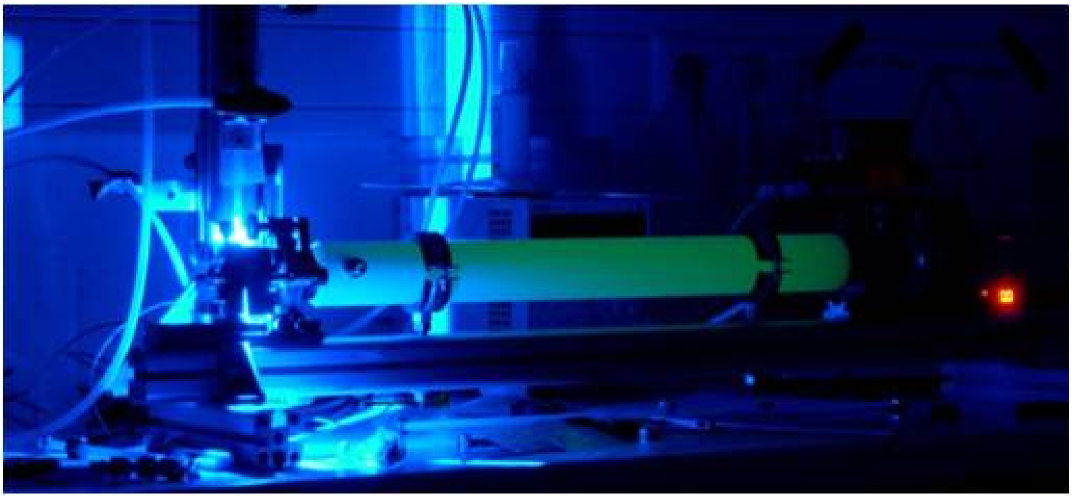
Advanced Lab Course
Cavity-Enhanced-DOAS



Institute of Environmental Physics

August 5, 2014

Safety instructions CE-DOAS lab course

Version 1.0 - July 2017

Before starting the experiment, students must familiarize themselves with the general laboratory regulations of the university. A printed version of the regulations can be found next to the laboratory entrance. In this lab course the following particular sources of hazard will be encountered during the course:

Ultra violet (UV) radiation

In this experiment, a UV light source is used. UV radiation irritates and damages the eyes. Skin irritation and even severe burns can occur in case of continuous UV exposure. When working with the lightsource wear appropriate protective goggles. Do not look directly into the light. Avoid direct exposure of the skin. If possible, screen the optical setup. Do not use the light source longer than necessary.

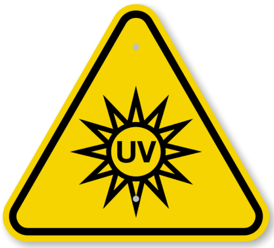
Nitrogen dioxide cuvette

For parts of the experiment a nitrogen dioxide (NO_2) cuvette with an NO_2 volume mixing ratio between 0.1 and 1.0 % will be used. NO_2 is harmful by inhalation. In case of nausea or respiratory tract irritation call a poison control center or doctor. In case of release of gas from the cuvette immediately leave the room and open windows if possible. Inform your experiment supervisor. Storage may only be carried out in well-ventilated areas. The cuvette must therefore be returned to an appropriate room after completion of the experiment.

Pressurised helium gas cyclinder

In this experiment a pressurised helium gas cyclinder is used for calibration purposes. Gas cyclinders can be pressured up to 200 bar and therefore have a condiserbale destructive potential when exploding. Furthermore, larger quantities of inert gases can displace breathing air leading to suffocation. **Only operate the gas cylinder after instruction and demonstration by your supervisor.** In case of a (uncontrolled) leak, if possible, close all valves and open the windows and leave the room.

Details on the listed hazards can be found in the information sheets attached to the respective hazard sources. By signing the 'Safety Briefing - Signature List', you confirm, that you have read and understood these instructions.



Contents

1 Introduction

Atmospheric chemistry is one of the main research topics at the Institute of Environmental Physics. The research group around Ulrich Platt is working towards gaining a better understanding of the chemical processes in the atmosphere. During research campaigns to locations all around the world, locally or globally important processes are analysed. The measurement technique utilized during most of these measurements is *Differential Optical Absorption Spectroscopy*, short DOAS. This method was first used by U. Platt and D. Perner and also by J. Noxon.

Absorption spectroscopy has been employed for several decades to study the earth's atmosphere. While the focus has been on remote sensing for a long time, lately there has been a renewed interest in in-situ methods, as point measurements allow an easier interpretation for highly inhomogeneous distributions of gases of interest compared to the integration approach of most remote sensing methods. One comparatively new method is Cavity Enhanced DOAS (CE-DOAS) which applies an optical resonator to perform sensitive in-situ measurements. The instrumental setup can be made relatively simple and also portable which is an important advantage for field measurements.

The goal of this lab course is to become familiar with the fundamentals of the CE-DOAS method and to learn how to operate such an instrument. The acquired knowledge is then practically applied to study the NO_2 chemistry in the lower urban atmosphere. A further goal is to get an impression of a scientists workday at the Institute of Environmental Physics.

For a succesful execution of this practical, it is important to be well prepared. So read this manual attentively to make sure you get the most out of it.

The experiment takes place on the second floor, room 230 at the Institute of Environmental Physics (INF 229).

2 Preparation at home

The practical will be a lot easier, if you thoroughly review these materials beforehand. You should be able to answer the following questions before starting the lab course:

- What are the sources of NO_2? What is its impact on atmospheric chemistry?
- Do you know the Law of Lambert-Beer?
- What does the term *differential* in DOAS mean?
- What is meant by cavity enhanced?
- What is the principle of CE-DOAS? Why is it a good method for the measurement of NO_2?
- What are preconditions to use CE-DOAS?
- A spectrum is the sum of different parts. Which components do you know?
- What is the difference between dark current, offset and noise?

Concepts:

- (CE-) DOAS
- DOASIS
- Absorption
- Chemistry of the atmosphere, especially ozone
- Spectrosopy
- Combustion processes

Instrumentation:

- Cavity with highly reflective mirrors
- High power LED with an emission at suitable wavelength
- Lenses for the optical setup
- Quartzfibre
- Spectrograph with CCD-detector
- Temperature control

- Generator for „zero-air“
- Flowmeter
- Switching valve
- Pump and filters
- Computer with data aquisition and evaluation software (DOASIS, Origin...)

3 Schedule

This list should help you keep track of the experiment. Detailed descriptions of each point are found in the main manual.

3.1 Preparation before the beginning

- You will need a lab book.
- Read the whole manual attentively.
- Mark points you didn't understand and discuss them with your lab partner.
- Create a subfolder with your name on the computer and copy the folder with the scripts into it.
- Every time you have to use scripts for measurements or evaluation, use those in your own folder.

3.2 First Experiments

- Record two offset spectra, call them *Offset_1* and *Offset_2*.
- Record two dark current spectra, *DC_1* and *DC_2*.
- Determine the instrumental noise.
- Record the spectrum of a Hg line emitter and conduct the wavelength calibration.
- Prepare the experimental setup for the I_0- and quartz cell measurement.
- Record some I_0 spectra.
- Evaluate the photon noise.
- Compare the different noise sources quantitively.
- Think about the wavelength range of the spectrometer and compare it to cross sections of trace gases.
- Record $I(\lambda)$ with the quartz cell inside the light path and $I_0(\lambda)$ without it.
- Determine the NO_2 concentration inside the cell.

- Answer the questions in the text.

3.3 Helium-Calibration

- Optimize the light throughput of the cavity. Do this accurately.
- Make yourself familiar with the concept of the He calibration again, as this is a particularly critical part.
- Answer the questions in the manuscript.
- Purge the cavity with zero air.
- Prepare the measurement script.
- Record two sequences of zero air and He and once again zero air.
- Determine the path length for 5 discrete wavelengths manually.
- Perform a polynomial fit to get an impression of the mirror reflectivity.
- Perform the evaluation using the script.
- Compare these two methods and their accuracy.

3.4 Experiments

- Find NO_2 sources which could be interesting to explore.
- Conduct some measurements and think about problems and difficulties.
- Evaluate the data as well as possible, using some of the tools you got and the knowledge you've acquired so far.

3.5 Long-term measurement

- Prepare the scripts for the I_0 measurement and the long term measurement.
- Record new offset and DC spectra.
- Record I_0 spectra and start the long term measurement.
- Record new I_0 spectra after the first half and the end of the experiment.
- Evaluate the dataset with 3 different fit scenario files.
- Investigate the influence of the iterative fit procedure.
- Try to explain the diurnal cycle of the NO_2.

4 Theoretical background

4.1 The Earth's atmosphere

The atmosphere of the earth surrounds us and protects life from extraterrestrial, high energy radiation. Without the atmosphere, life wouldn't be possible on our blue planet. There are other planets with atmospheres, but currently it is not known if life ever developed on any of them.

Since the atmosphere is bound by gravitation, there is a radial distribution and layers with characteristic parameters. The most important differentiating factor is temperature. Variations of temperature are a good indicator to distinguish between the different layers. In figure 4.1, the different parts of the atmosphere and their vertical extent are shown. The lowermost layer, the troposphere, is characterized by a decrease of the mean temperature with increasing altitude. It extends from the surface to an altitude of about 15km and contains about 90 % of the atmospheric mass. The main components of the atmosphere are nitrogen (78.08 %), oxygen (20.95 %), noble gases (0.93 %) and carbon dioxide (0.04 %). Besides these main constituents there are many so called trace gases with mixing ratios in the order of 10^{-6} down to 10^{-12}. Despite their low abundance these trace gases like ozone, nitrogen oxides and halogens drive the most important chemical processes in the atmosphere, which change its composition and thereby affect the conditions of life.

4.2 Units

This section provides an overview of some of the units used in atmospheric physics. The *concentration* of a trace gas is the number of particles per volume. The dimensionless *mixing ratio* is defined as the abundance of one component of a mixture relative to all components. The term can refer either to mole ratio or mass ratio. Commonly used are units of [ppm] (parts-per-million, 10^{-6}), [ppb] (parts-per-billion, 10^{-9}) or [ppt] (parts-per-trillion, 10^{-12}). If refering to mass an 'm' is attached, e.g. [ppmm], if refering to volume, a 'v' is attached.

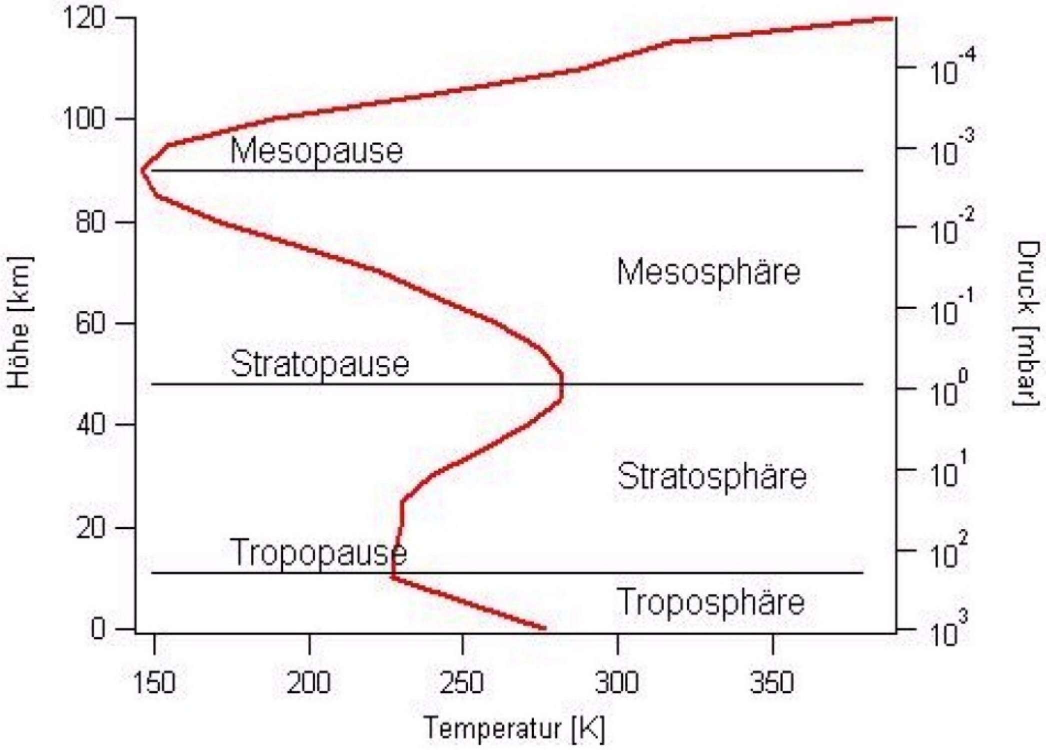


Figure 4.1: *Temperature profile of the atmosphere [Fleming et al., 1990].*

Table 4.1: *Overview of important units in atmospheric physics*

Name	Unit
Concentration	[molecules/cm^3], [µg/m^3]
Mixing ratio	[ppm], [ppb], [ppt]
Column density	[molecules/cm^2]
Dobson Unit	$1\,\mathrm{DU} = 2,6 \cdot 10^{16}\, molec/\mathrm{cm}^2$

The *column density* S is an important unit for remote sensing of trace gases. It is the concentration of a gas integrated along a path. This quantity is particularly useful for DOAS as you measure the integrated concentration along a light path.

$$S = \int c(s)\ ds \tag{4.1}$$

For ozone, a special unit exists. The *Dobson Unit.* 1 DU is equal to 2.6×10^{16} O_3 molecules/cm^2. This corresponds to a vertical ozone column of 1×10^{-5} m at a temperature of 0 °C and a pressure of 1013.25 hPa. In our atmosphere, normal ozone column densities are between 300 DU to 400 DU. Thus, the whole ozone in the atmosphere is equivalent to a thin layer of 3 mm to 4 mm thickness.

To get the average concentration from the column density, you have to divide the column density by the (optical) length of the measurement path. (In our case it will be the effective light path between the mirrors of the cavity, but more on that later (see sec. 4.6)). Then build the ratio with the calculated total number density of air particles.

$$\text{mixing ratio} = \frac{\text{the abundance of one component of a mixture}}{\text{amount of all components}} \tag{4.2}$$

To get the number density of air molecules we can use the ideal gas law:

$$N_A/V = P/(k_B \cdot T) \tag{4.3}$$

with $N_A = 6.022 \times 10^{23}$ particles, pressure P, temperature T, volume V and $k_B = 1.38 \times 10^{-23}$ J/K. In atmospheric chemistry the common unit for number densities is molecules/cm^3.

4.3 Nitrogen oxides

This lab course focuses on the nitrogen oxides NO (nitric oxide) and NO_2 (nitrogen dioxide), which are together refered to as NO_x. They are one of the most problematic pollutants in urban areas not only in developing, but also in industrialised countries. They are key species in the control of tropospheric ozone production and by this play an important role in the formation of the so called ”Los Angeles Smog”. Moreover, the concentration of NO_x has a strong influence on the atmospheric level of hydroxyl radicals (OH), which initiates the degradation of most oxidizable trace gases [Finlayson-Pitts and Pitts, 2000].

4.3.1 Sources and sinks of tropospheric NO_x

The global emissions of NO_x are caused by both human activities and natural processes. Table 4.2 shows the sources of NO_x and their contribution to the global emissions. New highly resolved satellite measurements allow to determine the

Table 4.2: *Summary of the main anthropogenic and natural sources for global tropospheric NO_x. Taken from e.g. [Lee et al., 1997].*

Source	Emission (10^{12} g/a)	Range of uncertainty (10^{12} g/a)
Fossil fuel combustion	22	13-31
Biomass burning	7.9	3-15
Soil microbial production	7.0	4-12
Lightning	5.0	2-20
Aircraft	0.8	0.59-0.95
Stratospheric	0.64	0.4-1
Total	44	23-81

global distribution of these NO_x sources. Figure 4.2 depicts the 18 month mean of a satellite measurement of NO_2, which was recorded by the SCIAMACHY instrument aboard the ESA satellite ENVISAT. Areas with high vertical column densities correlate with urban areas and therefore anthropogenic sources. In fact more than half of the global NO_x emissions are man made. The major source of anthropogenic NO_x is the combustion of fossil fuels in industrial processes, power plants and traffic. The most important mechanism for natural and anthropogenic production of NO_x is the Zel'dovic cycle [Zel'dovich, 1946] which describes the formation of *thermal* NO. The term *thermal* is chosen due to the high activation energy necessary for reaction 4.5 of 318 kJ/mol.

$$O_2 + M \longrightarrow O + O + M \tag{4.4}$$

$$O + N_2 \rightleftharpoons NO + N \tag{4.5}$$

$$N + O_2 \rightleftharpoons NO + O \tag{4.6}$$

$$N + OH \rightleftharpoons NO + H \tag{4.7}$$

NO_x is removed from the atmosphere mainly by further oxidation. During the day hydroxyl radicals oxidize NO_2 to nitric acid:

$$NO_2 + OH + M \longrightarrow HNO_3 + M \tag{4.8}$$

Another sink of NO_x is the reaction of NO_2 with ozone. Although the rate coefficient for this reaction is relatively small, it cannot be neglected in areas with high ozone concentrations in the absence of sunlight. During daytime this reaction plays no role because NO_3 is rapidly photolyzed. During the night, NO_3 reacts with NO_2 to form the anhydrite of nitric acid N_2O_5. The major sink of tropospheric N_2O_5 is the hydrolysis and subsequent wet or dry deposition [Mentel et al., 1996].

4.3.2 Photostationary state with ozone

Nitrogen dioxide is mainly a secondary pollutant. The oxidation to NO_2 is explained by Leighton [1961].

$$O(^3P) + O_2 + M \longrightarrow O_3 + M \tag{4.9}$$

$$O_3 + NO \rightleftharpoons NO_2 + O_2 \tag{4.10}$$

$$NO_2 + h\nu\ (\lambda_< 410\,\mathrm{nm}) \longrightarrow NO + O(^3P) \tag{4.11}$$

Photolysis in reaction 4.10 does only occour at wavelenghts below 410nm. The third reaction partner in 4.9 is required due to momentum conservation. The steady state concentrations of O_3, NO and NO_2 are linked by the Leighton ratio:

$$\frac{[NO]}{[NO_2]} = \frac{j_{NO_2}}{k_{O_3+NO} \cdot [O_3]} \tag{4.12}$$

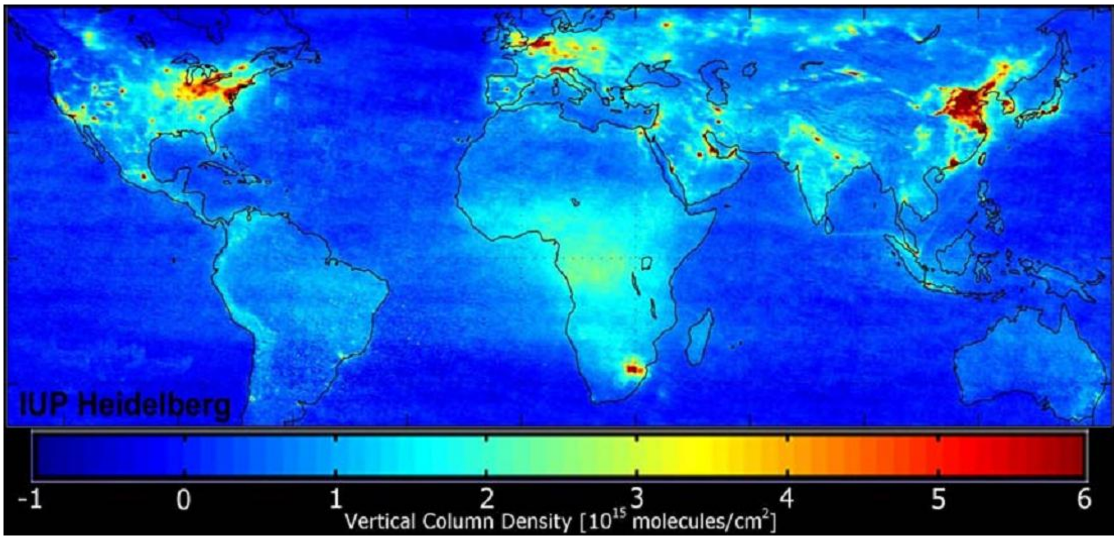


Figure 4.2: *Satellite measurement of the NO_2 vertical column densitiy averaged over the time period from January 2003 to June 2004. The measurements have been performed with the SCIAMACHY instrument aboard the ESA satellite ENVISAT. [Beirle et al., 2004].*

k_{O_3+NO} is the reaction constant for eqn. 4.10. Since the photolysis rate changes with solar zenith angle the Leighton ratio also changes during the course of the day. On a clear day, at noontime, when the photolysis rate has its maximum of about $j_{NO_2} \approx 8 \times 10^{-3}\,s^{-1}$ the Leighton ratio has its minimum and the lifetime of NO_2 is about 2 min. At typical O_3 mixing ratios of 30 ppb, $\frac{[NO]}{[NO_2]}$ is on the order of 1.

4.3.3 Photochemical smog

Since the first reports of photochemical smog in Los Angeles in the late 1940's, extremely high ozone levels have been measured in urban areas throughout the whole world. In Mexico City ozone levels over 400 ppb have been reported. Photochemical smog is worst when high levels of volatile organic compounds (VOCs) and NO_x are emitted into a thermal inversion layer, trapping them closely to the ground, and irradiated by sunlight during transport to downwind regions. The following section discusses the mechanisms responsible for the creation of photochemical smog.

Deviation from the photostationary state

The Leighton relation is only valid if reactions 4.9-4.11 describe the major sources and sinks of NO_2 and O_3. In the presence of VOCs, another reaction path for the conversion of NO to NO_2 exists, without the destruction of O_3. The OH radical which usually initiates the reaction chain is mainly formed by means of ozone

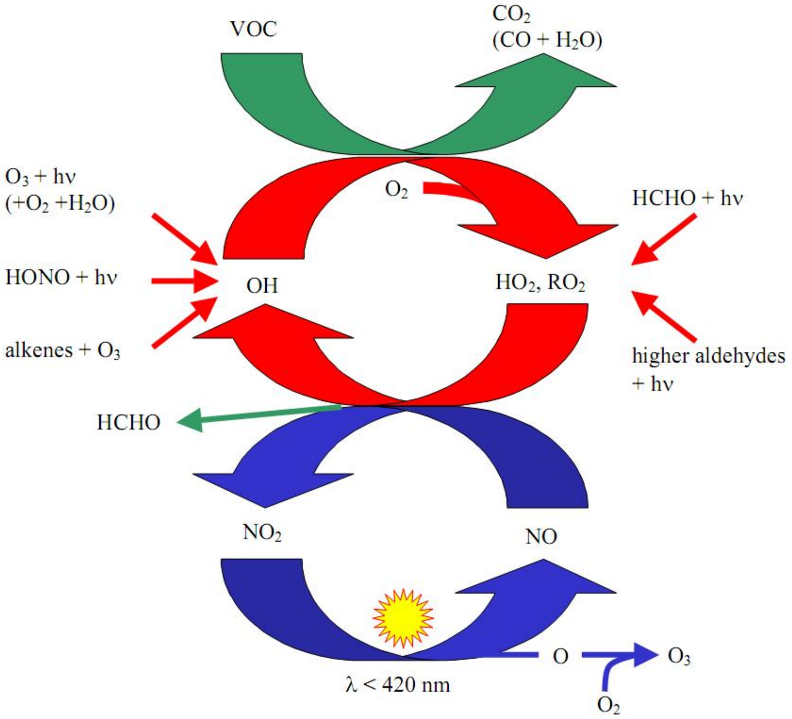


Figure 4.3: *Reaction cycles of tropospheric NO_x and ozone in a polluted atmosphere. The photostationary state of NO_x is illustrated by the blue cycle. It is disrupted by the presence of VOCs, which results in a net production of ozone. [Trick, 2004].*

photolysis:

$$O_3 + h\nu\ (\lambda_< 320\,\mathrm{nm}) \longrightarrow O(^1D) + O_2 \tag{4.13}$$

$$O(^1D) + H_2O \longrightarrow 2\,OH \tag{4.14}$$

The reaction chain is started by the oxidation of a hydrocarbon (RH) which may be described as

$$RH + OH \longrightarrow R + H_2O \tag{4.15}$$

$$R + O_2 \longrightarrow RO_2 \tag{4.16}$$

The peroxy radicals (RO_2) and (HO_2) react with NO and produce NO_2 without destroying ozone (e.g. see [Crutzen, 1970], [Parrish et al., 1986], [Carroll and Thompson, 1995])

$$RO_2 + NO \longrightarrow NO_2 + RO \tag{4.17}$$

$$RO + O_2 \longrightarrow R^{'}CHO + HO_2 \tag{4.18}$$

$$HO_2 + NO \longrightarrow NO_2 + OH \tag{4.19}$$

This scheme can be applied multiple times until the initial VOC is converted to CO_2 or CO and H_2O. Together with the reactions from 4.9-4.11 this can be written as an effective equation for the ozone production:

$$RH + 4\,O_2 + 2h\nu(\lambda_< 410\,\mathrm{nm}) \longrightarrow R^{'}CHO + H_2O + 2\,O_3 \tag{4.20}$$

The reaction system is illustrated in fig. 4.3 together with the most important sources of OH, hydroxyl and peroxy radicals.

Table 4.3: *Summary of health risks from NO_2, O_3 and particulate matter ($PM_{2.5}$).*

Pollutant	Effects related to short term exposure	Effects related to long term exposure
$PM_{2.5}$	Lung inflammatory reactions Respiratory symptoms Increase in hospital admissions Increase in mortality	Increase in lower respiratory symptoms Increase in chronic obfuscation pulmonary disease Reduction in lung functions in adults Reduction in life expectancy
O_3	Adverse effects on pulmonary function Lung inflammatory reactions Adverse effects on respiratory symptoms Increase in medication usage Increase in hospital admission Increase in mortality	Reduction in lung function development
NO_2	Effects on pulmonary function Increase in airway allergic inflammatory reactions Increase in hospital admissions Increase in mortality	Reduction in lung function Increased probability of respiratory symptoms

4.3.4 Health aspects of NO_2 air pollution

In addition to being a health hazard in itself, NO_2 is a precursor of a number of harmful secondary pollutants, including the formation of inorganic particulate matter via HNO_3, and photo oxidants (e.g. ozone and PANs[1]). These relationships are shown in figure 4.4.

In addition to being a health hazard in itself, NO_2 is a precursor of a number of harmful secondary pollutants, including the formation of inorganic particulate matter via HNO_3, and photo oxidants (e.g. ozone and PANs[2]). These relationships are shown in figure 4.4.

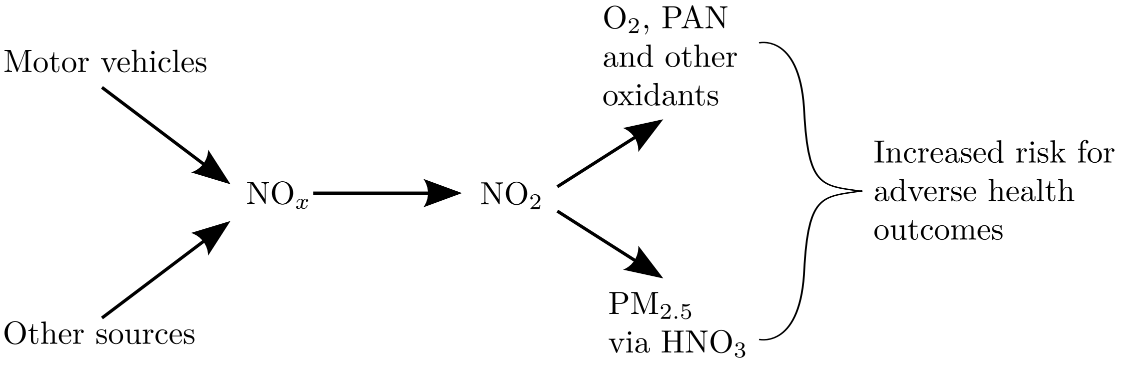


Figure 4.4: *Simplified relationship of NO_x emission with formation of NO_2 and other harmful reaction products including O_3 and particulate matter ($PM_{2.5}$) [WHO, 2003].*

A summary of health risks that may arise from NO_2 itself or its reaction products is given in table 4.3. The current WHO guideline values for NO_2 exposure are a 1-hour level of 200 µg/m^3 (106 ppb) and an annual average of 40 µg/m^3 (21 ppb).

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[1] peroxyacyl nitrates

[2] peroxyacyl nitrates

4.4 Differential Optical Absorption Spectroscopy

Quantitative statements about air chemistry require measurements of atmospheric trace gases. Differential Optical Absorption Spectroscopy (DOAS), developed by Platt et al. [1979], is a widely used method for quantitative measurements of atmospheric trace gases. It is a direct optical spectroscopy method, based on the Lambert-Beer law. In the following sections the theoretical foundations of DOAS are described.

4.4.1 Law of Lambert-Beer

The intensity of electromagnetic radiation decreases when it is transmitted through matter. This physical effect is described by the *Lambert-Beer* law.
If $I_0(\lambda)$ is the intensity of light before the transition through matter, then the intensity $I(\lambda, L)$ after the passage of a distance L is given by:

$$I(\lambda, L) = I_0(\lambda) \cdot exp(-\epsilon \cdot L) \tag{4.21}$$

where ϵ is the *absorption coefficient* which is proportional to the concentration c of the absorber with σ as absorption cross-section, also called *extinction*:

$$\epsilon = \sigma \cdot c \tag{4.22}$$

Generally, σ depends on pressure and temperature. Clearly, the concentration could also vary along the light path. The general form of Lambert-Beer's law with n absorbers is given by:

$$I(\lambda, L) = I_0(\lambda) \cdot \exp\left(-\int_0^L \sum_{j=1}^{n} \sigma_j(\lambda, p(s), T(s)) \cdot c_j(s)\, \mathrm{d}s\right) \tag{4.23}$$

For simplicity we will neglect pressure and temperature dependencies in the further discussion.

The logarithmic ratio of the intensities before and behind the transition through an absorber is called *optical density* D.

$$D(\lambda, L) := \ln\left(\frac{I_0(\lambda)}{I(\lambda, L)}\right) \tag{4.24}$$

If the concentration of the absorber is independent from the light path, the optical density can be simplified to:

$$D(\lambda) = L \cdot \sum_{j=1}^{n} \sigma_j(\lambda) \cdot \bar{c}_j \tag{4.25}$$

For a single absorber the average concentration $\bar{c}$ along a known path length L is then easily calculated:

$$\bar{c} = \frac{D(\lambda)}{\sigma(\lambda) \cdot L} \tag{4.26}$$

4.5 The DOAS method

Apart from the absorption by trace gases S, the light path through the atmosphere is also affected by scattering and absorption on aerosol particles and cloud droplets (Mie scattering) and by scattering on air molecules (Rayleigh scattering). The sum of both effects, scattering and absorption, are referred to as *extinction*. The extinction cross section can be separated into the components caused by molecular absorption as well as Rayleigh scattering (on air molecules) and Mie scattering (on aerosol particles):

$$\epsilon(\lambda) = \epsilon_S(\lambda) + \epsilon_{Mie}(\lambda) + \epsilon_{Ray}(\lambda) \tag{4.27}$$

This leads to the complete equation (with 4.22 and 4.23):

$$I(\lambda, L) = I_0(\lambda) \cdot exp\left(\sum_j L \cdot \sigma_j(\lambda) \cdot c_j + L[\epsilon_{Mie}(\lambda) + \epsilon_{Ray}(\lambda)]\right) \tag{4.28}$$

The essential principle of DOAS is to separate the measured spectra, as well as the laboratory absorption cross-sections into a narrowband (σ') and a broadband (σ^b) component (see fig. 4.5). The narrow part changes rapidly with wavelength, the broadband part doesn't.

$$\sigma(\lambda) = \sigma^b(\lambda) + \sigma'(\lambda) \tag{4.29}$$

This allows to rewrite equation 4.28 as:

$$I(\lambda, L) = I_0(\lambda) \cdot exp\left(\sum_j L \cdot (\sigma_j^b(\lambda) + \sigma'_j(\lambda)) \cdot c_j + L[\epsilon_{Mie}(\lambda) + \epsilon_{Ray}(\lambda)]\right) \tag{4.30}$$

$$\Rightarrow I(\lambda, L) = I'_0(\lambda) \cdot exp\left(\sum_j L \cdot \sigma'_j(\lambda) \cdot c_j\right) \tag{4.31}$$

where I'_0 is the product of the intensity of the light source and the broadband absorption.

Scattering processes have broadband cross-sections only, whereas looking at the narrowband structures, the effects of scattering are negligible. The narrowband structures are called *differential*, which is represented by the „D“ in the DOAS acronym. As the data evaluation only uses the narrowband structures, it is not necessary to know the absolute intensity I_0. Instead, an arbitrary reference spectrum can be used to cope with instrument characteristics.

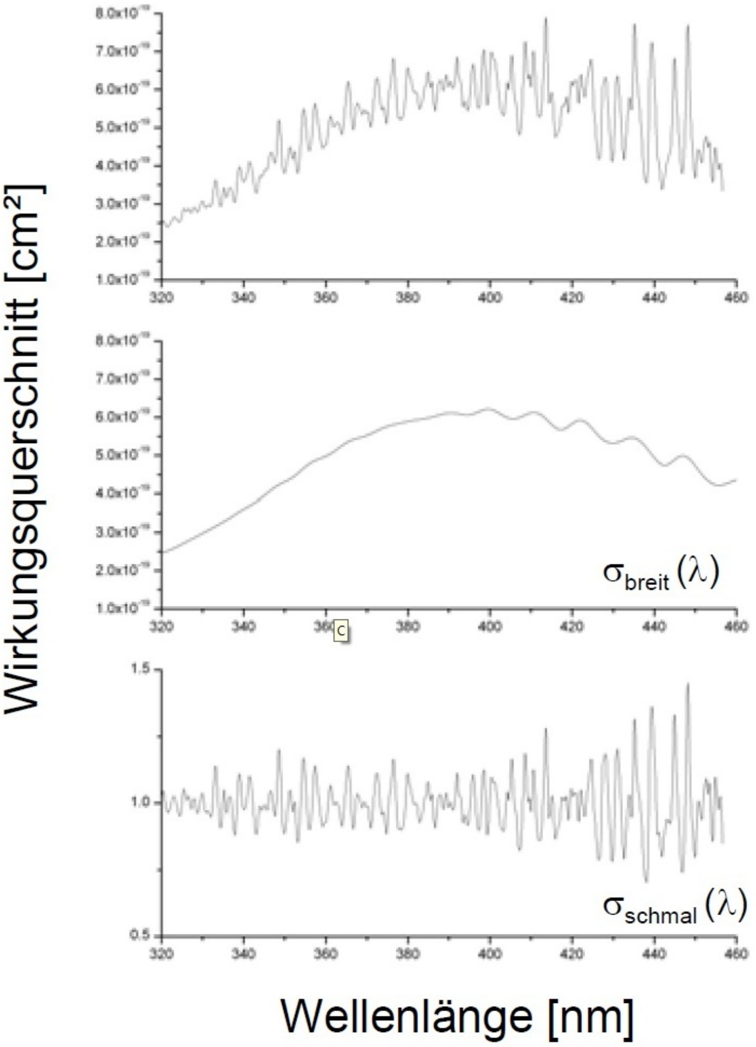


Figure 4.5: *The division of the absorption cross-section from NO_2 in broad- and narrowband parts: on top, the total cross section, below the broadband part, and on the bottom, the narrowband differential part [IUP, 2011].*

Analogous to eqn. 4.24, one defines the differential optical density D' as :

$$D'(\lambda, L) = ln\left(\frac{I'_0(\lambda)}{I(\lambda, L)}\right) = \sum_j L \cdot \sigma'_j(\lambda) \cdot c_j \tag{4.32}$$

All trace gases with distinct differential structures can be measured with the DOAS method, e.g. ozone, BrO, SO_2 or HCHO and many more. It is also possible to simultaneously measure several trace gases, as their differential absorption structures are unique fingerprints.

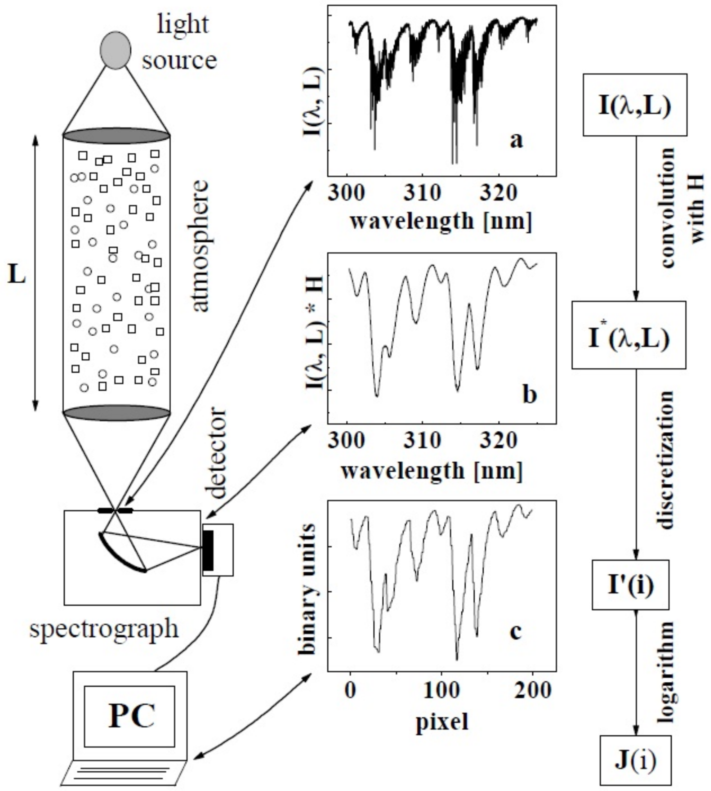


Figure 4.6: *Schematic view of a DOAS instrument used to measure trace gas concentrations. Collimated light undergoes absorption processes on its way through the atmosphere. In (a), an example of this light entering the spectrograph is given, where HCHO is assumed to be the only absorber and the light source has smooth spectral characteristics. This absorption spectrum shows the vibrational-rotational structure of the absorption bands. (b) The same spectrum convoluted by the spectrograph instrumental function reaches the detector. In the detector, the wavelength is mapped to discrete pixels. This spectrum (c) is then stored in the computer and can be analysed numerically.*

4.5.1 Convolution

The literature absorption cross sections that we use for the DOAS evaluation are usually recorded with high resolution spectrometers. However, typical spectrometers used for DOAS measurements have a much lower spectral resolution.

This means that a narrow emission line (FWHM much smaller than the spectral resolution) is smeared out to a peak whose width and shape are determined by the spectrometers imaging properties and CCD detector. This is called the instrument function H of the spectrometer.

Before performing a DOAS evaluation the high resolution reference spectra need to be adapted to this lower resolution. This is done by means of a convolution with the instrument function.

$$\sigma^*(\lambda) = \sigma(\lambda) \otimes H_{sp} = \int \sigma(\lambda - \lambda') \cdot H_{sp}(\lambda')\, \mathrm{d}\lambda' \tag{4.33}$$

For most low-resolution DOAS applications, atomic emission lines from low-pressure lamps provide an effective means to determine the combined instrument function, H. The natural line width of the emission lines is much smaller ($\sim$ 100 pm) than the typical resolution of DOAS spectrometers ($\sim$ 0.1 nm to 1 nm). The recorded emission line with the respective spectrometer detector system is therefore a very good approximation of H (see Fig. 4.7) [Platt and Stutz, 2008].

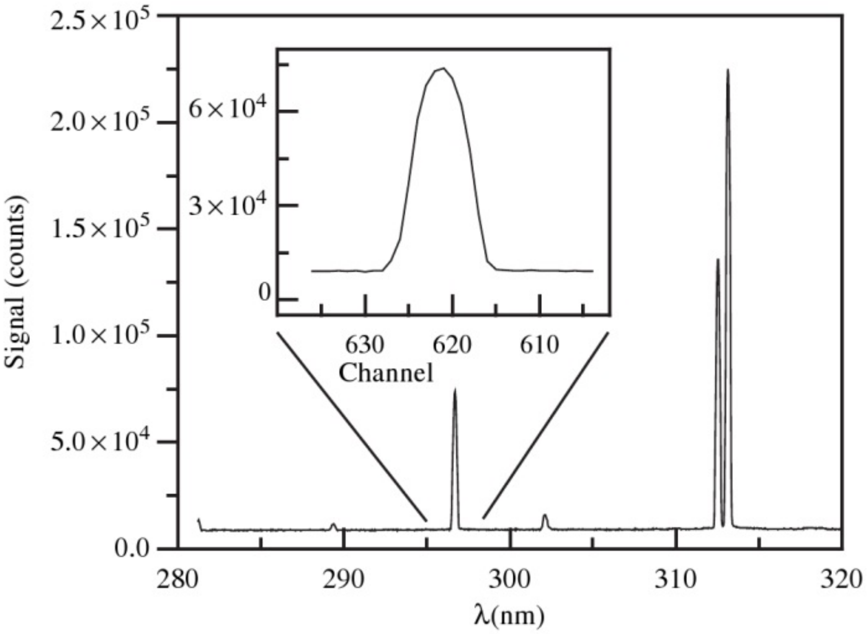


Figure 4.7: *Example of a mercury spectrum measured with a typical spectrometer-detector combination used for DOAS. The insert shows the shape of the mercury atomic emission line that is used for a convolution [Platt and Stutz, 2008].*

4.5.2 DOAS fit

The idea of the DOAS fit is fairly simple. A model is used to construct an optical density spectrum by taking into account all the physical effects the light entering the instrument undergoes. This modeled spectrum is then compared to the measured optical density. By varying the physical parameters of the modeled optical density spectrum, the difference between modeled and measured optical density is now minimized. When the minimum is reached, the physical parameters of the model are assumed to be retrieved. These parameters include the trace gas column densities. A DOAS measurement generally consists of a measurement spectrum $I(\lambda)$ with trace gas absorption and a reference measurement I_0 without absorbing trace gases.

The optical density is now modeled using the model parameters a$_i$ and a polynomial to account for broadband absorption:

$$\ln\left(\frac{I(\lambda)}{I_0(\lambda)}\right) = -\sum_i \sigma_i(\lambda)\cdot a_i + \sum_k b_k\lambda^k \tag{4.34}$$

Due to noise in the measurement, the modeled optical density can never perfectly match the measured optical density. Therefore, the DOAS fit searches for the minimum quadratic deviation:

$$min\left[\sum_i \sigma_i(\lambda)\cdot a_i + \sum_k b_k\lambda^k + R(\lambda) - \ln\left(\frac{I(\lambda)}{I_0(\lambda)}\right)\right]^2 \tag{4.35}$$

The minimum value achieved by varying the parameters a$_i$ and b$_k$ is called the fit residual. The smaller the residual, the better the fit has succeeded in modeling the trace gas absorption. Ideally, the residual is only composed of noise. In order to detect a trace gas, its optical density needs to be larger than the residual. This criteria can be used to estimate the detection limit for a particular species.

Once the minimum was found, the fit parameters a$_i$ represent the column densities of the individual trace gases which can be converted into concentrations by dividing through the light path length.

$$c_i = \frac{a_i}{L} \tag{4.36}$$

4.6 Cavity Enhanced-DOAS

As we could see in the section before, when radiation is transmitted through an absorber this leads to a characteristic absorption pattern. To use this for measurements of trace gases with very low concentrations, one needs a long optical path length. In open experimental configurations one can reach this simply by a long geometrical light path of several km. In Cavity Enhanced-DOAS (CE-DOAS), it is realized using two highly reflective mirrors to turn a short geometrical light path into a long effective light path. The setup is closed to isolate the measurement cell from the environment, which is a great advantage for in-situ measurements. This allows to sample the air over a long inlet tube from a well defined location. Furthermore it protects the sensitive optical setup and prevents contamination. A closed setup with a length of 50 cm and mirrors with a reflectivity R$=$ 0,9995 is used for the cavity in this practical. The reflectivity is wavelength dependent, the maximum is at $\lambda = 445\,$nm. (Section 4.6 is partly extracted from Horbanski [2010].)

4.6.1 Cavity Enhanced-DOAS Theory

The CE-DOAS approximation

After each round trip the primary beam is attenuated through the extinction in the gaseous medium and due to losses at the cavity mirrors. For a medium with a single pass optical density $D = \epsilon\, d$ (where ϵ is the extinction coefficient and d the length of the cavity), the fraction of the intensity transmitted in a single pass is calculated with Lambert-Beer as

$$T_{\text{gas}} = \exp\left(-\epsilon\, d\right) = \exp\left(-D\right) \tag{4.37}$$

Each time the light hits a cavity mirror, a fraction R_i of the light is reflected back into the cavity and a fraction $T_{\text{m},i}$ is transmitted through the mirror. The transmission through one cavity mirror can be written as

$$T_{\text{m},i} = 1 - R_i - A_i \quad i \in \{1, 2\} \tag{4.38}$$

where R_i is the mirror reflectivity, A_i the absorption loss in the mirror and i the index that identifies the mirror. As the light is coupled out on the side opposite to the light source, the total intensity I at the detector is calculated as the sum over the beams that exit after an even number of reflections [Fiedler, 2005].

$$\begin{aligned}
I =& I_{\text{in}} \cdot T_{\text{m},1} \cdot T_{\text{gas}} \cdot T_{\text{m},2} && \text{(zero reflections)}\\
&+ I_{\text{in}} \cdot T_{\text{m},1} \cdot T_{\text{gas}} \cdot R_2 \cdot T_{\text{gas}} \cdot R_1 \cdot T_{\text{gas}} \cdot T_{\text{m},2} && \text{(two reflections)}\\
&+ \ldots\\
&+ I_{\text{in}} \cdot T_{\text{m},1} \cdot T_{\text{m},2} \cdot T_{\text{gas}} \cdot R_1^n \cdot R_2^n \cdot T_{\text{gas}}^{2n} && (2n \text{ reflections})\\
&+ \ldots\\
&= I_{\text{in}} T_{\text{m},1} T_{\text{m},2} T_{\text{gas}} \sum_{n=0}^{\infty} R_1^n R_2^n T_{\text{gas}}^{2n} && (4.39)
\end{aligned}$$

To eliminate the unknown Intensity of the light source I_{in} an the mirror transmissions $T_{\text{m},i}$ we compute the cavity enhanced optical density:

$$D_{\text{CE}}(\lambda) = \left(\frac{I_0(\lambda)}{I(\lambda)}\right) \tag{4.40}$$

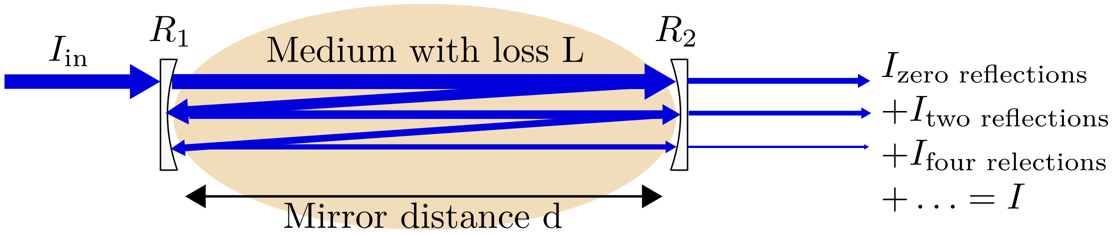


Figure 4.8: *Sketch of the light propagation through a CE-DOAS instrument [Horbanski, 2010].*

This compares the light intensity $I_0(\lambda)$ transmitted when the cavity is filled with zero air to the intensity $I(\lambda)$ transmitted when filled with an air sample containing additional absorbers. The respective extinction coefficients are $\epsilon_0(\lambda)$ for zero air and $\epsilon(\lambda)$ for the air sample.

At typical atmospheric concentrations, the trace gas absoption per roundtrip is very small ($\epsilon \to 0$). This allows us to convert the sum into an integral [Platt et al., 2009]. Furthermore the reflectivity is close to unity ($R \to 1$) which allows further simplification :
As $R \to 1$, it is possible to approximate it as $R = R - 1 + 1 \approx \exp(R-1)$.

These approximations allow to set up an equation for the *Cavity Enhanced optical density* D_{CE}.

$$\begin{aligned}
D_{\mathrm{CE}}(\lambda) &= \ln\left(\frac{I_0(\lambda)}{I(\lambda)}\right) \\
&= \ln\left(\frac{I_{\mathrm{in}} T_{\mathrm{m},1} T_{\mathrm{m},2} \displaystyle\int_0^{\infty} R^n \cdot \exp\left(-nd\,\epsilon_0\right)\,\mathrm{dn}}{I_{\mathrm{in}} T_{\mathrm{m},1} T_{\mathrm{m},2} \displaystyle\int_0^{\infty} R^n \cdot \exp\left(-nd\,\epsilon\right)\,\mathrm{dn}}\right) \\
&= \ln\left(\frac{\displaystyle\int_0^{\infty} \exp\left(-n(1-R+d\,\epsilon_0)\right)\,\mathrm{dn}}{\displaystyle\int_0^{\infty} \exp\left(-n(1-R+d\,\epsilon)\right)\,\mathrm{dn}}\right) \\
&= \ln\left(\frac{1-R+d\,\epsilon}{1-R+d\,\epsilon_0}\right) \\
&\underset{\epsilon_\Delta := \epsilon - \epsilon_0}{=} \ln\left(\frac{1-R+d\,\epsilon_0+d\,\epsilon\Delta}{1-R+d\,\epsilon_0}\right) && (4.41) \\
D_{\mathrm{CE}}(\lambda) &= \ln\left(1+\frac{d\,\epsilon\Delta(\lambda)}{1-R(\lambda)+d\,\epsilon_0(\lambda)}\right) && (4.42) \\
\Leftrightarrow \frac{I_0(\lambda)}{I(\lambda)} - 1 &= \frac{d}{1-R(\lambda)+d\,\epsilon_0(\lambda)} \cdot \epsilon\Delta(\lambda) && (4.43)
\end{aligned}$$

with

$I(\lambda)$	Measured intensity for an air sample that contains absorbing species.
$I_0(\lambda)$	Measured intensity for a reference gas without absorbing species, usually zero air.
$I_{\mathrm{in}}(\lambda)$	Intensity of the light source.
$T_{\mathrm{m},i}(\lambda)$	Transmissivity of cavity mirror i.
d	Displacement of the cavity mirrors.
$\epsilon(\lambda)$	Extinction coefficient for the air sample that contains absorbing species.
$\epsilon_0(\lambda)$	Extinction coefficient of the reference gas (zero air).
$\epsilon_\Delta(\lambda) = \epsilon(\lambda) - \epsilon_0(\lambda)$	Extinction of the air with absorber relative to the reference gas.

The Cavity-Enhanced optical density $D_{\mathrm{CE}}(\lambda)$ is given relative to the reference gas

$I_0(\lambda)$. It is important to remember that this approach also assumes a constant intensity of the light source. Since the trace gas measurements are usually carried out in air samples the interpretation of the results becomes a bit simpler if the $I_0(\lambda)$ measurement is assumed to be carried out in zero air. Then the extinction $\epsilon_\Delta(\lambda)$ only contains contributions from trace gas absorption as all other contributions cancel out. For an air sample that contains only one absorbing species it can be written as $\epsilon_\Delta(\lambda) = \sigma(\lambda) \cdot \bar{c}$ where $\sigma(\lambda)$ and $\bar{c}$ are the absorption cross section and the absorber concentration respectively.

The consequences of the nonlinear dependency of D_{CE} on the trace gas concentration in the cavity become clear when it is examined for two extreme (but realistic) cases.

1. For very good mirrors or very high trace gas aborption, i.e. $1 - R + d\epsilon_0 \ll d \cdot \epsilon_\Delta$

$$\begin{aligned} D_{\mathrm{CE}} &= \ln\left(\frac{1 - R + d\,\epsilon_0 + d\,\epsilon\Delta}{1 - R + d\,\epsilon_0}\right) \\ &\approx \ln\left(\frac{d\,\epsilon\Delta}{1 - R + d\,\epsilon_0}\right) \\ &\approx \ln(d\,\epsilon\Delta) - \ln(1 - R + d\,\epsilon_0) \\ &\approx \ln(d \cdot \sigma \cdot \bar{c}) + const \end{aligned} \tag{4.44}$$

   In these cases D_{CE} just depends weakly on the trace gas concentration $\bar{c}$. Therefore too high mirror reflectivities decrease the sensitivity of CE-DOAS.

2. For small trace gas absorption or relatively low mirror reflectivities, i.e. $1 - R + d\epsilon_0 \gg d \cdot \epsilon_\Delta$

$$\begin{aligned} D_{\mathrm{CE}} &= \ln\left(1 + \frac{d\,\epsilon\Delta}{1 - R + d\,\epsilon_0}\right) \\ &\approx \frac{d\,\epsilon\Delta}{1 - R + d\,\epsilon_0} \propto \bar{c} \end{aligned} \tag{4.45}$$

   In this regime the CE-DOAS signal is linear to the trace gas concentration. However, this linear behaviour is usually only obtained close to the detection limit of the instrument.

As we saw in chapter 4.4, the exact length of the light path has to be known (see eqn. 4.26). To get the equation for the path length in a more comprehensive form we define the effective path length $\bar{L}_{\mathrm{eff}}(\lambda)$.

$$\bar{L}_{\mathrm{eff}}(\lambda) = \frac{D_{\mathrm{CE}}(\lambda)}{\epsilon_\Delta(\lambda)} \Leftrightarrow D_{\mathrm{CE}}(\lambda) = \bar{L}_{\mathrm{eff}}(\lambda) \cdot \epsilon_\Delta(\lambda) \tag{4.46}$$

$\bar{L}_{\mathrm{eff}}(\lambda)$ corresponds to an absorption light path of a Lambert Beer absorption (e.g. LP-DOAS) with the optical density $D_{\mathrm{CE}}(\lambda)$. It is connected to the effective number of reflections via:

$$n_{\mathrm{eff}}(\lambda) = \frac{\bar{L}_{\mathrm{eff}}(\lambda)}{d} \tag{4.47}$$

Combining this with (4.43) gives

$$\bar{L}_{\text{eff}}(\lambda) = \frac{D_{CE}(\lambda)}{\exp(D_{\text{CE}}(\lambda)) - 1} \cdot \frac{d}{1 - R(\lambda)} \tag{4.48}$$

Futhermore we define

$$\bar{L}_0(\lambda) = \frac{d}{1 - R(\lambda) + d\,\epsilon_0(\lambda)} \tag{4.49}$$

finally yields

$$\boxed{\bar{L}_{\text{eff}}(\lambda) = \frac{D_{\text{CE}}(\lambda)}{\exp(D_{\text{CE}}(\lambda)) - 1}\,\bar{L}_0(\lambda)} \tag{4.50}$$

It is important to note that the effective path length is wavelength depended. This is mainly caused by the fact that we use high reflective dielectric mirrors whose reflectivity has a strong wavelength dependence. Furthermore, we have a wavelength depended path length reduction in the presence of absorbers which is described by

$$K(\lambda) = \frac{D_{\text{CE}}(\lambda)}{\exp(D_{\text{CE}}\,(\lambda)) - 1} \tag{4.51}$$

To visualize this dependency, it is plotted in figure 4.9. A medium with a higher optical density will reduce the effective path length because it increases the probability that a photon is scattered or absorbed in the cavity. Therefore especially those photons with a high number of reflections are removed from the transmitted light. To verify the effective pathlength for $D_{\text{CE}} \to 0$, i.e. for an absorber free cavity, the limit can be computed using L'Hospital's rule as

$$\lim_{D_{\text{CE}}\to 0}\left(\bar{L}_{\text{eff}}\right) = \lim_{D_{\text{CE}}\to 0}\left(\frac{D_{\text{CE}}}{e^{D_{\text{CE}}} - 1}\bar{L}_0\right) \underset{\text{L'Hospital}}{=} \lim_{D_{\text{CE}}\to 0}\left(\frac{1}{e^{D_{\text{CE}}}}\bar{L}_0\right) = \bar{L}_0 \tag{4.52}$$

The trace gas concentration can now be retrieved by combining eqn. (4.46) and eqn. (4.50)

$$\boxed{D_{\text{CE}}(\lambda) = \frac{D_{\text{CE}}(\lambda)}{\exp(D_{\text{CE}}(\lambda)) - 1}\,\bar{L}_0(\lambda)\,\epsilon_\Delta(\lambda)} \tag{4.53}$$

This equation can also be rearranged as

$$\boxed{D_{\text{eff}}(\lambda) = \frac{I_0(\lambda)}{I(\lambda)} - 1 = \bar{L}_0(\lambda)\,\epsilon_\Delta(\lambda)} \tag{4.54}$$

where D_{eff} defines the effective optical density.

4.6.2 Practical application with a DOAS evaluation

In a typical CE-DOAS application $I(\lambda)$ and $I_0(\lambda)$ are recorded over a wavelength range of several tens of nanometers. As described earlier, I_0 is acquired while the

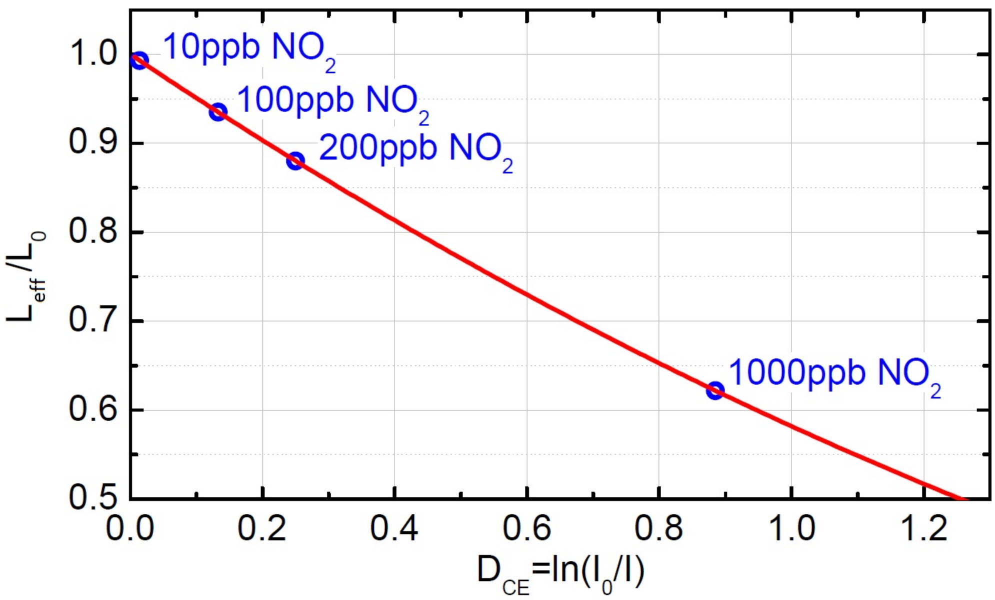


Figure 4.9: *Reduction of the effective path length as a function of the "Cavity Enhanced Optical Density" D_{CE}. In order to illustrate the magnitude of this effect the effective light path at $463\,\mathrm{nm}$ is shown for four realistic mixing ratios of NO$_2$ for a cavity with $d = 50\,\mathrm{cm}$ and $R = 0.9995$ [Horbanski, 2010].*

cavity volume is purged with zero air. From this, the Cavity-Enhanced optical density can be written as

$$D_{\mathrm{CE}} = \frac{D_{\mathrm{CE}}(\lambda)}{\exp(D_{\mathrm{CE}}\,(\lambda)) - 1}\,\bar{L}_0(\lambda)\left(\sum_{j\in J}\sigma_j i(\lambda)\,\bar{c}_j + \epsilon_{\mathrm{R}} + \epsilon_{\mathrm{M}}\right) \tag{4.55}$$

where J denotes the set of atmospheric trace gases that are found in the investigated air sample. Again σ_j and $\bar{c}_j$ refer to the absorption cross section and concentration respectively. The extinction coefficients ϵ_R and ϵ_M describe the contribution of Rayleigh and Mie scattering.

It is now also important to remember that $L_0(\lambda)$ varies with the wavelength due to the wavelength dependency of the mirror reflectivities. In a normal DOAS evaluation the absorption cross sections of trace gases are fitted to the measured optical densities in order to retrieve their column densities. The DOAS fit parameters are wavelength independent scalars. This requires all wavelength dependent quantities to be moved either into the fit references or into the measured optical density. There are now two different possibilities how eqn. (4.55) can be prepared for a DOAS evaluation:

1. The correction can be applied to the product of the average path length $\bar{L}_0(\lambda)$ of an empty cavity and the trace gas absorption cross section. This gives an effective reference which can be used in a DOAS evaluation.

$$r_j(\lambda) = \frac{D_{\mathrm{CE}}(\lambda)}{\exp(D_{\mathrm{CE}}\,(\lambda)) - 1}\,\bar{L}_0(\lambda)\,\sigma_j(\lambda) \tag{4.56}$$

The modeled spectrum for the DOAS fit then becomes:

$$D_{\text{Fit}}(\lambda) = \sum_j r_j(\lambda) \cdot \bar{c}_j + \mathcal{P}_r(\lambda) \tag{4.57}$$

where $\mathcal{P}_r(\lambda)$ is the DOAS polynomial. The fit parameters $\bar{c}_j$ are the actual trace gas concentrations.

2. It is also possible to correct the optical density D_{CE} by moving the cavity correction factor $D_{\text{CE}}/(\exp(D_{CE}) - 1)$ to the right hand side of eqn. (4.55). This transformation yields the approximation by [Fiedler, 2005] which uses the effective optical density D_{eff}:

$$D_{\text{eff}} = \exp(D_{\text{CE}}) - 1 \tag{4.58}$$

$$D_{\text{eff}} = \frac{I_0}{I} - 1 = \sum_j \underbrace{\bar{L}_0(\lambda)\sigma_j(\lambda)}_{\tilde{r}_j(\lambda)} \cdot \bar{c}_j \tag{4.59}$$

The equations above all compute the path length correction directly from the measured intensities I and I_0. However, this is only correct if all intensity changes can be attributed to extinction processes in the cavity. In real practice the measured Intensities can also change due to fluctuation of the light source (cause by changes in the ambient Temperature or the current supply), or by instabilities in the optomechanic setup. Using the measured intensities for the path length correction can therefore introduces an error which can be on the order of several 10 percent.

4.6.3 Practical determination of the cavity path length and mirror reflectivity

In the previous sections it is shown that the effective light path in a cavity depends on the absorber concentration in the cavity. It is also shown that it is sufficient to know the path length L_0 of a zero air cavity as it can be corrected for trace gas extinction. The calibration of L_0 also determines the mirror reflectivity R as both are linked by (4.49). In this section the method for the calibration of L_0, which is used during the practical is described.

From equation (4.54) it can be seen that the effective path length L_0 can be inferred by subsequently measuring the light transmitted by a cavity filled with zero air (I_0) and another gas sample (I) with different extinction. To get continuous information on the wavelength dependency of $L_0(\lambda)$ the extinction needs to be broadband. We will use Helium which is a very weak Rayleigh scatterer (about two orders of magnitude weaker than air) and therefore makes a relatively strong change in the Intensity signal when compared to zero air. This method, introduced by [Washenfelder et al., 2008], has several advantages over commonly used calibration gas mixtures with molecular absorbers:

1. Helium is easy to handle and as a pure inert gas it does not change its composition over time.

2. Literature Rayleigh scattering cross sections are generally more precise than molecular absorption cross sections.
3. Rayleigh scattering varies relatively slowly with the wavelength ($\sigma(\lambda) \propto \lambda^{-4}$). Therefore the wavelength dependency of the optical density $D_{\text{eff}}(\lambda)$ mainly comes from the variation of $L_0(\lambda)$.

Using (4.54) L_0 is then given by:

$$\boxed{\bar{L}_0(\lambda, T_{\text{air}}, p_{\text{air}}) = \frac{\frac{I_0(\lambda)}{I_{\text{He}}(\lambda)} - 1}{\epsilon_{\text{He}}(\lambda, T_{\text{He}}, p_{\text{He}}) - \epsilon_{\text{Air}}(\lambda, T_{\text{air}}, p_{\text{air}})}} \tag{4.60}$$

The extinction coefficient of helium only contains rayleigh scattering

$$\epsilon_{\text{He}}(\lambda, T, p) = \sigma_{\text{ray,He}}(\lambda) \cdot n_{\text{He}}(T, p) \tag{4.61}$$

$\epsilon_{\text{ray,He}}$ and $\epsilon_{\text{ray,Air}}$ are the product from the absorption coefficient σ_j and the number density $\bar{c}_j$. In the wavelength interval of interest (400 nm to 500 nm) the extinction coefficient of air also contains a contribution from the O_2 dimer O_4 which has absorption bands at 446 nm and 477 nm. The total extinction coefficient of air is then

$$\begin{aligned} \epsilon_{\text{air}}(\lambda, T, p) &= \sigma_{\text{ray,air}}(\lambda) \cdot n_{\text{air}}(T, p) + \sigma_{O_4} \cdot n^2_{O_2}(T, p) \\ &= \sigma_{\text{ray,air}}(\lambda) \cdot n_{\text{air}}(T, p) + \sigma_{O_4} \cdot (0.20946 \cdot n_{\text{air}}(T, p))^2 \end{aligned} \tag{4.62}$$

where σ_{O_4} is the O_4 absorption coefficient, taken from [Hermans et al., 1999]. The number density $n_j(T, p)$ of helium and air is calculated using the ideal gas law.

$$n_j(T, p) = \frac{p}{k_B \cdot T} \tag{4.63}$$

It should be noted that $\bar{L}_0(\lambda, T_{\text{air}}, p_{\text{air}})$ refers to the path length in a zero air cavity at a specific temperature and pressure. If temperature and pressure are different during the measurement then (4.49) can be used to adapt $\bar{L}_0(\lambda, T_{\text{air}}, p_{\text{air}})$. This equation can also be used to calculate the mirror reflectivity:

$$R = 1 - \frac{d}{\bar{L}_0(\lambda, T_{\text{air}}, p_{\text{air}})} + d \cdot \epsilon_{\text{air}}(\lambda, T_{\text{air}}, p_{\text{air}}) \tag{4.64}$$

5 Experimental setup

The experimental setup is shown in figure 5.1. The main component is the optical resonator, formed by the two highly reflective mirrors (see 5.3) which are mounted inside adjustable mounts. Together with the 50 cm teflon tube it forms the measuring cell. Other optical components are the LED light source, lenses and a fibre optic cable guiding the light into a temperature stabilized spectrograph for analysis. **Be careful when handling the fibre optic cable, it is very sensitive. It breaks easily if it is bent or twisted too much**.

The commercial miniature spectrograph-detector unit Ocean Optics USB2000 is used to analyse the incoming light. It is built in the *Czerny-Turner* design (see figure 5.4). The light entering the spectrometer through a slit is collimated by a spherical mirror and projected onto a grating as a parallel light beam. The grating disperses the light into its spectral components. A second spherical mirror focuses the light onto a detector, which consists of a one-dimensional CCD array with 2048 pixels.

The most important features of the detector are:

Number of pixels:	2048
Pixel size:	$14\mu m \times 200\mu m$
Full Well Capacity per pixel:	100 000 electrons
A/D - Converter:	12 bit (i.e., 4096 counts/pixel)
Integration time:	3 ms - 65 s

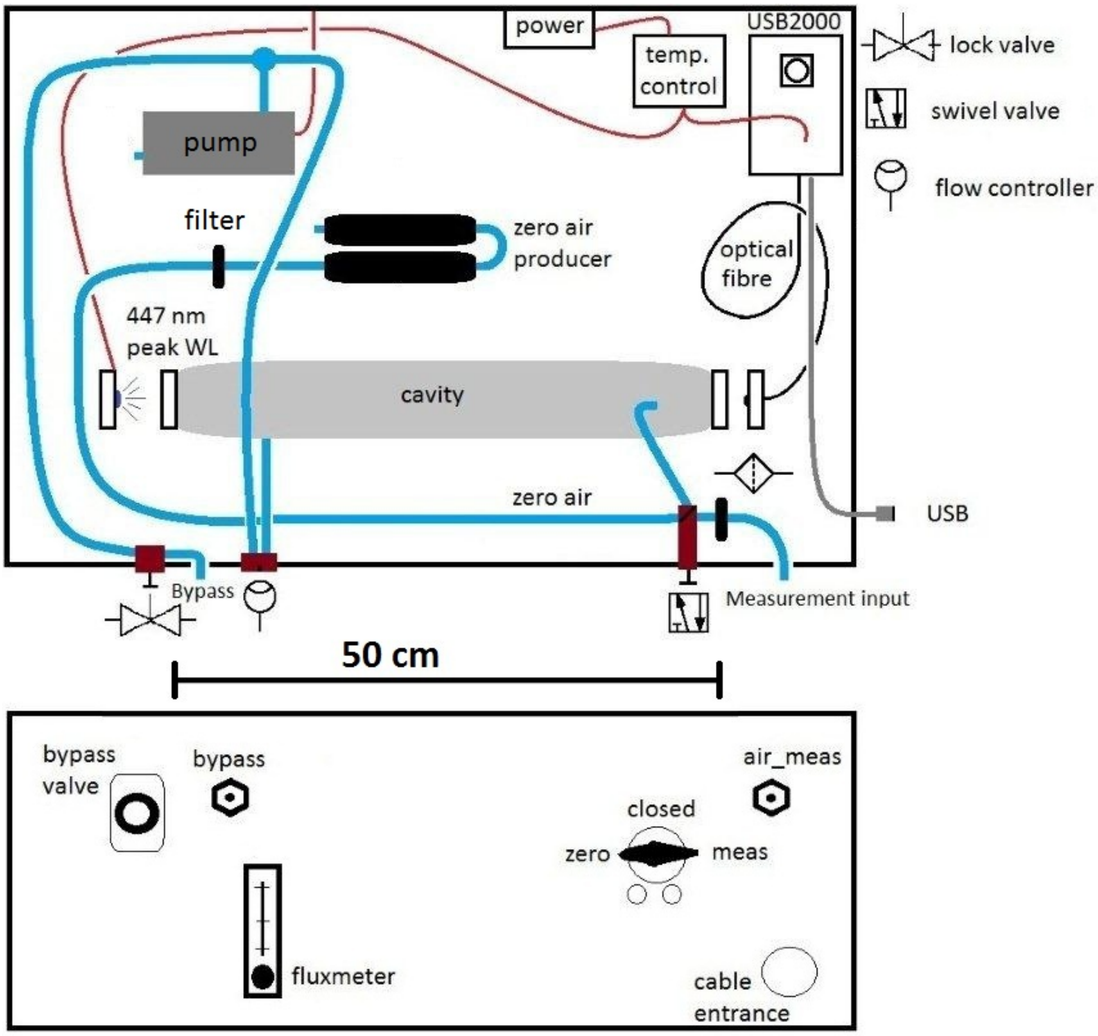


Figure 5.1: *Experimental setup: schematic view of the cavity. Two openings are used to let air into the cavity. The zero air input and the measurement input. The measurement input is also used for the He-calibration. When helium is in the cavity, the pump is switched off, and the bypass valve has to be opened to let the helium out. The bottom figure shows the front panel of the cavity setup.*

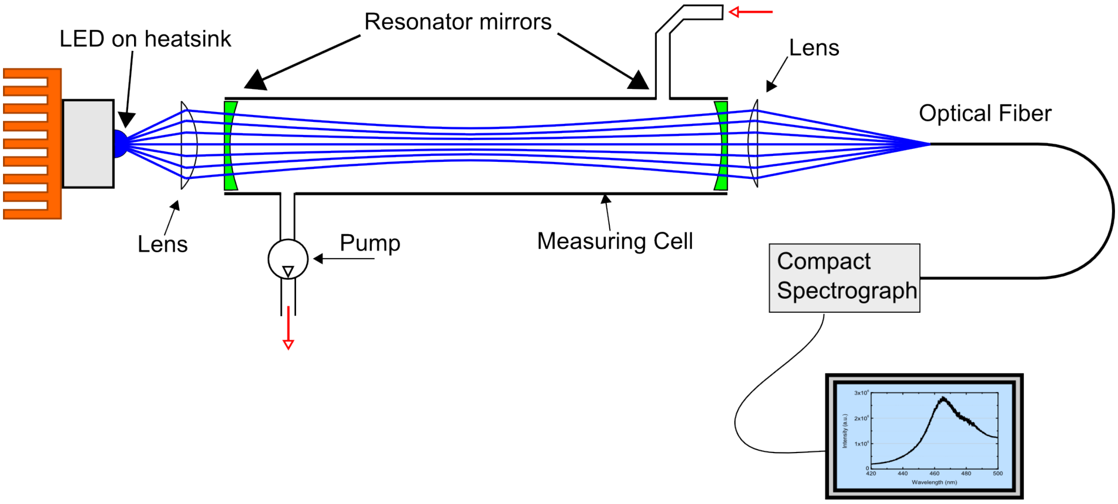


Figure 5.2: *Schematic diagram of the optics of the cavity system. Light from the LED is coupled into the cavity with a lens and on the other side coupled out of the cavity into a fused silica fiber into the spectrometer.*

Figure 5.3: *Picture of two highly reflective cavity mirrors. The mirrors in this image are still coated with a polymer to prevent dust and other particles from reaching the reflective surface.*

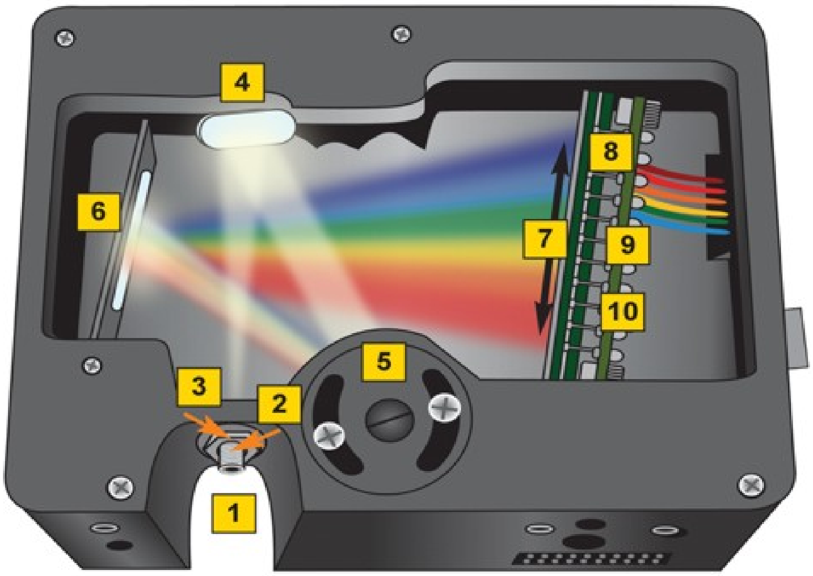


Figure 5.4: *The USB2000 spectrograph with detector. 1: Fiber connector; 2: entrance slit; 3: optical filter; 4: collimating mirror; 5: grating; 6: focusing mirror; 7: collection lens; 8: CCD detector.*

6 DOASIS

In this Practical you will use the DOAS Framework **DOASIS**. It is a library that offers the functionality to measure and evaluate DOAS spectra. All functionality can be accessed through a graphical user interface or a script based programming language (jscript). In this practical we will mainly use the graphical user interface as it also allows to visualize the spectra. A quick walk through the user interface is given in figure 6.1. A detailed description can be found in the DOASIS Tutorial that can be accessed over the Help menu.

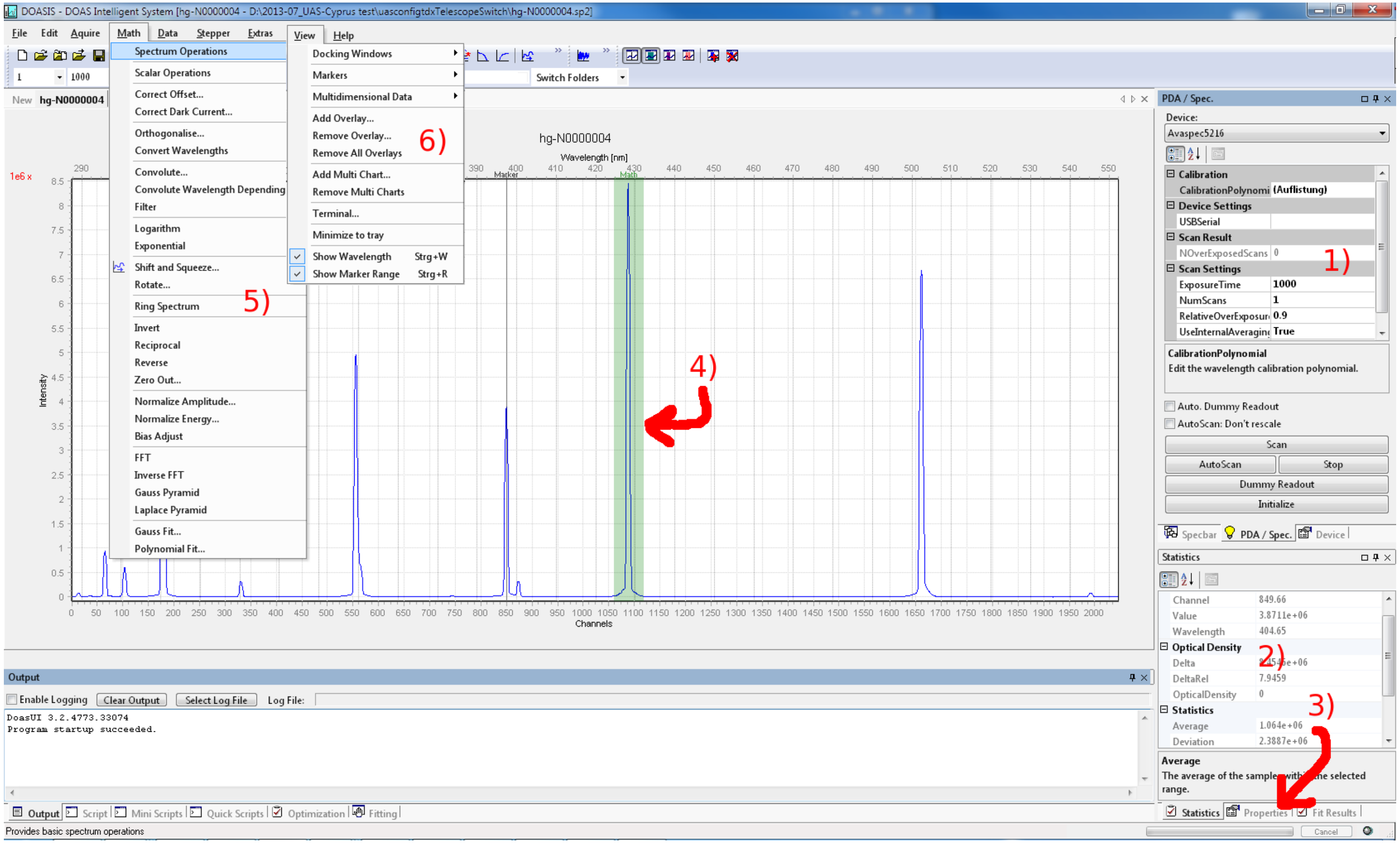
The central Object is a spectrum which can be created by **File/New...**. Make sure that the number of channels matches your spectrometer (2048). Attention: When DOASIS copies a spectrum, the copy still refers to the file name of the original spectrum. Simply saving the copy will overwrite the original spectrum. Therefore you have to use the **Save As ..** option which allows you to specify a new file name.

The **Math** menu offers basic mathematical operations that can be applied to spectra. **These operations are only applied to the area selected by the math marker**

Important properties of a spectrum can be accessed by the **Properties** and **Statistics** tabs generally found on the lower right hand side of the window.

To acquire a new spectrum with a spectrometer use the **PDS/Spec** tabs on the upper right hand side of the window. Make sure the device is selected as **Ocean Optics USB2000**. The ExposureTime property allows you to adjust the saturation of a spectrum make sure it does not exceed 50% of the maximum detector saturation. You can use the **NumScans** property to add up spectra to obtain a better signal to noise ratio.

More advanced operations like fitting and the convolution of spectra will be explained in the corresponding sections.



DOASIS - DOAS Intelligent System [hg-N0000004 - D:\2013-07_UAS-Cyprus test\uasconfigtdxTelescopeSwitch\hg-N0000004.sp2]

Device: Avaspec5216

Calibration
CalibrationPolynomi (Auflistung)
Device Settings
USBSerial
Scan Result
NOverExposedScans 0
Scan Settings
ExposureTime 1000
NumScans 1
RelativeOverExposur 0.9
UseInternalAveragin True

CalibrationPolynomial
Edit the wavelength calibration polynomial.

☐ Auto. Dummy Readout
☐ AutoScan: Don't rescale

Channel 849.66
Value 3.8711e+06
Wavelength 404.65
Optical Density
Delta 8.4546e+06
DeltaRel 7.9459
OpticalDensity 0
Statistics
Average 1.064e+06
Deviation 2.3887e+06

Average
The average of the samples within the selected range.

☐ Enable Logging
Log File:

```
DoasUI 3.2.4773.33074
Program startup succeeded.
```

Provides basic spectrum operations

Figure 6.1: *DOASIS User interface:*
1) ***PDA/Spec*** *Menue to acquire a spectrum. Make sure the Device is set to* ***Ocean Optics USB2000****. You will need to set the ExposureTime and NumberOfScans before recording a spectrum.*
2) ***Statistics*** *Gives you some basic statistical properties of the active spectrum. The values are with respect to the area selected by the math marker 4).*
3) ***Properties*** *Allows to access the meta information for a spectrum like a name, the start/stop date and the wavelength calibration etc.*
4) ***Math Marker*** *Selects the range to which all mathematical operations are applied.*
5) ***Math*** *Basic mathematical operations that can be applied to a spectrum.*
6) ***View/Add Overlay*** *Allows to create overlays of several spectra. Use the* ***Fit all overlays*** *property when using spectra of different magnitudes (e.g. a measured optical density and literature reference spectra)*

7 First experiments

The first thing you'll need to do is to give power to the LED and the spectrograph, the USB2000. They have to be at a stable temperature, which takes some time. The exact preparation of the experimental setup is the foundation of later measurements. Before you can proceed with the experiments, you have to learn to use this setup. The characterization of the spectrograph is the first thing to do. Here, one has to investigate the dark signal of which two parts are essential. The dark current and the offset. For the experiment it is important to record an offset and a dark current spectrum. Save them in the main folder → ...\Name_Vorname\... Furthermore a precise wavelength calibration is needed.
All measurements and a great part of the evaluation will be done using the program *DOASIS*. Step by step, its use will be explained.

7.1 Recording a spectrum

When recording a spectrum, two parameters must be taken into account: the *exposure time* and the number of exposures, also called scans. The exposure time is usually given in milliseconds and represents the time the detector is exposed to incoming light. The number of scans (called *NumScans* in DOASIS) tells the spectrometer how many exposures to add for each measurement.

7.2 Composition of a measured spectrum

Each measured spectrum is composed of several superimposed signals:

1. *Background*. The background signal is the measured signal when no light enters the spectrometer. It, in turn, is composed of two contributions:
    - *Electronic offset*: The electronic offset is added to each spectrum by the spectrometers electronics to avoid negative values in the analog-digital-converter. Since it is added to each spectrum, the total offset is proportional to the number of scans recorded.
    - *Dark current*: The dark current is caused by thermally excited electrons reaching the conduction band in the CCD detector without absorbing a photon. For a constant temperature, this contribution is proportional to the exposure time.

2. *Trace gas absorption.* Trace gases in the atmosphere create characteristic absorption structures in the measured spectra. The goal of the DOAS retrieval is to identify and isolate these structures, which typically feature optical depths of between 10^{-4} and 10^{-1}.

3. *Scattering effects.* Passive DOAS instruments usually measure scattered sunlight. As the scattering processes taking place in the atmosphere are wavelength dependent, the spectrum is influenced by these processes:

    - *Rayleigh & Mie scattering*: Most photons reaching the instrument are scattered either by air molecules (Raleigh scattering) or by small water droplets or particles called *aerosols* (Mie scattering). Both processes are elastic, i.e. the wavelength of the scattered photons remains constant during the process. The Rayleigh scattering probability is proportional to λ^{-4}, so shorter wavelengths are more likely to be scattered than long wavelengths. This is the reason why the sky appears blue. Mie scattering is much less dependent on wavelength, so clouds and fog appear white, as all wavelengths are equally scattered.

When recording a spectrum, it is important to use the dynamic range of the instruments detector. If the exposure time is chosen too short, the recorded spectrum will consist almost exclusively of electronic offset. On the other hand, if the exposure time is too long, the detector will be oversaturated and the top of the spectrum will be cut off.

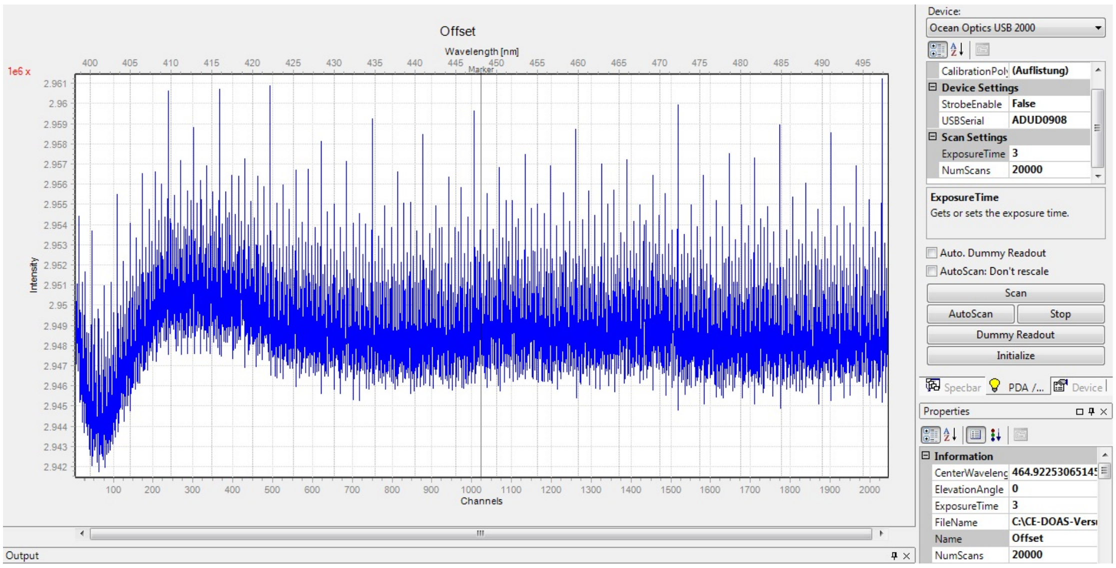
The *saturation* A of a detector pixel P is defined as:

$$A(P) = \frac{C}{N \cdot 4096} \cdot 100 \tag{7.1}$$

Here, C is the number of counts registered in the pixel, N is the number of scans. 4096 is the maximum number of counts one pixel can register. At saturations above 80%, the sensitivity of the CCD detector begins to drop off. Therefore, the measured signal is no longer proportional to the incoming photons. To avoid this, a saturation of about 70% is typically used for atmospheric measurements.

7.3 Preparing the measurements for the DOAS retrieval

In the following, the individual steps of a DOAS retrieval are described. First, the electronic offset and dark current must be corrected for, then the reference spectra and the fit routine must be prepared. Finally, the fit yields the trace gas concentration.



Device:
Ocean Optics USB 2000

CalibrationPol	(Auflistung)
Device Settings	
StrobeEnable	False
USBSerial	ADUD0908
Scan Settings	
ExposureTime	3
NumScans	20000

ExposureTime
Gets or sets the exposure time.

☐ Auto. Dummy Readout
☐ AutoScan: Don't rescale

CenterWaveleng	464.92253065145
ElevationAngle	0
ExposureTime	3
FileName	C:\CE-DOAS-Vers
Name	Offset
NumScans	20000

Figure 7.1: *Example for one offset spectrum. The offset signal is constant. Thus, it is possible to subtract the offset from the original spectra.*

7.3.1 Offset

The amplifier adds a constant voltage to the signal to avoid negative values. This is necessary because the ADC can only convert positive values. This constant voltage is the so-called offset. If a spectrum is the sum of N spectra, the offset will therefore be added N times.
The offset is not the same for all pixels but for each pixel it is constant for a given temperature. Thats the reason why it is possible and important to subtract the measured value every time from the recorded spectra. For N scans, the offset also has to be subtracted N times.
The required *offset spectra*, which contain only the offset signal, have to be measured at the minimal integration time of 3 ms. The optical fibre should be covered. To get a good statistical mean value, a lot of offset spectra should be recorded, normally around 10000 scans.
To subtract the offset signal, it is important to adapt the offset spectrum to the number of scans from the measured spectrum. After this step, the measured spectrum can be corrected from the offset.

$$I_{off-korr}(n) = I(n) - \frac{O(n)}{N_{offset}} \cdot N_{measuredspectrum} \tag{7.2}$$

I(n) is the intensity (in ADC counts) at pixel n. O(n) is the offset signal, N the number of scans.

The offset signal depends on the temperature. This is one reason why it is important to keep the detector, the USB2000, at a constant temperature. The standard is set to 15 °C.

7.3.2 Dark current

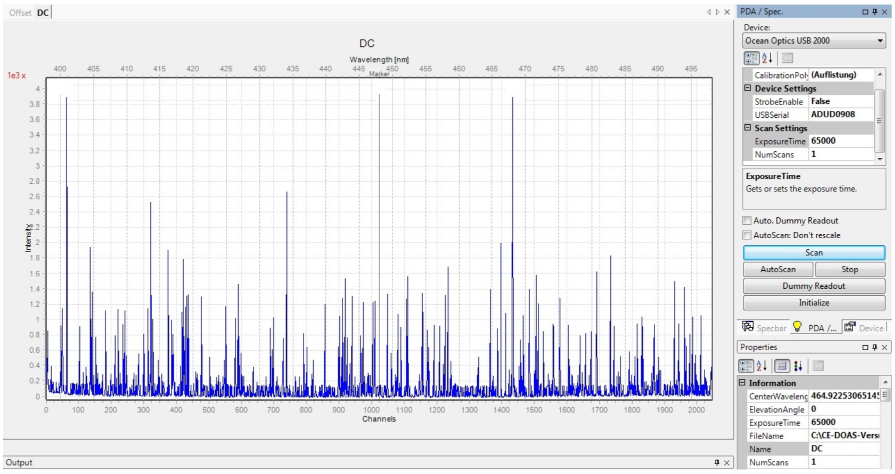
Electron-hole pairs arise not only through incoming photons. Thermal stimulation is also a reason, to bring electrons from the valence band to the conduction band. For silicon, the bandgap at 300 K is 1.17 eV. These electrons can reach the depletion zone, are stored and provide the dark current. Thus, the dark current I$_{DC}$ is temperature-dependent and proportional to the Boltzmann-factor:

$$I_{DC} \propto e^{-c \cdot E/kT} \tag{7.3}$$

Cooling the detector is an effective technique to reduce the dark current $Q_{DC} = \int I_{DC} dt$.
At constant temperature the dark current is constant and the assumption of a dark current, which is proportional to the exposure time is legitimate. To record a dark current spectrum one has to measure a single scan with a long exposure time with the fibre covered. For the USB2000 it is useful to integrate with the maximum exposure time of 60 000 ms.
To get the real dark current spectrum the offset has to be subtracted. Due to the dependence on the integration time, it has to be proportional to the duration of exposure:

$$I_{dark-corr}(n) = I(n) - \frac{D_{corr}(n)}{t_{DC}} \cdot t_{meas} \tag{7.4}$$

I(n) is the intensity, respectively count rate at the channel n. D_{corr} is the offset corrected spectrum, t the integration time of the spectrum.
Figure 7.2 shows a typical dark current spectrum. It is conspicuous that some pixels have an over-proportionally high dark current. These are the so called hot pixels, which occur as a result of production errors in the doping. The good thing is, that these hot pixels are constant. It is a characteristic fingerprint of the detector.



Device: Ocean Optics USB 2000

CalibrationPol (Auflistung)
Device Settings
StrobeEnable False
USBSerial ADUD0908
Scan Settings
ExposureTime 65000
NumScans 1

ExposureTime
Gets or sets the exposure time.

☐ Auto. Dummy Readout
☐ AutoScan: Don't rescale

Information
CenterWavelenc 464.92253065145
ElevationAngle 0
ExposureTime 65000
FileName C:\CE-DOAS-Vers
Name DC
NumScans 1

Figure 7.2: *Example for a dark current spectrum (integration time:* 65 000 ms*). The peaks come from hot pixels. Typically the dark current is around 3 counts per second. The hot pixels get many more, up to 60 counts per second.*

To do:

1. Use the black cloth to cover the space between fibre and lens so that no light can enter the fibre.
2. Record an offset spectrum.
   Each spectrum contains an electronic offset. Cover the fiber so no light enters the spectrometer and record an offset spectrum. You should use at least 10000 scans at the minimal exposure time (3 ms). Save the spectrum in the *.sp2 format.

   Determine the mean offset value per pixel per scan. Use the Statistics *tab and if necessary the menu entry Math → Scalar Operations → …*
3. Record a dark current spectrum.
   Use the maximum exposure time of 60 seconds. One exposure is enough here. Save the spectrum.

   Do you need to correct for the offset here? If so, use the menu entry Math → Correct Offset *and then save the spectrum again. Determine the average number of counts per pixel per second caused by dark current and compare this value to the offset.*
   Discuss the relevance of the dark current correction.

7.4 Noise

No two spectra will ever be perfectly identical, even if they are recorded under identical conditions. The reason for this is that there is always noise superimposed on all measurements. Statistics can help to quantify the noise. A measurement spectrum S is always composed of the background B and the signal induced by the incident photons P (see 7.2:

$$S = B + P$$

If multiple spectra are recorded under identical conditions, both contributions will fluctuate around a mean value. Gaussian error propagation yields the following equation for the total noise σ:

$$\sigma_S = \sqrt{\sigma_B^2 + \sigma_P^2} \tag{7.5}$$

The background noise σ_B is a property of the instrument and is therefore often referred to as instrument noise. It is composed of fluctuations in the electronic offset and the dark current.
The photon noise σ_P is a physical phenomenon that dictates the precision with

which electromagnetic radiation can be measured. The number of photons measured in a certain time interval fluctuates, even if the light entering the instrument has a perfectly constant intensity. The number of registered photons is then distributed according to the Poisson distribution: If M photons are registered on average for a given time interval, the root mean square (RMS) of the obtained distribution will be $\sqrt{M}$. Spectroscopy instruments are designed so that the photon noise, not the instrument noise limits the instrument precision. In this case, the photon noise dominates the total noise if the detector saturation is adequate.

To measure both the instrument and the photon noise, two spectra S_1 and S_2 are recorded in quick succession, so the magnitude of the noise contributions in the two spectra can be assumed to be equal. If the two spectra are then subtracted from one another, the noise of the difference σ_D calculates to:

$$\begin{aligned} \sigma_D &= \sqrt{\sigma_{S_1}^2 + \sigma_{S_2}^2} && (7.6) \\ &= \sqrt{2\sigma_S^2} && (7.7) \\ \Rightarrow \sigma_{S_i} &= \frac{1}{\sqrt{2}}\sigma_D && (7.8) \end{aligned}$$

To do:

Instrument noise

1. Take 2 offset spectra (10000 scans) immediately one after the other and calculate the difference.
   Math → Spectrum Operations → Subtract Spectrum. Determine the standard deviation (see *Statistics, Deviation*)

   How can the instrument noise of a single spectrum be calculated?

Total noise

1. Now purge the cavity with zero air. To do this select the switching valve at the front panel to "‘zero air"’, turn on the pump and set the air flow to 1 l/min and wait for about two minutes.
2. Uncover the fibre so that the light coming out of the cavity is guided into the spectrometer.
3. Set the exposure time so that a single scan spectrum has 50% saturation at the peak of the LED.

4. Record subsequently two spectra with 1, 10, 100 and 1000 scans respectively. Correct them for offset and dark current. Then take the quotient of each pair and determine the noise in the area where you have at least 50% saturation. Make a noise vs. number of scans plot. What do you see?

7.5 Wavelength calibration

The wavelength calibration is done using mercury emission lines of a PenRay rare gas lamp. An example of a wavelength calibration is shown in fig. 7.3.

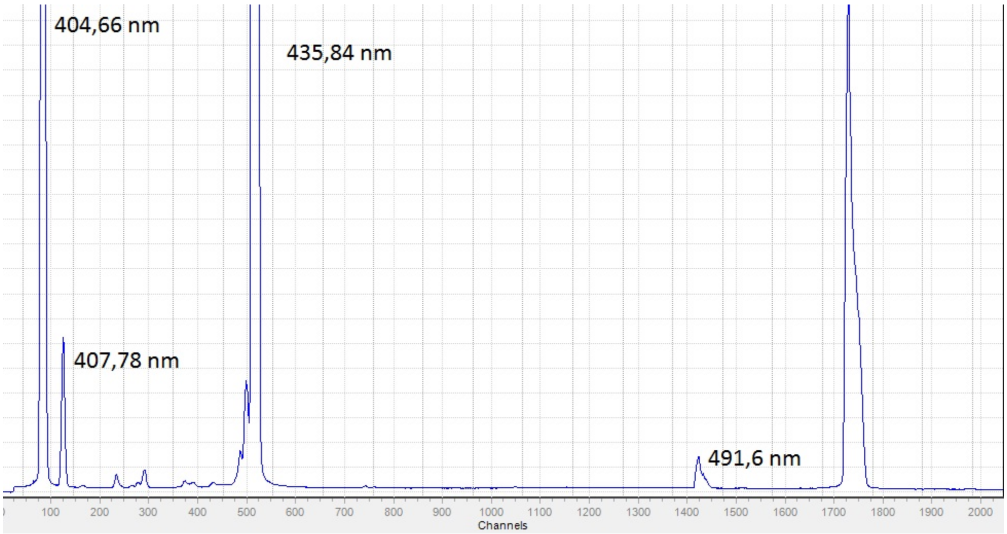


Figure 7.3: *An overview of the Hg emission lines used for the calibration.*

To do:

1. Connect the fibre to the mercury vapour lamp.
2. Record two Hg spectra. One where the strong peak has a 50% saturation, and one where the small peak at 491 nm has at least 20% saturation.
   From now on all Measured spectra need to be offset and dark curret corrected
   Save the corrected Hg spectra → ...\Name_Vorname\WLKalibration\.
3. Open the calibration assistant *Data* → *Calibration Assistant*
4. Go back to the Hg spectra and switch on the math markers
5. Starting from the Hg emission line with the lowest wavelength, select the area around the peak with the math marker. Make sure that only one peak is selected at a time and that the intensity is almost zero at the boundaries of the math range.
6. Make a gauss fit to determine the center of the peak *Math* → *Gauss Fit*.
7. Switch to the Calibration Assistant and press → *Get Marker*, then select the wavelength of the current peak and add it to the list.

8. Repeat this for all Hg peaks. After adding the last peak continue with the calibration assistant. Use a second order polynomial to fit the calibration curve. When the calibration is finished the polynomial parameters are written to the console. Copy them in your lab book for later. When prompted also select the option to transfer the calibration to all active spectra and set as default for new spectra.

9. The calibration result window also shows you the deviation between the polynomial fit and each Hg peak. Make sure the error does not exceed 0.1nm for any peak. Otherwise you probably selected a wrong Hg peak or a wrong wavelength information. In this case you have to repeat the procedure.

10. Now go to the Hg spectrum where the 435.8 nm peak has a 50% saturation. Select the 435.8 nm peak, make a Gauss fit to get the center of the peak. And save the Hg peak (not the Gauss Fit) as ...\Name_Vorname\ConvolutionKernel.sp2 $File \rightarrow SaveAs$..

7.6 Reference spectra

In this part of the course, you will prepare a reference cross section of NO_2 and measure the concentration of NO_2 in a gas cell. You will learn how to perform a DOAS fit.

As described in section 4.5.1, spectral analysis requires adapting the literature reference spectra to the spectrometer resolution. For this the following steps are performed.

1. Open the spectrum which you previously saved as ConvolutionKernel.sp2. **Make sure the math range still selects the 435.8 nm peak and the marker line is still at the center of the peak**. Otherwise readjust the math range and use another gauss fit to find the center of the peak.

2. Open a new spectrum ($File \rightarrow New$..), name it NO2 and make sure it is calibrated correctly, **that is has the correct number of channels (2048) and that the math range selects the entire spectrum**.

3. Load the NO_2 literature spectrum

4. Now perform the actual convolution $Math \rightarrow Convolute$... Select ConvolutionKernel as convolution kernel and NO2 as target spectrum. Leave the other option and press OK. Now the spectrum NO2 should contain a low resolution version of the literature spectrum.

5. Save the NO2 spectrum as Name_Vorname\Referenzspektren\NO2_conv.sp2

7.6.1 Recording a spectrum of the NO_2 gas cell

What happens to radiation as it passes through a medium? This is described by the Beer-Lambert law of absorption. (Equation 4.23).

$$I(\lambda, L) = I_0(\lambda) \cdot exp(-\int_0^L \sum_{j=1}^{n} \sigma_j(\lambda, p(s), T(s)) \cdot c_j(s) ds)$$

Now, we will bring the NO_2-filled cell with thickness L into the optical path. Then, the above equation simplifies to:

$$I(\lambda, L) = I_0(\lambda) \cdot exp(-\sigma_{NO_2}(\lambda) \cdot c_{NO_2} \cdot L)$$

1. From the previous sections the cavity should still be purged with zero air at a flow of 1 l/min.

2. Record a spectrum of the light coming out of the cavity. Use 1000 scans and a 50% saturation at the peak. In this experiment this is the light source spectrum I_0.

3. Place the NO_2 gas cell between the mirror holder and the lens at the fibre side and record a spectrum I.

4. Correct the spectra and compute the optical density $\ln(I/I_0)$. *Math* → *SpectrumOperations* → *Divide* and *Math* → *Logarithm*

5. You can immediately see the absorption features now.

7.6.2 Retrieving the NO_2 mixing ratio in the gas cell

This step is done by the fit routine in DOASIS. All the parameters needed for a fit are stored in a so called **fit scenario**.

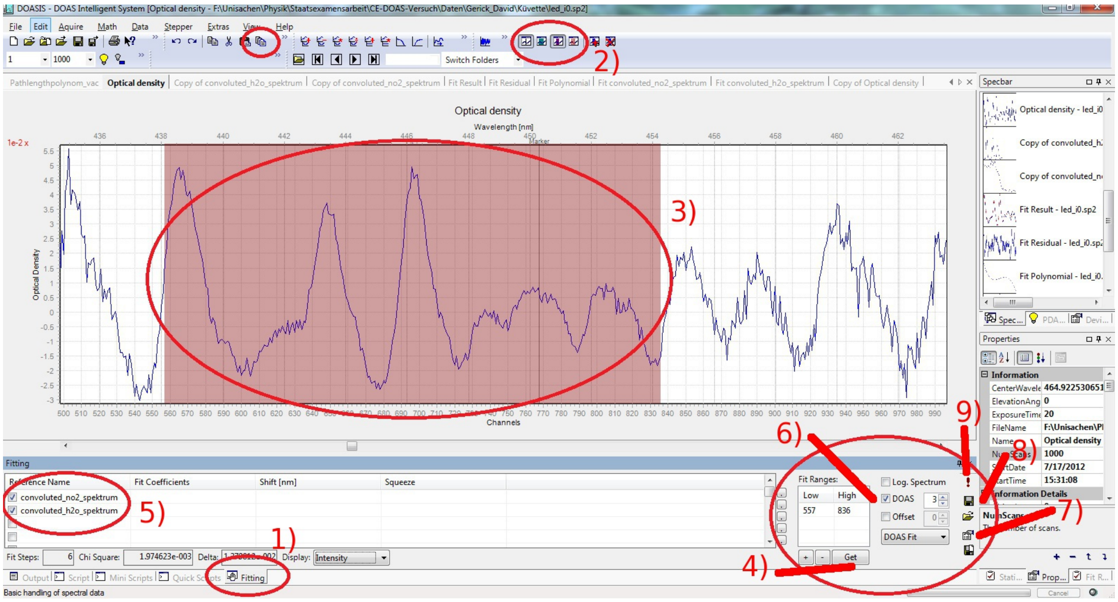


Figure 7.4: *DOASIS window in fit mode*

1. Click on the *Fitting* tab (1) on the bottom of the screen. This is the configuration window for the fit scenario.
2. Select the optical density spectrum. Activate the red fit maker by pressing **strg**+3 or using the icon in (2). Set the fit marker to the spectral range were the DOAS fit should be performed. You should ask yourself the following questions
    - How is the saturation of my spectrum? Don't include areas of the spectrum in which the saturation was low.
    - Where are the largest differential absorption structures of the trace gas you want to evaluate?
    - What other trace gases must be taken into account in this wavelength range? (In this case, the gas cell only contains NO_2, but in the atmosphere this will not be the case.)

    Press the **Get** button (4) below to fit ranges table to add it to the fit scenario.
3. Make sure the convoluted NO2 reference cross section **NO2_conv.sp2** is loaded. To select it as reference cross section click on the frist row of the *Reference Name* column (5) and select it from the drop down menu.
4. Make sure the DOAS Polynomial is activated and set to an order below five (6). Also make sure that Offset and Log Spectrum are deactivated.
5. For automated data evaluations it will be important to set the output parameters of the fit. These are found in the *additional properties* dialogue (7) under **Result Configuration** → **Select**. Here you should make sure that the **Select All** box is checked. This ensures that all available properties e.g. Fit Coefficients, Error ... are added to the output.

6. You can save the fitscenario using the save button (8),
7. Finally Start the fit by clicking on the red exclamation point (9).

After performing the fit, the fit coefficient for which the minimal χ^2 was found is given in the *Fit Coeff.* column of the *Fitting* register. Since the spectra were prepared according to the above equations, the fit coefficient represents the column density $\rho_{NO_2} \cdot L$ and the unit is molec/cm^2. The *Shift* value is the amount of pixels the spectrum was shifted to obtain an optimum fit, the *Squeeze* value is the factor by which it was squeezed or stretched. These values should be close to 0 and 1, respectively.
Now take a look at the *Fit Residual* spectrum and the obtained χ^2 value. How should the *Fit Residual* look like the case of an ideal fit? You can try varying the fit range and the Order of the DOAS polynomial. Does it have an influence on the fit result?

*When you have found the ideal fit range for this NO_2 measurement Calculate the NO_2 concentration and the mixing ratio (amount of NO_2 molecules per air molecule) in the gas cell assuming normal pressure and temperature (*1013 hPa *and* 298 K*)*

You have now completed the first steps and are ready for the cavity measurements.

8 He-Calibration

The evaluation of the concentration in the quarz cell is possible, because the path length L is known. In the case of the cavity the effective path length strongly depends on the cleanliness of the mirrors and the alignment of the resonator, the LED and the optical fibre. Therefore the path length has to be calibrated each time these parameters change. Another difference to classical DOAS is that the length of the effective light path depends on the wavelength. This is because the required high reflectivities can only be provided by interference mirrors which have a strong wavelength dependency in the reflectivity curve. In this section you will perform the calibration by the Rayleigh scattering method explained in 4.6.3.

To do: Make sure that the cavity is optimally aligned, because you will not have time for more than one path length calibration. As a rule of thumb, at an integration time of around 30 ms, at the 447 nm peak the CCD saturation should be between 40 % and 50 %. For the alignment set your spectrometer in the auto-scan mode with ten or less scans per spectrum. This allows you to follow the changes during the alignment procedure. The cavity is optimally aligned when the intensity of the peak at 447 nm is maximized.

Be careful with the mirror alignment, if they are tilted too far it can take you hours to realign the system.

You can turn the x-y-adjusting screws at the mirrors, change the z-position of the lenses or the x-y-position of the LED or the fibre coupling. The alignment procedure should be repeated iteratively until the optimal alignment is reached.

Once you finished the alignment, you have too keep it for the rest of the practical, so keep your hands off!!!

Now, the preparation is nearly complete. You aligned the optical setup, the spectrometer is wavelength calibrated and you have a dark current and an offset spectrum.

The last thing to do is to is the calibration of the light path length. You will use the strong difference in Rayleigh scattering of helium and air to calculate the light path length as explained in chapter 4.6.3. Helium has a far smaller cross section than zero air (without any absorbers). Figure 8.1 shows the cross sections in the wavelength window of interest.

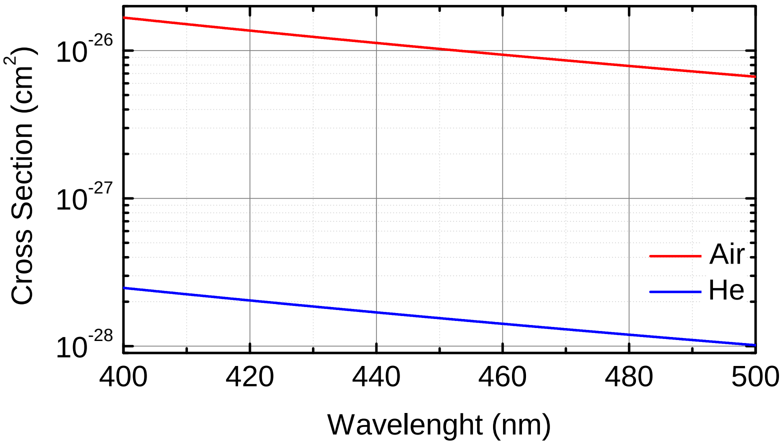


Figure 8.1: *Rayleigh scattering cross sections of helium and air [Horbanski, 2010].*

The comparison of the intensities gives us information, which makes it possible to calculate the path length as according to (4.60)).

$$\boxed{\bar{L}_0(\lambda, T_{\mathrm{air}}, p_{\mathrm{air}}) = \frac{\frac{I_0(\lambda)}{I_{\mathrm{He}}(\lambda)} - 1}{\epsilon_{\mathrm{He}}(\lambda, T_{\mathrm{He}}, p_{\mathrm{He}}) - \epsilon_{\mathrm{Air}}(\lambda, T_{\mathrm{air}}, p_{\mathrm{air}})}}$$

Think about the following questions: Why does the spectrum transmitted through the cavity look quite different to the LED spectrum? Is this normal? What is the green peak at the right edge? Where does it comes from? How long does it take to exchange the gas volume in the cavity? How can you see this in the spectra? How small should the intensity variation be, to get errors less than 10% in the resulting path length? Try to find answers and note them in your lab book.

8.1 Preparation of the script and cavity

We will use a DOASIS script to record the calibration measurements. This script saves the raw spectra in a structured way in the folders. Such scripts are a powerful tool and allow to operate automatic measurements or data evaluations. In DOASIS, you'll find the button *Script* in the left bottom corner. One can switch between output mode, script modes and the fitting operations. We need the **script mode** for the measurement of the path length. Its important to get an impression of the quality of the measurements. The He-calibration is a very sensitive matter.

To do: To save some time now start the zero air purge of the cavity as this should be performed for at least 15min before the measurement starts. Make sure that the switching valve at the front panel is set to zero air. Then start the air pump and use the flow meter at the front panel to adjust a air flow of 2 L/min.

Then copy the script folder with all scripts to your main folder: → ...\Name_Vorname\ Open the folder → ...\Name_Vorname\Scripte\Cal_CavityMessskriptv2.6.6.5 and edit the file: *UserVariables.js* with a txt editor (e.g. Notepad++):

```
/*
 *   Script for CE-DOAS Measurements: Variables and Parameters
 *
 *   Author: Martin Horbanski
 *
 *   Control variables adapted in this file.
 */

import System;
import System.IO;
import System.IO.Ports;
import System.Threading;
import DoasCore;
import DoasCore.Device;
import DoasCore.IO;
import DoasCore.Script;
import DoasCore.Spectra;
import DoasCore.HMI;
import DoasCore.Math;

//Folder Structure

/*** 1.1 Setup User Parameters   ******/
var BasePath =  "C:\\CE-DOAS-Versuch\\Daten\\Vorname_Nachname\\
    PLcalibration\\"
var NumberScans= 100;  //Number of Scans
var ExpTime= 20;       //Exposure Time
```

Only few changes need to be made: modify **Vorname_Nachname** to your names (please note that in jscript the backslashes in a file path have to be written as \\), set the **integration time and number of scans**.

Now we have to prepare the setup for the helium purge. First close the valve at the flow meter which comes directly behind the helium bottle. Connect the He gas line to the measurement input of the cavity.

The next steps involve the helium gas cylinder and should be performed together with your tutor.

First it is important to take a look at the pressure on the gas bottle. To do this you have to operate the pressure regulator (8.3). First screw out the pressure adjustment screw as far as possible (this separates the high and low pressure side). Then open the bottle valve and note the bottle pressure.

During the He calibration, the bottle pressure shouldn't decline more than 2 bar. If a higher bottle pressure drop is observed immediately close the bottle valve and inform your tutor.

This would be a sign for too high a gas flow through the cavity. The mirrors may then reposition themselves and this spoils the optical alignment. Before proceeding

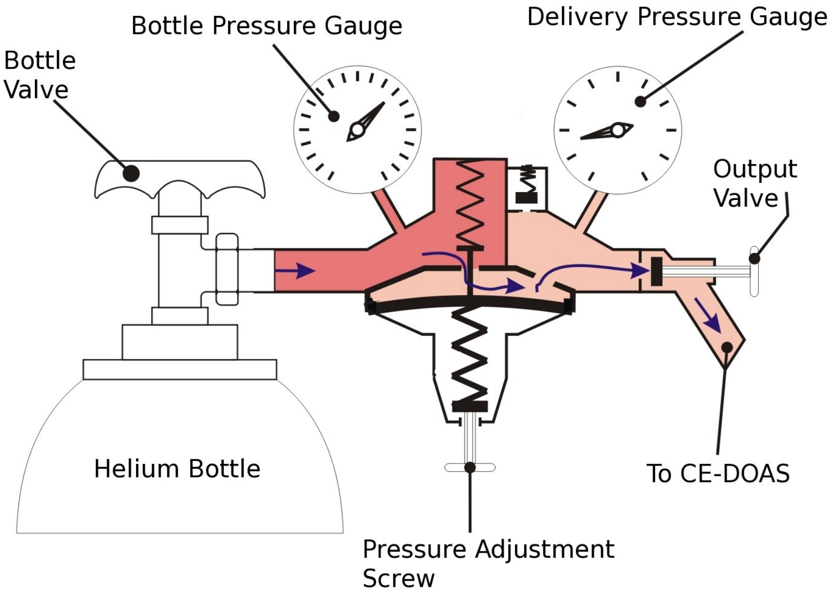


Figure 8.3: *Schematic of the helium pressure regulator. (Taken from Wikipedia)*

with the calibration, read the next chapters and make sure you understand it.

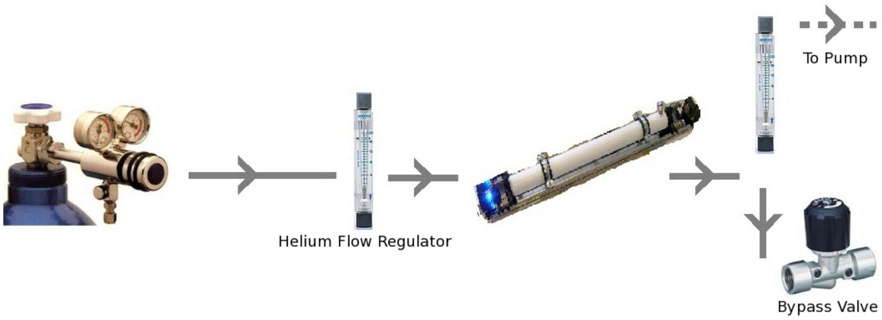


Figure 8.2: *How to arrange the He gas line and the needed valves.*

8.2 Path length measurement

The script will save the spectra and the quick evaluation data in preset folders. Now, it should be known, that the difference in the absorption from He and zero air is the point of interest. It is measureable through variations in the intensities. The script will output the deviations relative to the first recorded spectrum and show them in a new tab in DOASIS (name of it: *TrendIntI0*). If the absorption decreases, the relative intensity will increase. If the volume of the cavity is flushed completely (e.g. from zero air to He), the intensity should reach a stable equilibrium. These stable states have to be reached for the path length evaluation. A

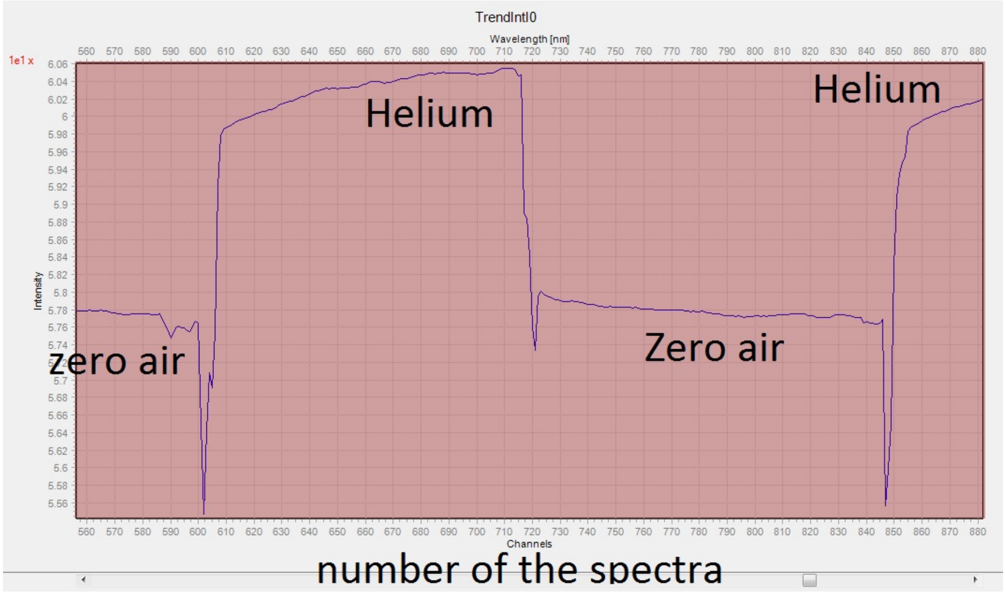


Figure 8.4: *Sequences of He and zero air measurements during the path length calibration.*

stable state is reached, when the variations go under the 0.1 %-level.
The whole path length calibration should take place rapidly. Thereby the drift of the experimental setup (temperature, LED intensity, pressure variations, dirt on the mirrors, etc.) can be minimized.

The path length calibration is the main source of the total measurement error. The error of the evaluation of trace gases can be up to 10 %. If the calibration is done well, it can sink to 5 %.

To make sure that the instrument is as stable as possible during the calibration procedure, close the door and the windows, as well as the cavity cover and avoid vibrations.

Make sure to write down the spectra numbers when changes are made (switch between gases, start/stop of pumps, change in gas flow rates) Also write down the number of spectra which you want to use for the calibrations, i.e. where you have stable intensity levels. These are important parameters for the evaluation.

When you switch to He, make sure that no overpressure comes into the cavity, that would change the experimental setup and the calibration is no more consistent. Be careful during the switching process, and always check that the pump is powered off during the He measurement and the bypass valve is opened. During the zero air measurement the opposite has to be done. The last zero air measurement gives you an indication of any drift from the beginning to the end of the calibration. You can measure this last zero air a long time. In figure 8.4 a part of the data acquisition is shown.

Follow this measurement sequence, do not deviate from this:

1. Start DOASIS and switch to the script mode
2. Load: → ... \Scripte\Cal_CavityMessskriptv2.6.6.5 \mobilemessung.jsp
3. Press *start* and make sure that the script is running
4. At this point you should have already purged the cavity with zero air for at least 15 minutes.
5. Reduce the air flow to 1 L/min (this avoids turbulences in the cavity)
6. Look at the *TrendIntI0* spectrum and make sure a stable state of zero air is reached.
7. Wait for at least 10 stable spectra (note the spectra numbers).
8. Now that the air measurement is finished, turn off the pump and open the bypass valve.
9. Make sure, that the valve at the flow meter behind the He bottle is closed.
10. Switch from zero air to the sample line where the He system is connected.
11. Use the pressure adjustment screw to set a regulator delivery pressure of 0.5 bar.
12. Now open the valve at the flow meter behind the He bottle and adjust it to a flow of 2 L/min.
13. After 20 s reduce the flow to 1 L/min.
14. Make sure that the intensity levels are stable and record at least 10 spectra. **After a maximum of 10 minutes the helium purge has to be stopped! If no stable level has been reached at that point ask you tutor for help.**
15. To stop the helium measurements first close the valve at the flow meter behind the helium bottle.
16. Then unscrew the pressure adjustment screw as far as possible.
17. Close the He bottle valve.
18. Switch back to zero air
19. Turn on the pump and close the bypass valve.
20. Purge with zero air at a flow rate of 2 L/min until the intensity level stabilizes.
21. Reduce the air flow to 1 L/min (this avoids turbulences in the cavity)
22. Look at the *TrendIntI0* spectrum and make sure a stable state of zero air is reached.
23. Wait for at least 10 stable spectra (note the spectra numbers). It is however good practice to keep it running until you start the next measurements.

8.3 Evaluation of the path length

8.3.1 Manual evaluation

In this part, you have to evaluate the path length manually. This is necessary to understand how it works. In the next chapter an automatic and more precise evaluation will follow.

To use the highly resolved cross sections for evaluation, they have to be convoluted. The spectrograph function is represented by the Hg-peak at 436 nm. Please proceed as follows and do the convolution of the air and the He cross sections:

1. Open the saved convolution kernel with the Hg-line at 435.8 nm
2. Mark the peak with the green marker
3. Fit a Gauss function with the same range as the wavelength calibration (refer to your lab book)
4. Open the highly resolved He-absorption cross section in the reference folder.
5. Create a new spectrum and include the calibration polynomial
6. Rename it *ConvolutedHeSpec*
7. Switch to the highly resolved He spectrum
8. Press: $Math \rightarrow$ *convolute*
9. Choose the convolution kernel and the newly created spectrum as the target
10. Save the convoluted He spectra in → ... \Name_Vorname\PLcalibration\Manuell\

Do the same with the highly resolved air Rayleigh scattering cross-section we will neglect the O_4 absorption for the manual evaluation to keep it simple.

To do: Evaluate the path length $\bar{L}_0(\lambda)$ using equation 4.60. You can do this either directly in DOASIS for the entire spectral range or choose five discrete wavelengths and do your calculation in Origin. Do a polynomial fit 3rd order to get a continuous path length curve. Its clear that you have to choose suitable wavelengths between 435 nm and 465 nm to cover the absorption bands of NO_2.

8.3.2 Script-based evaluation of the path length

The script based evaluation of the path length calculates a continuous path length curve and evaluates the spectra using more data, so the error will be much smaller. At the beginning look at the script → ... \Scripte\HeCalibration_v_3\ and try to check out, what's the difference between the manual evaluation and the script based one.

Before you can load the script *CalibratePathlength.jsp* to DOASIS, set up the following parameters in the *UserVariables.js*:

- ggBasePath, set it to your directory → ... \\Name_Vorname\\
- ggResultFolder = PLcalibration\\HeCal\\
- Convolution Kernel limits ggConvolutionKernelMinChannel and ggConvolutionKernelMaxChannel → set them to the rage which you used for the manual convolutions from the previous parts.
- copy the dark current and offset spectra into the ...\\PLcalibration\\folder
- Set up the names for your offset and dark current spectra.
- Set up the spectra which are to be evaluated for zero air
- Set up the spectra which are to be evaluated for He
- Make sure that the measuring cell pressure and temperature are set to ambient pressure and temperature.

Now you can start the script in DOASIS. It should load some spectra first, then convolute them and after this, the spectra are compared to each other for a mean value of the path length. You should find the evaluated data at:

→ ... \Name_Vorname\PLcalibration\HeCal\results_raw\
Airxxxxtoxxxx_Hexxxxtoxxxx\MeanOfL0_vac.xs

To do: In chapter 8.2 you measured twice with He. Do this evaluation for both stable sequences and open the two MeanOfL0_vac.xs and MeanOfL0_air.xs in one DOASIS window. You have to rename the two spectra to MeanOfL0_vac_1.xs and MeanOfL0_vac_2.xs to be able to open them simultaneously. Create a mean spectrum (from the two L0_vac and L0_air) and fit a 3rd order polynomial to this mean spectrum. These polynomials (vac and air) have to be saved at:

→ ... \Name_Vorname\PLcalibration\HeCal\results_raw\
Airxxxxtoxxxx_Hexxxxtoxxxx\Pathlength_polynom_vac.xs

This is later needed to determine the concentration of NO_2. Compare this method with the one above. Think about error sources and the magnitude of them. How could it be improved? Note your findings in your lab book.

9 Long term measurement

9.1 NO_2-diurnal variation

In chapter 4, you saw that the concentration of NO_2 changes systematically over a day. To verify this, long term measurements are needed. To start this long term measurement, some preparations have to be done.

To do:

1. You will use the measurement skript *Meas_CavityMessskriptv2.6.6.5* for ambient air measurements. Adapt *UserVariables.js* analogous to the calibration measurement script from the last section. The only difference is the **BasePath** which should point to ..\Vorname_Nachname\LongTermMeas\
2. Do the same with the script for the zero air measurements *I0_CavityMessskriptv2.6.6.5*
3. Connect the sample line to the measurement input of the cavity
4. Make sure the switching valve is set to zero air. Flush with zero air for at least 5 min. To switch from zero air to sample air use the switching valve.
5. Start the script *I0_CavityMessskriptv2.6.6.5* for new I_0 measurements
6. Record several I_0 spectra (~ 5)
7. Switch to sample air and start *Meas_CavityMessskriptv2.6.6.5*
8. At the end of the longterm measurement it is advisable to record some more I_0 spectra, i.e. repeat setup 4-6.

If you have the time, it could be interesting to measure longer than one day. Variable influences like rain, sunshine, wind, temperature, traffic and other factors can alter the outcome. You can use the data of the weather station on the roof. Ask your tutor to get access to the data. You will find it on the internal page of the homepage of the IUP.

To do: Evaluate the taken spectra as described in the next section and think about the results. To interpret the results, import them into *Origin*. Think about suitable plots to explain the different points of view. Discuss the errors in detail. Not only with words in the lab book (which is necessary and important to keep an overview), also try to assess them quantitatively. Questions that come up or problems which occur have to be noted. You are also encouraged to discuss other questions which might come up during the experiment or evaluation. Save the results in the folder: → ...\LongTermMeas\. The evaluation procedure is explained in chapter 10. These steps hold true for all evaluations you did/have to do.

Evaluations to do for the long term measurement:

- Experiment with different fit scenarios in the with a manual evaluation.
- The fit residual is the quantity of interest that should be optimized. But also keep in mind that generally wider fit ranges can also improve the detection limits if they include more absorption bands.
- Take the best fit scenario files and perform a script-based evaluation.
- Load the results in Origin and make plots to interpret the NO_2 time series with respect to air chemistry. You can ask your tutor for access to the data from the IUP Weather station.

10 Evaluation

Data evaluation is a relatively wide field. Think about your evaluation steps and how they could be improved or which phenomena are interesting to check out. A large part of a scientists work is to try new things to get better answers on existing problems or questions. Be serious and creative with the evaluation too. Use the tools you got, but follow the advice in this manual.

10.1 Manual evaluation

In this section it will be explained how the CE-DOAS equations are used for the manual evaluation. To recap the relations, look again on the effective optical density (4.59):

$$D_{\text{eff}} = \frac{I_0}{I} - 1 = \sum_j \underbrace{\bar{L}_0(\lambda)\sigma_j(\lambda)}_{\tilde{r}_j(\lambda)} \cdot \bar{c}_j \tag{10.1}$$

What is the difference to the Lamber-Beer law and what is the reason? To perform a DOAS fit, you need the following spectra and informations:

- Offset spectrum, DC spectrum, I_0 spectra and measurement spectra
- The wavelength calibration polynomial and the path length curve
- Highly resolved cross section spectra of the absorber
- Convolution kernel (make sure, that you use the same from the wavelength calibration)
- Think about a suitable wavelength range (see fig. A.1)

For the manual evaluation follow these steps:

1. Open offset, DC, I_0 spectrum, measurement spectrum, convolution kernel and the NO_2/H_2O cross sections.
2. Correct the I_0 and measurement spectrum with the DC and the offset.
3. Make a copy of the I_0-spectrum and divide this by the measurement spectrum: *Math → Spectrum Operations → Divide Spektrum*

4. Subtract one to get the effective optical density $Math \rightarrow ScalarOperations \rightarrow SubtractConst$.

5. Convolute the reference spectra (see section 8.3.1 and multiply them with the path length curve, $Math \rightarrow$ *Spectrum Operations...*.

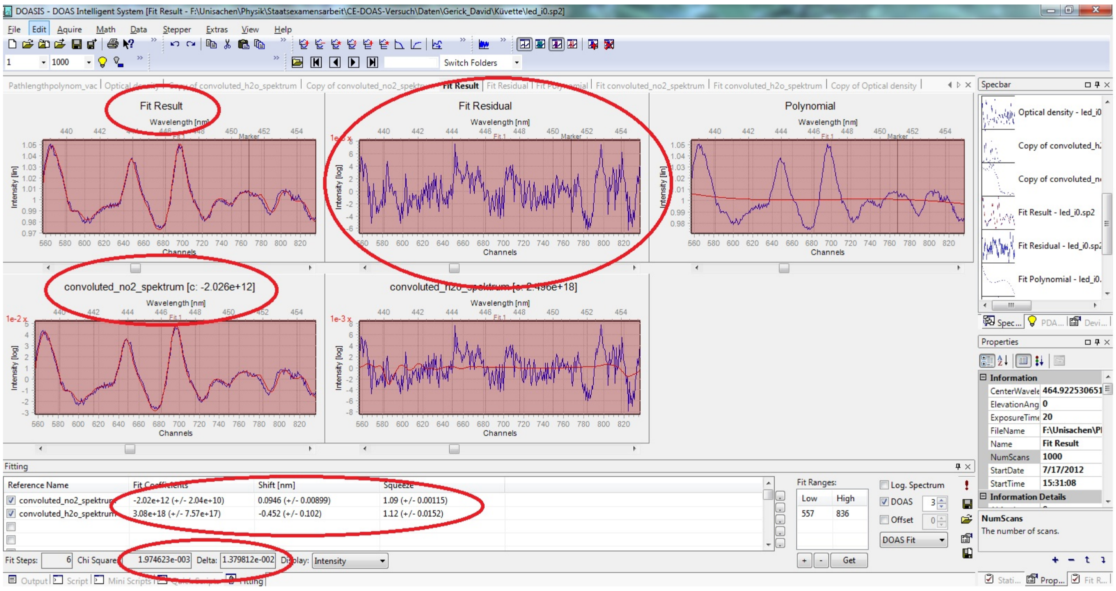
6. Apply a high pass filter to the optical density and the convoluted reference spectra, as described in the following to get rid of broadband structures.

How to get rid of broadband structures: Make a copy of the spectrum and set the green math marker to cover the whole range. Now press $Math \rightarrow Filter \rightarrow$ *Low Pass Binomial...* and choose 1000 iterations. This flattens the spectrum. Now you have to subtract this broadband spectrum from the original spectrum. The result is a new specrum without broadband structures. This procedure has to be done with the optical density and the reference spectra.

If you zoom into the optical density, you should see the absorption structures of the trace gases (see fig. 10.1). The Law of Lambert Beer makes clear that the path length is an important factor in the equation. **As the mirror reflectivity wavelength dependent, you need to multiply all reference spectra with the path length polynomial**. Then you can choose them as fit references for your fit scenario. The preparation of the fit scenario follows the description in section 7.6.2. The only difference is that you have multiple refernce spectra. **You should link the shift and squeeze properties of all references**. **Think about reasons why this should be done!** To do this determine one ”master reference” (typically the strongest absorber). For the other reference spectra double click in the shift column of the respective reference. This opens the *fit reference properties* dialogue. Go to the shift tab check the *Link Parameter* option and select the ”master reference”. Do the same procedure for the squeeze tab.

Now you can perform the fit. **You will note that the fit coefficients are negative, this is no error**. It is just an internal definition of the DOAS fit routine which expects the negative opitcal density. Multiplying the fit coefficients by (-1) gives you the number densities in molecules/cm^3. *How do you get the mixing ratios?*

Optimize the fit: Try other absorption bands and other/more trace gases and play with the wavelength range. Don‘t forget the convolution and the low pass filter on new trace gas reference spectra. Too few or too many bands can cause large errors. Look at shift, squeeze, fit residuals and fit coefficients with their errors. The shift should be close to 0, the squeeze should be 1. The residuals should be small and without characteristic structures (”noisy”) and the fit coefficient should be stable regardless of small changes to the fit settings. When you found a setting in which the fit has small errors, save the fit scenario file ...\LongTermMeas\ directory. Choose a suitable name that indicates which trace gases are fitted and which wavelength range is chosen.



Reference Name	Fit Coefficients	Shift [nm]	Squeeze
☑ convoluted_no2_spektrum	-2.02e+12 (+/- 2.04e+10)	0.0946 (+/- 0.00899)	1.09 (+/- 0.00115)
☑ convoluted_h2o_spektrum	3.08e+18 (+/- 7.57e+17)	-0.452 (+/- 0.102)	1.12 (+/- 0.0152)
☐			
☐			

Fit Steps: 6 Chi Square: 1.974623e-003 Delta: 1.379812e-002 Display: Intensity

Fit Ranges:

Low	High
557	836

☐ Log. Spectrum
☑ DOAS 3
☐ Offset 0
DOAS Fit

Information	
CenterWavele	464.922530651
ElevationAng	0
ExposureTime	20
FileName	F:\Unisachen\Pl
Name	Fit Result
NumScans	1000
StartDate	7/17/2012
StartTime	15:31:08

NumScans
The number of scans.

Figure 10.1: *DOASIS window with the fit results. Look at the circled areas, they shows important data output. With this information, you are able to assess the quality of the fit.*

10.2 Script-based evaluation

The Manual method is not a good procedure to evaluate large data sets. During field campaigns, typically ten thousands of spectra are acquired. To avoid long manual evaluations, you can use scripts which evaluate many spectra with the same fit procedure save in a *fit scenario*.

The script to conduct the evaluation for you is already existing. It is located in the folder *ClosedPathCEDOASEval20131115* and requires the following files to be in the ...\LongTermMeas\ directory:

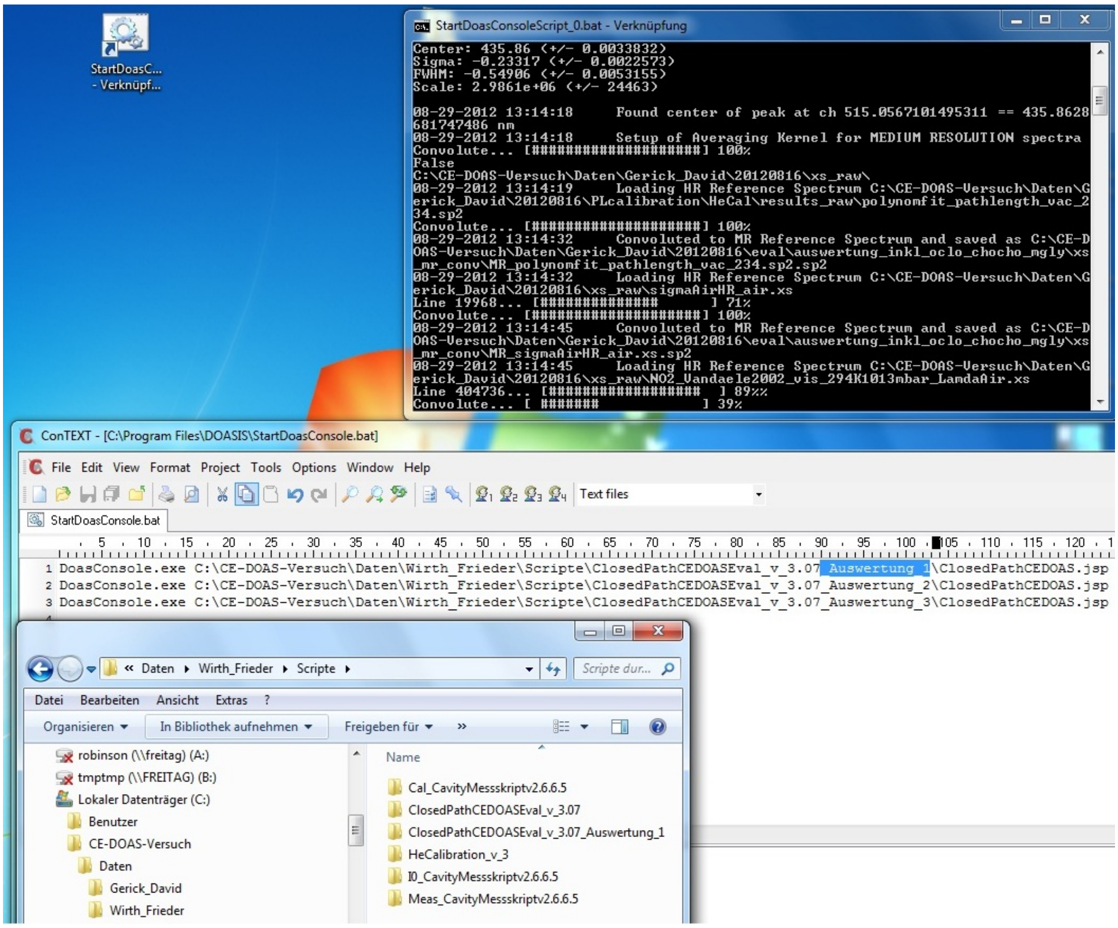
- Offset and Dark current
- Pathlength_polynom_vac.xs from chapter 8.3.2
- The fit scenario from the last section

Furthermore it is necessary to setup *UserConfig.js* this is similar to the helium-calibration script and should be straight forward.
Attention!: it is important that *ggGasNames* is adapted to the names of your fit references as they are named in your fit scenario. The *ggGasLFiles* list has to be extended if you want to use more reference spectra.

10.2.1 DOASIS via the console

It is possible to run DOASIS in console mode. The graphic interface needs a lot of computing performance and runs much slower. If you have found and tested the

script/scenario settings and checked that the script is working, it could be useful to run DOASIS in the console to save time.
To do this, you have to copy the file path of the script into the .bat file on the desktop (open it with the editor). Make sure, that no forbidden characters are used. At the beginning write: *DoasConsole.exe:* and then the path of the .jsp file of the script, which is needed.
If you want to do some evaluations in a row, e.g. the same data set with another fit scenario file, other parts of the spectra or other temperature and pressure values you have to write the paths of the scripts in a new line. The console will start them consecutively. In fig. 10.2 you can see an example.



```
Center: 435.86 (+/- 0.0033832)
Sigma: -0.23317 (+/- 0.0022573)
FWHM: -0.54906 (+/- 0.0053155)
Scale: 2.9861e+06 (+/- 24463)

08-29-2012 13:14:18     Found center of peak at ch 515.0567101495311 == 435.8628
681747486 nm
08-29-2012 13:14:18     Setup of Averaging Kernel for MEDIUM RESOLUTION spectra
Convolute... [####################] 100%
False
C:\CE-DOAS-Versuch\Daten\Gerick_David\20120816\xs_raw\
08-29-2012 13:14:19     Loading HR Reference Spectrum C:\CE-DOAS-Versuch\Daten\G
erick_David\20120816\PLcalibration\HeCal\results_raw\polynomfit_pathlength_vac_2
34.sp2
Convolute... [####################] 100%
08-29-2012 13:14:32     Convoluted to MR Reference Spectrum and saved as C:\CE-D
OAS-Versuch\Daten\Gerick_David\20120816\eval\auswertung_inkl_oclo_chocho_mgly\xs
_mr_conv\MR_polynomfit_pathlength_vac_234.sp2.sp2
08-29-2012 13:14:32     Loading HR Reference Spectrum C:\CE-DOAS-Versuch\Daten\G
erick_David\20120816\xs_raw\sigmaAirHR_air.xs
Line 19968... [###############       ] 71%
Convolute... [####################] 100%
08-29-2012 13:14:45     Convoluted to MR Reference Spectrum and saved as C:\CE-D
OAS-Versuch\Daten\Gerick_David\20120816\eval\auswertung_inkl_oclo_chocho_mgly\xs
_mr_conv\MR_sigmaAirHR_air.xs.sp2
08-29-2012 13:14:45     Loading HR Reference Spectrum C:\CE-DOAS-Versuch\Daten\G
erick_David\20120816\xs_raw\NO2_Vandaele2002_vis_294K1013mbar_LamdaAir.xs
Line 404736... [###################  ] 89%%
Convolute... [ #######             ] 39%
```

```
DoasConsole.exe C:\CE-DOAS-Versuch\Daten\Wirth_Frieder\Scripte\ClosedPathCEDOASEval_v_3.07_Auswertung_1\ClosedPathCEDOAS.jsp
DoasConsole.exe C:\CE-DOAS-Versuch\Daten\Wirth_Frieder\Scripte\ClosedPathCEDOASEval_v_3.07_Auswertung_2\ClosedPathCEDOAS.jsp
DoasConsole.exe C:\CE-DOAS-Versuch\Daten\Wirth_Frieder\Scripte\ClosedPathCEDOASEval_v_3.07_Auswertung_3\ClosedPathCEDOAS.jsp
```

Figure 10.2: *Illustration of the evaluation via console.*

11 Summary

In this practical you have measured different things with the CE-DOAS method. The law of Lambert-Beer was the basis for everything. From this, you came to the optical density and the circumstance that the concentration is determined with known absorption cross sections and the path length of the light through the gas.

It was essential to acquaint yourself with the workings of the experimental setup. The spectrograph and its characterisation was key for the preparation of later measurements. Also handling DOASIS and the data evaluation, manually and via JScript, was important to understand during the practical.

The first measurement was a quartz cell filled with NO_2. The concentration in the cell was very high to make this measurement possible, despite the extremely short optical path length. In the cavity however, the optical path length is not equivalent to the geometrical light path, but is extended. This circumstance leads to an a priori unknown path length. By comparison of the intensities from two different Rayleigh scatterers, helium and air, and with the known extinctions, the path length was possible to get.

With this foundation some different measurements have been done. The air from the urban environment was measured over a period of one day - hopefully, the chemistry of NO_2 was qualitatively validated. Also, different sources with combustion gases were measured. These data were evaluated with different methods. A manual evaluation and some script based, automatic evaluations have been done.

The aim to give you an impression of how environmental physicists work was hopefully successful. For the future, enjoy your studies. Till the next practical at the Institute of Environmental Physics, your team of advisors.

Appendix

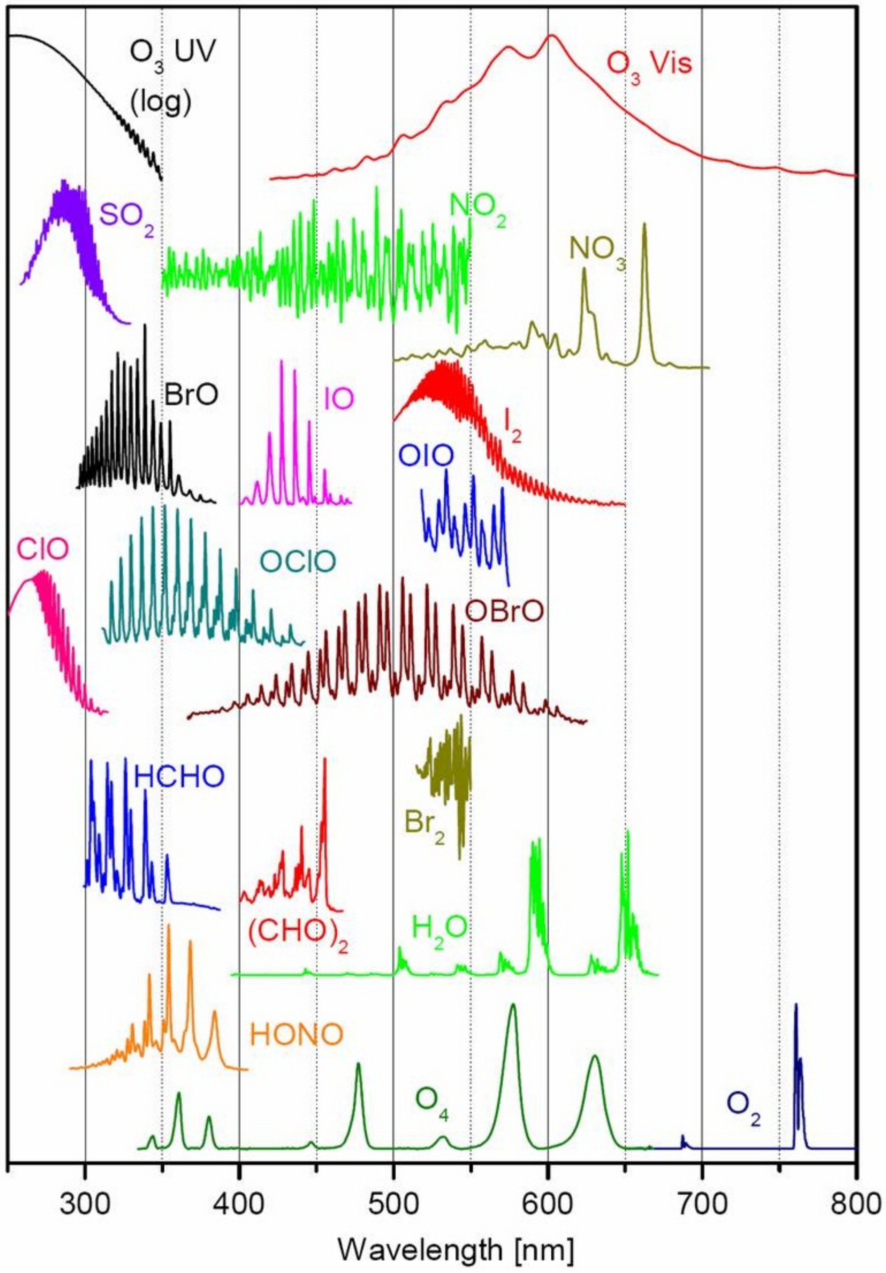


Figure A.1: ***Absorption bands of important trace gases:*** *The range of interest is around* $450\,\mathrm{nm}$.

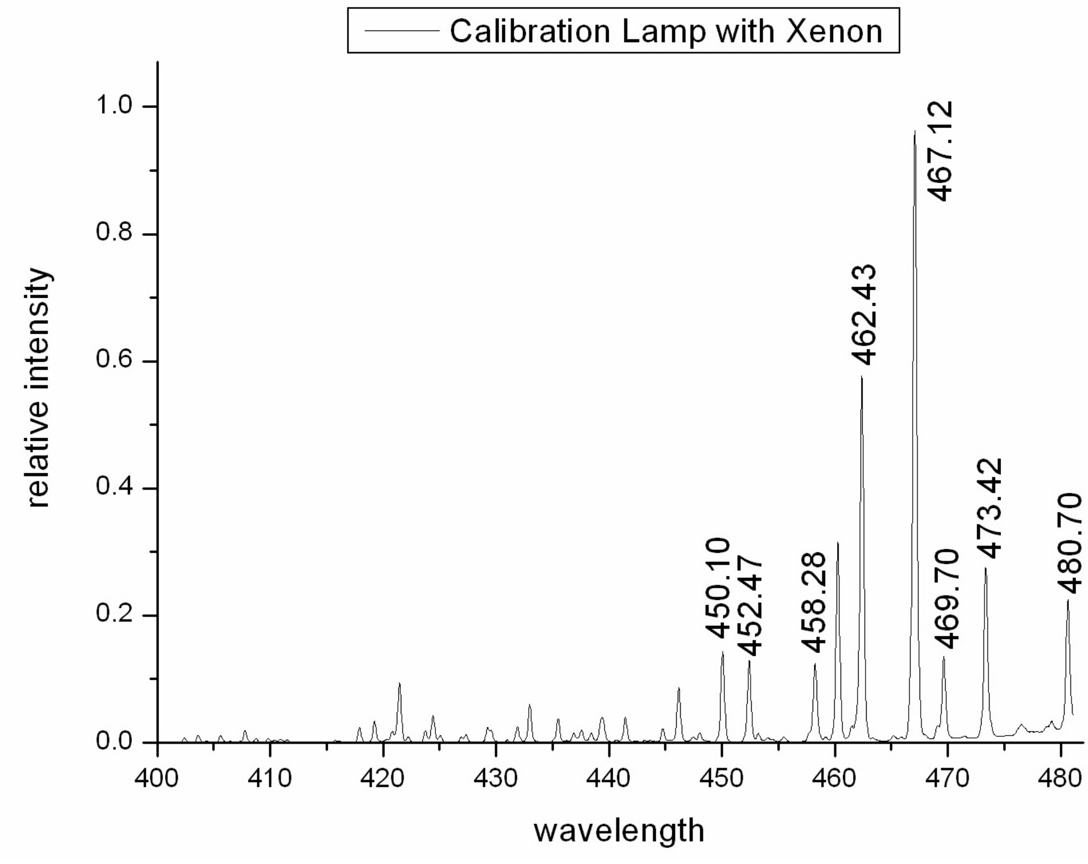


Figure A.2: *An overview of the Xe emission lines which can be used for the calibration.*

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