Fiber-laser-based Noise-Immune Cavity-Enhanced Optical Heterodyne Molecular Spectrometry

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In memory of my Brother
Abstract

Noise-immune cavity-enhanced optical heterodyne molecular spectroscopy (NICE-OHMS) is one of the most sensitive laser-based absorption techniques. The high sensitivity of NICE-OHMS is obtained by a unique combination of cavity enhancement (for increased interaction length with a sample) with frequency modulation spectrometry (for reduction of noise). Moreover, sub-Doppler detection is possible due to the presence of high intensity counter-propagating waves inside an external resonator, which provides an excellent spectral selectivity. The high sensitivity and selectivity make NICE-OHMS particularly suitable for trace gas detection. Despite this, the technique has so far not been often used for practical applications due to its technical complexity, originating primarily from the requirement of an active stabilization of the laser frequency to a cavity mode.

The main aim of the work presented in this thesis has been to develop a simpler and more robust NICE-OHMS instrumentation without compromising the high sensitivity and selectivity of the technique. A compact NICE-OHMS setup based on a fiber laser and a fiber-coupled electro-optic modulator has been constructed. The main advantage of the fiber laser is its narrow free-running linewidth, which significantly simplifies the frequency stabilization procedure. It has been demonstrated, using acetylene and carbon dioxide as pilot species, that the system is capable of detecting relative absorption down to $3 \times 10^{-9}$ on a Doppler-broadened transition, and sub-Doppler optical phase shift down to $1.6 \times 10^{-10}$, the latter corresponding to a detection limit of $1 \times 10^{-12}$ atm of C$_2$H$_2$. Moreover, the potential of dual frequency modulation dispersion spectrometry (DFM-DS), an integral part of NICE-OHMS, for concentration measurements has been assessed.

This thesis contributes also to the theoretical description of Doppler-broadened and sub-Doppler NICE-OHMS signals, as well as DFM-DS signals. It has been shown that the concentration of an analyte can be deduced from a Doppler-broadened NICE-OHMS signal detected at an arbitrary and unknown detection phase, provided that a fit of the theoretical lineshape to the experimental data is performed. The influence of optical saturation on Doppler-broadened NICE-OHMS signals has been described theoretically and demonstrated experimentally. In particular, it has been shown that the Doppler-broadened dispersion signal is unaffected by optical saturation in the Doppler limit. An expression for the sub-Doppler optical phase shift, valid for high degrees of saturation, has been derived and verified experimentally up to degrees of saturation of 100.
Sammanfattning

Brusimmun kavitetsförstärkt optisk-heterodyndetekterad molekylärspektrometri, NICE-OHMS (eng. noise-immune cavity-enhanced optical heterodyne molecular spectrometry), är en av de känsligaste laserbaserade absorptions teknikerna. Den höga känsligheten hos NICE-OHMS-tekniken uppkommer genom en unik kombination av kavitetsförstärkning (för ökad interaktionslängd med gasen) och frekvensmodulationspektrometri (för reduktion av brus). Tack vare närvaron av vågor med hög intensitet som propageras i motsatta riktningar ger tekniken även möjligheter till Dopplerfri detektion, vilket ger den en utmärkt spektral selektivitet. Trots detta har tekniken ännu inte använts i någon högre grad för praktiska tillämpningar, huvudsakligen på grund av dess tekniska komplexitet, framförallt förändrat av ett krav på en aktiv stabilisering (läsning) av laserns frekvens till en kavitetsmod.

Huvudsyften med det arbete som presenteras i denna avhandling har varit att vidareutveckla NICE-OHMS-tekniken mot en enklare och mer robust konstruktion, utan att försämra dess höga känslighet och selektivitet. En kompakt NICE-OHMS-instrumentering baserad på en fiberlaser och en fiberkopplad elektrooptisk modulator har konstruerats. Den främsta fördelen med den använda fiberlasern är dess mycket små linjebredd som avsevärt har förenklat dess läsning till en kavitetsmod. Mätningar har utförts på acetylen och koldioxid och det har visats att instrumenteringen kan mäta en relativ absorption ner till $3 \times 10^{-9}$ på en Dopplerbreddad övergång och en optisk fasförskjutning ner till $1,6 \times 10^{-10}$ på en Dopplerfri övergång, där det senare motsvarar en detektionsgräns på $1 \times 10^{-12}$ atm C$_2$H$_2$. Dessutom har potentialen av dubbelt frekvensmodulerad dispersionsspektrometri, DFM-DS (eng. dual frequency modulation dispersion spectrometry), som är en integrerad del av NICE-OHMS, för koncentrationsmätningar av gaser undersöks.

List of publications

This thesis is based on the following publications:

I  Fiber-laser-based noise-immune cavity-enhanced optical heterodyne molecular spectrometry for Doppler-broadened detection of $C_2H_2$ in the parts per trillion range.
   F. M. Schmidt, A. Foltynowicz, W. Ma, and O. Axner

II  Doppler-broadened fiber-laser-based NICE-OHMS - Improved detectability.
    F. M. Schmidt, A. Foltynowicz, W. Ma, T. Lock, and O. Axner

III  Theoretical description of Doppler-broadened noise-immune cavity-enhanced optical heterodyne molecular spectroscopy under optically saturated conditions.
     W. Ma, A. Foltynowicz, and O. Axner

IV  Doppler-broadened noise-immune cavity-enhanced optical heterodyne molecular spectroscopy signals from optically saturated transitions under low pressure conditions.
    A. Foltynowicz, W. Ma, F. M. Schmidt, and O. Axner

V  Sub-Doppler dispersion and noise-immune cavity-enhanced optical heterodyne molecular spectroscopy revised.
   O. Axner, W. Ma, and A. Foltynowicz

VI  Noise-immune cavity-enhanced optical heterodyne molecular spectroscopy: Current status and future potential.
    A. Foltynowicz, F. M. Schmidt, W. Ma, and O. Axner

VII Characterization of fiber-laser-based sub-Doppler NICE-OHMS for trace gas detection.
    A. Foltynowicz, W. Ma, and O. Axner
VIII  Wavelength modulated noise-immune cavity-enhanced optical heterodyne molecular spectroscopy signal line shapes in the Doppler limit.
A. Foltynowicz, W. Ma, F. M. Schmidt, and O. Axner

IX  Probing the free spectral range of an optical cavity using dual-frequency modulation: highly sensitive dispersion spectroscopy of C₂H₂.
F. M. Schmidt, W. Ma, A. Foltynowicz, and O. Axner
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Other publications by the author, not included in the thesis:

X  Absorption spectrometry by narrowband light in optically saturated and optically pumped collision and Doppler broadened gaseous media under arbitrary optical thickness conditions.
O. Axner, F. M. Schmidt, A. Foltynowicz, J. Gustafsson, N. Omenetto, and J. D. Winefordner
Appl. Spectrosc. 60, 1217-1240 (2006)

XI  Wavelength modulation absorption spectrometry from optically saturated collision-broadened transitions.
F. M. Schmidt, A. Foltynowicz, M. Gustafsson, and O. Axner

XII Wavelength modulation absorption spectrometry from optically pumped collision broadened atoms and molecules.
A. Foltynowicz, F. M. Schmidt, J. Gustafsson, and O. Axner
Abbreviations

AS absorption spectrometry
BP band pass
CE cavity enhanced
CEAS cavity enhanced absorption spectrometry
CRDS cavity ringdown spectroscopy
cw continuous wave
DAS direct absorption spectrometry
DB Doppler-broadened
DBM double balanced mixer
DC direct current
DFM-DS dual frequency modulation dispersion spectrometry
EDFL erbium-doped fiber laser
EOM electro-optic modulator
FM frequency modulated
FMS frequency modulation spectrometry
FP Fabry-Perot
FSR free spectral range
HWHM half-width at half maximum
ICOS integrated cavity output spectroscopy
KK Kramers-Kronig (relations)
LP low pass
OI optical isolator
PBS polarizing beam splitter
PD photodetector
PDH Pound-Drever-Hall
Ph phase shifter
PM polarization maintaining
PZT piezoelectric transducer
RF radio frequency
sD sub-Doppler
TEM transverse electromagnetic mode
VA variable attenuator
VCO voltage controlled oscillator
WM wavelength modulated
WMS wavelength modulation spectrometry
Symbols

\( B_p \) pressure broadening coefficient \([\text{Hz/ atm}]\)
\( c \) speed of light in vacuum \([\text{m/s}]\)
\( c_{\text{rel}} \) relative concentration of an analyte
\( e \) electronic charge \([\text{C}]\)
\( E \) real electric field \([\text{V/m}]\)
\( \hat{E} \) complex electric field \([\text{V/m}]\)
\( \hat{E}_A \) electric field transmitted through an analyte \([\text{V/m}]\)
\( \hat{E}_{\text{inc}} \) electric field incident on a FP cavity or an analyte \([\text{V/m}]\)
\( \hat{E}_r \) electric field reflected from a FP cavity \([\text{V/m}]\)
\( \hat{E}_t \) electric field transmitted through a FP cavity \([\text{V/m}]\)
\( E_o \) electric field amplitude \([\text{V/m}]\)
\( f \) Fourier frequency \([\text{Hz}]\)
\( \Delta f \) electronic bandwidth \([\text{Hz}]\)
\( F \) cavity finesse

\( F_{\text{SR}} \) free spectral range of a FP cavity \([\text{Hz}]\)
\( G \) degree of saturation
\( G_0 \) degree of saturation induced by the carrier of an FM triplet
\( G_{\pm 1} \) degree of saturation induced by a sideband of an FM triplet
\( h \) Planck constant \([\text{J—s}]\)
\( I \) intensity \([\text{W/m}^2]\)
\( I_A \) intensity of light transmitted through an analyte \([\text{W/m}^2]\)
\( I_c \) intracavity intensity \([\text{W/m}^2]\)
\( I_r \) intensity of light reflected from a FP cavity \([\text{W/m}^2]\)
\( I_{\text{sat}} \) saturation intensity \([\text{W/m}^2]\)
\( I_t \) intensity of light transmitted through a FP cavity \([\text{W/m}^2]\)
\( I_{\text{t}}^{\text{0}} \) intensity transmitted through a FP cavity on resonance \([\text{W/m}^2]\)
\( I_o \) intensity of light incident on an analyte or a FP cavity \([\text{W/m}^2]\)
\( I'_{\nu m} \) component of intensity at frequency \( \nu_m \) \([\text{W/m}^2]\)
\( k_o \) wave vector in vacuum \([\text{1/m}]\)
\( k_B \) Boltzmann constant \([\text{J/K}]\)
\( l \) mirror losses
\( L \) interaction length or cavity length \([\text{cm}]\)
\( n \) intracavity refractive index
\( n \) complex refractive index
\( n_A \) molecular density \([\text{molecules/cm}^3]\)
\( n_e \)  
refractive index for extraordinary wave

\( n_o \)  
refractive index for ordinary wave

\( p \)  
total gas pressure inside the cavity [atm]

\( P \)  
power [W]

\( P_c \)  
intracavity power [W]

\( P_{sat} \)  
saturation power [W]

\( P^0 \)  
power transmitted through a FP cavity on resonance [W]

\( P_o \)  
power incident on a detector in the absence of an analyte [W]

\( q \)  
cavity mode number

\( r \)  
mirror reflection coefficient

\( R^c \)  
cavity reflection (intensity)

\( \bar{R}^c \)  
complex cavity reflection function

\( R^c_A \)  
complex cavity reflection function in the presence of an analyte

\( R^c_{res} \)  
on-resonance cavity reflection (for intensity)

\( S \)  
transition line strength [cm\(^2\)/atm]

\( \dot{S} \)  
molecular transition line strength [cm\(^3\)/molecule/cm\(^2\)]

\( S^{in} \)  
signal at a frequency \( v_m \) [V]

\( S^{DB}_o \)  
unsaturated \( fm \)-NICE-OHMS signal strength [V]

\( t \)  
mirror transmission coefficient

\( \bar{T}^A \)  
complex transmission function of an analyte

\( T^c \)  
cavity transmission (intensity)

\( \bar{T}^c \)  
complex cavity transmission function

\( \bar{T}^c_A \)  
complex cavity transmission function in the presence of an analyte

\( T^c_{res} \)  
on-resonance cavity transmission (for intensity)

\( T_K \)  
temperature [K]

\( u \)  
most probable molecular velocity in Maxwellian distribution [m/s]

\( u_z \)  
molecular velocity in the z direction [m/s]

\( w \)  
Gaussian beam spot size [m]

\( w_{waist} \)  
minimum spot size of a Gaussian beam (at beam waist) [m]

\( x \)  
Doppler-width-normalized detuning

\( y \)  
Doppler-width-normalized saturated homogenous linewidth

\( y_0 \)  
Doppler-width-normalized homogenous linewidth

\( \alpha \)  
absorption

\( \alpha_{res} \)  
on-resonance absorption

\( \beta \)  
FM modulation index

\( \beta_1 \)  
FM modulation index at \( V_{fsr} \)

\( \beta_2 \)  
FM modulation index at \( V_{pdh} \)
\( \gamma_{tt} \) transit time broadening [s\(^{-1}\)]
\( \gamma_{12} \) decay rate of a dipole moment [s\(^{-1}\)]
\( \Gamma_c \) cavity mode width [Hz]
\( \Gamma_D \) Doppler half width at half maximum [Hz]
\( \Gamma_L \) homogenous linewidth [Hz]
\( \delta \) attenuation of electric field due to an analyte
\( \varepsilon_o \) electric permittivity of free space \([C^2\cdot s^{-2}\cdot kg^{-1}\cdot m^{-3}]\)
\( \eta_c \) detector current responsivity [A/W]
\( \theta_{fm} \) FM detection phase
\( \kappa \) intracavity power/intensity buildup
\( \lambda \) wavelength of light [m]
\( \mu \) transition dipole moment \([C\cdot m, mD]\)
\( \nu \) optical frequency [Hz]
\( \nu_a \) WM modulation amplitude [Hz]
\( \nu_c \) laser carrier frequency [Hz]
\( \nu_{fsr} \) FM modulation frequency for NICE-OHMS detection [Hz]
\( \nu_m \) general modulation frequency [Hz]
\( \nu_{pdh} \) FM modulation frequency for PDH locking [Hz]
\( \nu_q \) frequency of the \( q \)th longitudinal mode [Hz]
\( \nu_{qmn} \) frequency of a transverse cavity mode [Hz]
\( \nu_0 \) transition resonance frequency [Hz]
\( \Delta \nu \) laser (carrier) frequency detuning from the transition resonance [Hz]
\( \Delta \nu_q \) laser frequency detuning from the center of the \( q \)th cavity mode [Hz]
\( \Delta \rho_{11,22} \) difference in relative thermal population
\( \tau_{cav} \) cavity decay time [s]
\( \phi \) double-pass optical phase shift inside a FP cavity
\( \phi_{pp} \) phase shift of electric field due to an analyte
\( \phi_{00} \) peak-to-peak value of sub-Doppler optical phase shift
\( \chi \) complex susceptibility
\( \chi_{abs} \) area-normalized absorption lineshape function [cm]
\( \chi_{disp} \) dispersion lineshape function [cm]
\( \chi_{abs}^{peak} \) peak-normalized absorption lineshape function
\( \chi_{disp}^{peak} \) dispersion counterpart of peak-normalized absorption function
\( \chi_{abs}^{n} \) \( n \)th Fourier coefficient of the absorption lineshape function [cm]
\( \chi_{disp}^{n} \) \( n \)th Fourier coefficient of the dispersion lineshape function [cm]
\( \chi^0 \) peak value of the area-normalized lineshape function [cm]
\( \chi^0 \) peak value of the area-normalized Gaussian function [cm]
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1. Introduction

Laser-based absorption spectrometry (AS) is a well established and useful technique for detection and studies of atoms and molecules in gas phase. Although it is not the most sensitive of laser-based techniques (it cannot, for example, detect the presence of a single atom or molecule), its advantage over other laser-based techniques, e.g. fluorescence or ionization spectroscopy, is that it allows for quantitative measurements, e.g. an accurate assessment of the concentration of an analyte. In addition, since the signal is carried along the line of sight, measurements can be performed over very long paths.

The basic principle of AS is the Lambert–Beer law, which states that the intensity of a monochromatic electromagnetic field resonant with an atomic or molecular transition propagating through a gas of absorbers decreases exponentially, and that the exponent is proportional to the density of absorbers, the transition line strength and the interaction length [1]. The simplest absorption technique, referred to as direct absorption spectrometry (DAS), relies on a measurement of the relative absorption. The sensitivity (or detectability) of the technique, defined as the smallest relative absorption (or concentration) of the analyte that can be detected, is limited by the fact that a small signal has to be measured on top of a large background and is most often in the $10^{-3}$ range. This is far from enough for most applications and also far from the theoretical limit set by the shot noise, which is in the $10^{-8} - 10^{-7}$ range [2]. Moreover, transitions have a finite width, determined by the dominating type of broadening. Although each molecule has a unique spectrum, the transitions of different molecules might partly overlap, i.e., the center frequencies of transitions of different molecules might be separated by less than their width. The spectral selectivity of DAS performed under atmospheric pressure conditions is therefore limited by the collision broadening of transitions.

There is a constant strive for increasing the sensitivity and selectivity of absorption techniques. The latter can be improved by reducing the pressure of the sample and thus the collision broadening of the transition. This methodology works well until the broadening is reduced to the so-called Doppler limit, in which the width of the transition is determined by the thermal molecular velocity distribution. For further improvement sub-Doppler techniques have to be used, in which a single velocity group of molecules is addressed by two counter-propagating waves.

The sensitivity of AS is limited by the noise in the system. The dominating type of noise in DAS is the technical noise, e.g., noise of mechanical origin or laser intensity noise, which usually decreases with frequency. The noise in the system can therefore be reduced by shifting the detection to higher
frequencies. This is done by the use of modulation techniques, in which the information about the concentration of the analyte is encoded and detected at some higher frequency. There are two main types of modulation techniques, which differ by the frequency and amplitude of the modulation used.

In frequency modulation spectrometry (FMS) the phase of the light is modulated at a radio frequency (RF) with a small modulation index. As a result a pair of sidebands separated from the carrier by the modulation frequency appears, forming, together with the carrier, an FM triplet [3]. When FM light is incident on a detector, the three frequency components interfere with each other, creating beat signals at the modulation frequency, a process referred to as optical heterodyning. The two beat signals cancel in the absence of an analyte, whereas in the vicinity of a transition the balance of the FM triplet is disturbed and a net signal at the modulation frequency appears. Thus the technique is background free. Another advantage of FMS is that the modulated intensity carries information not only about the absorption of the light by the analyte, but also about the dispersion.

In wavelength modulation spectrometry (WMS) the frequency of the light is modulated at an audio frequency with an amplitude of the order of the transition linewidth [4]. In the absence of an analyte the intensity of the wavelength modulated light is constant. However, in the presence of a nonlinear absorber signals at various overtones of the modulation frequency appear. Although the analytical signal can be detected at any harmonic of the modulation frequency, the second harmonic is most often used.

Since the two modulation techniques are in principle background free, their sensitivity comes closer to the shot noise limit (which is similar to that of DAS). In practice, however, their sensitivity is in the $10^6 - 10^5$ range [2], limited by background signals originating from residual amplitude modulation (from the laser intensity modulation or from multiple reflections between optical surfaces, i.e., the so-called etalons). The modulation techniques are also not calibration free.

An alternative way to improve the sensitivity is to make the analytical signal larger. In order to do that one should, first of all, choose a transition with a large line strength. However, the choice is often dictated by the available laser sources. The strongest molecular transitions, between electronic states, lie in the ultraviolet wavelength range, where so far only a few tunable continuous wave (cw) lasers suitable for AS are available [5]. The fundamental vibrational transitions, whose line strengths are a few orders of magnitude smaller, lie in the mid-infrared wavelength range [6], corresponding to the working range of quantum cascade lasers, whose development has been rapid only recently. The most widely available lasers, distributed feedback (DFB) diode lasers in the telecom range around 1.5 $\mu$m,
can address the overtone transitions [6], which, in turn, are two or more orders of magnitude weaker than the fundamental vibrational transitions [1]. The lower part of the near-infrared range corresponds to even higher overtones, and thus even weaker transitions.

A more universal way to increase the signal size is to make the interaction path longer. This can most efficiently be done by placing the absorbing sample inside a multi-pass cell (either of White [7] or Herriott [8] type) or a resonant cavity (e.g. a Fabry-Perot cavity [9, 10]), in which the light travels many times back and forth between mirrors, thus interacting with the sample over a distance significantly longer than the physical length of the cavity. The multi-pass cells can enhance the signal by one or two order of magnitude, while a much larger enhancement, up to 5 orders of magnitude (given by $2F/\pi$, where $F$ is the finesse of the cavity, which can be as high as $10^4 - 10^5$), can be obtained with resonant cavities. Moreover, due to the presence of high intensity counter-propagating waves, a resonant Fabry-Perot (FP) cavity can provide conditions for sub-Doppler detection.

The transmission of light through a resonant cavity has a comb-like spectrum with longitudinal modes separated by the free spectral range (FSR, given by $c/2L$, where $c$ is the speed of light and $L$ is the cavity length). The width of the transmission modes is given by the ratio of the FSR and the finesse and is in the tens of kHz range for a high finesse cavity. This is less than the free-running linewidth of most tunable lasers, which makes continuous coupling of the laser power into the cavity problematic unless active stabilization of laser frequency is implemented.

There are a few types of cavity enhanced (CE) techniques, in which either the intracavity absorption or the cavity decay time are measured [11]. In the latter type, referred to as cavity ringdown spectrometry (CRDS), a pulse of light shorter than the cavity round trip time is injected into the cavity and the decay time is measured with and without the absorber or at two wavelengths, on and off resonance [12, 13]. CRDS can also be realized with the use of cw lasers, whose radiation is interrupted [14, 15] or whose frequency is rapidly scanned across the cavity mode [16, 17]. The foremost advantage of CRDS is that it is independent of laser amplitude noise and that no mode matching is needed. Sensitivities in the $10^{-8}$ range are routinely obtained [11, 18] but the technique is often limited by drifts in the system between two consecutive measurements [19].

Another approach is used in integrated cavity output spectrometry (ICOS), in which the cavity length and/or the laser frequency are dithered on a time scale much faster than the typical time for scanning across the absorption profile in order to randomize the input coupling of the light into the cavity, while the cavity output is integrated over a time longer than the dithering time but shorter than the sweep time [20]. In off-axis ICOS the
frequency dependence of the cavity transmission is reduced further by coupling the laser light to the cavity at an angle to the main axis, in order to induce many transverse modes, whose spacing is comparable to their width \([21]\). Both methods are, in general, limited by a low cavity transmission and a fluctuating coupling efficiency, and typically reach sensitivities in the \(10^{-7}\) range.

Yet another group of CE techniques is based on a *continuous coupling* of laser light into the cavity, which can be achieved by an active stabilization of the laser frequency to one of the cavity modes, either by electronic \([22-25]\) or optical feedback \([26]\). Cavity enhanced absorption spectrometry (CEAS) with optical feedback is capable of reaching sensitivities in the \(10^{-8}\) range, limited by parasitic interference fringes \([27]\). The electronically locked continuous wave CEAS can be used for highly sensitive sub-Doppler absorption spectroscopy \([22-24]\). However, any remaining laser frequency noise relative to the cavity mode is converted to amplitude noise in the transmitted light, which impairs the detectability. Due to the lack of noise reduction schemes, the shot noise limit, which is orders of magnitude below that of ordinary DAS, and can be as low as \(~10^{-13}\) \([2, 13]\), is usually not reached in locked CEAS techniques.

The most sensitive absorption technique is noise-immune cavity-enhanced optical-heterodyne molecular spectrometry (NICE-OHMS), which combines cavity enhancement with frequency modulation spectrometry. In NICE-OHMS the laser carrier frequency is locked to a cavity mode, while the modulation frequency is matched to the cavity *FSR*. In this configuration all components of the FM triplet are transmitted through the cavity in the same way and the balance of the triplet is undisturbed by any residual frequency noise of the laser with respect to the cavity mode. Thus the technique is immune to laser frequency noise, which implies that FMS can be performed inside the cavity as if the cavity was not present, yet fully benefiting from the increased interaction length. A WM dither is often additionally applied in order to remove any low frequency noise remaining after the FM demodulation process.

The history of NICE-OHMS is rather short. The technique was developed in the mid-90's at the Joint Institute for Laboratory Astrophysics (JILA), in Boulder, CO, by John L. Hall, Long-Sheng Ma, and Jun Ye. The aim was to create a technique with a high sensitivity that could be used to detect long-lived (and thereby narrow) molecular overtone transitions in the visible and near-infrared range for high precision frequency standard applications using sub-Doppler spectroscopy \([28]\). It has been demonstrated that NICE-OHMS performed with fixed-frequency lasers is capable of detecting relative absorption down to \(10^{-13}\), close to the shot noise limit, inside a cavity with a finesse of 100 000 \([2]\). A number of papers has been published by the group,
concerned mostly with application of NICE-OHMS to sensitive detection of sub-Doppler signals from C$_2$HD, C$_2$H$_2$, CO$_2$ for frequency standard applications at around 1 µm [2, 29-32]. A detailed description and summary of the achievements of the JILA group is presented in the doctoral thesis of Jun Ye [33]. After the first realization of the technique, NICE-OHMS has been performed only by a handful of research groups. Sub-Doppler NICE-OHMS has been used for high resolution spectroscopy of CH$_4$ and CH$_3$I in the 1630-1670 nm range [34, 35], for spectroscopic investigations of weak transitions of $^{13}$C$_2$H$_2$ in the 730-830 nm region [36], and for chemical sensing of N$_2$O at 8.5 µm [37]. Doppler-broadened NICE-OHMS was first performed on O$_2$ at 776 nm [38] and has been later used for measurements of O$_2$ at cryogenic temperatures at 761 nm [39], studies of ultraweak transitions of O$_2$ at 771 nm [40, 41], and of the sixth overtone band of NO at 797 nm [42, 43]. A more detailed summary of all works in the field of NICE-OHMS is given in paper VI in this thesis [44].

Although all realizations of NICE-OHMS have proven that the technique is capable of reaching very high sensitivities even with tunable laser sources (in the $10^{-9} - 10^{-8}$ range for Doppler-broadened detection, and in the $10^{-11} - 10^{-10}$ range for sub-Doppler measurements), NICE-OHMS has so far not been widely used for practical applications due to its technical complexity. The main constraint has been the requirement of an active stabilization of the laser frequency to a cavity mode. Although the requirement is released with comparison to ordinary CEAS techniques, due to the noise immune property, the locking servo must still have enough gain and bandwidth in order to couple all laser power into a cavity mode and in order for the laser to follow a cavity mode during a scan over a transition.

A few years ago a research project was initiated at the Department of Physics, Umeå University, Umeå, Sweden, with the aim of simplifying the technical realization of NICE-OHMS without sacrificing its extraordinary sensitivity and selectivity. The project, which the work presented in this thesis is a part of, has so far resulted in the construction of a compact NICE-OHMS setup based on a fiber laser, operating at a wavelength of 1.53 µm, and a fiber-coupled electro-optic modulator [45]. The first realization of the fiber-laser-based NICE-OHMS has already been described in the doctoral thesis of Florian Schmidt [46].

The main advantage of the fiber laser is its very narrow free-running linewidth, which considerably simplifies the laser frequency stabilization. It has been demonstrated that the fiber-laser-based NICE-OHMS system is capable of detecting relative absorption down to $3 \times 10^{-9}$ on Doppler-broadened transitions [47], which corresponds to a detection limit of 3.5 nTorr of C$_2$H$_2$, and sub-Doppler optical phase shift down to $1.6 \times 10^{-10}$ [48], which corresponds to a detection limit of 39 ppb of C$_2$H$_2$ at 20 mTorr total.
pressure (i.e., 0.8 nTorr of C₂H₂). The technical improvement has been accompanied by further development of the theoretical description of Doppler-broadened and sub-Doppler NICE-OHMS signals. In particular, it has been shown that the concentration of an analyte can be obtained from a Doppler-broadened NICE-OHMS signal detected at an arbitrary (and unknown) FM detection phase, provided that a fit of the theoretical lineshape to the experimental curve is performed [45]. The lineshapes of the Doppler-broadened NICE-OHMS signals in the presence of a WM dither have been characterized in detail, with emphasis on determining the optimum detection conditions [49]. The influence of optical saturation on Doppler-broadened NICE-OHMS signals has been described theoretically [50] and verified experimentally [51]. Moreover, a theory of sub-Doppler NICE-OHMS dispersion signal for high degrees of saturation has been developed and confirmed experimentally [52]. It has also been shown how the analyte concentration can be derived from the signal used for locking of the FM modulation frequency to the cavity FSR by a methodology referred to as dual frequency modulation dispersion spectrometry (DFM-DS) [53]. The publications referred to here [44, 45, 47-53] are the basis of this thesis and are appended at the end.

The first chapters of this thesis (2 – 7) serve as an introduction to the concepts needed for an understanding of NICE-OHMS. First, the basics of direct absorption spectrometry are revised in Chapter 2 in order to introduce the necessary nomenclature. The attenuation and the phase shift of an electric field interacting with molecules is derived in Chapter 3 for the cases of a single running wave and two counter-propagating waves with equal intensities. The principles of frequency modulation and wavelength modulation spectrometry are given in Chapter 4. Chapter 5 provides relevant information about the properties of Fabry–Perot cavities. The basics of control theory and laser frequency stabilization are presented in Chapter 6. Finally, the principles of NICE-OHMS are explained in Chapter 7.

After the theoretical section, the fiber-laser-based NICE-OHMS experimental setup and procedures are presented in Chapter 8 and the experimental results, with acetylene and carbon dioxide as pilot species, are summarized in Chapter 9. Chapter 10 contains conclusions and outlook, and is followed by a summary of the papers appended at the end of the thesis.
2. Direct Absorption Spectrometry

The basic principle of direct absorption spectrometry is the Lambert-Beer law. The formulation of this law for the case of narrowband light passing a gas of molecular absorbers with the most common types of absorption lineshapes is presented below. Moreover, the signal generation process and the noise sources in DAS are shortly discussed.

2.1 Lambert-Beer law

According to Lambert-Beer law, the intensity $I_A$ (W/m$^2$) of light transmitted through an absorbing sample of length $L$ (cm) (Figure 2.1) is related to the incident intensity, $I_0$, as

$$I_A(\Delta \nu) = I_0 e^{-\alpha(\Delta \nu)}, \quad (2.1)$$

where $\alpha(\Delta \nu)$ is the absorption (sometimes also referred to as absorbance) of the sample, given by

$$\alpha(\Delta \nu) = \hat{S} n_A \chi_{abs}(\Delta \nu), \quad (2.2)$$

where $\hat{S}$ is the molecular transition line strength (cm$^2$/molecule/cm$^2$), $n_A$ is the density of absorbers (molecules/cm$^3$), and $\chi_{abs}(\Delta \nu)$ is the frequency dependent area-normalized absorption lineshape function (cm). The frequency dependence of the transmitted intensity and the absorption is expressed in terms of the detuning of the laser frequency, $\nu$ (Hz), from the center of a molecular transition, $\nu_0$, defined as $\Delta \nu = \nu - \nu_0$.

![Figure 2.1. Absorption of light by a gaseous sample, characterized by an absorption $\alpha(\Delta \nu)$. The transmitted intensity, $I_A$, is detected with a photodetector, which produces a signal, $S_{det}$, proportional to the incident intensity.](image)

The transition line strength is defined as [54]

$$\hat{S} = \frac{2\pi^2 \nu_0 \mu^2}{3\cdot100\varepsilon_0 h c^2} \Delta \rho^{0}_{11,22}, \quad (2.3)$$

where $\mu$ is the transition dipole moment (C·m), $\varepsilon_0$ the electric permittivity of free space (C$^2$·s$^2$·kg$^{-1}$·m$^{-3}$), $h$ the Planck constant (J·s), $c$ the speed of light in vacuum (m/s), and where $\Delta \rho^{0}_{11,22}$ is the difference in relative thermal population of the two states, which under thermal equilibrium at a
temperature $T_K$ (K) is governed by Boltzmann statistics

$$\Delta \rho^{0}_{11,22} = \frac{g_1}{Q(T_K)} e^{-E_i/k_B T_K} \left( 1 - e^{-\hbar \nu_o/k_B T_K} \right),$$

(2.4)

where $E_i$ (J) and $g_1$ are the energy and the degeneracy of lower energy level, respectively, $Q(T_K)$ is the partition function, and $k_B$ is the Boltzmann constant (J/K) [54]. The factor of 100 in Eq. (2.3), and further below, converts the SI units to cgs units, in which the line strength and the lineshape functions are given. The dipole moment, in turn, is related to the Einstein A coefficient, $A_{21}$ (s⁻¹), as [54]

$$\mu^2 = \frac{3g_1 A_{21} \epsilon \mu^3}{16 g_2 \pi^3 \nu_0^3}, \quad (2.5)$$

where $g_2$ is the degeneracy of the upper energy level.

The product $\hat{S}n_A$ can also be written in terms of more practical entities, namely as

$$\hat{S}n_A = S c_{rel} p,$$

(2.6)

where $c_{rel}$ is the relative concentration of the analyte, $p$ the pressure (atm) and $S$ the line strength in units of cm⁻²/atm, related to $\hat{S}$ by

$$S = \frac{\hat{S}n_0 T_o}{P_{atm} T_K},$$

(2.7)

where $n_0$ is the Loschmidt number, i.e., the density of molecules at temperature of 0 °C ($T_o = 273.15$ K) and atmospheric pressure, $P_{atm}$, equal to $2.686 \times 10^{19}$ molecules/cm³. The product $c_{rel} p$ is the partial pressure of the analyte, denoted by $P_A$.

Direct absorption spectrometry is the simplest technique utilizing absorption of light for quantitative measurement. According to Eq. (2.1) the absorption of the analyte can be deduced from a measurement of the intensity of the light transmitted through a sample as

$$\alpha(\Delta \nu) = \ln \frac{I_0}{I_A(\Delta \nu)}.$$

(2.8)

The most commonly used entity in DAS is the integrated absorption, defined as

$$\int_0^\infty \ln \frac{I_0}{I_A(\Delta \nu)} d\sigma = \int_0^\infty \alpha(\Delta \nu) d\sigma = S c_{rel} p L \int_0^\infty \chi_{abs}(\Delta \nu) d\sigma = S c_{rel} p L,$$

(2.9)

where $\sigma$ is the frequency expressed in units of cm⁻¹, given by $\sigma = \nu/(100c)$.
The integrated absorption is independent of the prevailing type of 
broadening and gives directly the relative concentration of the analyte if the 
line strength, interaction length and sample pressure are known.

For optically thin samples, i.e., those for which $\alpha(\Delta \nu) \ll 1$, the exponent 
in Eq. (2.1) can be series expanded to

$$I_A(\Delta \nu) = I_0 \left[ 1 - \alpha(\Delta \nu) \right],$$

whereby the relative change of intensity (the relative absorption) becomes 
linearly dependent on the analyte absorption, i.e.,

$$\frac{\Delta I(\Delta \nu)}{I_0} = \frac{I_0 - I_A(\Delta \nu)}{I_0} = \alpha(\Delta \nu).$$

This implies that for optically thin samples the concentration of the analyte 
can be calculated from the area under the relative absorption, i.e.,

$$\int_0^{\infty} \frac{\Delta I(\Delta \nu)}{I_0} d\sigma = S\sigma_{rel}pL.$$ 

It is sometimes also of interest to write the absorption in terms of a peak-
normalized lineshape function, $\chi^{abs}(\Delta \nu)$, and the on-resonance absorption, $\alpha_0$, as

$$\alpha(\Delta \nu) = \alpha_0 \chi^{abs}(\Delta \nu),$$

where the peak-normalized lineshape function is related to the area-
normalized function as

$$\chi^{abs}(\Delta \nu) = \chi^0 \chi^{abs}(\Delta \nu),$$

and the on-resonance absorption can be written as

$$\alpha_0 = S\sigma_{rel}pL\chi^0,$$

with $\chi^0$ being the peak value of the area-normalized lineshape function.

### 2.2 Absorption lineshapes

The molecules in a gas move freely in all directions and at thermal 
equilibrium their velocity distribution is Maxwellian [55], given by

$$f(v_z) = \frac{1}{\sqrt{\pi}u} e^{-v_z^2/u^2},$$

where $v_z$ is the velocity component in the direction of propagation of the 
electric field, here chosen as $z$, and $u$ is the most probable velocity at 
temperature $T_K$, given by
\[ u = \sqrt{\frac{2k_B T_K}{m}}, \]  

where \( m \) is the molecular mass (kg). Due to the molecular motion the transition frequencies are Doppler shifted to

\[ \nu'_0 = \nu_0 (1 + v_z / c). \]  

Thus a monochromatic electric field with a frequency \( \nu \) can interact only with a group of molecules with a specific velocity within the thermal distribution, namely those with \( v_z = c(\nu - \nu_0) / \nu_0 \). This leads to an inhomogeneous broadening of the transition and a Gaussian absorption lineshape, given by [55, 56]

\[ \chi^{\text{abs}}_{\nu} (\Delta \nu, \Gamma_D) = \frac{100 \sqrt{\ln 2} c}{\sqrt{\pi} \Gamma_D} e^{-\left(\frac{2 \ln 2 \Delta \nu}{\Gamma_D}\right)^2}, \]  

where \( \Gamma_D \) is the Doppler width (half-width at half maximum, HWHM, in Hz) of a Gaussian profile, given by

\[ \Gamma_D = \frac{\sqrt{\ln 2} \nu_0 u}{c} = \frac{\nu_0}{c} \sqrt{2 \ln 2 k_B T_K / m}. \]  

Each velocity group of molecules is also homogenously broadened, mainly due to lifetime and collision broadening. The lifetime broadening is given by the inverse of the lifetime of the transition, \( \tau \), whereas the pressure broadening, which is proportional to pressure, can be characterized in terms of a pressure broadening coefficient \( B_p \) (Hz/atm). The lineshape of a homogenously broadened transition is given by a Lorentzian function [55, 56], namely

\[ \chi^{\text{abs}}_{\nu} (\Delta \nu, \Gamma_L) = \frac{100 c}{\pi} \frac{\Gamma_L}{(\Delta \nu)^2 + \Gamma_L^2}, \]  

where \( \Gamma_L \) is the homogenous linewidth (HWHM, in Hz), given by

\[ \Gamma_L = (2 \pi \tau)^{-1} + B_p P. \]  

Another type of broadening, referred to as transit time broadening, originates from the fact that molecules spend a finite time in the laser beam. The transit time broadening is not fully homogenous, but is often modeled as such with reasonable accuracy by the addition of a term \( \gamma_{tt} / 2 \pi \) to Eq. (2.22). For a Gaussian beam \( \gamma_{tt} \) can be written as

\[ \gamma_{tt} = \frac{\pi u}{4w}, \]  

where

\[ u = \sqrt{\frac{2k_B T_K}{m}}, \]  

and

\[ \Gamma_D = \frac{\sqrt{\ln 2} \nu_0 u}{c} = \frac{\nu_0}{c} \sqrt{2 \ln 2 k_B T_K / m}. \]
where \( w \) is the radius of the laser beam \([57, 58]\).

If the Doppler and homogenous widths are of comparable magnitudes, the lineshape function has a Voigt form, which is a convolution of a Gaussian and a Lorentzian lineshape function, given by \([56]\)

\[
\chi_{V}^{\text{abs}}(\Delta \nu, \Gamma_L, \Gamma_D) = \frac{100\sqrt{\ln 2} \nu_0 \Gamma_L}{\sqrt{\pi}} \int_{-\infty}^{\infty} \frac{e^{-(\nu_z/\nu_0)^2}}{(\Delta \nu + \nu_0 \nu_z/c)^2 + \Gamma_L^2} d\nu_z. \tag{2.24}
\]

However, if one of the phenomena dominates, any of the simpler formulas can be used. In the so-called Doppler limit, i.e., under low pressure conditions, the transitions are well described by the Gaussian lineshape function. At higher pressures, when collision broadening is dominating, the Lorentzian function can be used.

### 2.3 Detector signal

In DAS the light transmitted through the sample is incident on a photodetector, as shown in Figure 2.1, which produces a current proportional to the power of the laser beam, \( P \), defined as the area integrated intensity

\[
P = \int I dA, \tag{2.25}
\]

where \( A \) is the laser beam area. The detector current is given by

\[
i_{\text{det}} = \eta_c P, \tag{2.26}
\]

where the current responsivity of the detector diode, \( \eta_c \) (A/W), is related to the intrinsic quantum efficiency of the detector \( \eta_q \) (electrons/photons), as

\[
\eta_q e/(h\nu), \text{ where } e \text{ is the electronic charge (C)}.
\]

The detector signal, \( S_{\text{det}} \) (V), is given by

\[
S_{\text{det}} = g_{\text{det}} Z_{\text{det}} i_{\text{det}} = \eta P, \tag{2.27}
\]

where \( Z_{\text{det}} \) is the input impedance of the current to voltage converter (\( \Omega \)) and \( g_{\text{det}} \) is the voltage gain of the detector amplifier. In the last step an instrumentation factor \( \eta \) (V/W), equal to \( \eta_c g_{\text{det}} Z_{\text{det}} \), has been introduced.

In the presence of an analyte the detector signal is given by

\[
S_{\text{det}}(\Delta \nu) = \eta P_0 [1 - \alpha(\Delta \nu)], \tag{2.28}
\]

which can be separated into an analytical signal

\[
S_A(\Delta \nu) = (-) \eta P_0 \alpha(\Delta \nu), \tag{2.29}
\]

where the minus sign is often omitted for convenience, and a background
Here $P_0$ is defined as the power of the beam incident on the detector in the absence of the analyte.

### 2.4 Noise

The main disadvantage of direct absorption spectrometry is that the analytical signal is measured on top of a large background signal, through which noise can couple in. The fundamental limit of the noise is the shot noise, which originates from the quantum nature of light, namely the fact that the distribution of the photons arriving at the detector is Poissonian. The shot noise current can be written as

$$i_{\text{shot}} = \sqrt{2e\Delta f f_{\text{det}}},$$

where $\Delta f$ is the electronic bandwidth. This implies that the signal corresponding to the shot noise current is given by

$$S_{\text{shot}} = g_{\text{det}} Z_{\text{det}} \sqrt{2e\Delta f \eta_c P_0}.$$  

The measurements are shot noise limited if this noise dominates over the noise from other sources. The minimum detectable (shot-noise-limited) on-resonance absorption can be calculated by setting the signal-to-noise ratio, i.e., the ratio of Eq. (2.29) and Eq. (2.32), to 1, which yields

$$\left(\alpha_0\right)_{\text{DAS}}^{\text{DAS}} = \frac{2e\Delta f}{\eta_c P_0}.$$

For a detection bandwidth of 1 Hz, a detector current responsivity of 1 A/W and an incident power of 1 mW, the shot-noise-limited on-resonance absorption is equal to $2 \times 10^{-8}$.

The shot noise limit is never reached with direct absorption spectrometry due to the laser excess noise (technical noise, sometimes called the flicker noise), which has a 1/f frequency dependence and dominates at low frequencies, where the DAS signal is detected. Another source of noise is the thermal noise, which originates from thermal fluctuations of charge carriers in the electronics and has a flat frequency spectrum [59].
3. Doppler-broadened and sub-Doppler Absorption and Dispersion Lineshapes

The electric field propagating through a gaseous medium is not only attenuated but also phase shifted. However, since the information about the phase of the light is lost in a measurement of intensity, DAS is capable of detecting only absorption. On the other hand, an optical phase shift can be detected by interferometric techniques, such as frequency modulation spectroscopy. Thus it is not sufficient to describe light-matter interactions and the propagation of light through an absorber only in terms of intensity when these techniques are considered.

Moreover, light with low intensity interacts linearly with the medium, i.e., it only probes the difference in population of two energy levels without modifying it. However, when the intensity reaches a certain level, the light transfers a significant fraction of the population from the lower to the upper energy level at such a high rate that the excited molecules do not have time to deexcite spontaneously to the lower level. As a result the relative population difference decreases and a saturating wave, whose frequency is scanned across a transition, experiences attenuation smaller than an unsaturating wave would. Moreover, at each detuning a so-called Bennett hole is burned in the velocity distribution of the population of the molecular medium, as shown in Figure 3.1. The Bennett hole can be observed only if a second laser beam is used to probe the population difference in the vicinity of the velocity group of molecules resonant with the saturating ‘pump’ beam.

![Figure 3.1](image)

**Figure 3.1.** Thermal population difference between the two states of a Maxwellian velocity distribution of molecules in the presence of a saturating beam of light, which burns a Bennett hole at a velocity group for which $u_j = u$.

In many cases the pump and the probe waves originate from the same laser source, as for example takes place inside a Fabry-Perot cavity. In such configuration the two counter-propagating waves have the same frequency and intensity at all times. Each of them burns its own Bennett hole in the
population distribution, but does not interact with the hole burned by the
other wave unless both waves interact with the same velocity group, which
happens only on resonance, i.e., for $\nu = \nu_0$. Away from resonance each wave
experiences a reduced attenuation, as in the case of a single saturating
running wave, while on resonance a so-called Lamb dip is observed, as
shown in Figure 3.2. Detection of this narrow feature is the basis of sub-
Doppler spectroscopy.

![Figure 3.2. Absorption of a single unsaturating wave (upper curve), and of a
saturating wave in the presence of a counter-propagating wave with the same
intensity and frequency (lower curve), as a function of relative frequency
detuning.](image)

In this chapter the attenuation and the phase shift of an electric field
interacting with a molecular transition is described in some detail. The case
of a single running wave is considered separately from the case of two
counter-propagating waves with the same intensity.

### 3.1 Transmission of an electric field through a molecular
medium

A monochromatic linearly polarized electric field with an amplitude $E_0$
oscillating at a frequency $\nu$ and propagating in free space in the positive $z$
direction can be expressed as

$$E(\nu,z,t) = E_0 \hat{e} \cos(2\pi vt - k_0 z),$$

where $\hat{e}$ is the unit polarization vector, $k_0 = 2\pi / \lambda$ is the amplitude of the
wave vector in vacuum and $\lambda = c/\nu$ is the wavelength. The intensity, defined
as the time average of the square of the electric field, is given by

$$I_0 = c \varepsilon_0 \left\langle \left| E(\nu,z,t) \right|^2 \right\rangle = \frac{1}{2} c \varepsilon_0 E_0^2,$$

where $\langle ... \rangle$ denotes the time average over a suitable time interval. The
electric field can also be expressed in terms of a complex electric field,
$\tilde{E}(\nu,z,t)$, and its complex conjugate (c.c.), $\tilde{E}^*(\nu,z,t)$, as
Using the complex field representation the intensity can alternatively be calculated as

\[
I_0 = c\epsilon_0 \left| \hat{\mathbf{E}}(v,z,t) + \hat{\mathbf{E}}^*(v,z,t) \right|^2 = 2c\epsilon_0 \hat{\mathbf{E}}(v,z,t)\hat{\mathbf{E}}^*(v,z,t) = \frac{1}{2} c\epsilon_0 \mathbf{E}_0^2. \tag{3.4}
\]

The complex electric field transmitted through a sample of length \( L \) can be written as

\[
\tilde{\mathbf{E}}_A(\Delta \nu, z,t) = \frac{E_0}{2} e^{i(2\pi\nu-\nu_0)} e^{i(2\pi\nu L - \tilde{k}(\Delta \nu)L)}, \tag{3.5}
\]

where \( \tilde{k}(\Delta \nu) \) is the amplitude of the complex frequency dependent wave vector in the presence of an absorber. This field can also be written in terms of a complex transmission function of the analyte, \( \tilde{T}^A(\Delta \nu) \), as

\[
\tilde{\mathbf{E}}_A(\Delta \nu, z,t) = \tilde{T}^A(\Delta \nu) \hat{\mathbf{E}}(v,z,t), \tag{3.6}
\]

where \( \tilde{T}^A(\Delta \nu) \) is given by

\[
\tilde{T}^A(\Delta \nu) = e^{-\delta(\Delta \nu)-i\phi(\Delta \nu)}, \tag{3.7}
\]

with \( \delta(\Delta \nu) \) and \( \phi(\Delta \nu) \) being the frequency dependent amplitude attenuation and optical phase shift induced by the sample, given by \( \text{Im} \left[ \tilde{k}(\Delta \nu) \right] L \) and \( \text{Re} \left[ \tilde{k}(\Delta \nu) \right] - k_0 \), respectively. The intensity of light transmitted through a sample is therefore given by

\[
I_A(\Delta \nu) = 2c\epsilon_0 \hat{\mathbf{E}}_A(\nu,z,t)\hat{\mathbf{E}}_A^*(\nu,z,t) = I_0 e^{-2\delta(\Delta \nu)}, \tag{3.8}
\]

which has the same form as the Lambert-Beer law given in Eq. (2.1). This shows that the absorption of intensity is equal to twice the amplitude attenuation of the electric field, and also that the information about the phase of the electric field is lost in direct absorption spectrometry.

The complex wave vector is related to the complex frequency dependent refractive index of the sample as \( \tilde{k}(\Delta \nu) = 2\pi \tilde{n}(\Delta \nu)/\lambda \). With \( \tilde{n}(\Delta \nu) \) defined as \( n_R(\Delta \nu) - i n_I(\Delta \nu) \), where both \( n_R(\Delta \nu) \) and \( n_I(\Delta \nu) \) are real functions [50], the attenuation and phase shift can be expressed in terms of \( n_R(\Delta \nu) \) and \( n_I(\Delta \nu) \) by inserting Eqs (3.3), (3.5) and (3.7) into Eq. (3.6), which yields

\[
\delta(\Delta \nu) = \frac{2\pi n L}{c} n_I(\Delta \nu) \tag{3.9}
\]
respectively. The complex index of refraction can in turn be related to the complex susceptibility of the medium, \( \hat{\chi}(\Delta \nu) = \chi_R(\Delta \nu) - i\chi_I(\Delta \nu) \), as [56]

\[
\hat{n}(\Delta \nu) = \sqrt{1 + \hat{\chi}(\Delta \nu)}.
\]

Thus, for optically thin media, for which the susceptibility is much smaller than 1,

\[
n_R(\Delta \nu) = 1 + \frac{1}{2} \chi_R(\Delta \nu),
\]

and

\[
n_I(\Delta \nu) = \frac{1}{2} \chi_I(\Delta \nu),
\]

whereby the attenuation and phase shift are given by

\[
\delta(\Delta \nu) = \frac{\pi \nu L}{c} \chi_I(\Delta \nu),
\]

and

\[
\phi(\Delta \nu) = \frac{\pi \nu L}{c} \chi_R(\Delta \nu).
\]

The complex susceptibility relates the macroscopic polarization of a medium, \( \hat{P}(\Delta \nu) \), to the electric field that induces the polarization as

\[
\hat{P}(\Delta \nu, z,t) = \epsilon_0 \hat{\chi}(\Delta \nu) \hat{E}(\nu, z,t).
\]

The complex macroscopic polarization can also be written as an integration of the complex molecular dipole moments, \( \hat{p}(\Delta \nu, v_z, z,t) \), over the velocity distribution of the molecules, \( f(v_z) \), according to

\[
\hat{P}(\Delta \nu, z,t) = n_A \int_{-\infty}^{\infty} \hat{p}(\Delta \nu, v_z, z,t) f(v_z) dv_z.
\]

Under the condition that the medium can be modeled as a two-level system, with the levels denoted by 1 and 2, the complex dipole moment can be written as

\[
\hat{p}(\Delta \nu, v_z, z,t) = \mu \hat{\rho}_{12}(\Delta \nu, v_z, z,t),
\]

where \( \mu \) is the transition dipole moment, given by \( \langle 1 | \sigma | 2 \rangle \), and
\( \tilde{\rho}_{12}(\Delta v, v_z, z, t) \) is an off-diagonal element of the density matrix for the medium exposed to the electromagnetic field, which follows the electric field and can be written as

\[
\tilde{\rho}_{12}(\Delta v, v_z, z, t) = \rho_{12}^0(\Delta v, v_z, z, t)e^{i(2\pi v t - k_0 z)}, \tag{3.19}
\]

where \( \rho_{12}^0(\Delta v, v_z, z, t) \) represents an amplitude coefficient.

Equalizing the two expressions for the complex macroscopic polarization, Eqs (3.16) and (3.17), and utilizing the expressions for the electric field, Eq. (3.3), and for the off-diagonal density matrix element, Eq. (3.19), yields an expression for the complex susceptibility of the medium in terms of the amplitude of the off-diagonal density matrix element that reads

\[
\chi(\Delta v, z, t) = \frac{2n_0\mu_0 E_0}{\sqrt{\pi n_0 E_0}} \int_{-\infty}^{\infty} \tilde{\rho}_{12}^0(\Delta v, v_z, z, t)e^{-v_z^2/2} dv_z, \tag{3.20}
\]

The off-diagonal element of the density matrix for the medium exposed to an electromagnetic field can be calculated by solving the density matrix equations for the particular situation considered.

### 3.2 Single running wave – Doppler-broadened response

The density matrix equations for the interaction between molecules moving with a velocity \( v_z \) and an electric field, \( \mathbf{E}(v, z, t) \), have been formulated numerous times in the literature [60] and are also given in paper III. Solving these equations under steady-state conditions, with the rotating wave approximation and under the assumption that the electric field is constant across the laser beam, yields an amplitude coefficient for the off-diagonal element of the density matrices that can be written as

\[
\tilde{\rho}_{12}^0(\Delta v, v_z, G) = -\frac{\mu_0 E_0}{2\hbar} \Delta \rho_{11,22}^0 \frac{2\pi \Delta v - k_0 v_z + i\gamma_{12}}{\left(2\pi \Delta v - k_0 v_z\right)^2 + \gamma_{12}^2 (1 + G)}, \tag{3.21}
\]

where \( G \) is the degree of saturation of the transitions, given by

\[
G = \frac{I_0}{I_{sat}}, \tag{3.22}
\]

where the saturation intensity is defined as

\[
I_{sat} = \frac{3c\epsilon_0 h^2 \gamma_1 \gamma_2 \gamma_{12}}{\mu^2 \gamma_1 + \gamma_2}, \tag{3.23}
\]

where \( \gamma_{12} \) is the decay rate of the dipole moment, and \( \gamma_1 \) and \( \gamma_2 \) are the decay rates of the populations of the two energy levels. These decay rates have several contributions, of which the most important are the natural
broadening, transit time broadening and pressure broadening. For molecules passing a narrow laser beam the natural broadening can often be neglected with respect to the other broadening mechanisms. Under the assumption that the pressure dependence of all decay rates is similar and given by the sum of the transit time broadening and pressure broadening, i.e.,

\[ \gamma_1 = \gamma_2 = \gamma_{tt} + 2\pi B_p p, \]  

(3.24)

the saturation intensity can be expressed as \[ I_{sat} = \frac{3c\epsilon_o h^2}{2\mu^2} \left( \gamma_{tt} + 2\pi B_p p \right)^2. \]  

(3.25)

Inserting Eq. (3.21) into Eq. (3.20) and using the definition of the line strength, Eq. (2.3), provides an expression for the complex susceptibility of the medium under steady-state conditions that reads

\[ \chi(\Delta \nu, G) = -\frac{\hat{S}_n L}{2} \frac{2c}{\sqrt{k_0 u}} \int_{-\infty}^{\infty} \frac{(2\pi \Delta \nu - k_0 \nu_z + i\gamma_{12}) e^{-\nu_z^2 / u^2}}{(2\pi \Delta \nu - k_0 \nu_z)^2 + \gamma_{12}^2 (1 + G)} d\nu_z, \]  

(3.26)

where the fact that \((\mu \cdot \hat{e})^2 = \mu^2 / 3\) due to directional averaging has been used.

Thus the amplitude attenuation and the phase shift, related to the complex susceptibility of the medium through Eqs (3.14) and (3.15), can be expressed as

\[ \delta(\Delta \nu, G) = \frac{\hat{S}_n L}{2} \chi_0 \frac{2\nu}{100c} \int_{-\infty}^{\infty} \frac{\gamma_{12} e^{-\nu_z^2 / u^2}}{(2\pi \Delta \nu - k_0 \nu_z)^2 + \gamma_{12}^2 (1 + G)} d\nu_z, \]  

(3.27)

and

\[ \phi(\Delta \nu, G) = \frac{\hat{S}_n L}{2} \chi_0 \frac{2\nu}{100c} \int_{-\infty}^{\infty} \frac{(2\pi \Delta \nu - k_0 \nu_z) e^{-\nu_z^2 / u^2}}{(2\pi \Delta \nu - k_0 \nu_z)^2 + \gamma_{12}^2 (1 + G)} d\nu_z, \]  

(3.28)

respectively, where \(\chi_0 = 2 \cdot 100 \sqrt{\pi} / (k_0 u)\) is the peak value of the unsaturated area-normalized absorption Gaussian lineshape function (in units of cm), which can also be expressed in terms of the Doppler width, Eq. (2.20), as

\[ \chi_0 = \frac{100 \sqrt{\ln 2 c}}{\sqrt{\pi} \Gamma_D}. \]  

(3.29)

It is convenient to rewrite the two above expressions in terms of general absorption and dispersion lineshape functions, \(\chi^{abs}(\Delta \nu, G)\) and \(\chi^{disp}(\Delta \nu, G)\), as
\[
\delta(\Delta \nu, G) = \frac{S_{c, \text{rel}} P L}{2} \chi^{\text{abs}}(\Delta \nu, G),
\]

and

\[
\phi(\Delta \nu, G) = \frac{S_{c, \text{rel}} P L}{2} \chi^{\text{disp}}(\Delta \nu, G),
\]

where Eq. (2.6) has been used. As is shown in paper III, the two lineshape functions can be expressed more succinctly in terms of a Doppler-width-normalized detuning

\[
x = \frac{\sqrt{\ln 2} \Delta \nu}{\Gamma_D},
\]

and a Doppler-width-normalized saturated homogenous linewidth

\[
y = \sqrt{\ln 2(1+G)} \frac{\Gamma_f}{\Gamma_D},
\]

as

\[
\chi^{\text{abs}}(x, y, G) = \chi_0 \left( \frac{1}{\sqrt{1+G}} \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{ye^{-s^2}}{(x-s)^2 + y^2} ds \right)
\]

\[
= \chi_0 \left( \frac{1}{\sqrt{1+G}} \text{Re} \left[ \tilde{w}(x + iy) \right] \right),
\]

and

\[
\chi^{\text{disp}}(x, y, G) = -\chi_0 \left( \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{(x-s)e^{-s^2}}{(x-s)^2 + y^2} ds \right)
\]

\[
= -\chi_0 \text{Im} \left[ \tilde{w}(x + iy) \right],
\]

where \( s = v_z / u \) and \( \tilde{w}(z) \) is the error function of a complex argument, given by [61]

\[
\tilde{w}(z) = e^{-z^2} \left( 1 + \frac{2i}{\sqrt{\pi}} \int_{0}^{z} e^{s^2} ds \right).
\]

The general absorption lineshape function, Eq. (3.34), is a Voigt function, which in the absence of optical saturation is identical to that given in Eq. (2.24). The unsaturated Voigt lineshape (for \( G = 0 \)) and its dispersion counterpart are plotted with solid curves in Figure 3.3 for equal Doppler and homogenous widths (100 MHz).
Figure 3.3. Voigt, Gaussian and Lorentzian unsaturated area-normalized absorption lineshape functions (a) and their dispersion counterparts (b) for equal Doppler and homogenous linewidths of 100 MHz.

Under low pressure conditions, when collision broadening is negligible and the homogenous linewidth is much smaller than the Doppler width ($\Gamma_L \ll \Gamma_D$), i.e., in the Doppler limit, the imaginary part of the complex argument in Eq. (3.36) becomes negligible and the lineshapes simplify to

$$\chi_G^{abs}(x,G) = \chi_0 \frac{1}{\sqrt{1+G}} e^{-x^2} = \chi_0 \frac{1}{\sqrt{1+G}} \chi_G^{abs}(x), \quad (3.37)$$

and

$$\chi_G^{disp}(x) = -\chi_0 \frac{2}{\sqrt{\pi}} e^{-x^2} \int_0^x e^{s^2} ds = \chi_0 \chi_G^{disp}(x), \quad (3.38)$$

where a peak-normalized Gaussian function, $\chi_G^{obs}(x)$, and its dispersion counterpart, $\chi_G^{disp}(x)$, related to each other by the Kramers-Kronig (KK) relations, have been introduced. The dispersion lineshape function is independent of optical saturation, while the magnitude of the absorption lineshape function is decreased by a factor of $1/\sqrt{1+G}$. This shows that in the Doppler limit the absorption and dispersion lineshape functions are related through the KK relations only in the absence of optical saturation. The two functions are plotted with dashed curves in Figure 3.3 for a Doppler width of 100 MHz and $G = 0$.

Under high pressures conditions, i.e., in the collision dominated regime, when the homogenous linewidth is much larger than the Doppler width, i.e., when $\Gamma_L \gg \Gamma_D$, the value of the Lorentzian envelope can be assumed to be constant for each velocity group and taken in front of the integrals in Eqs (3.34) and (3.35). The resulting lineshapes, plotted with dotted curves in Figure 3.3 for $G = 0$, are thereby Lorentzian, given by
\[ \chi_{L}^{\text{abs}}(\Delta \nu, \Gamma_L, G) = \frac{100c}{\pi} \frac{\Gamma_L}{(\Delta \nu)^2 + (1 + G)\Gamma_L^2} \]

(3.39)

and

\[ \chi_{L}^{\text{disp}}(\Delta \nu, \Gamma_L, G) = -\frac{100c}{\pi} \frac{\Delta \nu}{(\Delta \nu)^2 + (1 + G)\Gamma_L^2} \]

(3.40)

where a peak-normalized Lorentzian function, \( \chi_{L}^{\text{abs}}(\Delta \nu, \Gamma_L, G) \), and its dispersion counterpart, \( \chi_{L}^{\text{disp}}(\Delta \nu, \Gamma_L, G) \), have been introduced. In the collision dominated regime the absorption and dispersion lineshape functions are affected by optical saturation in the same way, namely their linewidth is broadened by a factor of \( \sqrt{1+G} \) and their size is reduced by a factor of \( (1+G)^{-1} \).

### 3.3 Counter-propagating waves – sub-Doppler response

When two counter-propagating waves interact with the same velocity group of molecules, the expression for the amplitude coefficient for the off-diagonal element of the density matrix, \( \hat{\rho}_{12}^{\text{z}}(\Delta \nu, \nu_2, G) \), is no longer given by Eq. (3.21). It is shown in paper V that in the presence of two counter-propagating waves with equal intensities, under the same assumptions as Eq. (3.26) and additionally neglecting the coherences between the two excitations, i.e., treating the effect caused by the two traveling waves as a superposition of two separate interactions, the complex susceptibility can be expressed as

\[ \hat{\chi}(\Delta \nu, G) = -\hat{S}_{\text{A}} \frac{2c}{\sqrt{\pi}k_0u} \]

\[ \times \int_{-\infty}^{\infty} \frac{2\pi\Delta \nu - k_0\nu_z + i\gamma_{12}}{(2\pi\Delta \nu - k_0\nu_z)^2 + \gamma_{12}^2 (1 + G)} \frac{e^{-\nu_z^2/u^2}}{1 + G \left[ L_0^+ (\Delta \nu, \nu_z) + L_0^- (\Delta \nu, \nu_z) \right]} d\nu_z, \]

(3.41)

where

\[ L_0^0 (\Delta \nu, \nu_z) = \frac{\gamma_{12}^2}{(2\pi\Delta \nu \pm k_0\nu_z)^2 + \gamma_{12}^2} \]

(3.42)

are peak-normalized Lorentzian lineshape functions for the electric fields traveling in the positive and negative direction and interacting with the
velocity groups of molecules centered at $\pm v_\xi$, respectively. The general absorption lineshape function in the presence of counter-propagating waves is therefore given by

$$\chi^{abs\pm}(x,y_0,G) = \chi_0 \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{y_0}{(x + s)^2 + y_0^2} e^{-s^2} \left[ 1 + G \left( L_0^+ (x,y_0,s) + L_0^- (x,y_0,s) \right) \right] ds,$$

whereas the dispersion lineshape function is given by

$$\chi^{disp\pm}(x,y_0,G) = -\chi_0 \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{x \mp s}{(x + s)^2 + y_0^2} e^{-s^2} \left[ 1 + G \left( L_0^+ (x,y_0,s) + L_0^- (x,y_0,s) \right) \right] ds,$$

where

$$L_0^\pm (x,y_0,s) = \frac{y_0^2}{(x + s)^2 + y_0^2},$$

and where $y_0 = y(G=0) = \sqrt{\ln 2} \Gamma_L / \Gamma_D$ is the Doppler-width-normalized unsaturated homogenous linewidth.

These absorption and dispersion lineshape functions with a Doppler width of 100 MHz and a homogenous width of 1 MHz, for degrees of saturation, $G$, of 0, 0.5, 2, and 10, are plotted in Figure 3.4. As can be seen in panel (a), the Doppler-broadened absorption lineshape function is reduced due to optical saturation by a factor of $1/\sqrt{1 + G}$, and a Lamb dip appears on resonance. The corresponding dispersion lineshape function, displayed in panel (b), is not affected by optical saturation except for the appearance of the sub-Doppler response in the center.

![Figure 3.4](image.png)

**Figure 3.4.** Absorption (a) and dispersion (b) lineshape functions in the presence of two counter-propagating waves with equal intensity, for Doppler width of 100 MHz and a homogenous width of 1 MHz, and degrees of saturation as marked in the legend.
The size and shape of the sub-Doppler response depend mainly on the degree of saturation and the amount of collision broadening, which are both strongly pressure dependent. Molecular transitions are more easily saturated at low than at high pressures, since the saturation intensity, Eq. (3.25), increases with the square of the pressure. The sub-Doppler response can therefore usually be detected only in the Doppler limit.

The sub-Doppler absorption and dispersion lineshapes can be calculated by subtracting Eqs (3.34) and (3.35), describing the pure Doppler-broadened response, from Eqs (3.43) and (3.44), respectively. [Note that in the absence of the counter-propagating wave Eqs (3.43) and (3.44) reduce to the Eqs (3.34) and (3.35).] The resulting expressions are, under general conditions, given in integral form, although they reduce to Lorentzian lineshapes for low degrees of saturation \((G < 1)\) [33, 52, 55].

An analytical expression for the on-resonance value of the sub-Doppler attenuation, \(\delta_{00}\), can be obtained by putting \(x = 0\) in Eqs (3.34) and (3.43), and subtracting them from each other, which yields

\[
\delta_{00} = \left( \frac{1}{\sqrt{1+G}} - \frac{1}{\sqrt{1+2G}} \right) \alpha_0. 
\] (3.46)

This function, plotted in Figure 3.5 (a), reaches a maximum of \(\frac{0.13\alpha_0}{2}\) for a degree of saturation of 1.4 [31, 33].

It has been previously assumed that the sub-Doppler optical phase shift, \(\phi_{00}\), has the same power dependence as the sub-Doppler attenuation [13, 31, 33]. This originated from a tacit assumption that the two responses are related to each other by the KK relations. This is, however, not correct, since the KK relations are not valid for nonlinear responses. It has been shown in paper V that the peak-to-peak sub-Doppler optical phase shift, \(\phi_{00}^{pp}\), increases monotonically with the degree of saturation and approaches a
value of 0.45 of the on-resonance Doppler-broadened attenuation, $\alpha_o/2$
[52]. The dependence can be described with an empirical function

$$\phi_{pp} = 0.45 \frac{G}{1+G} \frac{\alpha_o}{2},$$

(3.47)

which is plotted in Figure 3.5 (b). The difference in power dependence of the
sub-Doppler attenuation and phase shift is significant, and implies dissimilar
optimum detection conditions for the two responses. While a specific
combination of laser intensity and sample pressure is required to maximize
the on-resonance value of the sub-Doppler attenuation, the peak-to-peak
sub-Doppler phase shift is always increased by increasing the laser power or
decreasing the pressure.
4. Modulation Techniques

The sensitivity of direct absorption spectrometry can never reach the shot noise limit since the analytical signal is detected at low frequencies where the technical noise is large. Since this type of noise has a roughly $1/f$ frequency dependence, reduction of noise can be obtained by shifting the detection to higher frequencies, which can be done by the use of modulation techniques. When modulated light is sent through a sample, the information about the analyte is encoded at the modulation frequency (and its overtones) and later retrieved by a demodulation of the detector signal. In frequency modulation spectrometry (FMS) the modulation frequency is in the RF range, of the same order of magnitude as the width of the probed transition, while in wavelength modulation spectrometry (WMS) the modulation is slower (at an audio frequency), while instead the amplitude is in the range of the transition width. Due to the different modulation frequencies and amplitudes the two techniques are described in a different way: The FM light is modeled as a carrier and a pair of modulation sidebands, while the WM light is more conveniently described as monochromatic, whose frequency changes sinusoidally in time.

The basic principles of the two modulation techniques are described below. Most common practical means of laser frequency modulation are presented and the limitations of the techniques are discussed.

4.1 Frequency modulation spectrometry

In FMS the phase of the electric field is modulated at an RF frequency $\nu_m$ with an amplitude represented by a modulation index $\beta$. The complex FM electric field can be written as

$$\hat{E}_{\text{fm}}(\nu_c, t) = \frac{E_0}{2} e^{i 2 \pi \nu_c t} e^{i \beta \sin(2 \pi \nu_m t)},$$

(4.1)

where $\nu_c$ is the carrier frequency [3]. This field can be rewritten in terms of a series of modes with amplitudes proportional to Bessel function of order $j$, $J_j(\beta)$, as [3, 62]

$$\hat{E}_{\text{fm}}(\nu_c, t) = \frac{E_0}{2} e^{i 2 \pi \nu_c t} \sum_{j=-\infty}^{\infty} J_j(\beta) e^{i 2 \pi j \nu_m t}. \quad (4.2)$$

Thus the field consists of a carrier and a number of sidebands, with amplitudes proportional to $J_j(\beta)$, separated from the carrier by $j\nu_m$, as shown in Figure 4.1 (a). For modulation indices smaller than 1, i.e., for $\beta < 1$, the Bessel functions of order higher than one take small values, whereby Eq. (4.2) simplifies to [63]
Figure 4.1. The spectrum of frequency modulated light for a high [(a), \( \beta = 4 \)] and low [(b), \( \beta < 1 \)] modulation index.

\[
\mathbf{E}_{\text{fm}}(v_c, t) = \frac{E_o}{2} e^{i2\pi v_c t} \left[ J_0(\beta) + J_1(\beta) e^{i2\pi v_m t} - J_1(\beta) e^{-i2\pi v_m t} \right],
\]

(4.3)

where the fact that \( J_{-1}(\beta) = -J_1(\beta) \) has been used. This shows that the light consists of a carrier and only one pair of sidebands with equal amplitudes (but opposite sign) at frequencies \( v_c \pm v_m \). The spectrum forms an FM triplet, shown in Figure 4.1 (b).

The intensity of a purely frequency modulated electric field, calculated as

\[
I_{\text{fm}} = 2e_o \mathbf{E}_{\text{fm}}(v_c, t) \mathbf{E}_{\text{fm}}^*(v_c, t),
\]

does not contain any component at the modulation frequency, since the beat signal of the lower sideband and the carrier cancels the beat signal of the upper sideband and the carrier completely. Thus no FM signal exists in the absence of analyte, which is the main advantage of FMS.

When the FM triplet passes through a gaseous sample in the vicinity of a transition the balance of the three components is disturbed. The transmitted electric field is then given by

\[
\mathbf{E}_{A_{\lambda}}(\Delta \nu, t) = \frac{E_o}{2} \left[ \mathcal{T}_0^A J_0(\beta) + \mathcal{T}_1^A J_1(\beta) e^{i2\pi \nu_m t} - \mathcal{T}_{-1}^A J_1(\beta) e^{-i2\pi \nu_m t} \right] e^{i2\pi \nu_c t},
\]

(4.4)

where \( \mathcal{T}_j^A \) is the complex transmission function of the analyte, given by Eq. (3.7), and the subscripts \( j = 0, \pm 1 \) denote the carrier and sideband frequencies, respectively, i.e., \( \mathcal{T}_0^A = \mathcal{T}^A(\Delta \nu) \), \( \mathcal{T}_{ \pm 1}^A = \mathcal{T}^A(\Delta \nu \pm \nu_m) \), and where \( \Delta \nu \) is now the detuning of the carrier from the center of the transition, i.e., \( v_c - \nu_0 \). The intensity of frequency modulated light transmitted through a sample, which again can be calculated as

\[
I_{A_{\lambda}} = 2e_o \mathbf{E}_{A_{\lambda}}(\Delta \nu, t) \mathbf{E}_{A_{\lambda}}^*(\Delta \nu, t),
\]

becomes
\[ I_A^{fm}(\Delta \nu, t) = I_0 \left\{ \hat{T}^A \hat{T}_0^A \hat{T}_1^A \hat{T}_{-1}^A J_2^2(\beta) \right. \]
\[ + 2J_0(\beta) J_1(\beta) \Re \left[ (\hat{T}^A \hat{T}_0^A - \hat{T}_1^A \hat{T}_{-1}^A) e^{i2\pi \nu_m t} \right] \]
\[ - 2J_1^2(\beta) \Re \left( \hat{T}^A \hat{T}_0^A e^{i4\pi \nu_m t} \right) \right\}. \] (4.5)

Thus the intensity has components at DC, at the modulation frequency and at twice the modulation frequency. The signal of interest is the one carried at the modulation frequency, namely
\[ I_A^{\nu m}(\Delta \nu, t) = 2I_0 J_0(\beta) J_1(\beta) \Re \left[ (\hat{T}^A \hat{T}_0^A - \hat{T}_1^A \hat{T}_{-1}^A) e^{i2\pi \nu_m t} \right]. \] (4.6)

Inserting the complex transmission function of the analyte from Eq. (3.7) yields, under the assumption of a weekly absorbing sample, for which both \[ |\delta_0 + \delta_1| \] and \[ |\phi_0 - \phi_1| \] are \( \ll 1 \), the intensity of the FM light transmitted through an absorbing sample
\[ I_A^{\nu m}(\Delta \nu, t) = 2I_0 J_0(\beta) J_1(\beta) \times \left[ (\phi_1 - 2\phi_0 + \phi_1) \sin(2\pi \nu_m t) + (\delta_1 - \delta_1) \cos(2\pi \nu_m t) \right], \] (4.7)

where \( \phi_j \) and \( \delta_j \) are the optical phase shift and amplitude attenuation of the \( j \)th mode of light, respectively. The sine (in-phase) term is proportional to the difference between the phase shift experienced by the carrier and the average phase shift experienced by the sidebands, while the cosine (out-of-phase) term is proportional to the difference of the attenuation experienced by the two sidebands [63].

In order to obtain the FMS signal, the detector signal is multiplied with a reference signal at the modulation frequency, \( \sin(2\pi \nu_m t + \theta_{fm}) \) in a double balanced mixer (DBM), where \( \theta_{fm} \) is the detection phase, and low pass filtered, as shown in Figure 4.2, which results in a DC signal

**Figure 4.2.** Schematic of a general setup of frequency modulation spectrometry. EOM – electro-optic modulator, Ph – phase shifter, LP – low pass filter, PD – photodetector.
\[ S_{A}^{\nu} (\Delta \nu, \theta_{fm}) = \eta_{fm} P_{0} J_{0} (\beta) J_{1} (\beta) \times \left[ (\phi_{1} - 2 \phi_{0} + \phi_{1}) \cos \theta_{fm} + (\delta_{1} - \delta_{1}) \sin \theta_{fm} \right], \] (4.8)

where \( \eta_{fm} \) (V/W) is an instrumentation factor including the gain of a possible amplifier. Inserting expressions for the optical phase shift and the attenuation from Eqs (3.30) and (3.31) yields

\[ S_{A}^{\nu} (\Delta \nu, \theta_{fm}) = \eta_{fm} P_{0} J_{0} (\beta) J_{1} (\beta) \frac{Sc_{rel}PL}{2} \times \left[ \chi^{\text{disp}} (\Delta \nu - \nu_{m}) \right] \cos \theta_{fm} \]
\[ + \left[ \chi^{\text{abs}} (\Delta \nu - \nu_{m}) - \chi^{\text{abs}} (\Delta \nu + \nu_{m}) \right] \sin \theta_{fm} \right]. \] (4.9)

The expression in the curly brackets is the FM signal lineshape, which in general consists of three dispersion and two absorption lineshape functions, whose separation is determined by the modulation frequency and whose weight can be adjusted by varying the detection phase. A pure dispersion and a pure absorption signal can be obtained by setting the detection phase to zero or \( \pi/2 \), respectively.

In the Doppler limit the dispersion and absorption lineshapes are given by Eqs (3.37) and (3.38). Figure 4.3 shows the pure absorption and dispersion FM lineshapes in the Doppler limit for a Doppler width of 200 MHz and a sideband spacing equal to 400 MHz, i.e., twice the Doppler width. The solid curves show the full FM lineshapes, while the dashed and dotted curves show the sideband and carrier contributions, respectively. The dependence of the FM lineshapes in the Doppler limit on the detection phase has been scrutinized in detail by North et al. [64].

![Figure 4.3](image-url)

**Figure 4.3.** Absorption (a) and dispersion (b) FM lineshape functions (solid curves) in the Doppler limit for a Doppler width of 200 MHz and modulation frequency of 400 MHz, with the sideband (dashed curves) and carrier (dotted curve) contributions.
The influence of the sideband spacing on the shape of the FM signals is shown in Figure 4.4, where the absorption and dispersion FM lineshapes for various modulation frequencies are plotted. For low modulation frequencies the contributions from the various modes cancel to some extent and the lineshapes have low amplitudes. The FM lineshapes become broader as the modulation frequency increases, and eventually the contributions separate.

For comparison, the absorption and dispersion FM lineshapes in the collision dominated regime are plotted for the same relative modulation frequencies in Figure 4.5. These lineshapes, given by a combination of Lorentzian lineshape functions [Eq. (3.39)] and their dispersion counterparts [Eq. (3.40)], have been analyzed by Bjorklund et al. [63].

The magnitude of the FM lineshape function depends on the modulation frequency as well as the detection phase. The optimum detection phase in the Doppler limit, defined as the phase at which the peak-to-peak value of the FM lineshape function is maximized, is plotted in Figure 4.6 (a) as a function of modulation frequency normalized to the Doppler width. This phase changes from that of absorption, i.e., $\pi/2$, at the lowest modulation
frequencies, towards that of dispersion at higher modulation frequencies. Figure 4.6 (b) shows the peak-to-peak value of the FM lineshape at the absorption, dispersion, and optimum detection phases in terms of the peak value of the unsaturated area-normalized absorption Gaussian lineshape function, $\chi_0$. The largest peak-to-peak value, equal to 3.6, is obtained for a modulation frequency equal to $2.2\Gamma_D$ at a detection phase of $0.1\pi$.

Figure 4.6. (a) Optimum detection phase and (b) the peak-to-peak value of the FM lineshape in the Doppler limit at the absorption, dispersion and optimum phase as a function of the modulation frequency normalized to Doppler width.

The optimum detection phase for FMS in the collision dominated regime is plotted in Figure 4.7 (a) as a function of modulation frequency normalized to the homogenous linewidth. Again, the phase changes from that of absorption at the lowest modulation frequencies, to that of dispersion at higher modulation frequencies. Figure 4.7 (b) shows the peak-to-peak value of FM lineshape at the absorption, dispersion and optimum detection phases in terms of the peak value of the area-normalized Lorentzian lineshape function, i.e., $c/(\pi\Gamma_L)$. The largest peak-to-peak value is 2.6, obtained with a modulation frequency of $2\Gamma_L$ at a detection phase of $0.15\pi$.

Figure 4.7. (a) Optimum detection phase and (b) the peak-to-peak value of the FM lineshape in the collision dominated regime at the absorption, dispersion and optimum phase as a function of the modulation frequency normalized to homogenous linewidth.
4.2 Wavelength modulation spectrometry

In WMS the phase of the light is modulated at a lower frequency, most often in the kHz range, but with a modulation index much larger than 1. This implies that more terms in the series expansion in Eq. (4.2) have to be kept, which makes the sideband representation inconvenient for WM light. Instead, the light in WMS is modeled as a monochromatic wave whose frequency is modulated sinusoidally in time. The instantaneous frequency of the light whose phase is modulated can be calculated as the derivative of the phase in Eq. (4.1), i.e., as

\[ \nu = \frac{1}{2\pi} \frac{d}{dt} \left[ 2\pi \nu_c t + \beta \sin(2\pi \nu_m t) \right] \]
\[ = \nu_c + \beta \nu_m \cos(2\pi \nu_m t) \]
\[ = \nu_c + \nu_a \cos(2\pi \nu_m t), \tag{4.10} \]

where the modulation amplitude, \( \nu_a \), is the product of the modulation index, \( \beta \), and the modulation frequency, \( \nu_m \). For example, for a typical modulation index of 0.4 and modulation frequency of 400 MHz the modulation amplitude is 160 MHz. In WMS the same modulation amplitude is obtained by the use of a significantly lower modulation frequency, which corresponds to a modulation index of the order of \( 10^{-2}-10^{-5} \). Actually, the modulation amplitude in WMS is most often of the order of or larger than the width of the transition, which corresponds to even larger modulation indices.

The wavelength modulated light transmitted through an absorbing sample does not carry information about the phase of the light. This can be seen by deriving Eq. (4.7) with more terms of the series expansion of the electric field representation [Eq. (4.2)], which shows that the attenuation terms add constructively, while the phase shift terms add destructively. Since the information about the phase of the light is lost when many sidebands are interacting with a transition, it is sufficient to describe the interaction of WM light with a transition in terms of the intensity.

WMS is a background free technique, since in the absence of an analyte, and when a possible background signal is frequency independent, i.e., given by Eq. (2.30), the intensity of the WM light is constant and does not contain any component at the modulation frequency. In the vicinity of a transition the power incident on the detector is periodically modulated, wherefore the detector signal can be expressed in terms of a Fourier series as [4]

\[ S_{A}^{um}(\Delta \nu, \nu_a, t) = \sum_{n=0}^{\infty} S_{A,n}^{um}(\Delta \nu, \nu_a) \cos(2\pi n \nu_m t), \tag{4.11} \]

where \( S_{A,n}^{um}(\Delta \nu, \nu_a) \) is the even component of the n\( \text{th} \) Fourier coefficient of
the detector signal (since the modulation is assumed to be purely cosine, with no phase lag between the modulation and absorption processes, all odd components are zero). The detector signal is demodulated at a suitable (nth) harmonic of the modulation frequency with a lock-in amplifier (Figure 4.8), in which the signal is multiplied with a reference signal at the corresponding, (nth) multiple of the modulation frequency, and low pass filtered. Assuming a demodulation with an in-phase reference signal, the magnitude of the resulting signal is proportional to the nth harmonic of the absorption, Eq. (2.29), i.e.

\[
S_{A,n}^{\text{wm}}(\Delta \nu, \nu_a) = \eta_{\text{wm}} P_0 \alpha_n(\Delta \nu, \nu_a) = \eta_{\text{wm}} P_0 \eta_{\text{rel}} Pl \chi_{n}^{\text{abs}}(\Delta \nu, \nu_a),
\]

where \( \eta_{\text{wm}} \) (V/W) is an instrumentation factor and \( \chi_{n}^{\text{abs}}(\Delta \nu, \nu_a) \) is the nth Fourier coefficient of the absorption lineshape function, given by

\[
\chi_{n}^{\text{abs}}(\Delta \nu, \nu_a) = \frac{2}{\pi} \int_{0}^{\tau} \chi_{n}^{\text{abs}}(\Delta \nu + \nu_a \cos(2\pi \nu_m t)) \cos(2\pi \nu_m t) dt,
\]

where the integration time \( \tau \) is the inverse of the modulation frequency, \( 1/\nu_m \) or an integer multiple thereof.

Figure 4.8. Schematic of the general setup of wavelength modulation spectrometry. PD – photodetector.

Analytical formulas for Fourier coefficients of Lorentzian [65] and Gaussian [66] functions have been given in literature, and their dependence on various parameters has been studied by Kluczynski et al. [4]. Most often, the signal at the second harmonic is detected, since it is the largest of the even Fourier coefficients, which are maximized on resonance. The signal at the first harmonic, on the other hand, has a dispersive shape and is affected by any linear background, e.g., that from a linear laser intensity modulation. The first and second Fourier coefficients of a Gaussian absorption lineshape function are plotted in Figure 4.9 for modulation amplitudes equal to 0.5, 1, 2 and 3 times \( \Gamma_p \), respectively. Figure 4.10 shows the corresponding Fourier coefficients of a Lorentzian lineshape function for a homogenous linewidth of 2 GHz and a modulation amplitude of 0.5, 1, 2 and 3 times \( \Gamma_L \).
4.3 Means of modulation – the electro-optic modulator

The frequency (or phase) of laser light can be modulated either directly, through the laser or its actuator, or by the use of an external modulator. WMS is usually performed with diode lasers, whose frequency can be controlled via the injection current. Such modulation, although simple to realize in practice, is accompanied by inevitable intensity modulation, which is linear with the injection current in the first order approximation. This leads to an offset in the detection of first harmonic WM signal, and an asymmetry of the analytical signals at all harmonics [4].

Most lasers lack a frequency actuator with sufficient bandwidth to allow for modulation at the high frequencies required in FMS. Moreover, although it is possible in some diode lasers to modulate the injection current at frequencies up to GHz, the associated intensity modulation would cause a background at the modulation frequency (i.e., the first harmonic), at which the FM signal is detected. Thus FMS utilizes most often an external electro-
optic modulator (EOM) to modulate the phase of the light, as was already indicated in Figure 4.2.

An EOM is basically a birefringent crystal whose refractive index can be modified by an external electric field, due to the linear electro-optic effect (the Pockels effect) [67, 68]. Assuming that the field is applied along the extraordinary axis of the crystal, the change of the refractive index, \( n_e \), is given by

\[
\Delta n_e = \frac{1}{2} n_e^3 r_e E_{rf},
\]

where \( r_e \) is the electro-optic coefficient and \( E_{rf} \) is the external electric field varying at the RF frequency, given by

\[
E_{rf} = \frac{V_{rf}}{d} \sin(2\pi v_m t),
\]

where \( d \) is the crystal thickness in the direction where the field is applied and \( V_{rf} \) is the amplitude of the applied voltage. The phase shift for the extraordinary wave in a crystal of length \( L_e \) is [67, 68]

\[
\theta_{rf} = \frac{2\pi L_e}{\lambda} \Delta n_e = \frac{\pi}{\lambda} n_e^3 r_e \frac{L_e}{d} V_{rf} \sin(2\pi v_m t).
\]

Thus, by comparison with Eq. (4.1), the modulation index can be identified as

\[
\beta = \frac{\pi}{\lambda} n_e^3 r_e \frac{L_e}{d} V_{rf}.
\]

An important parameter characterizing an EOM is the half wave voltage, i.e., voltage \( V_{rf} \) for which the phase shift is equal to \( \pi \), given by

\[
V_{rf} = \frac{\lambda d}{n_e^3 r_e L_e}.
\]

### 4.4 Shot noise and background signals

The shot noise limit for the modulation techniques is of the same order of magnitude as that of direct absorption spectrometry, although slightly higher, since only a certain harmonic of the signal is detected. The minimum detectable (shot-noise limited) on-resonance absorption for FMS is given by [2]

\[
(\alpha_{0})^{FMS}_{\min} = \frac{2e\Delta f}{\sqrt{\eta_c P_0} J_1(\beta) J_2(\beta)} \frac{\sqrt{2}}{\mathcal{K}_{pp}} \frac{1}{\sqrt{v_{m+\theta_{fm}}}},
\]
where $\chi_{PP}^{FM}(\nu_m, \theta_{fm})$ is the peak-to-peak value of the FM lineshape function for a given modulation frequency and detection phase, which was plotted in Figure 4.6 (b) and Figure 4.7 (b) in the Doppler-limit and for collision dominated regime, respectively. The maximum peak-to-peak values are 3.6 and 2.6 in the Doppler limit and in the collision dominated regime, respectively, and the product of the Bessel functions takes a value of 0.23 for a modulation index equal to 0.5. Thus the shot-noise limit for FMS is usually ~2 times higher than that of DAS.

The corresponding expression for WMS is

$$\alpha_0^{WMS} = \frac{2e\Delta f}{\eta_c P_0} \frac{\sqrt{2}}{\chi_{abs}^{o}(\nu_a)},$$

where $\chi_{abs}^{o}(\nu_a)$ is the on-resonance value of the second Fourier coefficient of the peak-normalized absorption lineshape function, which for a Gaussian lineshape function takes a maximum value of 0.42 for $\nu_a$ equal to 2.11 $\Gamma_D$ and for Lorentzian lineshape function – a maximum value of 0.34 for $\nu_a$ equal to 2.2 $\Gamma_L$ [4]. The shot-noise limit for WMS is thus ~4 times higher than that of DAS.

Since the FMS and WMS signals are less affected by 1/f noise than DAS, the detectability of these techniques comes closer to the shot noise limit than that of DAS. The main limitation to the sensitivity of the modulation techniques comes from interference fringes from multiple reflections between various optical components [69], including the EOM in FMS [70], since the width of these fringes is usually of the same order as the width of Doppler-broadened transitions.

Yet another type of background signal can appear at the dispersion phase in FMS when the polarization of light at the input of the EOM is not aligned along the principal axis of the crystal. Since the EOM is made of a birefringent crystal, the light polarized along the extraordinary (e-) and ordinary (o-) axes acquires different phase shift when passing the EOM. If the modulation is applied to the e-axis, the FM sidebands are produced only for the component of the light propagating along the e-axis, while the component along the o-axis passes unmodulated, although phase shifted with respect to the component of the carrier that is polarized along the e-axis. As a result, a balanced triplet, described by Eq. (4.3), is produced only along the e-axis of the EOM. This implies that a background signal appears if there is any polarization sensitive component between the EOM and the detector, with its polarization direction not aligned to the e-axis of the EOM.

Denoting the angle between the input polarization and the e-axis of the EOM by $\alpha_1$ and the angle between the output polarizer and the EOM e-axis by $\alpha_2$, the background signal is proportional to [71, 72]
\[ S_{EOM}^{\text{fm}} \sim J_1(\beta) \sin(2\alpha_1) \sin(2\alpha_2) \sin(\Delta \vartheta) \cos \theta_{\text{fm}}, \]  

(4.21)

where $\Delta \vartheta$ is the total phase difference between the light polarized along the o and e-axis directions, given by $\vartheta_{\text{in}} - \vartheta_{\text{in}}^e + \vartheta_{\text{EOM}}^o - \vartheta_{\text{EOM}}^e - \vartheta_{\text{DC}}^e$, where $\vartheta_{\text{in}}^o$ is the phase of the light entering the EOM polarized along the o-axis and $\vartheta_{\text{in}}^e$ is the phase of the light entering the EOM polarized along the e-axis, $\vartheta_{\text{EOM}}^o$ is the phase shift acquired in the EOM along the o-axis and $\vartheta_{\text{EOM}}^e$ is the phase shift acquired in the EOM along the e-axis and $\vartheta_{\text{DC}}^e$ is the phase shift induced by a DC voltage applied to the EOM along the e-axis. The $\cos \theta_{\text{fm}}$ dependence shows that this background signal appears only at the dispersion phase.

In order to reduce this background signal, the two polarization angles should be equal to an integer multiple of $\pi/2$. Note that an angle of $\pi/2$ corresponds to aligning any of the polarizers along the o-axis, in which case no modulation is produced; the angles should therefore be chosen as a multiple of $\pi$ or simply zero. Another way to remove the background is to make the total phase difference, $\Delta \vartheta$, equal to a zero or a multiple of $\pi$. Since the refractive indices of the crystal are temperature dependent, this phase shift can be adjusted by controlling the temperature of the EOM. However, this does not provide means of fast corrections of the phase, so a better solution is to apply a DC voltage to the EOM and control the phase shift actively in a feedback loop [71].
5. **Fabry-Perot Cavities**

An efficient way to increase the interaction length with the sample is to use an external optical resonator. The simplest and probably most commonly used type of resonator is the Fabry-Perot (FP) cavity (Figure 5.1), which is made of two parallel mirrors whose reflectivity is slightly smaller than unity and transmission is finite. The electric field incident on the input mirror can enter the resonator only if its frequency fulfills the standing wave condition inside the cavity; otherwise it is reflected. Once inside the cavity, the field is reflected multiple times between the two mirrors, which leads to a buildup of intensity, and an optical path that is much longer than the physical length of the cavity. A small fraction of the intracavity field leaks out of the cavity due to the finite transmission of the mirrors, at a rate proportional to the intracavity losses. The transmission of a FP cavity has a comb-like spectrum with equally spaced modes. The spacing of the modes, called the free spectral range (FSR), is inversely proportional to the cavity length, i.e., the mirror separation, while the width of the modes is determined by both the mirror reflectivity and the cavity FSR – the higher the reflectivity is, the narrower the transmission modes are. The ratio of the cavity FSR and the full width of the transmission mode is referred to as the finesse, which is a useful entity for characterization of FP cavities, since it depends solely on the reflectivities of the mirrors.

The basic properties of FP cavities are described in this chapter. The cavity transmission and reflection are derived for an empty cavity as well as in the presence of an analyte. The influence of mirror geometry on mode frequencies in a hemispherical cavity is shown. Moreover, the coupling of a Gaussian beam into a hemispherical cavity is described.

![Figure 5.1. Schematic picture of a Fabry-Perot resonator of length $L$.](image)

### 5.1 Empty cavity transmission and reflection

Figure 5.1 shows a FP cavity consisting of two parallel mirrors separated by a distance $L$. Each mirror is characterized by power reflection and transmission coefficients and losses, denoted by $r_j$, $t_j$, and $l_j$, respectively, where $j = 1$ and 2 for the input and output mirror, respectively. It follows from the energy conservation law that
For high reflectivity mirrors the reflection coefficients are close to unity, while the transmission coefficients and losses are close to zero (often as low as $10^{-4}$ or $10^{-5}$).

### 5.1.1 Electric field

The fraction of the incident electric field, $E_{\text{inc}}(\nu)$, that is reflected directly from the input mirror is given by [56]

$$E_r(\nu) = \sqrt{r_1} E_{\text{inc}}(\nu).$$

(5.2)

This field interferes with the field that has entered the resonator and leaked out from the cavity through the input mirror after one or more round trips between the mirrors. The leakage field, after $g$ round trips, can be written as

$$E_g^g(\nu) = \sqrt{r_1 r_2} (r_1 r_2)^{(g-1)/2} \sqrt{t_1} e^{-i[\varphi(\nu)+(2g-1)\pi]} E_{\text{inc}}(\nu),$$

(5.3)

where the factor of $(2g-1)\pi$ comes from the reflection from a medium with a higher refractive index (i.e., the surfaces of the mirrors), and where $\varphi(\nu)$ is the round trip phase shift given by

$$\varphi(\nu) = 2\frac{\pi n L}{c},$$

(5.4)

where $n$ is the refractive index inside the cavity (equal to 1 for an empty cavity). The total reflected electric field is then given by

$$E_r(\nu) = \left[\sqrt{r_1} - t_1 \sqrt{r_2} e^{-i\varphi(\nu)} \sum_{g=1}^{\infty} \left( \sqrt{r_1 r_2} e^{-i\varphi(\nu)} \right)^{g-1} \right] E_{\text{inc}}(\nu),$$

(5.5)

where in the last step the cavity reflection function, $\tilde{R}_c(\nu)$, has been introduced. Since the infinite series (for $\sqrt{r_1 r_2} < 1$) can be summed to

$$\sum_{g=1}^{\infty} \left( \sqrt{r_1 r_2} e^{-i\varphi(\nu)} \right)^{g-1} = \frac{1}{1 - \sqrt{r_1 r_2} e^{-i\varphi(\nu)}},$$

(5.6)

the cavity reflection function for the electric field can be expressed as

$$\tilde{R}_c(\nu) = \frac{\sqrt{r_1} - \sqrt{r_2} (1 - l_1) e^{-i\varphi(\nu)}}{1 - \sqrt{r_1 r_2} e^{-i\varphi(\nu)}},$$

(5.7)
where Eq. (5.1) has been used.

The transmitted field can be calculated in a similar manner as

\[
\hat{E}_t (\nu) = \sqrt{r_1 t_2} e^{-i\varphi(\nu)/2} \sum_{g=1}^{\infty} \left[ \sqrt{r_1 r_2} e^{-i\varphi(\nu)} \right]^{g-1} \hat{E}_{inc} (\nu) \\
= \hat{T}^c (\nu) \hat{E}_{inc} (\nu),
\]

which implies that the cavity transmission function for the electric field, \(\hat{T}^c (\nu)\), can be written as

\[
\hat{T}^c (\nu) = \frac{\sqrt{r_1 t_2} e^{-i\varphi(\nu)/2}}{1 - \sqrt{r_1 r_2} e^{-i\varphi(\nu)}}.
\]

(5.9)

The real and imaginary parts of the reflection and transmission functions are plotted in Figure 5.2 for a lossless cavity (i.e., for \(l_1 = l_2 = 0\)) and equal reflectivity of the mirrors, \(r_1 = r_2 = 0.81\). The real parts have a comb-like structure of distinct modes, while the imaginary parts have dispersive shape and are zero on resonance.

![Figure 5.2](image)

Figure 5.2. The real [(a), (b)] and imaginary [(c), (d)] parts of the cavity transmission [(a), (c)] and reflection [(b), (d)] functions around the qth cavity mode of a cavity with mirrors with equal reflection coefficients, \(r_1 = r_2 = 0.81\), as a function of optical frequency in terms of the cavity FSR.

The resonant frequencies, i.e., those transmitted by the cavity, are those for which the round trip phase shift is equal to a multiple of \(2\pi\), i.e.,
\( \varphi(v_q) = 2q\pi \). Thus, from Eq. (5.4), the center frequency of the \( q \)th cavity transmission mode is

\[
\nu_q = \frac{qc}{2nL},
\]

and the spacing of the modes, i.e., the cavity free spectral range (FSR), is equal to

\[
\text{FSR} = \nu_{q+1} - \nu_q = \frac{c}{2Ln}.
\]

The FSR of an empty cavity with a length in the range of 30 – 50 cm is in the 300 – 500 MHz range (higher for a shorter cavity).

The round trip phase shift can be rewritten in terms of a detuning of the laser frequency from the (nearest) \( q \)th cavity mode, \( \Delta \nu_q = \nu - \nu_q \), and the FSR as

\[
\varphi(v) = \frac{4\pi n L (\nu_q + \Delta \nu_q)}{c} = 2q\pi + \frac{2\pi \Delta \nu_q}{\text{FSR}} = 2q\pi + \varphi_q,
\]

where the round trip phase shift for frequencies in the vicinity of the \( q \)th mode, \( \varphi_q = \varphi(\Delta \nu_q) \), has been introduced in the last step.

The electric field stored inside the cavity leaks out through the mirrors at a constant rate, proportional to the intracavity round trip losses [13]. The decay of the intracavity field is exponential, with a time constant given by

\[
\tau_{\text{cav}} = \frac{4L}{c(t_1 + t_2 + l_1 + l_2)}.
\]

5.1.2 Intensity

The intensity transmitted through a FP cavity can be calculated from Eqs (5.8) and (5.9) as

\[
I_t(\Delta \nu_q) = I_0 \frac{t_1 t_2}{(1 - \sqrt{r_1 r_2})^2 + 4\sqrt{r_1 r_2} \sin^2 \left( \frac{\pi \Delta \nu_q}{\text{FSR}} \right)}.
\]

The cavity transmission, i.e., the ratio of the transmitted to the incident intensity, can therefore be written as

\[
T_c(\Delta \nu_q) = \frac{I_t(\Delta \nu_q)}{I_0} = \frac{T_{\text{c res}}}{1 + \frac{4\sqrt{r_1 r_2}}{(1 - \sqrt{r_1 r_2})^2} \sin^2 \left( \frac{\pi \Delta \nu_q}{\text{FSR}} \right)}.
\]
where

\[ T_{res}^c = \frac{t_1 t_2}{(1 - \sqrt{r_1 r_2})^2} \]  \hspace{1cm} (5.16)

is the on-resonance cavity transmission.

An important parameter describing a cavity is its finesse, defined as the ratio of the spacing of the modes (FSR) and their full width. The cavity mode HWHM, \( \Gamma_c \), i.e., the frequency detuning for which the transmission function becomes half of its on-resonance value, can be found by putting the denominator in Eq. (5.15) to 2, which yields,

\[ \frac{4 \sqrt{r_1 r_2}}{(1 - \sqrt{r_1 r_2})^2} \sin^2 \left( \frac{\pi \Gamma_c}{\text{FSR}} \right) = 1. \]  \hspace{1cm} (5.17)

Since for high reflectivity mirrors the mode width is much smaller than the FSR, i.e., \( \Gamma_c \ll \text{FSR} \), the HWHM of the cavity mode can be written as

\[ \Gamma_c = \frac{\text{FSR}}{\pi} \sqrt{(1 - \sqrt{r_1 r_2})^2} \]  \hspace{1cm} (5.18)

Thus the finesse is given by

\[ F = \frac{\text{FSR}}{2\Gamma_c} = \frac{\pi \sqrt{r_1 r_2}}{1 - \sqrt{r_1 r_2}}. \]  \hspace{1cm} (5.19)

For a cavity with high reflectivity mirrors, i.e., for \( r_j = 1 \), the finesse can alternatively be expressed as [31, 33]

\[ F = \frac{\pi}{1 - \sqrt{r_1 r_2}} = \frac{\pi}{1 - \sqrt{1 - t_1 - t_2}} = \frac{2\pi}{t_1 + t_1 + t_2 + l_2}. \]  \hspace{1cm} (5.20)

where Eq. (5.1) has been used. This shows that a cavity made of mirrors with losses and transmissions of the order of 10^{-5} has a finesse around, or above, 10^5 and the width of the transmission modes is in the tens of kHz range.

The cavity decay time, Eq. (5.13), can be expressed in terms of the finesse and FSR as

\[ \tau_{cav} = \frac{F}{\pi \text{FSR}} = \frac{1}{2\pi \Gamma_c}, \]  \hspace{1cm} (5.21)

which shows that it is proportional to the inverse of the cavity mode width. For a cavity with a finesse of a few thousand the decay time is of the order of a few microseconds.
The intensity transmitted through the cavity on resonance, $I^0_t$, can be calculated from Eq. (5.16) as

$$I^0_t = I_o T^\text{res}_c = I_o t_1 t_2 \left( \frac{F}{\pi} \right)^2,$$

where the definition of finesse from Eq. (5.20) has been used in the last step. The intracavity intensity, $I_c$, is related to the transmitted intensity through the transmission coefficient of the output mirror and is thereby equal to

$$I_c = \frac{I^0_t}{t_2} = I_o t_1 \left( \frac{F}{\pi} \right)^2.$$

The intensity that is absorbed or scattered at the mirrors, $I_l$, is given by

$$I_l = (l_1 + l_2) I_c = I_o (l_1 + l_2) t_1 \left( \frac{F}{\pi} \right)^2.$$

Finally, the on-resonance reflected intensity can be calculated as $I^0_r = I^0_o - I^0_t - I_l$, whereby the on-resonance cavity reflection becomes

$$R^\text{res}_c = \frac{I^0_r}{I^0_o} = \left( \frac{F}{2\pi} \right)^2 \left( l_1 + l_2 - t_1 + t_2 \right)^2.$$

The transmission of the input cavity mirror can be calculated by inserting the definition of the finesse, Eq. (5.20), into the above equation, which yields

$$t_1 = \frac{1 - \sqrt{R^\text{res}_c} \frac{F}{\pi}}{F}.$$

This implies that the intracavity intensity buildup, $\kappa$, defined as the ratio of the intracavity intensity [Eq. (5.23)] to the incident intensity, can be expressed in terms of cavity finesse and the on-resonance reflection as

$$\kappa = \frac{I_c}{I_0} = \left( 1 - \sqrt{R^\text{res}_c} \right) \frac{F}{\pi}.$$

A cavity is *impedance matched* if no intensity is reflected on resonance. Equation (5.25) shows that this is the case when the input mirror transmission is equal to the sum of the output mirror transmission and the losses of both mirrors, i.e., when $t_1 = t_2 + l_1 + l_2$. When this condition is fulfilled, the intracavity intensity buildup is equal to $F/\pi$. Since the cavity finesse can be as high as $10^5$, the intensity buildup in an impedance matched cavity can be well above $10^4$. Moreover, the on-resonance transmission of an impedance matched cavity becomes $t_2/t_1$, wherefore it can be well below 1 if the mirror losses are a significant fraction of the input mirror transmission.
An ideal cavity with mirrors with equal reflectivities and no losses is impedance matched and its on-resonance transmission is equal to 1. The cavity transmission, Eq. (5.15), for such a cavity can be rewritten in terms of the cavity finesse as

\[
T^c(\Delta v_q) = \frac{1}{1 + \left(\frac{2F}{\pi}\right)^2 \sin^2 \left(\frac{\pi \Delta v_q}{FSR}\right)}. \tag{5.28}
\]

For a laser frequency detuning much smaller than FSR, i.e., for \(\Delta v_q \ll FSR\), the sine term in the denominator can be series expanded yielding

\[
T^c(\Delta v_q) = \frac{\Gamma^2_c}{\Gamma^2_c + (\Delta v_q)^2} T^c_{\text{res}}. \tag{5.29}
\]

Thus a transmission mode of a high finesse cavity, whose width is much smaller than the cavity FSR, can be well modeled by a Lorentzian function.

In a lossless cavity all intensity that is not transmitted is reflected, thus the cavity reflection, \(R^c(\Delta v_q)\), becomes \(1 - T^c(\Delta v_q)\), which also can be written as

\[
R^c(\Delta v_q) = \frac{\left(\frac{2F}{\pi}\right)^2 \sin^2 \left(\frac{\pi \Delta v_q}{FSR}\right)}{1 + \left(\frac{2F}{\pi}\right)^2 \sin^2 \left(\frac{\pi \Delta v_q}{FSR}\right)} = \frac{(\Delta v_q)^2}{\Gamma^2_c + (\Delta v_q)^2}, \tag{5.30}
\]

where the latter equality is again valid for a detuning smaller than the cavity FSR. The cavity transmission and reflection are plotted in Figure 5.3 for the same mirror reflection coefficients as previously, i.e., for \(r_1 = r_2 = 0.81\), which yield a finesse of \(\sim 15\).

![Figure 5.3](image-url)
5.2 Cavity transmission and reflection in the presence of an absorber

The presence of a gas modifies the properties of the cavity. First of all, resonant frequencies are shifted by a change of the refractive index, \( n \), and their spacing decreases. Secondly, in the vicinity of a molecular transition the light entering the cavity is phase shifted by \( \phi(\Delta \nu) \) and attenuated by \( \delta(\Delta \nu) \) each time it passes the cavity, and the cavity reflection and transmission functions for the electric field are modified to

\[
\tilde{R}_A^e(\Delta \nu) = \frac{\sqrt{r_1} - \sqrt{r_2} (1 - l_1)e^{-i\phi(\nu)}e^{-2\delta(\Delta \nu) - i2\phi(\Delta \nu)}}{1 - \sqrt{r_1}r_2 e^{-i\phi(\nu)}e^{-2\delta(\Delta \nu) - i2\phi(\Delta \nu)}}
\]

(5.31)

and

\[
\tilde{T}_A^e(\Delta \nu) = \frac{\sqrt{r_1}r_2 e^{-i\phi(\nu)/2}e^{-\delta(\Delta \nu) - i\phi(\Delta \nu)}}{1 - \sqrt{r_1}r_2 e^{-i\phi(\nu)}e^{-2\delta(\Delta \nu) - i2\phi(\Delta \nu)}}
\]

(5.32)

respectively. The real and imaginary parts of the reflection and transmission functions in the presence and absence of an analyte are plotted with black and gray curves in Figure 5.4, respectively, for a cavity with lossless mirrors.

Figure 5.4. The real [(a), (b)] and imaginary [(c), (d)] parts of the cavity transmission [(a), (c)] and reflection [(b), (d)] functions in the absence (gray curve) and presence of an analyte (black curve), represented by a Gaussian absorption (dashed curve) and dispersion (dotted curve) lineshape functions with a HWHM equal to half of the cavity FSR (for a cavity with a finesse of 30).
with equal reflectivity, $r_1 = r_2 = 0.9$. The attenuation and phase shift due to the analyte are schematically illustrated with a Gaussian lineshape function and its dispersion counterpart by dashed and dotted curves in each panel, respectively. It is evident that in the vicinity of a molecular transition the cavity modes become wider and lower, and the center frequencies of the modes are shifted.

### 5.2.1 Cavity enhancement

The intensity of the light transmitted on resonance in the vicinity of a transition can be calculated from Eq. (5.32) as $I_t(\Delta \nu) = I_o T^c_\lambda(\Delta \nu) T^{c*}_\lambda(\Delta \nu)$, which yields [38]

$$I_t(\Delta \nu) = I_o \frac{t_1 t_2 e^{-2\delta(\Delta \nu)}}{1 - \sqrt{r_1 r_2} e^{-2\delta(\Delta \nu)}}^2. \quad (5.33)$$

The relative intensity change due to the presence of an analyte is given by

$$\frac{I_o^0 - I_t(\Delta \nu)}{I_o^0} = 1 - \frac{\left(1 - \sqrt{r_1 r_2}\right)^2 e^{-2\delta(\Delta \nu)}}{\left[1 - \sqrt{r_1 r_2} e^{-2\delta(\Delta \nu)}\right]^2}. \quad (5.34)$$

where $I_o^0$ is the transmitted intensity in the absence of absorber, given by Eq. (5.22). For small attenuation this expression can be series expanded to

$$\frac{I_o^0 - I_t(\Delta \nu)}{I_o^0} = \frac{2 \sqrt{r_1 r_2} 2\delta(\Delta \nu)}{1 - \sqrt{r_1 r_2} 2\delta(\Delta \nu)} = \frac{2F}{\pi} \alpha(\Delta \nu). \quad (5.35)$$

This shows, by comparison with Eq. (2.11), that the relative absorption in a high finesse cavity is enhanced by a factor of $2F/\pi$. This factor, which is of the same order of magnitude as the cavity finesse, can therefore be interpreted as the enhancement of the interaction length.

### 5.2.2 Detectability and noise

Since the absorption signal is enhanced by a factor of $2F/\pi$ by a resonant cavity, the minimum detectable (shot-noise-limited) absorption is decreased by the same factor with respect to that of DAS yielding

$$\left(\alpha^c_{\text{min}}\right) = \frac{\pi}{2F} \sqrt{\frac{2e\Delta f}{\eta_c P_o}}. \quad (5.36)$$

For a cavity with a finesse of $10^4$, the shot-noise-limited on-resonance absorption can be as low as $10^{-12}$, i.e. 4 orders of magnitude below that of DAS, Eq. (2.33). The shot noise limit is, however, most often not reached in cavity enhanced techniques based on resonant coupling of the laser light due
to the conversion of laser frequency noise to amplitude noise. When the laser frequency is locked to a cavity mode, any residual frequency noise of the laser with respect to the cavity will be converted to amplitude noise. Unless the lock is very tight, this noise usually limits the detectability.

5.3 Hemispherical cavity

The electric field coupled into a FP cavity must not only fulfill the standing wave condition, it must also produce a stable transverse intensity pattern at each plane inside the cavity. The intensity profile of a laser beam is most often Gaussian, thus for most efficient coupling the resonator should accept such a mode of light. However, a resonator constructed of two parallel flat mirrors does not support a beam with a Gaussian intensity distribution. Moreover, it is only marginally stable. Thus cavities are usually spherical, constructed from two concave mirrors, or hemispherical, with one concave and one flat mirror.

5.3.1 Gaussian beams

The complex electric field of a Gaussian laser beam at an axial position $z$ (counted from the beam waist), and at a radial distance $r$ from the center of the beam can be written as [56]

$$
\tilde{E}_G(v,r,z,t) = \frac{E_0}{2} e^{i 2 \pi \nu t} \frac{w_0}{w(z)} e^{i \left[ k_0 (z - \tan^{-1}(z/z_0)) \right]} e^{-ik_0 r^2 / 2R_G(z)} e^{-r^2 / w^2(z)}, \tag{5.37}
$$

where the spot size, $w(z)$, is given by

$$
w(z) = w_0 \sqrt{1 + z^2 / z_0^2}, \tag{5.38}
$$

where $w_0$ is the minimum spot size, $z_0$ is the Rayleigh range, which is a measure of the length of the waist region, given by

$$
z_0 = \frac{\pi w_0^2}{\lambda}, \tag{5.39}
$$

and $R_G(z)$ is the radius of curvature of the beam given by

$$
R_G(z) = z + \frac{z_0^2}{z}. \tag{5.40}
$$

Thus the intensity distribution of a Gaussian beam can be written as [56]

$$
I_G(r,z) = \frac{I_0}{1 + z^2 / z_0^2} e^{-2r^2 / w^2(z)}, \tag{5.41}
$$
where \( I_0^0 \) is the intensity at the center of the beam \((r = 0)\) at the beam waist \((z = 0)\), given by \( c \epsilon_0 E_0^2 / 2 \). The evolution of the Gaussian beam along the propagation direction in the vicinity of the waist is shown in Figure 5.5.

The power of a Gaussian beam can be calculated by integration of intensity over the beam area according to Eq. (2.25), and is given by

\[
P(z) = \int_0^{2\pi} \int_0^\infty I_G(r,z) \rho \, dr \, d\varphi = I_0^0 \frac{\pi w_0^2}{2}.
\]

(5.42)

This shows that it is possible to assign a Gaussian beam an effective area of \( \pi w_0^2 / 2 \).

Figure 5.5. The evolution of a Gaussian beam spot size, \( w(z) \), along the propagation direction in the vicinity of the waist. The Rayleigh range, \( z_0 \), spot size at beam waist, \( w_0 \), and the beam radius of curvature, \( R_G(z) \), are indicated, and the intensity profile is plotted at the beam waist and twice the Rayleigh range.

### 5.3.2 Resonator modes

If a Gaussian beam should form a resonator mode, its radius of curvature at each mirror must be equal to that of the mirror, \( R_j \) [56]. Obviously, a resonator with two flat mirrors will not sustain a Gaussian mode, wherefore the cavity must be hemispherical, as shown in Figure 5.6, or spherical.

Figure 5.6. A Gaussian resonator mode of a hemispherical cavity.

A resonator is stable if the beam is confined inside the cavity for an infinitely long time, i.e., it does not escape the resonator after an infinite number of reflections. The stability condition is usually written in terms of the \( g_j \) parameter, one for each mirror, defined as
\[ g_j = 1 - \frac{L}{R_j}, \quad (5.43) \]

and is given by [56]

\[ 0 \leq g_1 g_2 \leq 1. \quad (5.44) \]

The radius of curvature of the flat input mirror of a hemispherical cavity (Figure 5.6) is infinite, thus \( g_1 = 1 \) and the above condition reduces to

\[ 0 \leq L \leq R_2. \quad (5.45) \]

This shows that a hemispherical cavity is stable if its length is smaller than the curvature of the concave mirror.

The frequency of the \( q \)th longitudinal Gaussian beam mode of a hemispherical resonator is given by [56]

\[ \nu_q = \frac{c}{2L} \left( q + \frac{1}{\pi} \arccos \sqrt{g_2} \right). \quad (5.46) \]

The mirror curvature shifts the mode frequency with respect to the \( q \)th mode of a flat mirror resonator with the same length, while the mode spacing is still equal to the cavity FSR, as defined in Eq. (5.11). Moreover, there exist higher order Gaussian modes, denoted by \( \text{TEM}_{mn} \) (transverse electromagnetic, where \( m \) and \( n \) are positive integers), whose frequencies are given by

\[ \nu_{qmn} = \frac{c}{2L} \left[ q + \frac{1}{\pi} (m + n + 1) \arccos \sqrt{g_2} \right]. \quad (5.47) \]

Each transverse mode of order \((m,n)\) is associated with a \( q \)th longitudinal mode \((\text{TEM}_{00})\) and forms its own intensity pattern. A cavity is degenerate if the frequency of a transverse mode coincides with that of a longitudinal mode with a number higher than \( q \), i.e., if

\[ \nu_{qmn} = \nu_{(q+\Delta q)00}, \quad (5.48) \]

where \( \Delta q \) is a positive integer. Using Eq. (5.47) yields the condition for mode degeneracy as

\[ \frac{1}{\pi} (m + n) \arccos \sqrt{g_2} = \Delta q. \quad (5.49) \]

Solving for \( g_2 \) gives

\[ g_2 = \cos^2 \left( \frac{\Delta q \pi}{m + n} \right). \quad (5.50) \]

48
The ratios of the cavity length and the output mirror curvature corresponding to the solution of the above equation should be avoided when cavities are constructed, since it is difficult, if not impossible, to obtain a clean longitudinal mode spectrum in a degenerate cavity.

### 5.4 Spatial mode matching

A laser beam can be efficiently coupled into a cavity only if it is spatially matched to the geometry of the longitudinal TEM$_{00}$ mode of the cavity. The waist of the longitudinal Gaussian beam mode of a hemispherical resonator lies at the flat mirror, where the radius of curvature is infinite. This implies that the waist of the input laser beam should also be placed at the flat mirror. The radius of curvature of the laser beam at the position of the concave mirror, $R_G(L)$, should then be made equal to the curvature of that mirror, $R_2$. Figure 5.7 shows a Gaussian laser beam coupled into a hemispherical cavity with the help of a lens placed at a distance $d_1$ from the laser beam waist and $d_2$ from the cavity input mirror.

Figure 5.7. Mode matching of a Gaussian laser beam to a hemispherical cavity.

The geometry of a Gaussian beam can be fully described by a complex beam radius, $\tilde{q}$, defined as [56]

$$\frac{1}{\tilde{q}(z)} = \frac{1}{R_G(z)} + \frac{i\lambda}{\pi w^2(z)}.$$  \hspace{1cm} (5.51)

The propagation of a Gaussian beam through various optical elements can be calculated using the ABCD ray matrices, which transform the initial complex beam radius, $\tilde{q}'$, to a final, $\tilde{q}''$, according to [56]

$$\tilde{q}'' = \frac{A\tilde{q}' + B}{C\tilde{q}' + D}.$$ \hspace{1cm} (5.52)

The ray matrix for a beam propagating in free space over a distance $d$ is

$$\begin{bmatrix} A & B \\ C & D \end{bmatrix} = \begin{bmatrix} 1 & d \\ 0 & 1 \end{bmatrix},$$ \hspace{1cm} (5.53)

and for a beam passing a thin lens with a focal length $f_l$
\[
\begin{bmatrix}
A & B \\
C & D \\
\end{bmatrix} = \begin{bmatrix}
1 & 0 \\
-1/f_l & 1 \\
\end{bmatrix}. 
\] (5.54)

The propagation matrix for the beam shown in Figure 5.7 from the first beam waist to the input cavity mirror is calculated by multiplication of three matrices in inverse order, which yields

\[
\begin{bmatrix}
A & B \\
C & D \\
\end{bmatrix} = \begin{bmatrix}
1 - \frac{d_2}{f_l} & d_1 + d_2 - \frac{d_2 d_2}{f_l} \\
-\frac{1}{f_l} & 1 - \frac{d_1}{f_l} \\
\end{bmatrix}. 
\] (5.55)

According to Eq. (5.51), the complex beam radius at the waist of the laser beam, \( \tilde{q}' \) (see Figure 5.7), is fully imaginary and given by

\[
\tilde{q}' = -iz'_0, 
\] (5.56)

where \( z'_0 \) is the Rayleigh range of the laser beam given by Eq. (5.39). The complex beam radius of the cavity mode at the input mirror is also complex, and can be written as

\[
\tilde{q}^* = -iz'^{cav}_0, 
\] (5.57)

where \( z'^{cav}_0 \) is the Rayleigh range of the cavity mode. In order to match the spatial distribution of the laser beam to that of the cavity, the Rayleigh range of the laser beam after refraction in the lens, \( z'_0 \), should be equal to the Rayleigh range of the cavity mode, which can be calculated from Eq. (5.40) and the condition that \( R_L = R_2 \), as

\[
z^*_0 = z^{cav}_0 = \sqrt{(R_2 - L)l}. 
\] (5.58)

The two complex beam radii, \( \tilde{q}' \) and \( \tilde{q}^* \), are related through Eq. (5.52), which yields

\[
-iz^*_0 = \frac{BD + AC(z'_0)^2 - iz'_0}{C^2(z'_0)^2 + D^2}. 
\] (5.59)

Equalizing the real and imaginary parts of the above equation yields

\[
BD + AC(z'_0)^2 = 0, 
\] (5.60)

and

\[
C^2(z'_0)^2 + D^2 = z'_0 / z^*_0, 
\] (5.61)

respectively. Using Eq. (5.55) for the matrix components gives finally a set of
These equations can be solved for a given incident beam, i.e., a given \( z'_0 \), and a given cavity, i.e., a given \( R_z \) and \( L \) and thus a given \( z''_0 \), and for a given focal length, \( f_1 \), to yield the distances \( d_1 \) and \( d_2 \), which indicate where the lens should be placed to shape the beam correctly. The second equation gives directly an expression for \( d_1 \) as

\[
d_1 = f_1 - \frac{z'_0}{\sqrt{f_2 (f_2/z'_0 - z''_0)}}
\]

whereas \( d_2 \) can be calculated from the former expression.
6. Laser Frequency Stabilization

In order to make use of cavity enhancement of the interaction length, described in section 5.2, the laser light has to be resonantly coupled into the cavity. This is not trivial for high finesse cavities, as the free-running linewidth of the laser is usually comparable to or even larger than the cavity mode width. Moreover, the laser center frequency drifts due to mechanical disturbances and temperature changes. This prevents an efficient coupling of the power of a free-running laser into the cavity and, most of all, gives rise to frequency-to-amplitude noise conversion. Thus the laser frequency has to be actively stabilized to a cavity mode, either by optical or electronic feedback.

Laser locking by means of optical feedback from the cavity was originally developed by Romanini et al. for cw-CRDS [26]. The cavity needs to be V-shaped in order to avoid direct optical feedback from the cavity input mirror and ensure that the feedback comes only from the intracavity field [27, 73, 74]. The optical feedback from the intracavity field does not only provide an automatic locking of the laser frequency to the cavity mode; it also induces spectral narrowing of the laser linewidth thus eliminating the problem of a noisy cavity output [73] and allowing for a measurement of the cavity transmission with a fast response time. However, in order to ensure efficient locking, the phase of the reflected light has to be adjusted to provide maximum constructive feedback, which is usually achieved by active control of the position of a mirror in front of the cavity by a piezoelectric crystal. Moreover, the cavity length is usually not scanned, whereby molecular transitions can be probed only at the frequencies corresponding to the longitudinal cavity modes.

One of the most established techniques for electronic laser locking is the Pound-Drever-Hall (PDH) technique [75-79], which is also used in NICE-OHMS. An error signal with odd symmetry is derived from cavity reflected light with the use of FMS, filtered and fed back to the laser actuator. When the gain and bandwidth in the feedback loop are sufficient, the laser center frequency is stabilized to the center of the cavity mode and the linewidth of the laser is narrowed so that all power is coupled into the cavity. Moreover, once locked, the laser is able to follow a change of the cavity mode frequency induced by an alteration of the cavity length, and thus be scanned over a transition, which allows for a continuous signal acquisition.

The principles of the PDH technique are described below, preceded by a revision of the basics of negative feedback theory and followed by a discussion of the major issues concerning the servo design.
6.1 Basics of control theory

Consider a system depicted in Figure 6.1 producing a variable with a value $X$, which should be equal to a given reference value $X_{ref}$. The system has to be externally controlled, as it itself tends to wander off the set value due to external or internal disturbances, represented by $Z$.

![Figure 6.1. Block diagram of a negative feedback control loop.](image)

The output of the controlled system is compared to a reference value at point 1 and an error signal $X - X_{ref}$ is produced. The controller, which has a frequency dependent complex transfer function $H(f)$, amplifies the error signal and produces a correction signal $Y$, which is fed back to the system in order to correct the deviation of $X$ from $X_{ref}$. A possible disturbance $Z$ enters at point 2. Denoting the system transfer function by $G(f)$, the output of the system in a closed loop configuration can be expressed as [80]

$$X = G(f)(Z - Y),$$

(6.1)

where the correction signal is related to the error signal as

$$Y = H(f)(X - X_{ref}).$$

(6.2)

Thus $X$ can be expressed in terms of the reference value and the disturbance as

$$X = \frac{G(f)H(f)}{1 + G(f)H(f)} X_{ref} + \frac{G(f)}{1 + G(f)H(f)} Z.$$

(6.3)

The factor in front of the reference value is the closed loop transfer function, while that in front of the disturbance is the disturbance propagation function. This equation might be rewritten as

$$X = \frac{1}{1 + \frac{1}{G(f)H(f)}} \left( X_{ref} + \frac{1}{H(f)} Z \right),$$

(6.4)

which shows that if the open loop transfer function, $G(f)H(f)$, is much
larger than 1, the variable $X$ is close to the reference value $X_{\text{ref}}$, and the influence of any disturbance is reduced by the inverse of the transfer function of the controller, $1/H(f)$. Thus, when designing the control loop one should aim for as high open loop gain and controller gain as possible.

It is not possible to construct a control system with a proportional gain over all frequencies due to inevitable phase shifts that develop in any system. The control loop is unstable if the open loop transfer function is equal to -1, as then the denominator in Eq. (6.3) becomes infinite and the system starts to oscillate. In particular, at a frequency at which the phase is equal to $-180^\circ$ the denominator becomes $1 - |G(f)H(f)|$, which means that the gain of the open loop transfer function should not be equal to 1 at that frequency. In reality, there is both a phase and gain margin that have to be kept around this point in order for the system to be stable. Note, however, that the phase can in principle reach $-180^\circ$ if the gain is above 1, in which case the system is conditionally stable.

One way to determine the stability of a control system is to use a Bode diagram, which consists of separate plots of gain (in dB) and phase (in degrees) of the open loop transfer function with a common logarithmic frequency scale [81]. The bandwidth and the unity gain point (0 dB) can be found from the gain curve, while the corresponding phase can be seen on the other plot. The bandwidth should be large enough to allow for correction of disturbances at all frequencies that are possible in the system, while the phase at the unity gain point should not approach $-180^\circ$; in fact, a phase margin of ca $30^\circ$ should be maintained. According to the first Bode theorem [81] the slope of the asymptotic curve in the gain plot implies a certain corresponding phase. In particular, a slope of $-20m$ dB/decade (for integer $m$) corresponds to a phase of $-90^\circ$. This implies that the slope at the crossover point, and in a sufficiently large frequency range around it, should be $-20$ dB/decade in order to ensure that the phase is close to $-90^\circ$ at the unity gain point. For a detailed discussion about the stability criteria see Chapter 6 in Ref. [81].

### 6.2 The Pound-Drever-Hall technique

The PDH technique utilizes FMS to derive an error signal from the cavity reflected light, as shown in Figure 6.2. The phase of a linearly polarized laser light is modulated by an EOM at a frequency $\nu_{\text{pdh}}$, which is smaller than the cavity FSR but larger than the cavity linewidth, typically in the tens of MHz range. The FM light is incident on the cavity after passing a polarizing beam splitter (PBS) and a quarter-wave plate ($\lambda/4$), which changes its polarization to circular. After reflection the light goes back through the quarter-wave plate, whereby its polarization becomes linear and perpendicular to that of the incident wave, and the beam is reflected by the
PBS towards a photodetector, PD. The detector signal is multiplied with the reference signal (at a frequency of $\nu_{pdh}$) at the correct phase (adjusted by a phase shifter, Ph) in a double balanced mixer (DBM). The demodulated signal is low pass filtered (LP) to yield the PDH error signal, which is amplified and filtered in the control servo and fed back to the laser through its frequency actuator.

![Figure 6.2. Schematics of Pound-Drever-Hall laser frequency stabilization scheme. EOM – electro-optic modulator, PBS – polarizing beam splitter, $\lambda/4$ – quarter wave plate, PD – photodetector, DBM – double balanced mixer, Ph – phase shifter, LP – low pass filter.](image)

Using the nomenclature introduced in Figure 6.1, the laser is the controlled system and the laser frequency is the controlled variable. The reference signal (i.e., the frequency of the addressed cavity mode) is provided by the cavity, the error signal (i.e., the output of the LP filter) is created in the demodulation process, and the control signal is produced by the servo. A disturbance can enter anywhere in the system, it can be inherent in the laser or couple through the actuator. When the laser frequency is locked to a cavity mode and the cavity length is tuned, the laser frequency should, in a correctly designed system, follow the change of the reference value, i.e., the frequency of the cavity mode.

### 6.2.1 Error signal

When the phase of the electric field incident on a cavity is modulated at a frequency $\nu_{pdh}$, the reflected intensity has a component at the modulation frequency, which can be calculated according to Eq. (4.6) as

$$
I_r^{\nu_{pdh}}(v_c,t) = 2I_0J_0(\beta_1)J_1(\beta_1)\left[\text{Re}(\bar{R}_c^c \bar{R}_c^c - \bar{R}_0^c \bar{R}_1^c)\cos(2\nu_{pdh}t) - \text{Im}(\bar{R}_1^c \bar{R}_0^c - \bar{R}_0^c \bar{R}_1^c)\sin(2\nu_{pdh}t)\right],
$$

(6.5)

where $\bar{R}_0^c$ is the cavity reflection function for the carrier, and $\bar{R}_{\pm1}^c$ are the cavity reflection functions for the upper and lower sidebands, respectively, given by Eq. (5.7). Since the modulation frequency is larger than the cavity mode width, it can be assumed that when the laser carrier is in the vicinity of a $q$th cavity mode, the two sidebands are completely reflected, i.e., $\bar{R}_{\pm1}^c = 1$, 56
whereby the factor in front of the cosine term reduces to
\[
\text{Re}\left(\tilde{R}_1^c \tilde{R}_0^{c*} - \tilde{R}_0^c \tilde{R}_1^{c*}\right)_{\nu_c = \nu_q} = 0, \tag{6.6}
\]
while the one in front of the sine term becomes
\[
\text{Im}\left(\tilde{R}_1^c \tilde{R}_0^{c*} - \tilde{R}_0^c \tilde{R}_1^{c*}\right)_{\nu_c = \nu_q} = -2 \text{Im} \tilde{R}_0^c. \tag{6.7}
\]
Similarly, when the lower sideband is tuned close to a cavity resonance, the upper sideband and the carrier are fully reflected, thus
\[
\text{Re}\left(\tilde{R}_1^c \tilde{R}_0^{c*} - \tilde{R}_0^c \tilde{R}_1^{c*}\right)_{\nu_c - \nu_m = \nu_q} = -\text{Re} \tilde{R}_{-1}^c + 1, \tag{6.8}
\]
and
\[
\text{Im}\left(\tilde{R}_1^c \tilde{R}_0^{c*} - \tilde{R}_0^c \tilde{R}_1^{c*}\right)_{\nu_c - \nu_m = \nu_q} = \text{Im} \tilde{R}_{-1}^c, \tag{6.9}
\]
with corresponding expressions for the case when the upper sideband is close to a cavity resonance, i.e.,
\[
\text{Re}\left(\tilde{R}_1^c \tilde{R}_0^{c*} - \tilde{R}_0^c \tilde{R}_1^{c*}\right)_{\nu_c + \nu_m = \nu_q} = \text{Re} \tilde{R}_1^c - 1, \tag{6.10}
\]
and
\[
\text{Im}\left(\tilde{R}_1^c \tilde{R}_0^{c*} - \tilde{R}_0^c \tilde{R}_1^{c*}\right)_{\nu_c + \nu_m = \nu_q} = \text{Im} \tilde{R}_1^c. \tag{6.11}
\]
This implies that as the FM triplet is scanned across a cavity mode, the intensity at the PDH frequency can be written as a sum of all the above terms, i.e., as
\[
I^{\text{pdh}}_{\nu_c}(t) = 2 I_0 J_0(\beta_1) J_1(\beta_1) \left[ \text{Re} \tilde{R}_1^c - \text{Re} \tilde{R}_{-1}^c \right] \cos(2\pi \nu_{\text{pdh}} t) \\
+ \left( -\text{Im} \tilde{R}_{-1}^c + 2 \text{Im} \tilde{R}_0^c - \text{Im} \tilde{R}_1^c \right) \sin(2\pi \nu_{\text{pdh}} t). \tag{6.12}
\]

The cosine term has no contribution from the carrier, similarly to the ordinary FMS signal, and is therefore not useful for locking (it has a very weak frequency dependence in the vicinity of the cavity mode). A useful error signal with odd symmetry can instead be obtained from the sine term. The Pound-Drever-Hall error signal is obtained by demodulation of the detector signal with the in-phase reference signal, which yields
\[
S^{\text{pdh}}_{\nu_c}(t) = \eta_{\text{pdh}} P_0 J_0(\beta_1) J_1(\beta_1) \left[ -\text{Im} \tilde{R}_{-1}^c + 2 \text{Im} \tilde{R}_0^c - \text{Im} \tilde{R}_1^c \right]. \tag{6.13}
\]

The lineshape of the PDH error signal, i.e., the expression in parentheses, is
plotted in Figure 6.3 (a) as a function of frequency detuning from the cavity mode center (normalized to the modulation frequency).

![Figure 6.3. Pound-Drever-Hall error signal as a function of frequency detuning normalized to (a) modulation frequency and (b) cavity mode width, both for a cavity with a finesse of 150.](image)

The PDH error signal consists of three dispersion features, one for each sideband and one for the carrier, the latter with an opposite sign and twice the amplitude of the others. The carrier contribution, plotted in Figure 6.3 (b) as a function of detuning normalized to the cavity mode width, is proportional to the imaginary part of the cavity reflection function, Eq. (5.7), which for a lossless impedance matched cavity can be expressed in terms of the cavity finesse and the FSR as

$$2 \text{Im} \tilde{R}_q^c = -\frac{2F \sin \left( \frac{2\pi \Delta \nu q}{FSR} \right)}{1 + \left( \frac{2F}{\pi} \right)^2 \sin^2 \left( \frac{2\pi \Delta \nu q}{FSR} \right)}.$$  \hspace{1cm} (6.14)

For a high finesse cavity the mode width is much smaller than the cavity FSR, thus a useful approximation is obtained for $\Delta \nu q \ll FSR$ when the sine terms can be series expanded yielding

$$2 \text{Im} \tilde{R}_q^c \big|_{\Delta \nu q \ll FSR} = -\frac{2\Delta \nu q / \Gamma_c}{1 + \left( \frac{2\Delta \nu q}{\Gamma_c} \right)^2},$$  \hspace{1cm} (6.15)

where the definition of the finesse has been used. As long as the detuning is smaller than the cavity mode width, $\Delta \nu q \ll \Gamma_c$, the factor in the denominator can be neglected and the PDH error signal is linear with detuning, i.e.,
2\text{Im} \left\{ \tilde{R}_0 \right\}_{\Delta v_q \ll \Gamma_c} = -\frac{2\Delta v_q}{\Gamma_c}. \tag{6.16}

### 6.2.2 Servo design

The open loop transfer function of the feedback loop in the PDH technique is a product of the transfer functions of the cavity, the laser and the servo.

As shown above in Eq. (6.16), the PDH error signal provides proportional gain for noise with an amplitude below the cavity linewidth. This is, however, the case only for Fourier frequencies below the linewidth of the cavity. For frequencies higher than the cavity linewidth the slope of the error signal decreases as \(1/f\) due to the finite response time of the cavity, given by the inverse of the cavity linewidth, Eq. (5.21). Thus the cavity transfer function can be modeled as a low pass filter with a 3 dB frequency equal to the cavity mode width. The proportional gain of the error signal, in V/MHz, can be estimated by dividing the peak-to-peak value of the PDH error signal with twice the cavity linewidth.

The transfer function of the laser should be measured for frequencies within the desired bandwidth of the feedback loop, and preferably also at higher frequencies, as some resonances might exist there, which could later rise above the unity gain level giving rise to oscillations. The measurement can be done by applying a sinusoidal disturbance to the laser driver and observing the amplitude and phase of the laser frequency response using the cavity modes as frequency markers. Such a measurement yields the transfer function of the controlled system, where the gain is expressed in MHz/V.

The transfer function of the servo should be designed so as to yield the total open loop transfer function with a required gain and bandwidth. The bandwidth has to be larger than the linewidth of the laser in order to correct all frequency excursions of the laser. Note that the PDH modulation frequency should be at least one order of magnitude higher than the desired feedback bandwidth, so that the low pass filtering (to reject the sum frequency after the DBM) in the demodulation process does not introduce any phase shifts within the bandwidth.

The servo must basically be a PID (proportional-integral-derivative) controller. The integrator provides high gain at low frequencies and a -20 dB/decade slope of the gain curve at the unity gain point. In order to increase the gain at low frequencies, double integration can be used, which results in a slope of -40 dB/decade, wherefore a phase lead, i.e., a differentiator, has to be added at higher frequencies to lift the phase above -180° as the gain approaches unity. Moreover, the cavity roll-off has to be compensated for with a phase lead if the cavity linewidth is within the
desired bandwidth, which is usually the case when tunable lasers are locked to high finesse cavities. More phase leads in the servo might be needed to correct the phase in the laser transfer function. Finally, during the initial locking the gain at the lowest frequencies should be proportional, otherwise any possible offset in the error signal would be integrated to the supply voltage and no locking would occur. The integrator(s) should be turned on after the initial locking has been established and the error signal has been brought close to zero. An example of servo design, for the particular fiber laser used in this work, is given in section 8.5.1, and the locking procedure is described in section 8.5.2.
The uniqueness of NICE-OHMS originates from a successful merging of two previously mutually exclusive concepts used for improving the sensitivity of absorption techniques, namely cavity enhancement and frequency modulation spectrometry. In NICE-OHMS the carrier of an FM triplet is locked to a cavity mode with the PDH technique, while the modulation frequency, $\nu_{fsr}$, is matched to the cavity $FSR$, as is shown in Figure 7.1. In this configuration, the FM triplet is transmitted undisturbed by the cavity. Moreover, any shift of the laser carrier frequency results in an equal shift of the sidebands, i.e., in equal detuning of the three FM modes from their respective cavity modes. This implies that all components of the FM triplet are attenuated and phase shifted equally by the cavity, i.e., that $\delta_{-1} = \delta_{0} = \delta_{1}$ and $\phi_{-1} = \phi_{0} = \phi_{1}$. This leads to an important fact that no signal in cavity transmission or reflection is observed at the modulation frequency, since the attenuation of one sideband cancels that of the other, i.e., $\delta_{-1} - \delta_{1} = 0$, and the phase shift of the carrier cancels that experienced by the sidebands, i.e., $\phi_{-1} - 2\phi_{0} + \phi_{1} = 0$ [see Eq. (4.8)]. In other words, the balance of the triplet is not disturbed by the cavity and the technique is immune to the residual frequency noise of the laser carrier with respect to a cavity mode. This implies that FMS can be performed inside the cavity as if the cavity was not present, yet fully benefiting from the increased interaction length. Due to the ‘noise immunity’ NICE-OHMS is capable of reaching extraordinarily high sensitivities, close to the shot noise limit [2].

![Figure 7.1](image.png)

**Figure 7.1.** In NICE-OHMS the laser carrier frequency is locked to the $q$th cavity mode frequency and the electric field is phase modulated at two frequencies, $\nu_{pdh}$ and $\nu_{fsr}$, of which the former is smaller than the cavity $FSR$ but larger than the cavity mode width and used for PDH locking, while the latter is equal to the cavity $FSR$ and used for cavity enhanced FMS.

The cavity $FSR$ depends on the cavity length as well as the intracavity refractive index, and changes when the cavity length is scanned or when a gas is introduced to the cavity. Therefore, in order to automatically maintain the noise immune conditions at all times, the modulation frequency, $\nu_{fsr}$,
should be actively locked to the cavity FSR. An error signal for such a lock can be derived from the cavity reflected light at the sum or difference of the two modulation frequencies, $\nu_{\text{fsr}} \pm \nu_{\text{pdh}}$, as is further discussed below.

The light transmitted through the cavity is detected with a fast photodetector and demodulated at the $\nu_{\text{fsr}}$ frequency as in ordinary FMS, as shown in Figure 7.2. In the presence of an analyte a so-called $\nu_{\text{fm}}$-NICE-OHMS signal appears, whose lineshape is the same as that of ordinary FMS, but whose magnitude is increased by the cavity enhancement factor, $2F/\pi$. In order to reduce any remaining low frequency drift in the $\nu_{\text{fm}}$-NICE-OHMS signal, a WM dither can be additionally applied to the cavity length, whereby the signal needs to be further demodulated at the WM frequency, resulting in the so-called $\nu_{\text{wm}}$-NICE-OHMS signal.

![Figure 7.2. General NICE-OHMS setup.](image)

The lineshapes and parametric dependence of NICE-OHMS signals are described in this chapter. If the collision broadening is small (significantly smaller than the cavity FSR) the three modes (the carrier and the two FM sidebands) propagating in the same direction in the cavity interact with dissimilar velocity groups of molecules, which gives rise to an ordinary Doppler-broadened FMS response. The same velocity group can, however, be addressed simultaneously by one positively and one negatively propagating mode, giving rise to a sub-Doppler response. This means that both the Doppler-broadened and sub-Doppler signals can be obtained with the NICE-OHMS technique. Additionally, since the cavity mode spacing changes due to the dispersion of the gas, the correction signal used for locking of the modulation frequency to the cavity FSR can be used to detect the presence of an analyte. The latter detection scheme, referred to as dual frequency modulation dispersion spectrometry (DFM-DS), is also presented below.
7.1 Active FSR tracking

There are two possible ways to produce an error signal for locking of the modulation frequency to the cavity FSR. The first is to dither the tunable RF source at a frequency in the kHz range and demodulate the signal in cavity reflection at the dither frequency. An error signal is then created because the reflected power is higher when the sidebands are not matched to the FSR. However, this approach, which has been used in some of the NICE-OHMS implementations \([2, 30\text{-}32, 36, 38, 39, 43]\), is not optimal, since the error signal is derived at a low frequency, where laser noise is still significant \([38]\).

A better approach is the one proposed by deVoe and Brewer \([82]\), in which the error signal is derived from the cavity reflected light at the sum or difference of the two modulation frequencies that already exist in the setup, i.e., at \(v_{fsr} \pm v_{pdh}\). This has been used by van Leeuwen et al. \([40, 41]\) as well as in all experimental papers presented in this thesis \([45, 47\text{-}49, 51\text{-}53]\).

The electric field incident on the cavity modulated at two frequencies, \(v'_{fsr}\) and \(v_{pdh}\), can be written as

\[
\hat{E}_{\text{inc}}(v_c, t) = \frac{E_0}{2} \hat{e} e^{i2\pi v_c t} \left[ J_0(\beta_1) J_0(\beta_2) + J_0(\beta_2) J_1(\beta_1) \left( e^{i2\pi v_{pdh} t} - e^{-i2\pi v_{pdh} t} \right) \right. \\
\left. + J_0(\beta_1) J_1(\beta_2) e^{i2\pi v'_{fsr} t} - J_0(\beta_1) J_1(\beta_2) e^{-i2\pi v'_{fsr} t} \right] \\
+ J_1(\beta_1) J_1(\beta_2) e^{i2\pi v_{pdh} t} \left( e^{i2\pi v_{pdh} t} - e^{-i2\pi v_{pdh} t} \right) \\
- J_1(\beta_1) J_1(\beta_2) e^{-i2\pi v'_{fsr} t} \left( e^{i2\pi v_{pdh} t} - e^{-i2\pi v_{pdh} t} \right) \right].
\]

Thus the field consists of nine components, as shown in Figure 7.1. When the carrier is locked to the \(q\)th cavity mode, i.e., when \(v_c = v_q\), and the \(v'_{fsr}\) frequency is close to the cavity FSR, the components at frequencies \(v_c \pm v_{pdh}\) and \(v'_c \pm v'_{fsr} \pm v_{pdh}\) are fully reflected by the cavity, while the carrier is fully transmitted. The cavity reflection function is equal to 1 for the fully reflected components and zero for the carrier, whereby the total reflected electric field becomes...
\[ \hat{E}_r \left( v_q, v'_{\text{fsr}}, t \right) = \frac{E_0}{2} e^{i2\pi v_q t} \]
\[ \times \left[ J_0(\beta_2) J_1(\beta_1) \left( e^{i2\pi v'_{\text{fsr}} t} - e^{-i2\pi v_{\text{pdh}} t} \right) + J_0(\beta_1) J_1(\beta_2) \hat{R}_{c} e^{i2\pi v'_{\text{fsr}} t} + J_0(\beta_2) J_1(\beta_1) \hat{R}_{c} e^{-i2\pi v_{\text{pdh}} t} - J_1(\beta_1) J_1(\beta_2) e^{-i2\pi v'_{\text{fsr}} t} \left( e^{i2\pi v_{\text{pdh}} t} - e^{-i2\pi v_{\text{pdh}} t} \right) \right] \]

where the subscripts ±1 in \( \hat{R}_{c1} \) now refer to the cavity reflection function for the upper and lower sideband at the \( v'_{\text{fsr}} \) frequency, respectively, i.e., \( \hat{R}_{c1} = \hat{R}_{c} \left( v_q \pm v'_{\text{fsr}} - v_{\text{q} \pm 1} \right) \). The intensity of the reflected light has components at various beat frequencies, of which the one at \( v'_{\text{fsr}} \pm v_{\text{pdh}} \) is of importance for locking of the modulation frequency to the cavity FSR, and is given by [82]

\[ I_{r}^{v'_{\text{fsr}} \pm v_{\text{pdh}}} \left( v_{\text{fsr}} t \right) = \pi 2J_0(\beta_1) J_0(\beta_2) J_1(\beta_1) J_1(\beta_2) \]
\[ \times \left\{ \left( \text{Im} \hat{R}_{c1} - \text{Im} \hat{R}_{c1} \right) \sin \left[ 2\pi \left( v_{\text{fsr}} \pm v_{\text{pdh}} \right) t \right] + \left( \text{Re} \hat{R}_{c1} + \text{Re} \hat{R}_{c1} \right) \cos \left[ 2\pi \left( v_{\text{fsr}} \pm v_{\text{pdh}} \right) t \right] \right\} \]

In an empty cavity, the detuning of the lower sideband from the \((q-1)\)th cavity mode, given by \( v_{\text{fsr}} - \text{FSR} \), is equal in magnitude but has an opposite sign to the detuning of the upper sideband from the \((q+1)\)th cavity mode, given by \( \text{FSR} - v_{\text{fsr}} \), as is schematically shown in Figure 7.3. The cosine term in the above equation, which is proportional to the sum of the real parts of the cavity transmission function for the two sidebands, plotted in Figure 5.2 (b), is thus an even function of the detuning. On the other hand, the factor in

![Figure 7.3. The detuning of the sidebands from their respective cavity modes when the modulation frequency in the vicinity of cavity FSR.](image)
front of the sine, given by the difference of imaginary parts of the cavity transmission function [Figure 5.2 (d)] for the two sidebands, is an odd function and yields a useful error signal. Demodulation of this signal at a frequency $\nu'_{\text{fsr}} \pm \nu_{\text{pdh}}$ and at a phase corresponding to the sine term results in an error signal of the form

$$S^{\nu'_{\text{fsr}} \pm \nu_{\text{pdh}}} = \mp \eta_{\text{fsr}} P_0 J_0 (\beta_1) J_1 (\beta_1) J_1 (\beta_2) \text{Im}(\tilde{R}_c - \tilde{R}_c^*)$$ \hspace{1cm} (7.5)$$

where $\eta_{\text{fsr}}$ (V/W) is an instrumentation factor. The imaginary part of the cavity reflection function, given by Eq. (6.14), has odd symmetry with respect to the detuning, so the error signal in Eq. (7.5) becomes, for symmetric sideband detuning in an empty cavity,

$$S^{\nu'_{\text{fsr}} \pm \nu_{\text{pdh}}} = \mp 2 \eta_{\text{fsr}} P_0 J_0 (\beta_1) J_1 (\beta_2) J_1 (\beta_1) J_1 (\beta_2) \text{Im}(\tilde{R}_c)$$ \hspace{1cm} (7.6)$$

The lineshape of this signal, i.e., $\text{Im}(\tilde{R}_c^*)$, is plotted in Figure 7.4 as a function of the detuning of the frequency $\nu'_{\text{fsr}}$ from the cavity FSR in terms of the cavity linewidth. This lineshape is the same as that of the PDH error signal, wherefore the analysis presented in the sections 6.2.1 and 6.2.2 is valid also here, i.e., the error signal provides proportional gain for frequencies below the cavity mode width, and the gain decreases as $1/f$ for higher frequencies.

![Figure 7.4](image.png)

**Figure 7.4.** The lineshape of the error signal for locking of the modulation frequency to the cavity FSR as a function of detuning of the modulation frequency from the cavity FSR in terms of the cavity linewidth.

This error signal has to be amplified and filtered, and fed to the tunable frequency source, as shown in Figure 7.2. Once a lock is established, the modulation frequency is equal to the cavity FSR, i.e., $\nu'_{\text{fsr}} = \nu_{\text{fsr}} = \text{FSR}$. The whole FM triplet is then transmitted undisturbed through the cavity with each component locked to the center of its respective mode.
7.2 NICE-OHMS signals

As was shown in section 5.2 and Figure 5.4, the cavity transmission modes in the vicinity of a molecular transmission become lower and broader, and their center frequencies are shifted. The change of the cavity mode shape in the presence of the analyte can be interpreted as a local decrease of the cavity finesse. The finesse is inversely proportional to the intracavity losses [Eq. (5.20)], which are larger in the vicinity of a molecular transition due to the absorption of the analyte. However, under the assumption that the double-pass absorption of the analyte is much smaller than the intracavity losses, i.e., that

\[
\alpha(\Delta \nu) \ll \frac{F}{\pi},
\]

the influence of the analyte on the cavity properties is negligible, i.e., the finesse can be assumed to be constant and the shift of the cavity mode frequencies due to anomalous dispersion is negligible. When this condition, which for a cavity with a finesse of a few thousand corresponds to a single-pass absorption significantly lower than $10^{-4}$, is fulfilled, the NICE-OHMS signal, detected in cavity transmission, is an ordinary FMS signal given by Eq. (4.8), with the field attenuation and phase shift enhanced by the factor $2F/\pi$, derived in Eq. (5.35), i.e.,

\[
S_{\text{NICE-OHMS}}(\Delta \nu, \theta_{fm}) = \eta_{fm} \frac{2F}{\pi} P_t^0 J_0(\beta_1) J_1(\beta_1) \\
\times \left[ (\phi_{-1} - 2\phi_0 + \phi_1) \cos \theta_{fm} + (\delta_{-1} - \delta_1) \sin \theta_{fm} \right],
\]

where $P_t^0$ is the power transmitted on resonance in the absence of an analyte.

When the condition given in Eq. (7.7) is not fulfilled, the full transmission function given by Eq. (5.32) has to be used to derive an expression for the NICE-OHMS signal. Moreover, in the presence of significant amount of anomalous dispersion the spacing between consecutive modes is not constant, as shown in Figure 5.4. Since the modulation frequency can only be locked to the average mode spacing (see section 7.3), the frequency of the sidebands does not coincide exactly with the cavity resonances. This introduces additional attenuation and phase shift in the cavity transmitted light and further modifies the NICE-OHMS lineshape. Derivation of the expressions for the NICE-OHMS signal for arbitrarily high absorbances has not been seen as necessary, since NICE-OHMS is a technique designed for detection of ultra-low absorption, certainly below $10^{-4}$. 
7.2.1 Doppler-broadened NICE-OHMS

Under the assumption of low intracavity absorption, i.e., when Eq. (7.7) is valid, the Doppler-broadened \( fm \)-NICE-OHMS signal has the same shape as an ordinary FMS signal [Eq. (4.9)], but with its strength increased by the cavity enhancement factor. It is therefore given by [40, 45]

\[
S^{DB} \left( \Delta \nu, \theta_{fm} \right) = \eta_{fm} \frac{F}{\pi} P^0 t J_0 \left( \beta_1 \right) \beta_1 S_{rel} P L \\
\times \left[ \chi_{disp}^{\Delta \nu - \nu_m} - 2 \chi_{disp}^{\Delta \nu + \nu_m} \right] \cos \theta_{fm} \\
+ \left[ \chi_{abs}^{\Delta \nu - \nu_m} - \chi_{abs}^{\Delta \nu + \nu_m} \right] \sin \theta_{fm}.
\]

Under low pressure conditions, i.e., in the Doppler limit, the lineshape functions are Gaussian, given by Eqs (3.37) and (3.38) [45]. At higher pressures, when the collision broadening becomes significant, Voigt profiles, Eqs (3.34) and (3.35), have to be used [40]. For close to atmospheric pressures the lineshapes would be Lorentzian, Eqs (3.39) and (3.40).

The dependence of the signal shape on the detection phase and FM modulation frequency is the same as that of ordinary FMS, as discussed in section 4.1. Thus also the conditions that maximize the Doppler-broadened \( fm \)-NICE-OHMS lineshape are the same as in ordinary FMS. In the Doppler limit they are given by a modulation frequency (i.e., cavity FSR) of \( 2.2 \Gamma_D \) and a detection phase of \( 0.1 \pi \).

When WM dither is applied, the first Fourier coefficient of the above signal is detected whereby the \( wm \)-NICE-OHMS signal becomes

\[
S^{DB}_1 \left( \Delta \nu, \nu_a, \theta_{fm} \right) = \eta_{wm} \eta_{fm} \frac{F}{\pi} P^0 t J_0 \left( \beta_1 \right) \beta_1 S_{rel} P L \\
\times \left[ \chi_1^{\Delta \nu - \nu_m, \nu_a} - 2 \chi_1^{\Delta \nu + \nu_m, \nu_a} \right] \cos \theta_{fm} \\
+ \left[ \chi_1^{\Delta \nu - \nu_m, \nu_a} - \chi_1^{\Delta \nu + \nu_m, \nu_a} \right] \sin \theta_{fm}.
\]

where the subscript 1 denotes the first Fourier coefficient. The lineshape and strength of \( wm \)-NICE-OHMS signals depend not only on the detection phase and the ratio of modulation frequency to the linewidth, but also on the WM modulation amplitude, as shown in Figure 7.5, where \( wm \)-NICE-OHMS absorption and dispersion lineshapes are plotted for a modulation frequency equal to twice the Doppler width and for various WM modulation amplitudes. The parametric dependence of the \( wm \)-NICE-OHMS lineshapes in the Doppler limit has been investigated in detail in paper VIII. It has been shown that for cavities with FSR smaller than \( \Gamma_D \), the on-resonance
um-NICE-OHMS signal is maximized at FM detection phases close to that of pure absorption (between $\pi/4$ and $\pi/2$) and by relatively low WM modulation amplitudes (roughly equal to $\Gamma_D$). For cavities with larger relative FSRs (i.e., for shorter cavities or for detection of heavy molecules or at long wavelengths) the optimum FM detection phase shifts towards that of pure dispersion (detection phase around zero) and larger WM modulation amplitudes are needed to maximize the signal (up to ca $1.5\Gamma_D$). The range of WM modulation amplitudes and FM detection phases that give rise to a signal with a close-to-optimum magnitude is, however, relatively broad for each cavity FSR. Pure absorption um-NICE-OHMS signals are maximized in cavities whose FSR is $1.0 - 1.5$ times the HWHM of the Doppler-broadened transition, whereas the dispersion signals are largest for normalized FSRs in the $2.0 - 2.5$ range.

The largest on-resonance um-NICE-OHMS signal can be obtained for the same FM modulation frequency and FM detection phase as the one that maximize the peak-to-peak fm-NICE-OHMS lineshape, namely $2.2\Gamma_D$ and $0.1\pi$, respectively, and with a WM modulation amplitude of $1.45\Gamma_D$. This implies that the FSR of the cavity used for detection of Doppler-broadened NICE-OHMS signals in the Doppler limit should preferably be equal to $2.2\Gamma_D$, and that the optimum cavity length is given by

$$L_{opt} = \frac{c}{4.4\Gamma_D}. \quad (7.11)$$

The optimum cavity length (in cm) can be expressed in terms of the transition wavelength (in $\mu$m) and molecular mass (in atomic units, u) as

$$L_{opt} = 3.7\lambda_0\sqrt{m}, \quad (7.12)$$

where Eq. (2.20) has been used. This yields, for typical molecules with a
mass in the 15 – 50 µm range, detected at a wavelength of 1.5 µm, an optimum cavity length of 20 – 40 cm. In the mid-infrared region, however, longer cavities are needed for detection of the same molecules under optimum conditions, e.g., in the range of 70 – 120 cm at 5 µm.

In the absence of optical saturation, the $fm$-NICE-OHMS signal can be written as

$$S^{DB}(\Delta\nu, \theta_{fm}) = S_0^{DB} \bar{\chi}^{DB}(\Delta\nu, \theta_{fm}),$$  \hspace{1cm} (7.13)

where $S_0^{DB}$ is the unsaturated $fm$-NICE-OHMS signal strength, given by

$$S_0^{DB} = \eta_{fms} \frac{F}{\pi} P^0_{i} J^{-}_{0}(\beta_{i}) J^{-}_{1}(\beta_{i}) Sc_{rel} P L \chi^0$$  \hspace{1cm} (7.14)

and $\bar{\chi}^{DB}(\Delta\nu, \theta_{fm})$ is the Doppler-broadened $fm$-NICE-OHMS lineshape function, written in terms of peak-normalized absorption lineshape functions and their dispersion counterparts as

$$\bar{\chi}^{DB}(\Delta\nu, \theta_{fm}) = 
\begin{bmatrix}
\bar{\chi}^{abs}(\Delta\nu - \nu_{m}) - 2\bar{\chi}^{disp}(\Delta\nu) + \bar{\chi}^{disp}(\Delta\nu + \nu_{m}) \cos \theta_{fm} \\
\bar{\chi}^{abs}(\Delta\nu - \nu_{m}) - \bar{\chi}^{abs}(\Delta\nu + \nu_{m}) \sin \theta_{fm}
\end{bmatrix}.$$  \hspace{1cm} (7.15)

An important fact is that the $fm$-NICE-OHMS signal strength defined in this way is proportional to the partial pressure of the analyte but independent of the detection phase (paper I). This simplifies the experimental procedure, since a calibration curve measured at any detection phase can be used for measurements performed at all other phases. The concentration of the analyte can be deduced from a signal measured at any unknown detection phase provided that the theoretical Doppler-broadened NICE-OHMS signal is fitted to the measured data, with the detection phase and analyte concentration as fitting parameters.

However, this procedure works only in the absence of optical saturation or if the degree of saturation is known. The influence of optical saturation on Doppler-broadened NICE-OHMS signals has been described theoretically in paper III for general conditions, and verified experimentally in the Doppler limit in paper IV. It has been shown that in the Doppler limit the dispersion signal is virtually independent of optical saturation, while the absorption signal is reduced by a factor of $1/\sqrt{1 + G_{\pm}},$ where $G_{\pm}$ is the degree of saturation induced by the sidebands, given by

$$G_{\pm} = \frac{p_c}{P_{sat}} J^{\pm}_{1}(\beta_{i}),$$  \hspace{1cm} (7.16)

where the intracavity power, $P_c$, is related to the power incident on the
cavity according to Eq. (5.27), i.e., as

$$P_c = \left(1 - \frac{R_{res}}{\sqrt{R_{res}}} \right) \frac{F}{\pi} P_0,$$

(7.17)

while the saturation power, $P_{sat}$, is defined as the power for which the degree of saturation in the center of the beam is two, i.e., as [51]

$$P_{sat} = \frac{\pi w_0^2}{2} 2I_{sat} = \frac{3c\varepsilon_0 h^2}{2\mu^2} \pi w_0^2 \left( \Gamma + B_p P \right)^2,$$

(7.18)

where in the last step Eq. (3.25) for the saturation intensity has been used.

This means that the optically saturated Doppler-broadened $fm$-NICE-OHMS lineshape can be written as

$$\mathcal{X}_G^{DB}(\Delta v, \theta_{fm}, G_{\pm 1}) = \left[ \mathcal{X}_G^{disp}(\Delta v - \nu_m) - 2 \mathcal{X}_G^{disp}(\Delta v) + \mathcal{X}_G^{disp}(\Delta v + \nu_m) \right] \cos \theta_{fm}$$

$$+ \frac{1}{\sqrt{1+G_{\pm 1}}} \left[ \mathcal{X}_G^{abs}(\Delta v - \nu_m) - \mathcal{X}_G^{abs}(\Delta v + \nu_m) \right] \sin \theta_{fm}$$

(7.19)

Note that the absorption NICE-OHMS signal is affected much less by optical saturation than signals in other cavity enhanced techniques (detecting Doppler-broadened transitions). In ordinary DAS the amplitude of the absorption lineshape function decreases by a factor of $1/\sqrt{1+G}$, as shown in Eq. (3.37). In NICE-OHMS, however, the absorption signal has contributions only from the sidebands, which carry just a fraction of the power of the carrier, given by $J_1^2(\beta_2)/J_0^2(\beta_2)$. For example, for a modulation index of 0.35 the degree of saturation induced by a sideband is only 3% of that induced by the carrier. Nevertheless, optical saturation decreases the weight of the absorption contribution to the $fm$-NICE-OHMS signal. Unless the effect of optical saturation is taken into account, this can be incorrectly interpreted as a shift of the detection phase towards the dispersion phase.

The different behavior of absorption and dispersion NICE-OHMS signals under optically saturated conditions can be used to deduce the degree of saturation. In the Doppler limit the signal strength at dispersion phase is the same as the unsaturated $fm$-NICE-OHMS signal strength, i.e.,

$$S_{0,disp}^{DB} = S_0^{DB},$$

(7.20)

while the signal strength at absorption phase is reduced according to

$$S_{0,abs}^{DB} = S_0^{DB} \frac{1}{\sqrt{1+G_{\pm 1}}},$$

(7.21)
The degree of saturation can be determined from the measured ratio of the absorption and dispersion signal strengths as [51]

\[ R_{abs/\text{disp}} = \frac{S_{0,\text{abs}}}{S_{0,\text{disp}}} = \frac{1}{\sqrt{1 + G_{\pm 1}}}. \] (7.22)

Thus with the knowledge of the intracavity power and the modulation index it is possible to calculate the saturation power from Eq. (7.16).

### 7.2.2 Sub-Doppler NICE-OHMS

Sub-Doppler signals can be observed with NICE-OHMS due to the presence of high intensity counter-propagating waves inside the cavity. There are three waves propagating in each direction, thus as the triplet is scanned across a transition, there are nine occasions at which two waves interact with the same velocity group of molecules, occurring at five different detunings, as shown in Figure 7.6. First, when the detuning of the carrier from the transition center is equal to the modulation frequency, the sidebands propagating in opposite directions interact with the same group of molecules, namely those with a zero velocity component along the optical axis, as shown in panels (a) and (e). Next, when the detuning of the carrier is equal to half the modulation frequency, the carrier interacts with the same group of molecules as one of the sidebands going in the opposite direction, and, simultaneously, a sideband going in the positive direction interacts with the hole burned by the carrier propagating in the opposite direction, as shown in panels (b) and (d). Finally, when the carrier is tuned to resonance,
the two counter-propagating carriers interact with molecules with a zero velocity component, while the upper and lower sidebands propagating in the opposite directions interact with the groups of molecules that have a velocity component along the optical axis equal to $\pm \frac{2\pi v_{fr}}{k_0}$, see panel (c).

Figure 7.7 shows how the sub-Doppler signals appear in the NICE-OHMS absorption and dispersion signal as the FM triplet is scanned across the transition. The dashed and dotted curves show the sideband and carrier contributions, respectively (the latter present only in the dispersion signal), and the solid curves show the total NICE-OHMS signal. The signal at the detuning equal to the modulation frequency is the weakest and originates from the sideband-sideband interaction [Figure 7.6 (a) and (e)]. Thus this signals appears only when there is enough intensity in the sidebands to saturate the transition. At a detuning equal to half the modulation frequency the sub-Doppler absorption signal comes from the carrier-sideband interaction, i.e., the Bennett hole burned by the carrier and detected by the sideband, while the dispersion signal has an additional contribution from the Bennett hole burned by the sideband and detected with the carrier [Figure 7.6 (b) and (d)]. The largest signal appears on resonance at the dispersion phase and originates mainly from the carrier-carrier interaction, but has also a small contribution from the sideband-sideband interactions [Figure 7.6 (c)]. This signal is missing at the absorption phase due to the generic insensitivity of FMS to absorption of the carrier and the fact that the sideband-sideband interactions on resonance cancel (they have equal magnitude but opposite sign). Altogether five sub-Doppler signals appear on top of the Doppler-broadened signal at dispersion phase, and four at absorption phase.

**Figure 7.7.** Absorption (a) and dispersion (b) $\chi_3$-NICE-OHMS signals (solid curves) in the presence of optical saturation as a function of relative detuning from the center of the transitions in terms of modulation frequency, for a modulation index of 0.4 and degree of saturation of the carrier of 15. The dotted curve shows the carrier contribution to the dispersion signal, whereas the dashed curves show the sideband contributions.
It should be noted that the theory presented in section 3.3 and in paper V was derived for steady-state conditions in the molecular population, which is a correct assumption for the case of two counter-propagating waves with equal intensity. However, this assumption is not valid for the case of two counter-propagating waves with unequal intensities, which give rise to population pulsations. The theory given in paper V can thus only be used to model the center dispersion sub-Doppler signal and the signals at a detuning equal to the modulation frequency.

The center dispersion sub-Doppler signal is of most interest for practical applications, since it is the largest and resides on top of a nearly linear background. Moreover, the shape of this signal does not change with detection phase, as the absorption phase has no contribution on resonance.

The sub-Doppler dispersion signal can be expressed in terms of the sub-Doppler optical phase shift, \( \phi_{00}(\Delta \nu, G_0) \), as \([52]\)

\[
S_{DF}^{\text{disp}}(\Delta \nu, G_0) = -\eta_{\text{fms}} \frac{4F}{\pi} p_0^0 J_0(\beta_1) J_1(\beta_1) \phi_{00}(\Delta \nu, G_0),
\]

(7.23)

where \( G_0 \) is the degree of saturation induced by the carrier. The exact expression for the sub-Doppler optical phase shift has been derived in paper V. This expression is not analytical, but can be well approximated by a Lorentzian dispersion function up to high degrees of saturation, as has been shown in the same paper. The peak-to-peak value of the sub-Doppler optical phase shift for a beam with a constant intensity distribution was given by Eq. (3.47). It has been shown, again in paper V, that this expression should be modified to include a correction factor for the Gaussian intensity distribution of the laser beam according to \([52]\)

\[
\phi_{00}^{\text{pp}} = \phi(G_0) \frac{\alpha_0}{2} = 0.45 \frac{\alpha_0}{2} \frac{8}{w^2} \int_0^\infty \frac{G_0 e^{-4(r/w)^2}}{1 + 2G_0 e^{-2(r/w)^2}} r dr.
\]

(7.24)

The two expressions, for a constant and a Gaussian intensity distribution, are plotted in Figure 7.8 as a function of degree of saturation.

In conclusion, the center sub-Doppler dispersion NICE-OHMS signal can be written as

\[
S_{DF}^{\text{disp}}(\Delta \nu, G_0) = \eta_{\text{fms}} \frac{F}{\pi} p_0^0 J_0(\beta_1) J_1(\beta_1) S_{\text{rel}}^{\text{DL}} \chi_0 \Phi(G_0) \chi_{L}^{\text{disp}}(\Delta \nu, \Gamma_L)
\]

(7.25)

where \( \chi_{L}^{\text{disp}} \) is defined by Eq. (3.40) with \( G = 0 \).
Figure 7.8. Peak-to-peak sub-Doppler optical phase shift, in terms of the on-resonance Doppler-broadened absorption coefficient, as a function of the degree of saturation induced by the carrier. The dashed and solid curves show Eqs (3.47) and (7.24), respectively.

In order to remove the linear slope of the Doppler-broadened signal, the sub-Doppler dispersion signal is most often measured with WM dither, wherefore it becomes

\[ S_{1}^{DF} (\Delta \nu, \nu_a, G_0) = \eta_{ums} \eta_{fms} \frac{F}{\pi} \rho_{t} J_{0} (\beta_{l}) J_{1} (\beta_{l}) S_{cr} p L \chi_{\alpha} \Phi (G_0) \chi^{disp}_{L,1} (\Delta \nu, \nu_a), \quad (7.26) \]

where the first Fourier coefficient of the Lorentzian dispersion lineshape function, \( \chi^{disp}_{L,1} \), can be calculated by numerical integration as

\[ \chi^{disp}_{L,1} (\Delta \nu, \nu_a) = \frac{2}{\pi} \int_{0}^{\infty} \frac{\Gamma_{L} [\Delta \nu + \nu_a \cos (2 \pi \nu_m t)]}{[\Delta \nu + \nu_a \cos (2 \pi \nu_m t)]^2 + \Gamma_{L}^2} \cos (2 \pi \nu_m t) dt. \quad (7.27) \]

As has been shown in paper V and paper VII, although the shape of the sub-Doppler signal is modeled well by Eq. (3.40), the width of the signal does not follow the conventional \( \sqrt{1 + G_0} \) dependence on the degree of saturation. The cause of this is still not clear, although the presence of the sideband-sideband contribution is a possible explanation. A correct modeling of the width remains to be done.

### 7.3 Dual frequency modulation dispersion spectrometry

When the modulation frequency is locked to the cavity FSR, the error signal for active FSR tracking, Eq. (7.5), is equal to zero, whereby

\[ \text{Im} (\tilde{R}_{c1} - \tilde{R}_{c1}^*) = 0. \quad (7.28) \]

This condition is fulfilled also in the presence of an analyte in the cavity. As has been shown in Figure 5.4, the center positions of the cavity modes are shifted by anomalous dispersion. This means that in the vicinity of a
transition the cavity mode spacings, $v_q - v_{q-1}$ and $v_{q+1} - v_q$, change asymmetrically (except on resonance and at some other particular detuning) as is schematically illustrated in Figure 7.9. The lock tries to keep the modulation frequency equal to the cavity FSR, but due to the asymmetry the modulation frequency can only be locked to the average mode spacing. This means that as the FM triplet, with its carrier locked to the $q$th cavity mode, is scanned across a transition, there is a mismatch between the modulation frequency and the actual sideband spacing whereby the noise immune condition will be compromised.

The imaginary part of the cavity reflection function in the presence of an analyte [Eq. (5.31)], which was plotted in Figure 5.4 (d), is given by

$$\text{Im} \hat{R}_c^{\text{A,}\pm1} = -\frac{(1-r)\sqrt{r}e^{-2\delta_{11}}}{\left[1-\sqrt{r}e^{-2\delta_{11}}\right]^2} \frac{\sin\left(-\varphi_{q\pm1} - 2\varphi_{\pm1}\right)}{1 + \frac{2\sqrt{r}e^{-\delta_{11}}}{1-\sqrt{r}e^{-2\delta_{11}}} \sin^2\left(-\frac{\varphi_{q\pm1}}{2} - \varphi_{\pm1}\right)},$$

(7.29)

where equal mirror reflectivities, i.e., $r = r_1 = r_2$, have been assumed for simplicity. The round trip phase shift for the $(q\pm i)$th cavity mode can be found from Eq. (5.12) as

![Figure 7.9](image-url)
\[ \varphi_{q \pm 1} = \frac{2\pi \left( v_q \pm \nu_{\text{fsr}} - \nu_{q \pm 1} \right)}{\text{FSR}} = \pm \frac{2\pi \nu_{\text{fsr}}}{\text{FSR}} \pm 2\pi, \quad (7.30) \]

where \( \nu_{\text{fsr}} \) is the modulation frequency in the presence of the analyte under locked conditions. The relation between the modulation frequency and the concentration of the analyte in the cavity can be found by inserting Eq. (7.29) into Eq. (7.28). However, this yields a transcendental equation in terms of \( \nu_{\text{fsr}} \). On the other hand, for small attenuation and phase shift one can series expand Eq. (7.29), which gives, in the first order approximation,

\[ \text{Im} \tilde{R}_{A, \pm 1} = \sqrt{1 - r} \left( -2\varphi_{q \pm 1} - \varphi_{q \pm 1} \right) = \frac{F}{\pi} \left( -2\varphi_{q \pm 1} - \varphi_{q \pm 1} \right). \quad (7.31) \]

This implies that under locked conditions Eq. (7.28) corresponds to

\[ 2\varphi_1 + \varphi_{q+1} = 2\varphi_{-1} + \varphi_{q-1}. \quad (7.32) \]

Using Eqs (3.31) for the phase shifts due to the analyte and (7.30) for the round trip phase shift inside the cavity yields

\[ S_{\text{rel}} P L \chi^{\text{disp}} \left( v_c + v_{\text{fsr}} - v_o \right) - 2\pi + \frac{2\pi \nu_{\text{fsr}}}{\text{FSR}} = \quad (7.33) \]

which finally gives

\[ \nu_{\text{fsr}} \left( v_c \right) = \text{FSR} - \frac{c S_{\text{rel}} P r}{8\pi} \left[ \chi^{\text{disp}} \left( v_c - v_{\text{fsr}} - v_o \right) - \chi^{\text{disp}} \left( v_c + v_{\text{fsr}} - v_o \right) \right]. \quad (7.34) \]

This expression shows that the deviation of the modulation frequency from the empty cavity \( \text{FSR} \) is given by the difference of the dispersion experienced by the lower sideband and that experienced by the upper sideband due to the analyte. The analyte concentration can thus be assessed from a measurement of the frequency produced by the tunable frequency source under locked conditions, as is further discussed in paper IX.

### 7.4 Noise and background signals

Since the Doppler-broadened NICE-OHMS signal is basically a cavity enhanced FMS signal, the minimum detectable absorption is a factor of \( 2F/\pi \) lower than for ordinary FMS, and given by
\[(\alpha_o)_{\text{min}}^{DB} = \frac{\pi e^{\Delta\gamma}}{F \sqrt{\eta_c P_0}} J_1(\beta_1) J_2(\beta_1) \xi_{\text{pp}}^{\text{FM}}(v_{\text{fsr}}, \theta_{\text{fm}})^{-1}, \tag{7.35}\]

where \(\xi_{\text{pp}}^{\text{FM}}(v_{\text{fsr}}, \theta_{\text{fm}})\) is the peak-to-peak value of the lineshape function, which is the same as that for FMS in Eq. (4.19). For a cavity with a finesse of \(10^4\) the shot-noise limited absorption can be as low as \(10^{-12}\), which demonstrates the huge potential of the NICE-OHMS technique for trace gas detection.

The minimum detectable on-resonance absorption for sub-Doppler NICE-OHMS is given by

\[(\alpha_o)_{\text{min}}^{sD} = \frac{\pi e^{\Delta\gamma}}{F \sqrt{\eta_A P_0}} J_1(\beta_1) J_2(\beta_1) 2\Phi(G_0) \xi_{\text{L1}}^{\text{disp}}(0, \nu_a, \Gamma_L)^{-1}. \tag{7.36}\]

The maximum peak value of the first Fourier coefficient of a Lorentzian dispersion function, \(\xi_{\text{L1}}^{\text{disp}}(0, \nu_a, \Gamma_L)\), is 0.6 for a modulation amplitude equal to 1.27\(\Gamma_L\). Thus the factor of \(2\Phi(G_0) \xi_{\text{L1}}^{\text{disp}}(0, \nu_a, \Gamma_L)\) takes at most a value of 0.54. This implies that the shot noise limit for sub-Doppler NICE-OHMS is 6 times higher than for Doppler-broadened NICE-OHMS, thus in the \(10^{-11}\) range for the same cavity finesse.

Sensitivities close to the shot noise limit have been obtained mostly with sub-Doppler NICE-OHMS [44]. Doppler-broadened NICE-OHMS does not reach equally low detection limits mostly because of the residual amplitude modulation from the EOM or reflections between optical components, i.e., the so-called etalons.

Moreover, NICE-OHMS is affected by background signals at the dispersion phase originating from the EOM, discussed in section 4.4 around Eq. (4.21). Moreover, the noise immune principle is not valid if the FM triplet incident on the cavity is unbalanced, as then the phase shift and attenuation of the various components by the cavity modes is not equal and does not cancel. Thus in the presence of a background signal, the noise in the \(fm\)-NICE-OHMS signal is a copy of the laser frequency noise converted to amplitude noise (as in direct cavity transmission), with an amplitude proportional to the magnitude of the background signal.
8. Instrumentation and Experimental Procedures

8.1 Experimental setup

The experimental NICE-OHMS setup, on which the work presented in this thesis has been performed, has been modified numerous times during the course of the project. Its latest version, identical to that used in paper VIII, is shown schematically in Figure 8.1, and on photographs in Figures 8.2 – 8.4.

![Figure 8.1. NICE-OHMS experimental setup. EDFL – erbium doped fiber laser, EOM – electro-optic modulator, pol. – free space polarizer, $\lambda/2$ – half-wave plate, VA – variable attenuator, PBS – polarizing beam splitter cube, $\lambda/4$ – quarter-wave plate, OI – optical isolator, PD – photodetector, DBM – double balanced mixer, Ph – phase shifter, Gain – separate gain stage, BP – band pass filter, LP – low pass filter, Lock-in – lock-in amplifier, nodes (•) – power splitters/combiners. The dotted lines indicate the free space laser beam path.](image)

The light from an erbium-doped fiber laser (EDFL, see section 8.2) was led through a fiber-coupled polarizer (Phoenix Photonics, POL-50-15-PP-2-1) and electro-optic modulator (EOM, see section 8.3). All fibers were polarization maintaining with FC/APC connectors. After the EOM the light was coupled into free space by an output collimator (see Table 8.1 for a list of free space optical components). The polarization state after the EOM was cleaned with a free space polarizer and adjusted to the transmission direction of a polarizing beam splitter (PBS) with a half-wave plate. Mode matching to a longitudinal cavity mode was achieved with a single lens with a focal length of 1000 mm. A variable neutral density filter (variable attenuator, VA1) was used to adjust the input power to a desired level (affecting the degree of saturation inside the cavity). After the beam splitter...
the light passed a quarter-wave plate and reached the input mirror of the cavity. The reflected light passed the quarter-wave plate and was directed by the PBS on a high bandwidth photodetector (PD1). The cavity transmitted light was detected with an identical photodetector (PD2). Variable attenuators (VA2, VA3) were used to adjust the power incident on both detectors, in order to avoid saturation of the detectors and keep a constant power level for different cavity input powers (which was particularly important in reflection to ensure constant gain in the locking servo). Lenses with short focal lengths (20-50 mm) were used to focus the light on the small area of the detectors. All free-space optical components were arranged at an angle to the optical axis, as can be seen in Figures 8.3 and 8.4, to minimize the risk of multiple reflections. Moreover, in order to prevent multiple reflections between the cavity mirrors and detector windows the detectors were also tilted (Figure 8.4) and optical isolators (OI) were placed in front of the detectors. In transmission a quarter- and a half-wave plate were used to produce linearly polarized light with polarization direction suitable for the isolator.

**Table 8.1.** Free space optical components.

<table>
<thead>
<tr>
<th>device</th>
<th>model</th>
<th>company</th>
</tr>
</thead>
<tbody>
<tr>
<td>fiber collimator</td>
<td>F240APC</td>
<td>Thorlabs</td>
</tr>
<tr>
<td>polarizer</td>
<td>LPNIR050</td>
<td>Thorlabs</td>
</tr>
<tr>
<td>half-wave plate</td>
<td>-</td>
<td>Ekspla</td>
</tr>
<tr>
<td>quarter-wave plate</td>
<td>-</td>
<td>Ekspla</td>
</tr>
<tr>
<td>polarizing beam splitter</td>
<td>-</td>
<td>Ekspla</td>
</tr>
<tr>
<td>neutral density filter</td>
<td>ROO500-20</td>
<td>Reynard Corp.</td>
</tr>
<tr>
<td>optical isolator</td>
<td>1-15-UHP</td>
<td>Isowave</td>
</tr>
</tbody>
</table>

The characteristics of high bandwidth InGaAs detectors (New Focus, 1611) are summarized in Table 8.2. The DC outputs of these detectors were used to monitor the transmitted and reflected power levels, while the AC outputs were used to detect various RF signals. For some measurements, e.g. the cavity ringdown shown in Figure 8.10, a detector with 125 MHz bandwidth and DC response was used (New Focus, 1811).

**Table 8.2.** Characteristics of the high bandwidth InGaAs detectors.

<table>
<thead>
<tr>
<th>parameter</th>
<th>value</th>
<th>units</th>
</tr>
</thead>
<tbody>
<tr>
<td>DC output bandwidth</td>
<td>20</td>
<td>kHz</td>
</tr>
<tr>
<td>AC output bandwidth</td>
<td>0.03-1000</td>
<td>MHz</td>
</tr>
<tr>
<td>diode responsivity</td>
<td>1</td>
<td>A/W</td>
</tr>
<tr>
<td>transimpedance gain</td>
<td>700</td>
<td>V/A</td>
</tr>
<tr>
<td>cw saturation power</td>
<td>1</td>
<td>mW</td>
</tr>
<tr>
<td>detector diameter</td>
<td>1</td>
<td>mm</td>
</tr>
</tbody>
</table>
Two RF signals were applied to the EOM, one at 20 MHz, with a modulation index, $\beta_2 = \sim 0.2$, for PDH locking, and the other at \sim 380 MHz, with a modulation index, $\beta_1$, in the range 0.334 – 0.5, for NICE-OHMS detection. The two signals were produced by a fixed frequency source (see Table 8.3) and a voltage controlled oscillator (VCO), respectively. The AC output of the detector in reflection, PD1, was split and demodulated in a double balanced mixer (DBM) at 20 MHz, to provide the PDH error signal, and at 360 MHz to produce the error signal for active FSR tracking. The 360 MHz reference signal was obtained by multiplying the 20 MHz and 380 MHz signals in a DBM and filtering out all components except that at the difference frequency with a band pass (BP) filter. The two error signals were further filtered to produce correction signals that were sent to the laser frequency actuator and the tunable VCO, respectively.

**Table 8.3.** Electronic components.

<table>
<thead>
<tr>
<th>device</th>
<th>model</th>
<th>company</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF source @ 20 MHz</td>
<td>3363-B</td>
<td>New Focus</td>
</tr>
<tr>
<td>VCO @ 380 MHz</td>
<td>-</td>
<td>Metrinova</td>
</tr>
<tr>
<td>level 7 DBM</td>
<td>ZLW-1</td>
<td>Mini-Circuits</td>
</tr>
<tr>
<td>phase shifter @ 20 MHz</td>
<td>JSPH-26</td>
<td>Mini-Circuits</td>
</tr>
<tr>
<td>phase shifter @ 360/380 MHz</td>
<td>JSPH-446</td>
<td>Mini-Circuits</td>
</tr>
<tr>
<td>20 dB RF amplifier @ 380 MHz</td>
<td>ZRL-700</td>
<td>Mini-Circuits</td>
</tr>
<tr>
<td>19 dB RF amplifier @ 380 MHz</td>
<td>ZFL-500HLN</td>
<td>Mini-Circuits</td>
</tr>
<tr>
<td>low pass filters</td>
<td>PLP-series</td>
<td>Mini-Circuits</td>
</tr>
<tr>
<td>power splitters/combiners</td>
<td>ZFSC-2-1</td>
<td>Mini-Circuits</td>
</tr>
<tr>
<td>band pass filter @ 360 MHz</td>
<td>-</td>
<td>Metrinova</td>
</tr>
<tr>
<td>lock-in amplifier</td>
<td>SR830</td>
<td>Stanford Research Sys.</td>
</tr>
<tr>
<td>data acquisition card</td>
<td>NI PCI-6251</td>
<td>National Instruments</td>
</tr>
</tbody>
</table>

The signal from the detector in cavity transmission was amplified and demodulated at 380 MHz. The signal was further low pass filtered by a homemade low pass (LP) filter to yield an $fm$-NICE-OHMS signal or demodulated at the WM dither frequency in a lock-in amplifier to produce a $wm$-NICE-OHMS signal. The signals were recorded with a PC equipped with a data acquisition card and LabView. All fitting was performed with Matlab.

The cavity could be evacuated to a pressure below $10^5$ Torr with a rotary vacuum pump and a turbo molecular pump. The gas system provided connections for three different gases, and the cavity was separated from the rest of the vacuum system with a valve. The pressure was measured at both sides of this valve (thus separately in the cavity and in the rest of the gas system) with capacitive sensors working in the range of $10^5 – 1$ Torr (Leybold, Ceravac CRT 90). Volumetric mixing of two gases was possible using the cavity and the rest of the system as the two volumes.
Figure 8.2. Fiber-laser-based NICE-OHMS setup. The blue fiber in the foreground is the output of the fiber laser, which is led through a temperature stabilized PM fiber and EOM (in the aluminum box). The two aluminum boxes to the right contain demodulation, locking and detection electronics. The yellow bar is the cavity spacer made of Zerodur.

Figure 8.3. The optical part of the experimental setup. The short yellow fiber connected to the fiber collimator in the lower left corner is the output of the EOM. The yellow bar is the cavity spacer, with green low voltage PZTs. The gas system, connected to the cavity, is visible at the top of the picture.

Figure 8.4. Optics and detectors for detection of cavity reflected (to the left) and transmitted (to the right) light.
8.2 Fiber laser

An ideal laser for NICE-OHMS should first of all produce light in a wavelength range of interest and be easily locked, i.e., it should have a narrow free-running linewidth (preferably below the cavity linewidth), and frequency actuators with a bandwidth larger than the free-running linewidth (to allow for necessary frequency corrections) and no pronounced resonances or large phase shifts within the planned open loop bandwidth. The laser should also have a sufficient mode-hop free tunability, at least some hundreds of MHz for sub-Doppler detection and a few GHz for Doppler-broadened detection. Low intrinsic amplitude noise and the lack of intensity modulation are also an advantage, as well as a Gaussian mode structure of the output beam. For practical or commercial applications the size and cost of the laser are also of importance. However, since no laser fulfills all these requirements, some of these properties have to be compromised.

Various types of lasers have been used for NICE-OHMS and their advantages and disadvantages have been discussed in paper VIII. In the first realization of NICE-OHMS narrow linewidth solid state lasers (Nd:YAG and Yb:YAG) were used for frequency standard applications, in which the absolute frequency stability of the locked laser is of more importance than its tunability. Ti:sapphire lasers, which have a large tunability, have been used for both frequency standard and spectroscopic applications. Although the linewidth of these lasers is relatively narrow, they are not trivial to lock, and their size is large. External cavity diode lasers provide wide mode-hop-free tunability, but are susceptible to mechanical disturbances, and they have in general to be stabilized using at least two, or even three frequency actuators. In addition, their beam shape is often elliptical, which makes efficient mode matching difficult. The use of quantum cascade lasers for NICE-OHMS, demonstrated only once, is promising, since these lasers are tunable and have rather low widths, and are available in the mid-infrared wavelength range, which corresponds to strong fundamental vibrational transitions. A drawback is though that not all types of optical elements are presently available for the mid-infrared wavelength range.

The main advantage of the distributed-feedback-laser-pumped erbium-doped fiber laser (EDFL, Adjustik E15, Koheras) used in the experiments presented in this thesis was its very narrow free-running linewidth of 1 kHz (over 120 µs), which significantly simplified the frequency stabilization procedure. The wavelength of the particular laser used in this thesis could be temperature tuned in the 1530.8 – 1531.8 nm range. Fast modulation with a bandwidth of 100 kHz and maximum tuning range of 3 GHz could be obtained by modulating the laser cavity length with a piezoelectric transducer (PZT). The output of the laser was fiber-coupled (with a
polarization maintaining fiber) and the maximum output power was 14 mW. The intensity was virtually wavelength independent, i.e., it did not change with the PZT tuning. However, the spectrum of the laser intensity noise had a 35 dB peak at 300 kHz, as shown in Figure 8.5.

![Figure 8.5. Intensity noise spectrum of the fiber laser.](image)

### 8.2.1 Beam shape

The shape of the laser beam emerging from the fiber collimator was nearly perfectly Gaussian, which facilitated the spatial mode matching to a cavity. The position of the beam waist and the minimum spot size were measured with the razorblade method. In this method the power of the beam is measured at some distance from the output collimator, while the beam is gradually covered by a razorblade placed on a micrometer stage perpendicular to the beam. Since the measured power corresponds to the integral of the intensity, the power measured after the razorblade for a given position $x$ of the razorblade is given by

$$P(x) = \frac{P_0}{2 \sqrt{\pi}} \left[ 1 - \text{erf} \left( \frac{\sqrt{2} (x - x_0)}{w(z)} \right) \right],$$

(8.1)

where $x_0$ is an arbitrary offset of the razorblade position. Figure 8.6 (a) shows the beam power measured as a function of the razorblade position 20 cm after the output collimator (solid markers), where a fit of Eq. (8.1) (solid curve) yielded a value for the beam spot size, $w(z)$, of 0.650(5) mm. The measurement was repeated at different positions along the optical axis, giving rise to the data shown with solid markers in Figure 8.6 (b). Finally, Eq. (5.38) was fitted to this data (solid curve) with the waist position and the spot size at beam waist as fitting parameters. This particular fit yielded a beam waist position of 21.3(9) cm after the collimator and a spot size at beam waist of 0.659(2) mm.
8.2.2 Laser transfer function

The transfer function of the laser PZT actuator and the voltage driver (SVR 200/1, Piezomechanik GmBH) was measured by applying a sinusoidal modulation to the PZT driver and observing the cavity reflection (or transmission), with the cavity modes serving as frequency markers. The amplitude of the frequency response of the laser was measured by adjusting the amplitude of the sinusoidal modulation so as to yield a known peak-to-peak laser frequency response (e.g. 20 MHz, corresponding to the frequency difference between the carrier and the PDH sideband). The phase shift was measured by comparing where the turning point of the laser frequency modulation was with respect to the reference sinusoidal signal, as shown in Figure 8.7. In this example the cavity reflected signal (pink trace) was measured with the 125 MHz bandwidth detector, while the transmission signal (yellow trace) was measured with the DC output of the 1 GHz detector.
Since the DC output had a bandwidth of only 20 kHz, the ringing, which appears due to the interference of the incident field with the intracavity field leaking out through the input mirror (see section 8.4.2), is visible only in cavity reflection. At higher modulation frequencies this ringing can actually preclude precise measurement of the laser transfer function, as the tail of one cavity mode can overlap with the next mode.

The amplitude and phase (i.e., the Bode plots) of the fiber laser frequency response are shown in Figure 8.8. Below 1 kHz (not shown in the figure) the amplitude response was constant and equal to 95 MHz/V, which corresponded to a total tuning range of 2.85 GHz for the piezo driver input range of ±15 V, whereas the phase was close to zero. In the next decade (1 – 10 kHz) the amplitude response decreased and the phase decreases towards -90°. There were two resonances in the laser amplitude response, one at 35 kHz, and a second, smaller, at 46 kHz. At the frequency of the first resonance the phase dropped to -180°, and then at the frequency of the second resonance to -360°. Due to the associated phase shift, these resonances should be outside the bandwidth of the feedback loop. This limited the attainable bandwidth to less than 30 kHz. Since the laser linewidth was only 1 kHz, such a bandwidth was sufficient for locking.

![Figure 8.8.](image)

Figure 8.8. The amplitude (a) and phase (b) of the laser transfer function measured as a response to a sinusoidal modulation of the laser PZT.

### 8.3 Electro-optic modulator

The EOM used in this project was a z-cut, y-propagating fiber-coupled lithium niobate phase modulator (Photline, MPZ-LN-10), with the modulation applied along the extraordinary (slow) axis of the crystal. The main advantage of this modulator was its wide working frequency range, from 30 kHz to 10 GHz, which implied that both modulation frequencies needed in NICE-OHMS could be applied to the phase of the light with only one EOM. Moreover, the half wave voltage of this modulator was lower than that of typical free space resonant modulators, namely 5 V @ 5 kHz and 7 V @ 5 GHz, which yielded high modulation indices for low RF input powers.
and reduced the risk of electronic pickup. The input and output fibers were polarization maintaining and the insertion loss was 2.5 dB.

In order to reduce the influence of the temperature on the background signal (see section 4.4) the temperature of the EOM and the input PM fiber was stabilized. The EOM was placed between two copper plates, the temperature was measured with an AD590 sensor (Analog Devices) on the lower copper plate and controlled with an accuracy of 0.1 °C with a laser temperature driver (Newport, 3040) through three Peltier elements (Supercool) connected in series and placed below the lower copper plate. The PM fiber in front of the EOM was wound around a copper block, whose temperature was measured with an AD590 sensor and controlled with a laser temperature driver (Light Control Instruments, 325) through two Peltier elements connected in series.

8.4 Cavity

8.4.1 Geometry

The length of the cavity determines the cavity FSR and, together with the mirror reflectivity, the interaction length with the sample as well as the cavity mode width. For a given cavity finesse (i.e., mirror reflectivity) increasing the mirror separation provides a longer interaction length, while making the transmission modes narrower and the laser frequency stabilization more difficult. A convenient cavity length is in the tens of cm range, corresponding to a FSR in the hundreds of MHz range. As was discussed in section 7.2.1, the optimum cavity length for detection of Doppler-broadened NICE-OHMS signals in the Doppler limit at 1.5 µm is in the 20 – 40 cm range. For the two gases used in this experiment, C₂H₂ and CO₂, whose Doppler widths (at room temperature) are 236 and 182 MHz, respectively (see section 9.1), the optimum cavity length is 29 and 38 cm, respectively. According to the discussion in section 5.3.2, the length of the cavity should also be optimized with respect to the mirror geometry in order to produce a stable resonator. Moreover, the cavity should not have a degenerate spectrum and the transverse modes should not coincide with the PDH sidebands.

Three cavities with similar design have been used in the work presented in this thesis, and their parameters are summarized in Table 8.4. All were hemispherical, with a flat input mirror and a concave output mirror with a 1 m radius of curvature (Layertec) and with reflectivities in the 0.999 – 0.9994 range. The length of all cavities was similar, 37.8 – 39.4 cm, close to the optimum value for detection of CO₂. The transverse mode spacing for cavities 2 and 3, calculated from Eq. (5.47), was equal to
Table 8.4. Parameters of the three cavities used in the work presented in this thesis: length (mirror separation), free spectral range, finesse, linewidth, on-resonance transmission and reflection, and intracavity power buildup.

<table>
<thead>
<tr>
<th>cavity</th>
<th>$L$ [cm]</th>
<th>FSR [MHz]</th>
<th>$F$</th>
<th>$\Gamma_c$ [kHz]</th>
<th>$T_{c_{res}}$</th>
<th>$R_{c_{res}}$</th>
<th>$\kappa$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>37.82</td>
<td>396.32</td>
<td>140</td>
<td>140</td>
<td>7%</td>
<td>50%</td>
<td>130</td>
</tr>
<tr>
<td>2</td>
<td>39.48</td>
<td>379.92</td>
<td>4800</td>
<td>40</td>
<td>86%</td>
<td>2%</td>
<td>1300</td>
</tr>
<tr>
<td>3</td>
<td>39.37</td>
<td>381.02</td>
<td>5700</td>
<td>33</td>
<td>90%</td>
<td>1%</td>
<td>1600</td>
</tr>
</tbody>
</table>

$v_{qmn} - v_{qm(n-1)} = \frac{1}{\pi} \arccos\left(\sqrt{1 - 0.394^2}\right) FSR = 0.214 FSR, \quad (8.2)$

i.e., 82 MHz. Thus the cavity modes were not degenerate and the transverse modes did not overlap with the PDH modulation frequency.

The mirror spacers, and at the same time the gas chambers, were made of Zerodur (Schott AG), a glass ceramic material with an extremely small thermal expansion coefficient ($<10^{-7}$ K$^{-1}$, one order of magnitude below that of the best metal alloy, Invar) and a Young modulus of 90.3 GPa at 20°C, and provided good thermal and mechanical stability. The spacers were shaped as rectangular cuboids (Figure 8.3) with dimensions of 350 (or 335) × 70 × 70 mm, and had a hole with a 12 (or 20) cm diameter drilled lengthwise to provide passage for the light. Another hole was drilled perpendicularly for connection to the gas system. For a Zerodur bar with a length of 350 mm a change of the temperature by one degree resulted in a shift of the cavity mode frequencies by ~20 MHz and a change of the cavity $FSR$ by ~40 Hz @ 1.5 $\mu$m.

The tuning of the cavity length was obtained with the help of ring PZT actuators glued between the spacer and the mirrors. For a detailed description of how the PZTs were mounted on the Zerodur bar see ref. [46]. The first two cavities were built with high voltage actuators (Physik Intrumente), while in the third low voltage actuators (Piezomechanik), shown in Figure 8.9, were used. The properties of the two kinds of PZT actuators are summarized in Table 8.5. The disadvantage of the high voltage actuators was that they could not be operated in the pressure range of 1 – 500 Torr due to a risk of dielectric breakdown. This was why the low voltage actuators, which can be operated in the full pressure range up to atmospheric pressure, were used in the last cavity. Another advantage of the latter PZTs was the lower voltage required to obtain a given stroke (the maximum stroke was obtained for 150 V, as compared to 1000 V for the high voltage PZTs). A stroke of 30 $\mu$m (maximum for the longest PZT used) corresponds to a maximum shift of a cavity mode frequency by ~15 GHz and a cavity $FSR$ change of ~30 kHz @ 1.5 $\mu$m.
Table 8.5. The length, operating voltage, maximum stroke, outer (OD) and inner (ID) diameter of the high (1) and low (2) voltage PZT actuators used to modulate the length of the cavities. The two numbers correspond to PZTs of two different lengths.

<table>
<thead>
<tr>
<th>PZT length [mm]</th>
<th>V stroke [µm]</th>
<th>OD/ID [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 27/16 0-1000</td>
<td>30/15</td>
<td>25/16</td>
</tr>
<tr>
<td>2 27/13.5 -10-150</td>
<td>25/12</td>
<td>25/15</td>
</tr>
</tbody>
</table>

Figure 8.9. The input cavity mirror glued to a low voltage PZT and the Zerodur bar.

8.4.2 FSR, finesse and intracavity power

The FSR of each cavity was determined with high accuracy from a measurement of modulation frequency, \( \nu_{fsr} \), with a spectrum analyzer under locked conditions.

The cavity finesse can in principle be calculated using Eq. (5.19) and the mirror reflectivity. However, such estimate is limited by the accuracy with which the mirror reflectivity is specified by the manufacturer. Moreover, the mirror reflectivity might change due to aging and during the mounting and handling process. Thus it is important to determine the actual finesse of the cavity by other methods.

Since the cavity FSR was known, the finesse could be calculated from the ratio of the cavity FSR and the cavity mode width. The latter can be found from a measurement of the cavity decay time [83], given by Eq. (5.21). If the laser frequency is scanned around a cavity mode frequency, the incident electric field interacts with an intracavity field leaking out from the cavity, which has a different frequency, since it has entered the cavity at an earlier time. For a slow enough scan, the intracavity field will have decayed by the time the input field frequency changes, but for a faster scan a beating occurs [84]. A simple picture of this phenomenon is to assume that a field incident at time \( t \),

\[
E_{inc}(t) = E_1 \cos \left( 2\pi \left( \nu_{t_0} + st \right) t \right), \tag{8.3}
\]
where $s$ (Hz/s) is the scanning rate, interferes with the intracavity field with a frequency $\nu_{\text{to}}$ leaking out from the cavity

$$E_{\text{cav}}(t) = E_2 \cos\left(2\pi\nu_{\text{to}} t\right)e^{-t/\tau_{\text{cav}}}.$$ \hspace{2cm} (8.4)

As a result there is a beat signal in the reflected intensity proportional to

$$I_{\text{beat}} \sim \cos\left(2\pi st^2\right)e^{-t/\tau_{\text{cav}}}.$$ \hspace{2cm} (8.5)

Fitting Eq. (8.5) to the measured signal yields the cavity decay time. Figure 8.10 (a) shows the intensity reflected from cavity 3 as the fiber laser frequency was swept around a cavity mode with a saw-tooth function at 10 kHz. A closer look at each ringing event, Figure 8.10 (b), reveals the laser intensity noise at ~300 kHz, which distorted the exponential envelope of the signal. Unfortunately, this noise precluded an accurate determination of the cavity decay time by this method.

![Figure 8.10](image)

Figure 8.10. (a) Measurement of the cavity ringdown in cavity reflection (pink trace), when a saw-tooth scan at 10 kHz (green trace) was applied to the laser PZT. (b) A close-up of one ringing event, where the laser intensity noise at 300 kHz is visible.

The width of a cavity mode was instead found from fits of Eq. (6.14) to the measured PDH error signal. This method is limited by the relative laser to cavity frequency noise, as well as by the accuracy of the frequency scale calibration – the linewidth of the cavities was of the order of tens of kHz, while the frequency of the PDH sidebands, used as frequency markers, was 20 MHz, thus more than 2 orders of magnitude larger. The obtained values of the cavity finesse were verified by measurements of the on-resonance cavity transmission in the presence of a given partial pressure of an absorber, whose transition line strength was known. As an example, Figure 8.11 shows the relative power change measured in cavity transmission (cavity 3) around the P_{2(11)} transition of C_2H_2 for 102 ppm of C_2H_2 in 801 mTorr of N_2 (gray curve). Equation (5.34) was fitted to the data, as shown with the
black curve, with the product of mirror reflectivities, \( r_1r_2 \), as the fitting parameter, yielding a cavity finesse of 5700.

\[ \begin{align*}
\text{Figure 8.11.} & \text{ Direct intracavity absorption, i.e., the relative power change in the} \\
& \text{on-resonance cavity transmission (cavity 3), with 102 ppm of C}_2\text{H}_2 \text{ at 801 mTorr} \\
& \text{(gray curve) and a fit of Eq. (5.34) (black curve).}
\end{align*} \]

Once the cavity finesse was known, other parameters, such as the on-resonance cavity transmission, reflection, and the intracavity power buildup, were determined. The cavity transmission and reflection were measured under locked conditions, the latter by comparing the DC output of the reflection detector when the laser was locked and when it was unlocked (and off-resonance). One should remember that some of the incident power is carried by the PDH sidebands and possible transverse modes, which are reflected even when the laser carrier is in resonance with a cavity mode and the cavity is impedance matched. The intracavity power buildup was calculated using Eq. (7.17).

The first cavity had a significantly lower finesse than the other two due to a sparking that accidentally occurred in one of the cavity PZTs when the system was run at too high pressure and destroyed the coating of the input mirror. As a result, the impedance matching of this cavity was significantly deteriorated and the on-resonance transmission was very low, while the on-resonance reflection was 50%. The other two cavities were well impedance matched. Note that although the finesse of the first cavity was only 3.5 – 4 times lower than that of the other two cavities, the intracavity power buildup was one order of magnitude lower.

8.5 Laser frequency stabilization

8.5.1 Servo design

The transfer function of the fiber laser was modeled by a combination of first and second order phase-lag networks [81], namely as
where $G_{DC} = 90$ MHz/V is the DC gain, $f_1^{\text{res}}$ and $f_2^{\text{res}}$ are the center frequencies of the resonances, equal to 35 and 46 kHz, respectively, $f^{LP}$ is the 3 dB frequency of a low pass filter, equal to 10 kHz, and $a$ and $b$ are constants equal to $a_1 = 1/13$, $b_1 = 22$, $a_2 = 1/10$ and $b_2 = 11$. The gain and phase of this function are plotted in Figure 8.12 together with the measured laser transfer function. As can be seen in the figure, at frequencies lower than the first resonance frequency the phase was modeled correctly, while there was some error in the modeling of the gain. On the other hand, at higher frequencies the amplitude of the resonances was modeled well, while the phase deviated significantly from the measured values. This was a reasonable compromise, since it was more important to model the phase correctly within the desired bandwidth (~10 kHz) than the amplitude, while the correct modeling of the amplitude of the resonances was needed in order to prevent them from appearing above the unity gain level.

The transfer function of the cavity was modeled by a first order phase lag network, i.e., a low pass filter with a 3 dB frequency equal to the cavity mode width. The mode widths of all cavities used in this work were larger than the desired bandwidth of the control loop, so they did not influence the servo design to any larger extent. Note that this is not the case in general. The peak-to-peak value of the PDH error signal demodulated in the double balanced mixer, low pass filtered and detected after the first low-noise amplifying stage was 5 V. Thus the combined low frequency (DC) gain of the
laser and the demodulated error signal was 95 MHz/V × 5 V/80 kHz = 5940, i.e., 75 dB. This means that any voltage noise at the input of the laser PZT driver would produce a 75 dB larger voltage at the input of the servo electronics.

The Bode diagram of the transfer function of the control servo, which consisted of a double low pass filter with phase leads, is shown with solid curves in Figure 8.13. The 3 dB frequencies of the low pass filters were 30 and 70 Hz, respectively, and those of the phase leads were 2.5 and 4 kHz, respectively. Additional low pass filters with a 3 dB frequency of 1 MHz were added to reduce the gain above the unity gain frequency. The dashed curves in Figure 8.13 show the transfer function in the case when two integrators were activated, while the dotted curves show a notch filter at 35 kHz, which should eliminate the larger of the two laser resonances in order to prevent it from raising above the unity gain level.

Another feature implemented in the servo was a resonant gain at a frequency of the WM dither (250 Hz), shown with dash-dotted curves in Figure 8.13. In this way the gain at that particular frequency was significantly increased, forcing the laser to follow the cavity length dither more closely. An alternative to the resonant gain would be a feed forward, i.e., sending the dither signal simultaneously to the cavity PZT and the laser PZT driver so that the laser frequency follows the cavity mode closely even without the lock. However, the gain and the phase of the feed forward signal have to be carefully adjusted, which can be tedious. Moreover, the feed forward has to be reoptimized for each dither frequency, as the amplitude and phase response of the cavity PZTs usually change drastically with frequency (at frequencies in the tens and hundreds of Hz range). The resonant gain has the advantage that its center frequency can be tuned by changing a single capacitor.
The total open loop transfer function of the system consisting of the fiber laser (Figure 8.12), the cavity and the servo (Figure 8.13) is shown in Figure 8.14. High gain at low frequencies was achieved with double integrators (dashed curve) and the phase developed to \(-180^\circ\) at 12 kHz, which determined the bandwidth of the system. The unity gain point was crossed with a -20 dB/decade slope (shown with dotted line). The notch filter at 35 kHz (dotted curve) clearly prevented the first laser PZT resonance from appearing above the unity gain point, while the other resonance did not have to be reduced, as its amplitude was too low and it sat on a steep slope of the gain curve. With the integrators and the resonant gain on (dash-dotted curve) the system was conditionally stable, since the phase reached, or even exceeded, \(-180^\circ\) at frequencies within the bandwidth.

![Figure 8.14](image)

**Figure 8.14.** Bode plot of the open loop transfer function, i.e., the product of the laser, cavity and servo transfer functions. The solid and dashed curves correspond to PID controller without and with the integrators on, respectively, while the transfer functions with a notch filter and resonant gain are shown with dotted and dash-dotted curves, respectively. The two dotted lines in (a) indicate the -20 dB/decade and -40 dB/decade slopes.

In order to evaluate the performance of the control system, the (absolute value of the) closed loop transfer function and the disturbance propagation function, defined in Eq. (6.3), are plotted in Figure 8.15. The value of the closed loop transfer function is close to 1 for frequencies up to a few hundreds of Hz, which means that at these frequencies the laser will follow the change of the cavity mode center frequency well. The inset in Figure 8.15 (a) shows that without the resonant gain the relative error between the laser frequency and the cavity mode frequency modulated at 250 Hz will be 0.7%, while the resonant gain reduces this error to virtually zero. Note, however, that the use of a notch filter, apart from removing the resonance, increases the transfer function i.e., introduces noise, in the frequency range 1 – 10 kHz. The disturbance propagation function shows how the laser frequency changes in response to a voltage noise at the input to the PZT driver in a closed loop configuration (in logarithmic scale). For example, a noise with an amplitude of 1 mV at 10 Hz would cause a 1 Hz noise in the laser frequency.
However, the same noise at 1.2 kHz would result in a laser frequency noise of 15 kHz.

8.5.2 Locking procedure

Since the PDH error signal provides proportional gain only in the limited range within the cavity linewidth, the laser frequency had to be tuned into the vicinity of a cavity mode (or vice versa) before locking could occur. Since it was not possible to manually hold the laser frequency within the narrow cavity mode width, the cavity length was scanned at a frequency of a few Hertz, low enough to allow for coupling of the laser power into the cavity and high enough to reduce the influence of slow drift of the laser frequency, as is shown in Figure 8.16 (a). Once this was done, the gain in the servo, with the integration turned off, was gradually increased. In general, if the sign of the correction signal is wrong, the servo will push the laser carrier away from cavity resonance, and locking of the PDH sidebands will occur instead (since the PDH error signal has an opposite sign for the sidebands). If the sign is correct but the gain in the servo is too low, no action will occur or the system will be unstable, as the unity gain point would occur on the -40 dB/decade slope. If the initial gain in the servo is too large the system will overcorrect and quickly run into oscillations. Once the gain is sufficient, the cavity resonance, observed in either the transmission or reflection, will be widened, as is shown in Figure 8.16 (b). The flat section appearing at the top of the cavity resonance (the yellow and pink trace) indicates that the laser carrier stayed locked to a cavity mode for a fraction of the sweep.

Once the initial lock was established, increasing the servo gain made the laser follow the cavity for a larger fraction of the sweep. In Figure 8.16 (c) the gain was sufficient for the laser to stay locked during the whole sweep, but the sweep frequency was still visible in the error signal (green trace) and the
Figure 8.16. (a) The cavity reflection (pink trace), transmission (yellow trace) and the PDH error signal (green trace) when the cavity mode is scanned with a saw-tooth signal at 4 Hz (blue trace). (b) During initial locking the carrier stays locked to a cavity mode for a certain fraction of the sweep, while the sidebands are pushed away from resonance. (c) As the gain is increased the laser stays locked to a cavity mode during the whole sweep although the scan frequency is visible in the error signal. (d) When the integrators are on, the laser frequency follows the cavity mode much more accurately and the error signal is virtually zero even for larger sweep amplitudes. In (e) the gain is increased to cause oscillations. See text for details.

transmission decreased at the turning points of the sweep. In order to increase the gain at low frequencies, the integrators were turned on. First, however, the sweep amplitude was reduced to zero, so that the error signal was centered around zero, as any offset in the error signal would be
integrated to the supply voltage and the laser pushed out of lock. Once the integration was on, the laser followed the swept cavity mode frequency perfectly for a much larger sweep range – the transmission was constant during the sweep and the sweep frequency could not be seen in the error signal, as is shown in Figure 8.16 (d). Figure 8.16 (e) shows, finally, the consequence of increasing the gain further, so that the unity gain appeared at a frequency where the phase shift has reached -180° – oscillations were induced and the cavity transmission decreased.

Figure 8.17 illustrates the influence of the resonant gain. In Figure 8.17 (a) a WM dither at 25 Hz was applied to the cavity PZT (blue trace) and the servo produced a correction signal with proper gain and phase (pink trace). However, the gain was not sufficient to provide constant transmission (yellow trace) and the dither frequency appeared in the error signal (green trace). In Figure 8.17 (b) the resonant gain was turned on, and for the same dither amplitude the transmission was constant and the error signal was zero. One could expect to see an increase in the amplitude of the correction signal (pink trace) with respect to that shown in panel (a). Note, however, that in the absence of the resonant gain the cavity transmission decreased to 95% at the turning points, which means that at these points the detuning of the laser frequency from the center of the cavity mode was equal to 0.22 \( \Gamma_c \) [calculated from Eq. (5.29)]. For a cavity with a linewidth of 33 kHz this corresponded to 7.2 kHz. The WM dither amplitude in this example was ca 100 MHz, thus the mismatch between the laser and cavity mode frequencies was a small fraction (0.036%) of the total dither amplitude, which explains why there was no noticeable increase in the correction signal.

![Figure 8.17](image)

In order to check if the desired bandwidth (12 kHz, see discussion around Figure 8.14) had been achieved, the noise spectrum of the PDH error signal was measured, as shown in Figure 8.18. The lower curves show the spectrum of the error signal when the laser was unlocked and off resonance, while the
upper curves were measured with the laser locked. The two upper curves in Figure 8.18 (a) correspond to the optimum and a too high value of the servo gain. When the gain is increased above the optimum value, oscillations are induced at the frequency at which the phase reaches -180°. In the figure, a peak is visible at a frequency of 12.2 kHz, which agrees well with the predictions. Figure 8.18 (b) shows the noise spectrum at lower Fourier frequencies measured with a lower resolution bandwidth of the spectrum analyzer. The peak at 1.2 kHz originated from the turbo molecular pump and the wide bump slightly above 1 kHz from the rotary pump. The acoustic noise produced by the pumps was picked up by the laser and there was not enough gain in the servo at these frequencies to correct for those disturbances. The other peaks were the ubiquitous 50 Hz and its overtones. The inset in Figure 8.18 (b) shows that at the lowest frequencies the control loop reduced the noise in the error signal to the level set by the amplitude noise of the laser (lower trace).

![Figure 8.18](image_url)

**Figure 8.18.** Noise spectrum of the error signal when the laser is locked and unlocked (and off resonance, lower curves). See text for details.

### 8.6 Active FSR tracking

A perfect match of the modulation frequency to the cavity FSR is needed in order to ensure noise-immune conditions. A change in the cavity mode frequency of 3 GHz (corresponding to the maximum laser PZT tuning range) was accompanied by a change of the FSR by 6 kHz. If the modulation frequency would not follow the FSR change during the scan of the cavity length, the sidebands would at the end of the scan be detuned 3 kHz from their cavity modes, which is a significant fraction of the cavity linewidth and more than enough to disturb the balance of the FM triplet and introduce noise. It was therefore crucial, at least for detection of Doppler-broadened signals, to lock the FM modulation frequency to the cavity FSR. The lock was also used for sub-Doppler measurements, because any change in buffer gas pressure changes the FSR, and it was more convenient to have an active lock that traced these changes than to adjust the modulation frequency manually.
The frequency source was a custom made voltage controlled oscillator (VCO, Metrinova) with a center frequency of \(~380\) MHz and a free-running linewidth below 10 Hz. The center frequency of the oscillator could be manually adjusted within a few MHz range with a screw inside a helical resonator. The response of the VCO to the external input voltage is shown in Figure 8.19. The tuning range was 100 kHz, but the response was clearly nonlinear, which was slightly problematic, as it caused variations in the gain of the locking servo.

![Figure 8.19](image.png)

Figure 8.19. The response of the VCO to the input voltage.

The error signal for locking of the modulation frequency to the cavity FSR was obtained in cavity reflection, as described in section 7.1. The servo consisted of a PID controller with a switch for integration and resonant gain at the WM dither frequency. The correction signal was fed to the input of the VCO.

Before the lock could be established, the center frequency of the VCO had to be manually tuned into the vicinity of the cavity FSR, which was done with the help of a spectrum analyzer monitoring the output of the VCO. Alternatively, one can use the fact that the transmission through the cavity (with the carrier locked) is lower when the sidebands are detuned from their cavity modes, and higher when the modulation frequency is matched to the cavity FSR. A peak in cavity transmission can therefore be observed when the frequency of the VCO is scanned around the cavity FSR.

The width of the linear part of the error signal, Eq. (7.6), is equal to the full width of the cavity mode, i.e., 80 kHz for cavity 2. Since the VCO could only be scanned 100 kHz, the whole error signal could not be observed in a single sweep of the VCO frequency. This made the adjustment of the phase and offset of the FSR error signal somewhat troublesome. While a slight misalignment of the phase is acceptable, as long as the slope of the error signal is not affected too much, the offset setting is much more important, as it defines the locking point. There is, however, a way to adjust the locking point to the correct value.
If the modulation frequency is not matched exactly to the cavity $FSR$, the sidebands are detuned from the centers of their cavity modes, as shown in Figure 7.3. The cavity phase shift is linear in a small range around the resonance, which means that when the laser carrier jitters, the phase shift experienced by the carrier still cancels the phase shift experienced by both sidebands and no increase in the noise level is observed in the dispersion NICE-OHMS signal. However, this is not the case for the absorption signal. The cavity attenuation has a varying slope around the cavity resonance frequency and when the carrier frequency jitters, the change of attenuation of the lower sideband does not cancel that of the upper sideband, and noise appears. Figure 8.20 shows the background $fm$-NICE-OHMS absorption signal measured in front of the final low-pass filter (LP in Figure 8.1) as the offset of the $FSR$ error signal was tuned within the range corresponding to a shift of the VCO frequency of 0.7 kHz around the optimum setting. Clearly, a large change in the noise level is observed even for such a small detuning of the modulation frequency from the cavity $FSR$, which allows for a precise setting of the modulation frequency to within a few tens of Hz.

![Figure 8.20. Unfiltered $fm$-NICE-OHMS absorption background signal, as the offset of the error signal is adjusted around its optimum value, causing the VCO center frequency to move by 0.7 kHz.](image)

The importance of the active $FSR$ tracking is illustrated in Figure 8.21, which shows the $fm$-NICE-OHMS absorption and dispersion signals recorded with [(a), (c)] and without [(b), (d)] the $FSR$ lock (in front of the last low-pass filter in order to be able to see the noise). Without the lock the modulation frequency coincides with the actual cavity $FSR$ only at one particular frequency detuning, marked with an arrow in Figure 8.21 (b). At that detuning the noise immune condition is fulfilled, while at all other detunings the noise increases as the modulation frequency is farther detuned from the cavity $FSR$. Again, the absorption signal is affected much more by the mismatch between the modulation frequency and the cavity $FSR$ than the dispersion signal. Moreover, the inset in Figure 8.21 (b), which shows the
Figure 8.21. Absorption [(a), (b)] and dispersion [(c), (d)] $fm$-NICE-OHMS signals from 1000 ppm of C$_2$H$_2$ at 10 mTorr, with modulation frequency locked to the cavity FSR [(a), (c)] and unlocked [(b), (d)]. The insets in (b) and (d) show the low pass filtered signals.

low pass filtered signal, reveals that the shape of the absorption signal is distorted when the modulation frequency is unlocked.

8.7 Signal acquisition

The tuning of the laser frequency over the molecular transition was achieved by scanning the cavity length by applying a triangular voltage sweep from a home made (low noise) frequency generator to the input cavity mirror PZT. An optional WM dither, i.e., a sinusoidal signal from a lock-in amplifier, was applied to the output cavity mirror PZT. In the first fiber-laser-based NICE-OHMS realization (paper I) the scan and WM dither were applied to the same cavity PZT. This complicated the calibration procedure, as, due to its hysteresis, the PZT responded differently to the scan in the presence than in the absence of the WM dither. A better solution was to split the two signals, i.e., the scan and the WM dither, between the two PZTs, as was done in all subsequent papers.

As was already mentioned above, the $fm$-NICE-OHMS signal was obtained by demodulating the signal from the detector in cavity transmission at the frequency produced by the VCO. The signal was additionally low pass filtered, with a filter whose corner frequency could be adjusted freely to any value. For most measurements a relatively high bandwidth of 280 Hz was
used, in order to allow for fast signal acquisition (cavity length sweep frequency of 400 mHz) with a minimum of distortion of the lineshapes.

The WM dither frequency should be chosen in a low noise region of the noise spectrum and high enough to provide a good rejection of drifts. Due to the limited gain and bandwidth of the laser frequency control loop, the WM dither could only be applied at very low frequencies, in the tens of Hz range for Doppler-broadened detection (up to 25 Hz). This indicates directly that \( \nu_m \)-NICE-OHMS could not be performed under optimum conditions, as the 1/f noise is still significant in this frequency range. For sub-Doppler detection, which requires a much smaller modulation amplitude, a higher modulation frequency, namely 125 Hz, could be used.

A low dither frequency put a lower limit on the available lock-in integration time, which, according to the discussion around Eq. (4.13), has to be longer than the inverse of the WM dither frequency, \( 1/\nu_m \). For example, for a WM dither frequency of 25 Hz the shortest possible integration time was 6.3 ms. However, since the choice of time constants of the lock-in amplifier was 1, 3, 10, 30, 100 ms etc., a time constant of at least 10 ms had to be used. This, in turn, required very slow scanning (sweep frequency of 10 mHz) of the laser frequency (cavity length) in order to obtain undistorted lineshapes.

The DFM-DS signal should ideally be obtained by direct measurement if the output of the VCO under locked conditions. This could be done with the help of a spectrum analyzer, which, however, had a slow response time of 1 s. Instead, in order to acquire the signal continuously and at a higher acquisition rate, the correction signal at the input to the VCO was measured and recalculated to frequency using the VCO response curve shown in Figure 8.19.

### 8.8 Frequency scale and WM dither calibration

The optical frequency scale was calibrated after each series of measurements by unlocking the laser and scanning the cavity in exactly the same way (i.e., with the same amplitude and frequency) as during signal acquisition, and monitoring the cavity transmission, with the cavity modes serving as frequency markers. The maximum laser tuning range was 3 GHz, i.e., more than 7 cavity FSRs, wherefore up to 7 frequency markers, spaced by the cavity FSR, were visible each time. Due to the response of the cavity PZT the scan was nonlinear, and a polynomial had to be fitted to the positions of the cavity modes. For sub-Doppler measurements the frequency scanning range was of the order of a few tens of MHz, i.e., much smaller than the cavity FSR. For calibration of sweep with such a low range a signal at a low MHz frequency and with a large modulation index was applied to the
EOM so that two pairs of FM sidebands were created, which, together with the carrier, provided five frequency markers.

The response of the cavity PZT to the WM dither was calibrated using a cavity transmission mode as a reference. The laser was unlocked and the cavity length was scanned with the use of the input cavity PZT, while the WM dither was applied to the output cavity PZT. The signal from the cavity transmission detector was demodulated with a lock-in amplifier on the second harmonic of the WM frequency, yielding a second harmonic WM signal. Finally, the (second) Fourier coefficient of a Lorentzian lineshape function (with a width equal to the cavity mode width) was fitted to this signal with the modulation amplitude as a fitting parameter. This procedure worked well even though the WM signals obtained in this way were severely overmodulated (the cavity mode width was in the tens of kHz range, while the modulation amplitudes were in the MHz range). One should remember, however, that the laser frequency does not follow the cavity mode dither infinitely well under locked conditions, since the gain in the locking servo is finite. The error is, however, usually very small and the calibration provides a sufficiently good initial value for the fitting of analytical signals.
9. Experimental Results

A multitude of measurements have been performed with the fiber-laser-based NICE-OHMS instrumentation described in the previous chapter, both during the development stage of the setup, and as a part of the characterization of it. The most important results of these measurements are presented below. Some of them are the basis of the appended papers, while some are still unpublished. Typical Doppler-broadened and sub-Doppler NICE-OHMS signals are as well as the DFM-DS signals are shown. The detectability of the system in various modes of operation is assessed and the main limitations are discussed. First, however, the transitions of the two pilot species used in this thesis, namely C₂H₂ and CO₂, are characterized.

9.1 Acetylene and carbon dioxide transitions

Fiber-laser-based NICE-OHMS measurements have so far been performed on acetylene and carbon dioxide, on the transitions listed in Table 9.1. The transition wavelengths, \( \lambda_0 \), the Einstein A coefficients, \( A_{21} \), and the degeneracies of the two energy levels, \( g_1 \) and \( g_2 \), were taken from the HITRAN database [6]. The dipole moments were calculated using Eq. (2.5), where the definition of Debye, \( 1 \text{ D} = 3.3356 \times 10^{-30} \text{ C·m} \), was used. The room temperature line strengths were calculated from the molecular line strengths given in the HITRAN database using Eq. (2.7). The Doppler widths [Eq. (2.20)] of the two gases at 1531 nm and at a temperature of 23 °C are 236 MHz and 182 MHz, which implies that the peak values of the unsaturated area-normalized Gaussian lineshapes [Eq. (3.29)] are 59.6 and 77.6 cm, respectively.

<table>
<thead>
<tr>
<th>gas</th>
<th>transition</th>
<th>( \lambda_0 ) [nm]</th>
<th>( A_{21} ) [s⁻¹]</th>
<th>( g_1 )</th>
<th>( g_2 )</th>
<th>( \mu ) [mD]</th>
<th>( S ) [cm²/atm]</th>
</tr>
</thead>
<tbody>
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<td>0.133</td>
<td>2.560 × 10⁻⁶</td>
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<td>13</td>
<td>0.131</td>
<td>2.110 × 10⁻⁶</td>
</tr>
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<td>Pₑ(10)</td>
<td>1530.976</td>
<td>5.379</td>
<td>21</td>
<td>19</td>
<td>7.46</td>
<td>1.001 × 10⁻¹</td>
</tr>
</tbody>
</table>

Both C₂H₂ transitions listed in Table 9.1 belong to a relatively strong \( 0 \rightarrow v_1 + v_3 \) band. The Rₑ(38) CO₂ transition belongs to a weak \( 0 \rightarrow 3v_1 + v_3 \) band, while the Pₑ(9) and Pₑ(7) transitions belong to a hot band, \( v_2 \rightarrow 3v_1 + v_2 + v_3 \). It is worth to note that the line strengths of the C₂H₂
transitions are ~5 orders of magnitude larger than those of the CO2 transitions, while the dipole moments are almost 2 orders of magnitude larger.

The gases were available as pure CO2 and as 1000 ppm of C2H2 in N2. Pure N2 was used to obtain lower relative concentrations of C2H2 by volumetric mixing. Most Doppler-broadened measurements were performed on the P_e(11) transition of C2H2 and the nearby P_e(9) transition of CO2. Sub-Doppler spectroscopy was possible only on C2H2, due to the much lower dipole moment of CO2. In the Doppler limit, the single-pass absorption of 1000 ppm of C2H2 in cavity 2 at the P_e(11) transition, calculated using Eq. (2.15), was equal to

$$\alpha_{0}^{C_2H_2} = 9 \times 10^{-7} p,$$

where p is the total pressure of the C2H2/N2 mixture expressed in mTorr. Similarly, the single-pass absorption of pure CO2 detected at the P_e(9) transition in the same cavity was equal to

$$\alpha_{0}^{CO_2} = 1 \times 10^{-8} p,$$

where p is the pressure of CO2. This shows that for the same intracavity pressure the single-pass absorption of 1000 ppm of C2H2 was ~90 times larger than that of pure CO2. The intracavity losses in cavity 2 were equal to $2\pi/4800 = 1.3 \times 10^{-3}$, thus the double-pass absorption of 1000 ppm of C2H2 was 2% of the intracavity losses at an intracavity pressure of 15 mTorr, whereas the same condition for CO2 was reached at a pressure of 1.3 Torr. These pressures were chosen as the upper limits of low intracavity absorption for cavity 2, i.e., of the validity of Eq. (7.7) and thus also of Eq. (7.8) for the NICE-OHMS signal.

9.2 Doppler-broadened NICE-OHMS (Papers I, II, IV, VIII)

All Doppler-broadened measurements were performed in the Doppler limit due to two technical limitations. First, the high voltage cavity PZTs, used in cavities 1 and 2, could not be operated at pressures above 1 Torr. Second, the tuning range of the fiber laser was only 3 GHz, sufficient for acquisition of a Doppler-broadened NICE-OHMS signal in the Doppler limit, i.e., at low pressures, but not enough to measure pressure-broadened transitions whose widths are in the low GHz range.

Figure 9.1 shows some typical fm-NICE-OHMS signals (solid markers, for clarity only every tenth data point is displayed) from 93 mTorr of 1000 ppm of C2H2 recorded in cavity 1 at absorption, dispersion and optimum detection phases, where the latter was equal to 0.19π (paper I). Equation (7.9) was fitted to the experimental data with center frequency, signals strength and
detection phase as fitting parameters. The fits are shown with solid curves, while the residuals are displayed below each panel. The agreement between the theoretical expression and the measured signals is very good. The slowly varying structure in the residual originates from background signals, while the sharp features at detunings of ±200 MHz are the sub-Doppler signals.

Figure 9.1. Doppler-broadened fm-NICE-OHMS signals at absorption (a), dispersion (b) and optimum [34°, (c)] detection phase from 93 mTorr of 1000 ppm of C$_2$H$_2$ detected in cavity 1 (paper I). Measurement data are shown with circular markers, solid curves are the fits of Eq. (7.9), and the residuals are displayed below each panel.

Figure 9.2 shows wm-NICE-OHMS signals from 200 mTorr of pure CO$_2$, measured in cavity 3 at various FM detection phases and with different WM modulation amplitudes, as marked in the figure legend (paper VIII). Experimental data are again shown with circular markers, whereas the curves represent fits of Eq. (7.10). The residuals of the fits, displayed below each panel, show no systematic errors, and prove that the agreement between the theoretical lineshapes and experimental signals is satisfactory.

The concentration of the analyte can be deduced from fits of the NICE-OHMS lineshapes to the experimental curves with the detection phase and signal strength as the fitting parameters. In the absence of optical saturation, the signal strength is linear with partial pressure of the analyte irrespective of the detection phase. This is shown in Figure 9.3 (a), where the pressure dependence of the absorption and dispersion signal strength from 500 ppm of C$_2$H$_2$ in N$_2$ measured with low intracavity power (0.47 W) is plotted. At each pressure the signal strength is independent of the detection phase, thus a linear fit, shown in the figure, to data recorded at one detection phase can serve as a calibration curve for concentration measured at other detection phase.

An assessment of the analyte concentration from the measured signal strength is not equally straightforward in the presence of optical saturation. The reason is that the absorption signal is decreased by a factor of $1/\sqrt{1+G_{\pm1}}$, while the dispersion signal strength is unaffected by optical
Figure 9.2. Doppler-broadened um-NICE-OHMS signals from 200 mTorr of pure CO$_2$ measured at different detection phases and modulation amplitudes, as marked in figure legends, in cavity 3 (paper VIII). Measurement data are shown with circular markers, the curves are fits of Eq. (7.10), and the residuals are shown below each panel.

Figure 9.3. Pressure dependence of the fm-NICE-OHMS absorption and dispersion signal strength from 500 ppm of C$_2$H$_2$ for intracavity power of 0.47 W (a) and 3.8 W (b) measured in cavity 2 (paper IV). The lines show linear fits to the data.
saturation. Since the saturation intensity changes with pressure [Eq. (3.25)], this implies that while the pressure dependence of the dispersion signal strength is still linear, the absorption signal strength exhibits a nonlinearity with cavity pressure. This phenomenon is illustrated in Figure 9.3 (b), where the pressure dependence of the absorption and dispersion signal strength from 500 ppm of C$_2$H$_2$, measured with a saturating intracavity power (3.8 W), is plotted (paper IV). The dependence of the dispersion signal strength is truly linear, as shown by the linear fit, while the absorption signal strength is consequently below that of dispersion. Moreover, the ratio of the absorption and dispersion signal strength is different at different pressures, ranging from 0.5 (at the lowest pressure) to 0.97 (at the highest pressure), which is due to the fact that the saturation intensity increases with intracavity pressure.

The influence of optical saturation on Doppler-broadened NICE-OHMS signals is further illustrated in Figure 9.4, where fm-NICE-OHMS absorption [(a), (b)] and dispersion [(d), (e)] signals from a given partial pressure of C$_2$H$_2$ (10 µTorr) recorded under different total pressure and intracavity power conditions (i.e., for different degrees of saturation) are shown (paper IV). For comparison, the panels (c) and (f) show signals from 900 mTorr of

![Figure 9.4](image)

**Figure 9.4.** Doppler-broadened fm-NICE-OHMS absorption [(a) – (c)] and dispersion [(d) – (f)] signals from 100 ppm of C$_2$H$_2$ in 100 mTorr of N$_2$ [(a), (d)], 10 ppm of C$_2$H$_2$ in 1000 mTorr of N$_2$ [(b), (e)] and 900 mTorr of pure CO$_2$ [(c), (f)] at two different intracavity powers, as marked in the figure legends, measured in cavity 2 (paper IV).
CO₂, whose transition is unsaturated (due to the much smaller dipole moment). Experimental data are shown with circular markers, fits of Eq. (7.9) are shown with solid curves and the residuals are displayed below each panel. In Figure 9.4 (a) and (d) the intracavity power and total pressure were 0.47 W and 100 mTorr, respectively, which resulted in low degrees of saturation (0.5 and 0.015 for the carrier and the sidebands, respectively). In Figure 9.4 (b) and (e) the intracavity power and total pressure were 3.8 W and 10 mTorr, respectively, yielding much higher degrees of saturation (77 and 2.2 for the carrier and the sidebands, respectively). It is evident that the two dispersion signals from C₂H₂ [(d) and (e)] are virtually identical despite significantly dissimilar degrees of saturation, while the absorption signal [(a) and (b)] is reduced by a factor of 0.56, in agreement with Eq. (7.21). It is interesting to note that none of the Doppler-broadened NICE-OHMS signals is affected by optical saturation induced by the carrier.

The dependence of the Doppler-broadened NICE-OHMS absorption and dispersion signal strength from 1000 ppm of C₂H₂ at 10 mTorr on the intracavity power is shown in Figure 9.5 (a) (paper IV). The dispersion signal strength is virtually constant, in agreement with Eq. (7.20), while the strength of the absorption signal decreases, in agreement with Eq. (7.21). Figure 9.5 (b) shows the power dependence of the ratio of the absorption and dispersion signal strengths from 10 µTorr of C₂H₂ measured at different intracavity pressures as marked in the figure legend (solid markers). Equation (7.22) was fitted to each set of data with the saturation power as a fitting parameter (solid curves). These fits yielded the saturation power at each pressure, which is in turn plotted by the solid markers in Figure 9.6 (paper IV). The solid curve in this figure shows a fit of Eq. (7.18), which yields a transit time broadening and a pressure broadening coefficient of 94 kHz and 5.55 kHz/mTorr, respectively.

![Figure 9.5](image-url)
Intracavity pressure [mTorr]

Saturation power [W]

Figure 9.6. Pressure dependence of the saturation power for C\textsubscript{2}H\textsubscript{2} obtained from measurements displayed in Figure 9.5 (b) (paper IV).

9.3 Sub-Doppler NICE-OHMS (Papers V, VII)

The maximum possible intracavity power obtained in cavity 2, in which most of the sub-Doppler signals were measured, was 4.7 W, which corresponded to a degree of saturation of 100 for the P\textsubscript{e}(11) transition of C\textsubscript{2}H\textsubscript{2} at a total intracavity pressure of 10 mTorr. The possibility to obtain such high degrees of saturation allowed for studies of phenomena in previously unavailable saturation regimes.

As is illustrated in Figure 9.7, which shows fm-NICE-OHMS absorption and dispersion signal from 500 ppm of C\textsubscript{2}H\textsubscript{2} at 20 mTorr (paper VIII), the sub-Doppler signals reside on top of Doppler-broadened background. The intracavity power in this example was 4.6 W, yielding degrees of saturation of 50 and 1.5 for the carrier and the sidebands, respectively. Nine narrow sub-Doppler features can be seen on top of the Doppler-broadened background, in agreement with the predictions stated in section 7.2.2; four at the absorption and five at the dispersion detection phase, each originating from interaction of various pairs of FM light modes with specific velocity groups of molecules.

Figure 9.7. Fm-NICE-OHMS absorption (a) and dispersion (b) signals from 500 ppm of C\textsubscript{2}H\textsubscript{2} at 20 mTorr, for an intracavity power of 4.6 W, corresponding to a degree of saturation of 50 and 1.5 for the carrier and the sidebands, respectively, measured in cavity 2 (paper VII).
A \textit{wm}-NICE-OHMS signal from 1000 ppm of C$_2$H$_2$ at 10 mTorr detected in cavity 3 with an intracavity power of 5.3 W, at a detection phase of $3\pi/4$ with a WM modulation amplitude of 140 MHz, is shown in Figure 9.8. The degrees of saturation for the carrier and the sidebands were in this case 108 and 3.1, respectively. The sub-Doppler signal appears as a sharp overmodulated feature around resonance. Due to its resemblance to a bat, signals with this shape have been referred to as Bian Fu (Chinese for bat).

![Figure 9.8. Wm-NICE-OHMS signal from 1000 ppm of C$_2$H$_2$ at 10 mTorr measured in cavity 3 with an intracavity power of 5.3 mW, corresponding to degrees of saturation of 108 and 3.1 for the carrier and the sidebands, respectively, with a WM modulation amplitude of 140 MHz and at a detection phase of $3\pi/4$.](image)

The strength and linewidth of all sub-Doppler NICE-OHMS signals, and of the center dispersion signal in particular, depend strongly on the degree of saturation, and thus on the intracavity pressure and power. Figure 9.9 shows the center sub-Doppler dispersion signal from a partial pressure of 10 µTorr of C$_2$H$_2$ at three different intracavity buffer pressures and two different intracavity powers. The upper panels show the \textit{fm}-NICE-OHMS signals, while the lower panels display the corresponding \textit{wm} signals. The three vertical pairs of panels correspond to intracavity pressures of 10, 100 and 500 mTorr, respectively, whereas the two curves in each panel represent different intracavity powers (0.49 and 4.1 W, respectively). Evidently, the sub-Doppler signal is largest when the degree of saturation is highest, i.e., at the lowest pressure and for the largest power. The figure also shows that the linear Doppler-broadened background is removed by the WM process. Equation (7.26) was fitted to the \textit{wm}-NICE-OHMS signals with the center frequency, the linewidth and the signal strength as the fitting parameters. The theoretical lineshapes fit well and overlap the measured curves almost completely, as can be seen in the residuals shown below the panels. This shows that the sub-Doppler NICE-OHMS signals can be well modeled by the Lorentzian approximation.
Figure 9.9. (a) – (c) Sub-Doppler fm-NICE-OHMS dispersion signals from 10 µTorr of C₂H₂ at different buffer gas pressures (as marked in each panel) measured in cavity 2 at two intracavity powers: 4.1 W (black curve, larger signal) and 0.49 W (gray curve, smaller signal). (d) – (f) Sub-Doppler wn-NICE-OHMS dispersion signals taken under the same intracavity pressure and power conditions with modulation amplitudes of (d) 2.3 MHz, (e) 3.6 MHz, and (f) 5.4 MHz. Fits of Eq. (7.26) are also shown in the figure, with residuals displayed below, where the upper and lower residual correspond to the higher and lower intracavity power, respectively (paper VII).

Figure 9.10. The peak-to-peak optical phase shift in terms of the on-resonance Doppler-broadened absorption coefficient, as a function of the degree of saturation. Solid markers show the experimental data, measured in cavity 2, the solid curve is a plot of Eq. (7.24), dashed – of Eq. (3.47), and dash-dotted – of Eq. (3.46) (paper V).
The peak-to-peak sub-Doppler optical phase shift measured in cavity 2 as a function of the degree of saturation is shown by the solid markers in Figure 9.10. The large range of degrees of saturation (from 0.03 to 90) was obtained by using various combinations of intracavity power and buffer pressure with a constant partial pressure of $C_2H_2$. The solid and dashed curves are plots of the two expressions for the peak-to-peak sub-Doppler optical phase shift derived in paper V, namely Eqs (7.24) and (3.47), whereas the dash-dotted curve is a plot of the expression for the on-resonance sub-Doppler absorption signal that has previously been used to model the peak-to-peak sub-Doppler NICE-OHMS dispersion signal, i.e., Eq. (3.46) [13, 31, 33]. It is clear that the two former expressions, in particular the one that contains the correction factor for Gaussian intensity distribution of the beam, model the data much better than the latter. The latter expression, although correct for low degrees of saturation, underestimates the maximum signal size by a factor of 3.5. Moreover, the value of the peak-to-peak sub-Doppler phase shift predicted by this expression is wrong by more than an order of magnitude at high degrees of saturation.

Figure 9.11 (a) shows the pressure dependence of the strength of the sub-Doppler $um$-NICE-OHMS signal from a sample with a constant concentration of $C_2H_2$ (20 ppm) measured at four different intracavity powers, as marked in the figure legend. For each intracavity power there is an intracavity pressure at which the sub-Doppler NICE-OHMS signal is maximized (for smaller pressures the signal decreases because of a reduced partial pressure of the analyte, whereas for larger pressures the signal decreases because of a reduced degree of saturation). Since a higher degree of saturation can be obtained with a higher laser power, the maximum of the signal strength moves to higher pressures for higher powers.
The sub-Doppler $\nu m$-NICE-OHMS signal strength is expected to be linear with analyte concentration up to concentrations at which the double-pass absorption is a significant fraction of the empty cavity losses (provided that the buffer pressure is constant). This is shown in Figure 9.11 (b) (paper VII), where the signal strength is plotted as a function of concentration for three different intracavity pressures. A straight line was fitted to the data recorded at the lowest total pressure, 10 mTorr, whereas a polynomial fit was used for the data recorded at 100 and 500 mTorr in order to account for the nonlinear dependence at the highest concentrations. The slopes of the three calibration curves at low concentrations are dissimilar since the strength of the signal from a given concentration of the analyte depends on the intracavity pressure.

As was mentioned in section 7.2.2, the theory for the center sub-Doppler dispersion signal does not model well the sub-Doppler signal appearing at a detuning equal to half the modulation frequency, which originates from carrier-sideband interaction. Figure 9.12 shows a fragment of the $f m$-NICE-OHMS absorption signal from 1000 ppm of C$_2$H$_2$ measured in cavity 3 with an intracavity power of 5.3 W at four different intracavity pressures, 10, 5.7, 3.7 and 1.3 mTorr. The sub-Doppler signal at the detuning of -380 MHz originates from sideband-sideband interaction and its peak value follows Eq.

![Figure 9.12](image-url)
However the sub-Doppler signal at a detuning of -190 MHz shows an unexpected behavior, namely it changes sign and at the lowest pressure a peak (i.e., an inverted dip) appears instead. Figure 9.13 shows the same signal recorded at an even lower pressure (much below, 1 mTorr, outside the working range of the pressure gauge) and a C\textsubscript{2}H\textsubscript{2} concentration higher than 1000 ppm. The inversion of the dip indicates that no ordinary hole burning occurs at these low pressures and high degrees of saturation. This phenomenon remains to be explained.

![Figure 9.13. Fm-NICE-OHMS absorption signal from C\textsubscript{2}H\textsubscript{2} measured at an intracavity pressure below 1 mTorr. The inset shows a zoom of the inverted dip at a detuning of -180 MHz, originating from the carrier-sideband interaction.](image)

### 9.4 Dual frequency modulation dispersion spectroscopy (Paper IX)

Figure 9.14 shows a typical DFM-DS signal from 1000 ppm of C\textsubscript{2}H\textsubscript{2} in N\textsubscript{2} at a total pressure of 50 mTorr. As is shown in panel (a), the analytical DFM-DS signal (black curve) resides on top of a linear background, which originates from the change of cavity FSR as the cavity length is scanned. A pure analytical DFM-DS signal can be obtained by subtracting a background signal (gray curve, measured in an empty cavity). Such a net analytical signal is shown in Figure 9.14 (b) by the solid markers. The solid curve shows a fit of the numerical solution of Eq. (7.28) to the experimental lineshape. The residual of the fit is shown below the panel, confirming the agreement between the theoretical and experimental signal (paper IX).

Examples of DFM-DS signals obtained from 1000 ppm of C\textsubscript{2}H\textsubscript{2} at various intracavity pressures (20, 100, 200 and 400 mTorr) are shown in Figure 9.15, together with fits of Eq. (7.28), and with residuals displayed below each panel. The agreement between the theoretical model and the experimental signals is good also in this case.
Figure 9.14. (a) DFM-DS signal from 1000 ppm of C$_2$H$_2$ at 50 mTorr (black curve) and the empty cavity background signal (gray line), measured in cavity 2 (paper IX). (b) The DFM-DS analytical signal (solid markers) with a fit of numerical solution of Eq. (7.28) (solid curve) and residual (below).

Figure 9.15. DFM-DS signals from 1000 ppm of C$_2$H$_2$ at 20 (a), 100 (b), 200 (c), and 400 (d) mTorr, measured in cavity 2 (paper IX). Experimental data are shown by the solid markers, solid curves are fits of numerical solutions of Eq. (7.28) and residuals are shown below each panel.
The lineshape of the DFM-DS signal changes significantly with the concentration of the analyte. However, the on-resonance value of the DFM-DS signal is linear with partial pressure of the analyte. This is shown in Figure 9.16, where the experimental on-resonance DFM-DS signal (solid markers) is plotted together with the calculated on-resonance frequency shift (solid line). The theoretical values are in good agreement with the measured data.

![Figure 9.16. The on-resonance modulation frequency shift due to the partial pressure of the analyte, measured with DFM-DS in cavity 2 (paper IX).](image)

### 9.5 Detectability

One way to determine the detectability is to compare the size of the analytical signal from a known concentration or partial pressure of the analyte to the standard deviation of the noise in the background signal. For example, Figure 9.17 (a) shows an fm-NICE-OHMS dispersion signal from 30 mTorr of pure CO$_2$, corresponding to a single-pass absorption of $24 \times 10^{-8}$ (black curve) and the (empty cavity) background signal (gray curve). The background corrected analytical signal is plotted in Figure 9.17 (b) with solid markers, and a fit of Eq. (7.9) is shown with solid line. The signal-to-noise ratio can be estimated by comparing the peak size of the signal (0.7 V) with three times the standard deviation of the noise in the residual, which in this particular case was 23 mV. This yields a signal-to-noise ratio of 30, and thus a minimum detectable absorption of $8 \times 10^{-9}$ (paper II).

However, such method yields the detection limit only for the particular averaging time used to acquire the signal, but does not give information about the optimum averaging time. The latter can be obtained by the use of Allan variance [85]. In order to calculate the Allan variance, a large set of $N$ data (e.g. concentration values) has to be measured in equal time intervals, $\tau$. The time intervals should be as short as possible, though not shorter than the averaging time of the electronics, and are usually limited by the instrument response time. The data is then divided into $M$ subsets of $k$ elements, such that $k = N / M$, and the mean of each subset, $A_s(k)$, is
calculated. Each such average is equivalent to a data point taken with an integration time of $k\tau$. The Allan variance for a given integration time is calculated as the average of the differences of neighboring averaged data subsets, i.e., as [86]

$$\sigma_A^2(k) = \frac{1}{2(M-1)} \sum_{s=1}^{M-1} [A_{s+1}(k) - A_s(k)]^2,$$

(9.3)

where the mean of the subset is given by

$$A_s(k) = \frac{1}{k} \sum_{l=1}^{k} x_{(s-1)k+l},$$

(9.4)

where $x$ is the measured value. Thus, instead of calculating mean values and standard deviations for different integration times, one compares adjacent measurements to each other [85]. A logarithmic plot of the square root of the Allan variance as a function of integration time reveals information about the type of noise dominating in the system for different detection bandwidths. Most importantly, the square root of Allan variance of white noise, which has a $\tau^{-1/2}$ dependence, is equivalent to the standard deviation and corresponds to the detection limit [87].

Allan variance has been used to determine the detection limit for sub-Doppler NICE-OHMS (paper VIII). 25 ppm of C$_2$H$_2$ at 20 mTorr was let into the cavity and a scan over a sub-Doppler signal was acquired every 5 seconds (limited by the time constant of the lock-in amplifier). The concentration, which was retrieved from fits to the lineshapes, is shown in
the upper panel of Figure 9.18 as a function of measurement time. The square root of the Allan variance, expressed in terms of an optical phase shift, is shown in the lower panel of the figure as a function of the integration time, i.e., $k \tau$. The solid line shows the $\tau^{-1/2}$ dependence characteristic for white noise. The data follow this behavior for integration times up to $\sim 200$ s and the gray curve in the upper panel shows the concentration averaged over this integration times. The square root of the Allan variance up to the optimum integration time, normalized to $Hz^{1/2}$, gives the detection limit. In this case a minimum detectable single-pass optical phase shift of $2.2 \times 10^{-9} Hz^{1/2}$, which corresponds to a relative absorption of $3.9 \times 10^{-10} Hz^{1/2}$, was obtained. The drift, which starts at averaging times longer than $200$ s, was caused mainly by temperature induced changes of the refractive indices of the EOM and the PM fiber after the EOM, as is further discussed below.

![Figure 9.18](image)

**Figure 9.18.** Concentration of C$_2$H$_2$ (upper panel) measured in cavity 2 (paper VII) and the square root of the Allan variance of the sub-Doppler optical phase shift (lower panel). The gray curve shows the concentration averaged over the optimum integration time, i.e., $200$ s. The solid line shows the $\tau^{-1/2}$ dependence characteristic for white noise.

The detectability of various modes of operation of the NICE-OHMS instrumentation presented above is summarized in Table 9.2. For Doppler-broadened NICE-OHMS the detectability is listed for both $fm$- and $wm$-NICE-OHMS. The detectability of sub-Doppler NICE-OHMS is quoted in terms of the sub-Doppler optical phase shift and recalculated to single-pass absorption. Similarly, for DFM-DS the resolution of the modulation frequency measurement is given, and recalculated to the corresponding single-pass absorption.
Table 9.2. Detectability of NICE-OHMS in the three modes of operation – Doppler-broadened (DB), sub-Doppler (sD) and dual frequency modulation (DFM), quoted per unit length. The minimum detectable partial pressure, $p_A$, of C$_2$H$_2$ is quoted, together with the corresponding integration time $\tau$.

<table>
<thead>
<tr>
<th>Det. mode</th>
<th>Detectability</th>
<th>$p_A$ [nTorr]</th>
<th>$\tau$ [s]</th>
<th>Paper</th>
</tr>
</thead>
<tbody>
<tr>
<td>DB</td>
<td>$8.0 \times 10^{-11}$ cm$^{-1}$ (fm)</td>
<td>3.5</td>
<td>11</td>
<td>II</td>
</tr>
<tr>
<td></td>
<td>$2.4 \times 10^{-10}$ cm$^{-1}$ (um)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>sD</td>
<td>$5 \times 10^{-11}$ cm$^{-1}$ Hz$^{-1/2}$ ($\phi$)</td>
<td>0.8</td>
<td>200</td>
<td>VII</td>
</tr>
<tr>
<td></td>
<td>$1 \times 10^{-11}$ cm$^{-1}$ Hz$^{-1/2}$ ($\alpha_0$)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$@ 20$ mTorr</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DFM</td>
<td>$6$ Hz ($\nu_{fsr}$)</td>
<td>21</td>
<td>12.5</td>
<td>IX</td>
</tr>
<tr>
<td></td>
<td>$3 \times 10^{-9}$ cm$^{-1}$ ($\alpha_0$)</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

9.6 Limitations

The main limitation to the performance of the fiber-laser-based NICE-OHMS setup was a drifting background signal at dispersion phase originating from the birefringence of the PM fibers and the EOM. As was discussed in section 4.4, a background signal appears at the dispersion phase if the input and/or output polarization direction is not aligned along the e-axis of the EOM. Such perfect alignment is impossible to obtain for a fiber-coupled EOM. First of all the connector keys might not be aligned perfectly to the slow axis of the fiber. Moreover, polarization maintaining fibers have a built in stress birefringence [88], which means that they act like wave plates. If the input polarization direction is not aligned along the slow axis of the fiber, the electric field is projected on the two axes and the polarization state at the output of the fiber is different than at the input (due to the different propagation speeds along the two axes). Thus, when a PM fiber is used to connect the fiber-coupled polarizer and the EOM (see Figure 8.1), the polarization at the input of the EOM will most probably be elliptical. Similarly, the polarization state after the EOM will be disturbed by the output PM fiber.

Since it is not straightforward to control the polarization of the light propagating in the PM fibers, the background signal at the dispersion detection phase should be minimized by ensuring that the total phase difference between the light polarized along the o- and e-axis of the EOM [Eq. (4.21)] is zero. The relative phase of the two components is strongly temperature dependent, due to the dissimilar temperature dependence of the e- and o-axis refractive indices. The temperature dependence of the refractive indices of the LiNbO$_3$ crystal along the e- and o-axes, given by [89]
\[ n_e = 4.5567 + 2.605 \times 10^{-7} T_K^2 + \frac{0.970 \times 10^5 + 2.70 \times 10^{-2} T_K^2}{\lambda^2 - \left(2.01 \times 10^2 + 5.4 \times 10^{-5} T_K^2\right)^2} - 2.24 \times 10^{-8} \lambda^2 \] (9.5)

and

\[ n_o = 4.9130 + \frac{1.173 \times 10^5 + 1.65 \times 10^{-2} T_K^2}{\lambda^2 - \left(2.12 \times 10^2 + 2.7 \times 10^{-5} T_K^2\right)^2} - 2.78 \times 10^{-8} \lambda^2, \] (9.6)

where \( T_K \) is the temperature in K, is plotted in Figure 9.19 (a) for the range of temperature of 10 – 40 °C. In this range of temperatures, the change of \( n_e \) is \( 5 \times 10^{-4} \) K\(^{-1}\), while that of \( n_o \) is \( 1.7 \times 10^{-4} \) K\(^{-1}\), i.e., it is 3 times larger for the extraordinary wave than for the ordinary wave. This implies that the temperature will influence the relative phase of the light polarized along the two axes of the EOM. Figure 9.19 (b) shows the change of the \( fm \)-NICE-OHMS dispersion background signal for a change of EOM temperature of 2 °C induced through the temperature controller. The amplitude of this drift is comparable to the peak-to-peak size of a signal from 6 \( \mu \)Torr of \( C_2H_2 \). A drift of such magnitude can surely limit the detectability of the technique severely. In order to avoid it the temperature of the EOM and the PM fiber connecting the polarizer and the EOM was stabilized, as described in section 8.3. Before each series of measurements a combination of the EOM and fiber temperatures that provided a zero background signal was found. However, such solution was only temporary, since after some time the temperature induced change of refractive indices in the unstabilized fiber caused a drift again.

![Figure 9.19](image)

**Figure 9.19.** (a) Temperature dependence of extraordinary (solid curve) and ordinary (dashed curve) refractive indices of LiNbO\(_3\). (b) The variation of the \( fm \)-NICE-OHMS dispersion background signal as the temperature of the EOM is changed from 23 to 25 °C.

The best solution would be to apply DC voltage to the EOM in a feedback loop in order to actively correct the phase, as has been suggested by Wong.
and Hall [71]. Unfortunately, the particular z-cut fiber-coupled modulator used in this experiment lacked a response to pure DC due to an isolation layer between the electrodes and the crystal. This precluded the implementation of a feedback loop with this EOM.

The drift of the background signal can in principle be removed by the WM process. However, due to the limited gain and bandwidth of the laser locking servo, the WM dither frequencies used for Doppler-broadened NICE-OHMS detection were in the tens of Hz range, which did not allow for an efficient reduction of the drift. Higher WM dither frequencies were used for detection of sub-Doppler signals, wherefore the drift of the background was not observed in sub-Doppler detection. Unfortunately, this does not imply that the sub-Doppler signal was unaffected by the presence of the $f_{m}$ background. When the balance of the FM triplet in front of the cavity is disturbed by the dispersion in the fibers and the EOM, the 'noise immunity' is destroyed to a certain extent. The noise in the $f_{m}$-NICE-OHMS signal is then a copy of the laser frequency noise, with an amplitude proportional to the magnitude of the $f_{m}$ background. This causes, in turn, a varying noise level in the $w_{m}$-NICE-OHMS signal and thus in the sub-Doppler signal, which in turn limits the detectability.

An advantage of absorption $f_{m}$-NICE-OHMS signals is that they are unaffected by the drift induced by the unbalance of the phase. However, the peak-to-peak value of the absorption signal is in general smaller than that of the dispersion signal, and the strength of the signal is further reduced in the presence of optical saturation. The detection of Doppler-broadened absorption signals is limited by residual amplitude modulation from the EOM and multiple reflections between the optical elements (so-called etalons). The latter could be minimized by careful alignment of all free space optical components at an angle to the optical axis. The largest etalons, originating from the reflection between the cavity mirrors and the detector windows, were efficiently removed by the use of optical isolators in front of the detectors.

Finally, the DFM-DS signal is free from the background signal caused by the phase drift that originates from the EOM, since it is intrinsically insensitive to the dispersion of the carrier. The technique can in principle provide a high detectability if the VCO frequency is measured directly with a high resolution. However, in this project, the correction signal sent to the VCO was measured instead, in order to provide fast response time. Thus the noise level in the signal was determined by the stability and linewidth of the RF frequency source.
10. Conclusions and Outlook

This thesis describes the technical implementation of fiber-laser-based NICE-OHMS and summarizes the current status of the technique. It also contributes to an improved understanding of the NICE-OHMS technique by extending the theoretical description of the various types of signals that can be obtained.

It has been shown that fiber-laser-based NICE-OHMS is capable of detecting both Doppler-broadened and sub-Doppler signals with a sensitivity in the $10^{-9}$ range ($10^{14} \text{ cm}^3$). The linearity of the signal strength with analyte concentration has been demonstrated and the influence of optical saturation on Doppler-broadened NICE-OHMS signals has been investigated. It has been shown that the Doppler-broadened absorption signal is affected by optical saturation induced by the sidebands, and not by the carrier, and that the Doppler-broadened dispersion signal in the Doppler limit is not affected by optical saturation at all, which makes the NICE-OHMS technique less influenced by this phenomenon than other cavity enhanced techniques. It has also been shown that the dependence of the peak-to-peak sub-Doppler dispersion signal on the degree of saturation differs from what previously has been assumed; it does not have any maximum, instead it increases monotonically as a function of degree of saturation, and reaches a value 3.5 times larger than previously assumed. This thesis also presents a realization of a fiber-laser-based DFM-DS system, which has demonstrated a sensitivity in the $10^{-7}$ range.

The results presented in this thesis do not constitute the ultimate limits of performance of the fiber-laser-based NICE-OHMS technique. The detectability can be directly improved by removing the present main limitation, i.e., the background signals that result from an unbalance of the phase of the various components of the FM triplet incident on the cavity, primarily induced by the fiber-coupled EOM and PM fibers. Although not yet described in any publication, a feedback loop has already been implemented in the setup, similar to that suggested by Wong and Hall [71], which provides a balanced FM triplet in front of the cavity, and the preliminary results are promising. However, in order to make such a background reduction system effective, another type of fiber-coupled EOM should be used, viz. one that responds to a pure DC signal.

In the present implementation the power incident on the detector in cavity transmission was deliberately attenuated in order to avoid saturation of the detector by the background RF signal. Once the background signal has been eliminated, the power level should be increased in order to make the signal larger and the theoretical shot-noise limit lower. For the same reason,
and again in the absence of the background signal, the modulation index
should presumably be increased.

Further increase of the sensitivity can be obtained by the use of cavities
with higher finesse. A higher finesse would also result in a higher intracavity
power, which would enable saturation of transitions with a lower dipole
moment.

It would also be of interest to implement other designs of gas chambers,
e.g., flow cells, which would allow for performing measurements on sticky
gases, e.g., ammonia.

In order to make the system even more compact, the remaining free space
optical components, used for picking up the light reflected from the cavity in
order to obtain the PDH error signal, could be replaced with a fiber-coupled
optical circulator. This should, however, be done only when the problem
with dispersion in fibers has been removed by an active stabilization scheme.

All measurements presented in this thesis have been performed under low
pressure conditions, i.e., in the Doppler limit, due to technical limitations,
i.e., a restricted working pressure range of the cavity PZTs and the limited
tuning range of the fiber laser. A cavity with low voltage PZTs, which can be
operated up to atmospheric pressures, already exists, wherefore
measurements in the Voigt regime can be performed soon. With the present
fiber laser it will, however, not be possible to perform measurements at
atmospheric pressure, i.e., in the purely pressure-broadened regime, due to
the limited tuning range of the laser.

In order to be able to detect pressure-broadened molecular transitions
other types of lasers, with larger fast tuning range, should be used. In this
respect it would be especially interesting to investigate the applicability of
distributed feedback lasers for NICE-OHMS.

Although only two species were detected with NICE-OHMS in this work,
there exist a number of other molecules with transitions within the working
wavelength range of the fiber laser, e.g. N\textsubscript{2}O, CH\textsubscript{4}, NH\textsubscript{3}, H\textsubscript{2}S, and CH\textsubscript{2}O.
Moreover, narrow linewidth fiber lasers exist in several wavelength ranges,
presently corresponding to the emission windows of Yb, Er, and Tm doped
fibers, i.e., from 1030 to 1121 nm, from 1525 to 1585 nm, and from 1710 to
2100 nm, respectively. The application of NICE-OHMS can be extended into
other wavelength ranges by the use of different laser sources. Especially
promising are the quantum cascade lasers, which work in the wavelength
range corresponding to the fundamental molecular vibrational transitions
[37].

Finally, the theoretical description of NICE-OHMS signals should be
further developed. A correct modeling of the sub-Doppler carrier-sideband
interaction observed at a frequency detuning equal to half the cavity FSR
should be developed, as well as an analytical formula for the width of the
center sub-Doppler dispersion signal. Moreover, the influence of a higher modulation index on the shape and strength of Doppler-broadened and sub-Doppler NICE-OHMS signals should be investigated in order to find the optimum value of this parameter. The extension of the Doppler-broadened NICE-OHMS signal theory into the range of high intracavity absorption might also be needed for some applications.
11. Summary of the Papers

**Paper I**

**Fiber-laser-based noise-immune cavity-enhanced optical heterodyne molecular spectrometry for Doppler-broadened detection of C₂H₂ in the parts per trillion range.**

F. M. Schmidt, A. Foltynowicz, W. Ma, and O. Axner


In this paper fiber-laser-based NICE-OHMS was presented for the first time. The experimental setup was described in detail and the performance was evaluated using acetylene as pilot species. A detection limit of $2.4 \times 10^{-9}$ cm$^{-1}$ was obtained in a cavity with a finesse of 1400. A general theoretical description of Doppler-broadened $fm$- and $wm$-NICE-OHMS signals in terms of analyte concentration for arbitrary detection phase was presented and confirmed by experimental results in the Doppler limit. It was demonstrated that the signal strength is independent of the detection phase and linear with the partial pressure of the analyte.

I designed and built the electronics for the laser frequency stabilization and was involved in the optimization of the performance of the experimental setup. I was responsible for the final measurements, developed the Matlab fitting routines, and evaluated the data. I wrote parts of the manuscript.

**Paper II**

**Doppler-broadened fiber-laser-based NICE-OHMS - Improved detectability.**

F. M. Schmidt, A. Foltynowicz, W. Ma, T. Lock, and O. Axner


This paper presented an improved fiber-laser-based NICE-OHMS setup, based on a cavity with a finesse of 4800. Measurements were performed on C₂H₂ and CO₂ and a detectability of $8 \times 10^{-11}$ cm$^{-1}$ was obtained. The $fm$ and $wm$ detection modes at absorption and dispersion phase were compared and the optimum detection mode was discussed.

I was involved in the optimization of the performance of the experimental setup, conducted a large part of the experiments and evaluated most of the data. I contributed to the preparation of the manuscript.
Paper III

Theoretical description of Doppler-broadened noise-immune cavity-enhanced optical heterodyne molecular spectroscopy under optically saturated conditions.

W. Ma, A. Foltynowicz, and O. Axner

A theoretical description of Doppler-broadened NICE-OHMS signals under optically saturated conditions was presented in this paper. Expressions for the strength and shape of the Doppler-broadened NICE-OHMS signals were given for absorption and dispersion phase, in the Voigt regime as well as in the Doppler limit. It was shown that Doppler-broadened NICE-OHMS is affected less by optical saturation than other cavity enhanced techniques; in the Doppler limit the absorption signal decreases by a factor of \(1/\sqrt{1+G_{\pm1}}\), where \(G_{\pm1}\) is the degree of saturation induced by one of the FM sidebands, whereas the dispersion signal is virtually unaffected by optical saturation.

I contributed to the preparation of the manuscript and took part in the discussions about the theoretical modeling.

Paper IV

Doppler-broadened noise-immune cavity-enhanced optical heterodyne molecular spectroscopy signals from optically saturated transitions under low pressure conditions.

A. Foltynowicz, W. Ma, F. M. Schmidt, and O. Axner

This paper presented an experimental confirmation of the theoretical description of Doppler-broadened NICE-OHMS under optically saturated conditions in the Doppler limit. It was shown that Doppler-broadened dispersion signals in the Doppler limit are unaffected by optical saturation, while the absorption signals are reduced by a factor of \(1/\sqrt{1+G_{\pm1}}\), where \(G_{\pm1}\) is the degree of saturation induced by one of the FM sidebands. A methodology for assessments of the degree of saturation and the saturation power of a transition was given. The implications of optical saturation for practical trace species detection by Doppler-broadened NICE-OHMS were discussed.

I was responsible for all measurements and analysis of the results. I wrote a substantial part of the manuscript.
Paper V

Sub-Doppler dispersion and noise-immune cavity-enhanced optical heterodyne molecular spectroscopy revised.
O. Axner, W. Ma, and A. Foltynowicz

In this paper, the expression for the peak-to-peak sub-Doppler optical phase shift of two counter-propagating modes of light, to which the sub-Doppler NICE-OHMS dispersion signal is proportional, was derived. It was shown that the peak-to-peak sub-Doppler phase shift increases monotonically with the degree of saturation up to a value of $0.45 \frac{\alpha_0}{2}$, where $\alpha_0$ is the on-resonance absorption, and that the shape of the sub-Doppler NICE-OHMS dispersion signal is well modeled by a dispersion counterpart of the Lorentzian lineshape function. The new formula differs significantly from that previously used for weakly saturating conditions and modifies the optimum conditions for the sub-Doppler NICE-OHMS technique. The validity of the new expression was verified by experimental results up to a degree of saturation of 100.

I was involved in all measurements and wrote parts of the manuscript related to the experiment and the results.

Paper VI

A. Foltynowicz, F. M. Schmidt, W. Ma, and O. Axner

This is a review article, in which the experimental details, applications and performance of all previous realizations of NICE-OHMS were described. The principles of the technique were revised and various experimental issues of importance for the technique (e.g., the cavity design, suitable laser sources, laser frequency stabilization and active FSR tracking) were discussed. The performance of NICE-OHMS was compared to that of other cavity enhanced techniques. Its potential for practical applications was discussed.

I wrote a substantial part of the manuscript.
Paper VII

*Characterization of fiber-laser-based sub-Doppler NICE-OHMS for trace gas detection.*

A. Foltynowicz, W. Ma, and O. Axner


In this paper the potential of the sub-Doppler fiber-laser-based NICE-OHMS for trace gas detection was scrutinized. The non-linear dependence of the on-resonance sub-Doppler dispersion signal on the intracavity pressure and power was investigated and the optimum conditions with respect to these were determined. The linearity of the signal strength with concentration was demonstrated and the dynamic range of the technique was discussed. Measurements were performed on C$_2$H$_2$ up to degrees of saturation of 100. The minimum detectable sub-Doppler optical phase shift was $5 \times 10^{-11}$ cm$^{-1}$ Hz$^{1/2}$, corresponding to a partial pressure of C$_2$H$_2$ of $1 \times 10^{-12}$ atm for an intracavity pressure of 20 mTorr, and a concentration of 10 ppb at 400 mTorr.

I was responsible for all measurements and analysis of the results. I wrote a substantial part of the manuscript.

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Paper VIII

*Wavelength modulated noise-immune cavity-enhanced optical heterodyne molecular spectroscopy signal line shapes in the Doppler limit*

A. Foltynowicz, W. Ma, F. M. Schmidt, and O. Axner


In this paper a thorough analysis of Doppler-broadened *wm*-NICE-OHMS signals was presented. The dependence of the signal line shape and magnitude on FM modulation frequency, WM modulation amplitude and FM detection phase was investigated. The conditions that maximize the on-resonance signal were identified. The theory was verified by fits to experimental signals from C$_2$H$_2$ and CO$_2$.

I made all simulations and was responsible for the measurements and evaluation of the experimental data. I wrote most of the manuscript.
Paper IX

Probing the free spectral range of an optical cavity using dual-frequency modulation: highly sensitive dispersion spectroscopy of C$_2$H$_2$.

F. M. Schmidt, W. Ma, A. Foltynowicz, and O. Axner

in manuscript

This paper is the first demonstration of the application of DFM-DS to detection of trace amounts of a gas inside the cavity. A theoretical description of the signals is given, enabling assessment of the gas concentration from a fit of the theoretical lineshape to the experimentally obtained signal. The FSR shift of a cavity with a finesse of 4800 due to an acetylene transition has been measured with a resolution of 6 Hz (i.e., and accuracy of 1.5 parts in 10$^8$), which corresponds to a sensitivity of 3×10$^{-9}$ cm$^{-1}$ in terms of integrated absorption.

I was involved in the discussions about the theoretical description of signals, designed and constructed most of the electronics used for detection of the signals and contributed to the preparation of the manuscript.
12. Errata to the Papers

Papers I – VII

The expressions for the FMS, $f_m$-NICE-OHMS and $um$-NICE-OHMS signals in paper I, Eqs (8), (9) and (15), respectively, should be reduced by a factor of 2. The correct expressions are given by Eqs (4.9), (7.9) and (7.10) in this thesis. The reason for this discrepancy is that the factor of $1/2$, originating from the demodulation process, has been implicitly included in the instrumentation factor, $\eta_{fm}$. The same correction should be applied to the definition of $f_m$-NICE-OHMS signal strength in paper II [above Eq. (2)] and paper IV [below Eq. (11)]; to Eqs (6) and (29) in paper III, Eqs (2) and (6) in paper V, Eqs (1), (4) and (7) in paper VI and in Eq. (2) in paper VII.

Moreover, the phase angle, $\theta_{fm}$, used throughout papers I – VI, is not strictly the detection phase, as defined in this thesis. Instead, it follows the modulation convention used by North et al. [64], which is not valid for a reference signal with a sinusoidal form, as assumed in this work. The correct detection phase, $\theta'_{fm}$, should be defined as a shift of the reference signal with respect to the detector signal, i.e. with the reference signal being of the form $\sin(\omega_m t + \theta'_{fm})$. Thus the phase angle $\theta_{fm}$ used in the papers I – VI is related to the detection phase $\theta'_{fm}$ through

$$\theta'_{fm} = \pi/2 - \theta_{fm}.$$ 

This implies that absorption phase, which corresponds to $\theta_{fm}$ of $0$ or $\pm\pi$, corresponds to a detection phase, $\theta'_{fm}$, of $\pm\pi/2$. Likewise, dispersion phase, which corresponds to $\theta_{fm}$ of $\pm\pi/2$, corresponds to a detection phase, $\theta'_{fm}$, of $0$ or $\pm\pi$. The in-phase signal, for which $\theta'_{fm} = 0$, is thus the dispersion signal, not absorption.

None of these misprints affects any of the results or conclusions presented in these papers.

Paper III

Using the convention of writing the electrical field as given in Eq. (3) in this paper, i.e. as $-\exp[-i(\omega \eta_j t - k_j z)]$, the sign in front of the phase shift term in Eq. (5) should be positive, whereby Eq. (5) should read

$$T_j(\Delta \omega) = e^{-\delta_j(\Delta \omega)+i\phi_j(\Delta \omega)}.$$ 

Moreover, there are two minor misprints in this paper. Equation (32) should read
and the text above Eq. (36) should read “...whereby the real and imaginary parts of the error function reduce to \(\exp(-x_j^2)\) and \(\text{erfi}(x_j)\exp(-x_j^2)\), respectively.” Since all subsequent expressions are correct, none of these misprints have any consequence for the conclusions of the paper.
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