Determination of Rayleigh scattering coefficients in air using optical ring-down spectroscopy

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1. Short historical introduction and motivation

Sunlit Earth's atmosphere has a deep blue color resulting from light scattering in the upper troposphere. This phenomenon belongs to one of the most remarkable physical phenomena and certainly must have been observed by human individuals already in prehistoric times, even if its physical background was then unknown. It is also due to the scattering that at a sunrise or sunset the color of our star appears redder than at midday or that a piece of a milky glass – typically porous, characterized by refractive index fluctuations – has a bluish color when looked from the side while the orange light is transmitted through it, what is illustrated on the photographs of the Fig. 1.

Today it seems a common knowledge that the blue color of scattered light occurs if the objects interacting with photons are much smaller than the wavelength of a photons. However, first formal explanation of this fact was given in 1871 by the British scientist John William Strutt, the third Lord Rayleigh. It is, therefore, after him that the scattering of light on objects smaller than the wavelength was named the Rayleigh scattering.

In 1908, thirty seven years after publishing of works of Rayleigh, the German theoretical physicist Gustav Mie showed that molecular scattering explained by Rayleigh can only be considered as a part of a more general theory – the Mie theory.

Shortly, the Mie theory assumes spherical shape of uniform scatterers characterized by the index of refraction n and uses the so called size parameter x – a dimensionless constant defined by the ratio of the scatterer diameter, a, multiplied by 2π and divided by the wavelength, λ, to describe interactions with photons. In a limiting case of $x \ll 1$ it transforms into the Rayleigh theory.

According to the Mie theory the scattering of light depends in a rather complicated way on the size parameter revealing resonances for some specific values of x. Nonetheless, one can say that the larger the sphere the more light is scattered. This general dependency is in fact a power function of the radius giving rise to a large difference of scattering efficiency for small and larger particles. For example, the optical power scattered by a sphere of sub nm

Fig 1 Rayleigh scattering.
Above: on atmospheric molecules giving rise to a deep blue color of the sky and at the same time red color to the sunlight transmitted through the atmosphere.
Below: in a nano-porous milky glass "stones" gives rise to their bluish color and an orange color of transmitted light
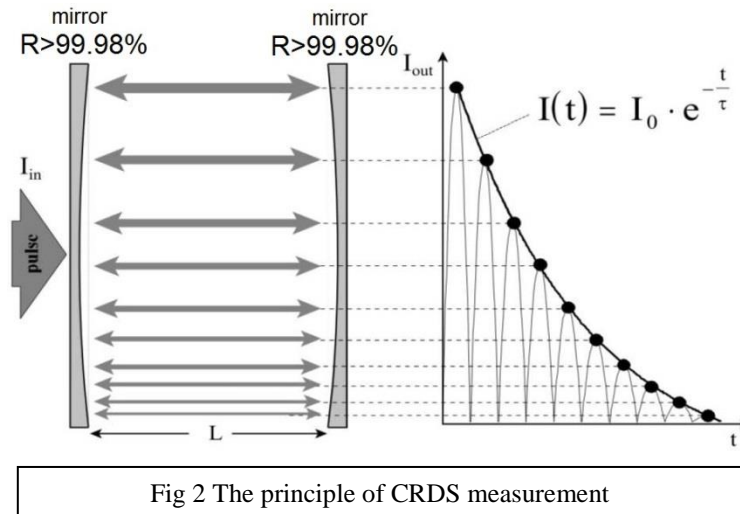
diameter is roughly 10^{20} times smaller than this scattered by a micrometer sized droplet and

corresponds in total to the small 10^{-26}–10^{-27} fraction of the overall intensity incident on the sphere if its transversal size is given in cm^2. This makes any measurement or visualization of the Rayleigh scattering a challenging task even if some of its features, like strong wavelength dependence or depolarization of scattered light – known as the Tyndall effect – may be demonstrated in colloid suspensions. Nevertheless, one should keep in mind that the Tyndal effect deals typically with micrometer sized particles that formally cannot be used as model systems for molecular Rayleigh scattering. Strictly speaking, the formula given by Rayleigh requires the wavelength of light to be far larger than the particle or oppositely the particle to be far smaller than the wavelength.

The experiment described in this proposal was thought and built with a main scope of demonstrating and visualizing molecular Rayleigh scattering to participants of university physics courses. It has a straightforward concept and uses an uncomplicated experimental setup, which can be easily operated by Bachelor or Master Degree students, for example, as a part of the *Physikalisches Praktikum* or *Fortgeschrittenes Physikalisches Praktikum*. On the other hand, the setup is suitable for detection of small values of the scattering coefficient in the order of 10^{-6}-10^{-8} cm^{-1}, what is sufficient to detect molecular scattering of an optical wave traveling in a diluted gas medium. Such high sensitivity is achieved through the use of an optical ring-down principle also known as the Cavity Ring-Down Spectroscopy (CRDS) technique. It provides means to determine scattering coefficients of gaseous substances, for example atmospheric air, but if desired also other gases.

2. Theoretical considerations
2.1 Cavity Ring-Down Spectroscopy

Cavity Ring-Down Spectroscopy (CRDS) is an ultrasensitive absorption spectroscopy technique that is relatively simple to implement experimentally. The technique has numerous

Fig 2 The principle of CRDS measurement

applications in spectroscopy, kinetics, analytical and atmospheric chemistry. It is based on injecting a laser pulse into a cavity bounded by two ultra-high reflective mirrors (reflection coefficient R>99.98%), as shown schematically on Fig. 2. The laser pulse is trapped within the cavity (retro-reflecting from both mirrors) for many thousands of round trips and thus a pathlength of many kilometres can be established within this cavity. For each reflection of the light pulse at a mirror of reflectivity R, a small fraction (1-R) of the light leaks out through the mirror and the light intensity decays gradually to zero. The intensity can be measured as a function of time by a time resolving photodetector. One can show that due to the constant energy losses by each round-trip reflection the cavity transmitted intensity, *I(t)*, decays exponentially in time *t* according to the equation:

$$I(t) = I_0 e^{-\frac{t}{\tau}},$$
(1.1)

where I_0 denotes the input intensity and τ – the decay constant or the so called ring-down time. If the cavity is evacuated, allowing to consider the magnitude of remaining molecular

scattering as negligible, in a stable optical arrangement, preventing for geometrical escape of photons beyond the mirrors' surface, and has a fixed length, L, the ring-down time becomes a function of the reflection coefficient, namely:

$$\tau(\lambda) = \frac{L}{c(1 - R(\lambda))},$$
(1.2)

where the constant c corresponds to the speed of light in vacuum. The ring-down time of an empty cavity is typically used as a reference decay time and is often denoted by τ_0. For a cavity bounded by two mirrors of reflectivity R, the number of round trips, N, performed in the time taken for the intensity to fall to 1/e of its initial value is obtained as $R^{2N} = 1/e$ or $N = -1/2\ln R$. Thus, for example, for a mirror reflectivity of 0.999, N=500 whereas for R=0.99999, N=50000, giving a path length in a 1-meter cavity of 100 km. Such high reflectivities are feasible with modern mirror coatings.

In the presence of scatterers, the decay of light is somewhat faster as some of the photons are deviated from their stable trajectories upon interaction with molecules. These photons do not reach the output mirror giving rise to the energy dissipation independent from this caused by the cavity mirrors. This additional energy loss is typically described in terms of the scattering coefficient, β, which has a unit of an inverse length and relates the intensity of the traveling wave with the distance over which it propagated. Accounting for the photon losses due to reflection and scattering the modified ring-down time formula takes the form:

$$\tau(\lambda) = \frac{L}{c(1 - R(\lambda) + \beta(\lambda)L)}.$$
(1.3)

By denoting the ring-down time of an empty cavity by τ_0 and substituting L in the above equation by the eqn. (1.2) one obtains:

$$\beta(\lambda) = \frac{1}{c}\left(\frac{1}{\tau(\lambda)} - \frac{1}{\tau_0(\lambda)}\right).$$
(1.4)

Apparently, the scattering coefficient depends on the ring-down time of an empty and gas filled cavity and is directly proportional to the difference of their inverses. In fact, it means that we can determine the Rayleigh scattering coefficient only via the ring-down times which depend only on geometrical parameters of the optical cavity and do not depend on parameters of laser pulse and its intensity inside the cavity.

2.2 Rayleigh scattering

According to the linear scattering theory, the power scattered by a single scatterer, for example a molecule or an aerosol particle, in a full solid angle of 4π is proportional to the incident intensity. The proportionality constant is known as a scattering cross section and is typically denoted by σ. It has a unit of the surface area. In a volume containing many scatterers the total scattered power is a superposition of power scattered by individual molecules. It is, therefore, convenient to multiply σ by the number concentration N. The proportionality obtained in this way is nothing else but earlier defined scattering coefficient β such that we may write the equality:

$$\beta(\lambda) = N\sigma(\lambda).$$
(1.5)

The Rayleigh theory approximates scattering molecules by oscillating Hertzian dipoles that reemit incident electromagnetic wave. One can show that in this case the scattering coefficient depends on the fourth power of the wavelength, namely:

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

(1.6)

Due to this strong fourth power dependence the blue photons (wavelengths) are scattered more efficiently than the red ones. Note, that by known wavelength the Eq. 1.6 allows to derive magnitude of the Rayleigh scattering coefficient, which may be directly compared with this obtained in CRDS measurement as given by the Eq. 1.4.

3. Experimental setup

Fig. 3 shows the experimental setup for measuring of Rayleigh scattering coefficients. The setup consists of a laser operating in pulsed regime. It can produce laser pulses with power up to 100 mW and with the repetition rate up to 100 Hz. The wavelength of the laser was carefully chosen to be far from any absorption resonances of most abundant air constituents. In this case radiation losses can be assumed to result only from the Rayleigh scattering. In our case the laser has a wavelength ~405 nm. Secondly, this wavelength was used in order to increase the Rayleigh coefficient because $\beta \sim \lambda^{-4}$. The laser is triggered externally by the delay generator (Stanford DG 545). Using the generator you can easily change a length of laser pulse and its repetition rate.
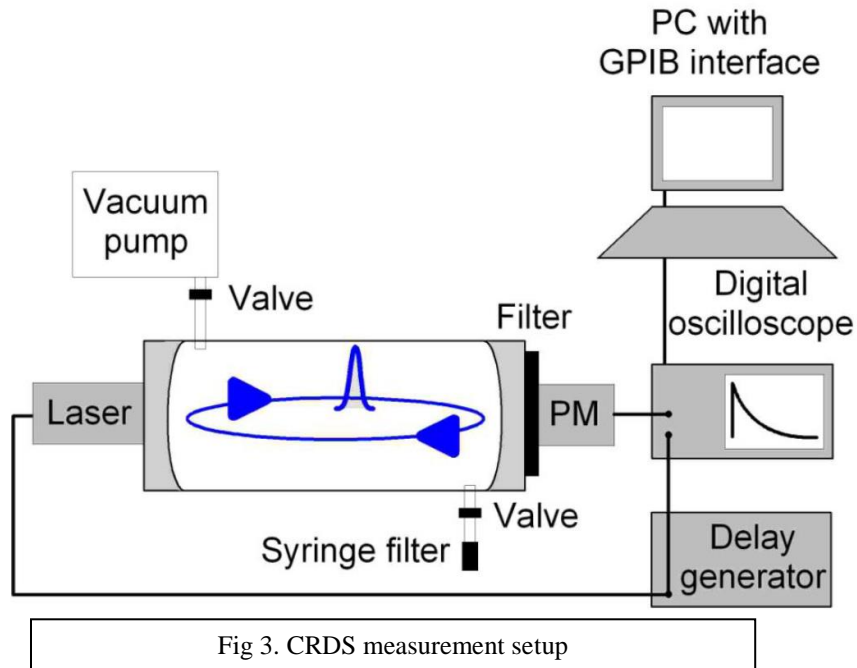

Fig 3. CRDS measurement setup

The optical cavity consists of two high reflective spherical mirrors spaced by the distance of 50 cm. The mirrors are coated with highly reflective dielectric coatings (Layertec) of R>99.98%.The radius of curvature of each mirror is 100 cm provides stable, non-confocal arrangement.

The photomultiplier (H7826, Hamamatsu Photonics) and the digital oscilloscope (HMO1522, Rohde & Schwarz) register the outgoing light from the cavity. The trigger for the oscilloscope device is generated by the same delay generator. The experimental data can be stored either on the internal storage device of the oscilloscope or transferred to the personal computer via the GPIB interface. To reduce background and improve sensitivity of the setup a

suitable band pass optical filter is used. It is located between the cavity and the photomultiplier.

The vacuum pump removes air from the cavity and the syringe filter with a 2 um pore diameter removes bigger aerosol particles from ambient air, which is next pumped into the cavity for investigations of Rayleigh scattering.

4. Description of measurement

For the determination of the Rayleigh scattering coefficient β (see eqn. (1.4)), students need to measure two ring-down times of the optical cavity: when the cavity is evacuated (time τ_0) and when the cavity is filled with air at atmospheric pressure (time τ).

For removing of air out of the cavity the vacuum pump has to be used. One needs to switch it on for a short time. During the pumping the pressure inside the cavity is continuously controlled with a manometer. The pump should be switched off as soon as the nanometer shows minimal possible value on its scale. The experience from our lab shows that the accuracy of an ordinary mechanical manometer is well sufficient to detect vacuum of required quality. After evacuation of air the cavity is ready for the measurement of the ring-down time τ_0.

For this measurement students need to properly align the optical system because output signal from the ring-down cavity is very sensitive to alignment of the optical system. In case of bad alignment of the system, the ring-down signal intensity becomes less than noise and any ring-down measurements are impossible. For this purpose one additional laser with wavelength ~532 nm (green light) should be used. The laser operates in continuous wave regime with output power ~0.8 mW and the wavelength is far away from the reflection band of the cavity mirrors. A good transmission of this laser beam through the cavity should help in the proper alignment of this optical system. Moreover, green light is more convenient for the alignment because it is much more visible by human eye than the violet light at 405 nm. When the optical system is proper aligned, then on the digital oscilloscope you will see the following signal (see Fig. 4). Here, a laser pulse at 405 nm has length 100 us, and the pulse decays by the exponential law (1.1).
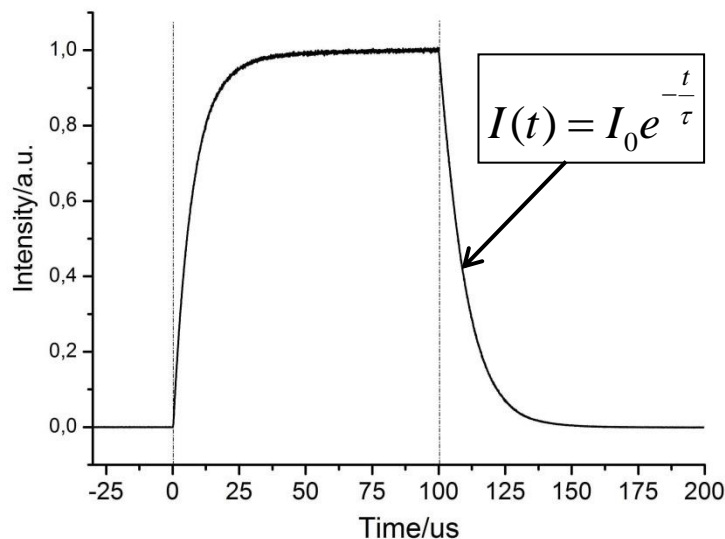

$$I(t) = I_0 e^{-\frac{t}{\tau}}$$

Fig 4. Ring-down signal observed on the oscilloscope after 100 us laser pulse at 405 nm.

Obviously, in case of ideal alignment, any optical losses inside the optical cavity will have minimal values. As follows from eqn. (1.2)-(1.3), minimal optical losses correspond to maximal ring-down time. Thus, students need to align the optical system in such way that the ring-down time has the highest possible value. In case of vacuum the value should be ~10-11 us.

Further, students need to fill the cavity with aerosol free ambient air at atmospheric pressure and measure a ring-down time again. Since the position of cavity mirrors is slightly changed after the pumping, it is necessary to align the cavity again. In case of proper alignment, you will be able to detect a ring-down time τ, which will be shorter (~8-9 us) than τ_0 due to presence of the Rayleigh scattering.

At the end of the measurements the registered ring-down signals has to be fitted with the single exponential function (1.1) to determine decay times. For convenience of observation of the ring-down decay and its fitting there is a LabVIEW platform on the computer. Using this platform, students can easily observe ring-down signals and process them on the computer. Also, during writing a protocol, students can use for processing of experimental data any computer programs like Origin, Mathematica or Matlab. Obtained Rayleigh scattering coefficient needs to be compared with theoretical value β as in eqn. (1.6).

5. Demonstration of measurements

The following graphs demonstrate measured CRDS signals in an evacuated (Fig. 5) and in air-filled cavity (Fig. 6). Tables in these figures indicate fitting parameters by the exponential function as in eqn. (1.1). Also, Fig. 7 shows normalized CRDS decays of these signals. As was told already, the ring-down time strongly depends on proper alignment of the optical system. Due to small difference between these ring-down times, in order to well distinguish these signal decays, students need to accurately align the optical system that the ring-down times have the highest possible values.
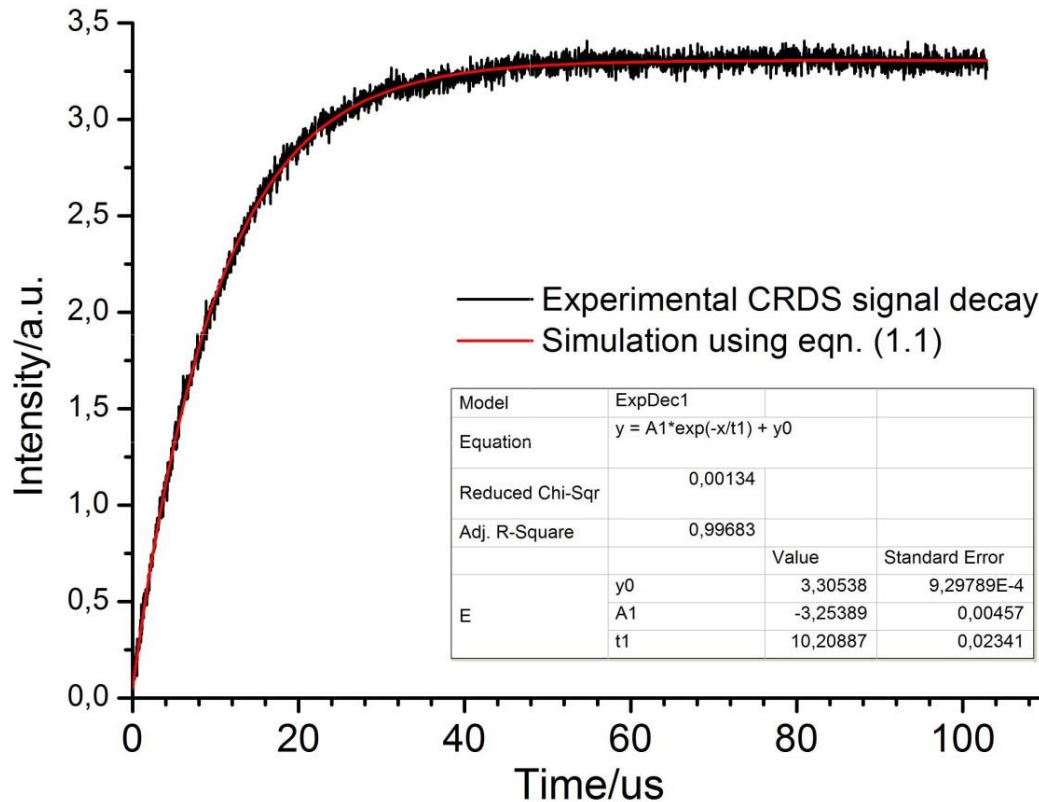
Model	ExpDec1		
Equation	y = A1*exp(-x/t1) + y0		
Reduced Chi-Sqr	0,00134		
Adj. R-Square	0,99683		
		Value	Standard Error
E	y0	3,30538	9,29789E-4
	A1	-3,25389	0,00457
	t1	10,20887	0,02341

Fig 5. CRDS signal decay in the evacuated cavity

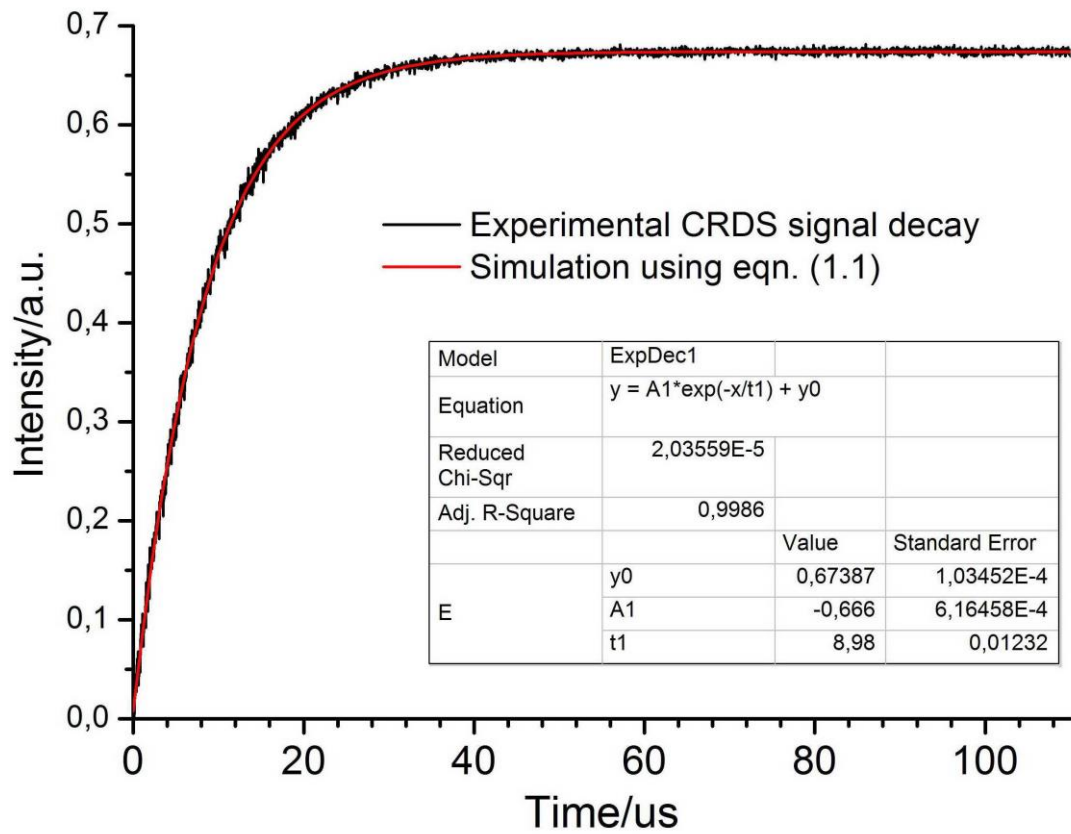| Model	ExpDec1		
Equation	y = A1*exp(-x/t1) + y0		
Reduced Chi-Sqr	2,03559E-5		
Adj. R-Square	0,9986		
		Value	Standard Error
	y0	0,67387	1,03452E-4
E	A1	-0,666	6,16458E-4
	t1	8,98	0,01232

Fig 6. CRDS signal decay in the air filled cavity at atmospheric pressure

Derived decay times in case of vacuum and air are $\tau_0 = 10.2$ us and $\tau = 8.98$ us, respectively.
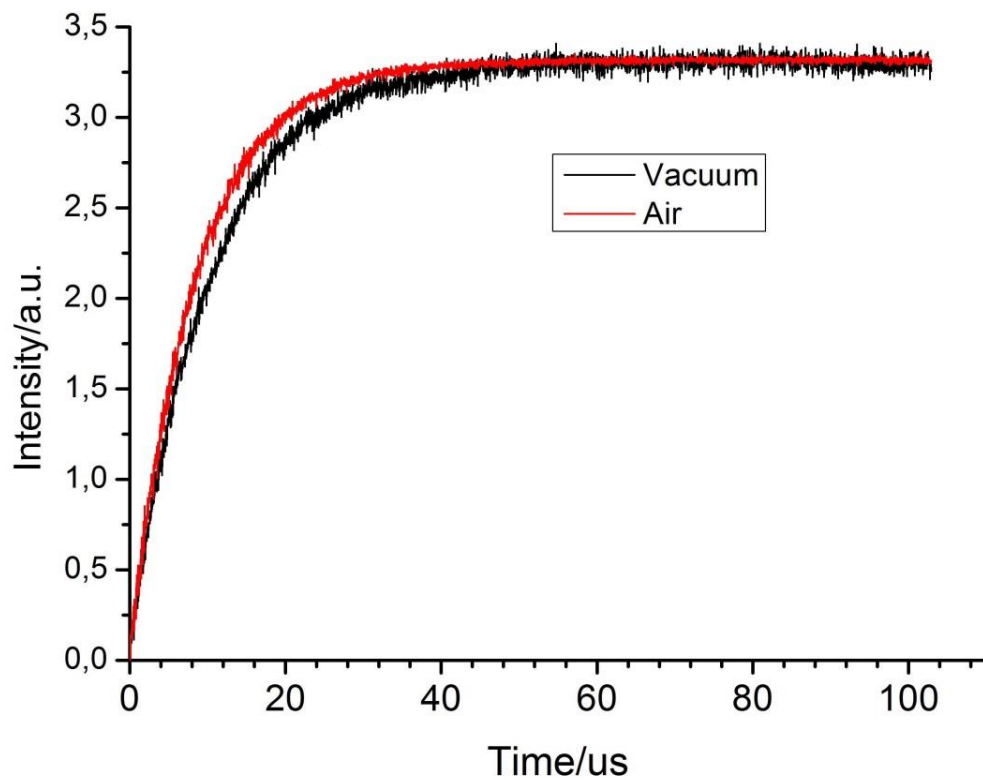

Fig 7. Superimposed CRDS decays of signals

6. Derivation of scattering coefficients

As it was said before, an experimental value of the Rayleigh scattering coefficient can be determined from eqn. (1.4), where τ_0 and τ experimentally measured ring-down times. In our case as follows from Fig. 5-6, these values are: $\tau_0 = 10.2$ us and $\tau = 8.98$ us. Thus, the scattering coefficient is:

$$\beta = 4.44 \times 10^{-5} \text{ m}^{-1}.$$

Theoretical calculation of the coefficient from eqn. (1.6) with current atmospheric pressure p=102070 Pa and temperature of air T~294 K and $\lambda = 405$ nm is:

$$\beta = 4.19 \times 10^{-5} \text{ m}^{-1}.$$

The discrepancy is probably caused by residual aerosol scattering (Mie scattering) in the cavity and due to non-ideal alignment of the optical cavity.

7. Preparation for this lab work

Before the experiment each student must know:
1. Basic principles Rayleigh scattering and observation of this scattering in nature. Other types of light scattering in nature. Criteria of applicability of these light scatterings.
2. How to explain Rayleigh scattering using classical electrodynamics.
3. Basic information about optical resonators. Criterion of stability of optical resonators.
4. Basic information about Cavity-Ring-Down Spectroscopy. Its advantages and disadvantages as compared with absorption spectroscopy.
5. How to detect Rayleigh scattering using our experimental setup.

Writing of the preparation
For the Lab course each group must bring a preparation (not longer than 5 pages) which consists of:
1. Introduction to this lab work including description of Rayleigh scattering and its observation in nature.
2. Theoretical description of the Cavity Ring-Down Spectroscopy and Rayleigh scattering. Students need to give corresponding formulae for determination of ring-down times and Rayleigh scattering coefficient.
3. Description of the experimental setup and experimental technique.

Literature

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