Mid- and Near-infrared NICE-OHMS
– Techniques for ultra-sensitive detection of molecules in gas phase

Thomas Hausmaninger
[...] to myself I seem to have been only like a boy playing on the seashore, and diverting myself in now and then finding a smoother pebble or a prettier shell than ordinary, whilst the great ocean of truth lay all undiscovered before me.

In der Wissenschaft gleichen wir alle nur den Kindern, die am Rande des Wissens hie und da einen Kiesel aufheben, während sich der weite Ozean des Unbekannten vor unseren Augen erstreckt.

Isaac Newton

Für Familie und Freunde
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Noise-immune cavity-enhanced optical heterodyne molecular spectrometry (NICE-OHMS) is a technique for ultra sensitive detection of molecular absorption and dispersion. For highest performance, the technique combines cavity enhancement (CE) with frequency modulation (FM); while the former increases the effective interaction length between the light and the analyte by several orders of magnitudes, the latter removes the in-coupling of $1/f$ noise and makes the signals background free. The combination of CE and FM also gives the technique an immunity to amplitude noise caused by the jitter of the laser frequency relative to the cavity resonance frequencies. All these properties make the technique suitable for ultra sensitive trace gas detection in the sub-parts-per-trillion (ppt) range. The aim of this thesis is to improve the performance of the NICE-OHMS technique and to increase its range of applications.

The work in this thesis can be divided into three areas: Firstly, a mid-infrared (MIR)-NICE-OHMS instrumentation was developed. In a first realization an unprecedented white-noise equivalent absorption limit for Doppler broadened (Db) detection in the MIR of $3 \times 10^{-9} \text{ cm}^{-1}\text{Hz}^{-1/2}$ was demonstrated. This was subsequently improved to $2.4 \times 10^{-10} \text{ cm}^{-1}\text{Hz}^{-1/2}$ allowing for detection methane and its two main isotopologues ($\text{CH}_3\text{D}$ and $^{13}\text{CH}_4$) at their natural abundance. Secondly, further development of an existing near-infrared NICE-OHMS system was performed. This resulted in an improved longtime stability and the first shot-noise limited NICE-OHMS system for Db detection with a noise equivalent absorption limit of $2.3 \times 10^{-14} \text{ cm}^{-1}$ detected over 200 s. Thirdly, models and theoretical descriptions of NICE-OHMS signals under strong absorption conditions and from methane under high laser power were developed. It was experimentally verified that the models allow for a more accurate evaluation of NICE-OHMS signals under a wide range of conditions.
SAMMANFATTNING


Avhandlingen kan delas in i tre delar: Inom den första utvecklades en mid-infraröd (MIR)-NICE-OHMS instrumentering. Vid en första realisering påvisades en aldrig tidigare uppnådd vitt-brus-ekvivalent absorptionsgräns för Dopplerbreddad (Db) detektering i MIR området på $3 \times 10^{-9}$ cm$^{-1}$Hz$^{-1/2}$. Detta förbättrades därefter till $2.4 \times 10^{-10}$ cm$^{-1}$Hz$^{-1/2}$, vilket möjliggör detektering av metan och dess två huvudsakliga isotopologer (CH$_3$D och $^{13}$CH$_4$) vid deras naturliga förekomst. Inom det andra området utfördes vidareutveckling av ett existerande NICE-OHMS-system verksamt i det när-infraröda (NIR) området. Detta resulterade i en förbättrad långtidsstabilitet och en brus-ekvivalent absorptionsgräns för Db detektion på $2.3 \times 10^{-14}$ cm$^{-1}$ mått över 200 s. Inom den tredje utvecklades modeller och teoretiska beskrivningar av NICE-OHMS under starka absorptionsförhållanden och från metan under hög laserintensitet. Det var experimentellt verifierat att modellerna möjliggör en mer noggrann utvärdering av NICE-OHMS-signaler under ett stort antal förhållanden.
This thesis is based on the following articles, which will be referred to in the text by their Roman numerals.

I. Doppler-broadened mid-infrared noise-immune cavity-enhanced optical heterodyne molecular spectrometry based on an optical parametric oscillator for trace gas detection
Silander I., Hausmaninger T., Ma W., Harren F. J. M., and Axner O.
doi:10.1364/OL.40.000439, ref.: [1]

II. Narrowing of the linewidth of an optical parametric oscillator by an acousto-optic modulator for the realization of mid-IR noise-immune cavity-enhanced optical heterodyne molecular spectrometry down to $10^{-10}$ cm$^{-1}$ Hz$^{-1/2}$
Hausmaninger T., Silander I., Axner O.
Optics Express (2015) Vol. 23, pp. 33641-33655
doi:10.1364/OE.23.033641, ref.: [2]

III. Doppler-broadened mid-infrared noise-immune cavity-enhanced optical heterodyne molecular spectrometry based on an optical parametric oscillator
Hausmaninger T., Silander I., Axner O.
Imaging and Applied Optics 2016, OSA technical Digest (online) (2016), paper LT2G.2

IV. Doppler-broadened NICE-OHMS beyond the cavity-limited weak absorption condition – I. Theoretical description
Ma W., Silander I., Hausmaninger T., Axner O.
V. Doppler-broadened NICE-OHMS beyond the cavity-limited weak absorption condition – II: Experimental verification

**Hausmaninger T.,** Silander I., Ma W., Axner O.


VI. Whispering-gallery-mode laser-based noise-immune cavity-enhanced optical heterodyne molecular spectrometry

**Zhao G., Hausmaninger T.,** Ma W., and Axner O.

doi: 10.1364/OL.42.003109, ref.: [6]

VII. Differential noise-immune cavity-enhanced optical heterodyne molecular spectroscopy for improvement of the detection sensitivity by reduction of drifts from background signals

**Zhao G., Hausmaninger T.,** Ma W., and Axner O.

*Optics Express* (2017) Vol. 25, pp. 29454-29471
doi: 10.1364/OE.25.029454, ref.: [7]

VIII. Shot-noise-limited Doppler-broadened noise-immune cavity-enhanced optical heterodyne molecular spectrometry

**Zhao G., Hausmaninger T.,** Ma W., and Axner O.

doi: 10.1364/OL.43.000715, ref.: [8]

IX. Depletion of the vibrational ground state of CH$_4$ in absorption spectroscopy at 3.4 µm in N$_2$ and air in the 1–100 Torr range

**Hausmaninger T.,** Zhao G., Ma W., Axner O.


X. Model for molecular absorption spectroscopy in the 1-100 Torr range in the presence of vibrational depletion

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X. High resolution ultra-sensitive trace gas detection by use of cavity-position-modulated sub-Doppler NICE-OHMS
Zhao G., Hausmaninger T., Schmidt F. M., Ma W., Axner O. in manuscript
arXiv:1810.13194[physics.ins-det]

XI. The structure of graphene oxide membranes in liquid water, ethanol and water – ethanol mixtures
doi:10.1039/c3nr04631a

XII. Noise-immune cavity-enhanced analytical atomic spectrometry – NICE-AAS – A technique for detection of elements down to zeptogram amounts
Axner O., Ehlers P., Hausmaninger T., Silander I., and Ma W.
doi:10.1016/j.sab.2014.08.016

XIII. Doppler-broadened noise-immune cavity-enhanced optical heterodyne molecular spectrometry down to $4 \times 10^{-13}$ cm$^{-1}$ Hz$^{-1/2}$: implementation of a 50,000 finesse cavity
Silander I., Hausmaninger T., Ma W., Ehlers P., and Axner O.
doi:10.1364/OL.40.002004, ref.: [10]

XIV. Model for in-coupling of etalons into signal strengths extracted from spectral line shape fitting and methodology
for predicting the optimum scanning
range—demonstration of Doppler-broadened,
noise-immune, cavity-enhanced optical heterodyne
molecular spectroscopy down to $9 \times 10^{-14}$ cm$^{-1}$
Silander I., Hausmaninger T., and Axner O.
doi:10.1364/JOSAB.32.002104

XVI. Sensitive and broadband measurement of dispersion in a
cavity using a Fourier transform spectrometer with kHz
resolution
Rutkowski R., Johansson A. C., Zhao G., Hausmaninger T.,
Khodabakhsh A., Axner O., and Foltynowicz A.
*Optics Express* (2017) Vol. 25, pp. 21711-21718
doi:10.1364/OE.25.021711

XVII. Gas modulation refractometry for high-precision
assessment of pressure under non-temperature-stabilized
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Silander I., Hausmaninger T., Zelan M., Axner O.
doi:10.1116/1.5022244

XVIII. Broadband calibration-free cavity-enhanced complex
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Johansson A. C., Rutkowski R., Filipsson A.,
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*Optics Express* (2018) Vol. 26, pp. 20633-20648
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ELFT extended-locking full-transmission 102
EM electro magnetic 5, 17–19, 28, 37
EOM electro-optic modulator 68, 71, 74, 91, 92

FF feed-forward 86, 87
FM frequency modulation 5, 7, 9, 27, 28, 32, 33, 46, 49, 52, 53, 67, 68, 71, 95
FMS frequency modulation spectrometry 5, 7, 17, 27, 30, 33, 45, 46, 48, 51, 52, 57, 82, 83
FPGA field programmable gate array 94, 97
FSR free spectral range 7, 39–41, 47, 52, 66, 105
FSR₀ empty cavity free spectral range 38, 39

HR highly reflective 35, 37–39
HWHM half width at half maximum 20, 38

IQ in-phase and quadrature 32, 96
IR infrared 13

LAS laser absorption spectroscopy 4–6

MIR mid infrared 9, 10, 81–83, 133

NEAL noise equivalent absorption limit 76, 77, 83, 84, 89–91, 136

NICE-OHVMS noise-immune cavity-enhanced optical heterodyne velocity modulation spectroscopy 82, 93

NIR  near infrared 9, 10, 73, 88

OPO  optical parametric oscillator 9, 10, 82–84, 86, 133

OS  optical saturation 108, 110

OWA  ordinary weak absorption 17, 18, 100, 101

PBS  polarizing beamsplitter 46, 69, 82

PDH  Pound-Drever-Hall 46, 48, 51–53, 59, 69, 71, 93, 105

PZT  piezoelectric transducers 66, 67, 70, 71, 83, 85, 86, 134

RAM  residual amplitude modulation 67, 74, 81, 82, 88

RCLWA  relaxed cavity-limited weak absorption 100, 102

RF  radio frequency 5, 27

sD  sub Doppler 8, 9, 25, 65, 72, 77, 81, 83, 91, 92, 94, 98, 106, 107, 138

SNR  signal-to-noise ratio 5, 8, 9, 35, 72, 74, 84, 86, 88, 90

TEM  transverse electromagnetic mode 36, 37

TEM<sub>00</sub>  fundamental TEM 37, 69

VCO  voltage-controlled oscillator 67, 71, 98

WGML  whispering-galley-mode laser 10, 87

WMS  wavelength modulation spectrometry 5, 27

WNEAL  white noise equivalent absorption limit 8–10, 76, 77, 83, 84, 88, 90, 91, 133, 134
### SYMBOLS

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<td>( \alpha )</td>
<td>absorption coefficient in cm(^{-1})</td>
<td>17–19, 21, 22, 99, 100</td>
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<td>( \alpha_0 )</td>
<td>absorption coefficient at the maximum of an absorption line in cm(^{-1})</td>
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<td>( A_{21} )</td>
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<td>( B_{12} )</td>
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<td>modulation index</td>
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<td>( \beta_{pdh} )</td>
<td>PDH modulation index</td>
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<tr>
<td>( c )</td>
<td>speed of light</td>
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<td>( \chi^{\text{abs}} )</td>
<td>area normalised absorption line shape function (in cm(^{-1}))</td>
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<td>( \chi^{\text{abs}}_V )</td>
<td>area normalised Voigt absorption line shape function</td>
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<td>( \chi^{\text{disp}} )</td>
<td>area normalised dispersion line shape function (in cm(^{-1}))</td>
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<td>( \chi^{\text{disp}}_V )</td>
<td>area normalised Voigt absorption line shape function</td>
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<td>( \chi^{\text{no}} )</td>
<td>area normalised dispersion line shape function (in cm(^{-1}))</td>
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<td>( \delta )</td>
<td>single pass absorption induced by molecular transitions</td>
<td>18, 19, 22, 30, 33, 40, 41, 43, 44, 57, 59, 100, 104</td>
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<td>( \delta_{fm} )</td>
<td>detuning between modulation frequency and FSR in absence of molecular transitions ((\nu_{fm} - \nu_{fsr}))</td>
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\( \Delta \nu \) detuning between the laser and the analyte 19, 21, 22, 24, 25, 63, 64, 72, 111

\( E_1 \) energy of lower level of a transition 14

\( E_2 \) energy of higher level of a transition 14

\( \tilde{E}_{\text{mod}} \) phase modulated electric field 28

\( \tilde{E}_{\text{mol}} \) electrical field after passing a gas sample 18, 30

\( \eta_{\text{det}} \) detector responsivity (in A/W) 73, 74

\( \eta_{\text{fm}} \) instrumentation factor for the demodulated FM signal 32, 33, 46, 47, 49

\( \eta_{\text{no}} \) instrumentation factor for the demodulated NICE-OHMS signal 56, 57, 72

\( F \) cavity finesse 39, 43, 44, 57, 74

\( G \) saturation parameter 24

\( \gamma_{21} \) decay rate from level 2 to 1 [Hz] 24

\( \Gamma_a \) analyte transition width (HWHM) 54, 63

\( \Gamma_c \) cavity mode width (HWHM) 38, 39, 41, 43, 44, 46, 54, 61

\( \Gamma_{\text{sat}}^L \) saturated Lorenzian width (HWHM) 24

\( \Gamma_L \) Lorenzian width (HWHM) 24

\( I \) intensity per unit frequency interval 16

\( J_j \) \( j^\text{th} \) order Bessel function of the first kind 28, 30, 31, 33, 46, 49, 55, 57

\( k_B \) Boltzmann constant 22, 23

\( L_c \) cavity length 35–39

\( \tilde{l} \) mirror electric field amplitude reflection coefficient 35, 39–41

\( \tilde{r} \) mirror electric field amplitude reflection coefficient 35, 38–41

\( \tilde{i} \) mirror electric field amplitude reflection coefficient 35, 39–41

\( N \) number density of analyte molecules (in m\(^{-3}\)) 21, 22

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\(n\)  index of refraction (non-resonant) 38, 39
\(N_i\)  number density of molecules in state \(i\), also referred to as population of state \(i\) (in \(\text{m}^{-3}\)) 14, 22
\(v_{\text{fsr}}\)  cavity free spectral range 39, 41, 44, 46, 49–51, 53–55, 61, 63, 64, 104, 105
\(v_{\text{fsr}}^0\)  empty cavity free spectral range 38, 39
\(v_j\)  frequency of the \(j\)th laser component of a frequency modulated laser 30–33, 41, 43, 44, 46, 49, 53–56, 101
\(v_l\)  frequency of a monochromatic laser 16–19, 28–33, 37, 38, 40, 43, 46–50, 53–58, 101, 102, 105
\(v_{\text{fm}}\)  modulation frequency for NICE-OHMS/FMS 28, 30, 31, 38, 45–56, 58, 63, 64, 95, 101, 102, 104, 105
\(v_{\text{mol}}\)  center frequency of a molecular transition 14, 15
\(v_{\text{pdt}}\)  modulation frequency for Pound-Drever-Hall 46–49, 52, 53, 94, 95
\(v_q\)  center frequency of the \(q\)th cavity mode to which the laser is locked 54
\(\text{OPL}_{\text{m}}\)  optical path length of cavity mirrors per single pass 37, 38
\(\phi\)  total cavity single pass phase shift 37, 38, 41, 105
\(\phi^0\)  empty cavity single pass phase shift 37, 38, 40, 43
\(\phi\)  single pass phaseshift additionally induced by molecular transitions 18, 19, 23, 30, 33, 38–41, 43, 44, 54, 55, 57, 61, 104, 105
\(\Phi\)  photon flux (in number of photons \(\text{m}^2 \text{s}^{-1}\)) 24
\(Q\)  total internal partition sum at a given temperature 22
\(q\)  cavity mode number (integer) 37, 44
\(R_c\)  cavity intensity reflection function 44
\(\tilde{R}_c\)  cavity electric field amplitude reflection function 40, 41, 44, 46, 47, 49, 53, 54, 101, 102, 104
spectral energy density (in $J m^{-3} Hz^{-1}$) 14–16
line-intensity, integrated line strength (in $cm^{-1}/molecule cm^{-2}$) 22, 23
$S_{fm}$ FMS signal after demodulation/amplification in $V$ 32, 33
$\sigma_A$ Allan Deviation 76
$\sigma_{ik}$ frequency dependent cross sections for absorption and stimulated emission 16, 22
$S_{no}$ NICE-OHMS signal after demodulation/amplification in $V$ 56, 57, 72
$S_{pdh}$ PDH error signal after demodulation/amplification in $V$ 46
$\xi_j$ detuning between the laser component $j$ and the corresponding cavity mode $q+j$ 41, 43, 44, 48, 54, 58, 101, 102, 105
$T_c$ cavity intensity transmission function 44
$\tilde{T}_c$ cavity electric field amplitude transmission function 40, 41, 43, 44, 55, 56, 101, 102, 104
$\tilde{T}_{mol}$ analyte electric field amplitude transmission function 18, 30–32
$\theta_{dvb}$ demodulation phase DVB error signal 49
$\theta_{fm}$ demodulation phase for the FMS/NICE-OHMS signal 32, 33, 56, 57, 63
$\theta_{pdh}$ demodulation phase PDH error signal 46, 47
$V_{\pi}$ halfwave voltage required to shift the phase by $\pi$ 68
$\omega_l$ angular frequency of a monochromatic laser 18
$\omega_{fm}$ angular modulation frequency for NICE-OHMS/FMS 31, 55, 58
Part I

BACKGROUND AND INTRODUCTION

A scientist in his laboratory is not a mere technician: he is also a child confronting natural phenomena that impress him as though they were fairy tales.

Marie Curie
Curiosity and the need to understand, predict and control things are widely spread among human beings. This results in many questions arising every day—both basic questions like "What’s the temperature outside?" or "What is the CO$_2$ concentration in this room?" and more complex ones like "Is the climate change fake news?" or "Do gravitational waves exist?". Many of these questions cannot be answered by observations based on human senses. Driven by curiosity mankind started to develop instrumentation for sensing various physical quantities so as to make them observable for human beings. With all the new questions arising every day, not only new instrumentation is required, but also the demands on the instrumentation increase. Such demands require often more sensitive, more compact, or more robust instrumentation. Moreover, also a good understanding of the functioning and limitations of the instrumentation and how to interpret their signals is crucial to give accurate answers to the questions of interest.

This thesis deals with the development of instrumentation answering the question about the presence or the concentration of molecular species (e.g. methane) in a gas sample. If the molecules of interest (referred to as the analyte) is present at high concentrations, it is in general easy to obtain this information (it can be as simple as smelling the gas of interest). To answer some questions though, it is necessary to detect gases that make up only an "extremely small" fraction of a given sample, where extremely small often means that the analyte is present at trace concentration of less than a few part per billion (ppb). The fields for which trace gas detection is of importance are widespread and include medicine (e.g. breath gas analysis [12, 13]), environmental monitoring (e.g. gas leak detection [14]), fundamental research (e.g. tracing methane sources in the environment [15, 16]), and indus-
trial process monitoring (e.g. combustion diagnostics [17]), just to mention a few.

As widespread the fields of application are, as varying are the requirements (sensitivity, accuracy, acquisition rate, cost, portability, etc.) of the instrumentation. Therefore, over the years, a multitude of different techniques and instrumentation for trace gas detection have been developed to address different demands and applications. These include both the group of mass spectrometry based techniques and the group of laser spectrometry based techniques [12]. The technique applied in the scope of this work belongs more specifically to the group of laser based absorption spectroscopy (AS) techniques.

The pioneer in the field of AS was Joseph Fraunhofer (1787-1826) who studied absorption lines in the optical spectrum of the sun. He found that the absorption of light by atoms and molecules has a spectral dependence that is characteristic for each atomic or molecular species. This enables a species selective detection of molecules. Furthermore, the amount of absorption can be directly related to the amount of analyte passed by light by the Lambert-Beer law, which allows for quantitative assessments. Based on these features, the invention of the lasers in the end of 1950s opened up for laser absorption spectroscopy (LAS) [18, 19]. The narrow bandwidth of lasers enabled both selective detection of spectral features (i.e. absorption lines) and sensitive detection of their absorption.

In the simplest LAS setups laser light is sent through a sample cell containing the gas sample while the laser intensity after the sample is measured. The relative absorption induced intensity change, $\Delta I / I_0$, can then be related to the analyte concentration by the Lambert-Beer law, where $\Delta I$ is the absorbed intensity and $I_0$ the incoming intensity (see section 2).

However, for low concentrations the absorption induced intensity change is in general very small compared to the total intensity and the detection sensitivity is limited by the noise of the incoming laser intensity. To improve on this, various techniques have been developed that reduce the influence of intensity noise or en-
hance the absorption signal so also to increase the signal-to-noise ratio (SNR) of LAS.

To reduce the influence of noise various modulation techniques were developed. As is discussed in section 3, the frequency spectrum of intensity noise has often a $1/f$ dependence. By modulation one can shift the absorption signal to a high frequency at which the intensity noise is low. By use of a demodulation process to retrieve the absorption signal the strong low frequency noise can be removed without losing information. An alternative explanation of this concept is that the signal is detected within a short time period over which the intensity is stable and not fluctuating due to acoustic noise. The maybe most straightforward modulation technique is wavelength modulation spectrometry (WMS) in which the wavelength is modulated back and forth over an absorption feature. Another modulation technique applicable to detection of ions is velocity modulation \[20\]. Also photo acoustic spectroscopy (PAS) uses either an intensity modulation or wavelength modulation approach to generate an acoustic wave originating from the periodically modulated absorption \[21, 22\].

A modulation technique closely related to WMS is frequency modulation spectrometry (FMS), which is discussed in detail in section 3.1. By modulating the laser frequency (or equivalently the phase) at a radio frequency (RF) a narrow single frequency laser is split into several frequency components separated by the frequency modulation (FM) frequency \[23, 24\]. As only the phase of the electro magnetic (EM) field is modulated, the modulation does not induce any modulation of the intensity at the FM frequency. However, when one of the spectral components of the laser is disturbed (attenuated or phase shifted) by an analyte the FM is partially converted to an amplitude modulation (AM) that can be detected in the laser intensity. A phase sensitive demodulation will then give a signal proportional to the absorption and/or the dispersion response of the analyte. This implies that in the absence of an analyte the signal is zero. FMS is therefore referred to as a background free technique. Because of the high modulation frequency the signal is not affected by $1/f$ noise whereby the instrumentation can provide extremely high detection sensitivity.
In particular it has been shown that, if other sources of noise have been eliminated, the noise levels of FMS can be reduced to the shot-noise limit \([25]\), which is the fundamental noise limit in AS that originates from the quantization of light energy.

While modulation techniques in general reduce the influence of noise, it is also possible to enhance the absorption of a gaseous sample by increasing the interaction length of the laser and the gas. It is in principle possible to just increase the length of a gas cell, but cells longer than 1 m are in general impractical to use. Another solution is to use so called multi-pass cells in which the laser beam is, after entering the cell, reflected multiple times back and forth in the cell before exiting the cell again. While it is feasible to construct multi-pass cells with several hundred passes they tend to have large sample volumes and can be challenging to align \([26]\).

Another common approach to enhance the response of LAS is to utilize a resonant optical cavity (shortly referred to as cavity, see section 4). Cavities are basically optical resonators (often formed by a pair of highly reflective mirrors as illustrated in figure 4.1) that only accept and transmit laser light if it matches one of its resonance frequencies. A weak absorber filled into the cavity can then induce strong changes of the transmission of the laser light. Here we refer to AS techniques making use of optical cavities as cavity enhanced (CE) techniques.

The maybe most straightforward CE technique is cavity enhanced direct absorption spectroscopy (CEDAS) (often also abbreviated CEAS \([26]\)). If the laser light is in resonance with the cavity, the light coupled into the cavity is trapped inside the cavity for a long time before it leaks out of the cavity again. This implies that with CEDAS the effective interaction length between the light and the molecules can be increased several thousand or tens of thousand times compared to a single passage (i.e. making a 20 km long interaction length out of a 40 cm long cavity). However, while for multi-pass cells the intensity noise remains constant, for CEDAS the intensity noise is often increased because the narrow cavity resonances convert laser frequency noise to amplitude noise. To solve this problem, techniques such as integrated ca-
vity output spectroscopy (ICOS) [27, 28], off-axis ICOS [29], and optical feedback-CEAS (OF-CEAS) [30] have been developed.

A widely applied CE technique that avoids the laser intensity noise is cavity ring-down spectroscopy (CRDS) [26, 31]. As for any other resonator, when a cavity resonance is excited by laser light it stores a part of the energy. If the excitation is stopped the damping will lead to an exponential decay of the stored energy. For optical resonators the damping is given by the sum of the losses in the mirrors and the absorption of molecules inside the cavity. The decay of the light stored inside the cavity can be observed by monitoring the power leaking out through one of the cavity mirrors (the leak-out power is a constant fraction of the intra-cavity power given by the mirror transmittance). CRDS makes use of this concept by abruptly turning off the laser excitation and then measuring the decay time constant (referred to as ring-down time). Since the ring-down time of this decay is independent of the initial intensity (at the switching off time) this measure is not directly affected by the laser intensity noise.

The technique addressed in this thesis, noise-immune cavity-enhanced optical heterodyne molecular spectrometry (NICE-OHMS), combines CE and FMS to obtain enhanced signals while maintaining a low noise level [32, 33]. The technique exploits the fact that cavity resonance frequencies are regularly spaced by the cavity free spectral range (FSR) and the FM light is composed of frequency components that are spaced by the modulation frequency. This makes it possible to couple the FM light into a cavity by matching the modulation frequency to the FSR. The FM light in the cavity experiences a CE interaction with the analyte. The resulting technique profits from cavity enhancement and the low noise and background free signals originating from the modulation process as described above. Additionally the FM light is immune to frequency to amplitude noise conversion. This so-called noise-immunity is the result of the nature of the matching of the FM frequency to the cavity resonance pattern (see section 6.5.2). Already with the first demonstrations of NICE-OHMS, utilizing an ultra-narrow fix-frequency laser, it was shown that these properties can make the technique shot-noise limited and that an
ultra low white noise equivalent absorption limit (WNEAL) in the order of $1 \times 10^{-14} \text{cm}^{-1}$ can be achieved [32, 33].

However, NICE-OHMS systems can provide both a narrow sub Doppler (sD) response that is not broadened by the velocity distribution of the molecules and a Doppler broadened (Db) response [34]. The first demonstrations of NICE-OHMS addressed, in fact, narrow (~100 kHz wide) sD signals with the aim for using them as an optical frequency standard [32, 35]. The excellent SNR demonstrated in those works promised also ultra low detection limits for trace gas detection. However, the sD response, which originates from optical saturation, is limited to low sample pressures [36]. The amount of absorption in general increases with the partial pressure of the addressed molecule. Therefore a limit on the pressure implies a limit on the sensitivity in terms of concentration. For this reason the Db-NICE-OHMS response is in general considered to give a better concentration detection limit (CDL) than what sD can do [34]. The first demonstration of Db-NICE-OHMS was performed by Gianfrani et al. in 1999 for measurements of $\text{O}_2$ transition line shapes with a WNEAL of $6.9 \times 10^{-11} \text{cm}^{-1}\text{Hz}^{-1/2}$. While this was a promising first demonstration, it turned out that it is in general difficult to obtain absorption detection limits for Db-detection as low as for sD-detection [37].

The reason for this is that, as for any other sensitive technique, imperfections in the implementation of NICE-OHMS do not always allow to reach fundamental detection limits under all conditions. NICE-OHMS realizations in particular are often limited by residual background signals, which can come from imperfections of the modulation process or from interference effects in the optical path. As discussed in section 6.7 of this thesis, these background signals are often instable and can cause signal drifts and couple other noise sources into the signal. In [37] it was concluded that Db detection is in general more sensitive to background signals than sD detection. Several techniques can be found in the literature that aim for alleviating this problem aiming at reduction of noise and improvement of longtime stability. One approach is the implementation of an additional modulation layer,
for example wavelength modulation or velocity modulation [32, 38, 39]. Alternatively the background signals can be actively suppressed by controlling the modulation or avoided by placing optical components at etalon-immune distances (EIDs) [25, 32, 40–43]. While these efforts resulted in impressive CDLs for acetylene (C₂H₂) in the sub-ppt (parts-per-trillion) range [10] to the authors knowledge, no shot-noise limited NICE-OHMS system for Db-detection had, until recently, been realized. To exploit the potential of Db-NICE-OHMS Publication VII, publication VIII and manuscript XI address this problem by the development of differential detection and background modulation approaches. In publication VIII the first shot noise limited NICE-OHMS system for Db-detection was demonstrated.

Besides reducing the noise by FM and increasing the interaction length by CE, it is also possible to improve on the SNR by addressing the strongest absorption features. The strongest fundamental vibrational transitions can be addressed with light in the mid infrared (MIR) (2–10 μm range). However, the first demonstration of NICE-OHMS by Ye and Ma et al. in the late 1990s [32, 33] as well as the subsequent development for Db-NICE-OHMS have been performed in the near infrared (NIR) (1–2 μm range) in which, for most molecules, only weak overtone transitions can be addressed (C₂H₂ transitions are an exception). The reason for this is that the electro optical components as well as the narrow laser sources required for NICE-OHMS are easily available for the NIR (since this range is used for telecommunication).

The invention of quantum cascade lasers (QCL) made the MIR range more accessible [44, 45] and also enabled the development of the first sD-MIR-NICE-OHMS instrumentation by Taubman et al. in 2004 [38]. Later, in 2012, Crabtree et al. and Porambo et al. demonstrated realizations of NICE-OHMS based on an optical parametric oscillator (OPO) and a difference frequency generation (DFG) source [39, 46]. While the former addressed sD signals of molecular ions and applied velocity modulation, the latter focused on sD detection using wavelength modulation. For the Db mode of detection in the MIR so far only a WNEAL 2 × 10⁻⁷ cm⁻¹Hz⁻¹/₂ has been demonstrated [46]. This is more
than five orders of magnitude above the detection limit for Db detection in the NIR [10].

To improve on this, publication I, publication II, and publication III in this thesis are concerned with the development of an OPO based NICE-OHMS system for sensitive detection of molecules by addressing Db absorption lines in the MIR. The specific aim of this system was to detect methane (CH$_4$) isotopologues, in particular the C-13 methane isotopologue ($^{13}$CH$_4$) and the deuterated methane isotopologue (CH$_3$D), which are of interest for environmental research [15, 16]. The developed system showed a WNEAL of $2.4 \times 10^{-10}$ cm$^{-1}$Hz$^{-1/2}$ and is to the authors knowledge the first MIR NICE-OHMS system for Db detection that opens up for detection of methane isotopologues with a detection limit in the low ppt range. This is well below the natural abundances in ambient air which are around 2 ppm, 20 ppb, and 1 ppb for CH$_4$, $^{13}$CH$_4$, and CH$_3$D respectively [47].

Besides realizing instrumentation addressing different molecules at various wavelength, it is also of importance to test laser sources that can make NICE-OHMS instrumentation more compact. During the last decade a significant amount of work was done in our group on improving the detection limit of Db-NICE-OHMS based on erbium doped fiber-lasers [10, 37, 43, 48–53]. In addition, in publication VI we demonstrated that it is possible to realize a NICE-OHMS system around a whispering-gallery-mode laser (WGML). Benefiting from the previous development the system could demonstrate a detection limit similar to the best previous realizations. WGMLs have the advantage that they have a narrow linewidth, similar to that of fiber lasers, while being more compact. Furthermore, they can be realized at a larger selection of wavelengths than fiber-lasers, which are limited to the wavelengths regions of the available gain media.

As mentioned above it is important to have a good understanding of the signals generated by an instrumentation. If a NICE-OHMS instrumentation is used close to the detection limit the signals are in general proportional to the analyte concentration. However, for stronger signals the NICE-OHMS response can become non-linear. This is often the case when systems are to be
calibrated. The publication IV and publication V scrutinize the response of a NICE-OHMS system with respect to the absorption and dispersion induced by the molecules. These works have resulted in a model that can describe and predict NICE-OHMS signals also when a significant amount of light is absorbed. They can also provide information about the conditions under which it is appropriate to assume a linear response and under which conditions more advanced models for the NICE-OHMS signals have to be applied. While these two publications are focused on the instrumental response, also the absorption by the molecules can show non-linearities with laser power and pressure. This can also sometimes make it difficult to relate signals—obtained by any AS based instrumentation—to analyte concentrations. Publication IX and manuscript X address laser power related effects at pressures above 1 Torr on the example of methane. The results show that optical saturation-like processes, referred to as vibrational depletion, can lead to signal distortions of up to 80%.

It is hoped that the works presented here have contributed to advancement of the NICE-OHMS technique in general and for its application to trace-gas analysis in particular.
MOLECULAR ABSORPTION AND DISPERSION OF LIGHT

NICE-OHMS is based on detecting the absorption and dispersion of light by molecular transitions. The following sections give a summary of the basic entities and processes giving rise to absorption and dispersion signals. Also the entities and functions relating these signals to the concentration of the molecules addressed by the spectrometer (the analyte) are given.

2.1 INTERACTION OF LIGHT AND MOLECULES

Molecules have several types of resonances corresponding to transitions between different types of energy levels. The transition energies for particular types of transitions differ, in general, by several orders of magnitude. Therefore the transition types can be classified according to the corresponding photon frequencies ($\nu$) and vacuum wavelengths ($\lambda$) \[^{[54]}\]. Transitions addressed by radio and microwave radiation ($\nu = 0.75$–$30$ GHz; $\lambda = 10$–$400$ mm) include nuclear magnetic spin resonances (NMR), electron paramagnetic spin resonances, and rotational transitions. Light in the infrared (IR) range ($\nu = 30$–$300$ THz; $\lambda = 1$–$10$ µm) addresses transitions between vibrational levels. And finally, light in the visible-UV range ($\nu \gtrsim 400$ THz; $\lambda \lesssim 700$ nm) corresponds to electronic transition energies.

The splitting of vibrational levels into rotational levels gives rise to the formation of rotational-vibrational (ro-vibartional) transition bands around the vibrational energies (see chapter 5.4 in \[^{[54]}\]). These ro-vibrational transitions are commonly addressed in molecular spectroscopy. For example in this work signals of transitions between ro-vibrational energy levels of $\text{C}_2\text{H}_2$ around $1.5$ µm and of $\text{CH}_4$ around $3.5$ µm were studied.
There are three main processes by which light can interact with transitions [36]. Firstly, a molecule in a lower state $E_1$ can absorb a photon and be excited to a higher level $E_2$ if the energy of the photon matches the energy difference between the two levels (i.e. $E_1 - E_2 = h\nu_{\text{mol}}$). This process is simply called absorption. Secondly, a photon fulfilling this condition can also stimulate a decay of a molecule in the higher state $E_2$, which then will emit an additional photon with the same energy and phase as the stimulating photon. This process is called stimulated emission. Thirdly, a molecule in the higher state can, by itself, spontaneously decay to a lower state by emission of a photon. This is referred to as spontaneous emission. These processes directly affect the intensity of the radiation as well as the number densities of molecules in the addressed states $N_i$ (given in units of cm$^{-3}$), where $i = 1, 2$ are the two states considered. $N_i$ is also referred to as population of the state $i$. Furthermore, also the population of other states (also states of other molecular species) that are coupled to the addressed states (e.g. by collisions) can be affected [9, 55]. To simplify matter in the following sections the latter effect will not be taken into account.

We will use the Einstein treatment to describe these processes. This is a rate-equation based treatment that is valid if the Rabi flopping at the Rabi frequency, $\omega_R$, is washed out, i.e if $\omega_R \ll \Delta\omega'$, where $\Delta\omega'$, is the larger of: (i) the radiation bandwidth; (ii) frequency width arising from phase-changing collisions" [56]. This condition is usually fulfilled with instrumentation built for molecular absorption spectroscopy.

The light field can be described in terms of the spectral energy density $\varphi(\nu)$ (in J cm$^{-3}$ Hz$^{-1}$). In this section we assume that $\varphi$ is given by such a broad distribution that it can be considered constant over the width of the transition, i.e. $\varphi(\nu) = \varphi(\nu_{\text{mol}}) = \text{constant}$.

The rate per unit volume at which molecules leave the lower state by absorption of light, $dN_1/dt$ is given by [36, 56]

$$
\left( \frac{dN_1}{dt} \right)_{\text{abs.}} = N_1 B_{12} \varphi(\nu_{\text{mol}}),
$$

(2.1)
where $B_{12}$ (in J$^{-1}$ cm$^3$ Hz$^2$) is the Einstein coefficient for absorption.

The rate for molecules in the upper state to experience stimulated emission, $dN_2/dt$, is given by

$$\left( \frac{dN_2}{dt} \right)_{\text{stim.}} = N_2 B_{21} \varrho (\nu_{\text{mol}}) = N_2 \frac{g_2}{g_1} B_{12} \varrho (\nu_{\text{mol}}),$$  \hspace{1cm} (2.2)

where $B_{21}$ is the the Einstein coefficient for stimulated emission, $g_{1,2}$ are the statistical weights of the upper and lower states, respectively, which thus relate $B_{21}$ and $B_{12}$ to each other.

Compared to absorption and stimulated emission, the molecular decay rate for spontaneous emission is independent of the external radiation field and is therefore, under all conditions, simply proportional to the Einstein coefficient for spontaneous emission $A_{21}$ (in Hz) and the number density $N_2$ [56],

$$\left( \frac{dN_2}{dt} \right)_{\text{spont}} = N_2 A_{21}.$$ \hspace{1cm} (2.3)

As a spontaneously emitted photon is directed in a random direction it will usually not directly contribute to an absorption related signal. In addition, for ro-vibrational levels the spontaneous emission rates are usually significantly lower than other types of decay processes. Therefore, this process in general plays a minor role for molecular absorption spectroscopy and will be neglected in the following discussion [9].

On the other hand, both the absorption and stimulated emission processes can noticeably affect the intensity of a light beam. This change in intensity is the measured quantity in absorption spectroscopy and will therefore be discussed in detail in the following section.

2.2 ATTENUATION OF THE INTENSITY - THE LAMBERT-BEER LAW

To describe the effects of absorption and stimulated emission on the intensity of light, in the following, we first rewrite the rate...
equations for a finite transition width and an arbitrary spectral distribution of the light-field. In a second step, the expressions are simplified under the condition of a narrow laser-linewidth.

As is described in section 2.4 spectral lines are never monochromatic due to broadening mechanisms [36]. Therefore it is useful to introduce the frequency dependent cross sections for absorption and stimulated emission $\sigma_{ik}(v)$ (in cm$^2$). On average the number of photons with frequency $v$ leading to absorption/stimulated emission on the transition $i \rightarrow k$ of a molecule in state $i$ is given by the number of photons with frequency $v$ passing through the circular area $\sigma_{ik}(v)$ around a molecule. With this definition the change in intensity of a collimated light beam propagating along the axis $z$ (in cm) can be written as

$$\frac{dI(z,v)}{dz} = I(z,v) \left[ \sigma_{12}(v)N_1 - \sigma_{21}(v)N_2 \right], \quad (2.4)$$

where $I(z,v)$ is the spectral intensity in the interval $[v, v + dv]$ (in W cm$^{-2}$ Hz$^{-1}$) which for a collimated laser beam is related to the spectral density by $I(z,v) = \varrho(z,v)c$.

This can be compared to eqs. (2.1, 2.2) while considering that the excitations and decays of molecules in a unit volume will absorb photons and emit photons with energies of $hv$. Since the total rates for absorption and stimulated emission over all frequencies from a broadened transition must be the same in the two descriptions this gives the relation (see Appendix B in [56])

$$B_{ik} = \frac{c}{hv} \int_0^\infty \sigma_{ik}(v)dv. \quad (2.5)$$

On the other hand, the narrow continuous wave (CW)-lasers used in absorption spectroscopy techniques addressed in this work are usually much narrower than the broadening of the line shapes. Therefore we can assume a collimated monochromatic laser radiation with the frequency $v_l$, which implies that $I(z,v) = \delta(v - v_l)I(z)$, where the intensity $I$ is given in W cm$^{-2}$ and eq. (2.4) can be rewritten in terms of the intensity as follows

$$\frac{dI(z,v_l)}{dz} = I(z,v_l) \left[ \sigma_{12}(v_l)N_1 - \sigma_{21}(v_l)N_2 \right]. \quad (2.6)$$
Finally, the absorption coefficient for a transition between the states 1 and 2, $\alpha(v)$, (in this work given in cm$^{-1}$) can be defined as

$$\alpha(v) = \sigma_{12}(v) \left[ N_1 - \frac{g_1}{g_2} N_2 \right]. \quad (2.7)$$

With this definition eq. (2.6) simplifies to

$$\frac{dI(z, v_1)}{dz} = I(z, v_1) \alpha(v_1). \quad (2.8)$$

Under the assumption that the populations $N_i$ and $\alpha(v)$ are independent of $z$, the solution of this differential equation is the Lambert-Beer-law which describes the decrease in intensity after light has passed an absorbing medium of length $L$,

$$I(v_1) = I_0 e^{-\alpha(v_1)L}, \quad (2.9)$$

where $I_0$ is the incoming intensity.

The direct absorption spectrometry (DAS) signal is often considered to be the relative absorption after the length $L$ defined as

$$\frac{\Delta I(v_1)}{I_0} = 1 - e^{-\alpha(v_1)L} \approx \alpha(v_1)L, \quad (2.10)$$

where $\Delta I(v_1) = I_0 - I(v_1)$ is the absolute difference in intensity before and after the absorber. The first order approximation given in the expression is valid in the case of small absorption ($\alpha L \ll 1$). The latter condition is also referred to as ordinary weak absorption (OWA) condition [4].

### 2.3 Electric Field Attenuation and Phase Shift Induced by Molecules

While for DAS mainly the attenuation of the intensity is of importance, techniques like NICE-OHMS or FMS are also sensitive to the phase shift of the EM waves. The electric field of polarized light in the polarization direction can be written as
\[ E(z, t) = E_0 \cos(\omega_1 t + k_0 z) = \frac{E_0}{2} \left[ e^{i(\omega_1 t + k_0 z)} + e^{-i(\omega_1 t + k_0 z)} \right] = \tilde{E}(z, t) + \tilde{E}^*(z, t), \]

where \( \omega_1 = 2\pi v_1 \) is the angular frequency of the light, \( k = 2\pi / \lambda \) is the wave vector, \( \lambda = n v / c \) is the wavelength, \( n \) is the broadband refractive index, \( \tilde{E} \) is the complex electric field, and \( \tilde{E}^* \) its complex conjugate.

The intensity (as the power per area unit measured by a photo diode over timescales orders of magnitude longer then the period of the EM wave [55]) can be conveniently written in terms of the complex electric field as

\[ I(z) = \frac{1}{2} c \varepsilon_0 E_0^2 = 2 c \varepsilon_0 \tilde{E}(z, t) \tilde{E}^*(z, t). \]

The molecular induced attenuation and phase shift of the electric field can be described by a complex electric field transmission function \( \tilde{T}_{\text{mol}} \) defined as [57]

\[ \tilde{E}_{\text{mol}}(v_l, L) = \tilde{T}_{\text{mol}}(v_l, L) \tilde{E}(v_l, L = 0), \]

where \( \tilde{E}_{\text{mol}} \) is the electric field in the presence of molecular transitions. The transmission function \( \tilde{T}_{\text{mol}} \) in turn can be expressed as

\[ \tilde{T}_{\text{mol}}(v_l, L) = e^{-\delta(v_l, L) - i\phi(v_l, L)}, \]

where \( \delta \) and \( \phi \) are the single pass attenuation (absorption) and phase shift of the electrical field due to molecular transitions after passing a length \( L \) in the medium. Under the OWA assumption, i.e. \( \alpha L \ll 1 \), the transfer function can be linearized in analogy to eq. (2.10), whereby \( \tilde{T}_{\text{mol}} \) can be expressed as

\[ \tilde{T}_{\text{mol}}(v_l, L) \approx 1 - \delta(v_l, L) - i\phi(v_l, L). \]

A comparison of eqs. (2.12) and (2.9) with the electric field given by (2.13) gives the relation between \( \delta \) and \( \alpha \):
\[ \delta(v_l, L) = \frac{\alpha(v_l)}{2} L, \]  
\[ (2.16) \]

where the factor 1/2 comes from the fact that \( \alpha \) is an intensity and \( \delta \) is a EM field related quantity. The relation between \( \delta \) and \( \phi \) is given in the simplest case by the Kramers-Kronig dispersion relations [36]. However, these relations are not applicable for inhomogeneous broadening in combination with optical saturation the relation [57].

### 2.4 Line Shapes and Broadening Mechanisms

As was alluded to above, the center frequency of a molecular ro-vibrational transition, \( v_{\text{mol}} \), is given by the difference in energy between the two ro-vibrational levels involved (\( \Delta E = h v_{\text{mol}} \)). However, due to different broadening mechanisms light is not only interacting with molecules at a discrete frequency, but rather in a range around the transition center frequency. The interaction strength as function of the detuning between the laser frequency and the transition center, \( \Delta \nu = v_l - v_{\text{mol}} \), is given by a probability distribution, which in turn often is described by a area normalized line shape function \( \chi_{\text{abs}}(\Delta \nu) \) for which the following holds [47],

\[ \int_0^{\infty} \chi_{\text{abs}}(\Delta \nu) d\nu \equiv 1. \]  
\[ (2.17) \]

Since transitions always affect both the amplitude and the phase of the light there exists for each type of absorption line shape a corresponding dispersion line shape \( \chi_{\text{disp}}(\Delta \nu) \) [36, 57].

The function \( \chi_{\text{abs}}(\Delta \nu) \) is different for different broadening mechanisms and can depend on various parameters. While in the following a overview over the most important broadening mechanisms is given, a detailed discussion of various types of broadening can be found elsewhere [36].

The most fundamental broadening is originating from the finite lifetime of the population in the laser addressed states. By the Heisenberg’s uncertainty principle a finite lifetime is directly
related to the uncertainty of the state energies which gives rise to a broadening of the transition frequency.

The broadening related to the lifetime limited by spontaneous emission is referred to as natural broadening [56]. For ro-vibrational transitions this broadening is in the order of tens of Hz and usually the smallest of all types of broadenings.

At higher pressures the lifetime of the populations is limited by collisions between molecules which will change the rotational state of the molecules leading to pressure broadening. The latter is proportional to the pressure and is, for example, for methane in N$_2$ approximately 2 MHz/Torr [9, 58].

At lower pressures molecules can have a mean free path between collisions similar to or larger than the laser beam diameter. Under this condition the transit time of a molecule through the laser beam puts boundaries on the laser-molecule interaction time that lead to a broadening of the transitions [59, 60]. This broadening, which is referred to as transit time broadening, is typically in the order of 100 kHz for a beam diameter of around 1 mm [57].

These broadening mechanisms—which all are based on a finite interaction time—lead to a line shape given by a Lorentzian function with a half width at half maximum (HWHM) $\Gamma_L$. If molecules are exposed to multiple Lorentzian broadenings, the total $\Gamma_L$ is given by the sum of all Lorentzian broadenings.

A different kind of broadening is the Doppler broadening. The thermal velocity of a molecule induces a Doppler shift of the transition frequency experienced by the light field interacting with the molecule. The molecular velocities are given by a distribution, but laser radiation of a given frequency will interact only with a given molecular velocity group. The resulting broadening of the line shape function is therefore often referred to as an inhomogeneous type of broadening. A Maxwellian distribution of the velocities leads to a Gaussian line shape with a HWHM $\Gamma_D$ [36, 56].

For pressures in the 1-100 Torr range, which often is used for trace-gas detection, both Doppler and pressure broadening are affecting the line shape. As long as the two broadening mechanisms can be considered independent of each other the combined
line shape can be described by a convolution of a Lorentzian and Gaussian function, i.e. the Voigt line shape.

At high pressures, typically above 50 Torr, also higher order collisional effects can influence the broadening. These are taken into account by more complicated line shapes, like speed-dependent Voigt [61], Galatry [62] and Hartmann-Tran [63, 64] profiles [65]. When sub-Doppler signals (see below) are studied with high accuracy, higher order effects can affect the signals also at low pressures [66].

For studies presented in this work the Voigt profile was in most cases considered sufficiently accurate. The Voigt line shape functions can be given in terms of the complex error function $W(x + iy)$ as [57]

$$\chi_{V}^{\text{abs}}(\Delta \nu) = \frac{c\sqrt{\ln(2)}}{\sqrt{\pi \Gamma_D}} \Re[W(x + iy)], \quad (2.18)$$

and

$$\chi_{V}^{\text{disp}}(\Delta \nu) = -\frac{c\sqrt{\ln(2)}}{\sqrt{\pi \Gamma_D}} \Im[W(x + iy)], \quad (2.19)$$

where $x$ is the Doppler-width normalized frequency detuning and $y$ the Doppler-width normalized Lorentzian width, given by

$$x = \frac{\Delta \nu \sqrt{\ln(2)}}{\Gamma_D} \quad (2.20)$$

and

$$y = \frac{\Gamma_L \sqrt{\ln(2)}}{\Gamma_D}, \quad (2.21)$$

respectively.

## 2.5 Line Strength – Relating Molecular Density to Absorption

When absorption spectrometry is applied to trace gas detection, and in particular for assessment of concentration, it is necessary to relate the measured absorption coefficient, $\alpha$, to the total number density of analyte molecules, $N$. As is shown by eq. (2.7),
α is directly related to the number densities of molecules in the laser addressed states \( N_i \) (referred to as the population of state \( i \)). Under thermal equilibrium the molecules populate a state \( i \) according to the Boltzmann distribution [47], i.e.

\[
N_i = N \frac{g_i}{Q(T)} e^{-E_i/k_B T},
\]

(2.22)

where \( k_B \) is the Boltzmann constant (in J K\(^{-1}\)), \( T \) is the absolute temperature (in K), and \( Q \) is the total internal partition sum. The latter is given by a summation over all states \( M \) of the molecule of interest,

\[
Q(T) = \sum_{j=1}^{M} g_j e^{-E_j/k_B T}.
\]

(2.23)

It is useful to define a line-intensity, \( S \), which is relating the absorption coefficient to the area-normalised line shape and the concentration under thermal equilibrium at a reference temperature (in this work 296 K). \( S \) is defined so that it is possible to write

\[
\alpha(\Delta \nu) = \frac{2}{L} \delta(\Delta \nu, L) = SN \chi_{abs}(\Delta \nu).
\]

(2.24)

If \( S \) is taken in units of cm\(^{-1}\)/(molecule cm\(^{-2}\)) as is done in the HITRAN database [58], \( N \) is given in units of cm\(^{-3}\) and \( \chi_{abs} \) in cm (i.e. inverse wavenumbers). \( S \) can also be interpreted as the absorption cross section for an analyte molecule integrated over the entire spectral range (given in wavenumbers). Therefore, it is also referred to as the integrated molecular line strength. It should be noted that both \( \sigma_{ik}(\nu) \) and \( S \) are cross-sections for a given transition \( ik \). However, \( \sigma_{ik}(\nu) \) is the (frequency dependent) cross section for a molecule in the state \( i \), but \( S \) is the (integrated) cross section for any analyte molecule in thermal equilibrium. The former implies that the probability for the molecule being in state \( i \) is—by definition—100%, the latter implies that the probability for the molecule being in state \( i \) is given by the Boltzmann distribution.
The corresponding relation for the phase shift, \( \phi(\nu, L) \), of the electric field is given by

\[
\frac{2}{L} \phi(\nu, L) = SN\chi^{\text{disp}}(\nu).
\]  

(2.25)

Comparison of eqs. (2.7, 2.22, and 2.24) gives the temperature dependence of the line strength and its relation to the Einstein coefficients [47],

\[
S(T) = \frac{\hbar \nu}{c Q(T)} (g_{12}B_{12}e^{-E_{1}/k_{B}T} - g_{21}B_{21}e^{-E_{2}/k_{B}T}).
\]  

(2.26)

It should be noted that for temperatures other then the reference temperature (296 K for the HITRAN database) it is necessary to recalculate the line-strength. In this work \( S \) refers always to the line strength as given in HITRAN. Furthermore, at room temperature the second term in the eq. (2.26) usually can be neglected, since the thermal energies are too low to populate the excited ro-vibrational state, i.e. since \( E_{2} \gg k_{B}T \Rightarrow N_{2} \approx 0 \). On the other hand, if the thermal equilibrium is disturbed by the laser (e.g. in case of optical saturation \( N_{2} \gg 0 \)) the line shape function can be redefined so that relation (2.24) still can be applied. It should be noted though, that in the latter case the line shape function of the transition is no longer area-normalized.

2.6 **OPTICAL SATURATION**

Up to this point we have mainly considered how the absorption process affects the light intensity. For this we have tacitly assumed that the laser light only probes the molecules. However, as shown in eqs. (2.1) and (2.2), the light also affects the population of the energy levels. If the laser induced excitation rate (i.e. the absorption rate) is in the order of the total relaxation rate the population \( N_{1} \) will be lower while while \( N_{2} \) will be higher than under thermal equilibrium. As a consequence the absorption coefficient is reduced and becomes a function of intensity [see eq. (2.7)]. This non-linear process is referred to as optical saturation [36].
Saturation is in the following modeled by a two level system, where the two levels are the laser addressed states. In this model these two levels are not coupled to any other levels. This simple model is often valid for solitary atomic transitions without hyperfine structure [36] and also for ro-vibrational transitions at low pressures. It should be noted though that deviations from predictions the two level model can be observed under experimental conditions for which collision induced coupling to neighboring rotational states is strong [9, 67].

To formulate the saturation process a simple rate equation can be set up, which for steady state can be written as [36]

\[
\frac{dN_1}{dt} = -\frac{dN_2}{dt} = -\Phi \sigma_{12}(\nu) N_1 + \Phi \sigma_{21}(\nu) N_2 + \gamma_{21} N_2,
\]

(2.27)

where \(\Phi\) is the photon flux (in number of photons m\(^{-2}\) s\(^{-1}\)) and \(\gamma_{21}\) is the sum of all decay rates other than stimulated emission.

For homogeneous broadenings (e.g. natural-, transit-time- and pressure-broadening) at any detuning the same molecules are addressed (i.e. all molecules populating the ro-vibrational states 1 and 2). However, for inhomogeneous Doppler broadening only molecules in the velocity group corresponding to \(\Delta \nu\) are addressed and affected by the laser light. Therefore these two conditions need to be dealt with differently.

For homogeneous broadening it can be shown that the saturated line shape is again given by a Lorentzian function, but with reduced amplitude and increased width. The additional broadening, also referred to as power broadening, is given by

\[
\Gamma_{L}^{\text{sat}} = \sqrt{1 + G \Gamma_L},
\]

(2.28)

where \(G\) is the unit less saturation parameter. The latter is in turn related to the laser intensity by the following expression

\[
G = \frac{I}{I_{\text{sat}}},
\]

(2.29)

where \(I_{\text{sat}}\) is the saturation intensity. An analytical expression for \(G\) as function of the decay rates and transition dipole-moment can be found elsewhere [36, 57].
For *inhomogeneous broadening* the laser only saturates the velocity group addressed by the laser. This "local" saturation burns a hole in the Doppler broadened lineshape function referred to as Bennet hole [48, 68, 69]. The Bennet hole can be observed as a dip in the Doppler profile if additional to a saturating laser the absorption is probed by a weak laser. Since the saturating laser always probes the Bennet hole as it is tuned over a Doppler broadened transition will experience a reduced absorption. It can be shown that the line shape measured by a saturating laser will be reduced by a factor of \( (1 + G)^{-1/2} \), although the Doppler width remains unchanged.

Counter-propagating electromagnetic waves — as present in optical resonators — can lead to so called sD responses. As discussed above for each \( \Delta \nu \) a different velocity group is addressed and probed. A velocity group includes molecules with a certain velocity, \( v_z \), relative to the laser propagation direction. Two counter propagating waves with the same frequency address (and saturate) therefore in general two groups of molecules with opposite velocity along the propagation axis, i.e. \( \pm v_z \). However at \( \Delta \nu = 0 \) molecules with \( v_z = 0 \) are addressed by both waves. This implies at zero detuning both counter-propagating waves address and saturate the same velocity group which increases the degree of saturation for this detuning/velocity group. This leads to the so called Lamb-Dip or sub-Doppler signal at the center of the absorption profile [48, 69, 70]. Since in NICE-OHMS counter-propagating waves with different frequencies are present in the cavity also sub-Doppler signals at various non-zero detunings can be observed [48].
One of the fundamental limitations of DAS is that the signal given by eq. (2.10) constitutes a small change ($\Delta I$) of a large background intensity ($I_0$). Therefore all the noise present in the laser intensity $I_0$ will directly couple into the absorption signal. However, the noise spectrum of lasers at low frequencies often has a $1/f$ dependence. This means that the noise can be high at low frequencies, but decreases with frequency until the white noise starts to dominate (which is by definition the same at all frequencies).

To avoid all this low-frequency noise various kinds of modulation can be applied. Any type of modulation has as a consequence that the signal appears at a high frequency whereby the low frequency noise can be filtered without losing the signal.

A common modulation-based technique is WMS. In WMS the wavelength of the laser is sinusoidally modulated at a kHz rate over a molecular transition. The Fourier components of the absorption signal will then be present in the transmitted intensity at multiples of the modulation frequency [71]. After detection using a photo detector they can be retrieved by demodulation using, for example, a Lock-In amplifier. The demodulation process involves steep band-pass filters efficiently removing the low-frequency noise.

Another less common example that can be applied to the detection of molecular ions is modulation of the drift velocity in an electrical field. The velocity modulation results in a modulation of the Doppler shift which can be detected and demodulated [72].

Finally, FMS makes use of FM, which is based on phase modulation of a laser at a RF [23, 24]. Since NICE-OHMS is based on this technique it will be described in more detail in the following section.
3.1 FREQUENCY MODULATION SPECTROSCOPY

Like for the phase shift induced by the molecular transitions described in section 2.3 phase modulation of laser light is best described by the complex electric field. If the phase of polarized laser light is sinusoidally modulated with a frequency \( \nu_{\text{fm}} \) it can be written as [52]

\[
\tilde{E}_{\text{mod}}(\nu_l, t) = \frac{E_0}{2} e^{-2\pi i \nu_l t} e^{-i \beta \sin(2\pi \nu_{\text{fm}} t)}, \tag{3.1}
\]

where \( \nu_l \) is the laser center frequency and \( \beta \) is the modulation index. Using the Jacoby-Anger expansion this expression can be written in form of a series, viz. as [73]

\[
\tilde{E}_{\text{mod}}(\nu_l, t) = \frac{E_0}{2} e^{i 2 \pi \nu_l t} \sum_{j=-\infty}^{\infty} J_j(\beta) e^{i 2 \pi j \nu_{\text{fm}} t}, \tag{3.2}
\]

where \( J_j(\beta) \) is the \( j^{\text{th}} \)-order Bessel function of the first kind. This notation reveals that phase modulated light can be seen as a superposition of EM waves with frequencies of \( \nu_l \pm j \nu_{\text{fm}} \). The amplitudes, \( J_j(\beta) \), of the components \( j=0,1,2,3 \), are plotted in figure 3.1a) as a function of the modulation index. As expected, for \( \beta = 0 \) (i.e. without modulation) only the 0\(^{\text{th}}\)-component is present; on the other hand with increasing \( \beta \) the number of higher order components with significant amplitude is increasing. For \( \beta = 0.7 \) the second order sidebands are plotted in figure 3.1b). The figure shows that under this condition the center component and the first order sidebands (i.e. the so called FM-triplet) dominate, but also the second order sidebands have a significant amplitude.
In this work the spectral components of the modulated laser light that correspond to the terms in (3.2) are referred to as *laser components*, since the often used term "mode" is easily confused with cavity modes. The $j$th laser component will shortly be denoted as $J_j$. The frequency of the *center component*, i.e. $J_0$, will be referred to as the *laser frequency* $\nu_l$ or center frequency. The often used term "carrier frequency" is avoided since it can be confused with the modulation frequency which also carries the spectroscopy signal. The remaining components, i.e. $J_{j \neq 0}$, are referred to as *sidebands*. Furthermore, the beating between two sidebands $J_m$ and $J_n$ is denoted as $J_m \leftrightarrow J_n$. 

**FM NOMENCLATURE**

*Figure 3.1:* Amplitudes of the modulation sidebands $j=1,2$ and $3$ as function of the modulation index (panel a) and the schematic of the laser components for a modulation index of 0.7 (panel b). The higher the modulation index the stronger the higher order sidebands.
An important property of the Bessel functions is that the positive and negative Bessel functions are related by

\[ J_j = (-1)^j J_{-j}. \] (3.3)

Since this implies that \( J_j J_{j+1} = -J_{-j} J_{-j-1} \) the beatings at \( \nu_{fm} \) between a pair of negative sidebands \( J_{-j-1} \leftrightarrow J_{-j} \) and the corresponding pair of positive sidebands \( J_j \leftrightarrow J_{j+1} \) cancel. Hence, the intensity of purely phase modulated light does not contain any oscillations at \( \nu_{fm} \).

However, according to eq. (2.14), a molecular transition will affect the amplitude and phase of the laser components. Moreover, since \( \delta \) and \( \phi \) are strongly frequency dependent functions, each component will be attenuated and phase shifted individually. Using the molecular transfer function the resulting electric field can be written as

\[
\tilde{E}_{mol}(\nu_l, t) = \frac{E_0}{2} e^{-i2\pi\nu_l t} \sum_{j=-\infty}^{\infty} J_j \tilde{T}_{mol}(\nu_j)e^{i2\pi j \nu_{fm} t}
\]

\[
= \frac{E_0}{2} \sum_{j=-\infty}^{\infty} J_j e^{i[2\pi j \nu_{fm} t - \phi(\nu_j)] - \delta(\nu_j)},
\] (3.4)

where \( \nu_j = [\nu_l + j \cdot \nu_{fm}] \) is the frequency of the \( j \)th laser component, and where we have treated \( L \) and \( \beta \) as constants. Due to the response of the molecular transitions the positive and negative sidebands are affected differently. As a result, the beatings do not fully balance and oscillations at \( \nu_{fm} \) arise in the intensity. This is the origin of the FMS signal.

It is possible to obtain the expression for the intensity of this signal at \( \nu_{fm} \) by inserting eq. (3.4) in eq. (2.12) and only keeping
terms corresponding to oscillations at \( \nu_{fm} \) which results in the following expression

\[
I(\nu, t)|_{\nu_{fm}} = I_0 \sum_{j=-\infty}^{\infty} J_j J_{j+1} \left\{ \tilde{T}_{mol}(\nu_j) \tilde{T}_{mol}^*(\nu_{j+1}) e^{-i\omega_{fm}t} + \tilde{T}_{mol}^*(\nu_j) \tilde{T}_{mol}(\nu_{j+1}) e^{+i\omega_{fm}t} \right\}
\]

\[
= 2I_0 \sum_{j=-\infty}^{\infty} J_j J_{j+1} \text{Re} \left\{ \tilde{T}_{mol}(\nu_j) \tilde{T}_{mol}^*(\nu_{j+1}) e^{-i\omega_{fm}t} \right\},
\]

where each term corresponds to a beating \( J_j \leftrightarrow J_{j+1} \).

It can be shown that the real part of the expression in curly bracket corresponds to a summation of two in quadrature oscillations at \( \nu_{fm} \) – i.e. a sine and a cosine term – as follows

\[
\text{Re} \{ \ldots \} = \text{Re} \left\{ \text{Re} \left[ \tilde{T}_j \tilde{T}_{j+1}^* \right] e^{-i\omega_{fm}t} + i \text{Im} \left[ \tilde{T}_j \tilde{T}_{j+1}^* \right] e^{-i\omega_{fm}t} \right\}
\]

\[
= \text{Re} \left[ \tilde{T}_j \tilde{T}_{j+1}^* \right] \cos (\omega_{fm}t) + \text{Im} \left[ \tilde{T}_j \tilde{T}_{j+1}^* \right] \sin (\omega_{fm}t),
\]

where we have used the shorthand notation \( \tilde{T}_{mol}(\nu_j) = \tilde{T}_j \). Using the relation (3.3) one can rewrite the beat signal at \( \nu_{fm} \) as

\[
I(\nu, t)|_{\nu_{fm}} = 2I_0 \sum_{j=0}^{\infty} J_j J_{j+1}
\]

\[
\left\{ \text{Re} \left[ \tilde{T}_j \tilde{T}_{j+1}^* - \tilde{T}_{j-1} \tilde{T}_{j-1}^* \right] \cos (\omega_{fm}t) + \text{Im} \left[ \tilde{T}_j \tilde{T}_{j+1}^* - \tilde{T}_{j-1} \tilde{T}_{j-1}^* \right] \sin (\omega_{fm}t) \right\}.
\]

This shows that the signal at \( \nu_{fm} \) is a function of the difference between the pairwise products of molecular transfer functions for neighboring positive and negative sidebands. As mentioned above, if no transitions are present, i.e. \( \tilde{T}_j = 1 \), the beatings \( J_j \leftrightarrow J_{j+1} \) and \( J_{j-1} \leftrightarrow J_{j-1} \) cancel and the signal at \( \nu_{fm} \) vanishes.

The signal at \( \nu_{fm} \) detected by the detector can be electronically demodulated to a DC signal by mixing it with the modulation
frequency and filtering the sum-frequency component. As the demodulation corresponds to a multiplication it can be shown that this process yields an electronic FM signal, \( S_{\text{fm}} \), that can be written as

\[
S_{\text{fm}}(\nu_l) = \eta_{\text{fm}} P_0 \sum_{j=-\infty}^{\infty} J_j J_{j+1} \left\{ \text{Re} \left[ \tilde{T}_{\text{mol}}(\nu_j) \tilde{T}_{\text{mol}}^*(\nu_{j+1}) \right] \sin(\theta_{\text{fm}}) + \right. \\
+ \left. \text{Im} \left[ \tilde{T}_{\text{mol}}(\nu_j) \tilde{T}_{\text{mol}}^*(\nu_{j+1}) \right] \cos(\theta_{\text{fm}}) \right\},
\]

where \( P_0 \) is the incident power (W) seen by the detector, \( \eta_{\text{fm}} \) is the instrumentation factor (V/W) taking into account for the detector responsivity and electronic signal amplification/attenuation, and \( \theta_{\text{fm}} \) is the demodulation phase. The demodulation phase is the phase shift between the local oscillator in the mixer and the detector signal without the phase shift due to molecular transitions.

**PHASE CONVENTION & IQ-DEMODULATION**

It should be noted that \( \theta_{\text{fm}} \) can be defined in different ways. In this work the demodulation phase is defined such that for \( \theta_{\text{fm}} = 0 \) only the imaginary part of the molecular transfer function products, \( \text{Im} \left[ \tilde{T}_j \tilde{T}_{j+1}^* \right] \), is demodulated. Both terms can be demodulated and acquired simultaneously by use of two mixers with two in quadrature local oscillators (also referred to as an in-phase and quadrature (IQ)-mixer). Furthermore, using two recorded in-quadrature signals the signal for an arbitrary \( \theta_{\text{fm}} \) can be calculated.

Equation (3.7) shows that the FM signal obtained after demodulation is proportional to a sum of the real and the imaginary part of the molecular transfer function evaluated at the frequencies of the laser components. Therefore, with a proper model for \( \tilde{T}_{\text{mol}} \) a recorded FM signal can be fitted and information about the molecular concentration can be extracted.
As for the intensity also the demodulated signal is zero in absence of molecular transition (i.e. $S_{\text{fm}} = 0$). FMS is therefore FMS is often referred to as a background free technique.

Furthermore FMS is often performed for detection of weak absorption signals for which $|\delta_j - \delta_{j+1}| \ll 1$, $|\phi_j - \phi_{j+1}| \ll 1$ can be assumed, where $\delta_j = \delta(v_j, L)$ and $\phi_j = \phi(v_j, L)$. Under this condition the FM signal can be approximated by \[52\]

$$S_{\text{fm}}(\nu_l) \approx \eta_{\text{fm}} P_0 e^{-2\delta_0} \sum_{j=0}^{\infty} I_j I_{j+1} \left[ (\delta_{j+1} + \delta_j - \delta_j - \delta_{j+1}) \sin(\theta_{\text{fm}}) + (\phi_{j+1} - \phi_j - \phi_j + \phi_{j+1}) \cos(\theta_{\text{fm}}) \right]. \ (3.9)$$

By choosing $\theta_{\text{fm}}$ to be 0 or $\pi/2$ one can chose between a FM signal given by either the phase shift or the attenuation induced by the molecules. These two responses are therefore also referred to as dispersion and absorption FM signals respectively.

In the case the modulation index is well below unity only the beating between first order side bands ($j=1$) and the center component ($j=0$) contribute significantly. This implies that terms with $I_{j>1}$ can be neglected and the FM-signal for a modulation tripplet is given by

$$S_{\text{fm}}(\nu_l) = \eta_{\text{fm}} P_0 e^{2\delta_0} I_0 I_1 \left[ (\delta_1 - \delta_1) \sin(\theta_{\text{fm}}) + (\phi_1 - 2\phi_0 + \phi_1) \cos(\theta_{\text{fm}}) \right]. \ (3.10)$$

It can be shown that for small absorption, the FM-signal is directly proportional to the analyte concentration. Therefore, after a calibration of $\eta_{\text{fm}}$, the FM signal can be used for quantitative assessments of molecular species.
Optical cavities (also termed optical resonators) are devices that show a resonant transmission of light at certain characteristic resonance frequencies. One important property of optical cavities is that the light entering the cavity will travel several round trips before it leaves the cavity again. Thereby the effective interaction length between the light and molecules inside the cavity can be prolonged by several orders of magnitudes as compared to a single passage. This and other properties of optical cavities are utilized for cavity enhanced spectroscopy techniques such as NICE-OHMS to obtain signals with high SNR.

The most commonly used type of optical cavity in NICE-OHMS and other cavity enhance techniques is the Fabry-Pérot cavity, which is illustrated in figure 4.1. Therefore the term cavity in this work in general refers to a Fabry-Pérot cavity although other types such as ring-cavities have been proven be suitable for NICE-OHMS as well [40].

Fabry-Pérot cavities consist of two highly reflective (HR) mirrors \( i = 1, 2 \) that are placed in parallel at a distance of \( L_c \) (referred to as cavity length). They are characterized by reflection, transmission and loss coefficients of the electric field denoted as \( \tilde{r}_i \), \( \tilde{t}_i \) and \( \tilde{l}_i \) respectively. For reasons of energy conservation the sum of their squares (i.e. the sum of the transmission, reflection and loss coefficients of the intensity) is always unity, i.e.

\[
\tilde{r}_i^2 + \tilde{t}_i^2 + \tilde{l}_i^2 = 1.
\]

In general if a laser beam is directed at the first mirror most of the light will be directly reflected (\( \tilde{r}_1^2 \approx 1 \)). However, if the optical path length for a round trip between the two mirrors is an integer multiple of the laser wavelength then the light after any number of round trips and the incoming light interfere constructi-
**Figure 4.1**: A Fabry-Pérot cavity with an illustration of the electric fields under a resonance condition. The incoming field (red) is in-phase with the light after one or multiple round trips inside the cavity (red inside the cavity), but the directly reflected light (green-dashed) is phase shifted by $\pi$ relative to the field leaking out of the cavity (blue dashed). Each internal reflection in the cavity adds an additional $\pi$ phase shift.

Vely – as is illustrated in figure 4.1. Under this resonance condition a standing wave with high intensity can build up between the two mirrors. Since the directly reflected field (green-dashed) and the field leaking out after several round trips (blue dashed) cancel, only a small part of the light (ideally no light) is reflected. This implies that a large part of the light (ideally all light) can be transmitted through the cavity (i.e. leak out through the second mirror). The two $\pi$ in the figure indicate that the two internal reflections (at a optical thin to thick interface) cause a $\pi$ shift of the electric field each, while the direct reflection (at a optical thick to thin interface) does not cause a phase shift.

For the standing wave to build up the incoming beam must also spatially match the light wavefront after one round-trip. Since a beam never can be fully collimated spherical cavity mirrors are used which keep the light focused and allow for stable transverse electromagnetic modes (TEMs) to build up. The spatial structure of the possible TEMs in a cavity is given by the radius of curvature of the spherical mirrors and the cavity length $L_c$ and can be calculated according to the theory for Gaussian beam propagation [55, 74]. A specific mirror geometry allows for many spatial TEMs of different orders. In general the higher the order the more complex the spatial mode structure and the larger area of the mirror.
is involved. In NICE-OHMS usually only the fundamental TEMs (TEM$_{00}$) are addressed which are also referred to as longitudinal modes since they follow the longitudinal cavity axis between the two mirrors. To make sure that only these can be excited by the laser light the incoming laser beam has to be spatially mode matched to the simple Gaussian shape of the TEM$_{00}$ [55]. In practice this can be achieved by placing suitable lenses or parabolic mirrors before the cavity [48, 52]. In case a problem with coupling to high order TEMs occurs (despite careful mode-matching) they can be eliminated by artificially reducing the cavity diameter by a pinhole as was done in [10].

4.1 CAVITY RESONANCE CONDITION

The resonance condition can also be formulated as the condition for which the phase shift of the EM field after one round trip equals an integer multiple $q$ of $2\pi$, i.e. as

$$2\varphi(\nu_l) \overset{!}{=} q2\pi,$$

where $\varphi$ is the single pass phase shift, $\nu_l$ is the frequency of the laser, $q$ is referred to as the cavity mode number, and $!$ is used as notation for a condition (which is not necessarily always fulfilled). The single pass phase shift depends in general on the cavity length, the phase shift of the mirror HR coating and the refractive index of the gas, where the refractive index includes a broadband response and the resonant contributions of molecular transitions. Due to the dispersion of these contributions $\varphi$ is in general a function of frequency, i.e. $\varphi(\nu)$.

The empty cavity single pass phase shift $\varphi^0$ is given by

$$\varphi^0(\nu_l) = \frac{2\pi \nu_l}{c} (L_c + \text{OPL}_m) \approx \frac{2\pi \nu_l}{c} L_c,$$

where $c$ is the speed of light and OPL$_m$ is the optical path-length of the two mirror coatings. In this work OPL$_m$ will be neglected for two reasons. The first is that it is negligible compared to $L_c$, i.e. OPL$_m(\nu) \ll L_c$. Secondly, in general its dispersion is rather weak.
over the frequency scale over which NICE-OHMS is sensitive to dispersion, i.e. $\text{OPL}_m(v) \approx \text{OPL}_m$ within the interval $[v, v + v_{fm}]$ (see section 6).

If the cavity is filled with gas the single pass phase shift (neglecting the OPL$^m$) can be written as

$$\phi(v_l) = \frac{2\pi L_c n}{c} v_l + \phi(v_l) = n\phi^0(v_l) + \phi(v_l), \quad (4.4)$$

where $n$ is the broadband index of refraction of the gas, while $\phi(v)$ is the additional single pass phase shift induced by the analyte transitions—given by eq. (2.14). In this work $n$ is assumed to be constant within the laser tuning range and the modulation frequency. On the other hand, the resonant contribution $\phi(v)$ is strongly frequency dependent. Quantitative measurements of the different contributions to the cavity dispersion over a large wavelength range can be found in $[11, 75]$.

### 4.2 Empty Cavity Properties and Resonance Pattern

It is useful to define some fundamental cavity parameters of an empty cavity.

Using the empty cavity single pass shift, eq. (4.3), and the resonance condition, eq. (4.2), the resonance frequencies of an empty cavity $\nu^0_q$ can be calculated as

$$\nu^0_q = \frac{qc}{2L_c}. \quad (4.5)$$

Two adjacent modes ($q$ and $q + 1$) are therefore separated by the frequency $\nu^0_{\text{fsr}}$, which is referred to as the empty cavity free spectral range (FSR$_0$) and given by

$$\nu^0_{\text{fsr}} = \nu_{q+1} - \nu_q = \frac{c}{2L_c}. \quad (4.6)$$

Assuming two HR mirrors (i.e. with $\tilde{r}_{1,2} \approx 1$) the HWHM of a cavity mode $\Gamma_c$ can be written as $[48]

$$\Gamma_c = \frac{\nu^0_{\text{fsr}}}{\pi} \frac{1 - \tilde{r}_1 \tilde{r}_2}{2\sqrt{\tilde{r}_1 \tilde{r}_2}}. \quad (4.7)$$
Finally, the cavity finesse, $F$, is defined as the ratio of the FSR$_0$ and the full width of a cavity mode, i.e. as

$$F = \frac{\nu_{fsr}^0}{2\Gamma_c}, \quad (4.8)$$

which for the simple case of a pair of equal HR mirrors, i.e. $\tilde{r}_1^2 = \tilde{r}_2^2 \equiv R \approx 1$, becomes $F = \pi/(1-R)$.

Light coupled into the cavity will decay exponentially (each round-trip a fraction is lost due to mirror losses and transmission through the mirrors). The decay time constant, $\tau_c$, can be given as [48]

$$\tau_c = \frac{4L_c}{c(\tilde{r}_1^2 + \tilde{r}_2^2 + \tilde{l}_1^2 + \tilde{l}_2^2)} = \frac{2F L_c}{\pi c}. \quad (4.9)$$

This implies that the effective length, $L_{\text{eff}}$, light travels inside the cavity after being coupled into the cavity until it leaks out again can be given as

$$L_{\text{eff}} = \frac{2F}{\pi} L_c. \quad (4.10)$$

The factor $2F/\pi$ is known as the cavity enhancement factor, since it is approximately the enhancement factor of the absorption for gas inside a cavity compared to the absorption for a single pass of a narrow laser in resonance with the cavity mode under weak absorption conditions [48].

### 4.3 Cavity Resonances in the Presence of FAS

If gas is let into the cavity the optical path length will change [see eq. (4.4)] and the resonance frequencies will shift accordingly. They are then given by

$$\nu_q = \frac{qc}{2L_c n} - \frac{\phi(\nu_q) c}{2\pi L_c n} = \nu_{fsr} \left[ q - \phi(\nu_q) / \pi \right], \quad (4.11)$$

where the cavity FSR has been defined as the mode spacing when not affected by any analyte transitions given as

$$\text{FSR} = \nu_{fsr} = \frac{c}{2n L_c}. \quad (4.12)$$
A comparison between the eqs. (4.11) and (4.5) reveals how the cavity modes are shifted after filling gas into the cavity. The first term of the equation shows that a cavity mode will be shifted due to the broadband refractive index. However since $q$ is a large number the first term gives a shift relatively similar for adjacent modes ($q$ and $q \pm 1$). More importantly this shift will keep the spacing between neighbouring modes (i.e. FSR) equal for all modes. The second term however corresponds to the mode shift due to the analyte transitions which is strongly frequency dependent and therefore can be very different (even of opposite sign) for adjacent resonances. As will be shown later the first term will not be picked up by the NICE-OHMS system, while the second term will in fact dominate the dispersion response of NICE-OHMS.

### 4.4 Cavity Reflection and Transmission Functions

As mentioned above if the laser frequency fulfills the resonance condition, given by eq. (4.2), and the beam is spatially mode matched light can be transmitted through the cavity. For an arbitrary $\nu_l$ and in case an analyte in the cavity introduces losses and phase shifts additionally to those of the mirrors a general expression for the cavity transmission and reflection can be calculated. The derivation is done by considering the superposition of the electric field amplitudes of the incoming laser light and the light after $n$ round trips in the cavity, where $n = 1, 2, 3, \ldots, \infty$ [48].

Such calculations give the complex electric field amplitude reflection function, $\tilde{R}_c$, and transmission function $\tilde{T}_c$ as a function of frequency in terms of the analyte induced single-pass phase shift $\phi(\nu)$ and losses $\delta(\nu)$ as [48]

$$
\tilde{R}_c(\nu) = \frac{\tilde{r}_1 - \tilde{r}_2(1 - \tilde{I}_1)e^{-2\delta(\nu) - i2\phi(\nu) - i2nq^0(\nu)}}{1 - \tilde{r}_1 \tilde{r}_2 e^{-2\delta(\nu) - i2\phi(\nu) - i2nq^0(\nu)}}
$$

(4.13)

and

$$
\tilde{T}_c(\nu) = \frac{\tilde{I}_1 \tilde{I}_2 e^{-\delta(\nu) - i\phi(\nu) - inq^0(\nu)}}{1 - \tilde{r}_1 \tilde{r}_2 e^{-2\delta(\nu) - i2\phi(\nu) - i2nq^0(\nu)}}.
$$

(4.14)
The cavity transmission function for a finesse of 150 as a function of laser-frequency is shown in figure 4.2. The left panels (a, c, e) and the corresponding right panels (b, d, f) show the same functions with different x-scales—the left panels show a few FSRs, while the right panels cover a few $\Gamma_c$. The panels (a-d) show the real and imaginary parts of $\tilde{T}_c(\nu)$ in presence (blue) and absence (black) of a molecular transition. Panel e) and f) show the single pass absorption (green) and dispersion (orange) induced by the transition. The figure shows that in the vicinity of a transition the amplitude of the modes gets attenuated and the center frequency of the mode shifts. Furthermore the width of the cavity modes increases.

To understand the regular pattern of the cavity modes, it is convenient to express the transfer functions of the $q^{th}$ cavity mode in terms of the detuning between the $j^{th}$ laser component and the mode center frequency, given by eq. (4.11),

$$\varsigma_j = \nu_j - \nu_q = \nu_j - \nu_{\text{fsr}} \left[ q - \phi(\nu_j) / \pi \right]. \quad (4.15)$$

It should be noted that the frequency detuning is defined as the detuning from a cavity resonance in the presence of molecular dispersion. Therefore it includes a term proportional to the molecular dispersion which is frequency dependent. However, as illustrated by figure 4.2 f), for $\varsigma_j \ll \Gamma_c$ the dispersion response can often be treated as constant, which implies that $\phi(\nu_j) \approx \phi(\nu_q)$.

Using this notation the single pass phase shift, eq. (4.4), can be rewritten as

$$\phi(\nu_j) = \phi(\varsigma_j, q) = q \pi + \frac{\varsigma_j}{\nu_{\text{fsr}}}. \quad (4.16)$$

The cavity transfer functions can be rewritten as function of $\varsigma_j$ as

$$\tilde{R}_c(\varsigma_j) = \frac{\tilde{r}_1 - \tilde{r}_2 (1 - \tilde{I}_1) e^{-2\delta(\nu) - i2\pi\varsigma_j / \nu_{\text{fsr}}}}{1 - \tilde{r}_1 \tilde{r}_2 e^{-2\delta(\nu) - i2\pi\varsigma_j / \nu_{\text{fsr}}}} \quad (4.17)$$

and

$$\tilde{T}_c(\varsigma_j) = (-1)^q \frac{\tilde{I}_1 \tilde{I}_2 e^{-\delta(\nu_j) - i\pi\varsigma_j / \nu_{\text{fsr}}}}{1 - \tilde{r}_1 \tilde{r}_2 e^{-2\delta(\nu) - i2\pi\varsigma_j / \nu_{\text{fsr}}}}, \quad (4.18)$$
Figure 4.2: The four first panels show the real (a,b) and imaginary (c,d) parts of the electric field cavity transmission function in presence of a strong molecular transition (blue) and without molecular transitions (black). Panel e) and f) show the single pass absorption (green) and dispersion (orange). The cavity finesse is 150, the FSR 400 MHz and the FWHM linewidth of the Doppler broadened transition is 270 MHz. The molecular attenuation and frequency shifts of the modes correspond to the cavity enhanced response to absorption and phase shift by the molecular transitions. Panel f) illustrates that even for this relatively low finesse the Doppler broadened molecular response is approximately constant over the cavity linewidth.
where the alternating sign for consecutive modes of the transmission function can be understood by considering that on resonance the phase shift in transmission is $q\pi$, which is half of the on resonance round trip phase shift of $q2\pi$, see also eq. (4.2).

### DETUNINGS AND ANALYTE DISPERSION

The dispersion response of the molecules adds an additional phase shift for each round trip which implies a shift of the resonance frequency, see eq. (4.4). Likewise a detuning of the laser frequency from a cavity resonance-frequency by $\varsigma_j$ implies a phase shift additional to a multiple of $2\pi$ for each round-trip, see eq. (4.11). Therefore it is possible to include the molecular dispersion response in the frequency detuning $\varsigma_j$ or, vice versa, relate the frequency detuning to a single pass phase shift—see also discussion around eq. (8.4).

As is shown below, in NICE-OHMS the frequency/phase shifts induced by the molecules directly translates into a phase shift of the modulation signal which is extracted in the demodulation process. With techniques like, for example, broadband cavity-enhanced complex refractive index spectroscopy (CE-CRIS) the molecular dispersion related mode frequency shifts are directly measured and then related to the dispersion response of the molecules [11].

The real and imaginary parts of $\tilde{T}_c$ can be approximated by a linear relation if the conventional cavity-limited weak absorption (CCLWA) condition (i.e. $(2F/\pi)|\delta(\nu) - i\phi| \ll 1$) is fulfilled and for small detunings between the laser components and the cavity modes, i.e. when $\varsigma_j \ll \Gamma_c$ [4, eqs. (49) and (50)],

$$\tilde{T}_c(\varsigma_j) \approx (-1)^q \left[ 1 - \left( \frac{2F}{\pi} \right) \delta(\nu_j) + i \frac{\varsigma_j}{\Gamma_c} \right]. \quad (4.19)$$

One can separate the imaginary part also into the contributions from the single pass phase shift in the absence of transitions, $n\phi^0(\nu_j)$, and the phase shift due to the transitions as follows.
\[ \tilde{T}_c(\varsigma_j) \approx (-1)^q \left\{ 1 - \left( \frac{2F}{\pi} \right) \left[ \delta(v_j) + i\phi(v_j) \right] + i\frac{v_j - qv_{fsr}}{\Gamma_c} \right\}. \] (4.20)

These two expressions illustrate that both the molecular induced absorption and phase shift are cavity enhanced if the frequency \( v_j \) is kept constant when adding the analyte into the cavity. However, when the \( v_j \) is locked to a cavity resonance, i.e. \( \varsigma_j = 0 \), the phase response is converted into a laser-frequency shift and only the cavity enhanced absorption response remains.

In case the intensity transmission function \( T_c(v) \) and reflection function \( R_c(v) \) of the cavity are of interest they can than be calculated as

\[ R_c(v) = \tilde{R}_c(v)\tilde{R}_c^*(v) \] (4.21)

and

\[ T_c(v) = \tilde{T}_c(v)\tilde{T}_c^*(v). \] (4.22)
LASER FREQUENCY STABILIZATION

While for some cavity based techniques, like CRDS, it is enough to spatially mode match laser light to the cavity, other techniques, like NICE-OHMS, make use of a continuous frequency stabilization of the laser to a cavity resonance. For NICE-OHMS the relative cavity-laser jitter should be well below the cavity mode width. The absolute stability is then given by the stability of the cavity resonances (i.e. the cavity length). Therefore the jitter and drifts of the cavity resonances should be kept significantly below the width of the transition addressed. The latter condition can be achieved by using a solid cavity spacer between the mirrors with little acoustic resonances, ideally made of a low thermal expansion material e.g. Zerodur.

**NOTE FM/FSR LOCKING**

It should be noted that only for an ideal (dispersion free) empty cavity all laser components are perfectly matched to a cavity mode frequency. This condition can be assumed for an empty cavity if the cavity mirror dispersion is weak over the range of $\nu_{fm}$. However, in the presence of analyte transitions single modes can be strongly shifted. This shift implies a detuning of the corresponding laser component from the cavity mode center. The latter leads in fact to the strong (cavity enhanced) dispersion response in NICE-OHMS, described below.

For NICE-OHMS a FMS scheme as described in section 3.1 is applied. This means that the laser is split into several components separated by $\nu_{fm}$. To match this modulated light to the cavity not only the center frequency of the laser is stabilized to a cavity reso-
nance, but also $\nu_{fm}$ is stabilized to $k \cdot \nu_{fsr}$ where $k = 1, 2, 3, \ldots$. As a result, each laser component is approximately (see note above) in resonance with a cavity mode.

5.1 PDH-LOCKING

In NICE-OHMS the laser frequency is locked to a cavity mode by the Pound-Drever-Hall (PDH) technique. In this an FM scheme as described in section 3.1 is applied, the difference being that a cavity mode resonance is probed instead of a molecular transition [76]. In the following a short summary of the principles of PDH locking is given. A thorough but graspable description of the PDH signal can be found in [77].

To obtain PDH locking the laser is phase modulated with a frequency $\nu_{pdh}$ that is chosen to be at least several times the cavity mode-width, $\Gamma_c$. The modulated light is spatially mode matched to the cavity and the light reflected from the cavity (or at least a part of it) is collected and directed onto a photo-diode. In NICE-OHMS instrumentation the reflection can be collected using for example a beam splitter, a polarizing beamsplitter (PBS) in combination with a quarter wave plate, or an optical circulator [1, 51].

An expression for the intensity detected on the photo-detector can be derived from the electric field of the incoming modulated light and the cavity reflection function, $\tilde{R}_c$, given in eq. (4.13). In analogy to the FMS signal, the PDH signal is given by [48, 77]

$$S_{pdh}(\nu_l, \nu_{fm}) = \eta_{fm} P_0 \sum_{j=-\infty}^{\infty} I_j I_{j+1} \left\{ \begin{array}{c} \text{Re} \left[ \tilde{R}_c(\nu_j) \tilde{R}_c^*(\nu_{j+1}) \right] \cos(\theta_{pdh}) + \\ \text{Im} \left[ \tilde{R}_c(\nu_j) \tilde{R}_c^*(\nu_{j+1}) \right] \sin(\theta_{pdh}) \end{array} \right\}, \tag{5.1}$$

where $\nu_j$ and $\nu_{j \pm 1}$ are the frequencies of the laser components separated by $\nu_{pdh}$. For the case of $\nu_{pdh} \gg \Gamma_c$ only one laser component at a time is affected by a cavity mode, while the remaining
components are directly reflected by the cavity mirror. This implies that if the center component of the laser is close to a cavity resonance, i.e. \( \nu_l \approx \nu_q \), the reflection functions for the other components are unity, i.e. \( \tilde{R}_c(\nu_{j \neq 0}) = 1 \), and that only the beatings of the first order sidebands with the center component are out of balance. Using these assumptions the expression can be simplified to

\[
S_{pdh}(\nu_l)\lvert_{\nu_l \approx \nu_q} = \eta_{fm} P_0 I_0 (\beta_{pdh}) I_1 (\beta_{pdh}) \cdot 2 \text{Im} \left[ \tilde{R}_c(\nu_l) \right] \sin (\theta_{pdh}). \quad (5.2)
\]

This implies that the PDH signal is proportional to the imaginary part of the cavity reflection function. Since the latter is an odd function around a cavity resonance (see figure 4.2 d) the PDH signal is very well suited as an error signal that is zero if \( \nu_0 \equiv \nu_l = \nu_q \) and, for \( \theta_{pdh} = \pi/2 \), positive and negative for positive and negative deviations of \( \nu_l - \nu_q \).

Furthermore, it can be shown that in case a side-band is in the vicinity of a resonance the frequency dependency is similar, but of opposite sign. This makes it possible to lock either one of the sidebands or the center frequency of the laser to a cavity mode by simply flipping the sign of a locking servo transfer function.

\section{5.2 Locking the Modulation Frequency – The DeVoe-Brewer Lock}

To lock \( \nu_{fm} \) to the cavity FSR an approach suggested by DeVoe and Brewer [78] is commonly applied for NICE-OHMS. It makes use of the two modulation frequencies, \( \nu_{fm} \) and \( \nu_{pdh} \), which already are used in NICE-OHMS. The spectral pattern resulting of this modulation is illustrated by the orange bars in figure 5.1. The DeVoe-Brewer (DVB) FSR lock uses the beating between the PDH sidebands of the center laser component and the adjacent FM side bands, which should be locked to the adjacent cavity modes. This corresponds to two possible beat frequencies \( \nu_{fm} \pm \nu_{pdh} \). The be-
ings for $\nu_{\text{fm}} - \nu_{\text{pdh}}$ are illustrated by the arrows in figure 5.1. Since the PDH sidebands are directly reflected the beatings are a measure of the cavity reflection function seen by the FM side bands.

In analogy to the FMS and PDH signals the DVB signal can be derived by considering only the spectral components with a frequency of $\nu_{\text{fm}} \pm \nu_{\text{pdh}}$. The PDH sidebands are directly reflected and their transfer functions are therefore unity. This implies that only one reflection function needs to be considered per beating. However, for each pair of neighboring FMS components there are two beatings to consider as shown by the solid and dashed arrows in figure 5.1. The intensity at the frequency $\nu_{\text{dvb}} = \nu_{\text{fm}} - \nu_{\text{pdh}}$ can thereby be written analogously to eq. (3.5) as

$$I(\nu_{\text{d}_{\text{v}}}, t) |_{\nu_{\text{dvb}}} \propto \sum_{j=-\infty}^{\infty} J_j J_{j+1} \text{Re} \left\{ \left( -\tilde{R}_j^c + \tilde{R}_{j+1}^e \right) e^{-i\omega_{\text{dvb}}t} \right\}, \quad (5.3)$$

where $J_j = J_j(\beta)$, and $\tilde{R}_j^c = \tilde{R}_j^c(\xi_j)$.
Again using the antisymmetric relation \( I_j I_{j+1} = -I_j I_{j-1} \) it is possible to write the full expression as

\[
2 I_0 J_0^{\text{pdh}} J_1^{\text{pdh}} \sum_{j=0}^{\infty} I_j I_{j+1} \left\{ \left( -\bar{R}_j^c + \bar{R}_{j+1}^c + \bar{R}_{j-1}^c - \bar{R}_j^c \right) e^{-i\omega_{\text{dvb}} t} \right\}
\]

(5.4)

where \( J_j^{\text{pdh}} = J_j(\beta_{\text{pdh}}) \).

This implies that the demodulated DVB error signal is given by

\[
S_{\text{dvb}}(v_j, v_{\text{fm}}) = \eta_{\text{fm}} P_0 \sum_{j=0}^{\infty} I_1(\beta_{\text{pdh}}) I_j(\beta) J_0(\beta_{\text{pdh}}) J_{j+1}(\beta)
\]

\[
\left\{ \begin{array}{c}
\text{Re} \left[ -\bar{R}_j^c + \bar{R}_{j+1}^c + \bar{R}_{j-1}^c - \bar{R}_j^c \right] \cos(\theta_{\text{dvb}}) + \\
\text{Im} \left[ -\bar{R}_j^c - \bar{R}_{j+1}^c + \bar{R}_{j-1}^c + \bar{R}_j^c \right] \sin(\theta_{\text{dvb}}) \end{array} \right\}, \quad (5.5)
\]

where \( v_j \) are the frequencies of the FM sidebands. A useful error signal is obtained for \( \theta_{\text{dvb}} = \pi/2 \), for which the signal is given by the imaginary part of the cavity reflection function. The same calculation with \( v_{\text{dvb}} = v_{\text{fm}} + v_{\text{pdh}} \) gives the same expression but with opposite sign.

In many NICE-OHMS implementations contributions from higher order sidebands can be neglected. This gives a simplified expression for the DVB error signal, viz.

\[
S_{\text{dvb}}(v_{\text{fm}}) = \eta P_0 J_1(\beta_{\text{pdh}}) J_0(\beta) J_0(\beta_{\text{pdh}}) J_1(\beta)
\]

\[
\text{Im} \left[ \bar{R}_c(v_{-1}) - \bar{R}_c(v_1) \right] . \quad (5.6)
\]

The expression shows that the carrier reflection function does not contribute since the two beatings (the dashed arrows in figure 5.1) cancel. As for \( v_{\text{fsr}} \neq v_{\text{fm}} \) the sidebands \( I_j \) and \( I_{-j} \) will be detuned in opposite directions from their corresponding cavity modes. Since the imaginary parts of the cavity reflection functions are odd around zero detuning, the locking condition (i.e. \( S_{\text{dvb}} = \)
0) is fulfilled if $\nu_{\text{fsr}} = \nu_{\text{fm}}$ for an empty cavity. From figure 5.1 it can also be seen that a change of the laser frequency will detune all laser components in the same direction and the beatings at $\nu_{\text{dmb}}$ will therefore cancel for any $\nu_l$.

For a cavity where the mode frequencies are shifted due to molecular transitions the locking condition is fulfilled less trivially and the side bands will no longer be locked to the center of the cavity modes (see section 6.3).
THE NICE-OHMS TECHNIQUE

6.1 PRINCIPLES

NICE-OHMS is a combination of CEDAS and FMS. It does not only take advantage of both techniques, but it is also immune to frequency-to-amplitude noise conversion which troubles CEDAS.

In short, the laser is modulated like in FMS, but with $v_{fm}$ locked to a multiple of $v_{fsr}$, often equal to $v_{fsr}$, using the DVB technique. After locking the center frequency component of the laser to a cavity mode, using the PDH technique all laser components are transmitted through their own cavity modes and experience a cavity enhanced interaction with the molecular transitions. The light transmitted through the cavity carries a cavity enhanced frequency modulation signal, which is the NICE-OHMS signal.

In more detail the origin of the NICE-OHMS signal can be understood by considering the following processes which are discussed in the subsequent sections:

1. Phase modulation of the laser
2. Locking of the laser components to the cavity resonances
3. Transmission of laser components through the cavity
4. Detection and demodulation of the transmitted laser light

The modulation (1) and demodulation (4) processes are independent of the absorption/dispersion of the analyte, and influence the NICE-OHMS signal similarly to the FMS signal described above. On the other hand both the locking process (2) and the transmission process (3) are both strongly influenced by the absorption and dispersion of the analyte in the cavity and the properties of the cavity itself.
The following description of the NICE-OHMS principle builds to a large part upon publication IV and publication V included in this work. However to discuss the principle in the following sections only the general expressions valid for strong absorption and the simplest expressions valid under the CCLWA condition \((F \alpha_0 L/\pi \ll 1)\) are considered. A discussion of various NICE-OHMS expressions for different conditions and how to compute them efficiently is found in section 8.1.

### 6.2 Phase Modulation of the Laser

In NICE-OHMS the laser is phase-modulated at two frequencies. The modulation with the lower frequency, denoted \(\nu_{\text{pdh}}\), induces sidebands used for locking the center frequency of the laser to a cavity resonance using the PDH technique. The higher modulation frequency, denoted \(\nu_{\text{fm}}\), corresponds to the modulation for the FMS and is therefore also referred to as the FM-frequency. While the principles of FM is described above, there are a few things to consider when choosing modulation parameters for a NICE-OHMS system.

For the PDH lock \(\nu_{\text{pdh}}\) should be chosen to be significantly larger than the cavity mode width and the necessary locking bandwidth. Furthermore care should be taken that the PDH sidebands do not overlap with a higher order transverse cavity mode which might be excited due to imperfect mode matching. A good choice of the PDH modulation index, \(\beta_{\text{pdh}}\), has proven to be around 1.2.

The \(\nu_{\text{fm}}\) has to be a multiple of the cavity FSR and follows similar criteria as for FMS: To get signal amplitude close to the maximum \(\nu_{\text{fm}}\) should be larger than the width of the transition addressed [50].

The choice of the FM modulation index, \(\beta\), has two important consequences for the NICE-OHMS signal. For \(\beta \lesssim 0.5\) the modulation induces solely a single pair of sidebands whereby the laser can be seen as a simple triplet with a strong carrier and two weak sidebands. For a higher modulation index multiple sidebands are generated (see figure 3.1). All significant sidebands need to
be taken into account when modeling the NICE-OHMS signal. Furthermore the amplitude of the demodulated signal is influenced by the modulation index. For addressing Doppler broadened transitions in the near-IR a modulation index of around 1.3 has been proven to give the maximum signal [50]; the optimum modulation index for a system can though be slightly different for different systems.

A scrutiny of the optimum modulation parameters can be found in [50].

6.3 Locking of the Modulated Laser to the Cavity Resonances

Using the PDH and DVB techniques described in section 5 the center frequency is locked to a cavity mode of choice and the sidebands are locked to neighboring modes separated by \( \nu_{fm} = k \cdot \nu_{fsr} \), where \( k \) is an integer which most often is taken as one. Two locking servos are actively controlling \( \nu_l \) and \( \nu_{fm} \) to keep the PDH and DVB error signals close to zero.

As illustrated by the yellow bars in figure 5.1, the simultaneous modulation at \( \nu_{fm} \) and \( \nu_{pdh} \) implies that not only the center component but also the FM sidebands are modulated with \( \nu_{pdh} \). This implies that also the FM sidebands contribute to the PDH error signal according to their amplitude given by the Bessel-functions. The locking condition for the PDH servo is in this case given by [4, eq. (9)]

\[
S_{pdh}(\nu_l, \nu_{fm}) \propto \text{Im} \left\{ J_0^2(\beta) \tilde{R}_c(\nu_l) + \sum_{j=1}^{\infty} J_j^2(\beta) \left[ \tilde{R}_c(\nu_{-j}) + \tilde{R}_c(\nu_{j}) \right] \right\} = 0, \quad (6.1)
\]

where \( \beta \) is the FM modulation index and \( \nu_j = \nu_l + j\nu_{fm} \).
The general locking condition for the DVB signal is given by

\[
S_{\text{dvb}}(v_{\text{fm}}, v_{l}) \propto \text{Im} \left\{ \sum_{j=1}^{\infty} I_{j-1}(\beta) I_{j}(\beta) \left[ \tilde{R}_c(v_j) - \tilde{R}_c(v_j) \right] \right\} \doteq 0. \quad (6.2)
\]

The \( v_l \) and \( v_{\text{fm}} \) for engaged locking servos can be obtained by solving the equation system of eqs. (6.1) and (6.2) with the presumption that \( v_l \approx v_q \) and \( v_{\text{fm}} \approx k \cdot v_{\text{fsr}} \), where \( k \) is a positive integer. For the general case this equation system needs to be solved numerically. However, under the CCLWA condition the mode shifts are small and under locked condition the laser-cavity detunings are small, i.e. \( \varsigma_j \ll \Gamma_c \). This implies that the imaginary part of the cavity reflection function can be linearized around the resonance frequency, i.e.

\[
\text{Im} \left\{ \tilde{R}_c(v_j) \right\} \propto \varsigma_j = v_j - v_{q+j} = \varsigma_j = v_j - v_{\text{fsr}} \left[ (q+j) - \phi(v_j)/\pi \right]. \quad (6.3)
\]

It is assumed here that the molecular dispersion lineshape is approximately constant over the cavity mode width, i.e. \( \phi(\varsigma_j) \approx \text{const.} \) for \( \varsigma_j < \Gamma_c \ll \Gamma_a \). If narrow sub-Doppler signals are addressed or if a very low finesse cavity is used it might be necessary to verify the validity of this assumption.

Using this linearization, the PDH and DVB locking conditions for a modulation triplet are fulfilled for

\[
\varsigma_0 \bar{I}_0^2 + \bar{I}_1^2 [\varsigma_{+1} + \varsigma_{-1}] \doteq 0 \quad (6.4)
\]

\[
[\varsigma_{+1} - \varsigma_{-1}] \doteq 0. \quad (6.5)
\]

For higher modulation indices the equations have to be expanded accordingly.
6.4 Transmission through the cavity

Using eq. (6.3) and \( \nu_j \equiv j \nu_{fm} \) one can solve the two conditions for \( \zeta_0 \) and \( \nu_{fm} \) which according to [4, eq. (46)] gives

\[
\zeta_0 = i \frac{1}{2} \nu_{fsr} \left[ -\phi(\nu_{q-1}) + 2\phi(\nu_{q+0}) - \phi(\nu_{q+1}) \right] \tag{6.6}
\]

\[
\nu_{fm} = \nu_{fsr} \left\{ 1 + \frac{1}{2\pi} \left[ \phi(\nu_{q-1}) - \phi(\nu_{q+1}) \right] \right\} \tag{6.7}
\]

It should be noted that eq. (6.7) does neither depend on \( \zeta_0 \) nor on \( \nu_l \). This shows that, to a first order, the \( \nu_{fsr} \) is locked independently of the state of the PDH lock and vice versa.

### 6.4 Transmission of the Modulated and Locked Laser through the Cavity

After the servos are engaged and the locking conditions are fulfilled most of the modulated light will be transmitted through the cavity. The small reflected part of the light consists of the PDH sidebands, the spatially mismatched light and the light reflected due to impedance mismatch.

The transmission of the electric field of each component is simply described by the cavity transmission function given by eq. (4.18).

The intensity of the oscillation at \( \nu_{fm} \) transmitted through the cavity can be written analogously to eq. (3.5) as

\[
I(\nu_l, t)|_{\nu_{fm}} = I_0 \sum_{j=-\infty}^{\infty} I_j I_{j+1} \text{Re} \left\{ \tilde{T}_c(\nu_j) \tilde{T}_c^*(\nu_{j+1}) e^{-i\omega_{fm}t} \right\} \tag{6.8}
\]

and similarly to eq. (3.7) it can be split into a sine and cosine term,

\[
I(\nu_l, t)|_{\nu_{fm}} = 2I_0 \sum_{j=-\infty}^{\infty} I_j I_{j+1} \left\{ \text{Re} \left[ \tilde{T}_c(\nu_j) \tilde{T}_c^*(\nu_{j+1}) \right] \cos (\omega_{fm}t) \right. \\
+ \text{Im} \left[ \tilde{T}_c(\nu_j) \tilde{T}_c^*(\nu_{j+1}) \right] \sin (\omega_{fm}t) \left\} \right. \tag{6.9}
\]
where $\widetilde{T}_c$ takes into account the response of molecules in the cavity, and the frequencies $\nu_j$ are given by the values of $\nu_l$ and $\nu_{fm}$ that are given by the locking conditions.

6.5 THE NICE-OHMS SIGNAL

6.5.1 Detection and demodulation of the transmitted laser

The NICE-OHMS signal is obtained by detection of the light transmitted through the cavity using a photo-detector and demodulating the electronic AC signal using a RF mixer with $\nu_{fm}$ as local oscillator. The general expression for the demodulated signal, i.e. the NICE-OHMS signal, is given by

$$S_{no}(\nu_l)(\nu_l) = \eta_{no} P_0 \sum_{j=-\infty}^{\infty} j_f j_{f+1} \left\{ \text{Re} \left[ \widetilde{T}_c(\nu_j) \widetilde{T}_c^*(\nu_{j+1}) \right] \sin(\theta_{fm}) + \right.$$  \hfill (6.10)

$$+ \text{Im} \left[ \widetilde{T}_c(\nu_j) \widetilde{T}_c^*(\nu_{j+1}) \right] \cos(\theta_{fm}) \right\}.$$

This is equivalent to eq. (38) in publication IV [4], which is written in terms of the real and imaginary parts of the transfer functions. To evaluate eq. (6.10) one needs to first solve the locking conditions, i.e. eqs. (6.1) and (6.2), to get the frequencies of the laser components, $\nu_j = \nu_l + j \nu_{fm}$. Then the cavity transfer function, eq. (4.14), has to be evaluated for each $\nu_j$. Both steps require the absorption and dispersion line shape functions of the molecular transitions to be addressed.

However, it can be shown that under certain conditions this procedure can be simplified. In particular under the CCLWA condition ($F \alpha L / \pi \ll 1$), the cavity transfer function can be linearized and the locking conditions simplified (see above), whereby the NICE-OHMS signal can be approximated by a simple analy-
tical expression which can be expressed for arbitrary modulation index as [4, 50, 52]

\[
S_{no}(\nu_l) \approx \eta_{no} P_0 \left( \frac{2F}{\pi} \right) \sum_{j=0}^{\infty} J_j J_{j+1} \left[ (\delta_{j-1} + \delta_j - \delta_{j+1}) \sin (\theta_{fm}) + (\phi_{j-1} - \phi_j - \phi_{j+1}) \cos (\theta_{fm}) \right].
\] (6.11)

Comparing this expression with the FMS signal in eq. (3.9) shows that under the CCLWA condition the NICE-OHMS signal can be seen as a FMS signal enhanced by the increased interaction length inside the cavity given by eq. (4.10), i.e. by a factor of \(2F/\pi\).

A discussion of different degrees of approximation of the NICE-OHMS line shapes can be found below in section 8.1.2 as well as in publication IV. An experimental verification and validity test of the same is given in reference publication V.

**Molecular Lineshape Functions**

It should be noted that both NICE-OHMS expressions given in eqs. (6.10) and (6.11) are valid for arbitrary types of molecular absorption and dispersion line shape functions used to calculate \(\phi\) and \(\delta\). However, for strong optical saturation or similar laser power related conditions one needs to take into account that not all laser components induce the same degree of saturation [9, 57].

### 6.5.2 Noise immunity and cavity enhancement in NICE-OHMS

As discussed above, the cavity allows for a strong enhancement of the absorption and dispersion response of the molecular transitions compared to a single passage of laser light. On the other hand, the narrow resonances imply that a small frequency jitter of the laser light give rise into a strong amplitude and phase jitter in the cavity transmission. This process is called frequency to amplitude noise conversion. Fortunately, the opposite sign of the
beatings of negative and positive sidebands does not only make the NICE-OHMS signal background free—it also results in a immunity to frequency to amplitude noise conversion. The latter property is referred to as noise immunity. Although the cavity enhancement and noise immunity can be seen directly from eqs. (6.11), in the following a more intuitive explanation is given.

For simplicity we will consider only two sidebands and refer to them as \( J_{\pm 1} \) and the center component as \( J_0 \). Furthermore it is easiest to understand the properties of NICE-OHMS signals by considering the signal before demodulation. Analogous to eq. (3.5) the sum of the beatings \( J_{-1} \leftrightarrow J_0 \) and \( J_0 \leftrightarrow J_1 \) can be expressed as

\[
I(v_l, t)|_{v_{fm}} = 2I_0J_0J_1 \text{Re} \left[ T^c_0 T^c_1 e^{-i\omega_{fm} t} - T^c_{-1} T^c_0 e^{-i\omega_{fm} t} \right],
\]

where \( T^c_j = T^c(\xi_j) \). The minus sign in the equation takes into account for the \( \pi \) phase shift of the \( J_{-1} \leftrightarrow J_0 \) beating with respect to the \( J_0 \leftrightarrow J_1 \) beating. This shows that if the cavity attenuations and the cavity phase shifts of the two beatings are equal, the beatings will cancel since both the amplitude and phase balance. These two conditions can be expressed as an amplitude balance equation,

\[
|T^c_0||T^c_{-1}| = |T^c_1||T^c_0|,
\]

and a phase balance equation,

\[
\arg(T^c_0) - \arg(T^c_{-1}) = \arg(T^c_1) - \arg(T^c_0),
\]

where \( \arg \) is the argument, i.e. the phase shift of the transfer function. The negative signs for the phase balance equation can be understood by the fact that the beat originates from the frequency-differences which are calculated consistently as the higher frequency minus the lower frequency.

The cavity enhancement of the absorption response of NICE-OHMS can be easily understood by the fact that the light coupled into the cavity travels in average \( F/\pi \) round trips before it leaves the cavity. This enhanced interaction length directly shows up in the cavity transmission function (4.19) and is illustrated in figure.
In this case, for which the finesse only is 30 (for illustrative purposes), a small absorption (orange curve) centered at $J_1$ results into a 20 times stronger reduction of the transmission (blue vs black curve) and thereby to a cavity enhanced attenuation of this sideband (blue vs black bars). In consequence the amplitude of the beatings is out of balance since $|T_c^1| \neq |T_c^0|$. This imbalance is $2F/\pi$ times stronger as compared to a single passage and leads therefore to an attenuation related signal proportional to $(2F/\pi)(\delta_j - \delta_{ij})$.

As mentioned above, also a small detuning of a laser component from the center of a narrow cavity mode will lead to an attenuation of the transmission. However, as illustrated in figure 6.1 panel b, if the laser center frequency is detuned from its cavity mode (blue bars), also the sidebands will be detuned with the same frequency from their cavity modes. This implies that all laser components are attenuated the same relative amount and the amplitudes of the beat signals is still balanced, i.e. $|T_c^0||T_1^0| = |T_c^0||T_0^0|$.

The cavity enhancement of the dispersion response of NICE-OHMS cannot be explained as straightforwardly. It starts by the fact that an additional molecular single pass phase shift gives rise to a shift of the resonance frequency. Due to the locking servos the laser components (partially) follow the shift of the cavity resonance.

Since the phase shift at the cavity resonance is $q\pi$, see eq. (4.2) the question arises: Why is there—despite the locking of the laser frequencies to the cavity resonances—a cavity enhanced phase response? The answer is that the PDH and DVB locks cannot keep all laser components locked exactly to the center of the corresponding cavity modes if the cavity modes are not equally spaced. In fact, it will be shown in the following that the servos will just redistribute the phase shifts between various modes while the phase imbalance between the beatings remains unchanged.

To illustrate this effect we consider a low modulation index for which the center component of the laser is dominating the PDH response and therefore always follow the frequency of its corresponding laser mode, i.e. $\arg(T_0^c) \sim \zeta_0 \approx 0$. This is illustrated in
Figure 6.1: Electric field amplitude transmission function of a cavity with a finesse of 30. Panel a) shows the function and the electric field components (illustrated by bars) in absence (black) and presence (blue) of molecular transitions together with the small molecular single pass attenuation (orange curve). Panel b) visualizes the noise immunity of the FM light by illustrating the amplitude attenuation for a small cavity-laser frequency detuning (blue bars) compared to zero detuning (black bars).
The NICE-OHMS signal

Figure 6.2 panel a) in which the $J_0$ is on resonance in the absence (black curve and bars) as well as in the presence (blue curve and bars) of a molecular induce phase shift (orange curve). The sidebands will be locked according to eq. (6.5) so that their detunings $\xi_{\pm 1}$ are equal.

Under the condition considered mainly the center cavity mode is affected by the molecular dispersion and shifted in frequency by $\nu_{\text{fsr}}\phi_0 / \pi$. However, the PDH lock keeps the $J_0$ locked, whereby $\xi_0 = 0$. Consequently, the phase of the $J_0$ component is not shifted in the cavity transmission. However, the sidebands are both detuned by the shift of $J_0$, consequently $\xi_{\pm 1} = \nu_{\text{fsr}}\phi / \pi$. This implies that in cavity transmission both sidebands are phase shifted by

$$\arg(T^c_{\pm 1}) = \pi\xi_{\pm 1} / \Gamma_c = 2F / \pi\phi_0.$$  \hfill (6.15)

Thus, the locking procedure transfers a phase shift/frequency-shift of the $J_0$ component to a frequency-detunings/phase-shifts of the $J_{\pm 1}$ components. As can be seen in the figure $\arg(T^c_i T^c_0)$ decreases while $\arg(T^c_i T^c_0^*)$ increases. Therefore the two phase shifts, i.e. the $(2F / \pi)\phi_0$, add up in the combined intensity beat signal, eq. (6.12), and consequently give rise to a NICE-OHMS signal, eq. (6.10).

It should be noted that in the case the laser frequency would not follow the mode shift (indicated by gray bars) $J_0$ would experience the phase shift of $-(2F / \pi)\phi_0$ which corresponds to the same shift relative to the sidebands as under locked conditions and will therefore result in the same NICE-OHMS signal. In the latter case the cavity enhanced phase shift can be seen as the analyte induced single pass phase shifts summed up for all roundtrips, i.e. $2F / \pi$ times.

The latter reasoning also explains the noise immunity of the phase response of the NICE-OHMS signal, illustrated in 6.2 panel b). If the center frequency is shifted (blue vs. black bars), all three modes will get shifted by the same angle and therefore the relative phase relation between the laser components will remain unchanged and the beatings will stay balanced (i.e. shifted by $\pi$).
Figure 6.2: Phase of the electric field transmission function for a cavity with a finesse of 30. Panel a) shows the function and the electric field components (illustrated by bars) in absence (black) and presence (blue) of molecular transitions together with the molecular single pass phase shift (orange curve). Panel b) visualizes the noise immunity of the phase of the FM light by illustrating zero (black bars) and a non-zero (blue bars) laser-cavity detuning.
6.5.3 Typical NICE-OHMS signals

As can be seen from eq. (6.11) the NICE-OHMS signal can be understood as a cavity enhanced dispersion and absorption of each laser component as it is scanned across the transition. By choosing the demodulation phase, \( \theta_{fm} \), to be 0 or \( \pi/2 \) one can choose between an out-of-phase and an in-phase signal. When eq. (6.11) is valid, they originate from the absorption and dispersion response of the molecules respectively and are therefore commonly referred to as Absorption- and Dispersion-NICE-OHMS signals.

Both signals are plotted as a function of laser-analyte detuning, \( \Delta \nu \), in the lower panels of figures 6.3 and 6.4 respectively. The upper panels (a–c) illustrate the laser components (red bars) together with the molecular absorption and dispersion line shapes (green) for \( \Delta \nu \) of -1, 0, and 0.45 \( \nu_{fsr} \) respectively. These three \( \Delta \nu \) are also marked with vertical dashed lines in the lower panels d of both figures.

For \( \Delta \nu = 0 \) (panels b) the attenuation is equal for both sidebands (for a symmetric line shape) and therefore the amplitude of the beatings of the two sidebands with the carrier is still canceling, giving a zero absorption signal (see panel a in figure 6.3). Also for detunings around zero the sidebands only interact with the flat wings of the absorption line shape function. Therefore, (and since the center component does not contribute to the absorption response) the absorption NICE-OHMS signal is relatively flat around \( \Delta \nu = 0 \). For the same detuning the phase shift of the center component is zero and the phase shifts of the sidebands are of opposite sign (see panel a in figure 6.4). Therefore the relative phase shift of the beatings is undisturbed (i.e. \( \pi \)) and the dispersion signal is also zero. However, because of the steep slope of the the dispersion lineshape function around \( \Delta \nu = 0 \) the center component experiences a phase shift already for small detunings, which in turn disturbs the phase balance of the two beatings with the sidebands. Therefore the dispersion NICE-OHMS signal has a steep slope at \( \Delta \nu = 0 \).

For \( \Delta \nu = \pm 0.46 \nu_{fm} \approx \pm \Gamma_a \) (panels c) the center component is at the maximum of the dispersion line shape (for this particu-
lar configuration). This implies that the phase of the beatings is maximally disturbed and the dispersion signal has its maximum. The amplitude of the sidebands is only weakly attenuated and therefore the absorption response is close to zero. This slope can be used for absolute frequency stabilization, in particular, if the dispersion response of a narrow sub-Doppler signal is addressed.

For \( \Delta \nu = \pm \nu_{\text{fsr}} \approx \pm \nu_{\text{fm}} \) (panels a) one of the sidebands is at the maximum of the absorption line shape. This implies that the amplitude of the sidebands is maximally out of balance which in turn results in a maximum of the absorption signal. The dispersion response on the other hand is only weakly affecting the other sideband and the carrier. Therefore the dispersion signal is close to zero at this detuning.

**Figure 6.3:** Illustration of three different laser analyte detunings relative to the molecular absorption response (panels a–c) and the absorption NICE-OHMS signal (panel d). The three dashed lines in panel d correspond to the three detunings illustrated in the panels a–c.
Figure 6.4: Illustration of three different laser analyte detunings relative to the molecular dispersion response (panels a–c) and the resulting dispersion NICE-OHMS signal (panel d). The three dashed lines in panel d correspond to the three detunings illustrated in the panels a–c.

6.6 EXPERIMENTAL IMPLEMENTATION – A TYPICAL NICE-OHMS SETUP

To successfully realize a NICE-OHMS instrumentation there are several things one needs to consider when choosing the components. In figure 6.5 a typical NICE-OHMS setup similar to the fiber-laser based NICE-OHMS setup presented in publication VIII is schematically illustrated and discussed in the following [8, 49]. Other NICE-OHMS setups realized as part of this work are discussed in chapter 7.

6.6.1 The laser and the locking actuators

The first component to choose is often the laser. When NICE-OHMS is intended to be used for frequency metrology by addressing narrow-band sD signals stable fixed frequency lasers can be
used [32]. For ultra sensitive trace gas detection often tunable lasers are used to record full Db absorption profiles as shown in figure 6.4 panel d). This has the advantage that the signal can be evaluated by a fitting procedure which can significantly reduce in-coupling of background signals [53] and furthermore the line center can be retrieved during a calibration measurement.

A NICE-OHMS setup in general requires a narrow laser with a linewidth significantly below the cavity FSR. It is desirable that the laser linewidth is in the order of the cavity mode-width. However, since the spectral width of the laser light can be reduced by locking the laser to the cavity no strict requirements for this parameter can be given. One should consider though that, the broader the laser width the higher the bandwidth of the PDH servo has to be. A rough estimate is that the servo bandwidth needs to be larger than the laser linewidth. Since the bandwidth of the PDH error signal is in the order of several MHz it is often the servo actuators that limit the bandwidth of the laser lock. Therefore a
broad laser requires a fast frequency control option as for example the current control of DFB lasers [79]. Narrow lasers require less locking bandwidth, but they often also have a limited tuning actuator bandwidth (not to be confused with tuning range). For example narrow fiber lasers or whispering gallery mode lasers can be tuned by a piezoelectric transducers (PZT) which has a limited bandwidth, often below 10 kHz. Despite their narrow linewidth this is often not enough bandwidth to lock them tightly to a cavity mode of high finesse cavities [6, 49]. One reason for this is that in the kHz range acoustic noise is present which induces a jitter of the cavity modes. To keep a stable lock the laser needs to follow this cavity mode jitter which requires sufficient gain also at kHz frequencies.

To increase the locking bandwidth a fiber coupled acousto-optic modulator (AOM) can be implemented after the laser source as illustrated in figure 6.5 [2, 49]. By controlling the frequency of a voltage-controlled oscillator (VCO) driving the AOM the frequency shift induced by the AOM can be controlled with a bandwidth to approximately 100 kHz (usually limited by the latency of the VCO response). While 100 kHz bandwidth is enough to compensate for most of the acoustic noise it still does not put high demands on the locking electronics. This makes the combination of a narrow linewidth laser and an AOM a robust and easy to operate solution.

6.6.2 The phase modulation

The next crucial part of a NICE-OHMS system is the implementation of the FM modulation. For this an actuator for phase modulation, which is responsive at RF frequencies, is required. For various types of semiconductor lasers the modulation can be directly applied to the current [38, 79, 80]. However, modulation of the laser current also results in an amplitude modulation, referred to as residual amplitude modulation (RAM) [80, 81]. For RAM the modulation sidebands are not balanced as for pure phase-modulation. This causes a background signal at the mo-
dulation frequency that also deteriorates the noise immunity of NICE-OHMS [43]. Therefore the phase modulation is often applied by use of an electro-optic modulator (EOM) as is illustrated in figure 6.5.

Also EOMs are not under all conditions providing pure phase-modulation [42]. However, there exist multiple approaches to alleviate problems with FM background from EOMs [25, 40–42]. Furthermore, it has been found EOMs with proton exchange waveguides show significantly less background signals [41]. Further approaches to reduce the influence of residual background signals are discussed below in section 7.3.

EOMs are available as free-space devices and as compact fiber-coupled models. Free-space EOMs require either high voltages (e.g. a half wave voltage of $V_\pi=205$ V) or are driven by a resonant electronic circuit whereby a separate EOM is required for each modulation frequency [40]. Since it is difficult to shield high voltage RF signals fiber coupled devices are preferred since they only require a few V modulation amplitude and are broadband, whereby multiple modulation frequencies can be applied with a single device [37].

6.6.3 Free-space optics

After generation of the FM light it is either collimated by a collimating lens in front of the laser or a fiber output coupler (FC). The resulting beam has to be spatially matched to the cavity. To get a Gaussian beam with a waist of the desired diameter and at the desired position so called mode-matching optics (MO) is placed in the free-space part before the cavity. To design the mode-matching optics first the Gaussian beam emitted from the last optical component (for fiber based systems often a fiber collimator) has to be characterized. Once this has been done different solutions for the mode-matching can be calculated [52]. To have more freedom a set of two lenses can be used instead of a single lens.
When choosing a solution for the mode matching and when placing other free-space optical components it should be considered to place them at so called EIDs—i.e. at multiples of the cavity length—since this reduces the influence of interference effects between the components [43]. Furthermore it is also possible to use parabolic mirrors for the mode matching optics and for focusing light onto the detectors. Mirrors in general do not give rise to etalons and can therefore be placed at an arbitrary position. To align the laser to the TEM\textsubscript{00} mode often two mirrors on kinematic mounts are used as shown in figure 6.5.

For implementation of the PDH and DVB techniques light reflected from the cavity has to be monitored. To collect the reflected light a PBS together with a half wave plate and a quarter wave-plate can be used as shown in figure 6.5. The half wave plate is placed before the beam-splitter and used to rotate the polarization of the light so that the light passes the PBS. A quarter wave-plate placed in front of the cavity is used to make the light entering the cavity circularly polarized. After the light is reflected from the cavity it passes the quarter wave-plate a second time and will be again linearly polarized, but 90 degree rotated compared to the incoming light. The PBS is therefore reflecting the light returning from the cavity onto the reflection detector without interfering with the incoming light. Alternatively also an optical circulator can be used to collect the reflected light [51]. It has however turned out that the optical circulators can induce background signals in the NICE-OHMS signal that are difficult to eliminate. If polarizing beam-splitters are not available at the wavelength of the system it is possible to use normal reflective beam-splitters [1].

6.6.4 The cavity

The heart of a NICE-OHMS system is the resonant optical cavity. The setups discussed in this work utilize Fabry-Pérot cavities consisting of two mirrors illustrated in figures 4.1 and 6.5. To be able to record a continuous NICE-OHMS signal it is necessary to tune
the frequency of the cavity resonance to which the laser is locked. As can be seen from eq. (4.5) this can be done by changing the cavity length. Therefore one of the cavity mirrors is mounted on a cylindrical PZT. When the PZT length is changed the cavity resonance frequencies will be shifted and the laser frequency will follow since it is locked to the resonance by the PDH servo. A is illustrated in figure 6.5 for the cavities constructed as part of this work both mirrors were mounted on PZTs. This adds additional tuning flexibility, in particular modulation of the cavity position as discussed in manuscript XI.

In the NICE-OHMS systems realized and utilized in this work, the mirrors are mounted on a spacer out of Zerodur with a cylindrical bore along the cavity axis as illustrated in figure 6.5. This bore hole, which is closed by the mirrors, has a connection to the vacuum system and can be filled with the analyte gas and pumped down to vacuum for background measurements. The Zerodur block has not only the advantage that it shows low thermal expansion, but also that it is very stiff and has a large mass and is therefore less sensitive to acoustic noise.

6.6.5 The detectors and demodulation electronics

Finally, a NICE-OHMS setup requires two high-bandwidth photo detectors. One detecting the light transmitted through the cavity that carries the NICE-OHMS signal and one for detection of the reflected light. Both have to have a minimum bandwidth of the modulation frequency. Furthermore, it is beneficial if they also have a DC monitoring output so that the intensity of the reflected and transmitted light can be monitored. The latter is in particular useful to monitor the state and quality of the lock. In some NICE-OHMS configurations, e.g. the one presented in publication VIII, a third reference detector monitors the background FM signal before the beam-splitter.

It should be noted that the NICE-OHMS signal is also present at the reflection detector [32]. Therefore it is in principle also an option to realize a NICE-OHMS system with a single detector. An
experimental study of different detection schemes can be found in publication VII and publication VIII which are summarized in section 7.3.

To bring the NICE-OHMS system to life it is required to implement RF electronics (for modulation and demodulation) and servo electronics (for locking the laser frequency and the modulation frequency).

As is shown in figure 6.5, the RF electronics is driven by two oscillators. One is a VCO generating the frequency for FM (380 MHz) and the other is generating a constant frequency for the PDH locking (20 MHz). Both frequencies are combined and coupled to the EOM. The frequencies are also used to demodulate the detector signals, which are all present at RF frequencies. The 20 MHz is mixed with the reflection detector signal to obtain the PDH error signal at DC. The 380 MHz signal is mixed with the signal detected in transmission to obtain the NICE-OHMS signal. Furthermore, the 20 MHz and 380 MHz signals are mixed to generate the sum- and difference-frequency. One of the latter is selected by a band pass filter and mixed with the reflection detector signal to obtain the DVB signal. The outputs of the mixers are then low-pass filtered to remove all high frequency components.

The PDH signal is sent through servo loop filter electronics to each laser frequency actuator (e.g. the laser PZT and the AOM VCO). The DVB error signal is also sent through loop filter electronics to the FM VCO. To avoid aliasing, the NICE-OHMS signal is low-pass filtered to less than half the acquisition rate of the AD converter used to digitize the signal.

6.7 TRACE GAS DETECTION SENSITIVITY OF NICE-OHMS SYSTEMS

When a NICE-OHMS system is designed for ultra sensitive trace gas detection, the assessment of the detection limit is a crucial part for characterization of the system. Unfortunately in the literature one can find different ways of assessing and defining the detection limit of spectrometry systems. This makes it often
difficult to compare the performance of different systems presented in the literature. To make a comparison possible it is important to clearly specify how the detection limits are evaluated. A thorough discussion about various noise contributions in NICE-OHMS systems and their assessment can be found in [74]. In the following the typical procedure for concentration measurements, typical noise sources, and the procedure for assessment of the detection limit used in this work will be summarized.

6.7.1 Assessment of the concentration in practice

To assess the analyte concentration NICE-OHMS signals are in general recorded over a spectral range of a few GHz for Db detection (see figure 6.4) and tens of MHz for sD detection (see manuscript XI). The acquisition rate is therefore given by the time it takes to scan the laser (and the cavity resonances) over the transition. For Db detection this acquisition rate is often in the order of Hz, but also tens of Hz are possible. Each recorded NICE-OHMS signal is then evaluated by fitting a line shape model, for example eq. (6.11) with $\alpha_0$ or the concentration as a free parameter. For trace gas detection the NICE-OHMS signal often can be assumed to be proportional to $\alpha_0$ and can be therefore eq. (6.11) can be rewritten in terms of a NICE-OHMS line shape function by

$$S_{no}(\Delta \nu) = \eta_{no} \alpha_0 \chi_{no}(\Delta \nu), \quad (6.16)$$

where $\chi_{no}$ is a line shape function for the instrumental response to the absorption and dispersion line shape functions.

To obtain the $\alpha_0$ from an arbitrary signal one needs to know the instrumentation factor $\eta_{no}$. The latter can be assessed by filling the cavity with a calibration gas with known concentration. The pressure is then preferably chosen such that the signal still is linear, but has a good SNR. Since under calibration conditions $\alpha_0$ is known, the instrumentation factor $\eta_{no}$ can be assessed by fitting eq. (6.16). Note that for high $\alpha_0$ the non-linearities of the NICE-OHMS signals have to be taken into account to obtain the correct $\eta_{no}$ (see also section 8.1).
Even for optimized NICE-OHMS systems there are residual background signals that contribute to the fitted $a_0$. However, often these background signals are stable over longer timescales. Under such conditions it is possible to first record them and then subtract them from subsequent measurements to obtain more accurate results for assessment of low concentrations. If an absolute frequency reference is available, which keeps the spectral range constant, the background signal can be simply recorded from an evacuated cavity. If one relies on the stability of the measurement cavity as the frequency reference it is best to fill the cavity with a buffer gas to the measurement pressure to make sure that the same spectral range is addressed for the background measurement and the concentration measurement.

### 6.7.2 Theoretical detection limit of a NICE-OHMS system

The most fundamental noise contribution in a NICE-OHMS system is the photon shot-noise. It originates from the quantum nature of the light and it represents the stochastic variation of the discrete number of photons that is passing a given area per time interval (i.e. the intensity). The variation can be described by a Poisson distribution and is therefore given by the square root of the number of photons passing the detection area.

In photo diodes not every indecent photon induces a electron-hole pair that contributes to the photo current. The number of electron-hole pairs induced per number of photons is referred to as quantum efficiency, $Q$, and can be for commercial high quality detectors in the NIR order of 0.8 [82]. From the quantum efficiency one can calculate the responsivity, $\eta_{\text{det}}$, which is defined as the photo current per incident optical power and given by

$$\eta_{\text{det}} = \frac{e}{\hbar \nu} Q,$$  \hspace{1cm} (6.17)

where $e$ is the electrical charge.
With this definition the shot-noise equivalent peak absorption coefficient for a NICE-OHMS signal (measured and evaluated by a fit as described in section 6.7.1), \( \alpha_{0}^{SN} \), is given by \[8, 74]\)

\[
\alpha_{0}^{SN} = \frac{\pi}{F L_c} \frac{\Lambda}{I_0 I_1 \kappa} \sqrt{\frac{e \Delta f}{\eta_{det}}} \frac{1}{\sqrt{P_0}},
\]

(6.18)

where the factor \( \Lambda \leq 1 \) takes into account for the fact that when scanning over a NICE-OHMS signal the SNR is not constant [53], \( \kappa \) is the ratio of the peak-to-peak value of the NICE-OHMS line shape function and \( \alpha_0, \Delta f \) is the detection bandwidth (scan rate), and \( P_0 \) is the power incident on the detector.

If \( P_0 \) is large enough, so that \( \sigma_P^{SN} \) is larger than the constant electronic background noise of the detector, then the NICE-OHMS system can in fact be shot-noise limited [8, 32]. However, as alluded to above (section 6.6), background signals from RAM or etalons can contribute noise that can be significantly above the shot-noise level.

One kind of noise contributions of background signals is in-coupling of intensity noise. Under background free conditions the NICE-OHMS signal is always zero even if the laser intensity is very noisy, since it affects all laser components simultaneously. However, if the triplet is not balanced, for example due to RAM, intensity noise will couple into the signal. This process can be dominating if strong background signals and high intensity noise is present (for example a DFB based system using current modulation).

For fiber-laser based NICE-OHMS systems using a proton exchange EOM both the intensity noise as well as the background signal amplitude are relatively low. Therefore these systems often are limited by the intrinsic instabilities related to the origin of the background signals. Background signals originating from etalons (interference between optical components) strongly depend on the distances of the surfaces involved. Any change in these lengths directly shifts the background relative to molecular signals and therefore results in a noise in the NICE-OHMS signal. On short time-scales below 1 second it can be acoustic noise which
causes a jitter of the background signals. In particular etalons in fiber coupled parts of the system can strongly pick up acoustic noise. On longer time scales, above several seconds, it is usually thermally induced length changes in the optical setup which causes a slow drift of the background signals (see for example Fig. 2 and publication VIII).

6.7.3 Experimental assessment of the detection limit

The detection limit is best assessed by a procedure similar to the actual measurements. It is then of interest to assess the limitations of the instrumentation without the influence of actual fluctuations or drifts of the analyte concentration. Therefore, in this work, the noise levels of various systems were assessed by recording empty cavity signals while scanning the same spectral range as for actual measurements. The signal were then evaluated by the same fitting procedure as described in section 6.7.1 to obtain $\alpha_0$ values for each empty cavity signal. The $\alpha_0$ values from measurements over several hours show the noise and background levels coupling into the $\alpha_0$ assessment.

As discussed in the previous section, different types of noise are dominating at different time scales. While white noise can be reduced by increasing the averaging time, slowly drifting background signals have to be eliminating by background measurements. To identify on which time scales a given type of noise is dominating longtime measurements of $\alpha_0$ are often evaluated by the use of Allan-Werle plots [83].

The Allan deviation is defined for a measurement series with $N$ samples $x_n$ (in our case $N$ measurements of $\alpha_0$), where $n = 1, \ldots, N$ [74, 83]. The samples are measured with a constant rate $f_s = 1/\Delta T$ (in our case the scan rate at which a full NICE-OHMS signal is acquired). The measurement series is then divided into $M$ adjacent subgroups of $k = N/M$ elements. The mean value of these subgroups is then calculated as
\[ A_s(k) = \frac{1}{k} \sum_{l=1}^{k} x_{s,k+l}, \quad (6.19) \]

where \( s = 0, \ldots, M - 1 \). The acquisition time for the \( k \) samples in each group is referred to as the integration time \( \tau_k = k \Delta t \). The Allan deviation, defined for a given integration time, is given by [83]

\[ \sigma_A(\tau_k) = \sqrt{\frac{1}{2(M-1)} \sum_{s=1}^{M-1} [A_s(k) - A_{s-1}(k)]^2}. \quad (6.20) \]

An Allan-Werle plot is then obtained by plotting \( \sigma_A \) from a measurement series of \( \alpha_0 \) as a function of \( \tau_k \) (see for example figure 7.2 below). To get reliable values of \( \sigma_A \) for integration times up to \( \tau_k = 1000 \) s usually a measurement series over approximately 12 hours is required (this corresponds to \( M = 43 \) subgroups).

In this work the noise equivalent absorption limit (NEAL) is defined as the Allan deviation of the \( \alpha_0 \) values from a series of empty cavity measurements for a certain integration time \( \tau_k \). Often the NEAL for the optimum integration time is given, i.e. the integration time giving the minimum \( \sigma_A \).

For white noise dominated integration times the Allan deviation for is equal to the standard deviation of the mean of \( k \) samples. This also implies that the deviation is given as a function of integration time by \( \sigma_A(\tau_k) = \sigma_A(\tau_1) / \sqrt{k} \). The WNEAL is then defined as the Allan deviation of the white noise at \( \tau_k = 1 \) and usually given in units of \( \text{cm}^{-1}\text{Hz}^{-1/2} \) (i.e. evaluated for one second integration time). The WNEAL can be calculated from a measured \( \sigma_A(\tau_{wn}^k) \) by

\[ \text{WNEAL} = \sigma_A(\tau_{wn}^k) \cdot \sqrt{\tau_{WN}^k}, \quad (6.21) \]

where \( \tau_{wn}^k \) should be chosen such that the measured \( \sigma_A(\tau_{wn}^k) \) is dominated by white noise.
It should be noted that if drifts dominate already before 1 second the WNEAL (in cm$^{-1}$Hz$^{-1/2}$) can have a lower number than the actual NEAL for $\tau_k = 1$ s. Furthermore, if the sampling time is longer than the white noise dominated integration time no reliable value for the WNEAL can be calculated.

In this work the same procedures and definitions are used for evaluating the detection limit for sD detection. This in particular means that $\alpha_0$ is always the peak absorption of the Db signal.

When comparing the detection limit of sD detection and Db detection it is important to note that the optimum pressure for Db detection is in the order of 50 Torr while for sD detection it is typically in the order of 100 mTorr [34]. Since $\alpha_0$ is approximately proportional to the pressure for a constant concentration the same NEAL value for sD detection and Db detection in general correspond to very different minimum detectable analyte concentrations.
Part II

RESULTS

My worthy friend, gray are all theories, and green alone
Life’s golden tree.

Grau, teurer Freund, ist alle Theorie und grün des Lebens
goldner Baum.

Johann Wolfgang von Goethe Faust I (1808)
DESIGN AND CONSTRUCTION OF NICE-OHMS INSTRUMENTATION

7.1 THE OPO-BASED MID-IR NICE-OHMS SYSTEM

The development of the Db Mid-IR (MIR) NICE-OHMS system is covered in publication I, publication II and publication III of this thesis [1–3]. The main reason for development of a Db NICE-OHMS setup for trace gas detection in the MIR region was that in this wavelength region strong fundamental ro-vibrational transitions can be addressed. For example the line strengths of CH$_4$ transitions in the band around 3.3 µm are two orders of magnitudes stronger than those of transitions in the band around 1.65 µm and six orders of magnitudes stronger than transitions in the telecommunication band around 1.55 µm. A system allowing for Db detection was preferred as it allows in general for lower concentration detection limits as compared to sD detection (see comment at end of section 6.7.3).

In the telecommunication bands in the NIR low noise lasers, fiber coupled modulators and other optical components are available off the shelf and a NICE-OHMS system can easily be constructed from standard components. Building a NICE-OHMS setup in the MIR turned out to be more challenging. In particular the pure phase modulation of MIR light at the FM frequency is non-trivial. A first realization of sD NICE-OHMS in the MID-IR based on a QCL and utilized current modulation, but it was only used in combination with an additional wavelength modulation layer to address sD signals [38]. As discussed in section 6.6, RAM makes it difficult to acquire low-noise Db signals using current modulation. The only demonstration of Db-NICE-OHMS in the MIR based on a difference frequency generation (DFG) source did not show the low detection limit expected from NICE-OHMS sys-
tems [46]. To improve on this an OPO based approach described in the following was chosen to realize the first MIR NICE-OHMS optimized of Db detection.

As was first shown by Lindsay et al. for FMS, phase modulated NIR light can be converted to a frequency modulated MIR light using a singly resonant OPO [84]. The same approach was then also successfully implemented by Crabtree et al. for noise-immune cavity-enhanced optical heterodyne velocity modulation spectroscopy (NICE-OHVMS) [39]. Based on these concept we could realized the first Db MIR NICE-OHMS system based on a commercial singly resonant OPO (Aculight, Argos 2400 SF, module C) as described in publication I. In this configuration a fiber coupled proton-exchange EOM is applied for phase modulation to minimize the RAM (see also section 6.6). As is illustrated in figure 7.1 we showed in publication II that it is possible to narrow the linewidth of the OPO output by implementation of an AOM after the seed laser. Using the sturdy locking of the AOM in combination with a feed forward circuit we could show in publication III that acquisition rates of Db signals of at least 21 Hz are feasible. Another major advantage of the OPO based system is that by tuning the height of the fan-out PPLN crystal in the OPO the idler can be tuned between 3.2 and 3.9 μm. This implies that transitions in a major part of the methane band around 3.3 μm as well as several other molecules of importance can be addressed.

The principle of the MIR system is the same as the system described in section 6.6 and the details of the experimental implementation is discussed in publication I and publication II. In the following only a few practical remarks are made. Since the alignment of the MIR beam to the cavity was non-trivial it came in handy that a visible green light (presumably from a weak second harmonic generation) was aligned with the MIR beam which could be used to pre-align the beam. Since the output beam of the OPO was not fully Gaussian, the beam-shaping optics included an aspheric lens focusing the light onto a pinhole to realize a spatial filter and obtain a clean Gaussian beam mode-matched to the cavity. Furthermore since no suitable PBS was available at this wavelength a 1% reflective beam-splitter was used. This
The first implementation of an OPO based Db MIR NICE-OHMS system, described in publication I, was based on a 500 finesse cavity with a mode width of approximately 380 kHz. The latter is significantly larger than the laser linewidth of 100 kHz and the width of the frequency jitter of the cavity modes from acoustic noise. It was therefore sufficient to implement a PDH servo with a bandwidth of approximately 1 kHz by giving feedback to the seed-laser PZT. The performance analysis by an Allan-Werle plot (red curve in figure 7.2) shows that for an acquisition time of one second the system was white noise limited with a WNEAL of $3 \times 10^{-9} \text{ cm}^{-1} \text{Hz}^{-1/2}$. For an integration time of 20 s the NEAL...
was assessed to be $1.5 \times 10^{-9}$ cm$^{-1}$. This NEAL corresponds to a concentration of 90 ppt of CH$_4$ when detected at its strongest transition and at a pressure of 40 Torr.

It was questionable whether this NEAL was sufficient for detection of CH$_3$D which has a natural abundance in the order of 1 ppb. Therefore a cavity with a finesse of approximately 4000 was implemented, as is described in publication II and shown in figure 7.1. Since this finesse corresponds to a cavity linewidth of 50 kHz an AOM was implemented to allow for a PDH servo with the required bandwidth of 100 kHz. An Allan-Werle plot (blue curve in figure 7.2) revealed that the WNEAL could be improved to $2.4 \times 10^{-10}$ cm$^{-1}$Hz$^{-1/2}$. This corresponds to a detection limit of methane concentrations in the low ppt range which is sufficient to detect $^{13}$CH$_4$ as well as CH$_3$D at natural abundance in atmospheric samples with a good SNR.

![Allan-Werle plot for Db detection at 3.5 µm with the OPO based NICE-OHMS system realized with a 500 finesse cavity (upper red curve) and a 4000 finesse cavity (lower blue curve) for a scan rate of 1 and 7 Hz respectively (figure adapted from [3]).](image-url)
7.2 LOCKING ELECTRONICS AND SERVO DESIGN

7.2.1 PZT resonances

As alluded to above and as is shown in publication II, the implementation of a higher finesse cavity often requires an increased locking bandwidth by implementation of an AOM. However, it was initially observed that despite the AOM the locking did not show a constant noise behavior, but the cavity-laser jitter increased sporadically. This resulted in dips in the intensity transmitted through the cavity. The origin of this was attributed to random excitation of the laser PZT resonances at 23.4 kHz. Possible sources leading to excitation of this resonance could be noise or too high gain at the resonance frequency in the servo electronics or acoustic noise in the laboratory.

By monitoring the FFT of the PDH error signal it was not conclusively verified that the noise originated from the PZT resonance. The reason was that the resonance was only sporadically excited while the data for a FFT is often recorded over longer timescales and therefore only presents an average excitation whose magnitude can be insignificant. Only after removing the resonance excitation by the action described below we could verify that it was causing the intensity noise.

As the phase response of the PZT changes by 180 degree within a narrow band around the resonance frequency, it is not straightforward to attenuate the noise by including it in the feedback bandwidth. One solution that effectively reduces electronic noise and avoids too high feedback gain at the resonance is the implementation of an electronic notch filter at the PZT resonance [85]. We presented an alternative solution in publication II. Servo electronics was implemented in parallel to the traditional PID servo that adds gain around the resonance frequency. Since the phase and gain of the parallel feedback path can be controlled independently the 180 degree phase jump can be tuned so that the open-loop transfer function fulfills the phase requirements for a stable feedback loop. This can attenuate electronic as well as acoustic noise at the resonance frequency. It should be noted that the feed-
back path that includes the AOM is dominating around the resonance frequency. This weakens the phase and gain constraints for a stable resonance feedback path and thereby makes the implementation less challenging.

After this implementation the intensity of the transmitted light was stable and furthermore the FFT of the error signal showed a dip instead of a peak at the PZT resonance frequency.

7.2.2 Feed-forward

For some applications it can be beneficial to acquire NICE-OHMS signals at a rate higher than 1 Hz. At the same time, to achieve a good SNR, it is necessary to record the NICE-OHMS signal over a GHz range around the center frequency of a Db transition [53]. For this the cavity resonance needs to be scanned over this range at the desired acquisition rate with the laser locked to the resonance frequency. Even if a well designed servo can provide very high gain at low frequencies (around 10 Hz) it is often not sufficient to keep the laser locked to the center of the resonance frequency if the cavity resonance is scanned over large ranges at these frequencies. This problem originates from the nonlinear response of the laser PZT in combination with the PZT drivers which leads to a reduced effective gain for high-amplitudes.

A well-known way to compensate for a pre-known disturbance of a system (such as a cavity length scan) is a feed-forward (FF) control. In publication III a FF circuit was implemented that feeds a phase and amplitude adjusted scanning signal to the laser PZT. Thereby the servo only needs to compensate for low amplitude responses present at multiples of the scanning frequency. By implementation of such a FF circuit in the OPO based NICE-OHMS system, signals were acquired with up to 21 Hz. The Allan-Werle plot for an acquisition bandwidth of 7 Hz after implementation of the FF circuit is shown by blue curve in figure 7.2 (which was originally presented in publication III).

It should be noted that the amplitude and phase responses of the laser PZT and the cavity PZT were different. Furthermore, the
PZT responses for large scanning amplitudes are non-linear. This implies that it is not straightforward to implement filter electronics that give a perfect FF response for all frequencies. It was therefore necessary to adjust the phase and amplitude of the FF signal for each scanning frequency. As is shown in publication III, an analog gain and phase control was for this purpose implemented in the FF path.

For publication VI a FF scheme was implemented to optimize the tuning range and scanning frequency of a WGML based NICE-OHMS system. WGML like the one used in publication VI have several advantages like a compact housing, availability at various wavelengths and narrow linewidth. This type of laser can provide a fast tuning by applying a voltage to a PZT stretching the whispering-gallery-mode microresonator of the laser. Since the tuning range of the PZT control was limited to 1 GHz, an additional FF path controlling the laser temperature had to be implemented.

To simplify the tuning of the FF signal it was generated digitally together with the cavity scan signal. This made it simple to flexibly adjust the FF phase and amplitude for different scanning conditions. Furthermore a digitally generated FF also included a second harmonic component of the scanning signal, which compensates for the non-linearities of the PZT responses. The FF scheme enabled a tuning range of 3 GHz for a scan rate of 0.5 Hz and 5 GHz for a scan rate of 0.1 Hz. Slower and faster scan rates decreased and increased the tuning ranges, respectively.
7.3 NOVEL DETECTION SCHEMES FOR NIR NICE-OHMS

As discussed in section 6.7 NICE-OHMS systems show a very low WNEAL and can be shot-noise-limited. However, this is most often not the case. Instead, the noise level is often limited by the presence of residual background signals. These background signals can couple in intensity noise, phase noise of the modulation frequency, or, in the worst case, even deteriorate the noise immunity of NICE-OHMS. Furthermore, the background signals themselves can be noisy and instable. While the in-coupling of other noise sources often results in an increased white-noise level, the unstability of the background signals often contributes to signal drifts over longer time-scales (tens of hundreds of seconds).

Reducing residual background signals that come from RAM or etalons in the system is therefore a crucial part when realizing a NICE-OHMS system for the lowest possible noise levels (ideally shot-noise-limited). In the literature one can find various approaches of how to reduce background signals or avoid their in-coupling into the signal [25, 40, 41, 53]. Publication VII, publication VIII and publication VI suggest methodologies to reduce the influence of background signals. The methodologies and detection schemes were experimentally implemented by adaption of an existing fiber-laser based NICE-OHMS system in the NIR. The discussed detection schemes are illustrated in figure 7.3.

7.3.1 Reflection and differential NICE-OHMS

As was suggested by Jun Ye et al. already in 1998, in one of the first NICE-OHMS papers, a NICE-OHMS signal can be detected in the light reflected by the cavity, as schematically drawn in figure 7.3 b), [32]. However, in the same work it was also concluded that in practice such a signal in general has a lower SNR compared to a NICE-OHMS signal detected in transmission. Therefore, according to my knowledge, except for two demonstrations by Ye and Silva [35, 86], NICE-OHMS signals have only been detected in transmission.
7.3 Detection Schemes for NICE-OHMS in the NIR

Figure 7.3: Schematics of the four NICE-OHMS detection schemes implemented in publication VII and publication VIII. For a more detailed description of a typical NICE-OHMS setup and the drawn components see figure 6.5. The noise equivalent absorption limit (NEAL) is stated for the optimum integration time and an integration time of 1000 s for each setup. The results show that the longtime stability can be significantly improved by the schemes with background canceling shown in c) and d).

a) Transmission NICE-OHMS

WNEAL: \(4 \times 10^{-13} \text{ cm}^{-1} \text{Hz}^{-1/2}\)
NEAL @50 s: \(7 \times 10^{-14} \text{ cm}^{-1}\)
NEAL @1000 s: \(6 \times 10^{-13} \text{ cm}^{-1}\)

b) Reflection NICE-OHMS

WNEAL: \(1 \times 10^{-12} \text{ cm}^{-1} \text{Hz}^{-1/2}\)
NEAL @100 s: \(1 \times 10^{-13} \text{ cm}^{-1}\)
NEAL @1000 s: \(6 \times 10^{-13} \text{ cm}^{-1}\)

c) Differential NICE-OHMS

WNEAL: \(5 \times 10^{-13} \text{ cm}^{-1} \text{Hz}^{-1/2}\)
NEAL @170 s: \(5 \times 10^{-14} \text{ cm}^{-1}\)
NEAL @1000 s: \(1 \times 10^{-13} \text{ cm}^{-1}\)

d) Balanced NICE-OHMS

WNEAL: \(2 \times 10^{-13} \text{ cm}^{-1} \text{Hz}^{-1/2}\)
NEAL @200 s: \(2 \times 10^{-14} \text{ cm}^{-1}\)
NEAL @1000 s: \(3 \times 10^{-14} \text{ cm}^{-1}\)
In publication VII we scrutinized the formalism and the SNR of the reflection NICE-OHMS signal. This revealed that when it comes to the shot-noise limited condition the reflection NICE-OHMS signal can in the best case be equal to the transmission NICE-OHMS signal. However, in practice, additional light is present in reflection which does not carry a NICE-OHMS signal, but increases the shot-noise as well as technical noise. Therefore, reflection NICE-OHMS signals are expected to be more noisy than transmission NICE-OHMS signals. More importantly, however, the formalism revealed that background signals carried by the light before entering the cavity will have opposite sign in transmission and reflection relative to the molecular NICE-OHMS signal. This implies that when adding the two signals the molecular NICE-OHMS signals add up while the background signals will cancel. This is referred to as differential NICE-OHMS.

With the experimental implementation of differential NICE-OHMS (as schematically drawn in figure 7.3 c), we could show that compared to the transmission NICE-OHMS signal the differential NICE-OHMS signal showed a factor of 7 lower longtime drifts of background signals while having a similar white noise level (publication VII). This resulted in a NEAL of \(4.7 \times 10^{-14} \text{cm}^{-1}\) for an integration time of 170 s without requiring additional optical components.

Another result presented the same publication worth to emphasize for practical reasons is that the white noise level of the reflection NICE-OHMS signal is only a factor of two higher than for that of the transmission NICE-OHMS signal while their longtime stability is similar. This implies that one can realize a simpler NICE-OHMS system with a single detector in case a larger WNEAL of \(9.7 \times 10^{-13} \text{cm}^{-1}\text{Hz}^{-1/2}\) and higher longtime drifts are acceptable.

7.3.2 Balanced NICE-OHMS detection

While the differential signal efficiently reduced the background, the white-noise still was a few times above the shot-noise limit.
Therefore another detection scheme was implemented. For this, a third reference detector was placed in the setup that detected a part of the light sampled by the polarizing beam splitter before the cavity (see figure 7.3 d). By tuning the polarization by use of a $\lambda/2$ plate the intensity of the sampled beam was controlled. The demodulated reference signal corresponds to the imbalance of the triplet at the sampling point and has in some NICE-OHMS realizations been used to give feedback to the EOM to reduce background signals [25, 40, 41]. In this case, we subtracted the reference signal from the transmission NICE-OHMS signal after acquiring both of them with a data acquisition card. We could show that this so called balanced detection scheme could not only reduce the longtime background drifts, but also the white noise in the system so as to make the resulting signal shot-noise-limited.

The Allan-Werle plot of a 12 hour longtime measurement for Db detection showed a WNEAL of $2.3 \times 10^{-13} \text{cm}^{-1}\text{Hz}^{-1/2}$ and, for the optimum integration time of 200 s, a NEAL of $2.2 \times 10^{-14} \text{cm}^{-1}$. Also for an integration time as long as 1000 s the Allan deviation was below $4 \times 10^{-14} \text{cm}^{-1}$. This indicates that longtime drifts were very efficiently suppressed.

In manuscript XI the method was applied for sD detection. It was shown that the NEAL for sD detection (see note in 6.7.3) for an integration time of 60 seconds could be reduced by a factor of 20, from $5 \times 10^{-12} \text{cm}^{-1}$ to $2.2 \times 10^{-13} \text{cm}^{-1}$.

This shows that the improvement of balanced detection for sD-detection is significantly stronger than for Db-detection. The reason is that Db and sD detection are limited by background structures that have different origin. As has been discussed in detail in [53] the in-coupling of drifting background signals does not only depend on their amplitude but also on the periodicity of their spectral structure. If the period of the background signal is similar to the width of the NICE-OHMS signal, a spectral drift of the background signal will strongly be picked up by a fit of the NICE-OHMS signal. Therefore, detection of Db signals (which typically have a GHz width) and detection of sD signals (which have a sub MHz width) are in general affected by background signals with different origin and periodicity. In the fiber-laser based NICE-
OHMS system the background structure that has a periodicity of GHz and limits the Db detection arises from the EOM. This structure is stable (i.e. contributes less than the white noise) over time scales in the order of 10 seconds. The background structure that has a periodicity in the order of MHz and limits sD detection, is originating from interference in the optical fibers that are several meters long. These etalons are highly instable already on the timescales of seconds.

7.3.3 Cavity position modulation

The detection schemes presented in publication VII and publication VIII were efficiently reducing the broad background signals originating from the EOM and narrow structures from the fibers. However, etalons originating from interference after the beam splitter could not be suppressed. While these etalons (with a periodicity of 120 MHz) are not strongly coupling into fits of Db NICE-OHMS signals they dominate the drifts observed in the sD mode of detection. Since in manuscript XI a sD signal was addressed it was necessary to reduce also these background structures. Although all components in the setup were placed at EIDs and their positions were optimized to reduce the etalons, it turned out very difficult to completely suppress all background signals. When identifying the origin of the remaining etalons we could first of all observe that, as expected, the strongest etalons were formed by one of the cavity mirrors and another free-space optical component. Furthermore, we also could observe that the dominating background structure was originating from an etalon between the in-coupling cavity mirror and the transmission detector. Note that this implies that etalons can include the optical cavity in their paths. A method to suppress background signals from etalons suggested 1985 by Webster is the Brewster-plate spoiler [87]. In that work, the optical path length of the etalon was modulated by periodically rotating a Brewster-plate placed in the path. By this modulation the background structure could be modulated at the rotation frequency and could then be efficiently filtered out.
7.3 Detection Schemes for Nice-OHMS in the NIR

from the spectroscopic signal. Also recently, this technique was successfully applied for NICE-OHVMS [88]. However, the implementation involves not only additional optical components and electronics, but also very careful alignment and optimization of the modulation. Therefore, in manuscript XI we suggested and applied a new method we here refer to as cavity position modulation (CPM).

Since both mirrors of our cavities are mounted on PZTs (see figure 6.5) it is possible to modulate the position of both synchronously without affecting the cavity length. To facilitate this two digitally generated 90 Hz modulation signals were sent to the two cavity PZTs. The amplitude and phase of the two signals was adjusted so that the length of the cavity was kept constant. To remove any residual length jitter from the modulation we tuned the amplitude and phase of one 90 Hz signal while monitoring the PDH feedback signal, which showed any residual length jitter at 90 Hz. The amplitude of the CPM was optimized to modulate one or a multiple of the etalon periodicity. The Allan-Werle plot shows that the longtime drifts were reduced by a factor of two, while the noise of the signal on short time scales increased only slightly, presumably due to some residual jitter at the CPM frequency.
7.4 FPGA BASED NICE-OHMS SYSTEM

As discussed above, NICE-OHMS systems can be extremely sensitive, they can return both Db dispersion as well absorption response, and they can provide narrow sD responses. However, to realize a NICE-OHMS system does not only require the implementation of the optical setup, but also of the servo, modulation and demodulation electronics. Furthermore, for the cavity scan, optionally a feed forward circuit and, in case of absolute frequency stabilization, a feedback servo to the cavity needs to be added. To adapt the system for different applications can also be time consuming.

To make the system easier to adapt and simpler to operate we have recently replaced a major part of the analog electronics of the fiber-laser based system with a digital field programmable gate array (FPGA) based system. The design of the first realization, the first signals recorded by the system, and the potentials of the system are discussed and presented in the following.

The system (shown in figure 7.4) is based on a FPGA (NI PXIe-7971R) that is directly connected to a Direct Digital Synthesizer (DDS, AD9915) and an Analog in-/output module (NI 5783). The latter has AD converters which digitize signals with 100 MSPS and DA converters that are generating signals with 200 MSPS. Both (the AD- and the DA-converter) have a resolution of 16 bits.

7.4.1 DDS and DDC based modulation and demodulation

It was demonstrated by Lam et al. that by implementing a digital demodulation scheme for PDH the influence of electronic offset drifts and low frequency disturbances (e.g. from ground-loops) can be removed [89]. To test the full potential of digitalization for NICE-OHMS all RF-signals (i.e. the PDH, the DVB and the NICE-OHMS signals) were digitally demodulated as described in the following.

The PDH modulation frequency \( \nu_{pdh} = 20 \text{ MHz} \) was generated directly on the FPGA with a DDS based on a simple 10
sample long static lookup table (LUT). The FM modulation frequency \( (v_{fm} \approx 380 \text{ MHz}) \) was generated by the external DDS with a rate of 2.5 GSPS. The clock of the external DDS was phase locked to the 20 MHz signal generated by the FPGA. Using digital IO pins directly coupled to the FPGA (provided by the NI 5783 module) the output DDS frequency was controlled with 10 MHz bandwidth. Both generated frequencies were bandpass filtered to attenuate high frequency spurs.

The four 100 MSPS DA converters enable acquisition of RF input signals at 20 MHz, which then can be demodulated to a DC signal by a digital down converter (DDC) on the FPGA. While the PDH signal can be directly digitized, the DVB and the NICE-OHMS signals needed to be down-converted by utilizing an analog mixer to the 20 MHz intermediate frequency by mixing them with a 380 MHz \( (v_{fm}) \) and a 360 MHz \( (v_{fm} - v_{pdh}) \) local oscillator (LO), respectively. To avoid aliasing of high frequency components the 20 MHz input signals were filtered with an analog passband filter (Minicircuits SIF-21.4+). The DDCs were clocked at the 100 MHz sampling rate multiplying each digitized signal.

**Figure 7.4:** Schematics of the FPGA based NICE-OHMS system.
with two in-quadrature 20 MHz sine waves. The sine waves were generated from 24 bit LUTs. The phases of the two sine waves were tunable in real-time by updating the LUTs using the controller PC. For the error signals only the dispersive responses suitable for locking were used and monitored. Typical digitally demodulated error signals are shown in figure 7.5. The IQ components of the NICE-OHMS signal were recorded as the NICE-OHMS absorption and dispersion response as shown by the red and blue curve in figure 7.6 panel a).

![Digital demodulation plots](image)

**Figure 7.5:** Digitally demodulated PDH (panel a) and DVB (panel b) error signals recorded with a 5 kHz sampling rate.

The DDC based demodulation scheme is not only potentially removing any low frequency electronic noise, it also does not require any analog phase shifters that can cause drifts and signal distortion. This is also true for the DVB and NICE-OHMS signals since the phase information of the original RF signal is conserved in the analog down-conversion process.

This implies that neither the servo signals, nor the NICE-OHMS signals, are affected by offset drifts of analog electronics. It also implies that both the in-phase (dispersion) and in-quadrature (absorption) signals can be acquired simultaneously [4]. The remaining analog part (gray in figure 7.4) only consists of RF-mixers for down conversion to 20 MHz and some standard amplifiers
Figure 7.6: Digitally demodulated NICE-OHMS signals of a CO$_2$ transition at 1576.9396 nm, at pressure of 0.5 mTorr pure CO$_2$. Panel a) shows the simultaneously recorded Db dispersion response (blue) and absorption response (red). Both signals were recorded with 0.5s acquisition time. Panel b) shows the sub-Doppler response in the center of the dispersion signal.

coupling the inputs and the outputs of FPGA to the detectors and actuators of the optical part of the NICE-OHMS system.

7.4.2 Digital servo design

When it came to the implementation of the servo filters the FPGA showed its flexibility. The filters were implemented as infinite impulse response (IIR) filters as described by Leibrandt and Heidecker [90]. With this type of filter it is possible to realize a phase and magnitude response similar to that from analog filters. The quantization noise of the filters can be reduced below the signal noise level by implementing all multiplications with sufficient bit depth. To reduce the required bit length of the filter coefficients the signal after the DDC, which comes with a rate of 100 MSPS, was down-sampled with a multirate filter to 1 MHz or 100 kHz depending on the required servo bandwidth. The latency between the analog input to the analog output was about 600 ns, which al-
allowed for a servo bandwidth for the AOM of approximately 200 kHz.

The filters were divided into consecutive second order IIR stages (in form of so called BiQuad filters) with freely programmable filter coefficients. That made it possible to adjust and optimize the filter parameters in real time. Furthermore it was possible to easily implement an additional servo for locking to a sD signal without additional components, as shown by the dashed lines in figure 7.4.

7.4.3 Preliminary conclusions and outlook

Despite that we could already successfully demonstrate that the digital demodulation for the PDH, the DVB and the NICE-OHMS signals and they showed noise levels in the same order of magnitude, a thorough performance comparison with comparable modulation parameters is missing.

Also we could successfully implement the digital locking for the PDH-lock, the DVB-lock, and for the absolute frequency stabilization to a sD response. Also for this part a thorough performance comparison with the analog realization is missing.

It was shown earlier that the modulation frequency locked to the cavity by the DVB technique can be directly used as a calibration-free measure of the molecular dispersion response [91]. The signal, i.e. the locked modulation frequency, is referred to as Dual-frequency modulation dispersion spectroscopy (DFM-DS) signal. The digital DVB feedback signal that is controlling the modulation frequency can directly be used as DFM-DS signal (without calibration by an external frequency counter as is necessary for an analog VCO). Therefore it is expected that it is straightforward to monitor a DFM-DS signal from the digital system without requiring further components.

I hope that the possibility to digitize the NICE-OHMS electronics can simplify the development of new systems and increase the range of applications of the technique.
MODELING OF NICE-OHMS SIGNALS

This thesis comprises three publications and one manuscript dealing with modeling of NICE-OHMS signals under different conditions. Publication IV and publication V scrutinize the principle of NICE-OHMS and give different degrees of approximations of the instrumental line shape function applicable to different degrees of absorption. Publication IX and manuscript X deal with the modeling of absorption by ro-vibrational transition under so-called vibrational-depleted conditions on the example of methane. The works include theoretical descriptions as well as experimental verifications of the models.

8.1 NICE-OHMS SIGNALS UNDER DIFFERENT ABSORPTION CONDITIONS

NICE-OHMS is best applied for detection of ultra-low concentrations. However, as for most other techniques, the instrumentation needs to be calibrated. For best accuracy, this is done by the use of a standard reference gas. For stability reasons these gases are not available with arbitrary low concentrations. Therefore the calibration gas can give rise to strong cavity enhanced absorption \( (2F/\pi\alpha) \), in particular for high finesse cavities. This implies that the response of a NICE-OHMS system might not be fully linear with the concentration over its entire working range. In particular, the conventional linear expressions for NICE-OHMS signals, such as eq. (6.11), might not be valid under the calibration conditions.

To enable for accurate calibration under all absorption conditions and to estimate in which absorption regime the NICE-OHMS signal amplitude can still be considered linear with concentration a general NICE-OHMS description is required. Such a description is given in publication IV [4] in this thesis and was verified
experimentally in publication V [5] using the fiber laser based NICE-OHMS system. The application of the FULL formalism to extend the dynamic range of a mid-IR NICE-OHMS system was also demonstrated in publication II [2].

The most general NICE-OHMS expression derived in these publications is already given in section 6.5. Therefore, in the following only the validity of various descriptions given in the publications will be summarized and a guideline for efficient computation of the most general expressions is given.

8.1.1 Definition of absorption regimes

In NICE-OHMS the absorption is usually not measured at a single frequency, but for each measurement the laser is scanned over a full absorption line profile while recording the NICE-OHMS signal. The recorded data is evaluated by fitting a model for the NICE-OHMS signal to the data, with the concentration as free parameter. To quantify the absorption strength corresponding to this signal the peak absorption $\alpha_0$ (per unit length) is defined as the maximum $\alpha$ addressed by the laser (if only one absorption line is addressed $\alpha_0$ in general corresponds to the absorption at the transition center frequency). Two quantities appearing in the series expansions of NICE-OHMS signals are half of the cavity enhanced absorption, i.e. $F\alpha L/\pi$, and the single pass absorption, i.e. $\alpha_0 L = 2\delta$. These two quantities can be used to define the following absorption regimes:

- The weakest requirement is the linearity of Lambert-Beer law for a single pass absorption, which is valid under the ordinary weak absorption (OWA) condition (i.e. $\alpha_0 L \ll 1$). This condition usually can be fulfilled with available calibration gases. Therefore this condition is always considered to be valid.

- The next stronger condition is to keep the cavity enhanced absorption low, i.e. $F\alpha_0 L/\pi < 1$. This condition is referred to as the relaxed cavity-limited weak absorption (RCLWA)
condition. The latter can often be fulfilled by available calibration gases even for high finesse cavities.

- The strongest conditions is that the cavity enhanced absorption is significantly below unity, i.e. $F_α L / π \ll 1$. This condition is referred to as conventional cavity-limited weak absorption (CCLWA) condition. For high finesse cavities this condition is sometimes difficult to fulfill with calibration gases. However, for trace gas detection close to the detection limit it is in general fulfilled and allows for simple and fast data evaluation.

8.1.2 Expressions for NICE-OHMS signals under various absorption conditions

Since eq. (6.10) or, equivalently, eq. (38) in [4] do not make any assumptions regarding the absorption they can, in principle, be applied for any $α_0$. However, to calculate the transmission functions $\tilde{T}_c(ν_j)$ first the exact frequencies of the laser components $ν_j$, or alternatively the laser cavity detunings $ς_j$, need to be calculated.

The detunings are in turn obtained by solving the locking conditions given by eqs. (5.5) and (5.1). Since both equations depend on $ν_l$ and $ν_{fm}$, in the general case, they have to be solved as a system of equations. In publication IV three approaches to find the solutions are suggested:

- The first approach, referred to as the FULL solution, is to solve the system without major assumptions. The only assumption is that the analyte transfer functions, given by eq. (2.14), are approximately constant over the width and shifts of the cavity modes. However, since these equations are depending on the non-linear cavity reflection functions, $\tilde{R}_c$, they can only be solved numerically. Under the OWA condition the simplified cavity transfer function given in [4, eq. (27)] can be used to speed up the computation slightly. Using eqs. (6.1) and (6.2) as the locking condition makes the FULL solution valid for high modulation indices.
The second approach is referred to as extended locking and is valid under the relaxed cavity-limited weak absorption (RCLWA) condition (i.e. $F\alpha_0 L/\pi < 1$). Under this condition a second order approximation $\tilde{R}_c$ of the cavity reflection function can be used to derive an analytical solution for the locking conditions. Such a solution, valid for $\beta < 0.4$, is given by eqs. (57)-(60) in ref. [4].

Finally, under the CCLWA condition (i.e. $F\alpha_0 L/\pi \ll 1$), the $\tilde{R}_c$ function can be linearised which gives the simple linear locking conditions given by eqs. (6.6) and (6.7).

After the locking conditions are solved the solution (i.e. $\nu_l$ and $\nu_{fm}$) can be used to calculate the detunings, $\varsigma_j$, the cavity transmission functions for all laser components, and subsequently the NICE-OHMS signal using eq. (6.10). In our work we suggest four formalisms to calculate the NICE-OHMS signal.

- The FULL formalism uses the numerical solution of the FULL locking conditions together with the exact $\tilde{T}_c$ given by eq. (4.18). Since $\tilde{T}_c$ is an analytic function the computation time is small once the locking conditions were solved numerically. In publication V this formalism was verified to be valid up to $F\alpha_0 L/\pi \approx 3.5$. Taking into account a sufficiently large number of sidebands this formalism is also valid for high modulation indices.

- The extended-locking full-transmission (ELFT) formalism uses the extended locking condition, but still applies the exact $\tilde{T}_c$ to calculate the transmission. This saves significant amount of computation time since the NICE-OHMS signal can be given as an analytical expression. In publication V this formalism was verified to be valid up to $F\alpha_0 L/\pi \lesssim 0.5$.

- The extended-locking extended-transmission (ELET) formalism uses not only the extended locking condition, but also a second order approximation of the $T_c$. This allows for a single analytical expression of the NICE-OHMS signal given
Figure 8.1: NICE-OHMS signal recorded under different absorption conditions (circular markers) together with simulations using different NICE-OHMS formalisms (figure published in [5]). The narrow panels below the signals show the difference between the measured signal and the various models. Note the differences in scales. The FULL formalism (black) shows good agreement with measured NICE-OHMS signals even under the strongest absorption conditions.
in eq. (64) in [4]. The results in publication V suggest that the formalism is valid for $F\alpha_0L/\pi \lesssim 0.1$.

- The conventional (CONV) formalism uses linear approximation for the $\tilde{R}_c$ and $\tilde{T}_c$ functions. This gives the analytical expression given in eq. (6.11). This expression is valid solely up to $F\alpha_0L/\pi \lesssim 0.01$. Under this condition the NICE-OHMS signal is simply proportional to the analyte concentration. Furthermore the expression can be evaluated for arbitrary modulation indices by calculating sufficiently many terms of the series.

The signals for different $F\alpha_0L/\pi$ values, calculated according to these formalisms, are shown in figure 8.1 together with some measured signals. A detailed experimental study and discussion of the validity of different formalisms can be found in publication V.

8.1.3 Efficient computation of NICE-OHMS signals using the FULL formalism

To solve the system of locking equations for the FULL formalism a few things can be considered which make the computation faster. First it is important to consider that the dispersion and absorption response of the molecules can often be assumed to be approximately constant over the mode-width and over analyte induced mode-shifts. Under this condition it possible to calculate the analyte responses for each cavity mode frequency (i.e. $\phi_j$ and $\delta_j$) before solving the equation system. While for a low modulation index it is enough to consider $j = 0, \pm 1$, for a higher modulation index more sidebands need to be taken into account.

Next it is important to notice that the detuning between the laser components and the corresponding cavity modes, as defined in eq. (4.15), can be calculated in terms of the $v_{fsr}$ and the $v_{fm}$ by [eq. (29) in publication IV]
\[ \zeta_j = \phi_0 \nu_{\text{fsr}} / \pi + \zeta_0 + j \nu_{\text{fm}} - j \nu_{\text{fsr}} + \phi_j \nu_{\text{fsr}} / \pi \]
\[ = \phi_0 \nu_{\text{fsr}} / \pi + \zeta_0 + j \delta_{\text{fm}} + \phi_j \nu_{\text{fsr}} / \pi, \]

(8.1)

where we have defined the detuning of the modulation frequency from the FSR as \( \delta_{\text{fm}} = \nu_{\text{fm}} - \nu_{\text{fsr}} \). As discussed above a frequency detuning from a cavity resonance corresponds to a deviation of the single-pass phase shift from the \( \phi \) which fulfills the resonance condition (4.2). This additional single-pass phase shift corresponding to a detuning of \( \zeta_j \) is given by

\[ \psi_j = \frac{\pi}{\nu_{\text{fsr}}} \zeta_j \]

(8.2)

while the additional single pass phase shift that corresponds to a detuning of \( \delta_{\text{fm}} \) can be defined as

\[ \psi_{\text{fm}} = \frac{\pi}{\nu_{\text{fsr}}} \delta_{\text{fm}}. \]

(8.3)

By dividing eq. (8.1) by \( \nu_{\text{fsr}}/\pi \) one gets the detuning relation in terms of "off-resonance single-pass phase shifts" as follows

\[ \psi_j = \phi_0 + \psi_0 + j \psi_{\text{fm}} + \psi_j. \]

(8.4)

Using these expressions one can change the variables \( \nu_l \) and \( \nu_{\text{fm}} \) to \( \psi_0 \) and \( \psi_{\text{fm}} \). Then the equation system of eqs. (6.1) and (6.2) can be solved numerically with the starting values \( \psi_0 = \psi_{\text{mod}} = 0 \).

Since the PDH and DVB locking condition are only weakly coupled one can also iteratively solve eq. (6.1) using \( \psi_0 \) as free parameter and eq. (6.2) using \( \psi_{\text{fm}} \) as free parameter.

By applying eqs. (8.1–8.3) the resulting \( \psi_0 \) and \( \psi_{\text{fm}} \) can be used to calculate all \( \zeta_j \) which in turn can be inserted in eq. (4.18) for calculation of the NICE-OHMS signal by eq. (6.10).
8.2 NICE-OHMS SIGNALS FROM METHANE ISOTOPOLOGUES

When aiming for detection of methane isotopologues the first problem we had to address was that the strongest lines of CH$_4$ and $^{13}$CH$_4$ always appear as a group of three lines in close proximity separated by less than one GHz [65]. As can be seen in figure 8.2 for the case of $^{13}$CH$_4$ this implies that the Db NICE-OHMS signals from the transitions will overlap.

To evaluate overlapping signals from multiple lines by fitting a model function, it is necessary to accurately calibrate the frequency scale of the signal and to know the separation of the transition frequencies. As was discussed in publication III, for the latter the sub-Doppler NICE-OHMS response is the perfect tool. The signal from a sample of pure methane (black curve in figure 8.3) shows that at low pressure the line-centers of each transition can easily identified by the narrow sD response. The frequency spacing obtained by such a measurement can be used to model Db signals at higher pressures. One such example is shown in figure 8.2 (by the black curve), which is detected at 100 Torr (~20 ppb of $^{13}$CH$_4$ in ambient air sample) and therefore shows no sD response. The red curve shows a fit based on the frequency scaling obtained from the sD signals in figure 8.3. As can be seen the agreement is good.

The residual of the fits shown in the lower panels of figures 8.3 and 8.2 also visualize the main limitation of the system. As can be seen there is a narrow irregular structure in the background. We traced back the origin of this structure to the fiber amplifier before the OPO (see figure 7.1). The background structure carries also noise induced by the fan of the amplifier which presumably dominates the noise-level of the system. It is expected that an ongoing refurbishment of the fiber amplifier will significantly reduce this problem.
Figure 8.2: Dispersion NICE-OHMS signal of $^{13}$CH$_4$ in ambient air at a pressure of 100 Torr. The signal (black) is composed of three $^{13}$CH$_4$ transitions at 3.27 µm. The concentration was estimated by fitting a model function (red curve) to be of the order of the natural abundance of 20 ppb $^{13}$CH$_4$.

Figure 8.3: Dispersion NICE-OHMS signal of $^{13}$CH$_4$ pure CH$_4$ at a pressure of 1 mTorr. The signal (black curve) is composed of three $^{13}$CH$_4$ transitions at 3.27 µm each giving rise to a Db and a sD response. The sD responses are not included in the model function (red curve) and therefore dominate the residual (lower panel).
8.3 DEPLETION AND SATURATION OF METHANE SIGNALS

As discussed the $^{13}$CH$_4$ signals from ambient air recorded at an intra cavity power of 160 mW (black curve in figure 8.2) were in good agreement with the modeled signal (red curve). However, as is shown in figure 8.4, methane signals from strong transitions (black x markers) recorded with higher intra cavity power were not at all in agreement with conventional models (green curves). The signals were in particular around the center frequency of the transition up to 80% smaller than predicted. The signals showed the strongest distortion at pressures around 10 Torr. At such pressures traditional optical saturation (OS) models predict a deviation from non saturated signals below 0.1%. One reason for this failure of the commonly used OS model for NICE-OHMS is that this model was developed under the assumption of relatively low pressure, predominantly below 1 Torr [57]. In publication IX and manuscript X it was concluded that above 1 Torr significantly different decay and transport processes dominate the population of the laser addressed molecules. It was therefore found necessary to find a model for these processes which can describe saturation like effects for pressures above 1 Torr.

Traditional OS models often use the rate of collisions changing the rotational state of molecules as the decay rate. However, these rates are not always the bottleneck in the deexcitation process. It was found that in particular for methane in N$_2$ the vibrational deexcitation processes are exceptionally slow [92]. In manuscript X it was shown that for pressures above 1 Torr the exceptionally low vibrational decay rates are the main cause for the non-linearity of the absorption response. It was concluded that the laser depletes the population of the entire laser addressed vibrational ground state. This differs from conditions traditional OS models describe under which it can be assumed that molecules in non laser addressed states and velocity groups act as a reservoir in thermal equilibrium, i.e. that they reside in the vibrational ground state. It should be noted that the depletion of the vibrational ground state can be seen as a type of optical saturation that affects the entire vibrational levels. However, to make a
Figure 8.4: NICE-OHMS signals in dispersion phase (panel a) and absorption phase (panel b) from a CH$_4$ transition at 3.392 µm for a methane concentration of 0.5 ppm in neat N$_2$ at a pressure of 15 Torr and an intracavity power of 2300 mW (every 10th point marked by black cross markers) and simulated without and with depletion effects (green and yellow curves, respectively. The lower parts of the panels show the difference between the simulations (including the depletion effects) and the measurements. Figure and caption adapted from publication IX [9, Fig. 4].
clear distinction, we chose to refer to this phenomenon as *depletion* instead of "vibrational OS".

At low pressures, the transport of molecules in and out of the laser beam is often modeled as a given transit time (i.e. a constant for all pressures). However, for pressures above 1 Torr the transport needs to be described by a diffusion model (e.g. Fick’s law) that predicts that the effective velocity of the molecules decreases with increasing pressure. Therefore, the exchange rate at which excited molecules in the laser beam are replaced by molecules in thermal equilibrium outside the beam is expected to decrease with pressure. Furthermore, simulations of the spatial dependence of the population of the vibrational states showed that the molecules outside the beam can also not be assumed to serve as a reservoir in thermal equilibrium.

To mathematically describe the depletion phenomenon a rate equation system that includes a diffusion term describing a cylindrical cavity was set up [9, eq. 2]. The degree of depletion $\gamma$ was then defined as the relative decrease of the absorption signal as compared to a non-depleted signal (e.g. if the depleted signal is 80% smaller than the corresponding estimated signal without the depletion phenomenon $\gamma = 0.8$, if the depleted signal is zero $\gamma = 1$, and if the signal is not affected by depletion $\gamma = 0$). Using excitation, decay and diffusion rates from the literature the pressure dependence of the degree of depletion was simulated. The simulations showed a good qualitative agreement with experimental data in the pressure range between 1 and 100 Torr.

As can be seen in figure 8.5 the simulations (solid lines) show that in the low pressure regime the depletion increases with increasing pressure. The reason for this is that in this pressure regime the transport of excited molecules away from the laser beam is dominating the decay process. However, with increasing pressure the diffusion rate decreases. In the upper pressure range the simulations predict a slow decrease of the depletion with pressure. This is attributed to the increasing collisional induced decay rates which are dominating at higher pressures.

However, the first simulation results (not shown here) predicted a significantly lower degree of depletion than the measured va-
Figure 8.5: Degree of depletion $\gamma$ as a function of pressure for a mixture of 0.1 ppm methane with pure $N_2$ for a laser-analyte detuning $\Delta \nu$ of 190 MHz. The latter corresponds to the maximum of the NICE-OHMS dispersion response. All data was recorded under the same condition with the intracavity power of 2300 mW and retrieved by fitting of the dispersion NICE-OHMS signal (for detailed procedure see publication IX). The data points show the measured assessed degree of depletion for the three $CH_4$ transitions, E (black + markers), A (orange o markers) and F (green x markers). The curves close to the data points show simulations of the measurements in the corresponding color. Figure and caption adapted from publication IX [9, Fig. 4].
ules over the entire pressure range. A closer look at the ro-vibrational energy level structure presented in the literature revealed that the ensemble of all CH$_4$ molecules is split into three different nuclear spin isomers. The nuclear spin conversion rate is relatively low compared to the excitation and decay rates [93]. Furthermore, the ro-vibrational energy levels of the different nuclear spin isomers are not degenerate. Therefore, a narrow CW laser addresses only a single nuclear spin isomer when addressing a specific ro-vibrational transition. After taking this into account when calculating the absorption cross section for the addressed transition (and the corresponding nuclear spin isomer) the simulated depletion did not only fit qualitatively, but also quantitatively as shown in figure 8.5. To validate the model, transitions of different nuclear spin isomers were experimentally addressed (by the transitions referred to as E-, A$_2$- and F$_2$-transition in figure 8.5). The good agreement of the measurements with the simulations confirmed that the model works for all three isomers and that it is valid to assume that the laser only affects the population of the addressed isomer. Using the final model also the line shapes of the depleted NICE-OHMS signals could be modeled and showed a good agreement with the measured signals as can be seen by the yellow curve in figure 8.4.

Furthermore, both the experimental data as well as the simulations showed that the depletion is significantly less severe for methane measured in air [9, fig. 6]. The reason for this has been attributed to the significantly higher vibrational decay probability upon collisions with oxygen molecules compared to nitrogen. This result implies that the use of a calibration gas with significantly different composition than that of the gas sample of interest the accuracy of the obtained results can be affected when not taking into account the depletion.

We hope that the results of publication IX and manuscript X help to accurately analyze absorption based signals of methane and to choose suitable system parameters such as pressure, laser power and calibration gas composition to minimize the effect of depletion. It should be noted that for depletion below 0.1 the line shapes are only weakly distorted and the effect of depletion can
be easily overlooked while it still adds a significant error to the concentration assessment.


[42] Isak Silander, Patrick Ehlers, Junyang Wang, and Ove Axner. “Frequency modulation background signals from fiber-based electro optic modulators are caused by crosstalk.” In:


Patrick Ehlers, Isak Silander, Junyang Wang, and Ove Axner. “Fiber-laser-based noise-immune cavity-enhanced optical heterodyne molecular spectrometry instrumentation for Doppler-broadened detection in the 10^-12 cm^-1 Hz^-1/2


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Kirstin – *Es gibt keinen Weg zum Glück, Glück ist der Weg*¹ – Danke, dass du dein Glück mit mir teilst!

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¹ Buddha
Part III

PUBLICATIONS

One never notices what has been done; one can only see what remains to be done.

Marie Curie
CONTRIBUTION REMARKS

PUBLICATION I

Doppler-broadened mid-infrared noise-immune cavity-enhanced optical heterodyne molecular spectrometry based on an optical parametric oscillator for trace gas detection
Silander I., Hausmaninger T., Ma W., Harren F. J. M., and Axner O.

In this work an optical parametric oscillator (OPO) was used to realize a NICE-OHMS system for addressing strong fundamental vibrational transitions in the mid infrared (MIR). A white noise equivalent absorption limit (WNEAL) of $3 \times 10^{-9} \text{ cm}^{-1}\text{Hz}^{-1/2}$ was demonstrated.

I constructed the MIR cavity. I worked out and implemented the conditions for mode matching and alignment of the MIR laser beam from the OPO to the cavity. I optimized the locking electronics for the system and performed the measurements presented. I took part in the writing and the internal revision processes.

was assessing the performance of the system and taking the measurements included in this publications. I was optimizing .

PUBLICATION II

Narrowing of the linewidth of an optical parametric oscillator by an acousto-optic modulator for the realization of mid-IR noise-immune cavity-enhanced optical heterodyne molecular spectrometry down to $10^{-10} \text{ cm}^{-1}\text{Hz}^{-1/2}$
Hausmaninger T., Silander I., Axner O.
Optics Express (2015) Vol. 23, pp. 33641-33655

In this work a new cavity with a finesse of 4000 and an acousto-optic modulator (AOM) was implemented in the OPO based
NICE-OHMS system developed in publication I. A WNEAL of $2.4 \times 10^{-10} \text{ cm}^{-1} \text{ Hz}^{-1/2}$ was demonstrated allowing for detection of methane and its two main isotopologues ($^{13}\text{CH}_4$ and $\text{CH}_3\text{D}$) at their natural abundance. Furthermore a novel servo design for active stabilization of the laser PZT resonance was suggested and implemented.

I was in charge of this project and was redesigning the system presented in publication I. I conducted the experimental implementation. In particular, I constructed the high-finesse cavity, implemented the AOM, and I designed and implemented the servo electronics for locking the laser to the high-finesse cavity. I took the measurements presented in the work. I wrote the major part of the manuscript.

**Publication III**

**Doppler-broadened mid-infrared noise-immune cavity-enhanced optical heterodyne molecular spectrometry based on an optical parametric oscillator**

Hausmaninger T., Silander I., Axner O.

*Imaging and Applied Optics 2016, OSA technical Digest (online) (2016), paper LT2G.2*

In this peer reviewed conference paper the acquisition rate was increased to above 7 Hz by implementation of a feed forward circuit. The first results of isotopologue measurements from the system developed in publication I and II were presented and

I was in charge of this project and was redesigning the system. I suggested and implemented the feed forward circuit for increasing the acquisition rate. I performed all measurements. I wrote the major part of the manuscript.

**Publication IV**

**Doppler-broadened NICE-OHMS beyond the cavity-limited weak absorption condition – I. Theoretical description**

Ma W., Silander I., Hausmaninger T., Axner O.
This work presents a theoretical derivation of NICE-OHMS signals under the conditions when the cavity enhanced absorption can not be considered small, i.e. when $F \alpha_0 L / \pi \ll 1$. The origin of the NICE-OHMS signal and the influence of the laser-cavity locking was scrutinized. Expressions with different levels of approximations were presented.

I was contributing to the development of the theoretical descriptions and involved in all discussions about the implications of the formalism. I was strongly involved in the writing and the internal revision processes.

**Publication V**

**Doppler-broadened NICE-OHMS beyond the cavity-limited weak absorption condition – II: Experimental verification**

**Hausmaninger T., Silander I., Ma W., Axner O.**


This work experimentally verifies the theoretical descriptions presented in publication IV. The validity of various simplified formalisms was studied for various absorption conditions.

I was in charge of planning of the experiments and the data analysis. I was responsible for the comparison between experimental results and the simulations based on the theoretical descriptions developed in publication IV. I was in charge of writing the manuscript in close collaboration with the co-Authors.

**Publication VI**

**Whispering-gallery-mode laser-based noise-immune cavity-enhanced optical heterodyne molecular spectrometry**

**Zhao G., Hausmaninger T., Ma W., and Axner O.**

In this work a compact whispering-gallery-mode laser (WGML) was implemented utilizing parts of an existing NIR-NICE-OHMS system originally based on an erbium-doped fiber laser (EDFL). The NEAL for the optimum integration time of 150 s was determined to be $6.6 \times 10^{-14} \text{ cm}^{-1}$.

I was consulted for the replacing the fiber-laser and the implementation of the WGML in the existing system. I was suggesting the implementation of a digitally generated feed forward signal with addition of a second harmonic component to increase the scan range and rate. I took part in the writing and internal revision processes.

**Publication VII**

**Differential noise-immune cavity-enhanced optical heterodyne molecular spectroscopy for improvement of the detection sensitivity by reduction of drifts from background signals**

Zhao G., Hausmaninger T., Ma W., and Axner O.

*Optics Express* (2017) Vol. 25, pp. 29454-29471

In this work a novel realization of NICE-OHMS, termed differential NICE-OHMS was presented and demonstrated utilizing an existing EDFL based NIR NICE-OHMS system. The work includes a description of the NICE-OHMS signal detected in cavity reflection and its relation to the signal detected in transmission. It was shown that differential NICE-OHMS both reduces background drifts and enhances the molecular signal. The NEAL for the optimum integration time of 170 s was determined to be $4.7 \times 10^{-14} \text{ cm}^{-1}$.

I contributed to the development of the theoretical description of the reflection and differential NICE-OHMS signal and their relation to the (conventional) transmission NICE-OHMS signal. I was strongly involved in the writing and the internal revision processes.
Publication VIII

Shot-noise-limited Doppler-broadened noise-immune cavity-enhanced optical heterodyne molecular spectrometry
Zhao G., Hausmaninger T., Ma W., and Axner O.

In this work a balanced detection scheme was implemented in an existing EDFL based NIR NICE-OHMS system. It was demonstrated that this can reduce the in-coupling of noise and background signals into the NICE-OHMS signal. It was verified that the resulting NICE-OHMS realization was shot-noise limited in the Db mode of detection.

I was involved in the discussions around the paper. I took part in the writing process and the internal revision processes.

Publication IX

Depletion of the vibrational ground state of CH₄ in absorption spectroscopy at 3.4 μm in N₂ and air in the 1–100 Torr range
Hausmaninger T., Zhao G., Ma W., Axner O.

In this work an experimental study of the depletion of the vibrational ground state when methane (CH₄) is addressed with laser in absorption spectroscopy in the 1-100 Torr range was presented. For this the OPO based NICE-OHMS system developed in the Publications I-III was utilized. The resulting distortion of the absorption line shape was measured under various conditions and for different gas mixtures. The experimental results were compared with the model that was presented in detail in manuscript X. It was shown that the model can predict the experimental results qualitatively and quantitatively under various conditions.

I was in charge of this project, conducting the experimental work as well as developing the theoretical model described in manuscript X. I wrote the major part of the manuscript.
Model for molecular absorption spectroscopy in the 1-100 Torr range in the presence of vibrational depletion
Hausmaninger T., Ma W., Axner O.
in manuscript

In this work a model for depletion of the vibrational ground state when methane (CH$_4$) is addressed with laser absorption spectroscopy in the 1-100 Torr range was presented. The dominating excitation and decay process were identified and included in the model. It was shown that the spatial diffusion of excited molecules is a strongly pressure dependent component of the decay process. It was predicted that under trace gas conditions the laser primarily affects only the populations of the nuclear spin isomer addressed by the laser.

I was in charge of this project. I was developing the theoretical model and performing the simulations. I wrote the major part of the manuscript.

High resolution ultra-sensitive trace gas detection by use of cavity-position-modulated sub-Doppler NICE-OHMS
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in manuscript

In this work sub Doppler (sD)-NICE-OHMS based trace gas detection of acetylene (C$_2$H$_2$) in breath samples was presented. For this an existing EDFL based NIR NICE-OHMS system was adapted. It was shown that the C$_2$H$_2$ signals can be detected in breath by sD NICE-OHMS despite a strong background from an interfering CO$_2$ line. To reduce the influence of background signals on the sD signals the balanced detection scheme presented in publication VIII was combined with a novel cavity position modulation technique. A procedure was worked out for simultaneous assessment of the CO$_2$ concentration. The 3$\sigma$ concentration detection limit (CDL) for C$_2$H$_2$ was assessed to be 130 ppt.
I was consulted for details in the experimental realization. I was suggesting the cavity position modulation for reduction of background signals. I was suggesting the procedure for the simultaneous assessment of the CO$_2$ concentration. I was strongly involved in the writing and the internal revision processes.