

Detection of Methane and Ethane by Continuous-Wave Cavity Ring-Down Spectroscopy Near 1.67 μm

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We report the simple detection method of the small hydrocarbons, methane and ethane, by continuous-wave cavity ring-down spectroscopy near 1.67 μm using an external cavity diode laser. The absorption lines of methane between 6002.48 cm^{-1} and 6003.37 cm^{-1} and ethane between 5955.65 cm^{-1} and 5956.4 cm^{-1} have been resolved and employed for the gas detection. The largest absorption cross sections were found to be $6.5 \times 10^{-20} \text{ cm}^2$ and $7.4 \times 10^{-21} \text{ cm}^2$ for methane and ethane, respectively, in each spectral range. The minimum detectable absorption limit of our spectrometer was $4.8 \times 10^{-9} \text{ cm}^{-1} / \sqrt{\text{Hz}}$, which corresponds to the detection limits of 3 ppb/ $\sqrt{\text{Hz}}$ and 27 ppb/ $\sqrt{\text{Hz}}$ for methane and ethane, respectively. The near-IR continuous-wave cavity ring-down spectroscopic detection method of the small hydrocarbons can be applied for medical diagnosis and environmental monitoring as a fast and convenient method.

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I. INTRODUCTION

Since the first demonstration of the high sensitivity of cavity ring-down spectroscopy (CRDS) by O'Keefe and Deacon [1], CRDS has proven its strong potential of various applications such as molecular spectroscopy, atmospheric chemistry, flame and plasma diagnosis, and analytical chemistry [2,3]. Very long effective path length up to tens of kilometers in the optical cavity consisting of a pair of high-reflectivity mirrors, and the immunity to the laser power fluctuations of CRDS provide a ultra-sensitive detection capability. The absorption lines of molecules from visible to infrared (IR) regions have been widely used for molecular spectroscopy and trace gas detection by CRDS. In view of trace gas monitoring, the availabilities of the strong absorption lines and the laser source providing the corresponding wavelengths for the molecules of interest are very important. Most of volatile organic molecules important in various fields (industry, environmental engineering, medical diagnosis, etc.) show strong absorption bands in the mid-IR region around $3 \mu\text{m} \sim 4 \mu\text{m}$ due to the excitation of their fundamental CH, OH, or CO vibrational modes. Recently, several kinds of mid-IR laser sources such as a quantum cascade laser [4,5], a lead-salt diode laser [6,7], and an OPO (optical parametric oscillator) [8-10] have been applied to cavity

ring-down, cavity enhanced absorption, and tunable diode laser absorption spectrometers for trace gas detection. However, these emerging mid-IR lasers have not yet been matured technically and commercially.

Alternatively, the more convenient approach is employing an external cavity diode laser (ECDL) providing the wavelengths in near-IR region. Currently, the commercially available ECDL provides wavelength from visible to near-IR range, tuning range of about 30 GHz without mode hopping, and linewidth of about 300 kHz. This suits ECDL to the laser source of CRDS with high sensitivity and selectivity. In the near-IR region around 1.6 μm , there are absorption bands due to the vibrational overtone or combination transitions of molecules. Usually, the absorption cross section of the overtone transition is weaker than that of the fundamental one by one or two orders of magnitude. This weaker absorption cross section may be the demerit of this near-IR CRDS approach in comparison with mid-IR CRDS. However, the technical improvements in optical alignments and data acquisition methods in continuous-wave cavity ring-down spectroscopy (cw-CRDS) have realized the minimum detectable absorption limit (MDAL) of a few $10^{-12} \text{ cm}^{-1} / \sqrt{\text{Hz}}$, which provides sub-ppb detection sensitivity for the near-IR cw-CRDS [11-15]. Therefore, the near-IR cw-CRDS using ECDL can be applied to various fields as the simple and sensitive gas

detection or monitoring method.

In this work, we report the simple detection method of cw-CRDS using ECDL near 1.67 μm for the small hydrocarbons, methane (CH_4) and ethane (C_2H_6). Environmentally, methane is one of the most serious greenhouse gases remarkably rising in concentration in the atmosphere like carbon dioxide. Also, methane and ethane in human breath gas can be disease or physiological markers for gut bacteria, and breast cancer and lipid peroxidation. Spectroscopic database of methane has been well established [16]. We employed one of the strong absorption lines located at 6002.59 cm^{-1} for the detection of methane. However, the accurate absorption line positions and cross sections of ethane near 1.67 μm have not been reported yet. We have obtained single-pass tunable diode laser absorption spectrum of ethane between 5950 cm^{-1} and 6050 cm^{-1} and the strong absorption line of ethane at 5955.97 cm^{-1} has been used for the detection. The detection sensitivities of our spectrometer are 3 ppb/ $\sqrt{\text{Hz}}$ and 27 ppb/ $\sqrt{\text{Hz}}$ for methane and ethane, respectively, which are mainly limited by the reflectivity of our cavity mirrors (99.89%). To our knowledge, the CRDS detection of ethane in near-IR region is reported for the first time. We have analyzed the signal-to-noise ratio (SNR) and MDAL of our spectrometer in detail and discussed the feasibility of applying this ppb-level detection method of the small hydrocarbons for environmental monitoring and medical diagnosis.

It would be helpful to review the recent research activities in CRDS in the near IR region in more detail. In the last decade, many tens of CRDS researches have been performed to analyze tens of kinds of trace gas molecules for the purpose of applying them to medicine, environment, agriculture, industry, *etc.* Except for several reports [11-13] where sub-ppb level sensitivity was realized for several kinds of gases, most of the sensitivities achieved by CRDS in the near IR region ranges from ppm to ppb level due to the weak absorptions of the molecular overtone vibrational bands. Using trace gas molecules such as CO_2 , NH_3 , and acetone as disease markers for medical diagnosis is the most prominent among the suggested applications. CO_2 is the most popular molecule studied in the near IR region. Since CO_2 has a transition line resonant to the wavelength of Nd:YAG laser at 1064 nm, it was used as an appropriate sample for CRDS researches where pushing the sensitivity toward shot-noise limit was tried and sensitivities as high as $10^{-12} \text{ cm}^{-1}/\sqrt{\text{Hz}}$ level or better were realized [11,12]. The isotope ratio of $^{13}\text{C}/^{12}\text{C}$ in CO_2 was determined by the precision which is enough for monitoring the presence of *Helicobacter pylori* due to the high detection sensitivity realized [14]. Acetone whose average mixing ratio in the human breath gas is around 1 ppm is the candidate for the marker of diabetes. Detection sensitivity of 150 ppb for acetone which is enough for diabetes monitoring was reported realized by cw-CRDS

near 1.67 μm [17].

B. L. Fawcett, *et al.* detected CH_4 with the sensitivity of 52 ppb through CRDS at 1.65 μm and suggested application for the monitoring of tropospheric methane, whose average concentration in the lower troposphere is 1.72 ppm [18]. The MDAL of their spectrometer was $1.5 \times 10^{-8} \text{ cm}^{-1}$. The strongest line used for the methane detection is located in the same overtone band as in our experiment and the maximum absorption cross section in the studied region is almost the same as ours. But this sensitivity seems not enough to monitor the small change in the average methane concentration in atmosphere (15 ppb/year), which will be discussed in the later part of this paper. But, the methane detection sensitivity of our CRD spectrometer is better than that of Fawcett, *et al.*'s by three times and enough for monitoring the small change of the average methane concentration in the atmosphere. Higher sensitivity ($5 \times 10^{-10} \text{ cm}^{-1}$) CRDS was performed to measure the CH_4 spectrum in the 1.55 μm transparency window for the purpose of astrophysical application by A. W. Liu *et al.* [19]. However, the largest absorption cross section in the band is smaller than that of the band in our experiment by 3 orders of magnitude so that the spectrum by Liu *et al.* is not appropriate for trace methane analysis.

II. DESIGN AND CHARACTERIZATION

The design of our cavity ring-down spectrometer is shown schematically in Fig. 1. ECDL (New-Focus Velocity 6300, tuning range = 1650 nm (1680 nm, maximum power ~ 3 mW) was used as a light source. Using a ramp signal from a function generator as an input to the piezoelectric translator (PZT) in the laser oscillator, the laser frequency can be tuned without mode hopping within 30 GHz. An optical isolator was located in front of the laser to keep the back reflected light from disturbing the laser. To switch off the laser input to the ring-down cavity rapidly, we used an acousto-optic modulator (AOM). Using a pair of lenses, the 1st-order-deflected laser beam was made match the TEM_{00} mode of the cavity optimally. The lenses of the mode matching package were carefully selected and positioned to make the beam waist and the Rayleigh range of the laser beam closest to those of a TEM_{00} mode of the cavity. A pair of high-reflectivity mirrors (reflectivity = 99.89%, radius of curvature = 2 m) were used for the ring-down cavity. The length of the cavity was 1 m. One of the mirrors was stuck to a ring-type PZT fixed to a kinematic mirror mount so that we could change the cavity length, which results in the movement of a cavity mode over one free spectral range. The CRDS cell was pumped out by a rotary pump (base pressure 10 m Torr) and filled with methane (Deokyang gas, ltd., 99.995%) or ethane (Intergas, ltd., 99.995%) gas. The

ring-down signal from the CRDS cell was collected by a lens and detected by a 125 MHz InGaAs photo-receiver (New-Focus 1811, gain 4×10^4 V/W at 1600 nm). The signal detected by the photo-receiver triggers a delay pulse generator (SRS DG535) and subsequently the delay pulse generator triggers the AOM and a digitizer (100 MHz, 14 bit). The acquired signal is fitted to an exponential function by Levenberg-Marquardt (L-M) algorithm to obtain the ring-down time, τ [20]. 40 single-shot τ 's were averaged and converted to the absorption coefficient of the medium in the cavity, a , using the following equation.

$$\tau = \frac{1}{(1-R) + ad + \gamma_{\text{scatt}}} \frac{L}{c} \quad (1)$$

R is the reflectivity of the mirrors, d is the length of the medium, γ_{scatt} is the scattering loss ratio from the mirror surfaces, L is the cavity length, and c is the speed of light in the cavity.

For wavelength calibration, we developed a Fabry-Perot etalon consisting of a pair of concave mirrors (reflectivity = 95% at 1650 to 1680 nm, radius of curvature = 30 cm, the frame made of invar) and a methane absorption cell (methane pressure = 50 Torr, length = 30 cm). The temperature of the Fabry-Perot étalon was stabilized within several mK. Therefore, the change of the free spectral range of the Fabry-Perot étalon due to thermal expansion is as small as several Hz. We sealed the Fabry-Perot etalon so that the refractive index of air within the étalon remained constant during the experiment. By using two absorption lines of methane, we determined that the length of the étalon is 29.96 (± 0.06) cm, and the free spectral range is 250.3 (± 0.5) MHz. The error (1σ) of the calibrated laser frequency is 60 MHz. The standard deviation of the laser frequency calibrated by polynomial fittings

with respect to the resonances of the Fabry-Perot étalon is 20 MHz and the error of the free spectral range of the Fabry-Perot étalon is 0.2%.

Fig. 2 (a) is the transmission signal of the ring-down cavity. The horizontal axis is time and its whole span represents the sweep of the cavity mode over one free spectral range. AOM switching was not performed during the measurement. As shown in Fig. 2 (a), only the TEM₀₀ mode was effectively excited in our experiment. Fig. 2 (b) shows the ring-down signal measured in a vacuum cavity. The single exponential curve fitted to the signal is also shown in the figure. From this, we can find the experimental data fits to a single exponential function very well. The ring-down time in the vacuum cavity, τ_0 is 2.9998 (± 0.0059) μs . The reflectivity of our CRDS mirrors determined from τ_0 is 99.89%. The scattering loss by the mirror surface was neglected.

Fig. 3 compares the absorption spectrum of methane measured by CRDS and the simulated spectrum based

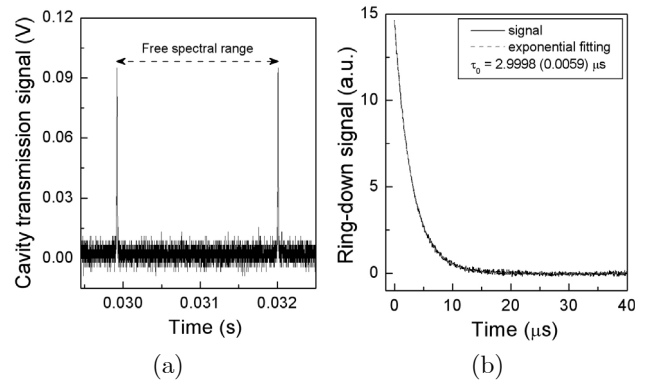


FIG. 2. (a) Measured transmission through the ring-down cavity for a continuous wave laser during the sweep of the cavity length over one free spectral range. (b) The signal of a ring-down event measured after switching off the input laser (black line) and an exponential line fitted to the experimental data (gray dashed line).

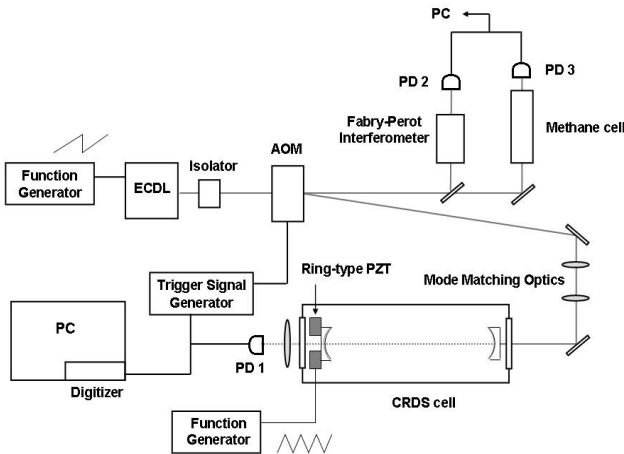


FIG. 1. Experimental setup of the cw-CRDS. ECDL: external cavity diode laser, AOM: acousto-optic modulator, PD: photo-diode.

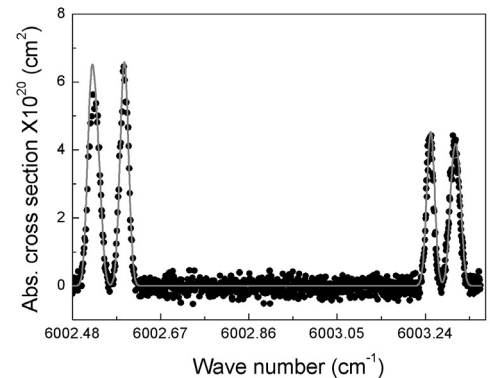


FIG. 3. Absorption spectrum of methane. Filled circles are experimental data, and the gray line is the reference spectrum calculated from HITRAN database [16].

on HITRAN database [16]. The pressure of methane in the CRDS cell was 2.3 mTorr. The absorption line located at 6002.59 cm^{-1} , which consists of three lines in the Q(6) of the $\text{CH}_4\ 2\nu_3$ band, has the strongest transition in the tuning range of our diode laser. When air pressure is lower than 0.1 Torr as in this case, collisional line broadening is smaller than 1 MHz ($\Delta\nu_{\text{coll.,methane}} = 1120\text{ MHz}$ at 150 Torr according to our measurement) [21]. Therefore, the linewidths of the transition lines are mainly due to the Doppler broadening, the value of which is 553 MHz at 300 K. The measured absorption cross section at 6002.59 cm^{-1} is $6.5 \times 10^{-20}\text{ cm}^2$ and the calculated value based on HITRAN database is $6.6 \times 10^{-20}\text{ cm}^2$. The discrepancy is about 2%, which is smaller than our experimental error, 6%. The main error sources of our experiment were the pressure error (3%) and the error in the absorption coefficient calculated from the finite SNR of the CRDS spectrum (5%).

Fig. 4 shows the absorption spectrum of ethane measured by CRDS between 5955.65 cm^{-1} and 5956.40 cm^{-1} and that measured by single-pass diode laser absorption spectroscopy between 5950 cm^{-1} and 6050 cm^{-1} (see the inset of Fig. 4). Rotationally-resolved spectrum of ethane near $1.67\ \mu\text{m}$ has not been reported yet. Previously, Smith reported the IR spectrum of ethane between $1.6\ \mu\text{m}$ and $13\ \mu\text{m}$ by absorption spectroscopy in the 133-mm long cell [22]. The spectrum between 5700 cm^{-1} and 6000 cm^{-1} reported in his work shows the partially-resolved sub-band progression in the spectral region corresponding to our observation. The cell temperature and pressure were 1400 mmHg and 25.5°C , respectively, and the 7200 -lines/inch grating was used for recording the spectrum. He tentatively assigned the observed progression to the combination band of the perpendicular type, of which the band origin is located at 5950.7 cm^{-1} . The absorption lines recorded in our

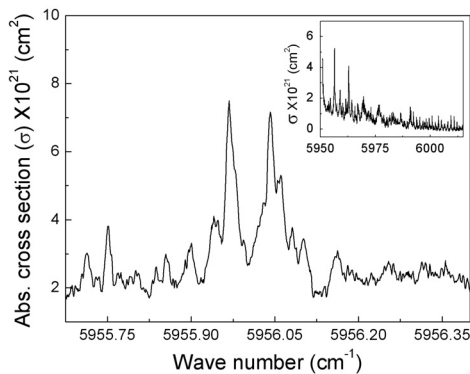


FIG. 4. High resolution spectrum of ethane. The inset figure shows the spectrum of ethane between 5950.96 and 6060.6 cm^{-1} measured by conventional absorption spectroscopy where the laser wavelength was roughly scanned and 50 Torr of ethane was filled in a cell of 1-m length.

single-pass diode laser absorption spectrum correspond to the ^RQ branch of the combination band. The pressure of ethane in our CRDS cell was 25 mTorr. For the strongest absorption line at 5955.97 cm^{-1} recorded in the single-pass diode laser absorption spectrum, the absorption cross section was determined to be $7.4 \times 10^{-21}\text{ cm}^2$ by CRDS.

The linearity of our CRDS spectrometer (absorption coefficient vs. gas pressure) is shown in Fig. 5. We measured the absorption coefficients of methane at 6002.59 cm^{-1} (1-30 mTorr) and ethane at 5955.97 cm^{-1} (1-150 mTorr) for various pressures. The absorption coefficients of methane and ethane were found to be proportional to the gas pressure (see Fig. 5 (a) and (b) for methane and ethane, respectively) within our experimental errors.

The MDAL of CRDS is expressed as the following equation [3].

$$\alpha_{\text{min}} = \left(\frac{\sigma_{\tau}}{\tau_0} \right) \cdot \frac{L}{c\tau_0 d} \cdot \sqrt{\frac{2}{N}} = \left(\frac{\sigma_{\tau}}{\tau_0} \right)_{\text{avg.}} \cdot \frac{1}{l_{\text{eff}}} \cdot \frac{L}{d} \quad (2)$$

Where, σ_{τ} is the standard deviation of single-shot τ , l_{eff} is the effective length of a medium, and N is the averaged number of data (single-shot τ). The factor of $\sqrt{2}\sigma\tau$ was introduced reflecting that the minimum noticeable change of the ring-down time is $\sqrt{2}\sigma$ rather than σ_{τ} . From Eq. (2), the detection sensitivity of CRDS becomes better as d (or L) is longer, the mirror reflectivity is higher, N is larger, and (σ_{τ}/τ_0) is smaller. In our experiment, τ_0 is $2.9998 (\pm 0.0059)\ \mu\text{s}$ and d (or L) is 1 m. The number of averaged single-shot τ per second, N was 40. The value of $(\sigma_{\tau}/\tau_0)_{\text{avg.}}$ determined from the background noise in a CRDS scan with 40-fold average for each data point is 4.4×10^{-4} . The resultant MDAL of our spectrometer was $4.8 \times 10^{-9}\text{ cm}^{-1}/\sqrt{\text{Hz}}$. From the MDAL of our spectrometer and the measured absorption cross sections, we could estimate the detection limit of methane and ethane.

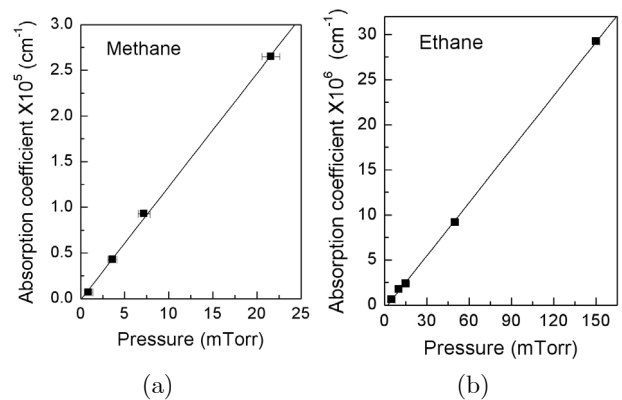


FIG. 5. Absorption values of methane (a) and ethane (b) for various gas pressures. The lines of (a) and (b) are linear functions fitted to the experimental data.

TABLE 1. Absorption line positions and cross sections of methane and ethane we measured and used for the gas detection, and the corresponding detection limits.

	Line position (cm ⁻¹)	Cross section (cm ²)	Detection limit (ppb/ $\sqrt{\text{Hz}}$)
Methane	6002.59	6.5×10^{-20}	3
Ethane	5955.97	7.4×10^{-21}	27

The detection limit of methane and ethane using our near-IR cw-CRDS spectrometer was 3 and 27 ppb/ $\sqrt{\text{Hz}}$, respectively. The performance of our spectrometer is summarized in Table 1.

While, the quantum or shot-noise limit of MDAL in CRDS is [12,20]

$$\alpha_{\min} = \frac{\sqrt{2} \left(\frac{\sigma_{\tau}}{\tau} \right)}{l_{\text{eff}}} = \frac{\sqrt{2}}{l_{\text{eff}}} \sqrt{\frac{e}{P_0 \mathfrak{R} \tau_0}} \quad (3)$$

Where, P_0 is the initial power of the ring-down signal, \mathfrak{R} is the photodetector responsivity (A/W), and e is the electron charge. Eq. (3) means that (σ_{τ}/τ) of the ring-down signal corresponds to the SNR of the continuous wave laser of P_0 with the detection bandwidth, $1/\tau_0$. From Eq. (3) and the parameters of our spectrometer, the MDAL from shot noise with 40-fold average is 2.4×10^{-10} cm⁻¹/ $\sqrt{\text{Hz}}$. The MDAL of our spectrometer is larger than the shot-noise limit by the factor of 20. Most of the extra noise is attributed to instruments such as photodetector, etc.. The experimental SNR of the ring-down signal is about 150:1 (see Fig. 2 (b)), which is about 13 times smaller than the signal to shot-noise ratio, 2000:1 for the given bandwidth, 30 MHz (the digitizer acquisition rate set in the experiment). The relatively large noise is mainly due to the amplifier voltage noise of the photodetector. Some part of the observed ring-down time fluctuation is thought to come from the non-weighted L-M fit algorithm used. According to D. Romanini, *et al.*, (σ_{τ}/τ) has the minimum value as in Eq. (3) when the L-M fit is weighted with the inverse square of the shot noise. The minimum value of (σ_{τ}/τ) obtainable with the non-weighted L-M method is known to be larger than that with the weighted algorithm by the factor of about 2 [19].

Compared with other methods of trace analysis, CRDS provides unprecedented sensitivity as well as speed. The simple detection method of near-IR cw-CRDS using ECDL with ppb-level sensitivity for small hydrocarbons, methane and ethane, can be applied for environmental monitoring and medical diagnosis. Methane is one of the major greenhouse gases (18% of total man-made green house gases [23]). During last two decades, the average concentration of methane in atmosphere has increased from 1.65 ppm to 1.77 ppm with the rate up to 15 ppb/year [24]. It has been found that several hundred kinds of

molecules exist in human exhaled breath [25-26]. Among them, several kinds of molecules have been found to be related to specific disease or physiological process of humans [25-26], and thus they can be employed as special markers in medical diagnoses. The general concentration of the human breath gases ranges from percent to ppb levels. Methane related with gut bacteria [25-26] is known to be included in human breath gas in the range between 2 ppm and 10 ppm, and ethane which can be used as a marker for breast cancer or lipid peroxidation is known to exist up to 10 ppb [25-26]. Therefore, our near-IR cw-CRDS spectrometer providing the ppb-level noise-equivalent sensitivity (during 1-s measurement interval) for methane and ethane can be applied for these environmental monitoring and medical diagnoses in a fast and convenient way. The current detection sensitivity of methane in our CRD spectrometer is enough for the proposed applications. But, higher sensitivity is needed for ethane for a medical application. Using mirrors of reflectivity higher than 99.99%, reducing the noise of the ring-down signal by a low noise photo-receiver, and enlarging the data-acquisition-and-analysis rate up to 1000 Hz, the sensitivity of our spectrometer can be improved enough for medical diagnosis using ethane.

III. CONCLUSION

In conclusion, we demonstrated the simple detection method of near-IR cw-CRDS for the small hydrocarbons, methane and ethane near 1.67 μm . The high sensitivity of our CRD spectrometer enabled us to measure very weak absorption lines of methane and ethane in low enough pressures to avoid collisional broadening. The analytical feasibility of our spectrometer was proven from the comparison of the measured spectrum of methane with the simulated spectrum based on HITRAN database and from the proportional relation between the measured gas pressure and absorption. The largest absorption cross sections were found to be 6.6×10^{-20} cm² and 7.4×10^{-21} cm² for methane and ethane, respectively. The MDAL of our CRD spectrometer was 4.8×10^{-9} cm⁻¹/ $\sqrt{\text{Hz}}$, which corresponds to the detection limit of 3 ppb/ $\sqrt{\text{Hz}}$ for methane and 27 ppb/ $\sqrt{\text{Hz}}$ for ethane, respectively. Finally, we proposed the applications of our spectrometer in environmental monitoring and medical diagnosis.

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