Cavity enhanced optical sensing

Isak Silander
“He e så he e nu“
Loosely translate:
“This is how it is now”
(so stop complaining and do something about it)
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Abstract

An optical cavity comprises a set of mirrors between which light can be reflected a number of times. The selectivity and stability of optical cavities make them extremely useful as frequency references or discriminators. With light coupled into the cavity, a sample placed inside a cavity will experience a significantly increased interaction length. Hence, they can be used also as amplifiers for sensing purposes. In the field of laser spectroscopy, some of the most sensitive techniques are therefore built upon optical cavities. In this work optical cavities are used to measure properties of gas samples, i.e. absorption, dispersion, and refractivity, with unprecedented precision.

The most sensitive detection technique of all, Doppler-broadened noise-immune cavity enhanced optical heterodyne molecular spectrometry (Db NICE-OHMS), has in this work been developed to an ultra-sensitive spectroscopic technique with unprecedented detection sensitivity. By identifying limiting factors, realizing new experimental setups, and determining optimal detection conditions, the sensitivity of the technique has been improved several orders of magnitude, from $8 \times 10^{-11}$ to $9 \times 10^{-14}$ cm$^{-1}$.

The pressure interval in which NICE-OHMS can be applied has been extended by derivation and verification of dispersions equations for so-called Dicke narrowing and speed dependent broadening effects. The theoretical description of NICE-OHMS has been expanded through the development of a formalism that can be applied to the situations when the cavity absorption cannot be considered to be small, which has expanded the dynamic range of the technique. In order to enable analysis of a large number of molecules at their most sensitive transitions (mainly their fundamental CH vibrational transitions) NICE-OHMS instrumentation has also been developed for measurements in the mid-infrared (MIR) region. While it has been difficult to realize this in the past due to a lack of optical modulators in the MIR range, the system has been based on an optical parametric oscillator, which can be modulated in the near-infrared (NIR) range.

As the index of refraction can be related to density, it is possible to retrieve gas density from measurements of the index of refraction. Two such instruments have been realized. The first one is based on a laser locked to a measurement cavity whose frequency is measured by compassion with an optical frequency comb. The second one is based on two lasers locked to a dual-cavity (i.e. one reference and one measurement cavity). By these methods changes in gas density down to $1 \times 10^{-9}$ kg/m$^3$ can be detected.

All instrumentations presented in this work have pushed forward the limits of what previously has been considered measurable. The knowledge acquired will be of great use for future ultrasensitive cavity-based detection methods.
Sammanfattning


Den mest känsliga detektionstekniken av alla, Dopplerbreddad brusimmunkavitetsförstärkt optisk-heterodyndetekterad molekylärspetskopisk (eng. Db NICE-OHMS), har i detta arbete vidareutvecklats till en ultrakänslig spektroskopisk teknik med tidigare överträffad känslighet. Genom att identifiera begränsade faktorer, realisera nya experimentella uppställningar, och identifiera optimala detektionsbetingelser har teknikens känslighet förbättras flera storleksordningar, från $8 \times 10^{-11}$ till $9 \times 10^{-14}$ cm$^{-1}$. Tryckintervallet där NICE-OHMS kan appliceras har utökats genom att dispersionsekvationen för s.k. Dickeavsmalning och hastighetsberoende breddningseffekter har härlemts och experimentellt verifierats. Den teoretiska beskrivningen av NICE-OHMS har utökats genom utvecklingen av en formalism som även gäller i området då kavitetsabsorptionen inte kan anses vara liten, vilket har utökat teknikens dynamiska område. För att möjliggöra analys av ett stort antal molekyler på deras mest känsliga övergångar (huvudsakligen deras fundamentala C-H vibrationsövergångar) har även NICE-OHMS instrumentering för mätningar i det mitt-infraröda (MIR) området utvecklats. Då detta tidigare har varit svårt att realisera p.g.a brist på optiska modulatorer i MIR-området har systemet baserats på en optisk parametrisk oscillator, som kan moduleras i det nära-infraröda (NIR) området.


Alla instrument som presenteras i denna avhandling har flyttat fram gränsen för vad som tidigare ansågs vara mätbart. Kunskapen som har samlats här kommer att vara viktig för framtida ultrakänsliga mätmetoder baserade på optiska kaviteter.
List of publications

This thesis is based on the following publications

NICE-OHMS – Technical realizations, Causes and reduction of background signals, Optimum detection conditions, and Improvement of performance

I. Reduction of background signals in fiber-based NICE-OHMS
   A. Foltynowicz, I. Silander, and O. Axner

II. Frequency modulation background signals from fiber-based electro optic modulators are caused by crosstalk
   I. Silander, P. Ehlers, J. Wang, and O. Axner

III. Fiber-laser-based noise-immune cavity-enhanced optical heterodyne molecular spectrometry instrumentation for Doppler-broadened detection in the 10^{-12} \text{ cm}^{-1} \text{ Hz}^{-1/2} region
   P. Ehlers, I. Silander, J. Wang, and O. Axner

IV. Fiber-laser-based noise-immune cavity-enhanced optical heterodyne molecular spectrometry incorporating an optical circulator
   P. Ehlers, I. Silander, J. Wang, A. Foltynowicz, and O. Axner

V. Use of etalon-immune distances to reduce the influence of background signals in frequency-modulation spectroscopy and noise-immune cavity-enhanced optical heterodyne molecular spectroscopy
   P. Ehlers, A. C. Johansson, I. Silander, A. Foltynowicz, and O. Axner
VI. **Doppler broadened noise-immune cavity-enhanced optical heterodyne molecular spectrometry: optimum modulation and demodulation conditions, cavity length, and modulation order**
P. Ehlers, **I. Silander**, and O. Axner

VII. **Doppler broadened NICE-OHMS beyond the triplet formalism: assessment of optimum modulation index**
P. Ehlers, J. Wang, **I. Silander**, and O. Axner,

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

IX. **Model for incoupling of etalons into signal strengths extracted from spectral line shape fitting and methodology for predicting the optimum scanning range – Demonstration of Doppler broadened NICE-OHMS down to $9 \times 10^{-14} \text{ cm}^{-1}$**
**I. Silander**, T. Hausmaninger, W. Ma, and O. Axner

X. **Doppler-broadened NICE-OHMS beyond the cavity-limited weak absorption condition – I. Theoretical Description**
W. Ma, **I. Silander**, T. Hausmaninger, and O. Axner
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XI. **Doppler-broadened NICE-OHMS beyond the cavity-limited weak absorption condition – II: Experimental verification**
T. Hausmaninger, W. Ma, **I. Silander**, and O. Axner
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Mid-IR OPO-based NICE-OHMS

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

XIII. Doppler-broadened noise-immune cavity-enhanced optical heterodyne molecular spectrometry in the mid-IR region down to $10^{-10}$ cm$^{-1}$ Hz$^{-1/2}$
T. Hausmaninger, I. Silander, O. Axner
In manuscript

Line shape studies

XIV. Dicke narrowing in the dispersion mode of detection and in noise-immune cavity-enhanced optical heterodyne molecular spectroscopy - Theory and experimental verification
J. Wang, P. Ehlers, I. Silander, and O. Axner

XV. Speed-dependent Voigt dispersion line-shape function: applicable to techniques measuring dispersion signals
J. Wang, P. Ehlers, I. Silander, J. Westberg, and O. Axner

XVI. Speed-dependent effects in dispersion mode of detection and in noise-immune cavity-enhanced optical heterodyne molecular spectrometry: experimental demonstration and validation of predicted line shape
J. Wang, P. Ehlers, I. Silander, and O. Axner
XVII. On the accuracy of the assessment of molecular concentration and spectroscopic parameters by frequency modulation spectrometry and NICE-OHMS
J. Wang, P. Ehlers, I. Silander, and O. Axner

Gas density measurements

XVIII. Optical measurement of the gas number density in a Fabry–Perot cavity
I. Silander, M. Zelan, O. Axner, F. Arrhén, L. Pendrill, and A. Foltynowicz
Measurement Science and Technology 24(10), 105207 (2013).

XIX. A dual Fabry-Perot cavity for fast assessments of gas number density
I. Silander, T. Hausmaninger, M. Zelan, O. Axner and A. Foltynowicz
In manuscript

Reviews and prospects

XX. NICE-OHMS — frequency modulation cavity-enhanced spectroscopy — principles and performance
O. Axner, P. Ehlers, A. Foltynowicz, I. Silander, and J. Wang

XXI. Noise-immune cavity-enhanced analytical atomic spectrometry — NICE-AAS — A technique for detection of elements down to zeptogram amounts
O. Axner, P. Ehlers, T. Hausmaninger, I. Silander, and W. Ma,
Introduction

Over the years, mankind has based its knowledge about our nature, environment, and world on observations. The first observations were made by our own senses; i.e. sight, hearing, taste, smell, and touch. When these were not sufficient, we developed instruments that could enhance our senses, or act in their place, e.g. telescopes and microscopes for enhanced viewing and stethoscopes and hydrophones for enhanced hearing. Taste and smell have been supplemented with a wide variety of detecting techniques for analyzing the chemical constituents of solid or liquid substances or gaseous samples, and the human touch has been replaced with thermometers, scales, and pressure gauges; although a fisherman will tell you that he can weigh his fish by hand you nowadays do not trust him over a scale. In addition to these, we have developed tools and techniques for assessments of a large range of physical entities, such as distances, electrical and magnetic fields, e.g. detectors for detection of radiation at frequencies at which the human eye is not sensitive and laser radars for assessment of distances and velocity. For every increase in accuracy or capability an improved understanding of the world or a scientific breakthrough has followed. For example, the introduction of high precision thermometers for breweries led to the discovery of the relation between mechanical motion and temperature and the development of the microscope led to the discovery of bacteria, which in turn led to the germ theory of disease. The quest for higher sensitivity, accuracy, and precision is hence not a quest solely for great scientific breakthroughs but also a strive to develop fundamental tools or instruments to see the invisible. In the work summarized here, the boundary of what is considered measurable has been further pushed forward by the development of a number of highly sensitive instruments utilizing optical cavities and photonics to measure what previously has been unmeasurable.

Photonics is a field that has evolved tremendously over the last decades. El-Hang Lee stated in an editorial in 2009 "Certainly, we are all witnessing, like the “age of electronics” in the 20th century, an “age of photonics” rising over the 21st century.” [1].

The age of electronics began with the invention of the transistor in the late 40’s, while the field of photonics, in turn, came to age with fiber communications in the 80’s. Since then, photonics has risen beside electronics; developments in electronics have advanced photonics and developments in photonics have benefited electronics. The combination of the two fields has for example advanced field such as optical fiber communication, optical data storage (CD/DVD/Blu-ray), and laser surgery.
One of the most important devices in photonics is the optical cavity also known as the optical resonator. Like microwave resonators were an integral part in the most sensitive measurement systems constructed during the 20th century, e.g. RADAR and atomic clocks, optical cavities are today an integral part of some of the most sensitive measurement systems conceived.

In an optical resonator light is circulated by spatially overlapping beam paths. At certain frequencies, this result in constructive interference and, in the case of linear resonators, a standing wave. At these frequencies, known as cavity mode frequencies, the wave inside the cavity will be amplified up to the point where the power losses equal the input power. The lower the losses the higher the power buildup, and the narrower the resonances. The spacing of these resonant frequencies is known as the free spectral range (FSR), \( v_{\text{FSR}} \), and the ratio of the FSR and the full width half maximum (FWHM) of the resonances is referred to as the finesse, \( F \). The optical cavity will transmit light only at these narrow resonances while other frequencies will be rejected (i.e. reflected). This frequency selectivity, in combination with inherent frequency stability, makes them extremely useful as frequency discriminators or references. Optical cavities are today therefore used in laboratories around the word for a variety of purposes.

Optical cavities can be divided into linear and ring resonators. Linear resonators, also known as standing wave resonators, are somewhat simplistically made so that light is bouncing between two mirrors resulting in contra propagating wave fronts, creating a time independent interference pattern, consisting of crests and valleys. Ring resonators, on the other hand, are made so that the wave fronts are circulating. They can therefore support modes propagating in two different directions, which in turn, can result in two output beams. Some examples of free space resonators utilizing mirrors are illustrated in Figure 1.

The simplest linear resonator is the Fabry-Perot, shown in panel (a) in Figure 1, which consists of two semitransparent mirrors. Another example of a linear resonator is the V-resonator, (b) in Figure 1. The advantage of this type is that it does not have any back reflection from its first surface (input mirror) and that it therefore can be used for so-called optical feedback locking. Linear resonators can also be made of optical fibers. In this case they often incorporate fiber Bragg-gratings, which are constructed by periodically inscribing a grating in the core of an optical fiber with varying refractive indexes. Such resonators are used for example in optical multiplexers, as strain sensors, and in fiber lasers. Examples of ring resonators are the three-mirror ring resonator shown in panel (c) in Figure 1, and the bow-tie, illustrated in panel (d). The latter type is often used in singly resonant optical parametric oscillators (OPOs). Ring resonators can
Figure 1. Illustration of four different types of optical resonators; (a) The Fabry-Perot resonator, (b) the V-resonator, (c) the ring resonator, and (d) the bow-tie resonator.

also be made as fiber loop resonators, which are used in laser gyroscopes and fiber loop ringdown spectroscopy [2].

Optical cavities are today made for a variety of applications. In its first application, in 1897, the Fabry-Perot etalon was used in an interferometer to obtain high resolution measurements of small distances between parallel surfaces [3]. In papers published in 1899 it was reported that the Fabry-Perot interferometer had been applied to study spectral lines of various metal vapors i.e. thallium, mercury, and cadmium [4, 5]. In these first realizations, silver coated glass plates were used as mirrors producing interferences fringes much sharper than those of a normal Michelson interferometer.

In 1958 concave spherical mirrors were introduced by Connes resulting in stable cavities [6]. This enabled a single mode of the cavity to be excited, which, in turn, resulted in a single Gaussian output beam instead of interference rings.

Albert Kastler stated in 1962, “It is shown that this device is equivalent to a long absorption path in an ordinary light beam” [7]. This pointed out the full potential of cavity enhanced measurements. In 1977 Brewster plates were introduced for input and output coupling [8]. This greatly reduced the losses from the silver mirrors, which increased the cavity finesse. The next major step in the development of optical cavities came with the introduction of dielectric mirrors, and by 1992 it was possible to construct cavities with astonishing finesse, viz. up to $1.6 \times 10^6$ [9].

Since the combination of amplification and discrimination is essential to produce coherent laser light, the majority of optical cavities are today used in
lasers, in particular for continuous wave (CW) lasers. The gain medium inside the optical cavity of such a laser will amplify one or a few cavity modes, resulting in one or a few standing waves; the wavelengths of the laser is hence determined by the lasing cavity modes.

In optical frequency combs (OFCs) the cavity is essential to achieve mode locking between the multitude of modes that simultaneously exist in the cavity. If the laser modes lock to each other, they will, by interference, produce a train of pulses. In the time domain, a mode-locked laser can therefore be seen as a single pulse that is circulated in an optical cavity. For each round trip, the pulse is amplified by the lasing media and a fraction of it is transmitted through the output mirror. To achieve the mode locking, pulsed lasers are often equipped with an intra-cavity acousto optical modulator (AOM) or an electro optical modulator (EOM) to modulate the intensity or the frequency, to suppress all other pulses developing inside the cavity. Alternatively, passive mode locking can be achieved by inserting a saturable absorber in the cavity. The output pulse train has a repetition rate given by the frequency of the pulses, which is equal to \( c/2L \), where \( L \) is the cavity length. If this pulse train is analyzed in the frequency domain the result will be a series of intensity peaks i.e. a frequency “comb”, with the teeth separated by the repetition rate, which also is the FSR of the laser cavity. In both cases the electrical field circulating inside the cavity is amplified by the gain medium and the output beam is a fraction of this field coupled out through the output mirror.

In Figure 2 the difference between a CW-laser and a mode-locked laser is illustrated. In the case of a single-mode CW-laser, as shown in panel (a), the circulating field produces a standing wave, resulting in an output wavelength that is an integer fraction of the cavity round trip length. In the case of a mode locked laser, as shown in panel (b), the circulating field consists of a number of modes locked to each other so they produce a series of pulses.

In a similar manner, a laser can also be used to excite a passive cavity. This can take place if the frequency (frequencies) of the laser matches one (or several modes) of the cavity. To achieve steady state conditions, which allows for a constant transmission through the cavity, the frequency of the laser needs to be locked to that of a mode of the cavity. Locking a laser to an external cavity will often stabilize the laser i.e. narrow its linewidth. It is worth noting that both CW lasers and OFCs can be locked to external optical cavities. While a CW laser can be locked to cavities with a length equal to an integer number of wavelengths of the light, an OFC can only be locked to cavities that have an FSR that is equal to an integer number of the repetition rate (if all light is to be coupled into the cavity) or an FSR that is an integer fraction
Figure 2. Illustration of the difference between continuous wave (CW) lasers (a), and mode locked lasers so called frequency combs (OFC) (b). In the latter case a single pulse exists inside the cavity and the separation of the pulses in time is both the inverse of the repetition frequency and the FSR.

of the repetition rate (only a fraction of the pulses are transmitted i.e. every second, third, etc.).

To the author’s knowledge, the CW-laser with the highest recorded stability was created in 2012 by an international collaboration of scientists at NIST/JILA in Boulder, CO and a group at Physikalisch-Technische Bundesanstalt (PTB). The laser, which utilized locking to an extremely stable external cavity, exhibited an fractional frequency variation lower than $1 \times 10^{-16}$, which represents a linewidth smaller than 40 mHz at 1.5 µm [10]. Both the cavity spacer and the mirror substrates are constructed from a silicon single-crystal that was cryogenically cooled to 124 K to minimize the thermal expansion of the cavity. One possible use of this ultrastability lasers is in combination with optical clocks. By phase locking two fields to each other, it is also possible to transfer this accuracy to other lasers enabling a variety of measurement with unprecedented accuracy.

This accuracy surpasses microwave resonators previously used as frequency standards. For example, with the GPS satellite system, which is based on atomic clocks, which in turn utilize microwave resonators that are stable to within $1 \times 10^{-12}$, it is possible to determine one’s position to within 1 m using differential GPS [11]. If the satellites were equipped with ultra-stable optical cavities with a stability of $1 \times 10^{-16}$ [10] the accuracy could conceivably be improved to less than 1 mm.

The best clocks, which today have an accuracy of $8.6 \times 10^{-18}$, are based on laser cooled quantum logic spectroscopy of an Al$^+$ ion. In these clocks ultra-stable cavities are used to narrow the laser sufficiently to probe a 8 mHz
narrow transition [12]. While these clocks are not practical to use in space i.e. in GPS satellites, the extreme accuracy might, in the same manner as the transition from mechanical instruments to electronics, lead to new scientific discoveries in other fields.

The Laser Interferometer Gravitational-wave Observatory (LIGO) is the largest of a number of ground based laser interferometers designed to detect gravitational waves. In LIGO optical cavities are used to increase the effective path length of the interferometer arms [13]. The interferometers at the Livingston Observatory and the Hanford Observatory consist of two 4 km ultra-vacuum arms. If a gravitational wave passes through the detector the space time will be altered in one or both interferometric arms, causing the light that is stored in the cavities to get partly out of phase with incoming light. By detecting the phase changes a relative change in distance of $10^{-21}$ can presumably be detected [14]. The original LIGO experiments ran from 2002 to 2010 with no reports of any gravitational waves. The upgraded “Advanced LIGO” experiment is scheduled to be operational in 2015 with an expected improvement sensitivity of one order of magnitude [15]. Other laser interferometer gravitational-wave observatories worth mentioning are TAMA300 located in Japan, the GEO600 in Germany, and VIRGO in Italy [16] which were first operational in 1995, 2001, and 2007, respectively. Currently upgrades are being implemented on both LIGO and VIRGO and future measurements hold the promise to settle the existence of gravitational waves.

Optical cavities are particularly applicable in spectroscopic techniques, in which the prolongation of the interaction length in combination with the narrow transmission modes can provide an exceptional selectivity and sensitivity.

The prolongation of the interaction length stems from the fact that photons of light coupled into a cavity are essentially trapped between the cavity mirrors. This will increase the time every photon spends in the cavity known as the cavity lifetime, $\tau_c$, and thereby the probability that a photon will be absorbed by analyte inside the cavity, e.g. gas. Every round trip a fraction of the trapped photons will be transmitted out through the first and the second cavity mirrors. When the wavelength is equal to an multiple of the cavity length the light reflected from and transmitted through the first cavity mirror will interfere destructively while the light transmitted through the second mirror will interfere constructively. By the conservation of energy, if there is no cavity losses (e.g. absorption), the sum of the photons transmitted through the second mirror will equal the in-coupled light. This result in an output beam equivalent with light passing through a significantly longer sample, one with an effective path length, $L_{\text{eff}}$ given by $c\tau_c$. In Figure 3 an
Figure 3. Illustration of the prolongation of the interaction length associated with light coupled into an optical cavity containing analyte. The sum of the out leakage fields will be equivalent to light passing through a significantly longer sample.

Illustration of the prolongation of interaction length associated with light coupled in to an optical cavity is shown.

By combining an optical cavity with lasers, which also have high selectivity (single wavelength) and sensitivity (stable intensity), highly selective and sensitive spectroscopic measurement system can be constructed. While these techniques, commonly known as cavity enhanced absorption spectroscopy (CEAS), have been applied to, for example, liquid-phase analysis of biomolecules [17], and detection of a single virus [18], the majority of realizations have targeted spectroscopic applications in gas samples, primarily as frequency standards or for trace gas analysis.

The simplest of these is integrated cavity output spectroscopy (ICOS), in which the transmitted power is integrated while the laser is swept across one or several cavity modes, or vice versa. The sensitivity of the technique is limited by the low transmitted power, which is inversely proportional to the cavity finesse, and its fluctuations. As the increase in interaction length is proportional to the finesse ICOS cannot therefore fully take advantage of the highest finesse cavities; the frequency noise of the laser is easily converted into amplitude noise by the sharp cavity resonances resulting in relatively high noise levels. In off-axis ICOS (OA-ICOS) the laser is purposely placed off-axis to the cavity so that also higher order transverse modes are excited. The result is that light can be transmitted also at frequencies between those of longitudinal cavity modes, increasing the amount of transmitted light.

By locking a CW laser to an optical cavity it is possible to measure the properties of a single cavity mode while keeping the stability and optical power of the laser. The two dominating methods of laser locking are the optical feedback (OF) and the Pound-Drever-Hall (PDH) [19] techniques.
Optical feedback locking requires a linear cavity whose input mirror does not reflect the light back to the laser e.g. an V-cavity as is shown in Figure 4. When scanning, the laser frequency is swept over a series of cavity modes. When the power is built up inside the cavity, light leaks out through the first mirror i.e. the input mirror, back into the laser. If the phase of the back reflected light is correct i.e. the distance between the cavity and the laser is an integer number of wavelengths, the frequency of the laser can lock to the frequency of the cavity. The result will be a laser that is jumping between consecutive cavity modes. While relatively simple, optical feedback locking can be applied only to a limited number of lasers e.g. diode and QC-lasers.

The PDH technique utilizes frequency modulation to lock the frequency laser to the cavity. The laser light is modulated at a frequency that is larger than the width of the cavity modes but smaller than half of the FSR of the cavity. By demodulating the back reflected light at the modulation frequency an error signal that is proportional to the phase difference between the electrical field built up inside the cavity and the laser output is obtained. For fluctuations of the laser wavelength that appear at a frequency that is lower than the cavity line width, i.e. at a time scale that is slower than the cavity lifetime, the error signal is proportional to the detuning of the optical frequency. For fluctuations that are faster than the cavity linewidth, the error signal is proportional to the fluctuations in phase. As the PDH method produces an electrical error signal it can be used to lock any laser whose frequency can be controlled by a voltage. Furthermore, it can also be used to control electro optical devices, such as EOMs and AOMs, when they are used to shift the phase or the frequency of the laser light.

To date the two most sensitive CW laser spectroscopic techniques are cavity ring down spectroscopy (CRDS) and noise-immune cavity-enhanced optical heterodyne molecular spectroscopy (NICE-OHMS).

CRDS measures the losses in a cavity mode, which can be related to the absorbance of any sample that is placed in the cavity. The best recorded sensitivity was achieved with heterodyne CRDS spectroscopy, which recently reported a shot noise limited sensitivity down to $6 \times 10^{-14}$ cm$^{-1}$ Hz$^{-1/2}$ for an optical power of 0.9 mW and a cavity finesse of 20 000 [20]. This value was calculated as the ratio of the theoretical peak value of a ring down event and the standard deviation of a zero measurement. A more realistic estimate of the performance of the system can be obtained by using the observed noise level of $4 \times 10^{-10}$ cm$^{-1}$ that was reported for a spectral measurement taken over 5.5 ms. Assuming white-noise limited conditions, this can be re calculated to $2 \times 10^{-12}$ cm$^{-1}$ Hz$^{-1/2}$. This is in parity with the best conventional CRDS demonstrations, which, using a cavity with a finesse of 450 000, has
Figure 4. Illustration of optical feedback locking with a V-cavity. The back reflection from the first cavity mirror (the dashed line) is re-directed away from the laser. The out leaked part of the field buildup in the cavity will be coupled into the laser if the distance between the laser and the cavity is correct i.e. it matches an integer number of wavelengths.

been reported as a noise equivalent absorption per unit length (NEAL) of $3 \times 10^{-12} \text{ cm}^{-1} \text{ Hz}^{1/2}$, or $1.4 \times 10^{-13} \text{ cm}^{-1}$.[21].

NICE-OHMS measures the relative absorbance and dispersion between cavity modes. As the absorption and dispersion of cavity modes can be related to the absorption and dispersion from the analyte inside the cavity, measurements of these measurements can be used to assess the latter. Hence, NICE-OHMS can detect both absorption and dispersion associated with molecular transitions. Furthermore, the technique can detect narrow sub-Doppler (sD) signals that can be used to determine transitions wavelengths or as frequency standards. In the first realization of NICE-OHMS, using a cavity with a finesse of 100 000, these sub-Doppler narrow signals were utilized for frequency metrology purposes resulting in an astonishing NEAL, of $10^{-14} \text{ cm}^{-1}$ over 1 s. As this number referred to the sub-Doppler signal which was assessed to be 13% of the Doppler broadened signal, the NEAL reported corresponds in practice to a noise equivalent absorption coefficient (NEAC) of $8 \times 10^{-14} \text{ cm}^{-1}$.

In addition to sub-Doppler signals NICE-OHMS can also detect Doppler broadened (Db) signals. The most sensitive realization of NICE-OHMS for Doppler broadened signals, utilizing a cavity with a finesse of 50 000, which has been realized as a part of the work presented in this thesis, has shown a NEAC of $2.6 \times 10^{-13} \text{ cm}^{-1} \text{ Hz}^{1/2}$ or $9 \times 10^{-14} \text{ cm}^{-1}$ at 30 s [IX]. If the technique is to be used for trace gas detection Doppler broadened signals have significantly higher potential than sub-Doppler signals. Since the absorption of the most accurate sub-Doppler and Doppler broadened realizations are similar, and Doppler broadened NICE-OHMS signals can be detected at significantly higher pressures than sub-Doppler NICE-OHMS, the former enables detection of much lower relative concentrations of analytes.
Also OFCs can be coupled to optical resonators. Theoretically, an OFC locked to an optical cavity can probe all cavity modes simultaneously enabling broad band detection of multiple species. However, in reality, cavity mirror dispersion will limit the number of modes that simultaneously can be excited. By simultaneously matching both the spacing of the comb teeth, i.e. the repetition rate of the laser, and the absolute frequencies of the comb lines, it is possible to achieve a cavity lock over a reasonably wide spectral range [22] (i.e. with an optical bandwidth that surpasses most CW lasers by orders of magnitude). By this approach, OFCs have been combined with optical cavities and applied to simultaneous spectral measurement over wide spectral ranges. An absorption sensitivity of $2.5 \times 10^{-10}$ cm$^{-1}$ Hz$^{-1/2}$ has been demonstrated for OFC CRDS [23] and of $4.3 \times 10^{-10}$ cm$^{-1}$ Hz$^{-1/2}$ for OFC NICE-OHMS [24].

In this thesis the author presents work primarily dealing with a refinement of NICE-OHMS, mainly focused upon improving the sensitivity and the dynamic range of the technique. In addition, also the realization of an accurate technique for assessment of gas number density by the use of optical cavities is presented.

As was alluded to above, NICE-OHMS and CRDS are two of the most sensitive spectroscopic techniques conceived to date. However, in contrast with CRDS NICE-OHMS has not so far been used in commercial instruments. The reason for this has mainly been that the technique has been considered too complicated for in situ realizations and uncertainties in the signal calibration. Recently, a large number of realizations with a wide variety of lasers has shown the first not to be true e.g. [VI, XII] and [25-31]. By extending the signal theory to higher absorption regimes the technique can now also be calibrated against direct absorption experiments [XIV, XV, XVI-XI]. Furthermore, for the most sensitive applications, e.g. isotopic studies, the sensitivity can still not rival that of mass spectrometers. On the other hand, if the sensitivity of NICE-OHMS could be sufficiently increased the fast signal acquisition time compared with a mass spectrometer and the high selectivity compared with CRDS could presumably make NICE-OHMS a potent technique for a wide range of applications e.g. in situ isotopic studies.

To move towards this, the sensitivity of NICE-OHMS has in this work been systematically improved by optimization of the signal strength, reduction of background signals and noise levels, and elimination of the causes of noise in the system [I-III, V-IX]. The dynamic range was improved by implementation of improved models of line shapes for higher pressure ranges [XVI-XI], and for higher absorbance ranges [XIV, XV]. NICE-OHMS systems for measurements on molecules in the mid infra-red wavelength range i.e. mid-IR NICE-OHMS, are also demonstrated and characterized. As
the mid-IR source (OPO) is tunable over a large wavelength range which includes the fundamental vibrations of a large number of important molecules, this significantly increases the numbers of species that can be detected with NICE-OHMS and the concentration detection limits [XII, XIII].

In many applications, as in the field of measurement standard, it is of importance to know the density of a gas with high accuracy. Conventional methods for the determination of gas density are based on measurement of pressure and temperature, which, by the use of the equation of state of a gas, i.e. the ideal gas law, are used to determine the gas density or changes in density. Hence the accuracy of a density measurement is given by the accuracy of either the pressure gauge or the accuracy of temperature measurement. By instead measuring the refractivity, which is given by $n - 1$ where $n$ is the refractive index, or the change of refractive index, $\Delta n$, it is possible to measure the gas density independent (to first order) of both the pressure and the temperature.

In this thesis, two new setups for accurate assessment of the gas number density by the use of optical cavities have been realized [XVIII, XIX]. While the accuracy of conventional techniques tend to be a fraction of the density, optical method exhibits an absolute error and hence will outperform conventional techniques at higher pressures. The ability to measure the density of gas with this high accuracy at any pressure can find a wide range of application where the most straightforward is leak detection i.e. measuring the change of density originating from a leak.

The intension of the first part of this thesis is to give a summary of the work done by the author to advance cavity enhanced sensing. The focus is not on the conventional theory of the techniques, since this has been scrutinized in earlier work, but rather on the origin of noise and background signals that limit the performance of these types of systems. The last part, which constitutes of the scientific papers produces, provides detailed information of the work done.
The Cavity

General description

An optical cavity or optical resonator is an optical device that circulates light by overlapping beam paths. The simplest form of an optical cavity is in turn the Fabry-Perot cavity, which consists of two highly-reflective mirrors separated by a distance, \( L \). Figure 5 shows a schematic description of a Fabry-Perot cavity.

Figure 5. Schematic illustration of a Fabry-Perot resonator of length \( L \) with an index of refraction between the mirrors of \( n \). The incident, reflected, and transmitted electrical fields are denoted \( E_0 \), \( E_R \), and \( E_T \), respectively. The corresponding powers are denoted \( P_0 \), \( P_R \), and \( P_T \) while the intracavity power is denoted \( P_c \). The mirrors’ intensity reflectivity, transmittance, and losses are in turn denoted \( r_i \), \( t_i \), and \( l_i \), respectively.

If the wavelength of light impinging on the cavity, \( \lambda_0 \), fulfills the condition \( \lambda_0 = 2Ln/q \), where \( n \) is the index of refraction and \( q \) is a positive integer, the latter known as the cavity mode number, the waves of consecutive reflections overlap and result in constructive interference. At these frequencies, here denoted \( v_q \), which are given by

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

and are known as cavity modes, the wave inside the cavity will be amplified up to the point where the losses equal the light input. The separation of two cavity modes, which is given by \( v_q - v_{q-1} \), is known as the free spectral range (FSR) of the cavity, here denoted \( v_{FSR} \), and can be expressed as

\[
v_{FSR} = \frac{c}{2nL}.
\]
The efficiency of the optical resonator depends on the quality of the mirrors used. As is shown in Figure 5, a mirror can be characterized by its (intensity) reflectivity, $r_i$, transmission, $t_i$, and losses, $l_i$. Energy conservation gives us the relation $r_i + t_i + l_i = 1$. It has been shown that for high reflective mirrors the half width half maximum (HWHM) of a cavity mode, $\Gamma_c$, is given by [32]

$$\Gamma_c = \frac{v_{FSR}}{\pi} \frac{1 - \sqrt{r_i r_2}}{2 \sqrt{r_i r_2}}. \quad (3)$$

An illustration the transmission of light through an optical cavity as a function of frequency can be seen in Figure 6.

The finesse of a cavity, $F$, is defined as the ratio of the FSR and the full width half maximum (FWHM) width of its resonance, which corresponds to two HWHM, i.e. $2\Gamma_c$. It can therefore be written as

$$F \equiv \frac{v_{FSR}}{2\Gamma_c} = \frac{\pi \sqrt{r_i r_2}}{1 - \sqrt{r_i r_2}}. \quad (4)$$

The finesse and the FSR are the two most important quantities for characterizing the properties of an optical cavity. Knowing these, it is possible to calculate other cavity properties.

An electrical field stored inside will decay exponentially as a result of the losses it experiences for every round trip. The time constant known as the cavity decay time, $\tau_c$, which is given by

$$\tau_c = \frac{4L}{c(t_1 + t_2 + l_1 + l_2)} = \frac{F}{\pi v_{FSR}}, \quad (5)$$

can be calculated from the mirror properties or the finesse and the FSR of the cavity.

As a result of the decay time an optical cavity will have a low-pass filter response, attenuating high-frequency fluctuations in the incoming electrical field with a 3-dB cutoff frequency that is given by

$$f_{3dB} = \frac{1}{2\pi} \frac{1}{\tau_c} = \frac{v_{FSR}}{2F}. \quad (6)$$

For spectroscopic purposes the effective interaction length of light with a sample inside a cavity, $L_{eff}$, which is given by
Figure 6. Illustration of power transmitted through an optical cavity. At the cavity mode frequencies, $v_q$, light is transmitted while between these light will be reflected. The spacing of the modes is known as the free spectral range, $v_{FSR}$, and the frequency discrimination around these modes is given width (HWHM) of the modes, $\Gamma_c$.

$$L_{eff} = \tau_c \frac{c}{n} = \frac{2F}{\pi} L,$$

(7)

is often the most relevant parameter. Finally, as light is circulated inside a cavity mode, the unidirectional intracavity power, $P_c$, will be significantly higher than the incident power, $P_0$. The unidirectional intracavity power for an impedance matched cavity (which has no reflection on resonance) is given by

$$P_c = \frac{F}{\pi} P_0.$$

(8)

Relations between parameters

All parameters given above can be considered constant as long as the losses, the length, and the index of refraction are constant. However, if any of these parameters change the result will be a change in the cavity properties.

For a small change in length, i.e. a $dL << L$, all parameters, except the cavity mode frequencies, can be considered constant. The change in frequency can be related to a shift in length by differentiating Eq. (1) with respect to $L$, which gives

$$\frac{dv_q}{dL} = -\frac{v_q}{L}.$$

(9)
Hence, a shift of cavity length, $\Delta L$, much smaller than the cavity length, i.e. $\Delta L \ll L$, will result in a shift in the cavity mode frequency by

$$\Delta v_q = -\frac{v_{q,0}}{L_0} \Delta L,$$  \hspace{1cm} (10)

where, $v_{q,0}$, is the frequency of the $q^{th}$ cavity mode for a cavity length of $L_0$.

In a similar manner, for a small change of the index of refraction, i.e. for $dn << n$, the change in the cavity mode frequencies can be obtained by differentiating Eq. (1) with respect to $n$, which gives

$$\frac{dv_q}{dn} = -\frac{v_q}{n}.$$  \hspace{1cm} (11)

For a small change of losses inside a high finesse cavity (for which $r_1 r_2 \approx 1$), i.e. for a small amount of absorption, hence for $\alpha L \ll 1$, the cavity decay time given by Eq.(5) will be given by

$$\tau_c = \frac{4L}{c(t_1 + t_2 + l_1 + l_2 + 2L\alpha)}.$$  \hspace{1cm} (12)

This shows that absorption inside the cavity will shorten the cavity decay time. The HWHM of a cavity mode, can, by the use of the Eqs. (4), (5) and (12), be written as

$$\Gamma_c = \frac{1}{2\pi \tau_c} = \frac{v_{\text{FSR}}(t_1 + t_2 + l_1 + l_2 + 2L\alpha)}{4\pi \tau_c}.$$  \hspace{1cm} (13)

Hence, for a small absorbance (i.e. $\alpha L \ll 1$), the change in cavity mode HWHM can be related to a shift in absorbance by differentiating Eq. (13), which gives

$$\frac{d\Gamma_c}{d(\alpha L)} = \frac{v_{\text{FSR}}}{2\pi}.$$  \hspace{1cm} (14)

A change in the cavity decay time can then be related to a change in absorbance for $\alpha L \ll 1$ by differentiating Eq. (13)

$$\frac{d\tau_c}{d(\alpha L)} = \frac{d\tau_c}{d\Gamma_c} \frac{d\Gamma_c}{d(\alpha L)} = -\frac{\tau_c F}{\pi}.$$  \hspace{1cm} (15)
The electrical field inside a cavity

The interaction of light with an optical cavity can be modeled with the help of the cavity reflection and transmission functions of an electrical field, \( R_c \) and \( T_c \), respectively. For an incident electrical field, \( E_0 \), the electrical field reflected from a cavity is given by [32]

\[
E_R = R_c E_0 ,
\]

while the transmitted electrical field is given by

\[
E_T = T_c E_0 ,
\]

where the reflection function is given by [32]

\[
R_c = \frac{\sqrt{r_1} - \sqrt{r_2} (1 - l_1) e^{-i\phi(v)}}{1 - \sqrt{r_1 r_2} e^{-i\phi(v)}},
\]

while the transmission function is given by

\[
T_c = \frac{\sqrt{t_1 t_2} e^{-i\phi(v)/2}}{1 - \sqrt{r_1 r_2} e^{-i\phi(v)}},
\]

where \( \phi(v) \) is the round trip phase shift of light in the cavity that is given by

\[
\phi(v) = \frac{2\pi v}{\nu_{FSR}}.
\]

The powers reflected from and transmitted through a cavity are given by

\[
P_R = R_c^* R_c P_0,
\]

and

\[
P_T = T_c^* T_c P_0,
\]

where \( R_c^* \) and \( T_c^* \) are the complex conjugates of the cavity reflection and the transmission function respectively, and \( P_0 \), in turn, is the power impinging onto the cavity. Figure 7 illustrates the powers reflected from, and transmitted through, a cavity, together with the phase shifts of the associated electrical fields. The figure shows that not only the transmission but also the phase shifts are concentrated around the cavity resonances.
Figure 7. Top panel: Schematic illustration of the power reflected, $R_c^2 R_c$, (blue) and transmitted through, $T_c^2 T_c$, (black) an optical cavity as a function of round trip phase, $\phi$. Bottom panel: The phase shift of the reflected and transmitted electrical fields, $\phi_{c,R}$ and $\phi_{c,T}$, respectively. The additional $\pi/2$ of the latter is a result of that the reflected and transmitted amplitudes are in quadrature.

The phase shifts of the electrical field associated with the cavity reflection and transmission are given by

$$\phi_{c,R} = \text{Arg}(R_c)$$

(23)

and

$$\phi_{c,T} = \text{Arg}(T_c),$$

(24)

where $\text{Arg}(x)$ denotes the argument of the entity $x$.

**Beams with a Gaussian intensity distribution**

The formalism above is valid assuming highly reflecting flat mirrors. In practice, optical cavities are made with spherical mirrors to produce a stable resonator. If a ray bouncing back and forth between the cavity mirrors stays indefinitely inside the cavity the cavity is considered stable.

This stability condition is usually written as,
where $g_1$ and $g_2$ are the two g-factors for the mirrors, which, in turn, are given by

$$g_i = \sqrt{1 - L/R_i} ,$$

where $R_i$ is the radius of curvature of the mirror. In a stable cavity the light field that excites a longitudinal cavity mode will have the form of a diffraction limited beam and have a Gaussian intensity distribution. In Figure 8 a stable Gaussian beam inside an optical cavity is illustrated.

![Figure 8. Illustration of Gaussian beam inside an optical cavity mode from two concave mirrors. The beam waist is in the center of the cavity. The curvature of the wave fronts matches the curvatures of the mirrors at the mirror surfaces.](image)

Such a beam can be described by a few parameters, e.g. the spot size and the radius of curvature of the wave front [33]. The spot size at a position $z$ along the optical axis is given by

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

where, $w_0$ is the radius of the beam waist and $z_0$ is known as the Rayleigh range, which is given by

$$z_0 = \pi w_0^2 / \lambda ,$$

where, in turn, $\lambda$ is the wavelength of the light. The radius of curvature of the wavefront, $R(z)$, is given by

$$R(z) = z + z_0^2 / z .$$

To couple light into such a cavity the radius of the wavefront of the beam must match the curvature of the mirrors at the mirror surfaces. To achieve this spatial mode matching one needs to design the in-coupling optics so that the beam waist matches that of the cavity. This is achieved by first measuring the propagation of the laser beam and then designing appropriate optics to be placed in front of the cavity with the help of expressions for Gaussian beam optics [34].
Transverse modes
In addition to the longitudinal modes, as a consequence of the curvature of the mirrors, also higher order transverse modes, can exist in the cavity. The electrical field of an excited transverse mode, $mn$, of a cavity can be written as [33]

$$E_{mn}(x, y, z) = E_0 \frac{w_0}{w(z)} H_m \left(\sqrt{2}x/w(z)\right) H_n \left(\sqrt{2}y/w(z)\right)$$

$$\times \exp \left[-(x^2 + y^2) \left(1/w^2(z) - ik/2R(z)\right) + ik - i(m + n + 1) \tan^{-1} (z / z_0)\right] \tag{30},$$

where $H_n$ represents the $n$:th Hermite polynomial, $k$ is the wave vector, and $m$ and $n$ are positive integers, the latter known as the transverse mode numbers.

The frequency of a transverse mode is given by

$$v_{qmn} = \frac{c}{2L} \left[ q + \frac{1}{\pi} (m + n + 1) \cos^{-1} \sqrt{g_1 g_2} \right]. \tag{31}$$

The laser is normally locked to a fundamental transverse mode (TEM$_{00}$), i.e. one with $m = n = 0$, also referred to as longitudinal mode, since such can support a laser beam with a Gaussian beam profile. The intensity distribution of an excited TEM$_{00}$ mode is given by

$$I_{00}(x, y, z) \propto E_{00}(x, y, z) E^*_{00}(x, y, z)$$

$$= I_0 \left(\frac{w_0}{w(z)}\right)^2 \exp \left[-2(x^2 + y^2)/w^2(z)\right], \tag{32}$$

where $E^*_{00}$ represents the complex conjugate and $I_0$ is the peak irradiance at the beam waist which is related to the total power, $P_{tot}$, by $I_0 = 2P_{tot} / \pi w_0^2$.

The intensity distribution of an excited TEM$_{nm}$ mode is, in turn, given by

$$I_{mn}(x, y, z) \propto E_{mn}(x, y, z) E^*_{mn}(x, y, z)$$

$$= I_0 \left(\frac{w_0}{w(z)}\right)^2 \left(H_m \left(\sqrt{2}x/w(z)\right) H_n \left(\sqrt{2}y/w(z)\right)\right)^2$$

$$\times \exp \left[-2(x^2 + y^2)/w^2(z)\right], \tag{33}$$

The intensity normalized mode pattern of a number of cavity modes, calculated from Eq. (33), which illustrates the extent of various TM modes, is schematically illustrated in Figure 9.
Higher order transverse modes can be excited if the light of the incident laser spatially overlaps with a transverse mode. This is the case if the laser is not aligned properly with respect to the TEM$_{00}$ mode or if the laser beam spatially overlaps several transverse modes. To avoid the latter the optics in front of the cavity should be made so that the physical extent of the laser light (the size and the position of the beam waist) matches the TEM$_{00}$ mode of the cavity, i.e. as was shown in Figure 8.

In general, when the laser is locked in frequency to one of the TEM$_{00}$ cavity modes, all light that is not spatially mode matched with the mode will be rejected. But if the frequency of a higher order transverse mode overlaps with the TEM$_{00}$ mode to which the laser is locked the higher order mode can also be exited. When designing the cavity, it is therefore of importance that the transverse mode frequencies do not overlap with the longitudinal transverse modes.

As is discussed further below, despite such precautions, it is possible through scattering, predominantly in high finesse cavities, that light can inadvertently simultaneously excite both a longitudinal and higher order transverse modes. Since the physical extent of higher order transverse modes is larger than that of a longitudinal mode, the number of transverse modes that can be excited in a cavity can be limited by inserting a pinhole into the cavity. The radius of a Hermite-Gaussian mode at a position $z$ in the cavity, $w_{mn}(z)$, can be approximated as [35]

\[
    w_{mn}(z) \approx w(z)\sqrt{m+n}.
\]  

(34)
The number of transverse modes (i.e. \( N_{\text{max}} = m + n \) ) that can fit within the pinhole with a radius of \( r \) is therefore simply given by the ratio between the area of the pinhole and that of the fundamental transverse mode,

\[
N_{\text{max}} = \frac{r^2}{w^2(z)}.
\]

In reality, however, alignment issues will further limit the number of excitable transverse modes. The pinhole is therefore generally chosen to be significantly larger than the fundamental mode, but smaller than any transverse mode that inadvertently might be excited by the light.

**The cavity mode frequency – a key to the assessment of gas density**

In the first application 1897, the Fabry-Perot etalon was used as an interferometer to obtain high resolution measurements of small distances between parallel surfaces [3]. As the experiment utilized flat mirrors the resulting output interference rings resembled those of a Michelson interferometer but with significantly higher contrast due to the phase shift associated with cavity transmission (illustrated in Figure 7). Hence the separation of the two surfaces could be measured with a precision of a fraction of a wavelength.

As was mentioned above, the most stable laser that has been locked to an extremely stable external cavity exhibited a relative frequency variation lower than \( 1 \times 10^{-16} \) at 1.5 \( \mu \)m [10]. If one such laser was to be locked to a measurement cavity, and another was to be used as a reference, it is theoretically possible to measure a fractional change of the length of the cavity, \( \sigma_L \), or the index of refraction, \( \sigma_n \), down to \( (\sigma_1^2 + \sigma_2^2)^{1/2} \approx 2 \times 10^{-16} \), where \( \sigma_1 \) and \( \sigma_2 \) denote the frequency variations of the two lasers. For a cavity with a length of 40 cm this corresponds to an change of 1 fm (10^{-15} m). As the size of a helium atom is in the order of 1 Å = 10^{-5} fm this implies that it is theoretically possible to assess the length of an optical cavity down to parts-per-million (ppm) of the length of an atom. Since the frequency of a cavity mode also depends on the index of refraction of gas in a cavity, it is also possible to assess gas density, \( \rho \), by measuring the frequency of a cavity mode. It can be shown [XVIII] that the uncertainty in the assessment in gas density, \( \sigma_\rho \), can be related to that of the index of refraction, \( \sigma_n \), by

\[
\sigma_\rho = \frac{d\rho}{dn} \sigma_n.
\]
Since the index of refraction for air at atmospheric pressure (for which the density is \(1.3 \text{ kgm}^{-3}\)) is \(~1.0003\), while it is \(1.0000\) in vacuum, the smallest measurable change in gas density is \(~1 \times 10^{-12} \text{ kgm}^{-3}\), which corresponds to a ng per cubic meter. The ability to measure the density of gas with this high accuracy at any pressure can find a wide range of application where the most straightforward is leak detection i.e. measuring the change of density originating from a leak.

The formulas for some of the fundamental properties of Fabry-Perot cavities presented above are compiled in Table 1.

\[
\begin{align*}
v_q &= \frac{q c}{2nL} \quad \text{Frequency of a cavity mode} \\
v_{\text{FSR}} &= \frac{c}{2nL} \quad \text{Free spectral range} \\
F &= \frac{v_{\text{FSR}}}{2\Gamma_c} \quad \text{Cavity finesse} \\
\Gamma_c &= \frac{v_{\text{FSR}}}{2F} \quad \text{Cavity mode width (HWHM)} \\
L_{\text{eff}} &= \frac{2F}{\pi} L \quad \text{Effective path length} \\
P_c &= \frac{F}{\pi} P_0 \quad \text{Unidirectional intracavity power} \\
\Delta v_q &= -\frac{v_{q,0}}{L_0} \Delta L \quad \text{The frequency shift of a cavity mode for a small length change (}\Delta L \ll L_0\text{)} \\
\Delta v_q &= -\frac{v_{q,0}}{n_0} \Delta n \quad \text{The frequency shift of a cavity mode for an index of refraction change (}\Delta n \ll n_0\text{)} \\
\Delta \Gamma_c &= \frac{v_{\text{FSR}}}{2\pi} \Delta(\alpha L) \quad \text{Change in the width of a cavity mode due to absorption (}\alpha L \ll 1\text{)} \\
\Delta \tau_c &= -\frac{F \tau_c}{\pi} \Delta(\alpha L) \quad \text{Change in the decay time of a cavity mode due to absorption (}\alpha L \ll 1\text{)} \\
w(z) &= w_0 \sqrt{1 + z/z_0} \quad \text{Spot size Gaussian beam (radius)} \\
z_0 &= \frac{\pi w_0^2}{\lambda} \quad \text{Rayleigh range} \\
R(z) &= z + z_0^2/z \quad \text{Radius of curvature of Gaussian beam}
\end{align*}
\]

Table 1. Compilation of properties of the Fabry-Perot cavity.
Interaction between light and matter – Absorption and dispersion

The Beer-Lambert law

The Beer-Lambert’s law relates the attenuation of narrow line width light to the properties of the material through which it is traveling. It states that there is a logarithmic dependence between the transmittance and the product of the absorption coefficient of the substance and the distance light travels through the material.

For a simple direct laser absorbance experiment, which is illustrated in Figure 10, light is passed through a volume of length \( L \), containing a molecular absorber. Whenever the frequency of the light is resonant with a molecular transition, the intensity will be attenuated.

\[
I(v) = I_0 e^{-\alpha(v)L},
\]

(37)

where \( I_0 \) is the intensity before the sample \([W/m^2] \) and where \( \alpha(v) \) is the absorption coefficient, given in units of \( 1/cm \). The absorption coefficient can, in turn, be written as [32]

\[
\alpha(v) = \hat{S} n_A \chi_{abs}^{abs}(v),
\]

(38)

where \( \hat{S} \) is the integrated molecular line strength for the transition addressed \([cm^{-1}/(molecule \cdot cm^{-2})] \), \( n_A \) is the number of (analyte) molecules per volume \([1/cm^3] \), and \( \chi_{abs}^{abs}(v) \) is the area normalized absorption line shape function likewise for the transition addressed. The relative absorption, or the relative change of intensity, which commonly is denoted \( \Delta I / I_0 \), can be written as

\[
\Delta I / I_0 = 1 - e^{-\alpha(v)L} \approx \alpha(v)L,
\]

(39)
where the approximation is valid for weak absorption, i.e. \( \alpha L \ll 1 \), which is the prevailing condition for ultrasensitive measurements.

**Attenuations and phase shifts of an electrical field due to the presence of an absorber**

Considering that light is an electromagnetic wave that gets attenuated when it passes through a medium, by symmetry, there will also be a phase shift associated with the absorption. The complex electrical field passing through an absorber of length \( L \) can be expressed as [36]

\[
E_A = T_A E_0 ,
\]

where \( E_0 \) is the undisturbed electrical field and \( T_A \) the complex transmission function of the absorber, which, in turn, can be written as

\[
T_A(v) = e^{-\delta(v)-i\phi(v)} , \tag{41}
\]

where \( \delta(v) \) represents the attenuation and \( \phi(v) \) is the phase shift of the electrical field. Since \( I \propto |E_A|^2 = E_A E_A^\ast \), which, in turn, can be written as \( T_A T_A^\ast |E_0|^2 \), and as \( \alpha = 2\delta \), it is possible to conclude that \( \delta(v) \) for a single transition can be related to the area normalized absorption line shape function by

\[
\delta(v) = \frac{\hat{S}_n L}{2} \chi^{abs}(v) . \tag{42}
\]

It is also possible to show that the corresponding phase shift can be written as

\[
\phi(v) = \frac{\hat{S}_n L}{2} \chi^{disp}(v) , \tag{43}
\]

where \( \chi^{disp}(v) \) is the dispersive counterpart to \( \chi^{abs}(v) \).

**Line shapes**

*Homogenous broadening; Natural, Collision, and Transit time broadening; The Lorentzian line shape function*

In a similar manner as the lifetime of a photon inside a cavity will determine the width of the cavity mode, the width of a molecular transition between two energy-levels will be given by the lifetimes of the states between which
the transition takes place. This can be related to the uncertainty principle, which states that \( \Delta E \Delta t \geq \hbar \). The uncertainty in the energy difference between the upper and lower state, \( \Delta E \), is therefore directly related to the lifetime of the states involved, \( \Delta t \), most often limited by that of the upper state. The finite lifetime will give rise to an uncertainty in the energy (i.e. frequency) resulting in a Lorentzian frequency distribution of the transition with a certain width. This effect is called natural broadening and it is the fundamental limit of line broadening.

In classical terms this can be exemplified by considering a damped oscillator for \( t > 0 \), with frequency \( v_0 \) and decay time \( \tau \), expressed as

\[
z(t) = e^{-i2\pi v_0 t} e^{-\pi t/\tau}.
\]

(44)

The Fourier cosine transform of an exponential decay function \( e^{-at} \) (if \( a > 0 \)) is \( a/(a^2 + \omega^2) \) (i.e. the real part of a Lorentzian function) and the Fourier sine transform is \( \omega/(a^2 + \omega^2) \) (i.e. the imaginary part of a Lorentzian function). As the Fourier transform of \( e^{iat} f(t) \) is \( F(\omega - a) \), the transform of (44) can be written as,

\[
Z_{\text{real}}(v) = \frac{1}{2\pi} \frac{\Gamma}{(v-v_0)^2 + \Gamma^2},
\]

(45)

and

\[
Z_{\text{img}}(v) = \frac{1}{2\pi} \frac{(v-v_0)}{(v-v_0)^2 + \Gamma^2},
\]

(46)

where \( \Gamma \) is the HWHM of the Lorentzian function, which is equal to \( 1/2\tau \).

Figure 11 illustrates the time response of a damped oscillator (seen in blue) and the corresponding real Fourier transform (seen in red), given by Equations (44) and (45), respectively. As the energy levels of a molecule can be related to oscillations (i.e. electronic, vibrational and rotational) the duration of these will hence determine the width of the energy band associated with a given energy level. Since the lifetimes of molecular states typically range from ms and upwards, a natural width is often in the kHz range or below. It is therefore seldom reached under normal experimental conditions. Instead, under most common conditions, other broadening mechanisms will dominate over the natural broadening. In the presence of collisions between molecules the lifetime of the states will be reduced, giving rise to what is called collision broadening. Since both the natural and the collision broadening appear as a consequence of a finite lifetime of the states involved, they can both be modeled by a
Figure 11. The time response of a damped oscillator seen in blue and the resulting spectrum seen in red. The spectrum has a Lorentzian lineshape with a linewidth inversely proportional of the decay time of the oscillator.

Lorentzian lineshape function. The area normalized Lorentzian absorption lineshape function and the corresponding dispersion lineshape function can be written as

\[ \chi^\text{abs}_L (\delta \nu) = \frac{c}{\pi} \frac{\Gamma_L}{\delta \nu^2 + \Gamma_L^2} \]  

and

\[ \chi^\text{disp}_L (\delta \nu) = \frac{c}{\pi} \frac{\delta \nu}{\delta \nu^2 + \Gamma_L^2} , \]  

where \( \delta \nu = \nu - \nu_0 \) represents the detuning from the transitions center frequency and \( \Gamma_L \) is the linewidth for the combined effect of natural and collision broadening, where, in turn, the latter is given as a product of the pressure and a pressure broadening coefficient, \( B_p \), i.e. as \[ \Gamma_p = B_p P . \] (49)

Since a typical broadening coefficient is \( \sim 2 \) GHz/atm, as is the case for the \( \text{P}_e(11) \) transition of \( \text{C}_2\text{H}_2 \) [37], this shows that collision broadening often supersedes natural broadening by orders of magnitude.
In laser spectroscopy, utilizing laser beams with finite widths, there is also a phenomenon termed transit time broadening. It originates from the fact that a molecule crossing the laser beam will experience laser irradiation only for a limited amount of time. Molecules passing a laser beam will experience a pulse of radiation with duration of $\tau = d / v$ where $d$ is the beam diameter and $v$ is the velocity component of the molecule that is perpendicular to the laser beam. At thermal equilibrium, the root mean square velocity can be estimated by

\[ v_{\text{rms}} = \sqrt{\frac{2 k_B T}{m}} , \]  

(50)

where $k_B$ is the Boltzmann constant (in J/K), $T$ is the temperature of the sample (in K), and $m$ is the molecular mass (in kg). For example, the rms velocity of C$_2$H$_2$ (with a molecular mass of 26) in a room temperature surrounding (i.e. at 293 K°) is 430 m/s. This implies that a molecule passing a 1 mm wide laser beam perpendicularly will experience a pulse of light with a duration of 2 µs.

It can be shown that also this type of broadening can be described by a Lorentzian lineshape function. It can be argued by the uncertainty principle that the transit broadening (FWHM) is given by

\[ \Gamma_r \approx \frac{1}{2 \tau}. \]  

(51)

Hence for 1 mm wide laser beam a typical transit time broadening is ~250 kHz. As typical pressure broadening coefficients are in the 2 GHz/atm range, transit time broadening will only affect measurements in the mTorr range.

**Inhomogeneous broadening; Doppler broadening: The Gaussian line shape function**

Doppler broadening is a result of the spread in velocity of a thermal ensemble of molecules. As molecules with different velocities will experience different Doppler shifts of light the absorption profile will be broadened.

Since the velocity distribution of an ensemble of molecules depends on temperature and molecular mass, also the Doppler shift will depend on the same parameters. Moreover, since the projection of the velocity-vectors of molecules in an ideal gas along the laser beam have a Gaussian distribution also the Doppler broadening will have a Gaussian distribution. For a transition with a center frequency of $v_0$ [Hz], the area-normalized Gaussian lineshape function and its dispersion counterpart are given by
\[ \chi^\text{abs}_G(x) = \frac{c}{\Gamma_D} \sqrt{\ln 2} e^{-x^2} \]  
\hfill (52)

and

\[ \chi^\text{disp}_G(\delta v) = \frac{2c\sqrt{\ln 2}}{\Gamma_D\pi} e^{-x^2} \int_0^x e^s ds, \]  
\hfill (53)

respectively, where \( \Gamma_D \) is the half width half maximum (HWHM) Doppler width, which, in turn, is given by

\[ \Gamma_D = \frac{v_0}{c} \sqrt{\frac{2\ln(2)k_bT}{m}}, \]  
\hfill (54)

and, \( x \), is the Doppler width normalized detuning, which is given by

\[ x = \frac{\sqrt{\ln 2}}{\Gamma_D} \delta v, \]  
\hfill (55)

where \( \delta v \) represents the detuning from the transitions center frequency.

**The intermediate case; The Voigt line shape function**

At low pressures, for which the collision broadening is small, the absorption profile will be Doppler broadened, whereby the lineshape function will have a Gaussian form. As the pressure is increased collisions between molecules will increase. At high pressures, typically at atmospheric pressures and above, the profile will be given by a Lorentzian lineshape. In the transition between these two regimes both processes will be contributing to the broadening, resulting in another type of profile. Under the conditions that collisional broadening and Doppler broadening are uncorrelated, it is represented by a Voigt lineshape function, which is a convolution of a Lorentzian and a Doppler line shape function. A comparison of the Doppler, Lorentzian and Voigt absorption lineshapes can be seen in Figure 12. The absorption and dispersion Voigt lineshape functions can be expressed as the real and imaginary part of common complex error function, \( W(x, y) \), respectively, viz. as

\[ \chi^\text{abs}_V(x) = \frac{c}{\Gamma_D} \sqrt{\ln 2} \Re\{W(x, y)\} \]  
\hfill (56)

and
Figure 12. Comparison of three area normalized absorption line shapes; the uppermost red curve represents a fully Doppler broadened lineshape with a $\Gamma_D$ of 250 MHz, the lowermost blue curve illustrates a Lorentzian lineshape with a $\Gamma_L$ of 250 MHz, while the intermediate black curve models a Voigt lineshape with both $\Gamma_D$ and $\Gamma_L$ being 250 MHz.

\[ X_{\text{disp}}^D(x) = \frac{c}{\Gamma_D} \sqrt{\frac{\ln 2}{\pi}} \text{Im}[W(x, y)], \]  

(57)  

respectively, where $y$ represents the Doppler width normalized collision broadening, given by

\[ y = \sqrt{\ln 2} \frac{\Gamma_L}{\Gamma_D} . \]  

(58)

This figure shows that the absorption from a Doppler broadened lineshape will be more concentrated around the transition than the Lorentzian counterpart. Hence, as the pressure is increased, the absorption from a given transition will be spread over a larger range of frequencies. This implies that for a given integrated molecular line strength $\hat{S}$ and a given number of molecules per volume $n_x$ the largest peak absorption is found on resonance in the Doppler limit. A comparison of the Doppler, Lorentzian, and Voigt dispersion lineshapes can be seen in Figure 13. This figure shows that the dispersion as absorption from a Doppler broadened lineshape will be more concentrated around the transition than the Lorentzian counterpart.
Figure 13. Comparison of the dispersion line shape functions that correspond to area-normalized Doppler, Lorentzian, and Voigt absorption lineshape functions. The notations of the curves are the same as in Figure 12.

Hence, as the pressure is increased, the change in dispersion from a given transition will be lower. This implies that for a given integrated molecular line strength \( \hat{S} \) and a given number of molecules per volume \( n \), the largest change of dispersion is found around resonance in the Doppler limit.

**Dicke narrowing**

The mean free path for a gas is given by the average distance a molecule can travel before it collides with another molecule. It can be written as

\[
\ell = \frac{k_B T}{\sqrt{2\pi d^2 P}},
\]

where \( d \) is the diameter of the particle. After a collision both molecules will change their velocity. As the average speed of the molecules is lower than the thermal speed (a straight line is shorter than the route molecules take) such collisions can lead to a narrowing of the Doppler profile [XIV]. This phenomenon can be understood as follows. The length over which the speed of the molecule is measured can be calculated with the help of the uncertainty principle,

\[
\Delta x \Delta p \geq \hbar,
\]
where $h$ is the Planck constant. This principle states that the position $x$ and the momentum $p$ cannot be measured simultaneously with infinite accuracy. As a result of this, a photon that carries a momentum of $2\pi h/\lambda$, can only assess a displacement of a molecule if it is larger than $\Delta x \geq \lambda/2\pi$. Hence the smallest spatial element the photon can resolve and the distance over which the speed of the molecule is measured, is $\lambda/2\pi$. If the mean free path is much larger than this i.e. $\ell \gg \lambda/2\pi$, the molecules can be seen as undisturbed but if the mean free path is in the order of or smaller than this, i.e. $\ell \leq \lambda/2\pi$, the measured velocity of the molecules will be reduced, which yields a narrowed Doppler profile. This effect, known as Dicke narrowing [38], leads to a simultaneous broadening of the Lorentzian components and narrowing of the Doppler profile in the Voigt line shape due to collisions [XIV].

The type of collision, which is determined by the collision partner, will also affect the lineshape. The two dominating collision models are the Galatry [39] and Rautian [40] models. The Galatry model assumes soft collisions, for which there is a strong correlation between the velocity before and after the collision, which is the case for collisions between heavy absorbers and light perturbers. The Rautian model assumes hard collisions, i.e. no correlation between the velocity before and after the collision, which is the case for collisions between light absorbers and heavy perturbers.

**Speed-dependent effects**

As was alluded to above, the Voigt profile is based on the assumption that the collisional broadening and Doppler broadening are uncorrelated and it is therefore represented by a convolution of a Lorentzian and a Doppler line shape function. However, in reality, the probability of a collision, and thereby the collision broadening, is higher for molecules with a higher velocity than for those with a lower. As a result, different velocity groups do not have the same Lorentzian width. The velocity is given by a Maxwell-Boltzmann distribution that is asymmetric with the most probable velocity being lower than the mean velocity. This gives rise to a narrowing of the Lorentzian profile and is referred to as speed dependent effects (SDEs) [XVI, XV].

**The peak lineshape function as a function of pressure**

For trace gas analysis the relative concentration, $c_{rel}$, is often the parameter of interest. As the integrated absorption, i.e. the amount of absorption obtained when scanning over the transition, depends the number of molecules per volume, $n_A$, which, in turn, increases with pressure as $pc_{rel}$,
the integrated absorption for a given concentration will increase with pressure.

The peak absorption, $\alpha_0$, on the other hand, will initially, in the Doppler limit, increase with increasing pressure according to

$$\alpha_0^D = \hat{\Delta}n \chi_G^{\text{abs}}(0) = c \sqrt{\frac{\ln 2}{\pi}} \frac{\hat{S}}{\Gamma_D} c_{\text{rel}} P.$$  \hspace{1cm} (61)

As the pressure is increased collisions between molecules will increase until the profile will be significantly affected by collision broadening. Eq. (61) will thereby no longer hold. Under fully pressure broadened conditions, for which the lineshape has a Lorentzian form, the peak absorption will, because of pressure broadening, no longer depend on the pressure, but only be proportional to the relative concentration through

$$\alpha_0^{\text{press}} = \hat{\Delta}n \chi_L^{\text{abs}}(0) = \frac{c}{\pi B_p} \frac{\hat{S}}{c_{\text{rel}}}.$$ \hspace{1cm} (62)

This implies that the peak absorption of a given transition will roll off with increasing pressure. As laser absorption experiments more often than not hinge on measuring a scan over a transition i.e. the difference between the peak and zero absorption, the optimum pressure is usually found in the Voigt regime.

In a similar manner as for absorption, in the Doppler limit, the peak dispersion will also increase with increasing pressure. In the pressure broadened regime one can find the peak dispersion by differentiating Eq. (48) with respect to frequency and equalize this with zero. The peak values are found at one Lorentzian width from the center of the transition i.e. for $\Delta \nu$ equals to $\Gamma_L$. Hence the maximum dispersion (per length units) will in this case be given by

$$\phi_{\text{max}}^{\text{press}} / L = \frac{\hat{\Delta}n}{2} \chi_{\text{disp}}(\Gamma_L) = \frac{c}{4\pi B_p} \frac{\hat{S}}{c_{\text{rel}}}.$$ \hspace{1cm} (63)

This implies that the peak dispersion, as the peak absorption, will roll off with increasing pressure and, for higher pressures, reach a value that is independent of pressure.

**The index of refraction of a gas**

In addition to the narrow features associated with molecular transitions discussed above there is a broad phase shift associated with light
propagation through a material lacking narrow absorption features. The electromagnetic wave will induce a disturbance in the charge distribution of the molecules, primarily affecting the electrons. This oscillation will, in turn, induce a new electromagnetic wave with the same frequency but with a slight phase delay. The transmitted electrical field will be a superposition of the remaining original electrical wave and all the induced electrical waves. The result will appear as a prolongation of the optical path length and is traditionally described in terms of an index of refraction of the material, \( n \). The susceptibility of a given type of molecule to have its charge distribution affected by light is wavelength dependent and can be expressed in terms of the molecular polarizability, \( \alpha \), which in turn can be related to the wavelength dependent molar refractivity, \( R_\lambda \), and to the wavelength dependent index of refraction, \( n_\lambda \), by the Lorentz and Lorentz relation as [41]

\[
R_\lambda = \frac{1}{\rho} \frac{n_\lambda^2 - 1}{n_\lambda^2 + 2} = A_R(\lambda) + B_R(\lambda)\rho + C_R(\lambda)\rho^2 + \cdots \approx \frac{4\pi N_A}{3} \alpha_\lambda. \tag{64}
\]

where \( \rho \) is the molar density and \( N_A \) is Avogadro’s number. \( A_R(\lambda) \) is the linear term given by \( 4\pi N_A \alpha_\lambda / 3 \), that is when the molecular polarizability is unaffected by collisions. The deviation from collisions affecting the polarizability is given by the terms containing the \( B_R(\lambda), C_R(\lambda) \), etc., which are known as the second, third, etc., refractivity virial coefficients [42]. The contributions from the viral terms are, in general, small compared with that of the leading term.

For a gas where the index of refraction \( n \approx 1 \), the density of the gas can be related to the measured index of refraction \( n \) by

\[
\rho = \frac{2}{3R_\lambda}(n-1). \tag{65}
\]

While measurement data for molar refractivity is not available for all gases the refractive index has been measured for a number of gases and gas mixtures. For example, the wavelength dependence of standard air, known as International Standard Atmosphere (ISA), characterized by 15 °C, 101.325 kPa, and 0% humidity, for which the density is 1.225 kg/m³, is given by [43]

\[
(n_{\text{air}} - 1) \cdot 10^8 = \frac{k_1}{k_0 - \lambda^{-2}} + \frac{k_1}{k_2 - \lambda^{-2}}, \tag{66}
\]

where \( k_0 = 238.0185 \, \mu m^{-2}, k_1 = 5792105 \, \mu m^{-2}, k_2 = 57.362 \, \mu m^{-2}, \) and \( k_3 = 67917 \, \mu m^{-2} \). The gas number density at a given pressure and temperature can be related to the Loschmidt constant, \( n_0 \), which states that the number of
ideal gas molecules per unit volume at a pressure of 101.325 kPa and a temperature of 273.15 °K (0°C) is 44.615036 mol/m³, by

\[ \rho = \left( \frac{pT_o}{p_oT} \right) n_o, \]  \hspace{2cm} (67)

where \( p_o = 101.325 \) kPa and \( T_o = 273.15 \) °K (0°C). Hence, one can calculate, by Eq. (65), the molar refractivity for any wavelength, which then can be used to relate the measured index of refraction to a number density.
Frequency Modulation Spectroscopy

As is further described below, the detection sensitivity of laser based spectroscopic absorption techniques is often limited by flicker noise originating from the laser intensity. This noise can be significantly reduced by moving the detection frequency into a frequency window less affected by such noise. In wavelength modulation spectrometry (WMS) the wavelength of the light is typically modulated by applying a modulation, often in the kHz range, to the laser frequency. When this is applied to semiconductor lasers, the modulation can be achieved by directly modulating the injection current of the laser. In frequency modulation spectroscopy (FMS), which uses a modulation frequency in the hundreds of MHz or low GHz [44-46] range, electro optical modulators (EOMs) are commonly used to achieve the modulation.

As frequency (or wavelength) can be seen as a continuous shift of phase, i.e. $\omega = \phi$, the derivative of the phase shift represents a frequency shift. A phase modulated electrical field can therefore be used to model both WMS and FMS. An optical field, e.g. that of a laser beam, with a sinusoidally modulated phase, $\phi(t) = \beta \sin \omega_m t$, can be expressed as

$$E(t) = E_0 \exp\left[i(\omega_0 t + \beta \sin \omega_m t)\right], \quad (68)$$

where $\omega_0$ and $\omega_m$ are the carrier and modulation angular frequencies and $\beta$ is the modulation index. In FMS it is common practice to rewrite Eq. (68) with the help of Bessel functions (using the Jacobi–Anger identity) as a series, viz. as

$$E(\omega_0, t) = E_0 \exp(i\omega_0 t) \sum_{k=-\infty}^{\infty} J_k(\beta) \exp(ik\omega_m t). \quad (69)$$

Bomse et al. stated in 1992 that “The difference between WMS and FMS is purely semantic; they are just limiting cases of the same method” [47]. Therefore, following the practice of WMS, the frequency shift that is associated with a modulation, $\Delta \omega(t)$, can, according to Eq. (68), be calculated as

$$\Delta \omega(t) = \dot{\phi} = \beta \omega_m \cos \omega_m t. \quad (70)$$

As was stated by Supplee et al. [48], in WMS the modulation frequency is smaller than the width of the spectral feature probed, i.e. $\omega_m << \Gamma$, while the modulation index is large, i.e. $\beta >> 1$, whereas for FMS the modulation frequency is larger than the width of the spectral feature probed, i.e. $\omega_m > \Gamma$, while the modulation index often is kept small, i.e. $\beta \leq 1$. Therefore one can
more generally state that WMS can be seen as FMS with a large number of sidebands and that FMS can be seen as WMS with a high modulation frequency. Figure 14 shows a simulated spectrum from a modulated laser for three different modulation indices, \( \beta \) equal to 1, 10, and 100, for a constant modulation amplitude, \( \beta \nu_m \) (of 400 MHz). The spectra are time averages illustrating the power distribution of the laser as seen by a spectrometer (averaged on a time scale larger than the inverse of the modulation frequency). The black curve illustrates typical FMS modulation conditions i.e. a modulation index of unity and a modulation frequency larger than the laser linewidth (400 and 10 MHz respectively). The red curve, in turn, represents the transition between the two regimes FMS and WMS i.e. \( \beta > 1 \) and a modulation frequency which is larger than the laser linewidth (40 and 10 MHz respectively). The blue curve, finally, represents WMS conditions, i.e. \( \beta >> 1 \) and a modulation frequency that is smaller than the laser linewidth (4 and 10 MHz respectively).

Thus, FMS conditions can be seen as a situation when the light simultaneously is composed of a number of modes (a carrier and a number of sidebands). As the modulation index is increased and the modulation frequency is decreased more sidebands are produced and the system approaches wavelength modulation condition. In this range the power of the laser will consist of two distinct peaks at the modulation amplitude \( \beta \nu_m \) corresponding to the turning points of the sinusoidal modulation.

As the resulting spectrum in frequency space, under WMS conditions, will contain a large number sidebands, it becomes complicated to describe the modulation with FMS formalism. Hence, while it is possible to express wavelength modulation signals with the same formalism as FMS, it is not an efficient way of describing the modulation. Since the modulation frequency in WMS is low, an alternative view of WMS is to interpret it as spectroscopy formed by a monochromatic wave that is repeatedly scanned across the transition. The conventional description of WMS is therefore that it is the frequency and not the phase of the light that is modulated [49].

In this work modulation is mainly done in the FM regime. Hence, the modulation frequency is much larger than the linewidth of the laser (the sidebands can be considered consisting of a single frequency). In these cases, the electrical field transmitted through an analyte can be expressed as a combination of Eq. (69) and a function of the absorbers’ transmission function at the frequency \( \omega_c = \omega_c + k \omega_m \), i.e. as

\[
E(\omega_c, t) = E_0 \exp\left(i \omega_c t \right) \sum_{k=-\infty}^{+\infty} T_k(\omega_k) J_k(\beta) \exp[ik \omega_m t], \tag{71}
\]
Figure 14. Simulation of the intensity spectrum from a modulated laser as a function of the detuning from laser center frequency (in MHz) for a laser with a linewidth $\Gamma_l$ of 10 MHz, for a constant modulation amplitude $\beta v_m$ of 400 MHz, for three different modulation indices $\beta = 1, 10, 100$, given by the black, red, and blue curves, respectively.

where, according to, Eq. (41), the absorbers’ transmission function, is given by

$$ T_k(\omega_k) = \exp[-\delta(\omega_k) - i\phi(\omega_k)], $$(72)

where $\delta(\omega_k)$ denotes the attenuation and $\phi(\omega_k)$ the phase shift of the electrical field at the frequency $\omega_k$. By the use of a photodetector, one can monitor the intensity of this electrical field, which is given by the electric field times its complex conjugate, as

$$ I(\omega_k, t) \propto E(\omega_k, t)E^*(\omega_k, t) $$

$$ = I_0 \left[ \sum_{k=-\infty}^{+\infty} J_k T_k \exp[i k \omega_m t] \right] \left[ \sum_{k=-\infty}^{+\infty} J_k T_k^* \exp[-i k \omega_m t] \right], $$

where, for simplicity, we have used the compressed notation $J_k \equiv J_k(\beta)$ and $T_k \equiv T_k(\omega_k)$.

In FMS, the signal is demodulated at the modulation frequency. By only considering these frequency components, Eq. (73) can be rewritten as
\[ S_{\text{FMS}}(\omega_c, t) = \eta I_0 \sum_{k=-\infty}^{+\infty} J_k J_{(k+1)} \left[ T_k T_{k+1}^* \exp\left(-i\omega_m t\right) + T_k^* T_{k+1} \exp\left(i\omega_m t\right) \right], \]  

(74)

where \( \eta \) is an instrumental factor. The products of the transmission functions can be expressed in terms of attenuation and phase shifts as

\[
T_k T_{k+1}^* = \exp\left[-\delta_k - \delta_{k+1} - i\phi_k + i\phi_{k+1}\right] \]

\[
T_k^* T_{k+1} = \exp\left[-\delta_k - \delta_{k+1} + i\phi_k - i\phi_{k+1}\right],
\]

(75)

where we, for simplicity, have used the notation \( \delta_k \equiv \delta(\omega_k) \) and \( \phi_k \equiv \phi(\omega_k) \).

By assuming that the attenuation and the dispersion are small, i.e. \( \delta_k << 1 \) and \( \phi_k << 1 \) the FMS signal can be written as

\[
S_{\text{FMS}}(\omega_c, t) = \eta I_0 \sum_{k=-\infty}^{+\infty} J_k J_{(k+1)} \left[ (\phi_k - \phi_{k+1}) \sin(\omega_m t) + (1 - \delta_k - \delta_{k+1}) \cos(\omega_m t) \right].
\]

(76)

As \( J_k = (-1)^k J_{-k} \) it is convenient to express Eq. (76) as

\[
S_{\text{FMS}}(\omega_c, t) = \eta I_0 2 \sum_{k=0}^{+\infty} J_k J_{(k+1)} \left[ (-\phi_{k-1} + \phi_k + \phi_k - \phi_{k+1}) \sin(\omega_m t) + (\delta_{k-1} + \delta_k - \delta_{k+1}) \cos(\omega_m t) \right],
\]

(77)

which, for low modulation indexes, i.e. \( \beta < 1 \), for which the contribution from second and higher order sidebands can be neglected, can be written as

\[
S_{\text{FMS}}(\omega_c, t) = I_0 2 J_0 J_1 \left[ (-\phi_0 + 2\phi_0 - \phi_0) \sin(\omega_m t) + (\delta_1 - \delta_1) \cos(\omega_m t) \right].
\]

(78)

In the presence of an analyte, the attenuation \( \delta_j \) and phase shift \( \phi_j \) of each mode can be related to the absorption and dispersion line profiles, \( \chi_j^{\text{abs}} \) and \( \chi_j^{\text{disp}} \), by the Eqs. (42) and (43), respectively. By choosing the demodulation phase, it is possible to detect either the pure in-phase or the pure out-of-phase signal or any linear combination thereof. Alternatively, by using an in-quadrature (IQ) mixer, it is possible to detect these two simultaneously. This implies that FMS enables simultaneous monitoring of both absorption and dispersion.
NICE-OHMS

General description

Noise-immune cavity-enhanced optical heterodyne molecular spectrometry (NICE-OHMS) is a powerful technique for detection of molecular compounds in gas phase. The sensitivity of the technique stems from a combination of FMS for reduction of noise and an optical cavity for increased interaction length with the analyte. Furthermore, by choosing the modulation frequency to be equal to the FSR of the cavity, all FMS sidebands are transmitted through the cavity. For an empty cavity all FM components will experience the same attenuations and phase shifts associated with laser frequency noise and as the demodulated FM signal is proportional to differences in attenuation and phase shifts between the FM components the technique is immunity to frequency-to-amplitude noise conversion. The basic principles of NICE-OHMS are schematically illustrated in Figure 15.

Figure 15. Illustration of the NICE-OHMS principle. The panels (i)-(iii) represent the frequency components of light; (i) the light emitted from an unmodulated single-mode, CW laser, thus consisting of a single frequency \( v_l \), (ii) the light after the EOM consisting of the laser frequency (the carrier) and two sidebands at ± the modulation frequency ±\( v_{FSR} \), and (iii) the electrical field inside the cavity together with the cavity transmission modes. Panel (iv) provides a schematic illustration of the experimental implementation. By demodulating the transmitted field at the modulation frequency, a NICE-OHMS signal is produced.
The Doppler broadened NICE-OHMS signal

For single pass absorption much lower than the cavity losses, i.e. for $\alpha_0 L << \pi / F$, the NICE-OHMS signal can be seen as an FMS signal, e.g. as given by Eq. (77), that is enhanced by the prolongation of interaction length from the cavity, given by Eq. (7), which can be written as

$$S_{FMS}(\omega_c, t) = I_0 \frac{F}{\pi} \sum_{k=0}^{\infty} J_k J_{(k+1)} \left[ (-\phi_{k-1} + \phi_k + \phi_{k+1}) \sin(\omega_m t) + (\delta_{k-1} + \delta_k - \delta_{k+1}) \cos(\omega_m t) \right].$$

(79)

As is shown in publication X, while this approximation holds for most practical cases, the real origin of the NICE-OHMS signal is much more complex. The NICE-OHMS signal is in reality a combination of several features, including locking of the laser frequency $\nu_l$ to one of the cavity modes with the Pound-Drever-Hall (PDH) method, locking of the modulation frequency $\nu_m$ to the cavity FSR with the DeVoe-Brewer method, which both are measured in the cavity reflection, Eq. (18), and the cavity transmission, given by Eq. (19). In the presence of an analyte, both the reflected and the transmitted light from the cavity will be affected. Firstly, as a result of the phase shifts associated with the absorption lines, the frequencies of the cavity modes will be shifted. This phenomenon, also known as cavity mode pulling, will not only affect the transmitted light but also the reflected light, which, in turn, will affect the locking points of both the laser PDH and the deVoe-Brewer lock. Secondly, as the intra-cavity losses increase as a result of absorption, the transmitted intensity will drop. As the transmitted light, in turn, depends on the locking points, these entities are inter-linked and the combined set of equations explicitly given in publication X have no known analytical solution. They have therefore to be solved numerically. A description of the origin of the NICE-OHMS signal is therefore that it is given by the interaction between the cavity, the analyte, and the laser locking. It can be shown though, that for the case when $\alpha_0 L << \pi / F$ things simplify and the NICE-OHMS signal can be seen as an FMS signal prolonged by the cavity as given by Eq. (79). An in-depth analysis and a description of this phenomenon can be found in the publications X and XI.

Sub-Doppler vs. Doppler broadened NICE-OHMS

In its original realization, NICE-OHMS was developed for metrology purposes utilizing a narrow linewidth fixed frequency Nd:YAG laser at 1.064 μm. The system could produce a detection sensitivity corresponding to a noise equivalent absorption per unit length (NEAL) of $10^{-14}$ cm$^{-1}$ over 1 s [50,
As these realizations utilized the narrow sub-Doppler response, stemming from the counter propagating waves inside the cavity, this type of detection is known as sub-Doppler (sD) NICE-OHMS. In contrast, Doppler broadened (Db) NICE-OHMS uses the whole lineshape of the transition addressed. However, it is worth to note that it is not like the name suggests, limited to the Doppler regime; it also includes situations when the transition is affected by collision broadening. Figure 16 illustrates a typical measurement in which both sD and Db NICE-OHMS signals are present.

The red curve represents a fit to the Db response. The discrepancies between the fit and the data are mainly the sub-Doppler responses. Starting from zero detuning there are several sD responses, viz., at detunings of zero, ±190, ±380, ±570 and ±760 MHz. Each of these originates from an interaction between the analyte with one forward and one counter propagating wave, each of which can either be the carrier or one of the sidebands.

The zero detuning sD signal originates from the forward propagating carrier and the first order-sidebands interacting with populations saturated by the counter propagating carrier and first order-sidebands, respectively. The sD signal at a detuning of 190 MHz originates from the forward propagating carrier and negative first-order sideband interacting with populations saturated by the counter propagating positive first-order sideband and carrier, respectively. The response found at 380 MHz originates mainly from the forward propagating negative first-order sideband interacting with populations saturated by the counter propagating positive first-order sideband. Additionally also the forward propagating carrier and the negative second-order sideband will interact with populations saturated by the counter propagating positive second-order sideband and carrier, respectively. The response found at 570 MHz originates from the forward propagating negative first- and second-order sideband, interacting with populations saturated by the counter propagating positive second and first-order sidebands. Finally, the response found at 760 MHz originates from the forward propagating negative second-order sideband that interacts with populations saturated by the counter propagating, positive second-order sideband. The responses found at -190, -380, -570 and -760 MHz are simply mirrors of the responses above (instead of interacting with a positive sideband the interaction is with a negative and vice versa).

As was mentioned above, the narrow sD-siganals are useful frequency references and have therefor been used as frequency standards [50]. They can also be used to determine exact relative line positions for multi-line fitting purposes [XIII] and as frequency scale references, i.e. for compensating PZT nonlinearities in scans. However, when the method is applied to trace gas detection optical saturation will have a profound effect
Figure 16. The black curve represents a NICE-OHMS signal from 10 ppm C2H2 in N2 at a pressure of 20 mTorr targeting the P_e(11) transition at 1.5316 µm taken in 0.5 s. The red curve represents a fit of Db NICE-OHMS at pure dispersion phase. The discrepancies between the two curves are the sD responses.

Figure 17 shows a simulation of the pressure dependence of the in-phase Db peak signal from our fiber-laser based NICE-OHMS system addressing a transition with a Voigt lineshape. In contrast, for a given relative concentration, \( c_{rel} \), the peak Db NICE-OHMS signal will increase with pressure until the pressure broadening increases the linewidth of the target transition to a point where it is too high for the FMS modulation frequency. For in-phase (dispersion) with a modulation index \( \beta \) of 1.06, the optimum modulation frequency for Doppler broadened transitions is found at \( v_m / \Gamma_D = 2.4 \) [VI]. This implies that the fiber NICE-OHMS system with a \( v_m \)
Figure 17. Simulation of the peak signal strengths pressure dependency $P_e(11)$ line at 1.531 detected with in-phase Db NICE-OHMS with $v_m$ at 381 MHz.

of 381 MHz, targeting the $P_e(11)$ transition in acetylene (which has a $\Gamma_D$ of 237 MHz) in the Doppler regime, is limited by the low modulation frequency. Hence, increasing the pressure will simultaneously increase the integrated absorption by increasing the amount of analyte and reduce the response of the system (due to under modulation). The peak response the Db NICE-OHMS fiber system addressing an unsaturated transition is estimated to be at 68 Torr. This is significantly larger than the optimum pressure for sD NICE-OHMS, which for a typical set of experimental conditions, is found to be around 400 mTorr [52]. Furthermore, the sub-Doppler absorption feature is always a fraction of the peak Doppler broadened absorption. This factor will vary depending on the degree of saturation but is usually in the order of 10%. Hence, a rough estimate of the theoretical ability to detect trace gases shows that Db is expected to outperform sD NICE-OHMS with three orders of magnitude.

**Locking procedures**

In general, if the frequency of the laser is actively regulated so it is within the linewidth of a cavity mode the laser is considered locked to the cavity. While this model is correct on time scales larger than the cavity lifetime it is not so for fluctuations on a shorter time scale. In this case one must consider the electrical fields and phases involved. Figure 18 illustrates schematically the
Figure 18. Illustration of the relevant frequencies and phase shifts associated with a laser locked to a cavity mode. The electrical fields at the first mirror surfaces are the incident and reflected laser fields with frequency \( \nu_i \), illustrated in red, and the forward and backwards propagating intracavity electrical field inside the cavity illustrated in blue with a frequency of \( \nu_c \). The corresponding phase shifts at the mirror surface one \( \phi_+^i \), \( \phi_-^i \), \( \phi_+^c \) and \( \phi_-^c \), respectively.

phases and frequencies of the relevant fields for a laser inducing an electrical field inside a cavity.

It is well known in the field of optics that there is a phase shift of \( \pi \) introduced every time light is reflected from a surface with a higher index of refraction (i.e. inside the cavity) while there is no such phase shift associated with transmission or reflection from a surface with lower index of refraction (i.e. reflections from outside the cavity). Hence, if the induced field is on resonance, so as to build up a high intracavity intensity, at the first mirror, the phase of the forward propagating electrical field in the cavity, \( \phi_+^c \), must be out of phase with the backwards propagating field, \( \phi_-^c \), that is \( \phi_+^c - \phi_-^c = \pi \). For the intensity to build up in the cavity, the phase of the incident field, \( \phi_+^i \), must be in phase with the forward propagating cavity field i.e. \( \phi_+^i = \phi_+^c \). In such a case the phase of the electrical field that leaks out from the cavity, which is equivalent to \( \phi_-^c \), and the reflected laser field, \( \phi_-^i \), will be out of phase i.e. \( \phi_-^c - \phi_-^i = \pi \). If the fields are of the same amplitude there will be no power reflected. Power conservation then demands that all the power is transmitted.

However, this ideal situation is seldom achieved, primarily due to intracavity losses (not an impedance matched cavity) or if the mode matching is not perfect or the laser is not perfectly phase locked to the intracavity field, or a combination of the above, and so only a fraction of the light will be coupled in to the cavity.

**Pound-Drever-Hall laser locking**

The PDH technique utilizes frequency modulation to lock the frequency of the laser to one of the cavity modes [53]. A schematic sketch of a typical PDH locking scheme can be seen in Figure 19. The laser light \((i)\) is modulated with
an EOM at a frequency higher than the cavity mode linewidth so that the resulting sidebands (ii) are rejected (reflected) by the cavity. When the laser frequency \( f_l \) is close to a cavity mode the carrier of the laser will induce an electrical field inside the cavity (iii). Under steady state conditions, the frequency of the induced field, \( f_c \), will be the same as the laser. The back reflected light will, in addition to the sidebands, contain the back reflected carrier and the out leakage from the buildup in the cavity (iv).

As was discussed above, when the light is on resonance with the cavity mode, the back reflected carrier and the electrical field that is buildup in the cavity are out of phase (i.e. \( \phi_i^+ - \phi_i^- = \pi \)) and hence there is no net reflection of the carrier.

By modulating the laser light at a frequency, \( v_{PDH} \), that is larger than the cavity linewidth, \( \Gamma_c \), and (in most cases) smaller than half of the FSR of the cavity \( v_{FSR} \), by a small modulation index (\( \beta = 1 \)) a pair of sidebands that are reflected when the carrier is on resonance is created. The back reflected light is monitored with a photodiode and the intensity is demodulated at the modulation frequency (e.g. by the use of a double balanced mixer). As the demodulated signal from the directly reflected (from the first mirror) sidebands and carrier is zero the PDH signal is, in fact, solely a function of the out leakage of the carrier and the reflected sidebands. It can be shown that for small detunings, the PDH error signal is, in general, proportional to

\[
S_{PDH} \propto \phi_i^+ - \phi_i^-. \quad (80)
\]

It is worth noting that for fluctuations faster than the cavity cutoff frequency, the field buildup inside the cavity can be considered constant. As the PDH signal is proportional to the phase shift between the laser and the field buildup inside the cavity, as is given by Eq. (80), the PDH signal will then be proportional to phase fluctuations \( \delta \phi_i^+ \) of the incident laser beam.

For fluctuations slower than the cavity cutoff frequency, the frequency of the field buildup inside the cavity will be equal to the frequency of the laser i.e. \( v_l = v_c \). If one considers that the Fabry Perot cavity prolongs the path length by a factor of \( L_{eff} / L = 2F / \pi \), it can be argued that also the single pass phase shift \( \phi(v) / 2 = \pi v / v_{FSR} \) will be increased with the same factor. Hence, the phase of the out-leaked electrical field, \( \phi_i^- \), for a small detuning is given by

\[
\phi_i^-(v) = \frac{2Fv}{v_{FSR}} + \pi, \quad (81)
\]

where the \( \pi \)-term comes from the \( \pi \)-shift associated with reflections inside the cavity i.e. \( \phi_i^+ - \phi_i^- = \pi \).
Figure 19. A schematic illustration of the principles and the realization of PDH locking. The panels (i) - (iv) represent the frequency components of light of various places of the system; (i) the light emitted from an unmodulated single-mode, CW laser, thus consisting of a single frequency \( v_l \), (ii) the light after the EOM consisting of the laser frequency (the carrier) and two sidebands at \( \pm \) the modulation frequency \( v_{PDH} \), (iii) the electrical field inside the cavity (blue), \( v_c \), and (iv) the back reflected light from the cavity i.e. the PDH sidebands and the laser carrier both reflected by the cavity and the out leakage from the buildup inside the cavity (primarily the carrier). Panel (v) provides a schematic illustration of the experimental realization. As the demodulation of the signal from the sidebands and the laser carrier of the laser is zero the PDH signal is solely a function of the out leakage of the carrier and the reflected sidebands.

If the frequency of the laser is not exactly equal to that of the cavity mode the phase of the out leaked electrical field, given by Eq. (81), will be shifted. As the back reflected and the buildup electrical field are no longer fully out of phase there will be an increase in the reflected intensity associated with this detuning along with a decrease of the intracavity build up. For a detuning of \( \pm \Gamma_c \) (HWHM) the phase of the out leaked electrical field \( \phi_c^- \) will experience a phase shift of \( \pm \pi/4 \). This implies that the cavity will serve as a very sensitive probe of the frequency of the laser and for slow fluctuations and small detuning the PDH error signal is proportional to the detuning of the laser frequency \( v_l \) from its cavity mode \( v_q \)

\[
S_{PDH} \propto v_l - v_q.
\]  

A typical PDH error signal is shown in Figure 20
Figure 20. Typical PDH error signal as the laser is swept over a cavity mode.

As the PDH method produces an error signal that is proportional to the detuning of the frequency of the carrier from that of the cavity mode, it can be used to lock any laser whose frequency can be controlled with a voltage. Furthermore, it can also be used to control electro optical devices, such as EOMs or AOMs, when they are used to shift the wavelength of the laser.

deVoe-Brewer locking

As the PDH technique locks the frequency of the laser to that of the cavity, the deVoe-Brewer method utilizes the PDH sidebands and the FMS sidebands to lock the FMS modulation frequency to the FSR of the cavity [53]. A schematic sketch of a typical deVoe-Brewer lock can be seen in Figure 21. The laser light is modulated at both at the PDH locking frequency, $v_{PDH}$, and at FMS frequency, $v_{FMS}$. For low modulation indexes, i.e. $\beta < 0.1$, these results in three triplets as illustrated in panel (i). In the deVoe-Brewer method the back reflected light is demodulated at the difference between the FMS and the PDH modulation frequencies i.e. $v_{FMS} - v_{PDH}$. This frequency is retrieved by mixing the signals in a double balanced mixer and band pass filtering out the difference frequency. Only considering these frequency components and that the laser is locked to the cavity, i.e. the net reflection of the laser center frequency is zero, one will find that only the phase of the out leaked FMS sidebands will contribute to the signal. This thus gives rise to an error signal for the FMS modulation frequency.
Figure 21. Illustration of deVoe-Brewer locking. The panels (i) and (ii) represent the frequency components of light; (i) the light after the EOM consisting of the three triplets from the FMS modulation at $v_{FMS}$ and the modulation for PDH locking $v_{PDH}$, (ii) the components responsible for the deVoe-Brewer error signal i.e. the back reflected PDH sidebands and the out leakage from the intra cavity FMS sidebands. Panel (iii) provides a schematic illustration of the experimental setup.

In a similar manner as the origin of the PDH signal can be traced to the carrier that is build up inside the cavity, the deVoe-Brewer signal utilizes the buildup of the FMS sideband. However, in contrast to the PDH error signal, the beat between the FMS sidebands and the PDH sidebands are in phase. This implies that there is a beating at the deVoe-Brewer frequency, defined as the difference between the PDH and FMS modulation frequencies, with an amplitude that is proportional to the intensity of the FMS sidebands back reflected from the first mirror.

Hence, if the FMS modulation frequency is tuned away from the cavity FSR the deVoe-Brewer error signal, which is proportional to the beating of the reflected FMS and PDH sidebands, will be nonzero. By demodulating off-phase with respect to this beating the deVoe-Brewer error signal will solely depend on the beat between the PDH sideband and the out leakage from the FMS sidebands that are buildup in the cavity. Considering the first positive and negative FMS sidebands and assuming a small detuning from resonance the deVoe-Brewer error signal is proportional to
where $\phi_{c-1}$ and $\phi_{c+1}$ denotes the phase of the forward propagating intracavity electrical field for the q-1 and q+1 cavity modes while $\phi_{l-1}$ and $\phi_{l+1}$ denote the incident field of the first negative and positive laser sidebands, all at the first mirror. The signs originate from the fact that the two beat frequencies are equal to $v_{PDH,-1} - v_{c-1}$ and $v_{c+1} - v_{PDH,+1}$, i.e., the difference between the negative PDH sideband of the laser light and the negative FMS intracavity electrical field, and the positive FMS intracavity electrical field and the positive PDH sideband.

As was alluded to above, the sidebands are locked if the phase difference between the forward propagating cavity field and the incident laser field are zero. If the FMS frequency ($v_{FMS}$) is detuned from the cavity FSR ($v_{FSR}$) the associated phase shifts for $\phi_{c-1} - \phi_{l-1}$ and $\phi_{c+1} - \phi_{l+1}$ will be of opposite signs and reinforce each other. Hence, the deVoe-Brewer error signal is proportional to detuning of the FMS frequency from the FSR of the cavity.

**Noise immunity**

In NICE-OHMS the FMS modulation frequency, $v_{FMS}$, is thus chosen to be equal to (an integer of) the free spectral range (FSR) of the cavity, $v_{FSR}$. This allows for FMS to be performed inside the cavity with an added benefit of the prolonged interaction length from the cavity. In addition, all spectral components of the FM triplet are transmitted through the cavity in an identical manner, whereby they are affected by any frequency-to-amplitude noise conversion in the same way. This implies that a jittering between the laser and the cavity will be mirrored in both the attenuations, $\delta_j$, and the phase shifts, $\phi_j$, of all components. Since the NICE-OHMS signal is proportional to the difference between various attenuations or phase shifts, any frequency jitter of the laser frequency will not affect the NICE-OHMS signal (as these components will cancel). Hence, for an empty cavity NICE-OHMS is not affected by the frequency to amplitude conversion which limits direct absorption cavity enhanced experiments. This is referred to as “noise immunity”.

**Background signals in NICE-OHMS**

While NICE-OHMS is considered to be immune to frequency to amplitude conversion, this statement holds only if there is no background signal present. As can be seen in Eq. (79), if the NICE-OHMS signal is non-zero the signal will be proportional to the intensity of the light impinging on the detector. This implies that all types of intensity noise, including that
produced by frequency-to-amplitude conversion from the jittering between the laser frequency and the cavity mode frequency, will couple in through the background signal. Furthermore, background signals also tend to be frequency dependent and drift, i.e. change over time. More often than not, this will limit the precision of the system. Hence, to achieve the lowest detection limits, one must eliminate background signals.

**Residual amplitude modulation**

The simplest way to achieve frequency modulation is to modulate the frequency of a laser directly (e.g. for a diode laser by applying a modulation to its injection current). Although simple, the frequency modulation is often associated with an intensity modulation, also referred to as residual amplitude modulation (RAM).

An amplitude modulation of an electric field component of a monochromatic beam of light can be expressed as

\[
E(t) = E_0 \left(1 + A \cos \omega_m t\right) \cos \omega_c t \\
= E_0 \left\{ \cos \omega_c t + \frac{A}{2} \cos[(\omega_c - \omega_m)t] + \frac{A}{2} \cos[(\omega_c + \omega_m)t] \right\},
\]

where \(A\) is the (relative) amplitude of the modulation. As is shown by the second step, in frequency space, this can be seen as a carrier with two sidebands. The intensity of light that experiences amplitude modulation contains therefore a term at the modulation frequency that is proportional to both the intensity of the light as well as the relative modulation amplitude, i.e.

\[
I(t) = I_0 A \cos(\omega_c t),
\]

which, in turn, gives rise to a FMS background signal proportional to both \(I_0\) and \(A\). Hence, in contrast to pure phase modulation, which does not give rise to any background signals, amplitude modulation produces a constant offset in NICE-OHMS that is proportional to the modulation amplitude. The reason for this difference is that with pure phase modulation, the \(2k+1\) and the \(-(2k+1)\) sidebands have 180 degrees phase difference. This implies that, the net contribution of all sidebands will in the absence of absorber, result in zero signal Eq. (68). As there is no phase difference between the two sidebands in AM modulation, which can be seen from Eq. (84), these signal will not cancel in FMS.
It should be noted that there are also other effects that do not involve amplitude modulation that commonly also are referred to as RAM. For example, cross coupling effects in EOMs [II], which mainly affect the carrier, are referred to as RAM although no amplitude modulation is associated with this effect.

**Parasitic etalons**

Inserting optical components into the beam path will more often than not result in that some part of the beam is reflected. The interference of laser light between various surfaces within the system will result in so-called etalons, which are common in all types of optical spectrometry, including FMS. The spectrum of such parasitic etalons is equivalent with that of a cavity with a low finesse and therefore they have a strong wavelength and temperature dependence. The temperature dependence is mainly caused by the thermal expansion of the optical table or the material supporting the components between which the etalons is created, but also the temperature dependence of the index of refraction of the medium between these surfaces will in some cases couple in. Parasitic etalons can be modeled as low finesse cavities. The transmitted intensity from such an etalon, \( I_{e} \), can therefore be calculated by Eq. (19), which gives

\[
I_{e} = T_{c} T_{e}^{*} I_{0} \approx \frac{t_{1}t_{2}I_{0}}{1 - \sqrt{r_{1}r_{2}} \cos \varphi(v)}, \tag{86}
\]

where \( \varphi(v) \) is the round trip phase shift in the etalon which, in turn, can be expressed in terms of the distance separating the components, \( L \), as \( \varphi(v) = 4\pi n L v / c \).

For instance, an uncoated surface, typically has a reflection coefficient of 4\% and a cavity mirror reflect typically 10\% on resonance, due to poor mode-matching and impedance matching. These reflections will give rise to an etalon with a finesse of 2.6. Equation (86) shows that the transmitted intensity fluctuation (peak to peak) from such an etalon will be 0.8\%. Since cavity-based detection techniques strive for detecting species in low concentrations (which give rise to absorption below this level) this is of course not acceptable and hence measures must be taken to reduce etalons.

The first measure is to use anti-reflection coated surfaces, since this can typically reduce the reflection from surfaces down to below 0.5\%. This will reduce the intensity fluctuation to 0.01\% of the total intensity. It is worth noting that the amplitude of the etalon will, for most well-conceived NICE-OHMS setups, be dominated by etalons stemming from the first or second cavity mirror as the back reflection tends to be in the order of 10\% even for a
well locked laser. This is orders of magnitude above any other typical reflection in an optimized system.

Secondly, to the extent it is possible, surfaces that produce back reflections should be placed at a non-perpendicular angle with respect to the laser beam. This approach is particularly important for objects that cannot be given an anti-reflection coating, e.g. detectors and polarizers. An estimate of how etalons can affect the detection sensitivity of NICE-OHMS and means to reduce them are discussed in some detail in the publication V and IX.

**Background signals from birefringent components**

One major source of background signals in FMS and NICE-OHMS is birefringent components, e.g. polarization maintaining (PM) fibers or electro-optic crystals. Birefringent components have different indices of refraction for light polarized along the primary axis, \(n_p\), and the secondary axis, \(n_s\), which results in two different optical path lengths for the different polarizations. If care is not taken to control the polarization and alignment of components this path difference will create interference between the light polarized along the two principal axes, resulting in an “etalon like” background with the periodicity (in optical frequency) given by \(c/|L(n_p - n_s)|\), where the denominator represents the path difference between two interfering beams. For PM fibers the birefringence is commonly expressed in the form of beat length, i.e. as

\[
L_b = \frac{\lambda}{|n_p - n_s|}. \tag{87}
\]

This represent the length of a PM fiber for which the phase difference between the primary and the secondary polarization modes equals \(2\pi\). For instance, a commonly used PM fiber for the 1.5 µm region (e.g. SM15-PS-U40D) has a beat length of 3 mm. Comparing with the periodicity of an etalon, which is \(c/(2L_n)\), it is possible to conclude that these two items produce significantly different types of background signals. An etalon with a length of 1 m will produce a background with periodicity of 150 MHz while 1 m fiber will produce a background with periodicity of 600 GHz. As the laser is typically swept a few GHz in NICE-OHMS, backgrounds from PM fibers appear as a constant or a sloping offset. It is also worth noting that, while fibers carrying modulated light can give rise to background signals, fibers carrying unmodulated light do not cause background FMS signals but can still indirectly cause disturbances through intensity fluctuations and changes in the initial polarization.
It is also possible to estimate the periodicity of background signal originating from the electro optical crystal in a fiber coupled EOM. For the case with a wavelength of 1.5 µm, an EOM crystal length of 10 cm (typical for fiber coupled EOMs) made from lithium niobate and for a crystal temperature of 25 °C, the indices of refraction for the extraordinary and the ordinary axis, $n_e$ and $n_o$, are 2.157 and 2.233, respectively [54]. Using the relation $c / |L(n_e - n_o)|$ it is possible to estimate the periodicity to be around 40 GHz. Hence, the NICE-OHMS background signals from fiber coupled EOMs will be a sum of two constant or sloping offsets.

Another type of background signals caused by birefringence is cross coupling in the EOM modulating the light. The effect, which historically also has been referred to as RAM, is caused by a combination of dissimilar electro optical effects and indices of refraction along the primary and secondary axis, i.e. the extraordinary and ordinary axis.

To separate the pure birefringent effect from the effects from modulation, the components along the ordinary axis are separated into a triplet with the same ratio between the carrier and sidebands as the triplet created along the extraordinary axis and one pure carrier. When these components interact with the triplet produced along the extraordinary axis the result is interference between two triplets (as for birefringent components) and a triplet and the carrier. The dominating effect for in-phase detection will be the interaction between the triplet (along the extraordinary axis) and the carrier (along the ordinary axis). As the out-of-phase signal does not contain any component from the carrier the triplet-triplet interaction will dominate in this phase.

Wong and Hall showed that background signals from free space EOMs can be eliminated by a careful alignment of a polarizer before or after the EOM [55]. However, it was thereafter observed that this procedure does not work for fiber coupled EOMs. Etalons from such systems were found to originate from cross-couplings between the principal axes of the polarization-maintaining fibers and those of the electro optic crystal. The origin of this background was extensively investigated in publication [II].

It was also shown that EOMs made with a proton exchanged waveguide do not suffer from these effects [I, II]. The reason is that this type of waveguide prevents propagation along the ordinary axis as the index inside the waveguide is lower for light polarized along the ordinary axis than in the substrate. This implies that light with this polarization is diffused out of the waveguide and not transmitted through the crystal.

The situation is different for EOMs with titanium diffused waveguides. In these, light can propagate with polarization along both the ordinary and the
extraordinary axes. In this case, the effect of cross coupling can be reduced by using the fact that the two axes have different electro optical coefficients i.e. that the index of refraction is changed differently if a voltage is applied across the crystal, and that the thermal dependence of the path length of the two axes also differ (the thermal dependence of the optical path is a combination of the thermal expansion and the change of index of refraction as a function of temperature). In publication I these effects were used to eliminate the background signals by simultaneous applying a temperature and a voltage feedback. This approach was successful in situations where the signal was dominated by incoupling of intensity noise $\sigma_I$, i.e. when the background signal times the relative intensity noise, $S_p\sigma_{I_p}/P_a$, dominates over other sources of noise. In cases when the setup was limited by technical noise, the use of an EOM with a titanium diffused waveguide together with additional feedback increased the noise level by a factor of two as compared to when a proton exchanged EOM was used. Although the cause for this has not yet been fully assessed one can speculate that the feedback loop, which is an copy of the FMS demodulation circuit, will add un-correlated noise to the signal while subtracting correlated noise sources.
Assessing the detection sensitivity of a technique

The Allan deviation and the Allan-Werle plot

In 1966, D.W. Allan proposed an M-sample variance to determine the stability of atomic clocks [56]. This concept was successively and efficiently applied to laser spectroscopy by Werle et al. in 1993 [57]. After the unfortunate demise of Werle, at FLAIR 2014 a decision was made to refer the use of the Allan deviation plots to spectroscopy as the Allan-Werle plots. A typical Allan deviation plot from a frequency stability measurement is shown in Figure 22. The data was acquired by recording the beat frequency between a laser locked to a cavity and an OFC referenced to a GPS stabilized rubidium source.

The Allan deviation is defined as follows. Consider a set of \( N \) data points, \( x_n \), where \( n = 1, \ldots, N \), taken with a specific sampling rate, \( f_s = 1/\Delta t \). This time series can, in turn, be divided into \( M \) sub-groups of \( k = N/M \) elements, each with the mean value of

\[
A_s(k) = \frac{1}{k} \sum_{i=1}^{k} x_{s,k+l},
\]

where \( s = 0, \ldots, M-1 \). The Allan deviation for a given averaging time, \( \tau = k \Delta t \), is then given by [56]

\[
\sigma_A(\tau) = \sqrt{\frac{1}{2(M-1)} \sum_{s=1}^{M-1} \left[ A_s(k) - A_{s-1}(k) \right]^2}.
\]

In contrast to the standard deviation the Allan deviation gives significantly different responses for different types of noise and is therefore a suitable means of analyzing the influence of various types of noise on a given instrumentation. For instance, in Figure 22 one can see two distinct regions with different slopes. For short integration times the slope is negative which implies that increased averaging will decrease the Allan deviation, that is increasing accuracy in the frequency determination. For long integration times the slope of the Allan deviation is positive which implies that the accuracy of the measurement is getting worse by averaging i.e. the signal is affected by drifts. The optimum measurement time is considered to be at the minimum of the curve.
Figure 22. Typical Allan plot of the frequency stability of the beat frequency between a laser locked to a cavity and an OFC stabilized to a rubidium source [XVIII].

Types of noise

Noise can be seen as an undesired disturbance in a signal. In cavity enhanced laser sensing techniques noise can for example originate from electronics, optical interference, mechanical vibrations and temperature fluctuations, or a combination of these. If the measurement system utilizes feedback loops and there is noise in error signal, it will couple in to the signal, through the locking procedures. In these cases, it is non-trivial to trace and eliminate the source of the noise. Allan plots can then be used to determine the types of noise present in the system and as different noise sources will produce different types of noise it is hence also possible (but not trivial) to determine the noise sources that limit the system.

White noise

White noise is a stochastic type of noise with a constant spectral distribution. The origin of this noise type is more often than not random processes of various kinds. Figure 23 shows simulated flicker noise and the corresponding Allan variance. In electronic circuits one source of white noise is thermal noise i.e. thermal fluctuations of electrons [58]. Considering a resistor, $R$, with a temperature of $T$, the standard deviation (the RMS) of the voltage produced over the resistor is given by
Figure 23. Simulated white noise and the corresponding Allan plot. The slope of the Allan plot has a $\tau^{-1/2}$ dependence.

\[ \sigma_{TN} = \sqrt{4k_B TR\Delta f}, \]  

(90)

where $\Delta f$ is the detection bandwidth. Hence, for example, for a 100 kΩ resistor at room temperature (i.e. at 300 K) the thermal noise will be $\sim 0.4 \mu\text{V Hz}^{-1/2}$.

Another type of noise related to electronics is shot noise whose origin is the quantified electrical current i.e. electrons. Shot noise was first introduced in the study of fluctuations of current in vacuum tubes [59]. The standard deviation of the shot noise current is given by

\[ \sigma_i = \sqrt{2ie\Delta f}, \]  

(91)

where $I$ is the current and $e$ is the elementary charge. The standard deviation of the shot noise voltage, measured over a resistor, $R$, is given by,

\[ \sigma_v = \sqrt{2e\Delta f \sqrt{RV}}. \]  

(92)

Hence, for example, a signal of 1 V measured over a 100 kΩ resistor will contain shot noise of $\sim 0.2 \mu\text{V Hz}^{-1/2}$.

Yet another type of shot noise is photon shot noise, which is discussed in detail in the section “shot noise” below. As for the electronic counterpart, photon shot noise originates from the quantified optical intensity i.e. photons.
The expected Allan variance for white noise can be calculated by considering the standard deviation of each sub group, which will be given by

\[ \sigma_{A(k)} = \sigma_{\Delta t} \sqrt{k} , \]  

(93)

where \( \sigma_{\Delta t} \) is the standard deviation for the sampling time. The fluctuation of \( A_i(k) - A_{i-1}(k) \) in Eq. (89) is given by the difference between the standard deviations of the two elements, which is equivalent to the standard deviation of the sum of two random variables, which, in turn, is given by

\[ \sigma_{X+Y} = \sqrt{\sigma_X^2 + \sigma_Y^2 + \text{cov}(X,Y)} , \]  

(94)

where \( \sigma_X \) and \( \sigma_Y \) are standard deviation of the variables \( X \) and \( Y \) respectively. As white noise is uncorrelated, \( \text{cov}(X,Y) = 0 \). The Allan deviation, \( \sigma_A(\tau) \), for white noise is therefore equivalent to the standard deviation of the mean \( \sigma_A(\tau) = \sigma_{\Delta t} \sqrt{k} \).

White noise tends to dominate all measurement systems at short integration times. As the power of white noise is distributed over all frequencies, low-pass-filters or, as shown in Figure 23, averaging will reduce this noise type.

**Flicker noise, 1/f-noise**

Flicker noise, also known as 1/f or pink noise, is a type of random noise with a spectral density that decreases with frequency. This implies that this type of noise contains a higher proportion of low frequencies than white noise. Figure 24 shows simulated flicker noise and the corresponding Allan variance.

In 1988, Weissman stated “In nearly all resistors, several lines of evidence indicate that resistance fluctuations are present in the absence of a driving current. Thus, for small currents, the spectral density of the measured voltage fluctuations is proportional to the square of the current, since \( \delta V = I \delta R \).” [60]. Hence, the origin of flicker noise has been related to fluctuations of the resistivity. Since the spectral density in the quote above refers to the square of voltage, flicker noise is proportional to the current. This type of noise can be reduced by limiting the current in the circuit so that the thermal noise given by Eq. (90) will dominate. A well-known source of flicker-noise is the laser intensity but also operational amplifiers and resistors have been related to this noise type.
Figure 24. Simulated flicker noise and the corresponding Allan plot. The Allan deviation for flicker noise is independent of $\tau$.

Flicker noise is considered to have a $1/f$ spectral dependence. Thus, the variance for any given sampling frequency, $f_b$, denoted $\sigma_b^2$, can be related to that taken at another frequency, $f_a$, $\sigma_a^2$, by

$$\sigma_b^2 = \sigma_a^2 \frac{f_a}{f_b}.$$  \hspace{1cm} (95)

Hence, the spread of points taken with longer integration time will be higher than that of points taken with shorter integration time, $\tau$. If one now considers a situation where a signal sampled with a sample frequency $f_a$ is summed over a given time interval $k / f_a$ that is equal to $1 / f_b$, the summed signal and its variance would grow with $f_b / f_a$. If the mean value of such a subgroup is taken the variance and the standard deviation would be constant and thereby also $\sigma_A = \sigma_{\Delta t}$ will be constant for all integration times.

**Brownian noise, $1/f^2$-noise**

Random-walk noise or Brownian noise has a $1/f^2$ spectral dependence. The signal can be seen as a number of consecutive random steps taken from the position of the previous point, which also is known as random walk. A simulation of Brownian noise and the corresponding Allan deviation are shown in Figure 25.
Figure 25. Simulated 1/f² type of noise, i.e. Brownian noise, and a corresponding Allan plot, which has a slope of $\tau^{1/2}$.

Thermal fluctuations are random deviations of the temperature from an equilibrium. As the temperature of a solid is a statistical ensemble of random microstates, e.g. vibrations around equilibrium position, the temperature at any given time will be given by a random sample of all states, where the probability of each state is given by the Boltzmann distribution.

Since random walk has a 1/f² spectral dependence, the variance for any given sampling frequency is given by

$$\sigma_b^2 = \sigma_a^2 \frac{f_a^2}{f_b^2},$$

(96)

where $f_a$ and $f_b$ are the sampling frequencies corresponding to the variances $\sigma_a^2$ and $\sigma_b^2$, respectively. Hence, the spread of points taken with longer integration times $\tau$ will be higher than points taken with shorter integration time. If one now considers a situation where a signal sampled with a sample frequency $f_a$ is summed over a given time interval that is $k / f_a$, which is equal to $1 / f_b$, the summed signal would grow with $f_b / f_a$, while the variance with $f_b^2 / f_a^2$. Hence, the mean value of each sub group used to calculate the Allan variance will experience an increasing standard deviation with increasing averaging time i.e. $\sigma_A = \sigma_\alpha \sqrt{k}$. This implies that the Allan variance will have an $\tau^{1/2}$ dependence.

Although usually very small, Brownian noise becomes a problem in ultra-precision measurement. It has, for instance, been reported that the
Brownian motion in the high-reflecting multilayer coatings of mirrors that make up a cavity is the main limiting factor for ultrastability lasers [61].

**Drifts, $1/f^3$-noise**

For long time scales many systems tend to be limited by drifts, which can be modelled as $1/f^3$ type of noise. As this type of noise tends to increase at a significantly higher rate than the Browning noise, it dominates the latter in most cases. These drifts are often temperature dependent. For instance, electronic offsets and gains tend to drift as a result of changing resistances due to temperature. For example, a resistor can typically have a temperature coefficient of 100 ppm/K. If used in an amplifying stage, this can result in a drift of a voltage of 100 ppm per degree. Furthermore, as the temperature in the lab changes, the alignment of the setup also changes whereby the power levels and the background in the setup also change.

For a constant drift the mean value will follow

$$A_i(k) = A_{i-1}(k) + Ck,$$

where $C$ is the drift constant, In such a case, the Allan deviation will be given by $\sigma_4(\tau) = Ck/\sqrt{2}$. Figure 26 shows some simulated $1/f^3$-noise together with the corresponding Allan deviation.

![Allan deviation and 1/f^3 noise](image)

**Figure 26.** Simulated $1/f^3$ type of noise, i.e. a steady drift, and a corresponding Allan plot, which has a slope of $\tau^1$. 

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**Periodic disturbances**

Another common type of disturbance is periodic disturbances. Such disturbances can originate from a variety of sources. If there is a periodical background, i.e. an etalon that drifts (with a constant drift of its length), the resulting signal will contain a periodical disturbance with an amplitude equal to the amplitude of the etalon. If, on the other hand, there is a background that periodically changes e.g. an etalon with a small periodic fluctuation in its phase the result will also be a periodical disturbance although with an amplitude given by a fraction of the total amplitude.

A periodical phase shift can be induced by oscillations in a temperature control circuit or by physical vibrations (low frequency acoustic noise). Finally, oscillations in laser servos can also affect the intensity and hence the signal strength. Hence, there is a multitude of sources of periodic disturbances. In Figure 27 a simulated periodical disturbance and the corresponding Allan deviation can be seen.

If the drift is periodical and the periodicity of the drift, \( \tau_{\text{drift}} \), is much larger than the averaging time i.e. for slow drifts, thus characterized by \( \tau_{\text{drift}} \gg k\Delta t \), the mean value of consecutive datasets can be written as

\[
A_s(k) = A_0 \sin\left(2\pi \cdot sk\Delta t / \tau_{\text{drift}} \right),
\]

where, \( A_0 \), is the drift amplitude. The difference between two consecutive mean values can be expressed (using the small angle approximation) as

\[
A_s(k) - A_{s-1}(k) = A_0 \left[ \sin\left(2\pi sk\Delta t / \tau_{\text{drift}} \right) - \sin\left(2\pi(s-1)k\Delta t / \tau_{\text{drift}} \right) \right]
\]

\[
= A_0 \left[ 2 \cos\left(\pi k\Delta t / \tau_{\text{drift}} (2s-1)\right) \sin\left(\pi k\Delta t / \tau_{\text{drift}} \right) \right]
\]

\[
\approx A_0 2 \pi k\Delta t / \tau_{\text{drift}} \left[ \cos\left(2\pi sk\Delta t / \tau_{\text{drift}} \right) \right].
\]

Since the mean square of \( \cos \) is 1/2 the standard deviation of a periodical drift with \( \tau_{\text{drift}} \gg k\Delta t \) (measured over a time \( \gg \tau_{\text{drift}} \)) will be given by

\[
\sigma_\delta(\tau) = A_0 \sqrt{2\pi k\Delta t / \tau_{\text{drift}}}. \]

This corresponds to the slope seen for short integration times in Figure 27, in this case for integration times shorter than 10 \( \Delta t \).

If the periodicity of the drift, \( \tau_{\text{drift}} \), is much smaller than the averaging time, \( \tau \), given by, \( k\Delta t \), i.e. when \( \tau \gg \tau_{\text{drift}} \), the mean value of the time elements will result in a series of peaks of \( \tau = \tau_{\text{drift}} (1/2 + 0.1...) \). As the average of the \( \sin \) function for half a period is \( \langle \sin \rangle_{\Delta \tau} = 2 / \pi \), the first peak will be found at \( \tau = k\Delta t = \tau_{\text{drift}} / 2 \) with an Allan deviation of \( \sigma_\delta = 2A_0 \sqrt{2 / \pi} \). The Allan deviation of every successive peak will drop off as the integration time increases i.e. the amplitude of the sequence of peaks will follow
Figure 27. A simulated periodical drift with $\tau_{\text{drift}}$ being 60 $\Delta t$ where $\Delta t$ is the time between consecutive measurements and the corresponding Allan plot. The slope for $\tau > \tau_{\text{drift}}$, given by the dashed line, has a $\tau^{-1}$ dependence.

$$
\sigma_\Delta(\tau) = 2 A_0 \sqrt{\tau_{\text{drift}} / \tau / \pi}, \quad (100)
$$

In reality a pure periodical drift is an ideal situation that seldom exists. If the spectrum of frequencies producing the disturbance is wide the resulting Allan variance will be given by a $\tau^{-1}$ noise level instead of a series of peaks.

Sources of noise in NICE-OHMS

**Photon shot noise**

Shot noise originates from the quantum nature of photons. This implies that the number of photons detected will always be an integer number. Hence, the smallest possible absorbance one can detect is given by the absorption of one single photon. As a given number of photons can be expressed as a given power, and as stochastic processes can be described by a Poisson distribution, it is possible to calculate the expected current noise level for a detector illuminated by a given power, $P_0$, as

$$
\sigma_{SN}^2 = 2 e \Delta f \eta_A P_0, \quad (101)
$$
where, $\eta_A$, is the responsivity of the detector in A/W. An expression for shot noise limited NICE-OHMS was first derived by Ye et al. [51]. As this expression was calculated for sub-Doppler signals and not utilizing Allan-Werle plots, which is the standard today, a revision of these formulas are in order and is therefore given here.

Starting from Eq. (78) and considering, for simplicity, only the in-phase response, the signal strength of an FMS signal before demodulation is proportional to the root mean square of a sinusoidal signal, which is $1/\sqrt{2}$, the average signal strength, after modulation, can be written as

$$S_{\text{FMS}}(\omega_c) = \eta P_0 \sqrt{2} J_0 J_1 \left(-\phi_1 + 2\phi_0 - \phi \right).$$  \hspace{1cm} (102)

As Ye et. al. were dealing with sub-Doppler signals they assumed that only the carrier, $\phi_0$, interacted with the lineshape. Furthermore, to give the detection sensitivity in terms of a sub-Doppler absorption, $\alpha_{sD}$, he assumed that the change in index of refraction at the center of the transition can be expressed as $\Delta n = c \alpha_{sD} / 2 \omega$, which corresponds to a phase shift of $\Delta \phi = \alpha_{sD} L / 2$. This resulted in a simple equation for the $sD$-FMS peak signal that is given by

$$S_{\text{FMS},sD}^{\text{peak}} = \eta P_0 \sqrt{2} J_0 J_1 \alpha_{sD} L.$$  \hspace{1cm} (103)

Adding the cavity enhancement factor, $2 F / \pi$, and assuming a detection limit in the form of a signal to noise ratio, $\text{SNR} = \sigma_{SN} / S_{\text{FMS},sD}^{\text{peak}}$, they derived the NICE-OHMS shot noise detection limit to be equal to

$$\alpha_{\text{SN},sD} L = \pi \frac{\text{SNR} \sqrt{e \Delta f}}{2 F J_0 J_1 \eta P_0}.$$  \hspace{1cm} (104)

Ye et. al. used an SNR of 2 but as the values are to be compared with detection limits retrieved from Allan-Werle plots, a SNR of 1 will be used in this work. This implies that the sub-Doppler shot noise detection limit will be considered to be half of this.

For Doppler broadened (Db) signals utilizing the relations (38) and (43), the FMS signal can be written as

$$S_{\text{FMS},Db} = \eta P_0 \frac{J_0 J_1}{\sqrt{2}} \left(-\chi_{1,1}^{\text{disp}} + 2\chi_0^{\text{disp}} - \chi_1^{\text{disp}} \right) \alpha_0 L,$$  \hspace{1cm} (105)

where, $\chi_{0,0}^{\text{abs}}$, represents the peak of the absorption lineshape function. It is convenient to introduce a constant, $\kappa$, representing the ratio of the peak of
the FMS line shape function and the peak of the direct absorption line shape function, given by

\[
\kappa = \max \left( -\chi_{-1} + 2\chi_0 - \chi_1 \right) / \chi_{0,0}.
\] (106)

This factor will be given by the specific condition of the experiment i.e. the pressure, the temperature and the \(v_{FMS}\) of the experiment. Although the lineshape function does not consider higher order sidebands the expression holds as long as \(J_0 > J_2\) that is for \(\beta < 1.84\).

This implies that the shot noise detection limit for Db NICE-OHMS can be written as

\[
\alpha_{SN}^D = \frac{\pi \text{ SNR}}{\kappa F J_0 J_1} \sqrt{\frac{e\Delta f}{\eta_i P_0}}.
\] (107)

At some typical conditions in the Doppler broadened regime, i.e. assuming a Doppler width \(\Gamma_D\) of 240 MHz and an FSR 380 MHz, \(\kappa\) will be 1.4. For a NICE-OHMS setup with an finesse of 50000, a modulation index of unity, an incident power of \(P_0=700\ \mu\text{W}\) impinging onto a detector with the responsivity of \(\eta_i=1\ \text{A/W}\), and a cavity length of 40 cm the shot noise limited detection limit \(\alpha_{SN}^D\) will be \(5 \times 10^{-14}\ \text{cm}^{-1}\text{Hz}^{-1/2}\).

**Detector noise**

Another type of noise often limiting the NICE-OHMS detection is detector noise. In contrast to shot noise the detector noise is not dependent on power but rather an omnipresent noise level. The detector noise level is often specified as a noise equivalent power (NEP) given in units of \(\text{W Hz}^{-1/2}\). This power represents the power of light that corresponds to the noise level for a SNR of 1. Hence, the detector noise limited detection limit for Db NICE-OHMS can be expressed as

\[
\alpha_{NEP}^D = \frac{\pi \text{ SNR NEP}}{\kappa F J_0 J_1} \Delta f^{1/2}.
\] (108)

For the same NICE-OHMS setup as above with a detector with a NEP of 30 pW \(\text{Hz}^{-1/2}\) the NEP detection limit, \(\alpha_{NEP}^D\), becomes \(1.5 \times 10^{-13}\ \text{cm}^{-1}\text{Hz}^{-1/2}\). This shows that for low optical powers the detection systems tend to be limited by detector noise while for high optical powers shot noise will dominate.
**Etalon noise and drifts**

It is also possible to calculate how big an influence an etalon of known amplitude will have on the NICE-OHMS signal with the same method used above. To estimate how etalons can affect the detection sensitivity of a NICE-OHMS setup we start from Eq. (108) and replace the NEP with the power fluctuation caused by etalons, \( \Delta P_E \), and as etalons cannot be averaged down, the bandwidth \( \Delta f^{1/2} \) is set to unity. This will result in an expression for an etalon-limited detection limit that is given by

\[
\alpha_E^{\text{Db}} L = \frac{\pi}{\kappa F} \frac{\text{SNR} \Delta P_E}{P_0}.
\]  

(109)

For an intensity fluctuation of 0.01%, i.e. a \( \Delta P_E / P_0 \) of \( 1 \times 10^{-4} \), and a NICE-OHMS setup with a cavity with a finesse of 50000, a modulation index of unity and a cavity length of 40 cm, this suggests a detection limit of \( \alpha_E^{\text{Db}} = 3 \times 10^{-10} \) cm\(^{-1}\) (under the assumption that the \( \kappa \)-factor is equivalent that given by a Db line shape i.e. 1.4).

In reality, the \( \kappa \)-factor, given by Eq. (106), will be highly dependent on the FSR of the etalon, \( \nu_{\text{FSR}} \), and the FMS modulation frequency. For etalons created between surfaces with low reflectivity, the \( \kappa \)-factor for out-of-phase NICE-OHMS signals is given by

\[
\kappa_{\text{abs}} = 2 \left| \sin(2\pi \cdot \nu_{\text{FMS}} / \nu_{\text{FSR}}) \right|,
\]  

(110)

while that for the in-phase detection signal is given by

\[
\kappa_{\text{disp}} = 4 \left| \sin^2 \left( \pi \cdot \nu_{\text{FMS}} / \nu_{\text{FSR}} \right) \right|.
\]  

(111)

The absorption-to-signal factor \( \kappa \) is plotted as a function of the ratio of the modulation frequency (\( \nu_{\text{FMS}} \)) and the etalon FSR (\( \nu_{\text{FSR}} \)) for both absorption and dispersion modes of detection in Figure 28.

For in-phase detection the \( \kappa \)-factor will take values from 0 to 4 and for out-of-phase detection from 0 to 2. For a fixed modulation frequency, and as the FSR of a etalon is a function of length, there will be distances for which (optical components) produce no FMS background signals. These are referred to as etalon immune distances (EIDs). In NICE-OHMS these distances correspond to integer numbers of the cavity length for in-phase detection and integer numbers of half cavity lengths for absorption. As NICE-OHMS is usually evaluated in dispersion phase, only the positions at integer numbers of the cavity length are in practice used as EID. The concept of (EID) has been scrutinized in detail in publication V.
Figure 28. Illustration of the EID concept. The $\kappa$-factor of etalon background signal for etalon lengths up to three cavity lengths i.e. $v_{\text{FMS}} / v_{\text{FSR}} = 3$. The black curve represents in-phase FMS detection while the red curve represents the out-of-phase detection.

As can be seen in Figure 28 the minima, for in-phase detection (black curve) are much wider than those for of the out-of-phase counter parts. Hence instrumentations implementing EIDs tend to be less affected by etalons in the dispersion than absorption mode of detection.

**Line shape fitting – General**

Retrieval of the signal strength of an analytical signal

Line shape fitting is a numerical procedure in which a model function is fitted to measurement data. A fit of a line shape function to a measured spectrum is equivalent to a wavelength filter that only accepts the predicted lineshape while rejecting other noise sources. Lineshape fitting is therefore commonly used in the most sensitive spectroscopic systems. The most common line shape fitting method is the least square fit, which is used in this work.

The fitting process performed in this work is based on the following concept. Consider a series of $N$ signals $S$. If the series of measurements is taken over a number of consecutive optical frequencies, $v_i$, the analytical signal, whose
strength is to be extracted from the total measured signal, can be expressed as

\[ S(v_i) = S_0 \overline{Z}_o(v_i) , \] (112)

where \( S_0 \) is referred to as the signal strength of the analytical signal and \( \overline{Z}_o(v_i) \) is the peak normalized analytical line shape function. Under the assumption that the model lineshape function, \( \overline{Z}(v) \), is well chosen, so it resembles the analytical line shape function, i.e. \( \overline{Z}(v_i) \approx \overline{Z}_o(v_i) \), the assessed strength of the signal, \( \hat{S} \), can be evaluated by least square fitting, i.e. by minimizing the error function

\[ F(\hat{S}) = \sum \left[ S(v_i) - \hat{S} \cdot \overline{Z}(v_i) \right]^2 . \] (113)

The minimum of this error function will be found when

\[ \frac{dF}{d\hat{S}} = \sum 2 \left[ S(v_i) - \hat{S} \cdot \overline{Z}(v_i) \right] \overline{Z}(v_i) = 0 , \] (114)

This implies that the signal strength retrieved by the fit, henceforth referred to as the fitted signal strength, can be obtained as

\[ \hat{S} = \frac{\sum S(v_i) \overline{Z}(v_i)}{\sum \overline{Z}^2(v_i)} = S_0 \frac{\sum \overline{Z}_o(v_i) \overline{Z}(v_i)}{\sum \overline{Z}_o^2(v_i)} . \] (115)

Hence if the model lineshape function matches the lineshape function of the analyte well, i.e. \( \overline{Z}(v_i) \approx \overline{Z}_o(v_i) \), the fitted signal strength, \( \hat{S} \), will be a good representative of evaluated experimental signal strength, i.e. \( S_0 \).

**In-coupling of noise**

It is possible to estimate how much noise such a fit will pick-up under some typical conditions. Consider a series of \( N \) signals, \( S \), with a standard deviation \( \sigma_S \). Under white noise limited conditions, if averaged, the standard deviation of the mean of signals is given by \( \sigma_S(N) = \sigma_S / \sqrt{N} \). If the series of measurements are taken over a series of frequencies, \( S(v_i) = S_0 \cdot \overline{Z}(v_i) \), where \( \overline{Z}(v_i) \) is the peak normalized lineshape function, one must take into consideration that the amplitude of the signal is not the same in every point. Hence, one must consider the effect a fluctuation in \( S(v_i) \) at one point \( v_i \) will have on the fitted line strength \( \hat{S} \). Since this is given by \( 1 / [dS(v_i) / d\hat{S}] \), the variance of the fitted signal can be written as
\[
\sigma^2_s(N) = \sum_{i=1}^{N} \left[ \frac{d\hat{S}}{dS(v_i)} \right]^2 \sigma^2_s, \tag{116}
\]

Moreover, since the derivative can be calculated from Eq. (115), as

\[
\frac{d\hat{S}}{dS(v_i)} = \frac{\bar{x}(v_i)}{\sum_{i=1}^{N} \bar{x}^2(v_i)}, \tag{117}
\]

this implies that the standard deviation of the fitted signal is given by

\[
\sigma_s(N) = \sqrt{\sum_{i=1}^{N} \bar{x}^2(v_i)} \sigma_s = \frac{\sigma_s}{\sqrt{N}}, \tag{118}
\]

It is here convenient to define an incoupling factor that relates the noise in the fitted signal, \(\sigma_s(N)\), to that of the signal averaged on resonance, \(\sigma_s(N)\), where the latter is given by \(\sigma_s / \sqrt{N}\), according to

\[
\varepsilon_{\text{inc}} = \frac{\sigma_s(N)}{\sigma_s(N)} = \frac{\sqrt{N}}{\sqrt{\sum_{i=1}^{N} \bar{x}^2(v_i)}} = \frac{1}{\sqrt{\left\langle x^2 \right\rangle}}, \tag{119}
\]

where \(\left\langle x^2 \right\rangle\) denotes the mean square of the lineshape function, averaged over the scan. As the RMS of a peak normalized line shape is always smaller than unity, this shows that under pure white noise limited conditions scanning will always yield a worse result than an on resonance measurement.

**In-coupling of background signals**

In most cases, the system is not limited by white noise but rather by a background signal and its drift. If this background signal is frequency dependent additional layers of modulation or filtering cannot eliminate its influence. In these cases, it is an advantage to use lineshape fitting to distinguish the analytical signal from the background signals. This is particularly the case with a frequency-dependent background signal that can drift in time, e.g. an etalon. For such a case, we will, for simplicity, assume that the background signal can be written as

\[
S(v_i, t) = S_e \cdot \bar{x}_e(v_i, t), \tag{120}
\]
where \( S_e \) is the peak signal of the etalon and \( \bar{\chi}(v_i, t) \) is its peak-normalized line shape function. Starting from Eq. (115) we find that the amount of the etalon signal that the fit will pick up can be expressed as

\[
\hat{S}_e(t) = S_e \frac{\sum \bar{\chi}(v_i, t) \bar{\chi}(v_i)}{\sum \bar{\chi}^2(v_i)}.
\] (121)

For the case with a periodical drift, i.e. a sinusoidal function that drifts over at least one period, the standard derivation will be given by

\[
\sigma_{\hat{S}_e} = \frac{S_e}{\sqrt{2}} \frac{\max \left\{ \sum \bar{\chi}_i(v_i, t) \bar{\chi}(v_i) \right\}_{\tau_{\text{app}}}}{\sum \bar{\chi}^2(v_i)},
\] (122)

where \( \max \{ f(t) \}_{\tau_{\text{app}}} \) corresponds to the maximum value taken over the time of one drift cycle.

It is once again convenient to define an in-coupling factor that relates the noise in the fitted signal to that of a signal acquired at a fixed frequency during the same drift cycle, i.e. the amplitude of the fitted signal over one drift cycle \( \max \{ \hat{S}_e(t) \}_{\tau_{\text{app}}} \) divided by the amplitude of the etalon \( S_e \),

\[
\varepsilon_e = \frac{\max \left\{ \sum \bar{\chi}_i(v_i, t) \bar{\chi}(v_i) \right\}_{\tau_{\text{app}}}}{\sum \bar{\chi}^2(v_i)} = \frac{\sigma_{\hat{S}_e}(N)}{\sigma_{S_e}(N)}.
\] (123)

**Line shape fitting in NICE-OHMS**

**In-coupling of noise and background signals as a function of scan range**

Both the incoupling of white noise and etalons are dependent on the fitted lineshape, \( \bar{\chi}(v_i) \), which, in turn, depends on the range of frequencies over which the fit is applied. For white noise limited systems, the optimum detection strategy is to stand on the peak of the lineshape so as to maximize the signal to noise ratio. For periodically drifting backgrounds, the optimum detection strategy comprises scanning over the line. The dependence of the incoupling of noise on the scanning range is scrutinized in paper IX. The optimum scanning range for some specific conditions was identified. This was used to improve on the detection sensitivity of the high finesse NICE-OHMS setup presented in paper VIII. Figure 29 displays two out of
Figure 29. Two peak-normalized Db NICE-OHMS line shape functions for in-phase i.e. dispersion detection. The red curve represents the line shape from a scan centered on the center of the transition, while the blue curve corresponds to the case when the scan is centered on one of the peaks of the profile.

Figure 30 shows a simulation of the in-coupling of white noise by Eq. (119), given by $\varepsilon_{wn}$, for the Db NICE-OHMS signals simulated in Figure 29 as a function of the scanning amplitude, $\Delta v$. As can be seen in Figure 29, for small scanning ranges of the peak centered scan (blue curve, small $\Delta v$) the incoupling factor will be close to unity. As the scan range is increased, $\varepsilon_{wn}$ increases. This is caused by the fact that the amount of analyte detected remains the same while the in-coupling of white noise increases. For the case of scans centered on the transition resonance, on the other hand, small scanning amplitudes will result in a large in-coupling of noise as the signal is zero around the center of the transition. As the scan is increased the scan picks up more of the signal and the incoupling factor decreases (improves). An optimum is reached for scans with an amplitude of 340 MHz. Thereafter, as the scan range is further increased, the in-coupling of white noise increases as parts of the scan are
Figure 30. The incoupling factor of white noise, $\varepsilon_{wn}$, as a function of scan amplitude $\Delta v$. The red curve represents the case when the scan is centered on the transition, while the blue displays the situation when the scan is centered on a peak of the NICE-OHMS signal.

made over frequency ranges in which very small amounts of the analytical signal are picked up. For amplitudes larger than 750 MHz, the in-coupling factor for transition and peak centered scans will be equivalent as the majority of the lineshape is included in both scans.

Figure 31 shows the in-coupling factor, $\varepsilon_v$, for the transition centered scan in the presence of an etalon i.e. the red curve in Figure 29 for etalons with various FSR, $v_{FSR}$, and various scanning amplitudes, $\Delta v$. The figure shows that for the majority of scans fitting will only pick up a fraction of the amplitude of the etalon signals (the yellow, the green, the blue, and the violet areas). There are some exceptions for which the fit will pick up substantial parts (and over 100%) of the etalons signal. These are seen as red areas enclosed by the black contour, some short scans (primarily those with amplitudes below 100 MHz) and for etalons with an FSR between 700-2000 MHz. For short scans the incoupling factor is basically given by the derivative of the etalon line shape function, whereby the maximum pickup will be large for large values of $\Delta v / v_{FSR}$. The region with etalons with an FSR between 700-2000 MHz represents the case where the periodicity of the etalons matches the periodicity of the NICE-OHMS line shape. Importantly, the figure also shows that there is an optimum range for scan amplitudes of 620 MHz that has a low incoupling ratio of all etalons with an FSR smaller than around 500 MHz, corresponding to optical elements.
Figure 31. The maximum fraction of an etalon signal amplitude that is picked up by a fit as the etalon drifts one full period, \( \varepsilon (\Delta v, v_{\text{FSR}}) \), given by Eq. (123), for an etalon with an FSR ranging from 10 MHz to 10 GHz for a scanning amplitude ranging from 2 MHz to 2 GHz. The color coded scale represents \( \varepsilon \) ranging from -100 dB to 20 dB. The black contour lines represent an \( \varepsilon \) of 0 dB (unity).

separated with more than 30 cm. Hence, for a NICE-OHMS system targeting the \( P_e(11) \) transition in C2H2 at 1.5316 \( \mu \)m under room temperature conditions, using a modulation frequency of 381 MHz with a modulation index \( \beta \) set to unity, and detecting the in-phase signal with all optical elements separated by more than 30 cm, the 620 MHz is an intelligent choice of scan amplitude. In fact, the Eqs. (119) and (123) can be used to evaluate the incoupling of white noise and periodical disturbances in any system utilizing lineshape fitting. Therefore, these expressions can be used to find the optimum scan range and the positioning of optics in any spectroscopic system.

For NICE-OHMS and FMS, there is the additional effect of EID to consider. As was shown above, the \( \kappa \)-factor for in-phase detection, \( \kappa_{\text{disp}} (v_{\text{FSR}}) \), given by Eq. (111), is also highly dependent on the FSR of the etalons. By multiplying this with the etalon in-coupling factor, \( \kappa_{\text{disp}} (v_{\text{FSR}}) \cdot \varepsilon (\Delta v, v_{\text{FSR}}) \), it is possible to assess the maximum fraction of an etalon amplitude that is picked up by a NICE-OHMS fit. This thus represents the fraction of the power fluctuation originating from the etalon that is picked up by the fitting routine. The fraction of the amplitude of an etalon that is picked up by a fit as the etalon drifts one full period is displayed in Figure 32. While Figure 31 represents the in-coupling into \( \hat{S} \) of an etalon with given signal amplitude, Figure 32
Figure 32. The maximum fraction of an etalon’s amplitude that is picked up by a fit as the etalon drifts one full period, \( \kappa_{disp}(\nu_{FSR}) \cdot \varepsilon(\Delta \nu, \nu_{FSR}) \), given by Eq. (111) and Eq. (123), for an etalon with a FSR ranging from 10 MHz to 10 GHz for a scanning amplitude ranging from 2 MHz to 2 GHz. The color-coded scale represents \( \varepsilon \) ranging from -100 dB (dark violet) to 20 dB (red). The black contour lines represent an \( \varepsilon \) of 0 dB (unity).

represents the in-coupling of an etalon created between two surfaces with a given reflectivity. A comparison with Figure 31 shows that there are additional horizontal minima, corresponding to the EID:s. Furthermore, for the largest FSRs, i.e. for etalons from optical components separated with the shortest distances, there is also a visible reduction in incoupling amplitude.
Experimental Details

NICE-OHMS

As is shown by the publications, in this work a number of realizations of NICE-OHMS have been implemented and optimized, primarily for ultra-sensitive trace gas detection. Furthermore, setups have been developed for assessment of gas number density, aiming at developing new calibration methods for gas leaks.

As the development of these techniques has taken place continuously during my involvement in this project, I will not describe all variations of the setup in this section but rather concentrate on the current status of some of the setups. Some experimental realizations not presented here but worth mentioning are the DFB-NICE-OHMS setup, which was used for lineshape studies (publications XIV, XV, XVI, and XVII), and the NICE-OHMS system that incorporated an optical circulator (paper IV).

Fiber-laser-based NICE-OHMS

The fiber-laser based NICE-OHMS setup has been the most important system for the development of Db NICE-OHMS. The system has been used in a variety of studies which resulted in 9 publications before I joined the group [28, 52, 62-65], and in 8 publications during my time in the group (I, II, III, V, VII, VIII, IX, and XI). The success of the system can to a large extent be attributed to the erbium-doped fiber-laser (EDFL, Koheras Adjustik E15), whose narrow linewidth and low noise resulted in a stable laser lock. This enabled a variety of investigations and further development of the system. A schematic illustration of the current status of the setup can be seen in Figure 33.

Light from an Er-doped fiber laser (EDFL, Koheras Adjustik E15), tunable from 1530.8 to 1531.8 nm, is sent through a fiber coupled acousto-optic modulator (AOM, AA Opto-Electronic, MT110-IR25-3FIO), whose first order output, shifted by 110 MHz, is fed to a fiber coupled electro optic modulator (EOM, General Photonics, LPM-001-15), the latter with a proton exchange waveguide to avoid residual amplitude modulation (RAM). The temperature of the EOM is stabilized using a Peltier element and a temperature controller (Thorlabs, TED200C). After the EOM, the light is coupled into free space and sent through a polarizer, a half-wave plate ($\lambda/2$), a polarizing beam splitter (PBS), a mode matching lens, and a quarter-wave plate ($\lambda/4$) before impinging on the cavity. The cavity spacer is made from Zerodur and the mirrors are mounted on cylindrical piezo-electric transducers (PZT) for
Figure 33. Schematic illustration of fiber-laser-based NICE-OHMS. Light produced in a Er-doped fiber laser (1.531 μm, blue) is sent through an AOM whose first order output is modulated in an EOM before it is coupled into free space. The light beam sent through a polarizer (P), a half-wave plate (λ/2), a polarizing beam splitter (PBS), a mode matching lens (L), and a quarter-wave plate (λ/4) before impinging on the cavity.

tuning of the FSR. The cavity has a finesse of 50,000 and an FSR of 381 MHz. To avoid mode coupling to higher order transverse cavity modes a 5 mm pinhole is placed inside the cavity. The back reflected light from the cavity is redirected by the PBS and focused by a lens onto a large bandwidth photo-detector (New Focus, 1611). The same type of detector is also used to monitor the light transmitted through the cavity, which carries the NICE-OHMS signal. The light is focused onto the detector by an off-axis parabolic mirror. To minimize the effect of etalons, as many as possible of the optical components were placed at EIDs [V].

To create sidebands for the Pound-Drever-Hall (PDH) locking and the FMS the EOM is simultaneously modulated at 20 and 381 MHz. This also enabled locking of the FMS modulation frequency to the FSR of the cavity by the DeVoe-Brewer (DVB) technique. To maximize the signal, the modulation index for the FMS is set to unity. The PDH and DVB error signals are created by demodulating the back reflected light at 20 and 361 MHz, respectively. The slow components (< 100 Hz) of the PDH error signal are sent through custom made electronics to the fiber laser PZT, while the fast components (> 100 Hz) are fed through a commercial PID controller (Toptica, FALC 110) to a 110 MHz voltage controlled oscillator (VCO) driving the AOM. The error
signal for the DVB locking of the FSR are sent to a 381 MHz VCO to lock the modulation frequency to the cavity FSR. The Db NICE-OHMS signal is in turn obtained by demodulating the transmitted light at 381 MHz.

The cavity is connected to a vacuum system, which allows changes of the amount of gas in the chamber as well as continuous measurement of the pressure inside the cavity by the use of a pressure gauge (Oerlikon Leybold Vacuum, Ceravac CTR91-1Torr).

**Optical parametric oscillator based NICE-OHMS**

While the fiber-laser based NICE-OHMS setup shows remarkable sensitivity the number of species it can address is limited by its restricted wavelength range, for the particular laser we have: 1530.8nm to 1531.8nm. For practical trace gas detection, both the tuning range of 1 nm and the center wavelength, which is in the near-IR region, is a problem. The tuning range limits the number of species that can be addressed with the same laser and the strength of the transitions in the near-IR wavelength range limits the sensitivity. Since there are a huge number of molecular constituents that have their strongest vibrational transitions in the mid-IR range it is beneficial to detect these in this wavelength range. One large group of importance is the hydrocarbons, as the wavelength region between 3.0 and 3.7 μm contains the stretching frequencies of molecules containing carbon-hydrogen bonds. A well-optimized NICE-OHMS system targeting this wavelength has the potential to detect a huge number of species with unprecedented accuracy.

To target this range, we have developed a NICE-OHMS system based on an optical parametric oscillator (OPO). This setup has so far resulted in two publications XII and XIII. A schematic illustration of the current status of the setup (as was used for paper XIII) can be seen in Figure 34.

Light from a seed laser, lasing at 1.064 μm, (NKT Photonics, Koheras Adjustik Y-10), is sent through a fiber coupled acousto-optic modulator (AOM, AA Opto-Electronic, MT110-B14-IR20-Fio-PMo), whose first order output, shifted by 110 MHz, is fed to a fiber coupled electro optic modulator (EOM, Photline, NIR-MPX-LN-05). Thereafter, the light is amplified by a fiber amplifier (IPG Photonics, YAR-10 K-1064-LP-SF) before it is used as the pump for the OPO (Aculight, Argos 2400 SF, module C).

The light that is produced in the seed laser (1.064 μm, blue) is modulated in an EOM before it is sent into the OPO. The OPO signal output (1.46 - 1.60 μm, green) is sent into a wave meter while the idler (3.2 - 3.9 μm, red) goes to the cavity, both attenuated by beam samplers with a reflectance of 1%.
Figure 34. Schematic illustration of the OPO based NICE-OHMS incorporating an AOM. Light produced in a seed laser (1.064 μm, blue) is sent through an AOM whose first order output is modulated in an EOM before it is sent through a fiber amplifier and into an OPO. The OPO signal output (1.46 - 1.60 μm, green) is sent into a wave meter while the idler (3.2 - 3.9 μm, red) goes to the cavity, both attenuated by beam samplers with a reflectance of 1%.

Since an OPO produces mid-IR light by a non-linear process (i.e. according to $\omega_{\text{pump}} = \omega_{\text{signal}} + \omega_{\text{idler}}$) and the signal is locked to a mode of its cavity, any minor change in the frequency of the pump will be transferred to the idler frequency. The result will be that any sidebands existing in the pump will be transferred into the idler.

The OPO signal output (1.46-1.60 μm) is split by the use of an uncoated 4º wedge (Thorlabs, PS811) and the small fraction reflected off its 1st surface is directed into a fiber-coupled wave meter (Burleigh, WA-1500-NIR-89). The wave meter can alternatively be connected to the monitor output of the seed laser to measure its frequency. The difference between these gives the frequency of the idler.

The OPO idler output (3.2-3.9 μm) is attenuated to ca. 50 mW by the use of an additional prism (Thorlabs, PS862). The unused parts of the signal and idler outputs, as well as the transmitted part of the pump beam, are sent into beam dumps. The idler is then sent into a closed plano-concave cavity with an FSR of 380 MHz. The cavity spacer is made from low-thermal expansion Zerodur and cylindrical piezo-electric transducers (PZT) for FSR tuning. The
mirrors were made on zinc selenide substrates (LohnStar), providing a finesse of 4000. The radius of the curved mirror was 1 m. Both the back reflected and the transmitted beams are sampled using a beam sampler with 1% reflectance (Meller Optics, SCD1553-01B). This has the advantages that the power is reduced below the saturation power of the detectors and that the etalons created between any cavity mirror and the detectors are reduced. Both the transmitted and the back reflected beams were monitored by fast detectors with a bandwidth close to that of the modulation frequency (~370 MHz, Vigo, PVI-4TE-8-1x1).

To generate sidebands for the PDH locking and the FM detection, the EOM is simultaneously modulated at 20 and 380 MHz. This also enables locking of the FM-modulation frequency to the FSR of the cavity by the DeVoe-Brewer method at 360 MHz [9]. The modulation index of the 380 MHz modulation was set to unity. As proton exchanged EOMs do not produce residual amplitude modulation (RAM) the triplets produced in the EOM are balanced.

The PDH and FSR error signals are generated by demodulating the back reflected light at 20 and 360 MHz respectively. The PDH error signal is sent through servo electronics, which, in turn, send the slow components (< 100 Hz) to the seed fiber laser, while the fast components (> 100 Hz) are fed through a separate servo to a 110 MHz voltage controlled oscillator (VCO) driving the AOM. The DVB error signal is sent to VCO driving the EOM to produce a modulation frequency that matches the FSR of the cavity. The NICE-OHMS signal is produced by demodulating the transmitted signal with the VCO frequency in an in-quadrature (IQ) mixer that gives rise to two in-quadrature signals.

**Optical measurement of the gas number density**

**Assessments using a single Fabry-Perot cavity and an optical frequency comb**

The refractometer setup used for assessing the gas number density utilizes the same locking electronics and vacuum system as the fiber-laser based NICE-OHMS setup. The system incorporated a new cavity with no PZTs for higher stability and an optical frequency comb to measure the frequency of the laser.

The experimental setup is illustrated in Figure 35. The light from a narrow linewidth Er:fiber laser (Koheras, Adjustik E15) is sent through a fiber coupled acousto-optic modulator (AOM, AA Opto-Electronic, MT110-IR25-
Figure 35. Schematic illustration of the instrumentation used for assessment of the gas number density using a Fabry-Perot etalon to which a narrow line width fiber laser is locked. The laser frequency is monitored with an optical frequency comb. Blue lines: optical fibers; red lines: free-space light paths; black lines: wires; OFC: MenloSystems FC-1500-250-WG; Fq (frequency) Counter: Agilent 53230A; EDFL: Koheras Adjustik E15; AOM: AA Opto-Electronic, MT110-IR25-3FIO; EOM: General Photonics, LPM- 001-15; P: polarizer; λ/2: half-wave plate; L: lens; PBS: polarizing beam splitter cube; λ/4: quarter-wave plate.

3FIO), whose first order output, shifted by 110 MHz, is fed to a 90/10 PM-fiber beam splitter. The larger fraction of the light from the beam splitter is combined with light from the optical frequency comb (OFC) (MenloSystems FC-1500-250-WG) to produce a beat note that can be measured with a large bandwidth photo-detector (New Focus, 1611). By band pass filtering the detected signal the frequency corresponding to the beating between the laser and the OFC can then be extracted and measured with a frequency counter (Agilent 53230A).

The smaller fraction from the beam splitter is sent to a fiber coupled electro optic modulator (EOM, General Photonics, LPM-001-15), the latter with a proton exchanged waveguide to avoid residual amplitude modulation (RAM) [I,II]. After the EOM, the light is coupled into free space and sent through a polarizer, a half-wave plate (λ/2), a polarizing beam splitter (PBS), a mode matching lens, and a quarter-wave plate (λ/4) before impinging on the
cavity. The cavity spacer is made from Zerodur onto which the mirrors are directly glued to produce in a cavity with a finesse of 7400 and a free spectral range of 428 MHz. The back reflected light from the cavity is redirected by the PBS and focused by a lens onto a large bandwidth photo-detector (New Focus, 1611).

To create sidebands for the Pound-Drever-Hall (PDH) locking the EOM is modulated at 20 MHz. The PDH error signals is created by demodulating the back reflected light at 20 MHz. The slow components (< 100 Hz) of the PDH error signal are sent through custom made electronics to the fiber laser PZT, while the fast components (> 100 Hz) are fed through a commercial PID controller (Toptica, FALC 110) to a 110 MHz voltage controlled oscillator (VCO) driving the AOM.

The repetition rate and the carrier envelope offset frequency of the comb are stabilized to a GPS referenced rubidium oscillator (Symmetricom, TSC4410A), and the values of the two parameters are chosen so that the frequency of the beat note between the cw laser and the nearest comb line is around 60 MHz, i.e. the center of the band pass filter. The number of the closest comb line is determined by measuring the frequency of the cw laser with a wavemeter (Burleigh, WA-1500), which provides 30 MHz resolution.

The cavity is connected to a vacuum system, which allows changes of the amount of gas in the chamber as well as continuous measurement of the pressure inside the cavity by the use of a pressure gauge (Oerlikon Leybold Vacuum, Ceravac CTR91-1Torr)

**Assessment using a dual Fabry-Perot cavity**

The system utilizing a single Fabry-Perot cavity together with an OFC presented in the previous section was found to be limited by the GPS referenced rubidium oscillator for short time scales and thermal drifts for longer. In an attempt to improve on both of these a new dual Fabry-Perot cavity was designed. The two cavities were bored in a common Zerodure spacer to lessen common mode thermal drift.

The experimental setup as illustrated in Figure 36 consists of two laser systems locked to the two cavities with the same method as used for gas number density measurements with a single cavity and fiber-laser based NICE-OHMS i.e. two narrow linewidth Er:fiber lasers (Koheras, Adjustik E15) with a fiber coupled acousto-optic modulators (AOM, AA Opto-Electronic, MT110-IR25-3FIO). These laser systems are locked to the measurement cavity and the reference cavity. A fraction of the light from each arm is split off and combined to produce a beat note that can be detected with a large bandwidth photo-detector (New Focus, 1611) and then
Figure 36. Schematic illustration of instrumentation for assessments of gas number density based on a dual Fabry-Perot cavity. Blue lines: optical fibers; red lines: free-space light paths; black lines: wires; Fq (frequency) Counter: Agilent 53230A; EDFL: Koheras Adjustik E15; AOM: AA Opto-Electronic, MT110-IR25-3FI; EOM: General Photonics, LPM-001-15; P: polarizer; λ/2: half-wave plate; L: lens; PBS: polarizing beam splitter cube; λ/4: quarter-wave plate.

measured with a frequency counter (Agilent 53230A). This enables the measurement of the frequency difference between a cavity mode of the reference cavity and a mode of the measurement cavity.
Pushing the detection limits

NICE-OHMS

Development of fiber laser based Db NICE-OHMS

When I joined the Laser Physics Group in the autumn of 2010 the NICE-OHMS project had been running for some years with the first papers focusing on Db-NICE-OMS published in 2007 [28, 62]. The system sensitivity was at this point at \(8 \times 10^{-11}\) cm\(^{-1}\) over 0.7 s, but had not been analyzed with Allan-Werle plots. The first time this was used was for sD NICE-OHMS in 2008 [52]. The limiting factor at this point was known to be in-coupling of noise due to an unbalancing of the triplet, which led to compromised noise immunity. The source for this unbalancing was known to be RAM from the fiber coupled EOM:s used in the setup.

To remedy this, we studied the phenomenon of RAM originating from EOMs in some detail and found that it stems from cross coupling between the birefringent axes in the EOM. To reduce the RAM from the EOM two separate approaches were tried. Firstly, an EOM incorporating a proton exchange waveguide was used instead of the normally used EOMs with Ti:diffused waveguides. As the former type of waveguide does not support propagation along the secondary axis no RAM will be produced in such EOMs. Secondly, by applying simultaneous temperature and voltage feedback to the EOM with a Ti:diffused waveguide the phases between the two birefringent axes could be kept constant, eliminating the RAM. Furthermore, as active feedback is applied also other background signals can be reduced by such an approach.

This work resulted in two publications, first one experimental paper [I] and soon thereafter a supporting theoretical description [II]. The experimental paper demonstrated a detection sensitivity (a NEAC) of \(9 \times 10^{-12}\) cm\(^{-1}\) over 100 s for an EOM with a proton exchange waveguide, and \(3.2 \times 10^{-12}\) cm\(^{-1}\) over 60 s for EOM with a Ti:diffused waveguide together with feedback. By simply using an EOM with a proton exchange waveguide the detection limit could thus be improved one order of magnitude. A further improvement by a factor of around 3 could be achieved by applying active feedback to the EOM with a Ti:diffused waveguide. This additional reduction was contributed to subtraction of omnipresent etalons.

After the completion of these projects the setups were disassembled and moved to other premises due to the renovation of the physics building. In Figure 37 one can see the setup a few weeks before it was moved to the
Figure 37. The fiber based NICE-OHMS setup in August 2010 before the move. The table is non-floating. Hence vibrations from the floor affect measurements. The plastic cover is used to reduce thermal fluctuations during operation.

temporary labs. The plastic cover is an early attempt to reduce environmental fluctuations mainly from air conditioning. Note that the rest of the lab equipment was already packed down at this point.

At the time of the move, we did a major overhaul of the fiber laser setup; we improved the mechanical insulation, upgraded the vacuum system, improved signal wiring and implemented an AOM for improved laser locking. Figure 38 shows a picture of the setup after the upgrades. In the center of the picture one can see the optical cavity with a Zerodur spacer. The setup is now placed on a separate optical table inserted in a Lexan box for additional environmental insulation. This dual-optical table setup was designed to reduce acoustic noise and thermal drifts of the setup. The vacuum system was rebuilt with high grade CF-flanges instead of previously used KF-flanges to decrease drifts of signal due to drifting pressure in the cavity. Additionally, the rough vacuum pump was placed outside the lab reducing acoustic noise in the lab.

The setup used an EOM with a proton exchanged waveguide, which in the old lab achieved a detection limit of $9 \times 10^{-12} \text{ cm}^{-1}$ over 100 s. The additional thermal and mechanical insulation resulted in an improvement of the detection limit to $4 \times 10^{-12} \text{ cm}^{-1}$ over 70 s. When an AOM was added to improve on the laser lock the detection limit was further improved to $1.8 \times 10^{-12} \text{ cm}^{-1}$ over 20 s. Hence, the environmental insulation in combination
with the AOM locking pushed the detection limit down a factor of 4. This work was described in some detail in a publication in 2012 [III].

Figure 39 shows a comparison between the Allan Werle plots from these realizations. The black, blue and magenta curves all represent measurement series with an EOM incorporating a proton exchange (PE) waveguide. The red curve represents a measurement using an EOM based on a Ti:diffused waveguide together with an active feedback. The black and red curves are recorded in the old lab with no additional environmental insulation. The blue and magenta lines are measured in the new lab with additional environmental insulation and, for the latter, with an improved laser locking obtained by the AOM.

At this point we tried to implement the same active EOM feedback that was used in publication [I]. While the implementation was successful in the old lab, before the implementation of the AOM, this did not improve the detection limit in the new lab, when the laser was additionally stabilized by the AOM. One plausible explanation for this is that, in the case of a poor laser lock, applying feedback to the EOM will provide an improvement as the noise immunity will be improved. At the instance of a good laser lock, as is the case when the AOM is implemented, there will be no such improvement as the incoupling of transmission intensity noise is not the dominating source of noise. Instead, as the feedback signal is produced by implementing
Figure 39. Allan Werle plot of the different realizations; in black proton exchanged (PE) EOM, in blue PE-EOM with improved insulation, in red Ti:diffused EOM with feedback, and magenta PE-EOM + improved insulation and AOM laser lock.

an additional FM demodulation circuit before the cavity, all uncorrelated noise (e.g. white noise) will be summed. Before this could be fully investigated the lab was disassembled again and moved back to the renovated labs in the old building.

To save time, as the setup was disassembled after the move, the first project to be run in the new lab was the realization of a NICE-OHMS instrumentation implementing an optical circulator. By implementing such a device a number of free space optical components could be eliminated. Figure 40 shows a picture of the setup incorporating the fiber circulator in the refurbished lab. It can clearly be seen that the number of optical components needed for fiber circulator NICE-OHMS is significantly lower than for the normal realization (as, e.g., is shown in Figure 38). The result was a significantly less complicated setup, although with a slightly reduced detection sensitivity (from 3 to $7 \times 10^{-12}$ cm$^{-1}$ Hz$^{-1/2}$) [IV].

The original setup was finally reassembled in the fall 2012, to perform an extensive investigation of the EID concept which previously already had been implemented into our setups (first appearance in publication [I]). This project resulted in publication [V]. By moving the transmission detector and hence altering the length of the etalon produced between the rear cavity mirror and the detector it was possible to reproduce the predicted response displayed in Figure 28. While the concept of eliminating etalons by choosing
Figure 40. The fiber based NICE-OHMS setup incorporating a fiber circulator (photo taken in May 2012 after the move back to the old but refurbished labs). The number of free space optical components need is significantly reduced. In the refurbished lab the setup is placed in its own temperature stabilized room.

an appropriate modulation frequency in FMS was known [66], this was the first paper expanding the concept to systems in which the modulation frequency cannot be freely chosen. This was achieved by instead placing the optical components at distances so as to reduce the influences of etalons in NICE-OHMS, referred to as at etalon-immune-distances (EIDs).

The next project aimed at improving the detection sensitivity of NICE-OHMS was initialized in the beginning of 2014. As the peak signal strength of NICE-OHMS based on a triplet is proportional to \( J_0(\beta)J_1(\beta) \), it was predicted that the signal strength could be enlarged by increasing the modulation index. However, it was also realized that for higher modulation indices, the light can no longer be seen as a triplet. A theoretical description for Db NICE-OHMS performed by light modulated to consist of several pairs of sidebands was therefore derived. Experiments showed that by increasing the modulation from the previously used value of 0.4 to 1.0 could increase the signal strength and improve on the detection limit. To set the modulation index, a variable amplifier was inserted between the VCO providing the FMS modulation frequency and the EOM. This work resulted in two publications, one comprising the theoretical description [VI], which presented the optimum modulating frequencies, indices and demodulation phases for different pressure conditions, and one providing the experimental verification [VII]. The experimental work showed only a small improvement of the detection limit from previous work [III], from \( 1.8 \) to \( 1.7 \times 10^{-12} \, \text{cm}^{-1} \) over 20 s and, for white noise limited conditions, from \( 5.6 \) to \( 4.9 \times 10^{-12} \).
cm$^{-1}$Hz$^{-1/2}$. This rather poor improvement was attributed to the higher amounts of environmental noise, and drifts in the new lab. However, the concept was validated by comparative measurements with the same setup showing white noise levels for $\beta$ of 0.4 and 1, as $7.3 \times 10^{-12}$ cm$^{-1}$Hz$^{-1/2}$, respectively.

To make a significant improvement of the system we decided in the autumn of 2014 to increase the finesse of our cavity from 5 200 to 50 000. Figure 41 displays a picture of the setup where the 50 000 finesse cavity has been implemented, taken in July 2015, 3 years after the move into the refurbished labs.

![Figure 41. The fiber based NICE-OHMS setup as it looked in July 2015. The additional environmental insulation, i.e. two-layer air-suspended optical table in a Lexan enclosure, is used also for gas number density measurements in publications [XVIII, XIX].](image)

The expected improvement of this was almost one order of magnitude, given by the ratio of the finesse values. However, after ordering higher reflectivity mirrors and realizing such a system twice (the first batch of mirrors were defective) we found that “sparks” appeared in the transmission signal. These were found to originate from coupling of light into higher order transverse modes through scattering from the cavity mirrors. The problem could be alleviated by inserting a pinhole in the cavity. By this all higher order transverse modes, which have a spatial extension that is larger than the size of the pinhole could be eliminated. Figure 42 displays two cavity enhanced direct absorption measurements; one with no pinhole inserted (black) and one with pinhole in cavity, offset with 0.4 V for clarity, red.
Figure 42. Cavity-enhanced direct absorption signals from 10 ppm of C\textsubscript{2}H\textsubscript{2} in N\textsubscript{2} at a pressure of 1 Torr targeting the P\textsubscript{e}(11) transition at 1.5316 \(\mu\)m. The lower and upper curves represent the transmitted intensity without and with a pinhole inserted in the cavity. The upper curve is offset by 0.4 V for clarity.

This work resulted in a publication that reported on these issues and presented an improved detection limit, reported as \(2.2 \times 10^{-13}\) cm\(^{-1}\) over 5 s [VIII]. The improvement in the white-noise-limited NEAC from the 5200 to 50000 finesse cavities was found to be from 49 to \(3.9 \times 10^{-13}\) cm\(^{-1}\) Hz\(^{-1/2}\), respectively. This shows that the white-noise-limited NEAC for the high finesse cavity system was a factor of 12.5 lower than that of the low-finesse system. This exceeded the expected improvement of 9 (given by the ratio of the finesse values) with 40%. This was contributed to filtering of fast frequency fluctuations by the increased cavity finesse. However, the improvement of the optimum NEAC (i.e. the lowest point of the Allan-Werle plot) was significantly less from \(1.7 \times 10^{-12}\) cm\(^{-1}\) over 20 s to \(2.2 \times 10^{-13}\) cm\(^{-1}\) over 5 s. While this manuscript was peer-reviewed a project dealing with the in-coupling of noise and background signals through lineshape fitting was pursued. The work addressed specifically the question whether there is any optimum length of a scan when line shape fitting is performed, and if so, how this optimum scan length should be found. This project resulted in a publication containing the theoretical description of the in-coupling processes, a method to optimize the data acquisition (basically how to choose the optimum scanning range), and an experimental verification [IX].

In Figure 43 the experimental results of different improvements are presented in the form of Allan-Werle plots. In addition to identifying the
optimum scanning conditions, this work encompassed two major
instrumentational developments that improved on the performance of the
system. Firstly, temperature stabilization was added to the EOM to stabilize
the remaining background (associated with internal reflection). Secondly,
the focusing lens for the transmission detector was replaced with an off-axis
parabolic mirror to reduce etalons produced between the detector and the
lens. Finally, following the theoretical estimates given in the paper, the scan
range was reduced to increase the time spent on the signal, effectively
increasing the signal strength. This resulted in the lowest ever recorded
detection limit for Db NICE-OHMS, i.e. $9 \times 10^{-14}$ cm$^{-1}$ over 20 s, and a
white-noise-limited NEAC of $2.6 \times 10^{-13}$ cm$^{-1}$ Hz$^{-1/2}$ [IX], shows by the
magenta curve in Figure 43.

Simultaneously with this development other realizations of Db NICE-OHMS
have been published by other groups. A few systems based on a few other
types of lasers and targeting other wavelength regions have been realized.
Table 2 presents a compilation of the different realizations of Doppler
broadened NICE-OHMS. Note that the table does not contain all
publications, only those reporting on a new system or an improved
detectability.
Table 2. The development of Doppler broadened NICE-OHMS over the years. The compilation comprises publishing year, cavity parameters, type of laser described in terms of a working wavelength, species addressed, and the detection sensitivity obtained, both in terms of a minimum absorption coefficient, $\alpha_0$, and white-noise limited detection sensitivity, NEAC. No sub-Doppler realizations are included in this compilation.

Figure 44 displays the data from Table 2 organized by year. The type of symbol indicates the type of laser used. Read markers represent publications from the Laser Physics Group at Umeå University. One can clearly see that during the last 5 years we have established ourselves as the leading group regarding the further development of Db NICE-OHMS.

Regarding, trace gas detection, Db NICE-OHMS and CRDS are generally considered the most sensitive methods. The presently most sensitive CRDS setup is based on a cavity with a finesse of 450 000 and has reported a NEAL of $3 \times 10^{-12}$ cm$^{-1}$ Hz$^{-1/2}$ and $1.4 \times 10^{-13}$ cm$^{-1}$ [21], where the latter number is in parity with the best NICE-OHMS value, which is $9 \times 10^{-14}$ cm$^{-1}$ over 20 s [IX]. Note, however, that NICE-OHMS can demonstrate a white-noise limited detection sensitivity (i.e. a NEAC or NEAL) that is one order of magnitude better than that of CRDS; $2.6 \times 10^{-13}$ vs. $3 \times 10^{-12}$ cm$^{-1}$ Hz$^{-1/2}$. Hence, we can state that we are also one of the leading groups in development of techniques for ultra-sensitive laser based trace gas detection in general.

Moore’s law states that "the number of transistors in a dense integrated circuit has doubled approximately every two years". As a result computing power has also doubled every two year as well. While the rate of development of computers is impressive the rate of development of
Figure 44. The development of Doppler broadened NICE-OHMS (Data taken from Table 2). The y-axis represents the detection limit in cm⁻¹ (i.e. α₀) while the x-axis denotes the year of publication. Read colored markers represent publications by the group at Umeå University. The dashed line represents an improvement of the detection limit with a factor of two per year.

Db NICE-OHMS as seen in Figure 44 has beaten that of Moore’s law by an improvement of a factor of 2 every year since 2004. If this speed of development is maintained the detection limit will be approximately 1 × 10⁻¹⁶ cm⁻¹, in ten years, which would open up for a number of interesting applications.

**Development of OPO based Db NICE-OHMS**

While the fiber-laser based NICE-OHMS setup shows remarkable sensitivity, the number of species it can address is limited by its wavelength range. For trace gas detection both the limited tuning range of 1 nm of each individual laser and the restricted availability of center wavelength in the near-IR (NIR) constitute a problem. The restricted tuning range limits the number of species that can be addressed with a given laser while center wavelengths solely in the NIR range, in which most molecules only have weak overtone transitions, limits the sensitivity. Since there are a huge number of molecular constituents that have their strongest vibrational transitions in the mid-IR (MIR) range it is beneficial to detect these at this wavelength. One large group of importance is the hydrocarbons, as the wavelength region between 3.0 and 3.7 μm contains the stretching frequencies of molecules containing
carbon-hydrogen bonds. A NICE-OHMS system targeting this wavelength has the potential to detect a huge number of species with unprecedented accuracy.

After investigating and rejecting the possibility to construct NICE-OHMS around a quantum cascade (QC) laser operating at these wavelengths in 2011, the possibility to construct NICE-OHMS around an Optical Parametric Oscillator (OPO) was investigated and found possible in early 2012. In the spring 2012 we moved back to our new renovated labs and at this point, we decided to not re-assemble the DFB-laser based system used for lineshape studies, presented in publications [XIV-XVII]. Hence from an empty table we initialized a project aimed at developing NICE-OHMS instrumentation for the MIR range based on an OPO.

This first realization was built around a cavity with a finesse of 500. It was demonstrated, in a publication submitted in November 2014, that this system could reach a detection sensitivity of methane of $1.5 \times 10^{-9} \text{ cm}^{-1}$ over 20 s [XII]. The corresponding Allan Werle plot, showing both the in- and out-of-phase response, is displayed in Figure 45.

![Figure 45. Allan Werle plot of the Allan deviation of the first realization of an OPO-based NICE-OHMS system [XII]. The black curve represents in-phase signals while the red displays out-of-phase signals, both evaluated by lineshape fitting.](image)

This result was comparable to that of Crabtree et al. in which ions were detected with an additional level of modulation, producing velocity modulated NICE-OHMS [31].
To improve on this we decided to implement a 4000 finesse cavity into our system. As the laser lock that was used in this first work was not sufficient to lock the laser to such a cavity we also needed to add an AOM to the locking scheme, similar to what was previously done on the fiber setup [IV]. An AOM (AA Opto-Electronic, MT110-B14-IR20-Fio-PM0) was hence inserted between the seed laser and the EOM to increase the bandwidth of the laser feedback. Figure 46 shows a picture of the OPO based NICE-OHMS when the AOM locking had been incorporated.

Figure 46. The OPO based NICE-OHMS setup incorporating AOM locking in June of 2015. The wavemeter seen in the bottom right of the picture is used to measure the wavelength of the seed laser and the signals beam of the OPO.

After extensive optimization of the electronics, this resulted in a system with a reported sensitivity of $1.3 \times 10^{-10}$ cm$^{-1}$ over 20 s [XIII]. This is an improvement of one order of magnitude from the original MIR-NICE-OHMS system incorporating the 500 finesse cavity. As the system is limited by etalons in the fiber amplifier, and not by the cavity lock, this is the improvement expected.

Figure 47 shows a calibration measurement from the OPO-NICE-OHMS system from that work. The measurement targeted the F2 - F1 transition in the R(6) manifold of the $v_2 + v_4$ band of CH$_4$ at 3.3928 µm. The point of calibration, made by the use of a reference gas with 45 ppm CH$_4$ in N$_2$ at 1 Torr, is specifically marked. The linearity of the system was checked by comparing fitted line strengths from measurement targeting the same line at pressures between 7 mTorr and 90 Torr and calculated absorption. The precision of the lowest points in this range were limited by outgassing and leaks in the vacuum system. Furthermore, for high pressures the weak cavity
Figure 47. Assessment of the dynamic range of the OPO-NICE-OHMS system expressed as the measured absorption as a function of the estimated absorption, both in units of \( \text{cm}^{-1} \). Blue dots represent measurements fitted with full theory (strong absorption) [X, XI], while red dots represent the conventional NICE-OHMS theory.

absorption condition, \( \alpha_0 L \ll \pi / F \), is not fulfilled. Hence, the full formalism, recently developed by our research group [X, XI] was implemented to demonstrate assessments of CH\(_4\) concentrations that range over 4 orders of magnitude.

Optical measurement of the gas number density

A discussion about the use of cavities and laser locking for purposes other than for gas assessment, molecular spectroscopy, and frequency standards, with Martin Zelan from SP Technical Research Institute of Sweden, Borås, was started in June 2012. They had, at that time, started a project aiming at locking a laser to a Fabry-Perot cavity. It was known that by measuring the frequency of a laser mode locked to a cavity mode the index of refraction, and hence the density of the gas inside the cavity, can be assessed with an unprecedented accuracy. We also realized that the Laser Physics Group in Umeå had the competence and equipment needed to perform such experiments while SP possessed the knowledge of other techniques and methods used in the field. Collaboration between SP and the Laser Physics
Group was then initialized with the aim of developing a system for calibration of test-leaks.

This collaboration resulted in a first paper in the fall of 2013, where a system measuring the gas number density by the frequency difference between a laser locked to a cavity and an OFC was presented [XVIII]. This work demonstrated that the gas number density could be assessed with a resolution of $1.4 \times 10^{-6}$ mol m$^{-3}$. The system was found to be limited by the GPS referenced rubidium oscillator for short time scales and thermal drifts for longer time scales.

In an attempt to improve on both of these limitations, a new dual Fabry-Perot cavity was designed. The two cavities were made with a common Zerodure spacer to lessen common mode thermal drift. These results are presented in a paper that presently is in manuscript form, sent out to a pre-review of collaborators in an ongoing EMPIR-project [XIX].

In Figure 48 the resulting Allan deviations from the beat frequency between the OFC and a laser locked to the measurement cavity (red) and the beat frequency between a laser locked to the reference cavity and the measurement cavity can be seen.

The data shows that the minimum Allan deviation for the two systems were found at 5 s and 150 ms, corresponding to a deviation of 900 and 50 Hz, for the single and double cavity systems, respectively. As the frequency of the laser is $2 \times 10^{14}$ Hz, these accuracies correspond to a relative change in index of refraction of $4.5 \times 10^{-12}$ and $2.5 \times 10^{-13}$, respectively. Taking into account the index of refraction of air calculated by Eq. (66) at 1.5 µm, which is 1.00024, and the density of air, which is 1.25 kg/m$^3$, this indicates that it is possible to detect a change of the density of air 1 µg/m$^3$ ($1 \times 10^{-9}$ kg/m$^3$).

The data from the single cavity measurement, shown by the red curve in Figure 48, were recorded during the night under a period of low cavity drifts, while the double cavity measurement, shown by the black line in Figure 48, was taken during day time, with the systems temperature still stabilizing. The drift tendencies for both systems are shown by the dashed lines. The data shows that the double (black curve) cavity experiences normal drifts, which have a $f^{-3}$ dependence, corresponding to a fractional length change of $3 \times 10^{-13}$ s$^{-1}$ while the single cavity system exhibits Brownian noise tendencies, i.e. a $f^{-2}$ dependence, corresponding to a fractional length change of $1.5 \times 10^{-12}$ s$^{-1/2}$. 

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Figure 48. Allan plot of the stability of the optical frequency, measured from evacuated cavities (i.e. under vacum) by the optical techniques realized. The black curve represents the beat frequency between two lasers locked to a dual Fabry-Perot cavity [XIX], while the red displays the beat frequency between a laser locked to a single Fabry-Perot cavity and an optical frequency comb [XVIII]. The dashed lines represent the slopes of the responses for long integration times, which have a $\tau^{1/2}$ and a $\tau^1$ – dependence (for the red and black curves, respectively).

Notcutt et. al. [72] reported fractional cavity mode creeping for a Zerodure spacer in the range from $3.5 \times 10^{-14}$ s$^{-1}$ (typical) to $5.3 \times 10^{-13}$ s$^{-1}$. Egan et. al. [73] reported fractional difference cavity mode creeping from a dual-cavity made from ULE-glass from $3.3 \times 10^{-15}$ s$^{-1}$ and $3.6 \times 10^{-16}$ s$^{-1}$. Furthermore, they found that the difference measurement reduced the drift by a factor of 3 compared with a single cavity measurement. For our dual Zerodure cavity we found a similar drift reduction.

Although the temperature stabilization was only rudimental the stability of the cavity spacers were found to be in the order of cavity creeping. This points to the fact that although one stabilizes the temperature there will still be cavity creeping and Brownian noise from the random generation of phonons in the crystal lattices in the layers of the cavity mirrors introducing drift in the system. Therefore, we conclude that to achieve the highest sensitivities, one needs to measure and calibrate on a short time scale.
Conclusions and Future prospects

The development of Db NICE-OHMS has, during my time in the project, been pursued on many fronts.

Firstly, work has been put in to understand and reduce the white noise that is present in most NICE-OHMS systems. In publications III and XII, a significantly improved white noise limited detection limit for Doppler-broadened NICE-OHMS was achieved by improving the laser lock and increasing the finesse. In publication III, the white noise reduction was related to lower intensity fluctuations in the transmitted laser light, while, in the publication XII, it was achieved by increasing the effective path length.

Secondly, extensive work has been pursued to understand, reduce, and control background signals. Background signals affect NICE-OHMS sensitivity in two ways; by coupling in intensity noise and by drifting backgrounds producing falls signals, where the latter will limit the effective integration time. The publications [I] and [II] present a reduction methodology and theoretical description of background signals caused by EOMs, while publication [V] presents a methodology to alleviate the influence of etalons.

Thirdly, the dynamic range of the setup has been increased by development of lineshapes theory for higher pressure ranges. The publications [XIV], [XVI], [XV], and [XVII] provide derivation and experimental verifications of dispersion lineshapes for higher pressures. This work is of great importance as the optimum pressure i.e. the pressure that enables the detection of the lowest relative concentration for a targeted species, often is in the regime in which the measurements are affected by both homogenous and inhomogeneous broadening mechanisms that not always are properly described by the ordinary Voigt lineshape function. It is shown that to evaluate measurements performed under such conditions correctly, one needs to use the correct broadening model.

Fourthly, the dynamic range has also been extended into the high absorption range. Theoretical derivations and experimental verifications of the Db NICE-OHMS signal in the range in which the absorbance is no longer considered low, i.e., when the single pass absorbance is not much lower than the intra-cavity losses, are presented in the publications [X] and [XI]. It is shown that in this range the conventionally used simplified model will break down and more elaborate lineshapes where cavity mode pulling and effects on the laser lock must be incorporated. This work can be of high importance when NICE–OHMS is to be used to measure two lines of significantly different strengths simultaneously i.e. isotopic analyses, or when calibrations are to be made using commercially available standard reference gases when
transitions with high integrated line strength are addressed by the use of high finesse cavities.

Fifthly, the sensitivity of the system has been increased in a series of actions taken to by optimize the signal strength. In [VI], [VII], and [IX] the NICE-OHMS signal strength is optimized with respect to a number of parameters; primary modulation index, modulation frequency, and scan range. As the detection limit can directly be related to the Signal to Noise Ratio (SNR) an improvement of the signal strength will in most cases be associated with an improved detection limit. Furthermore, the optimum conditions are more often than not related to a local maximum or minimum as a function of some parameters, where the derivative is zero, and therefore at these points, parameter fluctuations will have minimum effect on the signal.

Finally, additional NICE-OHMS realizations have shown that the technique can be simplified and possibly miniaturized [VI] and perform highly sensitive measurements in the MIR range [XII, XIII]. It has also been discussed to which extent the technique can be used for detection of atomic species then referred to as NICE-ASS [XXI]. It was concluded that if NICE-AAS can be made with the same detection sensitivity as now has been obtained for NICE-OHMS it would be possible to detect atoms in pps (parts-per sextillion) or zg/cm$^3$ concentrations.

All of the works done above show that the technique is truly versatile ultrasensitive and reliable. While this work was done for NICE-OHMS, many of the methods can be applied to other spectroscopic techniques. For example the model for incoupling of etalons through lineshape fitting [IX] can be applied to any spectroscopic technique utilizing least square fitting.

The work done with gas number density has also benefited from the knowledge gained from the NICE-OHMS projects. The laser locking procedures first developed in [III] was used to lock the lasers in the subsequent gas number density assessments [XVIII, XIX]. While we have received great interest from the measurement standards community for our work with density measurements, one goal for the next years is to apply this unprecedented accuracy to the measurement of pressure.

In the work presented here the limits of what are considered measurable have been further pushed back by applying optical cavities to measurements of absorption, dispersion and density of gases. The approach has been to systematically push the limit of what is considered possible to measure by eliminating the limiting factors from the measurement. It is hoped that the results presented here will be beneficial for future users of these types of techniques.
Scientific publications

Comment on the publications and my contributions to them. The publications are divided in sub-groups according to the main focus of the work presented in them.

NICE-OHMS – Technical realizations, Causes and reduction of background signals, Optimum detection conditions, and Improvement of performance

Publication I

Reduction of background signals in fiber-based NICE-OHMS
A. Foltynowicz, I. Silander, and O. Axner

This work presented a method for reducing background signals by applying active feedback to an EOM with a titanium diffused waveguide. The stability of a NICE-OHMS system realized around such an EOM with and without feedback and around an EOM with a proton exchanged waveguide which does not produce any RAM was compared. Finally, the concept of etalon immune distances was introduced for the first time.

My contribution to this work was the following. I build and tested the combined temperature and voltage feedback electronics. I took part in the planning and execution of the measurements. I also gave the first explanations for EID and why an FMS or NICE-OHMS system based on an EOM with a proton exchanged waveguide is free of RAM. I contributed to the internal revision process of the manuscript.

Publication II

Frequency modulation background signals from fiber-based electro optic modulators are caused by crosstalk
I. Silander, P. Ehlers, J. Wang, and O. Axner

This work is the theoretical description of the physical causes for background signals (RAM) in fiber coupled EOMs and the process used to eliminate such described in Publication I. The backgrounds are shown to originate from cross-coupling between principal the axes of the fibers and the crystal, which primal is due to misalignments in the production process.
I was responsible for the entire work from deriving the formalism to experimentally validating the result. I have written major parts of the manuscript.

**Publication III**

**Fiber-laser-based noise-immune cavity-enhanced optical heterodyne molecular spectrometry instrumentation for Doppler-broadened detection in the 10^{-12} cm^{-1} Hz^{1/2} region**
P. Ehlers, **I. Silander**, J. Wang, and O. Axner

In this work the noise level of the fiber laser NICE-OHMS setup was significantly reduced by implementation of an acousto-optical modulator (AOM). The performance of the laser lock was analyzed and the stability of the system with and without the additional AOM feedback was compared. Environmental influences were also reduced by a double-table-solution effectively placing the experiment inside an acoustic and temperature stabilized transparent plastic box.

My contribution to this work was mainly in designing and building the double-table and the acousto/thermal box. Furthermore, I assembled the new vacuum system used in this work and took part in the planning and problem solving around the measurements. I contributed to the internal revision process of the manuscript.

**Publication IV**

**Fiber-laser-based noise-immune cavity-enhanced optical heterodyne molecular spectrometry incorporating an optical circulator**
P. Ehlers, **I. Silander**, J. Wang, A. Foltynowicz, and O. Axner

To reduce complexity of the FBL-NICE-OHMS setup, a fiber optical circulator was incorporated into the setup. This resulted in a significantly reduced complexity experimentally but also a slightly reduced sensitivity, from 3 to 7 × 10^{-12} cm^{-1} Hz^{-1/2}. This approach might find a future application if a compact NICE-OHMS system, for in situ measurements, is to be realized.

I was involved in both the implementation of the optical circulator and the measurements presented in the paper. I took part in the internal revision process.
Publication V

Use of etalon-immune distances to reduce the influence of background signals in frequency-modulation spectroscopy and noise-immune cavity-enhanced optical heterodyne molecular spectroscopy
P. Ehlers, A. C. Johansson, I. Silander, A. Foltynowicz, and O. Axner

In this work the etalon immune distance (EID) concept is investigated both for FMS and NICE-OHMS. The effect of placing optical components on EID is shown for both FMS and NICE-OHMS signals. Furthermore, the effect of EID on NICE-OHMS detection sensitivity is investigated. Its different roles on the in-phase and out-of-phase signals are discussed.

This work constitutes the experimental verification of the EID concept conceived by me during the work with project [I]. I took part in the discussions around the work and planning of experiments. I also contributed to the internal revision process.

Publication VI

Doppler broadened noise-immune cavity-enhanced optical heterodyne molecular spectrometry: optimum modulation and demodulation conditions, cavity length, and modulation order
P. Ehlers, I. Silander, and O. Axner

A theoretical description of the optimum design of a NICE-OHMS instrumentation for Doppler-broadened signal detection. The influences of modulation index modulation frequency, i.e. the cavity length, and the modulation order are investigated.

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

Publication VII

Doppler broadened NICE-OHMS beyond the triplet formalism: assessment of optimum modulation index
P. Ehlers, J. Wang, I. Silander, and O. Axner,

This work constitutes an experimental validation the dependence of the Db NICE-OHMS signal on modulation index that is presented in paper VI. The detection sensitive is investigated for varies modulation indexing and was found to be improved for higher values compared to what had been
previously been used. This work thus verifies that the optimum conditions encompass modulation of the light to more than one pair of sidebands.

I took part in the modification of the fiber NICE-OHMS system and in discussions around the paper. I was involved in the internal revision process.

**Publication VIII**

**Doppler-broadened noise-immune cavity-enhanced optical heterodyne molecular spectrometry down to $4 \times 10^{-13} \text{ cm}^{-1} \text{ Hz}^{-1/2}$: implementation of a 50,000 finesse cavity**


In this work a high finesse cavity (with a finesse of 50 000) was implemented. It was shown that white noise detection sensitivity was reduced more than the increase in finesse (12.5 as compared to 9). This was attributed to a lower noise level. The lower noise level compared with VII was attributed to the change in cavity corner frequency. We also discuss the origin of recurrent dips in the cavity transmission, which were attributed to excitation of high order transverse mode by scattering from the mirrors. The effect of these was reduced by insertion of a small pinhole in the cavity.

I took part in the planning for the higher finesse cavity. I was responsible for all the measurements, and implemented the intra-cavity pinhole. I have written the major parts of the manuscript.

**Publication IX**

**Model for incoupling of etalons into signal strengths extracted from spectral line shape fitting and methodology for predicting the optimum scanning range – Demonstration of Doppler broadened NICE-OHMS down to $9 \times 10^{-14} \text{ cm}^{-1}$**


In this work, a theoretical description of how white noise and periodical disturbances couple into fits is presented. A model is presented how white noise etalons will couple in for different scan ranges. The results are experimentally validated. This resulted in an improved detection limit of $9 \times 10^{-14} \text{ cm}^{-1}$ which is the lowest recorded for Db NICE-OHMS.

I developed the major part of the theory in this paper and I was responsible for planning of the measurements. I have written the major parts of the manuscript.
Publication X

Doppler-broadened NICE-OHMS beyond the cavity-limited weak absorption condition – I. Theoretical Description
W. Ma, I. Silander, T. Hausmaninger, and O. Axner
To appear in Journal of Quantitative Spectroscopy and Radiative Transfer
doi:10.1016/j.jqsrt.2015.09.007

This work presents the theoretical derivation of Db NICE-OHMS signals for the case when the absorbance is not necessarily much smaller than the empty cavity losses. i.e. when $\alpha_0 L \ll \pi / F$. The true origin of the NICE-OHMS signal was found to be a combination of the laser lock, the FSR lock and the cavity transmission. Different degrees of approximations are derived for different absorption ranges.

I initiated the work by presenting an explanation to discrepancies in observed line shapes recorded with a high finesse cavity in measurements performed during project [VIII]. I also took part in the theoretical discussions and the internal revision of the manuscript.

Publication XI

Doppler-broadened NICE-OHMS beyond the cavity-limited weak absorption condition – II: Experimental verification
T. Hausmaninger, W. Ma, I. Silander, and O. Axner
To appear in Journal of Quantitative Spectroscopy and Radiative Transfer
doi:10.1016/j.jqsrt.2015.09.008

This work constitutes an experimental verification of the theoretical descriptions derived in paper X. It is shown that the full theory provides adequate description of the Db signal up to conditions for which $\alpha_0 L \approx 3\pi / F$. I initiated the work by presenting an explanation to discrepancies in observed line shapes recorded with the high finesse cavity in work VIII.

The measurement in this work was performed with the high finesse cavity which I designed. I took part in the data analysis and the internal revision process.
MIR OPO-based NICE-OHMS

Publication XII

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

In this work an optical parametric oscillator (OPO) is used as the light source. This enables NICE-OHMS to be performed in the 3.2–3.9 µm mid-infrared (MIR) region. As this region contains fundamental vibrational transitions which are much stronger than the overtones in the 1.53 µm region where the fiber laser system operates, this system opens up for sensitive detection of a range of new species and applications.

I was the driving force behind this project I planned the setup and ordered the necessary equipment. I was in charge of the initial construction of the setup and planed the measurements. I wrote the majority of the manuscript.

Publication XIII

Doppler-broadened noise-immune cavity-enhanced optical heterodyne molecular spectrometry in the mid-IR region down to $10^{-10}$ cm$^{-1}$ Hz$^{-1/2}$
T. Hausmaninger, I. Silander, O. Axner
In manuscript

In this work a 4000 finesse cavity was incorporated into the MIR NICE-OHMS system previously incorporating a 500 finesse cavity, described in publication XII. To enable locking of the high finesse cavity the bandwidth of the lock was increased by the use of an AOM. The resulting sensitivity of the system was found to be $1.3 \times 10^{-10}$ cm$^{-1}$ over 20 s which is the highest so far reported for MIR NICE-OHMS.

I designed the original system presented in publication XII, I formulated the plan of using an AOM, and I made the necessary inquiries to find a model suitable for our purposes. I was involved in the planning of the experiments and took part in internal revision proses.
Line shape studies

Publication XIV

**Dicke narrowing in the dispersion mode of detection and in noise-immune cavity-enhanced optical heterodyne molecular spectroscopy - Theory and experimental verification**

J. Wang, P. Ehlers, I. Silander, and O. Axner

This work is the first demonstration of Dicke narrowing in NICE-OHMS as well as detected in dispersion. Expressions for the dispersive Rautian and Galatry shape functions were derived and experimentally verified. These lineshapes were later used to extend the dynamic range of NICE-OHMS.

My main contribution to this work was mainly in designing the required electronics. I also contributed to the experimental setup designed by discussing possible solutions to various technical problems. I contributed to the internal revision of the manuscript.

Publication XV

**Speed-dependent Voigt dispersion line-shape function: applicable to techniques measuring dispersion signals**

J. Wang, P. Ehlers, I. Silander, J. Westberg, and O. Axner

This work constitute a theoretical derivation of the Speed-dependent Voigt dispersion line-shape function, which is experimentally verified in [XVI]. It was shown that for small speed dependent effects the function approached the ordinary Voigt line shape.

I took part in the theoretical discussions and the internal revision of the manuscript.

Publication XVI

**Speed-dependent effects in dispersion mode of detection and in noise-immune cavity-enhanced optical heterodyne molecular spectrometry: experimental demonstration and validation of predicted line shape**

J. Wang, P. Ehlers, I. Silander, and O. Axner

This work was the first demonstration of speed-dependent effects in dispersion which validated the expressions derived in XV.
My main contribution to this work was my involvement in the design, construction and problem shooting of the experimental setup. In particular the custom made electronics were designed and assembled by me. I also contributed to the internal revision of the manuscript.

**Publication XVII**

**On the accuracy of the assessment of molecular concentration and spectroscopic parameters by frequency modulation spectrometry and NICE-OHMS**

J. Wang, P. Ehlers, I. Silander, and O. Axner


In this work the accuracy of the assessment of molecular parameters through the use of NICE-OHMS was investigated. The accuracy of broadening parameters and line strength acquired through line shape fitting was assessed for different models i.e. Rautian, Galatry line shape functions and speed dependent Voigt.

I developed real time fitting routines to facilitate the laboratory work. I was involved in the discussions around the fitting routines and accuracy. This discussions led to the work presented in [IX]. I took part in the internal revision of the manuscript.

**Gas density measurements**

**Publication XVIII**

**Optical measurement of the gas number density in a Fabry–Perot cavity**

I. Silander, M. Zelan, O. Axner, F. Arrhéén, L. Pendrill, and A. Foltynowicz


In this work a method for determining the gas number density by measuring the optical frequency of a cavity mode was presented. By measuring the beat frequency of a laser locked to a cavity mode an optical frequency comb (OFC) the absolute frequency of the cavity mode could be determined. The resulting accuracy of refractivity measurements was $4.5 \times 10^{-12}$, which correspond to $1.4 \times 10^{-6}$ mol m$^{-3}$ for nitrogen. This accuracy is significantly higher than for existing non-optic methods.

I designed and assembled a large part of the experiment. I was involved in all the measurements and the error analysis. I participated in writing the manuscript.
Publication XIX

A dual Fabry-Perot cavity for fast assessments of gas number density
I. Silander, T. Hausmaninger, M. Zelan, O. Axner and A. Foltynowicz
In manuscript

In this work the optical method for determining the gas number density presented in XVIII was further developed. To increase the accuracy an dual cavity design was incorporated. This led to a significant reduction of noise. The resulting accuracy of refractivity measurements was found to be $2.5 \times 10^{-13}$. This accuracy was achieved at relatively short time scales which points towards the need of incorporation of automatic calibrations to enable field measurements.

I designed and assembled the main parts of the experiment. I was responsible for the measurements and I have written a substantial part of the manuscript.

Reviews and prospects

Publication XX

NICE-OHMS — frequency modulation cavity-enhanced spectroscopy — principles and performance
O. Axner, P. Ehlers, A. Foltynowicz, I. Silander, and J. Wang

This book chapter is a review of the principles and performance of the NICE-OHMS technique. It contains theoretical descriptions of all different modes of detection i.e. sub-Doppler, Doppler-broad, absorption, and dispersion different lineshapes. Furthermore, the different broadening mechanisms and there corresponding lineshapes are presented. Finally, noise and background signals in NICE-OHMS and some typical results are presented.

I contributed by writing the sub section “Noise and backgrounds” and by taking part in the internal revision process of the manuscript.
Publication XXI

Noise-immune cavity-enhanced analytical atomic spectrometry — NICE-AAS — A technique for detection of elements down to zeptogram amounts
O. Axner, P. Ehlers, T. Hausmaninger, I. Silander, and W. Ma,

In this work, the implementation of NICE-OHMS for analytical atomic spectrometry (AAS) is investigated.

Based on the, at the time prevalent detection sensitivity for Db NICE-OHMS for detection of molecules in gas phase, $4.9 \times 10^{-12} \text{ cm}^{-1} \text{ Hz}^{-1/2}$ over 10 s, this works predicts that for mercury (Hg) and sodium (Na) detection limits of 25 Hg-atoms and 15 Na-atoms per cubic should be achievable. Injecting a sample containing these species into graphite furnace the smallest detectable concentration will be in the parts-per-sextillion range corresponding to 10 zg/cm$^3$.

Since the publication of this project the Db NICE-OHMS detection sensitivity has been revised to $2.6 \times 10^{-13} \text{ cm}^{-1} \text{ Hz}^{-1/2}$ [IX]. If these new numbers are used to recalculate the detection sensitivities they will be in the order of one atom per cubic centimeter for both Hg and Na. This implies, if the same accuracy could be transferred to appropriate wavelengths, it would be possible to construct a sub-zeptogram NICE-AAS system. This shows the impressive potential of noise-immune cavity enhanced detection techniques.

I contributed with the analyses of the detecting sensitivities and took part in the internal review process of the manuscript.
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