

Direct Monitoring of Absorption in Solution by Cavity Ring-Down Spectroscopy

Alexander J. Hallock, Elena S. F. Berman, and Richard N. Zare*

Department of Chemistry, Stanford University, Stanford, California 94305

Cavity ring-down spectroscopy is applied to the liquid phase by placing the target solution directly into the optical cavity. We demonstrate that solutions in the cavity can be stirred and more importantly monitored in a flow. We report a minimum detectable absorption of 10^{-6} cm^{-1} for a range of organic solvents. This detection limit corresponds to picomolar concentrations for strong absorbers.

Absorption measurements are common means for detecting analytes in solution, but such measurements often lack sensitivity. Recently, the sensitivity of absorption measurements in the gas phase has been increased by 3–5 orders of magnitude. This sensitivity gain is achieved by placing a gas sample inside an optical cavity and observing the energy decay as a function of time (the ring-down rate) when a pulse of light is sent into this cavity.^{1–4} We report here progress in transferring the sensitivity gains for gas samples to liquid samples using cavity ring-down spectroscopy (CRDS).

Our methodology allows for the construction of a flow cell for real-time monitoring of absorption changes. Preliminary results show that we have the ability to detect analytes present in solution at concentrations less than one part per quadrillion by mass.

EXPERIMENTAL SECTION

Figure 1 illustrates the principle of CRDS. A measurement is made of the rate at which light leaks out of a stable, high-finesse, optical cavity. The simplest configuration is a pulsed laser source coupled to a cavity formed by two highly reflecting mirrors. Light escaping the cavity is detected by a photomultiplier, recorded on an oscilloscope, and analyzed by computer. Under a large variety of conditions, the ring-down rate is well described by an exponential decay.⁵ The ring-down lifetime τ is extracted by an exponential fit (weighted least squares).

$$\tau = \frac{t_r}{2[(1 - R) - \epsilon C l_s]} \quad (1)$$

- (1) O'Keefe, A.; Deacon, D. A. G. *Rev. Sci. Instrum.* **1988**, *59*, 2544–51.
- (2) Paldus, B. A.; Zare, R. N. In *Cavity-Ringdown Spectroscopy: An Ultratrace Absorption Measurement Technique*; Busch, K. W., Busch, M. A., Eds.; American Chemical Society: Washington DC, 1999.
- (3) Wheeler, M. D.; Newman, S. M.; Orr-Ewing, A. J.; Ashfold, M. N. R. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 337–51.
- (4) Berden, G.; Peeters, R.; Meijer, G. *Int. Rev. Phys. Chem.* **2000**, *19*, 565–607.
- (5) Zalicki, P.; Zare, R. N. *J. Chem. Phys.* **1995**, *102*, 2708–17.

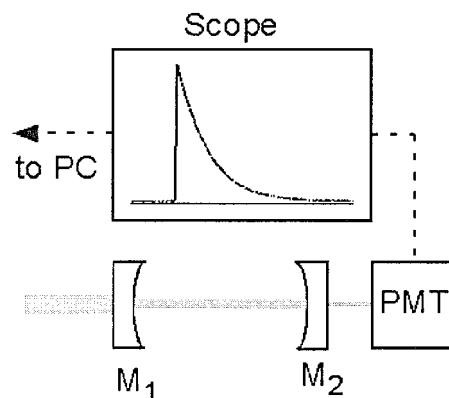


Figure 1. Experimental setup for signal generation, detection, and processing. Pulsed laser radiation is injected into an optical cavity composed of highly reflective mirrors M_1 and M_2 . A photomultiplier tube detects light leaking out of M_2 and the signal is recorded on an oscilloscope.

In CRDS, the ring-down time constant τ is related by eq 1 to the round trip time t_r , the mirror reflectivity R , the molar extinction coefficient ϵ , the concentration C , and the sample path length l_s . For an observed change $\Delta\tau$ in the ring-down lifetime τ between the pure solvent ring-down lifetime τ_1 and the ring-down lifetime of an analyte in solution τ_2 , the concentration can be extracted given the molar extinction coefficient ϵ using the relation

$$C = n\Delta\tau / c\tau_1\tau_2\epsilon \quad (2)$$

where c is the speed of light and n is the index of refraction of the solvent. When a change in τ , and the associated concentration, is being measured, it is important to note that the accuracy of the result is not affected by the accuracy of the measurement of the length of the cell or the reflectivity of the mirrors.

The increase in sensitivity over single-shot methods is caused in part by the fact that τ is insensitive to shot-to-shot intensity fluctuations of the light source. Also, the effective path length is greatly increased by the multiple reflections that the radiation pulse undergoes in the optical cavity. In this experiment, the effective path length is ~ 500 m, whereas the actual path length is only ~ 0.2 m.

Figure 2 shows the experimental setup. Tunable red light (DCM, 620–670 nm) from a Nd:YAG-pumped dye laser (Quanta Ray, PDL I) is shaped by focusing and iris and is steered into the ring-down cavity. Our cavity is formed by one flat and one curved ($r = 1$ m) highly reflecting mirror (Newport Supermirror,

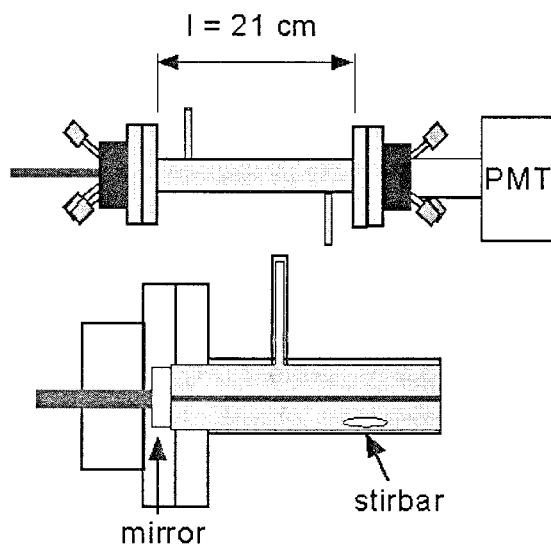


Figure 2. Detailed view of experimental setup showing construction of cell and location of mirror and magnetic stirbar.

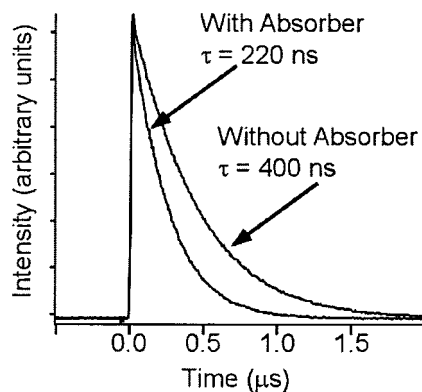


Figure 3. Representative ring-down traces showing a decrease in τ when an absorber is placed in the cavity. For these traces, the solvent is acetonitrile and the absorber is copper(II) acetate at 350 nM with $\epsilon \approx 350 \text{ cm}^{-1} \text{ M}^{-1}$.

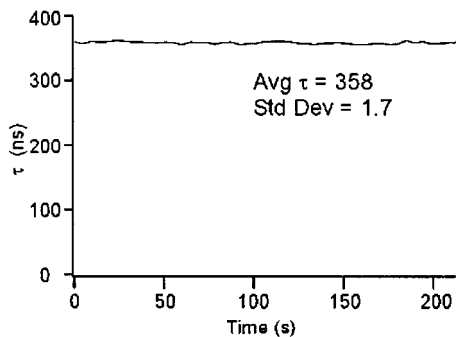


Figure 4. Ring-down lifetime as a function of time in a sample of pure acetonitrile.

$R = 99.98\%$ in air) spaced 21 cm apart. Typically, there is $\sim 1 \mu\text{J}$ of power stored in the cavity (input power of order 1 mJ/pulse). The chamber is constructed so that it can be filled entirely with liquid. The ring-down decay is typically fit over approximately three characteristic ring-down lifetimes.

RESULTS AND DISCUSSION

For an appreciable number of round trips, CRDS requires highly reflecting mirrors. The presence of solvent does not

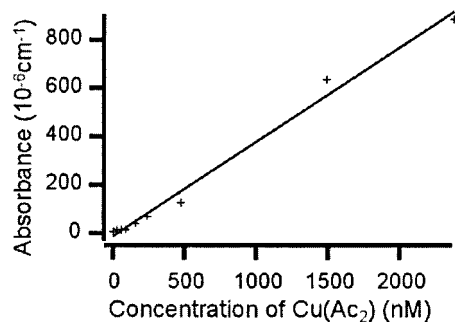


Figure 5. Calibration curve showing change in absorption against copper(II) acetate concentration spanning 3 orders of magnitude. A fit to the data gives an intercept near zero ($-1.26 \times 10^{-5} \pm 1.41 \times 10^{-5}$) and a slope of $388.7 \pm 14.7 \text{ cm}^{-1}$, which is in reasonable agreement with the value for ϵ for copper(II) acetate.

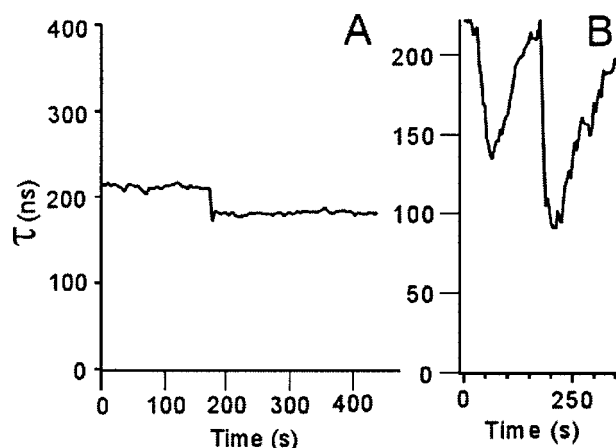


Figure 6. Ring-down lifetime τ vs time: (A) detection of $10 \mu\text{L}$ of 794 nM LD700 laser dye injected into 50 mL of solution inside the cavity while stirring; (B) two separate injections, first of 0.2 mL and second of 0.4 mL, of 0.54 mM Indigo Carmine in acetonitrile ($\epsilon \approx 18000 \text{ cm}^{-1} \text{ M}^{-1}$) flowing in to and out of the cavity. This trace shows a return to the baseline value of the ring-down lifetime between injections.

significantly alter the performance of the mirrors. Furthermore, long periods of exposure to various solvents have no deleterious effect on the mirrors.

While highly reflecting mirrors are necessary, they are not sufficient to produce ring-down times of practical length. To have adequate decay time, solvents must both absorb and scatter very weakly in the wavelength region of interest. This requirement necessitates both few impurities and minimal native absorption. Spectrophotometric grade cyclohexane, hexane, toluene, and acetonitrile show enough transparency in the red (620–670 nm) to be useful solvents, whereas water, tetrahydrofuran, carbon tetrachloride, methanol, and ethanol show too much background absorption.

The simplest experiment compares a chamber containing pure solvent to one with an absorber dissolved in the solvent (See Figure 3). We have experimented with many molecules from laser dyes (Rhodamine 700) to inorganic compounds (copper acetate). The measured ring-down lifetime of acetonitrile varies by less than 1% over several hundred seconds in the cavity (See Figure 4). Assuming a minimum detectable change of three times the standard deviation of the noise, we can resolve a 6-ns change in the value of the ring-down lifetime τ . From eq 2, this figure of

merit corresponds to a change in absorbance ϵC of a few parts in 10^6 cm^{-1} .

Because the case of no absorption corresponds to the highest value of τ and because sensitivity is inversely proportional to the product $\tau_i \tau_b$, the greatest sensitivity is obtained for smallest absorptions and thus lowest concentrations. We conclude that the detection limit corresponds to the best sensitivity achievable. A calibration curve (See Figure 5.) showing monitored absorption change against concentration and analysis of Figure 4 demonstrate that the detection limit for this method is an absolute absorption of 10^{-6} cm^{-1} , or 1–10 pM for an excellent absorber with a molar extinction coefficient of 10^5 – $10^6 \text{ cm}^{-1} \text{ M}^{-1}$. This limit corresponds to approximately 1–10 parts per quadrillion by mass.

The absorption sensitivity and detection limit may seem impressive for analytes in solution, but gas-phase CRDS experiments often achieve sensitivities of one part in 10^7 cm^{-1} in absorption and beyond.⁵ Our difference in sensitivity is accounted for by the fact that we are constrained to work with much shorter base ring-down times owing to background absorption and scattering of the solvent.

With very low concentrations, we encountered difficulties arising from analyte concentrations decreasing with time. The change occurs in the absence of light, so this effect is clearly not caused by photolysis. In an effort to make measurements more reproducible, we agitated the solution using a magnetic stir bar within the cavity. Agitation removed the problem, suggesting that solutes were preferentially segregating to the stainless steel cavity walls. At low stir speeds, motion of the solution does not significantly affect the ring-down measurement. We see a slight increase in noise and occasionally a reduced background. We can

clearly observe the drop in τ caused by adding an absorber to the cavity while stirring (see Figure 6). We also measured changes in τ while the solution flowed through the cell and could follow absorbers flowing in to and out of the cavity (see Figure 6). Multiple injections can be performed while the solution flows as the ring-down time returns to its background value after each sample. Sample injection was accomplished by using a syringe to introduce small volumes (0.1 mL) of an absorber into a flow of acetonitrile generated by a small pump. With moving solutions, either stirred or flowing, we generally observe stability on the order of 1% (σ_i/τ).

CONCLUSIONS

We have demonstrated that cavity ring-down spectroscopy can readily be applied to liquid samples by placing the sample in contact with the mirrors of an optical cavity. Moreover, this direct absorption method gives a significant enhancement in sensitivity compared to more traditional absorption measurements. We find that it will be necessary to make a careful choice of solvents for a given wavelength if maximum sensitivity is needed.

ACKNOWLEDGMENT

A.J.H. is grateful for a John Veach Memorial Fellowship and E.S.F.B. for an NSF Graduate Research Fellowship. This work is supported by the Office of Naval Research (Grant N00014-00-1-0364).

Received for review October 18, 2001. Accepted January 29, 2002.

AC011103I