Cavity Ring-Down Spectroscopy of Atmospheric Nitrogen Dioxide (NO_2) and Ozone (O_3)

Hendrik Fuchs (Forschungszentrum Jülich, University of Cologne)

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1 Preparation

1.1 Logistics

The experiment will be performed at Forschungszentrum Jülich in Jülich at the Institute for Energy and Climate Research, IEK-8: Troposphere. Please make an appointment to schedule time/date (e-mail: h.fuchs@fz-juelich.de, telephone: (02461) 61 6741). Before entering the campus, you need to register at the visitor centre at the main entrance of Forschungszentrum Jülich. A passport / ID-card is required for the registration.

1.2 Questions for preparation

Before performing the experiment, you should be prepared to answer the following questions:

- What is the measurement principle of cavity ring-down spectroscopy?
- Why is there only an effective path length for a photon inside the cavity?
- Which loss processes determine the ringdown time τ_0, when no absorber is present?
- How does CRDS spectroscopy compare to other absorption methods?

1.3 Literature

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2 Introduction

A large number of inorganic and organic gases are released into the atmosphere by anthropogenic activities for example by combustion processes, but also from plants. In fact, the largest fraction (approximately 90 %) of organic compounds is emitted by plants. These trace gases are transformed in our atmosphere by oxidation processes (often in several reaction steps) that lead to products that contain oxygen. These molecules can be small, chemically inactive molecules like carbon dioxide, but can also be larger oxygenated molecules such as acids that are water-soluble. Hydrophilic molecules that are produced can form particles or can condense on existing particles. Larger organic compounds are therefore eventually removed out of the atmosphere by rain or dry deposition after their chemical transformation. Although all these processes are cleaning the atmosphere from emitted trace gases, they have also negative consequences for air quality by causing secondary pollution like acidic rain, particles and ozone.

Nitrogen oxides ($NOx = NO + NO_2$) are mainly emitted from combustion processes in vehicles and power plants and are major air pollutants in urban areas. Primarily, nitric oxide (NO) is produced in the reaction of nitrogen atoms and

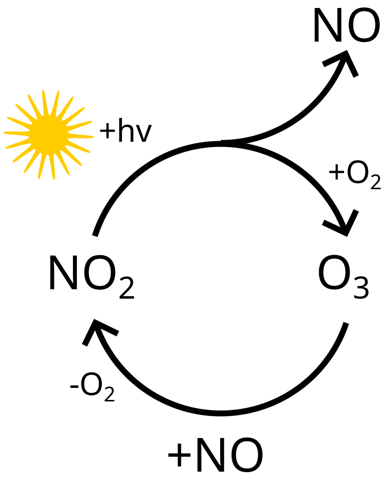


Figure 1: Equilibrium of atmospheric NO_2, NO and O_3.

oxygen atoms formed from the thermal decomposition of nitrogen and oxygen molecules at the high temperatures in the combustion process:

$$N_2 + O_2 + 180.62\,\mathrm{kJ} \rightleftharpoons 2\,\mathrm{NO} \tag{1}$$

At high concentrations in the exhaust, 2 nitric oxide molecules together with oxygen molecule can react to 2 NO_2 molecules. Catalytic converters made for example of platinum reduce substantially the NO concentration in the exhaust. In industrial exhaust treatment system and nowadays also in vehicles, a large fraction of NO_2 is removed in a selective catalytic reduction (SCR) catalyst that includes ammonia, which is produced from the thermal composition of liquid urea ("Add Blue").

In the atmosphere, NO, NO_2 and ozone O_3 concentrations are in a photo-stationary state. NO_2 is photo-labile and decomposes to NO and an oxygen atom, which further reacts with an oxygen molecule to ozone. NO_2 is reformed in the reaction of O_3 with NO:

$$\begin{aligned} NO_2 + h\nu\,(\lambda < 420\,\mathrm{nm}) + O_2 &\rightarrow NO + O_3 & (2)\\ NO + O_3 &\rightarrow NO_2 + O_2 & (3) \end{aligned}$$

Due to the fast reaction rate constant and photolysis rate, equilibrium concentrations ("photo-stationairy state") are established within minutes in sunshine conditions.

NO_2 is a hazardous gas that has a brown colour due to its strong absorption of light over a wid range of wavelengths in the visible region. Atmospheric mixing ration, however, are small (in the range of a few parts per billion, ppb) and even

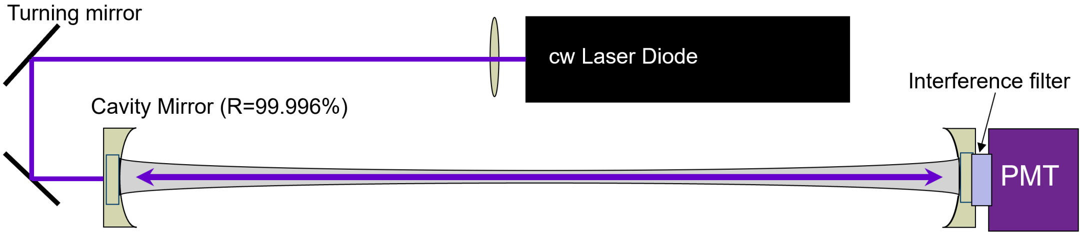


Figure 2: Schematics of the cavity ring-down instrument.

at high concentrations in exhaust plumes or in tunnels with high traffic, the absorption is too low to be visible for the human eye. NO_2 causes irritations of the respiratory system and increases symptoms in patients with asthma. Long-term exposure can lead to asthma and a decline of the lung function.

Therefore, NO_2 concentrations are regulated by law in most countries. In Europe, directives of the European commission set emission standards to limit the concentration of nitrogen oxides for example in the exhaust of power plants and vehicles. Air quality regulations also limit the maximum concentration of NO_2 to an average annual concentration of 20 ppb. Environmental authorities have a measurement network to monitor atmospheric NO_2 concentrations and governments must implement a plan to improve air quality, if limits are exceeded. In 2021, all monitoring stations in Germany were below the current limit, but even lower limits of 10 ppbv need to be met in 2030, which is still twice as high as recommendations by the World Health Organization.

3 Measurement principle

In the experiment, the concentrations of NO_2 and O_3 are determined using a cavity ring down system (CRDS). Cavity ring-down spectroscopy is an absorption technique, in which the temporal decay of light coupled into an optical cavity is observed (Fig. 2). Light of a pulsed laser is guided into an optical cavity. The cavity mirrors are highly reflective. Therefore, only a small fraction of the light is transmitted through the entrance mirror of the cavity, whereas the majority of light is reflected. In order to get light into the cavity, the mode of the light must match the cavity mode, e.g. the length of the cavity (= distance between the cavity mirrors, L) must equal a multiple whole number of half of the wavelength. In this instrument, the spectral width of the laser diode is approximately 0.5 nm, so that a large number of modes are available to fit the modes of the cavity. Behind the end mirror of the cavity, the intensity of the transmitted light is detected by a photomultiplier tube (PMT).

In cavity ring-down spectroscopy, the cavity is first filled with photons and then the light source is rapidly switched off. Photons in the cavity slowly "leak" out of the cavity due to the small transmission of the mirrors. If absorber molecules are present inside the cavity, the light is attenuated by absorption. In contrast to conventional absorption spectroscopy, however, there is no steady state condition reached, but the difference in the temporal behaviour of the transmitted light is compared. Eventually, the time constants with which the transmitted light decays with and without the presence of the absorber molecules are compared to determine the concentration of the absorber.

Analogue to the derivation of Lambert-Beer law, the change of the light intensity dI per length dl is described by the processes, with which the light is attenuated. Here, relevant loss processes include the transmission through the mirrors ($T = 1 - R$), Rayleigh scatter (cross section σ_{sc}, concentration of air molecules [M]) and absorption by various molecules $\mathrm{A_i}$ (cross section σ_i, concentration of absorber molecules $[\mathrm{A}_i]$). Mie scatter could add to the light loss. However, it does not play a role in this instrument, because particles are removed on a Teflon filter in the inlet or are not present in calibration gas mixtures.

$$\frac{dI}{dl} = -\left(\frac{1-R}{L} + \sigma_{sc}[\mathrm{M}] + \sum_i \sigma_i[\mathrm{A}_i]\right) I \tag{4}$$

Using the relationship $l = c \cdot t$ (c velocity of light), Equation 4 can be written as:

$$\frac{dI}{c \cdot dt} = -\left(\frac{1-R}{L} + \sigma_{sc}[\mathrm{M}] + \sum_i \sigma_i[\mathrm{A}_i]\right) I \tag{5}$$

The solution of this differential equation is a single-exponential decay function:

$$I(t) = I_0 \exp\left(-c\left(\frac{1-R}{L} + \sigma_{sc}[\mathrm{M}] + \sum_i \sigma_i[\mathrm{A}_i]\right) \cdot t\right) = I_0 \exp\left(-\frac{t}{\tau}\right) \tag{6}$$

The decay time τ is called ring-down time, which is is the lifetime of a photon in the cavity. A precise time-resolved measurement of the intensity of light leaking out of the cavity is needed to calculate the decay time.

In contrast to conventional absorption spectroscopy, there is no well-defined absorption path length, but an effective path length L_{eff} can be defined:

$$L_{eff} = c \cdot \tau \tag{7}$$

The value of the effective path length not only depends on instrumental parameters such as the reflectivity of the mirror and the length of the cavity, but also on the absorption of molecules present in the cavity. Typical ring-down times for high-performance instruments measuring the absorption of gases in the spectral range of visible light are several 10 to several 100 µs converting to effective absorption path lengths of several 10 to 100 km. This makes cavity ring-down spectroscopy a very sensitive absorption method.

In order to determine the concentration of one absorber molecule present in the cavity, the ring-down times with (τ) and without absorber (τ_0) are compared:

$$\begin{aligned}
\tau_0 &= c^{-1}\left(\frac{1-R}{L}+\sigma_{sc}[\mathrm{M}]\right)^{-1} && (8)\\
\tau &= c^{-1}\left(\frac{1-R}{L}+\sigma_{sc}[\mathrm{M}]+\sigma[\mathrm{A}]\right)^{-1} = \left(\tau_0^{-1}+c^{-1}\cdot\sigma[\mathrm{A}]\right)^{-1} && (9)\\
[\mathrm{A}] &= c^{-1}\cdot\sigma\left(\tau^{-1}-\tau_0^{-1}\right) && (10)
\end{aligned}$$

As can be seen from Equation 10, only 2 decay times need to be measured to calculate the concentration of the absorber. In contrast to conventional absorption spectroscopy, knowledge of the light instrumental parameters such as the intensity of the light source and length of the absorption pathway are not required to calculate the absorber concentration. This makes the method a robust measurement. However, to achieve a high precision, the cavity must be very stable and cleanliness of the mirrors must be maintained.

4 Experimental Setup

4.1 CRDS instrument

The CRDS instrument in this set-up consists of two approximately 50 cm long cavities. The cavity mirrors are highly reflective (reflectivity $R = 99.996\,\%$) and have a curvature radius of 1 m. The cavity mirrors are placed in holders that are mounted in adjustable mirror mounts.

The absorption cell between the cavity mirrors are made of stainless steel tubes that have a Silconert coating (outer diameter: 10 mm). The cavity tube and mirror mounts are connected via an O-ring connection that allows for a fine adjustment of the mirrors without putting mechanical stress to the tubes. All parts of the set-up are mounted on carbon fibre rods, which gives a stable structure with minimum temperature sensitivity.

The light source of the CRDS instrument is a blue laser diode with central wavelength of 405.4 nm (spectral width approximately 0.5 nm) and a maximum output power of 130 mW (class 3B laser). The laser is switch on and off by an external pulse which is generated by a National Instruments DAQ device. The

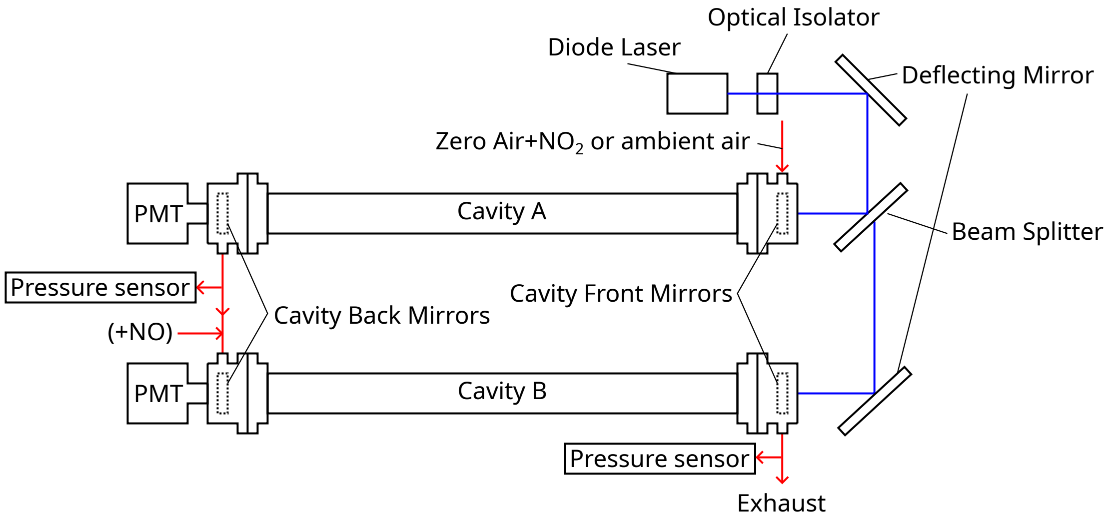


Figure 3: Set-up of the NO_2 CRDS instrument. The laser light path is indicated by blue lines and the path of the sampled air by red lines.

repetition rate is 2 kHz. The laser is 50 % on and 50 % off in each cycle (on/off duration: 250 µm).

After exiting the source, the laser beam passes an optical isolator, which consists of a combination of a polariser (Glan-Taylor prism) and a $\lambda/4$ plate. The latter rotates the polarization of the beam, so that any back-reflected light from optical components behind the optical isolator is blocked. Back-reflection of light into the laser could damage the laser diode. After reflection at a deflection mirror, the laser beam is guided into the cavities by 2 more deflection mirrors. The first one is a beam splitter, which splits the laser light approximately in half in intensity.

The laser light is coupled into the cavity through the front mirror of the optical cavity. Due to the high reflectivity the majority of the light is reflected and only a small fraction enters the cavity. This is the main reason, why the optical isolator is required to protect the laser diode.

At the opposite end, the a photomultiplier tube (PMT, Hamamtsu, 9-stage dynode structure) is mounted behind the end mirror of the cavity detecting the small amount of light that is transmitted by the cavity. A bandpass filter (Filtrop, central wavelength: 405 nm) in front of the PMT ensures that only light at the wavelength of the laser is detected.

The detected current signal of the PMT is electronically converted into a voltage signal and amplified and eventually measured by an oscilloscope computer card (National Instruments, 16bit resolution) with a sampling rate of 1MHz giving a time resolution of the recorded signal of 1 µs. The recorded signal is averaged over

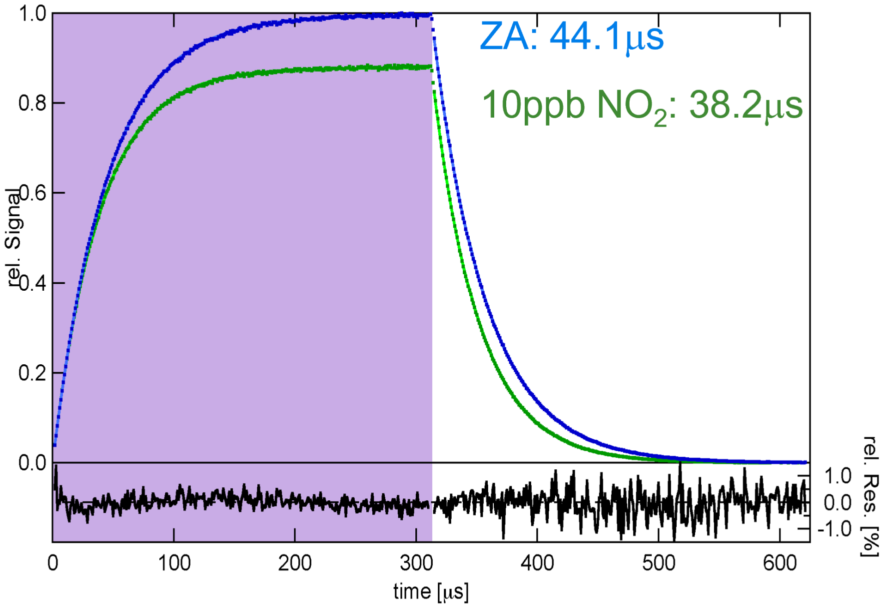


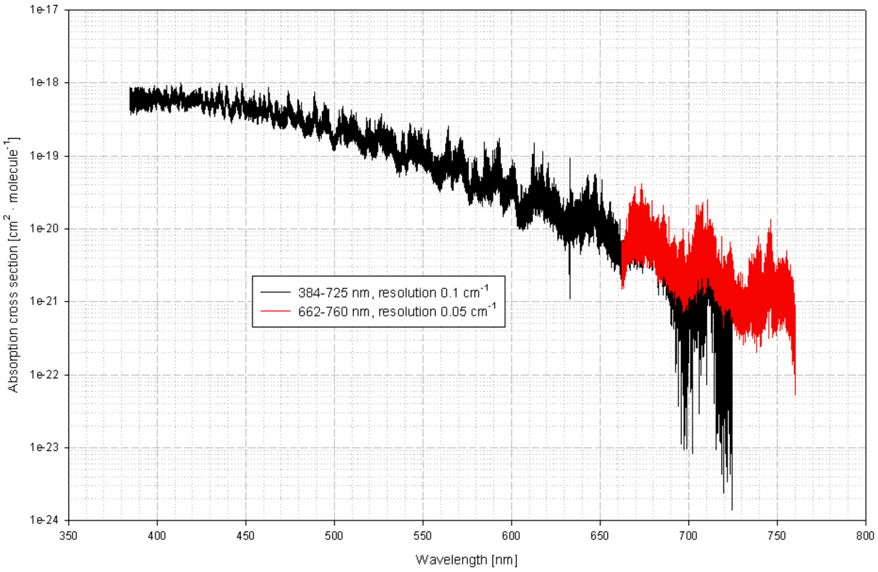
Figure 4: CRDS decay curves with and without the presence of NO_2 as absorber in the cavity. Note that ring-down times are approximately twice as high as in the set-up in this experiment, because a longer cavity was used.

2,000 on-off cycles of the laser in the operating software and thus, the effective time resolution of the measurement is 1 s.

The absorption cross section of NO_2 has a broad maximum around 400 nm (Fig. 5). The central wavelength of the laser of 405.4 nm is within that range allowing for the detection of NO_2 in the cavities by absorption. At lower wavelengths, photo-dissociation of NO_2 could happen that could introduce systematic errors in the measurement. At higher wavelengths, concurrent absorption of ozone gains in importance, so that the measured absorption could not be unambiguously attributed to NO_2 in ambient air measurement, if the concentration ratio of O_3 to NO_2 is high.

Figure 4 shows an example of a measurement of two decay curves in a CRDS instrument with and without the presence of NO_2 in the cavity. The ring-down time is determined by fitting the measured decay of the light leaking out of the cavity to a single-exponential decay function using a non-linear fit method (Levenberg-Marquard algorithm). Fitting is directly done in the operational software, which displays the fit result.

In the experiment, either synthetic air (79 % nitrogen, 21 % oxygen) containing nitrogen dioxide (NO_2) or ambient air is flowed through the cavity. Air is sampled through Teflon tubes (outer diameter: 6 mm or 0.32 mm). Teflon is a chemically inert material, so that the chemical composition of the air is not changed by wall



Ultra-high resolution absorption cross sections of nitrogen dioxide NO_2 at 294 K,
Vandaele et al., J. Geophys. Res. 107 (D18, 4348, doi:10.1029/2001JD000971) (2002) ACH 3-1

Figure 5: Absorption Cross Section of NO_2 in the 384-758nm range.

loss of reactive molecules.

In both cavities of the instrument the absorption at 405 nm is measured to detect NO_2. In the first cavity, the air composition is not altered. Between the 2 cavities, a small of air containing a high concentration of nitric oxide (NO) can be injected. If ozone is present in the sampled air, NO reacts with O_3 and chemically converts it to NO_2. The differential equation describing the change of the ozone concentrations is

$$\frac{\mathrm{d}[\mathrm{O}_3]}{\mathrm{d}t} = -k_{\mathrm{O3+NO}} \cdot [\mathrm{NO}][\mathrm{O}_3] \tag{11}$$

$k_{\mathrm{O3+NO}}$ is the bimolecular reaction rate constant of the reaction. The concentration of NO is much higher than that of O_3 in the sampled air, so that the reaction is pseudo first-order and the solution is:

$$[\mathrm{O}_3] = [\mathrm{O}_3]_0 \cdot \exp -k_{\mathrm{O3+NO}}[\mathrm{NO}]]t \tag{12}$$

The reaction time in the instrument is chosen, such that all ozone is converted before the air enters the second cavity. Therefore, the sum of NO_2 and O_3 is detected as NO_2 in the second cavity. The difference in the measured NO_2 concentration in both cavities gives then the initially present ozone concentration in the sampled air.

All flows are controlled by mass flow controllers (Bronkhorst El-Flow) that are digitally controlled and that provide highly precise and accurate flows of all gases in the experiment. Settings of the flows are done in the operational software. Additional sensors monitor the pressure in the cavities.

4.2 Software operation of the CRDS instrument

Figure 6 shows the graphical user interface (GUI) of the software written in LabView *NOxCaRD.vi* that is used to operate the instrument. You can find it in the Documents folder of the computer connected to the instrument. When opening the LabView software, the Labview programming environment (IDE) opens. To run the software, press the Run button in the IDE.

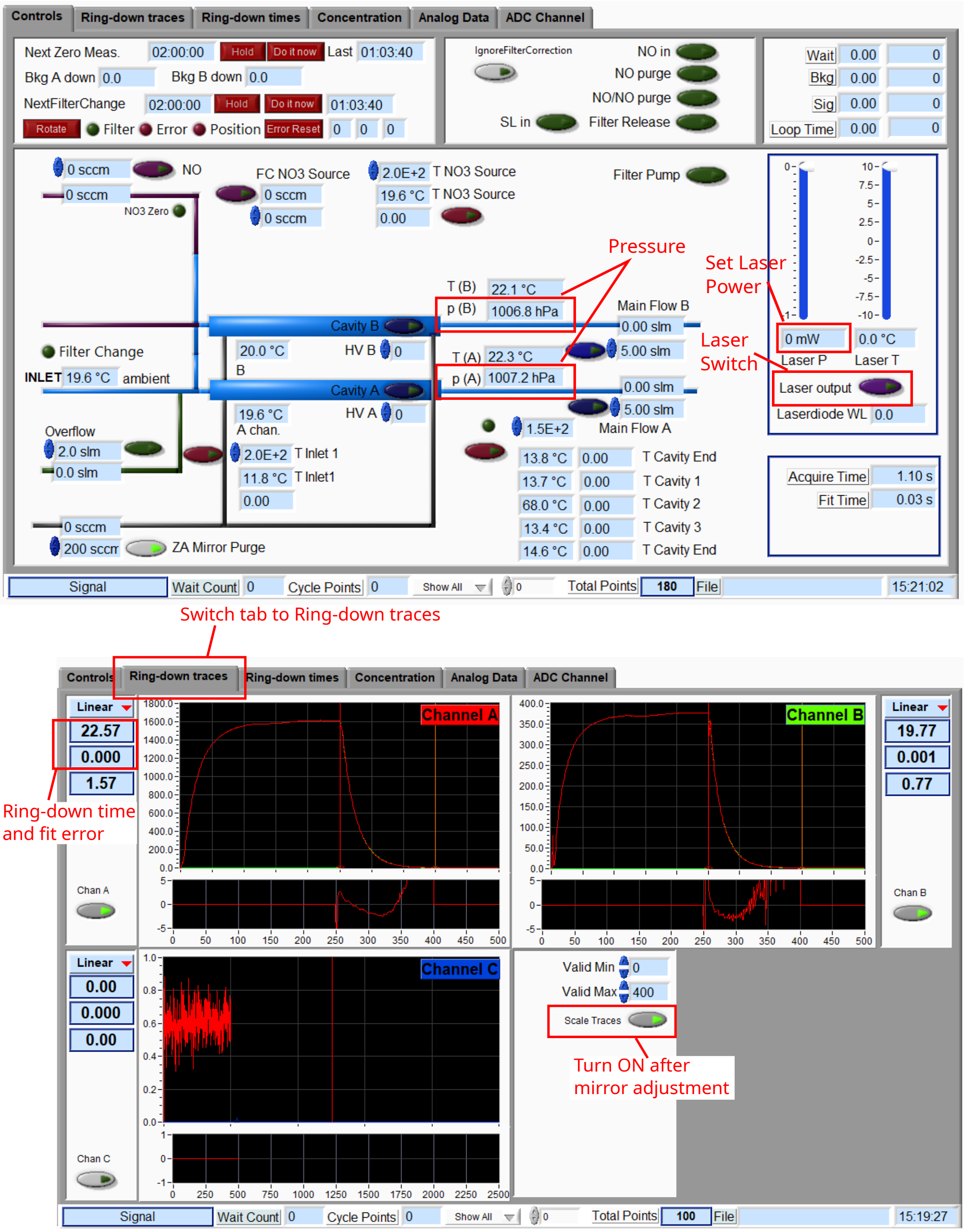
After a initialisation procedure, the readings of the pressure sensors behind each of the two cavities is displayed and the laser can be switched on, if the key lock switch at the power supply of the laser is turned on. A low laser power of 5 mW is sufficient and recommended for the measurements in this experiment.

The GUI of the software has several tabs. On the first tab, all switches for operating the instrument are displayed (Fig. 6). On the second tab *Ring-down traces*, ring-down traces and fit results of the decay times are displayed. “Set Traces” button is switched off until the mirror adjustment is finished. A mouse right-click on the y-axis opens a menu, which allows to do settings of the display like auto scaling of the axis, which can be useful while optimizing the cavity adjustment.

The PMT need a high voltage supply to amplify the signal. The photo-sensitive area of the PMT needs to be protected against bright light. Direct laser light without the cavity must not enter the PMT. The high voltage should only be turned on after checking that it is safe to turn it on. The high voltage can be set by software between 0 and 100 % of the maximum voltage (1 kV. As a second security measure, a shutter is mounted between the cavity mirror and the PMT.

The high voltage supply is turned on via a separate command line programme. The commands can be found in Fig. 7. To turn the PMT on, the following steps are necessary:

- Open the shutter on each PMT
- Open a command prompt window
- Change the working directory
- Switch on the PMTs
- Set high voltage to an initial value of 40 %



Next Zero Meas. 02:00:00 Last 01:03:40
Bkg A down 0.0
Bkg B down 0.0
NextFilterChange 02:00:00 01:03:40
Filter
Error
Position 0 0 0
NO in
NO purge
NO/NO purge
SL in
Filter Release
Wait 0.00 0
Bkg 0.00 0
Sig 0.00 0
Loop Time 0.00 0
NO 0 sccm
0 sccm
NO3 Zero
FC NO3 Source 0 sccm
0 sccm
T NO3 Source 2.0E+2
T NO3 Source 19.6 °C
0.00
Filter Pump
T (B) 22.1 °C
p (B) 1006.8 hPa
Main Flow B 0.00 slm
5.00 slm
Cavity B
20.0 °C B
HV B 0
T (A) 22.3 °C
p (A) 1007.2 hPa
0.00 slm
5.00 slm
Main Flow A
1.5E+2
Cavity A
19.6 °C A chan.
HV A 0
Filter Change
INLET 19.6 °C ambient
Overflow
2.0 slm
0.0 slm
T Inlet 1 2.0E+2
T Inlet1 11.8 °C
0.00
0 sccm
200 sccm ZA Mirror Purge
T Cavity End 13.8 °C 0.00
T Cavity 1 13.7 °C 0.00
T Cavity 2 68.0 °C 0.00
T Cavity 3 13.4 °C 0.00
T Cavity End 14.6 °C 0.00
Laser P 0 mW
Laser T 0.0 °C
Laser output
Laserdiode WL 0.0
Acquire Time 1.10 s
Fit Time 0.03 s
Signal Wait Count 0 Cycle Points 0 Show All 0 Total Points 180 File 15:21:02

Pressure

Set Laser Power

Laser Switch

Switch tab to Ring-down traces

Channel A: Linear 22.57 0.000 1.57

Channel B: Linear 19.77 0.001 0.77

Channel C: Linear 0.00 0.000 0.00

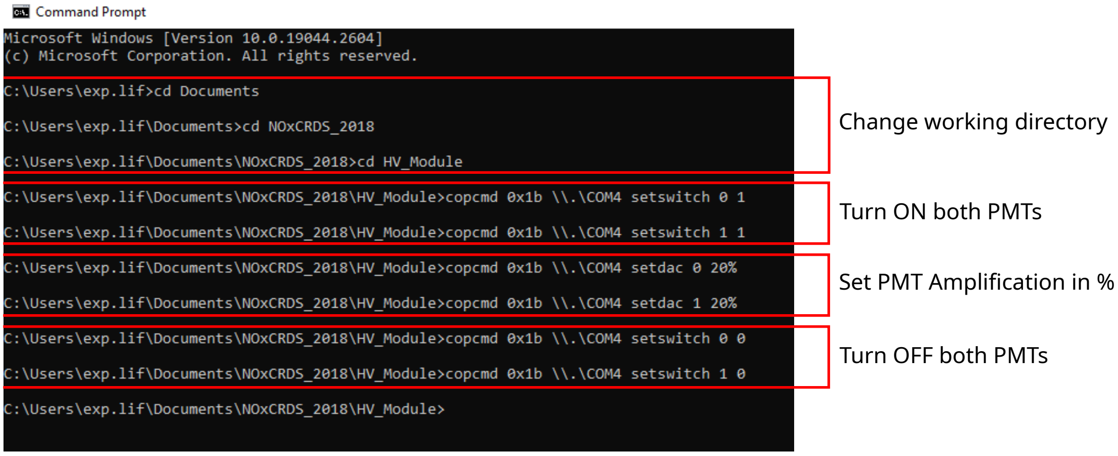
Ring-down time and fit error

Valid Min 0
Valid Max 400
Scale Traces

Turn ON after mirror adjustment

Signal Wait Count 0 Cycle Points 0 Show All 0 Total Points 100 File 15:19:27

Figure 6: GUI of the LabView software “NOxCaRD” for operating the CRDS instrument.



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Microsoft Windows [Version 10.0.19044.2604]
(c) Microsoft Corporation. All rights reserved.

C:\Users\exp.lif>cd Documents

C:\Users\exp.lif\Documents>cd NOxCRDS_2018

C:\Users\exp.lif\Documents\NOxCRDS_2018>cd HV_Module

C:\Users\exp.lif\Documents\NOxCRDS_2018\HV_Module>copcmd 0x1b \\.\COM4 setswitch 0 1

C:\Users\exp.lif\Documents\NOxCRDS_2018\HV_Module>copcmd 0x1b \\.\COM4 setswitch 1 1

C:\Users\exp.lif\Documents\NOxCRDS_2018\HV_Module>copcmd 0x1b \\.\COM4 setdac 0 20%

C:\Users\exp.lif\Documents\NOxCRDS_2018\HV_Module>copcmd 0x1b \\.\COM4 setdac 1 20%

C:\Users\exp.lif\Documents\NOxCRDS_2018\HV_Module>copcmd 0x1b \\.\COM4 setswitch 0 0

C:\Users\exp.lif\Documents\NOxCRDS_2018\HV_Module>copcmd 0x1b \\.\COM4 setswitch 1 0

C:\Users\exp.lif\Documents\NOxCRDS_2018\HV_Module>
```

Figure 7: Commands to switch on the high voltage supply of the PMT.

The high voltage can be increased to adjust the amplitude of the decay curve. The amplitude must not exceed values of $\pm 2000\,\mathrm{mV}$, because the electronics that is connected to the PMT signal cannot handle higher voltage values.

After the experiment: Switch off the PMTs and close the shutters! Turn off the laser by turning the key lock switch. Ensure that all gas cylinders are closed.

5 Experimental procedure

5.1 Optimization of the cavity alignment by adjusting the cavity mirrors and measurement of the zero ring-down time

The mirrors of the cavities are already pre-aligned, so that the laser beam is coupled into the cavity and a decay curve can be measured. With increasing quality of the alignment, the amplitude of the measured signal and the ring-down time in the cavity increase. The precision of the measurement and thus the ability to measure low concentrations increases with increasing ring-down time.

In a first step a optimization of the cavity mirrors shall be performed to improve the quality of the measurement. The mirrors are adjusted by adjusting precision screws at the mirror holders. These are located on the cavity side of the cavity mirror mounts (Fig. 8).

Screws tilt the mirror around one axis, thus turning them change the direction of the reflected beam and the position, where the beam hits the opposite mirror. The upper most screw changes the vertical position, the lower outer screw the horizontal position. The third screw in the corner tilts the mirror around a diagonal

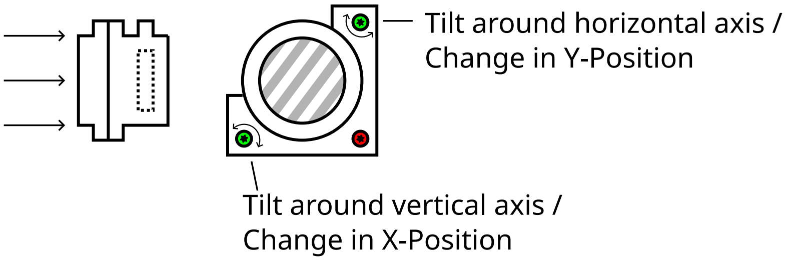

Figure 8: Schematics of the mirror mounts holding the cavity mirrors. Screws used to optimize the cavity alignment are indicated by green dots.

axis and should not be used for the alignment of the cavity. Optimization is achieved in iterative way by turning one screw after the other to the position at which the signal is highest and the ring-down time longest.

The optimization should be performed, while the inlet of the instrument is over-flowed with clean synthetic air controlled by a mass flow controller. Air is sucked into the cavity by a second flow controller. The flow rate of the zero air must be higher than the flow rate of the air sampled by the instrument to ensure that no air from the laboratory is mixed into the clean air. In this way also the zero ring-down time can be measured.

Task 1: Optimize the ring-down time.

Task 2: Measure the zero ring-down time. Calculate what the zero ring-down time would be, if there was no Rayleigh scatter from air molecules. Estimate the limit of detection for the measurement of NO_2 concentration from the noise of the zero measurement.

5.2 Measurement of NO_2 concentrations

5.2.1 Measurement of NO_2 concentration in synthetic air

In this experiment, the synthetic air used for measuring the zero ring-down time is mixed with a small flow of air containing a known concentration of NO_2. The flow is controlled by a mass flow controller and can be systematically varied to change the NO_2 concentration in the sampled air. Stable conditions should be reached within minutes.

Task 3: Determine the concentration of NO_2 in the gas bottle from measurements of NO_2 with different flows from the NO_2 bottle that is mixed into a constant (high) flow of synthetic air. Make use of a linear regression analysis. Choose an appropriate number of dilution steps.

5.2.2 Measurement of NO_2 and O_3 in ambient air

The inlet of the instrument can be switched from sampling synthetic air to ambient air to measure the NO_2 and O_3. Switch on the flow controller to inject NO between the 2 cavities.

Task 4: Sample 20 to 30 min ambient air and calculate NO_2 and O_3 concentrations from the time series of measured ring-down times. Ensure that the NO concentration and time for the conversion reaction is sufficient to completely convert O_3 to NO_2. Plot time series of concentrations and explain your observations.

5.3 Parameters needed for the evaluation of results

- Absorption cross section NO_2 @405.4 nm: $\sigma_{\mathrm{NO2}} = 6.09 \cdot 10^{-19}\,\mathrm{cm}^2$
- Rayleigh scatter cross section air @405.4 nm: $\sigma_{air} = 1.605 \cdot 10^{-26}\,\mathrm{cm}^2$
- Temperature dependent reaction rate constant of the NO_2+O_3 reaction: $k_{\mathrm{O3+NO}} = 2.07 \cdot 10^{-12} \exp\left(-1400/T\right)\mathrm{s}^{-1}\mathrm{cm}^3$

6 Security

Various potential hazards must be taken into account during the experiment.

Nitrogen oxides are irritant gases which can irritate the respiratory tract. Therefore, gas warning devices must be used when working with nitrogen oxides in order to detect possible leakages of the measurement setup. No hazardous concentrations will be reached in the laboratory during regular operation.

With a maximum power output of 130 mW the diode laser used is a class 3B laser. This makes the use of laser safety goggles mandatory when working with the experimental setup. A direct view into the beam path or specular reflections with the unprotected eye and contact with the skin by reaching into the beam path must be avoided. The set-up is made such that only little laser stray light is visible during regular operation.

The PMTs are operated with high voltage, so that no changes of the set-up of the PMT should be done by without advice of a supervisor.