

Cavity enhanced absorption spectroscopy of carbon dioxide using a DFB diode laser and a swept optical cavity

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A compact DFB tunable diode laser operating around 1.572 μm was used to study the cavity enhanced absorption spectroscopy of carbon dioxide near 1.572 μm . It was experimentally demonstrated that a narrow-band continuous wave laser could be used in combination with a high-finesse optically stable cavity to perform highly sensitive direct absorption spectroscopy using ideas from the field of cavity ring down spectroscopy in a simple experimental setup. Laser radiation was coupled into optical cavity via accidental coincidences of laser frequency with one of multitude modes of the cavity. Absorption spectrum of carbon dioxide was obtained, the absorption signals were extracted from the measurement recording only the highest light intensity that leaked out of the optical cavity. A wavemeter was used to record accurate frequency of the laser. An absorption sensitivity of about $3.39 \times 10^{-7} \text{ cm}^{-1}$ has been achieved.

Keywords: spectroscopy, cavity enhanced absorption spectroscopy (CEAS), carbon dioxide.

1. Introduction

Cavity ring down spectroscopy (CRDS) is a sensitive absorption technique for obtaining quantitative spectra of trace species [1]. A number of different forms of the technique have been developed [1]–[4], and it has been implemented using both pulsed and continuous wave laser sources. In general, the cw-CRDS method involves the build up of light in the optical cavity when the laser and cavity are in resonance. When the intracavity intensity reaches a threshold that is preestablished, the laser is rapidly switched off and the ringdown time of the light exiting the cavity is measured.

Recently, a new method of using an unstabilized cavity and recording the intensity of the light that leaks out of the optical cavity rather than the cavity ring down time has been developed. In this method, the laser radiation from the scanning laser is coupled into the optical cavity via accidental coincidences of the laser frequency with one of the multitude modes of the optical cavity. The laser and/or the cavity are scanned rapidly and the absorption signal is extracted from a measurement of the light intensity that leaks out of the cavity. This approach was developed almost simultaneously by

ENGELN *et al.* [5] in their cavity enhanced absorption spectroscopy (CEAS), and by O'KEEFE *et al.* [6] in their integrated cavity output spectroscopy (ICOS). These methods have the advantage of continuous data acquisition, and of operating without any expensive acousto-optic cell or any electro-optic modulation system, which makes the experimental setup simpler.

In CEAS, the laser frequency is not locked to the frequency of the optical cavity eigenmode. The cavity geometry is chosen such that the cavity mode is very dense. During the measurement, the laser and/or the cavity length are scanned, resulting in a quasi-continuous coupling of light into the optical cavity [5]. If the laser can be scanned repeatedly over a certain wavelength interval, a raw cavity enhanced absorption spectrum can be obtained very rapidly by summing several scans [5]. This feature offers flexibility in optimizing the experimental conditions in real time.

In this paper, we adopt an analogous method which is like CEAS developed by ENGELN *et al.* [5] and CHEUNG *et al.* [7]. We describe the implementation of CEAS to obtain absorption spectra of carbon dioxide using a cw tunable DFB diode laser near 1.572 μm . Our eventual aim is to use this CEAS system to detect OH radical near 1.51 μm , but for simplicity we conducted experiments using carbon dioxide. We demonstrated that with a relatively fast rate of scanning the cavity and low rate of scanning the diode laser, it is possible to obtain a CEAS of carbon dioxide at low pressure with high signal to noise ratio.

2. Theory

The technique of CEAS involves scanning the laser frequency repeatedly over the same spectral range or/and scanning the optical cavity length to build up a low-noise spectrum. Light is coupled into the optical cavity whenever resonance occurs between the laser frequency and a cavity mode. Aligning the cavity allows only TEM₀₀ mode of the cavity to be excited, contributing to a smoother baseline upon which absorption can be observed. An example of a progressively sparse cavity-mode structure as the cavity is aligned is shown in Fig. 1.

For a high finesse optical cavity, the laser intensity that transmits the optical cavity can be expressed as follows [8]:

$$I_T(t) \propto \int_0^{\infty} I(\nu) \exp\left(-\frac{t}{\tau(\nu)}\right) d\nu \quad (1)$$

Here, $\tau(\nu)$ is the optical cavity ring down time, and is given by:

$$\tau(\nu) = \frac{L}{c \left[\left| \ln(R(\nu)) \right| + \sum_i \sigma_i(\nu) \int_0^L N_i(x) dx \right]} \quad (2)$$

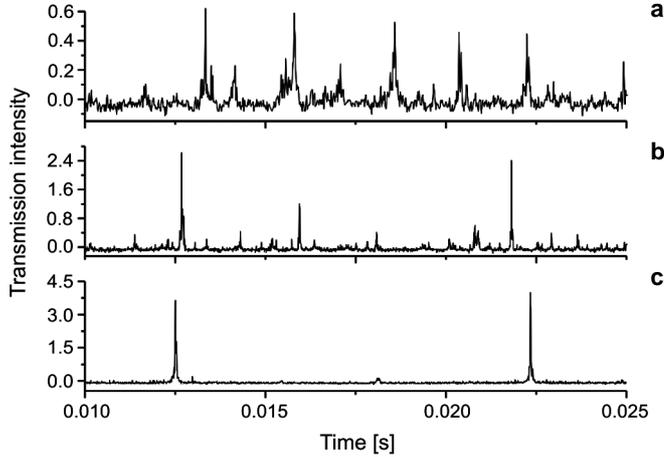


Fig. 1. Mode structure of a progressively aligned optical cavity (a)–(c), excited with a DFB diode laser source. With an aligned cavity the mode structure becomes far sparser as only TEM_{00} mode is excited in the cavity.

where c is the light speed, the sum $\left| \ln(R(\nu)) \right| + \sum_i \sigma_i(\nu) \int_0^L N_i(x) dx$ is over all light scattering and absorbing species with frequency dependent cross-sections $\sigma_i(\nu)$ and a line-integrated number density $\int_0^L N_i(x) dx$. The product of the frequency-dependent absorption cross-section with the number density $N_i(x)$ is commonly expressed as the absorption coefficient $\alpha(\nu)$. We use an effective loss coefficient $|\ln(R_{\text{eff}})|$ to express the optical cavity loss, and it does not include the absorption of the medium in the optical cavity. Compared with the optical cavity loss, the scatter loss can be neglected if the spectrum range is very narrow, so the effective loss coefficient $|\ln(R_{\text{eff}})|$ can be simplified as $|\ln(R)|$. Thus, the optical cavity ring down time $\tau(\nu)$ can be expressed as:

$$\tau(\nu) = \frac{L}{c \left[\left| \ln(R(\nu)) \right| + \alpha(\nu)L \right]}. \quad (3)$$

Commonly, in CEAS the mirror reflectivity is higher than 99%, *i.e.*, $R > 0.99 \approx 1$, so $|\ln(R)| \approx (1 - R)$. If the medium in the optical cavity is homogeneous, Eq. (3) can be written as:

$$\tau(\nu) = \frac{L}{c \left[(1 - R) + \alpha(\nu)L \right]}. \quad (4)$$

Equation (4) indicates that the cavity ring down time $\tau(\nu)$ is just determined by the cavity length L and the cavity mirror reflectivity R , as well as the absorption

coefficient $\alpha(\nu)$ of the medium in the cavity. When the cavity is empty, *i.e.*, $\alpha(\nu)L = 0$, Eq. (4) can be expressed as:

$$\tau_0(\nu) = \frac{L}{c(1-R)}. \quad (5)$$

In cavity enhanced absorption spectroscopy, we consider that the effective absorption path is the product of empty cavity ring down time $\tau(\nu)$ and the light speed c , so the effective absorption path in CEAS can be expressed as:

$$L_{eq} = \frac{1}{1-R} L. \quad (6)$$

Compared with the conversational absorption spectroscopy, the absorption path in CEAS is enhanced by a factor of $1/(1-R)$. Since the reflectivity of mirrors in CEAS is very high, $1/(1-R)$ has a very large value and the actual absorption path is very long, so CEAS can achieve a very great sensitivity.

3. Experiment

The experimental scheme of CEAS has been discussed by various researchers [5], [7], [9]–[11]; here we only give a very brief description of our experimental setup and conditions.

Our CEAS experimental apparatus is shown in Fig. 2. The laser radiation was coupled into a high finesse optical cavity formed by two plano-concave mirrors with a diameter of 35 mm and a radius of curvature of -1 m and reflectivity of $R \approx 0.994$ (near $1.573 \mu\text{m}$). Absorption measurements were made using a single mode, tunable DFB diode laser as the injection light source. The diode laser was tuned continuously in the region of 6358.4 and 6358.8 cm^{-1} with a 40 mW maximum power and a line width of less than 30 MHz. Absorption measurements were made in a closed-cell that could be evacuated and filled with controlled pressures of various gases. The cavity length was about 34 cm which results in cavity free spectral being about 477 MHz.

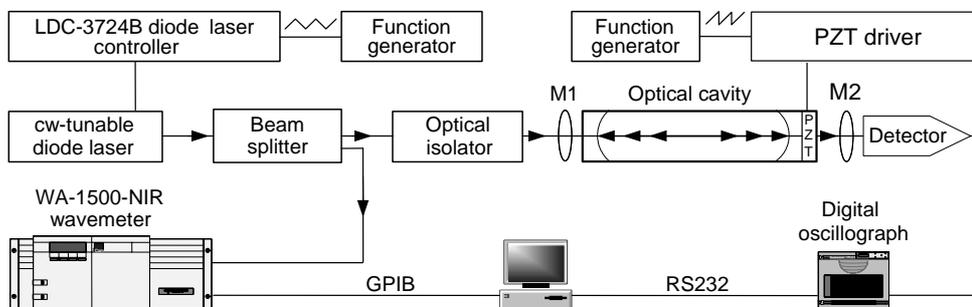


Fig. 2. Schematic diagram of CEAS experimental configuration.

A piezoelectric translator (PZT) was fixed to the end mirror to modulate the cavity length. A Faraday isolator was placed in the beam directly in front of the laser source to minimize the optical feedback from the cavity back to the laser. The laser frequency was scanned with a voltage from a function generator at a slow rate (about 200 s/cm). Another function generator was used to provide a voltage to the PZT controller to sweep the cavity at a rate of about 40 Hz. No care was required to stabilize the cavity or the experimental table upon which the cavity was placed. An InGaAs detector (New Focus, Inc., Model 2011) was used to detect the light exiting the end mirror. The detected signal was amplified and displayed on a digital oscilloscope (Tektronix, TDS3054). We used the method of recording the highest light intensity signal that leak out the optical cavity when scanning the laser. The data from the oscilloscope were transferred via an RS232 interface to a computer for further processing. The laser frequency was measured directly by a wavemeter (EXFO Burleigh Products Group, WA-1500-NIR) with an accuracy of about ± 0.2 ppm (± 0.0002 nm at 1000 nm).

4. Results and discussion

A spectrum of carbon dioxide in the region near $1.572 \mu\text{m}$ was measured, and then used to characterize the performance of the CEAS technique. Figure 3 shows the CEAS of a carbon dioxide centred at 6358.654 cm^{-1} , for 1300 Pa of carbon dioxide.

The line displayed in Fig. 3 is the P21 line of carbon dioxide near 6358.654 cm^{-1} . The position and absorption intensity of this line are listed in the HITRAN2003 Database as follows: $6358.6549 \text{ cm}^{-1}$; $1.816 \times 10^{-28} \text{ cm}^{-1}/(\text{molecule} \cdot \text{cm}^{-2})$. The line position obtained from our spectrum using the wavemeter readings is $6358.6538 \text{ cm}^{-1}$; the results of measurements compare extremely well with those listed in the HITRAN2003 database. The excellent agreement between our values and those in

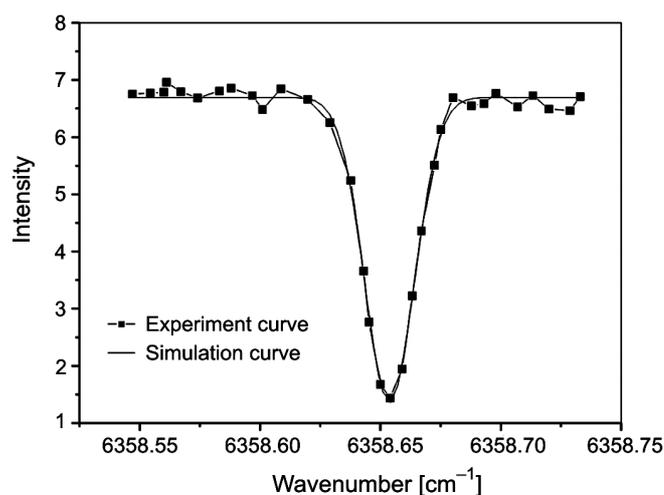


Fig. 3. CEAS of CO_2 near 6358.65 cm^{-1} at a pressure of 1300 Pa.

the database indicates that the spectrum obtained is of high quality and also high resolution. The full width at half maximum (FWHM) of the line is 0.0204 cm^{-1} ; this absorption linewidth is determined by both pressure broadening and Doppler broadening at room temperature. The result of a simulation using a Voigt profile is given in Fig. 3.

We have also examined the pressure dependence of the absorption spectrum. Figure 4 shows the same line recorded at pressures of 9.75, 8.25 and 7.5 mmHg. The intensity observed is directly proportional to the pressure of CO_2 in the cavity, which indicates that the technique is quantitative.

In order to estimate the sensitivity of our CEAS experiment, we measured the carbon dioxide absorption spectrum near 6358.65 cm^{-1} with the pressure of 33.3 Pa,

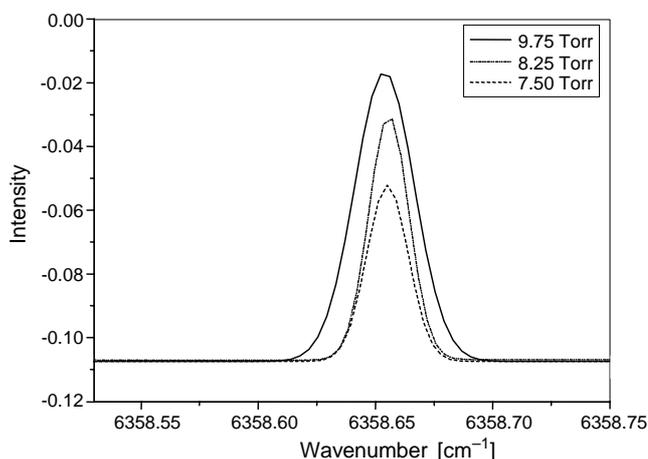


Fig. 4. Cavity enhanced absorption spectrum of carbon dioxide obtained at different pressures.

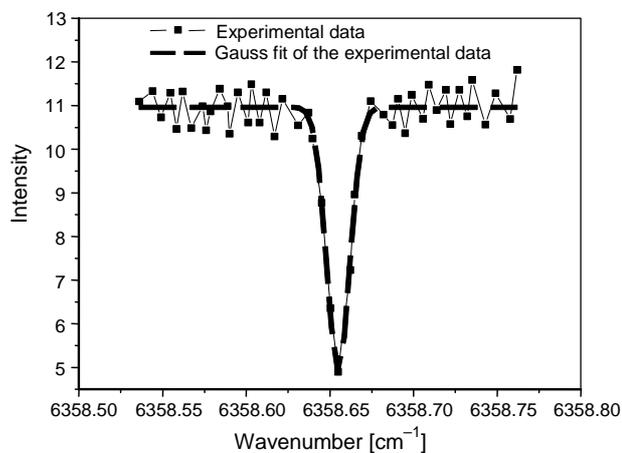


Fig. 5. Cavity enhanced absorption spectrum of CO_2 at the pressure of 33.3 Pa.

see Fig. 5. The line has an S/N ratio of about 5. The line listed in the Hitran2003 database has an absorption intensity of $1.816 \times 10^{-23} \text{ cm}^{-1}/(\text{molecule} \cdot \text{cm}^{-2})$. We performed a least squares fit to the line shape using a Gaussian function and obtained a line width of 0.0125 cm^{-1} . The absorption cross-section of this line is then worked out to be $1.5348 \times 10^{-22} \text{ cm}^2$, so the detection sensitivity expressed as carbon dioxide concentration for an signal to noise ratio of 1 reduces to $2.21 \times 10^{15} \text{ molecules} \cdot \text{cm}^{-3}$ and the absorption sensitivity is determined to be about $3.39 \times 10^{-7} \text{ cm}^{-1}$.

5. Conclusions

In this work, we have achieved the sensitivity of $3.39 \times 10^{-7} \text{ cm}^{-1}$ by CEAS technique using an unstabilized optical cavity which consists of two high reflectivity ($R \approx 0.994$ near $1.572 \mu\text{m}$) mirrors. We expect that this detection limit can be improved substantially if higher reflectivity mirrors are used. The advantages of the CEAS approach described here are in the system simplicity and ease of application, and the high sensitivity. We are currently working on this aspect of the technique for applications in quantitative OH radical analysis.

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