Cavity enhanced absorption spectroscopy for N$_2$O detection at 2.86 μm using a continuous tunable color center laser

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The cavity enhanced absorption technique is applied to N$_2$O detection around 2.86 μm using a continuous-wave color center laser. A high-finesse triangular ring cavity is used in this technology. Transmission through the cavity is obtained by jittering the cavity-length with a piezo on one of the cavity mirrors. A minimum detectable absorption coefficient of 2×10^{-6} cm^{-1} is achieved with a mirror reflectivity of 99.24%, corresponding to a N$_2$O detection limit of 600 parts per billion.

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Now there is a great deal of absorption spectroscopy techniques available to determine the concentration of gas molecules. Among these techniques, photoacoustic (PA) spectroscopy has been proved to be one of the most sensitive methods for trace gas detection[1]. As the acoustic signal is directly proportional to the input radiation intensity, high power laser source is needed for high sensitive measurement.

The trace gas detection technique that does not depend on the laser power is pulsed or cw cavity ring down (CRD) spectroscopy[2−4]. In CRD spectroscopy, the ring down time of the CRD cavity is measured, which is related to the total absorption losses. Pulsed lasers are normally very expensive and bulky, and cw-CRD requires a more sophisticated setup and is more sensitive to the environmental vibration than PA spectroscopy. So the pulsed and cw CRD are less suitable for trace gas detection.

Recently, a CRD related technology, called cavity enhanced absorption (CEA) spectroscopy has gained much attention[5−12]. Just like CRD, this technique does not depend on the laser power, and does not require a very sophisticated setup either. The minimum detectable absorption coefficients with CEA are typically around 10^{-8} cm^{-1}Hz$^{-1/2}$[8]. Although it is lower than that gained with CRD, CEA technique is still an alternative method for some applications.

As a versatile and sensitive tool for spectroscopic studies, the CEA technique has been applied to high-resolution absorption measurements with many kinds of lasers. For examples, a ring dye laser operating around 628 nm was used to study the γ-band of molecular oxygen[5]; diode lasers working at 1.5 μm were able to detect ammonia[7,8]; a CO$_2$ laser at 10.6 μm was utilized to detect ethylene[11], and lately a quantum cascade laser operating around 5.2 μm measured NO emissions from the human body[12].

In this paper, a color center laser based CEA spectroscopy around 2.86 μm is applied to the measurement of N$_2$O gas, which is known as an important greenhouse gas. In the experiment, a newly designed high-finesse tri-angular ring cavity sealed in absorption cell is used and a fine spectrum of N$_2$O gas is obtained.

The technique mainly utilizes a high-Q optical cavity in combination with a cw-laser. The light is coupled into the cavity by accidental coincidence with one of the cavity modes. Transmission of light from the cavity is time integrated and inversely proportional to the total cavity loss[4,5].

In CEA spectroscopy, the optical cavity is designed in a non-confocal way and a quasi-continuum of cavity modes is created[5]. In this way the light can be coupled into the cavity efficiently. The CEA spectroscopy depends on the scanning properties of the laser. When the laser frequency could be changed rapidly in time, one can scan the laser frequency at a high repetition rate in a certain frequency range. This is a method that is commonly used for diode lasers[7−10]. Alternatively, in the case that the laser is not allowed to be rapidly tuned, the coincidence between the laser mode and the cavity mode also could be realized by quickly scanning one of the cavity mirrors with a piezo. This method was only used with a line tunable CO$_2$ laser[11]. Here we implement this method with a color center laser that has a slow and continuous tuning rate (70 MHz/s).

The absorption of light through a molecular gas gives the following wavelength depending Ref. [13].

$$\int \kappa(\nu)\mathrm{d}\nu = \int \sigma g(\nu, \nu_0)N_{\mathrm{L}}P\mathrm{d}\nu = \sigma N_{\mathrm{L}}P, \qquad (1)$$

where $\kappa(\nu)$ is the gas absorption coefficient (in cm^{-1}), σ the molecular line intensity (cm^2 cm^{-1}/molecule), $g(\nu, \nu_0)$ the normalized line shape function (in cm), ν_0 the frequency at the line center (in cm^{-1}), N_{L} the Loschmidts number ($N_{\mathrm{L}} = 2.479 \times 10^{19}$ molecules cm^{-3} atm^{-1}), and P the partial pressure of the gas (in atm). In CEA spectroscopy, the absorption coefficient $\kappa(\nu)$ can be extracted from a measurement of the time-integrated intensity using[4]

$$S_0(\nu)/S(\nu) - 1 = \kappa(\nu)L/(1 - R), \qquad (2)$$

where $S(\nu)$ is experimentally determined, time integrated

absorption signal including sample absorption, $S_0(\nu)$ the same signal without absorption (i.e. base line), R the cavity total mirror reflectivity, and L the cavity length. The reflectivity is wavelength dependent, but for scans over a small frequency region we can approximate the reflectivity to be constant. Using Eq. (2) and assuming R to be constant, integration over the line profile gives

$$\int (S_0(\nu)/S(\nu) - 1)\mathrm{d}\nu = \sigma N_\mathrm{L} PaL/(1 - R). \qquad (3)$$

With the known mirror reflectivity R and gas absorption coefficient, the absorber concentration could be deduced using Eq. (3). Alternatively, the mirror R could also be determined with a known gas absorber concentration.

Figure 1 shows the experimental setup. A cw Burleigh FCL-20 color center laser operating with a Li:RbCl crystal allows continuous wavelength tuning over $2.65 - 3.35$ μm region with a laser linewidth of 2 MHz. The FCL was pumped by broadband red light from a standing wave linear dye laser (Spectra Physics 375B), which was pumped by an Ar^+ laser (Spectra Physics 2016-05B). Synchronous computer controlled tracking of the grating, the intra cavity etalon (ICE) and the cavity length of the laser results in continuous single mode tuning.

A low voltage 1-kHz jitter is applied to the ICE yielding a modulation depth of about 30 MHz, which is used to keep the laser single mode operating using a feedback loop. A wavemeter (Burleigh WA1000IR) and 8-GHz etalon were used to monitor the wavelength and to check for single-mode operation of the laser. The scan speed of the laser is 70 MHz/s and is limited by the speed of the feedback control loop.

Our high finesse CEA cavity, working as the absorption cavity, has a triangular ring cavity design to avoid feedback of laser light into the FCL system (Fig. 1)[14]. The two high reflecting flat mirrors ($R > 0.99$, Laser Optik, Garbsen, Germany) are separated 4 cm apart; the third mirror is curved (radius of curvature 2 m, $R > 0.99$, Laser Optik, Garbsen, Germany) and is located at a distance of 48 cm from the two flat mirrors, thus creating a round trip length of 1 m. The cavity is optimized to have as much cavity modes as possible and is modulated using a piezo controller attached on the curved mirror. The light escaping from the cavity towards a pyro-electric

photo detector was chopped and measured with a lock-in amplifier. A 40-Hz repetition rate for the piezo was found to give the strongest CEA signal. An integration time of 1 s was used for the lock-in to achieve the best signal-to-noise ratio (SNR) without loosing spectral resolution due to the laser scan speed.

During experiment, the CEA cavity is sealed and kept in a constant pressure. The gas is filled into the cavity through an inlet tube of the cell. The outlet tube is connected with a pump to control the pressure in the cell. In the experiment, the pressure is kept at 10 kPa.

A cavity-enhanced absorption spectrum around the 2.86 μm wavelength region of a 60 parts per million N_2O in nitrogen gas at 10-kPa pressure is shown in Fig. 2(a). For this scan we achieved a SNR of 33 over a 1 s integration time of the lock-in amplifier at peak I. The SNR is got via the division of the peak value and the signal jitter amplitude at the peak. The laser was scanned with 70 MHz/s over a frequency range of 54 GHz. Figure 2(b) shows the simulated molecular spectrum, using data from the Hitran database[15].

For a given gas concentration, the absorption peak ratio of peak I and II (see Fig. 2) is $\int(S_0(\nu_0)/S(\nu_0) - 1)_\mathrm{I}\mathrm{d}\nu/\int(S_0(\nu_0)/S(\nu_0) - 1)_\mathrm{II}\mathrm{d}\nu = 19.4$. This is comparable to the absorption strengths ratio $\sigma_\mathrm{I}/\sigma_\mathrm{II} = 18.9$ of the molecular line intensity derived from the Hitran database (Fig. 2(b)).

The SNR was improved by averaging over 4 scans (Fig. 3). In this case the 'noise' level is a result of residual mode structure on the baseline, averaging will smear out this mode structure with an improved SNR. The figure shows the absorption profile of a single line over a scanning range of 5.7 GHz under the same conditions as in Fig. 2(a).

Integration over the absorption line of Fig. 3 gives a value of 0.0302 cm^{-1} (Eq. (3)). With a given molecular line intensity from the Hitran database ($\sigma = 3.09 \times 10^{-20}$ cm^2 cm^{-1}/molecule) we derive a mirror transmission $(1 - R)$ of 0.0076, giving reflectivity $R = 0.9924$.

The absorption linewidth ($\Delta\nu_\mathrm{L} = 0.01726$ cm$^{-1} = 518$ MHz) is determined by both pressure broadening (0.0159 cm^{-1}[15]) and Doppler broadening (0.0065 cm^{-1}[13]). The results of a simulation using a Voight profile are given in Fig. 3.
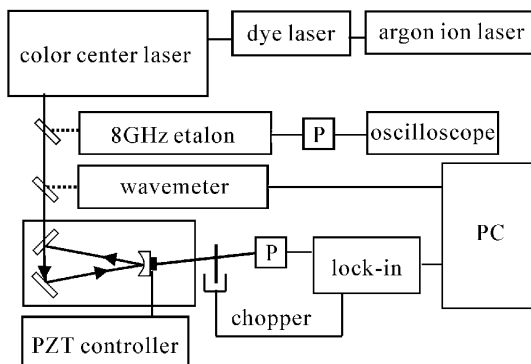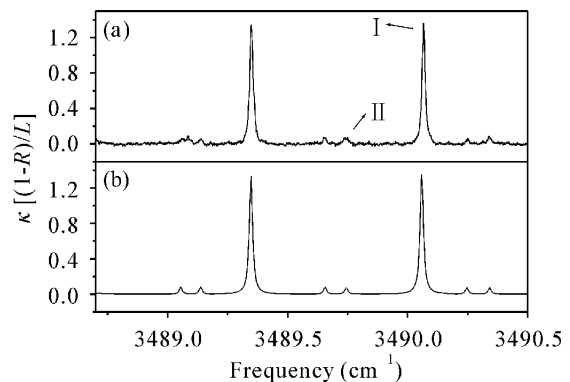

Fig. 1. The cavity enhanced absorption set-up using a color center laser in combination with a three-mirror ring cavity. The laser power is monitored using pyro-electric detectors (P).

Fig. 2. The cavity enhanced absorption spectrum recorded in a single wavelength scan (integration time 1 s) around 2.86 μm for a 60 parts per million N_2O mixture in N_2 at 100 mbar (a), and a simulation of the spectrum using data from the Hitran database (b).
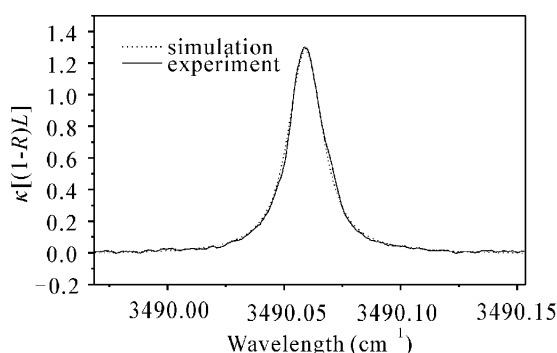
Fig. 3. Absorption line of N_2O, at 3490.059 cm^{-1}, taken under the same conditions as Fig. 2, but averaged over 4 consecutive data scans. The experimental curve fits well with a simulation using a Voight profile.

With Eq. (2), it is now possible to calculate κ at the center of the absorption line ($\kappa(\nu_0)$) to be 1.94×10^{-4} cm^{-1}. At the center of the absorption line (Fig. 3) at 3490.059 cm^{-1}, we achieved a SNR of 100, which gives a detection limit for N_2O of 600 parts per billion (SNR = 1). The equivalent minimum detectable absorption coefficient will then be $\kappa(\nu) = 2.0 \times 10^{-6}$ cm^{-1} (SNR = 1).

The cavity enhanced absorption method is extended to the 2.86 μm region using a color center laser. Next to that we've shown that a triangular ring cavity design is suitable for CEA spectroscopy. Further more, we demonstrated that CEA could be used with a slowly continuously tunable laser (70 MHz/s) combined with fast moving optical cavity modes. The SNR could be improved by averaging over repetitive scans, which shows that the 'noise' level is a result of residual mode structure on the baseline. With our combined mirror reflectivity of 0.9924 we achieved a sensitivity of 2.0×10^{-6} cm^{-1}Hz$^{-1/2}$, corresponding to a detection limit for N_2O of 600 parts per billion. We expect that this detection limit can be improved substantially if higher reflectivity mirrors are used.

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