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Cavity enhanced absorption spectroscopy in the 10 μm region using a waveguide CO_2 laser

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Abstract

The cavity enhanced absorption (CEA) technique is extended into the 10 μm region using a line-tunable continuous wave CO_2 laser. Part of the laser beam is deflected by an acousto-optical modulator (AOM), and is used to excite a mechanically unstable high-finesse optical cavity. In order to assure a stable and optimal transmittance of light through the cavity, the laser frequency and the cavity eigenfrequencies are modulated independently. The time-integrated intensity of the light exiting the cavity, which is inversely proportional to the cavity losses, is measured using a lock-in detection scheme. An absorption detection sensitivity of 1.5×10^{-6} cm^{-1} $Hz^{-1/2}$ is readily obtained with a rather simple setup.

1. Introduction

Cavity enhanced absorption (CEA) spectroscopy is a fairly new continuous wave (CW) sensitive absorption technique [1–7]. It makes use of efficient multipassing along the same optical path in a high-*Q* optical cavity. The laser light enters this optical cavity when the laser frequency and the frequency of one of the cavity eigenmodes accidentally coincide. The *time-integrated* intensity of the light transmitted through the cavity is measured and is inversely proportional to the total cavity losses [1]. As a result, the absorption coefficient of an absorber present in the cavity can be determined when the empty cavity losses are known.

In CEA spectroscopy, the laser frequency is *not* locked to the frequency of a cavity eigenmode. The cavity geometry is chosen such that the mode structure is very dense. During a measurement, both the laser frequency and the frequencies of the cavity eigenmodes are dithered, resulting in a quasi-continuous incoupling of light into the cavity. If the laser can be scanned repeatedly over a certain wavelength interval, as is the case for diode lasers, a 'raw' CEA spectrum can be obtained very rapidly (~1 s) by summing several scans [1]. This feature offers flexibility in optimizing the experimental conditions in real time.

As CEA spectroscopy makes use of CW lasers, it is possible to perform high-resolution absorption measurements. For example, rotationally resolved

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CEA spectra of combination and overtone bands of ammonia have been measured in a supersonic jet in the 1.5 μm region, with a Doppler limited resolution of 180 MHz [3]. These measurements were performed with a commercially available external cavity diode laser. Recently, we recorded CEA spectra of OH and hot water in flames using the same laser [5].

The CEA technique can be applied as an open-path setup, thereby allowing non-extractive in-situ measurements. This is of significance when measurements are carried out on polar molecules with strong adsorptive properties such as ammonia or water. In the 1.5 μm region, the sensitivity at atmospheric pressure has been determined to be 9×10^{-8} cm^{-1} Hz$^{-1/2}$ from CEA measurements in a climate chamber. This corresponds to a detection limit for ammonia of 100 ppb (1 s) [4]. Switching from the 1.5 μm region to the 10 μm region gives access to the fundamental ν_2 vibrational band of ammonia. This band is a factor of ~60 stronger than the overtone and combination bands present in the 1.5 μm region and a lower detection limit is therefore anticipated.

The Department of Molecular and Laser Physics of the University of Nijmegen houses the 'Life Science Trace Gas Exchange Facility', which operates several CW CO and CO_2 laser-based photoacoustic detectors to monitor trace gases at atmospheric conditions [8]. A sensitivity down to 10^{-10} cm^{-1} has been demonstrated with intracavity CO_2 laser photoacoustics [9], corresponding to a few ppt detection limit for ammonia with the 9R30 line. This estimate does not, however, account for the interference of ambient CO_2 or for the adsorptive properties of ammonia, which complicate all extractive techniques as well as CO_2 scrubbing. Other detection schemes have been developed which use an open-path setup in combination with a CO_2 laser, such as photo-thermal deflection spectroscopy [10] and CW cavity ring down spectroscopy [11,12].

In this Letter we describe the application of the CEA technique using a waveguide CO_2 laser. The measurements are performed in a closed cell system to allow rapid evacuation and control of the gas concentration during the experiments. It is shown that highly sensitive and fast, non-extractive measurements can be performed in the 10 μm region with a simple experimental setup.

2. Experiment

The CEA technique has been described in [1]. Up to now, CEA spectroscopy has been performed with continuously tunable lasers. The CW waveguide CO_2 laser which is used in the present experiments is line tunable, with a free spectral range limited intraline tunability of less than 100 MHz.

In CEA spectroscopy, light is coupled into the optical cavity whenever a resonance between the laser frequency and the frequency of one of the cavity eigenmodes occurs. Since the time-integrated intensity of the transmitted light is measured, it is important that the rate with which the light is coupled into the cavity is constant. Therefore, both the laser frequency and the frequencies of the cavity modes need to be modulated.

In Fig. 1 a schematic overview of the experimental setup is shown. The single-mode CO_2 waveguide laser [9] emits radiation between 9 and 11 μm. Line tuning of the laser is achieved by adjusting the grating angle. A piezoelectric element holding the output mirror of the laser cavity is used to modulate the laser frequency at a rate of 400 Hz. The laser beam passes through an acousto-optical modulator (AOM), which is switched on and off at a rate of about 30 Hz. The undeflected beam is used to monitor the power output of the laser. The deflected beam, which is shifted 90 MHz in frequency, is used to excite the high-finesse optical cavity. Apart from intensity modulating the laser beam, the AOM also prevents optical feedback into the laser.

The optical cavity is placed inside a stainless steel cell that can be evacuated. Light enters and exits the cell through ZnSe windows. The cavity consists of two highly reflective plano-concave mirrors (Laser Power Optics) separated by a distance d of 19.2 cm. The mirrors can be aligned independently from the outside of the cell. One of the cavity mirrors is mounted on a piezoelectric transducer, which is used to vary the cavity length (at a rate of 40 Hz). A ZnSe lens is placed just after the cell exit window in order to collect all the light

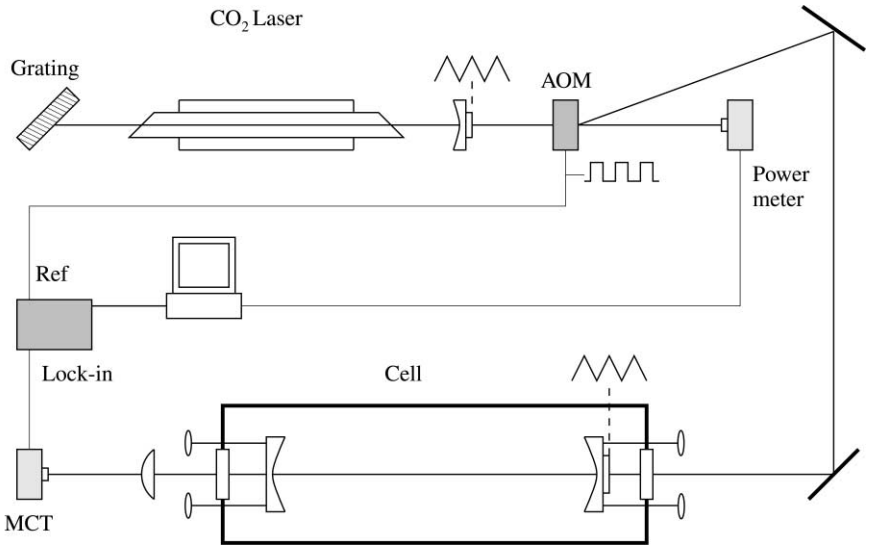

Fig. 1. Scheme of the CEA setup. Light from a waveguide CO_2 laser is modulated in frequency by a piezoelectric element mounted on the output mirror of the laser resonator. The beam passes through an acousto-optical modulator (AOM), of which the driving voltage is modulated. The undeflected beam is used to monitor the output power of the laser. The deflected beam is coupled into a high-finesse optical cavity that is mounted inside a cell that can be evacuated. The cavity length is modulated during the measurement using a piezo element mounted on one of the mirrors. The CEA signal is detected with a liquid-nitrogen-cooled MCT detector which is connected to a lock-in amplifier.

exiting the cavity. The intensity of the light is detected with a liquid-nitrogen-cooled MCT detector, which is connected to a lock-in amplifier. The modulation frequency of the AOM is used as the reference for the lock-in amplifier. The demodulated signal is digitized and stored in a computer.

The absorption coefficient κ can be extracted from a measurement of the time-integrated intensity via

$$\kappa(\nu) = \left(\frac{S_0(\nu)}{S(\nu)} - 1\right)\left(\frac{1-R}{d}\right), \tag{1}$$

where $S(\nu)$ is the signal recorded with the absorbing species, $S_0(\nu)$ is the signal without the absorbing species (i.e., the baseline), and R is the mirror reflectivity.

As can be seen from Eq. 1, the measured absorption in a CEA experiment is expressed in units of $(1-R)/d$. In order to put the absorption on an absolute scale, the effective mirror reflectivity must be known. Since the reflectivity of our mirrors was not known, it was determined by measuring the absorption of a molecule with a well-known absorption cross-section and concentration. For this purpose, we used a certified mixture of 1 ppm ethylene in air (80% N_2 and 20% O_2). Ethylene has an absorption coefficient of 30.4 atm^{-1} cm^{-1} at atmospheric pressure, at the 10P14 CO_2 laser line (949.479 cm^{-1}) [13].

The calibration procedure is as follows. The cell containing the cavity is filled with 1 bar pure nitrogen, and the CEA measurement is started. Next, the cell is evacuated, and filled with the 1 ppm ethylene/air mixture. During pumping and filling the measurement is halted, since the cavity alignment gets strongly distorted due to the rapid pressure fluctuations. After a minute, the cavity is stable again, and the measurement is continued. This cycle is repeated many times.

3. Results

Two parts of a more than 3 h measurement are shown in panels A and B of Fig. 2. The integration time of the lock-in amplifier is set to 1 s, while every 20 s a data point is recorded. The measurement in panel A starts with the 1 ppm ethylene

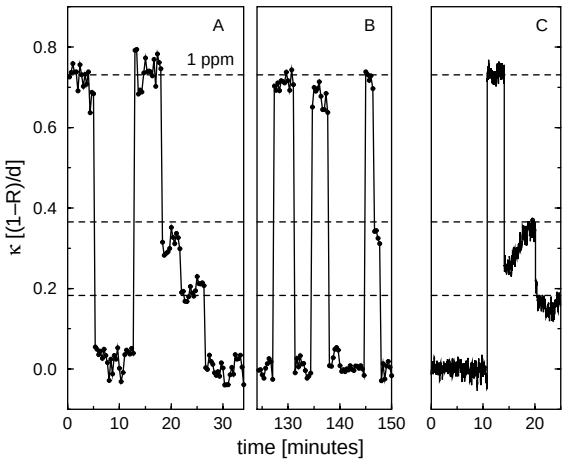

Fig. 2. Cavity enhanced absorption measurements of 1 ppm ethylene in 1 bar nitrogen. Panels A and B show parts of a more than 3 h measurement. The data points are sampled each 20 s, while the integration time of the lock-in amplifier is set to 1 s. Panel A shows measurements on the gas mixtures sequence 1 ppm C_2H_4, pure N_2, 1 ppm C_2H_4, 0.5 ppm C_2H_4, 0.25 ppm C_2H_4, and pure N_2. The 0.5 and 0.25 ppm dilutions are produced rather crudely (see text). The dashed horizontal lines indicate the expected 1, 0.5, and 0.25 ppm C_2H_4 signal levels. Panel B shows a sequence of pure N_2 and 1 ppm C_2H_4 samples. Right after the last 1 ppm measurement, a few data points are measured on a 0.5 ppm dilution. Panel C shows a similar measurement applying a different data-acquisition system: the lock-in integration time is 1 s, while the sampling rate is 3 Hz.

mixture, followed by pure nitrogen, and then the 1 ppm mixture again. The 1 ppm ethylene absorption coefficient amounts to $0.73 \times (1 - R)/d$. With a cavity length of 19.2 cm, the mirror reflectivity is calculated to be 0.9992.

By reducing the pressure to 0.5 bar, and adding nitrogen up to a total pressure of 1 bar, we tried to create a 500 ppb ethylene-in-nitrogen mixture. This was repeated in order to obtain a 250 ppb ethylene mixture. The results are shown in the last part of panel A. The dashed lines in Fig. 2 indicate the absorption coefficients corresponding to 1 ppm, 500 ppb, and 250 ppb, respectively. It can be seen that the measured absorption values do not exactly match the expected values. This is due to the rather crude way of making the leaner mixtures. The tube between the cell and the pump is rather long and has a volume comparable to that of the cell. The gas inlet and the pump connection are at opposite sides of the cell. Therefore, it is expected that it takes some time before the actual concentration at the axis of the cavity has reached the 500 ppb or 250 ppb value, as can be seen in the figure. Panel B is similar to panel A, and shows measurements about 1.5 h later. It is evident that the measured 1 ppm level is reproducible.

Panel C shows a measurement taken on another day with a different data-acquisition system, which is capable of measuring at a higher repetition rate. The integration time of the lock-in amplifier is again set to 1 s, while now a data point is recorded every 0.3 s. This panel shows again the absorption of 0 ppm, 1 ppm, 0.5 ppm, and 0.25 ppm ethylene in nitrogen. From these measurements we can determine the detection limit of this CEA configuration for ethylene to be 50 ppb (in 1 s), corresponding to a sensitivity of 1.5×10^{-6} cm^{-1}.

The advantage of the CEA technique is the open path character, which allows monitoring of fast concentration changes. Fig. 3 shows the result of such an experiment (0.1 s integration time of the lock-in amplifier, data points recorded every 0.06 s). We injected a small sample of pure ethylene at time point A. The measured absorption increases to a value corresponding to 48 ppm

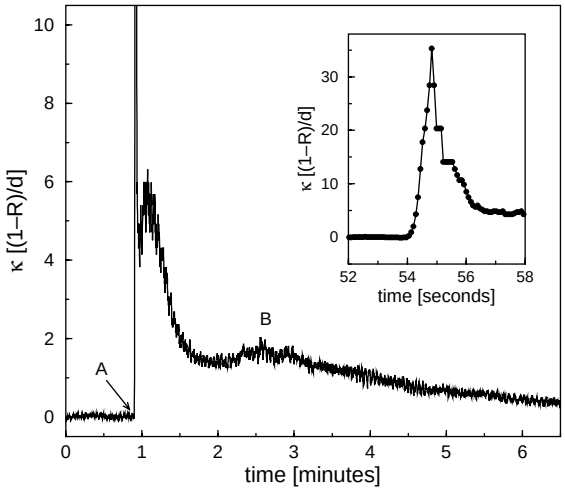

Fig. 3. Time response of the CEA setup. A small amount of pure ethylene is injected into the open cell at time point A. The ethylene absorption signal increases immediately to a value corresponding to about 48 ppm, as shown in the inset. The cell is flushed with pure nitrogen at time point B.

ethylene within a second (see inset of Fig. 3), followed by a decrease which results from diffusion of ethylene throughout the cell. At time point B, we supplied a flow of nitrogen to the open cell, which steadily removes the ethylene from the cell. Since the absorption curve is obtained by plotting the inverse of the measured signal, low signal levels, and thus high absorptions, as shown in the inset of Fig. 3, show bit-noise due to the analog-to-digital conversion.

4. Discussion

In a previous CEA study, we reported a sensitivity of 9×10^{-8} cm^{-1} for detection of species at atmospheric pressure [4]. In that study, a CW diode laser was used which can be scanned continuously over the spectral absorption feature contrary to the line-tunable CO_2 laser. The laser was scanned repeatedly (at a rate of 30 Hz) over the molecular absorption line, and the subsequent scans were summed during the CEA measurement. As a result, the on and off resonance absorption are measured simultaneously and the drift of the baseline is therefore cancelled. In the present experiment, the on and off resonance absorption are *not* measured simultaneously, which limits the sensitivity.

Furthermore, it is evident from Fig. 3 that there is a periodic noise superimposed on the signal. Experimentally, it was found that the intensity and frequency of this noise can be changed by adjusting the modulation frequencies of the AOM, the laser and cavity piezos, and it cannot be excluded that we have not found the optimum settings.

The sensitivity of our present setup is 1.5×10^{-6} cm^{-1} Hz$^{-1/2}$. This value can be compared with those obtained in other studies using a CO_2 laser with an open-path setup. Mürtz et al. [11] used the CW-CRD technique. In their setup, modematching optics are needed in order to excite mainly the longitudinal modes. The laser frequency is locked to the frequency of one of the longitudinal cavity eigenmodes. When sufficient light is coupled into the cavity, a threshold circuit triggers an AOM which switches off the laser beam. Subsequently, the intensity of the light exiting the cavity is measured time resolved. From the decay time, the so-called ring down time, the absorption coefficient is determined. In their study, Mürtz et al. [11] claimed a sensitivity of 3×10^{-7} cm^{-1} Hz$^{-1/2}$, with mirrors having a reflectivity of 0.995. In a similar experiment, Bucher et al. [12] reported a sensitivity of 4×10^{-9} cm^{-1} Hz$^{-1/2}$.

De Vries et al. [10] reported on photo-thermal deflection (PTD). In the PTD technique the deflection of a weak probe laser beam by the thermal refractive index gradient induced by trace gas absorption of an intense pump laser beam is measured. In their experiment the intra-cavity beam (100 W) of a CO_2 laser was used as the pump laser and a He–Ne laser was used as the probe laser in a multipass configuration. Part of the probe beam was used to correct for air turbulences. The reported sensitivity is 1.5×10^{-8} cm^{-1} Hz$^{-1/2}$. Although PTD spectroscopy is a non-extractive technique with a high sensitivity, the experiment is rather involved.

Comparing the sensitivities of the CEA, CW-CRD, and PTD techniques, it is clear that the CEA technique is the least sensitive one. On the other hand, the sensitivity of the present CEA setup is only a factor of 5 less than that of the CW-CRD setup reported by Mürtz et al. [11]. However, both the CW-CRD technique and the PTD technique are experimentally more involved than the CEA technique. Furthermore, our setup is rather insensitive to mechanical disturbances. Mechanical vibrations can even be used to enhance the sensitivity of CEA spectroscopy, since a more stable incoupling of light into the cavity will occur [3,4,6]. It is expected that the noise that limits our sensitivity can be reduced, since it is a result of beating between the frequencies of the applied modulations. Therefore, it is anticipated that the CEA setup will be of more practical use on remote locations.

The time response of our set up is, in principle, only limited by the integration time of the lock-in amplifier. This is also the case for the PTD technique. For the CW-CRD technique, the time response is limited by the rate at which the ring down decay transients can be recorded and analyzed, and by the time needed to re-lock the laser frequency to that of the cavity.

In this Letter, we have demonstrated that a line-tunable CO_2 laser can be used to perform CEA measurements. It is also shown that a lock-in detection scheme can be used in CEA spectroscopy in order to subtract background signal due to thermal radiation. At present the sensitivity is 1.5×10^{-6} cm^{-1} Hz$^{-1/2}$, which results in a 50 ppb (1 s) detection limit for ethylene on the 10P14 laser line. For detection of ammonia, this sensitivity corresponds to a detection limit of 25 ppb (1 s) on the 9R30 laser line [13]. Since the present sensitivity is limited by periodic noise (beating), it is expected that the sensitivity can be improved in future experiments.

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