Doctoral Thesis

Pulsed and modulated photoacoustic and transmission spectroscopy on trace gases employing continuously tunable CO₂-and diode-lasers

Author(s): Romann, Albert

Publication Date: 2007

Permanent Link: https://doi.org/10.3929/ethz-a-005461164

Rights / License: In Copyright - Non-Commercial Use Permitted
Pulsed and modulated photoacoustic and transmission spectroscopy on trace gases employing continuously tunable CO$_2$- and diode-lasers

A dissertation submitted to the

Swiss Federal Institute of Technology Zurich (ETH)

for the degree of

Doctor of Natural Sciences

presented by

Albert Romann
Dipl. Physiker ETH
Dipl. El. Ingenieur HTL
born 25 May 1966
citizen of Schleinikon ZH

accepted on the recommendation of

Prof. Dr. Markus W. Sigrist, examiner
Prof. Dr. Ursula Keller, co-examiner

2007
# Contents

Abstract iv  

Zusammenfassung vi

1 A brief introduction to spectroscopy and trace-gas sensing 1  
1.1 History 1  
1.2 Motivation 2  
1.2.1 Applications 3  
1.2.2 Qualitative and quantitative analysis 4  
1.3 Sensor requirements 7  
1.4 Spectroscopic techniques 8  
1.4.1 Absorption spectroscopy 8  
1.4.2 Cavity ring-down spectroscopy 9  
1.4.3 Photoacoustic spectroscopy 9  
1.5 Laser sources 9  
1.5.1 CO₂ laser 10  
1.5.2 CO laser 11  
1.5.3 Tunable diode laser 11  
1.5.4 Lead-salt diode laser 11  
1.5.5 Quantum cascade laser 11  
1.5.6 Chalcogenide laser 12  
1.5.7 Nonlinear optical frequency conversion 12  
1.6 Noncoherent sources 13  

2 Theory 14  
2.1 Light-matter interaction 14  
2.2 Frequency, wavelength, and wavenumber 14  
2.3 Absorption spectroscopy 15  
2.3.1 Beer-Lambert law 15  
2.3.2 Linestrength 16
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.3.3</td>
<td>Linewidth and line shift</td>
<td>17</td>
</tr>
<tr>
<td>2.3.4</td>
<td>Homogeneous and inhomogeneous line broadening</td>
<td>18</td>
</tr>
<tr>
<td>2.3.5</td>
<td>Natural linewidth</td>
<td>18</td>
</tr>
<tr>
<td>2.3.6</td>
<td>Doppler broadening at low pressure</td>
<td>19</td>
</tr>
<tr>
<td>2.3.7</td>
<td>Pressure broadening at high pressure</td>
<td>19</td>
</tr>
<tr>
<td>2.3.8</td>
<td>Combined broadening at intermediate pressure</td>
<td>20</td>
</tr>
<tr>
<td>2.3.9</td>
<td>Multipass cells</td>
<td>21</td>
</tr>
<tr>
<td>2.3.10</td>
<td>Practical aspects</td>
<td>21</td>
</tr>
<tr>
<td>2.4</td>
<td>Photoacoustic spectroscopy</td>
<td>22</td>
</tr>
<tr>
<td>2.5</td>
<td>Nonlinear optical frequency conversion</td>
<td>24</td>
</tr>
<tr>
<td>2.5.1</td>
<td>Second harmonic generation</td>
<td>24</td>
</tr>
<tr>
<td>2.5.2</td>
<td>Phasematching techniques</td>
<td>25</td>
</tr>
<tr>
<td>2.5.3</td>
<td>Second harmonic generation using quasi-phase matching</td>
<td>26</td>
</tr>
<tr>
<td>2.5.4</td>
<td>Quasi-phase matching materials</td>
<td>27</td>
</tr>
<tr>
<td>2.6</td>
<td>Signal extraction techniques</td>
<td>28</td>
</tr>
<tr>
<td>2.6.1</td>
<td>Definition of noise and background</td>
<td>28</td>
</tr>
<tr>
<td>2.6.2</td>
<td>Specific noise sources and backgrounds</td>
<td>28</td>
</tr>
<tr>
<td>2.6.3</td>
<td>Bandwidth narrowing techniques</td>
<td>29</td>
</tr>
<tr>
<td>2.6.4</td>
<td>Modulation techniques</td>
<td>30</td>
</tr>
<tr>
<td>2.7</td>
<td>Signal-to-noise ratio and detection limit</td>
<td>33</td>
</tr>
<tr>
<td>2.8</td>
<td>Selecting absorption features and laser wavelength</td>
<td>34</td>
</tr>
<tr>
<td>3</td>
<td>CO₂ laser-based spectrometer</td>
<td>35</td>
</tr>
<tr>
<td>3.1</td>
<td>Photoacoustic spectrometer employing two wavelengths simultaneously</td>
<td>35</td>
</tr>
<tr>
<td>3.2</td>
<td>Continuously tunable high-pressure CO₂ laser</td>
<td>36</td>
</tr>
<tr>
<td>3.2.1</td>
<td>Second harmonic generation</td>
<td>38</td>
</tr>
<tr>
<td>3.2.2</td>
<td>Summarized characteristics of the frequency doubled CO₂ laser</td>
<td>41</td>
</tr>
<tr>
<td>3.3</td>
<td>Photoacoustic cells</td>
<td>42</td>
</tr>
<tr>
<td>3.4</td>
<td>Measurements</td>
<td>43</td>
</tr>
<tr>
<td>3.4.1</td>
<td>Pressure dependence of the photoacoustic signal</td>
<td>43</td>
</tr>
<tr>
<td>3.4.2</td>
<td>Multicomponent mixture containing nitric oxide and water</td>
<td>45</td>
</tr>
<tr>
<td>3.4.3</td>
<td>Carbon dioxide measurement</td>
<td>47</td>
</tr>
<tr>
<td>3.4.4</td>
<td>Simultaneous detection at two wavelengths</td>
<td>48</td>
</tr>
<tr>
<td>3.5</td>
<td>Conclusions and further possibilities</td>
<td>50</td>
</tr>
</tbody>
</table>
## Contents

4 External cavity diode laser-based spectrometer 51

4.1 Intended use ................................................. 51
4.2 Spectrometer setups ........................................ 51
  4.2.1 Transmission spectrometer with amplitude modulation (AM) ...... 51
  4.2.2 Transmission spectrometer with wavelength modulation (WM) ...... 53
  4.2.3 Photoacoustic spectrometer with amplitude modulation (AM) ...... 53
  4.2.4 Photoacoustic spectrometer with wavelength modulation (WM) ...... 55
4.3 Equipment .................................................. 56
  4.3.1 External cavity diode laser .................................. 56
  4.3.2 Measurement cells ....................................... 59
  4.3.3 Photodetector ......................................... 62
  4.3.4 Tunics BT 1600 characterization ................................ 62
4.4 Direct absorption measurements ................................ 65
  4.4.1 Carbon dioxide in human exhaled breath .............. 65
  4.4.2 Carbon dioxide isotope ratio ............................... 65
  4.4.3 Motorcycle exhaust sample ................................ 66
  4.4.4 Methane measurement using wavelength modulation detection .... 68
4.5 Photoacoustic measurements .................................. 69
  4.5.1 Pressure dependent lineshape ................................ 69
  4.5.2 Wavelength modulation depth .............................. 70
4.6 Conclusion and further possibilities .............................. 71

Appendix A: Substances investigated 73

Appendix B: Spectral databases 76

Bibliography 78

Acronyms and symbols 91

Publications, presentations and patent 98

Supervised students and teaching activities 101

Acknowledgement 102

Curriculum vitae 104
Abstract

This thesis reports on laser-based spectroscopy for trace gas sensing in the mid- and near-infrared spectral region.

The fundamental absorption region in the mid-infrared is accessed by a photoacoustic spectrometer, which is based on a home-built, continuously tunable, high-pressure CO$_2$ laser employing periodically poled GaAs as non-linear material in first-order quasi-phase matching for second harmonic generation. Both, the fundamental 10$\mu$m- and the second harmonic 5$\mu$m-radiations are used, either individually, or, as a novel approach to trace gas sensing, simultaneously to excite the same region of the sample (i.e. coaxial beams). The continuous tunability is a crucial feature for selective detection in multi-component mixtures and is not offered by the usual line tunable CO$_2$ lasers (10$\mu$m range) or CO lasers (5$\mu$m range). The characteristics of our source include wide tuning ranges and narrow linewidths in both wavelength regions, i.e. the fundamental (9.2–10.7 $\mu$m [1087–935 cm$^{-1}$], and 540 MHz [0.018 cm$^{-1}$]) and frequency-doubled (4.6–5.35 $\mu$m [2174–1869 cm$^{-1}$], and 1050 MHz [0.0315 cm$^{-1}$]), respectively. Fundamental pulse energies range from 10 to 80 mJ, where as up to 1 mJ (typ. 0.04 to 0.4 mJ) can be achieved (external conversion efficiency up to 1.25%) in the frequency doubled regime (1 Hz repetition rate). The small photoacoustic cell (180 cm$^3$ gas volume) features an 80-microphone array and a built-in, battery-powered, low-noise preamplifier. The turbulence-free flow rate of up to 700 cm$^3$/s allows real-time monitoring of samples at room temperature and atmospheric pressures and below.

Selected measurements, emphasizing on applications of the 5$\mu$m wavelength extension of the CO$_2$ laser, are discussed. The nitric oxide $^{15}$NO/$^{14}$NO isotope ratio was measured in good agreement with the literature in a mixture containing NO and traces of water vapor (H$_2$O) as an impurity and interfering species. This demonstrates the high selectivity of the sensor. CO$_2$ was measured outside strong absorption bands to show the good sensitivity. The detection limits ($SNR$=3) of these species are 42.2 ppmV for NO, 136 ppmV for H$_2$O, and 2.55% for CO$_2$. As a novelty, simultaneous detection of NO, H$_2$O, and CO$_2$ using both laser wavelengths has been investigated and found feasible, although signal normalization issues remain.

Overtone and combination bands in the near-infrared were investigated using spectrometers based
on a fiber-coupled, continuous-wave, continuously tunable external cavity diode laser (ECDL) emitting in the telecommunication wavelength region around 1.6 μm. The source characteristics include a wide tuning range (1.54–1.66 μm, [6494–6024 cm⁻¹]) with a very narrow linewidth (<150 kHz, [0.5×10⁻⁶ cm⁻¹]) and 0.2–6.3 mW average output power. Wavelength modulation (WM) with frequencies <10 kHz can cause a maximum carrier frequency shift of ±2 GHz. Detection schemes implemented include transmission and resonant photoacoustic spectroscopy. Amplitude modulation (AM) and WM are employed with both detection schemes using a lock-in amplifier for demodulation.

The transmission spectrometer employs a White-type multipass cell (path length of 109 m at 80 passes and 4.31 sample volume) and home-made photodetectors. Measurements include the CO₂ concentration in exhaled human breath, the ν̈CO₂/ν̈CO₂ isotope ratio, and an exhaust sample from a motorcycle that demonstrates the analysis of a multicomponent sample. Detected species include CO, CO₂, methane (CH₄), and acetylene (C₂H₂). Their detection limits (SNR=3) achieved with AM are 1112 ppmV, 1390 ppmV, 39 ppmV, and 18 ppmV, respectively. Using 1f and 2f WM techniques, the detection limits (SNR=3) improve by an average factor of 4.8 and 9.3, respectively. The absorption spectrometer is now used as a teaching device for laser-based spectroscopy of trace gases for undergraduate students at the physics department of the ETH Zurich.

The resonant photoacoustic cell in Herriott-configuration (Q-factor of 70 at the resonance frequency of 1250 Hz, 2.31 sample volume, max. flow 1.5 l/min, flow mode time resolution of 5 min) employs a 16-microphone array and has a total absorption path length in the photoacoustic part of 15 m at 36 passes. An AM measurement of CH₄ resulted in a detection limit of 11 ppmV (SNR=3). This can be improved by employing WM techniques for which the optimal modulation depth is discussed.

This thesis comprises four chapters. Chapter 1 gives a brief introduction to trace gas sensing. Chapter 2 summarizes the theory relevant to the work presented. Chapter 3 reports on the frequency doubled CO₂ laser-based photoacoustic spectrometer and its applications. Finally, in chapter 4 discusses the ECDL-based transmission and photoacoustic spectrometers, as well as their operation modi and applications.
Zusammenfassung


Der Zugang zur Region der fundamentalen Absorptionen im mittleren Infrarot erfolgt durch ein photoakustisches Spektrometer, welches auf einem kontinuierlich abstimmbaren, Hochdruck-CO2 Laser (Eigenbau) basiert. Zur Frequenzverdoppe lung wird das nichtlineare Material periodisch-gepoltes GaAs in erster Ordnung Quasi-Phasenanpassung eingesetzt. Sowohl die fundamentale 10 μm, als auch die frequenzverdoppelte 5 μm Strahlung können eingesetzt werden. Entweder einzeln, oder, als Neuheit im Bereich des Spurengasnachweises', auch zeitgleich im selben Volumen (koaxiale Überlagerung beider Strahlen). Die kontinuierliche Abstimmbaarkeit der Laserquelle ist wesentlich für den selektiven Nachweis von Spurengasen. Die oft eingesetzten Alternativen, linienabstimmbare CO2 Laser (10 μm) und CO Laser (5 μm), bieten dies nicht. Die wesentlichen Eigenschaften der Quelle sind die grossen Abstimmbereiche und kleine Linienbreiten, sowohl im fundamentalen (9.2–10.7 μm [1087–935 cm⁻¹], und 540 MHz [0.018 cm⁻¹]), wie auch im entsprechenden frequenzverdoppelten Emissionsbereich (4.6–5.35 μm [2174–1869 cm⁻¹], und 1050 MHz [0.0315 cm⁻¹]). Die Pulsenergien im fundamentalen Bereich erreichen 10 bis 80 mJ bei einer Repetitonsrate von 1 Hz. Im frequenzverdoppelten Bereich werden bis zu 1 mJ (typ. 0.04 bis 0.4 mJ) erreicht (externen Konversions-Effizienz von 1.25%).

Die kompakte Photoakustik-Zelle (180 cm³ Gasvolumen) verfügt über eine 80-Mikrophon-Array mit einem integrierten, batteriebetriebenen und rauscharmen Mikrophonverstärker. Der turbulenzfrei Gasfluss (<700 cm³/s) erlaubte eine Beobachtung in Echtzeit bei Raumtemperatur und atmosphärischen oder kleineren Drücken.

Ausgewählte Messungen, hauptsächlich im erweiterten 5 μm Wellenlängenbereich des CO2 Lasers, werden diskutiert. Das Stickoxid ¹⁵NO/¹⁴NO Isopenverhältnis wurde in guter Übereinstimmung mit der Literatur in einem Gemisch, das neben NO als Verunreinigung und interferierende Substanz auch Wasserdampf (H₂O) enthält, gemessen. Dies demonstriert die hohe Selektivität des Sensors. Die gute Sensitivität wird anhand einer CO₂ Messung ausserhalb starker Absorptionen gezeigt. Die erreichten Nachweisgrenzen (SNR=3) sind 42.2 ppm für NO, 136 ppm für H₂O und 2.55% für CO₂. Als Neuheit wird der zeitgleiche Nachweis von NO,
H₂O und CO₂ beim Einsatz beider Laser-Strahlungen als praktikabel gezeigt.

Oberton- und Kombinationsbänder im nahen Infrarot wurden mittels verschiedener Spektrometern untersucht, welche auf einem glasfaser gekoppelten, kontinuierlich-abstimmbaren, Dauerstrich-Diodenlaser mit externer Kavität (ECDL) basieren. Seine Wellenlänge von 1.6 \( \mu \text{m} \) ist typisch Telekommunikations-Anwendungen und seine wesentlichen Merkmale sind der breite Abstimmbereich (1.54–1.66 \( \mu \text{m} \), [6494–6024 cm\(^{-1}\)]), die sehr kleine Linienbreite (<150 kHz, [0.5×10\(^{-6}\) cm\(^{-1}\)]) und eine mittlere optische Ausgangsleistung von 0.2–6.3 mW. Bei Wellenlängen-Modulation (WM) mit Frequenzen <10 kHz beträgt der maximale Trägerfrequenzhub ±2 GHz.


Chapter 1

A brief introduction to spectroscopy and trace-gas sensing

This chapter gives a brief introduction into the field of laser spectroscopy beginning with a historic view how spectroscopy came to age, a short motivation with main applications and a short comparison with alternative sensing techniques. Some general aspects include the absorption wavelength of various species and the availability of suitable laser sources. Gas sensor requirements are also discussed.

1.1 History

The beginning of spectroscopy can be accredited to Isaac Newton, who in the year 1666 used a prism to study sunlight after its passage through a hole. He observed a continuous band of colors, i.e. the spectrum. He concluded sunlight was composed of light of different colors and that prism refracts these colors differently. Another century passed until Thomas Melville, in 1752, observed discontinuities, or dark gaps and bright lines, present in the spectra of flames burning salts or metals. His experimental setup was similar to the one used by Newton. In 1802, William Hyde Wollaston refined the method by using a slit instead of the hole. This led to a brighter and clearer spectrum and enabled him to discover dark lines in the spectrum of the sun. Joseph von Fraunhofer, in 1814, independently rediscovered these lines when he increased the dispersion of his experimental setup using more than one prism. This enabled him to record several hundred lines, i.e. the Fraunhofer lines, in the spectra of the sun, but also in solar planets and bright stars. He could find some principal relations between the lines. William Herschel recognized that spectra would provide an excellent means to detect and identify small quantities of an element in a powder put into a flame. In 1880, he used a prism-based spectrometer to measure the radiant heat across the sun spectrum, first in the visible, and then beyond the red end of the spectrum. This marked the discovery of the non-visible spectrum. In the years from 1855 to 1863,
Robert Wilhelm Bunsen and Gustav Kirchhoff systematically investigated spectroscopic lines of alkali metals and absorbing vapors. Their method allowed the discovery of many new elements. Noteworthy, some new elements would first be seen on the sun before being discovered on earth. Although instrumentation had improved greatly over time, no explanation was given as to why atoms emitted or absorbed light at the frequencies they did. However, an atomic structure was assumed. Johann Balmer, in 1885, gave the first mathematical description of the distribution of the spectral lines, based on the hydrogen lines recorded by Anders Jonas Ångström. His formula predicted additional lines which where found subsequently. Johannes Rydberg independently presented a generalized formula in 1888. Niels Henrik David Bohr proposed a theory of the atom in 1913 in which the electrons occupied stable orbits with well-defined energy. Thus, absorption and emission of photons would be a direct result of an electron moving up or down from one orbit to another with different energy. This gave an explanation of the observation that atoms absorb and emit light at particular frequencies characteristic of the atom. In 1928, Chandrasekhar Venkata Raman observed weak inelastic scattering of light from liquids. The effect arises from the scattering of light by vibrating molecules and is now known as Raman scattering. These and many others made great contributions, paving the way for the development of quantum mechanics, lasers, and spectroscopic instrumentation [1, 2, 3].

1.2 Motivation

Several optical trace gas monitoring techniques have been developed [4, 5, 6]. Their spectral ranges stretch from ultra-violet (UV) over the visible (vis) to the near- (NIR) and mid-infrared (MIR). In particular, Fourier-transform infrared (FTIR) spectrometry is widely used with demonstrated high precision [7, 8, 9]. Other methods include chemiluminescence [10], and the separation techniques gas chromatography (GC) [11] and mass spectrometry (MS) [12], or a combination thereof [13]. Laser-based spectroscopic techniques offer some distinct advantages over above techniques namely increased resolution owing to the favorable narrow linewidth, wavelength tunability, and high spectral power of the laser source.

Spectroscopic studies have contributed to the understanding of the fundamental properties of gaseous compounds. In recent years, spectroscopy has gained importance as a noninvasive and fast means to qualitatively and quantitatively assess gas-phase samples. The number of applications is ever-increasing and selected examples are given in the following.

This thesis focuses on laser-based techniques, namely photoacoustic and transmission spectroscopy. Recent advances in tunable diode lasers and nonlinear optical frequency conversion
schemes and materials were a major motivation in the presented studies.

1.2 Applications

Some selected applications are given in the following and show the wide field of uses for spectroscopy today.

Environmental monitoring of gaseous pollutants For studying the greenhouse effect and the associated atmospheric chemistry it is essential to measure all active species. Spectroscopic techniques allow for the spatial and temporal monitoring of air pollutant distributions [4]. These include CO$_2$, methane and nitrogen oxides (NO$_x$). For environmental monitoring sulfurous oxides (SO$_x$), ammonia (NH$_3$) and nitrogen oxides are relevant.

Environmental surveillance of trace species Eruptive volcanic activities are preluded by an increased release of gaseous compounds such as water, CO$_2$ and SO$_2$ [14, 15]. Their isotope ratio points to the origins of the fumes. Monitoring these substances may help in the understanding of underlying mechanisms and serve as an early warning system for imminent outbursts. Evaluating the methane release of rice paddies, swampland, landfills and cattle, as well as the gas bubbling from melting permafrost from is needed for assessing their full greenhouse effect [16]. Oceanic CO$_2$-sinks need also to be studied for better understanding of the CO$_2$-cycle [17]. Leak detection in gas pipelines is another application [18, 19].

Occupational health Workplace safety in working environments such as mining or petrochemical refineries crucially depends on species found in the ambient air [20].

Medical applications Historically, sometimes doctors could use their trained sense of smell to diagnose diseases based on body fluids, exhalation, perspiration and excrements. Although trained dogs are still used today, the field was not followed up until technology offered new possibilities. Among other techniques, spectroscopy is well placed to occupy this field. Studies show direct correlation between ammonia in the breath, blood urea nitrogen and creatinine during hemodialysis [21]. The detection of isotopomers [22] is relevant for isotope labeled studies. Phillips [23] gives an introduction to these noninvasive diagnostic procedures. A recent review on clinical breath analysis including species and their physiological basis is given in [24].

Process control Many production process industries need tight control of relevant parameters such as water concentration in the semiconductor industries [25] or impurities in ethylene in plastic
Food and nutrition  Fruit and vegetables need optimal conditions for storage and transportation. Monitoring of relevant plant hormones such as ethylene indicates the stress of the crop [27]. Other applications include the internal oxygen balance of apples [28] or the kinetics of ethanol and acetaldehyde production in fermentation of wheat dough [29].

Chemical analysis  The petrochemical industry seeks to assess the quality, i.e. composition, of the natural gas after at the well or during pipeline transport, and it will be marketed accordingly [30]. Knowledge of the gas composition allows optimal combustion in engines and turbines.

Forensic science  Drugs, such as heroin, morphine and narcotine, can be detected using photoacoustic spectrometer [31]. Doping agents in sports might also be detected [32]. Fumes of explosives can be detected by cavity ring-down spectroscopy (CRDS) [33].

Homeland security  Spectroscopic techniques are being used in attempts to thwart terrorism. Governmental agencies test for fumes of explosives and nerve gases for example [34] and are looking for faster, portable and more extensive spectroscopic techniques.

Science and technology  Atomic clocks, laser stabilization and linewidth measurements rely on spectroscopic techniques [35]. Historically, astrophysics and spectroscopy developed jointly due to strong mutual exchange.

1.2.2 Qualitative and quantitative analysis

Both qualitative and quantitative analyses of sample composition are achieved by scanning across a spectral region of a species or composition that contains absorption lines with detectable strengths. The scan can either be continuous or discrete, e.g. on specific lines at certain wavelengths only.

Fingerprint  All polyatomic and heteronuclear diatomic molecules absorb radiation in the IR region. The absorption alters the rotation and vibration of the molecule. The wavelength dependent absorption pattern therefore depends on the physical properties of the molecule such as the number and type of atoms, as well as type, strength and angle of the bond. Each spectrum is unique and may be considered the molecular signature, or fingerprint, of the substance in the IR. The fingerprint reflects the internal energy transitions of atoms or molecules that make up the species
or compound [36]. The far-infrared (FIR) region, i.e. 25–1000 μm (10–400 cm⁻¹), has many rotational absorption features. The important mid-infrared (MIR) region, i.e. 2.5–25,000 μm (400–4,000 cm⁻¹), has fundamental vibrations and associated rotational-vibrational absorption features. The near-infrared (NIR) region, i.e. 0.71–2.5 μm (4000–14,000 cm⁻¹), has overtone and combination band absorption features. In this thesis, MIR and NIR studies are presented in chapter 3 and chapter 4, respectively.

Monoatomic gases, such as the noble gases, and homonuclear molecules like oxygen and nitrogen do not have significant IR bands and therefore must be measured by non-IR means. Diatomic molecules such as nitrous oxide (NO), carbon monoxide (CO), hydrogen chloride (HCl), and hydrogen fluoride (HF) have a single major band that is an array of individual lines. Linear polyatomic molecules like carbon dioxide (CO₂), nitrous oxide (N₂O) and acetylene (C₂H₂) also feature individual lines. Nonlinear polyatomic molecules like ozone (O₃), sulfur dioxide (SO₂), ammonia (NH₃), methane (CH₄) and water (H₂O) exhibit lines that can be resolved to small bundles of lines or bands. For large polyatomic molecules at atmospheric pressure there are also many lines overlapping each other. The resulting spectral features are broad and smooth except for strong "spikes" [36, 37]. However, spectra recorded at lower pressure reveal more details. A list with substances investigated during the course of this thesis is given in Appendix A.

Qualitative analysis  This is the identification of a single species or of a compound of species by the mere presence of absorption lines. Thus, for each species or compound the characteristic spectral distribution of absorption lines and bands must be known. Such information is obtained by measuring reference spectra of known substances or from databases supplied by manufacturers and laboratories, which are listed in Appendix B.

Quantitative analysis  This is the determination of the concentrations of single species or of a compound of species that make up a sample. Each species or a compound must be identified and its characteristic spectral absorption strengths of lines and bands known. Reference spectra or spectroscopic database provide the relevant information.

Interfering and unknown species  Ideally, the spectral information obtained form spectroscopic investigations of a gas sample is sufficient to unambiguously identify and quantify all components. However, unknown species can be present in the sample making the spectra difficult or impossible to understand. Furthermore, many species group into families of molecules with similar molecular structures or parts thereof, e.g. hydrocarbons (C-H bonds). The spectra of species belonging to
the same family may be very similar in structure and location, causing overlap in parts of the spectrum. These and other species that have spectral features that overlap are called interfering species.

**Absorption free windows** Often only one or a few selected species or compounds of the gas sample are of interest. Thus, to avoid interference, a spectral region is selected where other species, and especially strongly absorbing ones, exhibit either no or no significant absorption features. These selected regions are called spectral or atmospheric windows. Water vapor is always present in ambient air and it is the most abundant trace species after nitrogen and oxygen. Water also has absorption features throughout the spectral region. However, water and carbon dioxide (CO₂) have only negligible absorption in the regions from 3 to 5 \( \mu \text{m} \) and 8 to 14 \( \mu \text{m} \) (Fig. 1.1 taken from [4], page 88), making these preferred regions for trace gas sensing.

![Figure 1.1: Transmission after a path-length of 0.5 km through the atmosphere with water vapor (1%) being the major absorber (room temperature and atmospheric pressure).](image)

**Isotopomer (isotopic isomers)** Isotopomer (isotopic isomers) are molecules of the same structure, i.e. isomer, with the same total number of each isotopic atoms but differing in their position within the molecule. Except for the isotopic difference, the molecules have identical structure. Because of the differing positions of the isotopic atoms in the molecule structure, isotopomers have unique spectral features. Example: \(^{15}\text{N}^{14}\text{NO} \) and \(^{14}\text{N}^{15}\text{NO} \) have the same mass but different IR spectra.

**Mid-infrared spectroscopy** Most molecules exhibit strong, fundamental vibrational and rotational-vibrational transitions in the MIR region (2.5–25 \( \mu \text{m} \)). Applicable laser sources include CO₂-, CO₂-, quantum cascade- and lead-salt diode lasers, as well as laser pumped nonlinear frequency conversion schemes (see section 1.5).
Near-infrared spectroscopy  Overtones and combination band absorption features found in the NIR region (0.71–2.5 μm) can be more 100 to 10,000 times weaker than the fundamental lines and bands observed in the MIR. Applicable sources include overtone CO, diode-lasers, solid state lasers as well as nonlinear frequency conversion schemes (see section 1.5). The detection limits are generally lower in the NIR.

1.3 Sensor requirements

Because each application has specific needs, there is not one optimal sensor. However, an ideal laser-based trace-gas sensor should address or fulfill the following sensing requirements:

- **High sensitivity** to detect species with very low concentrations (at ppmV, ppbV, or pptV levels) or very weak absorbers.

- **High selectivity** to distinguish between species, isotopomers or isomers without cross-response.

- **Multicomponent capability** for the detection of numerous compounds with one sensor.

- **Large dynamic range** for monitoring high and low concentrations or weak and strong absorber with one sensor.

- **Continuous monitoring** with appropriate time-resolution for surveillance such as process control or traffic air pollution monitoring.

- **Fast response** to monitor species in (near) real time and good with temporal resolution so changes in concentrations or composition can be tracked (almost) instantaneously with sufficient data points.

- **Small sample volumes** are preferred when dealing with hazardous, expensive or rare analytes.

- **Noninvasive and nondestructive** to not disturb the sample or cause a chemical reaction.

- **No sample scrubbing or pre-concentration** to maintain the sample in original conditions.
Sample handling is another important issue and depends on sensor design. Some sample handling considerations include:

- **In-situ** measurement capability to study potentially unstable, locally extracted compounds continuously and in real time, thus avoiding sample handling.

- **Sample extraction** and collection for laboratory analysis should be reproducible and follow a well-defined procedure. Sample extraction always involves the risk of contamination or unstable samples.

- **Adsorption** of polar species that can cause false readings and compromise the time resolution can be reduced by flow-mode operation.

Still other considerations to be made in the design of a sensor include:

- **Remote location sensing** may require a lightweight and mobile system (minimal power requirements, easy to operate, maintenance friendly). Furthermore, it should be reliable and rugged and occupy a small volume.

- **Industrial applications** seek economic solutions.

- Gas sensors should be **tolerant to hostile environments**.

- Many applications require **autonomous operation** of the sensor. Thus it should have sufficient **storage space** for measured data, or a **communication link**, preferably wireless.

### 1.4 Spectroscopic techniques

Any spectroscopic technique based on laser instrumentation may in principle be studied with some other kind of light source, but usually at the expense of data quality in terms of signal-to-noise or spectral resolution. The distinctive features of laser light, notably the favorable narrow linewidth, wavelength tunability, high spectral power, and low intensity fluctuations, allow to resolve unique spectral absorption features and obtain high-resolution data.

#### 1.4.1 Absorption spectroscopy

In absorption spectroscopy the wavelength-dependent absorption of the sample is measured by registering the transmitted light beam with a photodetector [38]. This technique has been applied and is discussed in this thesis (see chapter 4).
1.4.2 Cavity ring-down spectroscopy

In cavity ring-down spectroscopy (CRDS) \[39, 40\] the decay time of laser light trapped inside a high-finesse optical cavity is measured. Each time light bounces off a high-reflectivity dielectric cavity mirror a small fraction leaks out and can be measured. This fraction depends on the initial intensity, which is affected by loss inside the cavity and after each reflection. Thus, the measured light over time follows an exponential decay from which the ring down time is extracted. The time constant, i.e. ring down time, predominantly depends on both the absorption of the sample present inside the cavity and mirror reflectivity losses. Scattering and other effects may also introduce minor losses. The high-finesse cavity \[41\] enables effective path-lengths of several kilometers in small volumes, which can result in very high sensitivity. Typical ring down times in the order of milliseconds allow near real-time monitoring. Additionally, the CRDS scheme is not prone to intensity fluctuations of the source since a decay rate is measured. However, the high reflectivity mirrors have limited wavelength range (few nm) and thus several mirror sets need to be employed with a tunable source for broad spectra recording. Additionally, these mirrors are costly and are not available for all wavelengths. They are scarce in the interesting fingerprint region in the mid IR.

1.4.3 Photoacoustic spectroscopy

Photoacoustic (PA) spectroscopy is based on the photoacoustic effect \[42\], in which an acoustic wave is generated after the absorption of modulated light by an absorbing species. The light absorption causes a transient temperature effect, which then transforms into a pressure variation in the absorbing media \[43, 44\]. The wavelength-dependent absorption of the sample is measured by registering the pressure wave, which is generated by the heat deposited in the sample through absorption \[45\]. This technique has been applied and is discussed in this thesis (see chapter 3).

1.5 Laser sources

Table 1.1 lists some laser sources commonly used in spectroscopic techniques. What follows is a description of each of these laser sources with particular emphasis placed on the sources used in this thesis, the high-pressure CO\(_2\) and tunable diode lasers.
1.5.1 CO₂ laser

CO₂ lasers emit in the MIR around 10 µm, operate at room temperature (RT) and have been employed in trace gas sensing. Two practical designs employed in our laboratory are the sealed-off line tunable CO₂ laser and the continuously tunable high-pressure CO₂ laser.

**Sealed-off line tunable CO₂ laser** Patel demonstrated the sealed-off line tunable CO₂ laser in 1964 [46]. Such lasers have long been successfully implemented in spectroscopic applications such as traffic emission monitoring [47] or studying ethylene metabolism in fruit storage [48]. They feature cw operation, high output power (up to 10 W), and good spatial mode profile. The tuning range in [48] includes a total of 67 lines from the 9R, 9P, 10R, and 10P branches covering a wavelength range from 914.4 to 1094.8 cm⁻¹ for the ¹²C¹₆O₂ isotope filling. Operation with isotopes ¹³C¹₆O₂, ¹₂C¹⁸O₂, ¹³C¹⁶O₂ and ¹³C¹⁸O₂ have been demonstrated and cover the wavelength range from 9 to 11.5 µm. The accurate wavelength of each line and isotopes can be found in [49].

**Continuously tunable CO₂ laser** To avoid tuning gaps between adjacent laser lines, a home-built high pressure CO₂ laser [50] has been employed in a continuously tunable pulsed spectrometer. It features a linewidth of 540 MHz and has been applied in high-resolution spectroscopy including a study of CO₂ isotopes [51, 52, 53]. The tuning range includes the branches 9R, 9P, 10R, and 10P and ranges from 9.2 to 10.7 µm. The pulse energies throughout the tuning range are minimum 10 mJ, while the pulse repetition rate is below 1 Hz. A further extension of the continuous tuning range into the 5 µm was realized in this study [54] (see chapter 3).
1.5.2 CO laser

Line-tunable cw CO lasers emit in the 5.1–8.0 \( \mu m \) region and have been employed in photoacoustic spectrometers for trace gas detection [27, 55, 56, 57, 58]. Output power of few Watts with linewidth of less then 100 MHz has been reported. However, cooling below room temperature (RT) is required for high output power. Line-tunable CO-overtone lasers emit in the 3 \( \mu m \) region [59] and emission from 2.3 to 4.1 \( \mu m \) has been demonstrated [58].

1.5.3 Tunable diode laser

Tunable diode lasers (TDL) based on III–V semiconducting compounds operating at room temperature (RT) cover a very wide spectral range including ultra-violet, visible, and the near-infrared [60], whereas the mid-infrared region (2.5–30 \( \mu m \)) is covered by lead-salt lasers [61, 62].

1.5.4 Lead-salt diode laser

Lead-salt lasers based on IV–VI compounds feature a wide tuning range combined with a narrow linewidth. The wavelength range from 3 to 30 \( \mu m \) is available but requires employing several devices. The typical mode-hop free range is below 1 cm\(^{-1}\). At RT or with TE cooling pulsed operation results in peak powers of several Watt [62]. Cryogenically cooled devices can operate continuous-wave and achieve typical output powers in excess of 0.1 mW. However, cryogenic operation may lead to condensation problems. More recent developments include cryogenically cooled laser-pumped vertical cavity emitting lasers (VCSEL) [63, 64] and edge emitting devices [65] operating at room temperature.

1.5.5 Quantum cascade laser

Since their first experimental realization in 1994 [66] quantum cascade lasers (QCLs) have progressed significantly [67] and can now operate at room temperature (RT) [68], emit single mode (distributed feedback, DFB) cw with powers up to 50 mW and a typical linewidth of a few MHz. QCLs use subband transitions created by a quantum confinement in a semiconductor heterostructure. The confinement is a design parameter and sets the emission wavelength range. However, the complex fabrication process involves many vapor phase depositions and is still challenging. Wavelength tuning is achieved by the change of the refractive index with temperature. The tuning range for the common DFB QCL employed in spectroscopic applications devices is few cm\(^{-1}\). At a fixed temperature, the injection current can be changed for fine-tuning or frequency modulation within a narrow wavelength range. Short wavelength emission at 3.4 \( \mu m \) [69], ultra-broadband
[70], and multi-wavelength [71] emission have been demonstrated. Recently, a cw broadly tunable TE cooled external cavity quantum cascade laser (EC-QCL) has been demonstrated [72] with a minimal power of more than 10 mW throughout the tuning range of 75 cm$^{-1}$ at 1850 cm$^{-1}$. This is a very promising source for trace gas sensing. QCLs have been employed in several spectroscopic detection schemes including cavity ring-down (CRDS) [73] and photoacoustic [74]. QCLs have been commercialized but only few selected wavelengths are available as DFB or Fabry-Perot (FP) devices that mostly require cryogenic cooling.

### 1.5.6 Chalcogenide laser

Chalcogenide lasers emit in the wavelength range from 2 to 3.1 μm in narrow-line cw operation with output power of up to 11 W and with 4 ps pulses at 400 mW in mode-locked regime [75, 76]. A PA spectrometer employing a chalcogenide laser operating at around 2.5 μm with a broad tunable range of 280 nm and with an output power of up to 100 mW has been reported [77]. The high output power combined with a wide tuning range render the chalcogenide lasers applicable for PA detection schemes in the near-infrared. An application as a tunable solid state source in nonlinear optical frequency conversion schemes is also feasible.

### 1.5.7 Nonlinear optical frequency conversion

Many interesting substances absorb in the spectral region between 2.8 to 4 μm. However, no primary laser source is readily available. Though quantum cascade lasers have the potential to narrow and eventually close the gap, laser pumped optical frequency conversion schemes employing nonlinear materials currently fill this gap [78, 79, 80]. While a phenomenological explanation is given below, a detailed discussion of the field relevant to the thesis is given in section 2.5.

**Second harmonic generation (SHG)** Two incident photons of the same frequency, i.e. $\omega_2 = \omega_1$, are converted to a single photon of frequency $\omega_3$ according to $\omega_3 = 2\omega_1$. The frequency of the photons of the incoming beam is doubled.

**Difference frequency generation (DFG)** Two incident photons of frequencies $\omega_3$ and $\omega_2$ are combined to a single photon with the difference frequency $\omega_1$ according to $\omega_1 = \omega_3 - \omega_2$. Employing a fixed and a tunable source, a new also tunable difference frequency can be generated.

**Optical parametric generation (OPG)** One incident photon of frequency $\omega_3$ is split into two single photons with different frequencies $\omega_1$ and $\omega_2$ according to $\omega_1 + \omega_2 = \omega_3$. By tuning
parameters of the nonlinear material, the incoming photon is split into two new photons.

1.6 Noncoherent sources

Any laser-spectroscopy technique for trace-gas sensing could in principle be implemented with some other sort of light source. However, while lasers in many respects have superior characteristics such as high monochromaticity, narrow linewidth, high output power, and tunability, noncoherent light sources are widely used in less sensitive and selective low-cost sensors.

**Black body emitter** The sun is a good approximation of a black body emitter. However, light fluctuates and lack of availability make sunlight impractical for most applications. An other black body source, hot filaments, often made from tungsten, have poor emissivity and thus the emitted radiation is moderate. Recently, micromachined black body-like IR-sources have been demonstrated and overcome limitations of hot filament sources [81] by exhibiting a high emissivity with a black body emission profile over a wide wavelength range. Their high thermal conductivity and low thermal mass make modulated operation up to 100 Hz feasible. Generally, black body emitters require a highly stable voltage supply to minimize fluctuations in radiation.

**Gas and vapor filled lamps** Hydrogen and deuterium lamps emit in the UV range (160–375 nm). Vapor filled lamps are less common as spectroscopic sources.

**Light emitting diode** Light emitting diodes (LEDs) are widely used in many applications. Recently, resonant-cavity LED (RC-LEDs) and detectors for mid-IR gas-sensing applications [82] have been reported and become a viable alternative in some sensing applications.

**Optically pumped frequency converter and photonic crystals** The band-gaps of photonic crystal-based (PC) emitters can be tailored to specific emission patterns exhibiting narrow bands [83, 84]. They can be electrically driven. Optical pumped semiconductor frequency converters [85, 86] have been demonstrated and are based on the ability to design specific band-structures.
This chapter summarizes the theory relevant for the studies presented in this thesis. This includes absorption and photoacoustic spectroscopy, modulation schemes and nonlinear optical frequency conversion.

2.1 Light-matter interaction

Light and matter interact with each other. Photons incident to a gas sample can be absorbed and excite rotational and vibrational states in the MIR, or combination band and overtones in the NIR. During relaxation, the photon energy is released through radiation or collisions with other molecules, atoms or the wall confining the sample. This results in lines and bands in the spectrum of the sample and is the basis of spectroscopic detection schemes. Quantum theory explains why only light of certain frequencies can be absorbed by one species. The well-defined energy levels of the species depend on the individual isotopes, structure and bonds of the molecule, as well on environmental parameters such as temperature, pressure and the presence and strength of electric and magnetic fields. These well-defined, unique absorption features enable species to be unambiguously identified.

2.2 Frequency, wavelength, and wavenumber

Besides the common variables frequency $\nu \ [\text{Hz}]$ and wavelength $\lambda \ [\mu\text{m}]$ in vacuum, IR spectroscopy also uses the wavenumber $\tilde{\nu} \ [\text{cm}^{-1}]$. The following definitions apply

$$\lambda = \frac{c}{\nu} \quad (2.1)$$

and

$$\tilde{\nu} = \frac{\nu}{c} \quad (2.2)$$
where \( c \) denotes the speed of light in vacuum. The conversion is summarized in Table 2.1.

\[
\begin{array}{|c|c|c|c|}
\hline
\nu [\text{Hz}] & \lambda [\text{\mu m}] & \tilde{\nu} [\text{cm}^{-1}] \\
\hline
\nu = 10^6 c/\lambda & \nu = 10^{-2} c \tilde{\nu} \\
\lambda = 10^{-6} c \nu & \lambda = 10^4 / \tilde{\nu} \\
\tilde{\nu} = 10^2 \nu / c & \tilde{\nu} = 10^4 / \lambda \\
\hline
\end{array}
\]

Table 2.1: Conversion between frequency \( \nu \), wavelength \( \lambda \), and wavenumber \( \tilde{\nu} \).

### 2.3 Absorption spectroscopy

In absorption spectroscopy, a light beam is passed through the sample under investigation and its wavelength-dependent intensity is recorded as depicted in Fig. 2.1. As a result of absorption, the transmitted light intensity \( I_T \) will be lower than the incident intensity \( I_0 \). It is this difference of the recorded intensities that permits the qualitative and quantitative analysis of the sample. Should the molecules' excited states have a radiative decay, the photon would still be lost, since generally emission is isotropic and thus not directed in the propagation direction of the incoming beam.

![Figure 2.1: Beer-Lambert absorption of a light beam passing through a sample.](image)

#### 2.3.1 Beer-Lambert law

The Beer-Lambert law empirically describes the absorption of light [5] and is fundamental for spectroscopy because it links absorption \( \alpha_{\text{gas}} \) and concentration \( c_{\text{gas}} \) of the absorbing species. It is given as

\[
I_T(\nu, l) = I_0 \exp \left[ -\alpha(\nu)c_{\text{gas}} l \right],
\]  

(2.3)

where \( I_T \) is the transmitted light intensity after the sample, \( I_0 \) is the incident light intensity, \( \alpha \) is the wavelength-dependent molecular absorption coefficient \( [\text{cm}^{-1}\text{molecule}^{-1}] \), \( c_{\text{gas}} \) is the concentration [molecules] of the absorbing species, and \( l \) is the length [cm] of the light path inside the absorbing sample. Thus, either the molecular absorption coefficient \( \alpha \) or the concentration \( c_{\text{gas}} \)
can be determined from the measurement of the incident and transmitted light intensities for a fixed absorption path-length \( l \), if either \( c_{\text{gas}} \) or \( \alpha \) are known. It should be noted that the absorption path-length \( l \) is the only free design parameter and has led to the development of employing open long-path and multipass cell absorption measurements techniques [4, 5, 6, 87] (see section 2.3.9). Using the total absorption coefficient \( \alpha_{\text{gas}} = \alpha(\nu)c_{\text{gas}} \text{[cm}^{-1}\text{]} \), the Beer-Lambert law has familiar form

\[
I_T(\nu, l) = I_0 \exp \left[ -\alpha_{\text{gas}} l \right].
\]

The molecular absorption coefficient \( \alpha(\nu) = N\sigma(\nu) \) depends on the number density \( N \) [molecules cm\(^{-3}\)] and molecular absorption cross-section \( \sigma \) [cm\(^2\) molecule] of the absorbing species. Thus the Beer-Lambert can also be written as

\[
I_T(\nu, l) = I_0 \exp \left[ -\sigma(\nu) N l \right].
\]

The transmittance \( T \) can be calculated from the Beer-Lambert law

\[
T(\nu) = \log_{10} \frac{I_0(\nu)}{I_T(\nu, l)}
\]

and relates to the absorbance \( A \) as follows

\[
A(\nu) = -\log_{10} T(\nu) = \frac{N\sigma l}{\ln 10} = \frac{\alpha(\nu)c_{\text{gas}} l}{\ln 10} = \frac{\alpha(\nu)_{\text{gas}} l}{\ln 10}.
\]

Note that the concentration \( c_{\text{gas}} \) is proportional to the absorbance \( A \) and not the transmittance. The absorbance is additive for overlapping absorption features of several species

\[
A = \frac{l}{\ln 10} \sum_i \alpha_i(\nu)c_i = \frac{l}{\ln 10} \sum_i N_i \sigma_i.
\]

Though other definitions of the absorbance are found in the literature, this definition is what will be assumed in this thesis.

### 2.3.2 Linestrength

For the absorption by a single vibration-rotation line [87], the absorption cross-section is given by

\[
\sigma(\nu) = S g(\nu - \nu_0),
\]
where $S$ is the integrated linestrength [cm molecule$^{-1}$], $g$ is the pressure dependent, normalized lineshape function [cm] and the frequency $\nu_0$ denotes the line position. For transitions from lower state $i$ to upper state $j$ the linestrength is given by

$$S_{ij} = \left( \frac{C\nu_{ij}}{Q_{vib}Q_{rot}} \right) \exp \left[ -\frac{\hbar \nu_{ij}}{k_B T} \right] \left( 1 - \exp \left[ \frac{\hbar \nu_{ij}}{k_B T} \right] \right) | R_{ij} |^2,$$

(2.10)

where $C$ is a constant, $\nu_{ij}$ is the transition frequency, and the vibrational and rotational transition numbers are given by $Q_{vib}$ and $Q_{rot}$, respectively. The factor $\left( 1 - \exp \left[ \frac{\hbar \nu_{ij}}{k_B T} \right] \right)$ accounts for induced emission and is relevant at high temperatures. $R_{ij}$ is the transition moment, $k_B$ the Boltzmann constant, and $T$ the temperature. The linestrength of line $\nu_i$ depends on the temperature through the population of the states, but is independent of pressure. Values of $S_{ij}$ are listed in databases such as HITRAN [88] or GEISA [89].

### 2.3.3 Linewidth and line shift

The absorption or emission of electromagnetic radiation in transitions in a two-level atomic or molecular system is not truly monochromatic, but is described by a range of wavelengths (Fig. 2.2). Additionally, the line center may be shifted from its nominal central wavelength. Several parameters can cause line broadening and shift [5, 87, 90]. In studies within this thesis, the dominating physical parameters were gas temperature and pressure. All measurements discussed in this thesis were recorded at room temperature with pressure ranging from few millibars to 1 bar (atmospheric pressure). Thus, the line shift is negligible with respect to the linewidth and has not been considered. What follows is a discussion of line broadening mechanism.

![Figure 2.2: Full width at half maximum (FWHM)](image-url)
A spectral distribution of emission or absorption intensity \( I(\nu) \) centered around \( \nu_0 \) is generally observed. The frequency interval \( \Delta \nu_0 = |\nu_2 - \nu_1| \) is defined by the frequencies \( \nu_2 \) and \( \nu_1 \) at which the intensity has dropped to half the maximum and is referred to as full width at half maximum (FWHM) as shown in Fig. 2.2. Spectral intervals such as linewidth or tuning ranges are often given in terms of frequency \( \nu \), wavelength \( \lambda \) or wavenumber \( \tilde{\nu} \). For short intervals a comparison is given with 

\[
\Delta \lambda_0 = -\frac{c}{\nu_0^2} \cdot \Delta \nu_0, \tag{2.11}
\]

\[
\Delta \nu_0 = -\frac{c}{\lambda_0^2} \cdot \Delta \lambda_0, \tag{2.12}
\]

and 

\[
\Delta \tilde{\nu}_0 = -\frac{1}{c^2} \cdot \Delta \nu_0. \tag{2.13}
\]

### 2.3.4 Homogeneous and inhomogeneous line broadening

If all parameters of a sample are the same, identical constituents (atoms and molecules) have the same probability for emission or absorption of radiation at resonance frequency \( \nu_0 \), with the same lineshape function \( g(\nu - \nu_0) \) and linewidth \( \Delta \nu_0 \). Thus, all atoms and molecules contribute equally. Processes that shorten the lifetime of a state, such as spontaneous emission or deactivating collisions cause a uniform line broadening by each atom or molecule in the sample [5, 87]. The resulting line broadening is homogeneous and results in a Lorentzian lineshape function 

\[
g_L(\nu) = \frac{\Delta \nu_L}{\pi} \cdot \frac{1}{(\nu - \nu_0)^2 + \Delta \nu_L^2} \tag{2.14}
\]

with linewidth \( \Delta \nu_L \).

Other processes shift the resonance frequency of individual atoms or molecules [5, 87]. The resulting line broadening is inhomogeneous and results in a Gaussian lineshape function 

\[
g_G(\nu) = \sqrt{\frac{\ln 2}{\pi}} \cdot \frac{1}{\Delta \nu_D/2} \exp \left[ -\ln 2 \left( \frac{\nu - \nu_0}{\nu_D/2} \right)^2 \right], \tag{2.15}
\]

with linewidth \( \Delta \nu_D \).

### 2.3.5 Natural linewidth

Classical radiation damping is a homogeneous line broadening process and is characterized by the natural linewidth \( \Delta \nu_n \) and the decay time \( \tau_{sp} \) of the excited state, which decays by spontaneous emission [5, 87]. Classically, the line broadening for the transition between the excited state and
the ground state is
\[ \Delta \nu_n = \frac{1}{2 \pi \tau_{sp}} = \frac{1}{3 \varepsilon_0} \cdot \frac{e^2}{c^2 \mu_e} \cdot \nu_0, \]  
(2.16)
where \( \nu_0 \) is the resonance frequency of the transition, \( \varepsilon_0 \) is the permittivity of vacuum, \( e \) and \( m_e \) are the charge and mass of the electron, and \( c \) is the speed of light. For transitions between two excited states \( i \) and \( j \), the lifetimes \( \tau_i \) and \( \tau_j \) of both levels contribute and the resulting linewidth is
\[ \Delta \nu_n = \frac{1}{2 \pi} \cdot \left( \frac{1}{\tau_i} + \frac{1}{\tau_j} \right). \]  
(2.17)
The natural linewidth \( \Delta \nu_n \) is usually small as compared with other line broadening processes and can be neglected [5, 87]. For example, transitions coupling vibrational states have a natural linewidth in the order of a few tens of kHz. The lineshape function is Lorentzian (Eq. 2.14).

### 2.3.6 Doppler broadening at low pressure

Thermal motion of atoms and molecules leads to a Doppler shift and results in an inhomogeneous line broadening with a characteristic Gaussian lineshape (Eq. 2.15) [5, 87]. The linewidth is
\[ \Delta \nu_D = \sqrt{8 \ln 2} \cdot \sqrt{\frac{k_B T}{m \cdot c^2}} \cdot \nu_0 \]  
(2.18)
with resonance frequency \( \nu_0 \), temperature \( T \), particle mass \( m \), Boltzmann constant \( k_B \), and speed of light \( c \). Doppler broadening dominates at low pressure.

### 2.3.7 Pressure broadening at high pressure

Elastic collisions amongst atoms and molecules cause homogeneous line broadening [5, 87, 90]. As expected, the collision rate increases with pressure \( p \). Pressure broadening has a characteristic Lorentzian lineshape (Eq. 2.14) and the linewidth is given as
\[ \Delta \nu_p = \sqrt{\frac{8}{\pi} \cdot \frac{p a^2}{\sqrt{m k_B T}}} \]  
(2.19)
with particle diameter \( a \) and mass \( m \). It is proportional to the classic cross section \( a^2 \pi \) for two identical particles. Pressure broadening dominates at high pressure.
2.3.8 Combined broadening at intermediate pressure

At intermediate pressures both Doppler and pressure broadening occur. The resulting lineshape is a convolution of the individual lineshape functions and is given by a Voigt function,

\[ g_V(\nu) = g_G(\nu) \ast g_L(\nu). \]  \hspace{1cm} (2.20)

This has no analytical solution, but can be solved numerically [91]. The linewidth can be approximated [92] to

\[ \Delta \nu_V = 0.5346 \cdot \Delta \nu_p + \sqrt{0.2116 \cdot \Delta \nu_p^2 + \Delta \nu_D^2}. \]  \hspace{1cm} (2.21)

Lorentzian, Gaussian and Voigt lineshape functions of the same width are depicted in Fig. 2.3. A comparison of the Lorentz and Gaussian line profile reveals that the spectral distribution associated with the natural or collision broadening is quite different from that arising from thermal motion. The wing content of the Lorentz profile is much greater than that of the Gaussian profile if they have comparable widths.

![Lorentzian, Gaussian, and Voigt lineshape functions](image)

**Figure 2.3**: Lorentzian, Gaussian, and Voigt lineshape functions of equal widths.

In the case of two independent homogeneous line broadening mechanisms, the resulting lineshape function is Lorentzian and the linewidths simply add \( \Delta \nu_{tot} = \Delta \nu_1 + \Delta \nu_2 \). For two independent inhomogeneous line broadening mechanisms, the resulting lineshape function is Gaussian and the linewidth can be calculated as \( \Delta \nu_{tot} = \sqrt{\Delta \nu_1^2 + \Delta \nu_2^2} \).
2.3.9 Multipass cells

According to the Beer-Lambert law (Eq. 2.4), the sensitivity of an absorption measurement can be improved by enlarging the absorption path-length \( l \). One way to increase the path-length within a sample is by employing a multipass cell. Two different designs are used: the White-type [93, 94] and the Herriott-type [95, 96] cells. Both types are compact, mechanically stable and are available in rugged designs. The White-type cell consists of three concave mirrors that bounce the light back and forth, and two flat transfer mirrors for in and out coupling of the light beam. The mirror spot pattern is in parallel rows. It features a good path-length to volume ratio, but requires a more elaborate adjustment when compared to the Herriott-type cell, which uses only two spherical or aspherical mirrors. In the Herriott-type cell, the mirror spot pattern resembles a Lissajous figure. The in and out coupling is through the same hole in one of the two mirrors. Generally, optical alignment is good, although additional external beam stirring mirrors are needed. The path-length to volume ratio is only fair. Experience in our laboratory showed more pronounced interference fringes in the transmission spectra obtained using a White-type cell (Infrared Analysis, Inc., Anaheim CA, USA) when compared to the Herriott-type cell (New Focus Inc., Model 5611, USA). This result is assumed to be due to the specific cells used, and not an inherent feature of the design. Both, White-type and Herriott-type cells have been used in the spectrometers employed in this thesis (see chapter 4).

2.3.10 Practical aspects

For good spectroscopic data two subsequent measurements must be performed. The first is with the sample in the measuring cell and the second is a control with a nonabsorbing filling, e.g. nitrogen or synthetic air, at the same pressure. By measuring a control, imperfections of the spectrometer such as pressure related sagging, reflection, window absorption, window scattering, and interference fringes can be taken into account.

Limitations of the Beer-Lambert law The derivation of concentrations from the the Beer-Lambert law (Eq. 2.4) breaks down in the case of very high concentrations due to electrostatic interaction between neighboring molecules. Photon loss through scattering, very high light intensities due to nonlinear optical processes, and the processes of fluorescence and phosphorescence also lead to errors. Optical fringes caused by parasitic etalons can lead to baseline distortion and external stray light resulting in a gain of false photons and detector saturation can also lead to significant errors.
2.4 Photoacoustic spectroscopy

Alexander Graham Bell, in 1880, first described the photoacoustic (PA) effect in which sound is generated in a material after illumination by a nonstationary source [42]. It occurs in solids, liquids and gases. In 1938, Viengerov first demonstrated a photoacoustic spectrometer using a thermal radiation source [43]. Kreuzer, in 1971, pioneered the field of laser-based photoacoustic trace-gas sensing in the MIR [44]. PA spectroscopy (PAS) is now widely used for environmental trace-gas sensing and as a spectroscopic technique [45]. PAS can be seen as an optical absorption spectroscopy, but can also be considered as calorimetry since it allows the measurement of internal heating of a sample.

The PA effect can be divided into three main processes (Fig. 2.4):

- **Laser radiation** modulated or pulsed
- **Absorption**
- **Excitation** rotational, vibrational, electronic
- **Deactivation** V-R, T
- **Heating** localized, transient
- **Expansion, contraction**
- **Acoustic wave** standing, pulsed
- **Detection**
- **Microphone**

**Figure 2.4:** Schematic view of the photoacoustic effect and the involved physical processes. The absorption of modulated or pulsed infrared laser radiation populates rotational (R) and vibrational (V) states in the absorbing species. Relaxation through collisional decays leads to localized transient heating (T). This causes an expansion of the sample and the resulting acoustic standing or pulsed wave can be detected with a microphone.
Local heat is released into the sample gas due to optical excitation and subsequent re-
laxation through collisional (nonradiative) decays.

Acoustic and thermal waves are generated due to localized transient heating and expansion.

Detection of the acoustic signal (pressure wave) in the PA cell is made by a microphone.

A detailed discussion of the PA effect and the physics of signal generation and detection can be
found in [97, 98]. PA spectrometer instrumentation issues including PA cell designs are discussed
in [45, 99].

Modulated photoacoustic signal Using a modulated MIR radiation source, rotational and vi-
brational states of a sample's gas molecules are excited. Assuming weak absorption, (with no
saturation or depletions effects) and fast relaxation to the ground state (with the relaxations time
\(\tau_{relax} \ll 1/f\), where \(f\) is the modulation frequency or pulse repetition rate of the excitation), the
recorded microphone signal \(S_{mic}\) is given as

\[
S_{mic} = C \cdot Q \cdot P_{las} \cdot N \cdot c_{gas} \cdot \sigma_{gas}.
\]  

(2.22)

\(C\) is the cell constant, \(Q\) the quality factor in case of a resonant PA spectrometer, \(P_{las}\) the incident
laser power, \(N\) the molecular density, and \(c_{gas}\) and \(\sigma_{gas}\) the concentration and absorption cross-
section of the absorbing of the sample. From Eq. 2.22 it is evident, that the detected signal scales
linearly with the incident laser power. Hence, lasers with powers of more than a few mW are
favored in modulated PAS. If different species in the gas sample, indicated by the index \(i\), absorb
at the wavelength of the incident radiation, then the recorded microphone signal comprises their
summed contributions

\[
S_{mic} = C \cdot Q \cdot P_{las} \cdot \sum_i N_i \cdot c_{gas,i} \cdot \sigma_{gas,i}.
\]  

(2.23)

The constant \(C\) is a characteristic of the PA cell and includes parameters such as the cell geometry
and microphone responsivity as well as thermodynamic properties (specific heats and pressure).
Although it can be calculated for a simple cell geometry, it is usually determined using a certified
gas mixture of known composition. All cavities used as PA cells exhibit acoustic resonances. The
quality factor \(Q\) of a resonance is a design parameter of the resonant cell [99]. It can be quite
high and has the benefit to increase the detected signal through resonant enhancement. However,
the use of a very high \(Q\)-value demands tracking of the narrow cell resonance by adjusting the
modulation frequency [48].
§2.5 Nonlinear optical frequency conversion

**Pulsed photoacoustic signal**  Pulsed photoacoustic signal generation lacks the possibility to resonantly enhance the signal. The registered microphone signal in pulsed operation is

\[ S_{mic} = C \cdot E_{las} \cdot N \cdot c_{gas} \cdot \sigma_{gas}, \]  

where \( E_{las} \) is incident laser pulse energy. From Eq. 2.24 it is evident, that the detected signal scales linearly with the incident laser pulse energy. Hence, lasers with high pulse energy are favored in pulsed PAS, i.e. few ten \( \mu J \) to few mJ depending on the detection scheme and the strength of the absorption feature.

In the case that several species absorb at the wavelength of the incident radiation the registered microphone signal becomes

\[ S_{mic} = C \cdot E_{las} \cdot \sum \limits_i N_i \cdot c_{gas,i} \cdot \sigma_{gas,i}, \]  

where the indices \( i \) indicate the different absorbing species of the gas sample.

2.5 **Nonlinear optical frequency conversion**

Nonlinear frequency conversion changes the frequency of incident light to other wavelengths by means of nonlinear optical processes in various materials. Not all wavelength ranges are directly accessible by lasers, and thus using nonlinear processes to generate the desired wavelength have become quite important. The demonstration of optical second harmonic generation by the irradiation of a quartz crystal with a ruby laser initiated nonlinear optics. This section covers only the theory relevant for this thesis. A good compilation about the theory of nonlinear optics is [78] while an extensive list of nonlinear optical materials is found in [79]. Useful is also the SNLO website [100] from which a free simulation tool and other information are available.

2.5.1 **Second harmonic generation**

Second-order frequency conversion exploits the high nonlinear susceptibility \( \chi^{(2)} \) in crystals lacking inversion symmetry and gives rise to sum and difference as well as second harmonic generation (SHG) in which incident light of frequency \( \nu_1 \) is converted to light of double the frequency. In a lossless medium in which energy is conserved, SHG can be described by

\[ \nu_2 = 2 \cdot \nu_1 = \nu_1 + \nu_1. \]  

(2.26)
In the same system, the wave-vectors of the pump $\vec{k}_\omega$ and the frequency converted beam $\vec{k}_{2\omega}$ add up, as

$$\vec{k}_{2\omega} = \vec{k}_\omega + \vec{k}_\omega.$$  \hspace{1cm} (2.27)

The underlying physical mechanism is quickly summarized in the following. The incident pump beam at the fundamental frequency $\nu_1$, causes nonlinear polarization due to the $\chi^{(2)}$ nonlinearity in the crystal. It oscillates at double the fundamental frequency and, following Maxwell’s equations, radiates with the same frequency. While propagating in the nonlinear medium, both radiation fields interact with each other which gives rise to energy transfer from the fundamental to the frequency doubled wave. In order to be efficient, frequency doubling requires high pump intensities and because it crucially depends on the phases of the involved waves, requires phase-matching (PM).

2.5.2 Phasematching techniques

Phasematching techniques are used to control the interaction of the pump and the frequency converted beams by maintaining the phase relations between the wave-vectors. PM is usually achieved by minimizing the phase mismatch vector $\Delta \vec{k}$ between the fundamental and frequency doubled beam where,

$$\Delta \vec{k} = \vec{k}_{2\omega} - (\vec{k}_\omega + \vec{k}_\omega).$$  \hspace{1cm} (2.28)

For small $\Delta \vec{k}$, or ideally $\Delta \vec{k} = 0$, the fields frequency doubled photons generated along the optical path in the crystal add coherently. Due to chromatic dispersion caused by the nonlinear medium, the wave-vectors, $\vec{k}_{2\omega}$ and $\vec{k}_\omega + \vec{k}_\omega$, generally have different lengths.

**Birefringent phase matching** To minimize this $\Delta \vec{k}$ mismatch, several parameters of the crystal can be tuned. The orientation of the crystal axis with respect to the optical axis can be varied. The operating temperature of the crystal can be changed to adjust the crystal’s index of refraction. And the polarizations of the photons of the interacting beams can be adjusted to make use of the crystals birefringence. A good discussion of the PM techniques possible in birefringent, homogeneous materials is given for example in [78].

**Quasi-phase matching** With normal PM as described in the previous paragraph, frequency conversion is possible only at a fairly limited number of frequencies. The quasi-phase matching (QPM) technique, which has been employed in our studies, achieves similar frequency conversion results and greatly increases the number of frequencies able to be produced [78]. Instead of employing a homogeneous crystal, materials with spatially modulated (or poled) homogeneous
domains are employed. The domain length is chosen so that when the pump and signal (frequency
converted) photons are 180 degrees out of phase, a new domain with reverse nonlinear properties
begins. As the phase mismatch oscillates the conversion continues to grow. In other words, the
period of poling is equal to two times the coherence length $l_c$ of the two beams propagating in
the crystal. If compared to perfect phase-matching, QPM results generally lower conversion ef¬
ficiency for the same nonlinear coefficient, i.e. the effective nonlinear coefficient is reduced by a
factor of $2/\pi$. However, QPM has several advantages. It allows the use of the same polarization
direction for all interacting waves, and consequently, the use of the element of the nonlinear tensor
with the highest $\chi^{(2)}$. As mentioned, QPM has greatly increased the number of frequencies able
to be both generated and converted. It has also allowed the use of isotropic materials including
GaAs in frequency conversion processes. QPM also allows for propagation in the direction along
of crystal axis, thus avoiding walk-off and resulting in larger acceptance angle. QPM was first
demonstrated by Armstrong [101], in 1962, and has strongly evolved since into, e.g. in the widely
used periodically polled LiNbO₃ (PPLN) [80] and orientation-patterned GaAs stacks [102, 103]
and films [104, 105, 106].

2.5.3 Second harmonic generation using quasi-phase matching

Sutherland [78] gives an in-depth discussion on SHG using QPM. The conversion efficiency em¬
ploying $j$th-order QPM interaction in a odd number of domains $N$ (e.g. stacks) in the infinite
plane wave approximation for nondepleted pump is given as

$$\eta_{2\omega} = \frac{P_{2\omega}}{P_\omega} = \frac{8 \cdot \pi^2 \cdot (2/j\pi) \cdot d_{eff}^2 \cdot L^2 \cdot I_\omega}{\varepsilon_0 \cdot n_\omega^2 \cdot n_{2\omega} \cdot c \cdot \lambda_\omega^2},$$

where $P_\omega$ and $P_{2\omega}$ are the optical powers of the fundamental and frequency converted beams,
$L = N \cdot l_c$ is the interaction length (often crystal length) in the nonlinear medium (under the
assumption of low incident fields $l_c$ can be approximated to be the coherence length), $d_{eff}$ is
the effective nonlinear coefficient, $I_\omega$ is the pump wave intensity, $n_\omega$ and $n_{2\omega}$ are the refractive
indices at the respective wavelength (calculated from Sellmeier dispersion formulae), and $\lambda_\omega$ is
the vacuum wavelength of the fundamental beam. The effective nonlinear coefficient in case of
first-order QPM can be calculated from the nonlinear coefficient of the employed materials as

$$d_{eff} = \frac{2}{\pi} \cdot \frac{2}{\sqrt{3}} \cdot d_{ij},$$

where $d_{ij}$ is the nonlinear coefficient of the material.
with $d_{ij}$ being the $ij$th element of the tensor describing the nonlinear properties of the employed material. From Eq. 2.29 an equation for the intensity of the frequency doubled beam is derived

$$I_{2\omega} \propto \left( \frac{d_{eff}^{QPM}}{n_\omega^2 \cdot n_{2\omega}} \right)^2 \cdot (N \cdot l_c)^2 \cdot I_\omega^2. \tag{2.31}$$

The intensity of the second harmonic scales with both the squares of the fundamental intensity and the overall crystal length $L = N \cdot l_c$. The conversion efficiency scales linearly with the pump intensity. The above relations were used in the following. It should be noted, that this nonlinear dependency causes spatial and temporal shaping of a pulse. As a consequence, the linewidth for pulsed pump beams changes.

### 2.5.4 Quasi-phase matching materials

QPM materials are employed for frequency doubling and optical parametric oscillations and include periodically polled lithium niobate (PPLN) [80] and in recent years also gallium arsenide (GaAs), the material employed in our studies. Ferroelectric materials, such as LiNbO$_3$ in PPLN, can be periodically poled by means of ferroelectric domain engineering, where a strong electric field is applied to the crystals for some time using structured microelectrodes. The applied field strengths exceed the material specific coercive field strengths to achieve permanent domain reversal. The poling period, or domain length, defines the wavelengths of for which the crystal can be used and the order of QPM. Domain lengths (poling periods) of typically 20 to 30 microns and crystal lengths of tens of millimeters are commonly achieved.

GaAs is not ferroelectric and thus cannot be poled in the way PPLN can be. The bulk material used in our studies was obtained by bonding polished wafers of a specific thickness and arranged in alternating crystal orientations to form a periodic structure [102, 103]. However, this technique is limited to long wavelengths and often uses higher-order QPM. More recently, an all-epitaxial process has been developed ([104, 105] and others) that permits lithographic definition of the QPM structure. The resulting materials are termed orientation-patterned GaAs (OP-GaAs). Through a combination of different growth techniques, OP-GaAs crystals can be fabricated with sufficient lengths (20 mm) and thicknesses (500 μm) for practical nonlinear interactions. In addition to having established material technology and well known dispersion relations [105], GaAs is also of interest because of its wide transparency range (from 1 to 16 μm), high nonlinear susceptibility ($d_{14} = 90 \text{ pm/V}$), low absorption, high laser damage threshold and high thermal conductivity (0.46 W/cmK).
2.6 Signal extraction techniques

2.6.1 Definition of noise and background

Signal extraction techniques are used to recover a measurement signal from a background or noise floor featured in an experiment. Background can be defined as inherent to the experimental setup and always present, but as such does not contain relevant information. Although constant background may simply be subtracted, specific noise reduction measures are taken dependent on the underlying noise mechanisms. Noise is comprised of a wide range of frequency components with uncorrelated phases and noise fluctuates in both the amplitude and frequency. An overview of relevant noise sources and backgrounds, as well as of commonly used signal extraction techniques, is given below.

2.6.2 Specific noise sources and backgrounds

Noise sources  
White noise is not dependent on the frequency and has a flat power spectral density. 1/f noise (or flicker noise) is present in electronic circuits, and elsewhere. It exhibits a frequency spectrum with a power density inversely proportional to the frequency. It can be minimized by part selection and circuit design. Detection and signal sampling above the 1/f-noise corner frequency is also an option and commonly achieved by modulation techniques. Shot noise [107] reflects the discrete nature of electric current or photons flux and its effects can be minimized for the system by the proper selection of the operating point.

In addition to these general noise sources there are several sources of noise common in spectroscopy. Electronic noise [108, 109] in detectors, microphones, and amplifiers must be minimized during circuit design. In PA detection acoustic noise and vibrations form the environment can be shielded mechanically, reduced by the use of resonance, and lock-in techniques. Microphone noise, i.e. the noise voltage present at the microphone output terminals, is the product of the normalized noise pressure value due to the pressure fluctuations (i.e. Brownian motion) at the diaphragm, the microphone responsivity at the corresponding frequency, and the square root of the measurement bandwidth. Microphone selection and signal recovery are discussed in [110]. Gas flow noise can be minimized by low flow rates, acoustic filtering (muffler) and design features like large tube diameter. Chopper vibrations can be mechanically isolated and must be incorporated into the design. Phase jitter is introduced by chopper speed fluctuations and can be minimized by selecting an appropriate device.


**§2.6 Signal extraction techniques**

**Backgrounds**  Window heating signal background is a common problem in PAS. It is caused when windows of the sample cell absorb incident laser light and can be minimized by arranging cell windows of the PA cell at Brewster-angle or by the use of high-grade antireflection (AR) coatings. Additionally window heating signal reduction can be achieved by employing buffer volumes, positioning the windows at acoustic nodes, or acoustic notch filter designs. The windows ideally face downwards to eliminate dust collection and are protected against other sources of contamination. The window material should feature low absorption and low scattering properties. Scattering of light inside a cell can cause generation of sound waves. Scattered light is also lost, which can lead to an error in absorption spectroscopy. Fringes can form at interfaces through which coherent light is transmitted and is often a problem with cell windows. The use of high-quality AR coatings, wedged windows or Brewster-angled cell windows reduces this problem. Furthermore, dithering of the coherent source may also be employed. Adsorption is the accumulation and formation of a layer of gas molecules on the surface. Adsorption and the reverse process, desorption, cause a background in a measuring cell and lead to false concentration readings. Using materials and surface finish with low adsorption potential [111, 112, 113] (i.e. high-quality finish and coatings) can reduce this problem. Because adsorption and desorption processes are relatively slow, the background error caused by adsorption can be reduced substantially by an increase in the flux of molecules (gas flow). However, detection at high flow rates may cause other problems, as the flow noise increases rapidly when the flow velocity exceeds a critical value. General design guidelines for PA cells are found in [99].

**2.6.3 Bandwidth narrowing techniques**

Limiting the bandwidth effectively reduces the noise and background signals present at the optical or acoustical detector or in the electronic signal path and is achieved by spectral, acoustic, and electronics filtering and signal processing. Two employed electronics signal processing methods employed are described in the following.

**Lock-in amplifier**

The basic idea behind lock-in amplifier is shifting the signal to a less noisy region for signal recovery. The frequency shift is accomplished by modulation of the stimulus, i.e. incident laser beam in spectroscopy. Between the modulated signal and the lock-in amplifier a phase-lock is established. This allows the signal to be measured at very narrow linewidth by a synchronous detector. A lock-in amplifier has been employed in the ECDL based spectrometers (chapter 4).
Averaging and boxcar averager

Due to the random nature of noise, a signal can be improved by averaging the time-domain signal $q$-times. This method is also applicable if the signal to be measured is not strictly periodically modulated, which is not the case with lock-in amplifiers. The accumulated signal increases linearly with $q$, while the noise contribution grows only with $\sqrt{q}$, assuming uncorrelated Gaussian noise. Averaging is often combined with a temporal filtering technique in which a trigger opens a predefined time-slot for signal acquisition. This combined technique is referred to as boxcar averager or integrator. Boxcar averaging has been used within this thesis to effectively acquire signals generated in the pulsed photoacoustic spectrometer (chapter 3).

2.6.4 Modulation techniques

Introducing a periodic change in one parameter, typically the excitation stimulus, of the experiment results in a modulated signal. The signal can be readout with a box-car averager, or a lock-in amplifier. Amplitude (AM) and wavelength (WM) techniques employing a lock-in amplifier have been used in the experiments in this thesis and are briefly discussed below.

Amplitude modulation

Modulating the amplitude (AM) of a carrier of frequency $\nu$ and having a small linewidth with a periodic function of frequency $\Omega$, where $\Omega \ll \nu$, results in a DC component and harmonics with frequencies $\Omega, 2\Omega, 3\Omega$ and so on. Performing phase-sensitive detection with a lock-in amplifier allows the measurement of individual Fourier coefficients. The Fourier series of the selected modulation signal elucidates the spectral distribution, amplitude and phase of each component. Normally a symmetric square-wave is chosen as the modulation signal and what results is strong DC and odd in-phase harmonics which quickly decay with higher harmonics. Usually the DC component is measured, unless excessive $1/\nu$-noise or other reasons suggest the detection of a higher harmonic. Practical implementations use a mechanical chopper with a modulation frequency $\Omega$ in the range of a few ten Hz (above the $1/\nu$-noise of the system) to few kHz (mechanical resonance of the chopper). The fundamental resonance frequency of the photoacoustic cell was selected and symmetric square-wave were selected in this study.

Wavelength modulation

In wavelength modulation (WM) schemes, a carrier of frequency $\nu$ and having a small linewidth is modulated with the frequency $\Omega$ and modulation depth $m$, where $m, \Omega \ll \nu$, and the carrier
frequency slowly increases and decreases by a small amount $m$. In the vicinity of an absorption feature (much wider than $m$ and $\Omega$), this WM is converted to AM, as shown here in Fig. 2.5. The conversion of WM to AM depends on the slope (or derivative) of the absorption feature at a particular frequency. In the center of Fig. 2.5, when the carrier is at the point of maximum absorption (i.e. line centre), the conversion goes to zero and the phase relationship between WM and AM changes sign. Far away from the absorption feature the conversion rate is zero. The resulting curve using phase-selective detection is shown in Fig. 2.6 and approximates the first derivative of the absorption feature.

If the frequency-shift (modulation depth) $m$ is small when compared to the broad absorption linewidth, the carrier $I_T(\nu + m \sin \Omega t)$ after transmission through an absorbing media can be

**Figure 2.5:** Scan across an absorption feature with a wavelength modulated carrier: wavelength modulation is converted to amplitude modulation depending on the slope of the absorption feature (top, bottom) and is zero at the line centre (center).
§2.6 Signal extraction techniques

Figure 2.6: The scan across the absorption line by wavelength-modulation techniques taking the phase into account: the signal depends on the sign of the slope of the absorption feature and a zero crossing indicates the line centre if phase-selective detection is used.

expanded in a Taylor series

\[
I_T(\nu + m \sin \Omega t) = I_T(\nu) \\
+ (m \sin \Omega t) \frac{dI_T(\nu)}{d\nu} \\
+ \left( \frac{m^2 \sin^2 \Omega t}{2!} \right) \frac{d^2I_T(\nu)}{d\nu^2} \\
+ \left( \frac{m^3 \sin^3 \Omega t}{3!} \right) \frac{d^3I_T(\nu)}{d\nu^3} \\
+ \ldots. \tag{2.32}
\]

Regrouping the terms by multiples of \( \Omega \) gives

\[
I_T(\nu + m \sin \Omega t) = \left[ I_T(\nu) + \frac{m^2}{4} \frac{d^2I_T(\nu)}{d\nu^2} + \ldots \right] \\
+ \sin \Omega t \left[ m \frac{dI_T(\nu)}{d\nu} + \frac{m^3}{8} \frac{d^3I_T(\nu)}{d\nu^3} + \ldots \right] \\
+ \cos 2\Omega t \left[ -\frac{m^2}{4} \frac{d^2I_T(\nu)}{d\nu^2} + \ldots \right] \\
+ \ldots. \tag{2.33}
\]

The coefficient of the second term of the right side is essentially \( m \) multiplied by first derivative of the transmitted intensity. Thus, an approximation of the derivative of the absorption feature can be retrieved. Analogously, detection at \( 2\Omega \) reveals the second derivative, and so on. In the literature, this is often referred to as derivative spectroscopy, or \( 1f \)- and \( 2f \)-detection, respectively. The harmonic at which data is recorded is a setting of the lock-in amplifier.

In this study absorption and photoacoustic spectroscopy using \( 1f \)- and \( 2f \)-detection schemes have been implemented.
2.7 Signal-to-noise ratio and detection limit

**Signal-to-noise ratio** The signal-to-noise ratio (SNR) compares the amplitudes of the mean value of the noise floor and the nominal signal level. As a convention used in this work, the noise floor of a spectrometer includes contributions that provide constant background and that cause increased noise fluctuations. The background noises are manifold, as they can be constant over time (e.g. chopper noise), scale with the incident intensity (e.g. window heating signal and cell noise caused by scattered light in PAS) or distort the baseline (optical fringes in transmission spectroscopy). These background contributions can often be assessed by reference measurements (e.g. calibrated gas mixtures or non absorbing gases) and thus eliminated by data manipulations (e.g. subtraction or baseline corrections). Various sources increase the noise fluctuations (e.g. laser intensity noise, detector and electronic noise, phase jitter, microphone noise, ambient noise, gas flow noise, discretization noise of the analog-to-digital conversion). Bandwidth narrowing techniques in combination with modulation schemes are commonly used to recover signals masked by noise. This emphasizes the importance of a good spectrometer design aiming at inherently low noise and background. However, noise fluctuations eventually limit the SNR and detection limits of a trace gas sensor. A fundamental limit is set by the photon shot noise or quantum noise limit \[107\]. At the expense of added complexity, this noise can be further minimized using squeezed states of light, states that have less uncertainty in one observable than does the vacuum state \[114, 115\].

**Detection limit** The detection limit is defined as the minimum concentration of a species that can be detected with a system. In the spectroscopy literature two definitions of the detection limit are commonly found: one with \(SNR = 1\) and a more conservative with \(SNR = 3\).

It is assumed, that the measured points, signal or noise, follow a Gaussian distribution centered around the mean value of the signal or noise floor. Both, the mean value, \(N_{\text{mean}}\), and the standard deviation, \(\sigma_{\text{stat}}\), can be calculated from this data set. An interval of \(|6\sigma_{\text{stat}}|\) includes 99.7% of all measured data points and defines the \(SNR = 3\). Thus, for equal amplitude (\(SNR = 1\)), signal and noise are indistinguishable. However, for \(SNR = 3\), signal and noise are distinguishable, as the amplitude difference (mean values) is sufficient to not have overlap between the noise distribution (centered around the noise floor level mean value) and the signal distribution (centered around the minimal signal level mean value). The detection limit definition using a \(SNR = 3\) has been used in this thesis to ensure that measured signals are distinguishable from noise (and background). The detection limit was derived from the minimal number density \(N_{\text{min}}\).
2.8 Selecting absorption features and laser wavelength

The selection of the most appropriate absorption feature is very important in trace-gas sensing. It impacts the design of the spectrometer as well as qualitative and quantitative analysis of the samples. A detailed discussion can be found in [22].

Tuning range and linewidth The identified absorption line must lie well within the tuning range of the spectroscopic light source. This prevents the loss of detection due to aging of the source or change in environmental parameters that may affect the source or other parts of the spectrometer. All light sources including lasers have a finite linewidth. Laser sources employed in spectroscopic trace-gas sensors should ideally sense absorption features which are wider than the laser linewidth, e.g. CO₂ absorption linewidth: 0.1 cm⁻¹ (3 GHz) or 0.03 cm⁻¹ (0.9 GHz) at room temperature and 1 bar or 0.1 bar, respectively. The recorded absorption profile is the convolution of the lineshape functions of both the laser and absorption feature.

Monitoring of several species The absorption features should be in a close spectral vicinity of each other but not overlap. The lines should also be of sufficient and similar strength well within the dynamic range of the sensor. This minimizes potential effects of nonlinearities, spectral dependencies of the detector and other system related errors, whilst maintaining similar high $SNR$.

Influence of temperature and pressure control Since the linestrength depends on the temperature through the population of the states (Boltzmann distribution, Eq. 2.10) and the lineshape reflects the elastic collisions (i.e. pressure) in the sample (line broadening, Eq. 2.19), if they cannot be controlled, lines should be selected that respond similar to changes in these environmental parameters. Temperature and pressure of the sample should also be monitored.

Interference with water and other species Water vapor is always present in ambient air and is often the most abundant absorbing species in infrared spectroscopic studies. Lines far from the water absorption line but also from other abundant species should be selected. For example, in medical diagnostics CO₂ and water vapor are these abundant species.
This chapter describes the photoacoustic spectrometer employing a frequency-doubled CO₂ laser. The unique continuously tunable laser source and measurements employing both the fundamental and frequency doubled radiation are discussed.

3.1 Photoacoustic spectrometer employing two wavelengths simultaneously

The basic experimental setup of the photoacoustic (PA) spectrometer employing two wavelengths simultaneously is shown in Fig. 3.1. As a novelty, both laser beams are available individually.

![Diagram](image)

**Figure 3.1:** PA spectrometer employing both the fundamental (FUN) and second harmonic (SHG) radiation of a pulsed, continuously tunable high-pressure CO₂ laser.
or simultaneously. The system is comprised of a pulsed CO\textsubscript{2} laser [51] emitting radiation in the fundamental (FUN, 10 µm) and frequency doubled (SHG, 5 µm) regime [54], a PA detection scheme and a data acquisition system. A computer is used for tuning the laser and recording the measured data. The zeroth-order grating reflection enters the small PA cell filled with 100 mbar CO\textsubscript{2}. The generated signal serves as a wavelength ruler. A small fraction of the FUN pulse energy is sampled by a ZnSe beam splitter and used as a monitoring and trigger signal. A second ZnSe beam splitter divides the incoming FUN pulse. The larger fraction pumps the nonlinear GaAs crystal for frequency doubling. The smaller fraction recombines coaxially with the optical path after the SHG stage. Both beams propagate through the PA cell [116] (see section 3.3). Dichroic mirrors combine and separate the FUN and SHG radiation. An 8-bit digital sampling oscilloscope (model 9450, LeCroy Europe SA, Meyrin, Switzerland) digitizes the PA signal. The pulse energies of the FUN and SHG beams, which are needed for normalization of the PA signal, are measured by calibrated pyroelectric detectors and are directly digitized in the smart display (PB50BB and PE10-SH probe heads with Dual Channel LaserStar, Ophir Optronics Ltd., Jerusalem, Israel). The PA and energy readings are transferred to the computer via GPIB interface for processing and storage. Gas samples were taken either from certified mixtures from gas bottles or prepared in a gas mixing unit (not shown in Fig. 3.1) equipped with mass flow controllers.

The PA spectrometer has several unique features not reported elsewhere. Although frequency doubled line-tunable CO\textsubscript{2} lasers [18, 102, 103, 117, 118] as well as continuously tunable lasers [51, 119, 120, 121, 122, 123] have been reported before, to our best knowledge, this is the only frequency doubled high-pressure laser [54]. Additionally, the possibility of employing both the FUN and SHG radiation (in coaxial alignment), either individually or coincidentally, in the same volume of the gas sample is unique. This enables measurements of the same gas sample in extended wavelength ranges in one spectrometer. This is relevant if the sample is of unknown composition and thus may also not be stable. Furthermore, the new spectroscopic technique enables trace gas sensing at multi-wavelengths simultaneously, thus allowing the sample to be quickly investigated for absorption features within the given spectral ranges. Finally, this technique makes gas kinetics studies of species excited at two wavelengths with fixed relation, namely the fundamental and second harmonic, at narrow line width, possible.

### 3.2 Continuously tunable high-pressure CO\textsubscript{2} laser

The home-built continuously tunable high-pressure CO\textsubscript{2} laser has been described previously in detail [50, 51] and is depicted schematically in Fig. 3.1. It operates with a gas mixture of 5% CO\textsubscript{2},
§3.2 Continuously tunable high-pressure CO$_2$ laser

5% N$_2$, and 90% He at a pressure of 10 bar in flow mode. The amplifier section has two 32 cm long electrodes for glow discharge excitation with preionization and is made from Makrolon (translucent high performance polycarbonate). A photo of the amplifier during glow discharge excitation is shown in Fig. 3.2. The laser is equipped with a Littman resonator [124] and wavelength tuning is achieved by rotating a flat cavity mirror by a computer controlled DC-drive. The incident angle of the metal diffraction grating is 77°. The grating has 150 lines/mm and is blazed for 943.4 cm$^{-1}$ (10.6 µm). The first-order reflection off the grating is reflected back and the zeroth-order is coupled out. An second zero-order reflection is available for emission wavelength recording employing a small PA cell filled with CO$_2$. This wavelength-tuning arrangement ensures a large tuning range (76 cm$^{-1}$ between 932 cm$^{-1}$ and 1088 cm$^{-1}$) and a very narrow linewidth of 540 MHz, making it well-suited for spectroscopic applications. Pulse energies of up to 80 mJ (around 10.6 µm) can be achieved and are limited by the damage threshold of the metal grating (arching), while 10 mJ are maintained throughout the tuning range. The laser pulse has a repetition rate of about 1 Hz. The laser source exhibits very strong longitudinal mode beating as shown in Fig. 3.3 and pulse-to-pulse fluctuations. Although the observed mode beating and the fluctuations pause no problem for PA studies in the FUN regime, efficient SHG is compromised as discussed below. A change in the design of the laser resonator would have been required to resolve this issue, which was beyond the scope of this thesis. However, inserting a saturable absorber [125] for passive mode-locking (suitable for the 10.6 µm range), a discharge triggered plasma switch mode-locking [123] (timing issues can be expected), a new resonator design optimized for single longitudinal modes [126], or a hybrid laser system employing a narrow linewidth tunable seed laser [127, 128] could potentially resolve the longitudinal mode beating and reduce the pulse fluctuations.
§3.2 Continuously tunable high-pressure CO₂ laser

3.2.1 Second harmonic generation

A bulk periodically poled, diffusion bonded GaAs crystal [102, 103] has been employed in a single pass frequency conversion stage for second harmonic generation in this thesis [54]. All-epitaxially-grown orientation patterned (OP) GaAs [104, 106] was not available when the nonlinear crystal was selected. However, GaAs is transparent in the range of 1 to 16 μm, features low absorption, high thermal conductivity, high average power handling capabilities and high damage threshold. The reported nonlinear coefficient for GaAs by Shoji et al. [129] is $d_{14} = (d_{36}) \approx 90 \text{ pm/V}$. The estimated figure of merit is 124 (pm/V)$^2$. Hence, GaAs compares well with other well-known nonlinear materials employed for the frequency conversion in the mid-infrared, such as ZnGeP₂, AgGaSe₂, CdGeAs₂, and GaSe [130]. Key parameters when selecting material for nonlinear frequency conversion include nonlinear coefficient, transparency range and damage threshold. Table 3.1 lists the properties of these materials commonly used for CO₂ laser frequency conversion [79].

ZnGeP₂ has a high nonlinear coefficient (75 pm/V) and high thermal conductivity (0.35 W/cmK). This material has been employed in OPOs [131] operating down to 2 μm employing birefringent PM. The ZnGeP₂ transmission range of 0.74–12 μm is limited by onset of the multiphonon absorption at around 8.5 μm, which results in a high thermal load at CO₂ laser doubling frequencies. AgGaSe₂ has an excellent long wave transparency range (from 0.7 to 19 μm) and is available with low intrinsic loss. Unfortunately, AgGaSe₂ has low nonlinear coefficient (half of ZnGeP₂). For CO₂ laser doubling the low nonlinear coefficient could be partly compensated by using long crys-
§3.2 Continuously tunable high-pressure CO₂ laser

Table 3.1: Selected nonlinear materials used for frequency conversion of 10 μm-radiation.

<table>
<thead>
<tr>
<th>Nonlinear optical material</th>
<th>Nonlinear coefficient at 10 μm [pm/V]</th>
<th>Transparency range [μm]</th>
<th>Damage threshold (pulse duration at given wavelength)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnGeP₂</td>
<td>d₃₆ = 75</td>
<td>0.74–12</td>
<td>60 MW/cm² (100 ns at 10.6μm)</td>
</tr>
<tr>
<td>AgGaSe₂</td>
<td>d₃₆ = 33</td>
<td>0.71–19</td>
<td>10 MW/cm² (125 ns at 10.6μm)</td>
</tr>
<tr>
<td>CdGeAs₂</td>
<td>d₃₆ = 235</td>
<td>2.4–18</td>
<td>33 MW/cm² (150 ns at 10.6μm)</td>
</tr>
<tr>
<td>GaSe</td>
<td>d₂₂ = 54.4</td>
<td>0.62–20</td>
<td>30 MW/cm² (150 ns at 9.3μm)</td>
</tr>
<tr>
<td>GaAs</td>
<td>d₁₄ ≈ 90</td>
<td>1–16</td>
<td>30 MW/cm² (90 ns at 10.6μm)</td>
</tr>
</tbody>
</table>

Table 3.2: Summarized properties of the employed diffusion bonded periodically poled GaAs crystal.

| GaAs crystal | Transparency range 1–16 μm | Damage threshold 30 MW/cm² | Nonlinear coefficient d₁₄ = (d₃₆) ≈ 90 pm/V | Figure of merit 124 (pm/V)² | First-order QPM 53 domains, 106 μm thickness | Size (l×h×w) 5.6×2×4 mm |

optical axis. As stated in [103] the conversion efficiency for this crystal is not equal across the crystal face. To avoid boundary effects, the pump beam was focused onto the center of the crystal face. This favors safe operation rather than high conversion efficiency. Fig. 3.4 shows the relation between the pump energy E_FUN (polarization along (111)) and the SHG beam energy E_SHG. As expected the measured data shows a quadratic relation (see Eq. 2.31). As Fig. 3.4 implies, SHG pulse energies E_SHG of 1 mJ are achieved at pump energies of E_FUN of 80 mJ, corresponding to an (external) energy conversion efficiency of 1.25%. Making a plane-wave, non-depleted pump approximation [78] (Eq. 2.31), with a maximum applied pump intensity I_w of 21.5 MW/cm², the
externally energy (flat-top pulse) conversion efficiency is estimated to 11.4%. Since the antireflection (AR) coating was damaged, it was ignored completely and Fresnel reflection was assumed. The crystal periodicity was assumed to be perfect. This estimation neglects the actual temporal pulse form exhibiting longitudinal mode beating shown in Fig. 3.3, spatial intensity distribution of the TEM00 mode, limited crystal transparency of 60% and deviation from ideal periodicity, as well as focusing parameters. Hence, this estimation gives an upper limit as some parameters needed for a more sophisticated theoretical approach, vary considerably from pulse to pulse, as is evident from Fig. 3.4. It should be noted that the actual conversion efficiency and hence the achievable SHG pulse energy is limited by the damage threshold of the crystal of 30 MW/cm² [103]. Fig. 3.5 shows SHG conversion efficiency as a function of pump wavelength. As expected from the given data of our crystal [103], the 9R and 9P branches of the CO₂ laser could not be exploited to generate significant SHG energies.

Figure 3.4: Generation of SHG energy as a function of incident FUN pulse energy at 10.55 μm.
§3.2 Continuously tunable high-pressure CO₂ laser

3.2.2 Summarized characteristics of the frequency doubled CO₂ laser

The main characteristics of the fundamental (FUN) and frequency doubled (SHG) continuously tunable high-pressure CO₂ laser are summarized in Tables 3.3 and 3.4. Table 3.3 gives the characteristic tuning ranges of both the fundamental (FUN, measurement) and the frequency doubled (SHG, calculated from FUN) radiation. The SHG characteristics listed in Table 3.4 are deduced from measurements. The pulse energies available form the frequency doubled CO₂ laser are sufficient for PA measurements in both the FUN (9R, 9R, 10P and 10R) and SHG (10P and 10R) wavelength regimes in the important MIR fingerprint region. The wide continuous tuning range, combined with the narrow linewidth of both the FUN and SHG radiation, allow for sensitive and selective trace gas sensing at atmospheric pressure and below. For example, the linewidths of both the FUN and SHG are considerably smaller than a typical absorption line for CO₂ at room temperature and atmospheric pressure (1 bar) and (0.1 bar), 0.1 GHz (0.1 cm⁻¹) and 900 MHz (0.03 cm⁻¹),

Table 3.3: Wavelength ranges of the FUN (10 μm) and SHG (5 μm) output of the frequency doubled CO₂ laser.

<table>
<thead>
<tr>
<th>CO₂ laser branch</th>
<th>FUN (10 μm) range [μm]</th>
<th>[cm⁻¹]</th>
<th>SHG (5 μm) range [μm]</th>
<th>[cm⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>9P P(28)–P(8)</td>
<td>1038.89–1056.89</td>
<td>9.63–9.46</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>9R R(4)–R(36)</td>
<td>1067.16–1087.69</td>
<td>9.37–9.19</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Figure 3.5: Generation of SHG radiation as a function of the FUN wavelength. The noise in the 9R and 9P branches is due to electric coupling from the high voltage discharge.
§3.3 Photoacoustic cells

Table 3.4: Characteristics of the FUN (10 \(\mu\)m) and SHG (5 \(\mu\)m) output of the frequency doubled CO\(_2\) laser.

<table>
<thead>
<tr>
<th>CO(_2) laser</th>
<th>FUN (10 (\mu)m) range</th>
<th>SHG (5 (\mu)m) range</th>
</tr>
</thead>
<tbody>
<tr>
<td>pulse energy</td>
<td>max. 80 mJ, min. 10 mJ</td>
<td>max. 1 mJ, typically 0.04 to 0.4 mJ</td>
</tr>
<tr>
<td>pulse repetition rate</td>
<td>1 Hz typically</td>
<td>same as pump source</td>
</tr>
<tr>
<td>pulse length (FWHM)</td>
<td>110 ns typically</td>
<td>73 ns typically</td>
</tr>
<tr>
<td>linewidth</td>
<td>0.018 cm(^{-1}) (540 MHz)</td>
<td>0.0315 cm(^{-1}) (1050 MHz)</td>
</tr>
<tr>
<td>laser gas mixture</td>
<td>5% CO(_2), 5% N(_2), and 90% He</td>
<td>N/A</td>
</tr>
<tr>
<td>operating pressure</td>
<td>10 bar typically</td>
<td>N/A</td>
</tr>
</tbody>
</table>

respectively. The unique laser source has been applied in both the FUN [53] and SHG regime [54]. As a novelty, simultaneous use of both the SHG and FUN radiation is demonstrated in this thesis.

3.3 Photoacoustic cells

During the course of this thesis different PA cells have been employed:

a) PA cell with 10-microphone array

The PA cell featuring a 10-microphone in-line array was employed to record spectra from dimethyl ether and bromomethane [53] in the FUN regime (10 \(\mu\)m). It has an optical absorption path-length of 52 cm and a volume of 500 cm\(^3\). It can be operated in stop and flow mode with rates up to 2 slm and gas pressures up to 1 bar.

b) PA cell for photo thermal beam deflection studies

For photo-thermal beam deflection studies [52], a specially designed PA cell with a single microphone and the possibility for out-coupling of the deflected beam was employed. This cell (diameter 70 mm, length 400 mm) was particularly employed in the FUN regime (10 \(\mu\)m) and for characterization of the SHG radiation.

c) PA cell with 80-microphone array

The nonresonant, single pass PA cell [116] shown in Fig. 3.6 features an 80-microphone array (BK 1751, Knowles Acoustics, Burgess Hill, UK) combined with a built-in bandwidth limited (bandpass with center frequency 15 kHz and bandwidth 10 kHz) low noise battery operated amplifier. The cell is sealed with BaF\(_2\) Brewster windows and operates in stop and flow mode. The small gas volume of 180 cm\(^3\), together with a turbulent-free flow rate of up to 700 cm\(^3\)/s, results in
a time constant of only a few seconds for a complete gas exchange. Additional high and low-pass filtering suppresses broadband and high frequency noise generated by the laser discharge. This cell was employed for the measurements discussed below.

![Figure 3.6](image.png)

**Figure 3.6:** PA cell employing an tubular 80-microphone array and built in low noise amplifier. The housing with the BaF Brewster windows is not shown. Microphones and a match are depicted for reference.

### 3.4 Measurements

Although measurements have been performed within both the FUN and SHG range of the CO$_2$ laser, we concentrate in the following studies on the 5 $\mu$m SHG regime.

#### 3.4.1 Pressure dependence of the photoacoustic signal

The strength of the PA signal [97, 98] depends not only on the absorption properties of the species in the sample, but also scales linearly with the energy of the incident laser pulse (Eq. 2.24) which is used for normalizing the PA signal. Other parameters (fixed in the PA experiment) include the laser linewidth, the profile and position of the beam relative to the PA cell and the properties of the employed microphone [110].

The response of the 80-microphone array PA cell was deduced from room temperature measurements on 1% nitric oxide (NO) diluted in nitrogen (N$_2$) for total pressures ranging from 58 mbar to 858 mbar. The solid line in Fig. 3.7 represents the theoretical pressure-dependent absorbance based on HITRAN data. The normalized PA signal remains nearly constant for total gas pressures from near atmospheric pressure down to 400 mbar, but decreases strongly for pressures below...
Figure 3.7: Measured microphone signal for 1% nitric oxide (NO) diluted in nitrogen (N2) vs. total gas pressure around 1881 cm⁻¹ at room temperature. HITRAN reference data (solid line) indicates the decrease in absorbance. Both the experimental data and HITRAN data are normalized to coincide at a pressure of 858 mbar. The deviation between measured data and HITRAN data is attributed to the pressure-dependent microphone responsivity, the reduction in the number of absorbing molecules and the reduction in the linewidth overlap between the absorption and laser lines.

400 mbar. For a pressure of 200 mbar, the signal has halved. The difference between the PA signal and the absorbance increases towards lower pressure and is also more pronounced at gas pressures below 400 mbar. This effect is attributed to three causes, namely the responsivity of the microphone employed here, the number density of the absorbing species and the overlap of the laser and absorption lines. The microphone responsivity depends on pressure and is an inherent property of the microphone. However, adsorption of molecules on the membrane, change of the membrane properties caused by reactive species, and aging also influence the responsivity. The number density of the absorbing species scales linearly with pressure, although its concentration, i.e. 1% NO diluted in N2, was constant in our measurement. The PA signal also depends on pressure (and the normally constant temperature). With lowering the pressure, the linewidth of the absorption line, with contributions from both Doppler (Eq. 2.18) and pressure (Eq. 2.19) broadening, is reduced (see also section 4.5.1). In this case, the amount of absorbed radiation is determined by the convolution of the laser linewidth (broad) and the absorption line profile (narrow). Hence, this effect will also reduce the recorded PA signal. Broader laser linewidths are thus favored at higher pressures, but result in reduced selectivity at lower pressures. Despite this drop in sensitivity, it should be emphasized that PA measurements at lower pressures may still be advantageous because absorption features become more distinct due to re-
duced pressure broadening. This is important in cases of multicomponent samples, which require high selectivity to be analyzed. This approach is, however, limited by the available laser linewidth.

### 3.4.2 Multicomponent mixture containing nitric oxide and water

**Concentrations of nitric oxide and water**

Fig. 3.8 shows a measurement of a multicomponent mixture containing nitric oxide (NO) and water vapor (H₂O), as an impurity and interfering species (see sections 1.2.2 and 2.8). The PA cell was operated in stop-flow mode. The two species were buffered in nitrogen (N₂) at a pressure of 402 mbar and room temperature and recorded in the spectral region 1870 to 1905 cm⁻¹. HITRAN data is given for reference. To determine the detection limit, an absorption line was scanned and the line profile was fitted to a Voigt profile. The amplitude of the fit was then compared to three-times the standard deviation ($SNR = 3$) of the baseline. The concentration was derived from HITRAN reference data and the concentrations (detection limits) obtained for NO and water vapor are 1% NO (42.2 ppmV) and 2.1% water vapor (136 ppmV), respectively.

The presence of an interfering substance, i.e. water vapor, demonstrated the selectivity of the spectrometer due to its wide tuning range combined with a narrow linewidth. This is important in the analysis of human exhalation [23, 24], which among traces of several substances contains high concentrations of the interfering species water vapor (H₂O) and CO₂ (see section 4.4.1).
Isotopomers of nitric oxide

A certified mixture of NO buffered in nitrogen (N₂) was measured at concentrations of 493 ppmV and 1% at various pressures and room temperature in stop-flow mode to find an suitable concentration and pressure regime for assessing the isotopomers. The measurement of 493 ppmV NO, buffered in nitrogen (N₂) at atmospheric pressure is depicted in Fig. 3.9. HITRAN data for NO

![HITRAN data](image)

**Figure 3.9:** Normalized PA spectra of 493 ppmV NO buffered in nitrogen (N₂) measured at atmospheric pressure and room temperature. a) HITRAN data (at 100 mbar) is given as a line position reference. The three spectral features indicated refer to the measurements below in b), c) and d). b) Q-branch measurement around 1874.1 cm⁻¹. c) Measurement of ¹⁵NO around 1878.468 cm⁻¹. d) Measurement of ¹⁴NO around 1881.039 cm⁻¹.

in the range of the frequency-doubled 10P branch of the CO₂ laser are given in Fig. 3.9 a) as reference. The Q-branch (centered around 1874.1 cm⁻¹) is shown in Fig. 3.9 b). Another important issue is the ¹⁵N/¹⁴N isotope ratio, which can be determined with our system. We derived the ¹⁵NO/¹⁴NO isotope ratio by measuring ¹⁴NO at 1881.039 cm⁻¹ (Fig. 3.9 c)) and ¹⁵NO at 1878.468 cm⁻¹ (Fig. 3.9 d)). The resulting value of \((3.58 \pm 0.55) \times 10^{-3}\) is in good agreement with literature data of \(3.700 \times 10^{-3}\). From Fig. 3.9, it should be noted that the precision of the isotope measurement could be substantially improved by measuring at an absorption line in the 1903 cm⁻¹ region and also if higher concentrations of NO were analyzed. However, this has not been possible because of the gap around 1903 cm⁻¹, which is beyond the continuous tuning range (Fig. 3.8). In general, all four tuning range intervals of the high-pressure CO₂ laser, i.e. 9P,
9R, 10P and 10R branches, exhibit gaps near their limits since the laser line overlap becomes less pronounced.

A noninvasive spectroscopic detection of $^{15}\text{N}$ (often together with $^{13}\text{C}_2\text{O}_2$), or other isotopomers would, provides an alternative to mass-spectrometry (MS) in medical diagnostics, for example, to study nitrogen metabolism, e.g. collagen turnover, amino acids, or in case of carbon dioxide, the Helicobacter pylori ($^{13}\text{C}_2\text{O}_2$/^{12}\text{C}_2\text{O}_2$ ratio) in humans. NO in the body, due to its small size, is a highly diffusible molecule and a ubiquitous bioactive molecule. It is a key biological messenger molecule, playing a role in a variety of biological processes. The detection of the $^{15}\text{N}/^{13}\text{C}$ isotope ratio from $\text{N}_2$ and $\text{CO}_2$ by mass-spectrometric measurements may be difficult. The nitrogen content is relatively low in organic compounds, for example amino acids contain 11-times more carbon than nitrogen. $\text{N}_2$ and CO (from incomplete combustion) produce an isobaric interference at $m/z = 28$ (mass-to-charge-ratio).

### Linewidth measurement of the frequency doubled CO$_2$ laser

The absorption line of 1% NO at 1881.039 cm$^{-1}$ recorded at a pressure of 58 mbar was used for the approximation of the laser linewidth in the SHG regime. Taking a Gaussian absorption profile (for simplicity) and a Gaussian laser line profile, a value of 0.0315 cm$^{-1}$ (1050 MHz) was deduced, as listed in Table 3.3.

### 3.4.3 Carbon dioxide measurement

Fig. 3.10 shows a measurement of CO$_2$, another relevant gas. Although the SHG CO$_2$-laser wavelengths are outside the strong absorption region of CO$_2$, monitoring is feasible as the experimental data that were recorded at room temperature and 249 mbar of pure CO$_2$ and their HITRAN

![Figure 3.10: Normalized PA spectrum of pure CO$_2$ measured at a pressure of 249 mbar and room temperature around 1899.115 cm$^{-1}$. HITRAN data is given as reference.](image-url)
The detection limit of CO₂ (SNR = 3) of 2.55% was derived from a measurement of pure CO₂ recorded at 1899.115 cm⁻¹ at 249 mbar and room temperature. The measured data was fitted with a Voigt profile as described above. The rather high detection limit for CO₂ is due to the low pulse energies of $E_{\text{SHG}} \leq 1$ mJ available in the 5 μm wavelength range, the fact that only nonresonant PA detection was feasible at the small pulse repetition rates involved, and the small absorption cross section of CO₂ outside the fundamental region. The time required to record a spectrum should also be crucial, as this can be important in selected monitoring applications, including industrial processes or metabolic studies. For each wavelength position of the scan shown in Fig. 3.10, 10 data points were collected, which corresponded to a measuring time of approximately 10 s. Neglecting the tuning of the laser between neighboring wavelengths positions, the total measurement time for the spectrum shown in Fig. 3.10 for example, with wavelength steps of $7.5 \times 10^{-3}$ cm⁻¹, was about 40 min. However, for the monitoring of a single species a complete line scan is usually not needed. Often measurements at the wavelength of the peak absorption feature are sufficient for monitoring the temporal evolution of a species’ concentration. Owing to the fast gas exchange and small volume of the 80-microphone array PA cell, monitoring of single species with temporal resolution below one minute is feasible and limited only by the pulse repetition rate. It should also be noted that based on the profile of the absorption line physical parameters [87] of the sample including the pressure and temperature can be derived (see section 2.3.8).

3.4.4 Simultaneous detection at two wavelengths

As a novel spectroscopic technique, simultaneous detection at two wavelengths is discussed in the following. Fig. 3.11 shows three measurements of a sample containing 1% NO and 2.1% H₂O buffered in nitrogen (N₂) at a partial pressure of 475 mbar and pure CO₂ at a partial pressure of 476 mbar. The data were recorded at a total gas pressure of 951 mbar and room temperature. In measurement Fig. 3.11 a) both the FUN and SHG radiations excited the gas mixture simultaneously in the same spatial region around 944 cm⁻¹ (FUN) and 1888 cm⁻¹ (SHG), respectively. The three absorption lines can be attributed to NO, CO₂ and H₂O. The measurement in Fig. 3.11 b) shows the same mixture using the SHG radiation only. In this region, only NO and H₂O absorb. The measurement in Fig. 3.11 c) used only the FUN radiation. The only absorbing species is CO₂. Simultaneous wavelength detection is clearly feasible and may offer an interesting possibility for trace gas sensing in systems with simultaneous dual or multi-wavelength emission. This can be a system with nonlinear frequency conversion scheme (see section 2.5) such as OPO, DFG or
§3.4 Measurements

Figure 3.11: Measurements of a gas mixture consisting of 0.5% NO and 1.05% water vapor (H$_2$O) buffered in nitrogen (N$_2$) and 50% CO$_2$ at a pressure of 951 mbar and room temperature. The sample is excited a) at two wavelengths around 944 cm$^{-1}$ (FUN) and 1888 cm$^{-1}$ (SHG) employed simultaneously, b) at only SHG, and c) only FUN wavelengths, respectively.

The demonstrated SHG. With OPO or DFG sources, signal and idler, or possibly a tunable pump could be combined. Another promising laser source is a fiber coupled array of diode lasers with species selected wavelengths. Simultaneous wavelength detection is not limited to photoacoustic detection schemes alone. In fact, the absence of the kinetic cooling effect [47, 132, 133] in, e.g., transmission measurements, may be advantageous. Future investigations should concentrate on the interferences between excited species through collisional coupling. Another important issue is the precise monitoring or control of the incident power, since the power signals are needed in data analysis, e.g., in photoacoustic spectroscopy for normalization.
3.5 Conclusions and further possibilities

Our pulsed photoacoustic spectrometer, based on a fundamental and frequency-doubled high-pressure CO₂ laser, features a wide and continuous tuning range in the FUN (10-μm) and SHG (5-μm) regimes and room temperature operation. It is well suited for spectroscopic investigations, with strong fundamental absorption lines of various species falling within these two wavelength regions. Its narrow linewidth in both regimes, combined with the fast access of a specific wavelength, enables both selective multicomponent trace gas monitoring and also fundamental spectroscopic studies on molecules, like the determination of isotope ratios. As a novelty, simultaneous detection of species at two wavelengths has been demonstrated. The wide emission wavelength ranges favor a photoacoustic detection scheme, with its inherent wavelength-independent response. The current, rather low, sensitivity of the system could be improved by applying a multipass PA arrangement [48] or by increasing the SHG pulse energies with the implementation of a longer nonlinear crystal. It should be noted, however, that even the current detection limits are of interest, for example in industrial gas monitoring. For example, the maximum permissible workplace concentration for NO (25 ppmV (30 mg/cm³) in Switzerland) is within reach of the present performance. Because of the inherent low pulse repetition rate, a high-pressure CO₂ laser is not suitable for fast scans over extended wavelength ranges, which would be necessary when investigating gas samples that may not be stable over time. In the future quantum cascade lasers (QCL, section 1.5.5) with tailored emission wavelengths [72] in combination with PA detection [74] could represent a suitable alternative in such cases. Should they become available, external cavity QCLs with extended tuning range, narrow linewidth and average power greater than 10 mW at room temperature would in fact provide an excellent spectroscopic tool for numerous applications.
External cavity diode laser-based spectrometer

This chapter describes the external cavity diode laser-based (ECDL) spectrometer. An account is given of the key characteristics of the ECDL, the spectrometer setup including sealed single pass, White-type and Herriott-type gas measuring cells. The spectrometer including modulation schemes as well as measured data are presented and discussed.

4.1 Intended use

Since the spectrometer's main design goal was the use as a teaching device in the advanced student laboratory of the physics department of the ETH Zurich, great effort was taken to build a robust and reliable setup that is easy to operate and align. This is shown in some added comfort, e.g. the single pass measurement cells are mounted on a precision translational displacement stage and simply slide into the beam line without the need for realignment. The available wavelength range in the near-infrared (NIR) gives access to combination and overtone bands of carbon monoxide (CO), carbon dioxide (CO₂), methane (CH₄), and acetylene (C₂H₂). However, one could not resist evaluating the possibilities of employing a NIR laser source in a resonant photoacoustic spectrometer using both amplitude (AM) and wavelength modulation (WM) detection schemes!

4.2 Spectrometer setups

4.2.1 Transmission spectrometer with amplitude modulation (AM)

The transmission spectrometer as available in the undergraduate student laboratory employing an amplitude modulation (AM) detection scheme is depicted in Fig. 4.1. The NIR tunable laser source is an external cavity diode laser (ECDL), described in detail below (section 4.3.1). A fiber collimator transforms the laser radiation into a collimated free space beam. A visible low-power
helium-neon (HeNe) laser beam ($\lambda = 632.8$ nm, $P_{cw} \approx 0.5$ mW) is coaxially superimposed using a dichroic mirror. It is available for alignment and for establishing the number of roundtrips inside the long-path multipass measuring cell. A mechanical chopper generates the amplitude modulation of the laser beam intensity and the reference signal for the lock-in detection. The modulation depth is 100% and the frequency is freely selectable. In practice a frequency above the $1/f$ noise corner frequency and below the resonance frequency of the mechanical chopper is selected. A beam splitter distributes radiation for each of the two arms of the spectrometer. The reference arm is fitted with two home-built single pass cells with fixed fillings. The cells are mounted on a translational displacement stage and allow convenient sample swapping. The probe beam propagates through the long-path multipass cell (custom built by Infrared Analysis, Inc., Anaheim CA, USA). This White-type cell is discussed in section 4.3.2. Two identical, home-built photo detectors are used in both arms. AR coated lenses with a focal length of 6.7 mm lens focus the beams onto the photodetectors. The lock-in amplifier (SR830, Stanford Research Systems, Inc., Sunnyvale CA, USA) records the voltage. The input signal is selected manually from either the probe or reference beam. A vacuum pump facilitates sample gas exchange in the multipass cell.
Temperature and pressure gages monitor the environmental parameters in the cell. Samples can be collected in gas-tight bags or balloons. A 2-micron particle filter (Swagelok Company, Solon OH, USA) at the cell inlet prevents dust, particles, smut or oil and water drops in the collected sample from entering the cell. This is important since the spectrometer is now used as a teaching device and the students are encouraged to spectroscopically analyze their own samples. AM spectrometer operation parameters include sample pressure, laser power, wavelength range and step size, and modulation frequency (blade type and revolution of the mechanical chopper). The measurement time $t_{\text{meas}}$ required to record spectra (wavelength interval ranging from $\lambda_{\text{start}}$ to $\lambda_{\text{stop}}$) depends on the selected wavelength range, the resolution (i.e. step size $\Delta\lambda_{\text{step}}$), as well as on the set lock-in amplifier time constant $\tau$ as

$$t_{\text{meas}} = 5 \cdot \tau \cdot \frac{\lambda_{\text{stop}} - \lambda_{\text{start}}}{\Delta\lambda_{\text{step}}}.$$  

(5 $\tau$ is the time required by the integration to reach > 99.32% of the applied signal in a step function response.) For example, a full scan with high resolution can take several hours, during which unstable samples might deteriorate or change composition and concentration. This is common problem for all high-resolution techniques.

### 4.2.2 Transmission spectrometer with wavelength modulation (WM)

The transmission spectrometer with the wavelength modulation (WM) detection scheme is depicted in Fig. 4.2. It is very similar to the setup employing an AM detection scheme discussed above and depicted in Fig. 4.1. The main differences are given in the following. Wavelength modulation (WM) of the laser beam is achieved by directly modulating the length of the ECDL with the amplitude and frequency adjustable reference signal from the lock-in amplifier. The mechanical chopper is thus obsolete and the chopper blade is turned into a non-blocking position with the aid of the HeNe laser (or removed). WM spectrometer operation parameters include sample pressure, laser power, wavelength range and step size, WM depth and frequency, and the measured harmonic ($1f$, $2f$, etc.).

### 4.2.3 Photoacoustic spectrometer with amplitude modulation (AM)

The photoacoustic (PA) spectrometer based on the near-IR ECDL employing an amplitude modulation (AM) detection scheme is depicted in Fig. 4.3. The laser beam is initially coupled into a resonant PA cell with the aid of a HeNe laser and two iris diaphragms, e.g. pin holes (not shown). A mechanical chopper generates the AM of the laser beam intensity and the reference signal for the lock-in detection. The modulation depth is 100% and the frequency is set to the resonance
Figure 4.2: ECDL based transmission spectrometer employing wavelength modulation (WM).

Figure 4.3: ECDL based photoacoustic spectrometer employing amplitude modulation.
frequency of 1.25 kHz of the homebuilt resonant Herriott-type multipass measuring cell [48] (see section 4.3.2). A battery-powered bandwidth-limited low noise amplifier enhances the signals from the microphone array, which is measured by the lock-in amplifier. The power-monitoring signal from the power stabilized ECDL was also recorded by the lock-in amplifier and is needed for normalizing the intensity dependent PA signal. Since the absorbed energy causes a temperature rise in the sample, the resonance frequency is frequently readjusted. A computer controls the setup and stores the measurements via GPIB interface.

4.2.4 Photoacoustic spectrometer with wavelength modulation (WM)

The PA spectrometer based on the NIR ECDL employing a WM detection scheme is depicted in Fig. 4.4. It is very similar to the setup employing an AM detection scheme (depicted in Fig. 4.3). PA WM spectrometer operation parameters include sample pressure, laser power, wavelength range and step size, WM depth, and the measured harmonic (1f, 2f, etc.).

![Diagram of ECDL based photoacoustic spectrometer employing wavelength modulation.](image)

In the direct absorption measurements, it became evident that optical fringes deteriorate the baseline of the detected signal, whereas these effects do not pose a problem when performing PA measurements. AM measurement schemes, however, suffer from window noise, which is minimized by a sophisticated cell design [99] with buffer volumes. However, since the window absorption is wavelength independent, its first derivative will be zero and hence will effectively be suppressed in 1f and higher harmonics WM PA schemes [134]. This has the added benefit of providing simpler cell designs. Therefore, the more simplistic setup, e.g. no mechanical chopper, than that offered by direct absorption or AM PA setup, would hence be ideal for such applications. A spectrometer setup without moving mechanical parts in addition excludes acoustic coupling to the microphone detection.
4.3 Equipment

4.3.1 External cavity diode laser

An external cavity diode laser (ECDL) is a non-monolithic laser source comprising a diode laser with one face antireflection (AR) coated as gain medium and external optical elements, which constitute the external cavity for tuning and linewidth narrowing. The external optical elements typically consist of a collimation lens, diffraction grating and end mirror. Common configurations are Littrow with a pivotable grating as end mirrors or Littman with a fixed grating within the cavity combined with a movable end mirror (see for example [135, 136, 137]). Wavelength tuning is achieved by rotating the grating or by changing the optical length of the cavity. The emission linewidth is narrow due to the grating single or double pass and the cavity length.

a) Tunics BT-1600 laser source

As near-IR ECDL source for the spectrometer a Tunics BT-1600 from Photonetics, Paris, France, (now a subdivision of GN Nettest A/S, Brøndby, Denmark) was selected. The external cavity is based on a Littman-Metcalf arrangement [124] is realized with a fixed grating and pivotable end mirror (dihedral reflector) for tuning. The mechanical parts made from Invar and ensure a long-term stable cavity with minimal mode hops. The ECDL is continuously tunable in a wide range with small step size, has a very narrow specified linewidth of 150 kHz, provides sufficient output power of several mW throughout the tuning range, and allows WM by means of cavity tuning (or alternatively by directly modulating the diode injection current at higher frequencies). Controls are readily accessible on the front plate and the GPIB interface allows integration into a computer controlled experimental setup and the monitoring of operating parameters.

b) Mode hops

The design of Tunics BT-1600 limits the mode hops to one over the entire tuning range. Generally, mode-hop-free tuning is obtained when the elongation of the cavity is proportional to the cavity length measured anywhere across the beam. Mode hops cause abrupt changes in the emission wavelength and manifest themselves as discontinuities in the recorded spectrum and thus should be minimized or avoided. However they can be detected not only in the spectrum, but also by recording the diode current (for stabilized systems). Fig. 4.5 shows the laser diode current as a function of tuning range for output powers of 3 mW and 6 mW. Single mode hops occur at output powers higher than 3 mW. The typical mode hop was estimated to cause a discontinuity (shift) in
the laser wavelength of 40 pm during tuning. The maximum current is limited to 120 mA to not exceed the absolute diode power dissipation.

c) Wavelength tuning

The Littman-Metcalf arrangement [124] with the dihedral reflector pivoting around point C indicated by angle $\Theta_2$ of the employed Tunics BT 1600 is shown in Fig. 4.6. This configuration allows a short and compact cavity with only one movable part. Hence, also the longitudinal modes are well separated in the order of tens of GHz as seen by $\Delta \nu = c'/2L_{opt}$ with $c'$ being the speed

\begin{center}
\begin{figure}
\includegraphics[width=\textwidth]{figure4.5.png}
\caption{Injected laser diode current as a function of the laser wavelength for optical output powers of 3 mW and 6 mW. Single mode hops occur for output power above 3 mW.}
\end{figure}
\end{center}

\begin{center}
\begin{figure}
\includegraphics[width=\textwidth]{figure4.6.png}
\caption{ECDL Tunics BT 1600 featuring a Littman-Metcalf [124] tuning arrangement.}
\end{figure}
\end{center}
of light inside the cavity. The resonance condition for the cavity $L_{opt} = q \cdot \lambda/2$ must be fulfilled $(q = 1, 2, 3 \ldots)$. The length of the optical cavity is given by

$$L_{opt} = AB + AD$$  \hfill (4.2)

or

$$L_{opt} = AC(\sin \Theta_1 + \sin \Theta_2).$$  \hfill (4.3)

Using the grating parameter $d$ (inverse of the distance between the equally spaced grooves) and wavelength $\lambda$ yields the grating equation

$$L_{opt}/\lambda = AC/d = C,$$  \hfill (4.4)

which must be satisfied for continuous wavelength tuning.

d) **Amplitude modulation (AM)**

Amplitude modulation (AM) of the laser radiation is achieved by a mechanical chopper wheel that periodically switches or modulates the intensity of a light beam. The modulation depth is 100% with the employed metal blades. Modulation frequencies can be up to several kHz and are limited by mechanical resonance when the chopping frequency approaches 5 to 10 kHz (depending on the blade).

e) **Wavelength modulation (WM)**

*Low frequency modulation* is obtained by actuating the dihedral mirror by a piezoelectric stage. This is achieved by applying a voltage to the Tunics BT 1600 fine scanning (FSC) input. The laser frequency can be offset by $\pm 2$ GHz with modulation frequencies from DC up to 10 kHz with a conversion rate of 0.3 GHz/V. Investigations indicated a slight hysteresis and nonlinearities for high signal levels and frequencies - possibly due to resonant enhancement. This can be expected from a mechanical system. However, this did not pose a problem for the low signal levels and modulation frequencies employed in the spectroscopic investigations using wavelength modulation.

*High frequency modulation* from 10 kHz to 1 GHz is available directly through diode-injecting current (beam modulation input). Exploiting high frequency modulations schemes require fast photo detectors, which typically employ small detector diodes. Thus beam steering effects caused by vibration or sound and focusing on the detector can pose a problem in long-path setups. Although
this possibility has been tested, it has not been followed up for the stated reasons. However, future efforts should include this exciting possibility by reducing the footprint of the setup to a single optical bench. Additional measures might include auto alignment of the beam onto the detectors [138].

4.3.2 Measurement cells

In trace gas sensing the concentration of the species under investigation is fixed and unknown. In direct absorption measurements (see section 2.3) lower detection limits can only be achieved by optimizing the product $\sigma(\nu) \cdot l$ of molecular absorption cross section and path-length (see Eq. 2.5). This can be achieved by selecting a laser source emitting in a spectral region where the species under investigation possesses a sufficiently large absorption cross section, and by extending the measuring path along which the laser radiation interacts with the species. Single pass cells are impractical already for medium lengths, say, of 1 m. Thus, measuring cells with folded optical path have been designed. However, regardless of the design of the long-path multipass measuring cells the conventional metal mirrors with finite reflectivity set an upper limit. As example, the transmission reduces to 36.6% after 100 reflections on a mirror with 99% reflectivity. A further development of the multi path approach is cavity ring-down spectroscopy (CRDS) [39, 40] in which dielectric mirrors with very high reflectivity (typically $> 99.99\%$) are employed. Effective length of several km's can be achieved. However, suitable mirrors are narrow band and not readily available in the interesting MIR region. Important in the field of air monitoring are open path measurements in free space employing beam expanding telescopes and a large back-reflection mirrors for a robust setup. Optical path-lengths of several kilometers can be achieved. The sample is a somewhat arbitrary compound of the entire air column and may fluctuate in composition and concentration.

a) Single pass cell

Two measurement cells with fixed 0.5 m path-length and 100 mbar fillings of CO$_2$ (100%) and CO (97.5%) mixed with methane (2.5%) were employed in the setup. The home-built cells were made from quartz glass tubes with 5° tilted flat windows of the same material. A precision translational stage holding the two cells allows a quick change and ensures repeatable positioning without the need of realignment.
b) White-type cell

The White optical system gives rise to a multiple-reflection long-path cell [93, 94]. The good energy conservation of this design is a result of re-focusing that occurs on every other pass. White cells have been used with success in atmospheric studies at total optical paths of more than a kilometer [139]. The only major cause of loss in the system is the absorption on the mirror surface, i.e. mirror loss. A basic set of four passes employing three mirrors is depicted in Fig. 4.7.

![Diagram of a White optical system](image)

**Figure 4.7**: The basic set of four passes of a White optical system. The field and two objective mirrors separation defines the cavity of length $L_{cell}$. The adjustable transfer mirrors facilitate beam coupling.

The field and two objective mirrors separation defines the cavity of length $L_{cell}$. The adjustable transfer mirrors facilitate coupling to the cell. Fig. 4.8 shows the placement of the images (commonly referred to as spots) on the field mirror. The number of images allowed in the row depends on the placement of the first image in the lower part of the field mirror. If it falls exactly on the vertical line, no more than four passes are possible. The farther right it falls, the greater the number or passes allowed. The number of passes is equal to the number on of the exit image, i.e. 80 passes in the figure. In practice, the number of passes is determined by counting the number of

![Image of image placement](image)
images on the bottom row $n_{\text{bottom}}$. The path-length in the cell is thus

$$L_{\text{path}} = n_{\text{bottom}} \cdot L_{\text{cell}}.$$  (4.5)

The custom made White cell (Infrared Analysis, Inc., Anaheim CA, USA) employed in the direct absorption spectrometer has a volume of 4.31, and is specified for 80 passes, i.e a path-length of 108.8 m. However 88 passes resulting in 119.68 m have also been achieved. Specified pressure range is from vacuum to 4 bar. After transmission through the empty cell the intensity fell to 28\% for 88 passes. Including the Fresnel losses caused by the two uncoated KBr made windows a mirror reflectivity of 0.982 was obtained, which is fair for the protected silver coated mirrors. The cell body is made from a borosilicate glass tube (diameter 70 mm, wall thickness 7 mm). The glass body is O-ring sealed on both ends and sandwiched between two end plates, which also hold the mirrors and windows. Four tension rods from end plate to end plate hold the cell together. Two valves control the sample gas exchange. The inlet valve is fitted with a filter (Swagelok, 2-micron) to keep out dust, particles, suds, and oil and water droplets. The cell can operate in closed mode or flow mode. A vacuum pump is available for cell evacuation. A pressure gage reads the cell pressure.

c) Resonant photoacoustic Herriott-type cell

In PA detection (see section 2.4), the generated signal scales with the absorbed power (see Eq. 2.22). To achieve highest detection sensitivity we combine a multipass configuration (for enhanced absorbed power) with a resonance (Q-factor enhancement) and microphone array (increased $SNR$). The resonant PA cell was embedded in a custom-made Herriott-type cell, which is in detail discussed in [48] and depicted in Fig. 4.9.

Figure 4.9: Multipass photoacoustic cell with Herriott cell, photoacoustic resonator, and cylindrical microphone array [48].
There are a total of 36 passes within the cell corresponding to an absorption path-length of 15 m (overall 23.68 m). The cell's Q-factor is approx. 70 at its resonance frequency of 1.25 kHz at the first longitudinal acoustic mode. This frequency is well above the $1/f$ noise corner frequency and below the mechanical resonance frequency of the chopper. It employs a 16-microphone array (KE 4-211-2, Sennheiser, Hannover, Germany) whose signal is enhanced by a battery powered bandwidth limited low noise amplifier. The cell has a volume is 2.31, operates at a maximum gas flow of 1.5 l/min, which is limited by increased ambient acoustic noise and onset of turbulence. A vacuum pump is available for cell evacuation and the pressure gage reads the cell pressure.

4.3.3 Photodetector

A range of photodetectors finds application in laser-based spectrometers. Selection criteria for the detectors include wavelength range, sensitivity, dynamic range, noise performance, damage threshold, operation temperature and price, and temporal resolution. If a tunable narrow linewidth radiation source is used, the photo detectors' spectral range must span the entire tuning range. The home-built low noise photodetectors employ InGaAs PIN photodiodes in combination with transimpedance amplifiers. The type G5832-11 (Hamamatsu Photonics K.K., Hamamatsu, Japan) has an AR coated window and can be thermoelectrically cooled to assure low noise measurements. It has an active area of 1 mm diameter and covers the spectral response range from 0.9 to 1.67 $\mu$m. The peak sensitivity wavelength is at 1.55 $\mu$m and the photosensitivity is 0.95 A/W. The generated photo current is linearly dependent on the incident intensity and converted to a proportional voltage by the transimpedance amplifier (OPA627 operational amplifier based). Due to the large active area of the detector, adjustment is facilitated. The low noise transimpedance amplifier is battery powered.

4.3.4 Tunics BT 1600 characterization

In this section, measurements for the characterization of the Tunics BT 1600 are shown. The effective emission range in dependence of the output power is depicted in Fig. 4.10. The cw power can be set between 0.2 mW and 6.31 mW. Limitation at the long end of the emission range is clearly visible. However, the long wavelength limit is well beyond the emission wavelength region specified by the manufacturer. It should also be noted, that the highest achievable output power drops to about 5.5 mW for very long lasting experiments, e.g. 24 hours. Fig. 4.5 shows the laser diode injection current as a function of the emission wavelength for 3 mW and 6 mW output power. At powers below 3 mW mode hop free tuning is achieved over the full tuning range of 114 nm. Single
mode hops of approx. 40 pm occur in the tuning range for power above 3 mW. Since the Tunics BT 1600 has stabilized output power, the diode injection current is adjusted to achieve the set output power. The injection current oscillates due to the two stage tuning arrangement employing a piezoelectric stage and a DC motor. The diode injection current is limited to not exceed the absolute allowable laser diode current density and power dissipation. Mainly the tuning characteristics and available output power have been validated. The specified laser linewidth of 150 kHz could not be directly measured, but appears feasible given the employed tuning arrangement (grating double pass). An upper limit of 150 MHz could be established by scanning a CO₂ absorption lines with width 0.013 cm⁻¹ at 2 mbar pressure. The laser line width is negligible when compared to absorption features. The main characteristics of the ECDL Tunics BT-1600 are summarized in Table 4.1.

Figure 4.10: Parameterized optical output power of the Tunics BT 1600 in function of the output wavelength range. The tuning range is limited towards longer wavelengths with increasing power.
Photonetics Tunics BT 1600
(with P6 and C options)

<table>
<thead>
<tr>
<th>parameter</th>
<th>manufacturer specifications</th>
<th>experimental verification</th>
</tr>
</thead>
<tbody>
<tr>
<td>tuning characteristics</td>
<td></td>
<td></td>
</tr>
<tr>
<td>wavelength range</td>
<td>1560 – 1640 nm</td>
<td>1540 – 1650 nm</td>
</tr>
<tr>
<td>$P = 0 \text{ dBm}$ ($P = 1 \text{ mW}$)</td>
<td>1570 – 1620 nm</td>
<td>1540 – 1645 nm</td>
</tr>
<tr>
<td>$P = 4 \text{ dBm}$ ($P = 4 \text{ mW}$; P6 option)</td>
<td>1570 – 1620 nm</td>
<td>1540 – 1634 nm</td>
</tr>
<tr>
<td>$P_{\text{max}} = 6.31 \text{ mW}$ (max. output power)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>mode hop free wavelength range</td>
<td>$&gt; 30 \text{ nm}$</td>
<td>max. 110 nm, min. 13 nm</td>
</tr>
<tr>
<td>absolute wavelength accuracy</td>
<td>$\pm 0.2 \text{ nm}$</td>
<td></td>
</tr>
<tr>
<td>tuning repeatability</td>
<td>$\pm 0.01 \text{ nm}$</td>
<td></td>
</tr>
<tr>
<td>wavelength setting resolution</td>
<td>0.01 nm</td>
<td></td>
</tr>
<tr>
<td>optical frequency fine-tuning</td>
<td></td>
<td></td>
</tr>
<tr>
<td>low frequency modulation $&lt; 10 \text{ kHz}$ (C option)</td>
<td>$\pm 2 \text{ GHz}$</td>
<td></td>
</tr>
<tr>
<td>tuning speed</td>
<td>10 s (70 nm)</td>
<td></td>
</tr>
<tr>
<td>laser output characteristics</td>
<td></td>
<td></td>
</tr>
<tr>
<td>power stability</td>
<td>$\pm 0.01 \text{ dB}$</td>
<td></td>
</tr>
<tr>
<td>linewidth (w/o coherence control)</td>
<td>typ. 150 kHz</td>
<td></td>
</tr>
<tr>
<td>linewidth (coherence control)</td>
<td>$&gt; 100 \text{ MHz}$</td>
<td></td>
</tr>
<tr>
<td>side mode suppression ratio</td>
<td>$&gt; 45 \text{ dB}$</td>
<td></td>
</tr>
<tr>
<td>relative intensity noise</td>
<td>$&gt; 145 \text{ dB/Hz}$</td>
<td></td>
</tr>
<tr>
<td>interface</td>
<td></td>
<td></td>
</tr>
<tr>
<td>optical connector</td>
<td>FC-APC</td>
<td></td>
</tr>
<tr>
<td>output fiber</td>
<td>SMF-28</td>
<td></td>
</tr>
<tr>
<td>output isolation</td>
<td>35 dB</td>
<td></td>
</tr>
<tr>
<td>return loss</td>
<td>$- 60 \text{ dB}$</td>
<td></td>
</tr>
<tr>
<td>remote control interface</td>
<td>IEEE-488-1 (GPIB) and RS-232 C</td>
<td></td>
</tr>
<tr>
<td>environment</td>
<td></td>
<td></td>
</tr>
<tr>
<td>operating temperature</td>
<td>$+15 \text{ to } +30 \text{ °C}$</td>
<td></td>
</tr>
<tr>
<td>power supply</td>
<td>100 – 240 VAC, 50 – 60 Hz</td>
<td></td>
</tr>
<tr>
<td>dimensions (w x h x l)</td>
<td>$320 \times 129 \times 308 \text{ mm}^3$</td>
<td></td>
</tr>
<tr>
<td>weight</td>
<td>7.5 kg</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.1: ECDL Tunics BT 1600 properties given by the manufacturer and measured characteristics.
4.4 Direct absorption measurements

4.4.1 Carbon dioxide in human exhaled breath

Spectroscopic breath analysis provides a noninvasive technique to detect diseases and malfunctions of the respiratory system or to study the metabolism (see section 1.2.1) [23, 24]. As an example, the CO₂ concentration in human exhaled breath of a healthy subject (Fig. 4.11) was measured around 6361.25 cm⁻¹ at a pressure of 950 mbar and room temperature employing the transmission spectrometer with AM depicted in Fig. 4.1. A concentration of (4 ± 0.1)% was obtained. The measured transmission data was baseline corrected (fringes), converted to an absorbance spectra, and fitted with a Lorentz function. The obtained amplitude was compared with HITRAN data (SNR = 3). Exhaled breath has high concentrations of water vapor (H₂O) and CO₂, which also are the main absorbing components in the used wavelength range. However, no interference with H₂O was observed due to the small line strength of H₂O and high concentration CO₂ of in the employed wavelength region.

![Figure 4.11: Carbon dioxide (CO₂) in human exhale of a healthy subject measured around 6360 cm⁻¹. The concentration is (4 ± 0.1)%. HITRAN data is given for reference.](image)

4.4.2 Carbon dioxide isotope ratio

The very narrow linewidth and the continuous tuning range of the Tunics BT 1600 laser source results in great selectivity, which is demonstrated by the $^{13}$CO₂/$^{12}$CO₂-isotope ratio of pure carbon dioxide around 6251.5 cm⁻¹ at a pressure of 2.5 mbar and room temperature (Fig. 4.12). The absorption line parameters were extracted from the transmission measurement as described above.
4.4 Direct absorption measurements

Using a Gaussian fit, the measured isotope ratio of $(1.12 \pm 0.01)\%$ is in good agreement with the literature value of $1.11\%$. Spectroscopic isotope measurements have many applications, including environmental surveillance of trace species. Eruptive volcanic activities [14, 15] have been linked to the isotope ratio of fumes. Measurements of the isotope ratio allow the distinction between natural and anthropogenic carbon dioxide. An other important field of application are isotope labeled foods and drinks that allow the study of metabolic functions and rates [23, 24].

4.4.3 Motorcycle exhaust sample

Fig. 4.13 shows the analysis of a multicomponent mixture, i.e. an exhaust sample from a two-stroke motorcycle, Piaggio Vespa 125 PX (1984 model), after cold start. The sample was collected at the exhaust outlet of the motorbike using a plastic bag. Two-stroke engines are notorious to be dirty, especially after cold start, where elevated pollution levels, due to incomplete combustion, can be expected. The 2-micron filter that prevents dust, particles, smut or oil and water droplets from entering the measuring cell is thus essential to prevent contamination of the spectrometer. Fig. 4.13 a) shows the high resolution data measured across the full wavelength range of the laser source (100 mbar and room temperature). Fig. 4.13 b) to f) show HITRAN spectra fitted to the measured data for the analyzed mixture and its components, i.e. $(0.43 \pm 0.1)\%$ carbon monoxide (CO), $(0.425 \pm 0.05)\%$ carbon dioxide (CO$_2$), $(100 \pm 10)$ ppmV methane (CH$_4$), and $(94 \pm 8)$ ppmV acetylene (C$_2$H$_2$). The roll-off in the transmission spectra towards lower wavenumbers is typical for the reduced spectral response of the employed InGaAs PIN photodetector at longer wave-
Figure 4.13: Analysis of a multicomponent gas mixture from a motorcycle containing 0.43% CO, 0.425% CO₂, 100 ppmV CH₄, and 94 ppmV C₂H₂.
lengths. Normalization of the transmission data is an integral part of the data processing required in the analysis of the sample, i.e. extraction concentrations and detection limits. The pronounced fringes, caused by parasitic étalon effects, are accounted for by baseline-correction during normalization of the transmission data. Thus, the observed roll-off and fringes do usually not pose a problem for data recorded at low pressure.

4.4.4 Methane measurement using wavelength modulation detection

A demonstration of the wavelength modulation (WM) techniques is given in the following. The WM transmission spectrometer (see section 4.2.2) was employed. The investigated substance is 100 ppmV methane buffered in air at 100 mbar and room temperature. The 1f- and 2f-detection measurements (Fig. 4.14) were recorded with a modulation depth of 0.21 GHz. The modulation frequency was adjusted to the resonance frequency of the PA cell. The 1f-detection data shown

![Image](image.png)

**Figure 4.14**: a) HITRAN data, b) 1f- and c) 2f-detection (bottom) measurements of 100 ppmV methane buffered in air, recorded at 100 mbar and room temperature.
in b) approximate the first derivative of the HITRAN transmission spectra a). The absorption line positions are given by zero-crossings through the baseline. This property of 1\textsuperscript{f}-detection greatly helps in the analysis of samples and in determination of line positions. Additionally, wavelength independent background and noise is removed. The 2\textsuperscript{f}-detection data shown in c) approximate the second derivative and first-order wavelength depended background and noise are removed. This is evident in the 2\textsuperscript{f} spectra. The distorted baseline in the 1\textsuperscript{f} data is removed in the 2\textsuperscript{f} spectra. However, the 2\textsuperscript{f}-detection spectrum have more pronounced features and thus the interpretation might become difficult. Measurements at lower pressure, due to the Gaussian-like lineshape function, may benefit from measurements employing WM detection. This is discussed in the following section below. For a discussion of the lineshapes and line broadening mechanisms see section 2.3.8. However, it should also be noted that the modulation depth should be selected so, as not to broaden the absorption features, and to achieve optimal signal amplitude.

### 4.5 Photoacoustic measurements

#### 4.5.1 Pressure dependent lineshape

An absorption feature of pure CO\textsubscript{2} around 1572.10 nm was measured at pressures ranging from 52.7 to 614 mbar and room temperature (Fig. 4.15) to study the role of collisional, or pressure broadening on the lineshape. The photoacoustic spectrometer with amplitude modulation (AM) discussed in section 4.2.3 was employed. At atmospheric pressure, the lineshape is dominated

![Figure 4.15: Pressure dependent lineshape of pure CO\textsubscript{2} from 52.7 to 614 mbar (data points connected to guide the eye)](image-url)
§4.5 Photoacoustic measurements

by pressure broadening and approximates a Lorentzian lineshape (see section 2.3.7). At reduced pressure the absorption line is dominated by Doppler broadening and approximates a Gaussian lineshape (see section 2.3.6). Thus, with the wings of the absorption line reduced, spectral features previously hidden in the wings of the dominating absorption feature appear in the spectrum. Spectroscopic measurements are often recorded at ambient pressure to keep the total number of absorbing molecules in the sample is high. Additionally, the complexity of the spectrometers is small, as the sample is exchanged by diffusion or by a pump that creates the gas flow through the cell. However, depending on the application, measurements at reduced pressure may add better selectivity, although at the cost of reduced sensitivity (see section 3.4.1).

4.5.2 Wavelength modulation depth

Selecting optimal wavelength modulation parameters (modulation depth and frequency) is essential when measuring with a WM spectrometer. The CO₂ absorption lines around 1584.15 nm were measured employing the PA spectrometer with wavelength modulation (WM) (see section 4.2.4). The sample pressure was 200 mbar at room temperature. Different wavelength modulation depths have been employed in Fig. 4.16, ranging from 60 to 1200 MHz (i) to (viii), respectively. The modulation frequency was set to the first longitudinal resonance of the PA cell. Employing a small modulation depth m in the 1/-detection scheme, i.e. m = 60 MHz, results in the close approximation of the absorption feature by its first derivative. However, to achieve the best possible sensitivity, the modulation depth is to be set to result in the highest signal strength, i.e. m the

![Figure 4.16](image)

**Figure 4.16:** Photoacoustic wavelength modulation (1/f-detection) detection with different modulation depths ranging from 60 (i) to 1200 MHz (viii), respectively.
range of 150 to 300 MHz. If the $m$ is further increased, the recorded signal remains approximately constant, but the spectral feature becomes more spread-out and results in reduced selectivity. Setting the modulation index $m$ to around 250 MHz in $1f$-detection schemes is a good compromise and results in high sensitivity and selectivity when measuring data at reduced pressures of, say 100 mbar to atmospheric pressure (i.e. 1 bar).

### 4.6 Conclusion and further possibilities

We have realized several spectrometers employing a fiber coupled NIR laser source emitting in the telecommunication wavelength region at 1.6 μm. The available wavelength range enables the detection of combination and overtone bands of carbon monoxide (CO), carbon dioxide (CO$_2$), methane (CH$_4$), and acetylene (C$_2$H$_2$). The wide continuous tuning range, combined with a narrow line width of the laser source, results in measurements with good selectivity. This has been demonstrated by the analysis of samples including exhaled human breath (CO$_2$) and exhaust from a motorcycle, i.e. the analysis of a multicomponent sample of previously unknown composition.

The output power of few mW is sufficient for sensitive photoacoustic detection and direct absorption measurements. Amplitude (AM) and wavelength modulation (WM) detection of $1f$ and $2f$ components have been demonstrated with both, the transmission and the resonant PA spectrometers. The optimal modulation depth was investigated for $1f$-detection. Backgrounds and noise can be effectively reduced when employing wavelength modulation.

The detection limits ($SNR=3$) for carbon monoxide (CO), carbon dioxide (CO$_2$), methane (CH$_4$), and acetylene (C$_2$H$_2$), employing a transmission spectrometer with amplitude modulation (AM), are 1112 ppmV, 1390 ppmV, 39 ppmV, and 18 ppmV, respectively. Using $1f$ and $2f$ WM techniques, the detection limits ($SNR=3$) improve and the sensitivity increases by average factors of 4.8 and 9.3, respectively. An AM PA measurement of CH$_4$ results in a detection limit of 11 ppmV ($SNR=3$).

One of the goals of this work was the implementation of a fully characterized laser-based transmission spectrometer to be applied for the analysis of gas samples of different origin. It is now employed as a teaching device in the undergraduate student laboratory in the physics department of the ETH Zurich.

Tunable diode lasers emitting in the telecommunications wavelength range, in combination with sensitive detection schemes, offer good performance at attractive cost. Employing an array of fiber coupled diode lasers with a resonant, wavelength modulation-capable photoacoustic detection scheme appears to be very attractive for future trace gas sensing applications that require
both high sensitivity and selectivity. Due to the employed wavelength modulation (elimination of window heating signal background), the resonant photoacoustic cell could be of a simple, yet effective and economic design. Combining the laser sources into a single fiber output would ease alignment issues and could allow a very compact sensor designs. Systems combining diode lasers in either photoacoustic [140] or transmission spectroscopic [141] detection schemes, although with separate propagating beams and detection paths, have recently been demonstrated. Ongoing developments in photoacoustics which, rather then employing microphones, use miniature tuning forks, i.e. quartz-enhanced photoacoustic spectroscopy (QEPAS) [142], or cantilevers [143] with interferometric detection [144] are very promising. An interesting way to improve the sensitivity of a near-IR photoacoustic sensors (the signal scales with the incident power) by employing a tunable diode laser in combination with an erbium-doped fiber amplifier is reported in [140, 144].
Appendix A: Substances investigated

Substances absorbing in the 10 \( \mu \text{m} \) (1000 cm\(^{-1}\)) wavelength range

Table A.1 lists selected substances with absorption features in the mid-s infrared region (MIR) accessible with tunable fundamental (FUN) CO\(_2\) laser. The maximum permissible workplace (MAK) [20], selected absorption features in the wavelength range and information about application and environmental relevance are given, where available.

<table>
<thead>
<tr>
<th>substance, formula</th>
<th>MAK [ppmV]</th>
<th>wavelength [( \mu \text{m} )]</th>
<th>wavenumber [cm(^{-1})]</th>
<th>application and environmental relevance</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetaldehyde, C(_2)H(_4)O</td>
<td>50</td>
<td>8.333–9.434</td>
<td>1060–1200</td>
<td>alcohol metabolism, fruit storage</td>
</tr>
<tr>
<td>acetone, C(_3)H(_6)O</td>
<td>500</td>
<td>10.526–10.753</td>
<td>930–950</td>
<td>medical analysis, dairy cattle health</td>
</tr>
<tr>
<td>ammonia, NH(_3)</td>
<td>20</td>
<td>10.309–10.870</td>
<td>920–970</td>
<td>agriculture, fertilizer dispersal, volcanic gas, acid rain, traffic, medical analysis, industrial processes</td>
</tr>
<tr>
<td>bromomethane (BM), CH(_3)Br</td>
<td>5</td>
<td>10.38–10.62</td>
<td>942–963</td>
<td>agriculture fumigant, ozone-depleting substance, greenhouse gas</td>
</tr>
<tr>
<td>carbon dioxide, CO(_2)</td>
<td>5000</td>
<td>9.217–10.204</td>
<td>980–1085</td>
<td>combustion, greenhouse gas, volcanic gas, medical analysis</td>
</tr>
<tr>
<td>dimethyl ether (DME), C(_2)H(_6)O</td>
<td>1000</td>
<td>10.40–10.58</td>
<td>945–961</td>
<td>aerosol spray propellant, alternative fuel</td>
</tr>
<tr>
<td>ethanol, C(_2)H(_6)O</td>
<td>500</td>
<td>9.804–9.174</td>
<td>1020–1090</td>
<td>alcohol metabolism, fruit storage</td>
</tr>
<tr>
<td>ethylene, C(_2)H(_4)</td>
<td>10000</td>
<td>10.526</td>
<td>950</td>
<td>plant hormone, fruit and vegetable storage and ripening</td>
</tr>
</tbody>
</table>

Table A.1: Substances available for investigation in the 10 \( \mu \text{m} \) wavelength range, which is accessible by the continuously tunable fundamental (FUN) CO\(_2\) laser.
Substances absorbing in the 5 μm (2000 cm⁻¹) wavelength range

Table A.2 lists selected substances with absorption features in the mid-infrared region (MIR) accessible with tunable frequency doubled (SHG) CO₂ laser. The maximum permissible workplace (MAK) [20], selected absorption features in the wavelength range and information about application and environmental relevance are given, where available.

<table>
<thead>
<tr>
<th>substance, formula</th>
<th>MAK [ppmV]</th>
<th>wavelength [μm]</th>
<th>wavenumber [cm⁻¹]</th>
<th>application and environmental relevance</th>
</tr>
</thead>
<tbody>
<tr>
<td>carbon monoxide, CO 630-08-0</td>
<td>30</td>
<td>4.72–4.545</td>
<td>2100–2200</td>
<td>combustion, medical analysis</td>
</tr>
<tr>
<td>carbonyl sulfide, OCS 463-58-1</td>
<td>N/A</td>
<td>4.808–4.926</td>
<td>2030–2080</td>
<td>fumigant, fruit storage, volcanic gas</td>
</tr>
<tr>
<td>nitric oxide, NO 10102-43-9</td>
<td>25</td>
<td>5.208–5.348</td>
<td>1870–1920</td>
<td>medical analysis gas</td>
</tr>
<tr>
<td>water, H₂O 7732-18-5</td>
<td>N/A</td>
<td>5.051–7.407</td>
<td>1350–1980</td>
<td>humidity, industrial processes</td>
</tr>
</tbody>
</table>

Table A.2: Substances available for investigation in the 5 μm wavelength range, which is accessible by the continuously tunable frequency doubled (SHG) CO₂ laser.
Substances absorbing in the 1.6 \( \mu \text{m} \) (6250 cm\(^{-1} \)) wavelength range

Table A.3 lists selected substances with absorption features in the near-infrared (NIR) region accessible with tunable diode lasers such as the ECDL Tunics BT 1600 employed in this thesis. The maximum permissible workplace (MAK) [20], selected absorption features in the wavelength range and information about application and environmental relevance are given, where available.

<table>
<thead>
<tr>
<th>substance, formula</th>
<th>MAK [ppmV]</th>
<th>wavelength [( \mu \text{m} )]</th>
<th>wavenumber [cm(^{-1} )]</th>
<th>application and environmental relevance</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetylene, C(_2)H(_2)</td>
<td>1000</td>
<td>1.52</td>
<td>6579</td>
<td>combustion</td>
</tr>
<tr>
<td>carbon monoxide, CO</td>
<td>30</td>
<td>1.5–1.59</td>
<td>6289–6410</td>
<td>combustion, medical analysis</td>
</tr>
<tr>
<td>carbon dioxide, CO(_2)</td>
<td>5000</td>
<td>1.31–1.35, 1.52–1.55, 1.57–1.67</td>
<td>7407–7634, 6452–6579, 5988–6369</td>
<td>combustion, greenhouse gas, volcanic gas, medical analysis</td>
</tr>
<tr>
<td>methane, CH(_4)</td>
<td>10000</td>
<td>1.65</td>
<td>6061</td>
<td>acid rain, smog, ozone formation, greenhouse gas</td>
</tr>
<tr>
<td>water, H(_2)O</td>
<td>N/A</td>
<td>1.39</td>
<td>7194</td>
<td>humidity, industrial processes</td>
</tr>
</tbody>
</table>

Table A.3: Substances available for investigation in the 1.6 \( \mu \text{m} \) wavelength range, which is available by the Tunics BT 1600 and other tunable diode lasers.
Appendix B: Spectral databases

Spectral databases and reference data are vital tools in gas phase spectroscopy. The free HITRAN database [88] has been used as main source of reference in this thesis. It is maintained and development is ongoing to include additional species and lines. A number of free and commercial software packages that are used for the extraction and manipulation of the HITRAN molecular spectroscopic database and associated molecular databases are available. The JavaHAWKS software package is free. The software has been written in the Java language so to maintain cross-platform performance, and at the same time maintaining a single source code. It is available from the HITRAN website given. Other databases, some share the HITRAN data format, are given below.

**HITRAN spectroscopic database [88]**
http://cfa-www.harvard.edu/HITRAN/

**GEISA spectroscopic database [89]**
http://ara.lmd.polytechnique.fr/

Jet Propulsion Laboratory Molecular Spectroscopy Catalog (Revision 4)
http://spec.jpl.nasa.gov/

Harvard-Smithsonian Center for Astrophysics, Atomic & Molecular Physics Division
http://www.cfa.harvard.edu/amp/

The Smithsonian Astrophysical Observatory, Terahertz Toolbox
http://www.cfa.harvard.edu/thztool/

The University of Denver, Atlas of High-Resolution IR Stratospheric Spectra
http://www.du.edu/~agoldman/atlas.html

Atomic & Molecular Database for Astronomy, Kurucz Atomic Line Database
http://www.cfa.harvard.edu/amdata/ampdata/kurucz23/sekur.html
The Cologne Database for Molecular Spectroscopy (CDMS)
http://www.phl.uni-koeln.de/vorhersagen/

Theoretical Atomic and Molecular Physics and Astrophysics Group, Department of Physics and Astronomy, Astrodata, University College London,
http://www.tampa.phys.ucl.ac.uk/

NIST: Quantitative Infrared Database (Version 1.10)
http://www.gases.nist.gov/database.html

Pacific Northwest National Laboratory, Vapor phase infrared spectral library
http://nwir.pnl.gov/

NIST: Wavenumber Calibration Tables From Heterodyne Frequency Measurements (Special Publication 821)

NIST: Recommended Rest Frequencies for Observed Interstellar Molecular Microwave Transitions (1991 Revision)

NIST: Atomic Spectra Database (Version 2.0)
http://physics.nist.gov/cgi-bin/AtData/main.asd

CHIANTI: Database for Astrophysical Emission Line Spectroscopy (Version 3.03)

EPA Reference Absorbance Spectra
http://www.epa.gov/tnn/emc/ftir/refnam.html
Bibliography


[100] SNLO software by A. V. Smith (free download), Sandia National Laboratories, Simulation tool for non-linear optical frequency conversions


Acronyms and symbols

Acronyms

1_f first harmonic
2_f second harmonic
9P, 9R, 10P, and 10R transition branches of CO2
AC alternating current, synonym for non-constant or non-zero frequency component
AM amplitude modulation
AR antireflection
CAS unique numerical identifiers for chemical compounds
cm^-1 wavenumber unit
CRDS cavity ring-down spectroscopy
cw continuous-wave
DAS direct absorption spectroscopy (or spectrometer)
dB decibel: power and intensity ratios
dBm decibel (dB) of the measured power referenced to 1 mW
DC direct current, synonym for constant or zero frequency component
DFB distributed feedback
DFG difference frequency generation
DL diode laser
ECDL external cavity diode laser
e.g. for example (Latin exempli gratia)
Eq. equation
ETH Eidgenössische Technische Hochschule (English Swiss Federal Institute of Technology)
EPA United States Environmental Protection Agency
Fig. figure
FP Fabry-Perot
FTIR Fourier transform infrared
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>FUN</td>
<td>fundamental</td>
</tr>
<tr>
<td>FWHM</td>
<td>full width at half maximum</td>
</tr>
<tr>
<td>GC</td>
<td>gas chromatography</td>
</tr>
<tr>
<td>GEISA</td>
<td>Gestion et Etude des Informations Spectroscopiques Atmosphériques (English study and management of atmospheric spectroscopic information)</td>
</tr>
<tr>
<td>GPIB</td>
<td>general purpose interface bus (IEEE 488)</td>
</tr>
<tr>
<td>HF</td>
<td>high frequency</td>
</tr>
<tr>
<td>HITRAN</td>
<td>high-resolution transmission molecular absorption database</td>
</tr>
<tr>
<td>i.e.</td>
<td>that is (Latin id est)</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
</tr>
<tr>
<td>L × H × W</td>
<td>dimensions: length × height × width</td>
</tr>
<tr>
<td>LED</td>
<td>light emitting diode</td>
</tr>
<tr>
<td>MAK</td>
<td>maximale Arbeitsplatz-Konzentration (English maximum permissible workplace concentration value) [20]</td>
</tr>
<tr>
<td>MAS</td>
<td>mass spectrometry or mass spectroscopy</td>
</tr>
<tr>
<td>MIR</td>
<td>mid-infrared</td>
</tr>
<tr>
<td>NIR</td>
<td>near-infrared</td>
</tr>
<tr>
<td>N/A</td>
<td>not applicable</td>
</tr>
<tr>
<td>NIST</td>
<td>National Institute of Standards and Technology</td>
</tr>
<tr>
<td>norm.</td>
<td>normalized</td>
</tr>
<tr>
<td>OPA</td>
<td>optical parametric amplification</td>
</tr>
<tr>
<td>OPO</td>
<td>optical parametric oscillation</td>
</tr>
<tr>
<td>PA</td>
<td>photoacoustic</td>
</tr>
<tr>
<td>PAS</td>
<td>photoacoustic spectroscopy (or spectrometer)</td>
</tr>
<tr>
<td>PC</td>
<td>photonic crystal</td>
</tr>
<tr>
<td>PD</td>
<td>photo detector or photo diode</td>
</tr>
<tr>
<td>PIN</td>
<td>p-type, intrinsic, n-type</td>
</tr>
<tr>
<td>PM</td>
<td>phase matching</td>
</tr>
<tr>
<td>ppbV</td>
<td>parts per billion (nmole/mole)</td>
</tr>
<tr>
<td>ppmV</td>
<td>parts per million (μmole/mole)</td>
</tr>
<tr>
<td>pptV</td>
<td>parts per trillion (pmole/mole)</td>
</tr>
<tr>
<td>QCL</td>
<td>quantum cascade laser</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>QEPAS</td>
<td>quartz-enhanced photoacoustic spectroscopy</td>
</tr>
<tr>
<td>QPM</td>
<td>quasi-phase matching</td>
</tr>
<tr>
<td>R</td>
<td>rotational</td>
</tr>
<tr>
<td>RC-LED</td>
<td>resonant cavity light emitting diode</td>
</tr>
<tr>
<td>RF</td>
<td>radio frequency</td>
</tr>
<tr>
<td>RT</td>
<td>room temperature</td>
</tr>
<tr>
<td>sccm</td>
<td>standard cubic centimeters per minute</td>
</tr>
<tr>
<td>SFG</td>
<td>sum frequency generation</td>
</tr>
<tr>
<td>SHG</td>
<td>second harmonic generation</td>
</tr>
<tr>
<td>slm</td>
<td>standard liter pre minute</td>
</tr>
<tr>
<td>SNR</td>
<td>signal-to-noise ratio</td>
</tr>
<tr>
<td>T</td>
<td>temperature</td>
</tr>
<tr>
<td>TDL</td>
<td>tunable diode laser</td>
</tr>
<tr>
<td>TE</td>
<td>thermoelectric</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>vis</td>
<td>visible</td>
</tr>
<tr>
<td>V</td>
<td>vibrational</td>
</tr>
<tr>
<td>VR</td>
<td>vibrational-rotational</td>
</tr>
<tr>
<td>VT</td>
<td>vibrational-translational</td>
</tr>
<tr>
<td>WM</td>
<td>wavelength modulation</td>
</tr>
</tbody>
</table>

**Substances and crystals**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgGaSe₂</td>
<td>silver gallium selenide</td>
</tr>
<tr>
<td>BaF₂</td>
<td>barium fluoride</td>
</tr>
<tr>
<td>BM</td>
<td>bromomethane or methyl bromide</td>
</tr>
<tr>
<td>CdGeAs₂</td>
<td>cadmium germanium arsenide</td>
</tr>
<tr>
<td>CH₄</td>
<td>methane</td>
</tr>
<tr>
<td>CH₃Br</td>
<td>bromomethane or methyl bromide</td>
</tr>
<tr>
<td>C₂H₂</td>
<td>acetylene</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>ethylene</td>
</tr>
<tr>
<td>C₂H₄O</td>
<td>acetaldehyde</td>
</tr>
<tr>
<td>C₂H₆O</td>
<td>ethanol</td>
</tr>
<tr>
<td>C₂H₆O</td>
<td>dimethyl ether</td>
</tr>
<tr>
<td>Chemical Symbol</td>
<td>Name</td>
</tr>
<tr>
<td>-----------------</td>
<td>--------------------</td>
</tr>
<tr>
<td>$C_3H_6O$</td>
<td>acetone</td>
</tr>
<tr>
<td>CO</td>
<td>carbon monoxide</td>
</tr>
<tr>
<td>$CO_2$</td>
<td>carbon dioxide</td>
</tr>
<tr>
<td>OCS</td>
<td>carbonyl sulfide</td>
</tr>
<tr>
<td>DME</td>
<td>dimethyl ether</td>
</tr>
<tr>
<td>GaAs</td>
<td>gallium arsenide</td>
</tr>
<tr>
<td>GaSe</td>
<td>gallium selenide</td>
</tr>
<tr>
<td>$H_2O$</td>
<td>water</td>
</tr>
<tr>
<td>He</td>
<td>helium</td>
</tr>
<tr>
<td>InGaAs$_3$</td>
<td>indium gallium arsenide</td>
</tr>
<tr>
<td>LiNbO$_3$</td>
<td>lithium niobate</td>
</tr>
<tr>
<td>$N_2$</td>
<td>nitrogen</td>
</tr>
<tr>
<td>Ne</td>
<td>neon</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>ammonia</td>
</tr>
<tr>
<td>NO</td>
<td>nitric oxide</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>nitrogen dioxide</td>
</tr>
<tr>
<td>NO$_x$</td>
<td>nitrogen oxides</td>
</tr>
<tr>
<td>$N_2O$</td>
<td>nitrous oxide</td>
</tr>
<tr>
<td>O$_2$</td>
<td>oxygen</td>
</tr>
<tr>
<td>OP-GaAs</td>
<td>orientation patterned gallium arsenide</td>
</tr>
<tr>
<td>PPLN</td>
<td>periodically poled lithium niobate</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>sulfur dioxide</td>
</tr>
<tr>
<td>SO$_x$</td>
<td>sulfur oxides</td>
</tr>
<tr>
<td>ZnGeP$_2$</td>
<td>zinc germanium diphosphide</td>
</tr>
<tr>
<td>ZnSe</td>
<td>zinc selenide</td>
</tr>
</tbody>
</table>

**Mathematical symbols**

- $A$: absorbance
- $a$: particle diameter
- $a^2\pi$: classical cross-section
- $\alpha(\nu)$: molecular absorption coefficient
- $\alpha_{gas} = \alpha(\nu)c_{gas}$: total absorption coefficient
- $\alpha_{gas,i}$: total absorption coefficient of the $i$-th gas compound in the mixture
$C$ constant or cell constant

c speed of light in vacuum: $c = 299,792,458 \text{ m/s (exact)}$ [146]

c' speed of light inside a cavity

c$_{\text{gas}}$ gas concentration

c$_{\text{gas},i}$ concentration of the $i$-th gas compound in a mixture

$\chi^{(2)}$ nonlinear susceptibility

d$_{\text{eff}}$ effective nonlinear coefficient

d$_{ij}$ $ij$-th tensor element

$E_{\text{FUN}}$ pulse energy of the fundamental radiation

$E_{\text{las}}$ laser pulse energy

$E_{\text{SHG}}$ pulse energy of the second harmonic radiation

e electron charge: $e = 1.602,176,53(14) \times 10^{-19} \text{ As}$ [146]

$\varepsilon_0$ vacuum permittivity: $\varepsilon_0 = 8.854,187,817 \ldots \times 10^{-12} \text{ As/Vm}$ [146]

$\eta$ conversion efficiency

$f$ modulation frequency or pulse repetition rate

$h$ Planck constant: $h = 6.626,069,3(11) \times 10^{-34} \text{ J s}$ [146]

$h = h/2\pi$ Planck constant: $h = 1.054,571,68(18) \times 10^{-34} \text{ J s}$ [146]

$hv = \hbar\omega$ photon energy

g($\nu - \nu_0$) normalized lineshape function

$g_{\text{G}}(\nu)$ Gaussian lineshape function

$g_{\text{L}}(\nu)$ Lorentzian lineshape function

$g_{\text{V}}(\nu)$ Voigt lineshape function

$I$ intensity

$i$ integer

$I_0$ incident intensity

$I_T$ transmitted intensity

$j$ integer

$k_B$ Boltzmann constant: $k_B = 1.380,650,5(24) \text{ J mol}^{-1} \text{ K}^{-1}$ [146]

$\vec{k}$ wave vector

$\Delta \vec{k}$ phase mismatch

$L$ crystal length

$l$ absorption path length

$l_c$ coherence length
\( L_{\text{cell}} \) \hspace{1cm} \text{optical length between cell mirrors} \\
\( L_{\text{opt}} \) \hspace{1cm} \text{optical length of the laser cavity} \\
\( L_{\text{path}} \) \hspace{1cm} \text{optical path length} \\
\( \lambda \) \hspace{1cm} \text{wavelength} \\
\( \Delta \lambda \) \hspace{1cm} \text{wavelength interval} \\
\( \Delta \lambda_{\text{step}} \) \hspace{1cm} \text{wavelength step} \\
m \hspace{1cm} \text{particle mass or modulation depth} \\
m_e \hspace{1cm} \text{electron mass: } m_e = 9.109,382,6(16) \times 10^{-31} \text{ kg} \quad [146] \\
m/z \hspace{1cm} \text{mass-to-charge ratio} \\
N \hspace{1cm} \text{number density of absorbing species or number of domains} \\
n_{\omega} \hspace{1cm} \text{refractive index at optical angular frequency } \omega \\
N_{\text{mean}} \hspace{1cm} \text{mean value} \\
n_{\text{bottom}} \hspace{1cm} \text{number of images on the bottom row} \\
\nu \hspace{1cm} \text{frequency or carrier frequency} \\
\nu_0 \hspace{1cm} \text{resonance frequency or line center frequency} \\
\nu_{ij} \hspace{1cm} \text{transition frequency between states } i \text{ and } j \\
\Delta \nu \hspace{1cm} \text{frequency interval or linewidth} \\
\bar{\nu} \hspace{1cm} \text{wavenumber} \\
\Delta \bar{\nu} \hspace{1cm} \text{wavenumber interval} \\
\Omega \hspace{1cm} \text{modulation frequency} \\
\omega \hspace{1cm} \text{optical angular frequency} \\
P \hspace{1cm} \text{power} \\
P_{\text{las}} \hspace{1cm} \text{incident optical laser power} \\
p \hspace{1cm} \text{pressure} \\
Q \hspace{1cm} \text{quality factor of the photoacoustic cell} \\
q \hspace{1cm} \text{positive integer} \\
Q_{\text{vib}} \hspace{1cm} \text{vibrational transition number} \\
Q_{\text{rot}} \hspace{1cm} \text{rotational transition number} \\
r \hspace{1cm} \text{radius} \\
R_{ij} \hspace{1cm} \text{transition moment between states } i \text{ and } j \\
S \hspace{1cm} \text{linestrength} \\
S_{ij} \hspace{1cm} \text{linestrength of transition between states } i \text{ and } j \\
S_{\text{mic}} \hspace{1cm} \text{photoacoustic signal registered with the microphone}
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma$</td>
<td>molecular absorption cross section</td>
</tr>
<tr>
<td>$\sigma_{gas}$</td>
<td>absorption cross section of the molecule</td>
</tr>
<tr>
<td>$\sigma_{gas,i}$</td>
<td>molecular absorption cross section of the $i$-th gas compound</td>
</tr>
<tr>
<td>$\sigma_{stat}$</td>
<td>standard deviation</td>
</tr>
<tr>
<td>$SNR$</td>
<td>signal-to-noise ratio</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature or transmittance</td>
</tr>
<tr>
<td>$t$</td>
<td>time</td>
</tr>
<tr>
<td>$t_{meas}$</td>
<td>measurement time</td>
</tr>
<tr>
<td>$\tau$</td>
<td>time constant</td>
</tr>
<tr>
<td>$\tau_i$</td>
<td>lifetime of state $i$</td>
</tr>
<tr>
<td>$\tau_{relax}$</td>
<td>relaxation time</td>
</tr>
<tr>
<td>$\tau_{sp}$</td>
<td>decay time of an excited state through spontaneous emission</td>
</tr>
<tr>
<td>$z$</td>
<td>distance along optical axis</td>
</tr>
</tbody>
</table>
Publications, presentations and patent

A list of all publications, conference presentations and a patent that originated in the course of this thesis is given below.

**Refereed journal publications**


**Conference proceedings and abstracts**


**Oral conference presentations**

A. Romann and M. W. Sigrist. *Simultaneous dual-wavelength photoacoustic detection of trace gases*, CLEO 2003, Baltimore MD (USA), June 1–6, 2003, paper CTuX2


A. Romann, R. Hitchen and M. W. Sigrist. *Multicomponent trace-gas sensing with compact 1.6 μm-external cavity diode laser photoacoustic system*, ACOLS 2001, Brisbane QLD (Australia), Dec 3–6, 2001, paper M(b)3


A. Romann and M. W. Sigrist. *High resolution spectra of bromo methane and dimethyl ether obtained by a continuously tunable 10-bar CO₂ laser based photoacoustic spectrometer*, Dig. 11th Int. Conf. on Photoacoustic and Photothermal Phenomena (11th ICPPP), Kyoto (Japan), June 25–29, 2000, paper P-01-05

M. W. Sigrist, A. Bohren, T. v. Lerber, and A. Romann. *Environmental applications in laser-based photoacoustic spectroscopy*, Dig. 11th Int. Conf. on Photoacoustic and Photothermal Phenomena (11th ICPPP), Kyoto (Japan), June 25–29, 2000, paper A-29-a1


M. W. Sigrist, A. Bohren, I. G. Calasso, M. Naegele, and A. Romann. *New developments in laser photoacoustic and photothermal spectroscopy applied to trace gas monitoring*, Dig. 14th Int. Conf. on Laser Spectroscopy (ICOLS99), Innsbruck (Austria), June 7–16, 1999, paper P2-72

**Patent**

*A method for measuring at least one physical parameter using an optical resonator,*

European Application No. 00 121 314.9 (date of application: 9 Oct. 2000),

Supervised students and teaching activities

A list of supervised student research projects and teaching and tutoring activities performed during the course of this thesis is given in the following.

Supervised diploma students

Robert Hitchen  
*An investigation into some of the various detection methods for trace gas analysis using a compact 1.6 μm external cavity diode laser* (diploma project)

Marcel Hintermann  
*Aufbau eines hochauflösenden Langwegabsorption-Spektrometers zum Spurengasanalyse basierend auf einem Diodenlaser mit externer Kavität* (diploma project)

Supervised semester work

Heidi Koivikko  
*Photothermal and photoacoustic trace gas detection on two examples* (semester project)

Teaching and tutoring activities

Lectures  
*Laser, Prof. M. W. Sigrist*  
*Laser für Ingenieure, Prof. M. W. Sigrist*

Laboratory courses  
*Laserspektroskopie*  
*Photoemission*
Acknowledgement

Firstly, I would like to thank my supervisor Professor Markus W. Sigrist for letting me join his research group, being approachable, and giving me the chance to present my work at international conferences and publications. Together with all present and past group members and visitors he has cultivated a stimulating research environment and filled the labs with many talented people. I also would like to thank Professor Ursula Keller for accepting to be the co-examiner of this thesis.

Without a doubt, the most direct influence on my work has come from Markus Nägele, Andreas Bohren, Tuomo von Lerber, Conny Fischer, and Irio Calasso. I have had the good fortune to be in the company of many nice people, both inside and outside my own small research group. Markus Nägele, Cornelia Fischer, Tuomo von Lerber, Andreas Bohren, Irio Calasso, Michael Seiter, Robert Hitchen, Heidi Koivikko, Daniel Vogler and Dylian Marinov have provided an upbeat and supportive environment and a constant supply of fresh humor. This is always important for lab work, which has the potential to be dull at times, especially when one has to constantly master and reanimate a moody CO₂-laser beast down in the dungeon. It seriously has been fun with these people. Outside of our group I'd like to thank especially the nonlinear ultra-cold spectroscopy basketball team. They all have contributed to the success of this project in some way.

I specially would like to thank Markus Nägele for among others for explaining and supporting me using his resonant PA setup, Andreas Bohren for his nice PA cell and being a nice person down in the lab, Irio Calasso for leaving a setup behind that was good to start with. The three of them also introduced me into many practical aspects of working in the lab with optics, lasers, and photoacoustic spectrometers as well as helping making me literate using LabView.

Marcel Hintermann during his diploma work has built a solid foundation for the diode-laser based experiments - quite a relevant contribution to the success of the laser spectroscopy experiment now being regularly used in the undergraduate lab and my thesis. I am also grateful to Robert Hitchen for making it a great and enjoyable summer 2001 and being willing to learn and work in the lab. Without him, the resonant photoacoustic and direct absorption experiments would hardly have been successful.

I very much appreciate all the stimulating discussions I had with Tuomo von Lerber. This was certainly a great and rewarding experience that included everything from brainstorming vague
ideas in unknown science land, to demonstrating and patenting our idea of fiber-based cavity
ring-down spectroscopy, and eventually involved attracting industrial partners.
The ETH Zurich offered a great environment that includes the great work done by the machine
shop and the glassblower. Thank you guys!
Outside work hours, there have been friends, flatmates, and family who have helped when things
would not go according to plan. Thank you all!
Last but not least, a big thank you goes to Amy for her support, English corrections and giving
advice. Merci beaucoup!

This study was financially supported by the Swiss National Science Foundation (SNF), the Ali-
liance for Global Sustainability (AGS, AVINA Funds), and the ETH Zurich. I also wish to ac-
knowledge Loïc Becouran and Eric Lallier, Thomson-CSF/LCR, Orsay, France, who kindly have
made the GaAs crystal available.
## Curriculum Vitae

<table>
<thead>
<tr>
<th>Year</th>
<th>Event</th>
</tr>
</thead>
<tbody>
<tr>
<td>1966</td>
<td>born in Zurich, citizen of Schleinikon (ZH)</td>
</tr>
<tr>
<td>1973–1982</td>
<td>primary school in Oberweningen-Schöfflisdorf (ZH), and secondary school in Niederweningen (ZH)</td>
</tr>
<tr>
<td>1982–1986</td>
<td>apprenticeship as electronics technician, Gretag Imaging AG, Regensdorf (ZH), and Trade School of the City of Zurich, Electrotechnical Department</td>
</tr>
<tr>
<td>1986–1989</td>
<td>study of electrical engineering, Winterthur Polytechnic</td>
</tr>
<tr>
<td>1989</td>
<td>graduation with diploma as dipl. El.-Ing. HTL (B. Sc. level), thesis in RF electronics: <em>Power Splitter-Combiners</em> (supervisor Prof. K. Bücher)</td>
</tr>
<tr>
<td>1990–1996</td>
<td>development engineer (full- and part time), R&amp;D department of RF electronics, Spectrospin AG, Fällanden</td>
</tr>
<tr>
<td>1990</td>
<td>entrance examination to the ETH Zurich (Swiss Federal Institute of Technology Zurich)</td>
</tr>
<tr>
<td>1991–1996</td>
<td>study of physics at the ETH Zurich</td>
</tr>
<tr>
<td>1993–1996</td>
<td>mathematics tutor (part time), Institut für Technische Ausbildung (ITA), Zurich</td>
</tr>
<tr>
<td>1996</td>
<td>graduation with diploma as dipl. Physiker ETH (M. Sc. level) thesis in computational astrophysics: <em>Doppelstern System γ²-Velorum</em> (supervisor Prof. W. Schmutz)</td>
</tr>
<tr>
<td>1996–1997</td>
<td>traveling the world</td>
</tr>
<tr>
<td>1997</td>
<td>support engineer, Sulzer Electronics AG, Zurich</td>
</tr>
</tbody>
</table>
1997–1998  research assistant, Positron Emission Tomography Group, Paul Scherrer Institut (PSI), Villigen

1998–2003  research assistant in the project presented in this thesis under the guidance of Prof. M. W. Sigrist at the Laser Spectroscopy and Sensing Laboratory of the Institute of Quantum Electronics, ETH Zurich

1998–2003  teaching assistant in courses of laser, and lasers and applications held by Prof. M. W. Sigrist, design and implementations of a new experiment for laser-based spectroscopy and tutoring in the undergraduate student laboratory

2003–2004  research fellow, Centre for Gravitational Physics (Prof. D. E. McClelland), The Australian National University, Canberra

2005–2006  project leader, Foundation for Research on Information Technologies in Society (Prof. N. Kuster), Zurich

2007    Ph. D. thesis and examination: *Pulsed and modulated photoacoustic and transmission spectroscopy on trace gases employing continuously tunable CO₂- and diode-lasers*