1. Goal

To show how the differential optical absorption spectroscopy (DOAS) technique can be applied to high resolution spectral measurements from space. In the ultra-violet region, where ozone has pronounced absorption lines, DOAS can be used to retrieve total ozone columns. The goal here is to show the physical principle behind the DOAS technique. Also the major assumptions behind the method, and uncertainties with DOAS from space will be highlighted.

2. Relevance

In 1985, the ozone hole over Antarctica was discovered. Ozone in the stratosphere (10-40 km altitude) is vital, because it filters the harmful ultraviolet (UV) radiation from the sun. Significant depletion of the ozone layer would mean more UV radiation at the surface, and higher occurrences of skin-cancer.

Ozone depletion is caused by persistent chloro-flouro-compounds (CFCs) which found a wide range of applications since the 1970’s. These compounds were thought to be harmless, because they were inert in the lower atmosphere. However, in the high stratosphere strong UV radiation breaks the CFCs, and active chlorine is released. Ultimately, this chlorine was shown to be responsible for stratospheric ozone depletion. Since the discovery of the ozone hole, the Montreal protocol (followed by numerous amendments) have been quite effective in banning the CFCs. However, CFCs have long lifetimes and it will take at least another 60 years before the ozone layer will be fully recovered. Currently, it is under active debate whether climate change will delay the recovery of the ozone layer.

For these reasons, monitoring the recovery of the ozone layer is of vital importance. Satellites, which their global view, play an important role here. Nowadays, the thickness of the ozone layer can be measured from space with an accuracy within a few percent. Ozone is measured from space since 1978, with the launch of the Nimbus-7 satellite. This satellite carried two instruments that were able to measure ozone: The Solar Backscatter Ultraviolet instrument (SBUV) and the Total Ozone Monitoring Spectrometer (TOMS). The latter instrument samples the solar ultraviolet (UV) light that is backscattered from the atmosphere at six wavelengths. From
these measurements, global maps of the total ozone column. The basic principle, that will also be explored in the exercises, is that some wavelengths are more strongly absorbed by ozone than others. As a result, the backscatter ratio depends on the amount of ozone that is present in the atmosphere.

A similar principle is employed by the Global Ozone Monitoring Experiment (GOME) that is currently still flying on the ERS-2 satellite that was launched in 1995. GOME measures the backscatter spectrum of the sun in the wavelength range 240 nm (far in the UV spectral region) up to 793 nm.

From these so-called Earth-shine spectra, column densities of ozone, nitrogen dioxide, water vapor, sulfur dioxide, and other trace gases can be retrieved. The nadir field of view of GOME is 320 km by 40 km. This view corresponds to the area on Earth that is seen by the satellite when it looks down. In this exercise, we will analyze measurements from GOME. We will focus on ozone. First, however, a short explanation of differential optical absorption spectroscopy (DOAS). This is the technique that form the basis of the retrieval algorithm of ozone and other gases from GOME spectra.

3. Theory
3.1 Differential Absorption

Gaseous absorption depends strongly on the wavelength. Suppose we have solar light with wavelength \( \lambda \) and radiance intensity \( L_\lambda \) in Wm\(^{-2}\)sr\(^{-1}\). This radiance is weakened due to gaseous absorption according to:

\[
dL_\lambda = -k_{\lambda,v} L_\lambda ds
\]

where \( k_{\lambda,v} \) (m\(^{-1}\)) is the volume absorption coefficient. Assuming that only absorption is important, the weakening of the radiance along the path \( s_1-s_2 \) can be written as:
The optical depth along the path due to absorption is then given by

\[ L_\lambda(s_2) = L_\lambda(s_1) \exp \left( - \int_{s_1}^{s_2} k_{\lambda,v} \, ds \right) \]

The optical depth along the path due to absorption is then given by

\[ \tau(s_1, s_2) = \int_{s_1}^{s_2} k_{\lambda,v} \, ds \]

Figure 2: Ozone retrieval from space. The satellite instrument measures the radiation of the sun that is scattered by the atmosphere. Scattering occurs mostly in the lower atmosphere, while ozone absorption occurs mostly in the stratosphere, where the ozone layer is located.

Figure 2 shows the geometry in which the thickness of the ozone layer is measured from space. The scattering in the lower atmosphere is caused by air molecules (Rayleigh scattering) and aerosols (Mie scattering). Moreover, the surface may be more or less reflective for solar UV radiation. Figure 1 shows that (Rayleigh) scattering in particularly efficient in the UV spectral region, where the reflectivity of the Earth goes up to 0.3.

Figure 3, relation between a vertical path dz and a slant path ds.

The radiation does not travel vertically through the atmosphere. The relation between a slant and a vertical path is outlined in figure 3.

Reading material for the hands-on exercises
The vertical optical depth due to ozone absorption depends on the solar zenith angle following:

\[ ds = \frac{1}{\cos(\theta)} \, dz = \frac{1}{\mu} \, dz \quad \tau(s_1, s_2) = \frac{\tau(z_1, z_2)}{\mu} \]

Now we consider two wavelengths: one more strongly absorbed by ozone than the other. Ignoring scattering of radiation (this process varies only weakly with wavelength), the radiative transfer for the two wavelengths can be written as:

\[
L_{\lambda_1} = L_{0,\lambda_1} \exp \left( - \int_{\text{path}} k_{\text{abs},\lambda_1} O_3(z) \, ds \right)
\]

\[
L_{\lambda_2} = L_{0,\lambda_2} \exp \left( - \int_{\text{path}} k_{\text{abs},\lambda_2} O_3(z) \, ds \right)
\]

\[
\ln \left( \frac{L}{L_0} \right)_{\lambda_1} - \ln \left( \frac{L}{L_0} \right)_{\lambda_2} = - \int_{\text{path}} (k_1 - k_2) O_3(z) \, ds
\]

Here \( k_{\text{abs}} \) denotes the absorption coefficient in the units \([m^3/kg/m]^{-1}\), since the concentration of ozone is given in \([kg/m^3]\). This formula forms the basis of differential optical absorption spectrometry (DOAS). DOAS can be applied by measuring the spectral absorption along a fixed path, e.g. at the surface. The known variation of the absorption coefficient \((k_1 - k_2)\) then leads directly to the \(O_3\) concentration along the path. GOME was the first instrument employ DOAS from space by measuring the Earth’s reflection at a relatively high spectral resolution. During the exercises the spectral features of ozone absorption in the UV spectral region will be fitted to the natural logarithm of Earth-shine spectra \((L/L_0\), see figure 1 for an example).

### 3.2 GOME measurements

DOAS from space is, in principle, less straightforward than DOAS on the ground. The reasons are:

- The light path through the atmosphere (see Figure 2) is not a straight line, like in ground-based applications of the DOAS technique.
- The light path is influenced by clouds, aerosols, surface reflection, solar zenith angle, ...
- Due to cloud masking, ozone below the clouds cannot be observed.
- The ozone volume absorption coefficient depends on temperature. What temperature should be used for a fit?
- The measured spectrum does not only depend on ozone. Other effects also influence the GOME measurements (e.g. Raman scattering, see figure 2).

Nevertheless, as you will see, the GOME spectra clearly contain information about the ozone abundance in the atmosphere. One of the main problems is the transformation of the measured amount of ozone to a vertical column density. The situation is illustrated in figure 4.
Figure 4: Possible light-paths of UV radiation. Some radiation that is received by the satellite is scattered by clouds. Another fraction comes from Rayleigh scattering, surface scattering, and multiple scattering. However, most of the ozone is in the stratosphere and is thus crossed two times by the measured radiation. At shorter wavelengths, however, ozone absorbs radiation more strongly and radiation may not reach the lower atmospheric layers.

Figure 4 shows that measuring tropospheric ozone will be difficult. However, 90% of the ozone resides in the stratosphere and GOME has a large sensitivity for stratospheric ozone.

A nice feature of the GOME measurements is that the method is self-calibrating by dividing the measured spectrum of the Earth by the measured spectrum of the sun. During the exercises we will investigate the following questions:

1. How well can the measured spectrum be fitted with the ozone absorption coefficient?
2. What factors are of influence on the retrieval result?

4. Analysis
First select from the main menu “DOAS on LVL1 GOME spectra”. This lets you select a so-called level 1 GOME spectrum, which has been corrected for all kinds of instrumental effects. After selection, the Reflectance spectrum of measured by GOME at a specific location on Earth will be plotted. In fact, the natural logarithm of $L/L_0$ is plotted as a function of wavelength. Standard, the wavelength runs from 320 nm to 360 nm. On top of the window, the solar zenith angle (degrees) is given. In the example, this solar zenith is 83.16 degrees, which corresponds to a measurement location at about 67 degrees North. GOME is a sun-synchronous...
orbit, which means that it has a fixed overpass time. In the case of ERS2 (the platform on which GOME is mounted) this overpass time is 10.30 local time (another overpass is at night). The green line corresponds to a polynomial fit to the GOME spectrum. This fit clearly shows spectral features that can be attributed to ozone absorption. To highlight these effects, a second panel displays the differential spectrum, which is the difference between the measured reflection spectrum and the polynomial fit (green line).

The window offers a number of options.

- Minimum wavelength: this corresponds to the minimum wavelength for the polynomial fit
- Maximum wavelength: similar for the maximum
- Show spectrum + fit: this is a drop down menu that lets you select the different program modes that will be explored
- New ground pixel: allows selecting a new spectrum without quitting the program
- Pixel info: Displays information about the 'official' GOME level-2 ozone product.

**Exercise 1: GOME spectra**

In this exercise different GOME spectra will be investigated. New spectra can be quickly loaded with the “new ground pixel button”. By selecting different ground pixels along the GOME orbit, address the following questions:

1. How does the solar zenith angle vary along the orbit?
2. How does the GOME spectrum vary with the cloudiness (see pixel info)?
3. For which situations (solar angle, cloudiness) are the spectral features of ozone strongest?

**Exercise 2: Ozone cross-section**

The second program mode displays information of the ozone cross-section. First change the program mode by changing the “Ozone spectrum and fit” drop down menu to “Show cross-section and fit.” This will display the ozone cross-section as a function of the wavelength.
This cross-section, which is another name of the absorption coefficient, has the units \([\text{Du}^{-1}]\). \([\text{Du}]\) stands for Dobson Unit, which is a common unit to express the vertical thickness of the ozone layer. Again, both the spectrum and the differential spectrum are displayed. The differential spectrum is the difference between cross-section and a differential fit. Address the following questions:

4. How does the ozone cross-section vary with the wavelength? How does this relate to the function of the stratospheric ozone layer in filtering UV?

5. Change the temperature slider. How does the differential cross-section change with the temperature that is taken? Why is a selection of one specific temperature an assumption?

6. Play around with the wavelength sliders. Is there an error involved in the “maximum” and “minimum” wavelengths that are selected for the fit?

Exercise 3: The DOAS fit

- Now the differential cross-section will be fitted to the differential spectrum. This fit will result in an estimate of the ozone amount “seen” by the satellite instrument in the light path between the sun and the instrument. To perform this “ozone retrieval”, select “Show DOAS fit” from the drop down menu. This will plot the differential spectrum \(\ln(L/L_0)\) and the differential ozone cross-section in one window. Moreover, new options will appear, which are explained below:

  - Minimum DOAS wavelength: this is the minimum wavelength of the so-called fit window. The fit window corresponds to the wavelength-range over which the DOAS fit is made.

  - Maximum DOAS wavelength: maximum of fit window

  - Slant ozone column (DU): this editable window gives the ‘slant’ amount of ozone. This amount is multiplied with the differential cross-section. The slider can be moved to change the amount of ozone.

  - Manual DOAS: can be toggled between “Manual DOAS” and “Automatic DOAS”. If “Automatic DOAS” is selected, a least squares fit is attempted of which the result is displayed in the window (which cannot be edited anymore).

Address the following questions:
7. Try to adjust the slant ozone column by moving the “slant ozone column slider”. Do you get a good fit? Are the spectral features in the spectrum all explained by ozone?

8. Modify the minimum and maximum DOAS wavelengths. Over which wavelength range are ozone features observed? Compare to question 4.

9. Toggle to “Automatic DOAS”. Do you get similar slant ozone columns?

10. Compare the retrieval result to the “pixel info” slant column. What is the % difference

The slant ozone column is related to the vertical ozone column by the Air Mass Factor (AMF). The AMF is the ratio of the average geometrical distance that is travelled by the measured photons, divided by the vertical height of the atmosphere. The air mass factor can be assessed by performing radiative transfer calculations. The AMF depends on (see figure 4):

- solar zenith angle
- satellite viewing angle
- cloud fraction and cloud top height (see figure 4)
- The surface albedo and orography

11. Using “pixel info”, assess the AMF conversion of the slant column to vertical ozone column.

12. Assess the accuracy of this DOAS implementation by varying
   - The DOAS fit window
   - The temperature taken for the ozone cross-section
   - The general wavelength range

13. What do you estimate as a % error?

14. Are these errors systematic for other ground pixels?