Trace gas detection and high-precision spectroscopy in the mid-infrared and visible wavelength regions

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Abstract

This thesis is based on four experimental spectroscopic studies where novel highly sensitive laser absorption spectroscopy spectrometers are developed and used for trace gas detection and precision spectroscopy. Most of the studies are carried out in the mid-infrared region between 3 and 4 µm, where a homebuilt continuous-wave singly resonating optical parametric oscillator is used as a light source. In addition, one study has been performed in the visible region using a commercial green laser at 532 nm.

Two of the developed spectroscopic applications are based on cavity ring-down spectroscopy. In this thesis, the first off-axis re-entrant cavity ring-down spectrometer in the mid-infrared is demonstrated and utilized for highly sensitive detection of formaldehyde. The second study presents an optical frequency comb referenced mid-infrared continuous-wave singly resonating optical parametric oscillator, which is applied to high-precision cavity ring-down spectroscopy of nitrous oxide and methane. Furthermore, this study presents a new method for referencing a mid-infrared optical parametric oscillator to a near-infrared optical frequency comb. This new method allows large mode-hop-free frequency tuning ranges in the mid-infrared region.

The other two experiments are based on cantilever-enhanced photoacoustic spectroscopy, presenting the first reported studies of cantilever-enhanced-based trace gas detection in the mid-infrared and visible region. These studies show the great potential of cantilever-enhanced photoacoustic detection for substantial enhancement of the sensitivity of trace gas detection. For instance, the best nitrogen dioxide detection limit ever reported using photoacoustic spectroscopy is presented in this thesis.
Preface

The present work has been carried out at the Laboratory of Physical Chemistry of the University of Helsinki and at the Centre for Metrology (MIKES) during the years between 2010 and 2015.

I owe my gratitude to a great many people who have contributed to this work. First of all, I would like to express my gratitude to my supervisor, Professor Lauri Halonen for giving me the opportunity to work in his group, and the interesting field of science. This work began essentially as early as 2008 when I started as an undergraduate to working with the development of mid-infrared laser sources. Ever since, Lauri has been supportive and has encouraged me throughout my studies and research.

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Jari Peltola
Helsinki, October 2015
List of publications

This thesis contains the following publications, which are referred to by the Roman numerals I-IV:


The author has prepared the manuscripts for Publications I, II, and III. He has also written the final version of the manuscript for Publication IV. In Publication I, the author has been responsible for most of the experimental work and data analysis. The author has been responsible for all the experimental work in Publication II. He has also analyzed most of the data presented in this publication. In Publications III and IV, the author has carried out all the experimental work and analysed all the measurements presented in these publications.

Related publications


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Chapter 1

Introduction

Trace gases are gases that exist in small concentrations in a gas mixture. A good example of such a gas mixture is the atmosphere around us, which is mainly composed of nitrogen, oxygen, and argon. Together these compounds account for about 99.9% of the total atmosphere. The remaining ~0.1% consists of trace gases including, among others, carbon dioxide (CO$_2$), ozone (O$_3$), methane (CH$_4$), hydrogen cyanide (HCN), nitrous oxide (N$_2$O), and oxides of nitrogen (NO$_x$). Of these, e.g., hydrogen cyanide is a highly toxic compound, which is used and released in many industrial processes and is formed during the combustion of nitrogen-containing compounds. In general, trace gases are involved in global warming, reduction of ozone layer, formation of photochemical smog and acid rain, and are the cause of health problems. Many of them are also absorbed (inhaled) and emitted (exhaled) by living organisms. Hence, the detection and quantification of the composition of trace gases for various scientific, industrial, medical, and environmental purposes is essential. Concentrations of trace gases vary typically from hundreds of parts-per-million (ppm) to a few of parts-per-trillion (ppt) by volume. Low concentrations and challenging measurement conditions create strict requirements for trace gas detection.

Laser-based absorption spectroscopy has provided versatile techniques for trace gas analysis [1–8], atmospheric monitoring [9–11], medical diagnostics [12–15], as well as for optical frequency metrology [16–19]. Spectroscopic methods such as cavity ring-down spectroscopy (CRDS) and photoacoustic spectroscopy (PAS) allow fast detection with high sensitivity and good spectral resolution, and need little or no pre-treatment of the sample. Tunable narrow linewidth lasers improve the selectivity and help to identify a molecule or its isotope from interfering compounds and background signals. This is the case especially in the mid-infrared (MIR), in the so-called fingerprint region, where many molecules have their characteristic strong fundamental vibrations and related rotational-vibrational structure. The MIR region covers wavelengths between 2.5 and 25 µm (400 – 4000 cm$^{-1}$). The strong absorption and the large number of detectable molecules make the mid-infrared region ideal for trace gas analysis. This is the case, in particular, in the wavelength region between 3.0 and 4.0 µm, which contains, for example, CH, NH, and OH stretching modes (see Fig. 1.1). In addition, the region has a relatively small absorption due to water vapor and carbon dioxide. However, laser manufacturing has proven to be very challenging for this region.

In this particular spectral region, 1064 nm pumped continuous wave (CW) optical parametric oscillators (OPOs), based on periodically poled lithium niobate (PPLN) non-
linear crystals, have been widely used as light sources for high-resolution MIR spectroscopy. These CW OPOs possess broad spectral coverage ($2.5 - 4.0 \, \mu m$), narrow linewidth ($\sim 1 \, MHz$), wide mode-hop-free tuning ($> 10 \, GHz$), and high output power ($> 0.5 \, W$) when configured as singly resonant OPOs (SROs).

In laser absorption spectroscopy, a measured spectrum presents the absorption of a sample as a function of light frequency. In particular, the frequency of light has previously been difficult to measure with high precision and accuracy. Consequently, one of the most important technological advances in the field of laser spectroscopy has been the invention of the optical frequency comb (OFC). The OFC enables one to synthesize and measure optical frequencies with extremely high accuracy, typically with relative uncertainties from $10^{-13}$ to $10^{-15}$. This has led to remarkable improvements in high-precision laser spectroscopy.

This thesis consists of four refereed publications, where novel highly sensitive laser absorption spectroscopy spectrometers are described and used for trace gas detection and precision spectroscopy in the mid-infrared and visible regions. A brief summary of each publication is given below.

Publication I describes the first re-entrant off-axis cavity ring-down spectroscopy spectrometer for the mid-infrared region, which provides high spectral resolution while maintaining high measurement speed. The spectrometer was applied to the spectroscopy of formaldehyde at 3.4 $\mu m$ using a mid-infrared CW-SRO as a light source.

Publication II describes a highly sensitive CW-SRO-based spectrometer, which utilizes photoacoustic spectroscopy for the detection of hydrogen cyanide and methane in the mid-infrared region. Very high sensitivity was achieved using a novel cantilever-enhanced photoacoustic detection combined with the high output power of the CW-SRO.

Publication III reports a simple cantilever-enhanced photoacoustic spectrometer for sensitive detection of nitrogen dioxide in the visible region reaching the lowest NO$_2$ detection limit (50 ppt in 1 s) ever reported using PAS. Unlike in the previous publications, the light source used in this work was a high-power continuous-wave intra-cavity frequency
doubled Nd:YVO$_4$ laser at 532 nm.

Publication IV presents a tunable mid-infrared CW-SRO, which is referenced to a fully stabilized near-infrared optical frequency comb using a new referencing method. The method is based on frequency doubling of the mid-infrared beam. The comb-referenced CW-SRO was applied to high-precision cavity-ring-down spectroscopy of nitrous oxide (N$_2$O) and water (H$_2$O) at 2.85 $\mu$m and of methane (CH$_4$) at 3.2 $\mu$m.

This thesis is organized as follows. Chapter 2 explains the general theory of the laser sources related to this thesis. In Chapter 3, I review the theoretical and experimental background of the spectroscopic techniques used and developed in this thesis. Chapter 3 also summarizes the results of the work presented in Publications I-IV. Chapter 4 summarizes and concludes the thesis.
Chapter 2

Laser sources

2.1 Continuous-wave optical parametric oscillator

All the CW-OPOs used in this thesis are self-developed and homebuilt. The more detailed description of their operation and design is described in publications \cite{20,21}. The following sections explain the main theory and principle of optical parametric oscillator that are relevant to this thesis.

2.1.1 Nonlinear frequency conversion

In a nonlinear optical interaction, the frequency of light can change. This effect enables creation of coherent mid-infrared radiation starting from visible or near-infrared laser radiation. When an electromagnetic field (EMF) $E$ interacts with a medium, it causes bound electrons (dipoles) to move inducing a changing dipole moment. The macroscopic polarization of the oscillating dipoles can be expressed as $P = \epsilon_0 \chi E$, where $\epsilon_0$ is the free space dielectric constant and $\chi$ is the susceptibility. The interaction with the magnetic field is small compared to the electric field and hence the magnetic part can generally be neglected. The susceptibility describes the response of a matter to an applied electromagnetic field. The induced polarization $P$ can be represented as a power series of the electric field

$$P = \epsilon_0 \chi^{(1)} E + \epsilon_0 (\chi^{(2)} E^2 + \chi^{(3)} E^3 + \cdots),$$

(2.1)

where the first term is the polarization induced by the linear susceptibility $\chi^{(1)}$ and the next two terms represent the polarization induced by the nonlinear susceptibilities $\chi^{(2)}$ and $\chi^{(3)}$. Normally, the intensity of electric field is small and the susceptibility will have only a linear dependence on the electric field. The effects of nonlinear susceptibilities become significant only when the intensity of the electric field is strong enough because their values are many orders of magnitude smaller than that of the linear one. In practice, nonlinear optical phenomena are only observed by using laser light.

When two electromagnetic fields with frequencies $\omega_1$ and $\omega_2$ interact with a second-order nonlinear medium, four additional frequencies, $2\omega_1$, $2\omega_2$, $\omega_1 + \omega_2$, and $\omega_1 - \omega_2$ are
created [22]. The first two frequencies are products of an effect called second harmonic generation (SHG) and the third and fourth effects are called sum frequency generation (SFG) and difference frequency generation (DFG), respectively. Optical parametric generation, which will be discussed in the next section, is based on the polarization induced by the second-order susceptibility $\chi^{(2)}$.

### 2.1.2 Optical parametric generation

Optical parametric generation (OPG) is a coherent three-wave mixing process (see Fig. 2.1a), where a pump field at frequency $\omega_p$, creates two new fields at frequencies $\omega_s$ and $\omega_i$, that obey the law of conservation of energy

$$\omega_p = \omega_s + \omega_i. \quad (2.2)$$

For historical reasons, the two output waves are called signal $\omega_s$ and idler $\omega_i$, where the output wave with a lower frequency (in the MIR) is called the idler. Unlike in the other second-order nonlinear processes, the new fields arise from optical parametric fluorescence, and the process does not have to involve input fields at $\omega_s$ and $\omega_i$. After that, DFG between the initial pump and a signal photon creates a new idler photon, which, in turn, creates a new signal photon by DFG with the pump. This process repeats itself throughout the medium amplifying the signal and idler fields. The amplification is possible only if the momentum is conserved in the process

$$k_p = k_s + k_i, \quad (2.3)$$

where $k_x, (x = p, s, i)$ are the wave vectors of the pump, signal, and idler fields. The wave vector depends on the refractive index ($n_x$) as $k_x = (n_x \omega_x/c)\hat{k}$, where $c$ is the speed of light, and $\hat{k}$ is a unit vector. Since all materials are in reality dispersive, the three waves propagate at different phase velocities corresponding to different refractive indices. This induces a phase-mismatch between the fields, which can be describe as

$$\Delta k = k_p - (k_s + k_i), \quad (2.4)$$

**Figure 2.1:** a) A three-wave mixing process. b) A singly resonant optical parametric oscillator configuration. The symbol HRM stands for a highly reflective mirror.
and it is illustrated in Fig. 2.2. The symbol $\Delta k$ is called the phase-mismatch parameter.

\[ k_s \quad \Delta k \quad k_i \quad k_p \]

Figure 2.2: Phase-mismatch in parametric generation.

The single pass parametric conversion efficiency of a nonlinear medium is typically very small. Because of this, a parametric device usually needs a positive feedback to amplify the generated fields. The feedback can be achieved by placing the nonlinear medium inside an optical cavity (see Fig. 2.1b). This configuration is called an optical parametric oscillator. The particular configuration, where only one of the wavelengths (in this case the signal) is in resonance inside the cavity, is called a singly resonant OPO. All the CW-OPOs used in this thesis are CW-SROs [20, 21]. In order for an OPO to reach the oscillation threshold, the single-pass parametric gain has to overcome the round-trip losses of the cavity. A typical pump power at threshold is a few watts for a CW-SRO [20].

The CW-SROs are considered as one of the most useful configurations for molecular detection in the mid-infrared region. Due to the CW operation, they possess narrow linewidth which is needed for selective high-resolution spectroscopy. In Publication I, we estimated that the 1-μs short-term and 1-s long-term linewidths of our SRO are approximately 200 kHz and 1 MHz, respectively. The CW-SROs have also a high idler output power of up to several watts [20, 23], which is useful, especially, for photoacoustic spectroscopy. But above all, they possess broad spectral coverage, which enables detection of numerous molecules in the mid-infrared. The wavelength tuning range of all periodically poled lithium niobate (PPLN)-based SROs used in Publications I, II, and IV is approximately $2.7 - 3.5 \, \mu m$, which covers, among other, the fundamental ro-vibrational transitions of formaldehyde ($CH_2O$), hydrogen cyanide (HCN), methane ($CH_4$), and nitrous oxide ($N_2O$).

### 2.1.3 Quasi-phase-matched lithium niobate crystal

The effect of phase dependence of the pump, signal, and idler fields inside the nonlinear medium on the parametric process has already been mentioned briefly in the previous section. Due to dispersion, a phase difference ($\Delta k$, see Equation 2.4) is induced between the pump, signal, and idler while they travel along the medium as seen in Fig 2.2. Phase matching is a method for achieving a constant phase relationship between the generated and propagating fields in order to obtain an effective parametric conversion. In the case of a phase-mismatched situation $\Delta k \neq 0$, the interference between the pump and other waves becomes destructive after the coherence length ($L_c = \pi/\Delta k$) after which the signal and idler waves are converted back to the pump frequency. This will create an oscillating power behaviour in the medium, which is illustrated by the bottom (red) line in Fig. 2.3. The top (purple) line presents the situation for perfect (birefringent) phase-matching ($\Delta k = 0$). The middle (green) line describes the principle of so called
quasi-phase-matching (QPM). In QPM, phase matching is achieved by reversing the crystal structure of the nonlinear material after every coherence length [24]. The inversion introduces an additional phase difference of \( \pi \), which makes the waves travel in phase again.

Lithium niobate is one the most used nonlinear materials, since it has a high nonlinear coefficient (see Table 2.1). In addition, it is transparent up to 5.5 \( \mu \)m (see Table 2.1). However, its use becomes difficult above 4 \( \mu \)m where the absorption becomes stronger (see Fig. 2.4). The quasi-phase-matching of lithium niobate is done usually by periodic poling. In the periodic poling, the dipoles of lithium niobate are permanently re-arranged under a high electric field. A typical poling period of PPLN crystal for MIR (\( \sim 3 \mu \)m) applications is around 30 \( \mu \)m. Using periodical poling, QPM can be done for the crystal orientation which has the strongest nonlinearity. The most common commercially available periodically poled nonlinear materials and their properties are listed in Table 2.1.
Figure 2.4: Transparency of lithium niobate between \( \sim 2 \) and \( 4 \) \( \mu \text{m} \) [21]. The absorption at \( \sim 2.8 \) \( \mu \text{m} \) is caused by OH. The measurement is carried out with the crystal used in this thesis using a Fourier transform infrared spectrometer. The crystal is 50 mm long and its both ends are antireflection coated for the pump, signal, and idler wavelengths.

2.1.4 Wavelength tuning

The wavelength of an SRO is determined by the energy conservation (Eq. 2.2) and the phase-matching condition (Eq. 2.3) within the parametric gain. While the signal wavelength is kept constant inside the SRO cavity, the idler wavelength can be tuned within the wavelength region supported by the gain curve by scanning the pump laser. Due to energy conservation, the pump frequency tuning is transferred entirely into the idler frequency. The width of the parametric gain is typically a few hundred gigahertz and using widely tunable pump lasers, it is possible to achieve wide continuous mode-hop free idler tuning ranges. For example, continuous mode-hop-free frequency-comb referenced tuning of the idler frequency over 40 GHz by pump tuning is demonstrated in Publication IV. In certain circumstances, a tuning range of up to a few terahertz can be achieved [26].

A tuning range larger than the width of the parametric gain curve requires a change in the phase-matching condition. This is typically done by changing the temperature of the nonlinear crystal. The temperature adjustment will change the length of the poling period by the thermal expansion. The effective poling period will also depend on the temperature dependence of refractive indices. Hence, a wide gapless tuning range is possible to achieve by combining the coarse temperature tuning of the crystal and the pump laser fine tuning [20]. A typical PPLN crystal has several poling periods in a single or fan-out configuration for different wavelength regions (see Fig. 2.5).

In addition, the signal frequency of an SRO depends on the cavity length (\( L_{\text{cav}} \)). The SRO tends to oscillate at the cavity mode that experiences the largest net gain, which is typically close to the maximum of the parametric gain curve. The parametric gain curve is usually wide compared to the spacing of the cavity modes. This is illustrated in Fig.
2.6. The spacing between two adjacent modes is called free spectral range (FSR) and it is determined for a standing wave cavity as $\text{FSR} = \frac{c}{2L_{\text{cav}}}$. A typical FSR of an SRO is $<1 \text{ GHz}$. Ambient perturbations (such as temperature variations and air flows) can cause frequency fluctuations of the cavity modes and the parametric gain, leading to mode-hops. These mode-hops can be prevented or reduced by stabilizing the crystal temperature and by covering the SRO cavity [20,27]. Often, an etalon is also placed inside the SRO cavity for improved single-mode operation and/or for frequency tuning [28–31].
CHAPTER 2. LASER SOURCES

2.2 Optical frequency comb

The frequency of electromagnetic waves in the optical region is typically hundreds of THz. Historically, absolute phase-coherent measurements of these frequencies have been challenging [33]. Electronically it is possible to measure and create directly radio frequencies (RFs) up to a few hundreds of GHz. The most stable and accurate frequency standards today are carried out in the RF region based on the 9.2-GHz cesium and the 1.42-GHz hydrogen hyperfine transitions of which the cesium transition defines the second in the international system of units (SI). An absolute measurement of frequency must be based on the time unit second, so the measurements in the optical region require a phase-coherent link to the microwave region.

In the past, there were only a few optical frequencies that were known relative to the primary standard and could be used as references for accurate frequency measurements in the optical region. These measurements were produced using frequency chains, which were complicated and their use required a lot of effort. The first phase-coherent measurement of visible radiation was performed as late as in 1996 [34].

A direct phase-coherent link between the radio frequencies and optical frequencies became possible at the end of the 1990s by the demonstration of the optical frequency comb (OFC) generator [35, 36]. The spectrum of a fully stabilized OFC consists of numerous equidistant laser lines whose frequencies are known extremely accurately. The OFC allows direct absolute measurement of any frequency within the comb range by optical heterodyne detection. The optical frequency comb has revolutionized the field of metrology since its discovery. It has enabled measurements of fundamental constants [37,38], frequency of lasers stabilized on transitions of atoms or molecules [17], or trapped and cooled ions [18] or atoms [19]. In particular, it has provided a versatile tool for spectroscopy to synthesize and measure optical frequencies with extremely low relative uncertainties [39–43], typically ranging from $10^{-13}$ to $10^{-15}$.

2.2.1 Principle of optical frequency comb

Consider a femtosecond mode-locked pulsed laser emitting a train of pulses with a repetition rate of $f_{\text{rep}}$. The pulsed laser has a wide spectrum due to the extremely short pulse duration. The electric field of the pulses circulates inside the laser cavity with a carrier frequency $f_c$ and can be represented as $E(t) = A(t)e^{-i(2\pi f_c)t}$. The pulse envelope function $A(t)$ is periodic in time having a period of $1/f_{\text{rep}}$, where the repetition rate of the pulses depends on the length $L_{\text{cav}}$ of the laser cavity and the group velocity $v_g$ of the pulse as $f_{\text{rep}} = v_g/2L_{\text{cav}}$. In frequency space, this periodicity of pulses creates regularly spaced frequency modes around the carrier frequency where the distance between adjacent modes is the repetition rate of the pulses (see Fig. 2.7). However, the pulses can have a constant pulse-to-pulse phase shift between the electric field and the pulse envelope. This phenomena shifts the spectrum of the comb by a factor of $f_{\text{CEO}}$ from zero and is referred to as carrier-envelope offset (CEO).

Taking the CEO into account the electric field can be now described as Fourier expansion [44]
where c.c. is the complex conjugate. The Fourier transformation of this equation corresponds to a comb spectrum in the frequency space. The frequency of the nth mode of the comb can be simply described as

\[ f_n = n f_{\text{rep}} + f_{\text{CEO}}. \] (2.6)

Figure 2.7: The principle of an optical frequency comb and f − 2f self-referencing technique.

In the optical region, n is usually a large number of the order of 10^6. Typically the pulse repetition rate and the CEO frequency are from tens of MHz to a few GHz and can be stabilized to a radio frequency standard, such as an atomic clock. The \( f_{\text{rep}} \) can be easily measured with a fast photodiode, whereas the measurement of the \( f_{\text{CEO}} \) is more difficult. It can be measured using an interferometric \( f − 2f \) self-referencing technique. The principle of this technique is schematically shown in Fig. 2.7. The comb frequency \( f_n \) from the red part of the spectrum is frequency doubled to a frequency \( 2f_n = 2(n f_{\text{rep}} + f_{\text{CEO}}) \). If the comb extends over an optical octave the doubled frequency \( 2f_n \) can be compared in a heterodyne measurement with the comb component \( f_{2n} = 2n f_{\text{rep}} + f_{\text{CEO}} \) in the blue part of the spectrum. The beat note of the heterodyne measurement between the frequency doubled mode and the mode \( 2n \) directly gives the value of the offset frequency since \( 2(n f_{\text{rep}} + f_{\text{CEO}}) - 2n f_{\text{rep}} + f_{\text{CEO}} = f_{\text{CEO}} \). When the \( f_{\text{rep}} \) and \( f_{\text{CEO}} \) are phase stabilized to a radio frequency standard, its accuracy is shifted to the optical region of the electromagnetic spectrum providing the phase-coherent link between radio and optical frequencies. In Publication IV, the repetition rate of 100 MHz and the CEO frequency of
20 MHz of a commercial OFC were stabilized to a hydrogen maser, which has a relative frequency stability of about $10^{-13}$ in 1 s.

The absolute frequency $f_{laser}$ of a laser within the comb spectrum can be determined from the beat note $f_{beat}$ between the laser and the closest comb line as

$$f_{laser} = nf_{rep} + f_{CEO} + f_{beat}. \quad (2.7)$$

The multiple integer (mode number) $n$ can be determined from a coarse measurement with a wavemeter or by measuring the beat note with at least two different mode numbers ($n$ and $n + 1$), which requires a change of the repetition frequency of the comb. However, normally this is not necessary because many laser frequencies are already known at a level much better than the comb mode spacing.

The first fully stabilized optical frequency combs were based on Kerr-lens mode-locked Titanium-sapphire (Ti:sapphire) lasers [33,35] whose spectra were broadened in a highly nonlinear microstructured fiber to cover a full octave between 500 and 1000 nm. Nowadays, fiber laser based solutions have become more popular because they provide higher stability and are more user-friendly. The most common realizations are based on erbium-[45] and ytterbium-doped [46] fiber lasers emitting around 1550 nm and 1030 nm, respectively. The spectrum of such femtosecond laser can also be broadened in a highly nonlinear microstructured fiber to cover a full octave [45, 46]. The erbium-based frequency comb produces a spectrum in the near-infrared region between 1100-2100 nm and can also be exploited as a frequency ruler for high spectral resolution spectroscopy in the mid-infrared region, as described in Publication IV. Optical frequency comb assisted mid-infrared spectroscopy is discussed in more detail in section 3.4.
Chapter 3

Laser absorption spectroscopy

3.1 Absorption of light

The familiar Beer-Lambert law expresses the transmitted intensity $I$ of the simplest direct absorption experiment (see Fig. 3.1) for a gas at frequency $\nu$, temperature $T$, and at pressure $p$ in the linear (weak field) regime according to

$$I(\nu, L_{OPL}) = I_0 \exp(-\alpha(\nu, T, p)L_{OPL}),$$

where $\alpha(\nu, T, p)$ is the absorption coefficient, and $L_{OPL}$ is the optical path length (OPL). The absorption coefficient $\alpha(\nu, T, p)$ can be expressed as [47]

$$\alpha(\nu, T, p) = S_{\eta\eta'}(T)f(\nu, \nu_{\eta\eta'}, T, p)N,$$

where $S_{\eta\eta'}$ is the line intensity for a non-degenerate transition at frequency $\nu_{\eta\eta'}$ between lower and upper states $\eta$ and $\eta'$, $f$ is the area-normalized line profile function, and $N$ is the number density of absorbing molecules. The spectral line intensity for a single molecule at HITRAN reference temperature $T_{ref} = 296K$ for the two states of a vibrational-rotational system is [47]

$$S_{\eta\eta'}(T_{ref}) = \frac{h\nu_{\eta\eta'}}{c} \frac{n_{\eta}}{N} (1 - \frac{g_{\eta}n_{\eta'}}{g_{\eta'}n_{\eta}})B_{\eta\eta'}$$

![Figure 3.1: A direct laser absorption experiment.](image)
where $B_{\eta \eta'}$ is the Einstein coefficient for induced absorption, $n_\eta$ and $n_{\eta'}$ are the populations of the lower and upper states, respectively, $g_\eta$ and $g_{\eta'}$ are the state statistical weights, and $\hbar$ is the Planck constant. The temperature dependent line intensity $S_{\eta \eta'}(T)$ can be calculated from the line intensity at reference temperature $S_{\eta \eta'}(T_{\text{ref}})$ according to [47]

$$
S_{\eta \eta'}(T) = S_{\eta \eta'}(T_{\text{ref}}) \frac{Q(T_{\text{ref}})}{Q(T)} \exp\left(-\frac{\hbar c E_\eta}{k} \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}} \right)\right) \frac{1 - \exp\left(-\frac{\hbar c E_{\eta'}}{kT_{\text{ref}}}\right)}{1 - \exp\left(-\frac{\hbar c E_{\eta'}}{kT}\right)},
$$

(3.4)

where $Q(T)$ is the total internal partition sum, $E_\eta$ is the lower state energy, and $k$ is the Boltzmann constant. The third term in Eq. 3.4 accounts for the ratio of Boltzmann populations between temperature $T$ and the reference temperature $T_{\text{ref}}$, and the last term for the effects of stimulated emission.

At pressures below 0.1 atm ($<100$ mbar, $<100$ Torr), the frequency dependence (broadening) of the absorption line profile is mostly determined by the Doppler effect caused by the thermal motion of the absorbing molecules relative to the light source. At a given temperature, different velocities determined by the Maxwell-Boltzmann distribution cause different Doppler shifts. The resulting line profile is called the Doppler profile. The Doppler profile, the function $f$ in Eq. 3.2, is defined as

$$
f(\nu, \nu_{\eta \eta'}, T) = \frac{1}{\gamma_D(T) \sqrt{\pi}} \exp\left(-\frac{(\nu - \nu_{\eta \eta'})^2}{\gamma_D(T)}\right)
$$

(3.5)

where $\gamma_D(T)$ is the Doppler profile’s full width at half maximum (FWHM) in frequency units (Hz) and it can be calculated as [48]

$$
\gamma_D(T) = 7.16 \cdot 10^{-7} \nu_{\eta \eta'} \sqrt{\frac{T}{M}}
$$

(3.6)

where $M$ is the molar mass.

An uncertainty in the energy of the states involved in the transition causes natural broadening of the line profile, and is characterized by a Lorentzian profile. Furthermore, the collisions between molecules interrupt the emission process decreasing the lifetime (broadening the line). This pressure dependent effect can also be characterized by a Lorentzian profile as

$$
f(\nu, \nu_{\eta \eta'}, T, p) = \frac{1}{\pi} \frac{\gamma(p, T)}{\gamma(p, T)^2 + (\nu - \nu_{\eta \eta'})^2}
$$

(3.7)

where $\gamma(p, T)$ is the FWHM of the Lorentzian profile. In many circumstances, the measured line profile is affected by both broadening mechanisms, and can be described as a convolution of the Doppler and the Lorentzian profiles, which results in a Voigt profile [48]. The normalized (area = 1) Lorentzian, Gaussian and Voigt line profiles of equal halfwidths are shown in Figure 3.2. For example, in the $3 \mu$m region, at a typical pressure of $\sim 0.1$ atm used in this thesis, the Lorentzian (pressure broadening) and Gaussian FWHMs are
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Figure 3.2: The area-normalized Gaussian (red), Lorentzian (blue) and Voigt (black) line profiles of equal halfwidths.

around 300 MHz for methane. The natural linewidth of methane ro-vibrational transitions in the MIR region is very narrow, even less than 100 Hz. Normally, the pressure broadened linewidth of a molecular transition in the MIR region is a few GHz at atmospheric pressure. The high resolution spectra fittings in Publication IV have been performed using an approximate solution [49] for Voigt line profile to speed up the fitting routine.

3.2 Continuous-wave cavity ring-down spectroscopy

The sensitivity of direct absorption spectroscopy is limited by the relatively short optical path length. Cavity ring-down spectroscopy (CRDS) is a technique where the OPL is enhanced by using an optical cavity [8, 50–53]. In CRDS, the laser beam is coupled into an external high-quality optical cavity, which is typically formed by two highly reflecting mirrors. The quality factor of the cavity is related to the reflectivities ($R$) of the mirrors through so-called finesse $F = \pi \sqrt{R/(1 - R)}$ [48]. The effective optical path length ($L_{\text{eff}} = 2F L_{\text{cav}}/\pi$) of the cavity can reach up to several kilometers already with a moderate finesse of ~5000 and a typical cavity length ($L_{\text{cav}}$) of 0.5 m.

Originally, the cavity ring-down technique was invented for measuring the reflectivity of mirrors in the early 1980s [54], but later in the same decade O’Keefe et. al. [55] noticed its usefulness for spectroscopy. Continuous-wave CRDS was introduced by Romanini et. al. [56] in 1997. A typical CW-CRDS setup is shown in Fig. 3.3. It consists of a tunable laser, whose output beam is passed through an acousto-optical modulator (AOM). The AOM is used as an optical switch to interrupt continuous light injection into the ring-down cavity (RDC). The light leaking out of the cavity is focused by a lens on the photodetector (PD).

The principle of CRDS is to measure the rate of absorption instead of the light intensity. When the light injection is interrupted, the intensity of light inside the cavity decays exponentially with a time constant $\tau$ [54, 55], which is called the ring-down time of the cavity. The ring-down time of the empty cavity ($\tau_0$) depends only on the reflectivity of
the mirrors (R) and the length of the cavity ($L_{\text{cav}}$). In the presence of an absorber, the ring-down time ($\tau$) is shorter due to the molecular absorption losses ($\alpha$) inside the cavity

$$\tau = \frac{L_{\text{cav}}}{c(1 - R + \alpha L_{\text{cav}})}.$$  \hfill (3.8)

The spectrum is obtained from the variation of the cavity ring-down time as a function of the laser frequency. The ring-down time does not depend on the initial power, which makes the CRDS independent of laser power fluctuations. The absorption coefficient (in cm$^{-1}$), at frequency $\nu$, can be calculated from the ring-down time variation as

$$\alpha(\nu) = \frac{1}{c} \left( \frac{1}{\tau(\nu)} - \frac{1}{\tau_0} \right).$$  \hfill (3.9)

The relative concentration ($C_{\text{rel}}$) of a molecular species in the sample can be calculated from the integrated absorption coefficient $\alpha_{\text{int}} = \int \alpha(\nu) \, d\nu$ as

$$C_{\text{rel}} = \frac{\alpha_{\text{int}}}{S_{\eta'\eta'}(T)N}.$$  \hfill (3.10)

It is worth mentioning that Eq. 3.10 is only valid for small absorption ($\alpha < 0.05$), when the Beer-Lambert law can be linearized. One of the benefits of CRDS is that, if the line intensity $S_{\eta'\eta'}(T)$ of the probed molecular transition is known, the measurement is calibration-free. It is clear that the sensitivity of CRDS depends on the molecular transition being probed, which favours the use of strong fundamental ro-vibrational transitions in the mid-infrared region for trace gas detection.

### 3.2.1 Off-axis injection with re-entrant configuration

The frequency resolution of a passive CRDS cavity is limited by the transmission comb determined by the cavity FSR (see Fig. 3.4). Normally, the injected laser beam is mode
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Figure 3.4: Schematic picture of transmission patterns of the conventional “on-axis” (left) and off-axis re-entrant (right) CRDS cavity within a molecular absorption profile.

matched to the lowest transverse electro-magnetic mode (TEM\(_{00}\)) of the cavity. The formula of eigenfrequencies \(\nu_{q,mn}\) of a spherical cavity formed by two mirrors is given by [57]

\[
\nu_{q,mn}^{\text{spherical}} = \frac{c}{2L_{\text{cav}}} \left[ q + (m + n + 1) \frac{\theta}{2\pi} \right],
\]  

(3.11)

where \(q\) is the longitudinal mode index, \(m\) and \(n\) are transverse mode indices \(\theta = 2 \arccos g\) is the Gouy phase shift of the TEM\(_{00}\) mode, and \(g = 1 - L_{\text{cav}}/R\) is the geometric cavity parameter. Generally, high spectral resolution is achieved by measuring the RD-signal with different cavity lengths [56, 58]. The cavity length is typically controlled with a piezoelectric transducer (PZT) attached to one of the cavity mirrors [56]. A small change in the cavity length shifts the eigenfrequencies according to Eq. 3.11, where already a \(\lambda/2\) change in length corresponds to one FSR shift in frequency. It is also clear that the spectral resolution improves if the cavity length is increased, but in many cases long cavities are impractical to use and more sensitive to ambient noise and vibrations. A typical 0.5 m cavity length corresponds to a FSR of 300 MHz, which would give only a few measurable data points within a molecular absorption profile at the typical measurement conditions used in this thesis (see section 3.1 or 3.2.2).

Alternatively, the spectral resolution of a CRD-measurement can be enhanced by using an off-axis (OA) injection technique [50, 51, 59–63]. Using the OA injection, it is possible to produce a dense or almost continuous cavity transmission comb, without active cavity modulation (see Fig. 3.4). Originally, the off-axis injection was used to create long optical path lengths in multipass cells [64, 65]. The dense transmission comb owes to the excitation of high order transverse electromagnetic modes of the cavity. Its use in cavity-enhanced absorption spectroscopy (CEAS) was first reported by Meijer et. al. [66] in 1994. Typically OA injection is used for integrated cavity output spectroscopy (ICOS) [51, 60], but it has been utilized for cavity ring-down spectroscopy as well [51, 52]. A real advantage of this approach is that the dense mode pattern enables rapid trace gas detection with high spectral resolution using fast tunable lasers [52, 60].
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The theory of off-axis technique can be derived by geometrical optics [64,65,67] or wave optics analysis [68]. The geometrical approach is presented in more detail in Publication I. In normal CRDS, the beam is injected into the cavity along the optical (on)-axis and the beam repeats itself every round trip. This is not the case in off-axis injection. The propagation of the beam during one round trip of the off-axis cavity can be described by a transfer matrix $T$, where the position $x_N$ and direction (angle $\varphi_N$) on the rear mirror after $N$ round trip can be expressed as

\[
\begin{pmatrix}
\varphi_N \\
x_N
\end{pmatrix} = T^N \begin{pmatrix}
\varphi_0 \\
x_0
\end{pmatrix},
\]

where $x_0$ and $\varphi_0$ are the beam initial position on the rear mirror and the angle between the ray and the optical axis, respectively. The off-axis injected beam repeats itself on the rear mirror after $N$ round trips if the transfer matrix $T^N$ is identity matrix $I$. The number $N$ is called the re-entrant order of the chosen cavity configuration. This happens if the cavity length is chosen as

\[
L_{\text{re-entrant}} = R\left[1 - \cos\left(\frac{K\pi}{N}\right)\right],
\]

where $K$ represents how many times the ray trajectory cycles around the optical axis. With the re-entrant length, the eigenfrequency formula becomes

\[
\nu_{q,mn}^{\text{spherical}} = \frac{c}{2LN} \left[Nq + (m + n + 1)K\right].
\]

If the re-entrant condition is fulfilled, the cavity length provides degeneracy of transverse modes where every mode family is separated by $K/N$. This divides the FSR to $N$ groups of degenerated modes which are equally frequency-spaced [67]. Due to the exact re-entrant length ($L_{\text{re-entrant}}$) of the RD-cavity, the off-axis technique provides a calibrated frequency axis with a better spectral resolution than the conventional on-axis injection technique.

In the MIR region, the off-axis injection has previously been used only for the integrated cavity output spectroscopy (ICOS) [59–63]. In this thesis, off-axis re-entrant CRDS has been utilized for the first time in the MIR. A detailed description of the developed measurement setup (Fig. 3.5) can be found in Publication I. In short, a simple two-mirror CW-SRO was used as the light source [20, 21]. The OPO pump laser system has a fast (up to 750 GHz s$^{-1}$) mode-hop-free tuning range of $\sim$100 GHz at 1064 nm. The SRO provides a high output power ($>0.5$ W) in the wavelength region 2.75 – 3.45 $\mu$m. The high SRO power is useful for reaching a good signal to noise ratio (SNR) in the measurement, since the optical power is divided equally between the generated modes, each group of modes having $1/N^2$ of the initial power [67].

An acousto-optic modulator (AOM) was used as an optical switch to interrupt light injection into the cavity so that a ring-down signal could be recorded. The ring-down cavity was formed by two concave mirrors which were connected to each other with a tube of flexible stainless steel. The re-entrant length of the cavity is 0.293 m ($K = 1$ and $N = 4$). The purpose of the "mode-matching" optics (M1 and M2) was to reshape the beam profile so that it would excite as many high order TEM$_{nm}$ ($n, m > 0$) modes of the ring-down cavity as possible [69]. The MIR beam leaking out of the cavity was focused on
### 3.2.2 Formaldehyde detection with off-axis re-entrant CRDS

The instrument described in the previous section can be used to record a spectrum with good resolution and high speed by scanning the fast tunable laser over several FSRs of the cavity. Since the cavity length is fixed, the system is simple compared to, for example, laser-locked CRDS instruments [70, 71], where the cavity length is actively locked to the laser frequency. In Publication I, the performance of the off-axis spectrometer was studied by measuring a mid-infrared spectrum of formaldehyde at $2943.08 - 2943.24 \text{ cm}^{-1} (3397.62 - 3397.80 \text{ nm})$. For this, we used a mixture of 10 ppmv (parts-per-million by volume) of $\text{H}_2\text{CO}$ in nitrogen. Because of strong adsorption of $\text{H}_2\text{CO}$ on the stainless steel surfaces of the ring-down cavity, the measurements were carried out in a continuous gas flow. The measurements were recorded at room temperature and at a sample pressure of about 0.1 atm. The FWHM of a pressure-broadened peak of formaldehyde at this pressure and wavelength is about 1 GHz which would result in only two measurable data points within the absorption profile using a passive 0.293 m long on-axis CRDS system.

Experimental results for the performance of the off-axis re-entrant CRDS spectrometer and formaldehyde detection are given in Publication I. The most important conclusions of the study can be summarized as follows:

- The off-axis injection divides the original FSR of 500 MHz into four groups of degenerated modes having the effective free spectral range ($\text{FSR}_{\text{eff}} = c/2LN$) of 125 MHz, which gives the needed spectral resolution for fast trace gas detection.
• The re-entrant condition of the cavity was found to be sensitive to deviations of the cavity length from the optimum re-entrant length. Already a deviation of $\Delta L \sim 250 \, \mu m$ caused splitting of the degenerate transverse cavity modes. The splitting decreases the sensitivity of the spectrometer due to the non-uniform excitation of the cavity modes.

• The optimum trigger level for AOM switching depends on the splitting of transverse mode degeneracy caused by mirror astigmatism and other imperfections. With low trigger levels, the ring-down distributions depend on the direction of the frequency scan. Due to the imperfect cavity mode degeneracy, the timing of the excitation of the different modes is not uniform.

• A detection limit of $\sim 75$ ppb for formaldehyde at $2943.176 \, \text{cm}^{-1}$ with a signal averaging time of 1 s was achieved. This results noise equivalent absorption (NEA) coefficient of $\sim 2.5 \times 10^{-8} \, \text{cm}^{-1} \text{Hz}^{-1/2}$.

• With the fast frequency tuning of the CW-SRO, we were able to measure the formaldehyde spectrum during a fast single 5 ms long sweep of the idler frequency over the wavenumber region $2943.12 - 2943.22 \, \text{cm}^{-1}$. This corresponds to a repetition rate of 4.6 kHz for the ring-down events. An example of a measured formaldehyde spectrum at $2943.176 \, \text{cm}^{-1}$ is shown in Fig. 3.6.

![Graph](image)

**Figure 3.6:** A fast 5 ms scan of 10 ppm $H_2CO$ spectrum at a pressure of 0.1 atm [Publication 1]. The red line is the least-square Voigt line shape fit to the measured data points.

Moreover, with the developed spectrometer, there is no significant difference between the sensitivity whether the injection is on-axis or off-axis. The achieved NEA coefficient
is of the same order of magnitude as to what has previously been reported for other mid-infrared cavity-enhanced absorption spectroscopy based spectrometers [72, 73] and other fast-scanning off-axis CRDS setups [52]. The achieved detection limit for formaldehyde is about two times better than the previously reported detection limit of 150 ppb in 3 s using an off-axis integrated cavity output spectroscopy with an interband cascade laser at 2832.485 cm$^{-1}$ [63]. Also note that the line strength of the formaldehyde transition at 2832.485 cm$^{-1}$ is approximately two times stronger than that the one used by us at 2943.176 cm$^{-1}$. Thus, the detection limit of our spectrometer can be increased by shifting the detection to the longer wavelengths, which was not possible with the ring-down-mirrors used in this study.

Although the sensitivity of our spectrometer is comparable to other simple off-axis CRDS and CEAS setups, a lower data-rate normalized minimum detectable absorption can be reached with other simple CW-CRDS techniques in the near-infrared. For example, using rapidly swept cavity [74] or laser [75] designs. In conclusion, the achieved detection limit of 75 ppb for formaldehyde is about 10 times higher than that required for breath and indoor air studies, since the ambient concentration of formaldehyde is $\sim 10$ ppb. In addition to the purchase of better mirrors, the required enhancement in the sensitivity could be achieved by improving the mechanical stability of the re-entrant cavity and by increasing the scanning speed of the OPO.

### 3.3 Cantilever-enhanced photoacoustic spectroscopy

Photoacoustic (PA) phenomenon is based on the conversion of optical energy into heat. It was discovered by Alexander Graham Bell in 1880 [76]. The PA signal originates from the absorption of light, which excites the ground state molecules to higher energy levels in the sample matrix. The relaxation of these excited states can happen either radiatively by emitting photons or nonradiatively through collisions with other molecules or atoms. In the gas phase, the time between collisions is typically shorter than the radiative life time of the excited transition. Therefore the optical energy is converted into translational energy in the sample, which leads to thermal expansion and produces a pressure wave that propagates away from its origin. This pressure wave can be detected by a pressure sensor, such as a microphone. When the amplitude of light is modulated, an acoustic signal is generated at a frequency equal to that of the modulation. For small absorptions, the amplitude of the photoacoustic signal $S$ is given by [77]

$$S = P \cdot R \cdot \alpha \cdot p_a,$$

where $P$ is the optical power, $\alpha$ is the absorption coefficient, $p_a$ is the partial pressure of the sample, and $R$ describes the responses of the PA cell and the microphone.

The amplitude of the PA signal depends linearly on all of the variables in Eq. (3.15). Therefore, high-power sources like CW-SROs combined with PAS permit high sensitivity in the mid-infrared region where the absorption is strong [1, 30, 78–81]. Such measurement systems enable trace gas detection in sub-ppb concentration levels. However, the sensitivity of commonly used condenser microphones has already been pushed close to the fundamental limit. In recent years, the development in PAS research has led to novel detection schemes, where the microphone is replaced with new type pressure sensors,
such as a quartz tuning fork [82], an optical fiber based microphone [83], and an optical cantilever microphone [84]. In this thesis, a cantilever based photoacoustic detection is combined, for the first time, with a CW-SRO operating in the mid-infrared region, as well as with a commercial high power continuous-wave laser at 532 nm. The review of the cantilever principles and the results of the trace gas measurements accomplished with cantilever based photoacoustic spectrometers are presented in the following sections.

### 3.3.1 Optical cantilever microphone

The cantilever-enhanced photoacoustic spectroscopy (CEPAS) is based on an extremely sensitive miniature silicon cantilever microphone introduced by Kauppinen et al. [84,85]. A schematic picture of a microfabrication manufactured cantilever structure is presented in Fig. 3.7. The typical length \((l_c)\) and width \((w)\) of the cantilever are \(\sim 5\) mm and \(\sim 1 - 2\) mm, respectively. The cantilever has a thickness \(h\) of \(5 - 10\) \(\mu\)m, and it is separated of its thicker frame with small gap \((\Delta = 3 - 5\) \(\mu\)m) from three sides. A pressure wave makes the cantilever move like a pendulum. The movement is about two orders of magnitude larger than that of a conventional membrane microphone. The response of the cantilever is also more linear, because the cantilever is connected to its frame just on one side, and thus only the bending motion is excited.

The movement of the cantilever is measured using a Michelson type laser interferometer, which is schematically shown in Fig. 3.8. A phase detection technique that utilizes multiple photodetectors enables measurement of over \(2\pi\) phase differences [86], which increases the dynamical range of the optical microphone. The phase change of \(2\pi\) corresponds to a displacement of \(\lambda/2\) of the cantilever, where \(\lambda\) is the wavelength of the interferometer laser. A typical cantilever has a resonant frequency around 600 Hz, depending on its effective mass and string constant, and the measurement conditions [87]. The frequency response of the cantilever is virtually constant below the resonant frequency (see Fig. 3.9). This means that the modulation frequency can be chosen freely below the resonance frequency. In many cases, the best SNR is achieved with modulation frequencies between 10 and 100 Hz [86].

Even though CEPAS is a rather new technique, it has already been used with many different light sources in the near- and mid-infrared region, such as black body radiators [85,88], tunable diode lasers [89–92], MIR light-emitting diodes (LEDs) [93], and QCLs [94,95]. In the previous studies, high sensitivities and excellent trace gas detection limits have been achieved for many molecules. For example, a carbon dioxide detection limit of 300 ppb has been reported using a tunable diode laser in the near-infrared [91]. In the MIR, sub-ppb detection of formaldehyde has been reached with a QCL [95]. The best reported normalized noise equivalent absorption (NNEA) coefficient \((3\sigma)\) with CEPAS spectroscopy is \(3.4 \cdot 10^{-10}\) \(\text{W cm}^{-1} \text{Hz}^{-1/2}\), which was achieved by measuring carbon dioxide at 1568.78 nm using a tunable diode laser [92]. Nevertheless, in order to reach extremely high detection sensitivities, a high power laser source is needed. Hence, in Publication II, we have combined cantilever-based detection with a CW-SRO. We show that this combination is capable of highly sensitive trace gas detection in the mid-infrared owing to the high watt-level output power of the CW-SRO. This study and its results are summarized in the following section.
Figure 3.7: Schematic picture of a cantilever.

Figure 3.8: A Michelson type laser interferometer.
Figure 3.9: Experimental frequency response of a silicon cantilever microphone without modulation (black) and with 90 Hz modulation of the optical power (red). The wide peak at around 600 Hz is the resonant peak of the cantilever. In addition to the sharp peak at the modulation frequency of 90 Hz, peaks at the harmonics of the modulation frequency are also observed.

3.3.2 Detection of HCN and CH$_4$ in the mid-infrared

The SRO-CEPAS system was used to measure HCN and CH$_4$ in the mid-infrared. The measurement setup presented in Publication II is shown in Fig. 3.10. The CW-SRO was similar to the one described in section 3.2.1 [20,21] except that the SRO cavity was a four mirror bow-tie ring cavity. The wavelength of the CW-SRO was tunable between 3.0 and 3.4 µm (3330 to 2950 cm$^{-1}$), where the single-mode idler output power was over 0.5 W. The long-term linewidth of the idler beam was of the order of 1 MHz. The idler wavelength was monitored with a wavemeter. Most of the idler power was focused through a commercial cantilever-enhanced photoacoustic analyser (PA201) manufactured by Gasera Ltd. The PA cell was 95 mm long and 4 mm in diameter with a total volume of about 7 ml. The transmitted SRO power was monitored after the analyser by a power meter (PM). The SRO wavelength was modulated at the frequency $f = 70$ Hz. The PA signal was detected at the harmonic frequency $2f$. The measurements were recorded at a sample temperature of 50°C and at a sample pressure of $\sim 400$ mbar ($\sim 0.35$ atm).

Photoacoustic spectroscopy is not an absolute absorption technique and needs to be calibrated with a reference gas. The calibration measurements were carried out by recording the photoacoustic signal with five different HCN concentrations, ranging from 8 ppb to 320 ppb. The calibration curve in Publication II shows a linear behaviour of the CEPAS signal as a function of HCN concentration measured at the center of the HCN transition at 3331.58 cm$^{-1}$. With the CW-SRO power of 0.5 W, a detection limit (1σ) of 190 ppt in 1 s was reached, which is, to our knowledge, the lowest HCN detection limit ever reported using PAS. This yields an NNEA of $1.8 \times 10^{-9}$ W cm$^{-1}$ Hz$^{-1/2}$. Hydrogen cyanide has also been measured with an OPO based PAS system [96]. In this study, a detection
limit of 400 ppt in 10 s at 3287.25 cm$^{-1}$ was reached. In addition, hydrogen cyanide has been measured with another novel PAS system. A detection limit (1$\sigma$) of 155 ppb in 1 s yielding an NNEA of $4.3 \times 10^{-9}$ W cm$^{-1}$ Hz$^{-1/2}$ has previously been reported using a PAS method where a quartz tuning fork is used as a pressure sensing element [97]. In this quartz enhanced photoacoustic spectroscopy (QEPAS) study, a 50 mW telecom diode laser was used to measure an HCN line at 6539.11 cm$^{-1}$.

The results reported in this thesis and in Publication II show the potential of our CW-SRO based CEPAS for significant enhancement in the sensitivity of PAS gas detection. However, it is worth noting that the CW-SRO power fluctuations become the dominant noise source in the measurement system when measuring high concentrations. This is illustrated in Fig. 3.11, where the behavior of the signal to noise ratio is shown as a function of PA signal level. The effect of SRO intensity noise is small or comparable with other noise sources up to 50 ppb and the SNR increases linearly. After that, the slope of the SNR starts to decrease and saturates at around 200 with high HCN concentrations. Consequently, this behavior is not critical for the performance of the measurement system when measuring low concentrations.

Figure 3.12 shows the result of a stability measurement of the SRO-CEPAS system. We used Allan deviation [98] to investigate of the optimum averaging time of the SRO-CEPAS system. Because of strong adsorption of HCN on the gold coated surfaces of the photoacoustic cell, we used methane for this measurement. The measurements were done by measuring the CEPAS signal at the center of the methane absorption line at 3057.68 cm$^{-1}$. A detection limit of 65 ppt with an averaging time of 30 s was reached when the CW-SRO power fluctuations were compensated. This is $\sim$4 times better than what can be obtained without the compensation (Fig. 3.12). In comparison with our results, a detection limit of $\sim$200 ppt with an averaging time of 100 s has been previously reported for methane using a CEPAS setup with a black body radiation source [85]. To the best of our knowledge, our detection limit is approximately by a factor of three better than the best previously reported photoacoustic spectroscopy measurement done with a mid-infrared CW-OPO and a resonant cell [78].
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Figure 3.11: Signal to noise ratios (SNRs) for different PA signal levels at the center of the absorption peak at 3331.584 cm$^{-1}$ with an OPO power of 0.6 W. The inset shows the SNR over a wider PA signal level range. The red slope is a linear least-square fit to the first three points of the SNR vs. the PA signal level plot [Publication II].

Figure 3.12: Allan deviation plots of the CEPAS system with compensation of OPO power fluctuations (red triangles) and without the compensation (black squares). The lower panel shows the measured PA signal without the power compensation [Publication II].
3.3.3 Detection of NO$_2$ using a high power green laser

Usually the best detection limits of trace gases are achieved by measuring their fundamental ro-vibrational transitions in the MIR region. However, usually, electronic transitions in the visible region are much stronger and, therefore, provide better sensitivity. One such example is nitrogen dioxide (NO$_2$), which has almost two orders of magnitude stronger absorption at around 400 nm than in the MIR region at 3.4 $\mu$m. The fundamental ro-vibrational transitions at around 6.1 $\mu$m are even almost five times weaker than the visible transitions. Publication III reports a CEPAS system, which is applied to NO$_2$ detection in the visible region. Nitrogen dioxide is a highly reactive gas and also an air pollutant that is released to the atmosphere mainly by combustion processes. The troposphere NO$_2$ concentration varies depending on the geographical location. It is typically a few tens of ppb, but can be in the sub-ppb level in clean areas and rise up to the ppm range in highly polluted areas. Since nitrogen dioxide has a wide and strong absorption spectrum in the visible region between 250 and 650 nm [99], a commercial high power continuous-wave intra-cavity frequency doubled Nd:YVO$_4$ laser at 532 nm was used as a light source. It is also worth mentioning that nowadays there are commercially available compact and affordable green lasers with relatively high output powers. Such a laser combined with the simple and sensitive measurement system described in this thesis provides an NO$_2$ sensor, which is capable of \textit{in situ} measurements with high sensitivity.

The experimental setup (Fig. 3.13) of the CEPAS system used Publication III is similar to the one described in Publication II. The same CEPAS unit model (Gasera, PA201) was used. The laser has a maximum optical output power of 10.5 W. The amplitude of the laser output was modulated at a frequency of 90 Hz using a chopper with a duty cycle of 50%. The measurements were recorded at room temperature (23°C) and at a sample pressure of 360 mbar (~0.35 atm).

The results of the experimental study for the performance of the CEPAS spectrometer are given in Publication III. The most important conclusions of the study can be summarized as follows:

- With the maximum laser power of 4.7 W, an NO$_2$ detection limit (1$\sigma$) of 50 ppt in 1 s was achieved.
- A linear increase of the CEPAS signal was observed within the entire optical power range without any indication of photochemical dissociation of NO$_2$.
- A normalized noise equivalent absorption coefficient of $2.6 \times 10^{-10}$ W cm$^{-1}$ Hz$^{-1/2}$ was obtained.

To our knowledge, the achieved NO$_2$ detection limit of 50 ppt (1 s) is the best that has been reported using photoacoustic spectroscopy [100]. Our excellent detection limit is mainly due to large electronic transition moment and the stable high power laser operating in the region where the photochemical dissociation does not occur [101]. Moreover, the high stability of the system makes it possible to improve the detection limit to as low as a few parts-per-trillion by using longer averaging times [Publication III]. Altogether, the NO$_2$ detection limit demonstrated here is among the best ever reported, even when comparing to more complex laser spectroscopy methods. For example, a detection limit (2$\sigma$) of 22 ppt in 1 s has previously been reported using cavity ring-down spectroscopy in the
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Figure 3.13: A schematic picture of the SRO-CEPAS setup [Publication III].

blue region [11]. With a more conventional NO$_2$ detection setup based on laser induced
fluorescence, a detection limit (1$\sigma$) of 15 ppt in 10 s has been reported [102].

3.4 Optical frequency comb assisted mid-infrared spectroscopy

It is difficult to exaggerate the impact of the optical frequency comb on absorption spec-
troscopy. The OFC is a versatile light source that provides excellent frequency accuracy
and high spectral purity within a broad spectral region. As mentioned in section 2.2.1,
optical frequency combs are commonly based on mode-locked Ti:sapphire lasers (0.5-1.1
µm) or mode-locked Er-doped fiber lasers (1-2 µm). They can be directly applied to
spectroscopy, enabling measurements of broad spectral spans at once [39, 103, 104]. An
individual comb mode can also be applied to probe narrow (< $f_{rep}$) one- or two-photon
excited atomic transitions [105, 106]. High finesse optical cavities have been used to in-
crease the sensitivity of direct OFC spectroscopy [40, 107–110]. Dual comb spectroscopy
utilizes the combination of two frequency combs with slightly different repetition rates as
an interferometric setup [111,112], which allows fast multiheterodyne spectroscopy over a
broad spectral range. In turn, a tunable single-frequency laser referenced to an OFC can
be used to measure gas absorption line parameters, such as line strength, center frequency,
width, and line broadening coefficients with high resolution and accuracy [41,43,113,114].

The extension of mode-locked laser based frequency combs to the MIR region has
proven difficult [115]. Although a mid-infrared comb can be realized using nonlinear
frequency conversion starting from a near-infrared frequency comb [116–129], these tech-
nologies are still rather complex. Thereby, MIR high precision spectroscopy is often done
by referencing the MIR laser source to an NIR OFC via nonlinear frequency conversion.
Figure 3.14 presents three often used approaches based on the frequency conversion in a
second order nonlinear crystal.

Difference frequency generation between two CW NIR laser sources produces MIR
radiation. Since the energy is conserved in the DFG process (see Eq. 2.2), the absolute
MIR (idler) frequency can be determined by measuring the pump and signal frequencies
with an OFC [130,131]. An advantage of DFG-based methods is that the carrier-envelope
Figure 3.14: Schemes for referencing a mid-infrared continuous-wave laser source to an OFC, based on nonlinear optical frequency conversion. The abbreviations DFG, SFG, and OPO stand for difference frequency generation, sum frequency generation, and optical parametric oscillator, respectively.

offset frequency of the comb is cancelled and the frequency of the idler can be determined as $f_{\text{DFG}} = (n_p - n_s)f_{\text{rep}} + f_{\text{beat}}^p - f_{\text{beat}}^s$. The $n_p$ and $n_s$ are the numbers of the closest comb modes of the pump and signal frequencies, respectively, and $f_{\text{beat}}^p$ and $f_{\text{beat}}^s$ are the corresponding beat frequencies of the pump and signal between the closest comb modes, respectively. Hence, only the repetition frequency of the comb needs to be stabilized in order to measure the absolute frequency of the MIR beam. The DFG-based frequency-comb referenced spectrometers have been used, for example, to measure absolute frequencies of CO$_2$ transitions near 4.2 µm [130] and CH$_4$ around 3.4 µm [131–133]. These high-precision spectroscopy setups are typically based on PPLN crystals, whose transparency starts to decrease above 4 µm (see Fig. 2.4). In addition, the optical power produced by CW-DFG in the mid-infrared is typically in the sub-milliwatt range.

In longer wavelengths, including most of the molecular fingerprint region, a different referencing scheme, such as SFG [134–143], is typically used. Commonly, the referencing process is implemented by taking a narrow part of the comb spectrum or a comb-referenced CW-NIR laser, which is then mixed, for instance, with the light of a QCL [134–140] or a CO$_2$ laser [141–143]. The SFG process produces a new frequency within the spectral region of the near-infrared comb. The SFG method is also independent of the carrier-envelope-offset frequency. Most spectroscopic studies with comb-referenced QCLs have been carried out around the 4.5 µm region [136–140]. However, the SFG referencing scheme has also been applied to phase-lock a QCL [135] at 9 µm and a CO$_2$ laser [141, 142] at 10 µm to an OFC.

The absolute frequency measurement of the idler beam of an OPO is usually done by measuring the frequencies of the near-infrared pump and signal beams with an OFC [144–147]. Often, the signal and pump frequencies are phase-locked to the comb in which case the wide scanning range of the idler is difficult to reach. The scanning of the repetition rate of the OFC results in scanning of both pump and signal frequencies, and since the signal is resonating inside the OPO cavity with a typical FSR of < 1 GHz, the mode-hop free tuning range is limited approximately to a FSR/2. This problem can be avoided by using an electro-optic modulator for scanning only one of the offset-locked frequencies, but even then the continuous scanning range of the MIR frequency is small, typically a few tens of MHz [144]. A much wider tuning range has been demonstrated only
recently, using a novel method that is not limited by the tuning range of the electro-optic modulator [148].

In Publication IV, a novel scheme for referencing the idler frequency of a CW-SRO to a fully-stabilized NIR OFC is presented. The principle of the method is shown in Fig. 3.15. The idler frequency is frequency doubled to the near-infrared in an MgO-doped PPLN crystal, after which its frequency can be directly referenced or locked to the NIR OFC. The benefit of the method is that now only one beam needs to be locked to the comb. However, this method requires a fully stabilized OFC where also the carrier-envelope-offset frequency is known. While the doubled frequency is locked to the OFC, the frequency of the idler beam can be simply tuned by scanning the repetition rate of the comb allowing for wide continuous tuning ranges.

### 3.4.1 Frequency-comb-referenced CW-SRO for precision spectroscopy

The experimental setup presented in Publication IV is shown in Fig. 3.16. The design of the CW-SRO was similar to that described in section 3.3.2. Coarse tuning of the MIR idler wavelength between 2.7 and 3.4 $\mu$m is done by changing the poling period and temperature of the crystal. Mode-hop-free fine tuning of the MIR frequency over 100 GHz can be done by tuning the frequency of the pump laser system. The single-mode idler output power is about 0.5 W with a 1-s linewidth of $\sim$1 MHz. The frequency-doubling system used in the Publication IV allows the doubling of the idler frequency within the whole wavelength tuning range of the CW-SRO. The frequency-doubled idler beam was guided through an optical fiber link to a beat frequency measurement with a commercial, fully stabilized OFC (Menlo Systems FC1500-100). The scanning of the MIR frequency of the SRO was done by adjusting the repetition rate of the OFC. The repetition rate and the offset frequency of the OFC were referenced to an active hydrogen maser, which was traceable to the SI-second. The OPO MIR frequency was locked to the OFC by stabilizing the beat note between the frequency-doubled idler beam and the OFC to a pre-set value (typically 20 MHz) by applying a correction from a proportional-integral (PI) controller to the OPO pump laser frequency. The bandwidth of the PI control was a few tens of hertz, which was limited by the shortest available gate time (4 ms) of the
frequency counter that was used to measure the beat frequency.

![Image of experimental setup](image-url)

Figure 3.16: The experimental setup of frequency-comb-linked SRO based cavity ring-down spectrometer

### 3.4.2 Precision spectroscopy of N\textsubscript{2}O and CH\textsubscript{4}

The frequency-comb referenced CW-SRO was used as a light source for high-precision cavity-ring down spectroscopy of N\textsubscript{2}O and CH\textsubscript{4}. The CRD spectrometer is briefly described below, and more details can be found in Publication IV. A small fraction of the idler beam was on-axis coupled into a 0.5 m long ring-down cavity formed by two highly reflecting concave mirrors (see Fig. 3.16). The ring-down signal was recorded by a photodetector, after switching off the MIR beam incident on the ring-down cavity using an AOM. The driving signal of the AOM caused a 50 MHz frequency shift to the MIR beam, which was directed to the CRD measurement. The 50 MHz driving signal was referenced to the same time base (hydrogen maser) as the OFC. For high frequency resolution, the ring-down cavity frequency was matched at every measuring point to the OFC referenced idler frequency by modulating the length of the cavity using piezoelectric actuators. The modulation frequency was typically 10 to 30 Hz and the recorded ring-downs were synchronized with the OFC-measurement of the MIR frequency.

The spectrometer is capable of large, mode-hop-free scans while maintaining locking of the idler frequency of the SRO to the OFC. As an example, a 40 GHz wide spectrum of an N\textsubscript{2}O sample at 2.85 \(\mu\)m in the presence of water was measured (Fig. 3.17a). The large tuning range of the spectrometer makes frequency calibrated measurements of several transitions possible in a single scan in the wavelength region below 4.0 \(\mu\)m where QCLs are not yet available. For comparison, a relatively wide phase-locked QCL tuning
range of $\sim 20$ GHz has previously been demonstrated at 4.3 $\mu$m [140]. True phase- or frequency-locking to an OFC, in many cases, increases the measurement time of the spectrum considerably. For example, the measurement presented in Fig. 3.17a took about one hour. The same measurement could be done much faster by reducing the number of acquired data points, or by performing the measurement without locking the SRO to the comb. These kind of OFC-referenced (but not locked) spectroscopic studies have been demonstrated with QCLs [136, 139]. Knabe et al. [139] achieved a tuning rate of $\sim 0.9$ GHz/s by referencing an external-cavity QCL at 4.5 $\mu$m to an NIR OFC using a SFG-based referencing method.

As has already been mentioned, accurate calibration of the frequency axis is needed for the precision measurements of absorption line parameters, such as the line intensity or center frequency. While the frequency axis is calibrated with the OFC, the absorbance axis can be accurately measured by cavity ring-down spectroscopy (see Section 3.2). In other words, the line intensity of, e.g., a molecular transition can be measured using CRDS by measuring the spectrum of a known concentration sample in a known measuring condition. The line intensity at the measurement temperature can be calculated from the determined integrated absorption coefficient of the measured spectrum using Eq. 3.10 while the line intensity at HITRAN reference temperature $T_{\text{ref}} = 296$ K can then be calculated using Eq. 3.4.

Figure 3.17b shows a measurement of the line intensity of the R44e transition of the $\nu_1 + \nu_3$ band of $\text{N}_2\text{O}$. In the spectrum, each frequency point (black marker) is an average of 50 ring-down events recorded during 5 s and the solid (red) line is a least-square Voigt fit to them. The line intensity deduced from the integrated absorption coefficient of the fitted spectrum was $S_{\eta\eta}(296$ K) = $2.7472 \times 10^{-21}$ cm$^{-1}$/ (molecule/cm$^{-2}$). The observed value deviated only 0.25 % from the HITRAN database value of $S_{\eta\eta}(296$ K) = $2.7540 \times 10^{-21}$ cm$^{-1}$/ (molecule/cm$^{-2}$) [99]. The uncertainty of the HITRAN value is between
2 and 5%. The estimated total uncertainty of our line intensity measurement was 3.4%. The biggest contribution to the uncertainty comes from the fitting procedure (3.0%). We also tried to fit with the Galatry line profile [149–151], which takes into account the effect of collisional, so-called Dicke narrowing, but the residual of the fitted profile showed no significant difference compared to the Voigt fit (see Fig. 3.17b). The uncertainty budget includes the statistical uncertainty of the ring-down fitting of 0.3%, mole fraction of 1.5%, temperature of 0.3%, and the pressure gauge of 0.2%.

The line intensity measurement was also part of an intercomparison of mole fraction measurements of $\text{N}_2\text{O}$ within the European Metrology Research Programme project "EUMETRISPEK". Four national metrology institutes (NMIs) from Germany (PTB), Netherlands (VSL), Denmark (DMF), and Finland (MIKES) were represented. The purpose of the intercomparison was to show that reliable molecular line data is important for accurate determination of mole fractions of molecules in the gas phase. In the comparison, each NMI measured the line intensity with their own spectrometer after which it was used for the determination of the mole fraction of a gravimetrically prepared reference sample. Our measurement was in good agreement with the reference value within the reported uncertainty.

In Publication IV, we also demonstrated the capability of the OFC-locked CRD spectrometer for saturated spectroscopy by measuring R8 transition of the $\nu_3$ band of methane at 3.2 $\mu$m. Owing to the high-finesse ring-down cavity, the intracavity power easily reached the watt-level even with modest input powers. High intracavity power is sufficient to saturate the strong fundamental rovibrational transitions of many molecules within the tuning range of the spectrometer. As an example, Fig. 3.18 shows the Lamb dip (saturated absorption feature) of the $F_1^{(2)}$ R8 component of CH$_4$ transition. The high spectral resolution at the center of the transition was achieved by scanning the repetition rate of the OFC in steps of $\sim 0.5$ – 1.0 Hz ($\sim 0.5$ – 1.0 MHz in the mid-IR). In the wings of the transition, the frequency step was larger. The saturation of the absorption allowed us to carry out measurements with sub-Doppler resolution, which significantly improved the precision in determining the absorption line center. The line center determined from the Lorentzian profile fit to the sub-Doppler spectrum was 93 064 092 684 662.80 Hz, which is in good agreement with the previously reported values for the same transition. The measured value is about 530 kHz smaller than an OFC-referenced value reported by Abe et. al [133] and 2.7 MHz smaller than the value reported in HITRAN [99].

Experimental results of the performance of the frequency-comb referenced CRD spectrometer are given in more detail in Publication IV. The most important conclusions of the study can be summarized as follows:

- The frequency-doubling method for referencing an MIR CW-SRO to an OFC is capable of large mode-hop-free scans while maintaining locking of the MIR frequency to the OFC.

- The maximum mode-hop-free scanning range of the MIR frequency is 410 GHz, which is limited by the repetition rate of the comb. In practise, it was limited to 100 GHz due to the SRO pump laser tunability.

- The Allan deviation of the OFC-locked idler frequency showed the achieved frequency stability of about 50 kHz in 1 s, which corresponded to a relative frequency stability of $\sim 4 \times 10^{-10}$. 
The noise-equivalent absorption coefficient of the CRDS spectrometer was $9.8 \times 10^{-8} \text{ cm}^{-1} \text{ Hz}^{-1/2}$, which is of the same order of magnitude as the sensitivity of the off-axis CRDS spectrometer presented in Publication I.

In addition to the accurate frequency axis calibration, the spectrometer also provides an accurate absorbance axis owing to CRDS, and is suitable for saturated spectroscopy.

In addition, the required beat-note SNR for reliable frequency counting could be obtained with an MIR power of as low as 100 mW, which is already in the achievable power region of current QCLs and interband cascade lasers between the 3 and 4 $\mu$m region [152].
Chapter 4

Conclusions

Four applications of two different spectroscopic methods have been demonstrated and studied in the laboratory for high sensitivity molecular gas-phase detection and high-precision spectroscopy. Most of the studies were carried out in the mid-infrared region with the exception of nitrogen dioxide detection in the visible. The mid-infrared experiments utilized continuous-wave singly resonating optical parametric oscillator (CW-SRO), a coherent high power light source in the mid-infrared wavelength region between 3 and 4 µm, which is one of the most important spectral regions for molecular spectroscopy. The demonstrated spectroscopic applications are based on cavity ring-down spectroscopy and photoacoustic spectroscopy, including, the first off-axis re-entrant CRDS experiment in the mid-infrared, two cantilever enhanced photoacoustic spectroscopy setups, and a high-precision CRDS spectrometer.

In this thesis, measurement of numerous trace gases with extremely high sensitivity was achieved by combining a versatile CW-SRO with state-of-the-art spectroscopic methods. As an example, a detection limit of 75 parts-per-billion in 1 s for formaldehyde was demonstrated by using off-axis re-entrant CRDS in the MIR. The off-axis re-entrant configuration provides a simple system for rapid trace gas detection with high spectral resolution without modulation of the ring-down cavity. Moreover, the high output power of the CW-SRO in the MIR shows great potential for significant enhancement of the sensitivity of trace gas detection by cantilever-enhanced photoacoustic spectroscopy. Using the CW-SRO based CEPAS setup developed in this thesis, noise equivalent detection limits of 190 ppt in 1 s and 65 ppt in 30 s were achieved for HCN and CH₄, respectively.

In this thesis, a new method for referencing a MIR CW-SRO to an optical frequency comb was demonstrated. The method is based on frequency doubling of the MIR beam used for spectroscopy, after which it can be referenced to a commercially available, fully stabilized Er-fiber-laser OFC in the near-infrared region. In this method, only one beam needs to be locked to the OFC, which significantly simplifies the scanning of the MIR frequency. Another benefit of this method is that it is not restricted to parametric sources, but can also be used with any other CW laser sources that have enough power (>100 mW) for the frequency doubling and are tunable in the MIR region, between 2 and 4 µm, so that the doubled frequency overlaps with the spectrum of the Er-fiber-laser OFC. In practice, the method can be combined with any standard absorption spectroscopy technique, such as direct absorption spectroscopy, wavelength modulation absorption spectroscopy, or cavity-enhanced spectroscopy. In this thesis, high-precision cavity ring-down
spectroscopy of nitrous oxide and methane was demonstrated using an OFC-referenced CW-SRO. In general, the OFC-referenced CRD spectrometer is a versatile tool for precision spectroscopy, allowing measurements of many absorption line parameters, such as line center frequencies, line shapes, broadening, as well as line intensities.

In addition to mid-infrared spectroscopy, this thesis shows the potential of cantilever-enhanced photoacoustic spectroscopy for extremely sensitive trace gas detection in the visible region. A noise equivalent detection limit (1σ) of 50 ppt in 1 s was achieved for nitrogen dioxide. This is the best NO$_2$ detection limit that has been reported using photoacoustic spectroscopy. Commercial availability of compact and affordable green high-power lasers makes our simple measurement setup potential for substantial enhancement in the sensitivity of NO$_2$ and also the other compound measurements, which have strong absorption in the green region.
Bibliography


