

Cavity-ringdown molecular spectroscopy based on an optical frequency comb at 1.45–1.65 μm

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Received September 22, 2006; revised October 20, 2006; accepted October 23, 2006; posted November 1, 2006 (Doc. ID 75366); published January 12, 2007

Optical frequency comb-based cavity-ringdown spectroscopy has recently enabled high-sensitivity absorption detection of molecules over a broad spectral range. We demonstrate an improved system based on a mode-locked erbium-doped fiber laser source centered at 1.5 μm , resulting in a spectrometer that is inexpensive, simple, and robust. It provides a very large spectral bandwidth (1.45–1.65 μm) for investigation of a wide variety of molecular absorptions. Strong molecular absorptions at 1.5 μm allow for detection at sensitivities approaching the 1 part in 10^9 volume level. We provide a detailed description of our spectrometer and present measurements of the rovibrational spectra for CO, NH₃, and C₂H₂ with an absorption sensitivity of $2 \times 10^{-8} \text{ cm}^{-1} \text{ Hz}^{-1/2}$ per detection channel. © 2007 Optical Society of America

OCIS codes: 300.6390, 140.4050, 140.3500.

In recent years, cavity-ringdown spectroscopy (CRDS) has found an increasing number of applications in a wide variety of research and commercial settings.^{1–4} The success of this technique for high-precision molecular concentration measurements and trace molecular detection can be attributed to its capability for simultaneously providing high sensitivity and excellent spectral selectivity. The sensitivity of cavity ringdown is attributed to the enhanced light–matter interaction length that is a consequence of coupling light into the resonant modes of a high-finesse optical cavity. The selectivity comes from the use of cavity resonance modes as high-resolution probes for individual molecular resonances. While cutting edge continuous wave (CW) CRDS systems provide excellent sensitivities of $2 \times 10^{-12} \text{ cm}^{-1} \text{ Hz}^{-1/2}$,¹ they are unable to investigate a large variety of molecules due to their limited spectral bandwidth of a few nanometers.^{1–4} In response to the limitations of CW CRDS there have been a number of efforts in recent years to develop highly sensitive broad-bandwidth spectroscopic techniques.^{5,6}

Broadband CRDS using an optical frequency comb emitted by a mode-locked laser source provides both high sensitivity and selectivity by efficiently coupling an optical frequency comb into a high-finesse optical cavity over a large spectral bandwidth.⁶ This technique allows cavity-ringdown measurements to be performed over hundreds of nanometers of spectral bandwidth, allowing a single CRDS system to perform measurements on a wide variety of molecules. In this Letter, we describe a broadband CRDS spectrometer based on a mode-locked erbium-doped fiber laser source. Using two chirped pulse amplifiers (CPAs) and a highly nonlinear fiber (HNLF), a spectral bandwidth of more than 500 nm is generated with an average spectral power density of 100 $\mu\text{W}/\text{nm}$. The laser source is coupled to a low-dispersion, high-finesse optical cavity to enable ringdown measurements over a large spectral bandwidth from 1450–1650 nm. The high sensitivity and selec-

tivity of this spectrometer are demonstrated with measurements of the overtone spectra of CO, C₂H₂, and NH₃ with a sensitivity of $2 \times 10^{-8} \text{ cm}^{-1} \text{ Hz}^{-1/2}$. Finally, an analysis is provided to identify further improvements to be made for the broadband ringdown sensitivity.

The mode-locked erbium-doped fiber laser⁷ is operated in the stretched-pulse regime (i.e., net normal dispersion) and provides a 100 MHz pulse train with pulse durations of 175 fs and 40 mW of average power (Fig. 1). The output of this laser is coupled into 15 m of anomalous dispersion single-mode fiber (SMF 28) that prestretches these pulses to 7.0 ps duration in preparation for two CPAs.⁸ Each CPA uses 2 m of highly doped erbium fiber as the gain medium and is pumped with two counterpropagating 980 nm laser diodes that each provide 500 mW of pumping power. The dispersion of each amplifier is slightly normal such that the pulses experience a small compression as they traverse the amplifiers. After the second CPA the pulses are 6.7 ps in duration and have an average power of 350 mW. A 40 cm piece of HNLF, with a nonlinearity coefficient of $\gamma = 30 \text{ W}^{-1} \text{ km}^{-1}$ and a zero dispersion point of 1580 nm, broadens the laser spectrum to several hundred nanometers [see Fig. 2(a)]. By launching highly chirped pulses into the nonlinear fiber, the onset of the nonlinearity occurs at higher average powers, leading to limited spectral broadening and consequently a higher spectral power density. The resulting spectrum has a peak spectral power density of 1 mW/nm at 1565 nm and $>200 \mu\text{W}/\text{nm}$ between 1420 and 1600 nm. The pulse train is then passed through an optical switch based on a Mach–Zender interferometer with an electro-optical modulator (EOM) in one arm of the interferometer. The switch is used to rapidly turn off the light incident on the cavity so ringdown measurements can be performed. The spectrum is monitored after the EOM switch by an optical spectrum analyzer. Due to optical losses in

the switch, collimator, and spectral monitoring, 100 mW are incident on the cavity for ringdown measurements.

The ringdown cavity is a two-mirror linear standing wave cavity designed to optimize the combined sensitivity and selectivity of the system by achieving a high finesse and low dispersion over a large spectral bandwidth. The reflectivity and dispersion curves for the mirrors used in this cavity are shown in Fig. 2(b). These mirrors provide a finesse of $F > 3100$ and dispersion $d < 15 \text{ fs}^2$ for 200 nm of spectral bandwidth between 1450 and 1650 nm with a peak finesse of $F=7200$ at 1545 nm. The cavity length is 1.5 m, corresponding to a free spectral range (FSR) of 100 MHz, matching the repetition frequency of the comb. Together, the length and finesse of the cavity lead to an effective absorption path length of $l_{\text{eff}} > (2F/\pi)l > 3 \text{ km}$. The empty cavity ringdown time is $\tau > 7.75 \mu\text{s}$ with a peak of $\tau=11.4 \mu\text{s}$ at 1545 nm.

The laser comb modes are coupled to the resonant cavity modes by adjusting the comb repetition frequency f_{rep} and the carrier offset frequency f_0 .⁶ The adjustment of f_{rep} is performed using two piezoelectric transducers (PZTs) and one picomotor inside the laser cavity. The first PZT provides a long range (17 μm) but slow response. A second PZT fiber stretcher is used for fast modulation (20 kHz) of f_{rep} . A picomotor allows for long range scans of f_{rep} (up to $\Delta l=2 \text{ cm}$ or $\Delta f_{\text{rep}}=1.5 \text{ MHz}$), which are useful for tracking large changes in the cavity FSR caused by pressure changes in the ringdown cavity. f_0 is adjusted by changing the driving current of the pump diode for the mode-locked fiber laser.

To perform ringdown measurements, the frequency comb is dithered around the resonant cavity modes at 500 Hz by the fast intracavity PZT, allowing the cavity to build up intensity and ringdown at 1000 times per second. The modulation amplitude of f_{rep} is $\Delta f_{\text{rep}} < 0.5 \text{ Hz}$ such that the comb frequencies and the cavity modes overlap for more than 10 μs during each sweep, allowing for more than 1000 pulses to contribute to each buildup and ringdown event. The cavity transmission is detected to monitor the buildup of light within the cavity. The periodic buildup signal is combined with the modulation signal to form a phase lock that maintains the phase relationship between

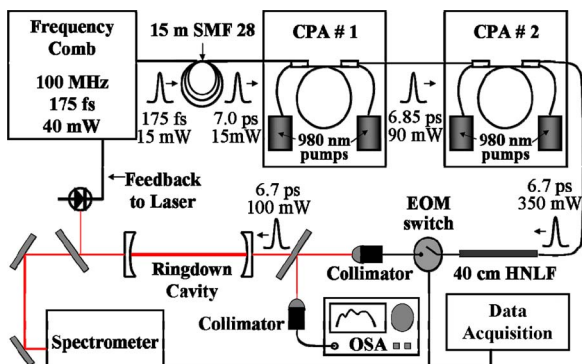


Fig. 1. (Color online) Schematic of the 1.55 μm frequency comb based cavity-ringdown spectrometer.

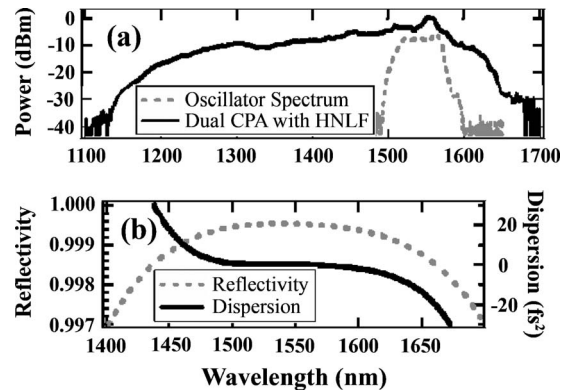


Fig. 2. (a) Spectral power density in (dBm/nm) for the fiber laser before and after amplification and spectral broadening. (b) Dispersion and reflectivity curves of the cavity mirrors show that low dispersion ($< 15 \text{ fs}^2$) and high reflectivity ($R > 0.999$) are maintained between 1450 and 1650 nm.

the buildup and the modulation signal at a low bandwidth (10 Hz). This locking scheme is robust and highly stable, permitting the comb to track the cavity and perform ringdown measurements for hours.

The light transmitted from the cavity is aligned into a 0.25 m monochromator and detected by an InGaAs photodiode followed by a 1 MHz bandwidth transimpedance amplifier permitting the detection of ringdown signals with a shot noise limit of 1 μW average optical power. The monochromator uses a 600 line/mm grating and 25 μm slits yielding a spectral resolution of 25 GHz. For the initial demonstration of this spectrometer, spectral scans are performed by scanning the monochromator grating and measuring the ringdown signal at each wavelength.

To demonstrate the capabilities of this spectrometer, we have measured the overtone spectra of CO, C_2H_2 , and NH_3 between 1450 and 1600 nm. To ensure that precisely measured concentrations of the target gas are introduced into the ringdown cavity, a two-stage dilution process is used. In the first stage, a pressure of 0.5 to 60 Torr of the target gas is combined with 600 Torr of Ar in a mixing container. After mixing, 1 to 50 Torr of the mixture is introduced into the ringdown chamber. Since the capacitive pressure gauge used here has an uncertainty of $\pm 50 \mu\text{Torr}$, pressures of the target gas between 0.8 mTorr and 5 Torr were achieved. Finally, the ringdown chamber is filled to 600 Torr with Ar to achieve a pressure-broadened linewidth of a few GHz for the target molecule.

The overtone spectra of CO, C_2H_2 , and NH_3 , shown in Fig. 3(a), contain 150 nm of spectral information, including the P-branch of the $\nu_1 + \nu_3$ overtone spectrum of C_2H_2 ,⁹ the $\nu=3$ overtone spectrum of CO,⁹ and more than 4000 rovibrational transitions in NH_3 between 1450 and 1560 nm.¹⁰ Due to our ability to resolve individual rotational lines of the CO overtone spectrum, these lines were used to measure the size of the ringdown signal as a function of the intracavity absorption α . Under a specific value of empty cavity loss, an increased level of intracavity gas absorption will lead to a gradual saturation of the ringdown sig-

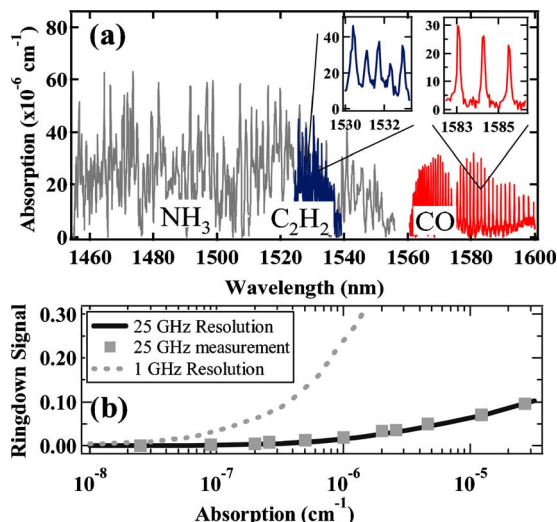


Fig. 3. (Color online) (a) Absorption spectra for 2 Torr CO, 10 mTorr NH_3 , and 1.5 mTorr C_2H_2 , showing 150 nm of spectral information. (b) Measured and calculated normalized ringdown signals for pressure-broadened (2 GHz linewidth) CO transition in the current system (25 GHz resolution). Calculated ringdown signals for 1 GHz resolution system performing the same measurements are also shown.

nal when the additional molecular loss becomes comparable with the empty cavity loss. In the case of low-resolution detection, the onset of saturation behavior occurs at much higher intracavity absorptions and is much less dramatic than in the high-resolution case as illustrated in Fig. 3(b). Here the measured and calculated ringdown signal sizes are plotted as a function of α , revealing a rather small change in the ringdown signal size with increasing absorption. This is the result of the low resolution of our spectrometer (25 GHz) relative to the pressure-broadened linewidth of the CO transitions being measured (~ 2 GHz). With 1 s of averaging time we are able to reach a signal-to-noise ratio of 1000 for the ringdown events, yielding an absorption sensitivity of $2 \times 10^{-8} \text{ cm}^{-1} \text{ Hz}^{-1/2}$. This level of sensitivity allows for the detection of 6 parts per million volume (ppmv) of CO, 20 parts per billion volume (ppbv) of NH_3 , and 8 ppbv of C_2H_2 at 1 s of integration time.

There are several avenues for improving the capabilities of this broadband CRDS system. Parallel acquisition of spectral information is an important first step. While technically challenging, especially in the IR spectral region where CCD technology is not available, the ability to simultaneously acquire an entire spectrum has profound implications for the way we define the sensitivity of absorption measurements. Currently the sensitivity is defined by the absorption α ($\text{cm}^{-1} \text{ Hz}^{-1/2}$) that can be measured by the system at a single wavelength. As a result, a CW system can report a superior high sensitivity for a particular absorption peak even though it might take minutes or hours to achieve this level of sensitivity across the entire spectrum of interest. Using the traditional definition of sensitivity, a broadband system with 10 times less sensitivity than a comparable CW system will already achieve the same performance if

the spectrum to be measured contains only 100 ringdown measurements. Obviously the broadband approach wins when a large number of spectral resonances are to be measured. Sensitivity can also be improved with the use of higher-reflectivity mirrors. By using higher-reflectivity low-dispersion mirrors for our next system, we will achieve an order of magnitude better sensitivity.

Another area for improvement is spectral resolution. The 1 GHz resolution ringdown signal size versus α , shown in Fig. 3(b), suggests that by reducing our resolution to the Doppler linewidth of CO we will increase our sensitivity by an order of magnitude. Though many technical challenges remain in realizing high resolution and massively parallel cavity-ringdown measurements, recent work by Weiner¹¹ and Diddams¹² demonstrated Doppler limited resolution using a virtually imaged phased array (VIPA) spectrometer. However, the current focal plane array detectors that are capable of reading out the parallel output of the VIPA spectrometer do not have the speed to record ringdown measurements. A direct absorption measurement that utilizes cavity enhancement will be an important first step toward the ultimate goal of highly sensitive, massively parallel absorption measurements using cavity-ringdown spectroscopy. Research along this line has already produced initial results in our laboratory and will be reported in a separate publication.

We thank K. Vogel and S. T. Cundiff for useful discussions. This work was funded by the Air Force Office of Scientific Research, the Office of Naval Research, NIST, and a University of Colorado Proof of Concept grant.

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