

# Use of Broadband, Continuous-Wave Diode Lasers in Cavity Ring-Down Spectroscopy for Liquid Samples

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Cavity ring-down spectroscopy (CRDS) is an extremely sensitive absorption technique that has been applied primarily to gas samples, which are characterized by having narrow absorption features. Recently, CRDS has also been applied to liquid samples, which have broad absorption features. The use of small inexpensive diode lasers as light sources for liquid samples is demonstrated. The low cost coupled with the ease and technical straightforwardness of application gives this technique wide appeal.

Index Headings: Absorption; Cavity ring-down spectroscopy; CRDS; Diode laser; Liquids.

## INTRODUCTION

Cavity ring-down spectroscopy (CRDS) is a relatively new technique heralded as an extremely sensitive measure of absorption.<sup>1</sup> It has generally been applied to molecules in the gas phase with excellent results.<sup>2</sup> CRDS employs highly reflective mirrors to form an optical cavity. Laser light is allowed to fill the cavity and is then shuttered. A photomultiplier or photodetector is used to detect the light as it leaks out of the cavity through the back mirror. The intensity of the detected light, the ring-down signal, decays exponentially with time constant  $\tau$ , which depends only on the characteristics of the cavity and any absorber within the cavity. Insensitivity to fluctuations in input laser intensity and a massive increase in effective pathlength owing to the multipass nature of the method provide the large increase in sensitivity relative to a traditional absorption measurement. Almost all CRDS studies have been performed on molecules in the gas phase. We report here a promising approach for carrying out cavity ring-down spectroscopy in liquid samples cheaply and easily. Because of the large linewidths of absorbers in liquids, we are able to develop a much-simplified approach to CRDS measurements.

## THEORY

Of critical concern is the linewidth of the laser compared with the linewidth of the absorption feature of interest. Use of a laser with a linewidth wider than or even comparable to that of the absorption feature produces systematic errors in the concentrations of absorber calculated

using a simple exponential-fit model to the data.<sup>3</sup> Of the two possible solutions to this problem, most experimentalists have chosen to use narrow-linewidth lasers rather than more complicated fitting routines.<sup>4</sup> Absorption linewidths in the gas phase are typically  $0.1 \text{ cm}^{-1}$  or narrower, so a very narrow linewidth laser is necessary.

Typical light sources used for gas-phase CRDS are thus either expensive pulsed lasers or very narrowband, continuous-wave (cw) diode lasers. The tunable pulsed lasers typically cover an entire bench top, require massive amounts of electricity to run, and cost several hundred thousand dollars. The narrowband diode lasers cost comparatively less (several thousand dollars) but require sophisticated instrumentation to couple the light into the cavity.<sup>5</sup>

Recently, we have been successful in adapting CRDS for use in liquids with a conventional Nd:YAG pumped dye laser.<sup>6</sup> Absorption linewidths in the liquid phase are much wider than those in the gas phase, on the order of  $1000 \text{ cm}^{-1}$ . Consequently, in the current work we were able to employ a hand-held, broadband, inexpensive (\$500) diode laser capable of running on just a few volts of electricity. In addition, little sophisticated instrumentation was needed to couple the laser light into the cavity other than an optical chopping device.

The laser beam may follow many stable trajectories in an optical cavity. These are generally divided into axial and transverse modes. Axial modes are different frequencies that "fit" in the cavity; a standing wave solution requires a half-integer number of wavelengths to fit between the boundary conditions imposed by the mirrors. Transverse modes are different cross-sectional shapes. In the case of cylindrical symmetry, as in our experiment, they are described by Gaussian-Laguerre polynomials. These transverse modes are the well-known TEM<sub>pl</sub> shapes.<sup>7</sup>

Each of the different modes supported by the optical cavity has a slightly different ring-down time. Nevertheless, under many experimental conditions the ring-down time constant,  $\tau$ , can be well approximated by:

$$I = I_0 \exp(-t/\tau) \quad (1)$$

where  $I$  is the intensity of the transmitted light,  $t$  is time, and  $\tau$  is the decay constant.<sup>8</sup> By carefully directing the laser light into the cavity, we are able to excite mostly

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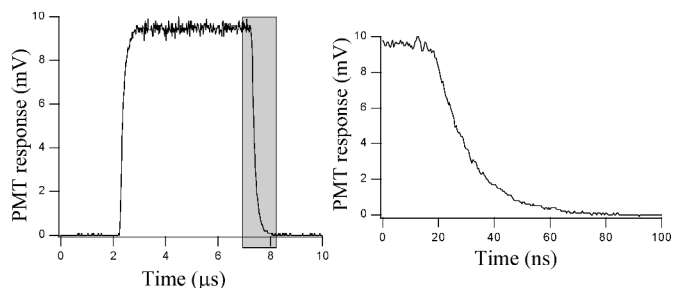


FIG. 1. Ring-up and ring-down signals taken in pure acetonitrile at 655 nm. The falling edge is expanded to show the exponential decay of the ring-down signal.

the TEM<sub>00</sub> transverse mode. This is the circular mode that exhibits the least amount of diffraction loss. Various schemes have been employed to excite a single axial mode of an optical cavity,<sup>5</sup> to average over multiple axial modes,<sup>2</sup> or to excite off-axis to avoid cavity mode structure with a concomitant loss of intensity.<sup>9</sup> Our system is the type that averages over many axial modes because the linewidth of the laser is much larger than the spacing between cavity axial modes. In this respect our setup is entirely equivalent to those using a pulsed system.

Although the power of the laser does not affect the exponential decay constant  $\tau$ , it does affect the signal-to-noise ratio on the detector. One might therefore expect that a relatively low-power diode laser would be unsuitable for CRDS. However, long pulses may constructively interfere over multiple reflections to store power in the cavity. Figure 1 shows intensity building up in our cavity and then ringing down.

## EXPERIMENTAL

The diode laser (Power Technology Inc., PM series, 655 nm) is driven by 5 V at 120 mA to produce approximately 35 mW of power. The laser is quite small, 12.60 × 50.93 mm, and is plugged into a normal wall socket. We used an acousto-optic modulator (AOM; Brimrose TM 200-58-658) to switch the light on and off to perform the experiments. The optical cavity is constructed from two highly reflective mirrors (Newport Supermirrors,  $R \approx 99.9\%$ ). Figure 2 shows the setup in more detail. We separated the first-order modulated beam (approximately 5 mW) with an iris and directed this beam into the optical cavity. The maximum switching rate is determined not by the AOM controller but rather by the amount of time needed for intensity to build up in the cavity and then ring down for each measurement. Because we work primarily in regions where decay constants are on the order of 100 ns (due to absorption by the solvent), we can switch as fast as 1 MHz. This signal-sampling rate is in sharp contrast to the typical pulsed setup, which typically runs at speeds on the order of 10 Hz. This massive increase in repetition rate is one of the sources of increased sensitivity with time for cw-CRDS. Narrowband cw diode lasers also enjoy this increase in repetition rate. With this particular experimental setup, we are limited by the data transfer rate of our oscilloscope (LeCroy LT372) to a data acquisition rate of 10 kHz. In future work this limitation will be eliminated by use of analog signal processing. In future work we also expect to address the

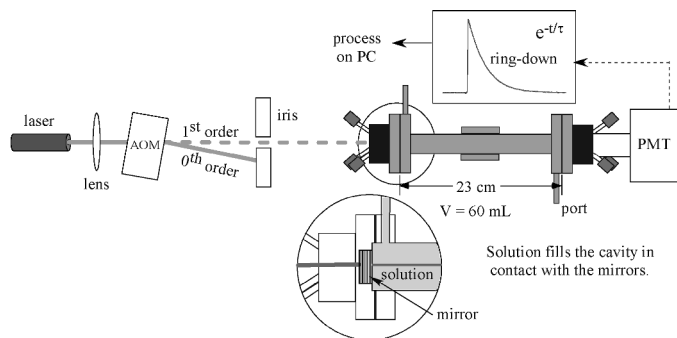


FIG. 2. Light from the laser is focused by a lens and chopped by an acousto-optic modulator. An iris selects the first-order beam. A photomultiplier records the decay, which is sent to an oscilloscope and computer for processing.

issue that the current diode laser operates at a single wavelength, either by employing a tunable diode or by coupling many diodes at once using fiber optics.

## RESULTS AND DISCUSSION

In this study we use a broadband, continuous-wave diode laser as the light source for CRDS. The measured ring-down lifetime varies by less than 2% ( $\sigma_r/\tau$ ) over several hours. This variation translates to a minimum detectable change in absorption coefficient of 1 part in  $3 \times 10^6 \text{ cm}^{-1}$  (one  $\sigma$ ). This corresponds to detecting ppb to ppt for good absorbers. This detection limit is only slightly higher than the limit reported for a standard CRDS setup with a pulsed dye laser under similar conditions.<sup>5</sup> Changes in experimental setup, particularly solvent and wavelength, have a large impact on the detection limit; therefore, future work is expected to improve the detection limit greatly.

Given the high repetition rate, our new methodology can be used to follow processes with time resolution as fine as microseconds. We have been able to monitor the kinetics of reactions in which an absorber is either created or destroyed under a variety of conditions. Figure 3 shows the decay in concentration of methylene blue as it undergoes a reduction in the presence of ascorbic acid to form leucomethylene blue, which does not absorb. We feel that the capability to monitor reactions at nanomolar concentrations with microsecond time resolution is very promising. In general, the study of reactivity over a broad

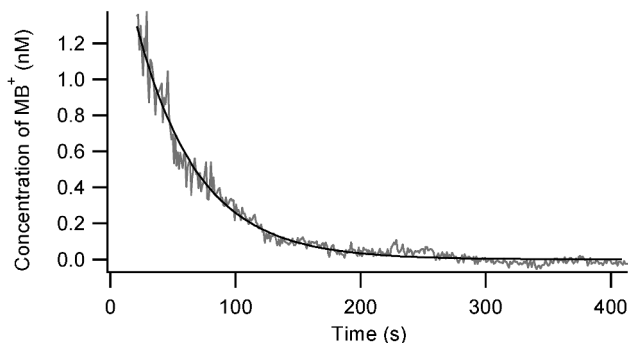


FIG. 3. The reduction of methylene blue (3.0 nM MB<sup>+</sup>) by ascorbic acid (0.33  $\mu\text{M}$ ) in a solution of 20% toluene/80% acetonitrile monitored at 655 nm. The fit shows an exponential loss of absorber concentration over time.

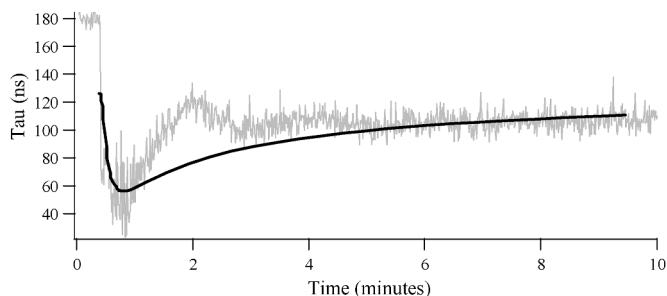


FIG. 4. Molecules of methylene blue are diffusing into the probe beam over several minutes. The fit is to a simple diffusion model. The oscillations, therefore, are not related to the diffusion process but are believed to be the result of photothermal beam steering caused by an inhomogeneous absorber distribution.

range of concentration and time regimes is important because elucidation of kinetic details often contributes greatly to mechanistic understanding.

Because CRDS is a line-of-sight technique, it can also be used to record events with spatial resolution. Methylene blue added to a volume of acetonitrile diffuses into the probe beam. Figure 4 shows the diffusion process over a few minutes. The fit was produced by equations that describe the diffusion of an instantaneous point source of heat in a metallic cylinder,<sup>10</sup> which have been easily adapted to describe diffusion of molecules in solution.

It is possible to simplify the experiment even further by removing the optical switch necessary to create regular pulses of light. In this case, light that does not couple into the optical cavity reflects directly back into the laser, causing chaotic instability in the lasing.<sup>11</sup> We can then take advantage of this self-pulsation-type effect.<sup>12</sup> Each time the laser stops producing light, a ring down can be measured as before. Under our conditions, the switching occurs at random times on the order of once a millisecond. This treatment does not adversely affect the laser in any permanent way. It makes the apparatus simpler and less expensive by removing the need to purchase and align a fast optical switch. Typical results are shown in Fig. 5.

## CONCLUSION

We are able to record cavity ring-down spectra in liquid samples utilizing an inexpensive, broadband cw diode

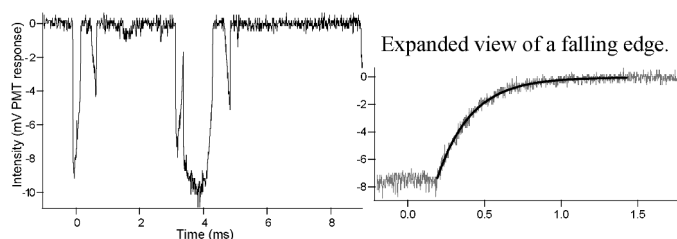


FIG. 5. Waveform produced by allowing feedback from reflected light to switch the laser. A higher-resolution picture of one such ring-down profile shows an exponential fit from which  $\tau$  may be extracted.

laser. This device, unsuitable for gas-phase measurements, is readily adapted to liquids because of the intrinsically large absorption features in the latter. We are able to follow reactions at very low concentrations. This study demonstrates an inexpensive, easy to implement, and sensitive form of cavity ring-down spectroscopy that can be applied to monitor absorbing species in liquid samples.

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1. A. O'Keefe and D. A. G. Deacon, *Rev. Sci. Instrum.* **59**, 2544 (1988).
2. G. Berden, R. Peters, and G. Meijer, *Int. Rev. Phys. Chem.* **19**, 565 (2000).
3. J. T. Hodges, J. P. Looney, and R. D. van Zee, *Appl. Opt.* **35**, 4112 (1996).
4. A. P. Yalin and R. N. Zare, *Laser Phys.* **12**, 1065 (2002).
5. B. A. Paldus, C. C. Harb, T. G. Spence, B. Wilke, J. Xie, J. S. Harris, and R. N. Zare, *J. Appl. Phys.* **83**, 3991 (1998).
6. A. J. Hallock, E. S. F. Berman, and R. N. Zare, *Anal. Chem.* **74**, 1741 (2002).
7. H. Kogelnik and T. Li, *Proc. IEEE* **54**, 1312 (1966).
8. P. Zalicki and R. N. Zare, *J. Chem. Phys.* **102**, 2708 (1995).
9. J. B. Paul, L. Lapson, and J. G. Anderson, *Appl. Opt.* **40**, 4904 (2001).
10. H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids* (Oxford University Press, New York, 1986).
11. G. C. Dente, P. S. Durkin, K. A. Wilson, and C. E. Moeller, *IEEE J. Quantum Electron.* **24**, 2441 (1988).
12. K. Otsuka and H. Iwamura, *Phys. Rev. A* **28**, 3153 (1983).