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OPTICS

DIRECT OPTICAL ABSORPTION MEASUREMENTS IN GASEOUS MEDIA BY THE CAVITY RING-DOWN SPECTROSCOPY TECHNIQUE FOR THE DEVELOPMENT OF A LOSSMETER

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Abstract. Direct absorption optical measurements with sensitivities better than 2 ppm/cm can be made using pulsed light sources and employing a simple optical cavity configuration. This paper demonstrates that the integrated absorption signal provides a quantitative total absorption measurement if the losses of resonant cavity are not dominated by mirror losses. This is possible when mirror reflectivities are ultra-high. This approach to making absorption measurement provides a sensitivity independent versus noise or fluctuation of optical source intensity.

Key words: spectroscopy, atmosphere monitoring, earth physics

1. INTRODUCTION

Since his introduction as a technique for quantitative optical absorption measurements in the 1988 [1], Cavity Ring-Down Spectroscopy (CRDS) has been employed in numerous configurations for spectroscopic studies in chemical physics and it has proven to be an absorption technique of broad application. One promising area of application is atmospheric monitoring of various pollutants. A number of such species can be detected by visible or near UV absorption analysis.

Because the absorption coefficients at various wavelengths are known for a large number of important pollutants, it is a simple task to transform the measured absorption signal to an absolute concentration. Since the equivalent path length over which the measurement is made is very long (10–20 km), the sensitivity is excellent. The principle of operation is based, not on the measurement of the absorbed signal strength for a given sample path, but of the time rate of absorption

of a sample located within a closed optical resonant cavity. The decay rate of a photon population in an optical cavity is used to obtain the associated total intra-cavity losses (per cm or per pass). When the cavity losses are dominated by cavity mirror scatter and mirror transmission, the frequency resolved "loss" curve maps out the mirror reflectivity function. When a narrow band absorbing species is present, absolute atomic or molecular absorption intensities can be inferred by subtracting the baseline (non-resonant) losses of the cavity, which are determined while the laser is off-resonance with transitions. The power of the CRDS method lies in the extremely high sensitivity and simplicity of the technique, together with the fact that it is an absorption-based method. It can provide absolute attenuation determinations. It is highly desirable for quantitative studies as absolute concentrations to be easily inferred from the absorption data. CRDS concentration detection limits for many species have been demonstrated to be in the part-per-billion (ppb) range [2]. The ability to utilize a single absorption feature ensures that the peak height or area is linearly proportional to the concentration and dramatically increases the probability that an absorption feature of the species of interest can be isolated from that of any interfering species. The spectral range is limited only by the availability of short pulse (several tens of nanosecond or shorter) lasers and high reflectors (better than 99% reflectivity) at a given wavelength.

2. EXPERIMENTAL METHOD

The system involved here is a closed path multipass absorption cell with effective path length of 10^4 meters for cavity mirrors with reflectivity of 99.9985%.

The ability to sample such large paths with a small 0.5 m cavity size optical system makes this approach useful in atmospheric or combustion analysis, especially in studies where spatially resolved sampling of trace constituents is desired. Experimental setup is shown schematically in Fig. 1.

Two wavelengths were involved for ring-down (RD) cavity pumping: 564 nm from a ND6000 Continuum dye laser for loss determination in atmospheric air and 1 064 nm from a Brilliant Quantel Nd:YAG laser for loss evaluation in CO_2 medium. Brilliant laser is used for dye laser pumping with a 2ω module as second-harmonic generator (532 nm) in order to obtain 564 nm output from Rhodamine 590 (Rh 590 Chloride) dye. The dye concentration in ethanol is adjusted to 3.7×10^{-4} (molar) in dye laser oscillator and 3×10^{-5} (molar) in dye laser amplifier. The laser mirrors have a damage threshold of 2 J/cm^2@532 nm and 3 J/cm^2@1064 nm for 10 ns pulsewidth. These values can be overreached with spikes from laser output when the resonance is touched in ring-down cavity. When the setup is involved to provide data from CO_2 with 1 064 nm, then the wavelength from Brilliant at 20 Hz is directly delivered to input of ring-down cavity. The output

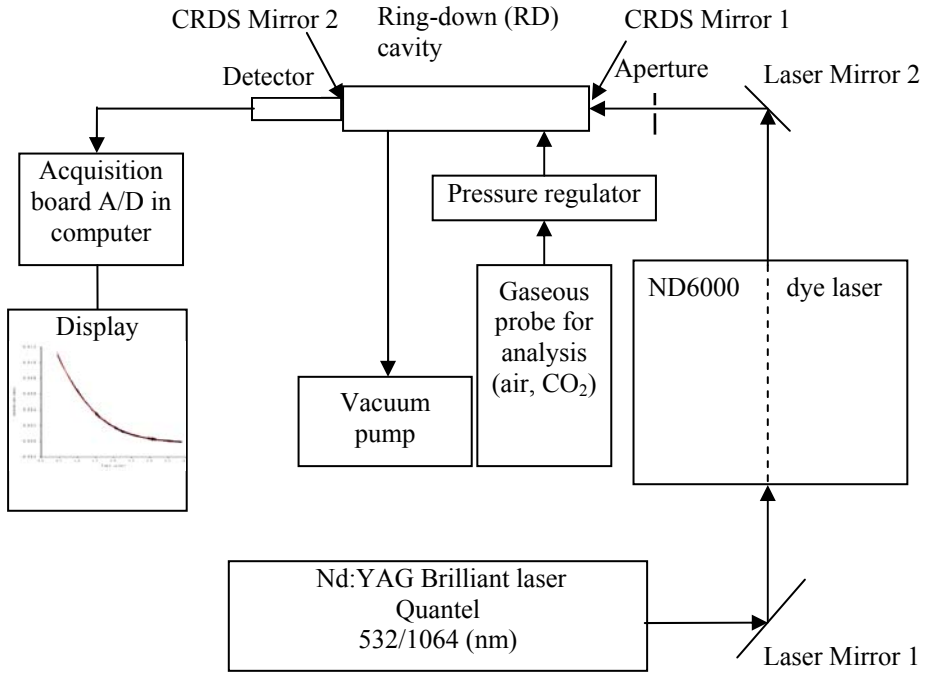

Fig. 1 – Experimental setup for CRDS of gaseous media.

signal from resonant RD cavity is detected with a metal package H5783-20 PMT module from Hamamatsu for 564 nm wavelength and a large area silicon photodiode (1 cm^2) from UDT Instruments for 1064 nm detection. The PMT module has 0.78 mA/W maximum cathode radiant sensitivity in 500÷650 nm range and the Si photodiode has 0.1 A/W@1064 nm absolute responsivity. The output CRDS signal is digitized with high speed Gage CompuScope CS12100-1M card and fit to an exponential waveform to obtain the ring-down time constant, which can be expressed as a loss per cm with Los Gatos Research Inc. CRD V4.0 software. The executable LGR CRD program provides a simple interface for aligning, evaluating and data logging a CRD setup. By wrapping these algorithms in a LabView shell, LGR has also provided a flexible, modifiable and efficient starting point for customer cavity ring-down data acquisition system to specific applications. Parameters for data acquisition are: averaging on 20 laser pulses, sampling rate 100 MHz, voltage gauge: 100 mV/step, 1 024 points/curve, 0.2 V trigger level, 1 MΩ input impedance, parameters fit in maximum 3 iterations, negative polarity for detectors, simultaneous display for signal, fit curve and difference for these traces for maximum of 100 curves in histogram. The external trigger signal is synchronized with the ring-down event. One pair of CRD mirrors

used for 564 nm measurements has 99.9985% maximum reflectivity at 540 nm and the second pair has the same maximum reflectivity at 1 064 nm. The mirrors can be used over a ±25 nm interval around mentioned wavelengths. All mirrors have 1 m radius of curvature and 1" diameter. The full system is exhibited in Fig. 2.

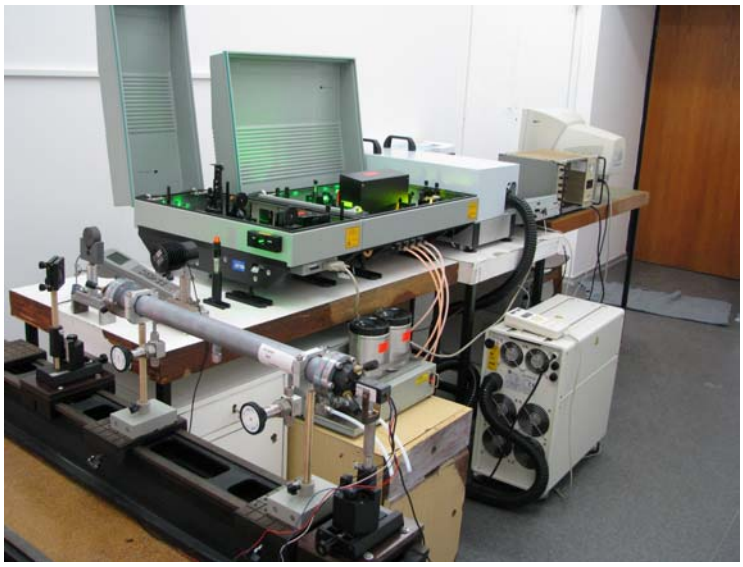

Fig. 2 – Experimental CRDS set-up for gaseous media.

The signal from photodetector is digitized and fed to computer, which fits the trace to a first-order exponential function to determine the decay time constant for each pulse. This constant is determined by two factors: the reflectivity of the mirrors and attenuation of the laser pulse by any absorbing medium inside the cavity. The time dependence of the pulse intensity is then given by Beer-Lambert relation:

$$I(t) = I_0 \exp(-\frac{t}{\tau_0} - \alpha c t), \tag{1}$$

where τ_0 is the time the laser pulse takes to decay to 1/e of its initial intensity in an empty cavity, α is the absorption coefficient of the absorbing medium and c is the speed of light. When there is no absorption inside the cavity (α=0) the decay rate is simple $1/\tau_0$. On the other hand, when a sample inside the cavity absorbs some of the light, the decay rate is given by:

$$\frac{1}{\tau} = \frac{1}{\tau_0} + \alpha c. \tag{2}$$

Therefore, by plotting the decay rate as a function of the laser frequency as it is scanned, an absorption spectrum is build up and because the difference between on- and off-resonance features is simple αc the recorded spectrum is quantitative. Time constant of empty cavity is defined by:

$$\tau_0 = 2L/[c(1-R)], \tag{3}$$

where: L – length of resonant cavity, c – speed of light, R – reflectivity of cavity mirrors. The computer extracts the exponential decay time (τ) of the signal and calculates the total loss:

$$\frac{1}{\tau c} = \alpha + \frac{1-R}{2L}. \tag{4}$$

For ultra-high R (R=0.999985 in this case*)* the absorption loss is dominant versus the losses at the mirrors. From ec. (1) for very small absorbance, for a single round trip ($2L=l$) in cavity, $ct=l$ and $\alpha l \ll 1$, it is obtained:

$$\delta I = \frac{I_0 - I}{I_0} \approx \alpha l. \tag{5}$$

Equation (5) can be written in terms of variation in ring-down rate, $\Delta k = 1/\tau - 1/\tau_0$, thus:

$$\delta I = \Delta k \frac{l}{c}. \tag{6}$$

Zalicki and Zare [3] shown that the variation in ring-down time $\Delta\tau = \tau_0 - \tau$ corresponding to the absorbance for a single pass is:

$$\alpha l = (1-R)\frac{\Delta\tau}{\tau}. \tag{7}$$

The condition of small absorbance can be achieved by obtaining the ring down times from the early part of the RD decay transient.

We can obtain the sensibility by minimum absorption coefficient α_{min} from eq. (7). Therefore, the CRDS sensibility is function of the accuracy of ring-down time measurement. If the measured ring-down time increases with the increasing of mirror reflectivity, then the accuracy is better for the determined value of $\Delta\tau/\tau$. On the other side, the sensitivity of CRDS stems in part from huge number of passes each pulse makes between the ultra-high reflectivity mirrors. For reflectivity of 0.999985 the number of round trips is about 10 000, giving an effective of 10 kilometers, far higher than for conventional multi-pass arrangements. By measuring the ring-down decay rate rather than absolute intensity of the laser pulse, shot-to-shot variations in laser output can be removed from the final spectrum.

3. RESULTS AND DISCUSSION

Experimental it's found that Nd:YAG laser output fluctuations increase to lower emission energies. Even the manufacturer gives a maximum value of 15% for variation of output laser, the measured value reaches 20%. In these conditions the TEM energy distribution of laser beam varies visibly. This distribution affects the stability of the oscillation modes from RD cavity (Fig. 3).

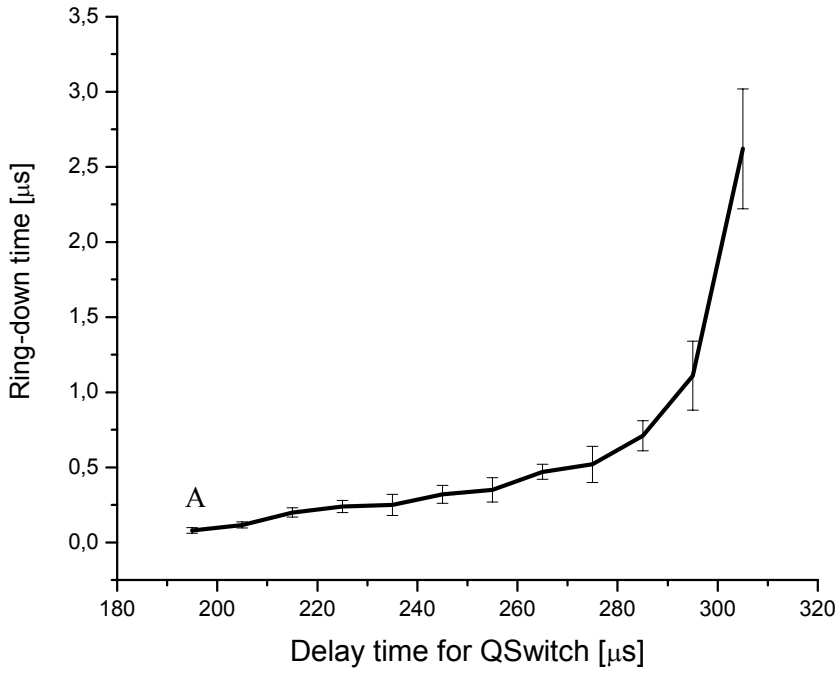

Fig. 3 – Ring-down time of laser pulse of 564 nm from RD cavity *versus* Q-Switch delay time of Brilliant laser.

The loss of an "empty" (actually with air) reference cavity is determined first and is later subtracted from that of the cavity with the sample inside. The difference is attributed to the absorption loss in sample. We chosen as working point for laser-RD system the point A from Fig. 3 corresponding to 195 μs Q-Switch delay time, where the baseline is 90 ppm/cm, for 564 nm pumping wavelength with air in RD cavity.

The measured loss baseline signal of resonant cavity with air in resonant cavity at atmospheric pressure for 564 nm is represented in Fig. 4 and for 1 064 nm pumping wavelength is shown in Fig. 5.

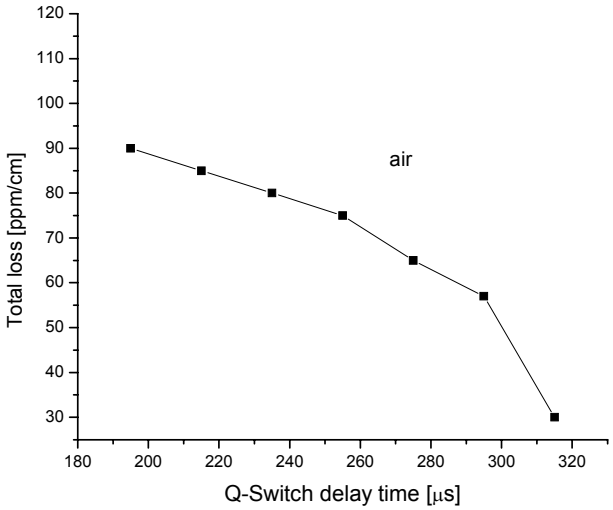

Fig. 4 – Total measured loss baseline versus Q-Switch delay time for air (1 atm.) in RD cavity at 564 nm pumping.

From Figs. 4–6 can be seen that the total losses of resonant cavity decrease with RD cavity pumping energy decreasing. The Nd:YAG laser output available for pumping decreases linear as the Q-Switch delay time increases respectively.

The losses are limited to a stable value of about 90 ppm/cm for absorption of the air at high energies of cavity pumping near. The maximum value of pumping is 360 mJ@1 064 nm at 195 μs Q-Switch delay time. The maximum value of losses is about 550–600 ppm/cm@1 064 nm with CO_2 in RD cavity. For 1 064 nm, to greater values of 307 μs with air in cavity, the instabilities of transmitted light are so high that the measured loss for RD cavity is random varying from 10 to 50 ppm/cm (Fig. 5).

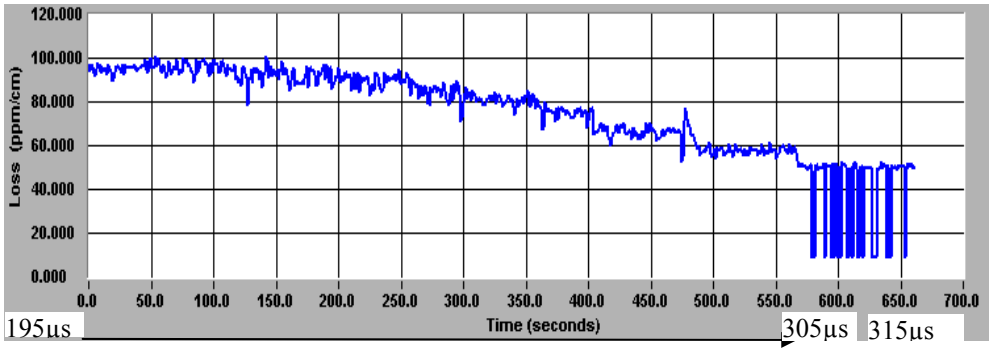

Fig. 5 – Total loss of resonant cavity with atmospheric air (baseline) at 1 bar in resonant cavity for a 660 s registration time, Q-Switch delay time ranging in 195–315 μs interval at 1 064 nm. Total loss are in 30–95×10^{-6} cm^{-1} range for 25 °C, laser energy: 360 mJ (195 μs Q-S delay time) to 17 mJ (315 μs Q-S delay time) step of 10 μs at every 50 s measurement.

The profiles of total loss curves from Figs. 4–6 coincide with the profiles of measured loss due to absorption and scattering in a medium inside of a resonant cavity [4]. The gains of superior oscillation transversal modes have the same allure, a profile coincident with inner loss.

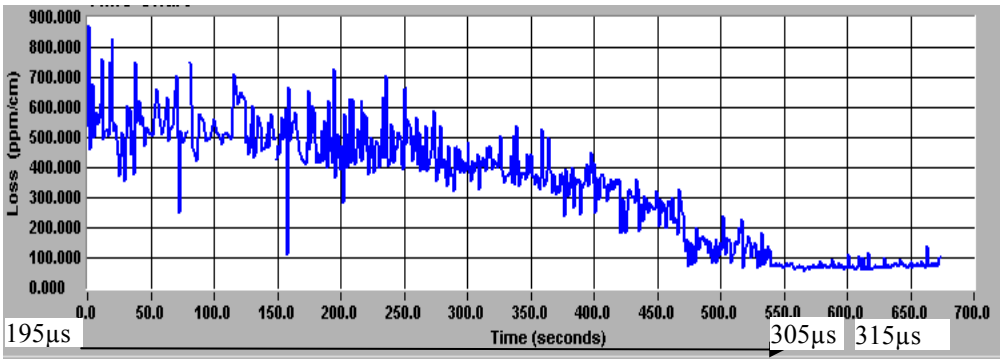

Fig. 6 – Total loss of cavity with CO_2 at 0.5 l/min continuous flow rate for a 660 s registration time, Q-Switch delay time ranging in 195–315 µs interval at 1 064 nm. Total loss are in $70–600\times10^{-6}$ cm^{-1} range for 25 °C, laser energy: 360 mJ (195 µs Q-S delay time) to 17 mJ (315 µs Q-S delay time) step of 10 µs at every 50 s measurement time.

In Fig. 7 the ring-down (RD) curves are acquired and averaged at the highest RD pumping energy.

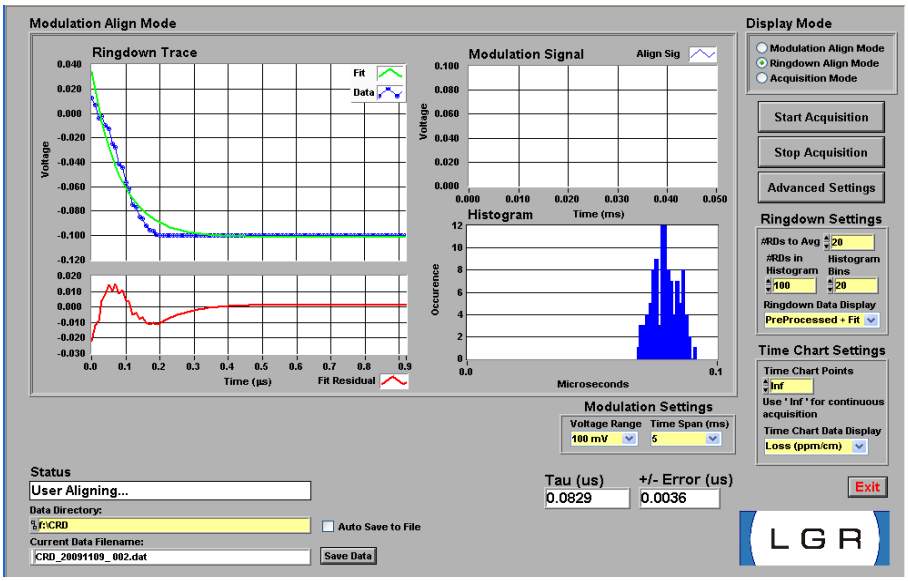

Fig. 7 – A screen capture with measurement for atmospheric air in cavity at 564 nm, 195 µs Q-Switch delay time, R = 99.8800@564 nm (maximum is R = 99.9985%@540 nm).

The RD and fit data are shown in upper left graph. The fit residual is shown in the graph just below left and the histogram on the lower right shows a running accumulation of the last captured ringdowns. The histogram from Fig. 7 represents the closest distribution of RD time measurements.

In Fig. 8 the total loss is recorded and plotted in the time trace at the bottom of the graph group at 564 nm for air in resonant cavity. The histogram in this case shows the distribution of the collected RDs, centered on 0.3117 μs value of ring-down time.

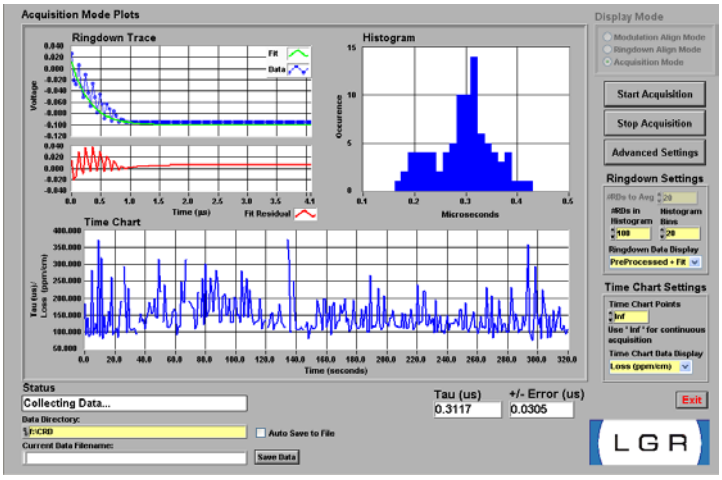

Fig. 8 – Measurement with atmospheric air in cavity at 564 nm, at a constant 260 μs Q-Switch delay time, R = 99.8800@564 nm, cavity loss = 105.87 ppm/cm.

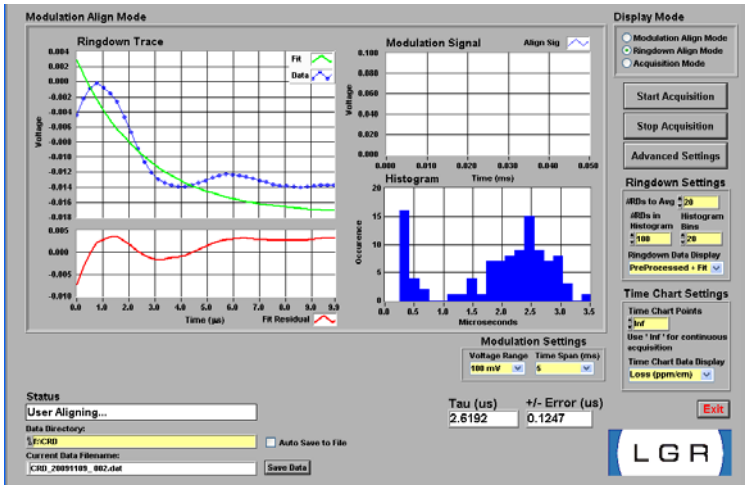

Fig. 9 – Measurement with atmospheric air in cavity at 564 nm, 307 μs Q-Switch delay time, R = 99.8800@564 nm.

The result from Fig. 9 is obtained at a maximum value of Q-Switch delay time where the cavity still resonates. To higher values than 307 μs the resonance is lost and CRDS measurements are not possible. When the wavelength of the injected light is resonant with an absorption feature of a species in the cavity, the ring-down time decreases linear versus concentration increasing of the species in cavity. If the wavelength injected in cavity does not match an absorption feature of any gas or impurity in the cavity, the decay time is dominated by mirror loss.

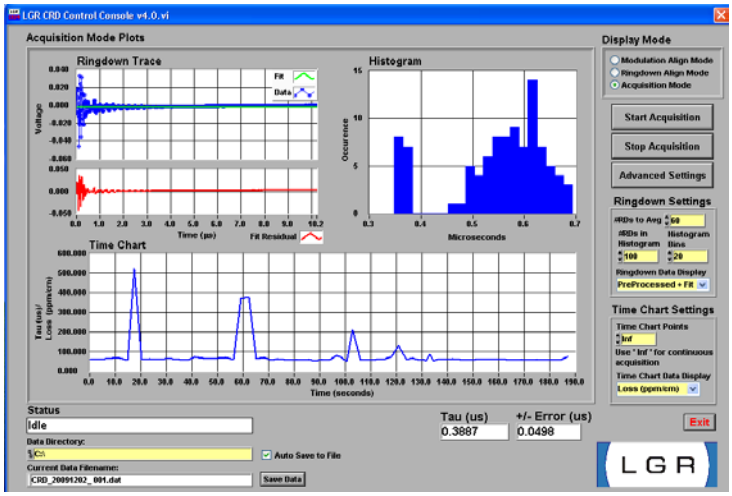

Fig. 10 – Loss registration at 1 064 nm in resonant cavity without CO_2 in chosen working point, average ring-down time: 0.52 μs and baseline: 79.71 ppm/cm.

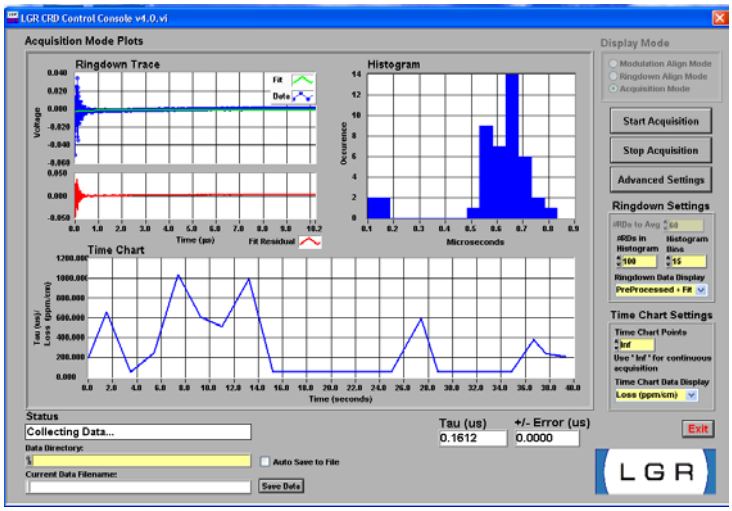

Fig.11 – Loss registration at 1 064 nm with CO_2 for first 14 s (600 ppm/cm), two spikes of 1 000 ppm/cm, 0.5 l/minute flow rate. Flowing of CO_2 is stopped after 14 seconds.

Ring-down times are 0.16 μs with CO_2 and 0.52 μs without CO_2 in resonant cavity, Q-Swith time is 195 μs (Fig. 11) and the baseline is about 80 ppm/cm. The investigated absorption line of CO_2 is ($20^03 \leftarrow 00^00$) R(6), which is weak [2].

Two effects can explain the spikes in the registrations from Figs. 10 and 11:

1. Multiexponentially decaying effect: the CRDS signal is only a single-exponentially decaying curve if the bandwidth of the laser radiation that is coupled into the cavity is much smaller than the width of the absorption features. But, if a strong but narrow absorption is detected with a broad bandwidth laser, whose centre frequency is set at the frequency of the absorption, then light with the frequency at the centre of the absorption line will have a short decay time, whereas frequencies in the wings of the laser profile will have the decay time of the empty cavity, which is much longer. The observed ring-down time, which is obtained by fitting the measured (multiexponentially decaying) transient to a single-exponentially decaying function, is predominantly determined by the contributions of the wings of the laser profile. Thus, in general, an absorption is underestimated if the bandwidth of the laser is comparable with or larger than the width of the molecular absorption. It is noted that this bandwidth effect is similar to that observed in conventional absorption spectroscopy when the instrumental resolution is lower than the width of the absorption features ([1, 3, 5]). These studies have shown that, for cases in which the bandwidth of the laser cannot be neglected, one can still extract the correct absorption coeficient from the measured decay transients, provided that the spectral intensity distribution of the light source is known. Zalicki and Zare [3] have also shown that for small absorbance the measured integrated absorption deviates only slightly from the true integrated absorption. This has experimentally been demonstrated by Newman et al. [6] who compared results from two spectroscopic techniques: high-resolution Fourier transform spectroscopy with a long-path absorption cell and CRDS.

By limiting the determination of the ring-down time to the first 0.5 μs of the decay transient (for a decay time of approximately 10 μs), the integrated absorption intensity Newman obtained from the CRDS experiment was in excellent agreement with that obtained from the Fourier transform experiment.

The width of 1 064 nm laser line from Nd:YAG Brilliant laser, used in our experiments, is larger than absorption line of CO_2 (much thinner than 1 cm^{-1}).

2. The rising of mode beating is the second effect. This event appears since the bandwidth of the excitation laser is often much larger than the (residual) mode spacing and many modes are excited or laser pulses are longer than the cavity round trip time [2]. For a empty cavity with 0.5 m length the round trip time is 3.3 ns. Hodges et al. [7] shown that the excitation of many (transverse) modes dramatically reduces the modulation depths of the beats observed in the RD transients. When the ring-down transients are averaged, the residual mode beating effects are further minimized, leading to a single-exponentially decaying transient.

Mode beating effects in the RD transient are often difficult to observe owing to a slow detector response or electronic filtering. However, the ultimate sensitivity is obtained if only one single longitudinal mode is excited in the cavity, giving a truly single-exponential decay [8].

In order to perform such an experiment, the mode spacing of the cavity should be larger than the spectral width of the laser and the cavity length should be carefully controlled in order to prevent drift of the modes.

Else, a cavity with long free spectral interval together a mode-locked laser are required to avoid this second effect [9].

Another key to the successful operation of this technique for optical absorption measurements is the use of a laser pulse with a coherence length so short that no interference can become established in the resonant cavity [10]. In the short pulse regime, for instance: 5–6 ns, the Fabry-Perot theory breaks down, permitting any frequency to be injected into cavity. The operation in this regime ensures that every pulse of the laser enter the cavity, producing stable and reproducible operation and continuous frequency scanning is possible without jumping from mode to mode as the frequency is scanned [11].

In our work, the losses within the cavity can be determined with a standard deviation on the order of 2 ppm/cm or 2×10^{-6} cm^{-1}@564 nm wavelength for air in RD cavity. If the empty cavity space between the mirrors is filled with an absorbing medium and the decay time is not dominated by mirror losses, then the system becomes an absorption spectrometer. The sensibility for this is evaluated using ec. (7) and values of ring-down times for empty cavity and with CO_2 cavity to α_{min}=0.14 ppm. By ensuring that each laser pulse produced with Brilliant laser for pumping and sent to the system is coupled into the cavity, it becomes feasible to use laser pulses with low duty cycle. The use of dye laser source greatly increases, through doubling or mixing, the spectral range which is available to this technique.

4. CONCLUSIONS

The absorption spectroscopy method with resonant cavity has been detailed and the concepts involved here were demonstrated in a proof-of-principle experiment which was carried out using a pulsed dye laser light source at 564 nm or directly a pumping of RD cavity with Nd:YAG laser radiation at 1064 nm. The experiment looked at the absorption signals produced by molecules from atmosphere at 564 nm and from CO_2 at 1 064 nm. The most exceptional aspect: it is not necessary to condition the gaseous probe in any way, including removal of water vapor. The absorption of H_2O is in 584–606 nm range. The development of CRDS system has resulted in the ability to make absorption measurements with the precision of 2 ppm/cm@564 nm in air. Total loss of cavity with CO_2 at 0.5 l/min continuous flow rate for a 660 s registration time was evaluated with Q-Switch delay time in 195–315 μs range at 1064 nm. Total loss are in $75–600\times10^{-6}$ cm^{-1}

interval for 25 °C, laser energy from 360 mJ (195 μs Q-Switch delay time) to 17 mJ (315 μs Q-Switch delay time) step of 10 μs at every 50 s measurement time, without additional calibration. It was necessary to choose a stable working point from laser output versus delay time Q-Switch graph for optimum resonance of spectroscopic cavity. The cavity is most stable to higher level of laser pumping.

Thus, the loss registration at 1064 nm with 0.5 l/min. CO_2 was evaluated to about 600 ppm/cm, respectively 520 ppm/cm over average baseline at maximum pumping energy, corresponding to absolute concentration of 26 000 ppm CO_2 for 50 cm RD cavity length. The ring-down time for CO_2 decreases of 3.2 times versus the ring-down time for air in resonant cavity at 1 064 nm. The sensibility of our set-up is 0.14 ppm. This work demonstrates that this spectroscopic approach can be used to record quantitative absorption signals of weak absorbers at signal collection rates which exceed that possible using the conventional spectroscopic technique.

This approach would be of great importance in the concurrent monitoring of several absorbing species in the spectral range of maximum reflectivity for CRDS mirrors.

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