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# CRDS Measurement Data Acquisition in Supersonic Expansion

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**Abstract.** Properties of molecular radicals with atmospheric relevance created in our experiment are measured spectroscopically. In order to enhance detection sensitivity we implemented the continuous wave cavity ring-down spectroscopy (cw-CRDS) technique. It enhances sensitivity by increasing effective path length through the sample while keeping small detection volume - contrary to other multi pass methods. Implementation of this method is described in this article along with approach taken to couple the cw-CRDS with the pulsed radical source and computer methods for data acquisition and processing of the measured data.

## Introduction

Spectroscopic measurements of both stable and transient molecules and their complexes in supersonic beams have a wide array of applications ranging from providing key data for theoretical chemistry to atmospheric research (Jenkin, 2002; Frost, 1999) and specific applications in combustion chemistry (Cheskis, 1998).

In our experiment we combine pulsed slit supersonic discharge nozzle as a source of cold transient molecules with methods of absorption spectroscopy as means of detection (Masat and Votava, 2008). Because of low concentrations of transient species produced in the source direct absorption methods often do not have sufficient sensitivity. Recently we have therefore implemented cavity ring-down spectroscopy (CRDS) detection method which has higher sensitivity due to longer effective path length through the sampled medium. This method is now used in many experiments but we implemented several new and unique approaches in combing this method with pulsed molecular source.

In the first part of this paper we describe the CRDS method and its application for continuous sources (cw-CRDS). Then in the second part we outline the timing issues in combining this method with pulsed molecular sources. Finally the third part focuses on the signal processing and last part shows preliminary measurement with all those techniques combined along with sensitivity limits estimation.

## CRDS experiment principle

Cavity ring-down absorption spectroscopy (CRDS) is a highly sensitive absorption detection technique that is based on measurements of photon decay times in high finesse Fabry-Perot type resonators: When a short light pulse is injected in a high finesse optical cavity, an exponentially decaying signal (ring-down) is observed at the resonator output. Time constant of this exponential decay is determined not only by the mirror reflectivities but also by absorption of the medium placed inside the resonator and can be calculated as:

$$\tau = \frac{d}{c(1 - R - \alpha L)}, \tag{1}$$

where $d$ is distance of mirrors creating the resonator, $c$ is the speed of light, $R$ is mirror reflectivity, $\alpha$ is the absorbance of measured medium and $L$ is the path length of beam through the absorbing medium.

### CRDS with cw lasers

Usage of CRDS with continual lasers (cw-CRDS) follows the same basic principles. However, to achieve effective coupling of the laser power into the resonator, laser frequency must be matched to one of the resonator longitudinal modes and fast optical switch (such as acousto-optic modulator AOM) is used to rapidly interrupt the incoming laser beam to observe the ring-down signal. Typically the resonator length is adjusted using a precision piezoelectric transducer (PZT) until the resonance condition $2L = n\lambda$ is fulfilled, where $\lambda$ is the laser wavelengths, and $n$ is an integer number. A typical layout of the cw-CRDS experiment is depicted in Figure 1.

In the most commonly used implementation of the cw-CRDS technique a saw-tooth voltage signal is applied to the PZT to repetitively sweep the cavity length over slightly more than one free spectral range (FSR) (see Figure 2). It is therefore ensured that at least one resonance between the laser and cavity is observed per sweep. At each resonance the ring-down time is measured and thus the absorbance is determined. This

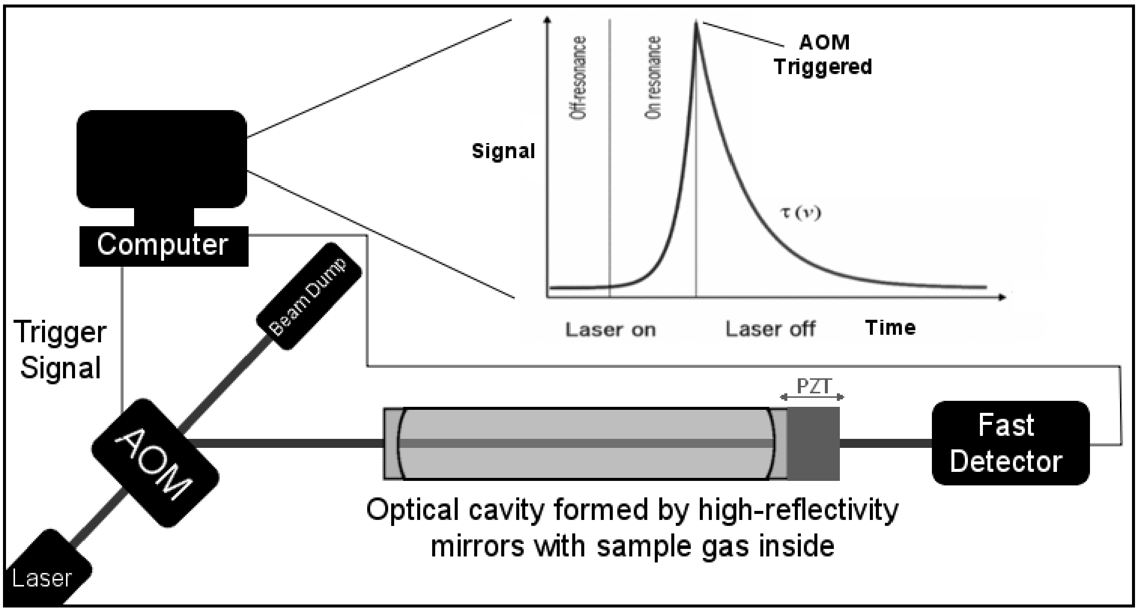


**Figure 1.** Typical layout of a cw-CRDS experiment. Single frequency laser beam is diffracted with AOM into the high finesse resonator. Resonator length is modulated with a PZT mounted end mirror. When the cavity is off resonance no measurable signal is observed on the detector. When resonance is achieved, signal on detector steeply rises. At predetermined threshold level, signal is sent to switch off the AOM and laser beam is interrupted. Decay of signal is then recorded and processed by computer. Laser frequency is stepped to measure the absorption spectra.

technique proved to be very useful for high sensitivity measurements in static samples, where precise timing of the ring-down events is not required.

**cw-CRDS in pulsed supersonic beam**

While the full-FSR sweep technique described above is very easy to implement it has limitations in terms of the repetition rate of the ring-down events. The sweep over a distance between two modes ($\Delta L = \lambda/2$) takes typically about 3–5 ms. Such repetition rate is sufficient in many experiments where the absorbance does not change on the millisecond time scale.

Our experiment however uses a pulsed supersonic nozzle with low duty cycle because we need to evacuate rather large amount of gas released from the nozzle during each gas pulse. Specifically the nozzle is fully opened for 0.5 ms at the repetition frequency of 3 Hz. With the 3 ms time separation of ring-down events majority of them (5 out of 6) would occur outside the nozzle opening window. This would be both waste of time and often expensive chemicals. To avoid these losses we implemented a method called cavity tracking to increase the ring-down event repetition rate.

In this approach the PZT is dithered over a range that is much narrower than the full FSR of the cavity and a DC offset is added to this oscillatory component to place a resonance close to the center of this narrow sweep range (see Figure 3). A feedback servoloop is then used to adjust the DC offset to compensate for slow drifts of the cavity lengths and/or for the laser tuning. This approach has been first reported by Romanini and coworkers (Romanini et al. 1997) and also used in other experimental setups (Macko et al. 2004).

We have however developed a novel tracking control unit based on a microcontroller—a single chip reprogrammable unit - that controls both the sweeping and tracking and provides high level of flexibility. Various tracking strategies can be implemented by simply changing the control software without the need to modify the circuit layout. Moreover, number of operation modes can be pre-programmed and easily software selected during the operation. The unit contains the ramp generator, CRDS event detection and the microcontroller CPU unit.

The control unit monitors when the CRDS event occurs and after a set delay it switches the direction of PZT ramp to opposite direction to sweep back towards the resonance. By this simple procedure the PZT sweeps around the resonance up and down switching the sweep direction each time the resonance is reached. The sweep range is set by the delay time between the ring-down event and ramp direction switch.

Narrowing this sweep range increases the frequency of ring-down events, but at the same time also increases the sensitivity to external disturbances. If the resonance is shifted outside the tracking range, on a time scale short compared to the servoloop response time, the lock is lost. The PZT control must then switch to the search mode until the resonance is detected again.

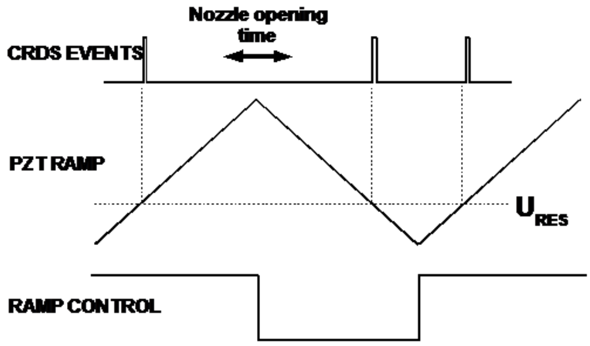


**Figure 2.** In commonly used full sweep mode the time distance between two ring-down events could be so big that in most cases the ring-down event is not present during the time when nozzle is opened.

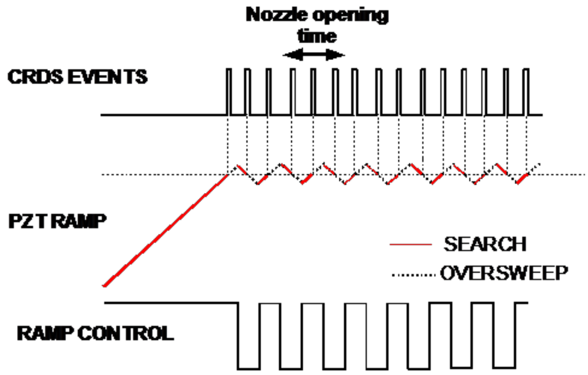


**Figure 3.** Once the resonance is found, in cavity tracking mode PZT sweeps only a small length and the ring-down events could be numerous.

Successful implementation of the tracking method therefore also requires sufficient mechanical stability of resonator length. Just a small jitter of resonator length caused by mechanical vibrations will project into time jitter of ring-down events. Taking into account our nozzle opening window (fully opened for 0.5 ms) the timing tolerance should be under ± 250 μs so the resonator length has to have stability of ± 25 nm if the PZT sweep rate is 5 ms/FSR and laser wavelength is 1000 nm. Our implementation achieves this stability with a robust construction of the whole resonator. Both resonator mirrors are fixed to a solid stainless steel frame built around the pulsed nozzle assembly. The frame is mechanically decoupled from the rest of the experiment so that vibrations do not directly transfer to the mirrors. We have found that using standard kinematic mounts for the mirrors already severely compromises resonator stability. Therefore the mirrors are pre-aligned and then glued with a high-vacuum epoxy directly to the end flanges of the resonator frame.

With our novel tracking system and this rigid cavity design the ring-down event frequency is up to 5 kHz. This ensures that at least one (typically 2 or 3) ring-down events are observed within each nozzle opening window. At these conditions during the measurement cycle we can measure ringdown decay constants before the nozzle opens, 2–3 time decay constants while the nozzle is fully opened and again several time decay constants to determine the baseline after the nozzle shuts.

## Data acquisition approach

While the PZT control works independently, laser tuning and data acquisition is operated with computer using National Instruments PCI6221 data acquisition card for laser control and fast Adlink PCI-9812 card for ringdown data acquisition, both controlled with custom built program. For each measurement step the program sets laser frequency and cards parameters. Data acquisition is started a set amount of time (usually 0.3 ms) before the nozzle opens and continuous stream of data are collected at maximum speed of 20 millions of samples (MS) per second. The Adlink card can store up to 32kS in internal memory, so even at maximum speed we sample 1.6 ms which samples the entire gas pulse (≈1 ms) and enough samples before and after the pulse to determine the baseline signal. After preset data point number is collected all data are sent to the computer.

The ring-downs are automatically detected and extracted from the full dataset. This procedure cuts the dataset into subsets which are further processed. Each subset starts just after the maximum of ring-down signal, and is 50 μs long, which corresponds to ≈3× the ring-down time with our current resonator mirrors. Ring-down time constants are fitted with fast CSI-fit algorithm (D. Halmer et al., 2004) for all the events in the dataset. Even though there is no synchronization between the ring-down events and nozzle opening we can assign the arrival

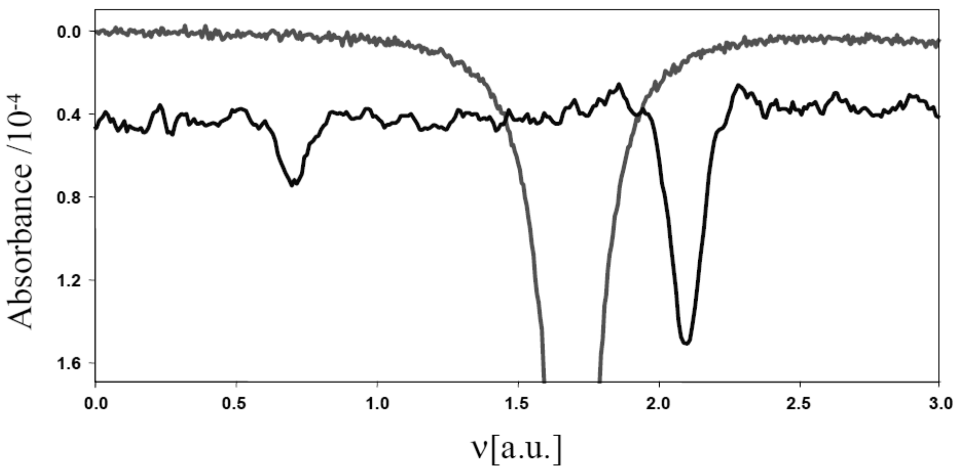


**Figure 4.** Comparison of the direct absorption and cw-CRDS measurements. Direct absorption wase shifted for clarity. When comparing sensitivity of those two methods we have calculated weakest detectable absorbance. As a detection limit a signal/noise ratio = 1 was taken. First measurement shows that the cw-CRDS system has 9 times lower detection limit.

time to each ring-down event because the dataset starts synchronously with the nozzle opening.. It is therefore possible to determine which ring-down events correspond to fully opened nozzle (signal window) and which were measured either before or after the pulse (baseline windows). Net absorption in the gas pulse is calculated from the difference of ring-down times in the signal and baseline windows respectively. Before the next nozzle opening the laser is tuned to new frequency and Adlink card is prepared for next data acquisition event.

## Sample CRDS measurement

First measurements serving as a proof of concept were made. Water was taken as a test molecule, in low concentration as a result of mixing laboratory air with argon.

Scanning over absorption line proved the control program to be fully functional, rigidity of the cell and electronic feedback PZT controller to be able to work in cavity tracking regime at 5 kHz. Sensitivity comparison was based on noise levels in direct absorption measurement and this cw-CRDS measurement as illustrated in Figure 4. With the limit of detection taken at the level noise/signal = 1, direct absorption can detect spectral lines with the $\alpha.l$ (absorbance multiplied by path through sample) higher than $2.0\times10^{-5}$ and cw-CRDS measurement needs just $\alpha.l > 2.3\times10^{-6}$, making cw-CRDS measurement nearly 9× more sensitive.

## Conclusion

We have built a new high sensitivity detection system based on cw-CRDS. Several unique solutions were applied to combine the cw-CRDS method with our pulsed radical source. With novelty electronic PZT control system and robust resonator construction high ring-down repetition rate up to 5 kHz is achieved. Relatively high signal data flow is processed with custom built application which copes with fast data processing at real time and laser control.

With the same measurement time as for direct absorption we are able to increase overall sensitivity more than nine times. Developed system is sufficiently universal to be used for improvement of performance in other spectroscopic experiments taken as whole or by its parts.

## References

Frost G.J., Ellison G.B., and Vaida V., Organic Peroxyl Radical Photolysis in the Near-Infrared: Effects on Tropospheric Chemistry, *J. Phys. Chem.,* Vol. 103, p. 10169–10178, 1999.

Cheskis S., Derzy I., Lozovsky V.A., Kachanov A., Romanini D., Cavity ring-down spectroscopy of OH radicals in low pressure flame, *Applied Physics B,* Vol. 66, p.377–381, 1998

Halmer, D., Golo von Basum, Hering, P., and Mürtz, M. Fast exponential fitting algorithm for real-time instrumental use, *Rev. Sci. Instrum.,* Vol. 75, p. 2187–2191, 2004

Jenkin M.E. et al., Development of a reduced speciated VOC degradation mechanism for use in ozone models, *Atmos. Environ.* Vol. 36, p. 4725–4734, 2002.

Macko, P., et al., Afterglow studies of $H_3^+$ (v=0) recombination using time resolved cw-diode laser cavity ring-down spectroscopy, *Int. J. Mass. Spectr.*, Vol. 233, p. 299, 2004.

Masat, M., Votava O. Characterization of supersonic radical source. In *WDS '08*. 2008.

Romanini, D., Kachanov, A. A., and Stoeckel, F., Diode laser cavity ring down spectroscopy, *Chem. Phys. Lett.*, Vol. 270, No. 5–6, p. 538–545, 1997.