Using quantum cascade lasers with resonant optical cavities as a diagnostic tool

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Abstract. Absorption spectroscopy based on optical resonators is known to be a very sensitive diagnostic technique. For many years the infrared spectral range could not be employed, because of the lack of suitable radiation sources with the required power and tunability. Recent advances in semiconductor laser technology, in particular the advent of quantum cascade lasers (QCL) provides new possibilities for highly sensitive and selective detection of molecular species. Cavity Enhanced Absorption Spectroscopy (CEAS) with a thermoelectrically (TE) cooled cw QCL emitting at 7.66 µm and employing a ~ 0.5 m long cavity yielded effective path lengths of 1080 m and a sensitivity of $2 \times 10^{-7}$ cm⁻¹Hz⁻¹/², mainly limited by incomplete averaging over cavity resonances. The molecular concentration detection limit with a 20 s integration time was found to be $6 \times 10^{8}$ molecules/cm³ for N₂O and $2 \times 10^{9}$ molecules/cm³ for CH₄ which is good enough for the selective measurement of trace atmospheric constituents at 2.2 mbar.

1. Introduction

Absorption spectroscopy in the mid infrared spectral region (MIR, 3 - 20 µm) using lasers as radiation sources is an effective method for monitoring molecular species in the fingerprint region. Conventional linear absorption spectroscopy employing multiple pass cells is a well-known method for achieving high sensitivity [1,2]. An alternative approach where path lengths up to several kilometres can be achieved is to combine a high finesse optical resonator with a pulsed or continuous wave (cw) source respectively for cavity ring-down spectroscopy (CRDS) [3], cavity enhanced absorption spectroscopy (CEAS) [4], or integrated cavity output spectroscopy (ICOS) [5,6]. In CEAS or ICOS the steady-state transmission or integrated transmitted intensity through the cavity is observed as a function of the laser frequency.

The majority of cavity based methods have used sources of radiation in the ultraviolet and visible regions. For many years the infrared spectral range could not be employed either for CRDS or for the CEAS or ICOS techniques, because of the lack of suitable radiation sources with the required power and tunability. Early experiments in the MIR were therefore carried out with bulky radiation sources,
e.g. optical parametric oscillators [7,8], Raman cells or shifters [9-11] or CO₂ and CO lasers [12-14]. In all these cases sophisticated optical geometries were developed which were more suitable for the research laboratory than for field applications. The combination of lead salt lasers with optical cavities suffered from low laser intensity [15]. Recent advances in semiconductor laser technology, in particular the advent of intersubband quantum cascade lasers (QCL) and interband cascade lasers (ICL) [16,17], provide new possibilities for highly sensitive and selective trace gas detection. Sensitivities of $5 \times 10^{-10}$ cm$^3$Hz$^{-1/2}$ were accomplished by means of multiple pass cells but at the expense of large sample volumes of a few litres and increased base lengths [2]. Distributed feedback (DFB)-QCLs combine single-frequency operation with tunability over several wavenumbers, and average powers over a mW. The relatively high output power permits the use of optical cavities with high finesse. The potential of such a combination was demonstrated in CRDS measurements with a cryogenically cooled cw DFB-QCL [18]. Several applications of QCLs combined with either the CRDS or the CEAS/ICOS techniques and with sensitivities down to $2 \times 10^{-9}$ cm$^3$Hz$^{-1/2}$ were reported [19]. The broader use of cavity based techniques in the MIR in industry or for field application has so far been hindered not only by space or weight restrictions, but also by the need for cryogenic cooling of either the laser or the detector. While pulsed QCLs working at room temperature have been commercially available for several years, room-temperature cw QCLs have only recently been introduced.

Moreover pulsed QCLs exhibit an intrinsic frequency chirp appearing as an increased effective laser line width [20] and exceeding the width of narrow molecular absorption features. Thus the application of TE cooled pulsed QCLs for ICOS and CRDS was found to be limited by the inevitable excitation of multiple cavity modes during one pulse [21-24]. Consequently the accuracy and advantage of an absolute internal absorption calibration, in theory inherent for CRDS experiments, is not achievable. Additionally, the chirped laser does not allow for an efficient build-up of the laser field in the cavity. CRDS using pulsed QCLs therefore has only a limited number of useful applications, e.g. for the determination of the reflectivity of the cavity mirrors without any absorption feature present or for the detection of complex and broad molecular absorptions at higher pressures where the width of absorption features exceeds the effective laser line width.

The essential narrow bandwidth emission from a QCL in combination with an optical resonator can be gained if the current of the laser is not switched or pulsed. Therefore a room temperature cw QCL emitting at 7.66 μm was used in a CEAS configuration aimed at achieving a sensitive, cryogen-free spectrometer for sampling small volumes. Apart from several studies on NO at 5 μm the MIR spectral region in general and the 7 - 8 μm region presently used have not been extensively investigated. The experimentally straightforward CEAS configuration would be of special interest for in-situ measurements of radicals, e.g. in low pressure plasmas, where multi-pass cell sampling ex-situ is not an option and where CRDS with a pulsed QCL suffers from the laser chirp and the low pressure, i.e. the width of the absorption lines cannot be arbitrarily matched to the effective pulsed QCL line width.

2. Experimental

The experimental arrangement for the CEAS experiments is shown in figure 1. The stable resonator was formed by two high reflectivity mirrors (Los Gatos Research) of diameter 25.4 mm and 1 m radius of curvature. It should be noted that a high reflectivity of the mirrors of better than 99 % can only be achieved for a relatively small wavelength window of typically 150 cm$^{-1}$. The mirrors also served to enclose the vacuum vessel which was made of standard vacuum components. Hence the vacuum cell determined the mirror separation of 0.432 m. In contrast to locked cavity studies, the cavity length here was not actively changed or dithered nor was the cavity locked to the wavelength of the laser source. Beam shaping optics (BSO) collected the radiation from the QCL firstly with an aspherical ZnSe lens (30 mm diameter, f/1.5) and then with a telescope formed by two off-axis parabolic mirrors (OAP) which reduced the beam diameter by a ratio of almost 1:5. No additional optics were added to suppress possible optical feedback to the laser, since feedback was assumed to be negligible for the current DFB-QCL device. The radiation leaking out of the cavity was collected by
an OAP of 25.4 mm diameter (f/0.64) and directed to a detector. A reference path could be used for calibration by inserting a beam flipping mirror. In the beginning, both signal and reference channel were equipped with liquid nitrogen (LN) cooled detectors (Judson Technologies). In addition, for validation experiments a TE cooled detector (neoplas control, VIGO element PDI 3TE 10/12) was employed for the signal channel.

A room temperature cw QCL (Alpes Lasers), emitting between 1300 cm\(^{-1}\) to 1311 cm\(^{-1}\) (~ 7.66 \(\mu\)m) was used for the experiments. It was operated in a standard housing (Starter Kit, Alpes Lasers), thermoelectrically cooled to - 5.9°C for calibration or + 2.2°C for trace gas measurements in room air and driven by a DC current source (Kepco, BOP100-2M) with a typical DC current of around 380 mA. An additional current ramp of 45 mA was impressed on it in order to sweep the laser frequency during the on-phase. The laser current was briefly reduced below the threshold value by -70 mA to record the offset of the zero signal (figure 2) in the off-phase. The sweep rate of the laser was 0.9 kHz for all measurements. For a mirror distance of 0.432 m the sweep of the laser frequency corresponded to a scan over 67 cavity modes, which was sufficient to avoid an overlap between the build-up and decay events of different cavity modes. On the other hand the sweep rate gave a full spectrum after slightly more than 1 ms. A given number of spectra were then averaged and simultaneously fitted. In order to smooth interference effects on the baseline of the spectra, mainly caused by longitudinal cavity modes, the whole cavity was arbitrarily destabilized mechanically, e.g. by an external vibrating source.

The laser sweep of 0.78 cm\(^{-1}\) or 23.4 GHz, with the current modulation applied, is illustrated at the top of figure 2 which shows the signal through a Germanium etalon (0.048 cm\(^{-1}\) free spectral range). Relative calibration of the frequency axis of the spectrum was provided by recording the fringes of a Germanium etalon in a reference channel and using interpolation. Absolute calibration and identification was achieved by comparison with standard gas absorption spectra recorded in the reference channel prior to the CEAS spectra.
3. Results

3.1. Calibration of the CEAS system

Spectra from different mixtures of N$_2$O in N$_2$ were recorded in order to determine the effective reflectivity of the cavity mirrors and to provide a calibration. The measurements were taken under flowing conditions at a constant pressure of 1.2 mbar. Figure 3 shows the result of the spectral scans, obtained with a liquid nitrogen cooled detector and averaged over 20 s to reduce the noise level below $\sim 2 \times 10^{-3}$ in transmission. The three dominant N$_2$O features appear at 1306.771 cm$^{-1}$, 1306.846 cm$^{-1}$ and 1306.929 cm$^{-1}$ respectively. The strongest line has a line strength $S$ of $1.0 \times 10^{-19}$ cm/molecule. For the lower intensity lines $S$ values of $9.7 \times 10^{-21}$ cm/molecule are reported in the literature [25].

The absorption coefficient $k(\nu)$, i.e. the product of the number density $n$ and the absorption cross section $\sigma$, is inferred from CEAS spectra through

$$n\sigma(\nu) = k(\nu) = \left( \frac{I_0(\nu)}{I(\nu)} - 1 \right) \frac{1 - R}{L}$$

where $L$ is the mirror spacing, $I_0$ and $I$ are the transmitted intensity of an empty cavity (baseline) and the cavity filled with the species of interest respectively. Obviously the reflectivity $R$ of the cavity mirrors must be known or calibrated in order to deduce absolute values for $k$. A fit of the transmission spectra (figure 2) resulted in an effective reflectivity of $R = 99.96\%$ for the cavity mirrors or an effective path length $L_{\text{eff}} = L/(1 - R)$ of 1080 m. Since in this approach the excitation of high order transverse modes may occur which could have different diffraction losses this value of $R$ should be regarded as an effective one [26]. No evidence was found that optical feedback from the cavity to the QCL caused line shifts or perturbed lines. Next, the three N$_2$O lines visible in figure 3 were analysed further using

$$\ln \left( \frac{I_0}{I} \right) \approx GA \sim n$$

where $G = R/(1 - R)$ and $A = (1 - \exp(-kL))$ [19]. If the natural logarithm is taken from the inverted transmission spectrum and plotted against $n$ a linear relationship is expected, as long as a weak absorber is present in the cavity.

![Figure 3. CEAS scans for different N$_2$O calibration mixtures (N$_2$O diluted in N$_2$) at a constant total pressure of 1.2 mbar: a) 5 ppm, b) 10 ppm, c) 50 ppm, d) 100 ppm The acquisition time was 20 s.](image)

![Figure 4. Calibration data for the maxima of the three absorption lines and the four mixing ratios of N$_2$O mentioned in figure 3: i) 1306.929 cm$^{-1}$, ii) 1306.846 cm$^{-1}$ and iii) 1306.771 cm$^{-1}$.](image)
Thus equation (2) serves as a check on the validity of the weak absorption limit \((k \rightarrow 0 \text{ and } R \rightarrow 1)\). For this purpose \(\ln(I_0/I)\) at the maximum of the N\(_2\)O lines was plotted against the concentration in the cavity (figure 4). Generally, it can be concluded that the linear approximation is valid for \(GA \leq 0.15\) whilst for absorption features bigger than 15\% a correction is necessary.

3.2. Test of validity and system performance

The CEAS system was validated with measurements on constituents of laboratory air, namely methane, nitrous oxide and water. In order to detect these species within one spectral scan the spectral range and therefore the heat sink temperature of the QCL was slightly changed compared to the calibration experiments. The spectrum expected to arise for the average mixing ratios of the three molecules was calculated and is plotted in the upper panel of figure 5. Some non-interfering absorption features were selected for analysis and these are summarized in table 1. The single water line in the spectrum consists of two unresolved lines with a spacing of 0.004 cm\(^{-1}\), so that an effective value for \(S\) (for simplicity the sum) is used whereas a third weaker line shifted by \(\sim 0.01\) cm\(^{-1}\) could be deconvoluted from the main lines and was not used for the quantitative analysis. The transmission spectrum recorded with a TE cooled detector is shown in the lower panel of figure 5. The measurements were performed at low pressure under flowing conditions at 2.2 mbar in order to increase line selectivity. The spectrum was averaged for 20 s. Qualitatively it agrees very well with the simulation. The line positions were fitted to a transmission profile (figure 5). This fit was then used to calculate the absorption coefficient using (1). Integrating over the absorption line of interest revealed the number densities and mixing ratios (table 1): 1.7 ppm of CH\(_4\), 350 ppb N\(_2\)O and more than 1\% of H\(_2\)O. A comparison with literature values for the abundance of these molecules in air (1.75 ppm for CH\(_4\), 320 ppb for N\(_2\)O and 0.1 ... 4\% for H\(_2\)O) yields fair agreement [27,28].

![Figure 5. Calculated spectrum (upper) for air containing CH\(_4\), N\(_2\)O and H\(_2\)O. Experimental conditions: 2.2 mbar, \(L_{eff} = 1080\) m. The corresponding CEAS spectrum (lower) was observed with a TE cooled detector (open circles) and fitted (solid line) to determine the actual concentrations.](image)

The measurements on laboratory air were repeated with a LN cooled detector and the results, in particular the relative measurement error after 20 s, were very similar. For the LN cooled detector \(\Delta I/I_0\) of 0.3\% was obtained whereas for the TE cooled detector 0.2\% was found. The corresponding noise equivalent absorption (NEA), defined by

\[
\text{NEA} = \frac{\Delta I}{I_0} \left( \frac{1 - R}{L} \right)^{1/2} \sqrt{\frac{2}{f}}
\]

Where \(f\) is the acquisition rate of the spectra, is then \(1.8 \times 10^{-7}\) cm\(^{-1}\)Hz\(^{-1/2}\) for the TE cooled detector if the calibration error in \(R\) is also included. It is possible to estimate the minimum detectable number density (MDND) \(n_{\text{min}}\) for each molecule by means of the absorption coefficient \(k_{\text{min}}\). Assuming that \(k_{\text{min}}\) corresponds to the maximum of the smallest absorption feature that can be distinguished from the
noise, the $n_{\text{min}}$ can be estimated. The MDNDs of the different molecules analysed are listed in Table 1. For N$_2$O a detection limit of $6.4 \times 10^8$ molecules/cm$^3$ is obtained, which transferred to CH$_4$ corresponds to $1.6 \times 10^9$ molecules/cm$^3$ for the strongest line in CH$_4$. If this is converted into a mixing ratio at 2.2 mbar the limits of detection for N$_2$O and CH$_4$ are 12 ppb and 46 ppb respectively.

| Molecule | Line strength $S$ [cm/molecule] | Mix. Ratio | $n$ [molecules/cm$^3$] | MDND ($n_{\text{min}}$) |
|----------|-------------------------------|------------|----------------------|------------------------|
| CH$_4$   | 1305.987 4.78 x 10^{-20}      | 1.72 ppm   | 9.2 x 10^{10}        | 2.5 x 10^{9}          |
| CH$_4$   | 1306.062 2.41 x 10^{-20}      | 1.82 ppm   | 9.8 x 10^{10}        | 4.9 x 10^{9}          |
| CH$_4$   | 1306.105 3.19 x 10^{-20}      | 1.68 ppm   | 9.0 x 10^{10}        | 3.7 x 10^{9}          |
| CH$_4$   | 1306.140 7.60 x 10^{-20}      | 1.66 ppm   | 8.9 x 10^{10}        | 1.6 x 10^{9}          |
| N$_2$O   | 1306.191 1.12 x 10^{-19}      | 346 ppb    | 1.9 x 10^{10}        | 6.4 x 10^{8}          |
| H$_2$O   | 1306.29 6.08 x 10^{-24} a)    | 1.1%       | 5.8 x 10^{14}        | 1.8 x 10^{13}         |

*effective line strength from two unresolved lines

4. Discussion and Summary

A thermoelectrically cooled QCL has been combined with a high finesse optical resonator in order to profit from the enlarged path lengths at reasonably small sample volumes in combination with the high absorption cross section in the infrared molecular fingerprint region. The sensitivity of $1.8 \times 10^{-7}$ cm$^1$Hz$^{1/2}$ presently achieved with the TE cooled CEAS system is comparable to other CEAS or ICOS studies exhibiting a NEA down to $4 \times 10^{-8}$ cm$^1$Hz$^{1/2}$ [26,29]. In comparison to entirely TE cooled based CRDS setups with pulsed QCLs the performance of the system is superior. For CRDS employing pulsed QCLs the fast frequency chirp of the laser causes an excitation from several to tens of cavity modes almost simultaneously. The result is an apparent linewidth effects, i.e. line broadening, loss of sensitivity and accuracy. It is concluded that the switching of the laser current and hence the rapid temperature changes of the QCL device should be avoided in order to benefit from the combination with a resonant cavity [21]. Narrow bandwidth radiation of typically less than 100 MHz ($\leq 0.003$ cm$^1$) can be provided by cw QCLs which is sufficient for the combination with the presently used cavity of 0.432 m and its free spectral range of 360 MHz (0.012 cm$^1$).

The NEA of the system is still almost a factor of ~50 less sensitive than CRDS employing a cw QCL as demonstrated by Paldus et al. [18] which may be explained by the commonly omitted cavity mode noise in CRDS. In the present case the system was aligned on-axis with respect to the laser beam which produces cavity mode noise inherent to CEAS/ICOS setups [29]. In order to achieve an accurate signal-to-noise ratio, a measurement interval of at least 5 s is necessary to smooth out the residual mode structure on the baseline. For CEAS or ICOS the minimum detectable absorption is typically limited to $10^{-2}$ to $10^{-3}$ due to incomplete averaging over the cavity resonances. Since this still dominates the total performance the choice of detector, i.e. TE or LN cooled, is of less importance for the sensitivity limits of the system as demonstrated in section 3. Due to an advantageous spectral position and a lower sampling pressure in our experiment the MDND of CH$_4$ was lower than in similar measurements carried out at 7.9 µm where a better sensitivity of $2 \times 10^{-9}$ cm$^1$Hz$^{1/2}$, but a $n_{\text{min}}$(CH$_4$) of $2.9 \times 10^7$ molecules/cm$^3$ were reported [19]. With a 20 s measurement interval detection limits for N$_2$O and CH$_4$ of $6 \times 10^8$ molecules/cm$^3$ and $2 \times 10^9$ molecules/cm$^3$ respectively could be achieved at 2.2 mbar indicating that sub-ppb levels could easily be measured at higher pressures.

Mode noise is absent in QCL spectrometers employing conventional long path cells which are today increasingly based on TE cooled lasers and detectors and hence exhibit higher sensitivities even down to $3 \times 10^{-10}$ cm$^1$Hz$^{1/2}$ [30]. However, the volume of commercial multiple pass cells covering effective path lengths up to 210 m, typically ranges from 0.5 to 5 l which may increase the dimensions of the system

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6 Value estimated by the authors from the cited data.
and the necessary pumping time. The aim has been to achieve maintenance free operation with a small sample volume, presently around 0.3 l, and with an optical geometry reduced in its complexity which would make the system field-deployable. The results achieved here are relevant both for the in-situ detection of radicals in plasma chemistry and for trace gas measurements with field-deployable systems. Additionally, trace gas measurements may also be carried out without pre-concentration procedures. The choice of an appropriate method depends on whether the important criterion is ultimate sensitivity or a more compact system. In the former case a multi pass cell spectrometer would be preferable because of its better signal to noise characteristics but this configuration would exclude the detection of processes on short time scales or certain types of in-situ measurements. To achieve a compact system small volume cavity based spectrometers employing cw QCLs would be more appropriate.

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