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Laser-locked, continuously tunable high resolution cavity ring-down spectrometer

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A continuous-wave cavity ring-down spectrometer with sub-MHz precision has been built using the sideband of a frequency stabilized laser as the tunable light source. The sideband is produced by passing the carrier laser beam through an electro-optic modulator (EOM) and then selected by a short etalon on resonance. The carrier laser frequency is locked to a longitude mode of a thermo-stabilized Fabry-Perot interferometer (FPI) with a long-term absolute frequency stability of 0.2 MHz (5×10^{-10}). Broad and precise spectral scanning is accomplished, respectively, by selecting a different longitudinal mode of the FPI and by tuning the radio-frequency driving the EOM. The air broadened water absorption line at 12 321 cm^{-1} was studied to test the performance of the spectrometer. © *2011 American Institute of Physics*. [doi:10.1063/1.3655445]

I. INTRODUCTION

Since the introduction by O'Keefe and Deacon in 1988,[1] cavity ring-down spectroscopy (CRDS) has been acknowledged as a very sensitive tool for absorption measurement, and has been widely applied in molecular spectroscopy[2,3] and trace gas detection.[4,5] Historic review of CRDS can be found in Refs. 6 and 7. The main idea of this method is to measure the decay rate of the light inside a resonant cavity composed of two high-reflectivity mirrors. The decay rate $1/\tau$ of the emitted light is proportional to the total optical losses inside the cavity, where τ is the "ring-down time"[8]

$$\tau = \frac{L/c}{-\ln R + \alpha L}. \qquad (1)$$

L is the length of the cavity, c is the speed of light, R is the reflectivity of a cavity mirror, and α is the sample absorption coefficient. α can be determined by

$$\alpha(\nu) = \frac{1}{c\tau(\nu)} + \frac{\ln R}{L}. \qquad (2)$$

Since the $\frac{\ln R}{L}$ term can be treated in the baseline, the absorption line profile can be obtained by fitting the measured curve $\frac{1}{c\tau}$.

In early CRDS studies pulsed lasers were used and eventually it was realized that the sensitivity was limited by multimode cavity excitation due to the wide bandwidth of the pulsed laser. Lehmann proposed to use narrow bandwidth continuous wave (cw) lasers to excite a single cavity mode to obtain higher sensitivity.[9] The first demonstration of cw-CRDS was performed by Romanini and his co-workers. Using a cw diode laser and a pair of mirrors with reflectivity $R \simeq 99.999\%$, a noise equivalent minimal detectable absorption loss $\alpha_{min} \simeq 2 \times 10^{-10}$ cm has been achieved.[10] We have obtained a sensitivity of 7×10^{-11} cm using a cw Ti:sapphire laser and a pair of mirrors with $R \simeq 99.995\%$.[11] Using a pair of mirrors of $R = 99.9987\%$ at $\lambda = 1652$ nm, Huang and Lehmann have obtained a sensitivity of 4.4×10^{-12} cm during an optimum integration time of about 30 min.[12]

In many applications, it is also desired to acquire high frequency precision as well as the high sensitivity. One obstacle is the frequency jitter of the scanning spectral laser used in cw-CRDS. Paldus *et al.* used two orthogonal beam polarization from a single laser but with different losses on the ring-down cavity, one used for stabilizing the cavity length and another one used for the ring-down measurement.[13] Since the stabilization of the cavity is still influenced by the frequency jitter of the scanning laser, Hodges *et al.* proposed frequency stabilized cavity ring-down spectroscopy (FS-CRDS). Here, frequency jitter is mitigated by stabilizing the ring-down cavity to an absolute frequency reference.[14] In their experiment, one of the ring-down cavity eigenfrequencies was locked to a frequency-stabilized He-Ne laser. Mode-matching of the spectral laser to the stabilized high-finesse ring-down cavity can lead to frequency resolution of about 1 MHz or less. The coarse scanning was limited by the separation between adjacent combs of the ring-down cavity (typically in 10^2 MHz) and the fine scanning was established by shifting the reference He-Ne laser frequency with a double passed acousto-optical modulator (AOM). Using 50 kHz scanning steps, relative frequency accuracy of about 0.1 MHz has been demonstrated.[15] Very recently, Cygan *et al.* applied the Pound-Drever-Hall method to lock the spectral laser on resonance to the ring-down cavity to increase the ring-down event acquisition rate.[16]

Here we present a different approach of FS-CRDS. The idea is to lock the spectral laser frequency to an external stabilized reference, as combs of a thermo-stabilized Fabry-Perot interferometer in our case, and the fine spectral scanning is accomplished by using a radio-frequency driven electro-optic modulator (EOM). In this case, throughout the fine spectral scanning, in the range of typically several GHz limited

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by the bandwidth of the EOM, the laser frequency is kept locked at the reference frequency. Such FS-CRDS scheme, we refer to "laser locked," is quite different from the one realized by Hodges *et al.*, in which the ring-down cavity is locked on resonance with a reference laser. The later one needs a frequency stabilized reference laser, and also a pair of specially designed dichroic cavity mirrors with relatively high transmittance at reference laser wavelength but low transmittance at spectral laser wavelength. It is also different from the laser-locked CRDS presented first by Leeuwen *et al.*[17] and later by Martínez *et al.*,[18] in which periodically locking the laser to a comb of the ring-down cavity was applied to increase the ring-down event repetition rate. As will be shown below, an important advantage of the method presented here is that the continuous frequency scanning can be performed with absolute frequency accuracy only limited by the stability of the frequency reference and the laser-locking scheme. In addition, such "laser-locked" FS-CRDS can be easily upgraded from an established cw-CRDS setup.

II. EXPERIMENTAL

The configuration of the CRDS setup is presented in Fig. 1. The laser source is a cw tunable Ti:Sapphire laser (Coherent 899-21) pumped with a 532 nm solid state laser (Coherent Verdi). The laser frequency (ν_0) is locked using the Pound-Drever-Hall method to a longitude mode of a Fabry-Perot interferer (FPI) built with ultra-low-expansion (ULE) glass. The length of the ULE FPI is 10 cm which yields a free-spectral-range (FSR) of 1.5 GHz. The finesse of the FPI is around 2000–5000 near 0.79 μm and 1.08 μm. The ULE-FPI is enclosed in an aluminium holder and installed in a vacuum chamber. The aluminium holder is also used as heat shield and the temperature drift was monitored with a thermal sensor (TH10K, Kapton) attached to the aluminium holder. A heating wire together with a feedback loop are used to stabilize the aluminium holder temperature at about 308 K. The temperature fluctuation has been continuously monitored for hours and it shows that the drift is below 10 mK.

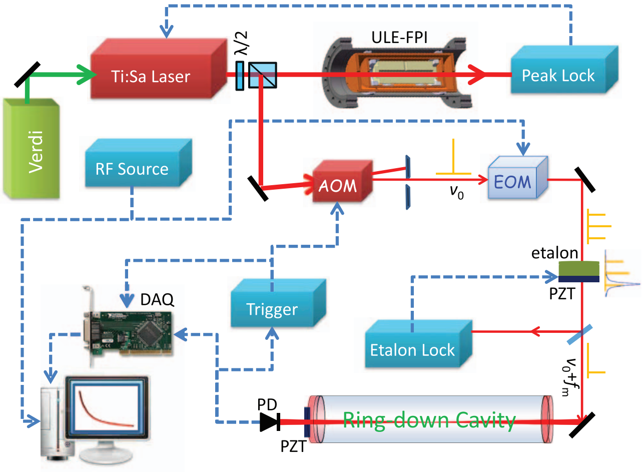

FIG. 1. (Color online) Schematic diagram of the laser-locked sideband cavity ring-down spectrometer. The abbreviations are as follows: AOM, acousto-optical modulator; DAQ, data acquisition card; EOM, electro-optical modulator; PD, photodiode; PZT, lead zirconate titanate piezoelectric actuator; ULE-FPI, Fabry-Perot interferometer made of ultra-low-expansion glass.

Part of the laser beam is led into an acousto-optical modulator (AOM, ISOMET) and then coupled to a broad-band fiber electro-optical modulator (EOM, New Focus). The AOM is used to switch on and off the laser and the EOM is used to produce sidebands ($\pm f_m$) on the carrier. The EOM is driven by a tunable radio-frequency (RF) source (Agilent 9320A) followed with an amplifier. The laser beam is then introduced into a homemade etalon. The etalon is composed of a pair of plano-concave mirrors and one of them is attached to a piezoelectric tube. It has a finesse of about 100 and FSR of 15 GHz. The length of the etalon is controlled with a feedback loop to keep one of its longitude mode on resonance to a selected sideband of the laser. In this case, only the selected sideband with frequency of $\nu_0 + f_m$ can go through the etalon while other sidebands and the carrier are reflected. The laser beam of frequency $\nu_0 + f_m$ is then coupled into the ring-down cavity for spectroscopy measurement. The cavity is 147 cm long and the curvature radius of the high reflectivity (HR) mirrors is 100 cm. Two HR mirrors (Los Gatos Inc.) have stated reflectivity of 99.995%. One of the HR mirrors is mounted on a piezoelectric actuator (Physik Instrumente GmbH) and the actuator is driven with a triangle wave (~100 Hz) from a function generator. The ring-down signal is detected by a photodiode and then recorded by a 14-bit digitizer (AD-Link PCI9820).

The fine spectral scanning is accomplished by tuning the radio-frequency f_m while the coarse tuning can be done by matching ν_0 to different longitude modes of the ULE-FPI. Since both the FSR of the ULE-FPI f_{FPI} and the RF frequency f_m can be measured to kHz accuracy or better, the relative precision of the spectrometer is at the same level. The absolute frequency accuracy is determined by the stability of the ULE-FPI. We have obtained the absolute frequency of the ULE-FPI by measuring the relative frequency shift between a comb of the ULE-FPI and the ^{87}Rb D_2 line at 780 nm. The used ^{87}Rb D_2 line has been precisely determined as 384, 228, 115.203(7) MHz by Ye *et al.*[19] In present measurement, the laser is locked to the Rb line using saturation spectroscopy and the ULE-FPI spectrum was recorded by scanning the sideband produced by the EOM. The resonance peak position of the ULE-FPI relative to the Rb line position was measured many times within a month or so to test the stability of the ULE-FPI. The results measured in one day (July-08) was shown in the left panel of Fig. 2, which gives 389.77(17) MHz. The statistical results obtained in other days are shown in the right panel of Fig. 2. Between the day-to-day measurements, the lasers were turned off to check the stability of the system. Figure 2 shows a fluctuation about 100–200 kHz in hours and slow day-to-day drift in the same order, which indicates a stability of about 5×10^{-10}. We believe that this fluctuation is mainly introduced by the Rb saturation spectroscopy and it actually gives an upper limit of the uncertainty of the ULE-FPI frequency. Since this accuracy is satisfied for present CRDS measurement, we did not take further effort to improve it.

It is also worth noting that the present setup has been upgraded from our previous cw-CRDS setup. Since all-fiber

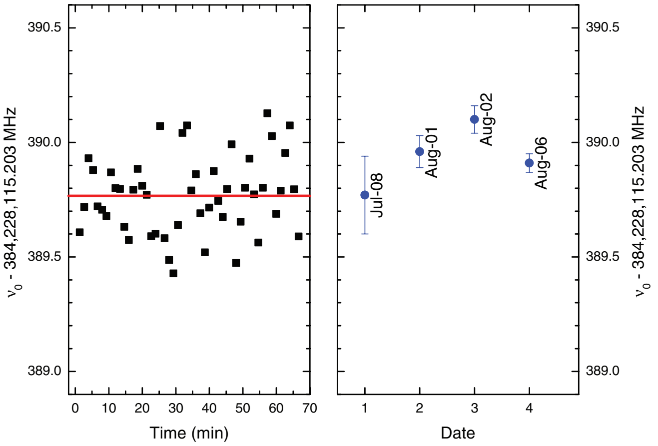

FIG. 2. (Color online) Measured ULE-FPI comb position relative to the Rb 780 nm D_2 line at 384, 228, 115.203(7) MHz. Left panel: the July-08 data. Right panel: statistical analysis of the data obtained at different dates.

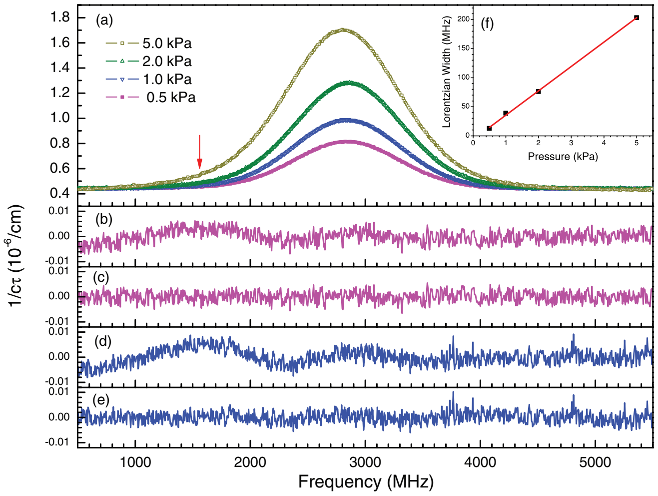

FIG. 3. (Color online) Air broadened H_2O absorption line at 12 321.08 cm^{-1} measured by laser-locked CRDS. (a) Spectrum measured with air pressure of 0.5, 1.0, 2.0, and 5.0 kPa. (b-d): the fitting residuals, (b) and (c) are for the 0.5 kPa spectrum, (d) and (e) are for the 1.0 kPa spectrum. In (b) and (d), only the 12 321.0774 cm^{-1} line was included in the fitting. (c) and (e), an additional weak line at 12 321.0365 cm^{-1} (position indicated with an arrow) was also included. (f) Lorentzian line width obtained from fitting of respective spectrum.

connections are used among different blocks in the apparatus, it allows us to switch the working mode easily between the "normal" mode and the "laser-locked" mode. Because accurate alignments of the ring-down cavity usually need higher laser power, we can simply bypass the fiber EOM and the sideband-selecting etalon during the optical alignments and put in them when the ring-down has been established. This advantage is very useful in daily operation.

III. PERFORMANCE TEST

To test the performance of the present frequency stabilized cavity ring-down spectrometer, a water absorption line at 12 321.0774 cm^{-1} was measured. The line is the $8_{2,6} \leftarrow 7_{2,5}$ transition of the $2\nu_1 + \nu_2 + \nu_3$ band of $H_2^{16}O$, with line strength of 3.23×10^{-24} cm^{-1} cm^2/molecule given in the HITRAN-2008 database.[20] Figure 3(a) shows the spectrum obtained under different air pressure. The spectrum was then fitted using a Voigt profile with the Doppler width fixed to the theoretical value. Figures 3(b) and 3(d) show the fitting residual of the spectrum obtained at 0.5 kPa and 1.0 kPa, respectively. It is clearly shown that there is notable discrepancy near the position indicated by the arrow on the figure. We concluded that there is a much weaker line which is absent from the HITRAN database. Assuming the strong and weak lines have the same profile, new fittings including both lines were carried out and the resulted fitting residuals are shown in Figs. 3(c) and 3(e). In this way, we also located the new weak line at 12 321.0365 cm^{-1} with intensity of about 33 times smaller than the line at 12 321.0774 cm^{-1}.

The Lorentzian width values obtained from the fitting of the spectrum are shown in Fig. 3(f), As expected, the pressure broadening Lorentzian width shows excellent linear dependence on the air pressure. Note that the Lorentzian width is actually much smaller than the Gaussian width (1.07 GHz) which was fixed at the theoretical Doppler broadening value in the fitting. The quality of the fitting also shows good resolution of the spectrometer.

Figures 3(b)–3(e) also illustrates the present noise-equivalent detection limit is about 2×10^{-9} cm, which is about 30 times worse than the best value we have achieved before[11] at "normal" working mode. The reason is that only about 1 mW laser power has been sent into the ring-down cavity, which is much smaller than that used in the "normal" working mode of this CRDS setup. The weak laser power is due to the loss in the sideband production and selection. Usually the EOM can only handle about 10 mW laser power and the EOM efficiency at high RF frequency is often quite low. The short FPI used as optical filter to select the specified sideband brings additional loss on the transmitted laser beam power. To pursue larger scanning range, sometimes we use high order harmonic frequency sideband produced in the EOM. In this case, the sideband laser power sent into the ring-down cavity can be very weak. A photo detector and pre-amplifier with sufficient bandwidth can overcome this problem. In fact, it has been reported that even microwatt light power is sufficient for a sensitive cavity ring-down spectrometer.[21] Since we concentrate more in the frequency resolution here, and also need to switch easily between the "normal" working mode and the "laser-locked" mode, we did not replace the detector and pre-amplifier in this work. In this case, the signal has not been amplified to fully satisfy the vertical resolution of the digitizer. Using a more proper amplifier can readily solve this problem.

IV. DISCUSSION AND CONCLUSION

As the conclusion, we have presented a frequency-stabilized sideband cavity ring-down spectroscopy using a continuous wave laser locked on to a thermo-stabilized Fabry-Perot interferometer made of ultra-low-expansion glass. The spectral scanning is performed by tuning the driven frequency of an electro-optic modulator to produce tunable laser sideband used for spectroscopy. We can obtain spectrum with absolute precision numbers in both axes: using absolute frequencies of the combs of the ULE-FPI plus the EOM sideband frequency as the x axis, as well as the very sensitive ring-down time as the y axis. This is very useful for quantitative spectroscopy applications, for example, line profile measurements and secondary frequency standards using molecular absorption lines. An interesting application is to determine the Boltzmann constant k_B by measuring the Doppler width of an absorption line of molecules at precisely maintained temperature.[22] Using CRDS for k_B determination has been proposed[11,16,23] and the possible precision is also discussed.[24]

The instrumental frequency accuracy demonstrated in present study is 170 kHz. Since the frequency of the microwave driving the EOM can be of extreme precision, the present instrumental accuracy is only limited by the frequency locking of the carrier laser. Using a passive optical cavity to lock the laser frequency in a compact system, subhertz accuracy ($\frac{\delta\nu}{\nu_0} \simeq 1 \times 10^{-15}$) has been reported.[25] The absolute frequency reference can also be replaced by a laser comb. Since the combs, either from a stabilized optical cavity or from a mode-locked femtosecond laser, can cover a very wide spectral region, the tunability of this “laser-locked” cavity ring-down spectrometer is only limited by the spectral laser in use. In this case, laser locked CRDS using a widely tunable laser (for example, a cw Ti:saphire laser) locked to a femtosecond laser comb can potentially cover a spectral range of hundreds nanometers with extremely high sensitivity and ultimate resolution as well.

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