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Fortgeschrittenen Praktikum Physik
Practical Environmental Measurement Techniques
Space Lab

DOAS Measurements of Atmospheric Species
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1 Background of the experiment

The Differential Optical Absorption Spectroscopy (DOAS) instrument at the Institute of Environmental Physics is used for continuous monitoring of atmospheric trace gases such as ozone (O_3), nitrogen dioxide (NO_2), bromine monoxide (BrO) and formaldehyde (HCHO).

One of the scientific questions behind the experiment is stratospheric ozone depletion in mid-latitudes and how dynamics, stratospheric temperatures and changes in chemical constitution of the stratosphere interact in their influence on the ozone layer. In mid-latitudes, ozone columns are mainly determined by transport of ozone from low to high latitudes and by dynamical changes of the tropopause height. The large variability from day to day and year to year makes the determination of reliable ozone trends difficult. However, from long-term measurements at many stations, an ozone reduction of approximately 4 percent per decade has been determined. Mixing of mid-latitude air with ozone depleted air from high latitudes in spring is one possible explanation, but *in situ* ozone destruction and long-term changes in transport patterns have also been proposed as reasons for the observed trend. In the last years, ozone decline has diminished and according to some studies even stopped in some latitudes, as would be expected from the effect of the Montreal Protocol on CFC emissions.

Other objectives of the DOAS-measurements at the Institute of Environmental Physics are validation of satellite instruments like GOME, SCIAMACHY, GOME-2, OMI or the TROPOMI instrument on the Sentinel 5 precursor satellite and the investigation of tropospheric air pollution. In Bremen, an important part of air pollution is caused by NO_x ($NO + NO_2$) emissions of traffic, power generation and industry.

With the DOAS method, trace species are identified using their distinct absorption structures in the UV/visible spectral range. The 'Differential' in DOAS indicates that only narrowband structures are analysed whereas the broadband structures - that are e.g. caused by extinction through scattering by molecules, aerosols or clouds, and that are difficult to quantify - are approximated by a polynomial in wavelength. Therefore, only those species that show significant and structured absorption in the UV/visible wavelength range can be observed, including O_3, NO_2, BrO, HCHO, CHOCHO, H_2O, OClO or IO. Unlike other techniques such as ozone sondes, LIDAR measurements, or microwave radiometry, DOAS measurements provide only little information on the vertical profile of the absorbers but rather yield the integrated column of a trace gas concentration in the atmosphere. This disadvantage is compensated by the simplicity of the experiment and the relatively large number of species that can be measured simultaneously. Another option to get some profile information at least for tropospheric absorbers is the analysis of light, scattered from different angles close to the horizon (see e.g. http://www.iup.uni-bremen.de/doas/maxdoas_instrument.htm).

1.1 Recommended reading

Most text books on atmospheric physics and chemistry have chapters dealing with ozone chemistry, both in troposphere and stratosphere and also have an introduction to tropospheric pollution. Some examples are

- Richard P. Wayne, Chemistry of Atmospheres, Oxford Science Publications
- Guy P. Brasseur, John J. Orlando, and Geoffrey S. Tyndall, Atmospheric Chemistry and Global Change, Oxford University Press
- T. E. Graedel, Paul J.Crutzen, Chemie der Atmosphäre, Spektrum Akademischer Verlag

If you are interested to learn more about UV/visible absorption measurements and DOAS, you might find the following books useful:

- The Remote Sensing of Tropospheric Composition from Space, Editors: John P. Burrows, Ulrich Platt, and Peter Borrell, Springer, ISBN 978-3-642-14790-6, online pdf
- Differential Optical Absorption Spectroscopy: Principles and Applications, Ulrich Platt and Jochen Stutz, Springer, ISBN: 978-3-540-21193-8 (Print) 978-3-540-75776-4

2 Experimental set-up

A DOAS instrument usually consists of a grating spectrometer, a CCD detector, a telescope, a quartz fibre bundle between spectrometer and telescope and a computer for data acquisition (see Figure 1).
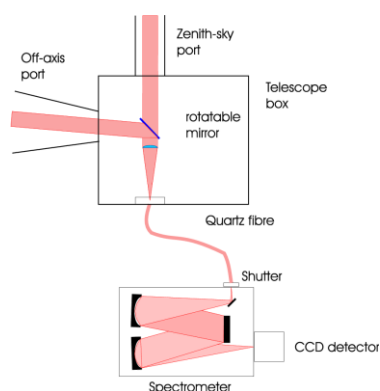

Figure 1: Simplified sketch of a DOAS set-up for zenith-sky and horizon observations

Light scattered from the atmosphere above the instrument is collected by the telescope through the zenith-sky port and fed into the spectrometer via a quartz fibre bundle. The spectrometer used in the practical is of the Czerny-Turner type, has a focal length of 0.275 m and is equipped with a flat ruled grating with 300 lines/mm. The CCD detector has 1024 pixels in the horizontal direction and is 251 pixels high. In the standard operation mode, the signal is integrated vertically resulting in a single spectrum with high signal-to-noise ratio. In automatic operation, the integration time is determined from the measurement taken prior to the measurement itself. In manual operation, the optimal integration time can be determined and set using the menu of the software.

In addition to the zenith pointing port, a second window is located at the side of the telescope to facilitate measurements of light scattered close to the horizon. This is achieved by moving a computer controlled motorised mirror into the line of sight. Depending on the mirror orientation, measurements at elevation angles between -5° and 30° can be performed. In contrast to zenith-sky observations, this type of measurements is most sensitive towards absorptions in the troposphere.

In the telescope housing, there are also two calibration lamps that are operated automatically during night and are used for the calibration of wavelength and relative radiometric response of the instrument.

3 Data analysis

3.1 Determination of absorption along light path

The basic quantity measured is the sky brightness I as a function of wavelength λ at different solar zenith angles (SZA) Θ and viewing elevation angles ϕ The analysis of the data is divided into two parts. First, the integrated amount of the absorber along the light path (called the *slant column*) is determined using the differential optical absorption spectroscopy method. In a second step, the average light path is computed with a radiative transfer model and used to convert the measured slant column into a vertical column that is the integral of the absorber along the vertical in the atmosphere. In the determination of the slant column, Lambert-Beer's law is used, accounting for extinction by molecular absorption of J species and in addition, Mie and Rayleigh scattering:

$$I(\lambda, \Theta, \phi) = \alpha(\lambda, \Theta, \phi) I_0(\lambda) \exp\left\{ -\int \left(\sum_{j=1}^{J} \sigma_j(\lambda) \rho_j(s) + \sigma_{Mie}(\lambda) \rho_{Mie}(s) \right. \right. $$
$$ \left. \left. + \sigma_{Ray}(\lambda) \rho_{Ray}(s) \right) ds \right\}$$

where σ_j is the absorption cross-section of species j, ρ_x is the density of absorber or scatterer x, I_0 is the radiance outside the atmosphere and the integral is taken along the light path s. The factor a determines the intensity of the scattered light and depends on the density of scatterers, the phase function and the viewing direction of the instrument and is a smooth function of wavelength.

Assuming that the absorption cross-sections do not vary significantly along the light path, the integral of the absorber column along the light path can be taken, leading to the slant columns $SC_j = \int \rho_j(s) ds$. This yields:

$$I(\lambda, \Theta, \phi) = \alpha(\lambda, \Theta, \phi) I_0(\lambda) \exp\left\{ -\sum_{j=1}^{J} \sigma_j(\lambda) SC_j - \sigma_{Mie}(\lambda) SC_{Mie} - \sigma_{Ray}(\lambda) SC_{Ray} \right\}$$

The cross-sections for Mie and Rayleigh scattering vary smoothly with wavelength:

$$\sigma_{Ray} \propto \lambda^{-4} \quad \sigma_{Mie} \propto \lambda^{-\kappa} \quad \kappa = 0 \ldots 2$$

and can be approximated by a polynomial. The basic 'trick' of the DOAS method is that all effects varying smoothly with wavelength are approximated by a low order polynomial including extinction by scattering, the factor a and also low frequency components in the molecular absorption:

$$I(\lambda, \Theta, \phi) = \alpha(\lambda, \Theta, \phi) I_0(\lambda) \exp\left\{ -\sum_{j=1}^{J} \sigma_j(\lambda) SC_j + \sum_{p} b_p \lambda^p \right\}$$

After taking the natural logarithm and including ln$a$ into the polynomial the DOAS equation reads:

$$\ln\left(\frac{I(\lambda,\Theta,\phi)}{I_0(\lambda)}\right) = -\sum_{j=1}^{J}\sigma_j(\lambda)SC_j + \sum_p b_p^*\lambda^p$$

Please note, that all multiplicative factors to I such as instrument sensitivity cancel if I and I_0 are measured with the same instrument. In the final analysis, this equation is solved for many wavelengths in a linear least squares analysis with the slant columns SC_j and the polynomial coefficients b_p^* as parameters.

In the simplified examples analysed in this practical, only one absorber has to be considered (NO_2) and the polynomial can be subtracted in a first step from both the absorption cross-sections σ and the logarithm of the radiances. The slant column can then be determined by simply scaling the absorption coefficient to the derived differential optical depth: $\tau(\lambda) = -\ln I(\lambda,\Theta,\phi)/I_0(\lambda)$

3.2 Light path

In the DOAS method, the signal is integrated along the light path. The longer the light path, the larger the signal. What the light path is depends on the viewing geometry used in the experiment.

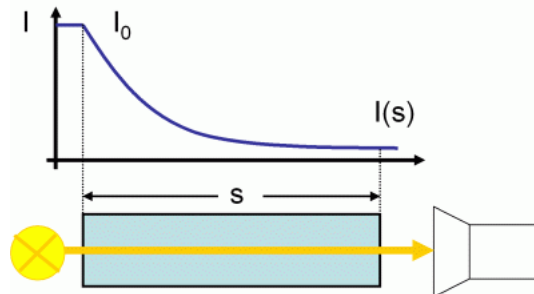### 3.2.1 Measurements in the lab / with NO_2 in a cell

Figure 2: Light path and decrease of intensity for a simple absorption experiment with a cell of length s containing a homogenous absorbing medium

In case of a measurement in the lab or using a cell filled with an absorber, the light path length is simply the physical size of the cell in the direction of the light path as shown in Figure 2.

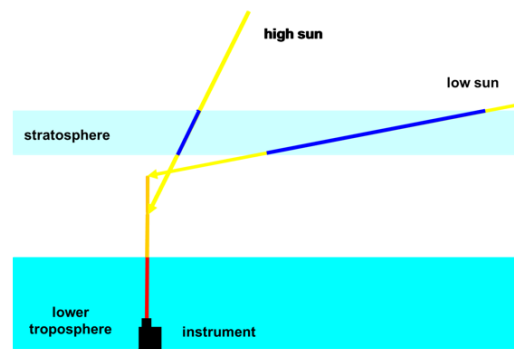### 3.2.2 Zenith-sky measurements of stratospheric absorbers

Figure 3: Sketch of the light path for a zenith-sky observation. Schematic light paths at two different solar zenith angles are shown. The larger the SZA, the longer the light path through the upper atmosphere.

In the case of zenith-sky absorptions, the light path can in first approximation be separated in two parts: First, the part coming from the sun and extending until the scattering in the atmosphere takes place. The length of this path through a given layer depends on the solar zenith angle and increases with increasing SZA. The second part of the light path is the vertical distance between the scattering point to the instrument. This part does not depend much on solar position. As indicated in Figure 3, zenith-sky observations are most sensitive to stratospheric absorbers and work best at low sun (twilight).

In reality, the light path is more complex because of many factors including the sphericity of the atmosphere, multiple scattering and the presence of aerosols and clouds. Accurate estimates of the light path length therefore need to be based on radiative transfer models.

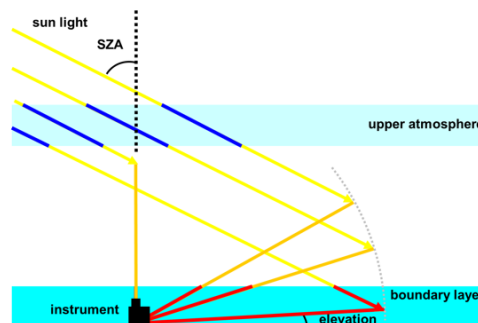### 3.2.3 Horizon measurements of tropospheric absorbers

Figure 4: Sketch of the light path for a horizon observation. Schematic light paths at four different elevation zenith angles are shown, including the view to the zenith ($\phi_0 = 90°$). The smaller the elevation angle, the longer the light path through the boundary layer.

If the telescope of the DOAS instrument is pointing to the horizon, the light path can again be separated into two parts (see Figure 4). The first part is similar to that of a zenith-sky observation and depends on the solar zenith angle. The second part depends on the elevation angle of the telescope, and determines how long the light path through the boundary layer is. This type of observation is best made at high sun and with small elevation angles of the telescope as it then maximizes the sensitivity to absorption in the boundary layer.

In real measurements, the length of the light path depends strongly on wavelength and the amount of aerosols contained in the boundary layer. In the presence of clouds, it is difficult to estimate the light path ad such measurements are usually discarded.

3.3 Choice of reference spectrum

As a complication, an extra-terrestrial spectrum $I_0(\lambda)$ cannot be measured with a ground-based instrument. Therefore, a reference measurement is taken with as low absorption as possible. Which measurement to take as reference depends on the target quantity:

3.3.1 Measurements in the lab / with NO_2 in a cell

If measurements of the absorber content in a cell are determined for example in the lab or when using the NO_2 cell in this experiment, the reference measurement $I_0(\lambda)$ is just the measurement without the cell.

3.3.2 Zenith-sky measurements of stratospheric absorbers

In the case of zenith-sky observations, a measurement at high sun at a solar zenith angle Θ_0 is used as I_0 in the case of zenith-sky observations as then the light path through the atmosphere is short. In this case, only the difference in absorption between the measurements taken at different SZA, $\Delta SC_j = SC_j(\Theta) - SC_j(\Theta_0)$ can be determined.

3.3.3 Horizon measurements of tropospheric absorbers

In the case of horizon observations, a measurement in zenith-sky direction is used, taken as close in time to the horizon measurement as possible. In the zenith direction, the light path in the troposphere is short and therefore the tropospheric absorption minimized. In this case, only the difference in absorption between the measurements taken at different elevation angles, $\Delta SC_j = SC_j(\phi) - SC_j(\phi_0 = 90°)$ can be determined.

3.4 Computation of vertical columns

The next step is the conversion from slant to vertical columns. This conversion relies on the concept of air mass factors (AMF). Air mass factors are defined as the ratio between the observed slant column and the searched quantity, the vertical column $VC_j = \int \rho_j(z)dz$ of absorber j:

$$AMF_j(\lambda, \Theta, \phi) \equiv SC_j(\lambda, \Theta, \phi)/VC_j$$

In general, air mass factors depend on wavelength, solar zenith angle, viewing angle and the vertical profile of the absorber. They are computed with radiative transfer models that simulate the measurement geometry for a standard atmosphere. In the practical, the appropriate air mass factor for NO_2 is supplied in a file.

As mentioned above, only the difference of slant columns can be determined from ground-based measurements, and some assumptions have to be made for the absorption already contained in the measurement at high sun. The simplest assumption is that the vertical column in the background measurement is the same as in the actual measurement, and the differences are only due to changes in light path. With this assumption, the vertical column can be determined as follows:

$$\Delta SC_j = SC_j(\Theta, \phi) - SC_j(\Theta_0, \phi_0)$$
$$= VC_j AMF(\Theta, \phi) - VC_j AMF(\Theta_0, \phi_0)$$
$$VC_j = \frac{\Delta SC_j}{AMF(\Theta, \phi) - AMF(\Theta_0, \phi_0)}$$

In the case of NO_2 cell measurements, the background measurement is the measurement without cell, and the light path within the cell is simply given by the length of the cell.

3.5 Recommended reading

There are many papers dealing with the DOAS method and with results obtained with these measurements. Several of them have been published of the Bremen group and are listed on our website www.doas-bremen.de. There is also some general information on the DOAS method and on applications available. A short introduction to the DOAS method is given in a lecture by Andreas Richter, which can be found here.

4 Experimental procedure and tasks

In the usual operating mode, DOAS measurements taken at twilight are analysed with a spectrum taken at noon as a background. As this takes too much time for a practical, you will be provided with such spectra for analysis. In addition, you will take measurements of NO_2 in a quartz cell and of NO_2 in the troposphere by taking measurements towards the horizon and to the zenith.

4.1 Experiment

4.1.1 NO2 cell measurements

During the practical, you will be introduced to the measurement system, and then take a series of measurements with and without a cell filled with NO_2. By analysing these spectra, you can deduce the amount of NO_2 in the cell. Be careful with the cell and avoid illumination before starting the experiment if possible (why?). In the lab, proceed as follows (a more detailed description is given in a 2nd document provided to you by the supervisor):

1. Familiarise yourself with the instrument and software
2. Take a few test measurements and discuss what you see
3. Switch the instrument to zenith-sky viewing mode
4. Insert the NO_2 cell into the zenith-sky viewing port of the telescope
5. Determine the optimal integration time
6. Take a measurement averaged over 20 individual measurements
7. Save your measurement
8. Remove the NO_2 cell.
9. Take a measurement averaged over 20 individual measurements. The two measurements with and without cell should be performed rapidly after each other. (Why?)
10. Save your measurement
11. Repeat the measurement sequence several times for at least 120 minutes.
12. For all exposure times used, take a dark signal measurement and save it to your stick.
13. Don't forget to make notes about the weather, filenames and anything else that might be of importance for the analysis, such as the length of the NO_2 cell.

4.1.2 Horizon measurements

As a second experiment, take one or a few measurements towards the horizon (1° - 15° elevation) and to the zenith (90°). If necessary, also take the dark measurements for the corresponding exposure times. From these data, you can estimate the amount of NO_2 in the boundary layer.

Once you have finished taking measurements, have the supervisor switch the instrument back to automatic operation, collect your data on a USB stick and other things and proceed with the data analysis on your own computer.

4.2 Data analysis

The supervisor will provide you with a set of measurement data and some auxiliary files necessary for the analysis. Your task is

1. to determine the concentration of the NO_2 in the cell from your cell measurements
2. to determine the NO_2 slant column in the boundary layer as a function of viewing angle from your horizon measurements
3. to compute the vertical column of stratospheric NO_2 above Bremen from a full day of measurements provided to you by the supervisor.

A detailed description of the data evaluation will be provided in the 2nd document.

4.3 Special precautions

- The NO_2 cell used in the absorption measurements is made of quartz glass and can break if not handled with care. Please use it carefully. If the cell breaks, leave it alone and get away. If it breaks indoors, leave the room immediately. Alarm your supervisor. **Nitrogen oxides at high concentrations are extremely harmful to human health.**
- The DOAS instrument is used for continuous monitoring of atmospheric constitution. It should therefore never be switched off, reset or moved by you. If any change in the instrument is necessary, the supervisor will take care of it.
- After your experiment, the instrument should be reset to run in automatic measuring mode to ensure continuous data sets. Please ask the supervisor for support.
- The DOAS lab is air conditioned. **Do not open the window and avoid keeping the door open.**

4.4 Prerequisites

For the DOAS practical, in addition to the usual things such as paper and a pocket calculator you will need the following items:

- a USB stick
- a coat (you need to go outside even if it rains)
- it is mandatory to do the practical at least twosome

5 Questions for the preparation

1. What are the basics of stratospheric and tropospheric ozone chemistry? What's the role of NO_2 in this context?
2. What are the main sources of nitrogen oxides in the atmosphere?
3. What is ozone depletion, what is ozone smog?
4. What is the magnitude of NO_2 columns to be expected in Bremen throughout the year?
5. What mixing ratios do you expect for NO_2 in the troposphere in Bremen?
6. What is the basic principle of a grating spectrometer? How is the spectral resolution determined?
7. What is the principle of a light fibre?
8. What are Fraunhofer lines?
9. Why do absorption spectra of molecules show structures in the UV/visible wavelength range?
10. What is a "fitting window"? How is it selected?
11. How does the DOAS algorithm differentiate between extinction by scattering and absorption by molecules?

12. Do you need to know the absolute intensities of the measurements for the DOAS analysis? Why?

13. Is the zenith-sky viewing DOAS instrument sensitive towards absorption in the troposphere? Why?

14. What is the schematic light path for horizon observations?

15. What is the basic quantity we get with the DOAS method?

16. What is the purpose of the "dark measurement"?

17. What is a slant column SC?

18. What is an air mass factor AMF?

19. What is a vertical column VC?