

Absorption spectroscopy of atmospheric species (ozone)

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Introduction

In the molecular spectroscopy laboratory we maintain set-ups for high and medium resolution spectroscopy of gases and mixtures of gases. The laboratory was created to supply the community with accurate reference data on absorption spectra and rate coefficients, important for atmospheric physics and chemistry investigations.

Objectives

In this practical you have the possibility to learn the technique of the classical absorption spectroscopy on the example of the ozone absorption spectrum in the ultraviolet and visible (UV-VIS) spectral range.

You will learn about optical beam path alignment, broad-band light sources operating in the UV-VIS spectral regions, and modern two-dimensional detectors (CCD, 'charge coupled device') allowing fast recording of broad spectra. You will work with an Echelle spectrometer using the cross-dispersion principle, which is operated via special software. You will obtain spectra and calculate optical densities using the Beer-Lambert law.

This practical guide will introduce you to the general ideas about the processes involved in the experiment. There are several suggestions for reading and you are very welcome to check internet pages using relevant keywords. It is in your own interest to collect the necessary amount of information using external sources, since it is not possible to describe everything in this practical guide.

Questions and examples are given throughout the text to give you the opportunity to check if you have understood the material. Please try to answer them!

Global monitoring of ozone

Ozone (O_3) is an important atmospheric component, responsible for UV absorption in the upper layers of the atmosphere (stratosphere). Long-term monitoring of the ozone distribution in the atmosphere and its trends are performed nowadays with an accuracy of better than 5% at many locations. Global coverage is provided by several satellites carrying instruments for remote sensing of ozone, which were launched in the past decades. New instruments are to be launched within the next years, since the life time of every instrument is limited. Also there is a network of ground-based stations measuring ozone concentration locally.

Reference data on the ozone absorption cross-sections are needed to retrieve the atmospheric ozone amounts from spectra delivered by satellites or ground-based instruments. Most of the instruments use the strong ozone absorption in the UV region (250 nm or near 330 nm), which has a very characteristic structure. Therefore knowledge of the absorption cross-sections at these wavelengths is of special interest.

Reading:

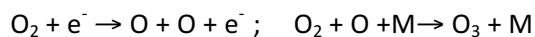
1. Please read the general information on the physical and chemical properties of ozone. There are numerous sources in the internet, you can simply try the <http://en.wikipedia.org/wiki/Ozone>
2. You can find a lot of information on the satellite instruments at the homepage of the European Space Agency. This is an optional reading. http://www.esa.int/Our_Activities/Observing_the_Earth
3. You can find a lot of information on the GOME and SCIAMACHY spectrometers on the homepages of the IUP. This is an optional reading. <http://www.iup.uni-bremen.de/sciamachy/index.html>, <http://www.iup.uni-bremen.de/gome/>

Questions 1.

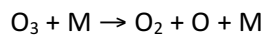
1. What does 'ozone' mean translated from the ancient Greek?
2. Why is ozone dangerous for humans?
3. Why do we need to measure ozone with high precision?
4. Why we are interested in the absorption at 330 nm?

Ozone measurements in the laboratory

Ozone is an unstable molecule. In the laboratory ozone is produced from oxygen, flowing through a vessel with electrical discharge causing the dissociation of the oxygen molecules in collisions with accelerated electrons:



Where M is a third body, usually an air molecule. In collisions with molecules ozone decays:



This process results in an exponential decay of the ozone in absence of any producing mechanisms:

$$n_{\text{O}_3}(t) = n_0 \exp\{-kn_M t\}$$

Here t is time, n_0 is an initial concentration, k the decay rate and n_M is the number density of the surrounding molecules. The decay rate depends on the temperature and the type of the surrounding molecules.

Please, note that ozone is harmful for humans if breathed in concentrations as low as 0.16 mg/m³

Example 1.

Calculate the time needed for an ozone decay of 10% at room temperature and a pressure of 50 mbar, assuming the surrounding molecules to be ozone and using the decay rate coefficient

$$k = 7.15 \cdot 10^{-10} \exp(-11195/T) \text{ [cm}^3/\text{molecule/sec]}, \quad T \text{ stands for temperature in Kelvins}$$

Use the ideal gas law (see example 2 for more details) and neglect the decay when calculating n_M . Compare this time with a typical duration of the experiment (1 hour).

Ozone absorption cross-sections

1. Electronic-vibrational-rotational spectra

Some information in this chapter is taken from the FTS practical description

http://www.msc-ep.uni-bremen.de/services/lectures/practicals/pr_fts_2015.pdf

You are welcome to read more details in the original text.

Atoms and molecules can only have a series of discrete values of energy with corresponding quantum numbers. Energy levels (E) are divided into electronic (E_{elec}), rotational (E_{rot}), vibrational (E_{vib}) and translational energy (E_{trans}), which is not considered further on in this description.

$$E = E_{elec} + E_{vib} + E_{rot} + E_{trans} \quad (1.1).$$

The absorption of radiation with frequency f (measured in Hz) occurs when a particle (atom or molecule) makes a transition from one state with energy E_k to another state with higher energy E_j :

$$E_j - E_k = hf \quad (1.2).$$

Here h is the Planck constant, which is depending on the units of energy, is

$$h \approx 6.626 \cdot 10^{-34} [J \cdot s] \text{ or } h \approx 4.14 \times 10^{-15} [eV \cdot s].$$

The Wavelength λ is typically measured in [nm] (10^{-9} m) or [Å] 'angstrom' (10^{-10} m) in the ultraviolet and visible spectral range and in [μ k] (10^{-6} m) in the infrared spectral range. Wavelength is connected with frequency by the simple relation:

$$c = f \cdot \lambda \quad (1.3).$$

Here c is the speed of light. Please, note that in spectroscopy sometimes the symbol ' ν ' is used for wavenumber which is inversely proportional to the wavelength and has units of [cm^{-1}].

Example 2:

Oxygen has an absorption band at wavelengths around 760 nm, which corresponds to an energy gap of about 1.63 eV, wavenumber of 13158 cm^{-1} and frequency 394.5 THz.

Questions 2:

Why do people often use [nm] in the ultraviolet region and [μ m] in the infrared?

Molecular spectra, especially when the number of atoms exceeds two, have a complex structure and involve electronic, vibrational-rotational and pure rotational transitions. The energy levels are described by a sum of corresponding terms:

$$T^{el} + G_v^{vib} + F_{v,J}^{rot} = \frac{E_{el}}{hc} + \frac{\hbar\omega}{hc} \left(v + \frac{1}{2} \right) + B \cdot J \cdot (J + 1) \quad (1.4)$$

and the wavelength of the transition is given by the difference of terms of the upper and lower levels involved in the transition.

In equation (Eq. 1.4):

- E_{el} - electronic energy,
- T_{el}, G, F – electronic vibrational and rotational energies in terms of wavenumbers (cm^{-1}).
- ω – is the angular frequency $\omega = 2\pi f$, historically connected with the vibrational motion of the harmonic oscillator;
- $\hbar = h/2\pi$;
- v ($v = 0, 1, 2, \dots$) – is the vibrational quantum number; this very common designation is somewhat confusing, since the very similar symbol ν is used for the wavenumber.
- B – is the rotational constant of the molecule, connected with the moment of inertia.
- J ($J = 0, 1, 2, \dots$) - is the vibrational quantum number.

Differences of quantum numbers for upper and lower states of a transition obey certain **selection rules**:

- vibrational transitions: $\Delta v = \pm 1, \pm 2, \pm 3, \dots$ with fast decreasing intensities;

- rotational transitions: $\Delta J = 0, \pm 1$. Observation of transition with $\Delta J=0$ depends on the symmetry of the molecular structure.
- Electronic transitions: the electronic energy of one electron is a result of the distance to the static atomic nuclei and the electronic system formed by further electrons. The transitions between two electronic states are ruled by the Franck-Condon principle, which states that an electronic transition occurs without changes in the nucleus positions during a transition. The syntax of the electronic transitions is not given in the description of this practical.

Example 3:

The lowest energy level of a molecule is described by the term

$$\frac{E_{el}}{hc} + \frac{\hbar\omega}{2hc}$$

The nuclei in a molecule are held together by the electrons. Depending on the quantum number of the electrons there are different electronic states of the molecule. Nuclei carry out their vibrations under influence of the potential energy which is a sum of the electronic energy and the Coulomb energy.

In the figure below, potential energy curves for a diatomic molecule are shown as function of the distance between nuclei. The black and blue curves correspond to states with different electronic energy: ground electronic state (black, S_0) and first excited electronic state (blue, S_1). The energy levels for the vibrational motion are shown as black and blue lines inside the curves. Red lines in the insert show rotational levels for the zero vibrational level of S_0 . Notice that the characteristic energy for the rotational motion is much smaller than that for the vibrational motion, and the latter is much smaller than the energy associated with electronic motion. There is an equilibrium distance with minimal energy which is not zero.

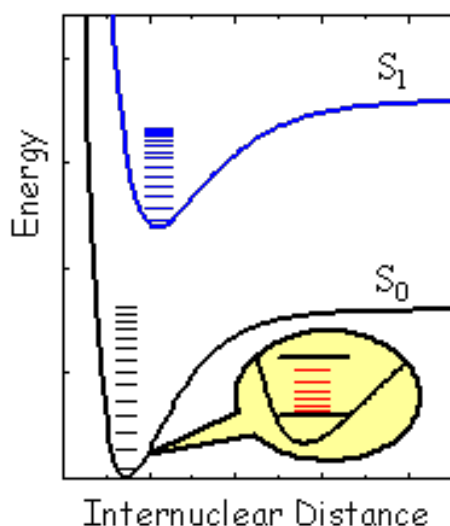


Fig.1. Potential energy curves of a diatomic molecule.

Picture adapted from "PHOTOCHEMISTRY
Theoretical Concepts and Reaction Mechanisms"
<http://www.photobiology.info/llichev.html>

In the ozone molecule which is not linear with 3 nuclei there are $3 \times 3 - 6 = 3$ relative coordinates; therefore the potential energy under which the nuclei move in a given electronic state can be

represented by a 3-dimensional surface in the in a 4-dimensional space. Every electronic state is represented by such a potential surface. Such hypersurfaces unlike the simple potential curves of the diatomic molecules are difficult to visualize.

Transitions between electronic states lead to spectra in the UV region. Transitions between vibrational-rotational levels belonging to the same electronic state produce spectra in the visible and infrared regions. Pure rotational transition within the same vibrational state leads to the spectra in the microwave region.

Reading:

A very detailed book on molecular spectra is the work of G. Herzberg "Molecular Spectra and Molecular Structure", consisting of three volumes:

"I. Spectra of Diatomic Molecules"

"II. Infrared and Raman Spectra of Polyatomic Molecules"

"III. Electronic Spectra and Electronic Structure of Polyatomic Molecules".

Unfortunately, this book is mostly for advanced spectroscopy readers. As a possible alternative with some experimental aspects the book "Molecular physics" by W. Demtröder can be recommended.

2. Beer-Lambert law

Measurements of the ozone absorption are based on the well-known Beer-Lambert law, which describes the intensity $I(\lambda)$ of the light at the wavelength λ transmitted through a medium, containing the absorbing gas:

$$I(\lambda) = I_0(\lambda) \int_0^L \exp\{-n(T, p, l) \cdot \sigma(\lambda)\} dl. \quad (2.1)$$

Here

I_0 - is the initial light intensity in absence of absorbing molecules (background);

n [molecule/cm³] - absorbing gas density which is a function of temperature T , pressure p and the position l

L [cm] – length of the absorbing medium;

σ [cm²/molecule] – absorption cross-section. The meaning of this quantity will be described below.

In the typical laboratory experiment, the gas of interest is filled into the cell, which has windows transparent for light with wavelength λ , defined by the aims of the experiment. In the current practical we investigate absorption at wavelengths around 330 nm (UV) for the reason described above.

If the absorbing gas is distributed uniformly along the optical beam, equation (Eq. 2.1) can be simplified:

$$I(\lambda) = I_0(\lambda) \cdot \exp\{-n(T, p) \cdot \sigma(\lambda) \cdot L\}. \quad (2.2)$$

There are several conditions to be fulfilled to use the equations (Eq. 2.2):

- The absorbing medium must be *homogeneously* distributed in the interaction volume and must *not scatter* the radiation;
- The incident radiation must consist of *parallel rays*, each traversing the same length in the absorbing medium;

- The incident light flux *must not influence* the atoms or molecules.
- In experiments two consequent measurements of intensity have to be done: one with and one without absorbing gas, all other parameters must be *constant*.

The product of cross-section, gas concentration and absorption length is called **optical density OD** and can be found from the ratio of the light intensities with and without gas:

$$OD = \ln \frac{I_0(\lambda)}{I(\lambda)} = n(T, p) \cdot \sigma(\lambda) \cdot L. \quad (2.3)$$

From the optical density the ozone concentration can be found if both cross-section σ and absorption length L are known. Therefore, precise information on the cross-sections is important for high quality remote sensing ozone measurements in the atmosphere.

In physics, the cross-section is a quantity describing the probability of a process. The absorption cross-section describes the ability of molecules to absorb radiation of a certain wavelength under certain conditions.

The absorption cross-section is connected with the probability of the transition between energy levels of the molecule. Therefore it is a function of wavelength and depends on parameters such as pressure and temperature. The absorption cross-section of ozone has a very strong dependence on wavelength in the UV region.

The dependence of cross-sections on pressure and temperature can be very complicated. For simple molecules cross-sections can be calculated using information on the energy levels of the molecule. However, even for molecules consisting of three atoms these types of calculations are very complicated, especially for transitions in the UV region, which involves electronic, vibrational and rotational levels. Despite all efforts, the accuracy of calculated ozone absorption cross-sections is still poor compared to experimental values. Nowadays, accurate cross-sections can be obtained under laboratory conditions only.

During the current practical, we will obtain **relative** cross-sections:

$$\sigma(\lambda) = \frac{1}{A(T, p)} \ln \frac{I_0(\lambda)}{I(\lambda)} \quad (2.4)$$

Here A is a scaling factor, which is the product of the ozone density and the absorption path length. We **will not** define this factor, since an additional experiment is needed to find the ozone density, which goes beyond the goals of this practical. **The main interest is on the qualitative dependence of the ozone cross-section on the wavelength.**

Note that in case of a small cross-section, the difference between the light intensity with and without the absorbing gas is very small and the resulting error bars for the cross-section are large. An obvious solution is to increase the absorbing length or the concentration of the absorbing gas. There are certain limits for the concentration of ozone from safety rules. Therefore, reflective optics is installed in the cell to increase path length by sending light many times through the gas (so called multipass cell of White type).

Questions 3.

1. How can light influence the gas?
2. Why are calculations of cross-sections complicated?
3. What does optical density $OD=0$ physically mean? And $OD=1$?
4. Why do we use multipass optics?

Example 4.

- a) Let's calculate the optical density for the following case:

A mixture at room temperature contains 10% of ozone in oxygen at a total pressure of 100 mbar, the length of the cell is 1 m, the cross-section is 10^{-18} cm²/molecule.

The ozone concentration n_{O_3} can be found from the ideal gas law:

$$n_{O_3} = \frac{p_{O_3}}{kT}$$

There p_{O_3} is partial pressure of ozone in Pa, k is the Boltzmann constant $k=1.38 \times 10^{-23}$ J/K and T is the temperature in Kelvin.

In our case $p_{O_3}=10^3$ Pa (100 mbar x 10% = 10 mbar; 1000 mbar = 10^5 Pa) and $n_{O_3} \approx 2.4 \times 10^{23}$ molecule/m³. Optical density (note the units!): $OD=2.4 \times 10^{17}$ molecule/cm³ x 100 cm x 10^{-18} cm²/molecule = 24.

This means that the intensity will be $I=I_0 e^{-24}$. This intensity is too low compared to the background intensity I_0 . Remember, that all parameters should be constant! If the sensitivity of the system was adjusted to the level of the background intensity I_0 , the signal I will be on the level of the noise.

- b) For a cross-section of 10^{-20} cm²/molecule the optical density $OD \approx 0.24$ and $I=I_0 e^{-0.24} \approx 0.8 I_0$. This condition belongs to the favorable region $0.1 < OD < 1$ and provides good results.
c) Calculate the range of the ozone partial pressure for measurements of cross-sections in the range

$$\sigma = 10^{-20} - 10^{-17} \text{ cm}^2/\text{molecule, assuming } OD=1.$$

Suggest conditions (L , total pressure, concentration of ozone in oxygen) to realize these experiments. Remember that: length can take discrete values of 1m, 2m etc but not more than 20 m (more details will be given in the experimental part of the description); total pressure cannot exceed 1000 mbar; concentration of ozone in oxygen cannot exceed 10%.

3. Spectral instruments with cross-dispersion

To obtain a spectrum in the UV region, broad-band radiation of a De or Xe lamp is sent through the cell and analyzed using a spectrometer. In our experiment we use a so-called "echelle" **grating** spectrometer (from French, *échelle*, meaning stairs or ladder), which uses the principle of cross-dispersion. In an echelle spectrometer there are two diffractive elements (a diffractive grating and a prism) mounted orthogonally in such a way that the highly illuminated orders are transversally separated.

A diffractive grating is a periodic structure, consisting of reflecting or transparent grooves with a characteristic size of the order of the magnitude of the wavelength. A grating is characterized by the groove density, usually counted in grooves per mm. A diffractive grating splits the incident light in several directions depending on the wavelength and the period of the grating.

$$d \times (\sin\phi + \sin\theta) = m\lambda \quad (3.1),$$

here

d is the period of the grating;

ϕ – the angle of the incident light relative to the perpendicular of the grating;

θ – the angle of the reflected (transmitted) light;
 λ – wavelength;
 m – an integer number (“order”).

The zeroth order ($m=0$) corresponds to specular reflection and is at the same angle for all wavelengths. The relation (Eq. 3.1) can be derived from the phase difference between beams reflected by neighboring periods. For light falling perpendicularly on the grating:

$$\sin\phi = m\lambda/d \quad (3.2)$$

From equation (Eq. 3.2) we immediately get that

$$m_1 \lambda_1 = m_2 \lambda_2 = m_3 \lambda_3 = \sin\phi \times d = \text{const} \quad (3.3).$$

Therefore wavelengths belonging to different orders will be refracted by the same angle. The second dispersive element, for example a prism, oriented orthogonally to the spectrum will shift the orders, forming a two-dimensional spectrum. This arrangement is very advantageous, when high resolution of a broad spectral region is needed.

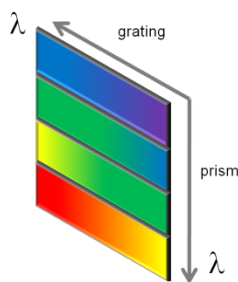


Fig.2. Simplified schematic illustration of the 2D spectrum formed from the “white” spectrum using prism and grating

Questions 4.

1. For a grating with a groove density of 100 gr/mm calculate the maximum diffractive wavelength in the order $m=100$ and order $m=50$ (light falls perpendicular to the grating).

4. Uncertainty estimation

There are two main sources of uncertainties of the cross-sections obtained using (Eq. 2.4):

- Statistical, arising from the stability of the intensities I and I_0 . This uncertainty can be found in terms of standard deviation of the (arithmetic) mean after averaging N spectra:

$$sd = \sqrt{\frac{\sum_i^N (I_{mean} - I_i)^2}{N(N-1)}}, \quad (4.1)$$

Here I_{mean} is the mean value, I_i the intensity of a single spectrum, and N the number of obtained spectra.

- Systematic, coming from the uncertainty of the scaling factor. This source of uncertainties is not estimated in this work.

In these terms, the systematic uncertainty characterizes the accuracy (difference between measured and real value) and the statistical uncertainty characterizes the precision (reproducibility) of the measurements.



Fig.3. Illustration of systematic and statistical errors: a) low accuracy, high precision; b) high accuracy, low precision

The total error is calculated using the usual equation

$$\delta F(x_i) = \sqrt{\sum \left(\frac{\partial F}{\partial x_i} \delta x_i \right)^2}$$

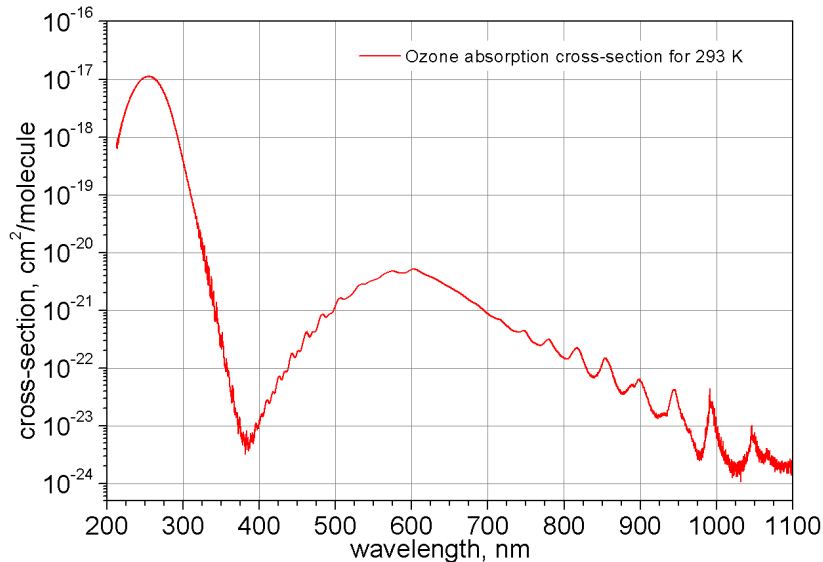
Questions 5.

Calculate the total uncertainty (in percent) for the optical density OD obtained from $I=20000$ and $I_0=40000$, both measured with 1% accuracy ($\delta I=200$ and $\delta I_0=400$)

Experiment

1. Challenges

Ozone cross-section values span over 6 orders of magnitude within 250-350 nm range:



Available scientific devices are not able to simultaneously cover the entire dynamic and wavelength range necessary for the whole absorption spectrum. In order to obtain full coverage of the spectrum it is necessary to perform multiple measurements under different conditions.

In our setup we can control:

- gas flow rate (100-600 sccm – standard cubic centimeters per minute. “Standard” means that the temperature is assumed to be 293K and pressure is atmospheric)
- ozone generator performance (80-300 arbitrary units on the ozone generator control dial, with higher value giving ca. 10% O₃ in the resulting O₂+O₃ mixture)
- gas mixture pressure (5-950 mbar) or pure ozone pressure (1-50 mbar) of the sample in the cell
- temperature of the cell (190-295K)
- absorption path (from 5 cm to about 30 meters)
- light source (Deuterium lamp for short/long single pass, Xenon or Laser-Driven Light source for all configurations)
- spectrometer settings

Each pair of spectra (with/without absorbing molecules) for otherwise stabilized experimental conditions yields one Optical Density (OD) spectrum. Due to specifics of the spectrometer it is only possible to obtain an OD spectrum spanning less than 3 orders of magnitude. Calculated OD spectra with values outside the 2-0,02 tend to be either saturated (strong absorption -> big difference between two spectra -> high ODs -> loss of information when almost all light is absorbed) or noisy (weak absorption -> small difference between two spectra -> low ODs -> high influence of white noise). We also estimate “dark current” background value. It represents the “background” originating from spontaneous signal caused by thermal quantum effects in the spectrometer sensor. Example below is a demonstration of cross-section spectrum derivation.

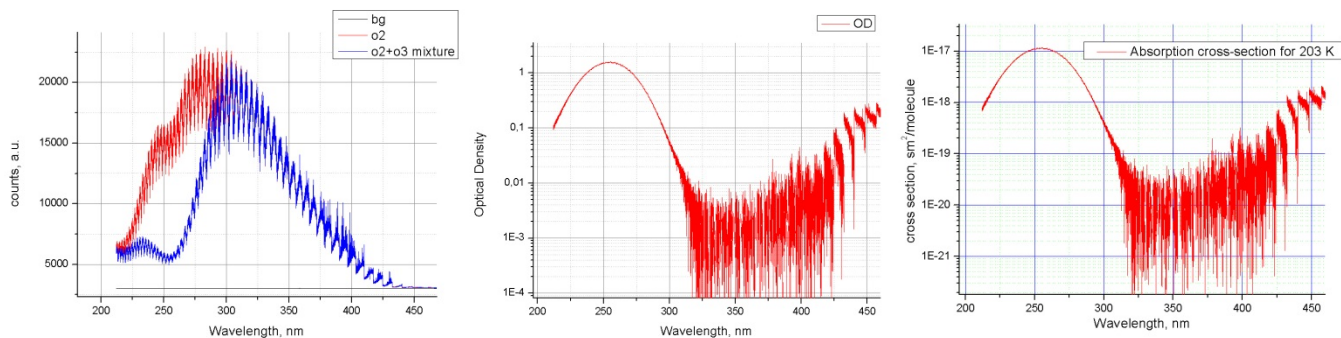


Fig.4. From single spectra to OD and cross-sections

a) Experimental setup scheme

The experimental setup consists of several major components (Fig.5):

- 1) Experimental cell (optionally coolable), in which gas sample is contained.
The cell has several possible alignment paths: single short (5 cm) pass, and a long multipass, resulting in 5-30 meters of effective absorption length (depending on alignment)
- 2) External cryostat for cell cooling/gas precooling. The cryostat cools down the liquid ethanol to the desired temperature and circulates it through the jacket of the cell
- 3) Gas flow meters/pressure regulators/pressure gauges
- 4) Ozone generator
- 5) Rotary and turbomolecular pumps for cell evacuation
- 6) Light sources – Deuterium (D_2) and Xenon (Xe) lamps, Laser-Driven Light Source (LDLS)
- 7) Spectrometer for spectra acquisition

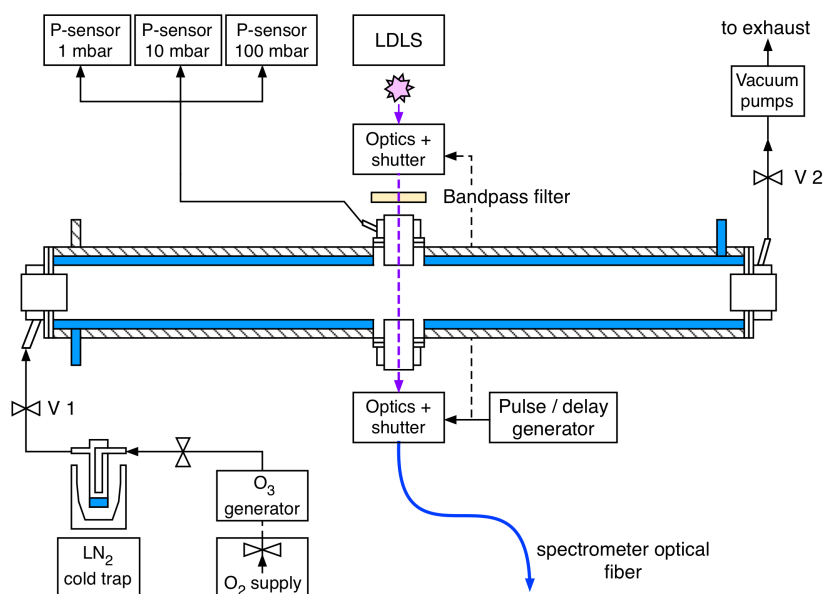


Fig.5. Experimental setup

b) Spectrometer

In our setup we use a spectrometer with two internal dispersive elements (prism and a special type of diffraction grating called *echelette*). It transforms the light fed via a quartz fiber into the two-dimensional pattern with spectral distribution and projects it upon an image intensifier (special quantum-electrical device used to amplify light intensity – microchannel plate MCP) and then a CCD sensor. The image is read out, digitized and processed into a spectrum automatically.

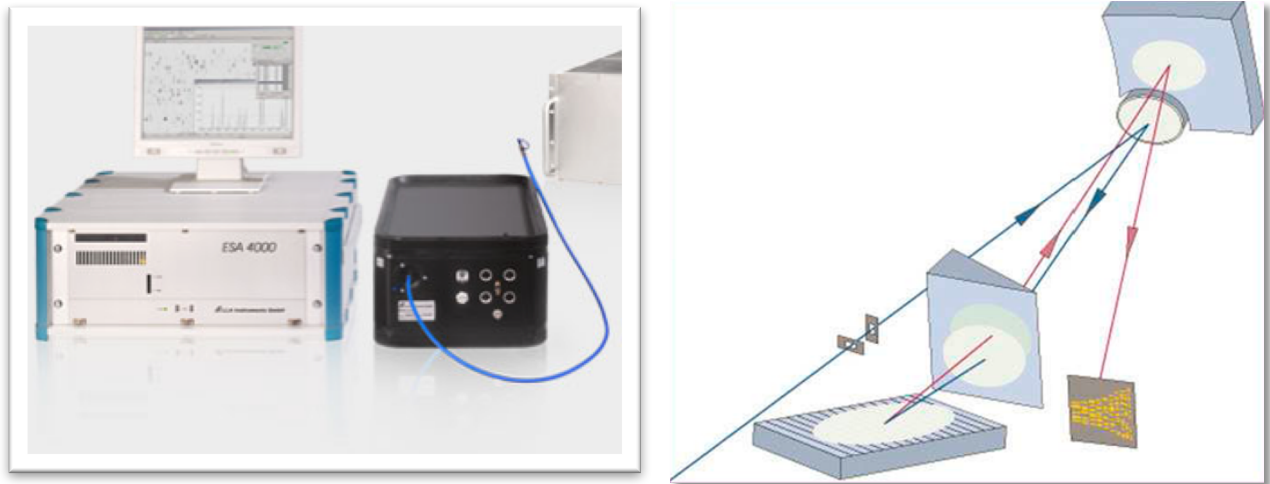


Fig.6. Echelle spectrometer

The spectrometer covers the wavelength range from 212 to 840 nm with a spectral resolution of about 0.02 nm, but due to some construction details gaps begin to appear in the spectrum starting from about 590 nm.

c) Data acquisition and processing software

The spectrometer is controlled via the ESAWIN package installed on the built-in PC. The user can change various parameters of the instrument depending on the current experimental demands.

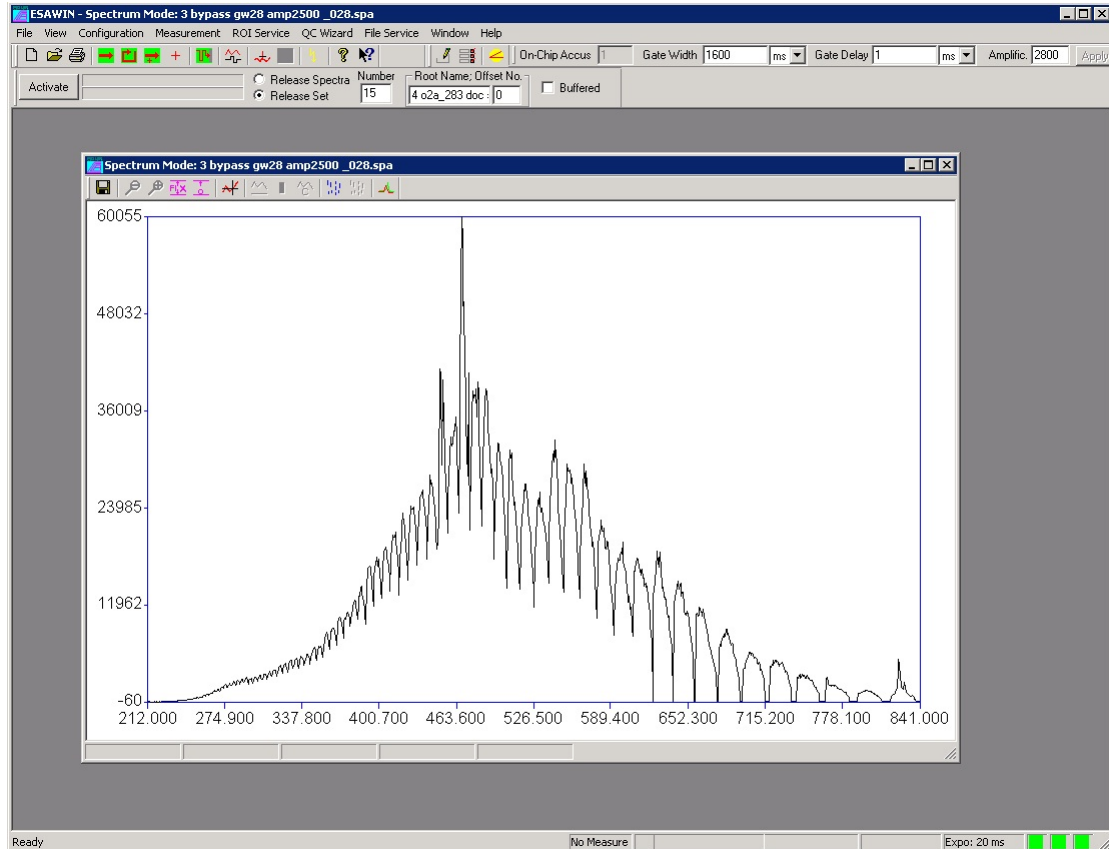


Fig.7. ESAWIN main window

Before acquiring spectra it is recommended to familiarize oneself with the software under supervision.

The most important settings are:

- **Gate width** which defines the duration (normally within 20-2000 ms) of the phase during which the intensifier is operational and the CCD is accumulating signal;
- **Amplification** defines the degree of signal intensification by setting the voltage on the MCP (available range 1200-4000 arbitrary units)

CAUTION! Always start a measurement with a combination of lower level settings. High values can result in oversaturation of the intensifier and can cause irreversible damage!

A safe starting point is a 20ms gate width and 2000 units for amplification. Our experience with available lamps and typical alignment options shows that gate width and amplification should never exceed 200 ms and 2800 units respectively. The resulting spectra are digitized and have an intensity range between 0 and 65535 ($0-2^{16}$) counts. The registered peak intensity grows linearly with gate width. The increment interval for amplification is 100 units.

To produce spectra with reasonable signal-to-noise ratio, we have to perform averaging of multiple individual spectra recorded by the spectrometer. There are several averaging modes available, but we will restrain ourselves to the following routine: the spectrometer measures 10 spectra and averages them before saving to file. Normally, we accumulate a 100 of such files. This results in the possibility to effectively average over 1000 single acquisitions.

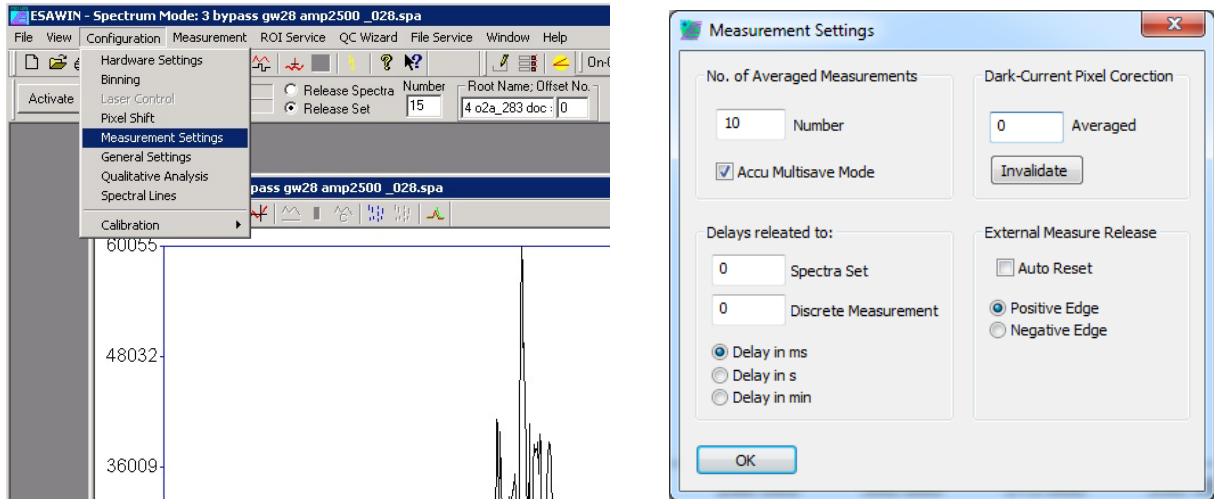


Fig.8. Measurement settings.

To extensively process and analyze spectra we use the Origin Pro software. You will be familiarized with required features and routines during the practical work, but feel free to download and try out the evaluation version here: <http://www.originlab.com/index.aspx?go=Downloads/OriginEvaluation>

You can install it on your PC and use in fully functional demo mode for 21 days.

2. Safety instructions

Many aspects of this practicum involve either the operation of fragile and sensitive equipment or handling of poisonous/flammable/explosive or otherwise hazardous materials.

In the event of any accidents occurring during your work first thing you should do is leave the lab and notify the personnel (although you will be supervised most of the time in the lab).

Ozone: subject to explosive decomposition (exothermic decay of O_3 to O_2), irritant, strong oxidizer. In our experiment we will deal with ozone concentrations up to 10% vol. It is thus necessary to wear safety masks during operations of gas pipes, cell facets etc.

Ethanol: flammable both as liquid and as vapor. Used as coolant circulating in the cell jacket.

Liquid Nitrogen LN_2 : a cryogenic liquid at $-195.79\text{ }^\circ\text{C}$ (77 K), can cause frost burns and suffocation (1 liter of liquid nitrogen will occupy about 650 liters as a gas once it has all vaporized).

Xenon and Deuterium lamps, LDLS: sources of intense UV radiation. It is not recommended to look directly at the lamp; safety glasses are required to avoid retina damage.

Spectrometer: might be damaged when wrong settings are applied. See above.

Questions 6.

1. Why is it desirable to maintain sub-atmospheric pressure in the cell?
2. What might happen if the cell cooled down to 203K is left with a gas mixture at a pressure of 900 mbar to warm up to 293K?

3. Tasks

In this work you will need to obtain the optical density spectra (which can be further scaled to the ozone cross-section spectra) around the 290-350 nm wavelength region. It is the region where spectral features are most noticeable and cross-section temperature dependence is most pronounced. The measurement will be done at room temperature of about 296K.

On the day of the practical work you will find the lab equipment in “warmed up” condition. Light source, spectrometer, and pumps will already be turned on. You will also be familiarized with other necessary lab devices. You will be assisted on performing some data processing operations in Origin Pro. Equipment-critical and dangerous tasks (spectrometer settings adjustment, pure ozone collection/sample preparation) will be performed by the supervisor.

Below is the typical sequence of actions necessary to obtain the ozone absorption spectrum.

a) Spectra acquisition

- **Stabilization of the light source**
 - Light source has to be on for at least half an hour prior to starting the measurements.
- **Collection of pure Ozone**
 - Using the condensation of ozone from the ozone-oxygen mixture flow from the ozone generator, a sufficient amount of pure ozone will be collected in a liquid nitrogen-cooled “cold trap”.
- **Determination of acquisition parameters**
 - Establish the level of amplification and gate width to obtain lamp spectra with reasonable peak counts (35 000 – 50 000)
- **Spectra acquisition - empty cell**
 - Record a set of spectra of the light source passing through the evacuated absorption cell.
- **Sample preparation - 1**
 - Release a small amount of ozone filling the cell up to 3-5 mbar pressure.
- **Spectra acquisition - low concentration (pressure) of the Ozone sample**
 - Record a set of spectra of the light source light passing through the cell filled with ozone gas sample at low pressure.
- **Sample preparation - 2**
 - Release an additional amount of ozone filling the cell to about 20-25 mbar pressure.
- **Spectra acquisition - high concentration (pressure) of the Ozone sample**
 - Record a set of spectra of the light source light passing through the cell filled with ozone gas sample at higher pressure.

b) Data evaluation

- i. **Conversion of the obtained spectra to ASCII files** is performed by ESAWIN.
- ii. **Import to Origin.** Using Origin Pro, import converted ASCII files into Origin and perform averaging of spectra obtained during measurements series. One of the products of the averaging routine in Origin is the “Standard Deviation of the Mean” value. It might be later used to estimate the error of the measurements.
- iii. **Calculation of the optical densities.** Using Beer-Lambert law, calculate optical densities for the obtained pairs of spectra: “empty”-“low O₃ pressure” and “empty”-“high O₃ pressure” (background should be individually estimated and subtracted from all three averaged sets of spectra).
- iv. **Concatenation** (using the “manual” and “Least Square Fit” approaches). After you get two OD spectra, perform a concatenation (up- or downscaling) based on the data available for both pieces in the wavelength region, where OD values lie within the 0.1-1 range. Routines will be explained on-site.

c) Conclusions

As a result of the completed tasks you will present two OD spectra, the results of their concatenation from two different approaches, and a set of uncertainty curves for mean spectra and calculated ODs. Major part of it will be performed on-site, with remaining processing and report compilation to be done at home.