Laboratory Report Rayleigh-Scattering

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Contents

1 Introduction **3**

2 Theory **3**
2.1 Cavity Ring-down Spectroscopy 3
2.2 Rayleigh-scattering 4

3 Experimental setup and technique **4**
3.1 Setup 4
3.2 Technique 6

4 Experimental procedure **6**

5 Analysis **7**

6 Discussion **10**

7 Sources **10**

1 Introduction

Rayleigh-scattering is the scattering of light on objects, which are much smaller than the lights wavelength. Observations in nature include for example the blue sky or a reddish sunset. Those phenomenons arise, because the sunlight scatters on particles in the atmosphere, which then emit light of a specific wavelength[1]. This experiment uses cavity ring-down spectroscopy to detect Rayleigh-scattering of a laser pulse on air particles, which will be used to determine the scattering coefficient.

2 Theory

2.1 Cavity Ring-down Spectroscopy

Cavity Ring-down Spectroscopy (CRDS) is a relatively sensitive form of spectroscopy[2]. There are different types of CRDS [2]. This protocol will focus on the laser pulse variant, since it is the variant used in the experiment.

Generally in CRDS a light pulse is coupled into a cavity consisting of two high reflecting mirrors[2]. High reflecting means in this case that 99 % or more of the light is reflected while the rest passes through the mirror. The reflectivity R of the mirror would be then $R = 0.99$. Because of this the intensity of the light inside the cavity and also the intensity of the light passing through the mirrors is decreasing over time. As mentioned, a light pulse is used as a source in CRDS [2]. To have control over the wavelength and to be able to compare the results with theoretical values, a laser pulse with a fixed wavelength is used in this particular setup[1]. In this case the intensity of exiting light can be written as[1]:

$$I(t) = I_0 e^{-\frac{t}{\tau}} \tag{1}$$

where I_0 is the input intensity and τ the decay constant which is called the ring-down time.

The ring-down time logically depends on the reflectivity of the mirrors because if more light can escape the cavity the decay of the intensity will be bigger. But there can also be a decay in intensity caused by scattering in form of absorption or similar. This happens if the cavity is filled with something that's interacting with the light, usually some gas, as in this case. Then the interacting photons don't reach the 'exit' mirror which is then detected as a greater decay in intensity[1,2].

The ring-down time can generally be written as[2]:

$$\tau(\nu) = \frac{L}{c(|\ln[R(\nu)]| + \sum_i \sigma_i(\nu) \int_0^l N_i(x)dx)} \tag{2}$$

where ν is the frequency of the light, L the length of the cavity, c the speed of light, R the mentioned reflectivity, σ the cross sections of the gas molecules and atoms and N a number density of the gas inside the cavity.

As a laser with a fixed frequency is used, the frequency dependencies can be neglected so $|\ln[R(\nu]|$ becomes an effective reflectivity $|\ln(R_{eff})|$. Since $R_{eff} \approx 1$, the logarithm can be expanded in a Taylor series around 1 so that[2]

$$|\ln(R_{eff})| = |R_{eff} - 1| = 1 - R_{eff} = 1 - R$$

because R_{eff}, conveniently R, can't be greater than 1.

When the whole cavity is equally filled with the scattering species, $N(x)$ becomes constant and l becomes L, so that[2] $\int_0^l N_i(x)dx = N \cdot L$.

The product $N \cdot \sigma(\nu)$ is generally expressed as $\beta(\nu)$ and is called the scattering coefficient, which will be discussed in the next section. Everything together plugged into equation 2 gives:

$$\tau(\nu) = \frac{L}{c[1 - R + \beta(\nu)L]} \tag{3}$$

From this equation it is clear that if there is vacuum in the cavity, the ring-down time only depends on the reflectivity R, because $\beta(\nu) = 0$. The ring-down time with vacuum in the cavity is called τ_0.

$$\tau_0(\nu) = \frac{L}{c[1 - R]} \tag{4}$$

It follows that $L = \tau_0(\nu)c[1 - R]$. Plugged in into equation 3 one can show that

$$\beta(\nu) = \frac{\tau_0(\nu) - \tau(\nu)}{c\tau_0(\nu)\tau(\nu)} = \frac{1}{c}\left(\frac{1}{\tau(\nu)} - \frac{1}{\tau_0(\nu)}\right) \tag{5}$$

So with two ring-down time measurements, one measured in a vacuum and one with the gas, which is to be examined, in the cavity, the scattering coefficient in the gas can be experimentally determined.

2.2 Rayleigh-scattering

In the linear scattering theory, the total power scattered by one particle is proportional to the intensity of the incident light[1]. The proportionality factor is the already mentioned scattering coefficient

$$\beta(\nu) = \sigma N \tag{6}$$

In the Rayleigh-scattering theory, the scattering of light on a molecule is approximated by a Hertzian-dipole, because the oscillating electromagnetic field (light) induces an oscillating dipole, by displacing the charged components of the molecule [3]. The dipole then emits electromagnetic waves with the same frequency as the incoming light, but in another direction. The intensity of the emitted light is maximal for the direction orthogonal to the direction of the induced dipole, with no light being reflected along the axis the dipole oscillates along [9] It can then be shown through classical electrodynamics that the scattering coefficient in this approximation is given by[2]

$$\beta(\lambda) = \frac{8\pi^3(n^2 - 1)^2}{3N\lambda^4} \tag{7}$$

Here λ is the wavelength of the incoming light and n is the refractive index. The proportionality of $\beta \propto \lambda^{-4}$ can be used to explain the blue sky, because blue light is the visible light with the smallest wavelength, which makes up a big portion of the sunlight. A smaller wavelength leads to a bigger scattering coefficient, which leads to more power scattered, so we see a lot of blue light. Technically violet light would have an even smaller wavelength, but the emitted light from the sun has more blue light than violet light[4].

This scattering is used in this experiment in the following way: The intensity of light escaping a cavity with two highly reflective mirrors is measured for vacuum and for air. In the vacuum the light does not scatter on any particles. For air, the light scatters on the air molecules, which leads to the light being scattered in random directions, because the direction of the induced dipole is basically random for a lot of particles. Therefore, less light exits the cavity and the measured intensity is lower for air.

3 Experimental setup and technique

3.1 Setup

The setup for this experiment can be seen in figure 1. A laser operating in pulsed regime (wavelength $\lambda \approx 405$ nm, repetition rate up to 100 Hz)[1] is pointing towards to optical cavity, which consists of two curved and highly reflective mirrors, which are $L = 50$ cm apart[1]. The curvature of these mirrors has a radius of $r = 1$ m, which leads to a stable optical resonator. For an optical resonator to be stable, it has to fulfill the stability criterion[2]

$$0 \leq L \leq r \qquad \text{or} \qquad r \leq L \leq 2r \tag{8}$$

This is obviously fulfilled in this setup. A vacuum pump and a syringe filter are attached to the cavity via two valves. The vacuum pump is used to create a vacuum, the syringe filter is able to remove bigger aerosol particles in the air, to get clean air for the measurement[1]. A photomultiplier (PM in fig. 1) multiplies the photons, which escape the cavity, so that they can be detected by the digital oscilloscope. The signal the oscilloscope recieves can then be seen in the GPIB interface on the attached PC. An additional delay generator attached to the laser and the oscilloscope ensures that the data aquisition is timed right.

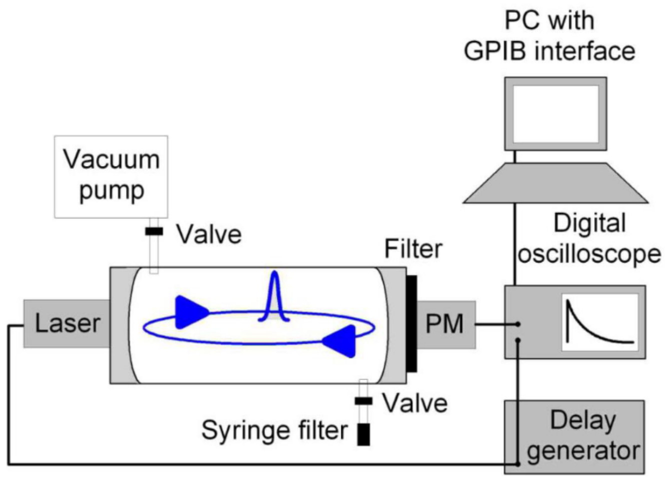

Figure 1: Schematic setup for Cavity Ring-down spectroscopy [1]

In Fig. 2 one can see the setup which was used for this experiment. The laser (1) is connected to a PC, where the rate and the intensity can be controlled via a software. Next to the laser there are two pinholes (3,4), which can be used to focus the laser and help with the adjustment. The cavity (5) consists of two mirrors on the inside of each side of it, which can be adjusted with two screws per mirror. On top of the cavity there are the two valves, one connected to a vacuum pump and the other connected to the room, and a barometer, which shows the pressure inside of the cavity. The exit of the cavity is connected to the photomultiplier (6), which sends the signal to the a digital oscilloscope (2).

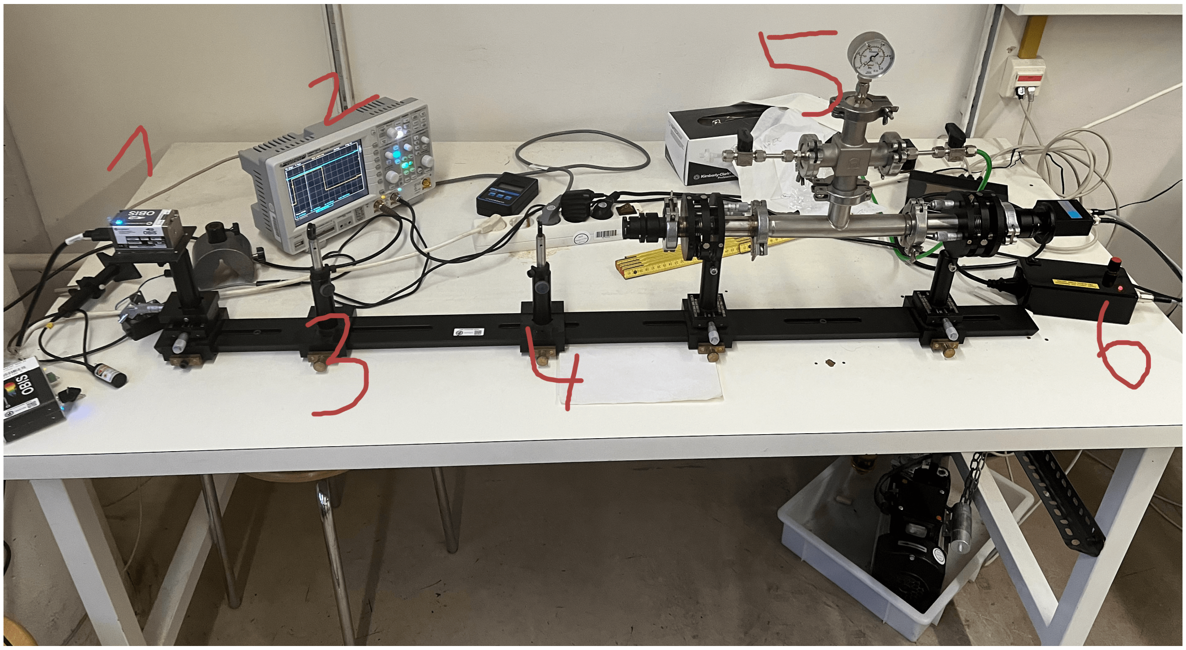

Figure 2: Experimental Setup

3.2 Technique

A light pulse of the laser gets trapped inside the cavity. The decay of the intensity of the exiting light can then be measured by the digital oscilloscope and plotted in the GPIB interface. This approach has the advantage, that inaccuracies in the laser pulse frequency do not matter[2]. Another advantage of CRDS is that there are no requirements, such as ionization or fluorescence, for the examined gas[2]. A disadvantage of CRDS is, that it is hard to calibrate[2], which is why there is an additional continuous fluorescence laser in this experiment, which helps with calibrating the path of the pulsed laser light[1].

The decay of the intensity will be in the form of Eq. (1), which enables one to determine τ, through linearization:

$$\ln[I(t)] = \ln(I_0) - \frac{1}{\tau}t \tag{9}$$

If the left side of Eq. (9) gets plotted over the time t, one will get a linear function with a slope of $-1/\tau$. With two values of the ring-down time, one for vacuum and the other one for air inside of the cavity, Eq. (5) can be used to calculate the scattering coefficient. This value will later be compared to a theoretical value, which will be attained by Eq. (7).

4 Experimental procedure

Before the start of the measurement, the setup has to be adjusted, such that the laser is perfectly aligned with the cavity and the signal reaches the oscilloscope. For this adjustment the photomultiplier is not connected to the exit of the cavity and there is a vacuum inside of it. A green laser is used for this adjustment, because the green light is more visible for the eye. The height, position and angle of the laser are set up in a way that the following requirements are met:

- Light goes trough the middle of both pinholes and enters the cavity in the center

- The light which is reflected back from the entrance of the cavity is also centered on the pinhole next to it.
- The light exits the cavity in the center, which can be checked by holding a piece of paper over it
- No light gets reflected orthogonally to the setup from the pinholes

Now the green laser gets swapped for the 405 nm laser and the photomultiplier is connected to the exit of the cavity. The mirrors get adjusted with the screws until the oscilloscope registers a signal, which fills the whole sreen on the oscilloscope. The intensity of the laser and the photomultiplier aswell as the scaling of the oscilloscope screen are kept constant during the measurements.

The intensity of the light exiting the cavity is measured six times for an air filled cavity and six times with vacuum. However, the intensity is measured alternatingly between air and vacuum. The intensity curve the oscilloscope measures is sent to a LabView-program on the PC. Switching from vacuum to air is done in the following way: Letting air flow in the cavity leads to small changes in the setup, which results in losing the signal on the oscilloscope. Because of that a smaller amount of air is admitted into the cavity first, which only messes up the signal on the oscilloscope a little bit. Doing this, one can retreive the signal everytime a portion of air is let into the cavity until the cavity pressure is equal to the atmospheric pressure, without losing the signal entirely. The same process is used to switch from air to vacuum.

5 Analysis

As described in the procedure, five measurements of the ring-down time were performed for both air and vacuum in the cavity. Since the same method was applied to all datasets, the procedure will be explained using an example, followed by the results of the other measurements. The example is the first measurement for air (Air_1)
First, the dataset is plotted (Fig.3). Here, the y-values, which represent the intensities, are multiplied by -1 to display the image correctly, as the oscilloscope does the same when collecting the data.

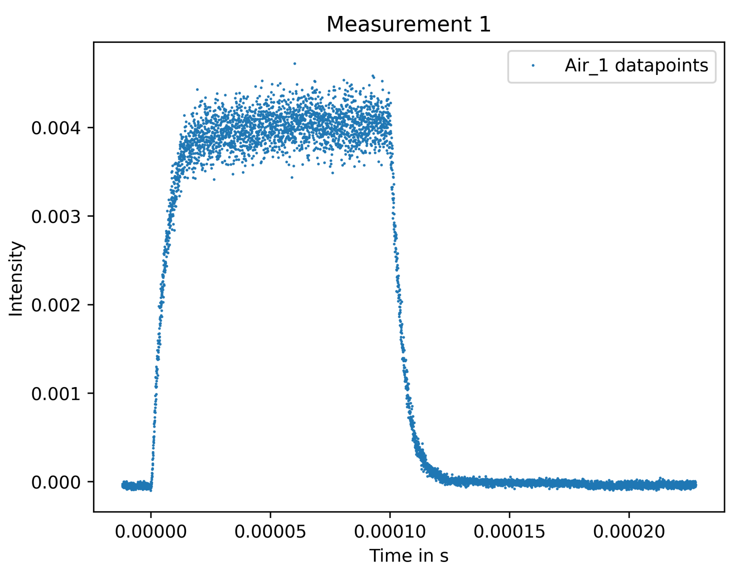

Figure 3: Datapoints of first measurement with air

The noise at the beginning is then cut off, and the remaining data is displayed in a semilogarithmic (semilogy) plot (Fig.4). The semilogy plot is used to identify the region where the function corresponds to an exponential function since the y-axis is logarithmic, transforming the exponential function into a straight line. One can see that from around 0.00012 s the spread of the measured values becomes so large that a clear straight line can no longer be determined. Therefore, the measured values to the right of 0.00012 s are cut off (this applies to all measurement series).

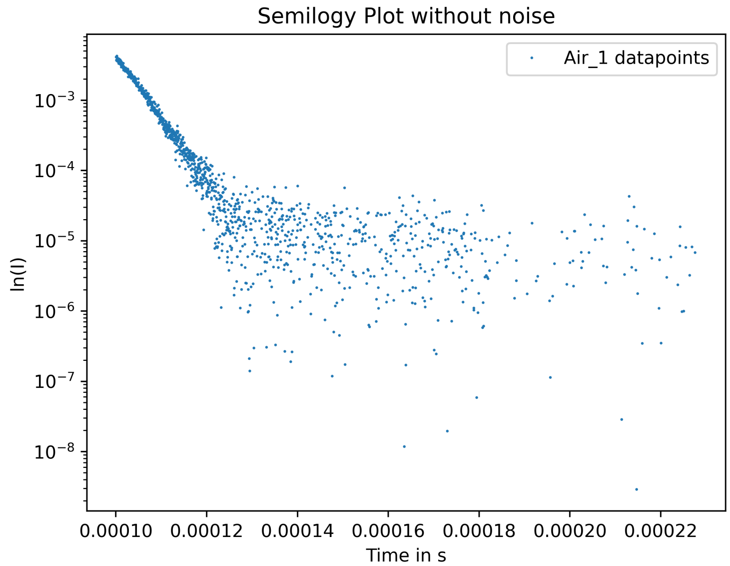

Figure 4: Semilogy plot of datapoints of first measurement with air

It is assumed that the selected region is described by the function from Equation (9). Next, the slope of the straight line in the semilogy plot, and thus the exponent of the exponential function, is determined using linear regression (Fig.5).

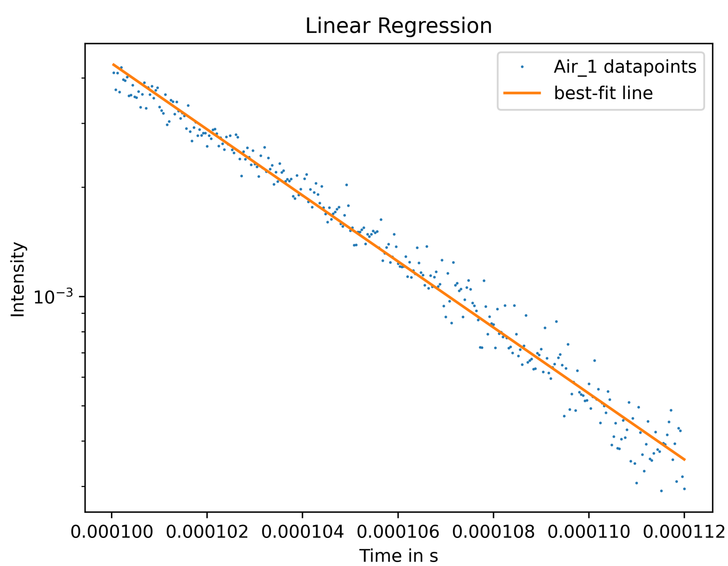

Figure 5: Linear regression of first measurement with air

The desired ring-down time τ is the reciprocal of the determined slope.
Since the measurement errors of the setup are not known, the mean value is calculated from the five data series for each condition in the cavity, and the standard deviation is used as the error for this result. The following ring-down times are obtained:

$$\tau_{air} = \tau = (5.1 \pm 0.2) \cdot 10^{-6}\ \mathrm{s} \qquad \tau_{vac} = \tau_0 = (5.7 \pm 0.2) \cdot 10^{-6}\ \mathrm{s} \tag{10}$$

In Figure 6 all best-fit lines are plotted for comparison. The difference between the measured ring-down times with vacuum and air is clearly visible.
Using these two results, the scattering coefficient β can now be calculated with Equation (5):

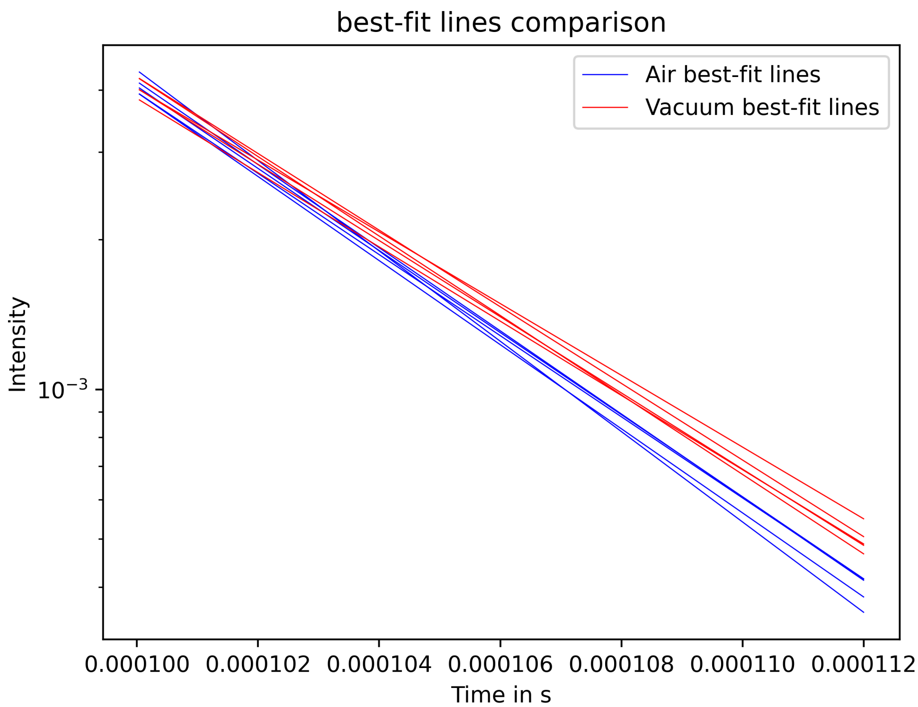

Figure 6: Comparison of best-fit lines of vacuum and air

$$\beta = \frac{1}{c}\left(\frac{1}{\tau(\nu)} - \frac{1}{\tau_0(\nu)}\right) = (7 \pm 4) \cdot 10^{-5}\frac{1}{m} \tag{11}$$

Where $c \approx 3 \cdot 10^9 \mathrm{ms}^{-1}$
The error is obtained through Gaussian error propagation which gives:

$$\Delta\beta = \frac{1}{c}\sqrt{\left(\frac{\Delta\tau}{\tau^2}\right)^2 + \left(\frac{\Delta\tau_0}{\tau_0^2}\right)^2}$$

The theoretical value for comparison is obtained from Eq. (7), where the refractive index of air[7] at STP is given by $n \approx 1,000283$ and the wavelength of the laser by $\lambda \approx 405$ nm. These values are assumed to be exact, because the other measured values have much bigger errors and the for the wavelength there is no more information in the given documents. The number density N is obtained via the ideal gas law with $N = \frac{p}{\mathrm{R}T}$, where p is the pressure, R is the universal gas constant and T is the temperature. Pressure und temperature were measured as $p = (1024 \pm 2)$ hPa and $T = (295,1 \pm 0,1)$ K.

The uncertainty for the temperature comes from a reading error and the uncertainty for the pressure is given by the uncertainty of the measurement device *GPB 3300 Behringer Barometer*[6]. Thus the error for the number density and the scattering coefficient can be calculated as follows with Gaussian error propagation

$$\Delta N = \sqrt{\left(\frac{\Delta p}{\mathrm{R}T}\right)^2 + \left(\frac{p}{\mathrm{R}T^2}\Delta T\right)^2} \qquad \Delta\beta = \frac{8\pi^3(n^2-1)^2}{3N^2\lambda^4}\Delta N \tag{12}$$

With[8] $\mathrm{R} \approx 8,314\mathrm{JK}^{-1}\mathrm{mol}^{-1}$ the theoretical value β_{th} can be calulated as:

$$\beta_{\mathrm{th}} = (3,918 \pm 0,008) \cdot 10^{-5}\mathrm{m}^{-1} \tag{13}$$

6 Discussion

The final result for the scattering coefficient β from the experiment is

$$\beta_{\mathrm{exp}} = (7 \pm 4) \cdot 10^{-5}\mathrm{m}^{-1}. \tag{14}$$

Using considerations with the ideal gas equation, it was possible to determine a theoretical comparative value that results in

$$\beta_{\mathrm{th}} = (3,918 \pm 0,008) \cdot 10^{-5}\mathrm{m}^{-1}. \tag{15}$$

This value lies within the simple error interval of the experimentally determined result.
However, it is noticeable that the experimental result has a very large error and that agreement with the theoretical value can only be established due to this very large error. There may be several explanations for the size of the error.
Firstly, despite many attempts, it was not always possible to perfectly minimize the noise in the measurement series, so that large fluctuations or uncertainties in the determined slopes are to be expected. One reason for this could be that the laser was possibly not optimally aligned and did not run exactly straight through the test setup. It turned out to be very difficult to adjust the laser so that the setup fulfils all requirements.
Another source of uncertainty lies in the choice of the size of the measurement range used for the further analysis. As can be seen in Figs. 4 and 5, only a very small section of the measured values is used for the fit, as the spread far to the right is much too large. However, it is not entirely clear how far to the right one cuts off and this can lead to significant deviations in the resulting value for τ.
Overall, it can be stated that an acceptable result could be achieved with the relatively simple measurement method, as it is in agreement with the theory. However, the method involves large measurement uncertainties that are difficult to minimize.

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