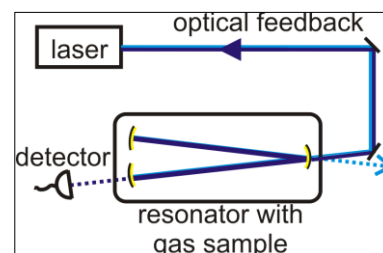


Rayleigh scattering of standard molecules using Cavity Ring-Down Spectroscopy



Supervisors:

1. Midhun George, room U3130, phone 62131, midhun@iup.physik.uni-bremen.de
2. M. D. Andrés Hernández, room U3135, phone 62110, lola@iup.physik.uni-bremen.de

Practical place: Lab room U4180_CRDS Labor

1 Practical objective

After successfully completing this practical, you should be familiar with the basics of optical resonators, ring-down signals and the experimental determination of scattering/absorption coefficients of different molecules.

Previous knowledge about the working principle of a laser, an optical resonator, and the theory of the Rayleigh scattering is required to finish successfully this practical exercise. This can be achieved by reading the references mentioned at the end of this script.

2 Rayleigh scattering

In the late nineteenth century the British physicist Lord Rayleigh derived for the light scattering by particles of smaller size than the wavelength of the incident light a cross section, which is since then known as Rayleigh scattering cross section. The particles can be atoms or molecules and the wavelength dependent Rayleigh scattering cross section can mathematically be defined as:

$$\sigma_{\bar{\lambda}} = \frac{32\pi^3}{3\lambda^4 N^2} (n - 1)^2. \quad (1)$$

with N being the concentration in molecule/m³, λ the wavelength in meters, and n the wavelength independent refractive index of the sample. If N is given in molecule/cm³, λ in terms of $\bar{\nu}$ (wave number in cm⁻¹), instead of n , the wavelength dependent refractive index $n_{\bar{\nu}}$ and F_k , related to the non-spherical shape of the molecule and known as King correction factor, are used, then the (1) can be written as:

$$\sigma_{\bar{\nu}} = \frac{24\pi^3 \bar{\nu}^4}{N^2} \left(\frac{n_{\bar{\nu}}^2 - 1}{n_{\bar{\nu}}^2 + 2} \right)^2 F_k(\bar{\nu}). \quad (2)$$

where:

$$F_k(\bar{\nu}) = \frac{6 + 3\rho_n(\bar{\nu})}{6 - 7\rho_n(\bar{\nu})} = \frac{3 + 6\rho_p(\bar{\nu})}{3 - 4\rho_p(\bar{\nu})} \quad (3)$$

During this practical you will experimentally determine the Rayleigh scattering cross section of the nitrogen (N₂) and Argon (Ar) molecules by using a diode laser and an optical resonator. The obtained experimental values will be compared with theoretical values to estimate the wavelength of the laser used.

Question 1: Calculate the King correction factor for nitrogen at a wavelength of 500nm if the ρ_n at this wavelength is equal to 0.0213. What will be the King correction factor for Argon at this wavelength and why?

3 Experimental Background

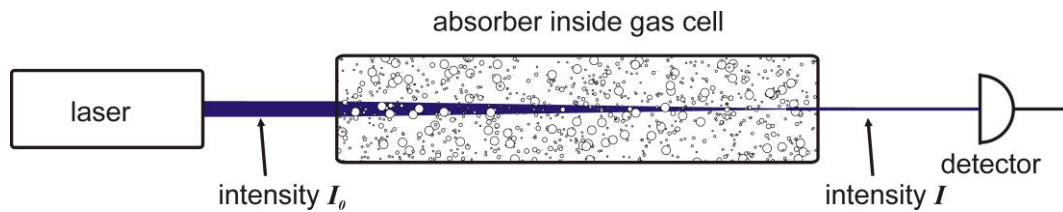


Fig. 1: Basic set up for absorption spectroscopy experiments

Absorption spectroscopy is a widely used technique to determine the concentration of certain gases of interest by relying on the ability of matter to absorb electromagnetic radiation, thus creating a measurable intensity change (see Fig. 1). The electromagnetic radiation attenuation for sufficiently small absorption is described by the BOUGUER-BEER-LAMBERT-Law:

$$I = I_0 \times e^{-\sigma \times N \times L} = I_0 \times e^{-\alpha \times L} \quad (4)$$

Where I_0 is the intensity of the incoming light, I is the intensity of the light after passing the cell with the absorbing gas, σ is the absorption cross section of the sample (in cm² / molecule) and N is the sample number density (in molecules / cm³). As atoms and molecules also cause scattering in their interaction with light according to their scattering cross section at a particular wavelength, the net attenuation of light is the result of absorption and scattering of the molecules inside the gas cell. If the absorption cross-section of the sample is negligible compared to the scattering cross-section, (4) is valid for

σ being the scattering cross-section. For this practical experiment we will use a laser with wavelength at which the absorption of sample gasses under investigation are negligible and therefore any extinction observed is caused by Rayleigh scattering. Now onwards we will only focus on Rayleigh scattering-cross sections. The scattering cross sections multiplied by the number density give the scattering coefficient α ($\alpha = \sigma \times N$, in cm^{-1}). L is the path length of the electromagnetic radiation -matter interaction, generally called the extinction path length.

Light extinction measurements require high specificity in order to assign the measurement signal to only one gas of interest, and sensitivity, to optimise the detection limit of the gas of interest.

Question 2: Using the table below, calculate the Rayleigh scattering cross section of Ar, N₂, CO, CO₂, CH₄, N₂O and SF₆ at 15°C and 1013.25 mbar near 532 nm.

Gas	$(n-1)/10^{-6}$	$F_k(\bar{\nu})$
Ar	268	1
N ₂	284	1.035
CO	325	1.016
CO ₂	427	1.145
CH ₄	481	1.000
N ₂ O	483	1.225
SF ₆	733	1.000

Question 3: Using the Rayleigh scattering cross section of Ar calculated in Question 2 find I/I_0 for a sample cell of 10m length kept at 15°C and 1013.25 mbar.

As it is clear from question 3, the light extinction caused by Rayleigh scattering is orders of magnitude lower than the incoming light intensity even for a 10m long sample cell. This makes the direct determination of Rayleigh scattering using conventional spectroscopic techniques challenging. Optical cavities with highly reflective mirrors (see Fig. 2) increase the effective path length of the sample cell, which in turn increases the possibility of electromagnetic radiation – matter interaction and consequently the measured light

extinction.

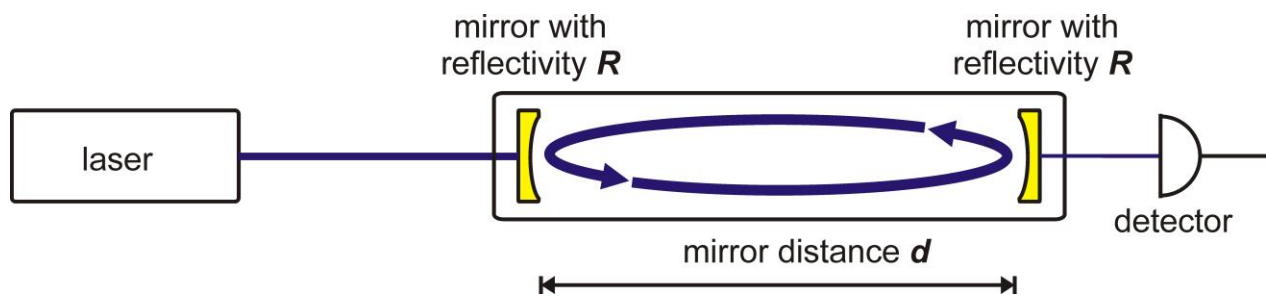


Fig. 2: Basic set up for experiments using cavity enhanced absorption spectroscopy

There is a high variety of different enhanced absorption methods relying on the use of optical cavities, as for example ICOS (integrated cavity output spectroscopy), IBBCEAS (incoherent broadband cavity enhanced spectroscopy), OF-CEAS (optical feedback cavity enhanced absorption spectroscopy), TDLAS (tunable diode laser absorption spectroscopy), and cw-CRDS (continuous wave cavity ring-down spectroscopy). The latter will be used in this practical. All these methods utilize the reflection of electromagnetic radiation by high reflective dielectric mirrors to enhance the optical path length and to increase sensitivity while maintaining a small sample cell size.

For example, mirrors with a reflection coefficient of $R \sim 99.993\%$ increase a (direct) resonator electromagnetic radiation path length from 40 cm to ~ 6 km! In order to reach this high path length, the resonator mirrors must be totally clean and properly adjusted. Even small mirror losses quickly add up and lead to poor results due to the high number of reflections.

Question 3: We use a multi-mode diode with a maximum output power of 100 mW. How does it work? Which laser class does it belong to?

3.1.1 Cavity ring-down spectroscopy (CRDS)

Most cavity enhanced absorption methods mentioned in the previous section measure the light intensity transmitted by the resonator and derive the value of the scattering coefficients, provided that absorption is not significant at this wavelength. Cavity ring-down spectroscopy does not! Instead, the intensity decay of a light-filled resonator is measured, and the scattering coefficient is derived by the decay time. Usually, an empty cell (i.e., the cell does not contain any scattering/absorbing species) is filled with light (termed “excited”) usually by a laser, which is then switched off rapidly when the resonator transmission reaches a certain threshold, while the resonator remains excited. The

subsequent decay of the transmission signal (aka the photons inside the resonator vanish by transmission through the mirrors) is then recorded, and its characteristic time constant, called ring-down time τ , typically between 1 - 100 μs , determined. This is depicted in Fig. 3 (black curve); the ring-down time calculation will be explained in chapter 5.

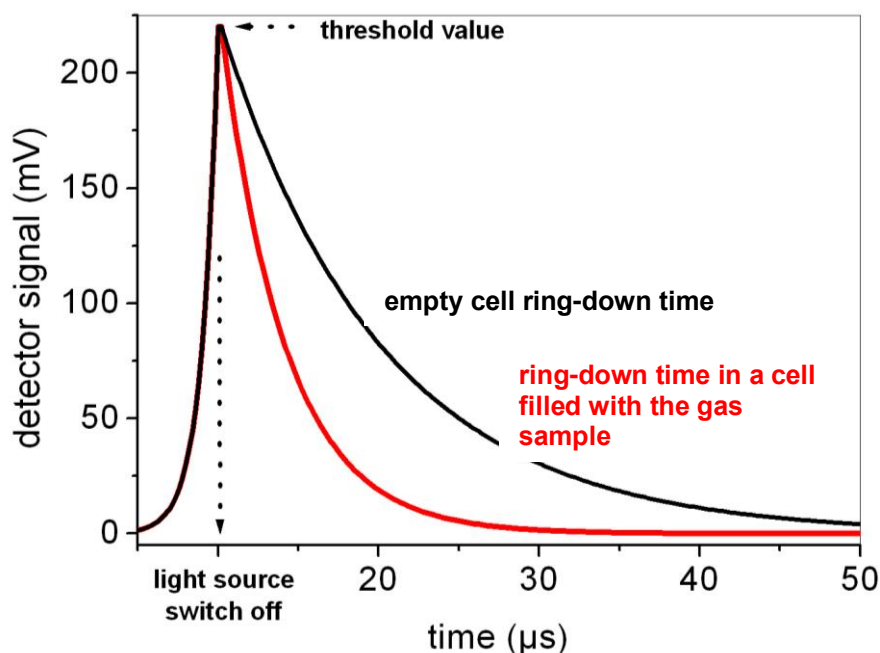


Fig. 3: Schematic ring-down signals with and without absorber

Once the ring-down time of the empty cell is measured, a known amount of the gas sample scattering the incident light is introduced into the resonator and the ring-down time measurement is repeated. Now, since the scattering represents an additional loss mechanism, the decay will be faster than before (red curve). The scattering cross-section of the sample can be calculated from the above mentioned ring-down times. More details will be given in the explanatory CRDS lecture to this practical.

3.2 Basic calculations

3.2.1 Empty cell: mirror reflectivity and ring-down time

Consider a set up for experiments using cavity ring-down time spectroscopy as depicted in Fig. 4. The resonator consists of two mirrors, which are assumed to have an identical reflectivity R , and to be at a distance d . Provided there is no scattering or absorbing sample present, the resonator properties can be determined. The measured ring-down time will be indexed by a zero (τ_0).

As long as the laser is on, the light reaches the cavity and is partly transmitted through it onto the detector where is measured as a voltage. When this voltage reaches a certain threshold value, the laser is switched off; either electronically (as is the case in the present practical) or by using an optical switch. The resonator remains excited, standing light waves inside, and the detector still receives a signal.

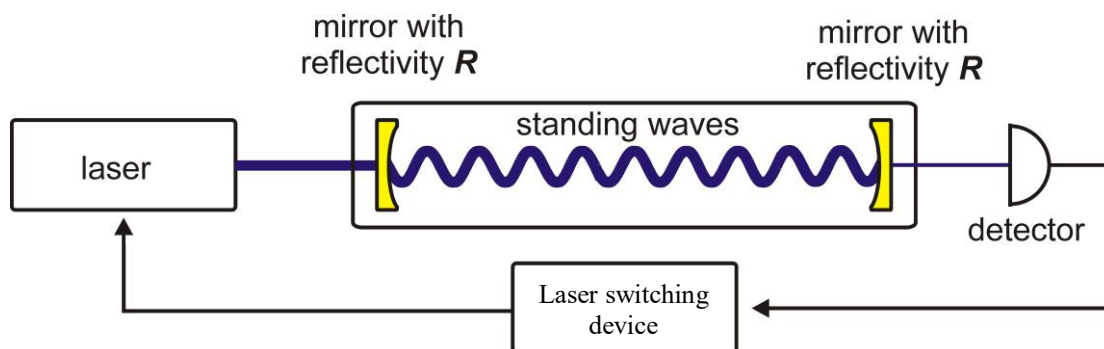


Fig. 4: Schematic setup for CRDS experiments

Let I_0 be the intensity inside the resonator at this moment, and let this intensity consist of photons which bounce back and forth between the mirrors. A photon will require a time t to cover the distance between mirrors, d . After $\Delta t = d/c_0$ (where c_0 is the speed of light in vacuum) all photons will have encountered one mirror in their path, and in an ideal case, they will have either being transmitted through the mirror or being reflected by the mirror, with a probability of R .

Let us consider the photons which are reflected back into the cavity. The remaining intensity I after Δt will be

$$I = I_0 \times R ,$$

and after $\Delta t_1 = 2 \times d/c_0$ (the index 1 now means one cavity round-trip)

$$I(1) = I_0 \times R^2 .$$

After n round-trips, it follows

$$\Delta t_n = 2n \times d/c_0 , \text{ and}$$

$$I(n) = I_0 \times R^{2n} . \tag{5}$$

The ring-down time τ_0 is defined as the time taken for the initial intensity I_0 to decrease to I_0/e . The ring-down time can be measured by detecting the intensity decay of the cavity.

Check your understanding: What are the ring-down times of the empty cell and the cell filled with an absorbing gas in Fig. 3? Can you quickly derive the ring-down time from such a measurement?

Related to the ring-down time is the associated number of round-trips m . The value of m is derived by using

$$I(m) = I_0 \times R^{2m} = \frac{I_0}{e}. \quad (6)$$

Dividing by I_0 and taking the logarithm on both sides gets us

$$2m \times \ln(R) = -1 \Leftrightarrow m = \frac{-1}{2 \times \ln(R)} \quad (7)$$

For high-reflective mirrors, i.e., with $R \sim 1$, $\ln(R)$ can be expanded in a Taylor series, and it follows $\ln(R) \sim R - 1$, thus

$$m \approx \frac{1}{2 \times (1-R)}. \quad (8)$$

As $\tau_0 = 2m \times d / c_0$,

$$\tau_0 = \left(\frac{d}{c_0}\right) \times \left(\frac{1}{1-R}\right). \quad (9)$$

Thus, for a known mirror distance d , the measurement of the ring-down time τ_0 enables the calculation of the mirror reflectivity R . This was the original purpose of developing cavity ring-down spectroscopy – to measure high mirror reflectivity with high accuracy.

Check your understanding: Derive the formula for two mirrors of different reflectivity forming an optical cavity (use R_1 and R_2 instead of R).

To extend the formula to the case of a resonator containing a scattering species, (4) and (5) must be combined:

$$I(n) = I_0 \times R^{2n} \times e^{-\alpha \times 2n \times d} \quad (10)$$

The ring-down time τ_α is different from the previously calculated τ_0 due to the light

extinction caused by the sample. The derivation of τ_α will be performed during the lecture presenting this practical, but you can do it yourself by following the derivation of τ_θ .

4 Practical description

During the practical session you will experimentally determine the scattering cross-sections of high purity N_2 and Ar using the experimental setup provided. This experimental setup will consist of an aligned optical cavity with a laser of unknown wavelength and a detector, an electronic switch, a data acquisition device, a flow controller, a pressure regulator, a temperature and pressure sensors and a vacuum pump as shown in Fig. 5.

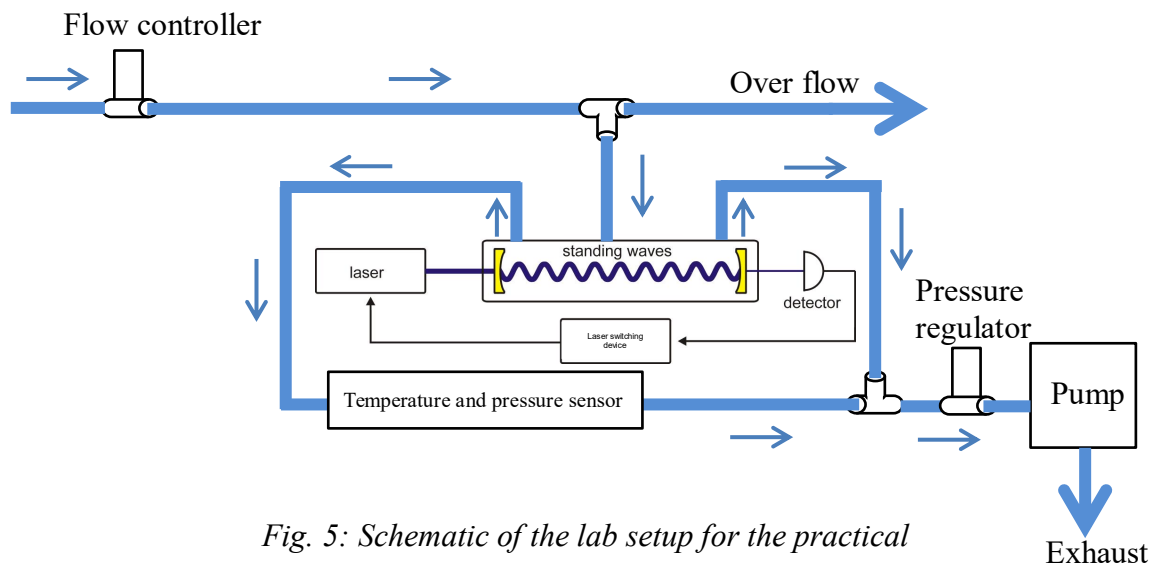


Fig. 5: Schematic of the lab setup for the practical

The setup will allow you to observe and save the cavity signal at different resonator pressures, which will be later used to calculate the ring-down time constants. From these measured ring-down time constants, the experimental value of Rayleigh scattering cross section and the τ_θ for the cavity will be calculated according to the detailed derivation provided in the explanatory lecture for the practical. Finally by comparison of the experimentally determined values of the Rayleigh scattering cross section with the theoretical values, the wavelength of the laser will be determined.

Check your understanding: Once you derive the formula to calculate τ_α find the expression for α by using (9). Based on this formula try to design an experimental procedure to determine scattering cross-sections. A detailed explanation will be given during the lecture. **Be prepared to present roughly/schematically the complete experiment during the testing interview at the beginning of the practical.**

4.1 Safety: Getting familiar with the lab space

Read the general lab safety instruction in the web page:

https://www.msc-ep.uni-bremen.de/services/lectures/Measurement_tech_SS19.html

Important! If you hear any alarm sound, leave the lab and corridor immediately and inform us!

- Eating, drinking, smoking is not allowed in the lab.
- Do not look into the laser; remove watches etc. which might reflect laser light.
- Do not touch any optical component (mirrors!) on their surface.
- Let us know if you think something is broken – do NOT attempt to fix it yourself.

Upon arriving in the lab, you will first be instructed of all necessary optical and electrical components; please verify the list:

- Aligned optical cavity and peripherals
 - comparator/pulse generator
 - oscilloscope
 - Temperature sensor
 - Pressure sensor
- Please restrict your experimental set up to the space reserved for your practical experiment. You can use a table or the wall counter for taking notes etc.

4.2 Measuring Rayleigh scattering cross-sections

You will be provided with an aligned V-resonator with all the necessary peripherals to successfully finish the experimental section. On the computer provided check if the PEP practical Rayleigh scattering study.vi program is running fine and you can see the signal from the photodiode. The gas under investigation will be flowing through the resonator at a constant mass flow rate. Your task is to change the pressure inside the resonator from 200 to 500 mbar with steps of 50 mbar with the help of the program. At least 10 minutes of detector signal at each pressure step should be recorded. Note that the values of the pressure, temperature and time at which the pressure is changed are required for future analysis. The difference in ring-down time for different resonator pressures can be observed on the oscilloscope.

Pure N_2 will be the first gas flowing through the cell for measurement. After completing the full set of measurements for N_2 you can ask the tutor to provide you with Ar and then repeat the measurement procedure.

Once you finished with all the measurements please contact the tutor again to provide you the file with the detector signals recorded for the full experiment.

4.3 Analysis of ring-down signals and calculation of Rayleigh scattering cross-sections

This part of the practical can also be finished after the lab practical time.

1. Determine the ring-down time from the signals you saved during the experiment. You can either fit a 1st order exponential decrease, or you can take the logarithm of the y-values and fit a linear slope.
2. Calculate the number concentration in the resonator for each pressure step assuming ideal gas behaviour.
3. Once the ring-down times and number concentrations are calculated with the help of (12) plot the number concentration vs inverse of ring-down time for both gases. What do you observe? Which function can you use to fit these data points?
4. Use the equation of the fit to calculate τ_0 , R and the scattering cross section of N_2 and Ar
5. Using the values provided by the tutor calculate the theoretical values of Rayleigh scattering cross-section for N_2 and Ar . Compare these with the experimental values. What do you see? What is the wavelength of the laser used?

5 Protocol

Please refer to the protocol guideline of the PEP practical. You do **not** have to submit a CD/DVD. Try to be concise and accurate. A good report consists of short, accurate descriptions and statements.

6 Relevant formulas

- The absorption coefficient α can be calculated if the ring-down time with and

without absorber (τ_α and τ_0) are both known. It then follows

$$\alpha = \frac{1}{c_0} \times \left(\frac{1}{\tau_\alpha} - \frac{1}{\tau_0} \right) \quad (11)$$

- Formula (11) can be re-written by substituting $\alpha = \sigma \times N/V$ to make a linear equation of the form $y = mx + c$:

$$\frac{c_0 N \sigma}{n V} = \left(\frac{1}{\tau_{\sigma N/V}} - \frac{1}{\tau_0} \right) \quad (12)$$

7 References

Chapter 5 of : Demtröder, W.: Laser spectroscopy: Basic Concepts and Instrumentation, 2nd edition Springer Berlin Heidelberg New York, ISBN 3-540-57171-X.

[Bereichsbibliothek PHY/ELT NW 1, signature: a phy 772.2 e/393(2)]

Chapter 1.2.4 of : Demtröder, W.: Laser spectroscopy 2: Experimental Techniques, Springer Berlin Heidelberg, ISBN 978-3-662-44640-9.

[Bereichsbibliothek PHY/ELT NW 1, signature: a phy 772.2 e/413(5)-2], ISBN 978-3-662-44641-6 (e-book)

Chapter 1.2.3 of : Demtröder, W.: Laser Spectroscopy Vol. 2: Experimental Techniques, Springer Berlin Heidelberg, ISBN 978-3-540-74952-3.

[Bereichsbibliothek PHY/ELT NW 1, signature: a phy 772.2 e/413(4)-1], ISBN 978-3-540-74954-7 (e-book)

Chapter 5 of : Demtröder, W.: Laser Spectroscopy Vol. 1: Basic Principles, Springer Berlin Heidelberg, ISBN 978-3-540-73415-4.

[Bereichsbibliothek PHY/ELT NW 1, signature: a phy 772.2 e/413(4)-1], ISBN 978-3-540-73418-5 (e-book)

Planet. Space Sa., Vol.32, No.6, pp. 7855790. 198

M. Snee, W. Ubachs / Journal of Quantitative Spectroscopy & Radiative Transfer 92 (2005) 293–310