Satellite remote sensing of cloud properties
in support of tropospheric trace gas retrievals

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Our planet is a lonely speck in the great enveloping cosmic dark. In our obscurity – in all this vastness – there is no hint that help will come from elsewhere to save us from ourselves. It is up to us.

—Carl Sagan in “Pale Blue Dot: A Vision of the Human Future in Space”, 1994, inspired by a portrait of planet Earth made by Voyager 1 from a distance of more than 6 billion kilometers.
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Introduction

1.1 The Earth’s atmosphere

The atmosphere is the complex, chaotic gaseous envelope of our planet. It consists mainly of molecular nitrogen (N$_2$, 78%), molecular oxygen (O$_2$, 21%) and argon (Ar, 0.9%) $^1$. Trace gases, such as carbon-dioxide (CO$_2$), ozone (O$_3$) and nitrogen dioxide (NO$_2$), account for the remaining 0.1%. Furthermore, the atmosphere harbors clouds and aerosols, which are suspended tiny particles. Many constituents of our atmosphere are crucial for Earth’s habitability. Furthermore, many of them play crucial roles in the Earth’s radiation balance and atmospheric chemistry. It is therefore very important to monitor and study changes in the atmosphere, which are either natural or induced by humans. Satellite measurements play a crucial role in the monitoring and studying of the atmospheric components. The accurate retrieval of tropospheric trace gas concentrations from these measurements in the presence of clouds is one of the most difficult challenges of present day Earth remote sensing. The retrieval of cloud properties which are needed to accurately retrieve trace gas information in the troposphere is the main subject of this thesis.

1.1.1 Tropospheric trace gases

The troposphere is the lowest layer of the atmosphere, extending from the surface to about 7 km at the poles and to about 17 km at the equator. Obviously, this part of the atmosphere is most directly affected by anthropogenic pollution due to e.g. agricultural processes and fossil-fuel

$^1$for dry air. Moist air can contain up to about 4% water vapor.
combustion. The increasing pollution can have profound effects on the atmosphere. In particular, changes in the Earth’s radiation budget due to increase of greenhouse gases and changes in the tropospheric chemistry are two major recent concerns.

**Greenhouse gases**

Solar radiation heats the Earth’s surface, which, as a result, emits thermal radiation. This thermal radiation is absorbed by greenhouse gases in the troposphere. In turn, the greenhouse gases partly re-emit this energy downwards, thereby essentially preventing the heat to escape to space. As a result, the surface temperatures is on average 32°C higher than it would be if no greenhouse gases were present (see e.g. Wayne, 1991). This process was discovered by Arrhenius (1896) and was later dubbed the greenhouse effect. The most important greenhouse gases, i.e. water vapor, carbon-dioxide, methane and ozone, naturally occur in the atmosphere. However, the concentrations of several greenhouse gases are increased by human activities (IPCC, 2007a). For instance, methane and nitrous oxide (N₂O) are emitted into the troposphere by agricultural processes. In the last century, the strong increase of fossil-fuel combustion resulted in a build up of carbon dioxide, ozone, methane, and other greenhouse gases in the troposphere. Furthermore, synthetic long-lived halocarbons, such as Chlorofluorocarbons (CFCs), escape from industrial processes, refrigerators and aerosol spray cans and add to the problem of the enhanced greenhouse effect. It is expected that the increase of greenhouse gases will lead to a global warming of about 2°C to 4°C in the coming century (IPCC, 2007a), possibly with devastating consequences (IPCC, 2007b).

**Tropospheric chemistry**

The chemistry of the troposphere is extremely complex due to the large number of reactive species, turbulent mixing, and the presence of clouds and aerosols (Wayne, 1991; Lelieveld and Crutzen, 1990; Andreae and Crutzen, 1997; Liu et al., 2006). A leading role in the tropospheric chemistry is taken on by hydroxyl (OH) radicals (see e.g. Wayne, 1991). The

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2Confusingly, this is not the same process which heats a garden greenhouse. There, convection of warm air is prevented by the glass.
OH radical reacts with almost all gases that are emitted into the atmosphere by natural processes and anthropogenic activities and is therefore often called the detergent of the atmosphere. Photolysis of ozone is the major source of OH. In turn, tropospheric ozone is mainly formed by a catalytic reaction chain in which nitrogen oxides (NO and NO$_2$), carbon monoxide (CO) and so-called volatile organic compounds (VOCs) react in the atmosphere in the presence of ultra-violet (UV) light from the sun. The burning of fossil fuels is a major source of these chemicals. Due to an increase of fossil fuel combustion, the tropospheric ozone concentration shows a steady increase in the twentieth century (Marenco et al., 1994), which in turn leads to an increased OH production rate (Lelieveld et al., 2004). In contrast, global OH concentrations and therewith the self-cleansing capability of the atmosphere appear very stable in the last century. This is due to the fact that emissions of compounds that deplete OH, such as carbon monoxide and methane, have also increased (Lelieveld et al., 2004). However, model calculations suggest the relative distribution of OH over the globe has changed due to such anthropogenic emissions (Lelieveld et al., 2004). Moreover, the apparent current stability of the atmosphere’s self-cleansing capability holds no guarantee for the future as relative emissions of trace gases may change (Prinn, 2003). Another issue of concern about the changing tropospheric chemistry is the increase of air pollution. Ozone, for example, is a key element of toxic photo-chemical smog, and its increase, together with many other trace gases, leads to poorer air quality, especially in large cities (Finlayson-Pitts and Pitts Jr., 1997). Also, acidic oxides, i.e. nitrogen dioxide and sulphur dioxide (SO$_2$), emitted by fossil-fuel combustion, can lead to acid rain after oxidation by OH radicals. Acid rain can cause severe damage to forests and aquatic life (Grennfelt and Hultberg, 1986).

1.1.2 Clouds

Heterogeneity and variability of clouds

Almost 70% of the Earth’s surface is covered by clouds at any given time (Rossow and Schiffer, 1999). Clouds are collections of particles mainly consisting of liquid or frozen water suspended in the atmosphere. The liquid droplets have sizes of about 1–50 $\mu$m. The ice crystals have many
possible shapes and sizes of about 20–2000 μm. From a macro-physical perspective, many cloud types can be distinguished by their shape, height, geometrical thickness, optical thickness, etc. Here, the optical thickness is an unit-less measure of the amount of extinction of light penetrating through the cloud. A very simplified but practical scheme to define several cloud types on the basis of only their top height and their optical thickness is used by the International Satellite Cloud Climatology Project (ISCCP, Rossow and Schiffer, 1999) and is shown in Fig. 1.1. Most common are cumulus, stratocumulus and cirrus clouds. Table 1.1 shows the 1986 annual mean global amounts of middle-level, low-level, cirrus and deep convective clouds and their average properties in the ISCCP database. Averaged over the globe and on annual timescales, the cloud amounts and properties vary

Table 1.1: Global annual mean amounts and properties of middle-level, low-level, cirrus and deep convective clouds in the ISCCP-D2 dataset of 1986 (Rossow and Schiffer, 1999).

<table>
<thead>
<tr>
<th>Cloud type</th>
<th>amount [%]</th>
<th>optical thickness</th>
<th>top pressure [hPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>low-level clouds</td>
<td>27.5</td>
<td>4.7</td>
<td>826</td>
</tr>
<tr>
<td>middle-level clouds</td>
<td>19.0</td>
<td>4.8</td>
<td>557</td>
</tr>
<tr>
<td>cirrus and cirrostratus</td>
<td>19.6</td>
<td>2.2</td>
<td>267</td>
</tr>
<tr>
<td>deep convective clouds</td>
<td>2.6</td>
<td>35.6</td>
<td>326</td>
</tr>
</tbody>
</table>

Figure 1.1: The ISCCP-D2 cloud classification scheme based on cloud optical thickness and cloud top pressure. The approximate cloud top heights corresponding to the cloud top pressures are indicated on the right axis. This figure is adapted from Rossow and Schiffer (1999).
only very little. On smaller spatial scales and shorter timescales, however, the variability of clouds is much larger. For instance, in some desert areas clouds are very rare, while in the mid-latitudes they are very abundant (See figure 1.2). Furthermore, their amounts have pronounced seasonal and diurnal cycles. Looking on the scale of individual clouds, one can spot clouds with horizontal sizes ranging from several hundred meters to thousands of kilometers, drifting through the atmosphere with speeds of up to about 30 m/s. Some clouds grow larger and thicker in time, others dissipate. Moreover, different cloud types can coexist at the same place and time in multi-layered systems. In fact, about 42% of the clouds are multi-layered (Wang et al., 2000). The heterogeneity and the variability of clouds make them one of the most difficult aspects of the atmosphere to study and to model.

Radiative effects of clouds

Clouds strongly affect the radiative transfer in the atmosphere and thereby the climate (Ramanathan et al., 1989; IPCC, 2007a). On the one hand clouds reflect incoming solar radiation, thereby cooling the atmosphere, and on the other hand absorb the long-wave radiation emitted by
the Earth’s surface, which tends to heat the atmosphere. Because of the large variation of cloud types and their different radiative properties, it was for long unclear what the net radiative effect of clouds in the Earth’s climate system is. Satellite measurements in the 1980s demonstrated that globally clouds have a net cooling effect (Ramanathan et al., 1989). In fact, if no clouds were present, the global net radiative flux to space would be about 20 Wm$^{-2}$ larger (Ramanathan et al., 1989), which is about 6% of the total average global incident solar radiation. To put this in perspective: the estimated change in outgoing radiative flux due to emissions of anthropogenic carbon-dioxide, which is the most important anthropogenic greenhouse gas, is 1.66 Wm$^{-2}$ (IPCC, 2007a). Small changes in the cloud amounts or shifts in the relative amounts of cloud types can have a dramatic effect on the Earth’s climate. In the last few decades, subtle changes of cloud properties have occurred due to anthropogenic emissions of small aerosol particles, which can act as cloud condensation nuclei on which cloud droplets form, and seem to lead to a cooling effect, significantly counteracting the global warming of the atmosphere due to increasing greenhouse gases (IPCC, 2007a). The strength of this cooling, however, remains the dominant uncertainty in climate change predictions.

The radiative effects of clouds also significantly affect the tropospheric photo-chemistry (Tang et al., 2003; Liu et al., 2006). Due to the shielding of UV light by clouds, the photo-dissociation frequency of e.g. ozone and nitrogen dioxide is significantly lower near the surface in cloudy regions compared to the clear-sky situation. Above clouds, the increased UV light due to the strong reflection of clouds leads to the opposite effect. This in turn leads to lower concentrations of hydroxyl radicals under the cloud and higher concentration above the clouds.

1.2 Satellite remote sensing of trace gases

Sunlight emerging from the Earth’s atmosphere has interacted with molecules and particles in the atmosphere and with the Earth’s surface. Therefore, information about these atmospheric constituents and the surface properties can be retrieved from measurements of the backscattered sunlight. The advantage of satellite remote sensing in comparison to in situ measurements is that measurements of the whole globe can be made
within a few days with the same instrument. This global coverage is crucial, for instance to study global changes in atmospheric compounds, to follow long-range transport through the atmosphere and to measure trace gases at remote locations.

1.2.1 Instruments

A satellite instrument developed to retrieve information about e.g. ozone, methane, carbon monoxide and other trace gases is the Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY, Bovensmann et al., 1999). SCIAMACHY is one of the 10 instruments on the European Environmental Satellite (ENVISAT) launched in 2002 by the European Space Agency (ESA). SCIAMACHY is a grating spectrometer, which measures the Earth radiance, i.e. solar radiation reflected by the Earth’s surface and its atmosphere, and the solar irradiance in six continuous bands in the wavelength range 240–1750 nm, and 2 additional bands measuring in the wavelength ranges 1940–2040 nm and 2265–2380 nm. The ratio of the Earth radiance and the solar irradiance is commonly referred to as reflectance. The spectral resolution ranges from 0.22 nm to 1.48 nm. The transmission efficiency of the instrument is sensitive to the polarization of the light. To correct for this, 7 broadband Polarization Measuring Devices (PMDs) are included in the instrument. SCIAMACHY can measure either in a nadir-geometry (looking downwards) or in a limb-geometry (looking through the limb of the atmosphere). In the nominal operation mode, the nadir and limb-measurements are alternated and both take place about 50% of the time. In this thesis, only nadir measurements are considered. The swath of the nadir scan has a width of 960 km. The nadir measurements footprints are about 60×30 km$^2$ or larger, depending on wavelength. The nadir PMD measurements are read out at a higher rate than the main science channels and therefore have smaller footprint sizes of 7×30 km$^2$. Global coverage is reached by SCIAMACHY in 6 days. The Global Ozone Monitoring Experiment (GOME, Burrows et al., 1999) is an instrument similar to SCIAMACHY, launched in 1995 on the second European Remote Sensing Satellite (ERS-2). It is a less extended version of SCIAMACHY as it covers a smaller wavelength range (240–790 nm) and observes only in nadir with a footprint size of 320×40 km$^2$. An improved version of GOME, GOME-2, was launched by EUMETSAT in 2006.
on the first Meteorological Operational spacecraft (MetOp-A). GOME-2 has a footprint size of $80 \times 40 \text{ km}^2$. Two additional GOME-2 instruments are scheduled to be launched on MetOp satellites guaranteeing GOME-2 observations until 2020. Another instrument similar to GOME and SCIAMACHY is the Ozone Monitoring Instrument (OMI, Levelt et al., 2006). OMI is a Dutch-Finnish Instrument launched on NASA’s EOS-Aura satellite in 2004. OMI measures in the wavelength range 270-500 nm and has a spatial resolution of about $13 \times 24 \text{ km}^2$. An overview of the mentioned satellite instruments is given in Table 1.2. This thesis is primarily focused on GOME and SCIAMACHY measurements.

Table 1.2: Characteristics of satellite instruments discussed in section 1.2.1.

<table>
<thead>
<tr>
<th>Spectrometer</th>
<th>Platform</th>
<th>launch year</th>
<th>spectral range [nm]</th>
<th>spectral resolution [nm]</th>
<th>footprint size [km$^2$]</th>
<th>global coverage</th>
</tr>
</thead>
<tbody>
<tr>
<td>GOME</td>
<td>ERS-2</td>
<td>1995</td>
<td>240–790</td>
<td>0.2–0.4</td>
<td>$320 \times 40$</td>
<td>3 days</td>
</tr>
<tr>
<td>SCIAMACHY</td>
<td>ENVISAT</td>
<td>2002</td>
<td>240–2380</td>
<td>0.2–1.5</td>
<td>$60 \times 30$</td>
<td>6 days</td>
</tr>
<tr>
<td>OMI</td>
<td>EOS-Aura</td>
<td>2004</td>
<td>270–500</td>
<td>0.5</td>
<td>$24 \times 13$</td>
<td>1 day</td>
</tr>
<tr>
<td>GOME-2</td>
<td>MetOp-A</td>
<td>2006$^b$</td>
<td>240–790</td>
<td>0.2–0.4</td>
<td>$80 \times 40$</td>
<td>1 day</td>
</tr>
</tbody>
</table>

$^a$Resolution can vary with wavelength. Minimum footprint size is given here in format (across track $\times$ along track).

$^b$Identical GOME-2 instruments are scheduled on future MetOp platforms until 2020.

1.2.2 Retrieval principle

All satellite instruments discussed in the previous section measure the reflectance of the atmosphere in the Ultra-Violet (UV) and visible wavelengths. Additionally, all of them, except OMI, measure up to the near infrared (800 nm). As shown in Fig. 1.3, many absorption bands of atmospheric gases, such as oxygen, ozone, nitrogen dioxide and water vapor, can be found at these wavelengths. These measurements in absorption bands allow to retrieve the vertically integrated concentrations of the absorbing gases, i.e. the gas column density. This is because the depth of the absorption features depends on the amount of gas that is encountered by the solar light. For a given gas column density, the depth of the corresponding absorption band can be modeled with a radiative transfer model. To re-
Figure 1.3: Three examples of SCIAMACHY measurements from orbit 18729 on 29 September 2005 over the North Atlantic ocean. Absorption features of oxygen, ozone, water vapor, nitrogen dioxide and carbon dioxide are indicated. To account for the (slightly) different solar zenith angles for each measurement, the measured reflectances are multiplied by $\pi/\mu_0$, where $\mu_0$ is the cosine of the solar zenith angle. The measurements are shown on a logarithmic wavelength scale.

trieve the gas column density from a measured spectrum, the gas column density used as input of the radiative transfer model is varied until the measured and modeled spectra are in optimal agreement. When the absorption strength of a gas varies substantially with wavelength, altitude resolved information can be obtained from the spectral dependence of the observed radiance. This is the case for ozone absorption in the UV, where the cross sections are large at short wavelengths and decrease rapidly with increasing wavelength (Chance et al., 1997), as illustrated in Fig. 1.4. Therefore, the radiances measured at short wavelengths (around 240 nm) contain information only about the ozone concentrations high in the atmosphere, as the light does not penetrate deeper. Light with longer wavelengths (around 320 nm) does intrude deeper into atmosphere and therefore also contains information about ozone concentrations in the lower atmosphere. This concept has been used extensively to retrieve ozone concentration profiles from nadir measurements of satellite instruments such as GOME (e.g. Munro et al., 1998; Hoogen et al., 1999; Hasekamp and Landgraf, 2001; Liu et al., 2005). Specifically, GOME measurements allow ozone profiles to be
Figure 1.4: Illustration of the retrieval of vertically resolved ozone concentrations from satellite based UV measurements. Measurements of the backscattered radiance at short wavelengths, e.g. at 290 nm, contain information about the upper parts of the atmosphere only because the ozone absorption is strong at these wavelengths. Measurements at longer wavelengths, e.g. 320 nm, where the ozone absorption is weaker, contain information about ozone concentrations at all heights.

retrieved with a Degrees of Freedom for Signal (DFS) of about 4.5–5.5 (Hasekamp and Landgraf, 2001; Liu et al., 2005). The DFS is a measure of the number of independent pieces of information that can be derived from the measurement. In the case of ozone profile retrievals these pieces of information correspond to vertical structures of the ozone profile, and thus the DFS is related to the vertical resolution of the retrieved profile. For GOME measurements, about 0.5–1.5 of the total DFS is contributed by the tropospheric layers (Liu et al., 2005). Ozone profile retrievals in the presence of clouds is the subject of chapter 5 of this thesis.

1.2.3 Importance of clouds

The satellite measurements are not only affected by atmospheric gases but also strongly by clouds. For example, Figure 1.3 shows measurements of SCIAMACHY in the 240–1800 nm wavelength range for a clear-sky and two different cloudy cases above the North Atlantic Ocean. Obviously, the reflectances for the cloudy scenes are generally much higher than the clear-sky measurements due to the relative high reflectance of clouds compared to that of a sea surface. Furthermore, the measured reflectances over the
Figure 1.5: The fraction of cloud-free observations as a function of sensor resolution (footprint area), as determined from 1×1 km² resolution MODIS TERRA cloud mask observations. Solid, dashed and dashed-dotted indicates results for which 0%, 5% and 20%, respectively, of the total area observed was allowed to contain clouds. Data are globally averaged from 70° S to 70° N. The dotted lines indicate the resolution of the sensors discussed in section 1.2.1. This figure is adapted from Krijger et al. (2007).

thick cloud are higher than those measured over the thin cloud. Another difference between the clear-sky and cloudy scenes is that the measurements over the cloudy scenes are spectrally flatter, i.e. whiter. This is simply because clouds are white and the clear sky is blue. Striking are also the differences in relative depths of the absorption bands between the three measurements; the absorption bands are only shallow in the clear-sky case and deepest in the case of a thick cloud. Due to the large variability of the cloud amount, their optical thickness and top height, the influence of clouds on the measurements such as those from SCIAMACHY is highly variable. Furthermore, since SCIAMACHY has a measurement footprint that covers a relatively large area of about 1800 km² and since almost 70% of the globe is covered by clouds, by far most of SCIAMACHY’s measurements are contaminated by clouds. The same is true for GOME, GOME-2, OMI and other instruments. Figure 1.5 shows the percentage of cloud-free measurements as a function of sensor resolution (Krijger et al., 2007). As seen in Figure 1.5, only about 6% of the SCIAMACHY pixels, 2% of the GOME pixels, 5% of the GOME-2 pixels and 12% of the OMI pixels, are com-
pletely cloud-free. Thus, when clouds cannot be accounted for sufficiently in the trace gas retrieval algorithms, 88–98% of the measurements cannot be used. Even when 20% of the pixel is allowed to be covered by clouds, as is often done in trace gas retrievals (e.g. Richter et al., 2005), still 77–83% of the measurements are not used. When clouds can be accounted for sufficiently in the retrieval, also measurements with higher cloud fractions allow the retrieval of information about the trace gases in the clear-sky part of the measurement footprint. Furthermore, relevant information can be then be retrieved about tropospheric trace gases of which significant amounts can be found above the cloud tops, such as ozone. Thus, at present, the full potential of these instruments is not exploited. Moreover, biases can be introduced in the retrieval products due to selection effects when only cloud-free measurements are included (Savage et al., 2004).

Thus, the effects of clouds on the measurements have to be known in order to accurately retrieve trace gas information in (partly) cloudy atmospheres. Important parameters that are needed for this are the cloud fraction, which is the relative amount of clouds in a measurement footprint, the cloud optical thickness (or reflection properties) and the cloud top height (Koelemeijer and Stammes, 1999). One of the objectives of this thesis work is the development of a new approach to retrieve cloud parameters using the same instruments as used to retrieve trace gas concentrations.

1.3 Remote sensing of clouds

1.3.1 Dedicated cloud instruments

Since the launch of the first Television Infrared Observation Satellite (TIROS) in 1960, clouds have been continuously observed from space by weather satellites. TIROS evolved into the currently operational TIROS-N/NOAA and MetOp series, carrying the Advanced Very High Resolution Radiometer (AVHRR). Other important present-day satellite instruments dedicated to retrieve cloud information are the Polarization and Directionality of the Earth’s Reflectances (POLDER), the Moderate Resolution Imaging Spectroradiometer (MODIS), the Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observation (CALIPSO) and Cloudsat. The satellites carrying these instruments are all in polar orbits. Cloud observa-
tions from geostationary satellites started in 1966 with the launch of the Applications Technology Satellite (ATS), which evolved into the Geostationary Operational Environmental Satellite (GOES) and MeteoSat series, of which several versions are currently operational.

Traditionally, thermal infrared camera’s are used to retrieve cloud information, such as their amount and their height. These thermal infrared camera’s measure the black-body radiation emitted by clouds. Since clouds have the same temperature as the surrounding atmosphere, the cloud height can be deduced from the measured cloud temperature, provided that the atmospheric temperature profile is known. When a temperature corresponding to the ground surface temperature is measured or when the measured visible radiance is below a certain threshold, the satellite observation is assumed to be cloud-free. Since the spatial resolution of these dedicated cloud remote sensing satellites is typically about 1 km\(^2\) or better, the footprints can be assumed either cloud-free or completely covered by clouds with little error. Modern satellite instruments dedicated to retrieve cloud information measure at several wavelengths from UV to radio, which allows the retrieval of many additional cloud properties, such as cloud optical thickness, droplet size and also information about the cloud phase (water or ice).

### 1.3.2 Cloud parameter retrieval with GOME and SCIAMACHY

The objective of SCIAMACHY, GOME and similar spectrometers is not to retrieve accurate cloud information, but to provide global trace gas measurements. However, as discussed in section 1.2.3, information about the cloud fraction, cloud optical thickness and cloud top height is necessary to accurately account for clouds in the trace gas retrieval algorithms. Therefore, several techniques to retrieve cloud information from their measurements have been developed. Most of them make use of the absorption band of molecular oxygen around a wavelength of 760 nm, the so-called oxygen A-band (Kuze and Chance, 1994; Koelemeijer et al., 2001). Since clouds shield the atmosphere below them, the light path of the reflected sunlight, and thus the depth of the oxygen A-band, decreases with increasing cloud height. This is illustrated in Fig. 1.6a where simulated SCIAMACHY measurements are shown for scenes with three different cloud top heights. With varying cloud top heights the continuum at 758 nm only
slightly changes, while the reflectance in the strongest part of the absorption bands at 761 nm varies significantly with varying cloud top height. The measured reflectance in and around the oxygen A-band is also sensitive to the optical thickness of the cloud, as shown in Fig. 1.6b. For increasing optical thickness, the continuum increases strongly. The measured reflectance at wavelengths in the deep absorption band is less sensitive to changes in the cloud optical thickness. This is because most light at these wavelengths is absorbed before reaching the cloud. Also the cloud fraction affects the reflectances in the oxygen A-band, as shown in Fig. 1.6c. Comparing Fig. 1.6c with Fig. 1.6b reveals that the sensitivity of the oxygen A-band to cloud fractions is very similar to its sensitivity to cloud optical thickness. It is this similarity in sensitivity for cloud fraction and cloud optical thickness that poses a problem in the simultaneous retrieval of both these parameters. However, because GOME and SCIAMACHY have such large footprint sizes, their pixels cannot be assumed either cloud-free or completely covered by clouds and a cloud fraction needs to be retrieved. For this reason, some cloud retrieval algorithms (e.g. Kurosu et al., 1999; Van Roozendael et al., 2006) use the higher spatial resolution measurements of the PMDs to determine the cloud fraction by setting thresholds for the PMD intensity values defining cloud-free and fully clouded scenes.
Subsequently, this value for the cloud fraction is used for the retrieval of cloud top height and cloud optical thickness from oxygen A-band measurements. A drawback of this approach is that the spatial resolution of the PMDs is also not high enough to assume their footprints to be either cloud-free or completely covered by clouds. Thus a cloud fraction has to be determined for every PMD measurement. However, these retrieved cloud fractions strongly depend on the chosen threshold values, as shown by Tuinder et al. (2004). Another commonly used solution is the retrieval of so-called effective cloud fractions (e.g. Koelemeijer et al., 2001). Effective cloud parameters are those that are retrieved from the measurements assuming a fixed cloud optical thickness (or reflection). For example, when for a certain GOME footprint the cloud optical thickness is 10, the cloud top pressure is 500 hPa and the cloud fraction is 0.5, the effective cloud fraction retrieved from measurements of the oxygen A-band under the assumption of a cloud optical thickness of 40, is 0.29 (see also Fig. 1 in Chapter 4 of this thesis). Thus, the effective cloud fraction differs significantly from the actual cloud fraction. The retrieved effective cloud top pressure is 524 hPa and thus differs only slightly from the actual cloud top pressure. In chapter 4 and 5 of this thesis, it is shown that the use of effective cloud parameters can result in significant biases in respectively tropospheric NO$_2$ columns and ozone profiles retrieved from GOME and SCIAMACHY measurements. This is because the effective cloud fraction is a wavelength dependent quantity. In the retrieval of effective cloud parameters, the measurement is simulated by a weighted sum of the reflectance of the cloudy and clear-sky parts of the measurement footprint. Since the effective cloud fraction differs significantly from the actual cloud fraction, also the estimated contribution of the clear-sky part of the measurement footprint differs from the actual one in this approach. The clear-sky contribution to the measurement can vary substantially with wavelength due to varying surface albedo, absorption features and, most importantly, Rayleigh scattering contribution. This in turn causes the retrieved effective cloud parameters to vary with wavelength. Therefore, a new method is introduced in this thesis to retrieve independent information about cloud fraction and optical thickness, in addition to the cloud top height, using the measurements at the oxygen A-band and in the UV. Since both the cloud fraction and optical thickness are retrieved with this
method, in contrast to an effective cloud fraction, the biases in retrieved trace gas amounts caused by the treatment of clouds are reduced.

1.4 Radiative transfer in cloudy atmospheres

In order to retrieve trace gas or cloud information from satellite measurements of backscattered sunlight, the measurements have to be modeled using a forward model. The major part of the forward model consist of a radiative transfer model to calculate the intensity vector emerging at the top of the atmosphere. For cloudy atmospheres, an important aspect of the radiative transfer model is the representation of clouds.

1.4.1 Cloud model

Since clouds have a relatively high scattering optical thickness, the radiative transfer calculations in cloudy atmospheres are generally very time consuming. To overcome this, many approximations have been proposed. The most widely used approximation is the treatment of clouds as reflecting and absorbing boundaries (e.g. Kurosu et al., 1997). This approximation neglects scattering and absorption within the cloud. Moreover, the cloud reflection is often assumed to be Lambertian (Koelemeijer et al., 2001), i.e. independent of geometry. However, several studies have shown that this approximate treatment of clouds can cause substantial errors in retrieved trace gas amounts and cloud properties (Liu et al., 2004; Ahmad et al., 2004). Therefore, a more advanced approximate treatment of clouds was proposed by Kokhanovsky (2001), in which the reflection matrices of clouds are analytically calculated using asymptotic relations. These relations are accurate for weakly absorbing clouds with a scattering optical thickness larger than 5 but can yield large errors when used in wavelength windows including strong absorption bands (Kokhanovsky and Rozanov, 2004).

In this thesis, clouds are described more realistically as scattering and absorbing layers. However, some simplifying assumptions still need to be made: Firstly, a single homogeneous cloud layer is assumed. Thus, the effect of multiple cloud layers and vertical inhomogeneity of the cloud layer is ignored. This approximation may cause errors in cloud retrieval results when multiple cloud layers and/or very inhomogeneous clouds are present in the measurement footprints (Rozanov et al., 2004). These issues are
briefly discussed in chapter 4 of this thesis. Secondly, horizontal inhomogeneities of the cloud are ignored. Thus, the atmosphere is divided in horizontal homogeneous clear-sky and cloudy parts. Furthermore, interactions of light from the clear-sky part and the cloudy part of the atmosphere are ignored. Thus, when $I_{\text{clear}}$ and $I_{\text{cloud}}$ are the simulated intensity vectors for the clear-sky and cloudy part of the measurement, respectively, the intensity vector $I$ at the top of a partly cloudy atmosphere is simply approximated by

$$I = f_c I_{\text{cloud}} + (1 - f_c) I_{\text{clear}}$$

(1.1)

where $f_c$ is the cloud fraction. This approximation is commonly called the independent pixel approximation. It has been shown that the independent pixel approximation performs sufficiently well at scales larger than about 1 km$^2$ (Marshak et al., 1995; Zuidema and Evans, 1998). Finally, the clouds are assumed to consist of liquid spherical water particles with a specified size distribution. With this assumption, the single scattering properties of the cloud particles can be calculated by Mie-theory. The fact that clouds can contain non-spherical (ice) particles is ignored by this approximation, which can lead to a significant overestimation in the retrieved cloud optical thickness, depending on geometry (Mishchenko et al., 1996). Furthermore, the variability in cloud droplets size distribution is ignored. This, however, will result in only small errors since the visible reflectance is only minimally dependent on the cloud particle size (see e.g. Minnis et al., 1998).

Although the cloud model is still a simplification of a real cloud, it describes important characteristics of clouds, such as their geometry dependent reflection, the absorption and scattering of light inside the cloud and the transmission of light through the cloud. Moreover, this model allows to accurately simulate GOME type measurements of cloudy atmospheres.

### 1.4.2 Solving the radiative transfer problem

**Monochromatic radiative transfer calculations**

To simulate the satellite measurements, a radiative transfer model is needed which solves the radiative transfer equation in a multi-layer, multiple-scattering and absorbing atmosphere, bounded below by a reflecting surface, and illuminated from above by the sun. Furthermore, because polarization effects cannot be neglected (Chandrasekhar, 1960; Liou, 1992;
Mishchenko et al., 1994; Lacis et al., 1998), a vector radiative transfer model is required, i.e. a model which solves the radiative transfer equation not only for the radiance but also for the polarization terms of the Stokes vector (Chandrasekhar, 1960; Hovenier et al., 2004; Mishchenko et al., 2006). Several methods to solve the atmospheric (vector) radiative transfer problem have been described in the literature (see e.g. Lenoble, 1985). For example, the doubling-adding (de Haan et al., 1987) and discrete ordinates (Schulz et al., 1999) methods are widely used. The radiative transfer model described in this thesis makes use of the Gauss-Seidel iterative method (Hasekamp and Landgraf, 2002). This is an efficient method for solving the radiative transfer problem in a clear-sky atmosphere. However, the Gauss-Seidel method is very inefficient for cloud layers due to their high scattering optical thickness. Therefore, we calculate the cloud reflection and transmission properties with the doubling method, which is efficient for homogeneous cloud layers. Subsequently, the Gauss-Seidel method is used to solve the radiative transfer problem in the whole atmosphere using the pre-calculated reflection and transmission properties of the cloud layer. This yields a relatively efficient model for monochromatic radiative transfer calculations.

Radiative transfer calculations in absorption bands

For the simulation of measurements in absorption bands, radiative transfer calculations have to be performed at high spectral resolution to resolve all significant absorption lines. This can lead to a high computational effort. To reduce the computing time, various approximation techniques are available (e.g. Stam et al., 2000b; Bennartz and Fischer, 2000). The underlying basic method of most of these techniques is the so-called k-distribution method (Lacis and Oinas, 1991). This method makes use of the smooth dependence of the radiances on the total absorption optical thickness. However, the radiance is not only dependent on the total absorption optical thickness but also on the vertical distribution of the optical thickness. Due to this, these techniques can yield large errors in strong absorption bands such as the oxygen A-band, especially in cloudy atmospheres (Stam et al., 2000b; Maurellis et al., 2004; Duan et al., 2005). Therefore, the radiative transfer model described in this thesis interpolates the reflection and transmission matrices of the cloud over the absorption
and scattering optical thickness within the cloud layer, while the radiative transfer calculations in the rest of the atmosphere are performed line-by-line. In this way, an efficient but accurate radiative transfer model for absorption bands is obtained.

1.5 Outline of this thesis

The goal of the research described in this thesis is to develop a new method for the retrieval of cloud parameters to improve the satellite remote sensing of tropospheric trace gas information in cloudy atmospheres. As discussed above, clouds have a big impact on the satellite measurements and thereby on the trace gas retrieval results. More specifically, the validation of ozone profiles retrieved from GOME measurements in the UV by Hasekamp et al. (Hasekamp and Landgraf, 2001; Hasekamp et al., 2002) revealed a large underestimation of the ozone concentration in the troposphere, which was partly attributed to the treatment of clouds in the retrieval. Simulations showed that using the readily available effective cloud parameters in the ozone profile retrievals leads to a smaller but still significant overestimation of the tropospheric ozone concentration. To further improve on this, a method is developed in this thesis to retrieve independent information about the cloud fraction, cloud optical thickness and cloud top pressure from GOME and SCIAMACHY measurements.

In chapter 2, we first evaluate the measurements of GOME and SCIAMACHY in the oxygen A-band at 760 nm, which are primarily used for the retrieval of cloud parameters. This is done by retrieving surface pressures from cloud-free GOME and SCIAMACHY measurements in the oxygen A-band. The validation of these retrievals with accurate meteorological model data can provide important insight into the quality of the oxygen A-band measurements and the forward model. Because aerosols are neglected in these retrievals, simulated measurements are used to assess the impact of the neglect of aerosols in surface pressure retrievals from the oxygen A-band. Using the validation of surface pressure retrievals from GOME and SCIAMACHY measurements, a cross-calibration of the two instruments is performed.

Accurate radiative transfer calculations in absorption bands in cloudy atmospheres are generally very time consuming. Therefore an efficient
vector radiative transfer model for vertically inhomogeneous cloudy atmospheres is introduced in chapter 3. A new approach to radiative transfer is taken by combining two solution methods, namely the Gauss-Seidel method, which is efficient for inhomogeneous cloudless atmospheres, and the doubling method, which is efficient for homogeneous cloud layers. In addition, to further reduce the computation time of radiative transfer calculations in absorption bands, the cloud reflection and transmission matrices are interpolated over the absorption and scattering optical depths within the cloud layer. By means of radiative transfer calculation in the oxygen A-band and the Hartley-Huggins ozone band, the efficiency and accuracy of the resulting model is discussed and compared to that of the well-known doubling-adding method. This radiative transfer model is used in the retrieval algorithms described in chapters 4 and 5.

A new method for the retrieval of cloud fraction, cloud optical thickness and cloud top pressure from GOME and SCIAMACHY measurements is presented in chapter 4. The presented algorithm uses the measurements of the oxygen A-band between 758 and 770 nm and measurements in the ultraviolet between 350 and 390 nm. The information content of these measurements is discussed and compared to the information content of measurements in the oxygen A-band only. The method is applied to a set of GOME measurements and the results are compared to cloud parameters retrieved from measurements of the Along Track Scanning Radiometer 2 (ATSR-2).

The effect of clouds on ozone profile retrievals is discussed in chapter 5. Three approaches to take clouds into account in ozone profile retrieval algorithms are evaluated, namely (1) to treat clouds as an effective ground surface albedo, commonly known as the cloud as albedo approach; (2) using effective cloud fractions and cloud top pressures retrieved from oxygen A band measurements assuming a cloud optical thickness of 40; and (3) using cloud fractions, optical thicknesses and top pressures retrieved from measurements at the oxygen A-band and in the UV from 350–390 nm, as proposed in chapter 4 of this thesis. The errors in the ozone profiles obtained with these different approaches are investigated by means of simulated GOME measurements. Finally, the ozone profiles retrieved from actual GOME measurements with these three approaches are validated with ozonesonde measurements.
The thesis is concluded with a summary and an outlook in chapter 6.
Chapter 2

Surface pressure retrieval from SCIAMACHY measurements in the O$_2$ A Band: validation of the measurements and sensitivity on aerosols

Abstract

We perform surface pressure retrievals from cloud-free oxygen A-band measurements of SCIAMACHY. These retrievals can be well validated because surface pressure is a quantity that is, in general, accurately known from meteorological models. Therefore, surface pressure retrievals and their validation provide important insight into the quality of the instrument calibration. Furthermore, they can provide insight into retrievals which are affected by similar radiation transport processes, for example the retrieval of total columns of H$_2$O, CO, CO$_2$ and CH$_4$. In our retrieval aerosols are neglected. Using synthetic measurements, it is shown that for low to moderate surface albedos this leads to an underestimation of the retrieved surface pressures. For high surface albedos this generally leads to an overestimation of the retrieved surface pressures. The surface pressures retrieved from the SCIAMACHY measurements indeed show this dependence on surface albedo, when compared to the corresponding pressures from a meteorological database. However, an offset of about 20 hPa was found, which can not be caused by neglecting aerosols in the retrieval. The same offset was found when comparing the retrieved surface pressures to those retrieved from co-located GOME oxygen A-band measurements. This implies a calibration error in the SCIAMACHY measurements. By adding an offset of 0.86% of the continuum reflectance at 756 nm to the SCIAMACHY reflectance measurements, this systematic bias vanishes.


text continues here
about 30 minutes, allowing a good comparison. Although SCIAMACHY
has been calibrated on ground, this calibration needs to be validated in
flight. Therefore, the results and validation of our retrievals are useful to
identify calibration inaccuracies.

The paper is constructed as follows. First the retrieval method is pre-
sented in Sect. 2.2. The effect of aerosols on the surface pressure retrieval
and on the oxygen A-band measurements is studied using simulated mea-
surements in Sect. 2.3. Then, in Sect. 2.4, the surface pressures retrieved
from SCIAMACHY measurements are presented and compared with the
findings from the simulated measurements and with surface pressures re-
trieved from GOME measurements. The discussion and conclusions follow
in Sect. 2.5.

2.2 The retrieval method

For the retrieval of a state vector $\mathbf{x}$ from a measurement vector $\mathbf{y}$, a forward
model $\mathbf{F}$ is needed that describes how $\mathbf{y}$ depends on $\mathbf{x}$, i.e.

$$\mathbf{y} = \mathbf{F}(\mathbf{x}) + \mathbf{e},$$

with error term $\mathbf{e}$. The measurement vector $\mathbf{y}$ contains the reflectances
measured at different wavelengths and the state vector $\mathbf{x}$ contains the un-
known parameters to be retrieved. For the surface pressure retrievals in
this paper the state vector $\mathbf{x}$ contains at least the following parameters: (1)
the surface pressure, (2) the surface albedo at 756 nm and (3) the linear
spectral dependence of the surface albedo. Additionally, $\mathbf{x}$ may contain
instrument parameters such as a wavelength shift and response function
parameters.

Since SCIAMACHY and GOME are polarization sensitive instruments,
the intensity $I_{pol}$ measured by a certain detector pixel $i$ at wavelength $\lambda_i$
is not only affected by the intensity of the light that enters the instrument
but also by its state of polarization, viz.

$$I_{pol}(\lambda_i) = \tilde{I}_{TOA}(\lambda_i) + m_{12}(\lambda_i)\tilde{Q}_{TOA}(\lambda_i) + m_{13}(\lambda_i)\tilde{U}_{TOA}(\lambda_i),$$

where $m_{12}$ and $m_{13}$ are elements of the instrument’s Mülller matrix nor-
malized to its element (1,1). Furthermore, $\tilde{I}_{TOA}$, $\tilde{Q}_{TOA}$, and $\tilde{U}_{TOA}$ are the
Figure 2.1: Example of an oxygen A-band reflectance spectrum at 0.005 nm spectral resolution (red) and at SCIAMACHY resolution (black).

Elements of the intensity vector $\bar{I}_{TOA}$ defined by

$$\bar{I}_{TOA}(\lambda_i) = \int_0^\infty d\lambda \ S(\lambda_i, \lambda) I_{TOA}(\lambda), \quad (2.3)$$

where $I_{TOA}(\lambda)$ is the intensity vector of the light at the entrance of the instrument. The spectral response function $S$ is described by

$$S(\lambda_i, \lambda) = \frac{a_1^2}{\left[(\lambda_i - \lambda)/\Delta_p\right]^4 + a_0^2}, \quad (2.4)$$

where $\Delta_p$ is the width of the detector pixels, assumed to be 0.217 nm. The width of the response function is determined by $a_0$. For SCIAMACHY and GOME, the value of $a_0$ is approximately 1.1772 and 0.7377, respectively. The normalization factor $a_1$ is determined by the requirement

$$\int_0^\infty S(\lambda_i, \lambda) d\lambda = 1. \quad (2.5)$$

Similarly to the earth radiances, SCIAMACHY and GOME also measure the solar irradiance $F_o$ to obtain the polarization sensitive reflectances $R_{pol}$
defined by

\[ R_{\text{pol}}(\lambda_i) = \frac{I_{\text{pol}}(\lambda_i)}{F_{\alpha}(\lambda_i)}. \] (2.6)

The common approach to account for the polarization sensitivity of SCIAMACHY and GOME is to apply a polarization correction to the radiances \( I_{\text{pol}} \) using the Polarization Measurement Devices (PMDs). However, the broadband PMD measurements are not sufficient to correct for the polarization sensitivity in spectral regions where the state of polarization is varying rapidly with wavelength, as is the case for the oxygen A-band \((\text{Stam et al., 2000a; Schutgens and Stammes, 2003})\). Moreover, the SCIAMACHY PMDs are not yet well calibrated. In our retrieval approach, these errors due to polarization sensitivity are avoided by using the polarization sensitive reflectances \( R_{\text{pol}} \) as the elements of the measurement vector \( \mathbf{y} \). This means that the forward model \( \mathbf{F} \) directly models the polarization sensitive reflectances \( R_{\text{pol}} \). This approach was introduced by \( \text{Hasekamp et al. (2002)} \) for the retrieval of Ozone profiles from GOME.

The main part of the forward model \( \mathbf{F} \) is an atmospheric radiative transfer model. In this study the SRON radiative transfer model \((\text{Hasekamp and Landgraf, 2002})\) is used, which uses a Gauss-Seidel iteration scheme to solve the plane-parallel radiative transfer equation. This model fully includes polarization and multiple scattering. A Rayleigh scattering atmosphere is assumed with 60 1 km thick layers. The absorption line parameters are taken from the HITRAN 2004 spectroscopic database \((\text{Rothman et al., 2005})\) and a Voigt lineshape is assumed. The cross-section sampling and radiative transfer calculations are performed on a 0.005 nm spectral resolution. Figure 2.1 shows an example of the oxygen A-band at 0.005 nm resolution and at SCIAMACHY resolution. The oxygen A-band consists of 2 branches which are resolved in the SCIAMACHY resolution, i.e. the deep R branch around 761 nm and the broader P branch around 765 nm. All retrievals are performed using iterative non-linear least squares fitting. For these fits, \( \ln(R) \) is used instead of \( R \).

### 2.3 Retrieval from simulated measurements

\( \text{Dubuisson et al. (2001)} \), among others, have shown that aerosols signifi-
Table 2.1: Characteristics at 765 nm of the two modes of the desert dust aerosols used in this study, based on aerosol model DL from Torres et al. (2001). A log-normal size distribution is assumed. The relative contribution of the modes to the number concentration is represented by the fraction. The aerosols are evenly distributed over the first 2 kilometres and decrease in number as $P^3$ from 2 to 10 kilometres, unless indicated otherwise. The single scattering albedo of the aerosols used is 0.97605. See Hansen and Travis (1974) for definitions of the parameters.

<table>
<thead>
<tr>
<th>mode</th>
<th>Effective radius</th>
<th>Size variance</th>
<th>Refractive index</th>
<th>fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.105 $\mu$m</td>
<td>0.323 $\mu$m$^2$</td>
<td>1.53-0.001i</td>
<td>0.99565</td>
</tr>
<tr>
<td>2</td>
<td>1.605 $\mu$m</td>
<td>0.418 $\mu$m$^2$</td>
<td>1.53-0.001i</td>
<td>0.00435</td>
</tr>
</tbody>
</table>

Significantly affect surface pressure retrievals from oxygen A-band measurements. Furthermore, they showed that the effects of aerosols depend on surface albedo. To study the effects of aerosols on the retrieval of surface pressure from SCIAMACHY, SCIAMACHY measurements are simulated for atmospheres with different aerosol loads and above several surface albedos. Subsequently, the apparent surface pressure from these simulated measurements is retrieved using a forward model with only Rayleigh scattering included. For these retrievals, the state vector $\mathbf{x}$ (see Eq. 2.1) contains only the surface pressure and surface albedo and the linear spectral dependence of the surface albedo. The SCIAMACHY measurements are simulated for a nadir viewing geometry with a solar zenith angle of 40° and the US standard atmosphere with a surface pressure of 1000 hPa. Desert dust aerosols are included of which the characteristics are given in Table 2.1. The optical aerosol properties are calculated using Mie theory.

Figures 2.2a and 2.2b show the difference between the true surface pressure and the retrieved apparent surface pressure ($\Delta P=P_{\text{true}}-P_{\text{apparent}}$) as a function of retrieved apparent surface albedo, for different aerosol optical thicknesses and height distributions, respectively. Figures 2.2c and 2.2d show $\Delta P$ as a function of apparent surface albedo for varying solar zenith angles and viewing geometries, respectively. Although depending on aerosol optical thickness, aerosol height distribution, aerosol type and geometry, two general effects are observed: (1) For low and moderate surface albedos the surface pressures are underestimated in the retrieval. This is due to the relatively high contribution to the measured radiances of
Figure 2.2: The difference between the true surface pressure used in the simulated measurements including aerosols and the apparent surface pressure retrieved ignoring aerosols, \( \Delta P = P_{\text{true}} - P_{\text{apparent}} \), as a function of retrieved apparent surface albedo. The true surface albedos are 0, 0.01, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6. The retrieved values are indicated by pluses. A nadir viewing geometry with a solar zenith angle of 40° is used. Panel (a) shows the retrieved values for different values of the total aerosol optical thickness \( \tau \) at 765 nm. To obtain \( \tau \) at the more common wavelength of 550 nm, the values have to be multiplied by 1.11. Panel (b) shows the retrieved values for different height distributions. Here, our standard aerosol distribution (see Table 2.1) is modified such that the lower layer with evenly distributed aerosols is extended to higher levels, indicated by the layer top. In panel (c), the retrieved \( \Delta P \) and surface albedos are shown for varying solar zenith angles (SZA) with a nadir viewing geometry. Panel (d) shows the retrieved values for different viewing angles (VA), when a relative azimuth angle of 50° is taken. Solid and dashed lines indicate negative and positive viewing angles, respectively. In Panels (b), (c) and (d) an aerosol optical thickness of 0.4 is taken.
Figure 2.3: Residuals between the simulated reflectance measurements $R_{\text{meas}}$ for an atmosphere including aerosols and the fitted reflectances $R_{\text{mod}}$ ignoring aerosols. The residuals are defined as $(R_{\text{mod}} - R_{\text{meas}})/R_{\text{meas}} \times 100\%$. A surface albedo of 0.1 is used. The residuals are shown for different values of the aerosol optical thickness (a) and different height distributions (b), similar to Fig. 2.2a and Fig. 2.2b respectively.

Figure 2.4: Similar to Fig. 2.2a, but when $\Delta P$ and the apparent surface albedo are retrieved while neglecting all scattering. The solid black line shows results of retrievals from simulated measurements for a clear-sky case including only Rayleigh scattering.
photons that are scattered back by the aerosol layer, reducing the photon path. Furthermore, most of the light penetrating through the aerosol layer is absorbed by the surface. This effect was also identified by *Dubuisson et al.* (2001). (2) At large surface albedos, the surface pressures are, in general, overestimated in the retrieval. Here, most photons penetrating through the aerosol layer are reflected by the surface and travel through the aerosol layer once more. Due to (multiple) scattering in the aerosol layer the photon path is enhanced, resulting in an overestimation of the surface pressure. This effect was not previously recognized by *Dubuisson et al.* (2001).

Furthermore, the results show that the effects of aerosols on the surface pressure retrieval increase with increasing aerosol optical thickness, while the aerosol height distribution only significantly impacts the surface pressure retrieval above low albedos. The solar zenith angles (SZA) impact the sensitivity of surface pressure retrieval on aerosols above all surface albedos. Starting at SZA = 10°, the values for ΔP first decrease towards larger SZA, reach a minimum for SZA ≈ 40°, and then increase towards larger SZA. This behavior is due to the fact that, on the one hand, an increase in SZA, and therewith geometrical path, causes (1) an enhanced optical path due to multiple scattering and on the other hand (2) leads to a decrease in optical path due to increased extinction. Below SZA ≈ 40°, the former effect dominates, while the latter effect dominates for higher SZA. Also the viewing geometry significantly impacts the sensitivity of surface pressure retrieval on aerosols above all surface albedos. Maximum values of ΔP occur at nadir geometries. The aerosol type affects the apparent surface pressure retrieval as well (not shown). Generally, a decrease in the aerosol particle size leads to an increase in multiple scattering and therewith, apparent surface pressures.

To summarize, Fig. 2.2 shows that due to varying aerosol optical thickness and height distribution and varying geometry, the expected range in ΔP is about 30 hPa above high surface albedos and about 300 hPa above low surface albedos. This is in agreement with what is found by other authors (*Vanbauce et al.*, 1998; *Dubuisson et al.*, 2001; *Ramon et al.*, 2004).

The spectral fitting residuals between the simulated measurements for an atmosphere including aerosols and the fitted reflectances ignoring aerosols are shown in Fig. 2.3a and b, for different aerosol optical thicknesses and
height distributions, respectively. The residuals show a large negative peak in the center of the deep R branch and positive values in the P branch. The amplitude of the residuals increases with increasing aerosol optical thickness (Fig. 2.3a) and increasing height of the bulk of the aerosols (Fig. 2.3b). Furthermore, it depends on type of the aerosols and slightly on the surface albedo (not shown). The shape of the residuals, however, is characteristic.

Figures 2.2 and 2.3 show a clear dependence of both $\Delta P$ and the spectral fitting residual on the aerosol height distribution and optical thickness. This implies that, when the true surface pressure and the aerosol type are known, information about the aerosol optical thickness and height distribution can be retrieved from the oxygen A-band measurements. This was previously demonstrated by Koppers et al. (1997).

In addition to aerosols, Rayleigh scattering also has a large effect on the surface pressure retrievals, although the Rayleigh scattering optical thickness at these wavelengths is relatively low ($\sim 0.025$). This effect is illustrated in Fig. 2.4, which shows $\Delta P$ retrieved while neglecting all scattering from simulated SCIAMACHY measurements for atmospheres including aerosols and, additionally, for a clear-sky atmosphere including only Rayleigh scattering. In the clear-sky case, neglecting Rayleigh scattering in the retrieval leads to an underestimation of the surface pressure above all surface albedos. For aerosol loaded atmospheres, a comparison of Fig. 2.4 with Fig. 2.2 shows that, at low albedos and for a low aerosol optical thickness, the effect of neglecting Rayleigh scattering dominates the effect of neglecting aerosols. Furthermore, at large albedos the effect of neglecting Rayleigh scattering can partly compensate for the effect of neglecting aerosols. The large effect of Rayleigh scattering can be explained by the fact that the oxygen A-band contains a large number of optically thick absorption lines (see Fig. 2.1) for which only few photons penetrate through the atmosphere to high pressure levels. At low pressure levels, aerosol optical depths are generally low and thus the reflectance at the wavelengths of these optically thick absorption lines is mainly determined by Rayleigh scattering. Therefore, neglecting Rayleigh scattering in the forward model leads to an increase in the depth of these absorption lines which leads to an underestimation of the surface pressure.

The simulations in this section show that aerosols significantly affect the oxygen A-band measurements. When retrieving surface pressure ne-
Figure 2.5: False color images produced with SCIAMACHY (left) and GOME (right) PMD measurements, which have a higher spatial resolution than the science channel measurements. For this study data from SCIAMACHY orbits 4700 (West) and 4699 (East) and GOME orbits 30 123 106 (West) and 30 123 092 (East) are used. The PMDs of SCIAMACHY and GOME measure in different wavelength ranges, resulting in different coloring.

glecting aerosol scattering, characteristic residuals as shown in Fig. 2.3 are expected. Furthermore, surface pressures retrieved using the oxygen A-band are expected to underestimate the actual surface pressure at low and moderate albedos and overestimate them at high albedos.

2.4 Retrieval from SCIAMACHY measurements

2.4.1 Data

For this study, the reflectances in the oxygen A-band measured by SCIAMACHY and GOME are analyzed. The characteristics of the oxygen A-band measurements for both instruments are summarized in Table 2.2. The SCIAMACHY reflectances (level 1b data) used in this study are improved by replacing calibration data using the NADC tools\(^1\). For both instruments all calibration options are applied, with the exception of the polarization sensitivity correction, which is not needed because the polarization sensitive measurement is modelled directly (see Sect. 2.2). Furthermore, on the

\(^1\)Available at http://www.sron.nl/~richardh/SciaDC/index.html
reflectances measured by SCIAMACHY a multiplicative correction factor of 1.2 is applied. This correction factor was found by Acarreta et al. (2004) and Acarreta and Stammes (2004) by comparing the measured reflectances with those measured by MERIS, also on ENVISAT.

Cloudy pixels are excluded from the data. To identify clouds in SCIAMACHY measurements, we use the SPICI method developed by Krijger et al. (2005) using the PMD measurements. For GOME, an adapted version is used.

As reference surface pressures for validation, the pressure profile data from the UKMO Stratospheric Assimilated dataset are combined with the TerrainBase surface elevation database. The UKMO dataset has a spatial resolution of 2.5×3.75° and the grid-box containing the center of the instrument footprint is taken. The TerrainBase data has a resolution of 5×5 arc-minutes and is averaged over the instrument footprint. To calculate the absorption cross-sections, the temperature profiles are taken from the UKMO dataset.
Table 2.2: Characteristics of the SCIAMACHY and GOME measurements in the oxygen A-band from 755–775 nm.

<table>
<thead>
<tr>
<th></th>
<th>SCIAMACHY</th>
<th>GOME</th>
</tr>
</thead>
<tbody>
<tr>
<td>Channel</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Spectral resolution</td>
<td>(\sim 0.4 \text{ nm} )</td>
<td>(\sim 0.25 \text{ nm} )</td>
</tr>
<tr>
<td>Spectral sampling</td>
<td>(\sim 0.22 \text{ nm} )</td>
<td>(\sim 0.22 \text{ nm} )</td>
</tr>
<tr>
<td>Footprint size</td>
<td>(60 \times 30 \text{ km}^2)</td>
<td>(320 \times 40 \text{ km}^2)</td>
</tr>
<tr>
<td>Scanning angles (East to west)</td>
<td>-30° to 30°</td>
<td>-30° to 30°</td>
</tr>
</tbody>
</table>

Table 2.3: Mean and standard deviation of the retrieved wavelength shifts \(\Delta \lambda\) and response function parameters \(a_0\).

<table>
<thead>
<tr>
<th></th>
<th>mean</th>
<th>standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta \lambda)</td>
<td>-0.0772 nm</td>
<td>0.00115 nm</td>
</tr>
<tr>
<td>(a_0)</td>
<td>1.09573</td>
<td>0.0356539</td>
</tr>
</tbody>
</table>

2.4.2 Retrieval results

First, SCIAMACHY and GOME measurements above southern Europe and northern Africa on 23 January 2003 are analyzed. False color images of the data used are shown in Fig. 2.5. In SCIAMACHY, Nadir and Limb measurements are alternated. Since for this study only Nadir measurements are used, the SCIAMACHY orbits are broken up into several blocks, generally referred to as states. The solar zenith angles and relative azimuth angles for these data range from about 40–60° and 30–60°, respectively.

To retrieve apparent surface pressures from SCIAMACHY measurements, the state vector \(\mathbf{x}\) (Eq. 2.1) contains (1) the surface pressure, (2) the surface albedo at 756 nm, (3) the linear spectral dependence of the surface albedo, (4) a wavelength shift \(\Delta \lambda\) and (5) the response function parameter \(a_0\) (see Eq. 2.4). The instrument parameters (4 and 5) did not significantly interfere with the other retrieved parameters and are very similar for each retrieval. The mean and standard deviation of the instrument parameters retrieved are given in Table 2.3.

Figure 2.6 shows the absolute differences between retrieved apparent surface pressures and the reference surface pressures \(\Delta P = P_{\text{reference}} - P_{\text{apparent}}\). Figure 2.7 shows \(\Delta P\) as a function of the retrieved surface albedo. Much
variation is seen, ranging from $\Delta P = 300$ to $-60$ hPa. Clearly, systematic differences are seen between retrievals above land and sea, i.e. high and low surface albedos. In general, $\Delta P$ is positive for albedos lower than 0.1 and negative for higher surface albedos. The few low surface pressures retrieved above high surface albedos are probably due to clouds not flagged by the cloud filter used.

Also shown in Fig. 2.7 are results from the simulated measurements as presented in Fig. 2.2, for an aerosol optical thickness of 0.1 and 0.3, respectively. The retrieved values match the results from the simulated measurements well for low albedos ($<0.1$). However, for higher albedos, the retrieved values for $\Delta P$ are systematically about 20 hPa lower. Several other aerosol types and height distributions were tried, none of which match these retrievals.

For comparison, surface pressures retrieved from the GOME measurements are shown in Fig. 2.8. Similar variations as in the SCIAMACHY retrievals of Figs. 2.6 and 2.7 are seen. However, the values of $\Delta P$ are systematically about 20 hPa higher than those retrieved from SCIAMACHY and are more in line with the simulations presented in Sect. 2.3.

To verify the observed systematic difference in $\Delta P$ retrieved by SCIAMACHY and GOME for other data, e.g. for other geometries and geolocations, values of $\Delta P$ are retrieved from an extended dataset. This dataset includes all cloud-free measurements in two orbits from 23 August 2002 and two orbits from 23 January 2003, all over Europe, Africa and the South Atlantic Ocean (i.e. orbits 2509, 2510, 4699 an 4700). The solar zenith angles and relative azimuth angles in this dataset range from about 20–80 ° and 0–60 °, respectively. Table 2.4 shows the mean values and standard deviations of $\Delta P$ retrieved from SCIAMACHY and GOME data, within several apparent surface albedo bins. Above low albedos ($<0.2$), the standard deviations become large, as expected from the conclusions made in section 2.3. Therefore, the comparison between $\Delta P$ retrieved by SCIAMACHY and GOME is very sensitive to varying atmospheric conditions and geometries. Above moderate and high albedos, on the other hand, values of $\Delta P$ retrieved by GOME are systematically about 20 hPa higher, confirming the conclusions made above.

Thus, it seems likely that the surface pressures retrieved from SCIAMACHY data suffer from a systematic error(s), probably due to a calibra-
Figure 2.7: $\Delta P$ as a function of apparent surface albedo for SCIAMACHY orbits 4700 (top) and 4699 (bottom). Results from the 5 individual SCIAMACHY states per orbit, as seen in Fig. 2.6, are color-coded in black, blue, green, yellow and red going from north to south. Two results from simulated measurements for atmospheres with aerosol optical thicknesses of 0.1 and 0.3, as presented in Fig. 2.2, are plotted with dashed lines.
Figure 2.8: $\Delta P$ retrieved by the GOME instrument, as a map-projection (a) and as function of apparent surface albedo (b), similar to Figs. 2.6 and 2.7, respectively.
Table 2.4: Mean values and standard deviations (in brackets) of $\Delta P$ retrieved from SCIAMACHY and GOME data of the extended dataset, within several apparent surface albedo bins.

<table>
<thead>
<tr>
<th>Apparent Surface albedo</th>
<th>$\Delta P$ SCIAMACHY [hPa]</th>
<th>$\Delta P$ GOME [hPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-0.05</td>
<td>133 (69.1)</td>
<td>133 (79.4)</td>
</tr>
<tr>
<td>0.05- 0.1</td>
<td>98.3 (106)</td>
<td>140.2 (129)</td>
</tr>
<tr>
<td>0.1- 0.2</td>
<td>20.7 (70.3)</td>
<td>66.7 (106)</td>
</tr>
<tr>
<td>0.2- 0.3</td>
<td>-12.5 (20.5)</td>
<td>11.3 (16.3)</td>
</tr>
<tr>
<td>0.3- 0.4</td>
<td>-14.3 (22.5)</td>
<td>2.25 (13.4)</td>
</tr>
<tr>
<td>0.4- 0.5</td>
<td>-25.7 (12.6)</td>
<td>-2.05 (16.7)</td>
</tr>
<tr>
<td>0.5- 0.6</td>
<td>-22.6 (28.2)</td>
<td>-0.257 (27.0)</td>
</tr>
</tbody>
</table>

The effect of several SCIAMACHY calibration errors on the retrieved surface pressures is investigated. First, it is found that changing the multiplicative factor applied on the measured reflectances (Acarreta et al., 2004, see Sect. 2.4.1) only minimally affects the retrieved surface pressure. The reason for this is that the relative depth of the oxygen A-band contains the surface pressure information. On the other hand, the retrieved surface pressures are affected when an offset is added to the measured reflectances. To determine a suitable calibration correction for SCIAMACHY, apparent surface pressures are retrieved from the SCIAMACHY measurements on which several offsets are applied. The offsets are defined as a percentage of the continuum reflectance around 756 nm, after multiplication by 1.2. Fig. 2.9 compares, for each applied offset, the mean surface pressure retrieved from SCIAMACHY with the corresponding mean surface pressure retrieved from GOME. For this, the extended dataset described above is used. GOME ground pixels are larger than those of SCIAMACHY and do not overlap perfectly. Therefore, surface pressures and apparent surface albedos retrieved from SCIAMACHY ground pixels with their center within a GOME ground pixel are averaged. Furthermore, SCIAMACHY and GOME observations with apparent surface albedos differing more than 2% are rejected. Because the $\Delta P$ retrieved by SCIAMACHY and GOME above low albedos is very sensitive to varying atmospheric conditions and sampling effects (see section 2.3), only observations with apparent surface albedos above 0.1 are used in this analysis. From Fig. 2.9 it follows that
the difference in retrieved apparent surface pressure between SCIAMACHY and GOME depends linearly on the applied offset. An offset of 0.86% of the continuum reflectance around 756 nm needs to be added to the SCIAMACHY oxygen A-band reflectance measurements, so that the retrieved surface pressures agree with those retrieved from the GOME data. Figure 2.10 shows $\Delta P$ as a function of surface albedo when this correction is applied. With this correction, the retrievals behave as expected from the study presented in Sect. 2.3 and compare well with the GOME retrievals shown in Fig. 2.8b. The offset found is probably related to the inaccuracies in the reflectance calibration (Lichtenberg et al., 2006; Acarreta et al., 2004; Nöel, 2004).

The different colors in Fig. 2.10 correspond to different SCIAMACHY states, i.e. different geolocations (see Figs. 2.6 and 2.7). Significant differences in the retrieved values of $\Delta P$ between states are seen. Because
Figure 2.10: Same as Fig. 2.7, but when the SCIAMACHY reflectances are corrected by adding an offset of 0.86% of the continuum reflectance to the reflectances.
Figure 2.11: Aerosol optical thicknesses at 558 nm retrieved using the MISR instrument on EOS Terra on January 23th, 2003. Data from MISR orbits 16486 (west) and 16485 (east) are shown. These data were obtained from the NASA Langley Research Centre Atmospheric Sciences Data Centre. The contours of the SCIAMACHY states are indicated by the red boxes.

Figure 2.12: Residuals of spectral fits of a SCIAMACHY (black) and a GOME (red) oxygen A-band measurement with a nadir viewing geometry and a solar zenith angle of approximately 40°. Both measurements are taken at approximately 13° latitude and -10° longitude and have an apparent surface albedo of ~0.16. Note that on the SCIAMACHY measurements the correction suggested in section 2.4.2 is applied. In blue, a residual from a simulated SCIAMACHY measurement, similar to those in Fig. 2.3, is shown. For this, an atmosphere including aerosols with an optical depth of 0.45 and a layer top of 8 km (see Fig. 2.2) is taken. The true surface pressure and apparent surface albedo are similar to those in the SCIAMACHY and GOME measurements.
all states have approximately similar geometries, it is likely that these differences are due to the varying aerosol optical thickness, as follows from Fig. 2.2. In particular, the retrievals from data from the most northern state of orbit 4700 (in black) match well with results from simulated measurements corresponding to an aerosol optical thickness of 0.05–0.2, while the most southern state of orbit 4700 (in red) matches better with results from simulated measurements for an aerosol optical thickness of 0.2–0.6. This increase in aerosol optical thickness at the location of the most southern state is confirmed by the aerosol optical thickness retrieved by the MISR instrument on EOS Terra (Diner et al., 2001) on the same day, as shown in Fig. 2.11. However, the absolute values of the MISR optical thicknesses do not match those derived from Fig. 2.10. As is illustrated in Fig. 2.2b, this can be due to an incorrect assumption about the aerosol height distribution in our forward model. Also, the true aerosol type can be different than the one assumed. Furthermore, the MISR optical thicknesses are given at a wavelength of 558 nm, while we use a wavelength of 765 nm. However, our results are in qualitative agreement with the aerosol optical thickness retrievals from MISR.

### 2.4.3 Spectral fitting residuals

A closer inspection of the spectral fitting residuals yields valuable information. Figure 2.12 shows residuals from a SCIAMACHY and a GOME measurement above approximately the same location with an apparent surface albedo of \( \sim 0.16 \). The residuals are very much alike. Also shown is a residual from a simulated measurement similar to those shown in Fig. 2.3. The residual from the simulated measurement is very similar to those from the real SCIAMACHY and GOME measurements. This confirms that the spectral fitting residuals are for a large part caused by neglecting aerosols in our retrieval.

However, also some high frequency scatter of about 2–5\% is seen in the residuals from the SCIAMACHY and GOME measurements, which are not observed in the simulations and can thus not be caused by neglecting aerosols in the retrieval. Again these features are very common in all our spectral fitting residuals. They might be due to errors in the spectroscopy data (Chance, 1997; Rothman et al., 2005) or the instrument response functions. Furthermore, solar Fraunhofer lines (e.g. at 766.5 nm) could
appear in the reflectances due to calibration errors.

2.5 Conclusions and discussion

In this paper we have presented surface pressure retrievals from cloud-free SCIAMACHY oxygen A-band measurements. The retrievals have been performed using a radiative transfer model that fully includes multiple Rayleigh scattering and polarization but does not include the effect of aerosols. Using synthetic measurements, the effects of neglecting aerosols on the retrieved surface pressures have been investigated. It was found that for low and moderate surface albedos, aerosols lead to an underestimation of the retrieved surface pressures due to a reduction of the light path. For high surface albedos, scattering by aerosols leads to an enhancement of the light path and thus to an overestimation of the surface pressure. The magnitude of these effects depends on aerosol optical thickness, the aerosol height distribution and the geometry. Variations in these parameters result in expected ranges in retrieved surface pressures of about 30 hPa above high surface albedos and about 300 hPa above low surface albedos. It has also been observed that aerosols cause a characteristic spectral feature in the fitting residuals, of which the amplitude depends on the aerosol optical thickness and height distribution as well.

The apparent surface pressures retrieved from SCIAMACHY have been validated with reference surface pressures from the UKMO meteorological dataset. The difference between the SCIAMACHY apparent surface pressures and the reference surface pressures shows a dependence on surface albedo that can be explained by the fact that aerosols are neglected in the retrieval. However, also a systematic offset of about 20 hPa was observed that cannot be explained by the effect of aerosols. The same offset was found by comparing the surface pressures retrieved from SCIAMACHY with surface pressures retrieved from co-located GOME measurements. This indicates the presence of a calibration error in the SCIAMACHY measurements. Adding an offset of 0.86% of the continuum reflectance at 756 nm to the SCIAMACHY reflectance measurements removes this systematic bias. This offset has been determined by comparing the surface pressures retrieved from SCIAMACHY measurements, on which several offsets are applied, with those retrieved from co-located GOME measure-
ments. The fitting residuals observed for the SCIAMACHY and GOME measurements are very similar and both show the characteristic spectral features due to neglecting aerosols in the retrieval, as were also found in the study using synthetic measurements.

The clear dependence of both the retrieved surface pressure and the spectral fitting residuals on the aerosol optical thickness and height distribution, as shown in this paper, indicates that both parameters may be retrieved from oxygen A-band measurements, when one assumes the surface pressure as known. This was previously demonstrated by Kopers et al. (1997).

For similar retrievals of total columns of other species than O₂, e.g. H₂O, CO, CO₂ and CH₄, similar effects due to aerosols as discussed in this paper, i.e. under- or overestimation of the total column, can be expected (Dubuisson et al., 2004; Houweling et al., 2005). The retrieved total column of these species are often scaled to oxygen to correct for the light path (Noël et al., 1999; O’Brien and Rayner, 2002; Kuang et al., 2002; Dufour et al., 2004) or to obtain volume mixing ratios of the species (Buchwitz et al., 2005a,b). As pointed out by O’Brien and Rayner (2002), the light paths are affected by the height distribution and optical thickness of the absorption lines of individual species, which needs to be considered when applying such a scaling. Indeed, comparing the results shown in Fig. 2.2 with those presented by Houweling et al. (2005) (Fig. 4a), it is apparent that aerosols impact the retrieval of CO₂ and O₂ differently. Furthermore, results shown in this paper imply that care must be taken when using the oxygen A-band for scaling of retrievals at other wavelengths, because the effects of aerosols are shown to depend significantly on surface albedo, which is wavelength dependent. Additionally, the optical thickness of Rayleigh scattering and therewith its relative contribution to the total scattering varies with wavelength as well. These problems can be avoided by retrieving aerosol properties simultaneously with the total column of the trace gas, the surface albedos and the surface pressure (Kuang et al., 2002).

To conclude, this paper shows that surface pressure retrievals can be used to validate the calibration of the oxygen A-band measurements. This approach could also be used to validate the calibration of the SCIAMACHY measurements of other oxygen bands, i.e. O₂ B and γ and O₄ bands.
Acknowledgements

SCIAMACHY and GOME data were provided by ESA. The SCIAMACHY data were processed using the NADC tools, available at http://www.sron.nl/~richardh/SciaDC/index.html. The MISR data were obtained from the NASA Langley Research Center Atmospheric Sciences Data Center. Part of this work was supported by the Dutch User Support Programme 2001–2005 (USP) under project number EO-069.
Chapter 3

Efficient vector radiative transfer calculations in vertically inhomogeneous cloudy atmospheres

Abstract

Accurate radiative transfer calculations in cloudy atmospheres are generally very time-consuming, limiting their practical use in satellite remote sensing applications. We present a model to efficiently calculate the radiative transfer of polarized light in atmospheres that contain homogeneous cloud layers. This model combines the Gauss-Seidel method, which is efficient for inhomogeneous cloudless atmospheres, with the doubling method, which is efficient for homogeneous cloud layers. Additionally, to reduce the computational effort for radiative transfer calculations in absorption bands, the cloud reflection and transmission matrices are interpolated over the absorption and scattering optical thickness within the cloud layer. We demonstrate that the proposed radiative transfer model in combination with this interpolation technique is very efficient for the simulation of satellite measurements for inhomogeneous atmospheres containing one homogeneous cloud layer. For example, SCIAMACHY measurements in the oxygen A-band (758–773 nm) and Hartley-Huggins ozone band (295–335 nm) with a spectral resolution of 0.4 nm can be simulated for these atmospheres within a minute on a 2.8 GHz PC with an accuracy better than 0.1 %.
3.1 Introduction

Satellite measurements of reflected sunlight in the ultraviolet (UV), visible and shortwave infrared play an important role in monitoring the atmospheric composition. For example, measurements of the Global Ozone Monitoring Experiment (GOME) (Burrows et al., 1999), the SCanning Imaging Absorption spectroMeter for Atmospheric CartograpHY (SCIAMACHY) (Bovensmann et al., 1999) and the Ozone Monitoring Instrument (OMI) (Levett et al., 2006), are used to monitor ozone, nitrogen-dioxide (NO₂), sulphur-dioxide (SO₂), water vapor, aerosols and other atmospheric compounds. Due to the large field-of-view of many of these satellite instruments, clouds are influencing most of their measurements. For example, the fields-of-view of GOME (320×40 km²), SCIAMACHY (60 ×30 km²) and OMI (13 × 24 km²) imply that, on average, about 98%, 94% and 90% of their measurements, respectively, is contaminated by clouds (Krijger et al., 2007). Clouds can have a large effect on the retrieval of trace gas amounts (Thompson et al., 1993; Koelmeijer and Stammes, 1999). Therefore, algorithms for the interpretation of these satellite measurements should take the effect of clouds into account. However, accurate radiative transfer calculations in cloudy atmospheres are generally very time-consuming. To overcome this, often simple approximations are used to describe clouds in retrieval algorithms. The most widely used approximation is the description of clouds as reflecting and absorbing surfaces that do not transmit radiation (e.g. Kurosu et al., 1997). Moreover, the cloud reflection is often assumed to be Lambertian (e.g. Koelmeijer et al., 2001).

Recent studies have shown that this approximative treatment of clouds can cause substantial errors in the retrieval products from satellites (Liu et al., 2004; Ahmad et al., 2004). For instance, Liu et al. (2004) showed that not accounting for ozone absorption within a cloud can result in errors in the total ozone amounts of about 1–10 %. Moreover, they showed that these errors greatly depend on viewing and illumination geometry and the amount and distribution of ozone within the cloud. Also in retrievals of cloud properties using absorption bands of oxygen (Fischer and Grassl, 1991; Koelmeijer et al., 2001; Daniel et al., 2003), neglecting the enhancement of absorption inside the clouds leads to an underestimation of the cloud top height (Kurosu et al., 1997; Rozanov and Kokhanovsky,
In addition, the coupling between scattering on cloud particles and molecular Rayleigh scattering needs to be taken into account, especially in the UV (Ahmad et al., 2004; Wang and King, 1997). Thus, a radiative transfer model used for the interpretation of satellite measurements of cloudy atmospheres should take scattering and absorption inside clouds into account.

Additionally, such a radiative transfer model should take polarization into account. Namely, clouds can polarize incoming solar radiation, or can depolarize radiation that has been scattered by molecules and/or aerosols, depending on scattering geometry (Hansen, 1971b; Liou, 1992; Stam et al., 2000a; Kokhanovsky and Weichert, 2002). These polarization effects should be taken into account in order to model the radiance correctly and in order to correctly model measurements of polarization sensitive instruments as GOME and SCIAMACHY (Stam et al., 2000a). Furthermore, satellite measurements of the state of polarization, as performed e.g. by the POLDER and PARASOL instruments (Deschamps et al., 1994) and the APS instrument, scheduled to fly on the NASA Glory Mission (Mishchenko et al., 2004), contain important information on e.g. cloud optical thickness and size distribution (Hansen, 1971b; Stam et al., 2000a; Kokhanovsky and Weichert, 2002; Parol et al., 2004; Mishchenko et al., 2004). Obviously, extraction of this information requires a radiative transfer model including polarization.

Current (vector) radiative transfer codes, based on e.g. the doubling-adding (de Haan et al., 1987), Gauss-Seidel (Hasekamp and Landgraf, 2002) and discrete ordinate (Schulz et al., 1999) techniques are generally very time consuming for inhomogeneous atmospheres that contain clouds. The efficient approximative treatment of cloud layers using asymptotic relations as described by Kokhanovsky (2001) can include reflection and transmission of polarized light. However, these relations are only accurate for weakly absorbing media with a scattering optical thickness larger than 5 and can yield large errors when used in wavelength windows including strong absorption bands (Kokhanovsky and Rozanov, 2004).

The aim of this paper is to present a radiative transfer model that is sufficiently efficient to be practically used in retrieval applications. For these applications, radiative transfer calculations have to be performed for atmospheres that contain a limited number of homogeneous cloud layers (in
most cases one cloud layer), whereas the rest of the atmosphere is described by homogeneous layers containing molecules and/or aerosols with a much smaller scattering optical thickness. The radiative transfer problem for such a model atmosphere can be solved in two steps. First, the radiative transfer equation is solved for each individual layer. For this step, we use the layer average intensity approximation for non-cloudy layers and the doubling method (de Haan et al., 1987) for cloud layers. Second, the boundary conditions at the layer interfaces are matched, which results in a matrix equation with respect to the corresponding intensity vectors. In the presented model, this equation is efficiently solved using the Gauss-Seidel iteration method. The efficiency of this COmbined Doubling And Gauss-Seidel (CODAGS) model is demonstrated by a comparison to the doubling-adding approach. Furthermore, we show how the number of Gaussian-quadrature streams in the optically thin atmospheric layers can be reduced with respect to that used in the cloud layer, significantly reducing the calculation time.

For most retrieval applications, radiative transfer calculations have to be performed at many wavelengths in an atmospheric absorption band. In order to optimize CODAGS for absorption bands, we significantly reduce the number of calculations for the cloud layer, which is by far the most time-consuming part of CODAGS. The number of cloud calculations is reduced by interpolating the cloud reflection and transmission matrices over the scattering and absorption optical thickness within the cloud layer. Here, the required accuracy of the Stokes parameters at the top of atmosphere can be specified beforehand. The accuracy and efficiency of this technique are demonstrated by its application on radiative transfer calculations in the oxygen A-band in the near infrared and the Hartley-Huggins ozone absorption band in the UV.

The paper is constructed as follows. In Section 3.2 we will discuss the theoretical background of the CODAGS model. The computational effort and accuracy of this model will be discussed in Section 3.3. In section 3.4, the reduction of Gaussian quadrature streams is discussed. Next, in Section 3.5, we present the interpolation technique for spectral windows including absorption bands. In Section 3.6, the practical application of the presented radiative transfer model is demonstrated by accurately simulating SCIAMACHY measurements. Finally, we conclude the paper in
Section 3.7.

3.2 Theory

3.2.1 The radiative transfer problem in matrix form

The radiance and the polarization of radiation can be described by an intensity vector $\mathbf{I}$, which has the Stokes parameters $I, Q, U$ and $V$ as its components (Chandrasekhar, 1960; Hovenier and van der Mee, 1983), i.e.

$$\mathbf{I} = [I, Q, U, V]^T,$$

where $T$ indicates the transposed vector. Here, we define $\mathbf{I}$ relative to the local meridian plane.

In this Section, a general solution for the radiative transfer problem for diffuse light is discussed. Here, the directional zenith dependence of the intensity field $\mathbf{I}$ is described by $N$ Gaussian quadrature streams and the azimuthal dependence by a Fourier series, as proposed by Hovenier and van der Mee (1983) (see Appendix 3.A).

Let us consider a plane-parallel, vertically inhomogeneous atmosphere containing $M$ homogeneous model layers. For several methods to solve the radiative transfer problem in a homogeneous model layer $k$, ranging from optical depth $\tau_{k-1}$ to $\tau_k$, the outgoing upward intensity at the upper layer boundary is subject to a set of linear equations of the type

$$\mathbf{I}^m(\tau_{k-1}, \mu_i) = \sum_{j=-N}^{N} a_j \left[ \alpha^m_k(\mu_j, \mu_i) \mathbf{I}^m(\tau_{k-1}, \mu_j) + \beta^m_k(\mu_j, \mu_i) \mathbf{I}^m(\tau_k, \mu_j) \right] + \gamma^m_k(\mu_i) \mathbf{F}_0 \exp(-\tau_k/\mu_0),$$

(3.2)

for each Fourier term $m$ and Gaussian quadrature angle $\mu_i$ (with $i < 0$ for downward directions and $i > 0$ for upward directions). Here, $a_j$ are the Gaussian quadrature weights. The vector $\mathbf{F}_0$ is defined by $\mathbf{F}_0 = [F_0, 0, 0, 0]^T$, where $F_0$ is the solar incident flux per unit area perpendicular to the solar beam in the direction $\mu_0$. A similar equation holds for the downward intensity at the lower layer boundary. Expressions for the $4 \times 4$ matrices $\alpha^m_k$, $\beta^m_k$ and the 4 dimensional vector $\gamma^m_k$ depend on the chosen radiative transfer solution technique.
Matching the continuity conditions at the layer boundaries, we obtain

\[
\Phi_{k-1}^+ = A_{++}^k \Phi_{k-1}^+ + A_{+-}^k \Phi_{k-1}^- + B_{++}^k \Phi_k^+ + B_{+-}^k \Phi_k^- + \Gamma_k^+ F_0 \exp(-\tau_{k-1}/\mu_0)
\]

\[
\Phi_k^- = A_{-+}^k \Phi_{k-1}^- + A_{--}^k \Phi_k^- + B_{-+}^k \Phi_k^+ + B_{--}^k \Phi_{k-1}^- + \Gamma_k^- F_0 \exp(-\tau_{k-1}/\mu_0)
\]

for \( k = 1, \ldots, M \). Here, the \( 4N \)-dimensional vectors are defined by

\[
\Phi_{\pm}^k = \begin{bmatrix} \Phi_{k}^{\pm} \\ \vdots \\ \Phi_{M}^{\pm} \end{bmatrix}, \quad \Gamma_{\pm}^k = \begin{bmatrix} \gamma_{k}^{\pm}(\mu_{\pm1}) \\ \vdots \\ \gamma_{k}^{\pm}(\mu_{\pmN}) \end{bmatrix}
\]

Furthermore, the \( 4N \times 4N \) matrices \( A_{\pm\pm}^k \) and \( B_{\pm\pm}^k \) in Eqs. (3.3) and (3.4) are given by

\[
A_{\pm\pm}^k = (\alpha_{k}^{m}(\mu_{\pm j}, \mu_{\pm i})) \quad \text{and} \quad B_{\pm\pm}^k = (\beta_{k}^{m}(\mu_{\pm j}, \mu_{\pm i})),
\]

with \( i, j = 1, \ldots, N \). The vector \( \Phi \) is subject to the boundary conditions

\[
\Phi_0^- = [0, 0, 0, 0]^T \quad \text{and} \quad \Phi_M^+ = A_S \Phi_M^- + \Gamma_S F_0 \exp(-\tau_M/\mu_0),
\]

where the \( 4N \times 4N \) matrix \( A_S \) is given by

\[
A_S = (\alpha_S^m(\mu_{-j}, \mu_i)),
\]

with the \( 4 \times 4 \) submatrices

\[
\alpha_S^m(\mu_{-j}, \mu_i) = 2\mu_j R_S^m(\mu_j, \mu_i),
\]

with \( i, j = 1, \ldots, N \) and where \( R_S^m \) is the \( m \)th Fourier term of the bidirectional reflection distribution matrix of the surface. The \( 4N \) dimensional vector \( \Gamma_S \) has the coefficients

\[
\gamma_S^m(\mu_i) = \frac{\mu_0}{\pi} R_S^m(\mu_0, \mu_i),
\]

with \( i = 1, \ldots, N \). For the whole model atmosphere, Eqs. (3.3), (3.4), (3.7) and (3.8) can be summarized in the matrix equation

\[
M\Phi = C,
\]
with the \((2M + 1)4N\) dimensional vectors

\[
\Phi = \begin{bmatrix}
\Phi_0^0 & \Phi_0^1 & \Phi_0^2 & \cdots & \Phi_0^{M-1} \\
\Phi_1^0 & \Phi_1^1 & \Phi_1^2 & \cdots & \Phi_1^{M-1} \\
\Phi_2^0 & \Phi_2^1 & \Phi_2^2 & \cdots & \Phi_2^{M-1} \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
\Phi_M^0 & \Phi_M^1 & \Phi_M^2 & \cdots & \Phi_M^{M-1} \\
\end{bmatrix}
\]

\[
C = \begin{bmatrix}
\Gamma_1 & \Gamma_1 & \Gamma_2 & \cdots & \Gamma_M \\
\Gamma_1 & \Gamma_1 & \Gamma_2 & \cdots & \Gamma_M \\
\Gamma_1 & \Gamma_1 & \Gamma_2 & \cdots & \Gamma_M \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
\Gamma_1 & \Gamma_1 & \Gamma_2 & \cdots & \Gamma_M \\
\end{bmatrix}
\] (3.13)

and the \((2M + 1)4N \times (2M + 1)4N\) sparse matrix

\[
M = 1 - \begin{bmatrix}
A_{1+} & B_{1-} & B_{1+} & 0 & \cdots & \cdots & 0 \\
B_{1+} & A_{1-} & A_{1+} & 0 & \cdots & \cdots & 0 \\
0 & A_{2-} & A_{2+} & B_{2+} & B_{2+} & \cdots & \cdots & 0 \\
0 & B_{2-} & B_{2+} & A_{2-} & A_{2+} & \cdots & \cdots & 0 \\
\vdots & \cdots & \cdots & \ddots & \ddots & \cdots & \cdots & \vdots \\
0 & \cdots & \cdots & 0 & A_{M-+} & A_{M+} & B_{M-+} & B_{M+} \\
0 & \cdots & \cdots & 0 & B_{M-+} & B_{M+} & A_{M-+} & A_{M+} \\
0 & \cdots & \cdots & 0 & A_S & 0 \\
\end{bmatrix}
\]

where 1 is the corresponding unity matrix. Hence, for known coefficients \(\alpha_k^m\), \(\beta_k^m\) and \(\gamma_k^m\), the diffuse intensity vector field at the layer boundaries is found from the solution of matrix equation (3.12). For this purpose, several techniques exist (see e.g. Press et al., 1992), of which the Gauss-Seidel and LU-decomposition techniques are most widely used. An efficient variant of the Gauss-Seidel technique was first proposed by Herman and Browning (1965) and worked out thoroughly by Landgraf et al. (2001). In the next two Subsections we will discuss the use of the ‘layer average intensity approximation’-method and the doubling method to obtain \(\alpha_k^m\), \(\beta_k^m\) and \(\gamma_k^m\) for an atmosphere that contains clouds.
3.2.2 Layer average intensity approximation for optically thin layers

To obtain expressions for $\alpha_k^m$, $\beta_k^m$ and $\gamma_k^m$, a common approach in radiative transfer models employing the Gauss-Seidel technique is to approximate the intensities by their layer average, i.e.

$$\bar{I}^m(\mu_i) = \frac{1}{2} \left[ I^m(\tau_l, \mu_i) + I^m(\tau_{l-1}, \mu_i) \right] \quad \text{for} \quad \tau_{l-1} < \tau < \tau_l, \quad (3.14)$$

for $i = -N, \cdots, -1, 1, \cdots, N$. Following Hasekamp (2002), $\alpha_k^m$ and $\beta_k^m$ are then defined by

$$\alpha_k^m(\mu_{\pm j}, \mu_{\pm i}) = \frac{\omega_k}{4} \mathbf{Z}_k^m(\mu_{\pm j}, \mu_{\pm i}) \left[ 1 - \exp(-\Delta \tau_k/\mu_i) \right]$$

$$\beta_k^m(\mu_{\pm j}, \mu_{\pm i}) = \alpha_k^m(\mu_{\pm j}, \mu_{\pm i}) + \delta_{ij} \exp(-\Delta \tau_k/\mu_i \mathbf{E}), \quad (3.15)$$

and $\gamma_k^m$ is defined by

$$\gamma_k^m(\mu_{\pm i}) = \frac{\omega_k}{4\pi} \frac{\mu_o}{\mu_o + \mu_i} \mathbf{Z}_k^m(-\mu_o, \mu_{\pm i}), \quad (3.16)$$

with $i, j = 1, \cdots, N$. Here, $\omega_k$ is the single scattering albedo, $\mathbf{E}$ is the $4 \times 4$ unity matrix and $\delta_{ij}$ is the Kronecker delta. Furthermore, $\mathbf{Z}_k^m$ is the $m$th Fourier term of the scattering phase matrix, which can be calculated by

$$\mathbf{Z}_k^m(\mu_j, \mu_i) = (-1)^m \sum_{l=-\infty}^{\infty} \mathbf{P}_l^m(-\mu_i) \mathbf{S}_k^l \mathbf{P}_m^l(-\mu_j), \quad (3.17)$$

where $\mathbf{S}_k^l$ is the expansion coefficient matrix and $\mathbf{P}_m^l$ is the generalized spherical function matrix (Hovenier and van der Mee, 1983; de Haan et al., 1987).

Thus, the layer average intensity approximation of Eq. 3.14 allows the coefficients $\alpha_k^m$, $\beta_k^m$ and $\gamma_k^m$ to be expressed directly in terms of the scattering phase function and the single scattering albedo. The layer average intensity approximation holds for optically thin layers. To limit the errors caused by Eq. 3.14, the model layers are split into thin sublayers, such that their scattering and absorption optical thickness do not exceed the thresholds $\Delta_{\text{scat}}$ and $\Delta_{\text{abs}}$, respectively. The layer splitting procedure is discussed by Landgraf et al. (2001).

The ‘layer average intensity approximation’-method is very efficient for solving the radiative transfer in clear-sky atmospheres, including Rayleigh
scattering, as well as in atmospheres including additional aerosols, as shown by Hasekamp and Landgraf (2002). However, as noted before by Hansen (1971a) and Herman et al. (1980) among others, the method becomes relatively time consuming when considering atmospheres with a large scattering optical thickness, such as atmospheres containing clouds. This is illustrated in Fig. 3.1, where the computation time is shown for the radiative transfer in a homogeneous cloud layer as a function of its scattering optical thickness, when using the layer average intensity approximation. This increase in computation time is mainly due to the splitting of thick model layers into thin sublayers, needed to make the approximation of Eq. 3.14 valid, which increases the size of \( M \). Also, the iteration to solve matrix equation \( M\Phi = C \) converges more slowly with increasing scattering optical thickness, due to the higher order of scattering in cloudy model layers.

Because the layer average intensity approximation is commonly used in combination with the Gauss-Seidel technique to solve matrix Eq. 3.12, we will refer to this combination simply as the Gauss-Seidel technique in the remainder of this paper.

### 3.2.3 Doubling method for optically thick layers

As discussed above, the Gauss-Seidel technique is not efficient to solve the radiative transfer in optically thick layers. Alternatively, when the reflection and transmission properties of these layers are known, \( \alpha_k^m \) and \( \beta_k^m \) can be defined for these layers by

\[
\begin{align*}
\alpha_k^m(\mu_j, \mu_i) &= \alpha_k^m(\mu_{-j}, \mu_{-i}) = 0 \\
\beta_k^m(\mu_{-j}, \mu_i) &= \beta_k^m(\mu_j, \mu_{-i}) = 0 \\
\alpha_k^m(\mu_{-j}, \mu_i) &= 2\mu_j R_k^m(\mu_j, \mu_i) \\
\beta_k^m(\mu_j, \mu_{-i}) &= 2\mu_j R_k^m(\mu_j, \mu_i) \\
\beta_k^m(\mu_{-j}, \mu_{-i}) &= 2\mu_j (T_k^m(\mu_{j}, \mu_i) + \delta_{ij} \exp(-\Delta \tau_k/\mu_i E)) \\
\beta_k^m(\mu_j, \mu_i) &= 2\mu_j (T_k^m(\mu_{j}, \mu_i) + \delta_{ij} \exp(-\Delta \tau_k/\mu_i E)) \quad (3.18)
\end{align*}
\]

and \( \gamma_k^m \) can be defined by

\[
\begin{align*}
\gamma_k^m(\mu_i) &= \frac{\mu_0}{\pi} R_k^m(\mu_0, \mu_i) \\
\gamma_k^m(\mu_{-i}) &= \frac{\mu_0}{\pi} T_k^m(\mu_0, \mu_i), \quad (3.19)
\end{align*}
\]
Figure 3.1: Mean calculation time $t_{\text{cloud}}$ per Fourier term of the intensity field in a non-absorbing cloud layer as a function of the scattering optical thickness of the cloud layer, when using the layer average intensity approximation. The scattering properties of the cloud layer are described by Mie-theory. Cloud particles with a two parameter gamma distribution, an effective radius of 6 μm, an effective variance of 0.5 μm and a refractive index of 1.335 are taken. The scattering properties are calculated at 550 nm. The scattering optical thickness threshold for the layer splitting $\Delta_{\text{scat}}$ is taken to be 0.01, yielding an accuracy of $10^{-2}$% (Landgraf et al., 2001). In these calculations, a nadir viewing geometry is taken with a solar zenith angle of 40°. Furthermore, circular polarization is neglected and 64 Gaussian streams are used. The calculations are performed on a Pentium 4 2.8 GHz computer.

with $i, j = 1, \cdots, N$. Here $R_{k}^{m}$ and $T_{k}^{m}$ are the $m$th Fourier terms of the reflection and transmission matrices, respectively, for light incident on the upper boundary of the layer. The Fourier terms of the reflection and transmission matrices for light incident on the lower boundary of the layer are denoted by $R^{*m}_{k}$ and $T^{*m}_{k}$.

An efficient method to calculate the reflection and transmission matrices of homogeneous cloud layers is the doubling method (Hovenier, 1971; de Haan et al., 1987). To briefly explain the doubling method, we consider a model atmospheric layer with scattering optical thickness $\Delta \tau$ of which the reflection and transmission properties are known. This layer is then placed
on another identical layer. The reflection and transmission properties of the combined layer with optical thickness $2\Delta \tau$ can now be calculated using the doubling equations given by de Haan et al. (1987). Repeatedly, the resulting layer can be placed on another identical layer and the reflection and transmission properties of this combined layer can be calculated. Thus, repeating this procedure $N$ times, the reflection and transmission properties of a homogeneous layer with optical thickness $2^N \Delta \tau$ are obtained. Therefore, the doubling method is an efficient method to calculate the reflection and transmission properties of optically thick homogeneous layers. The doubling method is started with a layer having a scattering optical thickness small enough so that the two orders of scattering approximation holds. The reflection and transmission properties of this initial layer can be calculated analytically as described by Hovenier (1971). A detailed discussion of the doubling method is given by de Haan et al. (1987).

### 3.3 Combined doubling and Gauss-Seidel model: Validation and numerical performance

Based on the theory discussed in Section 3.2, we introduce the combined doubling and Gauss-Seidel (CODAGS) model to efficiently perform monochromatic radiative transfer calculations in inhomogeneous atmospheres that contain a limited number of homogeneous cloud layers. In this model, the radiative transfer problem is solved using the matrix equation (3.12), for which the coefficients are calculated as described in Subsection 3.2.3 for a cloud layer and as described in Subsection 3.2.2 for the rest of the atmosphere. Here, we will discuss the efficiency and accuracy of the CODAGS model.

The accuracy $\epsilon$ of the CODAGS model is on the one hand determined by the optical thickness thresholds ($\Delta_{\text{scat}}$) used to split the model layers in the Gauss-Seidel method (see Eq. 3.14). On the other hand, the CODAGS accuracy depends on the optical thickness of the initial layer used in the doubling method for the calculation of the reflection and transmission properties of the cloud layer. For the doubling calculations, the absolute accuracy $\epsilon_{\text{cloud}}$ can be specified beforehand as described by de Haan et al. (1987). In principle both the Gauss-Seidel and doubling methods can obtain an arbitrary accuracy. However, there is a strong trade-off between accuracy and
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Table 3.1: Used settings of CODAGS

<table>
<thead>
<tr>
<th>TOA accuracy</th>
<th>Settings</th>
</tr>
</thead>
<tbody>
<tr>
<td>ε [%]</td>
<td>Δ_{scat}</td>
</tr>
<tr>
<td>10^{-1}</td>
<td>10^{-1}</td>
</tr>
<tr>
<td>10^{-2}</td>
<td>10^{-2}</td>
</tr>
<tr>
<td>10^{-4}</td>
<td>10^{-3}</td>
</tr>
</tbody>
</table>

computational effort for both methods, and thus for the CODAGS model. Here, especially $\Delta_{\text{scat}}$ in the Gauss-Seidel method plays a crucial role. We investigate the computational speed of CODAGS for several accuracies. The settings of $\Delta_{\text{scat}}$ and $\epsilon_{\text{cloud}}$ used are given in Table 3.1. As a reference we use doubling-adding calculations with an accuracy of about 10$^{-8}$ %.

For all calculations, a nadir viewing geometry with a solar zenith angle of 40° is taken. Furthermore, a 30-layered US standard (Anderson et al., 1986) Rayleigh scattering non-absorbing model atmosphere is used containing one homogeneous cloud layer with properties as described in the caption of Fig. 3.1. The cloud layer has an optical thickness of 20 and a geometrical thickness of 1 km. The cloud top height is chosen at 3 km. To account for the highly peaked scattering phase function in the cloud layer, we use the so-called MS method of Nakajima and Tanaka (1988). In this method, the radiative transfer of multiple scattered light is calculated using the $\delta$-M approximation, while the contribution of single scattered light is calculated analytically. Furthermore, we use 64 Gaussian quadrature streams, i.e. $N = 32$ in Eq. 3.2. Circular polarization is neglected, since its contribution is relatively small for the considered atmospheres (Hansen, 1971b). All calculations are performed on a Pentium 4 2.8 GHz computer.

For radiative transfer calculations in a model atmosphere containing one homogeneous cloud layer, the total calculation time $t_{\text{tot}}$ can be written as $t_{\text{tot}} = t_{\text{cloud}} + t_{\text{res}}$, where $t_{\text{cloud}}$ is the time needed for the calculation of the reflection and transmission matrices of the cloud and $t_{\text{res}}$ is the residual calculation time needed for the radiative transfer calculation in the non-cloudy part of the atmosphere. In Fig. 3.2, $t_{\text{cloud}}$ per Fourier term is shown as a function of cloud optical thickness for two absolute accuracies. A comparison of Fig. 3.2 with Fig. 3.1 shows that the doubling method is the most efficient for clouds with an optical thickness above about 2, while
Figure 3.2: Mean calculation time $t_{\text{cloud}}$ per Fourier term of the reflection and transmission matrices $R$ and $T$ as a function of cloud optical thickness. The solid and dashed lines correspond to absolute accuracies $\epsilon_{\text{cloud}}$ of $10^{-4}$ and $10^{-7}$, respectively.

the Gauss-Seidel method is the most efficient for a lower cloud optical thickness.

To study the numerical effort of CODAGS, we compare the computation times $t_{\text{tot}}$ and $t_{\text{res}}$ of CODAGS with that of doubling-adding calculations using the model of de Haan et al. (1987) for similar accuracies. We note that the invariant imbedding method (Mishchenko, 1990), which is also based on the adding equations, might be more efficient than the doubling-adding technique in some cases. Because both the doubling-adding model and CODAGS use the doubling method for the calculation of the cloud reflection and transmission properties, $t_{\text{cloud}}$ is the same in both models. For CODAGS, Fig 3.3 shows $t_{\text{res}}$ as a function of scattering optical thickness in the non-cloudy part of the model atmosphere. Here, CODAGS is about 10–30 times faster than the doubling-adding calculations for an accuracy of $10^{-2}$ %. For higher accuracies and large scattering optical thickness, the efficiency of CODAGS is decreased strongly. However, these higher accuracies are generally not needed for the interpretation of satellite measurements.
The relative calculation times mentioned above hold for one incoming solar angle. This is generally the calculation needed in retrieval algorithms. If simultaneous calculations are to be made for several incoming angles, e.g. for the calculation of look-up-tables, the efficiency of CODAGS relative to that of the doubling-adding method decreases, because the doubling-adding method provides reflection and transmission properties of the atmosphere for a large set of solar zenith angles. However, the CODAGS method can be adapted for this purpose by replacing the Gauss-Seidel method for solving matrix equation 3.12 by the LU-decomposition method (Press et al., 1992; Landgraf et al., 2001).

The high efficiency of CODAGS becomes less clear when we consider the total computation time $t_{\text{tot}}$, which also includes the numerical calculation for the cloud layer. Here, $t_{\text{tot}}$ is only 3–5 times larger for the doubling-adding calculations than for CODAGS with an accuracy of $10^{-2}$%. This is because the total computation time is dominated by the calculations for the cloud layer. Thus, to take advantage of the high efficiency of CODAGS for the non-cloudy part, $t_{\text{cloud}}$ has to be reduced. This will be discussed in the next Section.

The calculation times given in Fig. 3.3 and 3.4 represent simulations per Fourier term for Fourier terms with a full coupling between the cloud layer and the non-cloudy part of the atmosphere. However, if $Z^m = 0$ (see Eq. 3.17) for layers other than the cloud layer and $Z^m \neq 0$ for the cloud layer itself, essentially $t_{\text{res}} = 0$ and $t_{\text{tot}} = t_{\text{cloud}}$, both for CODAGS and the doubling-adding code. This situation occurs for example for Fourier terms $m > 2$ in a Rayleigh scattering atmosphere containing cloud layers with an off-nadir viewing and off-zenith solar geometry. However, for cloudy atmospheres with an additional aerosol loading, the results shown in Fig. 3.3 and Fig. 3.4 are representative for all Fourier terms. For a detailed discussion on the required number of Fourier terms we refer to King (1983).

### 3.4 Reduction of Gaussian quadrature streams

In radiative transfer calculations for Rayleigh and/or aerosol scattering atmospheres containing cloud layers, commonly the same number of Gaussian quadrature streams (see Eq. 3.2) is used in all model layers of the
Figure 3.3: Mean residual computation time per Fourier term as a function of the total scattering optical thickness using CODAGS. (a) Absolute calculation time $t_{res}$. (b) $t_{res}$ relative to the corresponding doubling-adding calculations. Solid, dotted and dashed lines are for accuracies of $10^{-1}$, $10^{-2}$ and $10^{-4}$ %, respectively.

atmosphere. The number of streams needed to obtain a required accuracy, depends on the shape of the considered scattering phase matrices, in particular on their peakedness (Nakajima and Tanaka, 1988). In general, cloud droplets have highly peaked scattering phase matrices in the ultraviolet to near-infrared wavelength region (Liou, 1992). Therefore, to describe phase matrices of cloud particles, more streams are needed than to describe Rayleigh or aerosol phase matrices. The separation of the cloudy and non-cloudy part of the model atmosphere for the solution of the radiative transfer equation, as is done in CODAGS, suggests to use a lower number of streams for the non-cloudy part. This will reduce the compu-
Figure 3.4: Mean total computation time $t_{\text{tot}}$ per Fourier term as a function of the total scattering optical thickness using CODAGS, relative to the corresponding doubling-adding calculations. The model atmosphere contains one cloud layer with a scattering optical thickness of 20. Solid, dotted and dashed lines are for accuracies of $10^{-1}$, $10^{-2}$ and $10^{-4}$ % respectively.

Computation time $t_{\text{res}}$ significantly with only a minor loss in accuracy. To obtain the reflection and transmission matrices of the cloud layer for the streams used in the non-cloudy part of the model atmosphere, an interpolation is used. Following a suggestion of Knibbe et al. (2000), we employ a bicubic spline algorithm (Press et al., 1992) for this interpolation.

To illustrate the errors due to this approach, simulations of backscattered sunlight are performed for a non-absorbing Rayleigh scattering model atmosphere containing one cloud layer. Using 64 streams for the cloud layer, Fig. 3.5 shows the resulting error as a function of the viewing angle, when using 8 or 16 streams in the non-cloudy part of the model atmosphere, instead of 64. Errors in $I$ are below 0.3 % and 0.05 % using 8 and 16 streams, respectively. Errors in $Q$ are generally below 4 % and 1.2 % using 8 and 16 streams, respectively, except for the region around a scattering angle of 160° where $Q$ is nearly 0. The errors in Fig. 3.5 mainly result from the decrease in coupling between the cloud layer and the surrounding layers.
Figure 3.5: Errors in $I$ and $Q$ due to the reduction of the Gaussian quadrature streams in the non-cloudy part of the model atmosphere as a function of viewing angle. The corresponding single scattering angle is indicated at the top axis. A solar zenith angle of 60° and a relative azimuth angle of 0° are used. For the calculation of the cloud properties 64 Gaussian quadrature streams are used. The solid and dashed lines show the errors made when 8 or 16 streams are used in the Gauss-Seidel calculations, respectively. Here, a total Rayleigh scattering optical thickness of 0.8 is taken, corresponding to a wavelength of 330 nm.

Results shown in Fig 3.5 are for a total Rayleigh scattering optical thickness of 0.8. Generally, similar or lower errors are obtained for other values of the total Rayleigh scattering optical thickness. Reducing the number of streams from 64 to 8 and 16, decreases $t_{\text{res}}$ by a factor of approximately 80 and 20, respectively.
3.5 Interpolation of the cloud reflection and transmission matrices

In the previous Section, we showed that the CODAGS model is highly efficient for radiative transfer calculations in the non-cloudy part of an inhomogeneous model atmosphere. However, the radiative transfer calculations in the cloudy part dominate the total calculation time, which is still too large for many practical applications, such as the retrieval of cloud properties or trace gases in cloudy atmospheres, for which many spectral calculations in a given absorption band have to be performed. Therefore, an interpolation technique is proposed here to significantly reduce the number of cloud calculations in a given spectral absorption band.

For the radiative transfer in absorption bands, various approximation techniques have been proposed previously to reduce the computing time (e.g. Stam et al., 2000b; Bennartz and Fischer, 2000). The underlying basic method of most of these techniques is the so-called correlated $k$-distribution method. However, due to the uncorrelated nature of overlapped absorption lines, these techniques can yield large errors in atmospheres containing clouds, especially in strong absorption bands such as the oxygen A-band (Duan et al., 2005). The recently published double-$k$ approach (Duan et al., 2005) significantly reduces these errors and obtains high accuracies ($< 0.5 \%$) in the oxygen A band for atmospheres containing one cloud layer. The concept of CODAGS allows to easily overcome any problem due to the uncorrelated nature of overlapping absorption bands. Utilizing the high performance of the CODAGS model in the non-cloudy part, we calculate the radiative transfer in this part of the atmosphere line-by-line. To reduce the numerical effort needed to calculate the transmission and reflection matrices of a homogeneous cloud layer, we make use of the fact that these matrices depend smoothly on the total (absorption) optical depth, a feature which is also used by $k$-distribution methods. Consequently, an interpolation scheme using calculations of the reflection and transmission properties of the cloud layer at selected optical depths allows to very efficiently incorporate a cloud layer in the CODAGS model. Since the cloud layer is assumed to be optically homogeneous, a correlation problem does not exists for this layer and therefore the approach converges to the accurate solution for an increasing number of interpolation points.
Furthermore, unlike the $k$-distribution methods, our approach allows to specify an approximate accuracy beforehand and it can be used in any wavelength range including a variation in scattering properties.

By means of the oxygen A absorption band around 760 nm, which is often used for the retrieval of cloud properties (Fischer and Grassl, 1991; Koelemeijer et al., 2001; Rozanov and Kokhanovsky, 2004), we will demonstrate how the reflection and transmission matrices of a cloud layer can be interpolated over absorption optical thickness in the cloud layer. This interpolation is applied to each Fourier term separately. For the first Fourier term, Fig. 3.6a and Fig. 3.6b show element $R_{11}$ of the cloud reflection matrix as a function of wavelength and the absorption optical thickness in the cloud, respectively. From Fig. 3.6 it follows that the cloud reflection and transmission matrices vary smoothly as a function of absorption optical depth in the cloud when evaluated at a fixed scattering optical depth. Thus, the elements of the cloud reflection and transmission matrices can be obtained by interpolation, from radiative transfer calculations at a reduced number $N_{\text{abs}}$ of absorption optical depths in the cloud layer. Here, the computational effort of the linear interpolation used is negligible. When the reflection and transmission matrices vary significantly with scattering optical depth as well, a double interpolation has to be performed over both the scattering and absorption optical depths. So, when evaluating the reflection and transmission matrices at $N_{\text{scat}}$ values of the scattering optical depths in the cloud layer, a total of $N_{\text{abs}} \times N_{\text{scat}}$ radiative transfer calculations have to be performed. Since the reflecting and transmission matrices vary approximately linearly with scattering optical depth in the cloud layer, generally errors below $10^{-2}$ % are obtained when taking $N_{\text{scat}} = 2$. Moreover, when the range of scattering optical depths in the considered band is smaller than 0.005, errors below $10^{-2}$ % are obtained when the scattering optical thickness is fixed at its average value, denoted as $N_{\text{scat}} = 1$.

For a given absorption band, the error due to this interpolation depends on the number of interpolation points and their distribution over the optical depths. A scheme to determine the distribution of interpolation points over the absorption optical depths to obtain a required accuracy in $I$ is described in Appendix 3.B. Here, in principle accuracies can be specified for each Stokes parameter, but it mostly suffices to only specify an accuracy on Stokes parameter $I$. In the interpolation scheme, first a range of
Figure 3.6: (a) Normalized element $R_{11}^0$ of the cloud reflection matrix as a function of wavelength and (b) as a function of absorption optical depth in the cloud layer for fixed scattering optical depth. The calculations are performed on a 0.005 nm spectral grid (3000 wavelengths in total) with a solar zenith angle of 40°, a viewing angle of 20° and a relative azimuth angle of 0°. Absorption cross-sections are taken from the HITRAN 2004 database (Rothman et al., 2005). The atmospheric setup as presented in Section 3.3 is used throughout this Section, unless specified otherwise.
absorption optical depths in which the interpolation has to be performed is determined. Then, interpolation points are added until the error on $I$ due to this interpolation is estimated to be below the required accuracy for all absorption optical depths. The distribution of interpolation points is calculated for each Fourier term separately. Generally, for increasing Fourier term $m$, the relative contribution of $I^m$ to the total intensity vector decreases. Therefore, the required number of interpolation points decreases with Fourier index.

Fig. 3.7 shows the difference between calculations in the oxygen A-band at 3000 wavelengths performed with a line-by-line model and one using the interpolation scheme. Here, the number of interpolation points corresponds to a required accuracy in Stokes parameter $I$ of $\delta_I = 0.1\%$ and $\delta_I = 0.5\%$. For several cloud top heights, Fig. 3.8 shows the required number of interpolations points, $N_{\text{abs}}$, for the first Fourier term as a function of accuracy. With increasing cloud height, the total absorption optical thickness above the cloud decreases, increasing the relative contribution of light reflected by the cloud to the top of atmosphere intensity. As a result, the required number of interpolation points increases with cloud height. For accuracies of 0.02 % to 1%, 140 to 18 interpolation points are needed for the first Fourier term. For the second and third Fourier terms 3 to 9 interpolations points are required to obtain these accuracies. For higher terms, 3 interpolation points are mostly sufficient. The required number of interpolation points is found to be rather independent of geometry. Furthermore, the range of scattering optical thickness in the cloud layer is 0.0002, which means that using $N_{\text{scat}} = 1$ is sufficient, as discussed above. As a result, in the example shown in Fig. 3.7 with $\delta_I = 0.1\%$ and $\delta_I = 0.5\%$ the total number of calculations for the cloud matrices is reduced by a factor of 576 and 761, respectively.

To illustrate the application of our interpolation scheme for spectral ranges where also the scattering optical thickness varies significantly with wavelength, it is applied to calculations in the Hartley-Huggins ozone absorption band from 295–335 nm at 400 wavelengths. This band is often used for the retrieval of ozone profiles and total ozone columns (Hasekamp and Landgraf, 2001; Liu et al., 2004). In this band, the range of scattering optical thickness in the cloud layer is 0.05 due to Rayleigh scattering. Therefore, we set $N_{\text{scat}} = 2$. The interpolation points required for the in-
Figure 3.7: The modeled Stokes parameters $I$ and $Q$ in the oxygen A band band at 3000 wavelengths (top panel) and the differences $\Delta I$ (middle panel) and $\Delta Q$ (bottom panel) between calculations performed with a line-by-line model and calculations performed using the interpolation scheme with $\delta_I = 0.1\%$ and $\delta_I = 0.5\%$. Here, the same atmospheric setup is used as in Fig 3.6. The Fourier series is truncated at a maximum of 28 terms.
Figure 3.8: Required number of interpolation points for the first Fourier term as a function of the relative accuracy of $I$ at the top of atmosphere in the oxygen A-band. Solid, dashed and dotted lines correspond to cloud top heights of 3, 6 and 10 km, respectively. The number of interpolation points are calculated using the scheme described in Appendix 3.B.

Interpolation over absorption optical depths are determined by the scheme presented in Appendix 3.B. The resulting errors for $\delta_I = 0.5\%$ are shown in Fig. 3.9. The obtained accuracy is well below 0.5\%. Since the range in absorption optical depth in the cloud layer is much smaller in the ozone band as compared to that in the oxygen A-band, the reflection and transmission matrices are more linear and only 3 interpolation points for each Fourier term are required for the interpolation over absorption optical depths. As a result, in this example the total number of calculations for the cloud matrices is reduced by a factor of 55.

3.6 Simulation of SCIAMACHY measurements

To demonstrate the practical use of the CODAGS radiative transfer model, including the interpolation technique discussed in the previous Section, it
Figure 3.9: Same as Fig 3.7, but for the Hartley-Huggins ozone absorption band. Here, $\delta_I = 0.5\%$ and $N_{\text{scat}}=2$. The calculations are performed on a 0.1 nm wavelength grid at 400 wavelengths in total. The ozone absorption cross-sections are taken from *Bass and Paur* (1985). The Fourier series is truncated at a maximum of 16 terms.
is applied to the simulation of measurements from the spaceborne spectrometer SCIAMACHY (Bovensmann et al., 1999) in the Hartley-Huggins ozone band and oxygen A-band, as shown in Fig. 3.7 and Fig. 3.9, respectively. Since SCIAMACHY is a polarization sensitive instrument, the intensity $I_{\text{pol}}$ measured at a certain wavelength $\lambda$ is not only determined by the intensity of the light that enters the instrument but also by its state of polarization (Hasekamp et al., 2002; van Diedenhoven et al., 2005, Chapter 2), viz.

$$I_{\text{pol}}(\lambda) = I_{\text{TOA}}(\lambda) + m_{12}(\lambda)Q_{\text{TOA}}(\lambda),$$  \hspace{1cm} (3.20)

where $m_{12}$ is an element of the instrument’s Müller matrix normalized to its element (1,1) and assumed to be 0.4 at the considered wavelengths (Lichtenberg et al., 2006). Here, the relatively small sensitivity of SCIAMACHY to $U$ is neglected. Furthermore, $I_{\text{TOA}}$ and $Q_{\text{TOA}}$ are the first two elements of the intensity vector convolved with the instrument’s response function, which is approximated by a Gaussian with a full width at half maximum of 0.4 nm. SCIAMACHY has a typical noise level of 0.1–0.5 % in the UV and visible wavelength ranges. Therefore, errors in $I$ below 0.1% need to be obtained at SCIAMACHY’s resolution. The required accuracy in $Q$ depends on the degree of polarization. In atmospheres containing clouds, the degree of polarization is typically < 30% at a scattering angle around 140° (the so-called rainbow geometry) and < 10% at other geometries (Hansen, 1971b; Liou, 1992). Because $m_{12}$ is 0.4, errors in $Q$ at SCIAMACHY’s resolution need to be below about 1% in the rainbow geometry and 2.5% in other geometries. We found that these requirements are met in the oxygen A-band when $\delta_I$ is set to 0.5%, $N_{\text{scat}} = 1$ and 8 streams are used in the non-cloudy part of the atmosphere. In the ozone absorption band the requirements are met when 16 streams are used in the non-cloudy part of the atmosphere, $\delta_I$ is set to 0.5% and $N_{\text{scat}} = 2$. Figs. 3.10 and 3.11 show the resulting errors in $I$ and $Q$ in the oxygen A-band and the ozone band, respectively. In both bands the error due to the interpolation of the cloud matrices is dominant in $I$, while the error in $Q$ is dominated by the reduction in streams, as follows from comparison of Fig. 3.10 with Fig. 3.7 and Fig. 3.11 with Fig. 3.9.

Using CODAGS with these settings, the calculations in the oxygen A and ozone band are performed in 60 and 44 seconds, respectively, on a Pentium 4 2.8 GHz PC. The calculation times are reduced for geometries
Figure 3.10: Accuracy of CODAGS in combination with the proposed interpolation scheme and the reduction of streams (Subsection 3.4) for calculations in the oxygen A-band at 3000 wavelengths on a 0.005 nm wavelength grid (grey) and at SCIAMACHY resolution (black). Here, $\delta_I$ is set to 0.5%, $N_{\text{scat}} = 1$ and 8 streams are used in the non-cloudy part of the atmosphere. The same atmospheric setup is used as in Fig 3.6. The Fourier series is truncated at a maximum of 28 terms.

for which less Fourier terms are required.

For retrieval purposes, not only the outgoing Stokes parameters at the top of atmosphere are needed, but also their derivatives with respect to atmospheric properties. Since both the Gauss-Seidel and doubling models calculate the internal radiation field with no or little extra computational effort (Hasekamp and Landgraf, 2002; Stammes et al., 1989), these derivatives can be efficiently calculated according to the method described by Hasekamp and Landgraf (2005b). Thus, CODAGS can be practically used for (off-line) retrieval algorithms.
Here, $N_{\text{scat}} = 2$ and $\delta_t$ is set to 0.5%. The Fourier series is truncated at a maximum of 16 terms.

3.7 Conclusions

In this paper, we have presented a model to efficiently calculate the radiative transfer of polarized light in atmospheres that contains a limited number of homogeneous cloud layers. This model is based on the concept that the radiative transfer problem in such atmospheres can be written in a matrix equation, which can be efficiently solved using the Gauss-Seidel iteration technique. The elements of this matrix equation are obtained using the commonly used layer average intensity approximation. However, using this approximation is inefficient for optically thick layers. Therefore, the elements of the matrix formalism for the optically thick cloud layers are obtained using its reflection and transmission properties calculated with the doubling method. Thus, in this combined doubling and Gauss-Seidel (CODAGS) model, for both the optically thin and optically thick parts of the atmosphere, the most efficient solution techniques are used. Furthermore, it was shown how the number of Gaussian-quadrature streams in the
optically thin atmospheric layers can be reduced with respect to that used in the cloud layer, significantly reducing the calculation time. Although an arbitrary number of homogeneous cloud layers can be incorporated in CODAGS, in this paper we restricted the application of CODAGS to atmospheres containing one homogeneous cloud layer, as this application is most important for retrieval purposes.

In order to optimize CODAGS for absorption bands, a method was proposed to reduce the computational effort for high spectral resolution radiative transfer calculations. Since the calculation time for monochromatic calculations in CODAGS is dominated by the calculation of the reflection and transmission matrices of the cloud layer, the number of calculations for these matrices was reduced by interpolating them over the absorption and scattering optical thickness within the cloud layer. In the scheme to interpolate over absorption optical thickness, the interpolation points needed to obtain an required accuracy in the top of atmosphere intensity vector are determined for each Fourier term separately. The number of interpolation points needed to obtain a certain accuracy depends on the strength of the absorption band considered. For example, in the oxygen A-band (758-773 nm), the total number of calculations for the cloud reflection and transmission matrices can be reduced by a factor of 576 at an accuracy in $I$ of 0.1 %. For calculations in the Hartley-Huggins ozone band (295-335 nm), where the cloud reflection and transmission matrices were also interpolated over the scattering optical thickness in the cloud layer, the total number of calculations for the cloud reflection and transmission matrices can be reduced by a factor of 55 at an accuracy in $I$ below 0.03 %.

CODAGS in combination with the proposed interpolation technique is well suited to efficiently simulate high or medium spectral resolution satellite measurements with an accuracy which is more than sufficient for the retrieval of atmospheric parameters. For example, it was shown that accurate simulations of the measurements of the SCIAMACHY instrument in the oxygen A-band and the Hartley-Huggins ozone band for an atmosphere containing one homogeneous cloud layer are obtained in the order of 15–60 and 12–45 seconds, respectively, on a Pentium 4 2.8 GHz PC.
3.A Fourier Expansion for Azimuthal Dependence

To handle the integration of the equations needed in our radiative transfer model over azimuth angles, the Fourier expansion proposed by Hovenier and van der Mee (1983), and de Haan et al. (1987) is used. For the intensity vector at optical depth $\tau$, zenith angle $\mu$ and azimuth angle $\varphi$ (measured clockwise when looking downward) this expansion is given by

$$I(\tau, \mu, \varphi) = \sum_{m=0}^{\infty} (2 - \delta_{m0})$$

$$\left[ B^m(\varphi_o - \varphi) I^m(\tau, \mu) B^{-m}(\varphi_o - \varphi) I^{-m}(\tau, \mu) \right], \quad (3.21)$$

where $\varphi_0$ is the azimuth angle of the incoming radiation, $\delta_{m0}$ is the Kronecker delta and

$$B^m(\varphi) = \text{diag}[\cos m\varphi, \cos m\varphi, \sin m\varphi, \sin m\varphi] \quad (3.22)$$

$$B^{-m}(\varphi) = \text{diag}[-\sin m\varphi, -\sin m\varphi, \cos m\varphi, \cos m\varphi]. \quad (3.23)$$

Furthermore, the vectors $I^m$ and $I^{-m}$ are given by

$$I^m(\tau, \mu) = \frac{1}{2\pi} \int_0^{2\pi} d\varphi \ B^m(\varphi_o - \varphi) \ I(\tau, \mu, \varphi)$$

$$I^{-m}(\tau, \mu) = \frac{1}{2\pi} \int_0^{2\pi} d\varphi \ B^{-m}(\varphi_o - \varphi) \ I(\tau, \mu, \varphi). \quad (3.24)$$

For matrices this expansion is given by

$$L(\tau, \tilde{\mu}, \tilde{\varphi}; \mu, \phi) = \frac{1}{2} \sum_{m=0}^{\infty} (2 - \delta_{m0})$$

$$\left[ B^m(\tilde{\varphi} - \varphi) L^m(\tau, \tilde{\mu}, \mu)(E + \Delta) + B^{-m}(\tilde{\varphi} - \varphi) L^m(\tau, \tilde{\mu}, \mu)(E - \Delta) \right], \quad (3.25)$$

where $E$ is the $4 \times 4$ unity matrix and

$$\Delta = \text{diag}[1, 1, -1, -1]. \quad (3.26)$$

Here $L$ stands for the matrices used in our model, i.e. the reflection and transmission matrices of a cloud layer, the reflection matrices of the surface and the scattering phase matrices.
For the radiative transfer problem with the solar source $F_0$, defined in Section 3.2, the Fourier series of Eq. 3.21 only contains terms of $I^{+m}$. Therefore, in this paper we omit the positive sign for $m$.

### 3.B A scheme to determine the distribution of interpolation points over the absorption optical depths in the cloud layer

For the interpolation of the cloud transmission and reflection matrices over absorption optical depth in the cloud layer (Section 3.5), a scheme is presented here to determine the distribution of interpolation points to obtain a relative accuracy better than a specified value $\delta_i$ in the $i$th Stokes parameter $I_i$ of the intensity vector $I$ at the top of atmosphere. In each step of this scheme, an interpolation point is added and the relative error in $I_i$ due to the interpolation of the cloud reflection matrix is estimated. When this error can be assumed below $\delta_i$ for every absorption optical depth in the cloud layer, the procedure is stopped. For every Fourier term, a new set of interpolation points is determined.

To obtain an accuracy better than $\delta_i$, for each Fourier term $M$, we require that (see Appendix 3.A)

\[ \left| \sum_{m=0}^{M} (2 - \delta_m) B^m(\varphi_o - \varphi) \Delta I^m(\tau_a) \right|_{I_i} < \delta_i, \quad (3.27) \]

where $\Delta I^m$ is the absolute error in $I^m$ due to an error in the cloud reflection and transmission matrices with an absorption optical depth $\tau_a$. Neglecting the transmission through the cloud and the multiple scattering above the cloud, $I_i$ in Eq. 3.27 is approximated by

\[ I_i \approx \left[ I_{SS\uparrow} + \sum_{m=0}^{M} (2 - \delta_m) B^m(\varphi_o - \varphi) R_c^m(\tau_a; \mu_0, \mu) \right] \frac{F_0}{\pi} \exp(-\alpha[\tau_c + \tau_s]) \right|_{i}, \quad (3.28) \]

where $R_c^m$ is the $m$th Fourier term of the cloud reflection matrix and $I_{SS\uparrow}$ is the single scattering solution for the atmosphere above the cloud layer,
which can be calculated analytically. Furthermore, $\tau_c$ and $\tau_s$ are the absorption and scattering optical thickness above the cloud layer, respectively, and $\alpha$ is the air mass factor given by $(1/\mu_0 + 1/\mu)$. Again by neglecting the transmission through the cloud and the multiple scattering above the cloud, $\Delta I^m$ in Eq. 3.27 is approximated by

$$\Delta I^m(\tau_a) \approx \Delta R_c^m(\tau_a; \mu_0, \mu) \frac{\mu_0 F_0}{\pi} \exp(-\alpha[\tau_c + \tau_s]), \quad (3.29)$$

where $\Delta R_c^m(\tau_a; \mu_0, \mu)$ is the error in the $m$th Fourier term of the cloud reflection matrix, estimated as explained below. Furthermore, $\tau_c$ can be approximated from $\tau_a$ using a linear relation, as illustrated in Fig. 3.12 for the oxygen A-band.

The interpolation points are distributed between the minimum absorption optical depth present in the cloud layer $\tau_{\text{min}}$ and a threshold absorption optical depth $\tau_{\text{thresh}}$, above which errors in the cloud reflection matrix of 100% or larger can be assumed to result in errors in $I_i$ below $\delta_i$. We first
calculate $R_c^m(\tau_{\text{min}})$. Next, $\tau_{\text{thresh}}$ is estimated by requiring
\[
\frac{R_c^0(\tau_{\text{thresh}})}{I_i} \exp(-\alpha[\tau_c + \tau_s]) = \delta_i.
\] (3.30)

In Eq. 3.30, $R_c^0(\tau_{\text{thresh}})$ is not known. Therefore, $R_c^0(\tau_{\text{min}})$ is used instead, which is a conservatively large value because $R_c^0(\tau_{\text{min}}) > R_c^0(\tau_{\text{thresh}})$. Furthermore, $I_i$ is approximated by the $i$th Stokes parameter of $I_{SS\uparrow}(\tau_c = 0)$.

We now can obtain $\tau_c$ by inverting Eq. 3.30 and subsequently determine $\tau_{\text{thresh}}$ from the linear relation between $\tau_c$ and $\tau_a$ in Fig 3.12. Next, $R_c^0(\tau_{\text{thresh}})$ is calculated.

The scheme proceeds with two alternating steps 1 and 2. To initialize step 1, the absorption optical depths $\tau_{a1}$ and $\tau_{a2}$ to be used are taken as $\tau_{\text{min}}$ and $\tau_{\text{thresh}}$ with the corresponding matrices $R_c^M(\tau_{\text{min}})$ and $R_c^M(\tau_{\text{thresh}})$, respectively.

1. The matrix $R_c^M(\tau_{a3})$ is calculated for $\tau_{a3} = -\ln[(e^{-\tau_{a1}} + e^{-\tau_{a2}})/2]$. Additionally, $R_c^M(\tau_{a3})$ is approximated by a linear interpolation between $R_c^M(\tau_{a1})$ and $R_c^M(\tau_{a2})$. Then, $\Delta R_c^M(\tau_{a3})$ is given by the difference between the interpolated and calculated values of $R_c^M(\tau_{a3})$.

2. When for $\tau_{a3}$, the condition of Eq. 3.27 is not fulfilled, the error on the reflection matrix due to interpolation between $\tau_{a3}$ and $\tau_{a2}$ cannot be assumed to be below $\delta_i$. Then, we set $\tau_{a1} = \tau_{a3}$ and the scheme returns to step 1. Otherwise, there are three options:

(a) If $\tau_{a1}$ equals $\tau_{\text{min}}$, the scheme is finished.

(b) If in the current and previous calculation of step 1, the same value for $\tau_{a1}$ was used, the accuracy of the interpolation for all values above $\tau_{a1}$ is assumed to be below $\delta_i$. Therefore, the scheme returns to step 1 with $\tau_{a2} = \tau_{a1}$ and $\tau_{a1}$ taken equal to the closest previously determined interpolation point for which $\tau_{a1} < \tau_{a2}$.

(c) In all other cases, the interpolation between $\tau_{a1}$ and $\tau_{a3}$ cannot be assumed below $\delta_i$. Then, we set $\tau_{a2} = \tau_{a3}$ and the scheme returns to step 1.

For values of $\tau_a$ above $\tau_{\text{thresh}}$, the cloud reflection and transmission matrices are interpolated between $\tau_{\text{thresh}}$ and $\tau_{\text{max}}$, at which the reflection and transmission matrices are assumed to be 0. For $\tau_{\text{max}}$, the value corresponding to the value of $\tau_c$ for which $e^{-\alpha\tau_c} < \epsilon$ is taken. We found that $10^{-12}$ is
a suitable value for $\epsilon$. The cloud reflection and transmission matrices for $\tau_a > \tau_{\text{max}}$ are set to 0.

It is important to note that some assumptions made in this scheme, i.e. only single scattering above the cloud and illumination of the cloud only by direct sunlight, become less valid at wavelengths for which the Rayleigh scattering cross sections are larger. This will result in an overestimation of the error calculated by Eq. 3.27. As a result, the scheme overestimates the required number of interpolation points for short wavelengths, resulting in a higher accuracy than requested.
Chapter 4

Retrieval of cloud parameters from satellite-based reflectance measurements in the ultraviolet and the oxygen A-band

Abstract

We present a new method for the retrieval of cloud fraction, cloud optical thickness and cloud top pressure from measurements of the Global Ozone Monitoring Experiment (GOME) and Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY), relevant for the retrieval of trace gas abundances in cloudy atmospheres. The presented algorithm makes use of the measurements of the oxygen A-band between 758 and 770 nm and additionally of measurements in the ultraviolet between 350 and 390 nm. In addition to the cloud parameters, information about the surface reflection is retrieved. It is shown that measurements in the oxygen A-band alone contain significant information about only two cloud parameters. By adding measurements in the ultraviolet, information about cloud fraction, cloud optical thickness and cloud top pressure can be retrieved. The cloud retrieval algorithm was applied to GOME data and the results are compared to cloud parameters retrieved from measurements of the Along Track Scanning Radiometer 2 (ATSR-2). The cloud fractions, cloud optical thicknesses and cloud top pressures retrieved by our algorithm and the corresponding ATSR-2 values have a median difference of -0.01, 2.5 and -33 hPa, respectively, with 68% confidence intervals of ±0.11, ±7.5 and ±111 hPa, respectively.
4.1 Introduction

Satellite measurements of reflected sunlight in the ultraviolet (UV), visible and infrared are extensively used to monitor atmospheric compounds, such as ozone, nitrogen-dioxide (NO₂), sulphur-dioxide (SO₂), water vapor and aerosols. For these purposes, the Global Ozone Monitoring Experiment (GOME-1 and GOME-2) (Burrows et al., 1999), the Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY) (Bovensmann et al., 1999) and the Ozone Monitoring Instrument (OMI) (Levett et al., 2006), measure the Earth’s reflectance in the wavelength ranges 240–800 nm, 240–2380 nm and 270–500 nm, respectively. The large fields-of-view of GOME (320×40 km²), SCIAMACHY (60×30 km²) and OMI (13×24 km²) imply that, on average, about 98%, 94% and 90% of their measurements, respectively, is contaminated by clouds (Krijger et al., 2007).

Clouds significantly affect the radiation field in the atmosphere, because of their relatively high reflectance, and because they partly shield the atmosphere below them. Therefore, it is essential to accurately take the effect of clouds into account in the retrieval of trace gas abundances (Thompson et al., 1993; Koelemeijer and Stammes, 1999; Liu et al., 2004; Wang et al., 2006). Here, the cloud parameters needed are the cloud optical thickness, the cloud top pressure and the relative amount of clouds in the field-of-view, i.e. the cloud fraction (Koelemeijer and Stammes, 1999).

For GOME and SCIAMACHY, several algorithms to retrieve one or several of these cloud parameters are available (e.g. Koelemeijer et al., 2001; Rozanov and Kokhanovsky, 2004; Joiner et al., 2004; Grzegorski et al., 2006; Van Roozendael et al., 2006). Many of these algorithms retrieve cloud information from measurements in the oxygen A-band and the continuum around it (Kuze and Chance, 1994; Koelemeijer et al., 2001; Rozanov and Kokhanovsky, 2004). These measurements are sensitive to the cloud fraction, cloud optical thickness and cloud top pressure. Since the amount of oxygen in the atmosphere is well-known, cloud information can be retrieved from these measurements. However, different combinations of cloud fraction and optical thickness produce nearly the same measurement at the oxygen A-band. For example, Fig. 4.1 shows that two very distinct combinations of cloud fraction and optical thickness, produce similar spectra.
Figure 4.1: Two forward model calculations in the oxygen A-band (top panel) and their differences (bottom panel). The solid line shows the result of a model calculation assuming a cloud with an optical thickness of 10, a top pressure of 500 hPa and a cloud fraction of 0.50. The dashed line shows the result of a model calculation assuming a cloud with an optical thickness of 40, a top pressure of 520 hPa and a cloud fraction of 0.30. All calculations are performed for a nadir viewing geometry with a solar zenith angle of 40° and the US standard atmosphere over a black surface. Here, the independent pixel approximation (e.g. Marshak et al., 1995) is used.

with differences below 0.6%. Given the fact that the total error in forward model and measurement may be expected to be larger than 0.6% (van Diedenhoven et al., 2005, Chapter 2), it is virtually impossible to retrieve both cloud fraction and optical thickness from oxygen A-band measurements. For this reason, some cloud retrieval algorithms (Kurosu et al., 1999; Van Roozendael et al., 2006) use the higher spatial resolution measurements of the Polarization Measuring Devices (PMDs) to determine the cloud fraction using thresholds for the intensity values defining cloud-free and fully clouded scenes. Subsequently, this value for the cloud fraction is used for the retrieval of cloud top height and cloud optical thickness from
oxygen A-band measurements. A drawback of this approach is that the retrieved cloud parameters strongly depend on the chosen threshold values (Tuinder et al., 2004). Alternatively, a fixed cloud optical thickness can be assumed and so-called effective values of the cloud fraction and cloud top pressure are retrieved (Kuze and Chance, 1994; Koelemeijer et al., 2001). However, the effective cloud parameters may differ significantly from actual cloud parameters. For example, assuming that the actual values of cloud fraction, cloud optical thickness, and cloud top pressure are 0.5, 10, and 500 hPa, respectively, the values of the corresponding effective cloud fraction and effective cloud top pressure are 0.29 and 524 hPa, respectively, when assuming a cloud optical thickness of 40 (see Fig. 4.1). This may cause problems in the retrieval of trace gas amounts. For example, Wang et al. (2006) have shown that the use of effective cloud parameters in DOAS based tropospheric NO2 column retrievals can cause errors >20% in the retrieved column for geometrical cloud fractions larger than 0.5, and errors >10% for geometrical cloud fractions larger than 0.2. Additionally, effective cloud parameters retrieved from oxygen A-band measurements are generally not representative for other spectral ranges. This is illustrated in Fig. 4.2, which shows two simulated UV reflectance spectra from 350 to 390 nm and their differences, for the same two combinations of cloud parameters as used for the simulations in the oxygen A-band shown in Fig. 4.1. From Fig. 4.2 it follows that the use of effective cloud parameters retrieved from measurements at the oxygen A-band results in errors larger than 3.5 % in the spectral range 350–390 nm. This is due to the much stronger contribution of Rayleigh scattered light to measurements in the UV than to measurements at the oxygen A-band. In turn, the large differences between the two spectra in Fig. 4.2 can be explained by the fact that the spectrum calculated for the effective cloud parameters has a too large contribution of Rayleigh scattering, due to the difference between effective cloud fraction and actual cloud fraction. On the one hand, this means that effective cloud parameters retrieved from oxygen A-band measurements introduce significant errors when used in the UV spectral range. On the other hand, it indicates that the combined use of measurements in the UV and at the oxygen A-band allows the retrieval of independent information about the cloud fraction, cloud optical thickness and cloud top pressure.

In this paper we present a new method for the independent retrieval of...
Figure 4.2: Same as Fig. 4.1, but for the 350–390 nm window.

cloud fraction, cloud optical thickness and cloud top pressure from GOME and SCIAMACHY measurements which is based on this concept. For this purpose, measurements at the oxygen A-band from 758–770 nm and in the UV from 350–390 nm are used. An advantage of our approach in comparison to approaches using only the oxygen A-band is that, in addition to the cloud top pressure, information about both the cloud fraction and cloud optical thickness can be retrieved, instead of only an effective cloud fraction. The retrieved cloud parameters are relevant for the retrieval of trace gas abundances in cloudy atmospheres. The paper is constructed as follows: In section 4.2, the retrieval approach is presented. Section 4.3 discusses the information content of the measurements, the retrieval noise and regularization errors on the retrieval result and the sensitivity of the retrieval approach to instrument calibration errors. Also the relevance of the retrieved cloud parameters to retrieval of tropospheric NO\textsubscript{2} columns is discussed in this section. Next, in section 4.4, the retrieval concept is applied to GOME measurements and the results are compared to results of
Chapter 4: Retrieval of cloud parameters from UV and the O\textsubscript{2} A-band

the Fast Retrieval Scheme for Cloud Observables (FRESCO) \citep{Koelemeijer2001} and cloud parameters retrieved from the Along Track Scanning Radiometer 2 (ATSR-2) instrument. Also the spectral fitting residuals are discussed in this section. Finally, we conclude the paper in section 4.5.

4.2 Retrieval approach

4.2.1 Forward model

Let us define a measurement vector $y$, containing the reflectances measured by GOME or SCIAMACHY in the spectral ranges 350–390 nm and 758–770 nm. Next, we define an atmospheric state vector $x$ that contains the parameters to be retrieved. In our case these are the cloud fraction, the cloud optical thickness at 550 nm, the cloud top pressure, the surface albedo in both wavelength windows and their linear spectral dependence. The geometrical thickness of the cloud is assumed to be known a priori. For the retrieval of an atmospheric state vector $x$ from the measurement vector $y$, a forward model $F$ is needed that describes how $y$ and $x$ are related, viz.

$$y = F(x) + e,$$

with error term $e$. To obtain $F$ for a partly cloudy measurement footprint, the independent pixel approximation \citep[e.g.][]{Marshak1995} is applied, viz.

$$F = (1 - f_c) F_{\text{clear}} + f_c F_{\text{cloud}},$$

where $f_c$ is the cloud fraction and $F_{\text{clear}}$ and $F_{\text{cloud}}$ are the components of the forward model for the clear-sky and cloudy parts of the measurement footprint, respectively. The main part of the forward models $F_{\text{clear}}$ and $F_{\text{cloud}}$ is an atmospheric radiative transfer model. Here, we employ the vector radiative transfer model of \cite{Hasekamp2002} and the CODAGS vector radiative transfer model of \cite{vanDiedenhoven2006} (Chapter 3) to describe the radiative transfer in the clear sky and cloudy part of the atmosphere, respectively. This provides an efficient forward model for partly cloudy atmospheres. The use of this model allows us to model the polarization-sensitive measurements of GOME and SCIAMACHY \citep{Hasekamp2002, vanDiedenhoven2005, Chapter
2). In this way, errors due to the polarization correction in the GOME and SCIAMACHY data processing (Stam et al., 2000a; Hasekamp et al., 2002; Schutgens and Stammes, 2003) are avoided. To simulate the spectral smoothing by the instruments, the instrument response function of Bednarz (1995) is used.

For the radiative transfer calculations, the absorption line parameters of the oxygen A-band are taken from the HITRAN 2004 spectroscopic database (Rothman et al., 2005) and a Voigt lineshape is assumed. The cross-section sampling and radiative transfer calculations in the oxygen A-band are performed on a 0.005 nm spectral resolution, which we found to be appropriate for a line-by-line simulation in this spectral range. For the calculation of the cross-sections of the weak oxygen dimer (O₂-O₂) absorption lines around 360 nm and 380 nm, a Lorentz lineshape is used with widths and center wavelengths taken from Greenblatt et al. (1990).

The Rayleigh scattering cross-sections and phase function are taken from Bucholtz (1995). The scattering properties of the cloud particles are calculated using Mie-theory (van de Hulst, 1957; de Rooij and van der Stap, 1984). The size distribution of the cloud particles is assumed to be log normal, with an effective radius of 6 μm and an effective variance of 0.5 (see Hansen and Travis (1974) for the definitions). Furthermore, we assume non-absorbing cloud particles with a refractive index of 1.335. This results in a scattering phase function with an asymmetry parameter of 0.841 at 550 nm. The cloud optical thickness τₐ at a wavelength λ is obtained from the value τ₅₅₀ at 550 nm via

\[
τ_λ = \frac{C_λ}{C_{550}} τ_{550},
\]

where \( C_λ \) and \( C_{550} \) are the Mie scattering cross sections at wavelength λ and 550 nm, respectively. The reflection of land surfaces and snow covered surfaces is modeled by a Lambertian albedo. For retrievals above sea surfaces, the surface reflection is characterized by a modeled ocean reflection matrix. For this, the Fresnel reflection on waves is calculated with the method of Mishchenko and Travis (1997), assuming the wind speed dependent distribution of surface slopes proposed by Cox and Munk (1954). The Lambertian surface albedo, which is a free parameter in the retrieval, is added to the sea surface reflection matrix.
4.2.2 Inversion

The aim of an inversion is to find a state vector \( \hat{x} \) for which forward model \( F(\hat{x}) \) and measurement \( y \) are in optimal agreement. Since the forward model is not linear in the unknown parameters, the solution of the inversion problem has to be found iteratively. Here, in each iteration step \( n \) we replace the forward model in Eq. 4.1 by its linear approximation, i.e.

\[
F(x) \approx F(x_n) + K [x - x_n],
\]

where \( x_n \) is the state vector for the iteration step under consideration and \( K \) is the Jacobian matrix containing the derivatives of the forward model with respect to the elements of \( x_n \). Thus, element \( K_{ij} \) of \( K \) is defined by

\[
K_{ij} = \frac{\partial F_i}{\partial x_j}(x_n).
\]

The derivatives are estimated using finite differencing. The measurement vector \( y \) considered here does not contain sufficient information to retrieve all 7 unknown parameters, and thus the corresponding inverse problem is ill-posed. This means that many combinations of the 7 parameters fit the measurement almost equally well within the noise. As a result, the least-squares solution to our inverse problem is overwhelmed by noise. In order to reduce the effect of noise, we employ the Phillips-Tikhonov regularization method (Phillips, 1962; Tikhonov, 1963) in a similar way as described in detail by Hasekamp and Landgraf (2005a). The most important aspects are summarized in Appendix 4.A.

Here, the retrieval result \( \hat{x} \) is a combination of information extracted from the measurements and a priori information and is related to the true state vector \( x_{\text{true}} \) and the a priori state vector \( x_a \) via

\[
\hat{x} = Ax_{\text{true}} + (I - A)x_a + e_x,
\]

where \( e_x \) represents the error in the retrieval result caused by the measurement error. Furthermore, \( A \) is the averaging kernel of the retrieval (see Eq. 4.17 in Appendix 4.A). The covariance matrix \( S \) of the error in \( \hat{x} \) is given by

\[
S = S_x + S_r.
\]

Here, \( S_x \) is the retrieval noise covariance matrix given by

\[
S_x = D S_y D^T,
\]
where $D$ is the contribution matrix (see Eq. 4.15 in Appendix 4.A) and $S_y$ is the measurement error covariance matrix. Furthermore, $S_r$ is the regularization error covariance matrix due to an error on $x_a$ and is given by

$$S_r = (I - A) S_a (I - A)^T,$$

(4.9)

where $S_a$ is the a priori error covariance matrix.

When the first-guess state vector is far from the true state vector, the linear approximation of Eq. 4.4 hampers the iterative solution of the inverse problem, resulting in no convergence of the fit. To improve the convergence, the Levenberg-Marquardt method (Levenberg, 1944; Marquardt, 1964) is used. The combination of the Levenberg-Marquardt method and the Phillips-Thikohnov method is summarized in Appendix 4.B. The convergence of the algorithm including the Levenberg-Marquardt method is checked using an ensemble of simulated measurements with randomly distributed cloud parameters. About 90% of the retrievals converged. This is in accordance with the convergence rate of retrievals on real GOME measurements. To improve on this convergence rate, an unconverged retrieval could be repeated with different first-guess values. This is however not yet implemented in the current version of the retrieval algorithm.

### 4.3 Sensitivity study

In this section we will investigate the information content of reflectance measurements in the UV from 350–390 nm combined with those at the oxygen A-band from 758–770 nm for cloud parameter retrievals. The information content will be compared to that of retrievals using only measurements in the oxygen A-band, as commonly used in cloud retrieval algorithms (Kuze and Chance, 1994; Koelemeijer et al., 2001; Rozanov and Kokhanovsky, 2004). For the combined oxygen A-band and UV measurements, also the retrieval noise and regularization errors are discussed. Furthermore, we will asses the sensitivity of the cloud parameter retrievals to instrument calibration errors.

For this study, GOME measurements are simulated for the US standard atmosphere using the cloud and surface parameters given in Table 4.1. A nadir viewing geometry is used with a solar zenith angle of 40 degrees. The
Table 4.1: Parameters in the sensitivity study, unless stated otherwise.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>cloud optical thickness at 550 nm</td>
<td>10</td>
</tr>
<tr>
<td>cloud top pressure</td>
<td>500 hPa</td>
</tr>
<tr>
<td>cloud bottom pressure</td>
<td>700 hPa</td>
</tr>
<tr>
<td>surface albedo O$_2$ A-band sea</td>
<td>0.01</td>
</tr>
<tr>
<td>surface albedo UV-window sea</td>
<td>0.05</td>
</tr>
<tr>
<td>surface albedo O$_2$ A-band vegetation</td>
<td>0.3</td>
</tr>
<tr>
<td>surface albedo UV-window vegetation</td>
<td>0.05</td>
</tr>
<tr>
<td>surface albedo O$_2$ A-band snow</td>
<td>0.9</td>
</tr>
<tr>
<td>surface albedo UV-window snow</td>
<td>0.9</td>
</tr>
<tr>
<td>surface albedo slope O$_2$ A-band</td>
<td>0</td>
</tr>
<tr>
<td>surface albedo slope UV-window</td>
<td>0</td>
</tr>
</tbody>
</table>

Wind speed needed to characterize Fresnel reflection on the sea waves is set to 7 m/s. To simulate the measurement noise, a Gaussian noise contribution is added to the simulated measurements. The GOME measurement noise in the UV and oxygen A-band windows is about 0.1 %. However, we use a noise contribution of 0.5 % to account for forward model and measurement errors with a random like structure, such as errors due to the 'undersampling' effect (Chance et al., 2005; van Deelen et al., 2007) and due to the Ring effect (Joiner et al., 2004; Landgraf et al., 2004) in the UV and errors in spectroscopy data and the instrument response function (Yang et al., 2005; Tran et al., 2006; van Diedenhoven et al., 2005, Chapter 2) in the oxygen A-band region. It is important to note that the conclusions made in this section are not significantly different when assuming noise contributions of 0.1–1%.

### 4.3.1 Information content

The information content of a measurement vector can be studied by investigating the sensitivity of the retrieved parameters to a priori information, $\partial \hat{x}_i/\partial x_{a,i}$. As can be concluded from Eq. 4.6, the diagonal terms $a_{ii}$ of $A$ describe this sensitivity, viz.

$$\frac{\partial \hat{x}_i}{\partial x_{a,i}} = 1 - a_{ii}.$$  \hspace{1cm} (4.10)
Figure 4.3: Derivatives of retrieved cloud and surface parameters with respect to their a priori values as a function of cloud fraction, for a measurement vector containing only measurements in the oxygen A-band above sea (left panel), vegetation (middle panel) and snow (right panel) surfaces. The solid, dotted and short-dashed lines correspond to the cloud fraction, cloud optical thickness and cloud top pressure, respectively. The long-dashed line corresponds to the surface albedo at the oxygen A-band.

For example when \( \partial \hat{x}_i / \partial x_{a,i} = 0 \), the corresponding retrieved parameter is not dependent on its a priori value and thus determined purely from the measurement.

Fig. 4.3 shows \( \partial \hat{x}_i / \partial x_{a,i} \) for a measurement vector containing only measurements in the oxygen A-band above sea, vegetation and snow surfaces. Above sea and vegetation surface types the oxygen A-band measurements contain significant information about the cloud top pressure and cloud fraction. However, these measurements contain little additional information about the cloud optical thickness. Information about the surface albedo is hardly available for sea and vegetation surfaces. Measurements above snow surfaces only contain significant information about the cloud top pressure and less about the other cloud parameters. Instead, information about the surface albedo is retrieved from the measurements. This is because the effect on the measurements of such highly reflective surfaces is very similar to that of clouds.

Figure 4.4 shows \( \partial \hat{x}_i / \partial x_{a,i} \) corresponding to the retrieved parameters when, in addition to measurements in the oxygen A-band, measurements in the UV-window are included. It can be seen that now all cloud parameters
can be retrieved from the measurements with little dependence on a priori information. Thus, the information content is significantly increased by including UV measurements. Furthermore, information about the surface albedos is retrieved. Above sea surfaces, the dependence of the retrieved surface albedo in the UV window on its a priori value is low for low cloud fractions but increases rapidly for increasing cloud fraction. The surface albedo in the oxygen A-band window is determined almost entirely from the a priori values for all cloud fractions. Above vegetation surfaces, the surface albedo in the oxygen A-band window is retrieved with only little dependence on a priori for all cloud fractions. The dependence on a priori for the surface albedo in the UV window is high but slightly decreases for decreasing cloud fractions. For other land surface types, excluding snow covered surfaces, the information content is similar to that of vegetation surfaces (not shown). Above snow covered surfaces the surface albedos are almost fully obtained from the measurements with only little dependence on a priori. Here, the high surface albedo enhances the contribution of Rayleigh scattering in the UV close to the surface. Therefore, the effect of the surface reflection to the measurements in the UV is not similar to that of a cloud, in contrast to the situation at the oxygen A-band. This avoids the use of a priori albedo values of snow covered surfaces, which are highly

Figure 4.4: Same as Fig. 4.3, but for a measurement vector containing measurements in the oxygen A-band and the UV-window between 350–390 nm. The dotted-dashed line corresponds to the surface albedo in the UV-window.
uncertain, for the retrieval of cloud parameters. The linear dependencies of the surface albedos are fully retrieved from the measurements in all cases and do not significantly depend on a priori values (not shown).

To summarize, using measurements in the UV in addition to the oxygen A-band for a large part solves the problem that cloud fraction and optical thickness cannot be independently retrieved from GOME and SCIAMACHY measurements.

### 4.3.2 Retrieval noise and regularization errors

The retrieval result given by Eq. 4.6 is affected by retrieval noise due to random measurement errors and by regularization errors due to uncertainties in the a priori information. Figure 4.5 shows the retrieval noise on the cloud fraction for measurements above sea, vegetation and snow covered surfaces. Above sea surfaces, the retrieval noise on the retrieved cloud fraction is below 0.01 for all cloud fractions. Above vegetation surfaces and snow covered surfaces, the retrieval noise on the cloud fraction is below 0.05 and increases slightly with increasing cloud fraction. The retrieval
noise on the cloud optical thickness is shown in Fig. 4.6. Above sea surfaces, the retrieval noise on the retrieved cloud optical thickness is below 1 for all cloud fractions. Above vegetation and snow covered surfaces, the retrieval noise on the cloud optical thickness is below 2 and 1, respectively, for cloud fractions larger than 0.2, but increases to about 3 for lower cloud fractions.

The regularization errors are dominated by errors due to errors on the a priori values of the surface albedos because the dependence of the cloud parameters on their a priori values is negligible for cloud fractions larger than 0.2. To give an indication of the regularization errors on the cloud parameters, Figs. 4.5 and 4.6 also show the regularization errors due to errors of 0.005, 0.01, 0.02 and 0.05 on the a priori surface albedo in the UV. Above sea surfaces, a maximum occurs in the regularization errors on the cloud fraction at a cloud fraction of ~0.4. This is because, with increasing cloud fraction, on the one hand the dependence of the retrieved surface albedo on its a priori value increases, while on the other hand the contribution of the surface albedo to the measurements decreases. (see Fig. 4.4). The regularization errors on the cloud fraction are below 0.1 for errors on the a priori surface albedo in the UV below 0.01, and increase up to 0.5 for a priori surface albedo errors of 0.05. Above vegetation surfaces, the largest regularization errors on the cloud fraction occur around cloud
fractions of 0.3. For errors on the a priori surface albedo in the UV below 0.01, the regularization errors are below 0.06. The regularization errors increase to 0.27 for a priori surface albedo in the UV errors of 0.05. Above snow covered surfaces, all regularization errors are negligible, because here the surface albedos are obtained fully from the measurements. As shown in Fig. 4.6, the regularization errors on the cloud optical thickness for retrievals above sea peak at a cloud fraction of 0.2. The regularization errors on the cloud optical thickness are below 7 for errors on the a priori surface albedo in the UV below 0.01, and increase up to 33 for a priori surface albedo errors of 0.05. Above vegetation surfaces, the regularization errors on the cloud optical thickness decrease with increasing cloud fraction. In contrast to the situation above sea surfaces, here no maximum occurs because the effect of the decreasing contribution of the surface albedo to the measurements with increasing cloud fraction is much larger than the effect due to the increase of dependence of the retrieved surface albedo on its a priori value. For a cloud fraction of 0.2, the errors are below 3 for errors on the a priori surface albedo in the UV below 0.01, and increase up to 15 for a priori surface albedo errors of 0.05. Again, all regularization errors are negligible for retrievals above snow covered surfaces. For errors on the a priori surface albedo in the oxygen A band, similar results as shown in Figs. 4.5 and 4.6 are obtained for retrievals above sea surfaces. For retrievals above vegetation and snow covered surfaces, these errors are negligible. The regularization error on the cloud top pressure due to errors in the a priori surface albedos up to 0.05 is generally below 5 hPa for all cases. In conclusion, accurate a priori information on surface albedo in both wavelength windows is needed for sea surfaces. Furthermore, for snow/ice-free land surfaces accurate a priori information on surface albedo in the UV is required.

4.3.3 Sensitivity to instrument calibration

GOME and SCIAMACHY measurements possibly have significant calibration errors (Koelemeijer et al., 1998; Tilstra et al., 2005; Tilstra and Stammes, 2007). Figure 4.7 shows the effect of calibration errors in the range -5–5 % on the retrieved cloud fraction and cloud optical thickness for retrievals over vegetation surfaces. Here, the relative calibration errors are assumed to be constant in the considered wavelength windows. Further-
Figure 4.7: Absolute errors in the cloud fraction (a) and the cloud optical thickness (b) for retrievals above vegetation surfaces when calibration errors are added on the UV and oxygen A-band windows. Here, a cloud fraction of 0.5 is used in the simulated measurements.

more, a cloud fraction of 0.5 is assumed. As seen in Fig. 4.7, small errors on the cloud fraction and optical thickness are obtained when the calibration in the two wavelength windows are correlated. Specifically, Fig. 4.7a shows that the error on the cloud fraction is 0 when the calibration error in the oxygen A-band is about 2.5 times the calibration error in the UV. Figure 4.7b shows that, when the calibration error in the oxygen A-band is about 1.5 times the calibration error in the UV, the error on the optical thickness is 0. To obtain errors in the cloud fraction below 0.1 and in optical thickness below 2, the calibration error in the oxygen A-band has to be about twice the calibration error in the UV plus or minus 1%. When the calibration errors in the two wavelength windows differ considerably, large errors on the cloud fraction and optical thickness can occur. Moreover, in these cases convergence of the inversion can become problematic. For decreasing cloud fractions, the regularization errors generally decrease. For example, for a calibration error of 2% at the oxygen A-band and no calibration error in the UV, the error on the cloud fraction decreases from 0.05 for a cloud fraction of 0.5 to 0.01 at a cloud fraction of 0.2. Furthermore, the error on the cloud optical thickness decreases with cloud fraction from 1.48 for a cloud fraction of 0.5 to 0.76 at a cloud fraction of 0.2.

For retrievals over sea surfaces, similar errors are obtained. For retrievals
above snow surfaces, the retrieval errors due to all calibration errors up to ±5% are significantly smaller and are generally below 2 in the optical thickness and below 0.05 in the cloud fraction. The retrieval errors on the cloud top pressure due to calibration errors are generally low for all surface types.

4.3.4 Relevance to tropospheric NO\textsubscript{2} retrievals

In this section, the relevance of our cloud retrieval algorithm for the retrieval of the tropospheric NO\textsubscript{2} column in cloudy atmospheres is discussed. Tropospheric NO\textsubscript{2} columns derived with the Differential Optical Absorption Spectroscopy (DOAS) technique (Platt, 1994) are an important product of GOME, SCIAMACHY and OMI measurements (e.g Beirle et al., 2003; Richter et al., 2005). These retrievals are particularly sensitive to clouds since the tropospheric NO\textsubscript{2} is generally below the cloud (Schaub et al., 2006; Wang et al., 2006).

In the DOAS technique, first the reflectance spectrum is separated into a spectrally smooth part, modeled by a polynomial, and in a differential part from which a slant gas column (SC) is retrieved. Then, this slant column is converted into a vertical column (VC) using an air mass factor (AMF), via

\[
VC = \frac{SC}{AMF}.
\]  

(4.11)

Here, the NO\textsubscript{2} AMF is given by

\[
AMF = \frac{-\ln(R/R_0)}{\tau_{NO_2}},
\]  

(4.12)

where \(R\) and \(R_0\) are the reflectances at the top of atmosphere at 440 nm with and without NO\textsubscript{2} absorption, respectively. Furthermore, \(\tau_{NO_2}\) is the total NO\textsubscript{2} absorption optical thickness. To calculate tropospheric NO\textsubscript{2} AMFs, we include NO\textsubscript{2} only in the lowest 2 km of the atmosphere. A NO\textsubscript{2} volume mixing ratio of 2.3 ppb is assumed, which corresponds to polluted situations. Furthermore, a surface albedo of 0.05 is assumed for the AMF calculations.

Here, we will investigate the errors in the AMF imposed by retrieval errors of our algorithm. Furthermore, we will show AMF errors that result from the use of effective cloud fractions and cloud top pressures retrieved...
from the oxygen A band to demonstrate the advantage of our approach compared to approaches that only retrieve effective cloud parameters. For this, an ensemble of 600 cases is constructed with randomly chosen cloud fractions between 0 and 1, cloud optical thickness values between 2 and 30 and cloud top pressures between 400 hPa and 600 hPa, above sea and vegetation surfaces. For these cases, measurements in the UV and oxygen A-band windows are simulated. Subsequently, the presented cloud retrieval algorithm is applied to these simulated measurements. For the cloud retrieval, an a priori cloud optical thickness of 5 and an a priori cloud top pressure of 500 hPa are taken. For the a priori cloud fraction the effective cloud fraction is taken that corresponds to the a priori cloud optical thickness. A random error of between -10% and +10% is assumed on the a priori surface albedos. In addition, effective cloud fractions and cloud top pressures are retrieved from the simulated measurements in the oxygen A-band, assuming a cloud optical thickness of 40. Then, for all cases AMFs are calculated for the cloud parameters in the simulated measurements, the retrieved cloud parameters and the effective cloud parameters. The cases for which our algorithm did not converge are removed from this study. Note that for all cases all NO2 is located below the height of the base of the cloud.

Figure 4.8 shows histograms of the differences between the reference AMFs and those calculated with the retrieved cloud parameters and effective cloud parameters. The use of effective cloud parameters generally results in an underestimation of the AMF. The asymmetric distribution of AMF errors has a mean of -12.4 %, a 68% confidence interval of ±10% and a significant wing toward negative errors. Using simulated measurements, Wang et al. (2006) also found a similar underestimation of the AMF for most solar zenith angles and cloud parameters. Thus, the use of effective cloud parameters generally leads to a significant overestimation of the tropospheric NO2 column. A similar systematic overestimation was observed by Schaub et al. (2006) for tropospheric NO2 column retrievals from GOME measurements in cloudy conditions when using effective cloud parameters obtained by FRESCO (Koelemeijer et al., 2001). When cloud parameters retrieved by the proposed algorithm are used, the errors in the AMF are symmetrically distributed around the mean of 0.4% with a 68% confidence interval of ±4.8%. Thus, the use of cloud parameters retrieved
by our algorithm may be expected to solve the systematic overestimation of tropospheric NO2 columns from GOME and SCIAMACHY measurements caused by effective cloud parameters in cloudy conditions.

4.4 Application to GOME measurements

In this section we apply our retrieval algorithm for cloud parameters to GOME measurements. Here we use 3400 measurements spread evenly over the year 1997, above the European area, North Africa and the Atlantic ocean. The areas and time-range are chosen since it provides a dataset with a considerable range of conditions. The retrieval results are compared with the effective cloud fractions and effective cloud pressures retrieved with the commonly used FRESCO algorithm (Koelemeijer et al., 2001) from the same measurements. Furthermore, we compare our results with cloud fractions, cloud optical thicknesses and cloud top pressures retrieved from ATSR-2 measurements using the Global Retrieval of ATSR
Cloud Parameters and Evaluation (GRAPE) algorithm (Watts et al., 1998; Poulsen et al., 2005).

In these comparisons, retrievals above snow covered surfaces, deserts and sea surfaces with a significant contribution of sunglint are avoided, since both the GRAPE and FRESCO retrieval results are unreliable or unavailable for these cases (Koelemeijer et al., 2001; Poulsen et al., 2005).

4.4.1 Retrieval input

To model the GOME measurements, scattering and absorption cross sections are calculated for atmospheric temperature and pressure profiles from the United Kingdom Met Office (UKMO) Stratospheric Assimilated dataset at the locations closest to the center of each GOME measurement footprint. Furthermore, the surface elevation averaged over the GOME footprint is determined from the TerrainBase surface elevation database. To account for the variation in viewing angle within a GOME footprint, measurements are simulated for 3 viewing angles corresponding to the middle, west and east boundaries of the GOME footprint. The simulations are linearly interpolated and subsequently integrated over viewing angle. In the UV window, systematic structures due to the Ring effect (Joiner et al., 2004; Landgraf et al., 2004) and the ‘undersampling’ effect (Chance et al., 2005; van Deelen et al., 2007) appear in the GOME measurements. These structures are partly removed by fitting theoretically calculated Ring spectra (Landgraf et al., 2004) and ‘undersampling’ effect correction spectra to the data in addition to the cloud parameters. For these spectra, an amplitude and a wavelength shift and squeeze is fitted.

The a priori surface albedos are obtained from the monthly 1° × 1° resolution Minimum Lambertian-Equivalent Reflectivity (MLER) database determined from cloud-free GOME observations (Koelemeijer et al., 2003). For this purpose, the MLER database gridboxes overlapping the GOME footprint are averaged, weighted by the amount of overlap. For GOME footprints containing more than 95% sea surfaces, the Fresnel reflection on the waves is characterized by a modeled ocean reflection matrix, as discussed in section 4.2.1. For this, the required windspeed is taken from re-analysis data of the European Center for Medium range Weather Forecasting (ECMWF) averaged over the GOME footprint.

The pressure difference between the top and bottom of the cloud is fixed
to 200 hPa, since this is a common geometrical thickness for middle- and low-level clouds (Wang et al., 2000). The a priori cloud optical thickness is set to 5, which is roughly the mean global value for middle- and low-level clouds (Rossow and Schiffer, 1999). The a priori values of the cloud fraction are the effective cloud fractions corresponding to the a priori cloud optical thickness. The a priori cloud top pressures are taken from data from the FRESCO algorithm (Koelemeijer et al., 2001). It is important to note however that the cloud fractions and cloud top pressures retrieved by our algorithm only minimally depend on their a priori values, as discussed in section 4.3.1.

4.4.2 Comparison to FRESCO results

In the FRESCO algorithm, clouds are approximated by reflecting boundaries with a Lambertian albedo of 0.8. Furthermore, surface albedos are taken from Koelemeijer et al. (2003). With these assumptions, effective cloud fractions and effective cloud pressures are retrieved from measurements in the oxygen A-band. Figure 4.9 shows the cloud fractions retrieved by our algorithm compared to the effective cloud fractions obtained by FRESCO (version 3). For clouds with a cloud fraction higher than 0.2 and an optical thickness between 30–60 (diamonds), the cloud fraction retrieved using our algorithm and effective cloud fractions from FRESCO agree well. For optically thinner and thicker clouds the cloud fractions obtained by our algorithm are generally higher and lower, respectively, than the effective cloud fractions from FRESCO. This is as expected since clouds with optical thickness around 40 have Lambertian equivalent albedos around 0.8, which is the value assumed in the FRESCO algorithm. When the cloud optical thickness is lower or higher than 40, this is compensated in FRESCO by respectively increasing or decreasing the effective cloud fraction. Thus, for cloud fractions larger than 0.2, the cloud fractions retrieved by our algorithm are consistent with the effective cloud fractions retrieved by FRESCO, given the definition of the effective cloud fraction in FRESCO. For cloud fractions lower than 0.2 above land, often the effective cloud fractions from FRESCO are higher than the cloud fractions retrieved by our algorithm. This is probably due to a difference in the surface albedo in the oxygen A-band window assumed by the FRESCO algorithm and that retrieved by our algorithm.
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Figure 4.9: Comparison of retrieved cloud fractions using the presented algorithm and the effective cloud fractions retrieved by the FRESCO algorithm. The different symbols correspond to selected ranges in retrieved cloud optical thickness $\tau_{\text{cloud}}$. Furthermore, $a$ represents the slopes of the linear functions fitted through the data in the selected ranges and the origin.

Figure 4.10 shows the histogram of the differences between cloud top pressures retrieved by our algorithm and the effective cloud pressures from FRESCO. These differences have a median of $-59 \pm 40$ hPa or $0.77 \pm 0.70$ km, where the value between brackets indicates the 68% confidence interval. The systematic difference depends on the optical thickness of the clouds included in the comparison, namely the difference increases for decreasing cloud optical thickness. This systematic difference is probably due to the neglect of scattering and absorption within the cloud and the transmission of light through the cloud by the FRESCO algorithm (Koelemeijer et al., 2001).

4.4.3 Comparison to ATSR-2 retrievals

In this subsection, our retrieval results are compared with cloud parameters retrieved from ATSR-2, which is on the same platform as GOME. ATSR-2 has a subsatellite footprint size of $1 \times 1 \text{ km}^2$ and its swath entirely overlaps
Figure 4.10: Histogram of $\Delta P_c$ defined as the cloud top pressures retrieved by our algorithm minus the effective cloud pressures from FRESCO. In this comparison all cases with a cloud fraction lower than 0.05 are excluded.

with the footprints of GOME for the used observations.

We use ATSR-2 cloud parameters retrieved by the GRAPE algorithm, version 1 (Watts et al., 1998; Poulsen et al., 2005, http://www-atm.physics.ox.ac.uk/group/grape/). At the time of preparation of this paper, version 2 GRAPE data were not yet available. In the GRAPE algorithm, first cloudy ATSR-2 pixels are identified using a cloudfilter. For these cloudy pixels, then an optimal estimation procedure is used to estimate cloud fraction, cloud optical thickness and cloud top pressure as well as the effective radius of the cloud particles, using measurements of the 0.67, 0.87, 1.6, 11 and 12 $\mu$m channels on ATSR-2. Furthermore, the cloud phase (water or ice) is determined.

To compare the retrievals on the GOME spatial resolution, the cloud fractions retrieved by GRAPE for ATSR-2 measurements within a GOME footprint are averaged. Furthermore, the GRAPE cloud top pressures and optical thickness values within a GOME footprint are averaged weighted by the GRAPE cloud fraction. ATSR-2 measurements for which the GRAPE algorithm retrieved a cloud optical thickness below 2 are considered as
clear-sky, since most of these cases are either thin cirrus clouds for which GOME is insensitive or pixels falsely identified as cloudy by the strict cloud filter used by GRAPE.

Figures 4.11 and 4.12 show histograms of the differences between the cloud fractions and optical thickness, respectively, retrieved by our algorithm and those from ATSR-2. For the comparisons of the optical thickness all cases with a cloud fraction lower than 0.05 are excluded. The cloud fraction and optical thickness values retrieved by our algorithm compare well to the corresponding ATSR-2 values. Here, the differences between the GOME and ATSR-2 values have median values of -0.01 (±0.11) for the cloud fraction and 2.5 (±7.5) for the cloud optical thickness. No obvious dependence of these results on geometry, location or surface albedos is found. Retrievals performed for a fixed cloud geometrical thickness values of 100 hPa instead of 200 hPa only yields mean differences in cloud fraction and cloud optical thickness of less than 0.01 and 0.5, respectively.

The distributions of the differences in cloud fraction and cloud optical thickness both show significant wings, where the cloud fractions are under-
Figure 4.12: Similar to Fig. 4.11 but for $\Delta \tau_c$ defined as the cloud optical thickness retrieved by our algorithm minus the ATSR-2 values. Here, all cases with a cloud fraction lower than 0.05 are excluded.

estimated by our algorithm as compared to the ATSR-2 values, and at the same time the cloud optical thickness values are overestimated. This is the situation for about 15% of all cases above land. The standard deviation of the ATSR-2 optical thickness values within the GOME pixels for these cases is about 20, which is about twice as high as compared to the average value. This indicates that the obtained biases for these cases could be due to the presence of horizontally inhomogeneous clouds. Furthermore, multilayered clouds could cause these biases. This is indicated by the fact that for these cases the cloud top pressures retrieved by ATSR-2 are on average about 67 hPa lower than those retrieved by GOME. This difference is expected for multilayered clouds since ATSR-2 is mostly sensitive to the top layer, while GOME retrieves a higher cloud top pressure in these cases (Rozanov et al., 2004). It is important to note that the $\chi^2$ values of the spectral fit to the measurements for these cases are very similar to those of other cases. This suggests that these retrieved parameters may still be very useful for the retrieval of trace gas abundances from the corresponding GOME measurements. Wavelength dependent effects due to
inhomogeneous or multilayered clouds are partly taken into account since cloud parameters are retrieved that describe the spectrum in both the UV and the oxygen A-band.

Figure 4.13 shows the histogram of the differences between the cloud top pressure retrieved by our algorithm and the ATSR-2 values. Again, all cases with a cloud fraction lower than 0.05 are excluded. The differences between the cloud top pressure retrieved by our algorithm and the ATSR-2 values have a median of $-33(\pm 111)$ hPa or $0.4(\pm 1.6)$ km. No obvious dependence of these results on geometry, location or surface albedos is found. Rozanov et al. (2006) find a similar bias and spread of $0.6(\pm 1.8)$ km between cloud top pressures derived from ATSR-2 and those derived from fully clouded GOME measurements with the Semi-analytical Cloud Retrieval Algorithm (SACURA) (Rozanov and Kokhanovsky, 2004). Thus, the retrieved cloud top pressures can be assumed to be consistent with those of SACURA. Rozanov and Kokhanovsky (2004) showed that the cloud top pressure derived from the oxygen A-band depends on the assumed geometrical thickness of the cloud. When in our algorithm the
cloud geometrical thickness is fixed at 100 hPa instead of 200 hPa, the mean retrieved cloud top pressure is about 50 hPa higher (or 0.8 km lower). Thus, the negative bias of the retrieved cloud top pressure compared to the ATSR-2 values could be due to an overestimation of the cloud geometrical thickness. To account for this, the geometrical thickness of the cloud layer could in theory be retrieved from the measurements as well. However, in practice this often leads to unphysical retrieval results with cloud bases under the ground surface due to the presence of multilayered or vertically inhomogeneous clouds (Rozanov and Kokhanovsky, 2004). The negative bias of the retrieved cloud top pressure compared to the ATSR-2 values could also be due to systematic overestimation of the cloud top pressures by ATSR-2, since cloud top pressures determined using infrared brightness temperature measurements, as in GRAPE, are known to be biased toward higher cloud top pressures (Rossow and Schiffer, 1999; Sherwood et al., 2004). Here, the difference between the cloud top pressures from GOME and ATSR-2 clearly depend on the optical thickness of the cloud, especially above land. For example, for clouds with an optical thickness higher than 40, the cloud top pressures retrieved by our algorithm are on average about 95 hPa higher (or 1.27 km lower) than the ATSR-2 cloud top pressures. However, when only clouds with an optical thickness below 10 are compared, the cloud top pressures retrieved by our algorithm are on average about 85 hPa lower (or 1.09 km higher) than the ATSR-2 cloud top pressures. It is not clear whether this dependency on optical thickness is caused by GRAPE or by our algorithm.

4.4.4 Spectral fitting residuals

Figure 4.14 shows the obtained mean spectral fitting residual in the UV-window and its standard deviation. Averaged over the whole wavelength range in this window, the mean spectral fitting residual is 0.005% and the mean of the standard deviations is 0.21%. The residuals show no significant broad spectral behavior, but many spectral fine structures are apparent. Similar fine structures were also found by Joiner et al. (2004) analyzing GOME data. These residuals are probably due to insufficient correction of the ‘undersampling’ effect (van Deelen et al., 2007) and the Ring effect (Joiner et al., 2004; Landgraf et al., 2004).

In Fig. 4.15, the obtained mean spectral fitting residual in the oxygen
Figure 4.14: Mean spectral fit residual between forward model and GOME measurements in the UV-window. The standard deviation around the mean is indicated with the grey area.

A-band and its standard deviation are shown. In this window, the mean spectral fitting residual and the mean standard deviation averaged over the wavelength range are -0.24% and 2.1%, respectively. Especially around the deep R-branch at 761 nm, the spectral fitting residual and the standard deviation are high. The mean residuals are very similar to those found by van Diedenhoven et al. (2005) (Chapter 2) retrieving surface pressures from SCIAMACHY and GOME measurements in the oxygen A-band. This indicates that many of these structures in the mean residuals may be due to errors in the spectroscopy data (Chance, 1997; Rothman et al., 2005), assumption of the spectral lineshapes (Yang et al., 2005; Tran et al., 2006) and insufficient knowledge of the instrument response function. The large spread and the large residual structure around 761 nm could be related to approximations made in the cloud model such as the fixed geometrical thickness and the use of a homogeneous cloud layer. The systematic structures in the residuals could lead to unaccounted biases in the retrieval.
4.5 Conclusions

In this paper we have presented a new method to retrieve information about cloud fraction, cloud optical thickness and cloud top pressure from GOME and SCIAMACHY measurements. Additionally, information on surface albedo is retrieved. The method makes use of measurements at the oxygen A-band from 758–770 nm and in the UV from 350–390 nm. The inversion is based on the Phillips-Tikhonov regularization method. An advantage of this approach in comparison to common approaches using only the oxygen A-band is that, in addition to the cloud top pressure, information about both the cloud fraction and cloud optical thickness can be retrieved, instead of only an effective cloud fraction. The retrieved cloud parameters are relevant for the retrieval of trace gas abundances in cloudy atmospheres.

It was shown that measurements at the oxygen A-band alone do not contain sufficient information for the independent retrieval of the cloud fraction, cloud optical thickness and cloud top pressure. Adding the UV window allows to retrieve significant information about all three cloud parameters. Furthermore, information about the surface reflection can be
obtained from these measurements. The UV-window adds information on the cloud fraction because in the clear-sky part of the measurement, the spectrum is dominated by Rayleigh scattering, which has a strong wavelength dependence. Due to the significant differences between the spectral signature of Rayleigh scattering and that of scattering by cloud particles, the UV window is especially sensitive to the cloud fraction.

Using simulated measurements, it was shown that the use of effective cloud fractions and cloud top pressures leads to a significant systematic underestimation of the tropospheric NO$_2$ AMF in cloudy atmospheres, which can be avoided using cloud parameters retrieved by the proposed algorithm.

The cloud retrieval algorithm was applied to GOME data and the results were compared to effective cloud parameters from the FRESCO algorithm (Koelmeijer et al., 2001). In the FRESCO algorithm, clouds are approximated by reflecting boundaries with a Lambertian albedo of 0.8. The cloud fractions retrieved by our algorithm are consistent with the effective cloud fractions retrieved by FRESCO, given the definition of the effective cloud fraction in FRESCO. Also the cloud top pressures retrieved by our algorithm generally agree well with the effective cloud pressures retrieved by FRESCO with a 68% confidence interval of ±40 hPa, although an offset of about -60 hPa is observed. Furthermore, our results were compared to cloud parameters retrieved from ATSR-2 measurements by the GRAPE algorithm. The distributions of the differences between the cloud fractions, cloud optical thicknesses and cloud top pressures retrieved by our algorithm and the corresponding ATSR-2 values have median values of -0.01 (±0.11), 2.5 (±7.5) and -33 (±111) hPa, respectively.

Acknowledgments

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4.A The Phillips-Tikhonov regularization method

The Phillips-Tikhonov regularization method (Phillips, 1962; Tikhonov, 1963) can be used to reduce the effect of measurement noise in ill-posed inverse problems. In the Phillips-Tikhonov regularization method, the solution $\hat{x}_{\text{reg}}$ is given by the least squares solution with an additional side constraint, viz.

$$\hat{x}_{\text{reg}} = \min_x \left( ||S_y^{-\frac{1}{2}}(F(x) - y)||^2 + \gamma ||\Gamma x||^2 \right),$$  \hfill (4.13)

where $\Gamma$ is a diagonal matrix that contains weighting factors for the different state vector elements in the side constraint and $\gamma$ is the regularization parameter. In its linear approximation, the solution $\hat{x}_{\text{reg}}$ in Eq. 4.13 can be written as

$$\hat{x}_{\text{reg}} = D \tilde{y},$$  \hfill (4.14)

where $\tilde{y} = y - F(x) + Kx$ and $D$ is the contribution matrix defined by

$$D = (K^T S_y^{-1} K + \gamma \Gamma)^{-1} K^T S_y^{-1},$$  \hfill (4.15)

where the superscript $T$ denotes the transposed matrix. Since the weighted norm of the state vector is a quantity that is very sensitive to noise contributions, these contributions are reduced by introducing the side constraint in Eq. 4.13. For the Phillips-Tikhonov solution, $\gamma$ should be chosen such that the minimizations of the weighted least squares norm $||S_y^{-\frac{1}{2}}(F(x) - y)||$ and the weighted solution norm $||\Gamma x||$ in Eq. 4.13 are well balanced. Such a value for $\gamma$ is found from the so-called L-curve (Hansen and O’Leary, 1993; Hansen, 1992).

The weighting factors in the matrix $\Gamma$ are defined relative to the elements of the corresponding state vector of the iteration step under consideration, making $\Gamma x$ dimensionless. Increasing the weighting factor in $\Gamma$ for a certain parameter decreases the information about this parameter that is obtained from the measurements, while for other parameters more information is taken from the measurements. Since the a priori information about the surface albedos in our retrieval scheme is more accurate than a priori information of cloud parameters and because we focus our retrieval scheme on the retrieval of cloud parameters, we increase the weights in
\( \Gamma \) corresponding to the surface albedos by a factor of 10 relative to the weights corresponding to the cloud parameters.

Owing to the inclusion of the side constraint in Eq. 4.13, the state vector \( \hat{x}_{reg} \) retrieved using Eq. 4.13 does not represent an estimate of the true state vector \( x_{true} \), but its elements represent weighted averages of the elements of \( x_{true} \). Since \( x_{true} \) contains several different cloud and surface parameters, the weighted averages in \( \hat{x}_{reg} \) have a limited physical meaning. Therefore, we include information from an a priori state vector \( x_a \) in the solution to make it a meaningful estimate of \( x_{true} \), viz.

\[
\hat{x} = \hat{x}_{reg} + (I - A)x_a.
\] (4.16)

Furthermore, \( A \) is the averaging kernel (Rodgers, 2000), given by

\[
A = \frac{\partial \hat{x}}{\partial x_{true}} = (K^T S_y^{-1} K + \gamma \Gamma)^{-1} K^T S_y^{-1} K.
\] (4.17)

For more details about the Phillips-Tikhonov regularization method we refer to the paper of Hasekamp and Landgraf (2005a).

### 4.B The Levenberg-Marquardt method

The Levenberg-Marquardt method (Levenberg, 1944; Marquardt, 1964) can be used to improve the convergence of a nonlinear iterative inversion problem. Applying the Levenberg-Marquardt method in combination with the Phillips-Thikhonov method described in Appendix 4.A, the solution \( \hat{x}_{n+1} \) for iteration step \( n+1 \) is given by (Rodgers, 2000)

\[
\hat{x}_{n+1} = \hat{x}_n + [\Gamma(\gamma + \lambda) + K_n^T S_y^{-1} K_n]^{-1}
\left[ K_n^T S_y^{-1}(y - F(x_n)) - \gamma ||\Gamma(\hat{x}_n - x_a)|| \right],
\] (4.18)

where the parameter \( \lambda \) is introduced to limit the change in \( x \) in each iteration step. We follow the procedure by Press et al. (1992) for the choice of \( \lambda \). When the Levenberg-Marquardt procedure has converged, \( \lambda = 0 \) and the Phillips-Thikhonov regularization described in Appendix 4.A is used. For more details about the Levenberg-Marquardt method we refer to Rodgers (2000).

Although the Levenberg-Marquardt method improves the convergence of the iterative inversion problem discussed in section 4.2.2, still many iterations are needed due to the strong nonlinearity of the problem. This
nonlinearity is mainly due to the strong dependence of the Jacobian matrix \( K \) on the cloud fraction. To reduce the computational effort, the forward models \( F_{\text{cloud}} \) and \( F_{\text{clear}} \) in Eq. 4.2 are approximated by their linear approximations

\[
\tilde{F}_{\text{cloud}}(x_{\text{cloud}}) \approx F_{\text{cloud}}(x_{\text{cloud}}^0) + K_{\text{cloud}}(x_{\text{cloud}}^0)[x_{\text{cloud}} - x_{\text{cloud}}^0]
\]

\[
\tilde{F}_{\text{clear}}(x_{\text{clear}}) \approx F_{\text{clear}}(x_{\text{clear}}^0) + K_{\text{clear}}(x_{\text{clear}}^0)[x_{\text{clear}} - x_{\text{clear}}^0],
\]  

(4.19)

where \( x_{\text{cloud}} \) is a subset of the state vector containing surface and cloud parameters, and \( x_{\text{clear}} \) is a subset containing only surface parameters. Furthermore, \( x_{\text{cloud}}^0 \) and \( x_{\text{clear}}^0 \) are the sets of parameters for which the exact calculation of \( F_{\text{clear}} \) and \( F_{\text{cloud}} \) were performed. \( K_{\text{cloud}} \) and \( K_{\text{clear}} \) are the Jacobian matrices for the cloudy part and clear-sky part of the measurement footprint, respectively. Using Eq. 4.19, the forward model \( \tilde{F} \) can be approximated by

\[
\tilde{F} = (1 - f_c) \tilde{F}_{\text{clear}} + f_c \tilde{F}_{\text{cloud}}.
\]  

(4.20)

The derivative of \( \tilde{F} \) with respect to the cloud fraction \( f_c \) is

\[
\frac{\partial \tilde{F}}{\partial f_c} = \tilde{F}_{\text{cloud}} - \tilde{F}_{\text{clear}}.
\]  

(4.21)

Furthermore, the derivatives of \( \tilde{F} \) with respect to the other parameters \( x_i \) are

\[
\frac{\partial \tilde{F}}{\partial x_i} = (1 - f_c) \frac{\partial F_{\text{clear}}}{\partial x_i}(x_{\text{clear}}^0) + f_c \frac{\partial F_{\text{cloud}}}{\partial x_i}(x_{\text{cloud}}^0).
\]  

(4.22)

Thus, using Eqs. (4.19), (4.20), (4.21) and (4.22), the forward model and the Jacobian matrix at state vector \( x \) can be approximated using exact forward model calculations at state vector \( x_0 \) without any significant computational effort. When the iteration using this approximate forward model has converged, a new exact forward model calculation is performed to initiate the next iteration.
Chapter 5

Effects of clouds on ozone profile retrievals from satellite measurements in the ultraviolet

Abstract

A new approach to take clouds into account in ozone profile retrievals from backscattered ultraviolet radiance measurements as performed by the Global Ozone Monitoring Experiment (GOME) is evaluated. In this approach ozone profiles are retrieved using cloud fractions, cloud optical thicknesses and top pressures retrieved from oxygen A-band measurements in addition to measurements between 350 nm and 390 nm. This approach (CUVO$_2$), is compared with two commonly used approaches in ozone profile retrievals, namely to treat clouds as an effective ground surface albedo (CaA); and using effective cloud fractions and top pressures retrieved from the oxygen A-band by assuming a cloud optical thickness of 40 (Ceff). Using simulated GOME retrievals we show that the CaA and Ceff approaches lead to significant biases in the mean ozone concentrations of up to $-85\%$ and 18\% near the surface, respectively. These biases significantly increase when the sensitivity to tropospheric ozone is increased due to measurement and forward model errors. With the CUVO$_2$ approach these errors are reduced to below 3\%. Retrievals from 141 GOME measurements using the three approaches were validated with ozonesonde measurements. For cloud optical thicknesses below 40, the mean differences between the ozone concentrations measured by the sondes and those retrieved with the CUVO$_2$ approach is less than 7\% and shows a clear improvement compared to the other approaches. In about a third of all cases, high optical thicknesses above 40 are retrieved erroneously. There are strong indications that these cases are related to inhomogeneous cloud fields within the relatively large GOME footprint. For these cases, all approaches lead to large errors in the mean ozone concentrations.
5.1 Introduction

Measurements of the global distribution of vertical ozone profiles are essential to monitor stratospheric and tropospheric ozone concentrations and to study physical and chemical processes in the atmosphere (e.g. Chandra et al., 1999; Ziemke et al., 2005; de Laat et al., 2007). Ozone profiles can be retrieved from satellite-based nadir reflectance measurements in the ultraviolet (UV) of sufficient spectral resolution (Chance et al., 1997). Such measurements are provided by the Global Ozone Monitoring Experiment (GOME-1 and GOME-2), the Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY) and the Ozone Monitoring Instrument (OMI). For GOME, several algorithms to retrieve ozone profiles are available (Munro et al., 1998; Hoogen et al., 1999; Hasekamp and Landgraf, 2001; van der A et al., 2002; Liu et al., 2005). These algorithms allow ozone profiles to be retrieved with a Degrees of Freedom for Signal (DFS) of about 4.5–5.5, of which 0.5–1.5 is contributed by the tropospheric layers (Liu et al., 2005). It was shown by Munro et al. (1998) and Liu et al. (2005) that valuable information about tropospheric ozone can be derived from these measurements.

Since about 98% of the GOME measurements are significantly influenced by clouds (Krijger et al., 2007), ozone profile retrieval algorithms need to accurately take clouds into account, especially to constrain the retrieval errors in the troposphere. However, clouds are generally included in ozone profile retrieval algorithms only in a simplified manner. For example, often clouds are treated as an effective ground surface albedo, thereby ignoring fractional cloud cover and the elevation of clouds. To accurately incorporate clouds into an ozone profile retrieval scheme, the cloud fraction, cloud optical thickness (or albedo) and the cloud top pressure are needed. However, the cloud retrieval algorithms available for GOME generally assume a cloud optical thickness and retrieve so-called effective cloud fractions and top pressures (e.g. Kuze and Chance, 1994; Koelmeijer et al., 2001). For DOAS based tropospheric NO$_2$ retrievals from GOME measurements it has been shown that the use of effective cloud parameters can lead to a significant systematic overestimation of the tropospheric NO$_2$ column in the order of 20–50% (Wang et al., 2006; van Diedenhoven et al., 2007, Chapter 4). We therefore introduced a scheme to retrieve independent information
about cloud fraction, cloud optical thickness and cloud top pressure from GOME measurements at the oxygen A-band and in the UV at 350–390 nm (van Diedenhoven et al., 2007, Chapter 4).

In this paper we investigate the effects of clouds on ozone profile retrievals from UV measurements in the spectral range 290–340 nm. Here, we evaluate the suitability of taking clouds into account in ozone profile retrievals by using cloud fraction, cloud optical thickness and cloud top pressure retrieved by the recently developed algorithm by van Diedenhoven et al. (2007) (Chapter 4). This approach is compared with two commonly used approaches to take clouds into account in ozone profile retrievals, namely: (1) to treat clouds as an effective ground surface albedo; and (2) using effective cloud fractions and top pressures retrieved from measurements at the oxygen A-band assuming a cloud optical thickness of 40.

In section 5.2 of this paper, the GOME measurements and the ozone profile retrieval approach are discussed. In section 5.3, the three different approaches to take clouds into account in the ozone profile retrievals are evaluated using simulated measurements. Then, in section 5.4, ozone profiles are retrieved from real GOME observations using the three different approaches and the results are validated with ozonesonde measurements. We conclude the paper in section 5.5.

5.2 GOME measurements and retrieval approach

5.2.1 GOME measurements

GOME was launched in 1995 and measures the Earth reflectance in four continuous bands from 237–794 nm, at 0.2–0.4 nm resolution (Bednarz, 1995). The instrument scans across track with a swath of 960 km, resulting in near global coverage in three days. For channels 2–4 (312–794 nm), the forward scan is divided into three observations of $320 \times 40$ km$^2$. Furthermore, a backscan of $960 \times 40$ km$^2$ is included in the scan cycle. Because of the large dynamical range in channel 1 (237–312 nm), this channel is split into channel 1a and channel 1b. Measurements of channel 1a (237–307 nm before 6 June 1998, 237–283 nm afterwards) have $960 \times 80$ km$^2$ sized footprints, corresponding to 2 nominal scan cycles. Therefore, we co-add the measurements of channels 1b and 2 to match the channel 1a observations. Thus, the spatial resolution of our retrievals is $960 \times 80$ km$^2$. 
In addition to Earth radiance spectra, GOME measures the Solar irradiance. To obtain Earth reflection spectra the Earth radiances are divided by the Solar irradiances. Here, the method of van Deelen et al. (2007) is used to account for wavelength shifts between the Earth and Solar spectra due to Doppler shifts between the measurements.

We use version 2.41 of the GOME Data Processor extraction software (DLR, 2002), including all standard corrections, e.g. leakage current and stray light. Furthermore, the seasonal dependence of the sun diffuser BSDF is corrected according to Slijkhuis (2004). The polarization correction is not applied since we use vector radiative transfer models to simulate the polarization sensitive measurements. This avoids errors due to an incorrect polarization correction (Hasekamp et al., 2002). Here, only data from early in the mission are used to avoid errors due to degradation of the instrument.

5.2.2 Retrieval approach

Ozone profile retrieval

For the retrieval of ozone profiles we use the algorithm of Hasekamp et al. (Hasekamp and Landgraf, 2001; Hasekamp et al., 2002). Reflectances and weighting functions for partly cloudy scenes are modeled using the independent pixel approximation (e.g. Marshak et al., 1995). We employ the vector radiative transfer model of Hasekamp and Landgraf (2002) and the CODAGS vector radiative transfer model of van Diedenhoven et al. (2006) (Chapter 3) to describe the radiative transfer in the clear sky and cloudy part of the atmosphere, respectively. Ozone concentrations at 24 atmospheric layers and the surface albedo are included in the retrieval. Their derivatives are calculated with the forward-adjoint perturbation theory (Landgraf et al., 2001, 2002; Hasekamp and Landgraf, 2005b). Measurements in the spectral range 290–313 nm and 326–340 nm are used. This wavelength range is extended in comparison to the algorithm of Hasekamp et al., which uses only measurements between 290 and 313 nm. The extension of the wavelength range is expected to increase the sensitivity of the retrievals to tropospheric ozone. Measurements between 313 nm and 326 nm are excluded to avoid the known large calibration errors of the GOME instrument in this wavelength range (Liu et al., 2005). The ozone absorption cross-sections are taken from Voigt et al. (2001). To account for Ring
structures in the GOME data, we include an amplitude and a wavelength shift and squeeze of a pre-calculated Ring spectrum (Landgraf et al., 2004) in the fit.

The inversion procedure in this algorithm is based on Phillips-Tikhonov regularization (Phillips, 1962; Tikhonov, 1963) with minimization of the norm of the first derivative with respect to altitude as a side constraint. The regularization parameter is determined by the L-curve technique (Hansen and O’Leary, 1993). Using Phillips-Tikhonov regularization, the retrieval result $x_{\text{ret}}$ is a smoothed version of the true profile $x_{\text{true}}$ and is given by

$$x_{\text{ret}} = Ax_{\text{true}} + e_{x},$$

(5.1)

where $e_{x}$ is the profile error caused by errors in the forward model and measurements, and $A$ is the averaging kernel matrix (Rodgers, 2000). The DFS of the retrieval is then given by the trace of $A$ (Rodgers, 2000). For more details about the ozone profile retrieval algorithm, we refer to the paper by Hasekamp and Landgraf (2001).

Note that the vertical resolution of the retrieval result at a certain height is determined by the corresponding row of the averaging kernel matrix. Thus, the retrieval result at a certain height does not represent the true ozone concentration at that height but rather the true profile smoothed by the corresponding row of the averaging kernel matrix.

**Treatment of clouds**

In this paper, we present ozone profiles retrieved using cloud fractions, cloud optical thickness and cloud top pressures retrieved from measurements at the oxygen A-band and in the UV from 350–390 nm (CUVO$_2$ approach). The applied cloud retrieval algorithm is described in detail by van Diedenhoven et al. (2007) (Chapter 4). In brief, cloud fraction, cloud optical thickness and cloud top pressure, in addition to the surface albedos in both wavelength windows and their linear spectral dependence, are simultaneously retrieved from these measurements using the Phillips-Tikhonov regularization method. In general, the regularization of the measurement inversion causes a dependence of the retrieval results on a priori information on cloud and surface parameters. However, in our case the retrieved cloud parameters depend only minimally on a priori cloud information for most cloud fractions, but still show a significant dependence on the a pri-
ori surface albedos. Thus, the errors in the retrieved cloud parameters are dominated by regularization errors due to errors on the a priori surface albedos. The retrieved cloud parameters compare well with those obtained by the Along Track Scanning Radiometer 2 (ATSR-2), which is on the same platform as GOME.

The CUVO$_2$ approach is compared with two commonly used approaches to take clouds into account in ozone profile retrievals. In the first alternative approach an effective ground surface albedo is retrieved to account for the enhanced reflection due to the presence of clouds, commonly known as the cloud as albedo (CaA) approach. This approach is used by e.g. Munro et al. (1998); Hoogen et al. (1999); Hasekamp and Landgraf (2001); van der A et al. (2002). The fractional coverage and the elevation of clouds are ignored in this approach. In the second approach, effective cloud fractions and cloud top pressures are used to account for clouds (Ceff approach). This approach is used by e.g. Liu et al. (2005) and in the current version of the ozone profile retrieval algorithm (OPERA) developed by the Royal Netherlands Meteorological Institute (KNMI) (see e.g. the overview paper by Meijer et al., 2006). Effective cloud parameters are those parameters retrieved when assuming a fixed cloud optical thickness (or reflection) (e.g. Koelemeijer et al., 2001). In this study, the effective cloud fractions and cloud top pressures are retrieved from measurements at the oxygen A-band, assuming a cloud optical thickness of 40. Such a high cloud optical thickness (or a corresponding cloud albedo of about 0.8) is commonly assumed in algorithms for effective cloud parameters (Koelemeijer et al., 2001; Liu et al., 2005). Koelemeijer and Stammes (1999) and Wang et al. (2006) have shown that a cloud albedo of 0.8 is an optimal choice for the retrieval of respectively total ozone columns and tropospheric NO$_2$ columns. Furthermore, since cloud optical thicknesses above 40 are rare, assuming a cloud optical thickness of 40 limits the possibility of retrieving effective cloud fractions exceeding 1 (Koelemeijer et al., 2001). In this approach, the surface albedo at the oxygen A-band is assumed a priori since no surface albedo information can be retrieved from the oxygen A-band measurements in combination with the effective cloud fraction and top pressure (van Diedenhoven et al., 2007, Chapter 4).
5.3 Effects of clouds on ozone profile retrievals using simulated measurements

In this section, the CUVO$_2$, CaA and Ceff approaches to take clouds into account in the ozone profile retrieval are evaluated using simulated measurements. To study the errors on retrieved ozone profiles due to these approaches, GOME measurements are simulated for an ensemble of 200 scenarios with randomly chosen cloud fractions between 0 and 1 and cloud top pressures between 400 hPa and 800 hPa. Furthermore, a difference between the cloud top and bottom of 200 hPa is assumed. The cloud optical thickness values are randomly chosen from a Gaussian distributed set with a median of 8, a standard deviation of 15 and a minimum cloud optical thickness of 2. This distribution roughly resembles global mean distributions of cloud optical thickness for water clouds, such as observed by e.g. Rossow and Lacis (1990) and Chang and Li (2005). A mean surface albedo corresponding to a vegetation surface is used, i.e. 0.01 between 290 and 340 nm, 0.05 between 350 and 390 nm and 0.3 at the oxygen A-band around 760 nm. In the ensemble, random variations of $\pm 10\%$ are introduced around the mean surface albedos. Then, ozone profiles are retrieved from these simulated measurements using the CaA, Ceff and CUVO$_2$ approaches to account for clouds.

For the CUVO$_2$ approach, an a priori cloud optical thickness of 5 and an a priori cloud top pressure of 500 hPa are taken. For the a priori cloud fraction, the effective cloud fraction that corresponds to the a priori cloud optical thickness of 5 is taken, with a maximum of 1. The mean vegetation surface albedos are used as the a priori surface albedos in the cloud parameter retrievals. All simulations are performed for a nadir viewing geometry with a solar zenith angle of 40$^\circ$. The atmospheric temperature and pressure profiles are taken from the US standard atmosphere. A single ozone profile is used for all simulations which is obtained by averaging all ozonesonde measurements above Payerne, Switzerland, in the years 1996 and 1997, available from the World Ozone and Ultraviolet Radiation Data Centre (WUDOC, http://www.woudc.org). The GOME noise error is modeld using the instrument noise model described by Landgraf and Hasekamp (2007). Additionally, a noise floor is added to account for other random-like errors, such as forward model errors. Results for two different
Chapter 5: Effects of clouds on ozone profile retrievals

5.3.1 Ensemble simulations

For a noise floor of 0.1%, Fig. 5.1 shows the relative mean differences $\langle \Delta x \rangle$ between the ozone profiles retrieved with the CUVO$_2$, CaA and Ceff approaches and the input profile used in the simulated measurements smoothed by convolution with the corresponding averaging kernels. The use of the common CaA approach leads to a large underestimation of the mean ozone concentrations below 10 km of up to 220% near the surface. Furthermore, an overestimation of up to 16% between 10–20 km is obtained. These errors are due to the neglect of the fractional cloud cover and the elevation of clouds in the CaA approach. The Ceff approach significantly improves on this. However, still an overestimation of the ozone

Figure 5.1: Relative mean differences $\langle \Delta x \rangle$ (left panel) and their standard deviation $\sigma_{\Delta x}$ (right panel) between ozone profiles retrieved from an ensemble of 200 simulated GOME measurements with randomly chosen cloud parameters and the corresponding smoothed ozone profiles used in the simulated measurements. Here, a noise floor of 0.1% is used. Solid, dashed and dashed-dotted lines correspond to the CUVO$_2$, CaA and Ceff approaches to take into account clouds, respectively. The dotted line indicates the retrieval noise. The standard deviation of the retrieval noise is determined by the standard deviation of the retrieval results where the correct cloud parameters are used in the retrieval. Here, $\Delta x$ and $\sigma_{\Delta x}$ are defined relative to the average smoothed input ozone profiles using the CUVO$_2$ averaging kernels.
mean concentrations below 10 km of up to 60% is obtained. Furthermore, between 10–20 km an underestimation up to 7% is obtained. These errors are due to the fact that the effective cloud fraction is a wavelength dependent quantity (van Diedenhoven et al., 2007, Chapter 4). This wavelength dependency is caused by the different contributions of the clear-sky part of the observation at different wavelengths due to varying atmospheric scattering and absorption optical thickness and the wavelength dependent surface albedo. Due to the strong increase in contribution of Rayleigh scattered light towards shorter wavelengths, the effective cloud fraction corresponding to measurements near e.g. 300 nm is significantly different to that corresponding to measurements around e.g. 330 nm. Thus, no single value for the effective cloud fraction in the 290–340 nm wavelength range exists. Therefore, using an effective cloud fraction retrieved from measurements around 370 nm instead of at the oxygen A-band, as proposed by Liu et al. (2005), lead to similar results as shown here. As shown in Fig. 5.1 these errors can be largely avoided by using the CUVO approach, which results in errors in the mean tropospheric ozone concentration below 11%. Furthermore, above 10 km the errors are below 1%. These errors are relatively small because in the CUVO approach information on both cloud fraction and cloud optical thickness is retrieved, in addition to cloud top pressure. The remaining error is caused by the regularization errors in the cloud parameters due to errors in the a priori cloud and surface parameters.

Fig. 5.1 also shows the standard deviation $\sigma_{\Delta x}$ of $\Delta x$. For altitudes higher than 10 km, $\sigma_{\Delta x}$ is below 5% for the Ceff and CUVO approaches, and somewhat higher (< 10%) for the CaA approach. Below about 8 km, the standard deviations strongly increase and are significantly larger than the standard deviation due to the retrieval noise, for all approaches. For the CUVO approach $\sigma_{\Delta x}$ is 42% near the surface, of which only 22% is caused by the retrieval noise. Apparently, random errors in the cloud parameters due to errors in the a priori surface albedos lead to an additional variation in the retrieved tropospheric ozone concentration.

The influence of clouds on the ozone profile retrievals decreases with decreasing contribution of the tropospheric layers to the DFS. In turn, the DFS decreases with increasing measurement and forward model error, and so does the tropospheric contribution to the DFS. The spectral fitting residuals observed in real GOME retrievals are about 0.8% on average,
which is much larger than the measurement noise. The reason for the spectral residuals can be manifold, e.g. errors in the forward model due insufficient correction of the Ring effect and the 'undersampling' effect \cite{vanDeelen2007}, errors in the ozone cross sections \cite{Orphal2003} or calibration errors of the GOME measurements \cite{vanDerA2002, tanzi2002, Liu2005}. In the measurement simulations we account for these errors by adding a noise floor. For a noise floor of 0.1\%, as used in Fig 5.1, the DFS is about 5.8, while the DFS obtained from real GOME measurements is about 4.8 \cite{Hasekamp2001}. Thus, to make the simulations more consistent with the results from real GOME measurements, we increase the noise floor to 0.8\%, which leads to an average DFS of about 4.7. Fig. 5.2 shows $<\Delta x>$ and $\sigma_{\Delta x}$ for a noise floor of 0.8\%. The stronger regularization of the inversion results in a significantly smaller effect of clouds compared to the situation shown in Fig. 5.1. The mean ozone concentration is underestimated by up to 85\% near the surface when using the CaA approach. The errors in the stratosphere are below 3\%. The Ceff approach leads to an overestimation of up to 18\% near the surface and below 1\% in the stratosphere. Thus, still significant biases are obtained in the troposphere due to the CaA and Ceff approaches. In contrast, the CUVO$_2$ approach leads to errors below
3% in the troposphere, and below 0.5% elsewhere. Also the part of the standard deviations $\sigma_{\Delta x}$ caused by cloud treatment is decreased with the increased noise floor. For the CaA approach, $\sigma_{\Delta x}$ is now 50% at ground level. For the Ceff and CUVO$_2$ approaches, standard deviations of up to about 25% are obtained, which is similar to the standard deviation of the retrieval noise.

### 5.3.2 Dependence of errors on cloud parameters

For the CaA and Ceff approaches, the obtained errors systematically depend on the cloud fraction and cloud optical thickness. Additionally, the errors due to the CaA approach depend on cloud top height. The errors due to the CUVO$_2$ approach do not significantly depend on cloud parameters since these are all independently retrieved in this approach. To study how the errors due to the CaA and Ceff approaches depend on cloud fraction, GOME measurements are simulated for a cloud optical thickness of 10 and a cloud top height of 5.6 km (500 hPa) and varying cloud fractions. Here, a noise floor of 0.8% is used. To minimize the effect of retrieval noise, results of 100 cases with different random measurements errors are averaged. Figure 5.3a shows the error $\Delta x_5$ in ozone concentration at a height of 5 km due to the CaA and Ceff approaches as a function of cloud fraction. Already for low cloud fractions of 0.1, the CaA approach leads to significant errors of about $-25\%$. For increasing cloud fraction up to 0.6 the errors due to the CaA approach increase to about $-70\%$. For cloud fractions larger than 0.6 the error slightly decreases. This is because the error due to neglect of fractional cloud cover decreases with increasing cloud fraction, while the error due to the neglect of the cloud elevation remains. For the Ceff approach, $\Delta x_5$ is 5% for cloud fractions of 0.1 and increases with cloud fraction to around 30% at a cloud fraction of 1.

Similarly, Fig. 5.3b shows the dependence of $\Delta x_5$ on the cloud optical thickness. Here, a cloud fraction of 0.5 and a cloud height of 5.6 km are used. The error due to the CaA approach increases with increasing cloud optical thickness, from about $-50\%$ at an optical thickness of 5 to about $-85\%$ at an optical thickness of 50. The error due to the Ceff approach peaks at about 20% around a cloud optical thickness of 10. A maximum occurs because of two competing effects that take place with increasing cloud fraction, namely on the one hand the influence of the
Figure 5.3: Errors $\Delta x_5$ in ozone concentration at 5 km altitude due to the CaA (dashed lines) and Ceff (dashed-dotted lines) approaches as a function of cloud fraction (a), cloud optical thickness (b) and cloud top height (c). The default cloud fraction is 0.5; the default cloud optical thickness is 10; and the default cloud height is 5.6 km. Here, a noise floor of 0.8% is used.
cloud on the measurements increases, while on the other hand the effective
cloud fraction approaches the geometrical cloud fraction. This leads to a
decrease of $\Delta x_5$ with increasing cloud optical thickness from 10 up to 40.
For a cloud optical thickness of 40 the effective cloud fraction is equal to
the geometrical cloud fraction and thus $\Delta x_5 = 0$. For optically thicker
clouds the error increases again with reversed sign.

Fig. 5.3c shows $\Delta x_5$ as a function of cloud top height. Here, a cloud
fraction of 0.5 and a cloud optical thickness of 10 are used. The error due
to the CaA approach increases with increasing cloud top height. This is
due to the neglect of elevation of clouds in the CaA approach. For the Ceff
approach, $\Delta x_5$ does not vary significantly with cloud top height. This is
because the Ceff approach adequately accounts for the cloud elevation.
5.3.3 Impact of clouds on averaging kernels

Clouds have a significant effect on the averaging kernels of the retrieved ozone profiles. To demonstrate this we perform retrievals from simulated measurements of a clear-sky case and a cloudy case. Here, a noise floor of 0.8% is used. In the cloudy case, a cloud is present with an optical thickness of 10, a top-height of 5 km (520 hPa) and a base-height of 2.8 km (720 hPa). Figure 5.4 shows the averaging kernels for the clear-sky case and for the cloudy case using the CaA and CUVO$_2$ (or Ceff) approach. For the clear-sky case, the tropospheric averaging kernels are relatively broad and all peak at a height of about 7 km. For the cloudy case the averaging kernels in the lower troposphere are generally more pronounced than those for the clear-sky situation. This higher sensitivity of the retrieval with respect to ozone in the lower model layers is due to the increase of light reflected in the troposphere by the presence of the cloud. However, using the CaA approach the averaging kernels in the troposphere peak at 1–3 km height, which is unrealistic since most light is reflected by the cloud top at 5 km altitude instead of by the surface. Using the CUVO$_2$ and Ceff approaches, the peak of the tropospheric averaging kernels is located at the correct height, namely at the cloud top. Furthermore, the averaging kernels rapidly decrease below the cloud top as most of the ozone in and below the cloud is effectively shielded.

In conclusion, the CaA approach leads to a significant underestimation in the mean tropospheric ozone concentrations, which increases with decreasing measurement and forward model errors. Furthermore, the underestimation increases with increasing cloud fraction, cloud optical thickness and cloud top height. The use of the Ceff approach reduces this bias. However, still a significant overestimation is obtained with this approach, which generally increases with cloud fraction, decreases with cloud optical thickness but is relatively insensitive to the cloud top height. By using the CUVO$_2$ approach, all biases can be largely avoided. Furthermore, the averaging kernels in the troposphere obtained with the CUVO$_2$ and Ceff approaches peak at the correct altitude at the cloud top, in contrast to those obtained with the CaA approach which erroneously peak near the surface.
5.4 Effects of clouds on GOME ozone profile retrievals

In this section we perform ozone profile retrievals from GOME data and compare results using the CUVO\textsubscript{2} approach with those obtained with the CaA and Ceff approaches. The retrievals are validated with Brewer-Mast ozonesonde measurements at Payerne (46.82° N, 6.95° E) and Hohenpeißenberg (47.80°N, 11.02°E) from April 1996 until April 1998, taken from the WOUDC. The sondes measure ozone concentrations up to a height of about 30 km with a precision of about 3–4\% (Beekmann et al., 1994). The a priori surface albedos needed for the Ceff and CUVO\textsubscript{2} approaches are obtained from the database of Koelemeijer et al. (2003).

In total 141 GOME ozone profile retrievals are evaluated. Cases in which the cloud retrieval algorithm of the CUVO\textsubscript{2} approach did not converge are excluded. This non-convergence is due to non-linear fitting effects and occurs in about 10\% of the retrievals with the current version of the algorithm (van Diedenhoven et al., 2007, Chapter 4). The effective cloud parameter retrievals converge in all cases. Also we exclude cases for which the peak-to-peak variability of the total ozone columns in the 6 sub-pixels within the large GOME ground footprints used here (excluding backscans) exceeds 15 Dobson Units. For this, we use total ozone columns retrieved by the TOGOMI algorithm (Valks and van Oss, 2003). In these cases, the ozonesonde measurement is probably not a good estimate of the ozone distribution as observed by GOME.

The average DFS of the retrieved ozone profiles is 4.8. In this paper results are evaluated for the altitudes 0–30 km, of which the layers between 0–10 km contribute on average 0.8 to the total DFS and layers between 10–30 km contribute 1.8 to the total DFS.

Figure 5.5 shows a time series of the ozone densities $x_5$ at 5 km altitude retrieved using the CUVO\textsubscript{2} approach and the corresponding smoothed and unsmoothed ozonesonde measurements. Figure 5.5 also shows the relative differences $\Delta x_5$ between $x_5$ retrieved using the CUVO\textsubscript{2}, CaA and Ceff approaches and the corresponding smoothed sonde measurements, respectively. For the CUVO\textsubscript{2} approach, the comparison of the retrievals with the smoothed sonde measurement shows a good agreement, with $\Delta x_5$ distributed around 0. $\Delta x_5$ is somewhat larger in winter. A similar comparison
Figure 5.5: Time series of 141 GOME ozone profile retrievals at Payerne, Switzerland (diamonds) and Hohenpeissenberg, Germany (squares). The upper panel shows the absolute concentrations $x_5$ at 5 km altitude retrieved using the CUVO$_2$ approach and the corresponding smoothed (solid line) and unsmoothed (dotted line) ozonesonde measurements. The bottom three panels show the relative differences $\Delta x_5$ between the retrievals and the smoothed sonde measurements for the CUVO$_2$, Ceff and CaA approaches, respectively. Here, $\Delta x_5$ is defined relative to the smoothed sonde values using the CUVO$_2$ averaging kernels.

is obtained with the Ceff approach. However, compared to the results from the CUVO$_2$ approach, $\Delta x_5$ obtained with the Ceff approach is somewhat more biased towards positive values in the winter months. Furthermore, an overall bias is present in the results of the Ceff approach which cannot be seen on this scale but will be shown below. In the results for the CaA approach a clear systematic bias of about 50% towards too low ozone concentrations can be seen. This is consistent with the results of Hasekamp et al. (2002) (Note that their $\Delta x$ is reversed in sign), showing a similar time series for Payerne using the CaA approach.

For the CUVO$_2$, CaA and Ceff approaches, Fig. 5.6 shows the mean differences $<\Delta x>$ between the retrieved ozone profiles and the corresponding smoothed sonde measurements for several ranges in cloud optical thickness.
Figure 5.6: Relative average differences $\langle \Delta x \rangle$ between GOME ozone profile retrievals and the corresponding smoothed ozone sonde measurements. GOME retrievals are performed using the CUVO$^2$ (solid lines), CaA (dashed lines) and Ceff (dashed-dotted lines) approaches. The top left panel shows the mean differences for all cases. The top right, bottom left and bottom right panels show the mean differences for retrieved cloud optical thickness values $\tau_c$ of above 40, between 5 and 40 and below 5, respectively. The number of comparisons in each optical thickness range is indicated. Here, $\langle \Delta x \rangle$ is defined relative to the mean smoothed sonde ozone profiles using the CUVO$^2$ averaging kernels.
\( \tau_c \) as retrieved by the CUVO\(_2\) approach. The CaA approach leads to a similar underestimation of the mean ozone concentrations in the troposphere as obtained in the simulations of Fig. 5.2. For \( 5 < \tau < 40 \) this underestimation is up to about 80\% near the surface and is significantly lower for \( \tau < 5 \), as expected from the results shown in Fig. 5.3b. For cloud optical thicknesses above 40 the underestimation in slightly lower than for cases with \( 5 < \tau < 40 \), although an increase is expected from the basis of Fig. 5.3b. The CUVO\(_2\) and Ceff approaches clearly improve the retrievals in the troposphere but still lead to an overestimation of up to 15\% and 27\% near the surface, respectively, when all cloud optical thickness values are taken into account. Perusing the results for the different optical thickness ranges shows that the overestimation in the case of the CUVO\(_2\) approach is mainly due to the cases for which a cloud optical thickness above 40 is retrieved. For these cases, the ozone concentration is overestimated by up to 45\% near the surface when using the CUVO\(_2\) approach. Furthermore, the Ceff approach leads to an even higher overestimation of up to 60\% for these cases, although Fig. 5.3b shows that a small underestimation due to the Ceff approach is expected for optically thick clouds. For about 38\% of the measurements a cloud optical thickness above 40 is retrieved, which is much more often than expected. As concluded by van Diedenhoven et al. (2007) (Chapter 4) from comparison to ATSR-2 cloud retrievals, for the majority of such cases the retrieved cloud optical thickness is significantly underestimated while the cloud fraction is underestimated due to the presence of horizontally inhomogeneous or multi-layered cloud fields. Clearly, the Ceff and CUVO\(_2\) approaches are not adequate in the case of inhomogeneous clouds. This is due to the assumption of a single homogeneous cloud layer and the independent pixel approximation. For cloud optical thickness values between 5 and 40, the CUVO\(_2\) approach leads to errors up to 7\% at 8 km and -2\% near the surface. The Ceff approach leads to an overestimation of up to 25\% at the surface, as expected from the simulations shown in Fig. 5.2. For cloud optical thickness values below 5, errors below \( \pm 4\% \) are obtained with the CUVO\(_2\) approach. The Ceff approach leads to an underestimation of ozone up to 8\%, although an overestimation of that order is expected from the study with simulated measurements. This is possibly due to a systematic overestimation of the surface albedo at the oxygen A-band, causing larger errors in the effective cloud parameters for
these optically thin clouds (Koelemeijer et al., 2001).

The standard deviation $\sigma_{\Delta x}$ for the CUVO$_2$ approach is shown in Fig. 5.7. Similar standard deviations are obtained for the CaA and Ceff approaches. For tropospheric layers, the standard deviation is about 65% near the surface, which is significantly larger than the 25% expected from the study on simulated measurements shown in Fig. 5.2. Furthermore, CUVO$_2$ and Ceff approaches do not yield lower standard deviations than the CaA approach as expected from Fig. 5.2. Also, no significant dependence of $\sigma_{\Delta x}$ on retrieved cloud parameters is observed. This insensitivity to cloud parameters indicates that these large standard deviations are due to other causes than clouds. At least part of the large standard deviations is very likely due to GOME sub-pixel ozone variability; the sonde and GOME measurements do not measure the exact same air masses. Sparling et al. (2006) showed that the horizontal variability of middle and upper tropospheric ozone concentrations is 15–25% across scales of about 150 km or larger.
5.5 Conclusions

In this paper we have evaluated a new approach to take clouds into account in ozone profile retrievals obtained from UV measurements in the spectral range 290–340 nm, as performed by GOME. In this approach, ozone profile retrievals are performed using cloud fraction, cloud optical thickness and top pressure retrieved from oxygen A-band measurements in addition to measurements between 350 nm and 390 nm, as described in van Diedenhoven et al. (2007) (Chapter 4). This approach (CUVO$_2$) was compared with two commonly used approaches in ozone retrievals, namely (1) to treat clouds as an effective ground surface albedo, commonly known as the cloud as albedo (CaA) approach; and (2) using effective cloud fractions and cloud top pressures retrieved from oxygen A-band measurements assuming a cloud optical thickness of 40 (Ceff approach). By means of simulated GOME retrievals for an ensemble of cases with varying cloud parameters we showed that the mean ozone concentrations are generally underestimated by up to 85% when using the CaA approach, while they are overestimated by up to 18% with the Ceff approach. The CUVO$_2$ approach leads to a relatively small underestimation of less than 3%. The errors generally peak near the surface. The underestimation due to the CaA approach is caused by the neglect of the fractional cloud cover and the elevation of clouds. The Ceff approach causes an overestimation due to the fact that the effective cloud fraction is a wavelength dependent quantity (van Diedenhoven et al., 2007, Chapter 4). The underestimation due to the CaA approach was shown to increase with increasing cloud fraction, cloud optical thickness and cloud top height. The overestimation due to the Ceff approach generally increases with cloud fraction, decreases with cloud optical thickness but is relatively insensitive to the cloud top height. In contrast, the errors due to the CUVO$_2$ approach do not significantly depend on cloud parameters since these are all independently retrieved in this approach. It was shown that the obtained biases caused by the CaA and Ceff approach significantly increase with increasing contribution of the tropospheric layers to the total DFS. This is for example the case when the measurement and forward model errors decrease.

The three different approaches were then applied to ozone profile retrievals from 141 GOME measurements and the results were validated with
co-located ozonesonde measurements. The mean differences $<\Delta x>$ between the retrieved ozone profiles and the corresponding smoothed sonde measurements were investigated for several cloud optical thickness ranges, i.e. $\tau_c > 40$, $5 < \tau_c < 40$ and $\tau_c < 5$. In accordance with the simulations, the CaA approach leads to an underestimation of the mean ozone concentrations in the troposphere up to about 70% for cloud optical thicknesses above 5, and up to 40% for optically thinner clouds. The Ceff and CUVO$_2$ approaches lead to an overestimation of up to 27% and 15% near the surface, respectively, when all cloud optical thickness values are taken into account. The unexpected overestimation with the CUVO$_2$ approach was shown to be mainly resulting from cases with a retrieved cloud optical thickness above 40, for which the mean ozone concentration is overestimated by up to 45% near the surface. The Ceff approach leads to an even higher overestimation of up to 60% for these cases. These very high cloud optical thicknesses above 40 are retrieved in about 38% of the measurements, which is much more often than expected. In van Diedenhoven et al. (2007) (Chapter 4), we showed that for the majority of such cases the cloud optical thickness is significantly overestimated while the cloud fraction is underestimated in the retrieval due to the presence of horizontally inhomogeneous or multi-layered cloud fields. Thus, the Ceff and CUVO$_2$ approaches are not adequate in the case of inhomogeneous clouds. For cloud optical thicknesses between 5 and 40, the Ceff approach leads to an overestimation of the mean ozone concentration of up to 25% near the surface, while the CUVO$_2$ leads to an overestimation below 7% at 8 km and about -2% near the surface, which is in accordance with the simulations. Also for $\tau_c < 5$, the CUVO$_2$ approach leads to low errors ($< 4\%$) in the mean ozone concentrations. The Ceff approach, however, leads to a small but unexpected underestimation for these optically thin clouds. This is possibly due to a systematically overestimation of the surface albedo at the oxygen A-band, causing errors in the effective cloud parameters for these optically thin clouds.

The standard deviations of the differences between GOME retrievals and sonde measurements are generally up to about 65% at ground level, which is about 20–40% higher than those obtained in the simulations. The standard deviations are similar for all three approaches and are not dependent on cloud parameters. This indicates that these large standard deviations are
not caused by clouds. At least part of these large standard deviations are very likely caused by errors in the validation with ozonesondes due to GOME sub-pixel ozone variability.

Thus, the CaA approach leads to significant underestimation in the mean tropospheric ozone concentrations retrieved from GOME measurements. The use of the Ceff approach reduces this bias but still leads to a significant overestimation in the mean tropospheric ozone concentrations. These biases can be largely avoided by using the CUVO\textsubscript{2} approach. The sensitivity of these retrievals to tropospheric ozone can be increased by further reducing the forward model errors. Then, the biases due to the CaA and Ceff approaches significantly increase and the use of the CUVO\textsubscript{2} approach becomes even more relevant. Application of the CUVO\textsubscript{2} approach to ozone profiles retrieval from higher spatial resolution measurements, such as performed by GOME-2 and future missions, is expected to further improve the performance since the problems with inhomogeneous cloud scenes will be significantly reduced. In addition, the validation with ozonesondes is expected to be more accurate for higher spatial resolution observations.

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Chapter 6

Summary and Outlook

6.1 Summary

The research described in this thesis concerns satellite remote sensing of cloud properties needed to accurately retrieve information about tropospheric trace gases. Two satellite instruments developed to retrieve information about atmospheric trace gases, such as ozone and nitrogen dioxide, are the Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY) and the Global Ozone Monitoring Experiment (GOME and GOME-2). Clouds have a large impact on satellite observations and therewith on trace gas retrieval results. To accurately account for clouds in trace gas retrievals, information about the relative amount of clouds within the instrument footprint (the cloud fraction), the cloud optical thickness and the cloud top pressure is needed. In this thesis, a new method to retrieve these three cloud parameters from GOME and SCIAMACHY measurements is developed. The retrieved cloud parameters are shown to improve the retrievals of ozone profiles in the troposphere. Here, the content and main conclusions of the chapters of this thesis are summarized.

In chapter 2, first the quality of the measurements of GOME and SCIAMACHY in the oxygen A-band at 760 nm, which are primarily used for the retrieval of cloud parameters, is evaluated. This is done by means of the retrieval of surface pressures from these measurements under cloud-free conditions. These retrievals can be well validated because surface pressure is a quantity that is, in general, accurately known. Therefore, surface pressure retrievals and their validation provide important insight into the quality of the instrument calibration and the forward model. In the surface
pressure retrieval we neglect aerosols. Using simulated measurements, it is shown that above low to moderate surface albedos this generally leads to an underestimation of the surface pressures, which ranges from about 50–300 hPa for surface albedos around 0.05 to about 10–50 hPa for surface albedos around 0.3. This underestimation is caused by the reduction of the light path due to scattering by aerosols. For high surface albedos (> 0.4), (multiple) scattering by aerosols can lead to an enhancement of the light path, which in turn leads to an overestimation of the surface pressure of up to 30 hPa. The magnitude of these effects is shown to be further dependent on aerosol optical thickness, the aerosol height distribution and observation geometry. Furthermore, aerosols cause a characteristic spectral feature in the fitting residuals. The amplitudes of these spectral features depend again on the aerosol optical thickness and height distribution. Surface pressures retrieved from SCIAMACHY measurements compare well with those from the UKMO meteorological dataset, taking into account the expected dependence on aerosols. However, a systematic positive offset of about 20 hPa is observed in the retrieved surface pressures. A similar offset was found in the comparison of surface pressures retrieved from SCIAMACHY and co-located GOME measurements. This bias was therefore interpreted as being caused by a calibration error on the SCIAMACHY measurements. Adding an offset of 0.86% of the continuum reflectance at 756 nm to the SCIAMACHY reflectances in the oxygen A-band removes this bias.

In chapter 3, a model is introduced to efficiently calculate the radiative transfer of polarized light in vertically inhomogeneous atmospheres that contain homogeneous cloud layers. Such calculations are generally very time-consuming. A novel approach to the radiative transfer problem in such atmospheres is taken by combining the Gauss-Seidel method, which is efficient for inhomogeneous cloudless atmospheres, with the doubling method, which is efficient for homogeneous cloud layers. For an atmosphere containing one optically thick cloud layer, this combined doubling and Gauss-Seidel (CODAGS) model is about 3–5 times faster than the doubling-adding model with an accuracy of 0.01%. The efficiency of the calculations is further increased by reducing the number of Gaussian-quadrature streams for the optically thin atmospheric layers in comparison to the number of streams used for the cloud layers. To optimize the model for radiative transfer calculations in absorption bands, the cloud reflec-
tion and transmission matrices are interpolated over the absorption and scattering optical thickness values within the cloud layers. The number of interpolation points that is needed to obtain a certain accuracy depends on the ranges of absorption and scattering optical thickness present in the evaluated wavelength range. For this, a scheme is developed to automatically determine the number of interpolation points and their distribution over optical thickness. The accuracy and efficiency of the CODAGS model, including the reduction of streams and the interpolation technique, is evaluated by means of radiative transfer calculations in the oxygen A-band and the Hartley-Huggins ozone band (295–335 nm). It is shown that SCIAMACHY measurements in these absorption bands for an atmosphere containing one optically thick cloud layer can be simulated with an accuracy better than 0.1% within 12–60 seconds on a Pentium 4 2.8 GHz PC. Overall a reduction of 2–3 orders of magnitude in the computational effort is achieved. This radiative transfer model is used for the research described in chapter 4 and 5.

In chapter 4, a new method is presented to retrieve information about cloud fraction, cloud optical thickness and cloud top pressure from GOME and SCIAMACHY measurements. The method uses measurements at the oxygen A-band in combination with measurements in the UV from 350–390 nm. It is shown that measurements of the oxygen A-band alone do not contain sufficient information to independently retrieve cloud fraction, cloud optical thickness and cloud top pressure. Adding the UV measurements allows to retrieve significant information about all three cloud parameters. Additionally, information about the surface reflection can be obtained from these measurements. Measurements in the UV add information on the cloud fraction because in this wavelength range, the spectrum of the clear-sky part of the measurement is dominated by Rayleigh scattering, which has a strong wavelength dependence. Due to the significant differences between the spectral signature of Rayleigh scattering and that of scattering by cloud particles, the UV window is especially sensitive to the cloud fraction. To illustrate the relevance of this cloud retrieval approach, it is shown that the common use of effective cloud fractions and cloud top pressures leads to a significant systematic underestimation of the tropospheric NO₂ Air Mass Factor in cloudy atmospheres. This underestimation can be avoided when all cloud parameters are retrieved independently, as is done with the here
developed method. The cloud retrieval is applied to GOME measurements. The results of the algorithm compare well to cloud parameters obtained by the GRAPE algorithm from co-located ATSR-2 measurements. The ATSR-2 measurements have a high spatial resolution $(1 \times 1 \text{ km}^2)$ and are therefore better suited to retrieve cloud parameters, particularly the cloud fraction, from. The distributions of the differences between the cloud fractions, cloud optical thicknesses and cloud top pressures retrieved by our algorithm and the corresponding ATSR-2 values have median values and 68% confidence levels (between brackets) of $-0.01 \pm 0.11$, $2.5 \pm 7.5$ and $-33 \pm 111$ hPa, respectively.

In chapter 5, the use of the cloud parameters retrieved by the algorithm described in chapter 4 to account for clouds in ozone profile retrievals is evaluated. This approach, dubbed the CUVO$_2$ approach, is compared with two commonly used approaches in ozone retrievals, namely (1) to treat clouds as an effective ground surface albedo, commonly known as the cloud as albedo (CaA) approach; and (2) using effective cloud fractions and cloud top pressures retrieved from oxygen A band measurements assuming a cloud optical thickness of 40 (Ceff approach). By means of simulated GOME retrievals for an ensemble of realistic cloudy scenes, we show that the mean ozone concentrations in the troposphere are retrieved with errors below 3% when using the CUVO$_2$ approach, while they are generally underestimated in the tropospheric layers up to 85% when using the CaA approach and overestimated by up to 18% with the Ceff approach. Generally, the highest errors are obtained near the surface. The underestimation due to the CaA approach is caused by the neglect of the fractional cloud cover and the elevation of clouds. The Ceff approach causes an overestimation because the effective cloud fraction is a wavelength dependent quantity, as was shown in chapter 4. Then, ozone profiles are retrieved from real GOME measurements using the CUVO$_2$, CaA and Ceff approaches and the results are validated with co-located ozonesonde measurements. The mean differences between ozone concentrations in the troposphere measured by the sondes and those retrieved using the CUVO$_2$, CaA and Ceff approaches are found to be 15%, -60% and 27%, respectively. The unexpected overestimation of the ozone concentration when using the CUVO$_2$ approach is shown to be caused by about a third of the retrievals for which too high cloud optical thickness values $(>> 40)$ are retrieved erroneously. For these
cases, a large overestimation of the mean tropospheric ozone of up to 45% is obtained when using the CUVO$_2$ approach. The Ceff approach leads to an even larger overestimation of the ozone concentration of up to 60% for these cases. As shown in chapter 4, the retrieval of such high optical thickness values indicates horizontally inhomogeneous or multi-layered clouds to be present in the GOME footprint. Thus, the Ceff and CUVO$_2$ approaches are not adequate in case of inhomogeneous clouds. For the cases with cloud optical thickness values between 5 and 40, the CUVO$_2$ approach results in an overestimation of the mean ozone concentrations of less than 7%, while the Ceff approach leads to an overestimation of up to 25%, similarly to what is observed in the simulations. Also for cloud optical thicknesses lower than 5, the CUVO$_2$ approach results in a low mean error below ±4%. The Ceff approach, however, leads to a small but unexpected underestimation in the mean ozone concentrations for these optically thin clouds. This is possibly due to the large sensitivity of the effective cloud parameters to biases in the applied surface albedo for these optical thin clouds. For all approaches, large standard deviations of up to about 65% are found, which are probably (in part) due to the variability of the ozone concentrations within the large (960 × 80 km$^2$) GOME footprints.

The main conclusions of this thesis are:

1. The retrieval of surface pressures can be used to evaluate the calibration of the SCIAMACHY and GOME measurements in the oxygen A-band. Comparing the surface pressures retrieved from the SCIAMACHY measurements to those from the UKMO meteorological dataset, a systematic positive offset of about 20 hPa is observed in the retrieved surface pressures. A similar offset is found in the comparison of surface pressures retrieved from SCIAMACHY and co-located GOME measurements. Adding an offset of 0.86% of the continuum reflectance at 756 nm to the SCIAMACHY reflectances in the oxygen A-band removes this bias.

2. The novel approach of combining the Gauss-Seidel and doubling radiative transfer calculation methods yields a model that efficiently and accurately calculates the radiative transfer in inhomogeneous atmospheres that contain cloud layers. For radiative transfer calculations in absorption
bands, the efficiency of this model is further increased by interpolating the reflection and transmission matrices of the cloud layers over the absorption and scattering optical thickness within the cloud layers. Overall, a reduction of 2–3 orders of magnitude in the computational effort is achieved while maintaining the required accuracy (< 0.1%).

3. Independent information about cloud fraction, cloud optical thickness and cloud top pressure can be retrieved by combining measurements in the oxygen A-band and in the UV between 350 and 390 nm.

4. By retrieving an effective surface albedo to take clouds into account in ozone profile retrievals, the tropospheric ozone concentrations are underestimated up to about 70% in the mean. Using effective cloud parameters in ozone profile retrievals generally leads to an overestimation of the tropospheric ozone concentrations of up to about 20% in the mean. By using the cloud parameters retrieved with the algorithm presented in this thesis, the mean differences between the tropospheric ozone concentrations retrieved from GOME measurements and those obtained from ozonesonde measurements are within 7% for most conditions.

6.2 Outlook

The presented method to retrieve cloud properties from measurements in the UV and the oxygen A-band was shown to be able to significantly improve tropospheric trace gas retrievals in cloudy atmospheres. The current version of the retrieval algorithm was developed to prove the feasibility of this method but is too slow to process a large amount of GOME and SCIAMACHY data. Even though quite some effort was already spent to develop an efficient radiative transfer model (chapter 3), the most time-consuming part of these retrievals is still the radiative transfer calculation. The bottleneck of these calculations is the computation of the cloud reflection and transmission matrices with the doubling method. To further reduce the computational effort of this model, the reflection and transmission matrices could be obtained efficiently from a pre-calculated look-up-table. Such a look-up-table should contain cloud reflection and transmission matrices for a variety of absorption and scattering optical thickness values. The
interpolation between these values can then be performed fast and accurately as described in chapter 3. The resulting model is then expected to be able to perform accurate radiative transfer calculations in absorption bands within about 1–10 seconds on a 2.8 GHz PC. With such an improved radiative transfer model, the cloud retrieval algorithm developed in this thesis can be expected to be fast enough to process large amounts of GOME and SCIAMACHY data.

As shown in chapter 4, the presented cloud retrieval algorithm retrieves too high cloud optical thickness values and too low cloud fractions in about 15% of the GOME measurements over land which contain inhomogeneous clouds. Furthermore, in chapter 5 large errors were obtained in the retrieved tropospheric ozone concentrations for exactly these cases regardless of the approach to account for clouds. The frequency of the problems due to horizontal cloud inhomogeneity is expected to increase with increasing footprint size. This is confirmed by the fact that the occurrence of these erroneous cloud retrievals increased by about 20% when the cloud retrievals were performed on the larger sized GOME footprints used for the ozone profile retrievals. SCIAMACHY and GOME-2 have considerably smaller footprint sizes than GOME and thus the problems due to the cloud horizontal inhomogeneity are expected to be substantially reduced when the presented cloud retrieval algorithm is applied to their measurements. Moreover, the inevitable increase of spatial resolution for future instruments will reduce the problem due to horizontally inhomogeneous clouds even further. Problems due to multi-layered clouds, however, will remain.

The sensitivity study on simulated measurements presented in chapter 4 revealed the potential of the presented cloud retrieval algorithm to retrieve cloud information above snow covered scenes. Moreover, the snow albedo can be retrieved simultaneously. Retrieval of cloud parameters above snow is of great importance since most available algorithms for GOME and SCIAMACHY are not able to distinguish clouds from snow covered surfaces. However, in the validation of the retrieved cloud parameters with ATSR-2 measurements presented in chapter 4, scenes with snow covered surfaces are excluded since the ATSR-2 retrievals are unreliable for these cases. Therefore, the quality of the retrieved cloud parameters above snow covered surfaces has not been evaluated in this thesis. In order to do so,
cloud parameters retrieved from SCIAMACHY above snow covered surfaces could be validated using MODIS, which is able to retrieve cloud optical thickness and cloud height above snow covered surfaces (King et al., 1997), although there is a time lag of about 30 minutes between the two observations. In addition, trace gas retrievals over snow covered surfaces using clouds retrieved with the presented algorithm should be validated.

The ozone profile retrievals presented in chapter 5 showed good agreement with the ozonesonde measurements in the mean. However, a large standard deviation of up to 65% was found in the troposphere, which are likely -at least partly- due to variation of ozone concentrations within the 960 \( \times \) 80 km\(^2\) sized GOME footprint. Ozone profiles retrieved from higher spatial resolution measurements are thus expected to show an improved comparison with ozonesondes. Moreover, as demonstrated by Sparling et al. (2006), the representation error in comparisons of ozonesondes to satellite measurements at spatial resolutions higher than 50 \( \times \) 50 km\(^2\) is within 10%. This in turn would enable effects of e.g. clouds on ozone profile retrievals to be studied in more detail. More importantly, well validated individual ozone profile retrievals are very valuable for studies of the physical and chemical processes in the atmosphere.

To also improve the vertical resolution of the ozone profiles retrieved from nadir measurements, the spectral fitting residuals have to be reduced. As discussed in chapter 5, the Root-Mean-Squared (RMS) values of the obtained residuals are in the order of 0.8% while the RMS of the measurement noise is 0.3%. These large residuals are probably due to errors in the forward model due to insufficient correction of the Ring effect and the ‘undersampling’ effect (van Deelen et al., 2007), errors in the ozone cross sections (Orphal, 2003) or calibration errors of the GOME measurements (van der A et al., 2002; Tanzi et al., 2002; Liu et al., 2005). Significantly more information about tropospheric ozone can be retrieved when the residuals are reduced to noise level by addressing these issues. However, then also the errors due to simplified treatments of clouds in the ozone retrieval strongly increase, as shown in chapter 5. The use of the here developed method then becomes more important.

An important application of GOME ozone profile retrievals is the validation of chemistry-transport models (e.g. de Laat et al., 2007). Until now, such validations were limited to ozone in the stratosphere because of the
low accuracy of the retrievals in the troposphere. In this thesis it is shown that the information on tropospheric ozone present in the GOME measurements (about 0.5–1.5 of the total DFS) can be accurately retrieved when clouds are properly taken into account. This allows to extend the validation of chemistry-transport models to tropospheric ozone. Furthermore, these retrievals can improve assimilations of global tropospheric ozone concentrations.
Samenvatting

Satellietwaarnemingen van wolkeneigenschappen voor de bepaling van sporengassen in de troposfeer

De atmosfeer is de dunne complexe schil van lucht rondom onze planeet. Het bestaat voor bijna 99,9% uit stikstof, zuurstof en argon\(^1\). De 0,1% die overblijft bestaat uit zogeheten sporengassen zoals koolstofdioxide, ozon en stikstofdioxide. Vele van deze sporengassen spelen een essentiële rol in het klimaat en de atmosferische chemie en zijn daarmee zeer belangrijk voor de leefbaarheid van de aarde. Door menselijke activiteiten zoals landbouw en de verbranding van fossiele brandstoffen is de samenstelling van de lucht de laatste eeuw sterk veranderd. Dit is vooral het geval in de troposfeer -de laag in de atmosfeer die vanaf de grond tot ongeveer 10 km hoog reikt. Door de luchtvervuiling verandert de delicate chemie in de troposfeer. Verder leidt deze uitstoot tot een verslechterde luchtkwaliteit, vooral in steden. Een andere grote zorg voor onze planeet is de toename van zogeheten broeikasgassen zoals koolstofdioxide, methaan en troposferisch ozon. Deze gassen absorberen de warmtestraling die door het aardoppervlak wordt uitgezonden en zenden een deel daarvan vervolgens weer terug naar beneden, wat resulteert in een netto opwarming van de lucht dichtbij het oppervlak. Dit wordt het broeikaseffect genoemd\(^2\). Broeikasgassen komen van nature voor in de atmosfeer en zijn cruciaal voor de leefbaarheid van de aarde. Een toename van broeikasgassen leidt echter tot een versterkt broeikaseffect en dus tot hogere temperaturen, mogelijk met desastreuze gevolgen, zoals bijvoorbeeld geconcludeerd door het *International Panel on Climate Change (IPCC, 2007a).* Het is daarom van groot belang om de veranderingen in de concentraties van de stoffen in de

\(^{1}\text{voor droge lucht. Vochtige lucht kan tot 4\% waterdamp bevatten}\)

\(^{2}\text{Verwarrend genoeg is dit niet hetzelfde effect dat een broeikas verwarmt. Daar wordt de convectie van warme lucht tegengehouden door het glas.}\)
atmosfeer mondiaal in de gaten te houden en te bestuderen.


Helaas worden satellietwaarnemingen van de troposfeer bemoeilijkt door de aanwezigheid van wolken. Bijna 70% van de aarde is gemiddeld genomen bewolkt. Omdat satellietinstrumenten een beperkte ruimtelijke resolutie hebben van vaak enkele honderden of duizenden vierkante kilometers, wordt meer dan 90% van hun waarnemingen beïnvloed door wolken. Om toch de troposferische samenstelling uit deze metingen zo nauwkeurig

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3 Zie figuur 1.3 op pagina 9 voor een voorbeeld
4 Zie figuur 1.2 op pagina 5 voor de mondiaal verdeling van de gemiddelde wolkenbedekking
mogelijk te bepalen moeten de wolken zo goed mogelijk gekarakteriseerd worden in het stralingstransportmodel. Hiervoor moeten de belangrijkste wolkeneigenschappen voor elke meting bekend zijn. Voor GOME en SCIAMACHY zijn drie wolkeneigenschappen zeer belangrijk: Ten eerste moet de optische dikte van de wolk bekend zijn. De optische dikte is een maat voor de hoeveelheid licht die door de wolk dringt en de hoeveelheid die gereflecteerd wordt door de wolk. Ten tweede moet, omdat GOME en SCIAMACHY een beperkte ruimtelijke resolutie hebben, per meting bepaald worden hoeveel van hun gezichtsveld bedekt wordt door wolken. Dit wordt ook wel de wolkenfractie genoemd, welke tussen 0 (onbewolkt) en 1 (geheel bewolkt) ligt. Ten derde is het nodig de wolkentophoogte te bepalen. Voor de bepaling van wolkeneigenschappen worden doorgaans GOME en SCIAMACHY metingen van de sterke absorptie band van moleculair zuurstof bij 760 nm (de zuurstof A-band) gebruikt. De diepte van de zuurstof A-band hangt direct af van de hoeveelheid waargenomen zuurstof. Omdat een wolk optisch dik is neemt het instrument weinig licht waar van onder de wolk. Hoe hoger de wolk, hoe groter het gedeelte zuurstof is dat wordt afgeschermd voor de satelliet. Hierdoor hangt de diepte van de zuurstof A-band af van de hoogte van de aanwezige wolken. Verder wordt de reflectie meting in het continuüm rondom de zuurstof A-band voornamelijk bepaald door de wolkenfractie en de wolken optische dikte. Het is echter onmogelijk om naast de wolkentophoogte ook de wolkenfractie en de wolken optische dikte beide te bepalen uit de zuurstof A-band metingen. Een veelgebruikte oplossing voor dit probleem is om een wolk optische dikte aan te nemen en zogeheten effectieve wolkenfracties te bepalen uit de metingen. In dit proefschrift wordt echter aangetoond dat het gebruik van effectieve wolkenfracties in algoritmes om sporengas informatie te bepalen significante fouten op kan leveren. Daarom is het herleiden van de onafhankelijke informatie van de wolkentophoogte, de wolkenfractie en de wolken optische dikte uit de GOME en SCIAMACHY metingen het voornaamste doel van dit proefschrift.

Om te beginnen wordt in hoofdstuk 2 de kwaliteit van de GOME en SCIAMACHY metingen in de zuurstof A-band geëvalueerd. Dit wordt gedaan

\[^{5}\text{Zie tabel 1.1 en figuur 1.1 op pagina 4 voor typische wolkeneigenschappen voor verschillende wolken-}\]

\[^{6}\text{Zie figuur 1.6 op pagina 14 voor de gevoeligheden van de zuurstof A-band voor de verschillende wolkeneigenschappen}\]
door middel van het bepalen van de gronddruk uit wolkenvrije metingen. De herleide gronddrukken kunnen heel nauwkeurig gevalideerd worden, omdat gronddruk over het algemeen goed bekend is uit weermodellen. Een validatie van de gemeten gronddruk kan dus belangrijke informatie over de kwaliteit van de metingen en het stralingstransportmodel prijsgeven. In de bepaling van de gronddruk zijn aërosolen -dat zijn kleine zwevende deeltjes in de atmosfeer zoals roet, zand en zeezout- genegeerd. Aan de hand van gesimuleerde metingen wordt aangetoond dat deze aanname in het algemeen leidt tot een onderschatting van de gronddruk. Dit komt doordat de aërosolen het licht terugverstrooien en zo het lichtpad verkorten. Boven sterk reflecterende oppervlaktes kunnen de aërosolen echter ook leiden tot een verlenging van het lichtpad en daarmee tot een overschatting van de gronddruk leiden. Deze effecten hangen sterk af van de optische dikte en de hoogteverdeling van de aërosolen. Gronddrukken herleid uit SCIAMA-CHY metingen komen goed overeen met die uit de UKMO meteorologische dataset als het effect van aërosolen in acht worden genomen. Er is echter wel een systematische overschatting van ongeveer 20 hPa te zien in de SCIAMACHY metingen. Een vergelijkbare overschatting is waargenomen bij de vergelijking tussen gronddrukken die herleid zijn uit SCIAMACHY metingen en die herleid zijn uit de gerelateerde GOME metingen. Er wordt aangenomen dat deze systematische afwijking veroorzaakt wordt door een kalibratiefout van de SCIAMACHY metingen. Als de SCIAMACHY reflectie metingen in de zuurstof A-band 0.86% van de continuümwaarde bij 756 nm wordt opgeteld, verdwijnt deze systematisch afwijking.

In hoofdstuk 3 wordt een nieuw stralingstransportmodel geïntroduceerd dat zeer efficiënt het transport van straling in atmosferen met wolkenlagen kan simuleren. Bovendien simuleert dit model tegelijk ook de trillingsrichting van het licht, oftewel de polarisatie. Dergelijke berekeningen, die nodig zijn om de GOME en SCIAMACHY metingen voor bewolkte gevallen goed te kunnen interpreteren, kosten in het algemeen veel tijd. Om tijd te winnen is een nieuwe aanpak van het stralingstransportprobleem toegepast door twee bekende methodes te combineren, namelijk de Gauss-Seidel methode, die snel is in het gedeelte van de atmosfeer zonder wolken, en de doubling methode, die snel is voor stralingstransportberekeningen in wolklagen. Voor stralingstransportberekeningen bij één golflengte en een atmosfeer met één wolklaag is dit combined doubling and Gauss-Seidel
(CODAGS) model 3–5 keer zo snel als het veelgebruikte doubling-adding model bij een nauwkeurigheid van 0.01%. Vervolgens is het model verder geoptimaliseerd voor simulaties van metingen bij meerdere golflengtes in absorptiebanden. Hiervoor worden de reflectie en transmissie van de wolklaag slechts voor een aantal waarden van de absorptie en verstrooiings optische dikte in de wolklaag exact berekend en vervolgens voor de overige waarden bepaald door middel van interpolatie. Tevens is hiervoor een manier om automatisch de hoeveelheid interpolatiepunten en hun verdeling over de optische dikte te bepalen ontwikkeld. De snelheid en nauwkeurigheid van het resulterende CODAGS model zijn aan de hand van stralingstransportberekeningen in de zuurstof A-band en de Hartley-Huggins ozon absorptieband (295–335 nm) geanalyseerd. Met het CODAGS model kunnen SCIAMACHY metingen van deze twee banden voor een atmosfeer met één dikke wolklaag gesimuleerd worden in ongeveer 12 tot 60 seconden met een nauwkeurigheid die beter is dan 0.1%. Dit is een tijdwinst van ongeveer 2 à 3 orders van grootte. Dit stralingstransportmodel wordt gebruikt voor het onderzoek beschreven in hoofdstuk 4 en 5.

Hoofdstuk 4 beschrijft een nieuwe methode om informatie over de wolkfragmentie, wolken optische dikte en wolkentophoogte te herleiden uit GOME en SCIAMACHY metingen. In deze methode wordt gebruik gemaakt van metingen van de zuurstof A-band en in het ultraviolet (UV) tussen 350 nm en 390 nm. In dit hoofdstuk wordt aangetoond dat metingen van alleen de zuurstof A-band onvoldoende zijn om genoeg informatie van wolkenfractie, wolken optische dikte en wolkentophoogte te bepalen. Als de UV-metingen worden toegevoegd is er wel voldoende informatie over deze drie wolkenparameters in de metingen aanwezig. Ook kan dan tegelijk informatie over de grondreflectie uit de metingen gehaald worden. De UV-metingen voegen informatie over wolken toe, omdat in dit golflengtegebied het licht afkomstig van het wolkenvrije gedeelte van het gezichtsveld van de satelliet gedomineerd wordt door Rayleigh verstrooiing aan luchtmoleculen, dat een zeer sterke golflengteafhankelijkheid heeft. Omdat het spectrale signatuur van de Rayleigh verstrooiing heel anders is dan die van verstrooiing aan wolkendruppels zijn de UV-metingen vooral gevoelig voor de wolkenfractie. Om de relevantie van deze aanpak te illustreren wordt aan de hand van simulaties aangetoond dat het gebruik van effectieve wolkenparameters tot een significante onderschatting kan lei-
den in de troposferische stikstofdioxideconcentratie bepaling uit GOME en
SCIAMACHY metingen. Deze onderschatting kan vermeden worden als
de wolkenparameters worden gebruikt die met de hier beschreven methode
worden bepaald. De methode is toegepast op GOME metingen. De resulte-
rende wolkeneigenschappen zijn vergeleken met de corresponderende waar-
den bepaald op dezelfde plaats en tijd door een ander satellietinstrument,
namelijk de ATSR-2. Door de hoge ruimtelijke resolutie van de ATSR-2
metingen (1×1 km²) zijn deze meer geschikt om met name de wolkenfrac-
tie en de wolken optische dikte uit te bepalen dan de GOME metingen.
De wolkeneigenschappen bepaald door de twee instrumenten komen in het
algemeen goed met elkaar overeen. De verdelingen van de verschillen tus-
sen wolkenfracties, wolken optische diktes en de wolkentophoogtes bepaald
met GOME en ATSR-2 hebben mediaan waarden en 68% betrouwbaar-
heidsinterval (tussen haakjes) van respectievelijk -0.01 (±0.11), 2.5 (±7.5)
and -33 (±111) hPa.

In hoofdstuk 5 worden de wolkeneigenschappen, die bepaald zijn met de
methode beschreven in hoofdstuk 4, gebruikt voor het bepalen van ozon
hoogteprofielen uit UV-metingen van GOME. Deze aanpak (CUVO₂ ge-
noemd) wordt vergeleken met twee andere veel gebruikte manieren om met
wolken rekening te houden in ozonprofiel bepalingen, namelijk: (1) door
een effectieve grondreflectie te herleiden uit de metingen (CaA aanpak); en
(2) door gebruik te maken van effectieve wolkenfracties en wolkentophoo-
gtes onder de aanname van een wolken optische dikte van 40 (Ceff aanpak).
Aan de hand van een set van gesimuleerde GOME metingen laten we zien
dat de gemiddelde ozonconcentratie in de troposfeer kan worden herleid
met fouten onder de 3% als de CUVO₂ aanpak wordt gebruikt, terwijl de-
ze wordt onderschat tot 85% als de CaA aanpak wordt gebruikt en tot 18%
wordt overschat als de Ceff aanpak wordt gebruikt. De grootste fouten zijn
in het algemeen dicht bij de grond te vinden. De onderschatting door de
CaA aanpak wordt veroorzaakt doordat de gedeeltelijke wolkenbedekking
en de hoogte van de wolken in deze benadering worden genegeerd. De Ceff
aanpak veroorzaakt overschattingen omdat de effectieve wolkenfractie van
golflengte afhangt, zoals in hoofdstuk 4 is aangetoond. Deze golflengteaf-
hankelijkheid geldt met name voor de UV-metingen die voor de ozonprofiel
bepalingen gebruikt worden. Daardoor is er geen eenduidige waarde voor
de effectieve wolkenfractie te bepalen voor deze metingen. Vervolgens zijn
Samenvatting

ozon hoogteprofielen uit GOME metingen herleid met de CUVO₂, CaA en Ceff methodes. De resultaten zijn gevalideerd met metingen die gedaan zijn met behulp van ballonsondes op dezelfde dag en ongeveer dezelfde plek. De gemiddelde verschillen tussen de ozonconcentraties in de troposfeer gemeten door de sondes, en die herleid uit de GOME metingen met de CUVO₂, CaA en Ceff aanpakken zijn respectievelijk 15%, -60%, en 27%. Er is aangetoond dat de onverwachte overschatting van de ozonconcentratie door de CUVO₂ aanpak veroorzaakt wordt door een derde van de gevallen waar ten onrechte zeer hoge wolken optische diktes (> 40) voor zijn afgeleid. Met de CUVO₂ aanpak wordt in deze gevallen een grote overschatting van de ozonconcentratie in de troposfeer van 45% gevonden. De Ceff aanpak leidt tot nog grotere fouten van 60% voor deze gevallen. In hoofdstuk 4 wordt aangetoond dat de foutieve bepaling van zulke hoge optische diktes waarschijnlijk veroorzaakt wordt door de aanwezigheid van horizontaal inhomogene of dubbele wolkenlagen in het gezichtsveld van GOME. De CUVO₂ en de Ceff aanpak zijn dus niet adequaat in het geval van inhomogene wolken. Voor de situaties met optische diktes tussen 5 en 40 geeft de CUVO₂ aanpak een overschatting in de gemiddelde ozonconcentratie van minder dan 7%, terwijl de Ceff aanpak een overschatting van 25% geeft, vergelijkbaar met wat in de simulaties is gevonden. Ook voor wolken optische diktes lager dan 5 geeft de CUVO₂ aanpak een lage gemiddelde fout van minder dan 4%. De Ceff aanpak leidt voor deze gevallen echter tot een kleine maar onverwachte onderschatting. Dit is mogelijk doordat voor deze lage wolken optische diktes de bepaling van de effectieve wolkenfracties zeer gevoelig is voor systematische fouten in de aangenomen grondreflectie. Voor alle methodes wordt een grote spreiding gevonden in het verschil tussen ozonconcentraties in de troposfeer, gemeten door de sondes en die bepaald zijn door GOME. Deze grote spreiding is waarschijnlijk (ten dele) te wijten aan variabiliteit van ozon binnen het grote (960×80 km²) gezichtsveld van GOME, waardoor de sondemetingen niet geheel representatief zijn voor de GOME metingen.

De belangrijkste conclusies van dit proefschrift zijn:

1. Het bepalen van de gronddruk uit SCIAMACHY en GOME metingen met behulp van de zuurstof A-band kan gebruikt worden ter evaluatie
van de kalibratie van deze metingen. Een vergelijking van de gronddruk herleid uit SCIAMACHY metingen en de corresponderende waarden uit de UKMO meteorologische dataset laat een systematische overschatting van 20 hPa zien. Eenzelfde verschil is waargenomen bij een vergelijking van de gronddruk bepaald uit SCIAMACHY metingen met die bepaald uit GOME metingen. Als bij de SCIAMACHY reflectie metingen in de zuurstof A-band 0.86% van de continuümwaarde bij 756 nm wordt opgeteld, verdwijnt deze systematisch afwijking.

2. Door het combineren van de Gauss-Seidel en doubling methodes is een efficiënt model verkregen voor het berekenen van het stralingtransport, inclusief polarisatie, in een atmosfeer met wolken. Dit model is verder ge-optimaliseerd voor simulaties van metingen in absorptiebanden door de reflecties en transmissies van de wolk te interpoleren over de absorptie en verstrooings optische dikte in de wolk. Al met al levert dit een tijdwinst op van ongeveer 2 á 3 orders van grootte.

3. Onafhankelijke informatie over de wolkenfractie, wolken optische dikte en wolkentophoogte kan worden herleid door metingen van de zuurstof A-band en metingen in het UV tussen 350 nm en 390 nm te combineren.

4. Wanneer bij het afleiden van ozon profielen een effectieve grondref-lectie wordt gebruikt om met wolken rekening te houden, levert dit een onderschatting op in de gemiddelde ozonconcentratie in de troposfeer tot ongeveer 70%. Door gebruik te maken van effectieve wolkenfracties en wolkentophoogtes onder de aanname van een wolken optische dikte van 40 wordt de gemiddelde ozonconcentratie in de troposfeer overschat met ongeveer 20%. Wanneer wolkeneigenschappen onafhankelijk worden bepaald met behulp van de methode ontwikkeld in dit proefschrift wordt het gemiddelde verschil tussen de ozonconcentratie in de troposfeer bepaald uit GOME metingen en die gemeten met behulp van ballonsondes gereduceerd tot minder dan 7% onder de meeste omstandigheden.
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Reviewed publications


