

Cavity ring-down spectroscopy of Doppler-broadened absorption line with sub-MHz absolute frequency accuracy

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Abstract: A continuous-wave cavity ring-down spectrometer has been built for precise determination of absolute frequencies of Doppler-broadened absorption lines. Using a thermo-stabilized Fabry-Pérot interferometer and Rb frequency references at the 780 nm and 795 nm, 0.1 – 0.6 MHz absolute frequency accuracy has been achieved in the 775-800 nm region. A water absorption line at 12579 cm^{-1} is studied to test the performance of the spectrometer. The line position at zero-pressure limit is determined with an uncertainty of 0.3 MHz (relative accuracy of 0.8×10^{-9}).

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OCIS codes: (300.6360) Spectroscopy, laser; (020.3690) Line shapes and shifts.

References and links

1. L. Rothman, I. Gordon, A. Barbe, D. Chris Benner, P. Bernath, M. Birk, V. Boudon, L. Brown, A. Campargue, J. Champion, K. Chance, L. Coudert, V. Dana, V. Devi, S. Fally, J.-M. Flaud, R. Gamache, A. Goldman, D. Jacquemart, I. Kleiner, N. Lacome, W. Lafferty, J.-Y. Mandin, S. Massie, S. Mikhailenko, C. Miller, N. Moazzen-Ahmadi, O. Naumenko, A. Nikitin, J. Orphal, V. Perevalov, A. Perrin, A. Predoi-Cross, C. Rinsland, M. Rotger, M. Šimečková, M. Smith, K. Sung, S. Tashkun, J. Tennyson, R. Toth, A. Vandaele, and V. Auwera, "The HITRAN 2008 molecular spectroscopic database," *J. Quant. Spectrosc. Radiat. Transfer* **110**, 533–572 (2009).
2. S. S. Brown, "Absorption spectroscopy in high-finesse cavities for atmospheric studies," *Chem. Rev.* **103**, 5219–5238 (2003).
3. B. A. Paldus and A. A. Kachanov, "An historical overview of cavity-enhanced methods," *Can. J. Phys.* **83**, 975–999 (2005).
4. P. Zalicki and R. N. Zare, "Cavity ring-down spectroscopy for quantitative absorption measurements," *J. Chem. Phys.* **102**, 2708–2717 (1995).
5. D. Romanini, A. A. Kachanov, and F. Stoeckel, "Diode laser cavity ring down spectroscopy," *Chem. Phys. Lett.* **270**, 538–545 (1997).
6. B. Gao, W. Jiang, A.-W. Liu, Y. Lu, C.-F. Cheng, G.-S. Cheng, and S.-M. Hu, "Ultra sensitive near-infrared cavity ring down spectrometer for precise line profile measurement," *Rev. Sci. Instrum.* **81**, 043105 (2010).
7. H. Huang and K. K. Lehmann, "Long-term stability in continuous wave cavity ringdown spectroscopy experiments," *Appl. Opt.* **49**, 1378–1387 (2010).
8. I. Galli, S. Bartalini, S. Borri, P. Cancio, D. Mazzotti, P. De Natale, and G. Giusfredi, "Molecular gas sensing below parts per trillion: Radiocarbon-dioxide optical detection," *Phys. Rev. Lett.* **107**, 270802 (2011).
9. A. Foltynowicz, T. Ban, P. Masowski, F. Adler, and J. Ye, "Quantum-noise-limited optical frequency comb spectroscopy," *Phys. Rev. Lett.* **107**, 233002 (2011).
10. J. T. Hodges, H. P. Layer, W. W. Miller, and G. E. Scace, "Frequency-stabilized single-mode cavity ring-down apparatus for high-resolution absorption spectroscopy," *Rev. Sci. Instrum.* **75**, 849–863 (2004).
11. D. Lisak, J. T. Hodges, and R. Ciuryło, "Comparison of semiclassical line-shape models to rovibrational H₂O spectra measured by frequency-stabilized cavity ring-down spectroscopy," *Phys. Rev. A* **73**, 012507 (2006).
12. S. Wójtcwicz, D. Lisak, A. Cygan, J. Domyslawska, R. S. Trawiński, and R. Ciuryło, "Line-shape study of self-broadened O₂ transitions measured by Pound-Drever-Hall-locked frequency-stabilized cavity ring-down spectroscopy," *Phys. Rev. A* **84**, 032511 (2011).

13. G. Giusfredi, S. Bartalini, S. Borri, P. Cancio, I. Galli, D. Mazzotti, and P. De Natale, "Saturated-absorption cavity ring-down spectroscopy," *Phys. Rev. Lett.* **104**, 110801 (2010).
14. H. Pan, C.-F. Cheng, Y. R. Sun, B. Gao, A.-W. Liu, and S.-M. Hu, "Laser-locked, continuously tunable high resolution cavity ring-down spectrometer," *Rev. Sci. Instrum.* **82**, 103110 (2011).
15. Y. R. Sun, H. Pan, C.-F. Cheng, A.-W. Liu, J.-T. Zhang, and S.-M. Hu, "Application of cavity ring-down spectroscopy to the boltzmann constant determination," *Opt. Express* **19**, 19993–20002 (2011).
16. J. Domysławska, S. Wójtewicz, D. Lisak, A. Cygan, F. Ozimek, K. Stec, Cz. Radzewicz, R. S. Trawiński, and R. Ciuryło, "Cavity ring-down spectroscopy of the oxygen B-band with absolute frequency reference to the optical frequency comb," *J. Chem. Phys.* **136**, 024201 (2012).
17. J. Ye, S. Swartz, P. Jungner, and J. L. Hall, "Hyperfine structure and absolute frequency of the ^{87}Rb $5P_{3/2}$ state," *Opt. Lett.* **21**, 1280–1282 (1996).
18. M. Maric, J. J. McFerran, and A. N. Luiten, "Frequency-comb spectroscopy of the D_1 line in laser-cooled rubidium," *Phys. Rev. A* **77**, 032502 (2008).
19. C. F. Cheng, Y. R. Sun, H. Pan, J. Wang, A. W. Liu, A. Campargue, and S. M. Hu, "Electric-quadrupole transition of H_2 determined to 10^{-9} precision," *Phys. Rev. A* **85**, 024501 (2012).

1. Introduction

Precise transition frequencies of atoms and molecules are widely applied in science and technology, such as tests of fundamental symmetries and high-level *ab initio* calculations, standards used for laser frequency stabilization and spectral calibration. Doppler free spectroscopy is frequently used in precision studies to avoid degrade of the frequency accuracy due to the Doppler-broadening, with experimental complexity at the expense. Particularly, it is more difficult to retrieve Doppler-free spectra of relatively weak molecular transitions in the infrared region. Meanwhile, transitions of molecules like water are widely used for spectral calibration for its extremely rich spectrum in the infrared. A huge archive of the transitions can be found in some spectroscopic databases including HITRAN [1]. Most of the available molecular absorption line frequencies are derived from the Doppler-limited spectra and with typical precision of 10^{-3} cm^{-1} . In principle, accurate line position can be retrieved from a broad line if the line profile has been recorded precisely, which requires a spectrometer with ultra-high sensitivity and resolution to detect delicate changes in the spectral profile.

Cavity ring-down spectroscopy (CRDS) has been acknowledged as a very sensitive tool for absorption measurement for over 20 years. It has been widely applied in molecular spectroscopy and trace gas detection. Historic reviews of CRDS can be found in Refs. [2, 3]. The main idea of this method is to measure the decay of the light power emitting from a resonant cavity composed of two high-reflectivity mirrors. The decay follows a simple exponential decay with a "ring-down time" τ . The sample absorption coefficient can be determined from [4]:

$$\alpha = \frac{1}{c\tau} - \frac{1}{c\tau_0}, \quad (1)$$

where c is the speed of light, τ_0 is the ring-down time of an empty cell. An absorption loss of $10^{-10}/\text{cm}$ or even less can be detected by a CRD spectrometer if the laser modes, both the spacial and the longitudinal, are matched to a high-finesse ring-down cavity [5–9].

To acquire high frequency precision in the CRDS measurements, Hodges *et al.* proposed frequency stabilized cavity ring-down spectroscopy (FS-CRDS) by stabilizing the ring-down cavity to an absolute frequency reference [10]. Mode-matching of the spectral laser to the stabilized high-finesse ring-down cavity can lead to frequency resolution of about 1 MHz or better. With a scanning step of 50 kHz, a *relative* frequency accuracy of about 0.1 MHz has been demonstrated [11]. FS-CRDS has been applied in the molecular line shape studies in the near-infrared [12] and in the mid-infrared [8, 13]. We have presented a different approach of FS-CRDS by locking the laser frequency to an external stabilized reference and scanning a sideband for spectroscopy through a radio-frequency driving electro-optic modulator [14]. FS-

CRDS can be favorable to determine the Boltzmann constant by measuring the Doppler width of a molecular line [15, 16].

In present work, we introduce CRDS with high precision over several hundred wavenumbers continuous scan range. Using a thermo-stabilized Fabry-Pérot interferometer calibrated with atomic frequency references, sub-MHz *absolute* frequency accuracy has been achieved in the near infrared, which is less than one thousandth of the Doppler width of the line. A Doppler-broadened ro-vibrational line of H_2^{16}O is studied to test the performance of the spectrometer.

2. Experimental

The configuration of the experimental setup is shown in Fig 1. Part of the experimental setup for cavity ring-down measurement is similar to our previous setup which have been presented in Ref. [6]. In brief, a CW tunable Ti:sapphire laser (Coherent 899-21) beam is coupled into a 1.4 m long resonance cavity. The cavity mirrors have a reflectivity of 99.995% and one of the two mirrors is mounted on a piezoelectric actuator. The piezoelectric actuator is driven with a triangle wave from a function generator. The Ti:Sapphire laser is running in a step-scan mode. On each step, typically about 100 ring-down events are recorded. A fitting program is applied to fit the exponentially decay curve yielding the decay time τ .

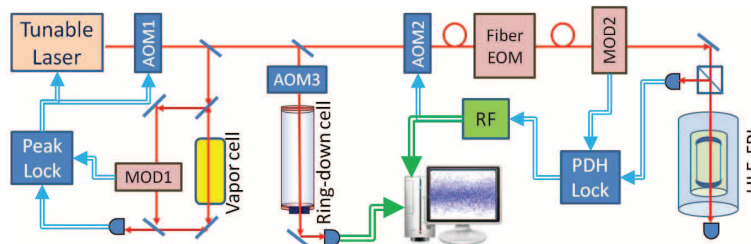


Fig. 1. Optic layout of the experimental setup. Abbreviations are as following: AOM, acousto-optical modulator; EOM, electro-optical modulator; MOD, frequency modulator; PDH, Pound-Drever-Hall locking; RF, radio frequency source driver; ULE-FPI, Fabry-Pérot interferometer made of ultra-low-expansion glass.

Precise calibration is accomplished by using the longitudinal modes of a 10 cm long thermo-stabilized Fabry-Pérot interferometer (FPI) built with ultra-low-expansion (ULE) glass. The finesse of the FPI is around 2000 – 5000 near $0.79 \mu\text{m}$. The ULE-FPI is enclosed in an aluminium holder sitting in a vacuum chamber. A heating wire together with a feedback loop are used to stabilize the aluminium holder temperature at about 303 K with a day-to-day temperature fluctuation of 10 mK (*rms*) measured by a thermal sensor. Beside the “free-scan” mode presented above, the spectrometer can also be switched to the “laser-locked” mode, where the laser frequency is locked to one of the longitudinal modes of the ULE-FPI using the Pound-Drever-Hall method. A sideband produced by a fiber electro-optical modulator (EOM) is selected and used for CRDS measurement instead of the carrier beam.

Absolute frequency calibration is accomplished by comparing the longitudinal mode frequencies of the ULE-FPI with available accurate atomic frequency references. The laser frequency is locked on an atomic saturation absorption line peak of Rb. The Rb vapor cell is installed in a magnetic shield (residual magnetic field $\simeq 0.2 \text{ mG}$) to eliminate the Zeeman frequency shift due to the residual magnetic field. The slow and fast feed-back control signals are delivered to the laser controller and an acousto-optical modulator (AOM1), respectively. After a frequency shift introduced by another AOM (AOM2), the carrier laser beam goes through a fiber electro-optic modulator (EOM) and two sidebands ($\pm f_s$) are added. The sideband frequency f_s

is tunable between hundred MHz to a few GHz controlled by a radio-frequency source (Agilent 9310A). The laser beam is then coupled into the ULE-FPI after a 10 MHz modulation introduced by a free-space electro-optic modulator. By demodulating the detected signal of the reflected beam from the ULE-FPI, we lock one of the sideband produced by the fiber EOM on a selected longitudinal mode of the ULE-FPI using the Pound-Drever-Hall method. The feedback control is accomplished by tuning the radio-frequency driving AOM2. In this way, the frequency difference between the atomic line and the selected ULE-FPI mode can be obtained by recording the radio-frequencies driving AOM2 and the fiber EOM.

The transmittance peaks of the ULE-FPI are indexed with integer numbers and the one adjacent to the ^{87}Rb 780 nm transition is chosen as $N = 0$. The frequency shifts of respective ULE-FPI peaks close to the ^{87}Rb $D1$ ($5S_{1/2} \rightarrow 5P_{1/2}$, 795 nm) and $D2$ ($5S_{1/2} \rightarrow 5P_{3/2}$, 780 nm) lines are measured and they are given in Table 1. The uncertainty of the $\Delta = \nu_N - \nu_{Rb}$ value is about 60 kHz, which consists of both the ULE-FPI frequency drift and the laser frequency drift. The later one is believed to be dominant since only fast changing fluctuation has been observed while the frequency drift of the ULE-FPI should be much slower. In this case, the absolute frequency drift of the ULE-FPI peaks is estimated to be less than 40 kHz.

Table 1. Frequency shifts of the ULE-FPI transmittance peaks to the respective ^{87}Rb transitions and the determined FSR.

λ/nm	Transition	ν_{Rb}/MHz	N^a	Δ^b/MHz	FSR/MHz
780	$5S_{1/2} \rightarrow 5P_{3/2}$, $F = 2 \rightarrow 3$,	384 228 115.203(8) ^c	0	389.213(63)	1497.02926(12)
795	$5S_{1/2} \rightarrow 5P_{1/2}$, $F = 2 \rightarrow 1$,	377 104 389.803(79) ^d	4759	-247.438(52)	1497.02863(39)

^a Index of the ULE-FPI longitudinal mode. ^b Measured frequency shift of the ULE-FPI peak to the atomic reference line, $\Delta = \nu_N - \nu_{Rb}$. ^c From Ref. [17]. ^d From Ref. [18].

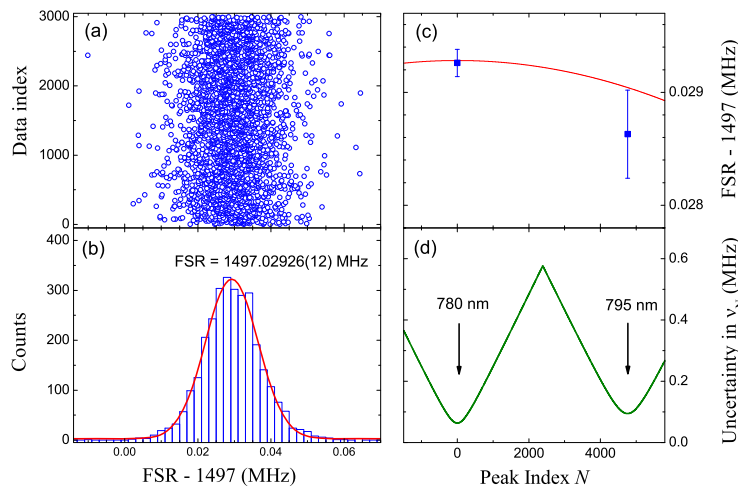


Fig. 2. Determination of the absolute frequencies of the ULE-FPI peaks. (a) FSR values at 780 nm from over 3000 measurements. (b) Gaussian function fitting of the histogram of the values from panel a. (c) The FSR value f , calculated (solid curve) and the experimentally determined (scattering points). (d) Uncertainty (1σ value) in the absolute frequency ν_N of the ULE-FPI peak with index N , where $\nu_N = \nu_M + (N - M)f$, ($M = 0$ or 4759).

By selecting two nearby ULE-FPI peaks as the locking positions, the free-spectral-range (FSR) of the ULE-FPI can be determined by measuring the difference of the the frequency shifts from the Rb line to these two ULE-FPI peaks. The FSR value f at $N = 0$ (780 nm) is measured in this way for over 3000 times and they are shown in Fig. 2(a). From the statistical distribution of the measured results, a most probable value of 1497.02926(12) MHz was obtained. The FSR value at $N = 4759$ near 795 nm has been obtained in the similar way which gives 1497.02863(39) MHz. Alternatively, an averaged FSR value can be obtained from $\bar{f} = \frac{\nu_{N1} - \nu_{N2}}{N1 - N2}$. Using the absolute frequencies of the ULE-FPI transmittance peaks $\nu_{N1=0}$ and $\nu_{N2=4759}$ which can be derived from the values shown in Table 1, we get $\bar{f} = 1497.02922(2)$ MHz.

The variation of the FSR value over the studied spectral range can be calculated using the group-delay-dispersion value given by the manufacturer of the ULE-FPI (ATFilms). The resulted curve of the FSR over the 775 – 800 nm region is shown in Fig. 2(c). The curve has been shifted to agree with the determined averaged \bar{f} value over this region. The FSR values determined at 780 nm and 795 nm are also shown in the same figure, and they agree well with the calculated FSR curve. According to the curve, the maximum deviation of the FSR value in this region due to group-delay-dispersion is 0.24 kHz. This value is used to estimate the uncertainty of the absolute frequencies ν_N of the ULE-FPI transmittance peaks with different N numbers. As shown in Fig. 2(d), the overall uncertainty of the ν_N value varies between 0.1 and 0.6 MHz in the spectral range of 775 – 800 nm. These absolute frequency markers can be easily used to calibrate the recorded spectrum.

3. Performance test: H₂¹⁶O line at 12579 cm⁻¹

To test the performance of the instrument, an absorption line of H₂¹⁶O at 12578.74 cm⁻¹ was recorded at room temperature (296 K). Distilled water sample was used and the water vapor pressure was measured by a capacitance gauge with 0.12 % accuracy (MKS 627B). Spectra with water vapor pressures in the range of 20-250 Pa were measured. Figure 3(a) illustrates the recorded spectrum with water vapor pressure of 28.4 Pa. The Doppler broadening width (full width at half maximum) is about 0.0365 cm⁻¹, which is dominant at the present experimental conditions. However, as shown in Fig. 3(b), a pure Gaussian function does not fit well the spectrum, even with the Doppler width unfixed. Taking into account a small contribution from the pressure-induced broadening effect, the spectrum can be better reproduced using a Voigt function with the Doppler width fixed at the theoretical value (Fig. 3(c)). In this way, the line parameters are obtained from least-square fitting of the spectrum.

The obtained water line positions and intensities at different sample pressures are shown in Fig. 3(d) and Fig. 3(e), respectively. The line strength can be obtained from a linear fit of the integrated intensities, which gives 9.328×10^{-25} cm molecule⁻¹ with an estimated uncertainty of about 3%. The uncertainty mainly comes from the water sample pressure drift due to water adsorbing on the wall of the sample cell. A linear fit of the positions versus sample pressures yields the frequency at the zero-pressure limit and also the self-broadening pressure-shift coefficient. Using the frequency of the corresponding transmittance peak of the ULE-FPI, the absolute frequency of the H₂¹⁶O line is determined to be 377 101 126.02(30) MHz or 12 578.739 590(10) cm⁻¹, with a relative uncertainty of 0.8×10^{-9} . In the HITRAN database [1], the H₂¹⁶O line is listed as the $J_{KaKc} = 2_{12} \rightarrow 2_{11}$ transition of the $\nu_2 + 3\nu_3$ band, with position $\nu = 12578.7401$ cm⁻¹ and strength $S = 9.520 \times 10^{-25}$ cm molecule⁻¹. Both the line position and line intensity values agree well with our values within the HITRAN data uncertainties ($\Delta\nu \sim 0.0001 - 0.001$ cm⁻¹, $\Delta S/S \sim 5\% - 10\%$). The self-broadened pressure-shift coefficient value determined here is -0.043(5) cm⁻¹/atm. It is not included in HITRAN where only an air-broadened value of -0.01169 cm⁻¹/atm is given for this line.

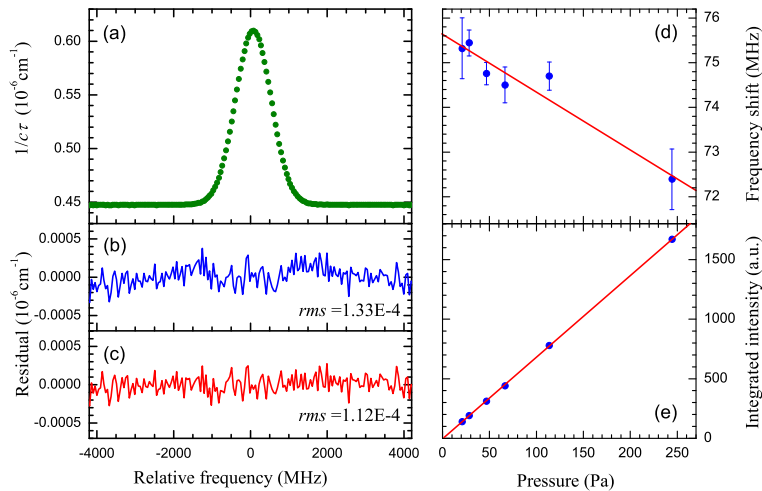


Fig. 3. CRDS spectrum of the H₂¹⁶O line at 12578.74 cm⁻¹. (a) Spectrum recorded with sample pressure 28.4 Pa. (b) Residuals of fitting with a Gaussian function. (c) Residuals of fitting with a Voigt function. (d) Obtained line position shifts relative to an adjacent mode of the ULE-FPI. (e) Integrated line intensities obtained from the fitting.

4. Summary

High-resolution cavity ring-down spectrometer has been built using a continuous-wave widely tunable Ti:Sapphire laser. Longitudinal modes of a thermo-stabilized Fabry-Pérot interferometer with long-term absolute frequency drift less than 0.1 MHz are used for frequency calibration. Taking into account the uncertainty in the determination of the free spectral range of the interferometer, the absolute frequency uncertainty is estimated to be 0.1 – 0.6 MHz in the spectral range of 775-800 nm. Combined with the ultra-high sensitivity, the spectrometer allows us to determine the precise positions of Doppler-broadened absorption lines. From the fitting of the recorded line profiles, the zero-pressure-limit position of the H₂O line at 12578.74 cm⁻¹ is determined to be 377 101 126.02 MHz with an uncertainty of 0.30 MHz, which is only 0.027 % of the Doppler width. The spectrometer can be applied to determine the precise frequencies of weak molecular absorption lines, which can be used for crucial test of high-level quantum chemistry calculations [19], or as secondary frequency standards.

The calibration of the spectrometer can also be accomplished by using femto-second laser combs [8, 16], which will lead to wider spectral coverage, but also much higher cost and experimental complexity. The present approach provides a relatively simple solution with moderate precision and spectral band-width, which is very suitable for the cavity ring-down spectroscopy of Doppler-broadened absorption lines.

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