Stratospheric O$_3$, NO$_2$, and NO$_3$ number density profiles from SCIAMACHY lunar occultation spectroscopic measurements: Retrieval, validation and interpretation

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Dedication
This thesis is dedicated to the Memory of my parents Trotter W. Amekudzi (my father) and Juliana A. Amevor-Dumashie (my mother).
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Deutsche Zusammenfassung


Es wurden gute Modellanpassungen von \( \text{O}_3 \), \( \text{NO}_2 \) und \( \text{NO}_3 \) erreicht, wobei die spektralen Residuen jeweils in der Größenordnung von 0,3%, 0,2% bzw. 0,2% liegen. Die Averaging-Kernels belegen eine signifikante Empfindlichkeit des Retrieval-Algorithmus gegenüber allen drei Spurengasen. Die theoretische Genauigkeit für \( \text{O}_3 \) und \( \text{NO}_2 \) ist besser als 14% bzw. 20% in Höhen zwischen 18 und 40 km, während die Genauigkeit für \( \text{NO}_3 \) besser als 35% ist im Bereich zwischen 20 und 55 km.


Um den gegenwärtigen Wissensstand über die \( \text{NO}_3 \)-Chemie zu untersuchen, wurden Vertikalprofile von \( \text{NO}_3 \) mit einem photochemischen Modell und einem einfachen Steady-State-Modell verglichen. In beiden Fällen wurden die gemessenen \( \text{O}_3 \)- und \( \text{NO}_2 \)-Profile als Startwert für die Modellberechnungen verwendet. Die Retrieval-Ergebnisse stimmen gut überein mit dem photochemischen Modell im Höhenbereich von 24 bis 45 km. Unterhalb von etwa 35–40 km werden die beobachteten \( \text{NO}_3 \)-Werte vom einfachen Modell gut reproduziert. Unterschiede zwischen beobachteten und simulierten Werten für \( \text{NO}_3 \) sind innerhalb der erwarteten Genauigkeit von 20–35%. Die Übereinstimmung zwischen beobachtetem \( \text{NO}_3 \) und dem photochemischen Modell zeigt, dass das Verhalten von \( \text{NO}_3 \) in der polaren Stratosphäre bereits gut nachzuvollziehen ist.
Abstract

Stratospheric number density profiles of O$_3$, NO$_2$, and NO$_3$ were retrieved from a moderate resolution atmospheric lunar transmitted spectra measured by the Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY) on board the European Environmental Satellite (ENVISAT), using the optimal estimation method. The measurements were taken over the high southern latitude (60$^\circ$S–90$^\circ$S), during the period of March to June 2003 and January to June 2004. The global spectral fitting method by the differential optical depth approach was applied to simultaneously fit O$_3$ and NO$_2$ using the spectral range of 430–460 nm and 510–560 nm within the Chappius absorption band of ozone. Furthermore, NO$_3$ was fitted using the visible spectral range of 615–680 nm containing NO$_3$ intense absorption bands at 623 nm and 662 nm.

Good fits of O$_3$, NO$_2$, and NO$_3$ were obtained with the spectral residual in the order of 0.3%, 0.2%, and 0.2% respectively. The averaging kernels show significant retrieval sensitivity for O$_3$, NO$_2$ and NO$_3$. The retrieval accuracy for O$_3$ and NO$_2$ between the altitude of 18 and 40 km is better than 14% and 20% respectively. Whereas the retrieval accuracy of NO$_3$ in the altitude range of 20–55 km is better than 35%.

Validation of the retrieved SCIAMACHY O$_3$ and NO$_2$ profiles were carried out. O$_3$ profiles were compared with HALOE, POAM-III, SAGE-II and -III, and MIPAS. Whereas NO$_2$ profiles were compared with HALOE, MIPAS, and SAGE-III. The validation results show that, the quality of SCIAMACHY O$_3$ profile is high, within 10–25% in the altitude range of 20–45 km. The quality of NO$_2$ is high within 10–35% in the altitude range of 20–40 km. These validation results give confidence that reasonable number density profiles of O$_3$ and NO$_2$ can be retrieved from SCIAMACHY spectroscopic lunar occultation data.

To test our current understanding of NO$_3$ chemistry, the retrieved NO$_3$ vertical profiles were compared with a full photochemical model and a relatively simple steady state model. The full photochemical model and a relatively simple steady state model used the retrieved O$_3$ and NO$_2$ results as input. The retrieved NO$_3$ profiles agree well with calculations from a full photochemical model constrained by retrieved O$_3$ and analyzed ECMWF temperatures in the altitude range between 24 to 45 km. Below about 35-40 km, observed NO$_3$ is well reproduced by photochemical steady state calculations. Differences between observed and modeled NO$_3$ are within the estimated accuracy of 20–35%. The agreement between the retrieved and photochemical model calculated NO$_3$ demonstrate that we have a reasonable understanding of the behavior of NO$_3$ in the polar stratosphere.
Part I

Introduction
Chapter 1

Motivation and objective

From the inception of the development of thought, the processes that underlie the formation and change of Earth have fascinated humans. These processes are linked, in the broader context, to the formation of universe(s) and the presence of life therein. Parallel to this inquiry, humans have struggled to adopt and modify Earth’s resources and environment to survive and enhance the quality of life. Through technology and economic activities coupled with quasi-exponential growth in the world population within the span of a few human generations, humankind have become one of the forces inducing a change on our earth system [NASA, 1986].

1.1 Motivation

Significant changes in the composition and behavior of the Earth’s Atmosphere over the last four decades, have been reported ([World Meteorological Organisation, 1994, 2003; Solomon, 1999] and references therein). The most important changes include:

1. Degradation of air quality (global air pollution) resulting from industrial combustion and biomass burning.

2. Increase in the abundance of tropospheric oxidants including ozone and related impact on the biosphere and human health.

3. Stratospheric ozone depletion resulting from tropospheric emission of chlorofluorocarbon compounds (CFCs and HFCs) [World Meteorological Organisation, 1994, 2003; Solomon, 1999] and references therein.
CHAPTER 1. MOTIVATION AND OBJECTIVE

4. Climatic changes (global warming) resulting from increasing emissions of greenhouse gases such as CO$_2$, CH$_4$, N$_2$O, and O$_3$ (Brasseur et al., 1999).

To understand the physical and chemical processes inducing these changes, and to assess the anthropogenic impact on climate, a number of scientific missions have been initiated. These missions include laboratory studies of atmospheric trace species, ground based atmospheric measurements, aircraft measurements and satellite measurements. In-situ measurements from ground-based instruments can provide detailed local tropospheric information about the atmosphere. However to obtain long-term global record necessary for monitoring atmospheric constituents (especially in the stratosphere and above) is only possible with remote sensing instruments on satellite platforms. Satellite missions have increased over the past three decades and its capability of monitoring and providing long-term data to the scientific community for studying changes in the atmospheric compositions has enhanced.

The focus of most today’s space-borne atmospheric measurement missions is on stratospheric ozone physics and chemistry, as ozone plays a unique role in absorbing the harmful UV radiation especially the UV-B. Depletion of stratospheric ozone will lead to almost no existence of life on our planet Earth, as this has harmful effects on biological organisms (human health, animals and plants).

Following the discovery of the Antarctic ozone hole (Farman et al., 1985), extensive scientific studies have been carried out to understand the basic mechanism of ozone hole formation. These studies have shown that gas-phase, and heterogeneous chemistry as well as transport are the major factors responsible for ozone depletion process leading to formation of the ozone hole (World Meteorological Organisation, 2003; Solomon, 1999 and references therein).

The earlier satellite missions to monitor the ozone layer, SBUV\(^1\) and TOMS\(^2\) were nadir viewing space-borne instruments. Later the scientific community introduced other instruments that observe our planet Earth’s atmosphere in limb and occultation viewing geometries. Today we have sensors on satellite platforms, which exploit solar, lunar, stellar, emission from the atmosphere, and satellite-crosslink signals. These sensors employ limb and occultation measurement technique to extract geophysical information from the atmosphere of relevance to climate and

\[^1\]SBUV stands for Solar Backscatter Ultraviolet is a spectrometer on board NASA’s Nimbus-7 satellite (11/1978 - 1990) (Heath et al., 1975; Fleig et al., 1990)
\[^2\]TOMS stands for Total Ozone Mapping Spectrometer on board Nimbus-7 /11/1978 - 1993) (Heath et al., 1975; McPeters et al., 1996)
Ozone research. The occultation space-borne sensors utilize a wide range of the electromagnetic spectrum from the UV via vis/IR and MW to radio waves, and exploit all kinds of atmosphere-radiation interactions such as absorption and scattering, both from molecules and aerosol, as well as refraction. The geophysical parameters obtained from occultation measurements, extend from temperature, pressure via trace gases to aerosols and cloud liquid water. Occultation data thus bear enormous utility for applications in atmospheric physics and chemistry as well as climate research. This thesis will demonstrate how trace gas information can be derive from spectroscopic data measured by the SCIAMACHY instrument using the lunar occultation measurement technique.

1.2 Thesis objectives

Observation and theoretical studies of nitrogen compounds have increased the recognition of the links between the nitrogen and chlorine chemistry in the Antarctic ozone depletion phenomenon ([Solomon, 1990] and references therein). Observations of nitrogen species such as NO, NO$_2$, NO$_3$, N$_2$O$_5$ and HNO$_3$ in the Antarctic regions have become a subject of increased scientific importance. [Noxon (1978); McKenzie and Johnston (1984)] were the first to report on surprisingly low twilight NO$_2$ abundances in Antarctica compared to theoretical gas-phase chemistry predictions, a condition now recognized as a key element in ozone depletion. Owing to the importance of NO$_2$ in reacting with ClO to convert reactive chlorine to ClONO$_2$, thereby limiting ozone loss.

To fully understand the long-term regional and global trends in catalytic destruction of O$_3$ in the stratosphere by NO$_x$, and the NO$_x$ budget, it is important to measure simultaneously NO$_3$, NO$_2$ and O$_3$. Lunar occultation performed on a satellite platforms, which is capable of providing nighttime measurements of atmospheric parameters is an excellent method to achieve this goal.

Nighttime measurements of trace gases (O$_3$, NO$_2$ and NO$_3$) using lunar and stellar occultation method have been performed successfully by ground based sensors and balloon platforms and the results have been reported by several authors, (see for example [Noxon et al. (1978); Platt et al. (1981); Norton and Noxon (1986); Solomon et al. (1989b); Smith and Solomon (1990); Naudet et al. (1981, 1989); Wayne et al. (1991); Rigaud et al. (1983); Renard et al. (1996, 2001)). These measurements, however, have not provided broader geographical coverage of the atmospheric trace species. Recent satellite platforms have introduced lunar and stellar occultation methods to measure nighttime atmospheric trace gases; these instruments are SCIAMACHY and SAGE-III, and GOMOS.
SCIAMACHY stands for SCanning Imaging Absorption spectroMeter for Atmospheric CHartography. It is a passive remote sensing moderate resolution UV, visible and short-wave infrared spectrometer on board the European Environmental Satellite (ENVISAT) launched in March 2002 ([Bovensmann et al., 1999]). SCIAMACHY instrument was designed to contribute to a better understanding of ozone chemistry, pollution and climate monitoring issues. SAGE-III stands for the third Stratospheric Aerosol and Gas Experiment. It is on board Meteor-3M launched in December 2001 and is designed to monitor aerosol extinction and ozone and nitrogen dioxide, in the upper troposphere and stratosphere ([McCormick et al., 2002]). The Global Ozone Monitoring by Occultation of Stars (GOMOS) is a UV, visible and short-wave infrared spectrometer on board the ENVISAT. By observing the Earth atmosphere using stellar occultation, GOMOS provides 400 profiles per day of O_3, NO_2 and NO_3 and H_2O ([Bertaux et al., 2000]).

The goal of the research presented in this thesis is to infer stratospheric vertical profiles of O_3, NO_2 and NO_3 from SCIAMACHY lunar occultation spectroscopic data and to validate the retrieved results. The focus of this work was to adapt the retrieval algorithms developed by Alexei Rozanov ([Rozanov, 2001]) and Jerome Meyer ([Meyer, 2004]) to retrieve trace gases from SCIAMACHY lunar occultation measurements and to validate and interpret the retrieved data. The major tasks of this research involve:

1. The calibration of SCIAMACHY lunar level-0 data including tangent height retrieval to improve the geometry information of the measurements using the O_2-A and O_2-B bands.

2. The retrieval of vertical profiles of O_3, NO_2 and NO_3 from SCIAMACHY spectroscopic data.

3. The Validation of O_3 and NO_2 with other space borne instruments such as HALOE, POAM-II, SAGE-II and III, and MIPAS.

4. Comparisons of the retrieved NO_3 with calculated NO_3 from photochemical model data to demonstrate how well the retrieved results agree with the current understanding of the stratospheric NO_3 chemistry.

3 HALOE stands for Halogen Occultation Experiment ([Russel et al., 1993b])
4 POAM-II stands for Polar Ozone and Aerosol Measurement III
5 MIPAS stands for Michelson Interferometer for Passive Atmospheric Sounding ([Endemann and Fischer, 1993] [Fischer and Oelhaf, 1996])
1.3 Thesis content

The thesis is divided into three parts. The first part is dedicated to general introduction of relevance to trace gas retrieval from the atmosphere. The second part is devoted to the instrumental description and the background theory necessary for the retrieval. A discussions of the results and the conclusions are given in the third part.

The first part has been subdivided into three chapters, the second part into four chapters and the third part into three chapters. In Chapter 2 a brief overview of the Earth’s atmosphere and ozone chemistry is presented. Chapter 3 provides an introduction to the nitrate radical: issues addressed in the chapter include importance, past history of measurements, and NO$_3$ chemistry. Instrumental description is given in Chapter 4 which includes measurement modes and optical design. Chapter 5 is devoted to characteristics of the Moon and lunar occultation measurements from the SCIAMACHY instrument. In Chapter 6 the radiative transfer modeling of the Earth’s atmosphere is considered. The optimal estimation theory and the retrieval methodology used in the thesis is described in chapter 7. The retrieval and validation results of O$_3$ and NO$_2$ are presented in chapter 8. Chapter 9 presents the retrieval results of NO$_3$ and interpretation of the retrieved NO$_3$ results. The last chapter, Chapter 10 summarizes the major findings of the study.
CHAPTER 1. MOTIVATION AND OBJECTIVE
Chapter 2

The Earth’s atmosphere

The Earth is one of the planets in our solar system and one of the three planets that have an atmosphere. The other planets possessing atmospheres are Venus and Mars. The atmospheres possessed by these planets are due to gases released from their interiors and the reactions these gases have undergone. The Earth’s atmosphere consist of a thin layer of different gases of varying compositions. In this chapter a brief overview of the Earth’s atmosphere is presented, starting with the major structure of the atmosphere followed by the atmospheric composition. The lastly section of the chapter is devoted to ozone chemistry.

2.1 Atmospheric layers

The Earth’s atmosphere is generally divided in four layers based on the average vertical temperature gradients: These layers are the troposphere, the stratosphere, the mesosphere and the thermosphere Fig. 2.1.

The lowest layer of the atmosphere is called the troposphere. This layer extends from the Earth’s surface up to the tropopause, which is at 8–18 km altitudes depending on latitude and time of the year. The height of the troposphere is up to approximately 18 km in the tropics, 12 km at mid-latitudes and 8 km near the poles. The highest height at the tropics is due to strong heating that causes vertical expansion of the lower atmosphere. The average height of the troposphere is approximately 11 kilometers as indicated in Fig. 2.1. About 85% of the total mass of the atmosphere is contained in the troposphere and this region of the atmosphere is often dynamically unstable with rapid vertical exchanges of energy and mass associated with convective activity. Most of atmospheric variabilities leading to meteorological process such as weather pattern occur in this region. Maximum air
CHAPTER 2. THE ATMOSPHERE

Figure 2.1: Atmospheric temperature profile based on US standard atmospheres (NASA, 1976). The horizontal lines indicate the various pause discussed.

The temperature of this layer occurs near the Earth’s surface; with increasing height, air temperature decreases uniformly at a lapse rate of approximately $9.7 \text{Kkm}^{-1}$ to an average temperature of 217 K, at the top of the troposphere. At the upper edge of the troposphere is a narrow transition zone called the tropopause and above the tropopause is the stratosphere.

The stratosphere is the layer that extends from an average altitude of 11 km to 50 km above the Earth’s surface. This region contains about 14.9% of the total mass of the Earth’s atmosphere and very little meteorological process occurs in this region. The lower stratosphere (11–20 km) is influenced by the polar jet streams and the subtropical jet streams. This region of the stratosphere is called isothermal layer, because its temperature remains constant with height. From an altitude of 20 to 50 km, temperature increases with altitude. The higher temperatures found in this region of the stratosphere occur because of a localized concentration of ozone gas molecules. This layer contains 90% of the Earth’s atmospheric ozone molecules, which absorb most of the ultraviolet sunlight creating heat energy that warms the stratosphere. This layer of ozone is called the ozone layer. At the upper edge of the stratosphere is a transition zone known as the stratopause.

The next atmospheric layer is the mesosphere located above the stratopause. The mesosphere extends from 50 to 85 km altitude. In the mesosphere, dynamical instability occurs frequently and is characterized by rapid vertical mixing due
2.2. ATMOSPHERIC COMPOSITION

to decrease in temperature with altitude, reaching the coldest atmospheric temperature of about 183 K at a height of approximately 85 km. At the top of the mesosphere is another transition zone called the mesopause.

The last atmospheric layer, as defined by vertical temperature gradient, has an altitude greater than approximately 85 km, and is called the thermosphere. The thermosphere is the warmest layer in the atmosphere. Heat in this region is generated from the absorption of short wavelength solar radiation by oxygen and nitrogen molecules. Temperatures in this layer can reach 500 K to 2000 K depending on the level of solar activity. Molecular diffusion producing atomic and ionic particles becomes the major process in this region, as vertical exchanges associated with dynamical mixing becomes insignificant. Details concerning these processes are provided in atmospheric physics and chemistry text books (Brasseur et al., 1999) and (Seinfeld and Pandis, 1998).

2.2 Atmospheric composition

Molecular O$_2$ and N$_2$ are the main constituents of the Earth’s atmosphere. Their atmospheric compositions are approximately 20.9% and 78.1% (i.e. O$_2$ and N$_2$ account for approximately 99% ) of the total mass of the atmosphere respectively. The noble gases argon and helium account for approximately 0.9% and other minor species known as trace gases constitute approximately 0.1%. Despite their negligible contribution to the total mass of air, many of these trace gases play important roles in the atmosphere. One of the most important trace gas in the atmosphere is ozone.

From the boundary layer up to 90 km, mixing by eddy fluid motions tends to produce uniform mixing ratios for all atmospheric major gaseous species. However most trace gases have significant sources and sinks in the stratosphere and mesosphere and therefore have spatial and temporal variability in their mixing ratios. For most of these trace species vertical variability is much greater than horizontal and temporal variability. It is therefore important to derive vertical profiles of trace gases so that their spatial and temporal compositions in the atmosphere can be known.

A number of variables are used to describe the vertical profiles (concentrations) of trace gases in the atmosphere. The concentration of a given trace gas in the atmosphere can be expressed in terms of number of molecules ($N_i$) per unit volume ($\text{cm}^3$) so called the number density $n_i$. The mass per unit volume ($\rho_i$), the partial pressure, $P_i$, or volume mixing ratios $\text{VMR}_i$, are other units used to express the atmospheric trace gas concentration. The $\text{VMR}_i$ is often given as parts per million
(ppm $10^{-6}$) or part per billion (ppb $10^{-9}$) or part per trillion (ppt $10^{-12}$). In this thesis, the vertical profiles of traces gases derived will be expressed in terms of number density. A relationship can be established between the other quantities and the number density based on the ideal gas law. For example the number density is related to the volume mixing ratio as

$$n_i = \frac{VMR_i P}{RT N_a},$$

(2.1)

where $R$ is the specific gas constant, $T$ is the temperature, $N_a$ is the Avogadro constant and $P$ is the atmospheric pressure. The density of air, $\rho$ is related to the number density through the molar mass of air, $M_{\text{air}}$, this relation is given as

$$n M_{\text{air}} = N_a \rho.$$ 

(2.2)

### 2.3 Stratospheric ozone chemistry

Stratospheric ozone plays a very important role in the Earth’s atmosphere, absorbing the harmful solar radiation (UV-B$^2$), which damages variety of life forms (unicellular organisms and surface cells of higher plants and animals) on the Earth surface. The absorbing of UV-B radiation by ozone in the stratosphere is the source of heat and thermal structure of the stratosphere [Andrews et al., 1987].

Systematic measurements of atmospheric ozone over many regions of the globe over the past decades have shown dramatic depletion in stratospheric ozone over the Antarctica, the Arctic and mid-latitude regions. The scientific interest to identify factors responsible for ozone destruction has been through a combination of laboratory studies, computer models and stratospheric observations. In this section, formation and loss processes of ozone would be presented.

#### 2.3.1 Chapman ozone chemistry

The photochemical theory governing ozone formation and destruction based on oxygen-only was first proposed by Chapman[1930]. Chapman’s theory stated that photolysis of oxygen molecule produces reactive atomic oxygen

$$O_2 + h\nu \rightarrow O + O.$$ 

(2.3)\]

Reaction 2.3 is possible only if the energy of the colliding photon has $\lambda \leq 242$ nm to dissociate molecular oxygen $O_2$ producing highly reactive oxygen atoms O.

---

1. The value of $R$ is $8.31441 \text{ J mol}^{-1} \text{ K}^{-1}$.
2. The wavelength range of UV-B is 280–320 nm.
The reactive atomic oxygen formed reacts rapidly with the surrounding oxygen molecules in the presence of a third body M (e.g. N$_2$, O$_2$ is required for simultaneous conservation of energy and momentum) to form ozone

$$O + O_2 + M \rightarrow O_3 + M.$$ (2.4)

$O_3$ formed according to Chapman theory can be removed from the atmosphere when incident radiation with $\lambda \leq 310$ nm is absorbed by the $O_3$ radical to produce electronically excited atomic oxygen, $O(^1D)$. If the absorbed radiation has wavelength in the range $310$ nm $\leq \lambda \leq 1100$ nm a ground state atomic oxygen, $O(^3P)$, is produced

$$O_3 + h\nu \rightarrow O_2 + O.$$ (2.5)

Reaction (2.5) can not be considered as ozone loss mechanism due to a very short lifetime ($10^{-2}$–1 s) of atomic oxygen in the stratosphere. Chapman therefore proposed that the loss mechanism for odd oxygen $O_x$ ($O$ and $O_3$) is

$$O_3 + O \rightarrow 2O_2,$$ (2.6)

$$O + O + M \rightarrow O_2 + M.$$ (2.7)

Chapman photochemical theory provide first step to better understanding of stratospheric ozone chemistry, however, it is incomplete due to the following reasons:

1. If this theory was correct then ozone columns should be highest in the tropics where ozone production is highest but rather ozone maximum is at moderate to high latitudes.

2. The Chapman’s ozone chemistry theory predicts ozone concentrations that are approximately factor of 2 higher than observed concentrations in the tropics (Chapman model produce global averaged total ozone column of 790 DU (Newman, 2000), whereas the actual observed value is approximately 300 DU).

3. At the polar latitudes the predicted value of ozone columns by Chapman’s model are too low.

These discrepancies in Chapman oxygen-only theory were corrected 40 years later (Solomon, 1999) when it was discovered that stratospheric ozone was chemically destroyed not solely by reaction of atomic oxygen, but also by hydrogen (Bates and Nicolet, 1950; Hampson, 1964) and nitrogen oxide chemistry (Crutzen, 1970, 1971; Johnston, 1971). Ozone destruction cycle involving halogens in particular chlorine from man-made chlorofluorocarbons transported to the stratosphere
Other factors such as Brewer-Dobson circulation and a slow stratospheric equator-to-pole motions are contributors to the observed stratospheric ozone trends.

### 2.3.2 Catalytic cycles

Catalytic ozone destruction cycles in the stratosphere involve a large number of atmospheric trace species that may either participate in gas phase or heterogeneous chemistry. A brief overview of this topic will be presented here. The catalytic cycles is summarized in the following form

\[
X + O_3 \longrightarrow XO + O_2 \quad (2.8)
\]

\[
XO + O_{2n+1} \longrightarrow X + (n + 1)O_2 \quad (2.9)
\]

\[
\text{net} \quad O_3 + O_{2n+1} \longrightarrow X + (n + 1)O_2 \quad (2.10)
\]

where \( X = \{H, OH, NO, Cl, Br\} \), these set of species belonged to families of \( HO_x, NO_x, ClO_x \) and \( BrO_x \) and \( n = \{0, 1\} \).

According to \cite{Bates and Nicolet, 1950} the gas phase catalytic cycle involving odd hydrogen family \( (HO_x) \) is

\[
\begin{align*}
\text{OH} + O & \longrightarrow H + O_2 \\
H + O_2 + M & \longrightarrow HO_2 + M \\
HO_2 + O & \longrightarrow OH + O_2 \\
\text{net} \quad O + O + M & \longrightarrow O_2 + M
\end{align*}
\]

The OH and HO\(_2\) radicals formed in Reaction (2.11) react with \( O_3 \)

\[
\begin{align*}
\text{OH} + O_3 & \longrightarrow HO_2 + O_2 \\
HO_2 + O_3 & \longrightarrow OH + 2O_2.
\end{align*}
\]

The net reaction is

\[ 2O_3 \longrightarrow 3O_2. \quad (2.13) \]

The catalytic cycle involving \( HO_x \) is the most important ozone destruction cycle above 40 km. In this cycle perturbation to the natural abundances of odd hydrogen arise through human modifications of source gases, which are mainly \( H_2O \) and \( CH_4 \) transported from the troposphere to the stratosphere.

Another important ozone depletion cycle is that involving the odd nitrogen \( (NO_x= NO + NO_2) \). This species get to the stratosphere through direct emissions
from aircrafts flying at high altitudes, by nuclear explosions or by photolysis of N\textsubscript{2}O transported from the troposphere into the stratosphere. The odd nitrogen cycle is believed to be the most important cycle responsible for ozone depletion in the altitude range of 20–40 km (middle stratosphere). This cycle can be summarized as

\begin{align}
\text{ON} + \text{O}_3 & \longrightarrow \text{NO}_2 + \text{O}_2 \\
\text{NO}_2 + \text{O} & \longrightarrow \text{ON} + \text{O}_2 \\
\text{net} \quad \text{O}_3 + \text{O} & \longrightarrow 2\text{O}_2
\end{align}

(2.14)

where the atomic oxygen source may be

\begin{align}
\text{NO}_2 + h\nu & \longrightarrow \text{O} + \text{NO}. \\
\end{align}

(2.15)

In 1974 it was shown that chlorine could also engage in a catalytic cycle contributing to stratospheric ozone destruction \cite{Stolarski and Cicerone, 1974}. The source of stratospheric chlorine was identified as the photolytic dissociation of man-made chlorofluorocarbons transported from the troposphere to the stratosphere \cite{Molina and Roland, 1974}. The major reactions involved in chlorine catalytic cycles are

\begin{align}
\text{Cl} + \text{O}_3 & \longrightarrow \text{ClO} + \text{O}_2 \\
\text{ClO} + \text{O} & \longrightarrow \text{Cl} + \text{O}_2 \\
\text{net} \quad \text{O}_3 + \text{O} & \longrightarrow 2\text{O}_2
\end{align}

(2.16)

\begin{align}
\text{Cl} + \text{O}_3 & \longrightarrow \text{ClO} + \text{O}_2 \\
\text{ClO} + \text{ClO} + \text{M} & \longrightarrow \text{Cl}_2\text{O}_2 + \text{M} \\
\text{Cl}_2\text{O}_2 + h\nu & \longrightarrow \text{Cl} + \text{ClO}_2 \\
\text{ClO}_2 + \text{M} & \longrightarrow \text{Cl} + \text{O}_2 + \text{M} \\
\text{net} \quad 2\text{O}_3 & \longrightarrow 3\text{O}_2.
\end{align}

(2.17)

\cite{Wofsy et al., 1975; Yung et al., 1980; McElroy et al., 1986} showed that stratospheric ozone loss could occur through catalytic cycle involving the coupling of bromine and chlorine chemistry. The reactions contributing to this cycle are

\begin{align}
\text{Cl} + \text{O}_3 & \longrightarrow \text{ClO} + \text{O}_2
\end{align}
$\text{Br + O}_3 \rightarrow \text{BrO + O}_2$

$\text{BrO + ClO} \rightarrow \text{Br + ClO}_2$

$\text{ClO}_2 + \text{M} \rightarrow \text{Cl + O}_2 + \text{M}$

\begin{equation}
\text{net} \quad 2\text{O}_3 \rightarrow 3\text{O}_2.
\end{equation}

The depletion of ozone by chlorine, bromine and the interactions between them is collectively referred to as halogen chemistry.

### 2.3.3 Antarctic ozone hole

[Farman et al. (1985)] shocked the scientific community with a report on the first observed massive annual decrease of stratospheric ozone in the Antarctic spring (September to October) at the British Antarctic Survey Station at Halley Bay (76°S, 27°W). These pioneering findings were confirmed by satellite measurements ([Stolarski et al. (1986)] and by other ground based observations at other Antarctic stations ([Komhyr et al. (1986), Mount et al. (1987)]). As the satellite measurements confirmed that the depletion extended over the entire Antarctica, the phenomenon became known as the Antarctic "ozone hole". Measurements of the vertical profiles of the depletion within the ozone hole were first reported by [Chubachi (1984)], this result was followed by other publications, see for example ([Hofmann et al. (1987), 1997; Iwasaka and Kondoh (1987); Gardiner (1988); Bevilacqua et al. (1997)].

[World Meteorological Organisation (2003)] assessment report for 2002 on ozone depletion have provided information on the amount of ozone loss in both Arctic and Antarctic regions. [Hofmann et al. (1997)] quantified ozone loss from the analysis of 10 years ozone-sonde measurements at the South Pole and made recommendations for the detection of Antarctic ozone recovery. The indicators for recovery include an end to springtime ozone depletion at 22 to 24 km and 12 to 20 km partial column value of more than 70 DU on September 15. Using POAM-II measurements over the Antarctic, [Bevilacqua et al. (1997)] derived the vortex average loss rates of ozone in August and September from 1994 to 1996 in the 450 to 800 K potential temperature range and found significant ozone loss over the three years period.

Different theories were proposed to explain the sudden stratospheric ozone loss over Antarctica ([Solomon (1999)] and reference therein], the most accepted theory is that involving heterogenous reaction occurring on the surface of PSCs (polar stratospheric clouds). Pre-requisite for PSCs formation are extremely low tempera-

---

3 Analyzed TOMS data of the vertical ozone column over the Antarctic were the first satellite ozone hole observations

4 PSCs are particles consisting of ternary mixtures of nitric acid, sulphuric acid and water
tures below 195 K, which occur more frequently in the Antarctic than in the Artic polar stratosphere. In the viewpoint of stratospheric meteorology and dynamics, the absence of solar illumination in high-latitude winter leads to cooling over the poles and hence a large temperature gradient near the polar terminator. This thermal gradient produces rapid zonal flow characterizing the "jet" at the edge of the vortex, while the air within the vortex is relatively isolated in comparison with surrounding mid-latitude regions leading to a core of very cold air within the vortex. The very low temperature in the vortex lead to formation of PSCs in the lower stratosphere. During winter and early spring the air at the polar latitudes is almost separated from that at lower latitudes due to the vortex. A downward circulation drives the polar air through the cold core of the vortex and the presence of PSCs in the cold core provides a platform for heterogenous chemistry.

The most important of the chemistry of the polar stratosphere is the conversion of reservoir compounds to catalytically active species or their precursors on the surface of the PSCs. The reservoir compounds which are mainly HCl and ClONO$_2$ are produced in the stratosphere from the reactions

\[ \text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3 \] (2.19)
\[ \text{ClO} + \text{NO}_2 + \text{M} \rightarrow \text{ClONO}_2 + \text{M}. \] (2.20)

The reservoir species HCl and ClONO$_2$, can react with each other on the surface of PSCs

\[ \text{ClONO}_2 + \text{HCl} \rightarrow \text{Cl}_2 + \text{HNO}_3. \] (2.21)

The outcome is that molecular chlorine is released as a gas and the nitric acid remains in the PSCs. Once solar photons reach the polar stratosphere in southern hemisphere the gaseous chlorine is photolyzed

\[ \text{Cl}_2 + h\nu \rightarrow \text{Cl} + \text{Cl} \] (2.22)
to chlorine atoms, which will result in catalytic destruction of ozone.
Chapter 3

The nitrate radical

This chapter provides introduction to the nitrate radical. The importance of the nitrate radical in the atmosphere is presented in the first section. This is followed by the NO$_3$ cross sections and then by the history of past measurements of NO$_3$. An introduction to NO$_3$ measurements from satellite platforms is given in the forth section of the chapter. The last two sections are devoted to chemistry of the nitrate radical and calculation of solar zenith angle, which is important for NO$_3$ interpretation.

3.1 Importance

The recognition of the contribution of nitrogen species in the Antarctic ozone depletion process ([Solomon] 1990) and references therein] have lead to increase observations of NO, NO$_2$, NO$_3$ N$_2$O$_5$, and HNO$_3$ in the polar regions. In this section the importance of the nitrate radical is presented.

The nitrate radical, NO$_3$ is one of the most important atmospheric species, because it plays a central role in the photochemistry of reactive nitrogen species in both the troposphere and the stratosphere ([Wayne et al. 1991]). At night, NO$_3$ controls the concentration of odd nitrogen, NO$_2$ (NO + NO$_2$). NO$_3$ plays a key role as an intermediate molecule in the conversion of NO$_2$ to N$_2$O$_5$, thus affects the abundance and diurnal variability of NO$_2$, a molecule which contributes significantly to stratospheric ozone chemistry. NO$_3$ contribute to heterogeneous chemistry in the lower stratosphere as N$_2$O$_5$ which is a temporary reservoir of oxides of nitrogen under favorable condition such as on the surface of stratospheric sulphate aerosol (SSA) in polar region react heterogeneously to form HNO$_3$, which is a long lived reservoir for NO$_x$ in the stratosphere. Yearly average yield of HNO$_3$
CHAPTER 3. THE NITRATE RADICAL

from nighttime NO$_3$ is comparable to HNO$_3$ produce from the OH oxidation of NO$_2$ in certain region of the earth ([Wayne et al., 1991]). In the troposphere, NO$_3$ reacts rapidly with dimethyl sulphide (DMS) in coastal regions, and alkene isoprene and terpene from forests to produce peroxy and hydroxy radicals and yielding products that may act as temporary reservoirs of oxides of nitrogen. Thus NO$_3$ acts as an effective nighttime oxidant in addition to OH, HO$_2$ and O$_3$ in the troposphere.

Another critical importance of tropospheric and/or stratospheric NO$_3$ in atmospheric chemistry is the existence of a possible scavenger. As NO$_3$ interchanges rapidly with other forms of reactive nitrogen (e.g., NO, NO$_2$, N$_2$O$_5$), scavenging of atmospheric NO$_3$ could affect the budgets of all reactive nitrogen species. These in turn play a key role in the photochemistry of both stratospheric and tropospheric ozone, also scavenging of NO$_3$ and other reactive nitrogen species play a notable role in nitric acid precipitation.

3.2 Absorption cross sections of NO$_3$

The absorption cross sections of the nitrate radical have been studied in several laboratories ([Sander et al., 2003] and references therein). The recommended value for the peak absorption at 298 K and 662 nm reported by [Sander et al., 2003] are $(2.00 \pm 0.25) \times 10^{-17}$ cm$^2$, which is the average of the results of several studies. The NO$_3$ absorption cross sections values in the wavelength range 600–670 nm at 298 K is shown in Fig. (3.1). The second intense absorption of NO$_3$ shown in Fig. (3.1) is at 623 nm and this value is approximately $1.5 \times 10^{-17}$ cm$^2$. The temperature dependence of NO$_3$ absorption cross sections at 662 nm band has been reported ([Wayne et al., 1991] Sander et al., 1997, 2003, Orphal et al., 2003) and references therein. Most of these studies showed that NO$_3$ cross section at 662 nm increases with decreasing temperature. In this thesis, NO$_3$ absorption cross sections used was taken from [Sander et al., 1997].

3.3 Past measurements

The Nitrate radical, NO$_3$, was first observed in the laboratory over 120 years ago. Hautefeuillue and Chappius [1881] postulated the formation of NO$_3$ within Chappius absorption band of O$_3$ with the most intense bands at $\lambda = 623$ and 662 nm, these results were first published in a table of wavelengths by Warburg and Leithäuser [1907] (see ([Wayne et al., 1991]).

The first atmospheric measurements of NO$_3$ were reported by [Noxon et al.]
Figure 3.1: Absorption cross sections of NO$_3$ at room temperature (298 K) covering wavelengths of 600–670 nm based on JPL recommendations [Sander et al. 1997].

[1978], who used a ground based scanning spectrometer to measure NO$_3$ column abundance above Fritz Peak observatory at latitude 40° N using the optical absorption near 660 nm of the Moon light. The theoretical aspects of those observations have been discussed by [Herman 1979], Herman calculated NO$_3$ from a detailed time dependent photochemical and diffusion model of the stratosphere and obtained different time behavior for NO$_3$ after sunset to just before sunrise. [Noxon et al. 1980] wrote a rejoinder to Herman’s theoretical observations to further explain their experimental observations. [Gelinas and Vajk 1981] reported on a comprehensive diurnal analysis of local variabilities for selected atmospheric volume elements along the lines of sight which was observed by [Noxon et al. 1978] as an alternative interpretations of those measurements to resolve the debated articles by [Noxon et al. 1980] and by [Herman 1979, 1980]. [Gelinas and Vajk 1981] analysis indicated that current photochemical theory is consistent with experimental observations of diurnal variations in total NO$_3$ and pointed out that factors such as absolute solar time, radiative rates, chemical rates, transport boundary fluxes, local trace species perturbations, and diurnal integration procedure could have plausibly contributed to the discrepancies in interpretation found in the debated articles. [Norton and Noxon 1986] reported on extensive measurements of total column abundance of stratospheric NO$_3$ at 19° N (Mauna Loa), 31° N (Hawaii), 40° N (Colorado), 51° N (Canada) and 64° N (Alaska) during spring and fall sea-
sons from 1978 through 1983. The instrument used by Norton and Noxon (1986) detected NO$_3$ vertical column abundances that were greater than $1.5 \times 10^{13}$ cm$^{-2}$. The seasonal and latitudinal variations in observed NO$_3$ abundances were far lower than theoretical predictions, but were well correlated with airflow patterns. These observations led Norton and Noxon to suggest that unknown “scavenging” process must exist for stratospheric NO$_3$ particularly at high latitude. Solomon et al. (1989a) measured NO$_3$ at 40° N and observed good agreement with model predictions and concluded that stratospheric NO$_3$ is not subject to significant scavenging.

The first ground based NO$_3$ measurements over Antarctica were reported by Sander et al. (1987), these measurements were carried out at 77.8° S (McMurdo station). Sander et al. (1987) observed that the bulk of the total column of NO$_3$ was located in the stratosphere and showed excellent agreements with model calculations, suggesting that the bulk of stratospheric NO$_3$ is not “scavenged”. Other measurements at McMurdo station during the fall, winter, and spring seasons were reported (Solomon et al., 1989b, 1993). These observations also do not support the existence of scavenger for stratospheric NO$_3$ in polar latitudes. However suggested that the main driving force of stratospheric NO$_3$ abundance were temperature and solar illumination. The arguments of all these articles are in support of already existing photochemical theory believed to govern the abundance and variability of stratospheric NO$_3$. Smith and Solomon (1990) carried out NO$_3$ measurements at a mid-latitude site (40° N), the Fritz Peak Observatory located at an altitude of 2.7 km in the Rocky mountains of Colorado using the moon as light source. The vertical profiles inferred from these measurements showed excellent agreement with theoretical predictions in th altitude range from 20 to 33 km. Smith and Solomon (1990) observed that at higher altitudes near 40 km, the NO$_3$ abundance is found to be quite sensitive to their adopted rate constant for thermal decomposition of N$_2$O$_5$ and suggested a relatively slow rate of N$_2$O$_5$ thermal decomposition in this region. Using visible and near-ultraviolet spectroscopy measurement technique at McMurdo station from October to April 1991, Solomon et al. (1993) determined the vertical column abundances of NO$_2$ and NO$_3$. Solomon et al. (1993) observed that the winter observations of both species deferred by a factor greater than 10 from the model predictions and said that the simultaneous observations of winter NO$_2$ and NO$_3$ provide unique information on the photochemical history of air parcels within the polar vortex. In particular their observations suggest that the concept of polar night as implied by zonally symmetric flow is not physically realistic for middle and upper stratospheric air in the region of their measurements.

The visible absorption spectroscopy technique using the Moon, stars or artificial light source was the most widely used atmospheric NO$_3$ measurement method. This method was used to measure tropospheric NO$_3$ both in polluted and remote environments (Platt et al., 1980, 1981, 1984; Noxon et al., 1983; Pitts et al., 1984;
3.4. NO$_3$ FROM SATELLITE INSTRUMENTS

Perner et al. (1985). Platt et al. (1981) considered the problem of overlap of the spectral features of NO$_3$ with other absorbers and discussed the absorption due to water vapor in the spectral range from 650 nm to 675 nm and that due to O$_2$ and O$_4$ near 626–630 nm. These measurements were carried out with an artificial lamp using an absorption path length of 4.8 km. Platt et al. (1981) measured the tropospheric NO$_3$ abundance using the two NO$_3$ absorption peak at 662 nm and 623 nm and demonstrated that the absorption due to water vapor could accurately be accounted for in their measurements. Platt et al. (1984) showed that the scavenging of tropospheric NO$_3$ was well correlated to relative humidity and suggested that surface reactions with aerosol particles may play a key role in the scavenging of tropospheric NO$_3$.

NO$_3$ vertical profiles have been derived from balloon-borne stellar occultation measurements at mid-latitudes (Naudet et al., 1981, 1989; Rigaud et al., 1983). According to Naudet et al. (1981, 1989), nighttime stratospheric NO$_3$ observations are between 5 and 160 ppt and display a maximum abundance near 40 km, which is in general agreement with theoretical models. NO$_3$ vertical profiles have also been inferred from balloon-borne instrument using the stellar and lunar occultation methods (Renard et al., 1996, 2001). The ground based and balloon-borne platforms however have not provided broader geographical coverage of the nitrate radical, which can only be achieved with satellite instruments.

3.4 NO$_3$ from satellite instruments

Although measurement of atmospheric trace gas from space-borne instruments started over three decades ago, measurement of NO$_3$ by space-borne instruments started recently. Owing to the fact that most of these satellite instruments were designed to measure scattered and/or absorbed solar photons, which render them incapable to measure NO$_3$, as NO$_3$ is rapidly removed from the atmosphere during the day. The daytime photolysis rate of NO$_3$ is 0.2 s$^{-1}$, however, at nighttime NO$_3$ concentrations build up to reach detectable values. The pre-requisite for NO$_3$ measurement by satellite instrument therefore is high sensitivity to measure lunar and stellar photons transmitted through the atmosphere. The satellite instruments which satisfy this requirement are SAGE-III, GOMOS, and SCIAMACHY.

SAGE-III stands for the third Stratospheric Gas and Aerosol Experiment launched in December 2001 on board the Russian Meteor-3M spacecraft. It is a multi-channel grating spectrometer capable of measuring atmospheric compositions using solar and lunar occultation measurement techniques in the UV-visible and near-infrared spectral region. The atmospheric parameters that are measured by SAGE-III instrument include aerosol particles, clouds, O$_3$, NO$_2$, H$_2$O, NO$_3$, OCIO, pressure
Global Ozone Monitoring by Occultation of Stars (GOMOS) is one of the ten instruments on board Envisat, which was launched by European Space Agency in March 2002. GOMOS is a UV-visible and near infrared spectrometer observing the Earth’s atmosphere using stellar occultation technique. The targeted atmospheric constituents include O$_3$, NO$_2$, H$_2$O, NO$_3$, aerosol particles, and Polar Stratospheric clouds (PSC (Bertaux et al., 2000). NO$_3$ derived from GOMOS stellar occultation measurements have been reported by Marchand et al. (2004).

3.5 Stratospheric nighttime chemistry

In the absence of heterogeneous processes the stratospheric nighttime NO$_3$ chemistry is believed to be governed by a relatively simple scheme involving NO$_2$, O$_3$, and N$_2$O$_5$ molecules:

\begin{align*}
\text{NO}_2 + \text{O}_3 & \rightarrow \text{NO}_3 + \text{O}_2 \quad (3.1) \\
\text{NO}_3 + \text{NO}_2 + \text{M} & \rightarrow \text{N}_2\text{O}_5 + \text{M} \quad (3.2) \\
\text{N}_2\text{O}_5 + \text{M} & \rightarrow \text{NO}_3 + \text{NO}_2 + \text{M} \quad (3.3)
\end{align*}

Reaction (3.1) is the main formation process of NO$_3$ and the nitrate radical is removed from the atmosphere by reacting with NO$_2$ to form N$_2$O$_5$ (Reaction 3.2), a reaction whose rate constant is temperature dependent (Norton and Noxon, 1986; Sander et al., 1987; Wangeberg et al., 1997). The reverse Reaction (3.3) serves as an additional NO$_3$ formation source when N$_2$O$_5$ in Reaction (3.2) is thermally decomposed to form NO$_2$ and NO$_3$. Assuming a steady state based on Reaction (3.1) to Reaction (3.3), the concentration of NO$_3$ can be calculated as

\[
[\text{NO}_3] = \frac{k_1[\text{O}_3]}{k_2[M]} + \frac{k_3[\text{N}_2\text{O}_5]}{k_2[\text{NO}_2]},
\]

(3.4)

where $k_1$, $k_2$ and $k_3$ are the reaction rate constants of Reactions (3.1), (3.2) and (3.3) respectively and $M$ is the number density of air. N$_2$O$_5$ builds up more slowly than does NO$_3$ after sunset (Solomon et al., 1989a). Thus in the early part of the night, the concentration of NO$_3$ depends largely on concentration of O$_3$ and temperature distribution. The effect of temperature is inherent in $k_1$; the rate constant $k_2$ is also a very important contributor to the absolute concentration of NO$_3$. For relatively low stratospheric temperatures the Reaction (3.3) is slow, and the second term in the right-hand side of Equation (3.4) can be neglected and NO$_3$ concentration is approximated as

\[
[\text{NO}_3] = \frac{k_1[\text{O}_3]}{k_2[M]},
\]

(3.5)
and the lifetime of NO$_3$, $\tau$, is given by

$$\tau = \frac{1}{k_2 [\text{NO}_2][M]} \quad (3.6)$$

(Norton and Noxon 1986; Sander et al. 1987). Sander et al. (1987) argued that if the second term in Equation (3.4) becomes important, then the growth of N$_2$O$_5$ can be reflected in growth of NO$_3$ with time during the night.

The temperature, $T$, dependence of NO$_3$ from Equation (3.5) is expressed as

$$\ln \left(\frac{[\text{NO}_3]}{[\text{O}_3]}\right) = -\frac{1180}{T} + \ln \left(\frac{2.67}{M}\right) \quad (3.7)$$

From the chemistry discussed above, it has been shown that three atmospheric variables are needed to calculate the time dependent growth of NO$_3$ concentration through the night. These variables are the O$_3$ concentration, the temperature, and the NO$_2$ concentration. The concentration of N$_2$O$_5$ becomes also an important variable for a relatively warm atmosphere.

The Reaction (3.1) in principle can be responsible for daytime production of NO$_3$, however rapid photolysis and the reaction with NO limit the concentrations of NO$_3$ to less than 1 ppt. There are other potential reactions that contribute to the daytime NO$_3$ chemistry in particular (see Appendix D) (Wayne et al. 1991). During the polar winter and spring, N$_2$O$_5$ reacts on the surface of stratospheric sulphate aerosol (SSA) heterogeneously to form HNO$_3$ and polar stratospheric clouds.

### 3.6 Calculation of solar zenith angle

In general, lunar occultation measurements have large Solar Zenith Angles (SZA) as these measurements are performed after sunset. Validation or comparison of trace gases that have strong diurnal cycles, for example NO$_2$ and NO$_3$, require the knowledge of the SZA, in addition to the geolocation information. For each SCIAMACHY measurement therefore a corresponding SZA is calculated based on the formula

$$\Theta = \arccos(\sin \phi \sin \vartheta + \cos \phi \cos \vartheta \cos H), \quad (3.8)$$

where $\Theta$ represent SZA, $\phi$ the latitude of lunar occultation measurement, $\vartheta$ the solar declination angle, and $H$ the hour angle (Seinfeld and Pandis 1998).

A plot of the SZA as a function of the day of the year is shown in Fig. (3.2). The measurements in 2003 have SZAs in the range of 95°–120°, whereas the measurements in 2004 have SZAs in the range of 92°–135°.
Figure 3.2: Solar zenith angle for each lunar occultation measurement as a function of the month of the year for 2003 (left) and 2004 (right).
Part II

Instrument and theory
Chapter 4

SCIAMACHY instrument

On March 1, 2002, ESA\(^1\) launched its first environmental satellite ENVISAT from Kourou, French Guiana carrying on board ten instruments. ENVISAT operates in a near-circular Sun-synchronous polar orbit having a mean altitude of about 800 km, period of 100 min (14 orbit per day) and moves with orbital velocity of approximately 7.45 km/s over ground crossing the equator on the descending node at about 10:00 local time. The inclination angle of the ENVISAT is 98°, moving always slightly against the rotation of the Earth and passing close to the poles. A repeated orbital cycle of ENVISAT is 35 days with respect to the position of the Earth’s surface. In this chapter, one of the ten instruments on board ENVISAT, the SCIAMACHY is described.

The Scanning Imaging Absorption Spectrometer for Atmospheric Chartography which was proposed in 1988 by the SCIAMACHY team (Burrows et al., 1988) and funded by Germany, The Netherlands and Belgium, is a UV visible and short-wave infrared, passive remote sensing moderate-resolution imaging spectrometer, contributed to the atmospheric physics and chemistry payload of ENVISAT. SCIAMACHY instrument has eight channels covering the spectral range of 240–2380 nm with a spectral resolution between 0.24 nm and 1.5 nm. SCIAMACHY is the first space-borne instrument that has the capability of measuring scattered photons in both nadir and limb observational geometries and also transmitted solar or lunar photons in occultation geometry (Bovensmann et al., 1999). Spectroscopic data from SCIAMACHY are expected to provide better understanding to a variety of issues of relevance to physics and chemistry of the Earth’s atmosphere. The scientific objectives of SCIAMACHY include:

- The impact of tropospheric pollution arising from industrial activity and

\(^1\)ESA stands for European Space Agency
biomass burning.

- Troposphere-stratosphere exchange processes (downward transport of stratospheric ozone, upward transport of ozone destroying precursor molecules).

- Stratospheric ozone chemistry, i.e., monitoring of ozone depletion over Antarctic and Arctic, monitoring of stratospheric halogen concentrations and global ozone budget.

- Mesospheric chemistry and dynamics (distribution of $H_2O$, ozone, NO and OH).

- Climate change, i.e., monitoring of greenhouse gases and radiation balance in the UV and near infrared.

4.1 Measurement modes

The multi-observational mode capability of the SCIAMACHY instrument provides the potential of obtaining a wide range of atmospheric information on traces gases, cloud and aerosol types. The measurement modes of SCIAMACHY instrument are briefly discussed in this section of the thesis.

4.1.1 Nadir

The atmospheric volume directly beneath the instrument is observed in nadir measurement mode. This observational mode have been applied successfully by other space-borne instruments including the predecessor of SCIAMACHY, the GOME instrument (Burrows et al., 1999) to remotely sense the earth’s atmosphere. In nadir mode, the nadir mirror scans across track in 4.0 s in forward direction followed by a fast 1 s back-scan. The scanning procedure is repeated several times for a total duration of approximately 65 s or 80 s depending on the orbital region. Each nadir scan covers an area on the ground of approximately 30 km along track and 960 km across track (960 km swath width), however there is an option for a smaller swath width of 120 km. A typical nadir scan is shown in Fig. 4.1. For the major constituents measured typically by SCIAMACHY in nadir mode, the ground pixel sizes are $30 \text{ km} \times 60 \text{ km}$ (Noël et al., 2000). $O_3$, $N_2O$, $H_2O$, $CO_2$, $CO$, $CH_4$, $H_2CO$, $NO_2$, $BrO$, $SO_2$, aerosol, and clouds are the expected scientific data products to be derived from SCIAMACHY nadir spectroscopic data (Bovensmann et al., 1999).

\(^{2}\text{GOME stands for the Global Ozone Monitoring Experiment on board of the second European Remote Sensing (ERS-2) satellite}\)
4.1. MEASUREMENT MODES

4.1.2 Limb

SCIAMACHY looks along the line of sight that travels through a tangential height with the Earth’s surface about 3000 km ahead of the sub-satellite nadir point at a particular time (see Fig. 4.1). The azimuth mirror thus scans in horizontal direction perpendicular to the satellite’s flight direction and the elevation (nadir) mirror scans through different tangential height. A complete limb scan cycle consist of 31 elevation step scans covering a tangential altitude range of 0–100 km in steps of approximately 3 km. Each horizontal scan of the atmosphere covers 1000 km across track in a duration of 1.5 s. A typical limb integration time is 0.375 s resulting in a horizontal resolution of 240 km. The vertical resolution of SCIAMACHY limb measurement is approximately 3 km. This is determined by the geometrical field of view, pointing stability of the instrument and multiple scattering processes in the atmosphere. From SCIAMACHY limb spectroscopic data it is possible to infer stratospheric and mesospheric vertical profiles of trace gases such as O$_3$, H$_2$O, OH, O$_2$, NO$_2$, NO, BrO (and ClO under ozone hole conditions) (Bovensmann et al., 1999). In addition information on polar stratospheric clouds (PSCs) (von Savigny et al., 2005b) and noctilucent clouds (NLCs) (von Savigny et al., 2004) in the mesosphere can be retrieved from limb measurements.
CHAPTER 4. SCIAMACHY INSTRUMENT

One unique feature of SCIAMACHY is the ability to observe the same air parcels in both limb and nadir observational modes; this so-called limb-nadir matching is achieved by observing an air parcel first in limb then about eight minutes later, the same air parcel is observed in nadir. By subtracting the limb stratospheric column from the near-simultaneous total nadir column, it is possible to derive tropospheric columns of various trace gases and aerosol parameters (Noël et al., 2000).

4.1.3 Solar occultation

The solar occultation measurement technique has proven to be a well established and a very valuable measurement method for remote sensing of the terrestrial and planetary atmospheres. This method has been used successfully to measure trace gases as well as temperature and aerosol concentrations in the Earth’s atmosphere by a number of space-borne instruments. These include the Stratospheric Aerosol Measurement (SAM-II) (McCormick et al., 1979), Stratospheric Aerosol and Gas Experiments (SAGE I, II and III) (Chu and McCormick, 1979; Chu et al., 1989; McCormick et al., 2002), the Halogen Occultation Experiment (HALOE) (Russel et al., 1993a), the Atmospheric Trace Molecule Spectroscopy (ATMOS) experiment (Gunson, 1992), and the Polar Ozone and Aerosol Measurement (POAM II and III) (Glaccum et al., 1996; Lucke et al., 1999). It is widely accepted that the occultation measurement methods are well suited to monitoring long-term trends in atmospheric composition, because the measurement is nearly self-calibrating and therefore relatively immune to long-term instrument degradation. In addition to the fore-mentioned advantage, the solar occultation method has high photon count rates due to the brightness of the source. This makes it possible to achieve high signal-to-noise ratios with a relatively small instrument field of view (FOV), resulting in measurements with high vertical resolution. The main disadvantage of SCIAMACHY solar occultation measurements is the limited spatial coverage. For example solar occultation measurements are performed at each orbit only during sunrise due to the sun-fixed orbit of ENVISAT and the forward viewing direction of SCIAMACHY. These measurements are therefore restricted to latitudes between 65° N and 90° N.

SCIAMACHY occultation measurements are performed using the elevation and the azimuth scan mirrors similar to that of the limb mode but with the Sun in the case of solar occultation in the instrument FOV so that only directly transmitted photons are collected by the detector. In the Sun scanning mode, the Sun follower is used to fix the azimuthal position of the Sun and then perform vertical scanning around 17.2 km for a pre-defined fixed time interval until the center of the geometric sun reaches 17.2 km. The Sun is then followed at a solar elevation rate of approximately 0.6°/s up to 100 km. A vertical scan over the complete sun takes
Figure 4.2: SCIAMACHY solar occultation scan strategy. Pink: Size of refracted sun. Yellow: Size of geometrical sun. The solid line represents the movement of the instrument FOV. [Noël et al., 2000; Meyer, 2004]

4.0 s. The resulting solar occultation scan strategy is illustrated in Fig. 4.2 [Noël et al., 2000; Meyer, 2004]. The vertical resolution at the tangent point for solar occultation measurements are approximately 2.6 km, and the horizontal resolution is 30 km.

## 4.2 Optical design and performance

The instrument is made up of a mirror system, a telescope, a spectrometer, and thermal and electronic subsystem. The movement of the scan mirrors depends on each measurement mode. For example for nadir measurements, the radiation from the Earth’s scene is directed by the elevation mirror into a telescope, which focuses the beam onto the entrance slit of the spectrometer. For limb and solar/lunar occultation measurements the radiation is reflected by the azimuth mirror to the elevation mirror and into the telescope, which focuses the beam onto the entrance slit of the spectrometer. For internal and subsolar calibration measurements the radiation of the internal calibration light sources or solar/lunar radiation is directed by the elevation mirror into the telescope. Spectra are recorded simultaneously in three spectral windows, 212–1750 nm, 1940–2040 nm and 2265–2380 nm. Stray
CHAPTER 4. SCIAMACHY INSTRUMENT

Figure 4.3: Optical diagram showing the components of sciamachy instrument.

Figure 4.4: A schematic view of light paths through the various channel within the sciamachy instrument (only layer 2, channel 3–8).
4.2. **OPTICAL DESIGN AND PERFORMANCE**

<table>
<thead>
<tr>
<th>Channel</th>
<th>Wavelength [nm]</th>
<th>Resolution [nm]</th>
<th>Detector material</th>
<th>Temperature [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>212–314</td>
<td>0.21</td>
<td>Si</td>
<td>200</td>
</tr>
<tr>
<td>2</td>
<td>309–404</td>
<td>0.22</td>
<td>Si</td>
<td>200</td>
</tr>
<tr>
<td>3</td>
<td>392–605</td>
<td>0.47</td>
<td>Si</td>
<td>235</td>
</tr>
<tr>
<td>4</td>
<td>698–709</td>
<td>0.42</td>
<td>Si</td>
<td>235</td>
</tr>
<tr>
<td>5</td>
<td>776–1056</td>
<td>0.55</td>
<td>Si</td>
<td>235</td>
</tr>
<tr>
<td>6</td>
<td>991–1750</td>
<td>1.56</td>
<td>In(0.53)Ga(0.47)As</td>
<td>200</td>
</tr>
<tr>
<td>7</td>
<td>1940–2040</td>
<td>0.21</td>
<td>In(0.81)Ga(0.19)As</td>
<td>150</td>
</tr>
<tr>
<td>8</td>
<td>2261–2380</td>
<td>0.24</td>
<td>In(0.83)Ga(0.17)As</td>
<td>150</td>
</tr>
</tbody>
</table>

Table 4.1: Characteristics of optical channels, detector material and cooling temperatures for channels 1–8 (Aben et al., 2002).

Light in the UV visible spectral window is minimized by the combination of a pre-dispersing prism and grating. Fig. 4.3 shows a schematic view of the various optical components of the SCIAMACHY instrument. Initially light from the spectrometer slit is collimated and directed onto the pre-dispersing prism. The selected beam of light leaving the predispersing prism forms a spectrum in the middle of the instrument, which is further separated into four components by means of reflective optics. The spectra with shorter wavelengths are directed to channel 1 (212–314 nm) and channel 2 (314–405) respectively. The majority of light in the spectrum (405–1750 nm) passes without reflection to channels 3–6, whereas the spectrum with the longer wavelength (1940–2380 nm) is reflected toward channels 7 and 8. Separation of light into the individual channels (3–6) is achieved with Dichroic mirrors (Goede et al., 1991; Burrows et al., 1995; Bovensmann et al., 1999). Each individual channel consist of a grating, transmission optics, and a diode array detector. Further dispersion of light is performed by the grating, which then focuses the light onto 8 linear 1024 pixel detector arrays. A schematic view of light paths through the various channel within the instruments is shown in Fig. 4.4 (for channels 3–8).

Dark current and detector noise are minimized by cooling the diode arrays to a desired temperature. The characteristics of the SCIAMACHY optics the material composition of each detector, and the detector temperature are provided in Table 4.1. To minimize the infrared emissions from the instrument that could influence the detectors of channels 6–8, the optical bench of the instrument is cooled and stabilized to 255 K.

As the SCIAMACHY instrument uses polarization sensitive optics like gratings, dichromic mirrors, prism and lenses, the instrument is very sensitive to the polarization state of the incident light (Aben et al., 2002). This implies that the spectrometer must be calibrated and characterized accurately with respect to its polarization sensitivity so as to derive correct radiometric values. The polarization
characteristic of incident light is therefore determined in SCIAMACHY by employing 7 broadband polarization channels similar to GOME instrument\(^3\) [Burrows et al., 1999].

\(^3\)GOME has only 3 PMD’s because of the reduced spectral range
Chapter 5

Occultation with the Moon

As the Moon is the light source for lunar occultation measurements, the first section of this chapter presents the literature review of the Moon and its characteristics. In the second section, the SCIAMACHY lunar occultation measurements method is presented.

5.1 The Moon

The Moon is the brightest object in the night time and the second brightest object in the sky after the Sun. Some nights, the Moon appears as a round globe and others it appears to be a thin slice. In reality, the Moon does not change in shape or size and its appearance changes as different parts of it are illuminated by the Sun. As the Moon is fairly close to the Earth (about 384,400 km), it seems larger than the stars and even as large as the Sun. The diameter of the Moon is approximately 3,476 km, which is about 400 times smaller than the Sun. However the apparent size of the Moon is about 0.5°, which is the same as the apparent size of the Sun. The Moon has no life on it in any form and has not changed much over the years. The Moon has no air, wind, or water. At night the temperature becomes colder than any place on Earth. In the daytime, it’s surface temperature become higher than boiling water. Compared to the Earth the Moon is less dense.

When the Moon is observed from the Earth with naked eye, it appears like a smooth sphere with dark and light patches of gray. This could provide some evidence that the Moon is made of two major types of terrain: relatively bright highlands and darker plains. With field glasses or a simple telescope one can see that the dark patches are flat plains, called maria. Studies on the Moon rocks identified it’s minerals composition, which includes aluminum, calcium, magne-
sium, silicon, and titanium. Some gases are also trapped in these rocks, such as hydrogen and helium. These gases are said to have reached the Moon by solar wind (Williams, 2004).

5.1.1 Lunar orbit

Following an elliptical orbit, the Moon travels around the Earth at 1022 ms\(^{-1}\). The Moon moves west to east on our sky, but seems to move east to west because the Earth spins much faster than the Moon can revolve around the Earth. Since the orbit is oval shaped, the Moon is not always the same distance away from the Earth. The point where it comes the closest to the Earth is called perigee; this is 354,330 km away. The farthest point, apogee, is 404,338 km.

The Moon has two main periods namely sidereal and synodic periods. To an observer on Earth, the Moon appears to be in orbit about the Earth, making one complete revolution with respect to the stars in 27.32 days, called sidereal month (period). The motion of the Moon about the Earth is in the same direction as the planets about the Sun, with a constant rotation rate; a situation described as (one-to-one) synchronous rotation. The gravitational pull keeps the Earth’s moon in its orbit. The Earth revolves around the Sun like all other planets, this implies that the Earth-Moon system also slowly revolves around the Sun. In principle it takes the Moon much longer (2 days) to complete a revolution with respect to the Sun about the Earth, this takes on the average about 29.53 days. This period is known as the synodic month, and this is the period used in lunar occultation measurement. A synodic month is one full day on the Moon. The lunar day is classified into two weeks of light and two weeks of darkness.

The Moon rotates on its axis only once during its movement around the Earth. The Moon rotates from the west to the east, the same direction that it travels around the Earth and at its equator, it rotates about 16 km/hr. Sometimes a short distance around the edge of the Moon can be seen, called the limb. It seems to swing up and down and from side to side during each revolution. These type of motions are called liberation. They are caused by changes in the Moon’s speed of revolution and by a tilt of 5 degrees. Liberation allow us to see about 59 percent of the Moon (Hamilton, 2005; Newhall and Williams, 1997; Bios et al., 1996; J. Chapront et al., 1999).

5.1.2 Moon phases

From any location on the Earth, the Moon appears to be a circular disk which, at any specific time, is illuminated to some degree by direct sunlight. Like the Earth,
5.1. **THE MOON**

The Moon is a sphere which is always half illuminated by the Sun, but as the Moon orbits the Earth we more or less see the illuminated half.

During a synodic month we see the moon change from a crescent to a full circle and back. These seemingly changes in shape and size are due to different lighting conditions. Different amounts of sunlight are reflected by the Sun to the Moon, causing these phases. The shape appears to change because we see different parts of the Moon’s surface as it makes its orbit. When the Moon is in between the Sun and the Earth, its far side is turned away from the Earth. It seems to be a darkened phase, which is called a new moon.

Fig. 5.1 illustrate the change in phase of the Moon as it is illuminated by the sunlight. In the new moon phase, the side of the Moon is illuminated by Earthshine, sunlight that is reflected from the Earth to the moon. A day after the new moon, a thins slice of light can be seen. The line between the Sunlit part and the dark part is called the terminator. After seven days, we see half of a full moon. This half circle is exposed to the Sun and can be seen from the Earth. It is called the first quarter. Seven days after the first quarter, the moon moves to where the Earth is between it and the Sun. This phase is the full moon. Seven days after the full moon, we see a half of a full moon once again. This is known as the last or third quarter. After one more week, the Moon returns to the new moon phase. As the Moon changes from a new moon to a full, it is called waxing. During the period from full to new, the Moon is waning. When it seems to be smaller than half of a moon, it is called a crescent. When it seems to be larger than half of a
CHAPTER 5. LUNAR OCCULTATION

moon, it is called a gibbous.

Although full moon occurs each month at a specific date and time, the Moon’s disk may appear to be full for several nights in a row. This is because the percentage of the Moon’s disk that appears illuminated changes very slowly around the time of full moon. For example the Moon may appear 100% illuminated only on the night closest to the time of exact Full Moon, but on the night before and the night after the Moon will appear 97-99% illuminated. Two days from Full Moon the Moon’s disk is 93-97% illuminated; this difference is not noticed usually (Williams, 2004; Bios et al., 1992).

The Moon rises and sets at varying times. With each passing day, the Moon rises about 50 minutes later and drops about 12°. By the end of a week, the Moon rises at noon and sets at midnight. During the full Moon, it rises as the Sun sets and sets as the Sun rises. During the last quarter, it rises at midnight and sets at noon.

5.1.3 Ecliptic and eclipses

The Moon’s orbit cuts the ecliptic at a shallow angle, around 5° which means that on the celestial sphere the Moon, follows a path through the zodiac. Half the time the Moon is north of the ecliptic. In another half time the Moon is in the south of the ecliptic. If the shadow of the Moon hits the Earth, the Sun is eclipsed in the shadow area. If on the other hand the shadow of the Earth covers the Moon, the Moon goes dark and we have an eclipse of the Moon. During a lunar eclipse, the Moon is a dark reddish color. This is because the Moon is illuminated by faint red rays from the Sun that have been refracted by the Earth’s atmosphere.

Eclipses can only happen when the Sun, Earth and Moon are on the same straight line. Since the Sun and Earth are in the plane of the ecliptic, the line is automatically in that plane. If the Moon is also on the same line, it must be in the plane of the ecliptic as well. It takes close to a month for the Moon to go around the Earth. During that time its orbit crosses the ecliptic twice, as it goes from one side to the other. At the time of crossing, the Sun may be anywhere along the ecliptic. Usually the Sun is not on the Earth-Moon line, and therefore an eclipse usually does not take place. Occasionally, however, it is on the ecliptic or close to it. If the Sun happens to occupy exactly the same spot on the celestial sphere, we get an eclipse of the Sun. This is because the Moon is then between the Earth and the Sun. On the other hand, if it occupies the spot exactly opposite from that of the Moon, the Earth’s shadow falls on the Moon and we have an eclipse of the Moon (Williams, 2004; J. Chapront and Chapront-Touzé, 1997).
5.1.4 Perturbation effects

The Sun attracts the Moon in such a way that it perturbs its orbit every 31.807 days. This phenomenon is called evection. Evection effect is mainly due to variation of the apparent value of eccentricity of the Moon’s orbit [Vuorilehto and Korpele [1994]]. The Sun and Moon, because of their varying distances and directions in relation to the Earth, constantly vary their gravitational attractions on the Earth. This makes the poles wander irregularly by about ±9 arc seconds from its average, or mean position. This produce a perturbation known as nutation, which has a period of about 18.6 years. It is called lunar nutation because the primary component of nutation is from the Moon.

5.1.5 Surface radiation

The thermal environment in orbit around the Moon is similar to that of Mercury since there is no atmosphere. It is dominated by the planetary infrared term. As an approximation, the surface temperature can be described as falling off from the subsolar point as a cosine function. Temperatures on the dark side of the Moon are of the order of 100K. The maximum temperature on the Sunlit side of the Moon peaks at 400K. These temperatures are not equivalent blackbody levels used for most other planets, but are combined with an overall surface emittance of 0.92 to obtain absolute values of the planetary infrared and reflected solar emission (Albedo). The mean planetary infrared minimum emission is $5.2 \text{ Wm}^{-2}$ and the mean subsolar peak is $1268 \text{ Wm}^{-2}$. The average lunar albedo is about 0.073, however the Moon’s surface has a variable albedo. The terrae region has an albedo ranging from 0.09 to 0.12 and the Marria region has an albedo ranging from 0.05 to 0.08 [Williams [2004]].

5.2 Lunar occultation measurements

The SCIAMACHY instrument performs lunar occultation measurements in the southern hemisphere of the Earth’s atmosphere, between 30° and 90° latitude, during local nighttime. SCIAMACHY Moon observations are possible above the northern hemisphere as well; however, these events usually coincide with sunrise. Also the lunar phase in these cases is less than 0.5, therefore it is impossible to perform useful lunar measurements. While sunrise is mainly defined by the relatively stable position of the Sun with respect to ENVISAT’s orbital plane, the properties of Moonrise in SCIAMACHY’s Limb Field Of View (LFOV) are determined by the orientation of the lunar orbital plane with respect to ENVISAT’s orbital plane and
CHAPTER 5. LUNAR OCCULTATION

Figure 5.2: The SCIAMACHY lunar occultation geographical coverage for 2003 (left) and 2004 (right). The blue crosses indicate the location of measurements.

the ecliptic. In this plane, the Moon completes one orbit within one synodic period of 29.53 days. Caused by the lunar orbital motion, the Moon moves through the LFOV from left to right at a rate of about 1° per orbit. Lunar occultation measurements start at a lunar phase of 0.6–0.7 and end shortly after full Moon. These measurements are performed in Moon pointing (staring) mode similar to the Halogen Occultation Experiment (Russel et al., 1993a). The SCIAMACHY instrument’s Instantaneous Field Of View in lunar occultation mode is 0.045° in vertical direction (height) and 1.8° in horizontal direction, the later is larger than the apparent diameter of the Moon, which is approximately 0.5°. To effectively track the Moon, the Moon Follower Device (MFD) is adjusted to the brightest point of the apparent Moon, as the Moon rises above the Earth’s horizon. Starting at approximately 17.2 km, the MFD follows the Moon up to 100 km (Noël et al., 2000). Below this critical altitude of 17.2 km, the apparent angular rate of the rising true Moon is significantly higher than that of the rising refracted images; as a result, tracking the rising Moon becomes almost impossible for the MFD. Above 100 km Moon measurements are performed for instrument calibration purposes. The integration time for SCIAMACHY lunar occultation measurements is 1.0 s, the vertical resolution is approximately 3 km and the horizontal resolution is 30 × 400 km².

SCIAMACHY lunar occultation can be successfully executed only when the lunar visibility occurs on the nightside. Due to the large field of view (2.2° × 2.2°), the MFD always detects in dayside occultations strong signal from the bright Earth’s atmosphere in addition to the moonlight. This prevents MFD control from acquiring and tracking the moon. In addition, variability in the lunar albedo, the perturbation effect of the motion of the moon, and seasons are other challenges

1MFD - the Moon follower device is made up of the Sun follower combined with a larger aperture providing a field of view of 2.2° × 2.2°
faced by interpretation of SCIAMACHY lunar occultation spectroscopic data \cite{Vuo-rilehto and Korpela, 1994}. The useful SCIAMACHY lunar occultation events where the Moon rises on the nightside are on the average 6–8 days per month and 4–8 months in the year. The locations of lunar occultation measurements performed in 2003 and 2004 is shown in Fig. 5.2.

The latitude point of each measurement as a function of the day of the year is shown in Fig. 5.3. The left panel plot corresponds to measurements carried out in 2003 and the plot in the right panel corresponds to measurement performed in 2004. These plots demonstrate the variability in lunar measurements. It can be seen that there are much less measurements in 2003 than in 2004. In addition, the measurements in 2004 have wider geographical coverage. Furthermore the measurements in 2004 extend from January to July whereas measurements in 2003 extend from February to June.
Chapter 6

Radiative transfer modeling

In this chapter, the background theory involving general radiative transfer in the Earth’s atmosphere is considered. The first section of the chapter is devoted to radiance followed by the calibration of lunar radiance spectra. The third section explain extinction processes in the atmosphere and the slit function is considered in the forth section. The radiative transfer equation is presented in fifth section and the last section is devoted to the lunar occultation forward model calculations.

6.1 Radiance

Radiance or intensity (I) is the radiant flux density per unit solid angle $\Omega$ (i.e. the electromagnetic radiation leaving or incident upon an area perpendicular to the beam), its unit is $\text{W m}^{-2} \text{sr}^{-1}$. The total radiant flux is called irradiance and radiance per unit wavelength interval is known as monochromatic radiance $I_{\lambda}$ ($\text{W m}^{-2} \text{sr}^{-1} \text{nm}^{-1}$). Spectroscopic instrument measured radiance is mainly over some spectral region, it implies measured radiance can be defined as

$$I_{\text{measured}} = \int_{\lambda-\Delta\lambda}^{\lambda+\Delta\lambda} \Psi \cdot I_{\lambda} d\lambda,$$

(6.1)

where $\Psi$ is the spectral response function of the instrument over its bandpass from $(\lambda - \Delta\lambda, \lambda + \Delta\lambda)$. Fig. 6.1 shows a simulated lunar radiance for SCIAMACHY instrument.

1radiant flux density in this content is the rate of flow of photon per unit area across a surface.
CHAPTER 6. RADIATIVE TRANSFER MODELING

Figure 6.1: Simulated lunar radiance for SCIAMACHY instrument, by S. Noël.

Figure 6.2: The measured SCIAMACHY lunar transmission spectra for selected altitudes. These spectra correspond to measurements of orbit number 5390 and sza = 105.8°, taken on 12th of March 2003 (left channel 3 and right channel 4).

6.2 Calibration of lunar radiance spectra

Retrieval of trace gas information from SCIAMACHY lunar occultation spectroscopic data can be divided into three separate steps: the conversion of the raw data (level 0 data) into calibrated spectra (level 1 data), tangent height correction procedure and retrieval of vertical profiles of trace gases (e.g., O₃, NO₂, and NO₃) from the calibrated spectra. In this section, the calibration process is described.

In general the calibration process (usually called the level 0 to level 1 processing) consists of wavelength calibration and radiometric calibration. The radiometric calibration involves several steps such as dark current correction, stray-light correction, instrumental noise correction, and polarization correction as the instrument optics are polarization sensitive (Burrows et al., 1999). Level 1 data are supplied by ESA for all other measurement mode except for lunar occultation, hence the need to begin the retrieval process with calibration. The calibration process of the SCIAMACHY lunar occultation involved the following procedure: wavelength calibration, removal of dead pixels, dark current correction, and stray-light correction. Instrumental noise polarization corrections are ignored in lunar occultation calibration process because occultation methods are nearly self-calibration methods: That is the measured lunar spectrum is divided by its corresponding measured lunar extra terrestrial spectrum.

Dark current correction is carried out by subtracting the measured signal for the instrument without any light source (leakage current) from all lunar occultation level 0 data. The dead/bad pixels are identified and removed in the calibration process. Wavelength calibration is carried out using the SCIAMACHY on board flight wavelength calibrated data file (key data file). This process involves assigning the correct pixel for each spectra point and measurement to its corresponding wavelength as in the key data file.

Instrumental noise, Fraunhofer structures, polarization effects, and Doppler shift are minimized by dividing each measurement by its corresponding reference
6.3. EXTINCTION PROCESSES

6.3. EXTINCTION PROCESSES

6.3. Extinction processes

6.3.1 Absorption

It is the loss of photon energy to a molecule, which leads to change of energy state of the molecule from lower energy level, \( E_l \) to a higher energy level, \( E_h \) (if the change in energy state is from \( E_h \) to \( E_l \) emission occurs). Information on absorption of gas molecules in the atmosphere must be known to accurately model the radiative transfer need for trace gas retrieval. The strength of the absorption is quantified with the molecular absorption cross sections \( \sigma_a \) (in cm\(^2\)). The absorption cross section is related to the absorption coefficient \( \alpha_a \) by

\[
\alpha_a = n \sigma_a, \tag{6.2}
\]

where \( n \) is the number density of the absorber. The electromagnetic radiation absorbed by gaseous molecules corresponds to their quantum mechanical transitions. Quantum mechanically, the intensity of absorption is proportional to the square of the transition dipole moment \( \mu_{1,2} \) given as

\[
\mu_{1,2} = \int \psi_1^* \mu \psi_2, \tag{6.3}
\]

where \( \psi_1 \) and \( \psi_2 \) are the wavefunctions for the two energy levels and \( \mu \) is the dipole moment operator. Molecules such as O\(_3\), NO\(_2\), and NO\(_3\) absorbed in the UV and visible regions therefore electronic transition is responsible for their observed absorption lines. If a molecule is absorbed in the infrared region then its absorption is due to vibrational transition. If absorbed in far infrared and microwave spectral
region then its absorption is due to rotational transition. The absorption spectra of molecules therefore depends on; which transition is permissible, the transition probability and the population of the involved state \cite{Atkins and de Paula 2002}.

**Absorption cross sections**

The absorption cross sections depend strongly on wavelength, temperature and pressure. The absorption cross section in the \textit{uv} visible spectral range are often available for most atmospheric constituents. However absorption cross sections for relatively weak absorbers such as O$_2$ and H$_2$O, in this spectral range are calculated by the so-called line-by-line method. The line-by-line calculations are also employed to calculate the absorption cross sections for short-wave infrared absorber. This method is formulated as

$$\sigma_a = \sum_{ij} S_{ij}(\nu,T)F(\nu,\nu_o,P,T),$$  \hspace{1cm} (6.4)

where \( S_{ij}(\nu,T) \) is the spectral line intensity at the temperature \( T \), \( F(\nu,\nu_o,P,T) \) is the line shape function. \( i \) and \( j \) are the indices of the lower and the upper energy levels of the transitions, and \( \nu_o \) is the center frequency. The center frequency and the energy levels of the transition, \( E_{i,j} \) are related as

$$\nu_o = \frac{E_i - E_j}{h},$$ \hspace{1cm} (6.5)

where \( h \) is Planck constant. The absorption coefficient in this case is calculated as

$$\alpha_a = \sum_q N_q \sum_{ij} S_{ij}(T)F(\nu,\nu_o),$$ \hspace{1cm} (6.6)

where \( N_q \) is the number density of the trace gases, \( \sum_q \) is the sum of all contributing absorbers. According to \cite{Goody 1964}, \( S_{ij}(T) \) can be obtained from one intensity \( S_o \) measured at temperature \( T_o \) as

$$S_{ij}(T) = S_o(T_o) \frac{n_i(T)(1 - \exp(-\frac{h\nu_o}{k_BT}))}{n_i(T_o)(1 - \exp(-\frac{h\nu_o}{k_BT_o}))},$$ \hspace{1cm} (6.7)

where \( n_i \) is the population of the lower energy level, \( k_B \) is the Boltzmann constant and \( c \) is the speed of light. \( n_i \) is described by the Maxwell-Boltzmann distribution as

$$n_i(T) = \frac{N g_i \exp(-\frac{E_i}{k_BT})}{\sum_i g_i \exp(-\frac{E_i}{k_BT})},$$ \hspace{1cm} (6.8)

where \( g_i \) is the degeneracy of the \( i \)th energy level with energy \( E_i \) and \( N \) the total number of electrons occupying the energy level. The denominator of Equation 6.8
is called the partition function\(^2\) In the atmospheric absorption when the partition function is considered as the combination of vibrational and rotational partition functions it can be approximated by a polynomial of temperature, \(T\), (Gamache \textit{et al.}, 1990) given as

\[
Q^{v,r} = a_0 + a_1 T + a_2 T^2 + a_3 T^3. \tag{6.9}
\]

Where the coefficients \(a_0\), \(a_1\), \(a_2\), and \(a_3\) are obtained by fitting to the calculated partition functions using a Simplex nonlinear minimization algorithm (Nelder and Mead, 1965). The spectral line database such as HITRAN uses the partition function storage given by Equation 6.9 to simplify the computation of the partition function.

### Line Broadening

An isolated, undisturbed and stationary molecule may absorb in narrow band determined by the natural line width but different processes can give a frequency distribution of the absorption, called line broadening. In the Earth’s atmosphere two major broadening mechanisms dominate due to thermal motion or pressure-induced collisions. These broadening mechanisms are pressure and Doppler broadening.

Pressure broadening is due to collisions between molecules in the atmosphere, which result in a shortened life time of the states involved in the transition and enabling the molecules to absorb at different frequencies. This broadening is relevant to the lower atmosphere below 40 km. Depending on the pressure, different line shape are obtained, for example at the pressures encountered in the troposphere and the lower stratosphere, the pressure broadening is described by the Lorentz frequency distribution function given as

\[
F_L(\nu, \nu_o) = \frac{1}{\pi} \frac{\alpha_L}{(\nu - \nu_o)^2 + \alpha_L^2}, \tag{6.10}
\]

where \(\alpha_L\) is the pressure induced width of the line. The full width at half maximum (FWHM) of the line shape function is \(2\alpha_L\). The temperature, \(T\), and pressure, \(P\), dependency of the Lorentz line width is normally calculated as

\[
\alpha_L(T, P) = \alpha_o(T_o, P_o) \left( \frac{P}{P_o} \right)^\beta \left( \frac{T}{T_o} \right)^\gamma, \tag{6.11}
\]

where \(\alpha_o\) is the Lorentz line width at reference pressure, \(P_o\), and reference temperature, \(T_o\), and \(\beta\) the exponent for the temperature dependency. (Goody, 1964)

---

\(^2\)The partition function characterizes how molecules in thermodynamic equilibrium are distributed among various energy states at particular temperature
express the Lorentz line width $\alpha_L$ in terms of the molecular kinetic energy given as

$$\alpha_L = \sum_j n_j \sigma_j^2 \sqrt{\frac{2k_B T}{\pi}} \left( \frac{1}{m} + \frac{1}{m_j} \right), \quad (6.12)$$

where $n_j$ is the number density of the $j$th species of perturber, $m_j$ is its mass, $m$ is the mass of the absorber, and $\sigma_j$ is the optical collision diameter.

In the upper stratosphere and the mesosphere, where molecular collision effects is relatively weak, Doppler broadening effect dominates. In this situation the broadening effect is due to the thermal motion of the molecules and the width of the spectral lines is determined by the Doppler shifts originated from the random thermal molecular motions. At thermal equilibrium the velocity of the atmospheric molecule has a Gaussian distribution and the line shape can be described by the Doppler function:

$$F_D(\nu, \nu_o, T) = \frac{1}{\alpha_D \sqrt{\pi}} \exp\left(-\frac{(\nu - \nu_o)^2}{\alpha_D^2}\right) \quad (6.13)$$

where

$$\alpha_D = \frac{\nu_o}{c} \sqrt{\frac{2RT}{M}} \quad (6.14)$$

where $M$ is the molecular mass and $R$ is the universal gas constant. When Doppler broadening exceeds the pressure broadening the height information in the line shape is lost because the Doppler line shape is independent of the pressure and the temperature dependence of the line width is low, $\sqrt{T}$. In the middle atmosphere, both broadening mechanisms are important and must be accounted for by a convolution of Lorentz and Doppler line shapes to produce a hybrid line shape. If no interaction between the two processes is assumed, a Voigt line shape is obtained, which is commonly used in radiative transfer models to approximate the shape of absorption lines in the atmosphere. The Voigt line function, $F_v$, is given as

$$F_v(\nu, \nu_o) = \int_{-\infty}^{\infty} F_L(\nu - \nu', \nu_o) F_D(\nu, \nu_o) d\nu'. \quad (6.15)$$

Substituting Equation 6.10 and 6.13 into Equation 6.15 we will obtain a Voigt profile, which is commonly used as an approximation to the shape of absorption lines in the atmosphere.

$$F_v(\nu, \nu, P, T) = \frac{\alpha_L}{\pi} \sqrt{\frac{m}{2\pi kT}} \cdot \left(\frac{1}{\nu - \nu^*_i - \frac{nu}{c}}\right)^2 \exp\left(-\frac{mu^2}{2kT}\right) du. \quad (6.16)$$
6.3. EXTINCTION PROCESSES

The Voigt profile is extensively tabulated in terms of the parameter \( d = 2\alpha L/\alpha D \) and fast numerical algorithms are available for its computation (Hui et al. 1982; Humlicek 1978).

6.3.2 Scattering

It is an event that leads to change in direction of the frequency of the incident photon on particles. The radiation scattered from a particle depends on the particle shape, size, and wavelength of the incident radiation. Scattering processes in the atmosphere are put into 3 categories: these are Rayleigh scattering \((\alpha < 0.1)\), Mie scattering \((0.1 < \alpha < 50)\) and geometric optics scattering \((\alpha > 50)\). Where \(\alpha\) is the size parameter, defined by Mie (1908) as

\[
\alpha = \frac{2\pi r}{\lambda},
\]

(6.17)

where \(r\) is the particle size radius.

Rayleigh scattering

Rayleigh scattering also known as molecular scattering is the interaction between an electromagnetic wave with gas molecules in the atmosphere leading to change in direction of the incident radiation. This theory consider the particles (gas molecules) as an oscillating and thus emitting dipole. The main result is the scattering efficiency factor is proportional to \(\lambda^{-4}\), an effect which can explain the blue color of the sky as short wavelengths are scattered more efficiently. In the first approximation the angular dependence of Rayleigh scattering is given by \((1 + \cos^2 \theta)\), where \(\theta\) is the scattering angle. The Rayleigh scattering cross section is calculated as

\[
\sigma_s(\lambda) \approx \frac{8\pi^3}{3\lambda^4} \frac{[n_s(\lambda)^2 - 1]^2}{N_s^2} F_k,
\]

(6.18)

where \(n_s(\lambda)\) is the real part of the refractive index of air under standard condition. \(N_s\) is the Loschmidt number and \(F_k\) is called the King correction (King 1923) given as

\[
F_k = \frac{6 + 3\rho}{6 - 7\rho},
\]

(6.19)

The Rayleigh scattering coefficient is proportional to \(n_s^2\). The atmospheric value of \(n_s\) is wavelength dependent and its variation is also due to the fact that
the atmosphere is a mixture of different gases, whose concentrations are highly variable. A common approximation for $n_s$ according to Edlén (1966) is given by

$$(n_s - 1) \cdot 10^8 = 8342.13 + \frac{2,406,030}{130 - \lambda^2} + \frac{15,997}{38.9 - \lambda^2}. \quad (6.20)$$

Mie scattering

The interaction between electromagnetic wave and spherical particles such as aerosol, resulting in scattering of the incident radiation is referred to as Mie scattering. Even though this theory was developed as early as 1908, it could not be calculated, owing to its complexity, until the last decades where computers were developed. According to Mie (1908); Deirmendjian (1969), the extinction coefficient due to aerosol scattering $\alpha_a(\nu)$ depend on the extinction efficiency $Q_a(r)$ and the particle size distribution function $f_a(r)$. $Q_a(r)$ is given as the ratio of the extinction cross section, $\sigma_{ext}$ to the geometric cross section of the particles, i.e,

$$Q(r) = \frac{\sigma_{ext}}{\pi r^2}. \quad (6.21)$$

The probability that the particle has a radius $r$ within the range $r$ to $r + dr$ is defined by the particle size distribution function, $f_a(r)$. According to Liou (1980); Goody and Yung (1995) and references therein $f_a(r)$ is given as

$$f_a(r) = \frac{1}{2\pi\sigma r} \exp\left\{ -\frac{1}{2} \left( \frac{\ln r - \ln R_m}{\sigma} \right)^2 \right\}. \quad (6.22)$$

The aerosol scattering extinction coefficient according to Deirmendjian (1969) is given as

$$\alpha_a(\nu) = \int_0^\infty \pi r^2 Q_a(r, n, \lambda) f_a(r) dr, \quad (6.23)$$

where $r$ is the radius, $n$ is the relative refractive index, and $\lambda$ is the wavelength. The aerosol profiles and optical properties are provided in the LOWTRAN (Low Resolution Atmospheric Transmission) aerosol model (Kneizys et al., 1988).

### 6.4 Slit function

The slit function suitable for SCIAMACHY instrument depends on the channel, for example, Ahlers and Dobber (2000) recommended that channels 6 and 8 of


6.5 Radiative transfer equation (RTE)

Consider an electromagnetic radiation with spectral radiance $I_\lambda(r, s)$ incident on small volume of atmosphere with an infinitesimal thickness $ds$ and cross-sectional area $A$. The radiance after emerging from the volume of atmosphere along the same direction $s(\theta, \phi)$ is $I_\lambda(r, s) + dI_\lambda$. There are three processes that contribute to the change in radiance $dI_\lambda$, these are absorption from the beam (direct term), scattering out and into the beam (depletion and source term) and thermal emission of the medium (source term). The equation involving all these contribution terms is generally referred to as the radiative transfer equation given as

$$dI_\lambda = -\alpha_{ab}(r, \lambda)I_\lambda(r, \lambda)ds - \alpha_{sc}(r, \lambda)I_\lambda(r, \lambda)ds$$

$$+ \frac{\alpha_{sc}(r, \lambda)}{4\pi} \int_S P(s, s'; r, \lambda) d\Omega' ds$$

$$+ \alpha_{em}(r, \lambda)B(T(r)) ds,$$

(6.27)
where the first term in Equation 6.27 is the absorption term, the second and third terms are the scattering contribution term and the last term is the thermal emission term. \( \alpha_{ab}, \alpha_{sc} \) and \( \alpha_{em} \) are absorption, scattering and emission coefficients respectively and \( P(s,s';r,\lambda) \) is the scattering phase function. The significant contribution to satellite remote sensing in occultation measurement mode is the absorption and scattering along the line of sight terms. Thus the radiation transfer equation in this case is given as

\[
dI_{\lambda} = -[\alpha_{ab}(r,\lambda) + \alpha_{sc}(r,\lambda)]I_{\lambda}(r,\lambda)ds. \tag{6.28}
\]

If

\[
\alpha_{ext}(r,\lambda) = \alpha_{ab}(r,\lambda) + \alpha_{sc}(r,\lambda), \tag{6.29}
\]

where \( \alpha_{ext}(r,\lambda) \) is called the extinction coefficient,

then Equation 6.28 becomes

\[
dI_{\lambda} = -\alpha_{ext}(r,\lambda)I_{\lambda}ds, \tag{6.30}
\]

and is called Beer-Lambert absorption law. Equation 6.30 can be re-written as

\[
\frac{dI_{\lambda}}{I_{\lambda}(r,\lambda)} = -\alpha_{ext}(r,\lambda)ds. \tag{6.31}
\]

Equation 6.31 is a first order differential equation whose solution is given as

\[
I_{\lambda}(r,\lambda) = I_{0}(\lambda) \exp(-\int_{0}^{s_{0}} \alpha_{ext}(r,\lambda)ds), \tag{6.32}
\]

where \( I_{\lambda}(r,\lambda) \) is the intensity of the direct electromagnetic radiation through the atmosphere and \( I_{0}(\lambda) \) is the extraterrestrial radiance. \( \int_{0}^{s_{0}} \alpha_{ext}(r,\lambda)ds \) is the optical light path through the atmosphere and \( s_{0} \) is the total path length. The symbol \( \tau \) is used to denote the optical light path through the atmosphere, i.e.

\[
\tau(r,\lambda) = \int_{0}^{s} \alpha_{ext}(r,\lambda)ds, \tag{6.33}
\]

and Equation 6.32 can be re-written as

\[
I_{\lambda}(r,\lambda) = I_{0}e^{-\tau(r,\lambda)}. \tag{6.34}
\]

The path length elements \( ds \) refer to the height layer grid, and can be calculated with and without refraction. The ray-tracing algorithm applied, is based on the
Snell’s law. A light ray hitting the boundary of two height layers $i$ and $j$ with angle $\theta_i$ to the perpendicular, will leave with angle $\theta_j$ given as
\[
\sin \theta_j = \frac{n_j}{n_i} \sin \theta_i, \tag{6.35}
\]
where $n_i$ and $n_j$ are the refractive indices, which are calculated with Equation 6.20.

$ds$ is related to the corresponding height steps $dh$ as
\[
ds = \frac{dh}{\cos \psi(h)} \tag{6.36}
\]

If we introduce a new function $\chi$ which is similar to the Heaviside function, the integration in Equation 6.33 can be re-written as
\[
\tau(\psi, \lambda) = \frac{h_t}{h_b} \int_{h_b}^{h_t} \frac{\chi(\psi, h')}{\cos \psi(h')} \alpha(\psi(h'), \lambda) dh'. \tag{6.37}
\]

Since the line of sight geometry is symmetric to the tangent point, it is sufficient to integrate only once from the bottom $h_b$ to the top $h_t$ of atmosphere with
\[
\chi(\psi, h') = \begin{cases} 
2 & \forall \ h' > h_g \\
0 & \forall \ h' \leq h_g 
\end{cases}, \tag{6.38}
\]
where $h_g$ is the geometrical tangent height. The geometrical tangent height $h_g$ and the lunar zenith angle $\psi$ at the top of atmosphere are related by
\[
h_g = (R_E + h_t) \sin \psi - R_E \tag{6.39}
\]
and
\[
\psi = \arcsin \left( \frac{h_g + R_E}{h_t + R_E} \right). \tag{6.40}
\]

$h_t$ is the defined height of the atmosphere above the surface and $R_E$ is the radius of the Earth.

In occultation geometry the Moon in SCIAMACHY field of view have a finite size, $\Omega$ with the instrument apparatus function $F(\omega)$. As SCIAMACHY is a multispectral instrument measuring over spectral range of 240–2380 nm, the simulated radiance has to be convolved with the instrument slit function $S(\lambda, \lambda')$. Applying these conditions to Equation 6.34 the radiance $\Upsilon^s(h_i, \lambda)$ measured by a real instrument can be calculated as
\[
\Upsilon^s(h_i, \lambda) = \int_{\Omega} \int_{\Delta \lambda} I_0(\lambda') S(\lambda, \lambda') F(\omega) e^{-\tau(h_i, \lambda')} d\lambda' d\omega. \tag{6.41}
\]
Here, $\Delta \lambda$ is the total width of SCIAMACHY slit function, $h_i$ is the tangent height and $i$ the tangent height index.
6.6 Forward model

The primary aim of a forward model in trace gas retrieval is to include the essential physics of measurement and all obtainable characteristics of the instrument that would allow a realistic simulation of direct measurement from the instrument. The forward model for evaluation of SCIAMACHY lunar occultation spectroscopic data is the same as the forward model scheme used to evaluate SCIAMACHY solar occultation data (Rozanov 2001) and (Meyer 2004). Given the appropriate observing conditions such as viewing angle, a-priori profile, absorption cross section of trace gases, atmospheric temperature and pressure distributions, and suitable instrument response function, the RTM stimulates the lunar transmitted radiance measured by SCIAMACHY instrument and also compute the Jacobian matrices of the derivatives of these simulated measurements with respect to the retrieval parameters, these Jacobian are preferably called the weighting function matrices. The simulated atmospheric transmission profiles are generated at a set of tangent heights or retrieval altitude grid. Although vertical resolution for the lunar measure is 3 km, a 1 km altitude grid was used, starting from 0 to 100 km. The simulated radiance $\Upsilon(h_i, \lambda')$ is calculated using Equation 6.41 and the full optical depth along the line of sight through the atmosphere $\tau(h_i, \lambda')$ in this case is given as

$$\tau(h_i, \lambda') = \int_0^{s_0} \alpha(h_i, \lambda', p, T),$$

and

$$\alpha(h_i, \lambda', p, T) = \alpha_a(h_i, \lambda') + \alpha_r(h_i, \lambda') + \sum_{j=1}^{M} \sigma_j(\lambda', P(h_i), T(h_i))N(h_i),$$

where $\alpha(h_i, \lambda', p, T)$ is the atmospheric extinction coefficient, for each tangent height and each wavelength. $\sigma_j(\lambda, T(h_i), P(h_i))$ is the absorption cross section of trace gas $j$, $\alpha_a(h_i, \lambda')$ is the aerosol extinction coefficient, and $\alpha_r(h_i, \lambda')$ is the molecular Rayleigh scattering coefficient. $T$ is the temperature and $P$ is the pressure. $M$ is the number of atmospheric trace gases having absorption features at $\lambda'$. The forward model simulation code has the possibility to use the HITRAN spectroscopic data and line parameter (Rothman et al. 1998) for line-by-line calculation of the absolute cross sections and fitting of line absorbers such as O$_2$ and H$_2$O.

The weighting function $W^j(h_i)$ is expressed as the derivative of the modeled transmission radiance with respect to the model parameters, given as

$$W^j(h_i, \lambda) = \frac{\delta \Upsilon^*(h_i, \lambda)}{\delta x^j_i},$$

where $\delta \Upsilon^*(h_i, \lambda)$ is the change in the modeled transmission radiance due to a change in the model parameter $x^j_i$. The derivatives of the absorption cross sections $\sigma_j$ with respect to the model parameters are calculated using Equation 6.43.
where \( x_i \) is the concentration of the trace gas of interest at a certain altitudes. \( i \) denotes the tangent height index and \( j \) the retrieval parameter index. Detail derivation of the weighting function formula for occultation measurement is given in {\cite{Rozanov2001}}.

The weighting function \( W_j(h_i, \lambda) \) is found by first computing variation in the measured radiance due to variation of the concentration of trace gas \( j \) given as

\[
\delta \Upsilon(\Psi, \lambda, N_1(h), ..., N_j(h), ..., N_J(h)) = \\
\Upsilon(\Psi, \lambda, N_1(h), ..., N_j(h) + \delta N_j(h), ..., N_J(h)) \\
- \Upsilon(\Psi, \lambda, N_1(h), ..., N_j(h), ..., N_J(h)).
\]  
(6.45)

Substitute the simulated radiance as given in Equation 6.41 into Equation 6.45 and using Equation 6.42 to calculate the variation of the optical depth due to variation of the concentration of trace gas \( j \), \( \delta \tau(\Psi, \omega, \lambda) \), we will get the following expression for \( \delta \Upsilon \):

\[
\delta \Upsilon(\psi, \lambda) = - \int_{h_b}^{h_t} dh' \delta N_j \int_{\Omega} d\omega f(\omega) \frac{\chi(\psi, h', \omega)}{\cos(\psi(h', \omega))} \\
\int_{\Delta \lambda} d\lambda' a(\lambda, \lambda') I_0(\lambda') e^{-\tau_j(\psi, \omega, \lambda')} \sigma_j(\lambda'),
\]  
(6.46)

and the weighting function can be calculated as

\[
W_j(\psi, x(h_i), \lambda) = - \int_{\Omega} d\omega f(\omega) \frac{\chi(\psi, h_i, \omega)}{\cos(\psi(h_i, \omega))} \\
\int_{\Delta \lambda} d\lambda' a(\lambda, \lambda') I_0(\lambda') e^{-\tau_j(\psi, \omega, \lambda')} \sigma_j(\lambda', h_i),
\]  
(6.47)

where the instrument apparatus function \( f(\omega) \) is commonly approximated as

\[
f(\omega) = \begin{cases} 
1 & \forall \omega \in \Omega \\
0 & \forall \omega \notin \Omega 
\end{cases}
\]  
(6.48)

Discretizing the equation for the variation of the measured radiance due to variation of atmospheric trace gas number densities, we will have

\[
\delta \Upsilon(\psi, \lambda, \bar{p}) = \sum_{j=1}^{J} \sum_{i=1}^{L} W_{ji}(\psi, \lambda, \bar{p}) \frac{\delta N_j(h_i)}{N_j(h_i)} q_i,
\]  
(6.49)

where \( q_i \) are the quadrature coefficients appropriate to the selected integration rule.
CHAPTER 6. RADIATIVE TRANSFER MODELING

The global spectral fitting method is used, this allow for the simultaneous fitting of interfering species in the retrieval window. The global spectral fitting employ the differential optical depth approach for the spectral fitting that is

$$\tau_i(\lambda) = \ln [I_i(\lambda)] - \sum_{i=0}^{N} c_k^i \lambda^i,$$  \hspace{1cm} (6.50)

where $I$ is the normalized lunar spectra, $i$ is the tangent height index, $k$ the retrieval parameter index, $c$ is the polynomial coefficient and $N$ is the order of the polynomial. The spectral fitting by the differential optical depth approach reduce the influence of systematical errors in the measured spectra and instrument calibration errors on the retrieval parameters, ([Rozanov, 2001]). In our situation the differential optical depth is applied to the measured and reference lunar occultation radiance, the simulated transmission spectrum and the weighting functions. The resulting differential spectra are $\tilde{I}_i^{m,ref}(\lambda), \tilde{T}_i(\lambda)$, and $\tilde{W}_j^k(\lambda)$, which corresponding to measured and reference radiance, the simulated spectra, and weighting function at each tangent height respectively. These differential spectra are calculated as

$$\tilde{I}_i^{m,ref}(\lambda) = \ln[I_i^{m,ref}(\lambda)] - \sum_{i=0}^{N} c_k^i \lambda^i \hspace{1cm} (6.51)$$

$$\tilde{T}_i = \ln \left[ \frac{I_i(\lambda)}{I_{ref}(\lambda)} \right] - \sum_{i=0}^{N} c_k^i \lambda^i \hspace{1cm} (6.52)$$

$$\tilde{W}_j^k(\lambda) = \frac{1}{I_i^s(\lambda)} W_i^k(\lambda) - \frac{1}{I_{ref}^s(\lambda)} W_{ref}^k(\lambda) - \sum_{i=0}^{N} c_k^i \lambda^i. \hspace{1cm} (6.53)$$

Further, shift and squeeze correction is performed to reduce errors due to wavelength calibration and Doppler shift by minimizing the following quadratic form:

$$||\tilde{T}_i^s(\lambda) + \sum_j \tilde{W}_j^s(\lambda) \frac{\Delta x_j}{x_j} - \tilde{I}_i^m(\lambda) + \tilde{I}_o(\lambda) -$$

$$\left( b_{sh}^s - b_{eq}^s \right) \frac{\delta \tilde{T}_i^s(\lambda)}{\delta \lambda} - \left( b_{sh}^m - b_{eq}^m \right) \frac{\delta \tilde{I}_o(\lambda)}{\delta \lambda} ||^2 \longrightarrow \text{min.} \hspace{1cm} (6.54)$$

Where $\tilde{W}_j^s(\lambda)$ is the vertically integrated weighting function (i.e., a change in the differential lunar transmission spectra due to a scaling of a trace gas vertical profile), and $\frac{\Delta x_j}{x_j}$ represents a scaling of the vertical profiles. The last two terms in Equation 6.54 account for the shift and squeeze correction within the retrieval code. The shift and squeeze correction is done for the ratio of the modeled transmission spectra with respect to the measured transmission spectrum. These are represented
by the coefficients $b_{sh}^s$ and $b_{sq}^s$. The shift and squeeze correction is also done for occultation measurements at the reference tangent altitude with respect to the measurements at atmospheric tangent altitude, represented by the coefficients $b_{sh}^m$ and $b_{sq}^m$. 

Chapter 7

The optimal estimation and retrieval scheme

An inverse problem in the atmosphere usually involve a system of non-linear equations of measurements (spectra) and atmospheric parameters (trace gases concentration, temperature, pressure, and aerosol extinction). The most commonly used inversion method to solve these system of non-linear equations (ill-posed physical problem) is the optimal estimation theory described by Rodgers (1976). The first section of this chapter will be devoted to the optimal estimation theory, followed by the description of the retrieval methodology applied to derive vertical profile of trace gases from SCIAMACHY lunar occultation spectroscopic measurement. The last section of this chapter is devoted to retrieval characterization and error analysis method.

7.1 Optimal estimation theory

Atmospheric measurements are not continuous function for example lunar occultation measurements perform at a tangent height interval of 3km. Measurement vector $\mathbf{y}$ of these measurements can therefore be represented by set of discrete values of $m$ dimension given as

$$\mathbf{y} = (y_1, y_2, y_3, \ldots, y_m)^T$$  \hspace{1cm} (7.1)

Geophysical parameters to be derived from these discrete measurements are usually continuous, this means for this goal to be achieved, the atmospheric parameters have to be discretize leading to inverse problem. Assuming that the atmospheric state vector $\mathbf{x}$ have $n$ dimension we can write in vector space $\mathbf{x}$ as

$$\mathbf{x} = (x_1, x_2, x_3, \ldots, x_n)^T$$  \hspace{1cm} (7.2)
In a situation where we have more independent measurements than unknown the inverse problem becomes overdetermined. The solution to such ill-posed problems is formulated in the context of Optimal Estimation (OE) theory, which allow for the inclusion of a priori information of the atmosphere (Rodgers [1976, 1990, 2000]).

The measurement vector \( y \in \mathbb{R}^m \) and the retrieval parameter state vector \( x \in \mathbb{R}^n \) are related through a non-linear radiative transfer model, \( F \), as

\[
y = Fx + \epsilon, \tag{7.3}
\]

where \( \epsilon \) is the \( m \)-dimensional measurement error vector. A more appropriate relation can be obtained by introducing a linearized radiative transfer (forward) model operator, \( K \). This formula is commonly obtain by the Taylor series expansion of the non-linear radiative transfer model

\[
F \approx F_0 + \frac{\delta F}{\delta x} \bigg|_{x_0} (x - x_0). \tag{7.4}
\]

If \( y_0 = Fx_0 \) and \( K = \frac{\delta F}{\delta x} \bigg|_{x_0} \) then the linearized form of Equation 7.3 will be given as

\[
y = y_0 + K(x - x_0) + \epsilon \tag{7.5}
\]

Where \( x_0 \) is the a priori state vector and \( y_0 \) the corresponding measurement vector to \( x_0 \). As \( m > n \) the inverse problem is a constrained least-squares problem in which optimal solution is find by minimizing a quadratic cost function (Rodgers, 2000):

\[
\| (y - y_0) - K(x - x_0) \|^2_{S_y^{-1}} + \| x - x_0 \|^2_{R} = [(y - y_0) - K(x - x_0)]^T S_y^{-1} [(y - y_0) - K(x - x_0)] + (x - x_0)^T R (x - x_0) \tag{7.6}
\]

where \( S_y \) is the measurement error covariance matrix and \( R \) is a regularization matrix. The second part of the righthand side of Equation 7.6 is the constrain- ing term, which adds additional knowledge about the solution to the information that comes from measurement. The superscripts \( T \) and \( -1 \) designate the matrix transpose and inverse, respectively. The retrieval solution is obtained iteratively following the Gauss-Newton iteration scheme, where the measurement vector \( x_i \) is used as linearization point for the \( (i+1) \)th iteration and optimal estimation solution for \( x_{i+1} \) is given by

\[
x_{i+1} = x_0 + (K_i^T S_y^{-1} K_i + R)^{-1} K_i^T S_y^{-1} (y - y_i + K_i(x_i - x_0)). \tag{7.7}
\]
The corresponding solution covariance matrix $\hat{S}$ is given as

$$S = (K^T S^{-1} y + R)^{-1}. \quad (7.8)$$

The theoretical precision of the retrieval of the $j$-th parameter is expressed in terms of elements of the retrieval error covariance matrix $S$ as,

$$s_j = \frac{\sigma_j}{x_j^j} \quad (7.9)$$

where $\sigma_j$ is a square root of the $i$-th diagonal element of $S$ and $x_j^j$ is the a priori value of the $j$-th parameter to be estimated.

### 7.2 Twomey-Tikhonov regularization

An a priori covariance matrix $S_a$ can be introduced in Equation (7.8) in the retrieval to represent the climatological constraint, where inverse of this matrix will replace the regularization matrix, $R$, in the retrieval Equation (7.7). To calculate this matrix requires a large number of independent profiles from a global database containing a large number of independent profiles measured at various conditions. However a single profile climatology taken from US Standard Atmospheres (NASA 1976) was used in this case, the major advantage of this climatology is that it is available for large number of retrievable atmospheric trace gases, but it is impossible to get a realistic a priori covariance matrix. It therefore becomes of paramount important that an ad hoc or smoothing constraints are included in the retrieval solution, which is referred to as Twomey-Tikhonov regularization. This form of regularization is so called, because it was first introduced independently by Tommey (1963) and Tikhonov (1963).

The purpose of Twomey-Tikhonov regularization is to modify the inverse of the a priori covariance matrix such that the optimal estimated solution will approach the desire state of the retrieved atmospheric parameter. Introduction of this constraint requires care to prevent a false retrieval solution, which will introduce unrealistic features and hence loss in measurement information. In the case of SCIAMACHY occultation retrieval scheme, the Twomey-Tikhonov regularization was applied by Meyer (2004), Meyer et al. (2005) to stabilize the retrieval solution for the retrieval of ozone and NO$_2$ from SCIAMACHY solar occultation measurements. The nature of the Twomey-Tikhonov regularization used in the SCIAMACHY lunar occultation scheme is the same as that applied to SCIAMACHY solar occultation retrieval scheme. The regularization operators are a constant and the second derivative operators, which controls the absolute value and the smoothness. In our algorithm, the constant parameter $T_j^1$ enhances the direct influence
on the a priori (i.e. $T_j^1$ replaces the inverse of the a priori covariance) and the second parameter, $T_j^2$, is the smoothing parameter, which account for the deviation of the a-priori state vector $x_0$ with respect to height $h_i$. The regularization matrix $R_j$ of the second parameter is written as

$$R_j = \begin{pmatrix}
\frac{T_j^2}{h_1-h_2} & \frac{T_j^2}{h_2-h_1} & 0 \\
\frac{T_j^2}{h_1-h_3} & 0 & \frac{T_j^2}{h_2-h_3} \\
0 & \frac{T_j^2}{h_3-h_4} & 0 \\
& \ddots & \ddots & \ddots & \ddots & 0 \\
0 & \frac{T_j^2}{h_{L-1}-h_L} & 0 & \frac{T_j^2}{h_L-h_{L-1}} \\
0 & 0 & \frac{T_j^2}{h_{L-2}-h_L} & \frac{T_j^2}{h_L-h_{L-2}} & \frac{T_j^2}{h_L-h_{L-1}}
\end{pmatrix}.$$  \hspace{1cm} (7.10)

where $j$ is the parameter index of each trace gas. The resulting regularization matrix involving the parameters discussed can be written as

$$R = \begin{pmatrix}
R_1 & 0 \\
\vdots & \ddots \\
0 & R_J
\end{pmatrix}.$$  \hspace{1cm} (7.11)

### 7.3 Retrieval methodology

One of the necessary steps in the retrieval of trace gases from SCIAMACHY occultation measurements is the tangent height correction, which is an independent algorithm from the main retrieval scheme. This section will first discuss briefly the tangent height correction procedure and this will be followed by the description of the trace gas retrieval scheme.

#### 7.3.1 Tangent height correction

The line of sight geometry is uniquely defined by its tangent height. The tangent height information is provided along side the spectroscopic data by European Space Agency, however this tangent heights are shifted due to misalignments of pre-calculated detector pointing geometry and refractive effects at lower tangent heights. The tangent height information are improved by an independent fitting
and subsequent retrieval of O\textsubscript{2} profiles \cite{Meyer et al., 2005} using O\textsubscript{2}-A-bands and O\textsubscript{2}-B-bands spectral window. The idea of tangent height correction using O\textsubscript{2} retrieval is stemmed from the fact that O\textsubscript{2} is a well mixed constituent of the atmosphere whose volume mixing ratio is well known. It turn out that the volume mixing ratio of O\textsubscript{2} is directly related to atmospheric temperature and pressure via the ideal gas law.

In general, the atmospheric pressure decreases exponentially with geometric height, a relation which is express as

\[
\frac{p(z)}{P_0} = e^{-\frac{z}{H(z)}}
\]

where \( H(z) = RT(z)/M_{air}g \) is called the scale height. The concept of scale height can be applied individually to atmospheric species \( i \). The scale height of atmospheric species \( i \) is given as

\[
H_i(z) = \frac{RT(z)}{M_i g},
\]

where \( M_i \) is the molecular weight of atmospheric species \( i \). Atmospheric species with less molecular weight than that of air will have large scale height. In the homosphere\footnote{The homosphere refers to the region from the earth surface to approximately 90 km, where major atmospheric constituents are uniformly mixed.} the scale height is approximately \( 7 \pm 1 \) km for air. The variation of the geometric height with the number density of atmospheric constituent can be approximated as

\[
n_i(z) \approx n_0 e^{\frac{z-z_0}{H_i(z)}},
\]

however if the scale height is equal to atmospheric scale height the constituent is well mixed and its mole fraction, \( f_i = \frac{n_i}{n_{total}} \), is constant with altitude. Based on this assumption a relation can be obtain between the mole fraction of O\textsubscript{2}, \( f_{oxy}^i \), a well mixed atmospheric constituent and the geometric altitude as

\[
h_{i+1} = h_i - H_{oxy}^i \ln \left( \frac{1 - f_{oxy}^i}{f_{oxy}^i} \right).
\]

An explicit derivation of this relation is provided in Appendix E. Similarly a relation for the tangent height can be formulated where the vertical profiles of O\textsubscript{2} is regarded as true information for the tangent height retrieval. The corresponding VMR, \( C_{oxy,i}^{ret} \), of O\textsubscript{2} retrieved from SCIAMACHY measurements is divided by the true profile, \( C_{oxy,i}^{true} \), and this is regarded as the measure of relative deviation from the true concentrations. An estimation for a better tangent height \( h \) at height layer \( i \) for iteration step \( k + 1 \) is then calculated as

\[
h_{i,k+1} = h_{i,k} - H_{oxy}^i \ln \left( \frac{C_{oxy,i}^{ret}}{C_{oxy,i}^{true}} \right).
\]
The superscript \( \text{ret} \) and \( \text{true} \) represent retrieval result and true information of O\(_2\) concentration, \( C_{\text{oxy}, i} \), respectively. \( H_{\text{oxy}}^2 \) the scale height of oxygen. The a priori information of temperature, pressure and O\(_2\) profiles used for the true tangent height retrieval are taken from US-standard climatology \((\text{NASA, 1976})\). The retrieval scheme uses lunar zenith angle, \( \psi \), in place of ESA’s tangent height as a priori tangent height information. This information is calculated using geometrical relation in Equation 6.40.

### 7.3.2 Retrieved profiles calculation

The final step of the retrieval is to invert the linear path integral in Equation 6.42 to derive vertical profile information of the fitted trace gases using the OE solution as given in Equation 7.7. The entire retrieval process is carried out iteratively using Gauss-Newton iteration scheme. The state vector \( x \) and \( x_0 \) defined as concentrations \( N_j \) for each height layer \( h_i \) and trace gas of interest \( j \) are express numerically as

\[
\begin{align*}
x_0 &= \begin{pmatrix} N_1(h_1) \\ \vdots \\ N_1(h_L) \\ \vdots \\ N_J(h_1) \\ \vdots \\ N_J(h_L) \end{pmatrix} \quad \text{and} \quad x &= \begin{pmatrix} \delta N_1(h_1) + N_1(h_1) \\ \vdots \\ \delta N_1(h_L) + N_1(h_L) \\ \vdots \\ \delta N_J(h_1) + N_J(h_1) \\ \vdots \\ \delta N_J(h_L) + N_J(h_L) \end{pmatrix},
\end{align*}
\]

(7.17)

where \( J \) is the total number of fitted trace gases and \( L \) the total number of height layers, this means each state vector contains \( M = L \times J \) elements. The numerical value of the estimated relative deviation of the true number density from its a priori value, \( x_t \), is given as

\[
\begin{align*}
x_t &= \begin{pmatrix} \delta N_1(h_1)/N_1(h_1) \\ \vdots \\ \delta N_1(h_L)/N_1(h_L) \\ \vdots \\ \delta N_J(h_1)/N_J(h_1) \\ \vdots \\ \delta N_J(h_L)/N_J(h_L) \end{pmatrix}.
\end{align*}
\]

(7.18)

The measurement vectors \( y \) and \( y_0 \) are written as radiance measured by the instrument at a set of discrete wavelengths and tangent heights given as
7.3. RETRIEVAL METHODOLOGY

\[
y = \begin{pmatrix}
\Upsilon(\psi_1, \lambda_1) \\
\vdots \\
\Upsilon(\psi_i, \lambda_i) \\
\vdots \\
\Upsilon(\psi_M, \lambda_1) \\
\vdots \\
\Upsilon(\psi_M, \lambda_J)
\end{pmatrix}
\quad \text{and} \quad
y - y_0 = \begin{pmatrix}
\delta \Upsilon(\psi_1, \lambda_1) \\
\vdots \\
\delta \Upsilon(\psi_i, \lambda_i) \\
\vdots \\
\delta \Upsilon(\psi_M, \lambda_1) \\
\vdots \\
\delta \Upsilon(\psi_M, \lambda_J)
\end{pmatrix}.
\]

(7.19)

Where \(i = 1, \ldots, J\) and \(\psi_m\) is the lunar zenith angle, \(m = 1, \ldots, M\). The linearized forward model operator \(K\) is from Equation 6.47 is computed as

\[
K = \begin{pmatrix}
\tilde{W}_{11}(\psi_1, \lambda_1)q_1 & \ldots & \tilde{W}_{ji}(\psi_1, \lambda_i)q_i & \ldots & \tilde{W}_{jL}(\psi_1, \lambda_1)q_L \\
\vdots & & \vdots & & \vdots \\
\tilde{W}_{11}(\psi_1, \lambda_J)q_1 & \ldots & \tilde{W}_{ji}(\psi_1, \lambda_J)q_i & \ldots & \tilde{W}_{jL}(\psi_1, \lambda_J)q_L \\
\vdots & & \vdots & & \vdots \\
\tilde{W}_{11}(\psi_M, \lambda_1)q_1 & \ldots & \tilde{W}_{ji}(\psi_M, \lambda_i)q_i & \ldots & \tilde{W}_{jL}(\psi_M, \lambda_1)q_L \\
\vdots & & \vdots & & \vdots \\
\tilde{W}_{11}(\psi_M, \lambda_J)q_1 & \ldots & \tilde{W}_{ji}(\psi_M, \lambda_J)q_i & \ldots & \tilde{W}_{jL}(\psi_M, \lambda_J)q_L
\end{pmatrix},
\]

(7.20)

where \(\tilde{W}_{ji}(\psi_m, \lambda_i)\) are the weighting functions appropriate to the relative variation of the corresponding fitted trace gases and is given as,

\[
\tilde{W}_{ji}(\psi_m, \lambda_i) = W_{ji}(\psi_k, \lambda_i)N_j(h_i).
\]

(7.21)

The spectral grid setting and number of discretize grid points generated have limitations. For example grid point generated by GOMETRAN, the occultation retrieval code can not exceed 60000 points. The recommended spectral grid setting for the trace gases fitted is summarized in the Table 7.1. Here it is observed that when line-absorbers such as \(\text{H}_2\text{O}\) and \(\text{O}_2\) are fitted the spectral grid, \(\Delta \lambda\), is very small, this implies much computing time is require for a full run of the retrieval code. The retrieval of \(\text{O}_2\) as discussed in Subsection 7.3.1 is necessary for tangent height correction, this for example takes computing time of about 1–2 hours.

7.3.3 The spectroscopic and a priori data source

Both the forward model calculations and the retrieval algorithms discussed earlier require absorption cross sections for the fitted gas and interfering species that have
CHAPTER 7. RETRIEVAL SCHEME

<table>
<thead>
<tr>
<th>Trace gas</th>
<th>Retrieval window [nm]</th>
<th>Spectral grid (Δλ) [nm]</th>
<th>Number of spectral points</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₂</td>
<td>425–465</td>
<td>0.1–0.2</td>
<td>400</td>
</tr>
<tr>
<td>O₃</td>
<td>520–580</td>
<td>0.1–0.2</td>
<td>600</td>
</tr>
<tr>
<td>O₂, NO₃</td>
<td>615–670</td>
<td>0.01–0.02</td>
<td>7200</td>
</tr>
<tr>
<td>O₃, H₂O</td>
<td>680–690, 757–767</td>
<td>0.001</td>
<td>14000</td>
</tr>
</tbody>
</table>

Table 7.1: Summary of the recommended spectral grid settings for the trace gases fitted so far in lunar occultation retrieval code.

significant extinction in the selected spectral window. O₃ and NO₂ absorption cross sections at five different temperatures in the spectral regions of interest measured at University of Bremen [Burrows et al., 1998] at spectral resolution to allow integration over the SCIAMACHY slit (optical filter) functions were used. Absorption cross sections of all other modeled trace gases in the selected windows, where O₃, NO₂, and NO₃ calculated from HITRAN spectroscopic data base [Rothman et al., 1998] and convolved with SCIAMACHY’s slit function. The spectral range used for O₃ and NO₂ retrieval is listed in Table 7.1. The spectral region less than 400 nm for SCIAMACHY lunar occultation spectral has comparable low signal-to-noise ratio hence this spectral region is not used for O₃ and NO₂ retrieval.

NO₃ absorption cross section at 298 K was taken from Jet Propulsion Laboratory [Sander et al., 1997]. This Absorption cross sections cover the spectral range from 600–670 nm. The retrieval of NO₃ focuses on the intense NO₃ absorption band near 623 nm and 662 nm. A plot of NO₃ absorption cross section at 298 K as a function of wavelength is shown in Fig. 3.1. NO₃ absorption band near 662 nm is overlapped with the absorption features due to water vapor. Whereas NO₃ absorption band near 623 nm is overlapped with absorption features of O₂-γ band and O₄ [Platt et al., 1981; Solomon et al., 1989b]. Absorption cross sections of O₂ and H₂O are calculated using the line-by-line calculation employing spectral parameters provided in the HITRAN data base [Rothman et al., 1998]. These parameters includes line positions, line strength at reference temperature, and air broadening half-widths. For line broadening function, the Voigt function is used [Rozenow, 2001 and references therein].

The a priori parameter for the retrieval i.e. the concentration profiles of all model and fitted atmospheric traces gases species, temperature, and pressure information. The temperature, pressure, NO₂, O₃ and all other trace gases a-priori profiles excluding NO₃ were taken from the US standard atmosphere [NASA, 1976]. The a-priori profile of NO₃ was taken from the results [Schlieter, 2001], obtained from ground based lunar occultation measurements [Aliwell, 1995].
7.4 Retrieval characterization and error analysis

The analysis used to characterize the possible errors for the SCIAMACHY lunar occultation retrievals adopts the general formalism described by \textit{Rodgers} (1990, 2000). In this section, information on how averaging kernel matrix and the retrieval errors are calculated or estimated for SCIAMACHY lunar occultation retrievals is presented.

7.4.1 Retrieval characterization

The averaging kernel matrix, $A$, is a quantity often used to characterize the dependence of the retrieved atmospheric state vector, $\hat{x}$, on variations of the true atmospheric state vector, $x$. $A$ is given as

$$A = \frac{\partial \hat{x}(h_i)}{\partial x(h_j)}.$$  \hfill (7.22)

In OE scheme the average kernels matrix has the following algebraic form:

$$A = (K^T S_y^{-1} K + R)^{-1} K^T S_y^{-1} K$$  \hfill (7.23)

The average kernels matrix can also be expressed in terms of the gain matrix, $G_y$, and the Jacobian matrix, $K$, this expression is given as

$$A = \frac{\partial \hat{x}(h_i)}{\partial x(h_j)} = \frac{\partial \hat{x}}{\partial y} \frac{\partial y}{\partial x} = G_y K$$  \hfill (7.24)

Using Equation \ref{eq:7.23} and taking into account Equation \ref{eq:7.7}, the retrieval solution, $\hat{x}$, can be expressed as

$$\hat{x} = x_0 + A(x_t + x_0).$$  \hfill (7.25)

Usually, the vertical resolution of each retrieval is characterized by examining the row of the averaging kernel that couple the true profile and the retrieved profile of a given trace gas. For an ideal scenario, $A$ is a unit matrix, but in reality the rows of $A$ are peaked functions with finite width. The width is regarded as a measure of the vertical resolution of the retrieved profiles. The gain matrix in Equation \ref{eq:7.24} is expressed as

$$G_y = (K^T S_y^{-1} K + R)^{-1} K^T S_y^{-1}$$  \hfill (7.26)

The gain matrix $G_y$ express in Equation \ref{eq:7.26} is an important quantity, which describes the sensitivity of the retrieval to changes in the measurement.
7.4.2 Error estimation

According to [Rodgers (2000)], the retrieved profile $\hat{x}$ is the result of operating on the measurement with an inverse (retrieval) method $\eta$, thus $\hat{x}$ is express as

$$\hat{x} = \eta(y, \hat{b}, x_a, c)$$  \hspace{1cm} (7.27)

Where $\hat{x}$ indicates an estimated quantity, rather than a true state, $\hat{b}$ is the best estimate of the true forward model parameters $b$, $x_a$ is the a priori estimate of the true state $x$ and $c$ comprise other parameters that do not appear in the forward model but have influence on the retrieval, an example of $c$ parameter is the convergence criteria. If we relate the retrieval to the true state by substituting Equation 7.3 into Equation 7.27 we will obtain a transfer function given as

$$\hat{x} = \eta(F(x, b) + \epsilon, \hat{b}, x_a, c)$$  \hspace{1cm} (7.28)

Linearizing the transfer function and including all the possible error terms due to measurement parameters, physics in forward model, and retrieval parameter we will get an expression for the total error estimate as

$$\hat{x} - x = (A - I)(x - x_a) + G_yK\Delta b + G_y\Delta f(x, b, b') + G_y\epsilon.$$  \hspace{1cm} (7.29)

Each of the terms in the right hand side of Equation 7.29 correspond to an error term in the final result. The first is the smoothing error term, $S_s$. In our retrieval scheme this is due mainly to Twomey-Tikhonov regularization. Owing to the fact that the true state is not normally known, it becomes difficult to determine the actual smoothing error, $(A - I)(x - x_a)$. What is therefore done is to find a realistic statistical estimate of the error, this is calculated as

$$S_s = (A - I)S_e(A - I)^T,$$  \hspace{1cm} (7.30)

where $I$ is the identity matrix and $S_e$ is the covariance matrix of the ensemble of state about the mean state. In our situation we estimate the smoothing error assuming that $S_e = S_x$. This is achieved by running the retrieval scheme without regularization at the measurement height resolution so that the only constrain is the a priori information. This implies Equation 7.30 can now be express as

$$S_s = (A - I)S_x(A - I)^T,$$  \hspace{1cm} (7.31)

and the estimate of the smoothing error $\sigma_s$ calculated as the square root of the diagonal of $S_s$.

The second term $G_yK\Delta b$ in Equation 7.29 is the model parameter error term and the third term $G_y\Delta f(x, b, b')$ is the forward model error term. The last term
$G_y \epsilon$ is the retrieval noise term. The retrieval noise term we will call the random error term is the easiest term to calculate. The random error $\sigma_r$ is calculated as the square root of the diagonal covariance of the retrieval noise, $S_r$. Where the covariance of the retrieval noise, $S_r$, is given as

$$S_r = G_y S_y G_y^T$$

or

$$S_r = (K^T S_y^{-1} K + R)^{-1} K^T S_y^{-1} K (K^T S_y^{-1} K + R)^{-1}.$$  

Equation (7.33) is used in this particular study to calculate the retrieved random error.

The model parameter error and forward model error terms we represent as systematic error term, $S_f$. The covariance of systematic error $S_f$ is express as

$$S_f = G_y K_b S_b K_b^T G_y^T,$$

where $S_b$ is the error covariance matrix of the model parameter $b$ and $K_b$ is the corresponding Jacobian matrix. The sensitivity $\Delta b_i$ due to uncertain $b_i$ parameter is calculated as

$$\Delta y_i = G_y \Delta b_i,$$  

where $\Delta y_i$ is the difference between the reference spectrum calculated using the retrieved profile $\hat{x}$ and a spectrum calculated with parameter $b_i$ perturbed by an assumed uncertainty of $1\sigma$ [Tsidu et al., 2004]. If $\Delta y_i$ is calculated then evaluation of the sensitivities $G_y$ and $K_b$ will become an easy task, which will lead to calculation of the systematic errors due to the model parameter $b_i$.

The total systematic errors includes the uncertainties from all interfering gases which are not jointly retrieved with the target gases. Others are uncertainties from: temperature, tangent height shift, instrumental line shape, spectral shift, and absorption cross sections of the retrieved trace gases.
Part III

Results and discussion
Chapter 8

O₃ and NO₂ results

In this chapter the results of O₃ and NO₂ retrieved from SCIAMACHY lunar occultation measurements are presented. Simultaneous measurement of NO₂ and O₃ will provide the opportunity not only for understanding NO₂ budget, but also these measurements will contribute to better a understanding of long-term trends in stratospheric O₃. The first section of the chapter is devoted to ozone results and ozone validation with other satellite instruments is presented in the second section. The last two sections present NO₂ retrieval results and NO₂ validation, respectively. A portion of the results presented here has been published (Amekudzi et al. 2005a).

8.1 Ozone retrieval results

The results of O₃ vertical profiles retrieved from lunar occultation spectra using the oe method are presented here. The data sets analyzed were measurement performed from March to June 2003 and January to June 2004. The retrieval was carried out using 430–460 nm and 510–560 nm within the Chappius absorption band of ozone with a 0.2 nm retrieval spectral resolution. The Huggins absorption band of ozone was not used because the uv spectral window for measured lunar spectra has low signal-to-noise ratio.

Details of the retrieval procedure have been presented in Chapter 7. A polynomial of order 3 was subtracted for simultaneous retrieval of O₃ and NO₂. Smoothing constraint parameters (Twomey-Tikhonov regularization) parameters used for O₃ retrieval were T₁ = 50 and T₂ = 100. The appropriate signal-to-noise ratio for the chosen spectral range and the retrieval altitude of 18–45 km is in the range of 1000–2000. Gaussian slit function was used and a constant a priori covariance of
Figure 8.1: Spectral fit of ozone at 21 km (left) and 30 km (right) tangent height (April 12, 2003, orbit number 5865, and SZA 109.3°). The dotted line represents the modeled differential optical depth and the solid line is the measured differential optical depth.

95% was applied as additional constraint to the retrieval solution.

8.1.1 Spectral fit and residual

The left panel of Figure 8.1 shows the spectral fit of O₃ at 21 km and the right panel the spectra fit of O₃ at 30 km. These fits correspond to a lunar occultation measurement of April 12, 2003, ENVISAT orbit number 5865 and SZA of 109.3°. The dotted line is the modeled differential optical depth and the solid line is the measured differential optical depth of O₃. The fit at 21 km shows higher value of the differential optical depth compared to the fit at 30 km. The quality of the spectral fits are high because they demonstrate good fit to the ozone absorption features.

The residual of the retrieval, i.e. the difference between the measured and the simulated differential transmission spectra is shown in Figure 8.2. The residual shown is the spectral residual of fitted gases in the spectral range of 510–560 nm (mainly O₃ and NO₂). In an ideal case, where the transmission is perfectly modeled, the residual should reflect the signal-to-noise ratio of the measurement. The quality of the retrieval therefore can be inferred from the residual. The spectral residual is in the order of 0.3% and shows a systematic structure for all relevant height layers. This value is reasonable and agrees favorably with the signal-to-noise ratio of the measurements.
8.1. OZONE RETRIEVAL RESULTS

8.1.2 Averaging kernels and retrieval errors

Averaging kernels

The left panel of Figure 8.3 presents a typical $O_3$ averaging kernel for selected altitudes calculated using Equation 7.23 for a spring scenario within the Antarctic ($76.9^\circ S, 089.6^\circ$). The geo-location information of this result is the same as that presented in Figure 8.1. From the averaging kernels, the highest averaging kernel of $O_3$ is approximately 0.5–0.55, which is in altitude range of 30–36 km. The averaging kernel for the altitude range of 19–26 km is approximately 0.37–0.45 and the averaging kernel near 40 km is 0.42. The averaging kernel at 42 km is approximately 0.30. The lowest averaging kernel is near 45 km and above 45 km the retrieval is weakly sensitive to ozone information in this region. The averaging kernel shown provide information on the vertical resolution of the measurement, which is in the range of 3–4 km. A negative maxima is seen in the averaging kernels shown, which is an indication of anti-correlation between the $O_3$ information content at the height of interest and the $O_3$ value in the vicinity (nearby altitudes).
Figure 8.3: Averaging kernel of selected altitudes for retrieved O\textsubscript{3} (left), this result is based on 1 km retrieval grid. Retrieval errors calculated from the O\textsubscript{3} (right). Solid lines is the random error, dotted lines the smoothing error and the dash line the total error.

retrieval errors

In general the errors on the retrieved profiles are random (measurement noise) error, smoothing error (error due to limiting vertical resolution of the measurement), and the systematic errors (error due to instrument pointing, calibration error, spectral line strength, absorption cross sections, and non-fitted interfering gases). Quantification of all these error sources in the retrieval is quite a tricky and difficult task. The first two error sources (random and smoothing errors) are determined using the method described in Section 7.4.

Typical results of the solution standard deviation (total error) and the respective contributions from measurement noise and smoothing errors standard deviations are displayed in the right panel of Figure 8.3. The smaller standard deviations are in altitude range where information content from measurements are high. In the altitude range of 18–35 km smoothing error is less than 5% and in the same altitude range the measurement noise and total errors are less than 10%. The smoothing error in the altitude range of 36–45 km is in the range of 5–14%, the measurement noise error in the same altitude range is in the range of 10–24% and the total error in the same altitude range is in the range of 15–30%.

The systematic errors in the retrieval includes: pointing error, calibration error, error in absorption cross sections, and error due to non-fitted interfering gases.

Calibration errors in the retrieval are negligible as the measured lunar spectra are divided by their corresponding measured lunar extra terrestrial spectrum. Temperature dependent absorption cross sections of ozone are used for the zone...
### 8.1. OZONE RETRIEVAL RESULTS

<table>
<thead>
<tr>
<th>Altitude [km]</th>
<th>Random error</th>
<th>Smoothing error</th>
<th>Total error</th>
<th>Pointing error</th>
<th>Absorption cross sections</th>
</tr>
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<td>20</td>
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<td>≤15</td>
<td>≤30</td>
<td>≤20</td>
<td>≤1</td>
</tr>
</tbody>
</table>

Table 8.1: Summary of the estimated retrieval errors: random due to spectral noise, smoothing error, total error, systematic error due to inaccurate pointing and absorption cross section for the ozone profile retrieval from SCIAMACHY lunar occultation. These values are in relative units (%).

retrieval, which contributes to the systematic error of less than 1% [von Savigny (2002)]. The Chappius band of ozone spectral window used for the retrieval, the non fitted interfering gases in this region are weak absorbers and hence the error due to the interfering of these gases are negligible. The major source of systematic error in the retrieval is the instrumental pointing error, as inaccurate knowledge of the satellite’s pointing direction will lead to a significant systematic error in the retrieval. These errors occur because the retrieved ozone profile is shifted vertically by the error in the tangent height assignment. Where the ozone density gradients are large (e.g. below and above ozone peak), tangent height shift will lead to relatively large systematic errors.

Sensitivity studies described in [Kaiser et al. (2004)] showed that scaling the ozone profiles by a factors of 0.8 and 1.2 leads to tangent height difference up to 1km. Scaling the ozone by a factors of 0.5 and 2.0 leads to tangent height difference up to 3km. [von Savigny et al. (2005a)] reported that retrieved tangent height offset of 1.13 km leads to systematic error in ozone profiles up to 25% above ozone concentration peak and up to 20% below the peak. In order to reduce the pointing errors in the retrieval to less than 5%, the tangent height accuracy has to be better than approximately 0.25 km. The corrected tangent height information used have accuracy in the range of 0.5–1 km this will lead to pointing error in the range of 10–20% in the retrieved profile. The summary of all estimated errors of the retrieval is presented in Table 8.1.

#### 8.1.3 Ozone number density profiles

A simple way to obtain first insight in the quality of the retrieved profiles is to compare the retrieved profiles with its own a-priori as the a priori is the first guess of the true profile. Figure 8.4 shows representative profiles of outside the vortex.
Figure 8.4: Ozone profiles (solid lines) as retrieved from sciamachy lunar occultation measurements. Retrieved profile for orbit 5413, 14/03/2003 at sza of 110.2° (left). Retrieved profile for orbit 5865, 14/04/2003 at sza of 109.3° (right). The dotted line is the a priori profile.

(1) derived from measurements performed at 06.44 hr local time, (62.8° S, 229.6°) on 14 March 2003 compared with the a priori profiles. At the right panel is the representative profiles for inside the vortex for measurements taken at 20.28 hr local time, (76.9° S, 089.6°) on 14 April 2003. The same a priori profiles were used in the retrieval. The maximum concentration of the a priori profile is approximately 5.0 × 10^{12} cm^{-3} near 23 km altitude. The retrieved ozone peak outside the vortex is approximately 4.4 × 10^{12} cm^{-3} and shifted about 3 km lower than the a priori value. The retrieved ozone peak inside the vortex is far less than the a priori value (3.6 × 10^{12} cm^{-3}), and about (4–5 km) lower in altitude than the a priori. In addition, the retrieved profiles turn close to the a priori values at the region of low sensitivity. The pronounced difference between the a priori profile and the retrieved profiles are an indication that in general the retrievals are not over constrained.

8.2 Ozone validation results

In order to assess the O₃ retrieval accuracy, the retrieved O₃ profiles are validated by comparison with other satellite instruments (HALOE, SAGE-II and -III, POAM-III and MIPAS). The result of these validation is presented in this section. As SCIAMACHY lunar occultation measurements are performed only when the Moon is visible there are a few measurements. The best criteria employed to obtain considerable coincidences for the validation is a large collocation distance corresponding to latitude and longitude difference of 5° and 10° respectively.
8.2. OZONE VALIDATION RESULTS

8.2.1 SCIAMACHY-HALOE ozone comparisons

The HALOE instrument on board Upper Atmosphere Research Satellite (UARS) has been in operation since October 1991. In this study the version 19 (v19) downloaded from (http://haloedata.larc.nasa.gov) was used. The validation and quality of HALOE ozone profiles was reported by Brühl et al. (1996). The accuracy of HALOE ozone profiles according to Brühl et al. (1996) are 20–30% in the altitude range of 15–30 km and 6–12% in the altitude range of 30–60 km. The SCIAMACHY-HALOE validation was based on 15 single collocated measurements. The geographical coincidence between matched measurements considered was in the range of 600–1000 km. The collocated events were taken on 13th and 14th March, 2003. Figure 8.5 presents examples of the SCIAMACHY-HALOE validation results. Ozone profiles of SCIAMACHY at (63.0° S, 84.0°) and HALOE at (68.9° S, 75.5°) are shown in left panel, whereas in the right panel the ozone profiles of SCIAMACHY at (62.0° S, 229.0°) and HALOE at (68.4° S, 244.5°) are shown. There is good agreement observed in the altitude range of 23–45 km for the result in the left panel of Figure 8.5. However, in the altitude range of 19–22 km SCIAMACHY result is slightly higher than HALOE result. The result shown in the right panel agree fairly well in the lower stratosphere (18–26 km), however above 26 km a slight bias is observed.

Figure 8.6 shows the statistical result of the 2003 comparison of SCIAMACHY ozone profiles with HALOE. There is a positive bias of SCIAMACHY to HALOE mean ozone density profiles in the middle stratosphere (23–45 km). The mean relative
Figure 8.6: Left: mean ozone density profiles for 15 collocated events in March 2003, for SCIAMACHY in grey and HALOE in black. The dotted lines are the standard deviations with respect to the mean. Right: the mean relative deviation (solid line) and the rms of the mean relative deviation (dotted line) of the comparison of 15 collocated SCIAMACHY ozone profiles with HALOE.

deviations is in the range of 10–25% of SCIAMACHY to HALOE and the root mean square of the mean relative deviations (rms) is in the range of 5–50% for the altitude range of 17–43 km.

The SCIAMACHY-HALOE validation was repeated for 2004 data using the same criteria as in the case of 2003 data. This validation was also based on 15 collocated events. The coincidence measurements were taken on 4th and 5th of March 2004. Example of this result is shown in Figure 8.7. In the left panel the results of March 4 2004 is shown. Good agreement is observed between SCIAMACHY and HALOE profiles in the altitude range of 26–35 km. Above 35 km SCIAMACHY result is slightly lower than the result of HALOE. There is a disagreement between SCIAMACHY and HALOE results in the altitude range of 20–25 km. The result of March 5 2004 is shown in the right panel of Figure 8.7. The March 5 2004 result displayed a systematically lower absolute value for SCIAMACHY ozone concentration compared to HALOE result.

The statistical results of 2004 SCIAMACHY-HALOE validation is shown in Figure 8.8. Good agreement is observed between SCIAMACHY and HALOE mean profiles shown in the right panel of Figure 8.8. However, SCIAMACHY mean profile is slightly higher than HALOE mean profile in the altitude range of 19–32 km. In addition, in the altitude range of 34–45 km SCIAMACHY mean profile is slightly lower than HALOE result. The mean relative deviations and the root mean square of the
8.2. OZONE VALIDATION RESULTS

Figure 8.7: Example of collocated ozone number density profiles for March 4 2004 orbit number 10518 (left) and March 5 2004 orbit number 10524 (right). The dotted line is SCIAMACHY result and the solid line is HALOE result.

The mean relative deviation is displayed in the right panel of Figure 8.8. The mean relative deviations is in the range of -30\% to +20\% between 18 and 45 km. The rms is in the range of 10–40\% in the altitude ranges of 18–26 km and 31–45 km. In the altitude range of 26–31 km the rms is in the range of 40–60\%.

8.2.2 SCIAMACHY POAM-III O₃ comparisons

The third Polar Ozone and Aerosol Measurement (POAM-III) is a solar occultation experiment instrument on board the French SPOT-4 spacecraft launched into a polar sun-synchronous orbit in March 1998. The POAM-III instrument performs occultation measurements in both hemispheres of the Earth’s atmosphere. The latitudinal coverage of the POAM-III instrument are (54° N–70° N) and (62° S– 87° S) (Lucke et al., 1999).

The first validation results of POAM-III was carried out with HALOE instrument, these results were reported by Lucke et al. (1999). A cross-validation with HALOE, SAGE-II and ozone sonde was the follow up publication, reported by Rusch et al. (2001). In these publications POAM-III ozone densities are systematically lower than HALOE ozone number densities by 7\% in the altitude range of 20–30 km. The POAM-III ozone number densities were also systematically lower than SAGE-II ozone number densities by 5\% in the altitude range of 20–40 km. In general validation for POAM-III with other instruments reveal that POAM-III overestimates the ozone densities by approximately 5\% at least in the altitude range of 20–40 km.
CHAPTER 8. \( \text{O}_3 \) AND \( \text{NO}_2 \) RESULTS

Figure 8.8: Left: mean ozone density profiles for 15 collocated events in March 2004, for SCIAMACHY in grey and HALOE in black. Right: the mean relative deviation (solid line) and the rms of the mean relative deviation (dotted line) of the comparison of 15 collocated SCIAMACHY ozone profiles with HALOE.

[Savigny, 2002] and references therein. The quality of POAM-III ozone number densities is in the range of 5–10% between 13 and 60 km. Here, the results of validation carried out for POAM-III retrieved ozone vertical profiles and SCIAMACHY lunar occultation retrieved ozone results are presented.

The criteria employed in this study to select coincidence measurements is that measurements were taken on the same day with collocation distance in the range of 300–900 km. In total, 51 coincidences were found, these coincidences correspond to measurement events of 13–15 April 2003, 11, 14 and 15 May 2003, and 12 June 2003. Examples of this study are displayed in Figure 8.9. In general there is a good agreement between the POAM-III and SCIAMACHY lunar ozone profiles with a very small bias between 22 and 40 km. From the results of the 51 profiles the mean profiles, the mean relative deviation (mean deviation) and the root mean square of the mean deviation (rms) were calculated. These results are shown in Figure 8.10. The mean deviations for SCIAMACHY compared to POAM-III are in the range of 1–28% in the altitude range of 24–45 km, with negative bias in range of 2–16% in the lower altitudes (18–23 km). The rms of the deviations are in the range of 10–45% in the altitude range of 18–45 km.
8.2. OZONE VALIDATION RESULTS

Figure 8.9: Example of ozone density profiles from coincident SCIAMACHY and POAM-III retrievals. The dotted line is the result for SCIAMACHY and the solid line for POAM-III. Results for 15th of April 2003 (left) and for 14th May 2003 (right).

Figure 8.10: Left: Mean ozone density profiles for 51 collocated events, with SCIAMACHY in grey and POAM-III in black. Right: the mean relative deviation (solid line) and the rms of the mean relative deviation (dotted line) of the comparison of 51 collocated SCIAMACHY $O_3$ profiles with POAM-III.
8.2.3 SCIAMACHY-SAGE II and III ozone comparisons

The results of SCIAMACHY and SAGE-II ozone comparisons are shown here. This is followed by SCIAMACHY-SAGE-III ozone comparisons.

SCIAMACHY-SAGE II ozone comparisons

The second Stratospheric Aerosol and Gas Experiment (SAGE-II) on board the Earth Radiation Budget Satellite (ERBS) launched in October 1984, is a solar occultation instrument, measuring the solar transmitted radiation through the Earth’s atmosphere in the UV-visible and near infrared spectral region. The SAGE-II instrument provides the longest record of satellite high-resolution ozone and NO\textsubscript{2} profile measurements, which have been extensively validated (Cunnold et al., 1989, 1991). The quality of SAGE-II ozone number density profiles is 10\% in the altitude range of 15–50 km (Cunnold et al., 1989). In this study, the validation results for SCIAMACHY ozone profiles with ozone profiles from the recently provided SAGE-II data version 6.2 (http://www.sage2.larc.nasa.gov/data) are presented.

The criteria employed in this study is that coincidence measurements were taken from the same day, having a collocation distance in the range of 600–1000 km. In addition a local time difference not more than 8 hrs was considered. Based on this criteria, 59 coincidences were found. These measurements were carried out from 1–6 February 2004. Figure 8.11 shows representative results of this study. A good agreement is observed for all relevant altitudes of SCIAMACHY measurements (18–45 km). The mean profiles show an underestimation of ozone number density in the altitude range of 18–42 km for SCIAMACHY results. The relative deviation calculated shows a slight negative bias in the range of 2–22\% for altitude range of 18–40 km. The standard deviation of the relative mean is in the range of 7–50\% (see Figure 8.12).

SCIAMACHY-SAGE III ozone comparisons

Ozone number density profiles derived from SCIAMACHY lunar occultation spectroscopic data were also compared with profiles retrieved from collocated SAGE-III lunar occultation measurements. SAGE-III ozone profiles are retrieved from 15 km to 50 km with vertical resolution of 0.5 km (McCormick et al., 2002). The criteria for this study was that coincident measurements were taken on the same day with a latitudinal and longitudinal difference less than 5° and 10°, respectively. These measurements were taken on the 12th of April, 2003 with a local time difference of 3–4 hours. Figure 8.13 shows the results of comparing the mean ozone number density profiles of 9 coincident SCIAMACHY and SAGE-III profiles. In general a good
8.2. OZONE VALIDATION RESULTS

Figure 8.11: Two examples of ozone density profiles from coincident SCIAMACHY and SAGE-II retrievals from 4th of February 2004. The dotted line is the result for SCIAMACHY and the solid line for SAGE-II.

Figure 8.12: Left: Mean ozone density profile for 59 collocated events, with SCIAMACHY in grey and SAGE-II in black. Right: The mean relative deviation (solid line) and the rms of the mean relative deviation (dotted line) of the comparison of 59 collocated SCIAMACHY $O_3$ profiles with SAGE-II.
agreement is observed, however SCIAMACHY results are slightly lower (2–8%) than SAGE-III.

8.2.4 SCIAMACHY-MIPAS ozone comparisons

Figures 8.14 and 8.15 are the results of the comparisons of SCIAMACHY and MIPAS (Michelson Interferometer for Passive Atmospheric Sounding) O$_3$ number density profiles. This study was carried out as a preliminary validation for both instruments, which carried out their measurements on the same satellite (ENVISAT). The distances between collocated events used for this study were in the range of 30–250 km and these measurements were taken from March to June 2003. Figure (8.14) shows the representative profiles of the SCIAMACHY-MIPAS comparisons. A typical result for 13 March 2003 is shown in the left panel and a result for 14 April 2003 is shown in the right panel. In general good agreement is observed in both examples, except for a slight bias observed in the altitude range of 27–35 km and 20–24 km for the result in the left panel.

The statistical results are presented in Figure 8.15, these study were based on 43 single profiles. A slight negative bias of SCIAMACHY mean ozone profiles...
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![Graphs showing ozone density profiles](image)

Figure 8.14: Examples of ozone density profiles from coincident SCIAMACHY and MIPAS retrievals. The dotted line is the result for SCIAMACHY and the solid line for MIPAS. Profiles for 13th of March 2003 (left) and for 14th April 2003 (right).

<table>
<thead>
<tr>
<th>Instruments</th>
<th>Altitude [km]</th>
<th>N</th>
<th>Mean difference [10^12 molec/cm^3]</th>
<th>Bias [%]</th>
<th>Rms [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>HALOE</td>
<td>24–45</td>
<td>15</td>
<td>≤ 0.5</td>
<td>≤ 25.0</td>
<td>≤ 50.0</td>
</tr>
<tr>
<td>POAM-III</td>
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<td>51</td>
<td>≤ 0.2</td>
<td>≤ 20.0</td>
<td>≤ 45.0</td>
</tr>
<tr>
<td>SAGE-II</td>
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<td>≤ 0.4</td>
<td>≤ 15.0</td>
<td>≤ 50.0</td>
</tr>
<tr>
<td>SAGE-III</td>
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<td>9</td>
<td>≤ 0.2</td>
<td>≤ 8.0</td>
<td></td>
</tr>
<tr>
<td>MIPAS</td>
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<td>43</td>
<td>≤ 0.5</td>
<td>≤ 15.0</td>
<td>≤ 30.0</td>
</tr>
</tbody>
</table>

Table 8.2: Summary of ozone validation results for SCIAMACHY compared with other instruments. N is the number of collocation of each comparison. The bias typifies the mean relative deviation of the SCIAMACHY to the other instruments compared to MIPAS between 18 to 45 km observed. The mean relative deviations of SCIAMACHY to MIPAS and the rms of ozone results are respectively in the range of -15% to -5% and 10–30% in the altitude range of 25–40 km.

8.2.5 Summary of ozone validation

Ozone profiles retrieved from SCIAMACHY lunar occultation measurements were compared with HALOE, POAM-III, SAGE-II and -III, and MIPAS profiles. In general, results from SCIAMACHY are systematically lower by 8–25% than the results of all the other instruments. Examples of ozone profiles for all the comparisons are displayed in Appendix A. The main statistical results of the SCIAMACHY lunar occultation ozone validation are summarized in Table 8.2. The systematic bias
found in the SCIAMACHY retrieved ozone profiles with profiles retrieved from other instruments is mainly due to pointing error. According to [von Savigny et al. (2005a) and references therein] 250 m shift in tangent height will translate to less than 5% error in ozone profiles and 500 m shift in tangent height will translate to about 10% systematic error in the retrieved profiles. Although tangent height correction procedure were applied to each data set, we found that there is pointing error of 0.5–1 km, will leads to systematic bias of 10–20% (Brinksma et al. 2005).
8.3. NO$_2$ RETRIEVAL RESULTS

This section presents the results of NO$_2$ vertical profiles retrieved from lunar occultation spectra using OE method. The data set analyzed were similar to those of O$_3$ retrieval. NO$_2$ and O$_3$ were fitted simultaneously using the retrieval window of 430–460 nm and 510–560 nm. Smoothing constraint parameter (Twomey-Tikhonov regularization parameters) used for NO$_2$ retrieval was $T_1 = 1 \times 10^2$ and $T_2 = 1 \times 10^3$ and the retrieval altitude range is 18–40 km.

8.3.1 Spectral fit and residual

The left panel of Figure 8.16 shows the spectral fit of NO$_2$ at 21 km and the right panel the spectra fit of NO$_2$ at 30 km. These fits correspond to lunar occultation measurements for April 14, 2003, ENVISAT orbit number 5865 and SZA of 109.3$^\circ$. The dotted line is the modeled differential optical depth and the solid line is the measured differential optical depth of NO$_2$. The fit at 21 km shows higher absolute value of the differential optical depth compared to the fit at 30 km. The spectral fits are good and show absorption features of NO$_2$.

The residual of the retrieved NO$_2$ is given in Figure 8.17. The residual shown is the spectral residual of fitted gases in the spectral range of 430–460 nm. The spectral residual of NO$_2$ is in the order of 0.2% for all relevant height layers.
8.3.2 Averaging kernels and retrieval errors

Averaging kernels for NO$_2$ for selected retrieval altitude is displayed in the left panel of Figure 8.18. The NO$_2$ averaging kernel shown correspond to the example presented in Figure 8.1. From the averaging kernels, the highest sensitivity of NO$_2$ is at altitude of 22 km and 32 km. The sensitivity for the altitude range of 25–30 km is approximately 0.40. The sensitivity near 40 km is approximately 0.16. Above 40 km and below 18 km the retrieval is not sensitive enough to NO$_2$ information. The vertical resolution of the measurement from the averaging kernels is in the range of 3–4 km.

The solution standard deviation (total error) and the respective contributions from measurement noise and smoothing are shown in the right panel of Figure 8.18. In general the maximum retrieval precision is less than 30 %. In the altitude range of 20–35 km the smoothing error is less than 7 % and in the same altitude range the measurement noise and total errors are less than 12 %. The smoothing error at the extreme altitudes 18 km and 40 km is approximately 10 % and 12 %, respectively. The measurement noise error at these extreme altitudes is about 13 % and 25 %, respectively, whereas the total errors at these same altitudes are about 23 % and 30 %, respectively. The summary of the retrieval errors in selected altitude ranged
8.3. NO$_2$ RETRIEVAL RESULTS

![Averaging kernel of selected altitudes for retrieved NO$_2$](image)

Figure 8.18: Averaging kernel of selected altitudes for retrieved NO$_2$ (left), this result is based on 1 km retrieval grid. Retrieval errors calculated from the OE for NO$_2$ (right). Solid lines is the random error, dotted lines the smoothing error and the total error.

<table>
<thead>
<tr>
<th>Altitude [km]</th>
<th>Random error</th>
<th>Smoothing error</th>
<th>Total error</th>
<th>Pointing error</th>
<th>Absorption cross sections</th>
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</thead>
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<td>$\leq 10$</td>
<td>$\leq 10$</td>
<td>$\leq 1$</td>
</tr>
<tr>
<td>25</td>
<td>$\leq 6$</td>
<td>$\leq 2$</td>
<td>$\leq 7$</td>
<td>$\leq 10$</td>
<td>$\leq 1$</td>
</tr>
<tr>
<td>30</td>
<td>$\leq 7$</td>
<td>$\leq 2$</td>
<td>$\leq 8$</td>
<td>$\leq 15$</td>
<td>$\leq 1$</td>
</tr>
<tr>
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<td>$\leq 15$</td>
<td>$\leq 6$</td>
<td>$\leq 18$</td>
<td>$\leq 15$</td>
<td>$\leq 1$</td>
</tr>
<tr>
<td>40</td>
<td>$\leq 30$</td>
<td>$\leq 20$</td>
<td>$\leq 40$</td>
<td>$\leq 20$</td>
<td>$\leq 1$</td>
</tr>
</tbody>
</table>

Table 8.3: Summary of the retrieval errors estimated for NO$_2$ retrieved from SCIAMACHY lunar occultation measurements. These values are in relative units (%).

Table is shown in Table 8.3. The systematic errors are the same as those discussed in Subsection 8.1.2.

8.3.3 NO$_2$ number density profiles

Figure 8.19 shows representative NO$_2$ profiles derived simultaneously with ozone, shown in Fig 8.4. The result corresponds to an outside vortex scenario (left) and an inside vortex scenario (right). The same a priori profiles were used in the retrieval, the maximum concentration of the a priori profile is $3.1 \times 10^9$ cm$^{-3}$ near 25 km altitude. The retrieved NO$_2$ peak outside vortex is shifted upward about 5 km and has approximately $1.1 \times 10^9$ cm$^{-3}$ more NO$_2$ concentration than its a priori value. The retrieved NO$_2$ inside the vortex shows a similar trend as the outside vortex result. The peak value for outside the vortex result is slightly less than 30 km and
Figure 8.19: NO$_2$ profiles (solid lines) as retrieved from SCIAMACHY lunar occultation measurements. Retrieved profile for orbit 5413, 14/03/2003 at sza of 110.2$^\circ$ (left). Retrieved profile for orbit 5865, 14/04/2003 at sza of 109.3$^\circ$ (right). The dotted line is the a priori profile. The error bar represent the maximum NO$_2$ retrieval error of 20%.

about 3–4 km higher in altitude than the a priori profile. The maximum number density for the inside vortex result is approximately 3.4×10$^9$ cm$^{-3}$, thus about 0.3×10$^9$ cm$^{-3}$ more than the a priori profile maximum. Below 20 km and above 40 km the retrieved profiles turn close to the a priori. The pronounced difference between the a priori information and retrieved NO$_2$ result prove that in general the retrievals are not over-constrained.

8.4 NO$_2$ validation results

NO$_2$ in the stratosphere is a relatively short-lived trace gas, and it has a significant diurnal variability. The concentration of NO$_2$ depends strongly on the sza (local-time and the history of exposure to sunlight), which makes validation of NO$_2$ measurements difficult. In particular as SCIAMACHY in lunar occultation mode starts measurements a few hours (1–3 hrs) after sunset and a few hours before sunrise, it is more difficult to get coincidence measurements both in location and local-time. To carry out validation study for SCIAMACHY measured lunar occultation NO$_2$ profiles at sza $\geq$ 95$^\circ$ with solar occultation measurement at sza $\leq$ 90, a 1-D photochemical model of the stratosphere is used (Bracher et al., 2005).

The 1-D photochemical model used for the photochemical correction of NO$_2$ is similar to the SLIMCAT photochemical model (Chipperfield, 1999; Sinnhuber et al., 2003). The reaction rates and absorption cross sections were taken from the JPL recommendation (Sander et al., 2003). The model includes 135 chemical
8.4. NO$_2$ VALIDATION RESULTS

reactions including gas-phase and heterogeneous reactions, 44 photolysis reactions of 52 species, which are of relevance to stratospheric chemistry. The model was run with a chemical time-step of 5 min and model output is every 15 min. The photochemical scheme in the 1-D model was driven from the chemistry scheme of the 2-D model, and considers exactly the same chemical reactions and species. The model is run over a period of 3 days. NO$_2$ profiles from HALOE sunrise measurements are transformed to the SZA of the SCIAMACHY lunar occultation measurement, then these two NO$_2$ results are compared. Detailed description of the NO$_2$ photochemical correction scheme is given in (Bracher et al., 2005). SCIAMACHY NO$_2$ results were also compared with MIPAS and SAGE-III but without photochemical correction scheme procedure applied, because only measurements at similar SZA were compared.

8.4.1 SCIAMACHY-HALOE NO$_2$ comparison

In this study HALOE version 19 data was used. The NO$_2$ data from HALOE version 19 are excellent within 10–15% from altitude range of 20–40 km in clear air conditions, but exhibit a low bias in the presence of aerosols loading (Gordley et al., 1996). The vertical resolution of HALOE data is around 2 km. The spatial and time criteria applied is similar to SCIAMACHY-HALOE ozone validation in Subsection 8.2.1. In addition, to avoid matches where the air volume sampled were coming from different air masses, all coincident measurements were checked for the Potential Vorticity (PV) according to the method described in (Bracher et al., 2004 and references therein). Figure 8.20 shows a representative NO$_2$ profiles for the SCIAMACHY-HALOE validation. Good agreement between the SCIAMACHY measurement and the model result with input of HALOE measurement at SCIAMACHY SZA is observed in the altitude range of 25–35 km for result in the left panel. However, the model underestimates the NO$_2$ number density in the lower stratosphere (altitude less than 25 km) and above 35 km. The figure in the right panel shows good agreement in the altitude range of 20–30 km, but above 30 km the model underestimates the NO$_2$ number densities. All the examples profiles are shown in Appendix B where there are a tangent height shift of 1–2 km for some cases between the SCIAMACHY and the model results with input of HALOE measurement at SCIAMACHY SZA.

The results of the mean profiles, the relative mean deviations and the rms are shown in Figure 8.21. Between the altitude range of 24–30 km a slight negative bias of less than 10% of SCIAMACHY to HALOE-Model is observed. The relative deviations of SCIAMACHY to HALOE-Model is in the range of -5–20% in the altitude range of 22–36 km and the rms is in the range of ±10% to ±45% for the same altitude range.
CHAPTER 8. \( O_3 \) AND \( \text{NO}_2 \) RESULTS

Figure 8.20: Examples of \( \text{NO}_2 \) density profiles for SCIAMACHY and HALOE comparison. The red line signifies the SCIAMACHY, the black line the HALOE, the green line the model at the HALOE SZA, and the blue line the model at the SCIAMACHY SZA. SCIAMACHY at SZA of 110.4\(^\circ\) and HALOE at SZA=90.0\(^\circ\) sunrise (left). SCIAMACHY at SZA of 110.2\(^\circ\) and HALOE at SZA of 90.0\(^\circ\) sunrise (right).

Figure 8.21: Left: mean \( \text{NO}_2 \) density profile for 15 collocated events, SCIAMACHY in grey and HALOE in black. Right: the mean relative deviation (solid line) and the rms of the mean relative deviation (dotted line) of these comparisons.
8.4. NO$_2$ VALIDATION RESULTS

8.4.2 SCIAMACHY-MIPAS NO$_2$ comparison

SCIAMACHY and MIPAS NO$_2$ number density profiles were compared. Due to strong diurnal variability of the NO$_2$ molecule it is important to use measurements close in SZA and geographical location. In the case of SCIAMACHY-MIPAS comparisons although both instruments are on the same satellite, SCIAMACHY looks forwards in its limb mode whereas MIPAS looks backwards. This means that there is a possibility for both instrument to have measurements with close SZA but sampling different air masses. To account for this disparity very close collocation distance criteria was apply in addition to close SZA. The collocation distance used were in the range of 40–100 km and the SZA differences less than 5° between collocated events were considered. Example of these comparisons are shown in Figure 8.22, SCIAMACHY number densities are slightly higher than MIPAS results in the altitude range of 25–40 km.

There is a positive bias of SCIAMACHY mean NO$_2$ profiles compared to MIPAS in the middle stratosphere (25–40 km). The mean relative deviations are in the range of 15–40% of SCIAMACHY to MIPAS and the rms is in the range of 10–30% between 25 to 40 km (see Figure 8.23).
CHAPTER 8. O₃ AND NO₂ RESULTS

Figure 8.23: Left: mean NO₂ density profile for 11 collocated events for SCIAMACHY in grey and MIPAS in black. Right: mean relative deviation (solid line) and the rms of the mean relative deviation (dotted line) of these comparisons.

Figure 8.24: Mean NO₂ density profile of 9 collocated events of SCIAMACHY (solid line) and SAGE-III (dashed line). The error bar represent the maximum retrieval error of the SCIAMACHY result of 20%.
8.4. NO\textsubscript{2} VALIDATION RESULTS

8.4.3 SCIAMACHY-SAGE III NO\textsubscript{2} comparison

NO\textsubscript{2} number density profiles derived from SCIAMACHY lunar occultation spectroscopic data are compared with collocated SAGE-III lunar occultation retrieved NO\textsubscript{2} profiles. Coincidence measurements were taken on the same day, using data sets with latitudinal and longitudinal difference of less than 5 and 10 degrees, respectively. These measurements were all taken on the 12th of April, 2003. Figure 8.22 shows the comparison of the mean number density profiles of 9 collocated SCIAMACHY and SAGE-III NO\textsubscript{2} profiles. The results generally show higher concentrations for SCIAMACHY in the range of 5–15\% for all relevant altitudes (18–40 km). Due to strong diurnal variation of NO\textsubscript{2}, difference in local time or SZA of measurement could lead to a some difference in the NO\textsubscript{2} concentration. SAGE-III measurement were taken between 18 and 19 hours local time corresponding to SZA in the range of 96\degree–100\degree, whereas SCIAMACHY measurements were taken later on the same day in the local time in the range of 21–22 hours corresponding to SZA between 114\degree and 115\degree. This result however is in agreement with known NO\textsubscript{2} chemistry, because just after sunset concentration of NO\textsubscript{2} starts to increase as NO is oxidized by the surrounding O\textsubscript{3} molecule to form NO\textsubscript{2}. The limiting factor being the reaction of NO\textsubscript{2} with NO\textsubscript{3} to form N\textsubscript{2}O\textsubscript{5}. The concentration of NO\textsubscript{2} 3–4 hours after sunset in the absence of its limiting factors, will be more than the concentration of NO\textsubscript{2} 1–2 hours after sunset Kumer et al. (1997).

8.4.4 Summary of NO\textsubscript{2} validation

The summary of the results of NO\textsubscript{2} validation is presented here. The SCIAMACHY lunar occultation retrieved NO\textsubscript{2} profiles compared with HALOE, SAGE-III, and MIPAS retrieved NO\textsubscript{2} results are general in good agreement. The mean relative deviation of SCIAMACHY is within -5\% to +20\% of HALOE-Model, which is also in agreement with the MIPAS and SAGE-III comparisons. The summary of the statistical results for NO\textsubscript{2} validation is shown in Table 8.4.

The systematic bias found may be due to differences in air masses analyzed in the case of SCIAMACHY-SAGE-III and SCIAMACHY-MIPAS comparisons. In the SCIAMACHY-HALOE comparison the bias may be due to uncertainties in the input parameters of the photochemical model used or systematic pointing errors in the SCIAMACHY retrieved profiles. The later has been discussed in the summary of ozone validation. The input parameters errors of the photochemical model include inaccuracies in the photolysis frequencies of the photochemical reactions and reaction rates. Other photochemical model parameter error sources are the influences of the initialized NO\textsubscript{x} and O\textsubscript{3} from measurement, temperature, and aerosol loading of the atmosphere. An estimate of the model input parameter error is less than
### Table 8.4: Statistical results of NO$_2$ profiles from SCIAMACHY compared with HALOE, MIPAS, and SAGE-III. N is the number of collocation of each comparison.

<table>
<thead>
<tr>
<th>Instruments</th>
<th>Altitude [km]</th>
<th>N</th>
<th>Mean difference [$10^9$ molec/cm$^3$]</th>
<th>Bias [%]</th>
<th>Rms [%]</th>
</tr>
</thead>
<tbody>
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<td>HALOE</td>
<td>23–38</td>
<td>15</td>
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<td>-5–20</td>
<td>5–40</td>
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<tr>
<td>MIPAS</td>
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<tr>
<td>SAGE-III</td>
<td>20–35</td>
<td>9</td>
<td>$\leq 0.2$</td>
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</table>

14 % in the altitude range of 15–40 km ([Bracher et al.](#)), 2005.
Chapter 9

NO$_3$ results

The first section of this chapter is devoted to the results of NO$_3$ vertical profiles retrieved over the Antarctic (60° S–90° S) from the SCIAMACHY lunar occultation spectra, using the visible spectral band (610–680 nm) containing NO$_3$ absorption bands at 623 nm and 662 nm. The interpretation of the retrieved results demonstrating our current understanding of NO$_3$ chemistry is given in the second section of this chapter. The retrieved NO$_3$ profiles agree well with calculations from a photochemical model constrained by retrieved O$_3$ and analyzed temperatures in the altitude range between 24 to 45 km. These results have been published in JGR atmospheres (Amekudzi et al., 2005b).

9.1 NO$_3$ retrieval results

After the first atmospheric measurements of NO$_3$ reported by Noxon et al. (1978), other ground based NO$_3$ measurements using the moon as light source followed (Platt et al., 1981; Gelinas and Vajk, 1981; Norton and Noxon, 1986; Sander et al., 1987; Solomon et al., 1989b; Smith and Solomon, 1990; Solomon et al., 1993). NO$_3$ vertical profiles have also been derived from balloon-borne stellar and lunar occultation measurements at mid-latitudes (Naudet et al., 1981, 1989; Rigaud et al., 1983; Renard et al., 1996, 2001). The ground based and balloon-borne platforms have not provided broader geographical coverage of the nitrate radical. In this section the first satellite (SCIAMACHY) measurement of NO$_3$ over high latitudes is presented.

NO$_3$ show a strong diurnal cycle and has two peak absorption bands at 623 and 662 nm. The abundance profile information of NO$_3$ is retrieved from these absorption peaks. The absorption bands of 623 nm and 662 nm, however have significant
contributions from other absorbers such as O$_3$, O$_2$, O$_4$, and H$_2$O. To accurately fit and retrieve NO$_3$ profiles, these strong absorbers were fitted in addition to NO$_3$. As O$_2$ and H$_2$O vapor are line absorber, their absolute cross sections were calculated using line-by-line spectral simulation code. Broadband absorption features of the atmosphere and instrument from the measured spectrum were removed by subtracting a third order polynomial. Detail of this procedure is found in Chapter 7. Twomey-Tikhonov regularization parameters used for NO$_3$ retrieval were $T_1 = 100$ and $T_2 = 1000$. The signal-to-noise ratio is in the range of 1000–2000, the retrieval spectral resolution is 0.01 and altitude range is 20–55 km. Gaussian slit function was used and a constant a priori covariance of 90% was applied as additional constrain to the retrieval solution.

9.1.1 NO$_3$ spectral fit and residual

Figure 9.1 shows an example of the spectral fit and residual at 39 km tangent height for March 12, 2003, corresponding to ENVISAT orbit number 5390, and Solar Zenith Angle (sza) of 105.8°. The dotted line is the differential optical depth of the modeled NO$_3$ and the solid line represents the measurement contribution of NO$_3$. The quality of the fit is good and the absorption band of NO$_3$ at 623 nm and 662 nm are accurately fitted. The residual shown in the bottom panel of Figure 9.1 is the spectral residual of fitted gases in the spectral range of 615–670 nm. The spectral residual is in the order of 0.2% for all relevant height layers.

9.1.2 Averaging kernel and retrieval error

Averaging kernels for selected altitudes for retrieved NO$_3$ is displayed in the left panel of Fig 9.2. From the averaging kernel, the highest sensitivity of NO$_3$ is at 35 km followed by the sensitivity at 40 km. The sensitivity at 27–30 km and 45 km are approximately half of the sensitivity at 35 km. Below 20 and above 60 km, no significant information about the NO$_3$ concentration is retrieved.

Precision of the retrieved NO$_3$ profile was calculated using a-priori covariance of 90% and signal-noise-ratio of 1000. In the absence of systematic error, NO$_3$ vertical profile distribution can be retrieved from SCIAMACHY lunar occultation data with an accuracy better than 20% and the retrieval error is less than 10% for regions of higher sensitivity (35–45 km) (see the right panel of Figure 9.2).

In addition to the statistical error of less than 20%, there are other possible significant errors sources in the NO$_3$ retrieval. The uncertainty in the NO$_3$ absolute cross sections is less than 10% \citep{Orphal2003, Sander2003}. The water vapor absorption band (640-665 nm) overlaps with NO$_3$ absorption line.
9.1. NO$_3$ RETRIEVAL RESULTS

Figure 9.1: The fit (top) and residual (bottom) at 39 km tangent height (for March 12, 2003, orbit number 5390, and sza 105.8°). The dotted line represents the modeled differential optical depth of NO$_3$ and the solid line is the measured differential absorption spectrum of NO$_3$. 
Figure 9.2: The averaging kernels of selected altitudes for the retrieved profile of NO₃ (left). This result is based on 1 km vertical resolution. The precision of the retrieved NO₃ number density profile is shown at the right panel. This result is based on a measurement vertical resolution of 3–4 km.

at 662 nm although this effect was considered in the forward model part of the retrieval code, it could introduce a systematic error in the simulated transmission spectra. The systematic error due to interfering gases (H₂O, NO₂, and O₄) is less than 5 %. Due to varying brightness of the moon, higher detector noise and stray light could influence the measured lunar signal and could introduce a random error of less than 15 % in the measurement. Although shift and squeeze correction has been used in the retrieval code to correct for wavelength shift, a wavelength calibration error of less than 1 % could remain in the retrieval result (Meyer et al., 2004). Although retrieval of O₂ is used to improve the information on tangent height, there could still be a systematic error of less than 1 km resulting from a pointing error of less than 0.012°, which could affect the number of photons absorbed (von Savigny et al., 2005a). Other sources of error include systematic errors in the a-priori temperature, pressure, and NO₃ profiles and smoothing error of less than 12 %, as Twomey-Tikhonov regularization was applied in the retrieval process to obtain smooth NO₃ profiles. The retrieved results thus have uncertainties in the measurement and atmospheric a-priori information. These uncertainties have contributed to random noise, smoothing and systematic errors of 20–35 % in the retrieved NO₃ profiles.

9.1.3 NO₃ number density profiles

The retrieved NO₃ monthly and zonal means are presented in Figure 9.3 and 9.4 respectively. The March result is derived from measurements in the moderately high latitudes (60° S–65° S), having maximum number density near 38 km (approx-
9.2. INTERPRETATION OF NO₃ BY USING O₃ AND NO₂

approximately 1.4\times10^7 \text{ cm}^{-3}, \text{ this value is } 0.5\times10^7 \text{ cm}^{-3} \text{ higher than the a priori value. The April, May and June results have maximum near 41 km, which have concentrations less than the a priori value. April and May maximum concentration values are approximately 0.4\times10^7 \text{ cm}^{-3} \text{ and June value is about } 0.5\times10^7 \text{ cm}^{-3}. In addition the retrieved profiles turn close to the a priori values at the region of low sensitivity. The pronounced difference between the a priori information and the retrieved results are indication that, in general the NO₃ retrievals are not over constrained.

The zonal mean profiles of NO₃ concentration retrieved from SCIAMACHY lunar occultation measurements between March and June 2003 shown in Figure 9.4 indicates higher concentration of retrieved NO₃ were in the moderately high latitudes (60°S–65°S), corresponding to an altitude range of 36–40 km. These high values were mainly due to the contribution from measurement data of March where the stratosphere was relatively warm. The low values of retrieved NO₃ were observed in the high latitude (70°S–85°S). These values are derived from measurements in April, May, and June where the temperature in the stratosphere was relatively low.

9.2 Interpretation of NO₃ by using O₃ and NO₂

In order to test, how well the SCIAMACHY measurements agree with our current understanding of the NO₃ nighttime chemistry and to check the internal consistency of the observations, the observed NO₃ profiles were compared with calculations of a photochemical model. In the first case the retrieved NO₃ was compared with a full photochemical model and then with a relatively simple model that assumed that at steady state the nighttime concentration of NO₃ depend on the concentration of O₃ and temperature.

9.2.1 Comparison with model calculations

The model is a 1-D photochemical box model based on the photochemical scheme from the SLIMCAT model (Chipperfield, 1999). The model is similar to the photochemical correction scheme discussed in Section 8.4, details of this model are given in (Sinnhuber et al., 2003) and references therein. The model is initialized with the output of a global 2-D chemistry and transport model for the geolocation and day of the SCIAMACHY measurements. It uses reaction rate constants and photolysis cross sections according to the latest JPL recommendation (Sander et al., 2003). The 1-D model is constrained by temperature and pressure profiles
Figure 9.3: The monthly mean profiles of NO$_3$ retrieved from SCIAMACHY lunar occultation from March to June 2003. March result (a), April (b), May (c) and June (d). The dotted line is the a priori NO$_3$ profile and error bars show the maximum possible error of 35%.
9.2. INTERPRETATION OF NO$_3$ BY USING O$_3$ AND NO$_2$

Figure 9.4: The zonal mean profiles of NO$_3$ retrieved from SCIAMACHY lunar occultation from March to June 2003 for latitude band of 60° S–65° S (black) and 70° S–85° S (grey). The shaded region show the maximum possible error of 35%. The analysis is based on 35 profiles for 60° S–65° S and 95 profiles for 70° S–85° S.

from ECMWF analyses and ozone and NO$_2$ profiles from SCIAMACHY observations. NO$_2$ is constrained by scaling the modeled NO$_y$ (in particular NO, NO$_2$, N$_2$O$_5$, and HNO$_3$) until the modeled NO$_2$ agrees with measured NO$_2$ at the time of the SCIAMACHY measurements.

Figure 9.5 shows the comparison of retrieved NO$_3$ with calculated NO$_3$ from the photochemical model for 14 March 2003 (a) and for 12 April 2003 (b). In general a good agreement between observed and modeled NO$_3$ within the expected error of 35% between the altitude range of 24–45 km. There is a relatively large uncertainty in the modeled NO$_3$ concentration as a result of uncertainties in the temperature profile. It was observed that 1 K increase in temperature increases the NO$_3$ concentration by about 6%. A 5 K uncertainty in the temperature profile – which seems realistic for the Antarctic winter stratosphere – will then result in a 30% uncertainty in the modeled NO$_3$ profile.

In steady state, the nighttime NO$_3$ concentration can be described by Equation 3.4

$$[\text{NO}_3] = \frac{k_1[\text{O}_3]}{k_2[\text{M}]} + \frac{k_3[\text{N}_2\text{O}_5]}{k_2[\text{NO}_2]}.$$ 

The second term on the right hand side of Equation 3.4 accounts for the production of NO$_3$ due to the thermal decomposition of N$_2$O$_5$. If this term is neglected, then the night time steady state concentration of NO$_3$ is simple and depends only on
Figure 9.5: NO\textsubscript{3} profile retrieved from SCIAMACHY lunar occultation compared with NO\textsubscript{3} profile calculated from 1-D box model and ss model. Solid line is the retrieval result, the dashed-dotted line is the 1-D box model output and the solid line with diamond points is the ss model output. (a) Example of NO\textsubscript{3} profile for 14th of March, 2003 (at sza of 110\textdegree). (b) Example of NO\textsubscript{3} profile for 12th of April, 2003 (at sza of 115\textdegree).

Ozone and temperature:

\[
[\text{NO}_3] = \frac{k_1 [\text{O}_3]}{k_2 [\text{M}].}
\]

In order to identify the altitude regions where the second term in Equation 3.4 can be neglected, it was assumed that the concentration of N\textsubscript{2}O\textsubscript{5} during night is in the same order of magnitude as the concentration of NO\textsubscript{2} or smaller. Then Equation 3.5 is a reasonable approximation, if the ratio \(k_3/k_2\), which is the inverse of the equilibrium constant for Reactions 3.2 and 3.3, is much smaller than the NO\textsubscript{3} concentrations. Based on the conditions investigated here, the simple steady state formulation is expected to be valid below an altitude of about 35 to 40 km. This is because, below 35 km the time scales of Reactions 3.2 and 3.3 to reach steady state are in the order of an hour or less (\textcite{Norton and Noxon, 1986}; \textcite{Sander et al., 1987}). Also included in Figure 9.6 is the steady state (ss) model calculation according to Equation 3.5. As expected, a good agreement between the full time dependent model calculations and the ss model below 35 km, where the agreement is better for the April profile where temperatures are lower. Above 40 km the ss model overestimates the NO\textsubscript{3} concentrations. A comparison between retrieved NO\textsubscript{3} profiles and profiles of NO\textsubscript{3} calculated using the ss model carried out is shown in Figure 9.6. The results shown here are the monthly mean profiles, the dash lines are the retrieved NO\textsubscript{3} profiles and the solid lines with diamond points are the ss model outputs. In general the ss model outputs are in good agreement with retrieved profiles between 24 and 35 km, however some discrepancies could be observed between 30 and 35 km for March, April and May. The ss model outputs
Figure 9.6: Monthly mean of NO₃ profiles retrieved from SCIAMACHY lunar occultation compared with NO₃ profiles calculated from SS model for (a) March, (b) April, (c) May, and (d) June of 2003. Dashed lines are the retrieval results and solid lines with diamond points are the model outputs. The error bars show the maximum possible error of 35%.
CHAPTER 9. NO₃ RESULTS

Figure 9.7: Retrieved NO₃ concentration from SCIAMACHY lunar occultation as a function of NO₃ calculated from the steady state approximation model. (a) The result for latitude band of (60–65° S), the correlation coefficient for this graph is 0.83. (b) The result for latitude band of (66–72° S) the correlation coefficient for this graph is 0.98

underestimate or overestimate the NO₃ concentration retrieved from SCIAMACHY data between 30 and 35 km. The discrepancies are due to a large temperature gradient observed at such altitudes ([Solomon et al., 1993; Renard et al., 2001]). Another possible source of error in the steady state profiles is the systematic error of less than 13% in the SCIAMACHY O₃ profiles used ([Amekudzi et al., 2005a]).

In order to verify the consistency in the retrieved NO₃ profiles, the retrieved NO₃ concentrations are plotted as a function of corresponding NO₃ concentrations calculated from the steady state model. Contribution of NO₃ concentrations above 40 km were removed from this study, as it was shown from Figure 9.6 that steady state condition cannot be assumed above 40 km for NO₃. These results are displayed in Figure 9.7. Figure 9.7(a) is the result for latitude band of 60–65° S and Figure 9.7(b) is the result for latitude band of 66–72° S. High positive correlations are observed between the retrieved NO₃ and steady state model NO₃ with correlation coefficients in the range of 0.8–0.98.

9.2.2 Variability of NO₂ and NO₃

NO₂ and NO₃ show strong diurnal cycles, during daytime atmospheric NO₂ is produced from NO and NO₂, as NO₃ is rapidly photolyzed. The daytime stratospheric NO concentration is however far more than the concentration of NO₂. Just after sunset, the stratospheric NO is rapidly oxidized to NO₂ by O₃ and NO₂ is further
9.2. INTERPRETATION OF NO$_3$ BY USING O$_3$ AND NO$_2$

Figure 9.8: Solar zenith angle dependence of NO$_2$ and NO$_3$ for 2003 SCIAMACHY lunar occultation measurements, NO$_2$ result at 30 km (left) and NO$_3$ result at 40 km (right).

oxidized by O$_3$ to NO$_3$. The concentration of both NO$_2$ and NO$_3$ thus build up few minutes after sunset, the limiting factors being complete removal of NO, temperature and reaction of NO$_2$ and NO$_3$ in the presence of collision partner to form N$_2$O$_5$.

Kumer et al. (1997) have shown that at relative warm temperatures (T>290 K), reaction (O$_3$ + NO$_2$) that forms NO$_3$ has lifetime less than a day. In addition, above 275 K concentration of N$_2$O$_5$ in upper stratosphere is strongly limited by its thermal decomposition that leads to formation of NO$_2$ + NO$_3$. The lifetime of N$_2$O$_5$ at 290 K is few minutes and about a day for NO$_3$. This implies as NO$_3$ rich warm air parcel move through a pool of cool air they are converted to N$_2$O$_5$ and the vice versa. The maximum nighttime concentration of NO$_3$ is expected at sza$>100^\circ$, T$>255$K and about 2 or more hours after sunset. Under similar conditions the concentration of NO$_2$ is also expected to be relatively high.

In Figure 9.8, the highest concentration of NO$_3$ (March) corresponds to sza in the range of 105$^\circ$–110$^\circ$, the highest NO$_2$ concentration is also in March and within the sza range of 105$^\circ$–110$^\circ$. A diurnal cycle is observed for both NO$_2$ and NO$_3$ number densities retrieved in April and May. The peak of these cycles occur at sza of 102$^\circ$, 111$^\circ$, 115$^\circ$ for April. The peak for May occur at 105$^\circ$ and 110$^\circ$. The result for June show maximum value near 101$^\circ$ for both NO$_2$ and NO$_3$. The variations seen in the monthly peak values are due to temperature changes, which strongly affects the reaction NO$_2$ + NO$_3$ $\rightleftharpoons$ N$_2$O$_5$ + M above 30 km.

Further study was carried out to observe a close correlation between the NO$_2$ and NO$_3$ results, these results are shown in Figure 9.9. The results shown here are results of NO$_2$ and NO$_3$ number densities averaged over 2 hours.
Figure 9.9: Vertical profiles of NO$_2$ and NO$_3$ averaged over 2 hours equivalent local time for sciamachy lunar occultation measurements for 2003. NO$_2$ result (left) and NO$_3$ result (right).

(white) region between 0 and 2 hour corresponds to sunrise and that between 14 and 20 hour corresponds to sunset. In absence of biases observed near 20 km for NO$_2$ results, hours of higher NO$_2$ number density corresponds to hours of higher NO$_3$ number density. These agreements occurred after 20 hours local time in the altitude near 25–35 km. Solar zenith angle was plotted as a function of the local time for each measurement, this result is displayed in Figure [9.10]. The aim of this plot was to identify the contributions of each month (March–June) to the observed number density values in Figure [9.9]. It was observed that some March measurements were taken in the early hours before sunrise, these measurements were responsible for higher number density value observed before sunrise. The higher values obtained just after 20 hours were due to contributions from all the month, but more especially from May and June measurements.

In general we observed that NO$_3$ and NO$_2$ concentrations have strong diurnal cycle in addition to latitudinal and temperature dependence. These findings are in agreement with NO$_x$ chemistry of the polar stratosphere ([Solomon et al. 1989b], [Smith and Solomon 1990]). Further studies using sciamachy lunar occultation data and photochemical model to understand the diurnal variability of NO$_3$ and NO$_2$ in polar region (Antarctic) will be interesting.
Figure 9.10: Solar zenith angle as a function of local time of measurements for 2003. The different symbol represents a particular month of measurements, diamond (March), triangle (April), square (May) and cross (June)
Chapter 10

Conclusion

10.1 Summary of O\textsubscript{3} and NO\textsubscript{2} results

O\textsubscript{3} and NO\textsubscript{2} number density have been derived from SCIAMACHY lunar occultation measurements using the optimal estimation method. Good spectral fits showing absorption features O\textsubscript{3} (520–560 nm) and NO\textsubscript{2} (430–460 nm) were presented. The spectral residuals are in the order of 0.3\% and 0.2\% for O\textsubscript{3} and NO\textsubscript{2}, respectively. The averaging kernels show reasonable retrieval sensitivity for O\textsubscript{3} and NO\textsubscript{2}. O\textsubscript{3} vertical profile distribution can be retrieved from 18–40 km with an accuracy better than 14\% and from 40–45 km with accuracy better than 27\%. The NO\textsubscript{2} vertical profile distribution can be retrieved from 18–35 km with an accuracy better than 20\% and from 35–40 km with accuracy better than 30\%.

Comparisons of collocated SCIAMACHY O\textsubscript{3} profiles with HALOE, POAM-III and SAGE-II show that the quality of O\textsubscript{3} retrieved from SCIAMACHY lunar occultation is high, within 10–25\% between 20 to 45 km. SCIAMACHY O\textsubscript{3} results are in good agreement with the results of MIPAS and SAGE-III in the altitude range of 20–45 km. The mean deviations and rms of the mean deviations of SCIAMACHY-MIPAS comparisons are in the order of 10–15\% and 10–30\%, respectively.

SCIAMACHY-HALOE NO\textsubscript{2} comparisons were carried out using photochemical correction. A slight negative bias was observed in the altitude range of 24–30 km with relative deviations in the range of -5\% to +10\%. SCIAMACHY-MIPAS NO\textsubscript{2} comparisons show relative deviations in the range of 5–40\% and the rms values in the range of 10–30\% between 24–40 km. The number density of NO\textsubscript{2} inferred from SCIAMACHY lunar occultation is slightly higher than that derived from SAGE-III lunar occultation measurement. A complete validation of these results will justify the quality of the scientific data products derived from SCIAMACHY lunar occultation measurements.
occultation measurement. The data set presented here provides a valuable basis for studies of the NO\textsubscript{x} budget and will be valuable for modeling studies, which will improve our understanding of nighttime O\textsubscript{3} chemistry. Furthermore this data will be useful for data simulation of other nitrogen trace species such as N\textsubscript{2}O\textsubscript{5}.

10.2 Summary of NO\textsubscript{3} results

The first retrieved NO\textsubscript{3} profiles from SCIAMACHY lunar occultation measurements over the Antarctica using the optimal estimation method have been presented. The spectral fits are of high quality and show absorption features of NO\textsubscript{3} at 623 nm and 662 nm. The retrieval error is less than 10\% in the regions of higher sensitivity showing that the quality of the results are good.

Understanding of NO\textsubscript{3} chemistry at the location of the measurements were tested using a full photochemical model and relatively simple steady state model. The NO\textsubscript{3} profiles calculated from the full 1-D photochemical model are in good agreement with retrieved NO\textsubscript{3} profiles between 24 to 45 km within the estimated accuracy of 20–35\%. The steady state model NO\textsubscript{3} agree with retrieved NO\textsubscript{3} in the altitude range of 24–40 km. The agreement supports the use of the steady state approximation model to calculate globally NO\textsubscript{3} concentrations in the middle stratosphere (24–40 km) and the use of a full photochemical model to calculate NO\textsubscript{3} concentration above 40 km.

It was observed that NO\textsubscript{3} chemistry in the stratosphere depends strongly on temperature and inaccuracy in stratospheric temperature of less than 5 K will contribute approximately 30\% error in the observed NO\textsubscript{3} concentrations. In addition the concentration of NO\textsubscript{3} and NO\textsubscript{2} have strong diurnal, seasonal, and latitudinal variations.

A small temperature dependence of the strong (0-0) band around 662 nm of NO\textsubscript{3} absorption cross section due to changing population of the ground vibrational state have been observed, see \cite{Orphal et al., 2003} and references therein. The combination of temperature and temperature-dependent cross sections will therefore improve the retrieval accuracy for NO\textsubscript{3}.

The lunar occultation measurements of SCIAMACHY demonstrate that we have a reasonable understanding of the behavior of NO\textsubscript{3} in the high latitude stratosphere and mesosphere. The ratio of NO\textsubscript{3} to N\textsubscript{2}O\textsubscript{5} is very sensitive to temperature. Significant information about changing condition in the upper atmosphere will be monitored by long-term measurements of NO\textsubscript{3}, NO\textsubscript{2}, O\textsubscript{3} and temperatures from instruments like SCIAMACHY. Our understanding will benefit from linking measurements (N\textsubscript{2}O\textsubscript{5}) made by IR sensors such as MIPAS \cite{Tsidu et al., 2004} and
the stellar occultation measurements of GOMOS (Marchand et al., 2004).

10.3 Outlook

Future studies will be carried out in the following:

1. Further validation of NO\textsubscript{2} using photochemical correction is desirable with SAGE-II and POAM-III retrieved NO\textsubscript{2}.

2. Comparison of NO\textsubscript{3} profiles retrieved from SCIAMACHY lunar occultation measurements with NO\textsubscript{3} profiles retrieved from GOMOS and SAGE-III measurements.

3. Further studies on the diurnal variation of NO\textsubscript{3} and NO\textsubscript{2} using analysis based on kinetics equations derive for species number densities in the local atmospheric air parcel which are actually observed (Gelinas and Vajk, 1981).

4. It will be interesting to assimilate N\textsubscript{2}O\textsubscript{5} concentration from the SCIAMACHY lunar occultation retrieved \textit{O}_3, NO\textsubscript{2} and NO\textsubscript{3}. In this direction, a proposed collaborated research with MIPAS group in Forschungszentrum Karlsruhe will be helpful, as the group have successfully retrieved nitrogen species such as HNO\textsubscript{3}, ClONO\textsubscript{2}, NO, NO\textsubscript{2} and N\textsubscript{2}O\textsubscript{5}. This task will be possible if all the reaction rate constants in equation (3.4) are known, in addition to temperature information.

5. Retrieval of OC\textsubscript{1}O during ozone hole condition using lunar occultation measurements that were taken after May. To perform this task it will be desirable to first identify signature of psc from the lunar occultation spectra using the similar method employed by von Savigny et al. (2005b).
Appendix A

Examples of ozone comparisons
APPENDIX A. EXAMPLES OF OZONE COMPARISONS

Figure A.1: Examples of SCIAMACHY-HALOE ozone profiles comparisons for 2003. The dotted lines are results of the SCIAMACHY and the solid line the results of the HALOE.
Figure A.2: Examples of SCIAMACHY-HALOE ozone density profiles comparisons for 2004, results of the SCIAMACHY (dotted lines) and the HALOE (solid lines).
Figure A.3: Examples of SCIAMACHY-POAM-III ozone comparisons for 2003. The dotted lines the results of the SCIAMACHY and the solid line the results of the POAM-III.
Figure A.4: Other examples of SCIAMACHY-POAM-III ozone density profiles comparisons for 2003.
Figure A.5: Other examples of sciamachy-POAM-III ozone density profiles comparisons for 2003.
Figure A.6: Other examples of SCIAMACHY-POAM-III ozone density profiles comparisons for 2003.
Figure A.7: Other examples of SCIAMACHY-POAM-III ozone density profiles comparisons for 2003.
Figure A.8: Examples of SCIAMACHY-SAGE-II ozone comparisons for 2004, the results of the SCIAMACHY (dotted lines) and the results of the SAGE-II (solid lines).
Figure A.9: Other examples of SCIAMACHY-SAGE-II ozone density profiles comparisons for 2004.
Figure A.10: Other examples of SCIAMACHY-SAGE-II ozone density profiles comparisons for 2004.
Figure A.11: Other examples of SCIAMACHY-SAGE-II ozone density profiles comparisons for 2004.
Figure A.12: Other examples of SCIAMACHY-SAGE-II ozone density profiles comparisons for 2004.
Figure A.13: Other examples of SCIAMACHY-SAGE-II ozone density profiles comparisons for 2004.
Figure A.14: Examples of SCIAMACHY-MIPAS ozone profiles comparisons for 2003. The dotted lines are results of the SCIAMACHY and the solid line the results of the MIPAS.
Figure A.15: Other examples of SCIAMACHY-MIPAS ozone density profiles comparisons for 2003.
Figure A.16: Other examples of SCIAMACHY-MIPAS ozone density profiles comparisons for 2003.
Figure A.17: Other examples of SCIAMACHY-MIPAS ozone density profiles comparisons for 2003.
Figure A.18: Other examples of SCIAMACHY-MIPAS ozone density profiles comparisons for 2003.
Appendix B

Examples of NO$_2$ comparisons
Figure B.1: Examples of NO$_2$ density profiles for SCIAMACHY and HALOE comparison. The red line signifies the SCIAMACHY, the black line the HALOE, the green line the model at the HALOE SZA, and the blue line the model at the SCIAMACHY SZA.
Figure B.2: Examples of SCIAMACHY-MIPAS NO$_2$ comparisons for high latitudes for 2003. The dotted lines are the results of SCIAMACHY and the solid lines for MIPAS.
APPENDIX B. EXAMPLES OF NO$_2$ COMPARISONS
Appendix C

Moon characteristics and geolocation information

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Table C.2: This table provides information on the date, time, geographical location and solar zenith angle of SCIAMACHY lunar occultation measurements for 2003.
Appendix D

NO$_3$ further reactions

The reactions presented here are some possible reactions that can lead to either production or loss of NO$_3$ molecules. Most of these reactions can only occur during and in the troposphere.

\[
\begin{align*}
OH + HNO_3 & \longrightarrow NO_3 + H_2O \quad \text{(D.1)} \\
ClONo_2 + hv(\lambda < 330 \text{ nm}) & \longrightarrow Cl + NO_3 \quad \text{(D.2)} \\
Cl + ClONo_2 & \longrightarrow Cl_2 + NO_3 \quad \text{(D.3)} \\
OH + ClONo_2 & \longrightarrow HOCl + NO_3 \quad \text{(D.4)} \\
O + NO_2 + M & \longrightarrow NO_3 + M \quad \text{(D.5)} \\
N_2O_5 + hv(\lambda < 330 \text{ nm}) & \longrightarrow NO_3 + NO_2 \quad \text{(D.6)} \\
N_2O_5 + hv(\lambda < 280 \text{ nm}) & \longrightarrow NO_3 + NO + O \quad \text{(D.7)} \\
HO_2NO_2 + hv(\lambda < 330 \text{ nm}) & \longrightarrow OH + NO_3 \quad \text{(D.8)} \\
\end{align*}
\]
The steady state concentration of NO$_3$ in the stratosphere can be approximated as

$$[\text{NO}_3] = \frac{k_1 [\text{O}_3]}{k_2 [\text{M}]},$$  \hspace{1cm} (D.9)

where reaction reaction rate constants $k_1$ and $k_2$ are respectively given by

$$k_1 = 1.2 \times 10^{-13} \exp \left( \frac{-2450}{T} \right)$$  \hspace{1cm} (D.10)

$$k_2 = 4.5 \times 10^{-14} \exp \left( \frac{-1260}{T} \right),$$  \hspace{1cm} (D.11)

Substituting equation (D.10) and (D.11) in equation (D.9) and taking the natural logarithm of the resulting equation we will get

$$\ln \left( \frac{[\text{NO}_3]}{[\text{O}_3]} \right) = - \frac{1180}{T} + \ln \left( \frac{2.67}{M} \right)$$  \hspace{1cm} (D.12)
Appendix E

Tangent height and number density

The number density $n$ of trace gas is related to the atmospheric scale height, $H(h)$, and geometric height, $h$, through the hydrostatic equation:

$$n_i(h) = n_0 \exp \left(-\frac{h_i - h_0}{H(h)}\right).$$  \hspace{1cm} (E.1)

Similarly,

$$n_{i+1}(h) = n_0 \exp \left(-\frac{h_{i+1} - h_0}{H(h)}\right).$$  \hspace{1cm} (E.2)

Let $a = \frac{h_{i+1} - h_0}{H}$ and $b = \frac{h_{i+1} - h_0}{H}$ implies

$$n_i(h) = n_0 e^{-a},$$  \hspace{1cm} (E.3)

and

$$n_{i+1}(h) = n_0 e^{-b}.$$  \hspace{1cm} (E.4)

Now mole fraction $f_i$ is given as

$$f_i = \frac{n_i}{n_i + n_{i+1}},$$  \hspace{1cm} (E.5)

substituting equation E.3 and E.4 into equation E.5 we will get

$$f_i = \frac{n_0 e^{-a}}{n_0 e^{-a} + n_0 e^{-b}},$$  \hspace{1cm} (E.6)

multiplying equation E.6 by $n_0 e^{-a} + n_0 e^{-b}$ we will get

$$f_i e^{-a} + f_i e^{-b} = e^{-a}.$$  \hspace{1cm} (E.7)
APPENDIX E. TANGENT HEIGHT AND NUMBER DENSITY

Implies

\[ f_i e^{-b} = (1 - f_i) e^{-a}, \]  

(E.8)

which can be re-written as

\[ \frac{e^{-b}}{e^{-a}} = \frac{1 - f_i}{f_i}, \]  

(E.9)

or

\[ e^{-b(-a)} = \frac{1 - f_i}{f_i}. \]  

(E.10)

Taking natural logarithms of both sides and replacing \( a \) and \( b \) we will get

\[ -\left( \frac{h_{i+1} - h_0}{H} \right) + \left( \frac{h_i - h_0}{H} \right) = \ln \left[ \frac{1 - f_i}{f_i} \right], \]  

(E.11)

implies

\[ \frac{-h_{i+1} + h_i}{H(h_i)^2} = \ln \left[ \frac{1 - f_i}{f_i} \right]. \]  

(E.12)

Re-arranging the result in equation (E.12) we will have

\[ h_{i+1} = h_i - H(h_i)^2 \ln \left[ \frac{1 - f_i}{f_i} \right]. \]  

(E.13)
Acknowledgment

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