

## **Pomiar stężenia NO<sub>2</sub> wytwarzanego w powietrzu metodą spektroskopii strat we wnęcie (ang. Cavity ring down spectroscopy, CRDS)**

### **Przebieg ćwiczenia**

- 1) Przygotowanie układu pomiarowego, zjustowanie optycznej wnęki rezonansowej.
- 2) Rejestracja zaniku czasowego impulsów laserowych transmitowanych przez wnękę "pustą" (tj. wypełnioną powietrzem)
- 3) Rejestracja zaniku czasowego impulsów laserowych transmitowanych przez wnękę wypełnioną powietrzem zawierającym absorber (cząsteczki NO<sub>2</sub>).
- 4) Obliczenie współczynnika odbicia zwierciadeł rezonatora oraz koncentracji NO<sub>2</sub> w badanym powietrzu.

### **Wymagania wstępne:**

1. Podstawy fizyki laserów
  - a) absorpcja i emisja światła (spontaniczna i wymuszona), współczynniki Einsteina, prawdopodobieństwa przejść;
  - b) ośrodek wzmacniający światło, inwersja obsadzeń;
  - c) rezonatory laserowe, mody rezonatora.
2. Metoda spektroskopii strat we wnęcie (CRDS).
3. Zanieczyszczenia powietrza i ich powstawanie.
4. Znajomość działania elementów układu doświadczalnego
  - a) fotopowielacz;
  - b) oscyloskop cyfrowy.

### **Zalecana literatura**

1. W. Demtröder, Spektroskopia laserowa, PWN.  
(w pliku PDF)
2. T. Stacewicz, P. Wasylczyk, P. Kowalczyk, M. Semczuk, "Cavity ring down spectroscopy experiment for advanced undergraduate laboratory".
3. "XYZs of oscilloscopes".

# Cavity ring down spectroscopy experiment for advanced undergraduate laboratory

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**Abstract.** A simple experiment is described that permits advanced undergraduates to learn the principles and applications of the cavity ring down spectroscopy technique. The apparatus is used for measurements of low concentrations of NO<sub>2</sub> produced in air by an electric discharge. We present the set-up, experimental procedure, data analysis and some typical results.

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## 1. Introduction

Cavity ring down spectroscopy (CRDS) is a conceptually simple but highly effective laser technique for measurement of weak absorption, particularly of gas phase species. As such, it deserves to be introduced to students of physics and chemistry at a relatively early stage of their education. Among many applications, CRDS is used to detect and qualitatively measure trace concentrations of air pollutants. In our opinion the combination of a problem of natural concern to many young people with a modern experimental method for its investigation provides a topic particularly attractive for students. Therefore we have designed an experiment for an advanced undergraduate (third year) physics laboratory in which the pulsed CRDS technique is employed to detect low number densities of laboratory produced  $\text{NO}_2$  in air. The following sections present an overview of the CRDS technique, a brief discussion of sources of  $\text{NO}_2$  in the Earth's atmosphere, a description of the apparatus used in this experiment, some remarks about the experimental procedure, and the process of data analysis as well as typical results.

## 2. Principles of the CRDS technique

The cavity ring down spectroscopy technique is based on the measurement of the decay rate of light trapped inside an optical resonator of particularly high finesse (i.e. composed of two mirrors characterized by very high reflectivity). This decay is linked with losses that depend on the residual mirror transmission and on the absorbing medium between the mirrors. As the light is often said to 'ring' backwards and forwards between the cavity mirrors, the gradual decrease of its intensity gives the origin of the method's name. Initially this technique was proposed by Herbelin *et al.* [1, 2] for testing mirrors of high reflectivity. Then O'Keefe and Deacon in 1988 [3] applied it for measurements of gas absorption spectra. By now several modifications of the CRDS method are known [4, 5, 6]. They are widely used in experiments in physics, chemistry and biology.

To understand the basis of the CRDS technique, consider an empty optical resonator consisting of two highly reflective mirrors (with reflectivities  $R$  typically greater than 0.999) separated by a distance  $d$ . A short laser pulse is directed into the back face of one of the mirrors. For the sake of clarity we initially assume that the pulse duration is smaller than the round trip time in the cavity. A small fraction of the pulse enters the resonator through the mirror and becomes trapped inside, moving back and forth between the mirrors. In each round trip the pulse intensity decreases by a factor  $R^2$  because of mirror losses. Thus, after  $k$  round trips the intensity of the bouncing pulse decreases as

$$I_k = I_0 R^{2k} = I_0 \cdot \exp(2k \ln R) . \quad (1)$$

This decay is monitored by positioning a sensitive photodetector behind the second mirror to detect the tiny amount of light leaking out of the resonator through the

mirror on each pass. The recorded signal would consist of a train of pulses with intensity decreasing exponentially according to (1). However, in most experiments the laser pulse is actually longer than the time for a single round trip and the pulse train is smoothed to an envelope of pulse amplitudes that decrease continuously in time. As the number of cavity round trips  $k$  can be related to the time  $t$  the pulse has spent in the resonator by  $k = t/t_r$ , where  $t_r = 2d/c$  denotes the time for one round trip and  $c$  is the speed of light, the observed continuous decay assumes the form

$$I(t) = I_0 \exp\left(\frac{ct \ln R}{d}\right). \quad (2)$$

Since the mirrors of the resonator are highly reflective, i.e.  $R \approx 1$ , we may approximate  $\ln R \approx -(1 - R)$  and rewrite eq.(2) as

$$I(t) = I_0 \exp\left(-\frac{c(1 - R)}{d} \cdot t\right) = I_0 \exp(-t/\tau_0). \quad (3)$$

The decay time constant

$$\tau_0 = \frac{d}{c(1 - R)} \quad (4)$$

is called a ring down time of the empty resonator.

Instead of vacuum (or non-absorbing gas) filling an 'empty' resonator, a molecular absorber can be placed inside. This increases losses of pulse intensity due to absorption and scattering. In the gas phase scattering can usually be neglected as compared to absorption and the losses per round trip are described by the Lambert-Beer law, i.e. an additional factor  $\exp(-2k\sigma Nd)$  has to be introduced in formula (1), with  $N$  being the number density of the absorbers and  $\sigma$  the absorption cross section. Then the time dependence of the output signal can be written as

$$I(t) = I_0 \exp\left(-\frac{c[(1 - R) + \sigma Nd]}{d} \cdot t\right) = I_0 \exp(-t/\tau), \quad (5)$$

with a decay time (a ring down time of the filled resonator)

$$\tau = \frac{d}{c[(1 - R) + \sigma Nd]}. \quad (6)$$

If the absorption cross section of the gaseous medium is known, the number density of its molecules can be determined by fitting eqs. (5) and (6) to the measured intensity decay curves for the empty and filled resonator, respectively, and subtracting the reciprocal ring down times:

$$N = \frac{1}{c\sigma} \left(\frac{1}{\tau} - \frac{1}{\tau_0}\right). \quad (7)$$

On the other hand, if the laser wavelength is tuned, the ring down time recorded at each wavelength can be transformed into an absorption cross section, yielding the absorption spectrum of the gas in the resonator.

The CRDS technique is highly sensitive. For values of  $R = 0.999$  and  $d = 1$  m, we calculate from (4) that  $\tau_0 = 3.3 \mu\text{s}$  and the light pulse travels 1 km by the time its intensity drops by a factor of  $e$ . Therefore the cavity ring down spectrometer is analogous to an absorption cell with a kilometre length. Another advantage of the method is its immunity from pulse-to-pulse fluctuation of the laser light because the measured decay rates are independent of the pulse intensity.

### 3. Sources and environmental impacts of atmospheric $\text{NO}_2$

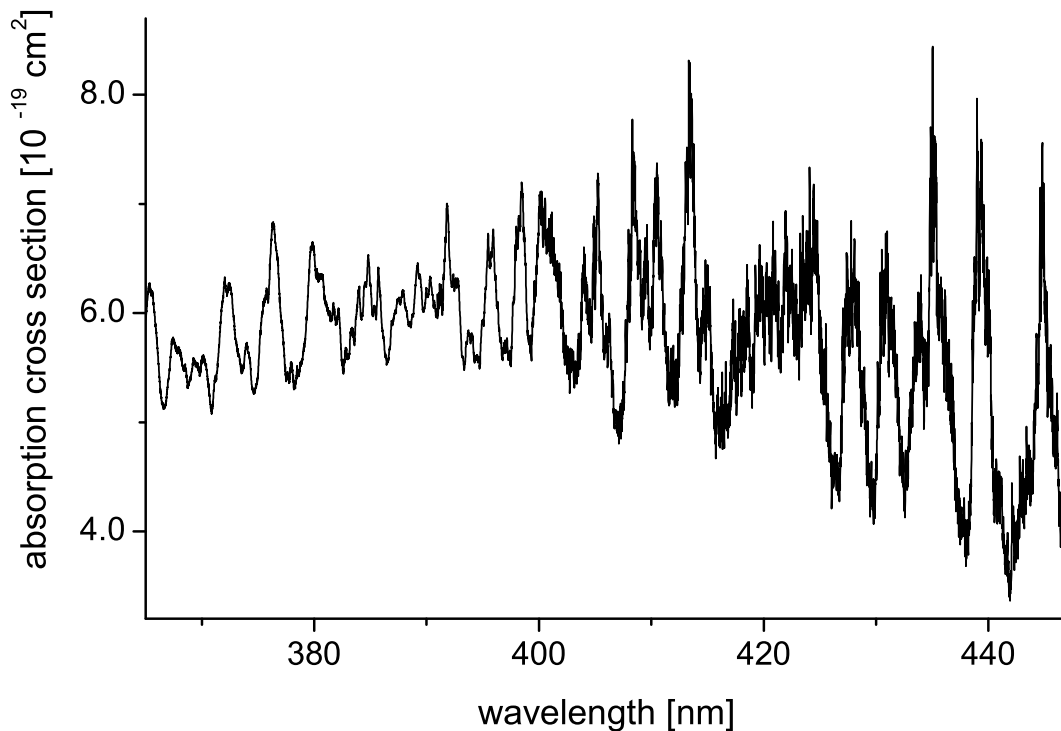
Nitrogen dioxide ( $\text{NO}_2$ ) is a highly reactive gas present at low concentration in atmospheric air. Natural sources of nitrogen dioxide include biological processes in soil, atmospheric oxidation of ammonia, atmospheric discharges, forest fires etc., and provide  $\text{NO}_2$  at concentrations usually below the threshold for adverse biological or environmental effects. Of much more importance are man-made sources, especially emissions from fuel combustion in motor vehicles, electric power plants and other industrial, commercial and residential sources that burn fossil fuel. These emissions are primarily in the form of nitric oxide ( $\text{NO}$ ) which is subsequently oxidized in the atmosphere to  $\text{NO}_2$  [8].

Atmospheric  $\text{NO}_2$  is very important to urban air quality as it has a variety of health and environmental impacts. It can irritate the lungs, cause bronchitis and pneumonia and lower resistance to respiratory infections. In the presence of sunlight, it reacts with hydrocarbons to produce other pollutants such as ozone, the most toxic component of urban smog. When absorbed by water droplets in clouds,  $\text{NO}_2$  is ultimately converted to  $\text{HNO}_3$  and forms acid rain which harms plant and animal life, accelerates corrosion, and acidifies lakes and streams.

At present  $\text{NO}_2$  is commonly detected using methods based on chemiluminescence [8]. Their sensitivity reaches a few parts per billion (ppb). Recent development of GaN and InGaN laser diodes provides an opportunity to construct fully optoelectronic detectors of this compound. These laser diodes generate radiation in the 370 - 445 nm range that coincides well with the  ${}^2\text{B}_1 \leftarrow {}^2\text{A}_1$  and  ${}^2\text{B}_2 \leftarrow {}^2\text{A}_1$  absorption bands of the  $\text{NO}_2$  molecule (Fig. 1) [9]. CRDS with pulsed and cw diode lasers working at around 410 nm has already been used for  $\text{NO}_2$  detection by several groups; some of them achieved the detection limit of 0.7 ppb [10, 11].

### 4. Design of the apparatus

Our experimental setup is presented in Fig. 2. As a light source we use a blue pulsed GaN diode laser (VLMB1, TopGaN, Poland) working at  $\lambda \approx 414$  nm, that generates pulses of about 100 ns duration and  $5 \cdot 10^{-9}$  J energy at repetition rate of 1 KHz. The laser light is incident almost normally on a diffraction grating (1800 grooves per mm) and diffracted in first order into two beams on both sides of the incident laser ray. The main purpose of using an optical grating at this position is to get rid of the background



**Figure 1.** Part of the absorption spectrum of  $\text{NO}_2$  [7].

luminescence of the diode. The dielectric mirrors used in the ring down cavity are highly reflective only over a limited spectral range ca. 30 nm wide. Although much weaker than the laser radiation, the luminescence is spectrally broad and when falling into a region of higher transmission of the mirrors it may easily leak through the resonator, affecting the output signal. One of the diffracted beams is attenuated by neutral density filters and directed onto a photocathode of a low efficiency photomultiplier providing trigger pulses for the detection system (note that because of low sensitivity at the blue end of the visible spectrum, common photodiodes cannot usually serve this purpose). The other beam, after passing through a pinhole bored in a metal screen, to eliminate the unwanted luminescence, is directed with a mirror to the resonator.

The ring down cavity consists of two identical, highly reflective plano-concave mirrors with a radius of curvature of 2 m, coated for optimum performance ( $R \approx 0.999$ ) at wavelengths around 414 nm (we use mirrors supplied by Vigo Systems, Poland, but any mirrors of similar specification can be employed). The mirrors are positioned 60 cm apart, in mounts allowing fine adjustment in order to align the resonator. The mounts are connected via flexible bellows to a metal tube, provided with three side openings. Two of them, placed symmetrically at the ends of the tube, serve as inlets for the ambient air, whereas at the middle one, the outlet, a small propeller fan is mounted that ensures a gentle gas flow through the tube. At both inlets a HV spark discharge

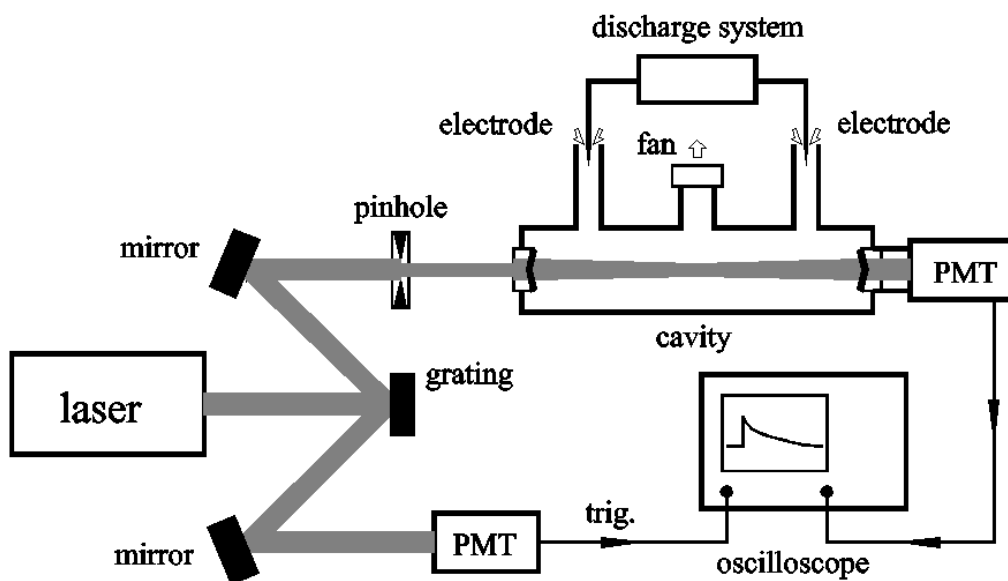
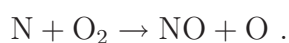
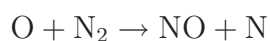
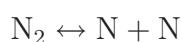
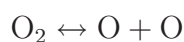


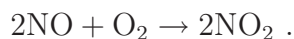
Figure 2. Schematic view of the experimental setup.

can be ignited in the air. The discharge is driven by a generator built from a typical ignition coil and electronic module from a car. It provides electric pulses at about 100 Hz repetition rate and produces sparks between electrodes placed roughly 1 cm apart.

In the hot discharge channel nitric oxide is produced by the break up of  $N_2$  and  $O_2$  in a chain of reactions [8]



Subsequently, NO is oxidized to nitrogen dioxide:



Note that the process is similar to that following a lightning stroke.

The light exiting the ring down resonator through its end mirror is monitored using a photomultiplier tube protected with a narrowband interference filter and placed in close proximity. The photoelectric signal is fed into a digital oscilloscope (TiePie HS-4) with 12 bit vertical resolution and horizontal resolution of 50 MS/s. The decay curve is recorded over a period of three or four decay times. Typically 512 decays are averaged in the on-board memory of the oscilloscope and then transferred via an USB-2 port to a personal computer for further analysis.

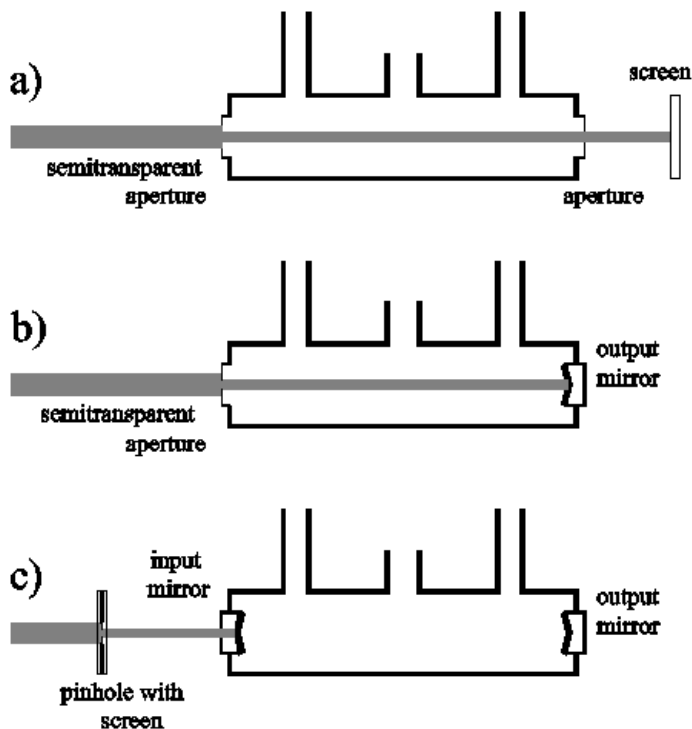
## 5. Alignment, measurements and data analysis

The initial part of the experiment consists of the precise alignment of the ring down cavity so that the laser beam inside the resonator does not walk off the mirrors after repeated reflections. The following procedure, illustrated in Fig. 3, is suggested to the students. First, both mirrors are replaced by centred apertures ca. 2 mm in diameter and the laser beam is sent through them, to be then approximately in line with the optical axis of the resonator (Fig. 2a). Next, the end mirror is mounted in place (it should be pointed out to the student that the coated surfaces of both mirrors must face into the resonator). Since the first aperture is made in a semitransparent material (e.g. white cardboard), a spot of laser light back reflected from the mirror should be visible on it and the mirror position can be adjusted slightly so that the spot overlaps the aperture (Fig. 2b). Otherwise, the following method, specific to the adjustment of optical cavities has to be used. The mirror should be put slightly askew, for example by adjusting the horizontal knob so that the mirror points slightly to the right or left. Then the mirror should be rocked about the horizontal axis with the other knob, sweeping it through the range of angles that includes the correct orientation required for cavity alignment. The search procedure calls for a systematic two-dimensional search over all vertical and horizontal mirror positions. Each time a small adjustment of the horizontal knob should be followed by a large movement of the other knob to pass over the full range of vertical orientations. These two different motions ought to be performed independently but in succession. The search eventually produces a spot of back reflected laser light on the cardboard and then the end mirror can be finally aligned with ease. As the next step, the front mirror is installed. To find its (approximately) correct position a fraction of light that is reflected from the back, flat part of the mirror towards the laser is used, visible as a spot on the screen around the pinhole installed some 20 cm before the cavity (Fig. 2c). The mirror is adjusted until the spot overlaps the forward propagating beam. Now the resonator is close to being aligned. At this stage the photomultiplier can be positioned behind the end mirror and the ring down decay curve should be seen on the oscilloscope. An ultimate, fine alignment of both mirrors is then necessary in order to get a signal of maximum intensity and maximum duration.

As the first stage of the measurements, the decay curve of the 'empty' (i.e. filled only with the ambient air) resonator is recorded. Because the time dependent signal is of a form

$$f(t) = A \exp[-(t - t_0)/\tau_0] + B , \quad (8)$$

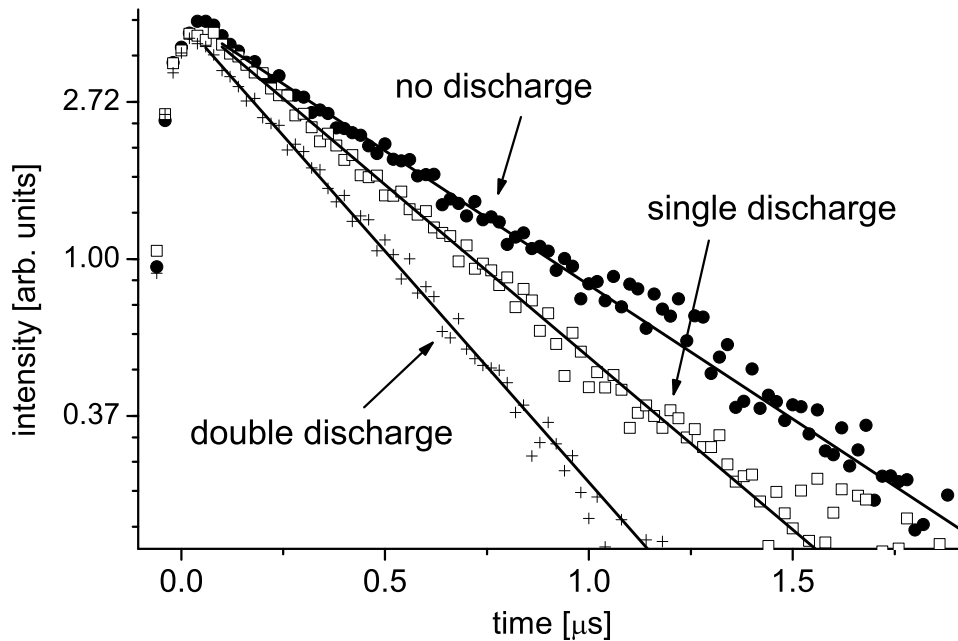
the computer routine subtracts the baseline offset  $B$  and fits a straight line to the natural logarithm of the data in a user-specified region which excludes the tail of the decay where the noise is amplified (Fig.3). Typically we found the decay time constants to have values  $\tau_0 \approx 500 - 700$  ns, which give mirror reflectivities calculated from eq. (4) of  $R \approx 0.997$ , below their specifications. We attribute this fact mainly to degeneration of reflectivity due to dust gradually settling on mirror surfaces as a result of the constant



**Figure 3.** Three steps of the cavity alignment procedure. See text for the detailed description.

flow of air through the cavity. To prevent this, the incoming air is passed through paper filters (we use a layer of a commercial lens paper for this purpose). Occasional cleaning of mirrors is unavoidable but should be only done by instructors rather than by inexperienced students. In addition, filtration of the incoming air serves also to remove aerosol particles present in the air which may cause scattering of the laser light inside the resonator, thus increasing the losses. As concentration of aerosol particles typical for urban atmospheres is known to give extinction of the order of  $10^{-6} \text{ m}^{-1}$  [8], this sets an obvious limit to the sensitivity of  $\text{NO}_2$  detection.

Subsequently, the air entering the resonator is enriched with  $\text{NO}_2$  produced first in a discharge ignited at one gas inlet, then at both of them. A gradual shortening of the decay times can be observed. As an illustration we can consider experimental results presented in Fig. 4, where the values  $\tau_0 = 585.7 \pm 4.3 \text{ ns}$ ,  $\tau_1 = 455.3 \pm 4.9 \text{ ns}$  and  $\tau_2 = 339.9 \pm 2.7 \text{ ns}$  are measured. Taking the absorption cross section of nitrogen dioxide at the laser wavelength as  $\sigma = 6.2 \pm 0.5 \times 10^{-19} \text{ cm}^2 \cdot \text{molecule}^{-1}$  (see Fig. 1), the mean number density of  $\text{NO}_2$  molecules in the resonator can be calculated from eq.(7). For the decays shown in Fig. 4 we obtain  $N_1 = 2.6 \pm 0.2 \times 10^{13} \text{ molecules/cm}^3$  and  $N_2 = 6.6 \pm 0.5 \times 10^{13} \text{ molecules/cm}^3$  with a discharge at one and two inlets, respectively, where the errors result mainly from uncertainty of the absorption cross section. These values can be related to the number of molecules in the air at room



**Figure 4.** Typical ring down decay traces (shown in semilogarithmic scale) measured in the resonator filled with the 'pure' air, air enriched with  $\text{NO}_2$  produced in discharge at one gas inlet and at two inlets. Solid lines represent the fitted exponential decays corresponding to decay times  $\tau_0 = 585.7 \pm 4.3$  ns,  $\tau_1 = 455.3 \pm 4.9$  ns and  $\tau_2 = 339.9 \pm 2.7$  ns, respectively.

temperature and pressure of 1 atmosphere, which may be calculated from the ideal gas law as  $\approx 2.5 \times 10^{19}$  molecules/cm<sup>3</sup>, and expressed as mixing ratios of 1.1 ppm and 2.74 ppm. Alternatively, by making use of the weight of a single  $\text{NO}_2$  molecule, approximately equal to  $14+2 \cdot 16=46$  atomic mass units or  $7.64 \times 10^{-23}$  g, the number densities  $N_1$  and  $N_2$  can be converted to densities of 2.0 mg/m<sup>3</sup> and 5.1 mg/m<sup>3</sup>, respectively. Note that the values obtained are above the limit of safety given by the World Health Organization, which for 1-hour exposure to  $\text{NO}_2$  amounts to 200  $\mu\text{g}/\text{m}^3$  [12].

Equation (7) allows us also to estimate the sensitivity of our cavity ring down measurements in terms of a minimum detectable concentration of nitrogen dioxide. Assuming conservatively that the smallest detectable change in the ring down time when an absorber is present inside the resonator amounts to  $\Delta\tau_{min} \approx 10$  ns, we obtain the relative precision of decay time determination in our experiment equal to

$$F = \frac{\Delta\tau_{min}}{\tau_0} \approx 1.5 \cdot 10^{-2} \quad (9)$$

and

$$N_{min} = \frac{F}{c\sigma\tau_0} \approx 10^{12} \text{ molecules/cm}^3 \quad (10)$$

corresponding to an atmospheric mixing ratio of  $\sim 40$  ppb. Note that this result is achieved with relatively cheap dielectric mirrors. When the mirrors specially designed for CRDS technique are used (with  $R > 0.9999$ ) a detection limit better than 1 ppb can be reached.

## 6. Conclusion

We have presented a laboratory experiment to study trace concentrations of  $\text{NO}_2$  molecules generated in electric discharge in ambient air. Its principal pedagogical value is that it demonstrates how modern laser spectroscopy methods can be applied to monitor toxic emissions with a high sensitivity. This project is suitable particularly for training of undergraduates with an interest in laser physics, optics, molecular spectroscopy and environmental physics. We have found that students' involvement in the experiment is high, resulting in quality performance.

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