Cavity ringdown spectroscopy with a continuous-wave laser: calculation of coupling efficiency and a new spectrometer design

Jae Won Hahn, Yong Shim Yoo, Jae Yong Lee, Jae Wan Kim, and Hai-Woong Lee

For the efficient operation of a cavity ringdown spectroscopy (CRDS) system utilized with a continuous-wave (cw) laser, we numerically analyze the coupling efficiency of a cw laser to a ringdown cavity in terms of changes in the scanning rate, the laser linewidth, and the mirror reflectivity. We also demonstrate a new simple design for a CRDS system that can produce a CRDS signal with only a piezoelectric transducer (PZT), without the acousto-optic modulator that is usually adopted to switch off the cw laser beam that enters the cavity. Furthermore, we investigate the feasibility of the cw CRDS technique with a fast-scanning PZT by recording a CRDS spectrum of acetylene overtones. The detection sensitivity that corresponds to the noise-equivalent absorption is found to be $\sim 3 \times 10^{-9}$/cm. © 1999 Optical Society of America

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1. Introduction

If we make a cavity with high-reflectance mirrors ($R \sim 99.99\%$), photons can be trapped in the cavity and remain there for a few microseconds as they bounce back and forth between the mirrors. Cavity ringdown spectroscopy (CRDS) measures the decay time of the photons in the cavity to yield the absolute loss of the cavity. CRDS is a technique capable of making ultrasensitive ($<1 \times 10^{-6}$ fractional absorption change) direct absorption measurements on microsecond time scales. Because of its high sensitivity and simplicity, CRDS is now being widely used for studying chemical kinetics and absorption bands of molecules[1–10] and for measuring the concentration of minor species in flames,[11,12] etc. It is also considered one of the most promising techniques for detecting the absolute concentrations of trace species for measurement standards.[13]

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The cavity ringdown technique was originally developed to measure the reflectivity of high-reflectance mirrors.[15–17] Using an intensity-modulated light source, Herbelin *et al.*[15] demonstrated that the photon decay time could be determined from the phase shift of the light that has passed through the cavity. For the same purpose, Anderson *et al.*[16] produced a photon decay signal with a high-speed Pockels cell, directly measuring the decay time of the photons in a cavity.

In 1988 O'Keefe and Deacon[1] demonstrated CRDS with a pulsed laser source. Most CRDS experiments performed thereafter used pulsed lasers because the pulsed laser is a convenient source of high-intensity photon bursts, even though the energy coupling efficiency is small. Many studies of the response function of the ringdown cavity to the pulse laser source and the photon dynamics in the cavity have been performed.[18–21]

CRDS with a continuous-wave (cw) laser was successfully demonstrated by Romanini *et al.*[22–24] in 1997. The basic principle of the cw CRDS setup was similar to that of Anderson *et al.* Romanini *et al.* used an acousto-optic modulator instead of a Pockels cell to interrupt the cw laser beam introduced into the cavity. Using a piezoelectric transducer (PZT), they slowly scanned the cavity length to build up a high-intensity photon burst in the cavity. After the photon intensity exceeded a certain threshold, they quickly interrupted the cw laser beam with the acousto-optic modulator to obtain a photon decay signal. More recently, Paldus *et al.*[25] also performed cw CRDS by locking a high-finesse resonator to a cw laser source. Using the cavity-locking technique, they could greatly improve the system performance by reducing the shot-to-shot fluctuation in the photon decay signal.

To produce a sufficient number of photon bursts, one should keep the high-finesse cavity on resonance for some time. A single-mode cw laser has a narrow linewidth of ~1 MHz, and a cavity used for the CRDS experiment has a narrow bandwidth because of its high finesse (larger than 10^4). Hence locking the cavity mode directly to the narrow laser linewidth is extremely difficult, because a small thermal drift of the cavity length or a tiny mechanical vibration can cause the cavity mirror to go off resonance. Because the orthogonal polarization components of light have different reflectivities, the cavity finesse can be reduced in a specific wavelength range because of the change in reflectivity corresponding to the new polarization. Paldus *et al.*[25] stabilized the cavity with one polarization component and produced photon decay signals with the other polarization component, but complex optical locking systems were needed. Instead of actively stabilizing the cavity length on resonance, one can easily accumulate photons in the cavity by sweeping one resonance mode of the cavity through the cw laser linewidth, trading off the performance of a cw CRDS system.

To set up an efficient cw CRDS system we need to understand in detail the process of photon dynamics in the cavity. When we scan the cavity near resonance, the photon intensity transmitted through the cavity will depend on the laser linewidth, the scanning speed of the cavity, the finesse of the cavity, etc. The theory of the coupling of a cw laser beam to the cavity has not been well studied in detail, however. Here we numerically calculate the coupling efficiency of a cw CRDS system with respect to the laser linewidth, the scanning speed of the cavity, and the finesse of the cavity. We also demonstrate a new simple CRDS setup that yields photon decay signals by using only a PZT instead of an acousto-optic modulator as an optical switch.

2. Description of a Ring-Down Signal Produced with a cw Laser Source

For a change in cavity length accomplished by moving one mirror, some theoretical analyses were performed by several authors.[26–29] Here we give only a brief description of the analytical equation and extend it to include the laser linewidth effect.

Considering a Fabry–Perot cavity with two mirrors that have identical electric field reflectivity $\mathcal{R}$ and transmissivity $\mathcal{T}$, let us assume a monochromatic radiation coming into the cavity whose length L_0 is slowly changed with speed ν. We also assume that the cavity is on resonance with the incident field at time $t = 0$ and that the cavity round-trip time t_r ($=2L_0/c$, where c is the velocity of light) is much smaller than the cavity decay time τ_d [$=L_0/(-c\ln \mathcal{R}^2)$]. Time t is described in units of cavity round-trip time: $t = t_r l$ (l is an integer). We obtain the electric field inside the cavity by summing all multiply reflected wave components, so the electric field emerging from the cavity is derived by

$$E_{out}(t) = \mathcal{T}^2 E_0 \exp[i(kz - \omega t_r)] \times \sum_{n=0}^{\infty} \mathcal{R}^{2n} \exp[ik\nu t_r n(2l - n)] \qquad (1)$$

and the intensity that corresponds to the monochromatic wave is

$$I_0^M(t) = T^2 I_0 \left| \sum_{n=0}^{\infty} R^n \exp[ik\nu t_r n(2l - n)] \right|^2, \qquad (2)$$

where k and ω are the propagation vector and the frequency of the incident radiation, respectively, and R and T are the intensity reflectivity ($\mathcal{R}^2$) and transmissivity ($\mathcal{T}^2$), respectively.

The results derived for monochromatic laser excitation should be extended to describe the realistic situation in which the excitation laser has a finite linewidth. If we assume that the spectral broadening has originated from a random phase jitter of the electric field of the laser, the effect can be described by addition of a random phase factor $\exp[i\phi(t)]$ according to the Gaussian white-noise model.[30] Equivalently, the effect can also be taken into account by summation of all intensity contributions to the ringdown signal from the spectral components that constitute a Lorentzian line shape of the excitation laser. Therefore we finally obtain the intensity of the ringdown signal:

$$I_{out}(t) = \frac{1}{\pi} \int_0^{\infty} T^2 R^{2[l+\delta(\omega)]} \times \left| \sum_{n=-[l+\delta(\omega)]}^{\infty} R^n \exp\left[-i\omega t_r \left(\frac{\nu}{c}\right) n^2 \right] \right|^2 \times \frac{I_0 \Delta\omega d\omega}{(\omega - \omega_0)^2 + (\Delta\omega/2)^2}, \qquad (3)$$

where ω_0 is the line-center frequency and $\Delta\omega$ is the FWHM of the Lorentzian line shape. For the summation and multiplication of R we take the integer value of $\delta(\omega)[=-(c/2\pi)(\omega - \omega_0)/\omega_0]$.

3. Experiment

A. Experimental Setup

The apparatus for the experiment is shown schematically in Fig. 1(a). A cw ring dye laser (Coherent 899-21) pumped by an Ar^+ laser was used as a light source. We operated the ring dye laser at a wavelength of ~570 nm with a power output of 200 mW. The linewidth of the laser was estimated to be <500 kHz. The Fabry–Perot cavity consisted of two high-reflectance mirrors (Research Electro Optic, Inc.) with 1.27-cm diameters and 4-m radii of curvature. The reflectivity of the mirror was >99.99% in the

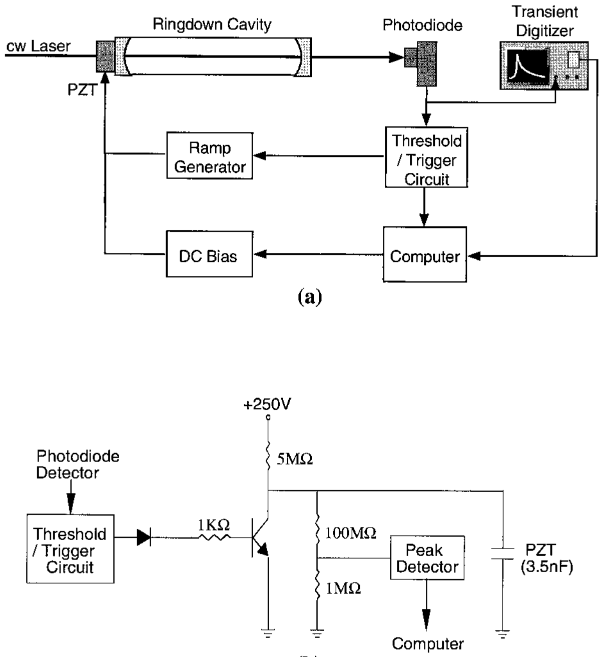

Fig. 1. (a) Schematic diagram of the apparatus for a cw CRDS system. (b) Electronic circuit for driving the PZT.

wavelength range from 570 to 610 nm. The PZT was a 1.27 cm in length and a 1.27 cm in diameter and had a 10-mm-diameter hole in it. The cavity had a length of 30 cm and was contained in a high-vacuum chamber evacuated to 0.2 Pa. To prevent feedback of the laser beam from the cavity to the cw ring dye laser we placed an optical isolator (Optics for Research, 10-5-VIR-HP) in the beam path. The isolation ratio of the laser beam incident upon the cavity was ~43 dB. The size of the laser beam at the center of the cavity was matched to the TEM_{00} cavity mode (350 μm in radius) with a lens (f = 75 cm).

B. Spectrometer

To realize the CRDS technique with a cw laser source we need to accumulate high-intensity photon flux in the cavity and then quickly switch off the cw laser source to obtain a photon decay signal. Here we pay attention to the two well-known intrinsic properties of a Fabry–Perot cavity. One is trapping of photons in the cavity, and the other is fast switching of a cw laser beam. To understand the basic concept of trapping a burst of photons in the cavity, let us assume that the light source is purely monochromatic and that the energy loss by absorption and scattering upon the cavity-mirror surface is negligibly small. When a Fabry–Perot cavity stays on resonance at the wavelength of the light source for a time comparable with the cavity ringdown time, the photon intensity coupled into the cavity increases by a factor equal to the finesse of the cavity; then almost the same intensity of light as was incident upon the cavity emerges from the cavity. When the cavity stays off resonance, however, only a small fraction of the cw light will be transmitted through the cavity; the transmittance of the cavity is given by multiplication of the transmissivities of the two mirrors that constitute the Fabry–Perot cavity. This means that, if we quickly scan the cavity from an on-resonance position to an off-resonance position, we can rapidly switch off the cw laser source coupling into the cavity. Therefore, by using only these two intrinsic properties of the Fabry–Perot cavity, we can not only accumulate abundant photons from a cw laser in the cavity but also quickly switch off the cw laser without any additional optical switching device, such as an acousto-optic modulator or an optical Q switch.

An *et al.*[28] previously demonstrated the switching of a cw laser beam coupling into a cavity with the fast-cavity-scan technique. They applied this technique to measure the ultralow relative velocity of mirrors as well as the linewidth of the probe laser. In this case, to avoid interference in the leading part of the photon decay signal as a result of the coupling of the incident cw laser beam into the cavity, they needed to scan the mirror very fast ($\sim 1.2 \times 10^4$ GHz/s), trading off the photon intensity accumulated in the cavity. Here we note that the magnitude of the signal depends strongly on the scanning speed, as we discuss in Section 4.

The electronic circuit for driving the PZT is shown in Fig. 1(b). We modulated the cavity length with a PZT that had an inherent capacitance of ~3.5 nF. A high voltage of ~250 V was applied to the PZT through a 5-MΩ resistor. As the applied voltage at the PZT increases with a time constant of 17.5 ms, one of the cavity modes can be coincident with the wavelength of the cw laser. We slowly increased the voltage applied to the PZT to sweep the cavity slowly. When the photon intensity coming through the cavity reached a threshold intensity, we triggered only a transistor [Fig. 1(b)] to decrease the voltage applied to the PZT. The cavity length changed by a quarter wavelength in 1 μs, causing the cavity mirror to move off resonance within a few nanoseconds after the trigger; then it stayed off resonance until most of the photons in the cavity decayed out.

In addition to producing the photon decay signal, the PZT could simultaneously compensate for the thermal drift of the cavity and track the cavity length according to laser frequency tuning. To maintain the photon decay signal at the same temporal position during the cavity sweeping, we added a dc bias voltage to the voltage applied for scanning the cavity. As shown in Fig. 1(b), we monitored the peak of the sweep voltage applied to the PZT where the ringdown event took place, and the dc bias voltage was determined with a feedback routine in a control program. When the bias voltage reached that which corresponded to one cavity free spectral range (FSR) (~250 V), it was reset to 0 V for continuous tracking.

The output beam transmitted through the cavity was monitored with a photodiode (New Focus 1801; bandwidth, 125 MHz) placed behind the end mirror. The signal from the photodiode was digitized on a

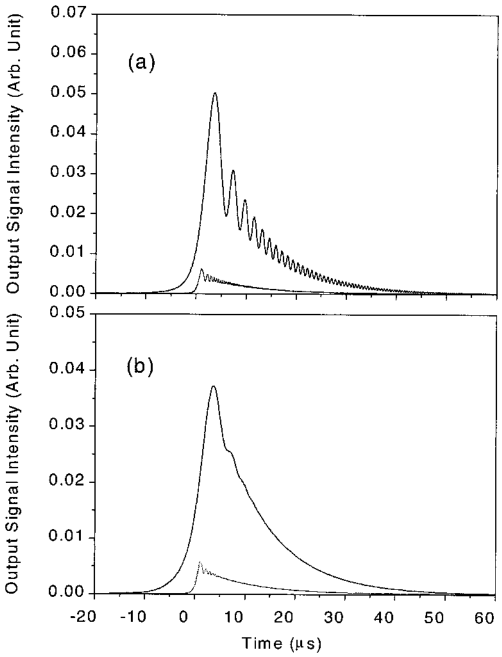

Fig. 2. Calculated intensity of a cw laser transmitted through a scanning Fabry–Perot cavity. The spectral linewidth of the cw laser is (a) monochromatic and (b) 100 kHz. The mirror was scanned with at a speed of 100 FSR/s (larger curve, upper trace) and 1000 FSR/s (smaller curve, lower trace). For the calculation, $\lambda_0 = 570$ nm and $L_0 = 30$ cm.

digital oscilloscope (Tektronix 2440; 300-MHz bandwidth) with 8-bit resolution.

4. Results and Analysis

A. Calculation of the Transient Peak Generated with a Fast-Scanning Mirror and the Coupling Efficiency of a cw Laser to a Ringdown Cavity

Using Eq. (3), we calculated the intensities of the transmitted cw laser through a 30-cm-long Fabry–Perot cavity with a mirror reflectivity of 99.99%. The results of the calculations for a monochromatic light source and for a cw laser with a linewidth of 100 kHz are plotted in Figs. 2(a) and 2(b), respectively. In the calculation, the wavelength of the light source was 570 nm, and the wavelength of the cavity mirror was scanned at the speed of the cavity-length change, 100 FSR (FSR $= 1/t_r$) per second or 1000 FSR per second. Because the cw laser light couples into the cavity only during resonance, the intensity of the transmitted light exhibits a transient behavior that has a peak near $t = 0$.

From Fig. 2 one can see that the peak intensity of the decay signal is greatly reduced with an increase in scanning speed. When the mirror velocity is increased by a factor of 10, the peak intensity of the output signal is reduced by a factor of ~7. Furthermore, because of the Doppler shift induced by a moving mirror, several modulation peaks are superimposed upon the decay signal; this complicates the fitting of the photon decay signal to a simple exponential function. In Fig. 2(a) several modulation peaks appear in the leading part of the photon decay signal, whose frequency is linearly chirped as the signal decays. Analyses of the modulation peak were made by several authors,[26,28,29] and here we give a brief interpretation of the frequency chirping and smoothing of the modulation peaks.

In case of monochromatic light we can find from the last term of Eq. (1) that the phase shift of the electric field caused by the Doppler shift depends on both the mirror speed and the reflection number n. The phase shift increases quadratically with the increase in the reflection number, yielding modulations of the photon decay signal. Hence the modulation frequency of the photon decay signal becomes higher as the signal decays. Also, we can easily expect that, as the phase shift increases, the randomness of the phase of multiply reflected wave components in the complex plane[29] will become greater, leading to a smoothing of the modulation peaks in the photon decay signal that is obtained by the summation of the all multiply reflected wave components. Moreover, the modulation peaks are smoothed by superposition of different frequency components that originate from the linewidth of the cw laser. Figure 2 shows that when the mirror speed increases, the frequency of the modulation peaks becomes higher and the amplitude of the peaks becomes smaller. Also, the high-frequency modulation peaks in Fig. 2(b) become invisible in the tail of the signal.

To set up a ringdown cavity spectrometer with a cw laser it is important to estimate how much laser power is transmitted through the cavity. Inasmuch as the CRDS signal intensity depends on the initial photon density confined in the cavity before the photon decay, one needs to scan the cavity slowly so that photon bursts are accumulated in the cavity as much as possible. We have defined the coupling efficiency of the cw CRDS system as the ratio of the peak power of the photon decay signal to that of the incident cw laser, which is the peak transmissivity of a cw laser through the cavity. By changing the linewidth of the cw laser, the cavity length, and the reflectivity of the mirror, we calculated the coupling efficiencies with Eq. (3).

The coupling efficiencies calculated as a function of the linewidth of the cw laser are plotted in Fig. 3. For the calculation, the reflectivity of the mirror and the cavity length were 99.99% and 30 cm, respectively. The scanning rate of 1 Hz denotes the cavity scanning of one FSR per second. The calculations were performed with several scanning rates of the cavity mirror. The scanning rate used for the calculation is indicated for each curve in the figure. A scanning rate of 0 Hz means that the resonance frequency of the cavity stands on the center frequency of the cw laser. The curve calculated for the scanning rate of 0 Hz illustrates the ratio of integration of multiplication of the transmission function of the cavity and the spectral line-shape function of the cw laser in the frequency domain to the area of the spectral line-shape function.

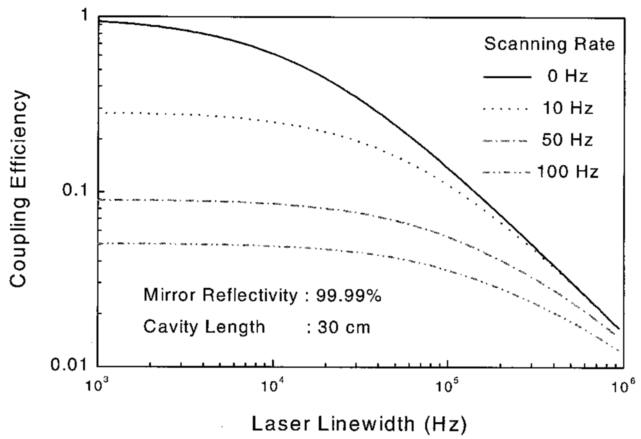

Fig. 3. Coupling efficiency calculated as a function of laser linewidth for various scanning rates.

The intensity transmission function of a Fabry–Perot cavity versus frequency consists of a series of narrow transmission peaks separated by a FSR. A transmission peak can be described with an Airy function, and its FWHM ($\Delta\nu_F$) is equal to FSR/finesse. The finesse of a Fabry–Perot cavity with a mirror reflectivity of 99.99% is 3.14×10^4, and the FSR of a 30-cm-long cavity is 500 MHz. Therefore, $\Delta\nu_F$ is approximately 15.9 kHz. The solid curve in Fig. 3 (0-Hz scanning rate) shows that the coupling efficiency decreases with an increase in the laser linewidth and nearly reaches 1 as the laser linewidth approaches 10 kHz or less. We can easily expect that the coupling efficiency will be inversely proportional to the scanning rate that determines the duration of the transmission peak's overlap with the spectral linewidth of the cw laser. In Fig. 3, however, the coupling efficiency is not exactly proportional to the inverse of the scanning rate. The ratios of the coupling efficiencies for scanning rates of 10 and 100 Hz to those for scanning rates of 50 and 100 Hz are 5.7 and 1.7, respectively, at the beginning, and decrease to 1.4 and 1.2 as the linewidth of the laser increases from 1 kHz to 1 MHz. As a result, it is found that, for a fixed $\Delta\nu_F$, the coupling efficiencies are correlated with two factors, the spectral density of the laser in unit frequency and the overlap time of the laser linewidth and the transmission peak during the cavity scan. If the laser linewidth increases, the spectral density decreases, leading to decreased coupling efficiency, but the overlap time increases, leading to higher coupling efficiency. In the region of a laser linewidth less than 10 kHz the laser linewidth does not affect the coupling efficiency at all. In the region of laser linewidth larger than 20 kHz, however, $\Delta\nu_F$ is smaller than the laser linewidth, and the coupling efficiency is gradually reduced as the laser linewidth increases. Therefore, for efficient operation of a cw CRDS setup, we need to choose the scanning rate properly by taking account of the linewidth of the cw laser and the FWHM of the transmission peak of the cavity. In this manner we can easily expect that the coupling efficiency will be inversely proportional to the cavity length because the FWHM of a transmission peak decreases with an increase in the cavity length.

We also calculated the coupling efficiency as a function of mirror reflectivity. For the calculation, the cavity length and the scanning rate are 30 cm and 50 Hz, respectively. The calculated coupling efficiencies for laser linewidths of 10 and 100 kHz are plotted in Fig. 4. As the mirror reflectivity increases, the coupling efficiencies decrease greatly; for example, if the mirror reflectivity increases from 99.99% to 99.999%, the detection sensitivity will be improved in principle but the coupling efficiencies will be reduced by factors of more than 60 for laser linewidths of both 10 and 100 kHz. We also note that, even if we replace a cw laser with a linewidth of 10 kHz instead of with a linewidth 100 kHz, the coupling efficiency is improved by only ~30%. Here we found that, because the cw beam coupled into the cavity is proportional to the mirror transmissivity, the coupling efficiency decreases with increasing mirror reflectivity. If the mirror reflectivity increases from 99.99% to 99.999%, the FWHM of the transmission peak is reduced by a factor of 10 and the cw beam coupled into the cavity decreases again by a factor of 10 owing to the reduced transmissivity. Therefore the coupling efficiency is roughly proportional to the square of the transmissivity.

B. Calculation of the Photon Decay Signal

In Section 3 we proposed a new apparatus that produces a ringdown signal by use only of a PZT. To estimate the performance of the CRDS apparatus we used Eq. (3) to calculate the temporal shape of a photon decay signal. For the calculation, the laser linewidth and the cavity length were 100 kHz and 30 cm, respectively, and, to accumulate enough photon burst in the cavity, we assumed the cavity length to be slowly scanned with a scanning rate of 100 Hz. The mirror reflectivity and the center wavelength of the laser were 99.99% and 570 nm, respectively. We

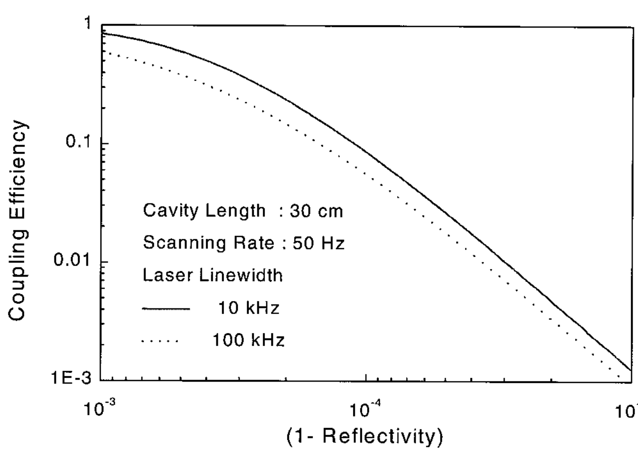

Fig. 4. Coupling efficiency calculated as a function of mirror reflectivity.

also assumed that after the photon intensity reached a given threshold the cavity length was fast scanned with a PZT.

If we discharge the voltage applied to the PZT with the switching circuit shown in Fig. 1(b), the applied voltage of the PZT will decrease exponentially, causing the length of the PZT to contract as a function of the applied voltage. Therefore, to calculate the ringdown signal obtained by fast scanning of the cavity length, we describe the cavity length $L(t)$ by the following equations:

$$L(t) = L_0 + \nu t, \qquad t < t_{\mathrm{sw}},$$
$$L(t) = L_0 + \nu t - \Delta L\{1 - \exp[-\Gamma_{\mathrm{sw}}(t - t_{\mathrm{sw}})]\}, \quad t \geq t_{\mathrm{sw}}, \tag{4}$$

where ΔL is the total change in cavity length as a result of the discharge of the applied voltage on the PZT and where Γ_{sw} is the decay time constant of the applied voltage. In the calculation, ΔL and Γ_{sw} were given by a quarter wavelength of the cw laser and 1 μs, respectively. Figure 5 shows the calculated ringdown signal obtained with PZT. The modulation peaks superposed upon the decay signal are invisible, and the signal exhibits a smooth exponential decay. The decay time constant of the exponential decay is 9.99962 μs, which is very close to the theoretical cavity decay time of 9.99950 μs. These results indicate that the cw CRDS system with a PZT produces a good photon decay signal whose decay time constant is close to the theoretical one with negligibly small error.

C. Measurement of an Acetylene Spectrum

A CRDS signal obtained by a single event is shown in Fig. 6. As was predicted in the calculation, the signal does not exhibit any modulation peaks, and it decays sharply in an exponential form. By fitting the data of the decay signal, we obtained a decay time constant of 23.2 μs. Even though the laser power incident upon the cavity was only 5 mW, the signal-to-noise ratio of the CRDS signal shown in Fig. 7 is fairly good. In practice, we usually took an average of 64 sequential signals to record a CRDS spectrum; in that case the noise superposed upon the signal was reduced near the digitizing limit.

We made a performance test of the CRDS spectrometer by recording a spectrum of the overtone transition of acetylene near 570 nm, which is the same CRDS spectrum as that previously measured by Romanini *et al.*[22] with the acousto-optic modulator. The measured spectrum is plotted in Fig. 7. The ringdown cavity was filled with acetylene at a pressure of 2700 Pa, and the scanning rate of the cavity was 100 Hz. As the wedge of the mirrors used in this experiment is $<1 \times 10^{-3}$ rad, we observed quite a large baseline oscillation during the dye laser scanning. The amplitude of the oscillation was ~3%, and the period was ~17 GHz. The origin of the baseline oscillation is the etalon effect of the mirror itself, which changes the effective reflectivity of the mirror as a function of the frequency of the incident beam. Hence it is known that one can remove the oscillation by using mirrors with wedges of $>1.7 \times 10^{-2}$ rad.[25] The baseline oscillation that appeared during the laser scanning was reproducible,

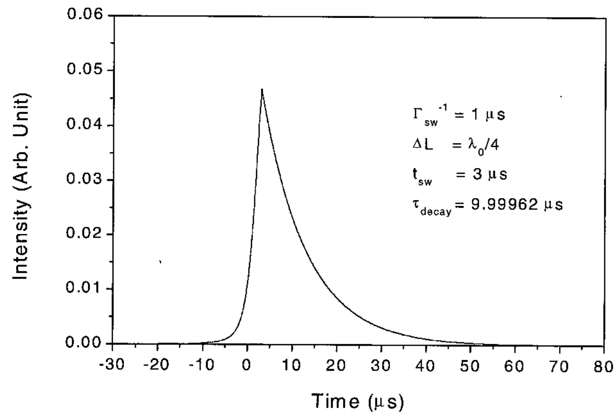

Fig. 5. Calculated cavity ringdown signals obtained with a fast-scanning PZT. For the calculation, $\lambda_0 = 570$ nm, $R = 0.9999$, $L_0 = 30$ cm, and $\Delta\nu = 10$ kHz.

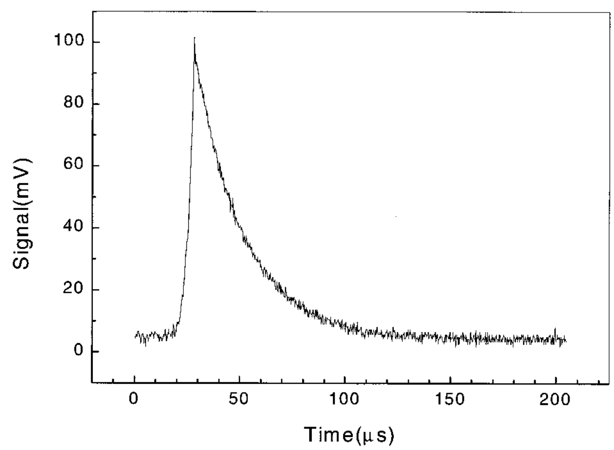

Fig. 6. Single trace of the experimental cavity ringdown signal obtained by scanning the cavity with a PZT.

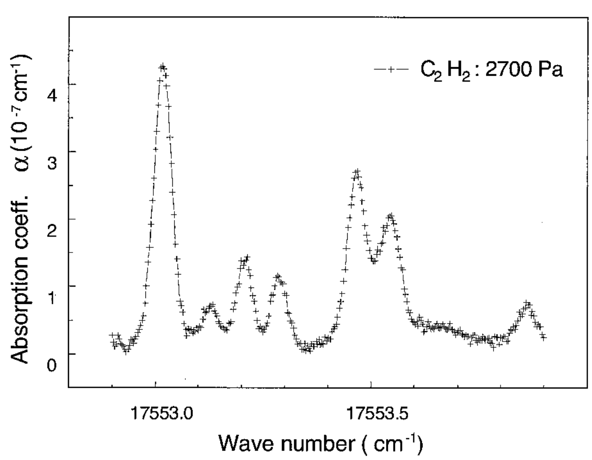

Fig. 7. CRDS spectrum of a weak overtone of acetylene measured with a scanning laser frequency of 30 GHz.

and the CRDS spectrum was subtracted from the baseline measured with an empty cavity.

In addition to baseline oscillation, we found that a baseline shift related to the displacement of the PZT that was used to make the ringdown event to appear at the same position during PZT scanning. The baseline shift depended on the displacement of the PZT and increased as the beam was shifted away from the cavity axis. We need to change the voltage applied to the PZT according to the wavelength of the incident beam. So when we tuned the wavelength of the laser, the baseline oscillated with the period of the FRS of the cavity (500 MHz), which was much smaller than that which was due to the etalon effect of the mirror. When the system was well adjusted, the baseline shift oscillated with an amplitude of 0.5%.

We suspected that the small tilt between the PZT axis and the cavity axis made the incident beam strike a different point upon the mirror surface, leading to variation of the effective reflectivity because of inhomogeneity of the mirror surface or because of the etalon effect that was due to the change in the thickness of the concave mirror. We found that only a $2 \times 10^{-5}\%$ change in the reflectivity can lead to a 0.5% baseline shift. However, when we calculated the etalon effect that was due to the displacement of the PZT, assuming that the tilt between the PZT and the cavity axis was 10^{-2} rad and that the displacement of the PZT was half a wavelength, the calculated baseline shift was only $\sim$0.02% at maximum. We suspect that the tiny misalignment of the cavity induced by the PZT displacement could contribute to the baseline shift, but this possibility is still under investigation. We found that we could minimize the baseline oscillation by aligning the beam carefully to pass along the cavity axis.

Shot-to-shot variation of the photon decay time was $\sim$2%, but it was reduced to $<$0.1% by averaging of 64 events. However, the oscillation that was due to baseline shift during the laser scanning reached $\sim$0.5%. Because the period of the oscillation that is due to the baseline shift is small and is not reproducible, we could not subtract the oscillation term from the CRDS spectrum. The rms noise level determined with the standard deviation of several baseline sections of the CRDS spectrum shown in Fig. 7 is 0.5%, and we found that the noise of the CRDS spectrum is caused mainly by the baseline shift that is due to the displacement of the PZT. The calculated minimum absorption coefficient of our CRDS system that corresponds to the shot-noise limit[31] is $\sim 3 \times 10^{-10}$/cm. However, the absorption coefficient that corresponds to the noise level of the spectrum is $\sim 3 \times 10^{-9}$/cm, which is larger by factor of 10 than that derived from the shot-noise limit. Therefore, further research to reduce the background noise in the spectrum is needed.

5. Conclusions

The coupling efficiency of a cw CRDS system has been analyzed with a numerical calculation of the peak CRDS signals. We performed the numerical calculation by changing the scanning rate of the cavity length, the laser linewidth, the mirror reflectivity, and the cavity length; and efficient operation of a cw CRDS system has been discussed. From the results of the calculation, we found that the coupling efficiency depends mainly on the spectral density of the cw laser, the mirror transmissivity, and the duration of the FWHM of the transmission peak of the cavity that is overlapping the spectral linewidth of a laser. For efficient operation of a cw CRDS setup one needs to choose the scanning rate properly by taking account of the linewidth of the cw laser and the FWHM of the transmission peak of the cavity. Also, we found that the efficiency is roughly proportional to the square of the mirror transmissivity and inversely proportional to the cavity length, but it does not depend much on the laser linewidth.

We have demonstrated a new, simple method for detecting the photon decay in a Fabry–Perot cavity with a cw laser source, and we found that a simple spectrometer design that uses a PZT instead of an acousto-optic modulator can produce good cavity ringdown signals. The cavity ringdown signals were numerically calculated for use of a PZT to switch off the cw laser coupling into the cavity. Furthermore, we investigated the feasibility of applying this technique for CRDS by recording the CRDS spectrum of acetylene overtones; the absorption coefficient that corresponded to the noise level was 3×10^{-9}/cm.

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References

1. A. O'Keefe and D. A. G. Deacon, "Cavity ringdown optical spectrometer for absorption measurements using pulsed laser sources," Rev. Sci. Instrum. **59,** 2544–2551 (1988).
2. A. O'Keefe, J. J. Scherer, A. L. Cooksy, R. Sheeks, J. Heath, and R. J. Saykally, "Cavity ringdown dye laser spectroscopy of jet-cooled metal clusters: Cu_2 and Cu_3," Chem. Phys. Lett. **172,** 214–218 (1990).
3. T. Yu and M. C. Lin, "Kinetics of phenyl radical reactions studied by the cavity-ringdown method," J. Am. Chem. Soc. **115,** 4371–4372 (1993).
4. K. Nakagawa, T. Katsuda, A. S. Shelkovnikov, M. de Labachelerie, and M. Ohtsu, "Highly sensitive detection of molecular absorption using a high finesse optical cavity," Opt. Commun. **107,** 369–372 (1994).
5. D. Romanini and K. K. Lehmann, "Cavity ringdown overtone spectroscopy of HCN, $H^{13}CN$ and $HC^{15}N$," J. Chem. Phys. **102,** 633–642 (1995).
6. R. T. Jongma, M. G. H. Boogaarts, I. Holleman, and G. Meijer, "Trace gas detection with cavity ringdown spectroscopy," Rev. Sci. Instrum. **66,** 2821–2827 (1995).
7. P. Zalicki, Y. Ma, R. N. Zare, E. H. Wahl, J. R. Dadamio, and T. G. Owano, "Methyl radical measurement by cavity ringdown spectroscopy," Chem. Phys. Lett. **234,** 269–274 (1995).
8. D. Romanini and K. K. Lehmann, "Calculation of the Herman–Wallis in Π–Σ vibrational overtone transitions in a linear molecule: comparison with HCN experimental results," J. Chem. Phys. **105,** 68–80 (1996).

9. E. H. Wahl, T. G. Owano, C. H. Kruger, P. Zalicki, Y. Ma, and R. N. Zare, "Measurement of absolute CH_3 concentration in a hot-filament reactor using cavity ringdown spectroscopy," Diamond Related Mater. **5,** 373–377 (1996).
10. L. Zhu, D. Kellis, and C. Ding, "Photolysis of glyoxal at 193, 248, 308 and 351 nm," Chem. Phys. Lett. **257,** 487–491 (1996).
11. G. Meijer, M. G. H. Boogaarts, R. T. Jongma, D. H. Parker, and A. M. Wodtke, "Coherent cavity ringdown spectroscopy," Chem. Phys. Lett. **217,**ke 112–116 (1994).
12. J. J. Scherer, and D. J. Rakestraw, "Cavity ringdown laser absorption spectroscopy detection of formyl (HCO) radical in a low pressure flame," Chem. Phys. Lett. **265,** 169–176 (1997).
13. T. Etzkorn, J. Fitzer, S. Muris, and J. Wolfrum, "Determination of absolute methyl- and hydroxyl-radical concentrations in a low pressure methane–oxygen flame," Chem. Phys. Lett. **208,** 307–310 (1993).
14. J. T. Hodges, J. P. Looney, and R. D. van Zee, "Laser bandwidth effects in quantitative cavity ringdown spectroscopy," Appl. Opt. **35,** 4112–4116 (1996).
15. J. M. Herbelin, J. A. McKay, M. A. Kwok, R. H. Ueunten, D. S. Urevig, D. J. Spencer, and D. J. Benard, "Sensitive measurement of photon lifetime and true reflectance in an optical cavity by a phase-shift method," Appl. Opt. **19,** 144–147 (1980).
16. D. Z. Anderson, J. C. Frisch, and C. S. Masser, "Mirror reflectometer based on optical cavity decay time," Appl. Opt. **23,** 1238–1245 (1984).
17. M. Billardon, M. E. Couprie, J. M. Ortega, and M. Velghe, "Fabry–Perot effects in the exponential decay and phase shift reflectivity measurement methods," Appl. Opt. **30,** 344–351 (1991).
18. P. Zalicki and R. N. Zare, "Cavity ringdown spectroscopy for quantitative absorption measurements," J. Chem. Phys. **102,** 2708–2717 (1995).
19. K. K. Lehmann and D. Romanini, "The superposition principle and cavity ringdown spectroscopy," J. Chem. Phys. **105,** 10,263–10,277 (1996).
20. J. T. Hodges, J. P. Looney, and R. D. van Zee, "Response of a ringdown cavity to an arbitrary excitation," J. Chem. Phys. **105,** 10,278–10,287 (1996).
21. J. Martin, B. A. Paldus, P. Zalicki, E. H. Wahl, T. G. Owano, J. S. Harris, Jr., C. H. Kruger, and R. N. Zare, "Cavity ringdown spectroscopy with Fourier-transform-limited light pulses," Chem. Phys. Lett. **258,** 63–70 (1996).
22. D. Romanini, A. A. Kachanov, N. Sadeghi, and F. Stoeckel, "Cw cavity ringdown spectroscopy," Chem. Phys. Lett. **264,** 316–322 (1997).
23. D. Romanini, A. A. Kachanov, and F. Stoeckel, "Diode laser cavity ringdown spectroscopy," Chem. Phys. Lett. **270,** 538–545 (1997).
24. D. Romanini, A. A. Kachanov, and F. Stoeckel, "Cavity ringdown spectroscopy: broadband absolute absorption measurements," Chem. Phys. Lett. **270,** 546–550 (1997).
25. B. A. Paldus, C. C. Harb, T. G. Spence, B. Wilke, J. Xie, J. S. Harris, and R. N. Zare, "Cavity-locked ringdown spectroscopy," J. Appl. Phys. **83,** 3991–3997 (1998).
26. Z. Li, R. G. T. Bennett, and G. E. Stedman, "Swept-frequency induced optical cavity ringing," Opt. Commun. **86,** 51–57 (1991).
27. Z. Li, G. E. Stedman, and H. R. Bilger, "Asymmetric response profile of a scanning Fabry–Perot interferometer," Opt. Commun. **100,** 240–246 (1993).
28. K. An, C. Yang, R. R. Dasari, and M. S. Feld, "Cavity ringdown technique and its application to the measurement of ultraslow velocities," Opt. Lett. **20,** 1068–1070 (1995).
29. J. Poirson, F. Bretenaker, M. Vallet, and A. L. Floch, "Analytical and experimental study of ringing effects in a Fabry–Perot cavity. Application to the measurement of high finesse," J. Opt. Soc. Am. B **14,** 2811–2817 (1997).
30. B. E. A. Saleh and M. C. Teich, *Fundamentals of Photonics* (Wiley, New York, 1991).
31. D. Romanini and K. K. Lehmann, "Ring-down cavity absorption spectroscopy of the very weak HCN overtone bands with six, seven, and eight stretching quanta," J. Chem. Phys. **99,** 6287–6301 (1993).