NOISE MITIGATION TECHNIQUES FOR HIGH-PRECISION LASER SPECTROSCOPY
AND INTEGRATED PHOTONIC CHEMICAL SENSORS

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Abstract

In this dissertation, laser spectroscopy is utilized to monitor trace-gas species for environmental and health applications. Due to their non-invasive and in situ sensing capabilities, optical platforms are attractive for on-site, real-time diagnostics. Two main techniques are investigated: (i) Faraday rotation spectroscopy (FRS) and (ii) tunable diode laser spectroscopy (TDLS), where noise reduction techniques are implemented in both cases for precise and accurate quantification of analytes. A variety of sensing configurations are demonstrated, including benchtop laboratory sensors [Chapters 4, 6, 7], transportable extractive point sensors [Chapter 5], and on-chip integrated sensors [Chapter 7].

Chapters 4 to 6 demonstrate FRS for detection of paramagnetic molecules. Using a combination of phase-sensitive signal recovery, balanced-detection and polarizer angle optimization, these sensors consistently demonstrate near shot-noise limited performance with minimum fractional absorption $\sim 10^2 \times$ beyond conventional TDLS. Given that FRS is an ideal platform for implementation of common noise reduction techniques, it presents a viable solution to precision spectroscopy of chemical radicals.

Chapter 7 contributes toward a new generation of integrated spectrometers, with the goal of scalable precision sensing nodes. To this end, we present examples of compact TDLS sensor modalities, including integrated sources for broadband, multi-heterodyne spectroscopy, and evanescent waveguide spectroscopy on a silicon-photonic chip. We conclude this dissertation with a vision of a fully integrated TDLS sensor node applicable for real-time sample quantification and localization.
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\( c_2 \) \hspace{1cm} \text{second radiation constant: 1.439 cm} \cdot \text{K} \hspace{1cm} 7.3.5

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\([^{m}\text{N}]_{\text{S/R}}\)  
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Chapter 1:
Introduction and Motivation

In this thesis we study noise reduction techniques in optical spectroscopy, implemented in configurations ranging from benchtop free-space optics to silicon photonic on-chip platforms. In this first Chapter we provide a background to optical sensor development and a summary of the relevant techniques addressed within the body of this dissertation.

1.1 Motivation and applications

One of the important goals of optical spectroscopy is the precise and accurate determination of unknown quantities of chemical substances of interest (analytes). Within this context, precision is the consistency of repeated measurements of the same analyte quantity over a given measurement time, while accuracy is the proximity of the measurement to the true value.\(^1\) Stringent performance requirements for such sensors arise in applications ranging from security [1, 2] to health [3, 4] and environmental [5-7] monitoring, with the latter two being a particular focus of this dissertation. In these applications, laser spectroscopy plays an increasingly important role due to the non-destructive and (highly specific, or spectral crosstalk-free) real-time detection capabilities, with some instances outlined below.

A significant biomedical application example involves quantification of biomarkers within the human body, through either breath [4, 8-10], blood [11, 12] or urine analysis [13, 14]. This is presently an active area of study for the purpose of real-time clinical diagnostics, a particular

\(^1\) Generally, any precise system can be made accurate via calibration with a known quantity of analyte, and is expected to maintain this accuracy up to a zero-drift time, after which sensor recalibration is required. These concepts are quantified in Chapter 3.
example being the measurement of nitric oxide and its isotopes (denoted by $^{14}\text{NO}$ and $^{15}\text{NO}$) [15, 16]. Breath analysis of $^{14}\text{NO}$ can be used as an indicator of respiratory health [15], and isotopically labeled precursors may be injected into a patient to study metabolic pathways [14] and their associated syndromes. Generally, present technologies for biomolecular sensing rely on chemiluminescence [17] or electro-chemical techniques [18], with isotopic analysis performed using mass spectrometry [19, 20]. The former methods do not provide isotopic selectivity, and mass spectrometry presents intensive maintenance and cost limitations [21]. Optical sensors combine capabilities of both technologies to satisfy a gap niche; isotopic selectivity is accomplished by targeting the respective molecular transitions, and near shot-noise limited sensitivity can be accomplished using appropriate noise mitigation techniques [16, 22]. Recent development of transportable extractive spectrometers [23] enables real-time, in-situ sensing capabilities as demonstrated in Chapter 5.

For reasons similar to those outlined above, laser spectroscopy is also particularly well suited to environmental monitoring and geoscientific studies [7]. Examples of the former include detection of primary pollutants, examples being oxides of nitrogen ($\text{NO}_x$), sulfur ($\text{SO}_x$), and carbon (CO), and secondary pollutants (chemical/photochemical reaction products of the primary) such as sulfuric acid ($\text{H}_2\text{SO}_4$) and ozone ($\text{O}_3$) [24]. Additionally, a presently active area of research involves the disruption of global carbon and nitrogen cycles due to the rapid intensification of fossil fuel combustion and industrial processes [25, 26]. A particular application example in Chapter 4 involves part-per-million (ppmv) level oxygen ($\text{O}_2$) detection for bio-respiratory diagnostics, which in marine ecosystems can be used to constrain biological productivity of marine biota [27]. In Chapters 5 and 6, we develop tools for the analysis of fixed nitrogen (a critical nutrient in photosynthetic growth) and its isotopes. In particular, nitrates ($\text{NO}_3^-$) are the dominant
factor in phytoplankton growth, which acts as an atmospheric carbon sink via the ocean’s ‘biological pump’ [28]. Toward the conclusion of this thesis, compact modalities for environmental sensing are presented (Chapter 7) [29], and an on-chip methane spectrometer for fugitive emissions quantification on oil well pads (and localization when implemented in a wide-area sensor network) is demonstrated (Section 7.3). A future vision of portable and compact optical sensor development is presented, ideally incorporating precise and accurate measurements within a low-power, spatially efficient hardware footprint with scalable production potential.

1.2 Historical developments

Quantitative spectroscopy was first demonstrated by Fraunhofer, building on Newton’s study of refraction via glass prisms [30]. This spatial separation of optical frequencies was extended to grating spectrometers for the absolute wavelength measurement of spectral features, notably those from sunlight [30]. The significance of such lines was recognized by Kirchhoff in 1859 who demonstrated the correspondence between physical constituents and their respective spectral signatures, thus enabling quantitative study of atomic and molecular composition of the sun’s atmosphere [31]. More recently, non-dispersive infrared spectroscopy (NDIR) utilizing broadband transmission measurements have been used for composition analysis, although molecular selectivity is problematic due to the spectral crosstalk from alternate species [24].

Recent advances in laser technologies, first demonstrated by Maiman in 1960 [32] has facilitated rapid development of modern techniques based on tunable diode laser spectroscopy (TDLS). In particular, quantum cascade laser (QCL) technology first demonstrated by Faist in 1994 [33] provided a means to target the mid-infrared (MIR) wavelength range (2 µm to 24 µm) via bandstructure engineering of GaAs and InP based heterostructures, thus enabling selective
measurement of fundamental ro-vibrational transitions (and eliminating crosstalk) of various molecular species shown in Figure 1.1.

1.3 Technologies for modern spectroscopy

The evolution of semiconductor laser sources and detector design have enabled high-resolution, molecule specific, real-time detection with part-per-trillion (pptv) detection limits [24]. For example, distributed feedback (DFB) QCL sources provide single mode operation with linewidths < 100 MHz with typical injection current tuning ranges of 3-4 cm\(^{-1}\) (Figure 1.2) and up to 20 cm\(^{-1}\) via thermal tuning [34]. Utilization of the full gain spectrum has been demonstrated in external cavity (EC-QCL) configurations for broadband spectroscopy, with tuning ranges up to 432 cm\(^{-1}\) and watt-level peak output power [35]. For power efficient MIR applications, interband cascade laser (ICL) sources spanning 3 to 6 µm have been increasingly employed due to their low current threshold density [36]. Toward even shorter near-infrared (NIR) wavelengths, gallium-arsenide (GaAs) based diodes and vertical cavity surface emitting lasers (VCSELs) are particularly widespread due to their relevance to optical communications, and can be used for detection of overtone bands of fundamental ro-vibrational transitions [6]. Common to all the above sources are narrow laser linewidths that resolve absorption spectral features within the tuning range, thus providing high molecular specificity via suitable wavelength selection [24]. Moreover, semiconductor lasers may be modulated up to MHz rates, enabling signal-to-noise (SNR) enhancement techniques such as wavelength modulation (Section 2.2) for 1/f noise reduction [24].

MIR optical detection schemes primarily rely upon mercury-cadmium telluride (MCT) and indium antimonide (InSb) based materials [37], with thermoelectrically cooled MCT detectors typically utilized up to 6 µm, and potentially up to 25 µm with cryogenic cooling [38]. In conjunction with low noise preamplifier electronics, near shot-noise performance for detector
noise-equivalent power (NEP) have reached widespread commercial availability [39], and have been implemented in the sensors demonstrated in Chapters 4, 5 and 6. Further noise suppression techniques such as electronic noise cancellation via balanced-detection, first demonstrated by Hobbs [40], can be utilized for reduction of laser technical noise and optical fringing, described in Chapter 4. Alternative technologies such as quantum-well infrared photodetectors (QWIPs) have been developed for long-wave infrared (LWIR) wavelengths, using intersubband transitions in a way similar to QCL technologies [41].

1.4 An overview of spectroscopic techniques

Conventional absorption-based TDLS (TDLAS) utilizes line-scanning across the spectral feature to ‘self-reference’ [24] by measuring peak absorption relative to zero-absorption in the spectral wings. Voigt least-mean squares (VLMS) fitting of baseline-normalized spectra allows direct extraction of analyte concentration, given experimental parameters (temperature, pressure, optical path length, etc.). Typically, \((aL)_{\text{min}} \approx 10^{-4} \text{ Hz}^{1/2}\) in the absence of further noise mitigation techniques [24]. On-chip modalities of TDLAS are demonstrated in Chapter 7.

Wavelength modulation spectroscopy (WMS, Section 2.2) is an alternate TDLS technique involving modulation of laser frequency via current injection [42], followed by narrow-band detection at modulation harmonics to filter out frequencies (and noise) unrelated to the signal of interest [42]. Due to derivative-like WMS spectra, operation in line-locked mode is possible, whereby active feedback via proportional-integral-derivative (PID) control locks the laser frequency to zero-crossings of odd harmonics for continuous and real-time measurement of even harmonic spectral peak signals. Typical WMS techniques demonstrate \((aL)_{\text{min}} \approx 10^{-5} \text{ Hz}^{1/2}\) [24], corresponding to an order-of-magnitude improvement from TDLAS due to equivalent noise bandwidth (ENBW) reduction.
TDLS techniques outlined above are subject to the Beer-Lambert law [43] and are thus limited in linear dynamic range. Dispersion spectroscopy utilizes correspondence between real and imaginary components of the complex susceptibility via the Kramers-Kronig relations [44], and overcomes the nonlinearity of optically thick samples. An example particularly relevant to this dissertation is Faraday rotation spectroscopy (FRS), whereby the induced circular birefringence of paramagnetic molecules via Zeeman splitting of $\Delta m_I = \pm 1$ transitions [45] results in rotation of linearly polarized light. A developmental timeline is shown in Figure 1.3, where the initial concept arose in the study of Electron Paramagnetic Resonance (EPR) by Zavoisky in 1944 [46] for split transitions of a single $J$-rotational quantum number (typically microwave frequencies), and was extended to the infrared wavelengths by Mizushima in 1953 [47] (Laser Magnetic Resonance, or LMR). More conventional FRS techniques, namely AC-FRS (magnetic field, or sample modulation, described in Section 2.4.4) and balanced-detection (BD-FRS) were implemented by Litfin in 1980 [48] and Adams in 1984 [49], with a variety of prototype FRS sensors for biogenic and isotopic NO detection demonstrated shortly thereafter [50-55]. Further developments by Lewicki [45], So [50], Brumfield [22], and Wang et al. [16] demonstrated the potential for near shot-noise capabilities of FRS systems with $(aL)_{\text{min}} < 10^{-6}$ Hz$^{-1/2}$, and validated FRS as an ultrasensitive technique for the detection of paramagnetic species. In this thesis we show that in addition to linearity for optically thick samples, FRS is an ideal platform for noise reduction techniques via balanced-detection (Chapter 4), sample modulation (Chapters 5 and 6) and optical subtraction for real-time referencing (Chapter 6), with consistent demonstration of near shot-noise limited measurements in each case.

Given the multitude of FRS techniques available, the challenge is to select the method appropriate to applications demands. A summary of methods explored in this thesis is provided in
Table 1.1 which shows performance converging toward the shot-noise limit for each FRS technique, along with $\Theta_{\text{NEA}}$ (the smallest detectible FRS angle, Section 3.3.4) approaching $10^{-8}$ rad·Hz$^{1/2}$ levels. In all cases, short-term precision is excellent regardless of technique; rather, the selection is primarily dependent upon limiting factors such as laser output power (90º methods preferable), long-term stability requirements (DM-FRS, dDM-FRS), and power budget (45º method using permanent magnets).

A large range of advanced spectroscopic techniques beyond the scope of this thesis are presently undergoing intensive research and development. Such methods include cavity enhanced absorption spectroscopy (CEAS), whereby high finesse cavities with small physical footprints are utilized for path-length enhancement, and cavity ring-down spectroscopy (CRDS) where the optical intensity decay time in the cavity is used to measure the analyte concentration [24]. A particularly sensitive technique, termed noise-immune cavity-enhanced optical heterodyne molecular spectroscopy (NICE-OHMS) utilizes cavity path-length enhancement in conjunction with frequency modulation at the cavity free-spectral range (FSR) such that frequency noise of the laser is common-mode and cancels in the signal demodulation process [56]. Through this technique, near shot-noise absorption sensitivities down to $10^{-14}$ Hz$^{1/2}$·cm$^{-1}$ can be achieved. Much focus has also been placed on photo-acoustic trace-gas spectroscopy (PAS) and its quartz-enhanced analogue (QEPAS), which involves conversion of the intensity variations of laser light (e.g. pulsed) to pressure waves detected via microphones (PAS) or piezoelectric tuning forks (QEPAS) [57]. Present areas of investigation include tuning fork geometries [58] and micro-resonators for signal enhancement [57]. The above is intended as a sampling of modern techniques, and further detail may be found in recent review articles [24].

1.5   Research directions of this thesis
The work in this dissertation is divided into two main sections: (I) the development of high precision point/extractive Faraday rotation spectrometers near the shot-noise limit, with a vision toward (II) the development of miniature sensing modalities with scalable production potential. In (I), FRS sensors present an ideal testbed for investigating noise mitigation techniques, and demonstrate the true potential of balanced-detection, sample modulation (AC-FRS) techniques, and optical referencing schemes (Chapters 4 to 6). Proof of concept on-chip sensing modalities are experimentally demonstrated in (II), and implementation of unique noise reduction methods is studied for each platform, (e.g. beat-note frequency stabilization (Section 7.2), or the dynamic etalon fitting-routine (Appendix A5.2) etc.). Naturally, the chosen sensor configuration depends primarily upon the application demands (weight/size, power consumption, precision/accuracy, dynamic range etc.), and chip-scale sensors are not intended to replace or reduce the relevance of alternate configurations; rather, scalable miniaturized sensors provide added capability in particular application spaces. For example, with the benefit of mass-production potential, such sensor nodes may be deployed in a wide-area sensor network for high resolution temporal and spatial analyte quantification (Sections 7.1 and 7.3). On the other hand, extractive sensors such as those described in Chapters 5 and 6 are applicable to clinical diagnostics and are not subject to those same limitations of power and size, with the main goal of ultra-high sensitivity and accuracy required by these demanding applications.
References


Chapter 2:
Spectroscopic Theory and Modeling

In this Chapter a detailed exploration and mathematical modeling of spectroscopic techniques relevant to this thesis is performed. Absorption-based tunable diode-laser spectroscopy (TDLAS) is modeled via the Beer-Lambert law, followed by the extension to wavelength-modulation spectroscopy (WMS). Through the Kramers-Kronig relation (KKR), the corresponding dispersion lineshapes and the Zeeman split transitions for modeling of Faraday rotation spectra are calculated. The Allan-deviation will be introduced as a quantifier of sensor precision, stability, and accuracy.

2.1 Absorption spectroscopy

Absorption-based TDLAS (TDLAS) will be used as a starting point in this Chapter from which more sophisticated methods are derived. Although TDLAS typically does not reach sensitivities achievable through alternative methods [1], its attractiveness stems from the simplicity of implementation (thus serving as a commercially viable solution) and well documented computational algorithms allowing fast spectral modeling [2, 3]. In this Section the basic theory is introduced, followed by numerical results and concluded with experimental considerations for reduction of TDLAS noise.

2.1.1 Basic formulation

A conceptual schematic of TDLAS is shown in Figure 2.1(a). A laser beam emitted by a tunable diode laser impinges upon a detector after passing through some quantity of analyte, with the goal being the determination of this unknown quantity through spectral modeling. Assuming a macroscopic number density of analyte, the fractional intensity degradation per unit distance is constant [4], leading to an exponential decay in the initial optical intensity $I_0$ given by the Beer-Lambert law [5]:
\[ I_r = I_0 \exp \left[ -L \cdot \frac{T_R}{T} \cdot p \cdot S \cdot \chi_{abs}(\tilde{\nu} - \tilde{\nu}_0) \cdot C_r \cdot L \right] \]  

(2.1)

where \( L = 2.686 \times 10^{19} \text{ cm}^{-3} \) is the Loschmidt constant, indicating the particle number density at partial pressure \( p = 1.0 \) and \( T_R = 273.15 \text{ K} \). Of the remaining terms, \( T \) is the temperature of measurement (K), \( L \) is the optical path length (cm), \( S \) is the integrated molecular linestrength (cm\(^{-1}\)•molecule\(^{-1}\)•cm\(^2\)), \( \chi_{abs}(\tilde{\nu} - \tilde{\nu}_0) \) is the area-normalized spectral lineshape, and \( C_r \) is the relative molecular concentration of interest. Typically, \( T \) and \( p \) are measured in conjunction with spectral acquisition, \( S \) is retrieved via the HITRAN molecular database [6], and \( L \) is a known experimental parameter. TDLAS involves the direct measurement of the relative optical intensity throughput \( I_r/I_0 \), yielding a solution to \( C_r \) (the remaining unknown quantity in Equation 2.1). It is important to note that the presence of baseline (due to \( I_0 \) in Equation 2.1) is inherent to TDLAS, as shown in the example in Figure 2.1(b).

Near atmospheric conditions \( \chi_{abs}(\tilde{\nu} - \tilde{\nu}_0) \) is accurately approximated by a homogenously broadened Lorentzian lineshape (a specific example for the \(^{15}\text{NO} \text{Q}(3/2) \) transition is shown in Figure 2.2(a), where collision broadening is dominant above \( \sim 25 \text{ torr} \)), and for reduced pressure operation a Voigt profile is used (Section 2.1.2), which is the convolution of a Lorentzian (homogeneous) and Gaussian (inhomogeneous) components. Following the development of [7], the resulting expression for the full calculation of an absorption Voigt profile is given by:

\[ \chi_{abs}(\tilde{\nu}_d) = \frac{1}{\delta \tilde{\nu}_D} \cdot \int \frac{\ln 2}{\pi} \cdot \frac{\zeta_I}{\pi} \cdot \int_{-\infty}^{\infty} \frac{\exp(-\varphi^2)}{\zeta_R^2 + (\zeta_I - \varphi)^2} \cdot d\varphi \]  

(2.2)

where we define \( \tilde{\nu}_d = \tilde{\nu} - \tilde{\nu}_0 \) to be the wavenumber detuning from the line-center, \( \delta \tilde{\nu}_D \) to be the Doppler half-width at half maximum (HWHM), and \( \zeta_R \) and \( \zeta_I \) to be the real and imaginary components of \( Z \), given by:
\[
Z \equiv \zeta_R + i \cdot \zeta_I = \sqrt{\ln 2} \cdot \left( \frac{\tilde{\nu}_d}{\Delta \tilde{\nu}_D} + i \cdot \frac{\delta \tilde{\nu}_L}{\Delta \tilde{\nu}_D} \right)
\]  

(2.3)

Furthermore, using the expression for \(Z\) from above, Equation 2.2 can be re-written as:

\[
\chi_{\text{abs}}(\tilde{\nu}_d) = \frac{1}{\Delta \tilde{\nu}_D} \cdot \sqrt{\frac{\ln 2}{\pi}} \cdot \text{Re} \left[ i \cdot \int_{-\infty}^{\infty} \frac{\exp(-\varphi^2)}{Z - \varphi} \cdot d\varphi \right]
\]  

(2.4)

The term in square brackets is the complex error function (or plasma dispersion function) [8], whose real and imaginary parts are related through the KKR [9].

2.1.2 Spectral modeling

In modeling Voigt lineshapes, calculation via discrete summation of terms using the trapezoidal approximation in Equation 2.2 is computationally costly and not feasible for real-time VLMS fitting. Instead, a polynomial series expansion developed by Weideman is implemented [8] using fast Fourier transform (FFT) based coefficient calculations, with excellent accuracy achievable using relatively few terms. In Figure 2.2(b), Examples of numerical lineshape calculations at different pressures are conducted for \(^{15}\text{NO}\) Q(3/2) line near 1842.76 cm\(^{-1}\) in the \(^2\Pi_{3/2}\) subsystem (molecules relevant to Chapters 5 and 6), showing dominant homogeneous broadening mechanisms above \(\sim 25\) torr (\(\sim 0.03\) atm), where a simple Lorentz approximation is accurate and significantly reduces computational time. Only in the regime where \(\delta \tilde{\nu}_D \approx \delta \tilde{\nu}_L\) is the full Voigt approximation necessary for the accuracy of concentration retrieval.

2.1.3 Experimental considerations

An example of typical TDLAS measurement sequence is shown in Figure 2.3, where the laser is scanned (via current ramping) over the absorption transition of interest. The time resolution of measurement is given by the scan time of a single ramp, and sufficient points must occur within
the lineshape HWHM for adequate VLMS fitting accuracy (Appendix A2.2), placing lower-bound constraints on the data acquisition sample rate.

It is also interesting to note that higher ramp rates act as a high-pass filter due to baseline normalization prior to VLMS fitting, which linearizes slowly varying 1/f noise in the time domain. This flattens the amplitude spectral density (ASD) to white-noise like below the ramp frequency (numerical demonstration shown in Appendix A2.1). Typically, 1/f noise dominates until the detector noise floor (typically white) is reached at higher frequencies, and the frequency of the noise crossover point defines the optimum ramp rate beyond which precision no longer improves. Integration (in quadrature) of the ASD plot provides the precision of a single acquisition point, and VLMS fitting reduces the ENBW by (approximately) averaging the single-point noise over the number of points within the lineshape FWHM (Appendix A2.2).

2.2 Wavelength modulation spectroscopy (WMS)

TDLAS precision is improved by increasing the ramp frequency until the detection noise floor becomes the dominant noise contribution, and spectral fitting effectively reduces ENBW through averaging. A more refined method is to encode the absorption spectra to high-frequency via laser current modulation known as wavelength modulation spectroscopy (WMS).

2.2.1 Concept of WMS

A conceptual operating principle of WMS is depicted in the inset of Figure 2.4(a). Modulation of the laser frequency at amplitude $\tilde{v}_m$ and frequency $f_L$ causes modulated output intensity in the presence of frequency dependent absorption (i.e. spectral features). By probing variations in absorption features, WMS lineshapes are derivative-like [3], and converge to true derivative spectroscopy in the small modulation amplitude limit. The purpose of modulation is to encode the WMS signal away from 1/f noise, and the subsequent phase-sensitive detection reduces ENBW by
appropriate bandwidth selection, which rejects frequencies outside the signal of interest. Using WMS, line-locked operation is possible, whereby a proportional-integral-derivative (PID) controller actively locks to the zero-crossing of an odd harmonic (1f, 3f, etc.). The maxima of even harmonics (typically 2f) are then measured continuously for real-time concentration retrieval. Fundamentally, the performance of WMS and TDLAS are identical for a single sample point measurement; however, we note that in the experimental case of line-scanned TDLAS, the impact of Voigt least-mean squares (VLMS) spectral fitting is to effectively average over the duration of the FWHM for each acquired spectrum (Appendix A2.2), resulting in a SNR degradation compared to on-line (line-locked) measurement of the signal peak in the case of WMS.

2.2.2 Spectral modeling and signal optimization

Numerically, WMS spectra can be calculated using a direct Fourier expansion introduced by Wilson [10], where non-zero signal harmonics (denoted by N) are given by:

\[ H_N(\tilde{\nu}_d) = \frac{G_{LIA}}{\sqrt{2}} \cdot \frac{2}{\pi} \int_0^\pi I_r(\tilde{\nu}_d + \tilde{\nu}_m \cos \theta) \cdot \cos(N\theta) \cdot d\theta \]  \hspace{1cm} (2.5)

In Equation 2.5, \( \tilde{\nu}_m \) denotes wavenumber modulation depth and \( G_{LIA} \) represents the lock-in amplifier transimpedance gain. The \( \sqrt{2} \) factor in the denominator of the first term is due to root-mean square (RMS) amplitude measurement during the demodulation process. Figure 2.4(a) demonstrates the effect of modulation depth on the WMS signal strength; intuitively, increasing \( \tilde{\nu}_m \) at the absorption peak increases the \( 2f_L \) harmonic until distortion from the spectral wings occur, resulting in signal degradation. This is seen in Figure 2.4(b) where over-modulation causes \( 2f_L \) spectral broadening and reduction in peak amplitude. In the case where real-time analysis of WMS spectra is required, various techniques have been investigated for fast fitting of modulated lineshapes [2, 11]. Recently, analytic expressions have been derived for modulated Lorentzian
lineshapes [11], and the numerical non-approximative Westberg-Wang-Axner (WWA) method [7] is applicable to Voigt profiles where collisional and Doppler broadening are comparable.

2.3 Dispersion spectroscopy

In Equation 2.4, $\chi_{abs}(\tilde{\nu}_d)$ was demonstrated to be proportional to the real part of the complex error function $w(Z)$, defined as [8]:

$$w(Z) = \frac{i}{\pi} \int_{-\infty}^{\infty} \frac{\exp(-\varphi^2)}{Z - \varphi} d\varphi$$  \hspace{1cm} (2.6)

whose real and imaginary components are related through the KKR. Using Equations 2.3 and 2.6, we write the dispersion lineshape $\chi_{disp}(\tilde{\nu}_d)$ as (proportional to) the corresponding imaginary part of $w(Z)$:

$$\chi_{disp}(\tilde{\nu}_d) = \frac{1}{\delta \tilde{\nu}_D} \cdot \sqrt{\ln \frac{2}{\pi}} \cdot \frac{1}{\pi} \cdot \int_{-\infty}^{\infty} \frac{\exp(-\varphi^2)}{\zeta_1^2 + (\zeta_2 - \varphi)^2} \cdot (\zeta_2 - \varphi) \cdot d\varphi$$  \hspace{1cm} (2.7)

Substituting Equation 2.7 into Equation 2.1 (the Beer-Lambert law) and remembering that the optical intensity is proportional to the square of electric field, we determine the optical phase change as:

$$\phi(\tilde{\nu}_d) = \frac{L}{2} \cdot \frac{T}{T} \cdot p \cdot S \cdot C_r \cdot L \cdot \chi_{disp}(\tilde{\nu}_d)$$  \hspace{1cm} (2.8)

An example of this calculation is shown in Figure 2.5, which depicts calculated lineshapes for both absorption and dispersion of the R4 line of 1 % CH$_4$ at 6057.1 cm$^{-1}$. The one-to-one correspondence between $\chi_{abs}(\tilde{\nu}_d)$ and $\chi_{disp}(\tilde{\nu}_d)$ indicates that absorption and dispersion provide fundamentally the same information regarding analyte concentration; however, dispersion spectroscopy involves the direct measurement of the optical phase (or refractive index of the medium) which avoids nonlinearity caused by the Beer-Lambert law [9]. Dispersion techniques are therefore particularly useful in applications requiring large dynamic range in addition to
precision; a particular example being O\textsubscript{2} in the atmosphere, where single ppmv sensitivity is required for bio-respiratory studies [12, 13] on top of an atmospheric baseline of 20.8 %. Furthermore, in contrast to TDLAS, dispersion methods do not inherently require baseline normalization because the phase change is zero in the absence of spectral absorption. In the following Section we investigate Faraday rotation spectroscopy (FRS) [14-20], a dispersion technique particularly relevant to this dissertation (Chapters 4 to 6), which relies on the Zeeman split dispersion profiles of orthogonal (i.e. left/right handed) circularly polarized light.

2.4 Faraday rotation spectroscopy (FRS)

In this Section the basic concept and theory of Faraday rotation spectroscopy (FRS) is covered, and implementations relevant to this thesis are discussed. Specifically, we introduce modulation techniques for both the sample (field modulation) and laser (wavelength modulation) [17, 18, 20], and numerically investigate lineshapes related to these methods.

2.4.1 The origin of FRS signals

A general schematic of an FRS sensor is shown in Figure 2.6. Incoming incident laser light is initially linearly polarized, which can be decomposed into two orthogonal circular polarizations (left/right circularly polarized light, or LCP/RCP). Induced magnetic circular birefringence (MCB) causes Zeeman splitting of Δm\textsubscript{J} = ±1 transitions [14] and leads to a refractive index variation between LCP and RCP light. The relative phase change acquired results in a polarization rotation at the output, which is translated back into optical intensity variation via an analyzer (second polarizer) and measured on a photodiode. The physical origin of Faraday rotation signal may be understood by the introduction of energy isotropy (Zeeman splitting) to the orientation of the molecular magnetic dipoles (in this case, paramagnetic molecules) due to the applied magnetic field. LCP/RCP, which interacts with opposite dipole moments, thus observes macroscopic
differences in molecular absorption/dispersion at a given optical frequency. A significant benefit of FRS is the immunity to non-paramagnetic (i.e. diamagnetic) species such as CO$_2$ and H$_2$O [15], leading to zero-baseline measurements in the atmospheric windows where such molecules occur. Note that Figure 2.6 is intended only to conceptually show a common scheme of FRS whereby the analyzer is nearly crossed with respect to the polarizer (90º method). The purpose of this nearly-crossed scheme is to extract the polarization rotation signal by measuring the projection on a nearly orthogonal axis; this effectively removes much of the intensity-noise in the orthogonal axis that does not contribute toward the signal. Alternative implementations include those shown in Figures 4.1 (DC-FRS) [16, 19], and 5.2 (AC-FRS/DM-FRS) [17, 18, 20]. Typically, the 90º method is dominated by laser excess noise and detector noise, and Chapters 4 to 6 are intended to demonstrate various noise mitigation techniques to overcome these limitations.

2.4.2 Faraday rotation angle spectra (DC-FRS)

A more rigorous visualization of the origin of induced MCB is seen in Figure 2.7, where the applied constant (DC) magnetic field causes splitting of the degeneracy of rotational $J$-quantum levels. Treatment with perturbation theory gives a frequency deviation $\delta \tilde{\nu}_{m' \rightarrow m''}$ from the non-perturbed state [7]:

$$\delta \tilde{\nu}_{m' \rightarrow m''} = (m'' \cdot g'' - m' \cdot g') \cdot \mu_B \cdot B$$  \hspace{1cm} (2.9)

where $m'$ and $m''$ denote the lower and upper state respectively, $\mu_B = 4.67 \times 10^{-5}$ cm$^{-1}$/G is the Bohr Magneton, and $B$ is the magnetic field (Gauss). The resulting polarization rotation $\Theta_{FRS} = \Delta \phi_{T}/2$, where $\Delta \phi_{T}$ is the total relative phase shift by summation across all $m' \rightarrow m''$ transitions yielding [21]:

$$\Theta_{FRS}(\tilde{\nu}_d) = \frac{L}{4} \cdot \frac{T_R}{T} \cdot p \cdot S \cdot C_r \cdot L \cdot \sum_{m'm''} (\Delta m_j) \cdot W(m', m'') \cdot \chi_{disp}(\tilde{\nu}_d - \delta \tilde{\nu}_{m' \rightarrow m''})$$  \hspace{1cm} (2.10)
where the $\Delta m_J$ term within the summation subtracts RCP from LCP for relative phase calculation, and $W(m',m'')$ is a weighting factor\(^2\) for each $m' \rightarrow m''$ transition [7, 21]. Following the development of [22] and using Equation 2.10, Figure 2.8 shows broad spectral calculation of Faraday rotation angles for the P ($\Delta J = -1$), Q ($\Delta J = 0$), and R ($\Delta J = +1$) branches of the fundamental rovibrational transitions of $^{14}$NO using g-factors obtained from [23]. The calculation was performed at a relatively low pressure of 35 torr and $B = 100$ G field strength. Note that despite the weakly absorbing Q-branch, the FRS signals are strong due to the equal g-factors within the same $J$-transition (rotational levels), which allow constructive addition of each $\Delta m_J$ transition. Using $\Theta_{FRS}$ calculated in Equation 2.10 enables the determination of photodetector voltage signal $V_{sig}$ in Figure 2.6 (Appendix A1.1) through the application of Malus’ law [24], given by $P_{sig} = P_0 \cdot \sin^2 \theta$ (the signal power transmission through two polarizers uncrossed by angle $\theta$):

$$V_{DC-FRS}^{\nu_d} = G_V \cdot R_I \cdot \frac{dP_{sig}}{d\theta} \cdot \Theta_{FRS}(\nu_d) = G_V \cdot R_I \cdot P_0 \cdot \sin(2\theta) \cdot \Theta_{FRS}(\nu_d)$$  \hspace{1cm} (2.12)

$G_V$ denotes the detector voltage transimpedance gain (V/A) and $R_I$ denotes the current responsivity (A/W). The derivative in Equation 2.12 arises because a rotation in the angle of polarization may

\(^{2}\) The weighting factor $W(m',m'')$ is related to the Wigner 3-j symbol and is given by [7]:

$$W(m',m'') = 3 \cdot \begin{pmatrix} J'' & 1 & J' \\ -m'' & \pm 1 & m' \end{pmatrix}^2$$  \hspace{1cm} (2.11)

where again the $J'$ and $J''$ notations denotes the lower and upper transition state respectively. The numerical pre-factor is a normalization requirement to ensure the total integrated linestrength is conserved.
be equivalently viewed as a rotation in the analyzer (thus the derivative with respect to $\theta$), and may be intuitively understood from Figure 4.4 (Section 4.5), which displays the signal retrieval in hybrid-FRS. The signal given in Equation 2.12 is rigorously derived in Appendix A1.1 through the Jones calculus.

An example of spectra for the $^{15}$NO Q(3/2) line modeled using Equation 2.10 is given in Figure 2.7(b), which shows the individual Zeeman split dispersion spectra for each $\Delta m_J = \pm 1$ transition, and the difference between the RCP/LCP components which yield the Faraday rotation angle (black curve, right axis). Conversion to detector voltage signal may be accomplished through Equation 2.12, and LMS fitting is used to retrieve real-time analyte concentrations.

2.4.3 Wavelength modulation in DC-FRS

Similar to the case of WMS, laser modulation may be applied in the DC-FRS case for reduction of $1/f$ noise. Spectral modeling follows the same Fourier expansion procedure in Equation 2.5 [10], where the direct (non-modulated) DC-FRS spectra is used instead of optical transmittance:

$$V_N^{WMS}(\tilde{\nu}_d) = \sqrt{2} \cdot G_V \cdot R_f \cdot \sin(2\alpha) \cdot P_0 \cdot \frac{G_{LIA}}{\pi} \cdot \int_0^\pi \Theta_{FRS}(\tilde{\nu}_d + \tilde{\nu}_m \cos \theta) \cdot \cos(N\theta) \cdot d\theta$$  \hspace{1cm} (2.13)

An example of $2f$ harmonic wavelength modulated DC-FRS spectra is provided in the inset of Figure 2.9, and the signal strength (normalized to direct DC-FRS) is calculated as a function of modulation depth at 40 torr pressure and 125 G magnetic field. Although the maximum signal attainable through wavelength modulated DC-FRS is $\sim 60\%$ of that with direct DC-FRS, the combination of low-frequency noise reduction and narrow-bandwidth phase-sensitive measurement enhances detection sensitivity. An additional technique that may be introduced is the 45° method, where both the ordinary and extraordinary polarizations are utilized for electronic subtraction in a balanced-detection scheme (Chapter 4) [16, 19]. Commercially available auto-
balancing detectors are widely available, which allow a stable low-frequency common-mode rejection ratio (CMRR) without attenuating the modulation signal amplitude. A detailed study of balanced-detection 45° method FRS (BD-FRS) and a generalized hybrid-FRS technique (a superset of 45° and 90° methods) [19] will be explored in Chapter 4.

2.4.4 Sample modulation (AC-FRS)

A unique capability of FRS is the possibility of sample modulation, by oscillating the amplitude of the Zeeman shift via magnetic field oscillations at some frequency $f_M = \omega_m/(2\pi)$. The result is an etalon-free spectral baseline measurement because only magnetically susceptible materials (in this case only the sample) are modulated at the frequency of interest. In this case, it is important that $f_M$ is faster than typical baseline variations caused by etalon drifts so that during the demodulation process, temporal variations within one modulation period $1/f_M$ are insignificant. In this sense, AC-FRS behaves like quasi-simultaneous BD-FRS but is not limited by finite CMRR (therefore allowing leakage of optical fringing), thus serving as a true zero-baseline technique.

The introduction of magnetic field modulation $B(t) = B_0 \cos(2\pi f_M t)$ implies time dependence of $\Theta_{\text{FRS}}(\nu_d, t)$ in Equation 2.10 due to the time dependence of $\delta \nu_{m'\rightarrow m''}$ for each $\Delta m_J = \pm 1$ transition. In this case, numerical calculation of individual $\chi_{\text{disp}}(\nu_d, t)$ transitions are summed repeatedly at discrete times due to the different transition $g$-factors for non Q-branch ($\Delta J = \pm 1$) transitions. Examples of resulting $\Theta_{\text{FRS}}(\nu_d, t)$ are given by the black curves in Figure 2.10(a). Demodulation of the black curves occur at each $\nu_d$, yielding a result which is analogous to Equation 2.13 for wavelength modulation signals:

$$V_{N_{\text{AC-FRS}}}^{\nu_d} = \sqrt{2} \cdot G_v \cdot R_I \cdot \sin(2\alpha) \cdot P_0 \cdot \frac{G_{\text{LIA}}}{\pi} \cdot \int_0^{\pi/\omega_m} \Theta_{\text{FRS}}(\nu_d, t) \cdot \cos(N \cdot \omega_m t) \cdot dt$$ (2.14)
In principle, fast coil modulation can reduce $1/f$ noise contribution from the laser, but the frequency of field modulation $f_M$ in AC-FRS is experimentally constrained due to the presence of Eddy currents in the solenoid causing undesirable magnetic field distortion within the sample measurement region. It is therefore necessary to keep $f_M$ fairly slow, within the kHz range. AC-FRS therefore remains susceptible to low-frequency laser technical noise, and is addressed in Section 2.4.5 using dual-modulation FRS (DM-FRS).

Figure 2.10(b) shows the calculations of the AC-FRS signal dependence on magnetic field amplitude, for a variety of pressures. Note that the optimum magnetic fields increase with rising pressure, which is consistent with the expectation of optimum splitting near the FWHM. Additionally, the optimum signal saturates at higher pressures. This can be understood by noting that the area-normalized lineshapes broaden almost linearly in a collision-broadened (Lorentzian) regime, leading to a degradation in peak absorbance by roughly the same factor. Increasing the number density of molecules therefore presents diminishing signal gains, with the caveat that greater magnetic field (and therefore power consumption) is required to optimize the Zeeman splitting of transitions.

2.4.5 Dual-modulation FRS (DM-FRS)

In Sections 2.4.3 and 2.4.4, modulation of the laser and sample were investigated separately; the former provides $1/f$ laser intensity noise reduction and the latter allows true zero-baseline measurements by decoupling the sample spectrum from background optical etalon effects [15]. In this Section we investigate the simultaneous use of both techniques to achieve baseline free operation with low-frequency noise reduction. This technique is termed dual-modulation and was first investigated by Wang et al. [17, 24].
Using the same formalism as presented in the previous sections, DM-FRS spectra are modeled as

\[ V_{N_1}^{DM-FRS}(\tilde{\nu}_d) = \int_0^{\pi} V_{N_1}^{AC-FRS}(\tilde{\nu}_d + \tilde{\nu}_m \cos \theta) \cdot \cos(N_2 \theta) \cdot d\theta \]  

(2.15)

where \( N_1 \) and \( N_2 \) denote the field and wavelength demodulation harmonics respectively. Figure 2.11(b) shows an example of \( N_1 = 1 \) and \( N_2 = 2 \), yielding 2\( f_L \)-like spectra with a peak amplitude \(~60\%\) of the 1\( f_L \) AC-FRS spectral maxima. Again, despite the degradation in signal maximum, the ability to perform phase-sensitive detection for reduction of 1/\( f \) noise renders DM-FRS a particularly powerful technique with demonstrated performance near the shot-noise limit [17, 18, 20]. Minimum fractional absorptions for DM-FRS systems approach \((\alpha L)_{\text{min}} = 10^{-8} \text{ Hz}^{-1/2}\) levels, representing sensitivities \(~10^2\times\) greater than what is achievable using a well implemented TDLAS system. Due to their sensitivity, DM-FRS sensors are particularly well suited for trace-gas sensing with a short path length, enabling single pass sensors capable of reaching sub-ppbv\(\cdot\)Hz\(^{-1/2}\) level precisions. These sensors will be investigated at length in Chapters 5 and 6, which involve isotopic ratiometry of NO for medical and environmental studies.

Figure 2.11(a) shows the DM-FRS spectral peak amplitude as a function of wavelength modulation depth for a variety of pressures (each with optimized Zeeman splitting at the FWHM). The numerical results show essentially consistent optimum depths occurring near 2.1\( \times \) the HWHM of the absorption spectrum.

2.4.6 Notes regarding choice of FRS technique

In addition to the technique summary provided in Table 1.1, a functional map of FRS methods is depicted in Figure 2.12, with orange boxes indicating contributions from this thesis. Toward the right are non-sample-modulation techniques; instead, wavelength modulation, BD-FRS, and
hybrid-FRS are used to improve SNR performance. Toward the left are more power intensive systems offering true zero-baseline performance; these are better suited as diagnostic tools for applications requiring more stringent constraints on both accuracy and precision (e.g. medical, geoscientific studies), but consume substantially more power. In Chapter 3 we investigate the origin of noise in each of these techniques, and subsequent chapters explore the details of their implementation.
References


Chapter 3: Noise Considerations in FRS Systems

In this Chapter common dominant noise sources in optical sensors are discussed and the minimum fractional absorption is introduced as a quantitative measure of detection sensitivity. Allan deviation analysis is introduced for characterization of sensor accuracy and precision. The bulk of this Chapter focuses on sources of imprecision in FRS sensors, using experimental results detailed in [1, 2], with the goal of optimizing SNR and determining fundamental system performance limits.

3.1 Manifestations of noise

Conventional sensor systems suffer from three main sources of imprecision [3]: (i) optical intensity-noise of the light source, (ii) thermal/Johnson noise of the detector and associated detection subsystems, and (iii) shot-noise due to the Poisson distribution of photo-generated carriers. These contributions are respectively given by:

\[ \sigma_{\text{int}} = G_V \cdot R_I \cdot \sigma_{\text{RIN}} \cdot P_{\text{sig}} \cdot \sqrt{\Delta f} \]  \hspace{1cm} (3.1)

\[ \sigma_{\text{det}} = G_V \cdot R_I \cdot \sigma_{\text{NEP}} \cdot \sqrt{\Delta f} \]  \hspace{1cm} (3.2)

\[ \sigma_{\text{shot}} = G_V \cdot \sqrt{2e \cdot R_I \cdot P_{\text{sig}}} \cdot \sqrt{\Delta f} \]  \hspace{1cm} (3.3)

where we have defined \( P_{\text{sig}} \) as the total optical power incident upon the photodetector, and \( \Delta f \) as the equivalent-noise bandwidth (ENBW). The quadrature sum of these uncorrelated sources provides a measure of the total system noise \( \sigma_T \):

\[ \sigma_T = \sqrt{\sigma_{\text{int}}^2 + \sigma_{\text{det}}^2 + \sigma_{\text{shot}}^2} \]  \hspace{1cm} (3.4)

Techniques for noise reduction in an optical sensor system depends on the dominant noise contribution, with the goal of all these methods (i.e. laser modulation, detector cooling, etc.) being
fundamental shot-noise limited performance. Each of the above noise contributions (Equations 3.1 to 3.3) will be discussed in the sub-Sections below.

3.1.1 Relative intensity-noise (RIN)

Relative intensity-noise (RIN) in Equation 3.1 is denoted $\bar{\sigma}_{RIN}$ and is defined as the root-mean-square (RMS) of the power-normalized noise spectral density $\sigma_{RIN}(f)$:

$$
\bar{\sigma}_{RIN} = \sqrt{\frac{1}{M} \int_{0}^{M} [\sigma_{RIN}(f)]^2 \cdot df}
$$

(3.5)

RIN is intended to generally cover any unpredictable intensity related variations resulting from laser instability (e.g. thermal [4] and technical [5]) or mechanical instability [6], resulting in $1/f$ like ASD trends. Various methods exist to reduce the impact of low-frequency noise on spectroscopic measurements; in the case of conventional line-scanned TDLAS, this noise may be partially mitigated by ramping at higher frequencies (Appendix A2.1) to high-pass filter the $1/f$ noise contributions, resulting in white-noise detector limited performance. This is typically followed by spectral fitting algorithms (e.g. VLMS) which effectively average the noise over the lineshape FWHM (Appendix A2.2). Alternatively, wavelength modulation spectroscopy (WMS) may be utilized to encode signals at frequencies where the detector-noise floor dominates, followed by phase-sensitive detection for ENBW reduction (Section 2.2).

3.1.2 Detector noise-equivalent power (NEP)

In this thesis we deal primarily with photodiode noise such as MCT for MIR detection or GaAs based semiconductor detectors for NIR, where noise-equivalent power ($\sigma_{NEP}$) in $\text{W} \cdot \text{Hz}^{1/2}$ units (watts per one-hertz ENBW), is used as a measure of noise in the absence of incident optical input and defines the amount of optical power required for unity SNR. The detector NEP arises from
two primary contributions; (i) thermal (Johnson-Nyquist) noise [3] and (ii) generation-recombination noise due to random carrier generation [7], where the former typically dominates:

\[ \sigma_{\text{NEP}} = \sqrt{\frac{4k_B T}{R}} \]  

(3.6)

In Equation 3.6, \( k_B = 1.31 \times 10^{-23} \text{ m}^2\text{kg}^{-1}\text{s}^{-2}\text{K}^{-1} \) is the Boltzmann constant, \( T \) is the detector temperature, and \( R \) is the input impedance of the preamplifier. A heuristic demonstration of this thermal current is given in [8], and is rigorously derived using the fluctuation-dissipation theorem [9]. Although direct application of Equation 3.6 may be used for detector-noise analysis, measurements such as those given in Figure 7.15 (Section 7.3.4) are sufficient for empirical noise characterization of \( \sigma_{\text{NEP}} \) and will be used for analysis of the forthcoming sensor systems.

3.1.3 Shot-noise

Shot-noise as described by Equation 3.3 is computed by the power spectral density of photocurrent for a constant incident power \( P_{\text{sig}} \) [3], and is treated in this thesis as the fundamental performance limit of conventional sensor systems limited by a Poisson distribution of photo-generated carrier statistics [10]. Note that Equation 3.3 does not distinguish between the origin of shot-noise, that is, whether it primarily arises from photon or detection statistics. Given a typical current responsivity \( \sim 1 \text{ A/W} \) [1] and a wavelength of 5.4 \( \mu\text{m} \) (Chapters 5 and 6), the photon and charge carrier count per unit time are comparable \( (\sim 10^{14} \text{ counts/s}) \); therefore, any differences in statistical distributions become significant. In this dissertation we deal only with coherent light, which demonstrates Poissonian statistics such that Equation 3.3 may be applied without modification.

3.1.4 Quantifying detection sensitivity

Given the sources of noise expressed in Equations 3.1 to 3.3, we may write the total effective optical noise (denoted as \( P_\sigma \)) as:
\[ P_{\sigma} = \frac{\sigma_{\text{tot}}}{G_V \cdot R_I} = \sqrt{(\bar{\sigma}_{\text{RIN}} \cdot P_{\text{sig}})^2 + (\sigma_{\text{NEP}})^2 + \left( \frac{2e \cdot P_{\text{sig}}}{R_I} \right)} \]  
(3.7)

To introduce a general measure of spectrometer sensitivity, note that for a transmission measurement \( P_{\text{sig}} = P_0 \cdot e^{-\alpha L} \) according to the Beer-Lambert law from Equation 2.1. We quantify sensor performance by indicating the smallest fractional absorption signal \( \Delta P_{\text{min}}/P_0 \) resolvable, where \( \Delta P = (P_0 - P_{\text{sig}}) \). For optically thin samples, a first-order Taylor expansion gives:

\[ \frac{\Delta P}{P_0} \approx \alpha L \]  
(3.8)

From Equation 3.7, we have determined the smallest power fluctuation \( \Delta P_{\text{min}} = P_{\sigma} \), and in the absence of absorbing species (such that \( P_{\text{sig}} = P_0 \)) we may write the minimum fractional absorption \((\alpha L)_{\text{min}}\) as:

\[ \frac{\Delta P_{\text{min}}}{P_0} = \sqrt{\bar{\sigma}_{\text{RIN}}^2 + \frac{\sigma_{\text{NEP}}^2}{P_{\text{sig}}^2} + \frac{2e}{R_I \cdot P_{\text{sig}}}} \equiv (\alpha L)_{\text{min}} \]  
(3.9)

Equation 3.9 has three limiting cases, dominated by RIN, detector NEP, and shot-noise. These can be respectively written as:

\[ (\alpha L)_{\text{int}} = \bar{\sigma}_{\text{RIN}}, \quad (\alpha L)_{\text{det}} = \frac{\sigma_{\text{NEP}}}{P_{\text{sig}}}, \quad (\alpha L)_{\text{shot}} = \sqrt{\frac{2e}{R_I \cdot P_{\text{sig}}}} \]  
(3.10)

Given that SNR \( \sim 1/(\alpha L)_{\text{min}} \), minimum detection limits (MDL) improve (with increasing \( P_{\text{sig}} \)) only in the case where sensors are detector- or shot-noise limited. Where a sensor is limited by \( \sigma_{\text{NEP}} \), it is merely sufficient to increase power until either intensity-noise or (preferably) shot-noise limits are reached; the latter limit still allows sensitivity enhancement by \( \sqrt{P_{\text{sig}}} \), whereas the former case remains independent of optical power. The existence of the shot-noise regime for a spectrometer is not guaranteed, and is covered in more detail in Section 3.3.1 for FRS systems.
Using the formulation described above, we may generally say that sensors with smaller \((aL)_{\text{min}}\) are superior, although an instrument with poor \((aL)_{\text{min}}\) may perform well by increasing optical path length \(L\). Therefore, \(a_{\text{min}} = (aL)_{\text{min}}/L\) is frequently used as another figure of merit representing sensitivity with the path length taken into account. While \(a_{\text{min}}\) is a direct measure of analyte MDL, \((aL)_{\text{min}}\) is more useful for inter-comparison involving spectrometers utilizing different spectroscopic techniques.

### 3.2 Allan deviation analysis for spectroscopy

Spectroscopic sensitivity is quantified through the Allan deviation \((\sigma_{\text{ADV}})\) [11], or two-sample deviation, initially devised as a frequency stability metric for timekeeping. In contrast to conventional deviation calculations, \(\sigma_{\text{ADV}}\) converges for common types of noise, in particular, those with 1/f ASD (Figure 3.1).

The Allan deviation can be viewed as a moving standard deviation; rather than choosing the time-series mean as a reference, \(\sigma_{\text{ADV}}\) ‘bins’ the time-series into a duration \(\tau\) and references the deviation with respect to a previous bin:

\[
\sigma_{\text{ADV}}(\tau) = \sqrt{\frac{1}{2(M + 1) \sum_{i=1}^{M-1} (\nu_{i+1} - \nu_{i})^2}} \tag{3.11}
\]

In Equation 3.11, \(M\) denotes the number of total bins, and \(\nu_i\) the bin average. Sensor precision and accuracy (zero-drift time) are defined as:

(a) **Precision**: detectivity obtained in the shortest \(\tau\) (typically 1 s), i.e. \(\sigma_{\text{ADV}}(\tau = 1\ \text{s})\)

(b) **Stability time**: maximum \(\tau_{\text{stab}}\) under which \(\sigma_{\text{ADV}}\) follows Gaussian (Hz \(^{-1/2}\)) performance

(c) **Zero-drift time**: the integration time \(\{\tau_{\text{min}}, \tau_{\text{ZD}}\}\) between which the \(\sigma_{\text{ADV}}\) falls under a tolerance threshold \(\sigma_{\text{TOL}}\), i.e. \(\sigma_{\text{ADV}}(\tau < \sigma_{\text{TOL}}) < \tau < \tau_{\text{ZD}}\)

### 3.3 Noise analysis and optimization for FRS
In the following we study the impact of laser intensity-noise, detector-noise, and shot-noise on the sensitivity of Faraday rotation systems, and explore techniques used in Chapters 4 to 6 for SNR optimization. In particular, the detailed study of analyzer uncrossing angle is performed for intensity-noise suppression. In Section 3.3.4, a unique quantifier termed the noise-equivalent angle ($\Theta_{\text{NEA}}$) is used to characterize FRS spectrometers, and its correspondence with $(\alpha L)_{\text{min}}$ is studied.

3.3.1 Relative noise contributions

We consider noise contributions in the conventional 90° methods (AC-FRS and DC-FRS techniques included). Through the use of Equations 2.12 and 3.7, we write the SNR as:

$$SNR_{\text{tot}}^{90°} = \frac{\xi(N_f L) \cdot \sin(2\theta) \cdot \Theta_{\text{FRS}}(\nu_d)}{\sqrt{[\sigma_{\text{RIN}} \cdot \sin^2(\theta)]^2 + \left(\frac{\sigma_{\text{NEP}}}{P_0}\right)^2 + \left(\frac{2e \cdot \sin^2(\theta)}{R_L \cdot P_0}\right)^2}}$$  \hspace{1cm} (3.12)

where we have introduced a signal degradation factor $\xi(N_f L)$ due to $N$th harmonic detection. Similar to Section 3.1.4, we consider the three limiting cases in Equation 3.12:

$$SNR_{\text{int}}^{90°} = \frac{\xi(N_f L) \cdot 1}{\sigma_{\text{RIN}}} \cdot \frac{\sin(2\theta)}{\sin^2(\theta)} \cdot \Theta_{\text{FRS}}(\nu_d)$$ \hspace{1cm} (3.13)

$$SNR_{\text{det}}^{90°} = \frac{\xi(N_f L) \cdot P_0}{\sigma_{\text{NEP}}} \cdot \frac{\sin(2\theta)}{\sin^2(\theta)} \cdot \Theta_{\text{FRS}}(\nu_d)$$ \hspace{1cm} (3.14)

$$SNR_{\text{shot}}^{90°} = \frac{\xi(N_f L) \cdot \sqrt{R_L \cdot P_0}}{2e} \cdot \frac{\sin(2\theta)}{\sin \theta} \cdot \Theta_{\text{FRS}}(\nu_d)$$ \hspace{1cm} (3.15)

Although Equations 3.13 to 3.15 appear to independently vary with $P_0$ and $\theta$, the optimum analyzer uncrossing angle $\theta$ is dependent upon $P_0$ and will be studied in the next Section.

Given the noise contributions outlined above, the conditions under which a shot-noise dominated regime exists requires $\sigma_{\text{shot}} > \{\sigma_{\text{int}}, \sigma_{\text{det}}\}$ for some incident power $P_0$, that is,
\[
\frac{2e \cdot \sin^2(\theta)}{R_i \cdot P_0} > \left\{ \left( \frac{\sigma_{\text{NEP}}}{P_0} \right)^2 \cdot \left[ \sigma_{\text{RIN}} \cdot \sin^2(\theta) \right]^2 \right\}^{1/2}
\]  

(3.16)

Solving for Equation 3.16 gives an inequality for \( P_0 \), where monotonically increasing bounds ensures existence of shot-noise. The resulting condition is given by [12]:

\[
\sigma_{\text{NEP}} \cdot \sigma_{\text{RIN}} < 2e \cdot (R_i)^{-1}
\]

(3.17)

From Equation 3.17, it is clear that an excess of either detector- or laser intensity-noise will mask shot-noise, and can be intuitively visualized from Figure 3.2(a).

3.3.2 Optimization of analyzer uncrossing angle

Generally, optimization of SNR is required for FRS spectrometers due to different contributions of detector-noise (\( \sigma_{\text{det}} \)), laser intensity-noise (\( \sigma_{\text{int}} \)), and shot-noise (\( \sigma_{\text{shot}} \)), as outlined in Section 3.3.1. These noise contributions are characterized by controlled variation of the analyzer uncrossing angle \( \theta \), thereby altering the signal power as \( P_{\text{sig}} = P_0 \cdot \sin^2(\theta) \). In the following we use the DM-FRS system described in Chapter 5 as an example, with \( P_0 = 6.4 \text{ mW} \) being the power incident upon the analyzer [1]. Experimental characterization of noise contributions (the shot-noise is calculated based on incident signal power) is provided in Figure 3.2(a) Analysis of the noise yields a laser RIN of \( 2.19 \times 10^{-7} \text{ Hz}^{-1/2} \), and a photodetector NEP of \( 1.25 \times 10^{-12} \text{ W} \cdot \text{Hz}^{-1/2} \). The corresponding total noise fit to the measured data is given by the quadrature sum of the individual component contributions as described using Equation 3.7, where we have assumed an ENBW of \( \Delta f = 1 \text{ Hz per sideband} \) (corresponding to a 2 Hz total ENBW for DM-FRS as described in Section 5.2). The optimum uncrossing angle occurs exactly when

\[
\sigma_{\text{det}}^2 = \sigma_{\text{shot}}^2 \cdot \frac{\sin^2(\theta)}{\cos(2\theta)} + \sigma_{\text{int}}^2 \frac{1}{\cos(2\theta)}
\]

(3.18)
Equation 3.18 describes the zero-derivative condition of the total SNR given by the ratio in Equation 3.12, resulting in an analytic solution for \( \theta_{opt} \) given by (Appendix A1.2):

\[
\theta_{opt} = \sin^{-1} \left( \frac{\sigma_{det}}{\sigma_{sig} + \sigma_{det}} \right), \quad \text{where} \quad \sigma_{sig}^0 = \sqrt{(\sigma_{det}^0)^2 + (\sigma_{shot}^0)^2 + (\sigma_{int}^0)^2}
\]

(3.19)

where we have used \( \sigma_{int}^0 = G_V R_I \bar{\sigma}_{\text{RIN}} P_0 \) and \( \sigma_{shot}^0 = G_V (2 e R_I P_0)^{1/2} \) to denote the intensity- and shot-noise incident upon the analyzer. Additionally, the extinction ratio of the system is assumed to have negligible noise contribution \( (\varepsilon = 1.86 \times 10^{-4} \text{ from [1]) and has been ignored in the above derivations (full expressions can be found in Section 3.3.3). Note that even in a fairly low-power case, \( \sigma_{int}^0 \) is the dominant contributor to \( \sigma_{sig}^0 \) in Equation 3.19. Thus, we may nominally assume \( \sigma_{int}^0 \gg \{\sigma_{shot}^0, \sigma_{det}\} \), which yields:

\[
\theta_{opt} \approx \sin^{-1} \left( \frac{\sigma_{NEP}}{\bar{\sigma}_{\text{RIN}} P_0} \right) = 1.71^\circ
\]

(3.20)

Using Equation 3.20, we also see that at \( \theta_{opt} \), the detector signal power \( P_{\text{sig}}^{opt} \) is given by:

\[
P_{\text{sig}}^{opt} = \frac{\sigma_{NEP}}{\bar{\sigma}_{\text{RIN}}}
\]

(3.21)

Therefore, to reach optimum SNR performance it is necessary for the detector saturation limit \( P_{sat} \) to be above the power defined by Equation 3.21, i.e. \( P_{sat} > P_{\text{sig}}^{opt} \). Referring to Figure 3.2(b) and using Equation 3.18, we find that the optimum uncrossing angle is well approximated (for small \( \theta \)) by the point where \( \sigma_{int} = \sigma_{det} \), yielding a calculated optimum angle consistent with the measured \( \theta_{opt} = 1.71^\circ \) at \( P_{\text{sig}} = 5.7 \mu W \).

Prior expressions of SNR in FRS for limiting noise cases were derived in Equations 3.13 to 3.15; it is now possible to use Equation 3.19 to understand the power dependence of SNR in each scenario.
Note that in all cases (regardless of the dominant noise source), SNR for 90° methods obey $\sqrt{P_0}$ trends with analyzer angle optimization (Equation 3.22 is identical for both intensity- and detector-noise because $\sigma_{int} = \sigma_{det}$ at $\theta_{opt}$). This is a unique feature of FRS, whereby even in the intensity-noise limited regime, SNR may be enhanced through power increase (compare with Equation 3.10 for TDLAS, where SNR remains constant in the intensity-noise limit). Intuitively, this may be understood from FRS signal enhancement due to $P_0$ increase (Figure 4.4), combined with $\theta$ reduction such that $P_{sig}$ stays constant (thus keeping the total noise unchanged). This is implemented in hybrid-FRS (Chapter 4) to remove the detector saturation limit, and is not a limiting factor in conventional 90° methods.

Using shot-noise limited SNR in Equation 3.23 as reference, we compare the relative SNR for the other noise cases:

$$SNR_{\text{int},det}^{90°} = \frac{\sqrt{2} \cdot \xi(N_f) \cdot \Theta_{\text{FRS}}(\tilde{v}_d) \cdot \sqrt{P_0}}{\sqrt{\sigma_{\text{RIN}} \cdot \sigma_{\text{NEP}}}}$$  

(3.22)

$$SNR_{\text{shot}}^{90°} = \frac{\sqrt{2R_i} \cdot \xi(N_f)}{\sqrt{e}} \cdot \Theta_{\text{FRS}}(\tilde{v}_d) \cdot \sqrt{P_0}$$  

(3.23)

Given that the noise is inversely proportional to SNR, Equation 3.24 indicates that the system operates at factor $\Lambda_{\sigma}$ above the shot noise limit, given by

$$\Lambda_{\sigma} = \sqrt{1 + \frac{\sigma_{\text{RIN}} \cdot \sigma_{\text{NEP}}}{e/R_i}}$$  

(3.25)

Using experimental values $\sigma_{\text{NEP}} = 1.25 \times 10^{-12}$ W$\cdot$Hz$^{-1/2}$, $\sigma_{\text{RIN}} = 2.19 \times 10^{-7}$ Hz$^{-1/2}$, $R_i = 3.8$ A/W, and $e = 1.602 \times 10^{-19}$ C, we obtain $\Lambda_{\sigma} = 2.73$, and is consistent with the experimental value of $\Lambda_{\sigma,\text{expt}} =$
2.78 obtained in Chapter 5. Note that Equation 3.25 is independent of \( P_0 \); it is merely necessary to optimize \( \theta \) to maintain \( \Lambda_\sigma \) for the incident power. In other words, the 90º method can be maintained at the same factor \( \Lambda_\sigma \) above the shot-noise limit for all \( P_0 \). For comparison, in an identical experimental configuration, TDLAS operates at 60.4\( \times \) the shot noise limit; and in this case FRS presents superior performance due to intensity-noise suppression via nearly-crossed polarizers.

### 3.3.3 Impact of polarizer extinction ratio

In Section 3.3.2, \( \theta \) is optimized to maximize SNR, which occurs at an angle \( \theta_{opt} \), where the detector- and intensity-noise are approximately equal. However, this assumes a polarization extinction ratio (PER) \( \epsilon \) such that the intensity leakage through the analyzer (\( \sigma_{int,e} \)) is negligible compared to the detector noise floor, or \( \sigma_{int,e} \ll \sigma_{det} \). During the initial developmental phase of the differential DM-FRS experimental scheme described in Appendix A3 [2], an empirically sharp degradation of \( \epsilon \) was observed when the incident beam polarization is varied even very slightly from \( s \) and \( p \) type prior to the retro-reflector, resulting in a poor extinction ratio (\( \epsilon = 1.62\times10^{-3} \)) and thus invalidating the above assumption. Additionally, the initial use of Rochon polarizers resulted in significant beam crosstalk between the ordinary and extraordinary polarizations due to the very small exit angle (\( \sim 1^\circ \)). Although such limitations have since been overcome by replacement using wire grid polarizers, it is instructive to calculate the impact of PER on the optimal analyzer angle in a general case. We quantify this by repeating the above calculations with PER included by replacing the nominal signal power \( P_{sig} = P_0\sin^2(\theta) \) with \( \tilde{P}_{sig} \) to account for the effect of leakage of the ordinary polarization beam (Appendix A1.2):

\[
\tilde{P}_{sig} = P_0 \cdot [\sin^2(\theta) + \epsilon \cdot \cos^2(\theta)] = P_{sig} + P_{leak}
\]  

(3.26)

Again solving for the zero-derivative condition \( d(SNR_{tot})/d\theta = 0 \), \( \theta_{opt} \) occurs when:
\[(\text{eff } \sigma_{\text{det}})^2 = (\sigma_{\text{shot}}^P)^2 \cdot \frac{\sin^2(\theta)}{\cos(2\theta)} + (\sigma_{\text{int}}^P)^2 \cdot \frac{1}{\cos(2\theta)} \] (3.27)

Note the similarity to Equation 3.18, where \( \sigma_{\text{shot}}^P = G_V (2 e R_f P_{\text{sig}})^{1/2} \) and \( \sigma_{\text{int}}^P = G_V R_f \sigma_{\text{RIN}} P_{\text{sig}} \) are the shot- and intensity-noise contributions from the signal (not leakage) power, and is identical to the right-hand side of Equation 3.18. The effective detector noise \( \text{eff } \sigma_{\text{det}} \) is defined by a quadrature sum of nominal detector baseline and polarization leakage terms:

\[ \text{eff } \sigma_{\text{det}} = \sqrt{(\sigma_{\text{det}})^2 + \left(\frac{\sigma_{\text{int}}^P \cdot \cos^2(\theta)}{\cos(2\theta)}\right) + \left(\frac{\sigma_{\text{shot}}^P \cdot 1}{\cos(2\theta)}\right)} \] (3.28)

In the case of nearly-crossed polarizers (small \( \theta \)), leakage terms are well approximated by \( \sigma_{\text{int}}^P \approx \varepsilon \cdot \sigma_{\text{int}}^P \) and \( \sigma_{\text{shot}}^P \approx \sqrt{\varepsilon} \cdot \sigma_{\text{shot}}^P = G_V (2 e R_f e^2 P_0)^{1/2} \) resulting in a constant effective detector noise term that can be directly measured by completely crossing the polarizers. Again, only the latter term in Equation 3.27 remains significant, and the uncrossing angle is well approximated by \( \text{eff } \sigma_{\text{det}} = \sigma_{\text{int}}^P \), corresponding to:

\[ \theta_{\text{opt}} = \sin^{-1} \sqrt{\frac{\text{eff } \sigma_{\text{det}}}{\sigma_{\text{int}}^P + \text{eff } \sigma_{\text{det}}}} \] (3.29)

Note that in the very high-power limit where leakage power dominates the effective detector-noise, Equation 3.29 converges to

\[ \theta_{\text{opt}} \approx \sqrt{\frac{\varepsilon}{1+\varepsilon}} \quad \Rightarrow \quad P_{\text{sig}}^{\text{opt}} = \left(\frac{\varepsilon}{1+\varepsilon} + \varepsilon\right) P_0 \] (3.30)

The consequence of this power leakage in an intermediate power case of Equation 3.29 is graphically shown in Figure A3.4, whereupon the introduction of finite PER increases the effective detector NEP, causing \( \theta_{\text{opt}} \) to increase and degrading the optimum SNR. In FRS sensors, the effect of depolarization (e.g. by multi-pass measurements and multiple intermediate optical interfaces)
needs to be carefully mitigated as it affects the smallest detectible polarization angle (noise-equivalent angle $\Theta_{NEA}$), described below.

3.3.4 Noise-equivalent Faraday rotation angle

We characterize the sensitivity of Faraday rotation systems based on the smallest detectable polarization rotation angle, termed the noise-equivalent Faraday rotation angle ($\Theta_{NEA}$).

Substitution of Equation 3.20 into Equation 3.12, and setting $\Theta_{NEA} = \Theta_{FRS}(\bar{\nu})$ when $SNR_{tot}^{90^\circ} = 1$ (minimum detectable limit at unity SNR), we obtain [13]:

$$\Theta_{NEA} = \frac{1}{\xi(Nf_L)} \sqrt{\frac{\sigma_{RIN} \cdot \sigma_{NEP} + e/R_I}{2P_0}}$$

(3.31)

In the shot-noise limit, $\sigma_{RIN} \cdot \sigma_{NEP} << e/R_I$ from Equation 3.25, and Equation 3.31 reduces to:

$$\Theta_{NEA}^{shot} = \frac{1}{\xi(Nf_L)} \sqrt{\frac{e/R_I}{2P_0}}$$

(3.32)

A direct correspondence between the noise equivalent angle $\Theta_{NEA}$ and the minimum fractional absorption $(aL)_{min}$ exists in the simple case of optimum splitting of a single line. This can be demonstrated analytically (Appendix A1.3) in the typical case of homogeneously broadened (Lorentzian) spectra, where application of Equation 2.2 with $\delta\nu_D << \delta\nu_L$ yields an area normalized absorption lineshape $\chi_{abs}(\bar{\nu}_d)$, and through the KKR (or equivalently, Equation 2.2 and 2.7) a dispersion lineshape given by [3]:

$$\chi_{abs}(\bar{\nu}_d) = \frac{1}{\pi} \cdot \frac{\delta\nu_L}{\bar{\nu}_d^2 + \delta\nu_L^2} \cdot \chi_{disp}(\bar{\nu}_d) = \frac{1}{\pi} \cdot \frac{\bar{\nu}_d}{\bar{\nu}_d^2 + \delta\nu_L^2}$$

(3.33)

Differentiation of $\chi_{disp}(\bar{\nu}_d)$ gives maxima at $\bar{\nu}_d \approx \pm \delta\nu_L$ which indicates a peak-to-peak variation of equal to $\chi_{abs}(\bar{\nu}_d = 0) = (\pi \cdot \delta\nu_L)^{-1}$. At optimum splitting, this peak-to-peak variation is
probed using the LCP/RCP light, and application of Equation 2.8 demonstrates that \( \Delta \phi_{\text{max}} = \Delta \phi(\tilde{V}_d = \pm \delta \tilde{V}_L) = \alpha L/2 \). Given that the FRS angle \( \Theta_{\text{FRS}} = \Delta \phi_{\text{max}}/2 \) [3], it follows that:

\[
\Theta_{\text{NEA}} = \frac{1}{4}(\alpha L)_{\text{min}}
\]  

(3.34)

In practice, slight deviations from Equation 3.34 may occur for a number of reasons, including sub-optimal magnetic field, over/under-modulation amplitude of the laser, or multiple lines with varying g-factors causing unequal Zeeman splitting.

At this point, it is also instructive to consider the comparison between FRS and TDLAS in the fundamental shot-noise limited case, using the noise-equivalent angle formulation above. From Equations 3.32 and 3.34, the minimum fractional absorption for shot-noise limited FRS is:

\[
(aL)_{\text{min}}^{90^\circ \text{FRS}} = \frac{2}{\xi(N \tilde{f}_L)} \cdot \sqrt{\frac{2\cdot e/R_f}{P_0}}
\]  

(3.35)

and in conjunction with Equation 3.10 (using the minimum fractional absorption in the shot-noise limited case), we find that

\[
\frac{(aL)_{\text{min}}^{90^\circ \text{FRS}}}{(aL)_{\text{min}}^{\text{TDLAS}}} = \frac{2}{\xi(N \tilde{f}_L)}
\]  

(3.36)

From Equation 3.36 above, we see that TDLAS fundamentally performs \( \sim 2\times \) better (within the harmonic signal reduction factor). However, this is based on the limit of shot-noise, which is difficult to achieve through conventional TDLAS techniques (due to the presence of laser RIN, low-frequency 1/f noise, spectral baseline structure and fringe drifts, etc.). In practice FRS systems can reach this shot-noise limit much more readily using appropriate noise mitigation techniques described in Chapters 4 to 6, and generally present superior sensitivities when compared to TDLAS.
References


Chapter 4:
Hybrid Faraday Rotation Spectroscopy

Faraday rotation spectroscopy (FRS) of $O_2$ is performed at atmospheric conditions using a DFB diode laser and permanent rare-earth magnets [1, 2]. Polarization rotation is detected with a hybrid detection method that combines the advantages of two approaches: balanced optical-detection (45º method) and conventional FRS with an optimized analyzer offset angle (90º method) for maximum sensitivity enhancement. A measurement precision of $0.6 \text{ ppmv} \cdot \text{Hz}^{-1/2}$ at $1.4 \times$ the shot-noise limit for atmospheric $O_2$ is demonstrated, and a theoretical model of hybrid detection is described, with calculated detection limits in good agreement with experiment.

4.1 Introduction

The significant role of oxygen ($O_2$) in geochemical and biological cycles necessitates its detection in various scientific and environmental settings [3-8]. Modern applications are increasingly stringent, requiring greater accuracy, stability and shorter acquisition times [3, 5]. Magnetodynamic detection of $O_2$ by exploiting its paramagnetic properties is one technique that has been explored to meet these requirements [9, 10], but is susceptible to mechanical vibrations and drifts. Alternate techniques include solid-state sensors for combustion diagnostics [11], and more recently miniature $O_2$ sensors, where alteration of the electrical or chemical properties of nanostructures is used [12, 13]. Despite substantial progress in such $O_2$ detection technologies, in situ measurements remain challenging due to issues involving environmental contamination, operating pressure constraints and interfering molecular species.

Optical spectroscopic systems have received strong interest due to their sensitivity and specificity [14-23] and are frequently built for low-power, field deployable operation. Sub-part-per-million (sub-ppmv) $O_2$ detection limits have been achieved with vacuum-ultraviolet absorption
[24] and fiber-based techniques [25], although portability, dynamic range and in situ capabilities hinder their application. To date, we have not identified any sensor in literature that performs in situ atmospheric O₂ detection with the target sub-ppmv sensitivity required for bio-respiratory diagnostics [3].

Recent work [26-28] has identified promise for sub-ppmv O₂ detection at atmospheric pressure using Faraday rotation spectroscopy (FRS) that targets the A-band of oxygen at 762 nm [29]. In O₂ FRS, an applied magnetic field splits the \( ^3\Sigma^- \) O₂ ground state, and quantum selection rules allow only \( \Delta m_J = +1 \) and -1 for rovibronic transitions in the A-band, which interact with right-handed (RCP) and left-handed circularly polarized (LCP) light respectively. The resulting circular birefringence, detailed in Chapter 2, causes rotation of linearly polarized light as it travels through an O₂ sample, and is detected by projection onto a nearly-crossed polarizer. So et al. [27, 28] performed atmospheric pressure FRS on the O₂ \(^{3}P^{1}\) transition [29] using a modulated (AC) magnetic field, yielding an AC-FRS detection limit of 10 ppmv·Hz\(^{-1/2}\). Brumfield et al. [26] employed rare-earth magnets for static (DC) field generation and conventional balanced-detection FRS (BD-FRS) for fringe removal and intensity-noise suppression. This configuration was used to achieve a shot-noise limited sensitivity of 6 ppmv·Hz\(^{-1/2}\).

In the present work we demonstrate further sensitivity enhancement using a DFB laser diode to: (i) increase the laser power and maintain near shot-noise performance for signal-to-noise ratio (SNR) enhancement, and (ii) employ a hybrid FRS system that combines balanced-detection and optimization of the analyzer offset angle typical for conventional AC-FRS systems. The hybrid-FRS technique, which also uses a DC magnetic field, achieves a 10× enhancement beyond the sensitivity reported in [26].

4.2 Conventional FRS methods
As described in Section 1.4, there are two distinct FRS signal detection methods reported in literature: (1) 90° method implemented with nearly-crossed polarizers [28, 30, 31] and (2) 45° method employing balanced optical-detection [26, 31-33]. The former is more popular [32, 33] because it is simpler to implement, requiring only a single photodetector and two nearly-crossed polarizers (before and after the sample) to measure $\Theta_{\text{FRS}}$ of the light polarization [33]. In this nearly-crossed configuration, the laser intensity-noise is effectively suppressed, providing improved SNR in the FRS measurement compared to TDLAS. As described in Section 3.3.2, $\theta_{\text{opt.}}$ is determined by equalizing detector NEP with laser RIN or quantum shot-noise generated from the laser radiation incident on the photodetector. In the 45° method, the laser intensity-noise suppression is performed electronically by splitting the laser beam emerging from the sample cell into orthogonally polarized components (usually equal power achieved with $\theta = 45^\circ$) and performing balanced-detection using two photodetector elements. In this configuration, the component FRS signals measured on both photodetector elements are out of phase, while the intensity-noise is in phase allowing for laser noise suppression. Auto-balanced photodetectors (e.g. Nirvana model 2007 by New Focus) that require other than a 50/50 split ratio have also been successfully used in BD-FRS systems (the split ratio can be conveniently adjusted by varying $\theta$) [26]. Both the 45° and 90° methods present unique advantages and limitations (discussed in Section 4.5), and prior experimental work has assumed them to be distinct [30, 32, 33]; that is, the use of one method precludes the other. In what follows, we experimentally show that these two techniques can be used in a complementary fashion resulting in a hybrid-FRS method that can achieve a better SNR than either one alone. To identify the benefits of hybrid-FRS, we first present results of the conventional 45° method and compare this with hybrid-FRS in Section 4.6.

4.3 Experimental Setup
The studies and experiments have been performed using the optical configuration shown in Figure 4.1. The setup is similar to that reported by Brumfield et al. [26], but the VCSEL laser used in [26] has been replaced with a DFB diode laser (Sacher Lasertechnik, $\lambda = 762$ nm, targeting the $^3P_1(1)$ $O_2$ transition in the A electronic band [29]), with some important modifications made to the polarization optics to enable hybrid-FRS measurement (detailed below). The laser current is modulated at $f_L = 6$ kHz with a modulation depth optimized to maximize the $2f_L$ FRS signal. The ambient laboratory air at room temperature and atmospheric pressure is used as the sample gas for our studies. The laser light is first transmitted through a Glan-Thompson polarizer (GTP) to establish a clean polarization state prior to entering a cylindrical-mirror multi-pass cell (MPC). The cell provides $L = 6.8$ m path length with $40\%$ optical throughput. An array of rare-earth magnets generates a 554 G axial magnetic field in the active region probed by the laser beam within the MPC. Light passing through the cell undergoes polarization rotation due to interaction with the sample and is split (after exiting the cell) into orthogonal components by a Wollaston prism (WP). Balanced-detection and demodulation is performed using a Nirvana auto-balancing photodetector (New Focus, model 2007) and lock-in amplifier (Signal Recovery 7265), with automated data acquisition using a DAQ board (NI-USB-6529) and customized LabVIEW software. The auto-balancing function is employed with an optimal 2:1 reference-to-signal-photodiode split-ratio (480 $\mu$W on the signal-photodiode), resulting in laser intensity-noise suppression of $> 20$ dB (the 21.6 dB common-mode rejection-ratio (CMRR) of the balanced detector (BPD) is determined experimentally). The system is used to perform detection using the $45^{\circ}$ method and hybrid-FRS methods. As the DFB laser is capable of providing up to 30 mW of output optical power, a nano-particle polarizer (NPP) (shown as NPP1 in Figure 4.1) is placed after the laser output to attenuate the laser radiation and avoid detector saturation in the $45^{\circ}$ method.
In hybrid-FRS the NPP1 is set to maximum transmission and the detector saturation is avoided by combination of the appropriate $\theta$ setting and attenuation of the reference branch using the NPP2. Since the optical fringes introduced by the NPP2 are very stable, the auto-balancing circuit is capable of compensation of any slow optical power drift between the reference- and signal-photodiodes. It should also be noted that NPP2 is relatively thin resulting in a large fringe free spectral range (> 10× the $^3P_1(1)$ linewidth), so any parasitic intensity modulation induced by the laser wavelength modulation creates a negligible baseline offset in the measured FRS signal.

To assess the proposed hybrid-FRS method and establish a performance baseline, conventional BD-FRS is implemented using the same system components. In our prior work we used a VCSEL [26] capable of delivering 20 µW of optical power to the signal-photodiode. This resulted in a minimum detection limit (MDL) for $O_2$ of 6 ppmv·Hz$^{-1/2}$. Application of a more powerful DFB laser that can easily deliver up to 480 µW to the signal-photodetector (detector saturation occurs at 500 µW) is expected to result in a 4.9× improvement in $O_2$ sensitivity. At $P_0 \approx 1.4$ mW (which provides 480 µW to the signal detector at a split ratio of 2:1), the MDL for $O_2$ measured with the conventional balanced FRS system using DFB laser is 1.8 ppmv·Hz$^{-1/2}$, and is detailed below.

4.4 Balanced-detection FRS of $O_2$

The 2f$_i$ FRS $^3P_1(1)$ spectral line is shown in Figure 4.2. The laser is thermally tuned by 2.5 °C corresponding to 3.3 cm$^{-1}$ wavenumbers, and the asymmetry in the lineshape is due to residual amplitude modulation as the DFB optical output increases with decreasing temperature. The inset in Figure 4.2 shows an expanded view of the 36 °C to 37 °C baseline, exposing a weak $^{16}O^{18}O$ isotopic feature. The inset also shows minor CMRR-suppressed fringing with a FSR of ~ 0.1 cm$^{-1}$ and is consistent with the GTP length.
System noise is characterized by measuring CMRR-suppressed laser intensity-noise and total noise as power on the BPD increases (Figure 4.3). The measured CMRR of 20.3 dB for these BD-FRS experiments indicates a target shot-noise regime between 20 µW and 480 µW. VCSEL results in [26] use 20 µW of signal-photodiode incident power to achieve a sensitivity of 6 ppmv·Hz\(^{-1/2}\), hence a 4.9× improvement factor may be expected from our simple power increase in the shot noise regime. At 480 µW, our minimum detection limit (MDL) improves to 1.8 ppmv in 1 sec., corresponding to an improvement of 3.3×, or 70 % of the expected enhancement. The 30 % discrepancy has been attributed to the higher laser relative intensity-noise (RIN) of 5.3×10\(^{-7}\) Hz\(^{-1/2}\) (2× the VCSEL RIN), roughly at 2× the quantum shot-noise limit. However, it should be noted that due to the detector saturation limit only a fraction of the available laser power \(P_0 \approx 1.4\) mW vs. 8 mW maximum available after the MPC could be used to perform this measurement.

The SNR trend in Figure 4.3 can be explained as follows: in the low-power shot-noise regime, \(\text{SNR} \sim P_0^{1/2}\) (\(P_0\) is total power incident on the BPD). As power increases, intensity-noise increases faster than shot-noise, resulting in the SNR increasing as \((P_0)^n\), where \(n \rightarrow 0\) in the intensity-noise regime. Beyond the shot-noise to intensity-noise crossover point (480 µW), no benefit is derived from further power increase.

4.5 Limitations of the 45° and 90° method

Based on the results obtained with the 45° method in the previous Section, one can realize that its main limitation is related to detector saturation, which limits the amount of total laser power that can be used in the FRS measurement. On the contrary, the 90° method is free from this limitation, because the amount of light transmitted through a nearly-crossed analyzer is significantly lower; however, laser noise and electromagnetic interference (EMI) limits the achievable sensitivity. In
order to discuss the main limitations in both techniques, an analysis of signal and noise in both methods is performed below.

In the 45º method (where $\theta = 45^\circ$), the signal ($V_{45^\circ}$) and noise ($\sigma_{45^\circ}$) is expressed as:

$$V_{45^\circ} = 2 \cdot \xi (N_f) \cdot G_v \cdot R_i \cdot P_0 \cdot \Theta_{FRS}$$

$$\sigma_{45^\circ} = 2 \cdot G_v \cdot R_i \cdot P_0 \cdot \sqrt{\left(10 \cdot \frac{CMRR}{20} \cdot \frac{\sigma_{BIN}}{4} \cdot \sqrt{\Delta f}\right)^2 + \left(\frac{\sigma_{NEP}}{2 P_0} \cdot \sqrt{\Delta f}\right)^2 + \frac{e}{2 P_0 \cdot R_i} \cdot \Delta f}$$

Where $G_v = 10^5$ V/A is the transimpedance gain, $R_i = 0.5$ A/W is the detector responsivity, and $P_0$ and $\Theta_{FRS}$ are the incident power (Watts) on the analyzer and FRS polarization rotation angle respectively. The factor of 2 in Equation 4.1 originates from the dual contribution to the FRS signal from the signal and reference beams. The corresponding signal and noise for the 90º method can be found in Equation 3.12.

Theoretically both the 45º and 90º methods can ultimately be shot-noise limited. With an assumption that the shot-noise limit is achieved when the photocurrent shot-noise becomes equal to either the detector- or laser intensity-noise, one can express the total noise of the system as:

$$\sigma_{45^\circ}_{\text{shot}} = \sqrt{2} \cdot G_v \cdot \sqrt{4 e \cdot R_i \cdot P_0 \cdot \Delta f} = G_v \cdot \sqrt{4e \cdot R_i \cdot P_0 \cdot \Delta f}$$

$$\sigma_{90^\circ}_{\text{shot}} = \sqrt{2} \cdot G_v \cdot \sqrt{2e \cdot R_i \cdot P_0 \cdot \sin^2(\theta) \cdot \Delta f} = G_v \cdot \sqrt{4e \cdot R_i \cdot P_0 \cdot \sin^2(\theta) \cdot \Delta f}$$

The factor $\sqrt{2}$ represents a quadrature sum of two noise contributions of the same magnitude. The SNR in the shot-noise limited ($SNR_{\text{shot}}$) case for both methods becomes:

$$SNR_{45^\circ}_{\text{shot}} = \frac{V_{45^\circ}}{\sigma_{45^\circ}_{\text{shot}}} = \sqrt{\frac{R_i \cdot P_0}{e}} \cdot \Theta_{FRS} \cdot \sqrt{\Delta f}$$

$$SNR_{90^\circ}_{\text{shot}} = \frac{V_{90^\circ}}{\sigma_{90^\circ}_{\text{shot}}} = \sqrt{\frac{R_i \cdot P_0}{e}} \cdot \cos(\theta) \cdot \Theta_{FRS} \cdot \sqrt{\Delta f}$$

55
Therefore, assuming $\theta \ll 10^\circ$ in the 90° method both techniques should provide comparable ultimate performance. However practical limitations exist, (detailed below as sub-sections (A) and (B) for the 45° and 90° methods respectively) and result in SNRs significantly lower than $SNR_{\text{shot}}$ determined in Equations 4.5 and 4.6.

(A) Detector saturation limit in the 45° method

Given the total laser power on each detector element is limited by some specified saturation power $P_{\text{sat}}$, there is a limit to the total analyzer power $P_0$ that can be used in the FRS measurement. To understand this point, we may consider a high power ($P_{0,A}$) and low power ($P_{0,B}$) case of Malus’ law in Figure 4.4(a), where conventional BD-FRS may be used in the case of $P_{0,B}$ (since both signal and reference branches are below saturation, denoted by the green curve). Using small signal analysis and assuming shot-noise limited performance (Equation 4.5), it is clear that SNR enhancement will require increasing $P_{0,B}$, and is limited by detector saturation, i.e. $P_{0,B} < 2 \cdot P_{\text{sat}}$. Thus despite excellent laser noise suppression provided by BD-FRS that enables operation in the shot-noise regime, there is a hard limit in the maximum achievable SNR with this technique (Figure 4.4(b)). Therefore, application of more powerful lasers does not bring the $P_0^{1/2}$ improvement in SNR predicted by Equation 4.5, but only allows for maximum power of $P_0 = 2 \cdot P_{\text{sat}}$ which limits the ultimate performance of the system.

(B) Laser intensity-noise limit in 90° method

As predicted by Equations 4.5 and 4.6, the 90° method should be capable of the same ultimate sensitivity as provided by the shot-noise limited 45° method. However, the lack of balanced-detection that provides an additional $\geq 20$ dB of CMRR makes it difficult to suppress the laser intensity-noise in the FRS system using the 90° method. As a result, laser noise reduction based solely on optical suppression through decrease in $\theta$ may not be sufficient to achieve shot-noise
limited operation (note that the signal in Equation 3.12 scales with \(\sin(2\theta)\) while the laser noise is proportional to \(\sin^2(\theta)\), which allows for improvement in SNR in the intensity-noise dominated regime by decreasing \(\theta\) until the detector-noise floor is reached; in such a configuration the shot-noise limited operation can only be obtained with ultra-low noise photodetectors and high-quality polarizers). Therefore, most of the FRS systems utilizing the 90º method operate in the laser intensity-noise dominated regime. Using Equation 3.12 and the experimental parameters relevant to our setup with \(\sigma_{NEP} = 5.4 \times 10^{-12} \text{ W} \cdot \text{Hz}^{-1/2}\), \(\bar{\sigma}_{RIN} = 5.3 \times 10^{-7} \text{ Hz}^{-1/2}\), and \(P_0 = 8 \text{ mW}\) (obtained from our 30 mW DFB diode after optical losses in the system primarily from the MPC), the best \(\text{SNR}^{90\circ}\) is achieved at \(\theta_{opt.} = 2^\circ\) as shown in Figure 4.5(a). For ease of comparison, the \(\text{SNR}^{90\circ}\) values presented in Figure 4.5(b) were normalized to the peak SNR of the hybrid-FRS method at \(P_0 = 8 \text{ mW}\).

4.6 Hybrid-FRS

Theoretically, the benefit of hybrid-FRS can be explained using SNR calculations. The hybrid-FRS signal \((V_{\text{hybrid}})\) equation is derived as generalized BD-FRS for an arbitrary \(\theta\) \((0^\circ < \theta < 45^\circ)\), with the NPP2 (Figure 4.1) and auto-balancing circuit suppressing \(P_{\text{ref}}\) by \(\gamma = \tan^2(\theta)\) and analyzing the difference \(P_{\text{sig}} - \gamma \cdot P_{\text{ref}}\), which yields [26]:

\[
V_{\text{hybrid}} = G_v \cdot R_j \cdot P_0 \cdot [(1 + \gamma) \cdot \sin(2\theta)] \cdot \Theta_{\text{FRS}}
\]  

(4.7)

We also consider the noise of hybrid-FRS, given as the quadrature sum of detector-, shot- and laser intensity-noise:

\[
\sigma_{\text{hybrid}} = G_v \cdot R_j \cdot P_0 \sqrt{\frac{\text{CMRR}_{\text{20}}}{10} \cdot \bar{\sigma}_{\text{RIN}} \cdot \sin^2(\theta) \cdot \sqrt{\Delta f} + \left(\frac{\sigma_{\text{NEP}}}{P_0} \cdot \sqrt{\Delta f}\right)^2 + \frac{4e \cdot \sin^2(\theta)}{R_j \cdot P_0} \cdot \Delta f}
\]  

(4.8)

When shot-noise limited operation is achieved the total noise of the system can be expressed as:
and the SNR in the shot-noise limited case becomes:

\[
SNR_{\text{shot}}^{\text{hybrid}} = \frac{V_{\text{shot}}^{\text{hybrid}}}{\sigma_{\text{shot}}^{\text{hybrid}}} = \frac{\sin(\theta) + \cos(\theta)}{\sqrt{2}} \cdot \sqrt{\frac{R_f \cdot P_0}{e}} \cdot \Theta_{\text{FRS}} \cdot \sqrt{\Delta f}
\]  

(4.10)

It is clear that in the case of \( \theta = 45^\circ \) the shot noise limited SNR for the hybrid method becomes equivalent to Equation 4.5 derived for 45º method. For small \( \theta \), the ultimate shot-noise limited SNR tends to be slightly smaller (\( \sqrt{2} \) times) than \( SNR^{90^\circ} \) for the shot-noise limit in Equations 4.5 and 4.6. However, given the effective laser noise suppression through balanced-detection that helps approach the shot-noise regime, a \( \sqrt{2} \) decrease in ultimate SNR represents only a small penalty for the use of a second detector (the \( \sqrt{2} \) factor originates from the dual contribution of uncorrelated photocurrent shot-noise).

4.6.1 Comparison of hybrid-FRS to 45º and 90º methods

The impact of laser noise suppression through balanced-detection in hybrid FRS is clearly noticeable in Figures 4.5(a) and (b) which compare the \( SNR^{\text{hybrid}} \) with SNR achievable with the conventional 90º method using experimental parameters relevant to our optical setup. For easier comparison all values of the SNR presented in the Figure 4.5 are normalized to the maximum SNR achieved with the hybrid method at \( P_0 = 8 \text{ mW} \). For the experimental maximum \( P_0 \) of 8 mW, the 90º method achieves optimum operating conditions at \( \theta_{\text{opt.}} = 2^\circ \) with the SNR nearly 50 % of that achievable with hybrid-FRS. The hybrid method achieves an optimal SNR at \( \theta_{\text{opt.}} = 7.3^\circ \), indicating a lower effective laser noise achieved with the balanced-detection that permits opening the analyzer further to increase the laser power on the photodetector. Similar calculations were performed for other laser powers with an assumption of the same RIN and NEP. Figure 4.5(c) shows that in all cases the hybrid method demonstrates better performance than the 90º method. It
is also clear that for low-power lasers (e.g. VCSELs, see the \( P_0 = 1 \) mW plot) there may be no optimum point on the SNR plot and the \( \theta_{opt} \) becomes 45º, making hybrid-FRS equivalent to the conventional 45º method.

In the case of low laser power such that the incident power on the signal-photodiode remains always below detector saturation even at an analyzer uncrossing angle of \( \theta = 45^\circ (P_{sig} = P_0/2) \), the 45º method is usually expected to provide better performance than the 90º method. This is due to efficient laser noise suppression by balanced-detection while operating the FRS system at the point of maximum signal generated at \( \theta = 45^\circ \). This is also indicated in Figure 4.5(c) that shows \( \text{SNR}^{90^\circ} \) and \( \text{SNR}^{\text{hybrid}} \) at \( P_0 = 1 \) mW (effectively \( \text{SNR}^{45^\circ} \)) as a function of \( \theta \) for low-power. If the conventional 45º method is used the \( \text{SNR}^{45^\circ} \) can only be improved through an increase of optical power, but once the detector saturation is reached, further increase of signal in the 45º method is not possible (black line \( P_{sig,B} \) in Figure 4.4(b)). Therefore, at higher laser power it is beneficial to use hybrid-FRS and decrease \( \theta \) to achieve an increase in FRS signal while keeping the \( P_{sig} \) constant and below detector saturation (red line \( P_{sig,A} \) in Figure 4.4(b)). If the laser noise is effectively suppressed by the BPD, the shot-noise limited operation can be maintained and SNR follows the \( P_0^{1/2} \) increase predicted by Equation 4.10.

In conclusion hybrid FRS eliminates the detector saturation limitation of 45º method and reduces intensity-noise through balanced-detection, thus enabling shot-noise limited operation that is rarely achieved in practice with the conventional 90º method.

4.6.2 Power constraints

We now consider minimum and maximum power limitations in hybrid FRS. It has been observed in Figure 4.5(c) for the given experimental parameters, that when \( P_0 \) is low (~ 1 mW), the SNR curve increases monotonically with no local maximum. In this case we see that there exists a
minimum power $P_{0,\text{min}}$ under which no benefit is derived from decreasing $\theta$, and conventional BD-FRS is superior (i.e. one should work as close as possible to 45º when operating below saturation of the BPD). One can solve for this condition as the minimum laser power which satisfies $d(SNR)/d\theta = 0$ for $0^\circ < \theta < 45^\circ$. The angle $\theta$ where $d(SNR)/d\theta = 0$ is the optimal analyzer uncrossing angle $\theta_{\text{opt}}$, which is plotted for varying $P_0$ in Figure 4.6(a). We calculate that below $P_{0,\text{min}} = 1.5$ mW our system requires conventional BD-FRS, while for $P_0 > 1.5$ mW hybrid-FRS provides better SNR.

To optimize system performance, the operating point should lie upon the solid black line in Figure 4.6(a), while maximizing available laser power $P_0$. Our experimental operating point is indicated by the red circle, with $\theta = 8.3^\circ$ at $P_0 = 7.6$ mW, which is close to the theoretical $\theta_{\text{opt}} = 7.5^\circ$. Slight deviations of $\theta$ do not affect the SNR as each point on Figure 4.6(a) represents a zero-derivative SNR condition at $\theta_{\text{opt}}$.

To estimate the maximum power limit one has to consider polarization extinction ratio (PER, or $\varepsilon = 1/R_\varepsilon$), which has been neglected so far but will play a significant role for large $P_0$ and small $\theta$, as light leakage will be comparable to the total power transmitted through an ideal polarizer. This effect of finite $R_\varepsilon$ manifests itself as a transformation of the reference-photodiode suppression factor $\gamma \rightarrow \gamma \cdot \zeta$ in Equation 4.7, and signal power $P_0 \cdot sin^2(\theta) \rightarrow P_0 \cdot sin^2(\theta) \cdot \zeta$ in Equation 4.8 where $\zeta = 1 + (\gamma \cdot R_\varepsilon)^{-1}$. Using these considerations, the maximum power $P^{\text{max}}_0$ after which the SNR no longer improves (i.e. where leakage begins to dominate the total noise) occurs approximately when (Appendix A1.4):

$$G_\gamma \cdot R_L \cdot 10^{ \frac{CMRR}{20} } \cdot \sigma_{RIN} \cdot (\varepsilon P^{\text{max}}_0) \approx \sigma^{\text{opt}}_{\text{sig}}$$

(4.11)
In Equation 4.11, $\sigma_{\text{sig opt}}^2$ is the total noise due to the signal power at optimum analyzer uncrossing, given by Equation 4.8. Solving for the maximum power gives:

$$P_0^{\text{max}} \approx \frac{1}{\epsilon} \cdot \sqrt{2\left(P_{\text{sig opt}}^2\right)^2 + \frac{4\epsilon \cdot P_{\text{sig opt}}}{R_t} \cdot \left(10 \frac{\text{CMRR}}{20} \cdot \bar{\sigma}_{\text{RIN}}\right)^2}$$

(4.12)

Where the optimum power $P_{\text{sig opt}}$ is obtained from Equation 3.21. The impact of good polarizers (smaller $\epsilon$) is therefore the increase of the maximum allowable power $P_0^{\text{max}}$ before diminishing returns on the SNR, and scales according to $P_0^{\text{max}} \sim \epsilon^{-1}$.

Graphically, the effect of the non-ideal polarizers is shown in Figure 4.6(b) which shows SNR as a function of $P_0$ for different $R_c$. The SNR indeed increases as $P_0^{1/2}$ but only until the laser noise leaking through the polarizers begins to dominate and outweighs any benefit derived from increasing $P_0$. In our experiment, although the GTP and WP have $R_c \sim 10^4$, due to depolarization in the MPC an effective extinction ratio of $R_c \sim 10^3$ has been determined (corresponding to the red curve in Figure 4.6(b)). Therefore, in our current system the maximum power limit is $\sim 100$ mW, beyond which no SNR improvement is expected.

4.7 Hybrid-FRS: measurement results

Hybrid-FRS measurements were performed using the system in Figure 4.1. The hybrid system is optimized subject to limitations of detector-noise (dominating at $P_{\text{sig}} < 20 \mu\text{W}$), intensity-noise (dominating at $P_{\text{sig}} > 660 \mu\text{W}$), detector saturation (occurring at $P_{\text{sig}} = 500 \mu\text{W}$) and available laser power of $P_0 = 8 \text{ mW}$. Figure 4.7(a) shows a plot of total noise as a function of optical power $P_0$ and analyzer offset angle $\theta$ derived from experimental measurements of laser intensity- and detector-noise. Since each constraint is delimited by a given $P_{\text{sig}}$, the curves determining the operation area of the system follow the form of $P_0 = P_{\text{sig}}/\sin^2(\theta)$. The laser intensity-noise is
calculated assuming a CMRR of 21.6 dB ± 1.8 dB, determined as an average of numerous measurements (similar to that in Figure 4.3) over different optical powers and split ratios.

It is always desirable to operate in the shot-noise regime (shaded) which provides the ultimate sensitivity for a given power and allows for the $\sim P_0^{1/2}$ increase in SNR. In other noise regimes (detector- or intensity-noise limits) the SNR is sub-optimal and requires more stringent PER requirements and laser power to attain comparable performance. It is important to note that the shaded area is the desirable parameter space accessible by the hybrid-FRS method, and measurement optimization occurs at the point with the highest SNR.

Within the same parameter space, the FRS signal from $^3P_1(1)$ O$_2$ transition is calculated using Equation 4.7 and plotted together with the values measured experimentally (Figure 4.7(b)). DC-FRS peak signal levels were measured at $P_{sig} = 160 \mu W$, and the Figure 4.7(b) inset shows examples of hybrid-FRS spectra of the $^3P_1(1)$ line acquired with varying $\theta$. Asymmetries in the lineshape are due to residual amplitude modulation of the DFB laser, and peak signal measurements are in excellent agreement with calculations. In Figure 4.7(c) a SNR map has been generated using the signal and noise from Figures 4.7(b) and (a) respectively. It is clear from the figure that conventional balanced-detection that operates at a constant $\theta$ (e.g. 45º) will not approach the highest SNR area through a simple increase of the optical power (the detector saturation level will be reached first). However, for hybrid-FRS which operates at constant $P_{sig} = 160 \mu W$, the highest SNR that coincides with the line of the available optical power can be conveniently approached. The minimum detection limit (MDL) of O$_2$ for each experimental measurement is labeled on the SNR plot and the measured MDL values are in reasonable agreement with the calculated MDL shown in the inset of Figure 4.7(c). Taking horizontal cross-sections (fixed $P_0$) of the SNR map, we re-obtain SNR curves shown in Figure 4.5(c).
The 0.6 ppmv·Hz$^{-1/2}$ MDL is 1.4× the shot-noise limit and corresponds to a noise-equivalent polarization rotation $\Theta_{NEA} = \sigma_{hybrid}^2 / \left[ (1+\gamma) \cdot \sin(2\theta) \cdot P_0 \cdot G_V \cdot R_I \cdot \zeta(2f_l) \right] = 1.6 \times 10^{-8}$ rad·Hz$^{-1/2}$ ($\zeta(2f_l)$ given in Figure 2.9 and obtained through Equation 2.13 is the signal reduction due to second harmonic detection). We may also calculate the minimum fractional absorption ($aL_{\text{min}}$) for comparison with other methods. For a 6.8 m path length we observe ~ 5 % optical absorption, which translates to $(aL_{\text{min}}) = 1.5 \times 10^{-7}$ Hz$^{-1/2}$ and compares very favorably to sensitive absorption spectroscopy techniques [34].

4.8 Concluding remarks

A hybrid-FRS system that combines optimization of the analyzer angle $\theta$ with balanced detection is demonstrated and characterized (summary description in Figure 4.8). The system detects atmospheric oxygen with an MDL of 0.6 ppmv·Hz$^{-1/2}$ and consumes < 5 W due to application of permanent magnets for magnetic field generation.

The hybrid-FRS technique has been established as a superset of the 90º and 45º FRS detection methods, and the parameter space of operation for our system has been defined. SNR improvements with varying $\theta$ and $P_0$ are in good agreement with predictions. For a given set of experimental parameters, hybrid-FRS will always outperform the 90º method due to CMRR-suppressed intensity-noise, and eliminates the detector saturation limitation in FRS systems based on the 45º method.

For comparison, Table 4.1 summarizes alternative atmospheric oxygen detection techniques published in literature. The hybrid-FRS result is a 10× enhancement beyond DC-FRS with a VCSEL emitting only 200 µW [26], and our MDL is also a significant improvement over alternate optical techniques (WMS, QEPAS). Furthermore, FRS is a dispersion-based measurement, thus providing inherently linear response to analyte concentration (in contrast to conventional
absorption-based systems, in which the upper bound of dynamic range is limited to $\leq 10\%$
absorption according to the Beer-Lambert It is instructive at this point to consider a limitation of balanced-detection FRS that is addressed in the forthcoming Chapter (dual-modulation FRS); the presence of finite CMRR indicates that spectral features unrelated to the FRS signal (e.g. optical fringes) are only suppressed, not eliminated. In this sense hybrid-FRS is not considered a true zero-baseline technique, except for the extreme case where baseline fringes can be suppressed below the white-noise floor of the sensor. This may be resolved using sample modulation (AC-FRS/DM-FRS described in Section 2.4 and demonstrated in Chapters 5 and 6), which is a noise reduction feature unique to FRS, though their implementation requires a generous power budget to drive a solenoid at audio frequencies. Nevertheless, with the above demonstration of excellent short-term precision of hybrid-FRS, long-term accuracy may be ensured through the use of periodic calibration or spectral correlation [35] techniques beyond the zero-drift time.
References


Chapter 5:

Dual-modulation Faraday Rotation Spectroscopy

Following the discussion at the conclusion of Chapter 4, the long-term accuracy of FRS sensors can be addressed using sample modulation for baseline removal (Section 2.4.4). In this Chapter, we demonstrate a transportable spectrometer for analysis of nitrogen isotopes [1-4]. The spectrometer is based on dual-modulation Faraday rotation spectroscopy of nitric oxide isotopologues with near shot-noise limited performance and baseline-free operation. Noise analysis indicates minor isotope ($^{15}$NO) detection sensitivity of 0.36 ppbv·Hz$^{-1/2}$, corresponding to noise-equivalent Faraday rotation angle (NEA) of $1.31 \times 10^{-8}$ rad·Hz$^{-1/2}$ and minimum fractional absorption $(\alpha L)_{\text{min}} = 6.27 \times 10^{-8}$ Hz$^{-1/2}$. White-noise limited performance at 2.8× the shot-noise limit is observed up to $\sim 10^3$ s, allowing reliable calibration and sample measurement within the drift-free interval (stability time) of the sensor. Integration with a wet-chemistry reactor based on acidic vanadium(III) enables conversion of aqueous nitrate/nitrite samples to gaseous NO for total nitrogen isotope analysis. Isotopic ratiometry is accomplished via time-multiplexed measurements of two NO isotope transitions. For 5 μmol potassium nitrate samples, the instrument consistently yields ratiometric precision below 0.3 ‰, thus demonstrating potential as an in situ diagnostic tool for environmental nitrogen cycle studies.

5.1 Introduction

Ratiometric analysis of nitrogen isotopologues ($^{14}$N, $^{15}$N) provides unique insight into nitrogen cycling dynamics [5-9] and enables environmental diagnostics by differentiating various natural and anthropogenic chemical processes [10, 11]. This bears particular significance in light of recent studies [12, 13] indicating comparable rates of anthropogenic and natural nitrogen fixation due to combustion of fossil fuels and fertilizer production (via the Haber-Bosch process). Additionally,
nitric oxide (NO) is known to play a key physiological role as a signal molecule in the human body [14], and isotopic analysis of nitrogen isotopes (in the form of nitrates/nitrites in blood and urine as well as NO in breath) are utilized in medical diagnostics of physio-pathological processes [15, 16]. In the case of environmental studies, sub-permil precision is frequently required [5, 8, 9] as deviations from natural abundance remain small; in the case of medical analysis, isotopically labeled precursors may be introduced into the patient’s body for metabolic studies and the requirements for isotopic sensitivity can be relaxed [15, 17]. Presently, isotope ratio mass-spectrometry (IRMS) is the state-of-art technique for precision isotopic ratiometry [9-11, 15, 16], which can be used with a variety of front-end N to N₂ conversion methods (e.g. Dumas combustion using CN elemental analyzers [18]), or N to N₂O via the “denitrifier” method [19]. However, substantial capital investment and maintenance requirements required for IRMS-based systems prevent nitrogen isotope analysis from being used as a mainstream diagnostic tool. Furthermore, lack of instrument transportability eliminates the possibility of in situ measurements, thus requiring samples to be shipped to the laboratory, which presents practical limits on sample sizes.

In this Chapter, we present a transportable analyzer based on dual-modulation Faraday rotation spectroscopy (DM-FRS) [1-4, 17] of NO, with near-fundamental quantum shot-noise limited sensitivity. The transportability of the system [1] allows in situ measurements and practically eliminates the sample size limitation characteristic in the case of external laboratory analysis. Integration of the spectrometer with a compact wet-chemical vanadium(III) conversion setup [1, 20] enables measurement of nitrate/nitrite fluid samples. Sub-permil isotopic ratiometric precision for micro-mole (µmol) nitrate samples has been achieved, demonstrating our spectrometer as an enabling technology for in situ environmental and medical diagnostics.

5.2 SNR in DM-FRS: theory and practical limitations
According to the discussion in Section 2.4.5, individual use of either AC-FRS or DC-FRS allows for only mutually exclusive noise reduction techniques [1]. Recent work on hybrid-FRS (Chapter 4) combined DC-FRS with balanced-detection for etalon suppression and intensity-noise reduction, enabling measurements near (1.4×) the shot-noise limit. However, the lack of low-noise, high common-mode suppression balanced-detectors in the mid-infrared limits the implementation of these techniques in this highly desirable molecular fingerprint spectral region.

An introduction to DM-FRS spectral modeling was given in Section 2.4.5, utilizing simultaneous laser wavelength ($f_L$) and B-field ($f_M$) modulation, which encodes the FRS signal into high-frequency sidebands ($Nf_L \pm f_M$), whereupon the appropriate harmonic ($N$) may be chosen for signal demodulation (Figure 5.1). DM-FRS thus combines laser intensity-noise reduction with etalon-free measurements to enable near shot-noise and baseline-free detection, consistently yielding near-record noise-equivalent angles ($\Theta_{NEA}$) below $10^{-8}$ rad·Hz$^{-1/2}$ [1, 17]. In addition to the benefits detailed previously, it is instructive to consider these techniques operating in ideal conditions and examine their ultimate capabilities in the regime of the fundamental limit.

In DM-FRS, magnetic field modulation of the sample produces an amplitude modulation which appears as two sidebands around a carrier frequency associated with fast wavelength modulation of the laser. The sidebands must be separately demodulated and summed to produce the resultant FRS signal [1]. This can be generally understood as a two-step process of signal generation involving the harmonic detection of a wavelength-modulated spectrum of an AC-FRS lineshape (Equation 2.15). Since harmonic detection reduces the maximum available signal by $\xi(Nf_L)$, and dual-sideband demodulation doubles the bandwidth required for signal retrieval (i.e. for ENBW of $\Delta f = 1$ Hz, dual sideband detection introduces noise from actual bandwidth of $2 \cdot \Delta f = 2$ Hz), these effects are taken into account in signal and noise modeling. We thus have:
\[ V_{DM-FRS} = \xi(Nf_L) \cdot G_v \cdot R_I \cdot P_0 \cdot \sin(2\theta) \cdot \Theta_{FRS} \quad (5.1) \]

\[ \sigma_{DM-FRS}^{DM-FRS} = G_v \cdot R_I \cdot P_{sig} \cdot \sqrt{\left( \frac{\sigma_{RIN} (f_{DM}) \cdot \sqrt{2\Delta f}}{P_{sig}} \right)^2 + \frac{2e}{R_I \cdot P_{sig}} \cdot (2\Delta f) + \left( \frac{\sigma_{NEP} \cdot \sqrt{2\Delta f}}{P_{sig}} \right)^2} \quad (5.2) \]

where the laser relative intensity-noise (RIN) is considered to be frequency dependent and measured at frequencies that correspond to harmonics of laser wavelength modulation. Consistent with the notation defined in Chapter 2, \( P_0 \) is the power incident upon the analyzer, with \( \theta \) and \( \Theta_{FRS} \) denoting the analyzer uncrossing angle and Faraday rotation angle respectively. The signal power incident on the photodetector is given by \( P_{sig} = P_0 \cdot \sin^2(\theta) \). \( 2\Delta f \) is the ENBW for DM-FRS (due to doubling of the ENBW required for recovery of the signal), related inversely to the minimum time between adjacent data samples ensuring independent (uncorrelated) measurements. The corresponding analysis for the 90º method is given in Equation 3.12, and for fundamental SNR considerations, we may consider the quantum shot-noise limiting case with:

\[ \sigma_{shot}^{90º} = G_v \cdot R_I \cdot P_{sig} \cdot \sqrt{\frac{2e}{R_I \cdot P_{sig}}} \cdot \Delta f \quad (5.3) \]

\[ \sigma_{shot}^{DM-FRS} = G_v \cdot R_I \cdot P_{sig} \cdot \sqrt{\frac{2e}{R_I \cdot P_{sig}}} \cdot \sqrt{2\Delta f} \quad (5.4) \]

Thus, the fundamental SNR limit for both measurements becomes (assuming small \( \theta \)):

\[ SNR_{shot}^{90º} = \frac{V_{90º}}{\sigma_{90º}} = \frac{2R_I \cdot P_0}{e \cdot \Delta f} \cdot \Theta_{FRS} \quad (5.5) \]

\[ SNR_{shot}^{DM-FRS} = \frac{R_I \cdot P_0}{e \cdot \Delta f} \cdot \Theta_{FRS} \cdot \xi(Nf_L) \quad (5.6) \]

As expected, an additional modulation process in DM-FRS results in an additional degradation of the SNR by a factor of
\[ \sigma_{\text{tot}}^{\text{DM-FRS}} = \sqrt{2} \cdot \sigma_{\text{tot}}^{90\circ} \Rightarrow \frac{\text{SNR}_{\text{tot}}^{\text{DM-FRS}}}{\text{SNR}_{\text{tot}}^{90\circ}} = \frac{\xi(Nf_L)}{\sqrt{2}} \] (5.7)

with respect to idealized 90° methods, consistent with the ENBW considerations above (the \( \sqrt{2} \) factor arises from the dual sideband demodulation process which doubles the ENBW). In the nominal case of 2\(^{nd}\)-harmonic demodulation, \( \xi(2f_L) = 0.595 \) (Figure 2.11); hence, fundamentally DM-FRS can achieve \( \sim 40\% \) of the detection limit of shot-noise limited AC-FRS techniques. However, the ultimate shot-noise limit is difficult to attain in conventional FRS methods, whereas DM-FRS is able to reach this limit far more easily in practical systems [1-4, 17].

It is useful at this point also to clarify the notational meaning of bandwidth normalized values in this paper: we take the normalization unit Hz\(^{1/2}\) to represent the signal demodulation bandwidth about each DM-FRS sideband (Figure 5.1), which is understood to be the fastest rate at which we are able to resolve signal changes. Although this notation symbolizes only half the noise bandwidth under consideration, figures of merit quoted in Hz\(^{1/2}\) (implying values normalized to \( \Delta f = 1 \) Hz ENBW) represent single-sideband ENBW (consistent with AC-FRS notation), and should be understood as having already accounted for the \( \sqrt{2} \times \) noise increase from the dual-sidebands.

5.3 Spectrometer design

Following the early developments published in Wang et al. [17], measurement of NO is performed by targeting the \(^{15}\)N\(^{16}\)O Q(3/2) transition at 1842.763 cm\(^{-1}\) (minor isotope) and \(^{14}\)N\(^{16}\)O P(19/2)e doublet at 1842.946 cm\(^{-1}\) (major isotope) using a DFB-QCL (Alpes Lasers). A MCT photodetector (Vigo System, PVI-3TE-6, current responsivity \( R_I = 3.8 \) A/W and voltage transimpedance \( G_V = 4.5 \times 10^4 \) V/A) is utilized for optical detection. Substantial spectrometer size/weight reduction is accomplished by replacement of the water chiller with a fan and coolant-based heat-sink (Corsair H100i), and a miniaturized class-D audio amplifier (Sure Electronics TK2050), data acquisition
card (NI USB-6001) and vacuum pump (KNF UN84.3 ANDC). Sample measurement is conducted through the triple pass gas cell \(L_{cell} = 15\) cm) operating in continuous flow configuration at 80 Torr and magnetic field \(B = 150\) Gauss. The DM-FRS spectrometer (Figure 5.2) utilizes simultaneous modulation of laser wavelength \(f_L = 50\) kHz and magnetic field \(f_M = 100\) Hz [1-3], where the former reduces \(1/f\) noise and the latter eliminates optical etalon effects as described in Section 2.4.5. The magnetic field modulation frequency is reduced from [4, 17] to lower electromagnetic interference (EMI) effects, eliminating the need for high-permeability shielding.

Spectral analysis of the noise is shown in Figure 5.3, demonstrating the reduction in EMI at low frequencies \(f_M = 100\) Hz in [1-3]) compared to higher frequencies \(f_M = 1.554\) kHz in [4]). Retrieval of DM-FRS spectra is performed via demodulation at signal sideband harmonics \((2f_L \pm f_M)\), which provides low laser intensity-noise, near baseline-free measurement capability, and intrinsic immunity to interferences from \(\text{H}_2\text{O}\) and other diamagnetic absorbers in the MIR region.

A reference branch with a gas cell containing both NO isotopes \((\sim 1.5\%^{15}\text{NO}, \text{and} \sim 2.5\%^{14}\text{NO in} \text{N}_2)\) is used to perform spectral line-locking of the laser wavelength to the major or minor NO isotope transitions for continuous measurements.

The spectrometer is housed in a 12U 19” rack (Rackmount Solutions 212024-L) and integrated with a wet-chemistry nitrate/nitrite to NO conversion unit based on [20] for fluid sample analysis shown in Figure 5.2(c). Gas samples containing NO can be introduced directly to the system for isotopic analysis (Figure 5.2(b) also shows a Loccioni® commercial human breath sampler, used with the system for medical studies).

5.4 DM-FRS system performance

In the following sections system performance analysis is characterized through (i) spectral acquisition and baseline performance (Section 5.4.1), (ii) measurement stability, accuracy, as well
as detection limits for $^{15}\text{NO}$ (Section 5.4.2). In addition, Section 5.4.1 details the mechanism newly developed in this system to provide time-multiplexed isotopic analysis via line-switching between the major and minor NO isotopes.

5.4.1 DM-FRS spectra and time-multiplexed isotope analysis

Following the description in [1], SNR optimization is performed by determination of analyzer uncrossing angle (detailed in Section 3.3.2). Analysis of measured system noise yields laser relative intensity-noise (RIN) of $2.19 \times 10^{-7}$ Hz$^{-1/2}$, and a photodetector noise equivalent power (NEP) of $1.25 \times 10^{-12}$ W·Hz$^{-1/2}$. The optimum uncrossing is well approximated (for small $\theta$) by the point where $\sigma_{\text{int}} = \sigma_{\text{det}}$ and the effective extinction ratio of the optical system ($\varepsilon = 1.86 \times 10^{-4}$ [1, 3] through the polarizers and optical gas cell) is assumed to contribute negligibly to the total noise, yielding a calculated (and measured) optimum angle $\theta_{\text{opt}} = 1.71^\circ$ at $P_{\text{sig}} = 5.7 \mu\text{W}$, and $P_0 = 6.4 \text{ mW}$ (power incident upon the analyzer).

Signal spectra for both $^{14}\text{NO}$ and $^{15}\text{NO}$ are obtained by current-tuning of the laser across both transitions (Figure 5.4). A G-Cal permeation device (Vici Metronics) is used to generate the NO gas sample, which includes both $^{14}\text{NO}$ P(19/2)e at 1842.946 cm$^{-1}$ and $^{15}\text{NO}$ Q(3/2) at 1842.763 cm$^{-1}$ lines (blue and red respectively) in the fundamental $v_2$ ro-vibrational band of NO. The spectrum is acquired using 1500 points at $\Delta f = 1$ Hz ENBW per point, resulting in a total acquisition time of $\sim 1500$ s. The inset of Figure 5.4(a) shows a corresponding typical $3f_L$ wavelength modulated absorption spectrum for $^{14}\text{NO}$ measured in the reference channel, which is used to line-lock to the maxima of the DM-FRS spectra of the major isotope. Qualitative analysis of line-locking stability yields a lock-speed of $\sim 2.5$ s, whereupon the oscillations of the PID controlled feedback loop results in signal oscillations below the detection limit of the system. Within the lock-speed limitations, line-switching (isotopic multiplexing) is performed by hopping
the laser current set-point between the $^{15}$NO and $^{14}$NO transitions at predefined time intervals for quasi-simultaneous measurements of isotopic variations. It is important to note that the ratio of raw FRS signals is not directly indicative of the isotopic abundance as system parameters are optimized for maximum $^{15}$NO sensitivity by targeting the Q(3/2) transition with the highest effective magnetic moment, which despite lower line intensity produces the highest FRS signals at low magnetic fields. Therefore, appropriate signal calibration must be utilized to measure relative isotopic abundances (see Section 5.5.3 for details).

Figure 5.4(b) depicts the $^{15}$NO spectra acquired with pure nitrogen as sample gas, indicating zero-baseline performance near the fundamental shot-noise limit. This demonstrates the benefit of lower magnetic field modulation frequency which reduces EMI without the need for extraneous shielding material for our laser or detector systems. Figure 5.4(c) shows the $^{15}$NO Q(3/2) transition measured for an uncalibrated cylinder gas containing ~ 1-2 ppmv of NO in $N_2$ mixture. Along with the measurement is simulated spectra for the same transition using the model from Equation 2.15 [21]. The spectral fit yields a $^{15}$NO concentration of 4.56 ppbv; this translates to a $^{14}$NO concentration of 1.24 ppmv assuming natural abundance (0.368 %), which is consistent with the expected concentration levels in this non-certified gas mixture.

5.4.2 Minimum detection limit and long-term stability

Characterization of the spectrometer stability is performed in line-locked mode using the $^{15}$NO transition (Figure 5.5(c), inset shows the $^{15}$NO WMS spectrum used for line-locking). Pure $N_2$ is utilized for the test, and all drifts are therefore attributable to instrumental instabilities. Raw measurement data over a span of ~ 1 hr is shown in Figure 5.5(a). A slow positive signal drift is noticeable over this long measurement period, indicating possible electronic interferences that indirectly modulate optical etalons into FRS signal sidebands. In the case of practical
implementation of the system for small liquid sample measurements, residual NO produced in the
c hemical conversion unit must be nulled for each measurement, which requires baseline correction
based on the data acquired before and after the sample peak. Typically, sample measurements
follow known reference injections, each lasting approximately 500 s at a typical system flow rate
of ~ 100 sccm. A linear correction for each 500 s measurement interval utilizing the first 50 s and
last 100 s is used for baseline correction for small sample analysis; therefore, to understand
instrumental stability in a practical measurement scenario, this peak baseline correction technique
is applied to the data in Figure 5.5(a) followed by Allan-deviation analysis in Figure 5.5(c)
(corrected data shown in Figure 5.5(b)). In Figure 5.5(c), system precision is set by a noise level
of 234 nV·Hz$^{-1/2}$, which is 2.8× the shot-noise limit ($\sigma_{\text{shot}} = 84$ nV·Hz$^{-1/2}$). Calculation of the shot-
noise factor $\Lambda_\sigma$ described by Equation 3.25 using measured RIN and NEP yields $\Lambda_\sigma = 2.73$, in
excellent agreement with the experimentally determined value. The system is white-noise limited
up to ~ $10^3$ s, indicating that sequential reference and sample measurements (500 s each) may be
performed with linear baseline correction without introducing substantial drifts in measurement
accuracy. Furthermore, the detection limit for $^{15}$NO is derived using the ratio of $^{15}$NO signal
(Figure 5.4(c)) and system noise (Figure 5.5(c)): $\text{SNR} = 3 \mu\text{V}/(234 \text{ nV·Hz}^{-1/2}) = 12.8 \text{ Hz}^{1/2}$,
resulting in a bandwidth normalized $^{15}$NO MDL of 4.56 ppbv/(12.8 Hz$^{1/2}$) = 0.36 ppbv·Hz$^{-1/2}$. This

$$\text{SNR} = \frac{3 \mu\text{V}}{234 \text{ nV·Hz}^{-1/2}} = 12.8 \text{ Hz}^{1/2}$$

$$\text{SNR} \approx \frac{4.56 \text{ ppbv}}{12.8 \text{ Hz}^{1/2}} = 0.36 \text{ ppbv·Hz}^{-1/2}$$

corresponds to a noise-equivalent Faraday rotation angle $\Theta_{\text{NEA}}$ of [1]:

$$\Theta_{\text{NEA}} = \frac{\sigma_{\text{tot}}}{\sigma_{\text{shot}}} \cdot \Theta_{\text{SNEA}} = \frac{\sigma_{\text{tot}}}{\sigma_{\text{shot}}} \cdot \sqrt{2} \frac{h\nu}{\xi(Nf_L)} \sqrt{\frac{\eta P_0}{2}} = 1.31 \times 10^{-8} \text{ rad·Hz}^{-1/2}$$

(5.8)

where $\Theta_{\text{SNEA}}$ is the shot-noise equivalent Faraday rotation angle (i.e., $\Theta_{\text{FRS}}$ corresponding to shot-
noise fluctuations). To indicate relative sensitivity of DM-FRS, we calculate a minimum fractional
absorption of \((\alpha L)_{\text{min}} = 6.27 \times 10^{-8} \text{ Hz}^{-1/2}\), which compares favorably to typical TDLS systems which provide \((\alpha L)_{\text{min}}\) in the \(~ 10^{-5} \text{ Hz}^{-1/2}\) range [22].

5.5 Isotopic ratiometry and real-time fractionation studies

For fluid sample analysis a full integration of the spectrometer and chemical conversion setup (Figure 5.2(a) and (c)) is performed. Fractionation-free spectrometer performance during isotopic analysis of gas samples is demonstrated, along with measurement of real-time fractionation during sample injection. Error analysis indicates consistent sub-permil precision for micro-mole (μmol) sample sizes.

5.5.1 Ratiometric definitions and terminology

In Section 5.4.2, spectrometer noise characterization revealed a drift-free performance of approximately 1000 s, and it is expected that within this time frame the DM-FRS spectrometer provides high accuracy, and does not introduce measurement artefacts (i.e., modification of the ratiometric value via instrument fractionation). The system measurements that are used to evaluate the isotopic ratios \(\delta^{15}\text{N}\) are typically presented as permil (‰) values, defined according to [9]:

\[
\delta^{15}\text{N} = \left( \frac{[^{15}\text{N}]_S}{[^{14}\text{N}]_S} \right) - 1 \times 10^3 \text{ ‰} \quad (5.9)
\]

where \([^{\text{m}}\text{N}]_S\) and \([^{\text{m}}\text{N}]_R\) represent true sample and reference volume NO concentrations. In the case of experimentally signals, we define an analogous ratiometric quantity:

\[
\delta^{15}\bar{N} = \left( \frac{[^{15}\bar{\text{N}}]_S}{[^{14}\bar{\text{N}}]_S} \right) - 1 \times 10^3 \text{ ‰} \quad (5.10)
\]
where we use the corresponding tilde notation to denote raw measured signals on the spectrometer (typically measured in μV). The equality between volume concentration ratio (ppmv) defined in Equation 5.9 and raw signal ratio (μV) in Equation 5.10, i.e. $δ^{15}N = δ^{15}Ñ$ generally holds true since $[^{15}Ñ] = [^{15}N] \cdot γ^{15}$ and $[^{14}Ñ] = [^{14}N] \cdot γ^{14}$ where $γ^m$ is the ppmv to μV instrumental conversion factor for each isotope. Assuming sequential reference and sample measurements are made within the drift-free time-frame of the instrument (i.e., the reference ratio remains unchanged, see Section 5.4.2), we expect $γ^m$ to remain the same (i.e., $γ^{14}_S = γ^{14}_R$ and $γ^{15}_S = γ^{15}_R$), and therefore $δ^{15}N = δ^{15}Ñ$ within the stability time of the spectrometer. Within the above stability constraints and for notational clarity, we use $δ^{15}N$ to denote the measured isotopic ratio in the following discussion.

5.5.2 Real-time analysis of gas samples

To evaluate the isotopic ratiometry performance of the system, we first consider the instantaneous ratiometric error $Δ(δ^{15}N)(t)$:

$$δ^{15}N(t) \pm Δ(δ^{15}N)(t) = \left(\frac{[^{15}Ñ]_S(t) \pm Δ[^{15}Ñ]_S}{[^{14}Ñ]_S(t) \pm Δ[^{14}Ñ]_S} \cdot \frac{[^{14}N]_R}{[^{15}N]_R} - 1\right) \times 10^3‰ $$  \hspace{1cm} (5.11)

where we have defined our instantaneous signals $[^{15}Ñ]_S(t)$ and $[^{14}Ñ]_S(t)$ to be time dependent and our uncertainties $Δ[^{15}Ñ]_S$ and $Δ[^{14}Ñ]_S$ represent noise for data reported every 1 s (1 Hz measurements with 2 Hz ENBW). The reference measurement error is assumed to be negligible, which can be assured through application of high concentration reference gases/liquid samples.

By applying isotopic line switching with 50 % measurement duty cycle between major and minor isotopes, it is appropriate to assume $Δ[^{15}Ñ]/[^{15}Ñ]_s >> Δ[^{14}Ñ]/[^{14}Ñ]_s$. Propagation of uncertainties in Equation 5.11 then gives:
\[
\Delta(\delta^{15}N)(t) = \frac{[^{15}\tilde{N}]_s(t)}{[^{15}\tilde{N}]_R}
\frac{1}{\sqrt{[^{14}\tilde{N}]_s(t)}} \sqrt{\left(\frac{\Delta[^{15}\tilde{N}]_s(t)}{[^{15}\tilde{N}]_s(t)}\right)^2 + \left(\frac{\Delta[^{14}\tilde{N}]_s(t)}{[^{14}\tilde{N}]_s(t)}\right)^2} \times 10^3
\]

(5.12)

\[
\approx \left(\frac{\delta^{15}N(t)}{10^3} + 1\right) \left(\frac{\Delta[^{15}\tilde{N}]_s(t)}{[^{15}\tilde{N}]_s(t)}\right) \times 10^3
\]

For samples with near-natural abundance, Equation 5.12 reduces further to a straightforward relation between ratiometric error and relative precision of \(^{15}\text{N}\) detection:

\[
\Delta(\delta^{15}N)(t) \approx \left(\frac{\Delta[^{15}\tilde{N}]_s(t)}{[^{15}\tilde{N}]_s(t)}\right) \times 10^3
\]

(5.13)

From Equations 5.12 and 5.13, it is evident that error contributions of the spectrometer are inversely proportional to the minor isotope signal strength \([^{15}\tilde{N}]_s(t)\). Thus, any noise and drifts in the system can be compensated by increasing the sample size for isotopic ratiometry measurements. As a rough approximation, with \(\Delta[^{15}\tilde{N}]_s = 234 \text{nV·Hz}^{-1/2}\) indicated in Figure 5.5(c), sub-permil precision can be achieved for 1 Hz measurements if \(~120 \text{ ppmv NO samples are used, which would result in} [^{15}\tilde{N}]_s > 240 \mu\text{V}\). With this relationship, one can predict minimum sample size required to achieve desirable instantaneous ratiometric precision (see Figure 5.8(b)).

Both the ratiometric precision and its concentration dependence as well as any potential fractionation effects of the gas analyzer can be conveniently evaluated using gas samples. To this end, we use the NO in \(\text{N}_2\) mixture from the cylinder (with 1.24 ppmv \(^{14}\text{NO}\) concentration determined in Section 5.4.1), which is manually diluted over 1200 s by mixing with dry \(\text{N}_2\) to produce a gradual variation in the sample gas concentration with no modification to the relative isotopic composition of NO. For this test, only relative excursion from the mean isotopic composition is of importance, and the sample is assumed to have natural abundance of NO isotopes with nominal \(\delta^{15}\text{N} = 0\). The line-switch interval was set to 50 s (Figure 5.6), with the gray shaded
regions denoting $^{14}$NO measurement periods and the non-shaded regions denoting $^{15}$NO. Inherent to the line-switch process is the presence of gaps in the measurement of each isotope. To enable direct ratiometric calculation in the measurement regions of $^{15}$NO, we perform high-order polynomial interpolation of the $^{14}$NO signal (which has significantly higher SNR and negligible effect on the ratiometric error as shown in Equation 5.12).

The results of isotopic analysis are shown in the top graph of Figure 5.6, demonstrating negligible fractionation effects over the duration of NO variation. It is also clearly visible that the precision is degraded with smaller sample concentrations, which was predicted by Equations 5.12 and 5.13. Despite the varying precision during this test, statistically the permil ratio does not deviate from the mean (0 ‰ assumed here), which confirms that the accuracy of the sensor is preserved over the ~ 1000 s measurement time, a result consistent with the Allan deviation analysis in Figure 5.5(c). Within a single 50 s measurement segment we estimate a concentration normalized ratiometric precision of 120 ‰·ppmv·Hz$^{-1/2}$. This confirms the previous estimate predicting that a sub-permil precision for a 1 Hz measurement near natural abundance requires NO concentrations of > 100 ppmv.

5.5.3 Instrument calibration procedure for isotopic analysis

The definition of permil (‰) isotopic ratio given in Equations 5.9 and 5.10 relies upon knowledge of a well-known reference concentration $[^{15}\text{N}]$ and $[^{14}\text{N}]$ with corresponding measured signals $[^{15}\tilde{\text{N}}]$ and $[^{14}\tilde{\text{N}}]$ respectively. Two main considerations follow: (i) the reference gas must be a stable concentration such that $[^{15}\text{N}]$ and $[^{14}\text{N}]$ remain consistent, and (ii) the measurement of sample must occur within the stability time of the spectrometer, such that $\gamma^{15}$ and $\gamma^{14}$ remain within the drift-free interval and therefore $[^{15}\tilde{\text{N}}]$ and $[^{14}\tilde{\text{N}}]$ are accurate. In the following (Sections 5.5.4 to 5.5.6), measurements within the stability time are performed after calibration with a permeation device.
Figure 5.7 shows time-multiplexed measurements at 50 s line-switch intervals performed at two flow-rates corresponding to different NO concentrations (the darker colors and faded colors correspond to 10 sccm and 75 sccm respectively). Based on the mean value of the $[\text{^{15}N}](t)$ and $[\text{^{14}N}](t)$ signals at both flow-rates, given by

$$\bar{\eta}_R = \frac{\langle [\text{^{15}N}](t) \rangle_T}{\langle [\text{^{14}N}](t) \rangle_T}$$  \hspace{1cm} (5.14)

the instantaneous values $[\text{^{15}N}](t)$ and $[\text{^{14}N}](t)$ are used to calculate the permil isotopic ratio through linear interpolation of $[\text{^{14}N}]$ during the line-switch intervals. Utilization of Equation 5.10 relates the time-dependent permeation gas measurements to $\bar{\eta}_R$ (i.e., itself) for determination of the instantaneous isotopic ratio:

$$\delta^{15}\tilde{N} = \left( \frac{[\text{^{15}N}]_S}{[\text{^{14}N}]_S} \cdot \frac{1}{\bar{\eta}_R} - 1 \right) \times 10^3 \text{‰}$$  \hspace{1cm} (5.15)

Inspection of the results in Figure 5.7 show that both flow-rates converge to a ratiometric null, indicating the independence of flow-rate to the isotopic composition of the permeation reference gas. Flow-rates up to 140 sccm are tested for ratiometric consistency, though at lower flow-rates (and higher concentrations) the noise is proportionally smaller (as described in Section 5.5.2). In principle it is desirable to use larger signals such that the reference can be determined precisely within a reasonably short averaging time to reduce calibration overhead.

### 5.5.4 Fluid sample analysis

To study real time fractionation effects in the chemical conversion system for liquid sample analysis, it is necessary to preserve high ratiometric precision. Therefore, in order to produce NO concentrations above 100 ppmv, we use $> 1 \mu\text{mol}$ samples of liquid nitrate/nitrite solutions. As a demonstration of the quasi-simultaneous isotope measurement of fluid samples, 5 $\mu\text{mol}$ (500 $\mu\text{L}$
∗ 10 mM) KNO₃ (potassium nitrate) is injected into the acidic vanadium(III) for measurement of NO isotopes as shown in Figure 5.8. Broad peaks of ~ 100 s full-width half-maximum (FWHM) were obtained at a flow-rate of 64 sccm, and line-switching at 15 s intervals was selected to ensure sufficient time resolution during the sample peak. In principle, the measurement duty cycle for each isotope (¹⁴NO and ¹⁵NO) should be optimized such that the majority of time is spent on ¹⁵NO measurement (which has a lower SNR); however, this results in sparse and short ¹⁴NO segments, which in turn yields lower peak interpolation accuracy. From these experimental considerations we have chosen a simple 50% duty cycle between major/minor isotope switching. As mentioned in Section 5.4.1, the PID line-lock requires ~ 2.5 s settling time, and such an interval of data at the beginning of each measurement segment has been discarded prior to analysis. The final isotopic ratio (δ¹⁵N<T>) is referenced to the permeation gas described in Section 5.5.3, whose isotopic ratio (ηᵣ) has been characterized to remain independent of flow rate (tested from 10 sccm to 140 sccm) and concentration, and is therefore suitable as a stable reference for our measurements. The permil isotopic ratio calculated according to Equation 5.10 is shown in Figure 5.8(a), clearly demonstrating a varying instantaneous permil ratio over the sample peak. Provided that the spectrometer itself is fractionation-free as shown in Section 5.5.2, we conclude that the fractionation observed during the liquid sample analysis originates from the chemical conversion unit. Mass fractionation may result in shifted ¹⁵NO and ¹⁴NO peaks, and δ¹⁵N(t) at any given point in time may not be an accurate representation of the sample composition. Therefore, to reduce the effects of time-dependent fractionation it is critical to measure the entire peak (i.e., integrating the entire peak ensures we have accounted for all chemically produced NO molecules). To calculate total permil value δ¹⁵N<T> the ratio of the integrated peaks is used according to:
\[
\delta^{15}N_T = \left( \int_{t}^{T} \frac{[^{15}\tilde{N}]_s(t)}{[^{14}\tilde{N}]_s(t)} \cdot \frac{1}{\tilde{\eta}_R} - 1 \right) \times 10^3 = \left( \frac{\left( [^{15}\tilde{N}]_s(t) \right)_T}{\left( [^{14}\tilde{N}]_s(t) \right)_T} \cdot \frac{1}{\tilde{\eta}_R} - 1 \right) \times 10^3
\]  

(5.16)

where \(\tilde{\eta}_R\) is the reference ratio (from the G-Cal permeation device), and \(T\) as the time-span used for \(^{15}\text{NO}\) measurement (peak integration time is \(\sim 50\%\) total peak time due to isotope switching).

Using \([^{15}\tilde{N}]_s(t) = \tilde{\eta}_R \cdot [^{15}\delta N(t)/10^3 + 1] \cdot [^{14}\tilde{N}]_s(t)\) from Equation 5.10, we obtain (Appendix A1.5):

\[
\delta^{15}N_T = \frac{\left( \delta^{15}N(t) \cdot [^{14}\tilde{N}]_s(t) \right)_T}{\left( [^{14}\tilde{N}]_s(t) \right)_T}
\]  

(5.17)

This demonstrates that the final isotopic ratio can be considered as a weighted average of instantaneous permil ratio (Figure 5.8(a)) over the major isotopic peak. Furthermore, Equation 5.17 indicates that as \([^{14}\tilde{N}]_s(t)\) degrades near the peak wings, the relative contribution of \(\delta^{15}N(t)\) to \(\delta^{15}N_T\) becomes proportionally smaller. Qualitatively, accuracy of the final ratiometric calculation is hardly affected by the integration of the wings, and any residual accuracy deviation is corrected via calibration with known references.

Error propagation in Equation 5.17 (\(\Delta[^{15}\tilde{N}]_s\) at \(\Delta f = 2\) Hz ENBW are uncorrelated and sum in quadrature), result in a simple extension of Equation 5.13 of the following form (Appendix A1.5):

\[
\Delta(\delta^{15}N_T) = \frac{\Delta[^{15}\tilde{N}]_s}{\sqrt{T}} \cdot \left[ \frac{\delta^{15}N_T}{10^3} + 1 \right] \times 10^3
\]  

(5.18)

Intuitively, Equation 5.18 is understood as the quotient of time-averaged noise and signal for the \(^{15}\text{N}\), multiplied by a conversion factor (\(\sim 10^3\) for samples near \(\tilde{\eta}_R\) abundance) to convert to ratiometric (‰) units. Since in case of the liquid samples the entire sample peak is used for measurement, the time-averaging further improves ratiometric precision, which is also sample size
dependent. The effect of sample size variation on ratiometric precision is plotted above Figure 5.8(b), which indicates sub-permil precision for sample sizes > 1 μmol. For the peak shown in Figure 5.8(a) derived from a 5 μmol KNO₃ sample, we calculate $\delta^{15}N_{T} = 200.1 \%$ and $\Delta(\delta^{15}N_{T}) = 0.25 \%$, demonstrating precision well within sub-permil range. Multiple repeat injections yields very similar isotopic ratios (three $[^{15}\text{N}]_{s}(t)$ measurements are shown in the inset, and $[^{14}\text{N}]_{s}(t)$ is excluded for clarity) with the average isotopic ratio of $(\delta^{15}N_{T})_{avg} = 199.0 \%$. The standard deviation of $(\delta^{15}N_{T})_{stdev} = 5.08 \%$ was calculated for the best four out of five injections, which is significantly higher than: (i) instrument precision of 0.25 \% (calculated for 5 μmol KNO₃) and (ii) instrument drift (sub-permil for $\sim 10^3$ s as calculated from Figure 5.5(c)); therefore, we conclude the principal contribution to measurement error originates from uncertainty introduced by chemical reduction of nitrates within the sampling front end.

5.5.5 Time-dependent fractionation via isotopic line switching

In Sections 5.5.2 and 5.5.4, time-multiplexed isotopic measurements via line-switching was demonstrated for observation of isotopic fractionation over the duration of an injected sample peak. The question of the necessity of quasi-simultaneous measurements arises, and whether a simple two-peak measurement by a repeated sample injection for each $^{15}$N and $^{14}$N isotope is in fact sufficient to achieve the required accuracy. Figure 5.9 is a demonstration of the two measurement methods: (A) two sample injections for separate measurement of $^{15}$N and $^{14}$N; (B) a single sample injection with line-switched measurements at a 50 % duty cycle. An identical flow configuration (41.4 sccm) and sample size (5 μmol KNO₃) is used during the experimental comparison of (A) and (B).

Figure 5.9(a) shows the ratiometric analysis of method (A) performed by aligning 10 % peak rise times for both isotopes, resulting in a monotonically increasing fractionation curve calculated
using $\tilde{\eta}_R$ determined in Section 5.5.3. Precision analysis indicates $\Delta(\delta^{15}\text{N}_T) = 0.18 \%$, consistent with time averaging of permil standard deviation (3.0 \%o Hz$^{-1/2}$, inset of Figure 5.9(a)). Peak integration of $^{15}\text{N}(t)$ and $^{14}\text{N}(t)$ yield total isotopic ratio of 200.5 \%o ± 0.18 \%o. In Figure 5.9(b), 25 s switch intervals are used in a measurement scheme similar to Section 5.5.4. High-order polynomial interpolation is used for $^{14}\text{NO}$ peak gap intervals, resulting in a total ratiometric value of 175.9 \%o ± 0.27 \%o according to Equation 5.18. The time dependent $\delta^{15}\text{N}(t)$ shows a standard deviation consistent with Figure 5.9(a), and the slight degradation in precision after peak integration is due to the 50 % duty cycle of measurement inherent to the line-switch procedure.

Comparison of Figures 5.9(a) and (b) demonstrate that integration over the entirety of the sample peak yields similar measured ratiometric precisions. However, it is apparent that real-time ratiometric variation over the peak (notably in the vicinity of the peak maxima) are not captured in separate isotope injections, and the resulting total $\delta^{15}\text{N}_T$ deviates significantly (200.5 \%o vs. 175.9 \%o). In addition to this inaccuracy of temporally separate injections, dynamics of the flow and wet-chemistry system (e.g. kinetic fractionation) are not observable without quasi-continuous line-switched analysis.

5.5.6 Small sample analysis

Prior measurements in Section 5.5.4 utilized 5 µmol KNO$_3$ samples to achieve sub-permil precisions (calculated by Equation 5.18 and displayed in Figure 5.8(a)). Given the transportability of the present DM-FRS spectrometer, the same sample size limitations defined by IRMS-based systems can be overcome with the present FRS technology (e.g. by on-site deployment of the DM-FRS sensor), and improvement in precision is proportional to the sample size (and also the measurement duration, described in Section 5.5.4), as indicated by Equation 5.18. Nevertheless, it is instructive to demonstrate a more extreme case of small (~ nmol) size sample injections, similar
to those used in IRMS systems, particularly the state-of-art denitrifier method pioneered by Sigman [19].

Figure 5.10 shows a sequential measurement of ~ 70 nmol sample and reference KNO₃ injection within a 10³ s stability time of the spectrometer, utilizing USGS-41 (δ¹⁵N = 47.57 ‰) and USGS-40 (δ¹⁵N = -4.52 ‰) standards respectively, leading to a relative per-mil ratio of δ¹⁵N_S/R = ([δ¹⁵N_S − δ¹⁵N_R] · 10³) / (δ¹⁵N_R + 10³) = 52.3 ‰. Measurements are performed at 103 sccm flow rate and 15 s line-switch interval, totaling 500 s per peak for adequate capture of any baseline offsets. Based upon the KNO₃ injection quantity, a signal degradation of ~ 70× is expected, and therefore baseline fluctuations due to residual NO and peak crosstalk become particularly significant. Qualitatively, we note that to first-order with similar sample and reference sizes, baseline corrections become necessary when the non-zero ¹⁵N baseline offset is on the same order as δ¹⁵N(t) = [¹⁵N]S(t) − [¹⁵N]R(t). ¹⁴N interpolation followed by peak integration via Equation 5.17 for both sample and reference yields a relative δ¹⁵N = 43.8 ‰ ± 28.2 ‰, which is within one standard deviation of the expected 52.3 ‰ and demonstrates the potential of small sample analysis (on the same ~ 10 nmol sample requirement as IRMS based systems [23]) using the current DM-FRS spectrometer. In order to further improve precision, increased analyte residence time in the sample chamber is investigated below.

5.5.7 Preliminary measurements of gas sample trapping

According to Equation 5.18, two methods exist for improvement of ratiometric precision: (i) increasing sample size [¹⁵N]S(t), and (ii) increasing averaging time T. Typically, it is desirable to increase the former due to the linear proportionality of improvement, whereas the latter time averaging improves with the square-root of measurement time. Nevertheless, in precision isotopic analysis, time is generally not the limiting constraint, and the non-destructive sample handling
inherent to optical measurements allows the continuous use of the sample while it remains present within the sensor measurement cell.

To demonstrate the effect of time averaging with gas trapping, solenoid valves (ASCO Model 8320) were inserted at the inlet and outlet of the gas cell in Figure 5.2(a) and synchronized for simultaneous closure. Figure 5.11(a) shows an initial gas-trap measurement with NO gas from the G-Cal permeation device, using a carrier flow corresponding to 10 ppmv $^{14}$NO and 25 s line-switch intervals. Upon valve closure ($t = 0$ s), signal decay is observed for both isotopes, primarily due to leakage of ambient air ($\sim$ 0.05 torr/s) into the gas chamber which causes collisional broadening and decreases peak absorbance, and renders the applied magnetic field ($B = 150$ G) sub-optimal. Experimental characterization of the signal decay as a function of increasing pressure enables calculation of the expected signal levels (shown in gray and black for $^{14}$NO and $^{15}$NO respectively), and subsequent signal normalization allows determination of permil ratios. Over the span of the ~2000 s measurement, the trapped gas is observed to slowly enrich in $^{15}$NO, likely due to reaction with ambient air ($O_2$) leaking into the gas cell. At 10 ppmv $^{14}$NO, the isotopic precision is determined to be $\Delta(\delta^{15}N) = 1.41 \%_0$ given the spectrometer noise and 2000 s averaging time. For the expected $> 100$ ppmv ($5 \mu$mol KNO$_3$) concentrations from the wet-chemistry NO$_3$ conversion system, we expect the precision $\Delta(\delta^{15}N)_{100ppmv} < 0.14 \%_0$. Area integration under the $[^{14}N]$, $[^{15}N]$ curves yield an average isotopic ratio of 83.7 %, although the real time $\delta^{15}N(t)$ is more representative of isotopic composition as it tracks true $^{15}$N enrichment of the gas at any given time.

Identical gas-trap measurements are repeated in Figure 5.11(b) for 5 $\mu$mol KNO$_3$ injections where the solenoid valves are sealed at the sample peak. Pressure normalized signals are shown as gray dashed lines, and normalization yields isotopic $\delta^{15}N(t)$ that enriches in $[^{15}N] < 2\times$ faster than results shown in Figure 5.11(a) using the permeation device. The faster increase in $[^{15}N]$
abundance indicates the possible presence of active chemical reagents in the reactor vapor (most significantly \( \text{H}_2\text{O} \) and \( \text{NO}_2 \) [24]) that result in significantly faster NO degradation (e.g. through formation of \( \text{HNO}_2 \) [24]), which is qualitatively noted by the clear isotopic fractionation (~ 200 ‰) observable in the sample injection peaks in previous measurements (Sections 5.5.4 and 5.5.5). Calculation of the measurement noise yields \( \Delta(\delta^{15}\text{N}) = 0.07 \text{‰} \) which is ~ 3.6× improved over the result obtained in Section 5.5.4 (\( \Delta(\delta^{15}\text{N}) = 0.25 \text{‰} \)) for integration over a single injection peak.

The aforementioned experimental results demonstrate the efficacy of gas-trapping for precision enhancement; however, two considerations arise based on the data in Figure 5.11 that results in ratiometric inaccuracies: (i) ambient leakage causing contamination of the NO gas in the measurement cell, and (ii) the increased rate of NO decay from the wet-chemistry system due to the reactor vapor. The former is easily resolved with appropriate system engineering; the latter through the possible use of filters (e.g. Nafion dryers) for removal of \( \text{H}_2\text{O} \) prior to the trapping process. These preliminary measurements in Figure 5.11 are intended to demonstrate the potential of sample averaging, and will be further developed in the next generation DM-FRS prototype.

5.6 Ratiometric linearity

In Section 5.5.2, fractionation-free system performance was demonstrated, supporting the conclusion that the real time fractionation described in Section 5.5.4 may be attributed to \( \delta^{15}\text{N} \) variations in the sample gas. Here we consider how ratiometric accuracy varies with isotopic composition. This sensor linearity test is conducted by performing 400 nmol injections of samples with known isotopic compositions with ratiometric values of 5 ‰, 1111 ‰, 2218 ‰, and 5536 ‰ prepared using a mixture of 99% \( ^{15}\text{N} \) enriched potassium nitrate (Cambridge Isotopes) with natural abundance nitrate (Fisher Scientific). The samples injected are substantially smaller (by roughly 12.5×) than prior injections demonstrated in Section 5.5.4, thus yielding a lower ratiometric
precision of $\Delta(\delta^{15}N) = 2 \%o$ (consistent with Equation 5.18 and Figure 5.8(b)). Four repeat injections are conducted for each ratiometric sample, with results plotted in Figure 5.12(b). Ratiometric analyses demonstrate excellent linearity ($R^2 = 0.999$), with a permil offset of 177.9 \%o consistent with measurements using near-natural abundance samples shown in Figure 5.8(a). It is notable that the measured to calculated isotopic ratio is not unity ($d\delta^{15}N_{\text{meas}} / d\delta^{15}N_{\text{calc}} = 0.782$), indicating possible $^{14}$NO preference in the vanadium(III) conversion process. Different temperature dependence of the transition linestrength between $^{14}$NO and $^{15}$NO have been considered as a source of this effect, but calculations yield slope modification factors far below the observed deviation for temperature differences up to hundreds of Kelvin [1]. Nevertheless, the excellent linearity demonstrates consistency in sample conversion and measurement, allowing any sample to be calibrated via known references.

5.7 Limitations of the present ratiometric method

In Section 5.5.3, a simple calibration method is used, whereby a G-Cal permeation device is characterized to maintain consistent isotope ratio independent of carrier flow-rate, and is therefore suitable as a ratiometric reference. However, prior to sample measurements, this calibration method must take place within the zero-drift interval of the spectrometer, and therefore involves a brute-force measurement of all terms ($[^{15}N]_{S/R}(t), [^{14}N]_{S/R}(t)$) in Equation 5.10 for $\delta^{15}N$. In addition to substantial calibration time overhead, systematic errors (e.g. fractional error $\rho$) in determination of any of the above sample and reference $[\tilde{N}]_{S/R}(t)$ terms, i.e. $[\tilde{N}]_{S/R}(t) \rightarrow (1 \pm \rho)[\tilde{N}]_{S/R}(t)$ results in measured $\delta^{15}N_{\text{meas}}$ of:
where we have defined $O_1(\rho) = \rho \cdot 10^3 \%$ and $O_2(\rho) = \delta^{15}N_{\text{true}} \cdot \rho$, and $\delta^{15}N_{\text{true}}$ to be the true permil ratio for $\rho \to 0$. From Equation 5.19 it is clear that the additive first-order term $O_1(\rho)$ is responsible for the bulk of the inaccuracy; a 1 % error ($\rho = 10^{-2}$) in $[\tilde{N}]_{S/R}(t)$ results in $|O_1(\rho)| = 10 \%$ offset. The second order term is multiplicative and results in a fractional error in $\delta^{15}N_{\text{true}}$, which is typically within acceptable limits. Examples of sources of $\rho$ include imperfect baseline removal described in Section 5.5.6, or residual NO from prior sample injections. For larger sample sizes as demonstrated in Sections 5.5.4 and 5.5.5, Equation 5.19 does not constrain the ratiometric accuracy, although in the case of small sample sizes such artefacts will appear if the spectrometer noise or residual NO in the flow system is not appropriately controlled. To mitigate this effect, a differential DM-FRS method will be proposed and demonstrated in Chapter 6 which eliminates the $O_1(\rho)$ uncertainty for more reliable ratiometry.

5.8 Concluding remarks

A dual-modulation Faraday rotation spectrometer is demonstrated for isotopic ratiometry via line-switching. Noise characterization demonstrates 0.36 ppbv·Hz$^{-1/2}$ $^{15}$NO sensitivity, at 2.8× the shot-noise limit and $1.31 \times 10^{-8}$ rad·Hz$^{-1/2}$ noise-equivalent angle with baseline-free performance. Ratiometric analysis indicates sub-permil precision for $\mu$mol level nitrate samples, allowing real-time ratiometric diagnostics with excellent linearity ($R^2 = 0.999$) up to $10^3 \%$ levels. The combination of sensitivity and transportability demonstrates promise for in situ environmental and medical diagnostics. Development of a next-generation portable prototype is underway, with goals
of further miniaturization of the signal processing electronics, gas-trapping capability and integration with a total-nitrogen combustion-based conversion unit for measurement of organic nitrogen samples, which is expected to eliminate isotopic uncertainty introduced by the current chemical conversion unit. Finally, to mitigate the effect of unfavorable additive errors in the presence of systematic signal inaccuracy, a differential scheme is developed in Chapter 6 for real-time sample referencing via in-line optical subtraction.
References


Chapter 6:
Differential DM-FRS for Real-time Calibration

In this Chapter, we overcome limitations of direct ratiometry via separate sample and reference measurements described in Chapter 5. To this end, we devise a real-time, in-line referencing scheme [1, 2] to simplify the calibration procedure by measuring Faraday rotation difference (i.e. polarization subtraction) signals $15\tilde{\eta}(t) = [15\tilde{N}]_S(t) - [15\tilde{N}]_R(t)$ and $14\tilde{\eta}(t) = [14\tilde{N}]_S(t) - [14\tilde{N}]_R(t)$. The mathematical formulation for $\delta^{15}N$ based on $15\tilde{\eta}(t)$ and $14\tilde{\eta}(t)$ will be presented. Implementation of this optical subtraction scheme for in situ sample referencing, termed differential DM-FRS (dDM-FRS), is demonstrated for NO isotopic analysis. $^{15}$NO MDL of 3.1 ppb·Hz$^{-1/2}$ is measured through only 15 cm optical path length, and Allan-deviation stability indicates Gaussian-noise performance up to ~ 300 s at 1.9× the quantum shot noise limit, corresponding to a $(\alpha L)_{\text{min}} = 1.2 \times 10^{-7}$ Hz$^{1/2}$ and $\Theta_{\text{NEA}} = 1.70 \times 10^{-8}$ Hz$^{1/2}$ for $^{15}$NO. Excellent sensor linearity is determined using single-cell isotopic analysis of IAEA-NO-3 ratiometric standard ($\delta^{15}N = 4.7$ ‰) by conversion to gaseous NO via nitrate reduction in an acidic solution of vanadium(III). Initial demonstration of differential measurement of $^{15}$NO yields 19.2 dB magneto-optical CMRR, and demonstrates sub-permil ratiometric precision for > 200 s averaging. Implementation details of dDM-FRS for precision ratiometry will be discussed.

6.1 Introduction

In Chapter 5, DM-FRS was utilized for time-multiplexed, quasi-simultaneous isotopic fractionation studies of NO, yielding $(\alpha L)_{\text{min}}$ of 6.27×10$^{-8}$ Hz$^{1/2}$ and $\Theta_{\text{NEA}} = 1.31 \times 10^{-8}$ rad·Hz$^{-1/2}$ at 2.8× the quantum shot-noise limit [3-6]. Long-term sensor stability ($\sim 10^3$ s) allowed peak-averaging at ~ 10$^3$ s time scales, enabling sub-permil precisions for sub-μmol nitrate (NO$_3$-) injection quantities. Particularly significant to isotopic ratiometry as described in Chapter 5 is the
procedure for sample referencing, which ensures that all measurements are quantified with respect to the same standard $[^{15}\text{N}]_R/[^{14}\text{N}]_R$. The calibration procedure, outlined in Section 5.5.3, relies upon direct measurement of a calibration reference gas, followed by measurement of an unknown sample $[^{15}\text{N}]_S/[^{14}\text{N}]_S$ within the stability time of the spectrometer. This direct ratiometric measurement suffers from various drawbacks including calibration time overhead and poor handling of systematic errors, as described in Section 5.7. In particular, ratiometric accuracy of the system (particularly for small sample sizes), is predicated on the assumption that (i) any measurement baseline correction (due to residual remaining NO in the flow system from prior sample/reference injections) remains linear and small with respect to the sample peak and (ii) the reference and sample peaks are acquired within the stability time of the spectrometer to ensure that measurement results are not affected by sensor drift over time.

In what follows, we present a differential DM-FRS (dDM-FRS) sensor [1, 2] to resolve the previous limitations by using real-time polarization subtraction (reversing the sense of Faraday rotation) between the sample and reference gases. We begin with an experimental scheme for implementation of optical polarization subtraction (Section 6.2), followed by the mathematical formulation for differential ratiometric measurements (Section 6.3) to understand how the temporally concurrent sample and reference difference measurement $^{15}\hat{\eta}(t)$ and $^{14}\hat{\eta}(t)$ improve accuracy. In particular, each measurement peak is always referenced to a known reference quantity of NO, and the first order error term $O_1(\rho)$ described in Section 5.7 is eliminated. A key parameter for dDM-FRS is the CMRR, which through the mathematical formulation of differential measurement, behaves as an offset calibration term in the permil isotopic ratio, and requires characterization to ensure differential measurement accuracy. Experimentally, we determine a magneto-optical CMRR of 24.8 dB and 19.2 dB (Appendix A3 and Section 6.4.2) for $^{14}$NO and
\(^{15}\text{NO}\) respectively, yielding estimated sub-permil ratiometric uncertainty in the calibration offset for µmol sample sizes and ~ 200 s peak averaging.

6.2 Differential DM-FRS (dDM-FRS) sensor design

The present dDM-FRS system follows a similar design pattern outlined in [3-6] but with relaxed dimensional and power constraints as a benchtop prototype. The dDM-FRS benchtop system has undergone two generations of development, where the 2nd-generation prototype is the focus of this Chapter and depicted in Figure 6.1.

The 1st-generation dDM-FRS spectrometer (described in Appendix A3) demonstrates long term stability and near (2.4×) shot-noise limited performance. However, limitations include: (i) the relatively high \(f_M = 1.04 \text{ kHz}\) B-field modulation frequency resulting in EMI and the necessity of baseline removal (Appendix A3.3), and (ii) the poor PER (Appendix A3.4) due to crosstalk between the ordinary and extraordinary polarizations exiting the Rochon polarizer (Foctek RCP5010). In the following, we describe development of the separately constructed 2nd-generation dDM-FRS spectrometer that resolves the above limitations, and with which the mathematical formulation described in Section 6.3 is rigorously tested (Section 6.5).

The design follows the development of Chapter 5 [3-6] and Appendix A3 [1, 2]. A DFB QCL (Alpes Lasers) is employed to target the \(^{15}\text{N}\text{^{16}O}\) Q(3/2) and \(^{14}\text{N}\text{^{16}O}\) P(19/2)e transitions at 1842.76 cm\(^{-1}\) and 1842.95 cm\(^{-1}\) respectively, and laser modulation occurs at \(f_L = 50 \text{ kHz}\) [2]. Similar to [3], a compact (~ 3.3 lbs) water circulator and fan system (Corsair H100i) is appended to a customized QCL housing for thermal control. Anti-reflection (AR) coated wire grid polarizers (ISP Optics POL-3-5-SI-25) are used to eliminate crosstalk between the ordinary/extraordinary beams exiting the Rochon polarizers, and the 2.5 % \(^{14}\text{NO}\) reference cell for line-locking has been repositioned to utilize the partial reflection from P1 (initial polarizer). The optical path is single-pass (15 cm),
and the two cells (reference and sample gas cells) are housed within the solenoid to minimize magnetic field dissimilarities, where the field is driven through the use of a miniaturized class-D audio amplifier (Sure Electronics TK2050). Additionally, the coil modulation frequency $f_M$ is reduced from 1.04 kHz (Appendix A3.1) to 100 Hz for EMI suppression [1], with a peak field of 169 Gauss, close to the optimum calculated in Figure 2.10(b). Sample and reference cell operating pressure is set to 80 Torr (Varian IDP3B01 scroll pump) for future compatibility with compact vacuum pumps (e.g. KNF UN84.3 ANDC diaphragm pump [3]). The resulting detector signal (Vigo PVI-3TE, current responsivity $R_I = 3.3$ A/W, voltage transimpedance $G_V = 5 \times 10^4$ V/A) undergoes two-stage demodulation for the dual sidebands at $2f_L \pm f_M$ via phase-sensitive detection (Zurich Instruments HF2LI) as described in Section 2.4.5 and Chapter 5.

Integration with the wet chemistry for sample measurement and cylinder NO for ratiometric referencing is shown in Figure 6.1 and follows the development of Section 5.3. The reference cylinder may be optionally replaced with an automated dilution tracker for minimization of $^{14}\eta(t)$; this will be performed in another developmental iteration and is beyond the scope of this Chapter.

Given the introduction of AR-coated wire-grid polarizers, substantial improvement of the PER is observed ($\varepsilon = 1.34 \times 10^{-5}$). SNR optimization based on analyzer uncrossing angle is performed as described in Section 3.3.2, using a measured $\tilde{\sigma}_{\text{RIN}} = 2.89 \times 10^{-7}$ Hz$^{1/2}$ and $\sigma_{\text{NEP}} = 1.15 \times 10^{-12}$ W·Hz$^{-1/2}$. Calculation of optimum uncrossing angle yields $\theta_{\text{opt}} = 2.56^\circ$ using Equation 3.20, which is consistent with the results determined in Figure 6.2.

To perform the optical subtraction, two bare-gold mirrors angled at 45º are used to retro-reflect the optical beam back through the solenoid. As the beam reflects off each mirror, the sense of circular polarization changes; i.e. clockwise becomes anticlockwise and vice versa. The retro-reflection process thus maintains the same circular polarization sense in both the sample and
reference cells, resulting in an opposite polarization rotation in the return trip as the magnetic field is reversed with respect to the beam path [2]. This is to be contrasted with a multi-pass cell, whereby each path iteration through the cell undergoes only one reflection, thus allowing additive polarization rotation.

6.3 Theory of differential ratiometry

To derive an expression for the isotopic ratio for our differential system described in Section 6.2, we begin with the standard ratiometric definition [7] as described in Equation 5.10 for $\delta^{15}\text{N}$, with time-dependent variations included explicitly in the permil ratio:

$$
\delta^{15}\text{N}(t) = \left( \frac{[15\text{N}]_S(t)}{[14\text{N}]_S(t)} - 1 \right) \times 10^3 \text{‰}
$$

(6.1)

In the case of our optical spectrometer, there exists a concentration (ppmv) to signal (voltage) conversion factor $\gamma_{15}^S$ and $\gamma_{14}^S$ (also introduced in Section 5.5.1) such that $[15\text{N}]_S(t) = \gamma_{15}^S \cdot [15\tilde{\text{N}}]_S(t)$, $[14\text{N}]_S(t) = \gamma_{14}^S \cdot [14\tilde{\text{N}}]_S(t)$, along with analogous definitions for $\gamma_{15}^R$ and $\gamma_{14}^R$. For notational clarity, we define parameters $\kappa_{15} = \gamma_{15}^S / \gamma_{15}^R$ and $\kappa_{14} = \gamma_{14}^S / \gamma_{14}^R$, which is related directly to the magneto-optical CMRR measured in Section 6.4.2. Using the above notation, we may therefore write:

$$
\delta^{15}\text{N}(t) = \left( \frac{\kappa_{15}}{\kappa_{14}} \cdot \frac{[15\tilde{\text{N}}]_S(t)}{[14\tilde{\text{N}}]_S(t)} - 1 \right) \times 10^3 \text{‰}
$$

(6.2)

Presently, it is useful to note that in the case of a differential measurement, the only signal of direct interest (and directly accessible from measurement) is given by the optical subtraction $^{15}\tilde{\eta}(t)$ and $^{14}\tilde{\eta}(t)$:
To consider the impact of the CMRR on the isotopic ratio, we may consider a scenario where an identical reference gas is passed simultaneously through both reference and sample cells, i.e. $[^{15}\text{N}]_S(t) = [^{15}\text{N}]_R(t)$, or $\gamma_{15}S[^{15}\text{N}]_S(t) = \gamma_{15}R[^{15}\text{N}]_R(t)$, with similar relations for the major isotopologue. Calculation of the difference signal $^{15}\tilde{\eta}$ yields a definition for the CMRR ($^{15}R_{CMR}$ and $^{14}R_{CMR}$) given by:

$$^{15}R_{CMR} \equiv \left(\frac{\langle^{15}\tilde{\eta}(t)\rangle_T}{\langle[^{15}\text{N}(t)]_R\rangle_T}\right) = \frac{1 - \kappa_{15}}{\kappa_{15}}$$  

$$^{14}R_{CMR} \equiv \left(\frac{\langle^{14}\tilde{\eta}(t)\rangle_T}{\langle[^{14}\text{N}(t)]_R\rangle_T}\right) = \frac{1 - \kappa_{14}}{\kappa_{14}}$$  

Rearranging Equation 6.4 for $\kappa_{15}$ and $\kappa_{14}$, and substituting the resulting expressions (and Equation 6.3) into Equation 6.2 yields:

$$\delta^{15}\text{N}(t) = \left(\frac{1 + {^{14}R}_{CMR}}{1 + {^{15}R}_{CMR}} \cdot \frac{^{15}\tilde{\eta} + [^{15}\text{N}]_R(t)}{^{14}\tilde{\eta} + [^{14}\text{N}]_R(t)} \times 10^3 \% \right)$$  

We consider the limit where $^{14}\tilde{\eta}(t)$ is kept small, i.e. $[^{14}\text{N}]_S(t) \approx [^{14}\text{N}]_R(t)$ via real-time concentration tracking such that $^{14}\tilde{\eta}(t) \ll [^{14}\text{N}]_R(t)$. This may experimentally be realized using a gas dilution system with real-time signal feedback to maintain near-zero differential $^{14}\tilde{\eta}(t)$. Under this assumption, we may write the numerator term in Equation 6.5 as:

$$\frac{^{15}\tilde{\eta} + [^{15}\text{N}]_R(t)}{^{14}\tilde{\eta} + [^{14}\text{N}]_R(t)} = \frac{^{15}\tilde{\eta}(t)}{^{14}\tilde{\eta}(t)} \frac{[^{15}\text{N}]_R(t)}{[^{14}\text{N}]_R(t)} \left(1 - \frac{^{15}\tilde{\eta}_R(t)}{[^{14}\text{N}]_R(t)} \right) \frac{[^{15}\text{N}]_R(t)}{[^{15}\text{N}]_R(t)}$$  

Combining Equations 6.5 and 6.6 provides the final real-time isotopic ratio $\delta^{15}\text{N}(t)$ using differential ratiometry:
\[ \delta^{15}N(t) = \frac{1 + 14^{14}R_{CMR}}{1 + 15^{15}R_{CMR}} \left\{ \Omega_{O(1)}(t) - \Omega_{O(2)}(t) - \Omega_{O(3)}(t) + \tau(14^{14}R_{CMR} , 15^{15}R_{CMR}) \right\} \times 10^3 \% \quad (6.7) \]

\[ \Omega_{O(1)}(t) = \frac{15^{15} \eta(t)}{[15^{15}N]_R(t)} , \quad \Omega_{O(2)}(t) = \frac{14^{14} \eta(t)}{[14^{14}N]_R(t)} , \quad \Omega_{O(3)}(t) = \frac{15^{15} \eta(t)}{[15^{15}N]_R(t)} \cdot \frac{14^{14} \eta(t)}{[14^{14}N]_R(t)} \quad (6.8) \]

\[ \tau(14^{14}R_{CMR} , 15^{15}R_{CMR}) = \frac{14^{14}R_{CMR} - 15^{15}R_{CMR}}{1 + 14^{14}R_{CMR}} \quad (6.9) \]

\( \Omega_{O(1)}(t) , \Omega_{O(2)}(t) , \Omega_{O(3)}(t) \) are introduced to denote the first to third order terms respectively (in order of decreasing contribution to the final \( \delta^{15}N \) calculation), and are defined in Equation 6.8. In the case of fast dilution feedback to maintain zero major isotope differential \( 14^{14}N(t) \) signal, only \( \Omega_{O(1)}(t) \) is relevant. The final term \( \tau(14^{14}R_{CMR} , 15^{15}R_{CMR}) \) in Equation 6.9 is a measure of the contribution due to imperfect common-mode suppression or \( \{|14^{14}R_{CMR}|, |15^{15}R_{CMR}| > 0 \} \), which manifests as an additive permil offset, and can be quantified through reference calibration. Using the nominal scheme whereby \( 14^{14} \eta(t) \ll [14^{14}N]_S(t) \), only the first order term \( \Omega_{O(1)}(t) \) remains significant in \( \delta^{15}N(t) \):

\[ \delta^{15}N(t) = \frac{1 + 14^{14}R_{CMR}}{1 + 15^{15}R_{CMR}} \cdot \Omega_{O(1)}(t) \cdot 10^3 \% = \frac{1 + 14^{14}R_{CMR}}{1 + 15^{15}R_{CMR}} \cdot \frac{15^{15} \eta(t)}{[15^{15}N]_R(t)} \cdot 10^3 \% \quad (6.10) \]

From the expression above, two main benefits are apparent when compared to a direct isotope measurement ratio from Equation 6.1 (described in Chapter 5): (i) real-time calibration of all sample measurements, and (ii) resistance to systematic deviations, thus improving both ratiometric accuracy and precision. These are considered below in turn.

First, in case (i), the measurement implicit in Equation 6.1 and described in Section 5.5.1 involves the temporally distinct measurement of sample and reference gas. Consequently, reference samples need to be taken within the stability time of the spectrometer to maintain adequate ratiometric accuracy and avoid inaccuracies from long-term noise or baseline drifts. The
differential sensor is resistant to such deviations since at any given measurement time, $^{15}\tilde{\eta}(t)$ is directly measured and $[^{15}\tilde{N}]_R(t) = [^{15}\tilde{N}]_R(t)/\gamma_S^{15}$ can be calculated from the dilution factor and $\gamma_S^{15}$, which may be quantified prior to the start of the measurement process. Furthermore, regarding (ii), any uncertainties in the signal conversion factor $\gamma_S^{15}$ and dilution factor, which result in uncertainty in the calculated $[^{15}\tilde{N}]_R(t)$, as well as $\kappa_{14}/\kappa_{15}$ (corresponding to the $R_{CMR}$ for each isotope) translate fractionally into permil uncertainty. For example, instrumental drift causing relative CMRR isotope variation cause some fractional change $(\kappa_{14}/\kappa_{15}) \rightarrow (1\pm\rho)\cdot(\kappa_{14}/\kappa_{15})$, which in turn results in a measured ratiometric value $\delta^{15}N_{\text{meas}}(t)$:

$$\delta^{15}N_{\text{meas}}(t) = (1 \pm \rho) \cdot \delta^{15}N_{\text{true}}(t) = \delta^{15}N_{\text{true}}(t) + O_2(\rho)$$

Note that in comparison to Equation 5.19, only the second order term $O_2(\rho) = \delta^{15}N_{\text{true}} \cdot \rho$ exists, and the differential sensor is no longer limited by $O_1(\rho)$ additive errors.

Presently, we also consider instantaneous ratiometric precision $\Delta(\delta^{15}N)(t)$ provided by the dDM-FRS system. The ratiometric precision $\Delta(\delta^{15}N)$ is calculated assuming that the imprecision from $\Omega_{O(1)}(t)$ is dominant, which can be validated by writing the error contributions to $\Delta(\delta^{15}N)$ from each $\Omega_{O(N)}(t)$ order term (we assume $^{14}R_{CMR}$ and $^{15}R_{CMR}$ are well known prior to sample measurement such that $\Delta^\tau$ can be neglected):

$$\Delta[\Omega_{O(1)}(t)] \approx \frac{^{15}\sigma_{\text{tot}}}{\left[\left[^{15}\tilde{N}\right]_R(t)\right]_T}, \quad \Delta[\Omega_{O(2)}(t)] \approx \frac{^{14}\sigma_{\text{tot}}}{\left[\left[^{14}\tilde{N}\right]_R(t)\right]_T}$$

$$\Delta[\Omega_{O(3)}(t)] \approx \Omega_{O(1)}(t) \cdot \Delta[\Omega_{O(2)}(t)]$$

where $^{15}\sigma_{\text{tot}} \approx ^{14}\sigma_{\text{tot}}$ is the total measurement noise of minor and major isotopes respectively. Given that $[^{15}\tilde{N}]_R(t) << [^{14}\tilde{N}]_R(t)$ near natural abundance, and $\Omega_{O(1)}(t) > \{\Omega_{O(2)}(t), \Omega_{O(3)}(t)\}$ it follows that:

$$\Delta[\Omega_{O(1)}(t)] \gg \Delta[\Omega_{O(2)}(t)] \gg \Delta[\Omega_{O(3)}(t)]$$

(6.13)
and therefore to first-order (using Equation 6.10), we obtain:

$$\Delta(\delta^{15}N)(t) = \delta^{15}N(t) \cdot \sqrt{\left(\frac{\Delta(\delta\tilde{\eta})^2}{\langle\delta\tilde{\eta}\rangle^2} + \frac{\Delta[\tilde{N}]_{R}^2}{[\tilde{N}]_{R}(t)^2}\right)10^3} \%_o$$

$$= \frac{\Lambda_{\sigma} \cdot \sigma_{shot}}{[\tilde{N}]_{R}(t)} \cdot \frac{1 + [14]_{CMR}^{15}R_{CMR}}{1 + [15]_{CMR}^{15}N_{R}} \cdot 10^3 \%_o$$

(6.14)

where $\sigma_{shot}$ is the quantum shot-noise contribution as determined in Figure 6.3, and $\Lambda_{\sigma}$ is the factor of performance from the shot-noise limit (Section 3.3.2), and we have assumed that $^{15}\tilde{\eta} < \langle [15\tilde{N}]_{R}(t)\rangle$. Note the similarity between Equations 6.14 and 5.13, which is as expected given that the ratiometric precision should scale linearly with system noise and inversely with sample size. Based on the above considerations, we therefore see that the differential measurement as given by Equation 6.7 provides enhanced accuracy via simultaneous reference and sample measurements (Equation 6.11), without any degradation in precision performance (Equation 6.14).

In what follows, we describe the instrumentation development for differential ratiometry using the method described by Equation 6.7. In particular, we follow the developments of [3-6] described in Chapter 5 to extend the use of DM-FRS for detection of NO isotopologues, which has routinely demonstrated near-quantum shot-noise limited sensors with NEA on the order ~ $10^{-8}$ rad·Hz$^{-1/2}$ [1, 3, 6, 8, 9].

6.4 dDM-FRS sensor performance

We experimentally characterize the dDM-FRS sensor detection limits and long-term stability. The magneto-optical CMRR of $^{15}$NO and ratiometric precision is analyzed, demonstrating potential for sub-permil measurements over 100 s. Line-switched measurements as described in Chapter 5 are implemented for quasi-simultaneous $^{15}$NO, $^{14}$NO ratiometry. Based on the measured CMRR, we verify the mathematical formulation of differential ratiometry (Equations 6.7 to 6.9) through self-referencing of a sample gas.
6.4.1 Spectral acquisition and sensor stability

Given the adequate demonstration of $^{14}$NO measurements and $^{14}$NO CMRR characterization in Appendix A3.4, present measurements for the 2nd-generation dDM-FRS sensor will primarily focus on $^{15}$NO analysis. Spectral acquisition from a calibrated 50 ppmv $^{14}$NO (184 ppbv at 0.368 % natural abundance) cylinder is performed at $\Delta f = 1$ Hz ENBW per point, shown in Figure 6.3(a). Reduction of $f_M$ essentially eliminates EMI, thus negating the requirement of baseline removal used in Appendix A3.3. The top graph of Figure 6.3(a) shows laboratory air measurement, which may be treated as zero-gas given the negligible contribution of ambient $^{15}$NO, and demonstrates zero-baseline as expected for DM-FRS techniques. Wavelength modulation spectroscopy ($3f_L$) of the reference gas (2.5 % $^{14}$NO and 1.5 % $^{15}$NO in N$_2$ balance) is performed for line-locking to the spectral peaks for real-time NO diagnostics, demonstrating performance at 1.9× the shot-noise limit ($\sigma_{\text{shot}} = 102.7$ nV·Hz$^{-1/2}$) with Gaussian noise performance up to $\sim$ 300 s. Based on the measured $^{15}$NO Q(3/2) signal peak ($V_{\text{sig}} = 11.6$ µV) and $\sigma_{\text{tot}} = 195.3$ nV·Hz$^{-1/2}$, we calculate a SNR = 59.4 Hz$^{-1/2}$ corresponding to a MDL of 3.1 ppbv·Hz$^{-1/2}$ and $\Theta_{\text{NEA}} = 1.7 \times 10^{-8}$ rad·Hz$^{-1/2}$, or $(\alpha L)_{\text{min}} = 1.2 \times 10^{-7}$ Hz$^{-1/2}$. Similar analysis for $^{14}$NO in Appendix A3.4 yields a $^{14}$NO detection limit of 20.3 ppbv·Hz$^{-1/2}$, corresponding to $(\alpha L)_{\text{min}} = 1.79 \times 10^{-6}$ Hz$^{-1/2}$. Note the proximity of both $(\alpha L)_{\text{min}}$ and $\Theta_{\text{NEA}}$ to previous work [3-6, 8], which is consistent with the performance of near shot-noise limited FRS sensors.

6.4.2 Measurement of the magneto-optical CMRR

The impact of a finite CMRR, denoted by $R_{\text{CMR}}$ in the previous Section manifests as an additive offset to the final permil isotope ratio. Ideally this offset term $\tau(R_{\text{CMR}}, R_{\text{CMR}})$ should remain static (i.e. the CMRR should be stable) and can therefore be quantified prior to isotopic analysis and used as an accuracy offset to obtain the true permil value. In addition, note that comparison of
Equations 6.4 and 6.10 shows that in the limiting case of $\Omega_{O(1)}(t)$ approximation and measurement of identical gas in the sample and reference cells, the sensor CMRR is in fact proportional to the permil ratio; i.e. $\delta^{15}N \approx ^{15}R_{CMR} \cdot 10^3 \%$. This indicates that measurement of $^{15}\bar{\eta}(t)$ stability for fixed $[^{15}N]_S$ and $[^{15}N]_R$ provides both sensor stability and CMRR stability; that is, the CMRR stability time is exactly the same as the sensor drift-free interval.

In addition to the above considerations, it is preferable that the relative contribution of $^{15}R_{CMR}$ with respect to $\Omega_{O(1)}(t)$ is small, i.e. $\tau(^{14}R_{CMR},^{15}R_{CMR}) \ll \Omega_{O(1)}(t)$, to reduce the impact of inaccuracies in the determination of $^{14}R_{CMR}$ and $^{15}R_{CMR}$. In the optimum case only $\Omega_{O(1)}(t)$ should determine the isotope ratio and its precision as quantified in Equation 6.14 should be the dominant uncertainty.

Figure 6.4(a) shows a demonstration of real-time optical subtraction in the dDM-FRS sensor, using line-locked operation to measure the same cylinder $^{15}$NO through both sample and reference cells. A three stage measurement procedure is used for CMRR characterization: initially, the gas flows through the (i) reference cell (between ~ 200 and 600 s), resulting in a Faraday rotation in the opposite sense as the (ii) sample cell measurement (between ~ 800 and 1200 s), which results in an inverted signal ($V_{ref} < 0$) with respect to the sample ($V_{sample} > 0$). Finally, (iii) simultaneous flow (~ 1200 and 1400 s) of identical NO gas through both cells is to determine the efficacy of magneto-optical subtraction, and is displayed in the boxed region (and expanded in the inset). Calculation of $^{14}R_{CMR}$, $^{15}R_{CMR}$, and $\tau(^{14}R_{CMR},^{15}R_{CMR})$ is then accomplished through direct application of Equation 6.4 and 6.9.

From Figure 6.4(a), we note that the calculated difference $^{14}\bar{\eta}_{calc} = <[^{15}N]_S>_T - <[^{15}N]_R>_T = -1.41 \mu V$ and measured $^{14}\bar{\eta}_{meas} = -1.28 \mu V$ are similar, which suggests that a significant portion of the imperfect CMRR is due to systematic differences in the measurements cells, and is
correctable (e.g. via adjustment of relative gas-cell lengths or placement within the solenoid to minimize field variation between the sample/reference). We therefore consider the true suppression capability of the differential sensor, quantified by the deviation between $^{14}\tilde{\eta}_{\text{meas}}$ and $^{14}\tilde{\eta}_{\text{calc}}$,

$$^{14}\text{CMRR}_{\text{true}} = 10 \cdot \log \left( \frac{\langle ^{14}\tilde{\eta}_{\text{meas}}(t) \rangle_T - \langle ^{14}\tilde{\eta}_{\text{calc}}(t) \rangle_T}{\langle ^{14}\tilde{N}(t) \rangle_R \rangle_T} \right)$$

(6.15)

$$= 10 \cdot \log \left( \frac{0.201 \ \mu V - 0.336 \ \mu V}{11.23 \ \mu V} \right) = 19.2 \ \text{dB}$$

corresponding to a ‘true’ suppression factor $^{14}R_{\text{true}} = 3.3 \times 10^{-3}$, or $^{15}\text{CMRR}_{\text{true}} = 19.2 \ \text{dB}$.

Figure 6.4(b) shows a ~ 2500 s line-locked measurement of a $^{15}$NO differential signal (from the certified NO cylinder), where the raw time series is displayed in the inset. Allan deviation analysis again indicates precision at 1.9× the shot-noise limit, with Gaussian-noise performance up to ~ 400 s. The raw time series measurement $^{15}\tilde{\eta}(t)$ is shown in the inset, and using Equation 6.7, conversion to permil precision $\Delta(\delta^{15}N) = 17.1 \ \%_o \ \text{Hz}^{-1/2}$ is accomplished by scaling with respect to the time average reference signal $\langle [^{15}\tilde{N}]_R(t) \rangle_T = 11.21 \ \mu V$. Note that in the shot-noise limit, isotopic precision for 50 ppmv $^{14}$NO is 9.2 $\%_o \ \text{Hz}^{-1/2}$, which represents a fundamental ratiometric precision limit (at 50 ppmv) for this sensor.

Typical 5 µmol KNO$_3$ sample injections yield > 200 ppmv $[^{14}\tilde{N}]$ peak concentrations (Section 5.5.4) with FWHM ~ 100 s (variation exist depending on carrier gas flow rate). From the $\sigma_{\text{ADV}}$ in Figure 6.4(b) (using a 50 ppmv $^{14}$NO differential measurement), $\Delta(\delta^{15}N) \approx 1 \ %_o$ at 200 s averaging time, which allows sub-permil range for µmol NO$_3$ sample sizes previously used in our wet-chemistry setup. Moreover, as described in Section 6.4.2, $^{15}R_{\text{CMR}} = \Omega(1)(t)$ for this constant gas differential measurement, and thus Figure 6.4(b) is also a measure of the stability of the CMRR.
Within the stability time of the sensor, the \(^{15}R_{CMR}\) and \(^{14}R_{CMR}\) CMRR values may thus be considered drift-free.

6.5 Line-switched dDM-FRS for isotopic ratiometry

Temporally separate isotope measurement, such as those described in Appendix A3.5 have demonstrated utility in \(^{15}\)N labeled studies [10-13]. In precision isotope ratiometry however, isolated analysis of each isotope does not capture the time dynamics of sample fractionation (as described in Section 5.5.5), and is also susceptible to sample-to-sample variations which result in ratiometric inaccuracy. This is addressed by implementation of line-switching for quasi-simultaneous analysis of \(^{14}\)N and \(^{15}\)N isotopologues.

6.5.1 Demonstration of in-line self-referencing

Figure 6.5 shows a preliminary demonstration of line-switched differential measurements at 50 s intervals. Sample, reference, and difference signals are sequentially measured for both isotopes. Data traces such as those shown in Figure 6.5 are utilized for determination of \(^{14}R_{CMR}\) and \(^{15}R_{CMR}\), and subsets of the three regions (sample, measurement, difference) are superimposed and plotted in Figure 6.6. The darker blue and red lines indicate sample measurement, while the faded colors indicate reference. Dashed lines near the signal null denote optical subtraction signals \(^{14}\tilde{\eta}(t)\) and \(^{15}\tilde{\eta}(t)\), used in Equation 6.7 to calculate the \(\Omega_{O(N)}(t)\) terms of \(\delta^{15}\)N. Note that the identical gas flowing through both sample and reference in Figure 6.6 is an example of self-referencing, whereby application of Equation 6.7 is expected to yield null ratiometric deviation, and is a working demonstration of self-referencing to validate the mathematical formulation derived in Section 6.3.

Given that an unchanging, constant NO concentration from a certified cylinder is flowing through both measurement cells, we estimate signal and reference levels by time averaging over
the ~ 600 s interval in Figure 6.6. The sample and reference $^{14}$N and $^{15}$N signals are given respectively as 158.7 µV and −151.35 µV ($^{14}$NO), and 11.7 µV and −10.8 µV ($^{15}$NO). Calculation of the mean optical subtraction yields $^{14}R_{CMR} = 5.6 \times 10^{-2}$ and $^{15}R_{CMR} = 4.0 \times 10^{-2}$. Presently, due to the lack of active control for minimization of $^{14}\eta(t)$, it is necessary to account for higher-order $\Omega_{O(\text{N})}(t)$ terms, and the final summation result of $\delta^{15}\text{N}(t)$ is shown on the top of Figure 6.6. Standard deviation of $\delta^{15}\text{N}(t)$ yields 16.9 ‰∙Hz$^{-1/2}$, which is in excellent agreement with 17.1 ‰∙Hz$^{-1/2}$ obtained from Figure 6.4(b). Furthermore, averaging over the measurement scan time yields an offset from null of −0.68 ‰, which is within the expected precision for ~ 300 s averaging (600 s at 50 % switch interval duty cycle). The present confirmation of null ratio from self-referencing is a direct validation of the strength of real-time calibration using the dDM-FRS sensor.

6.5.2 Demonstration of fractionation free dDM-FRS performance

Figure 6.7 shows a five-step dilution of the 50 ppmv cylinder NO gas. The blue curve is the expected $[^{15}\text{N}]_R$, calculated from the finite $^{14}R_{CMR}$ which leaves visible subtraction residuals for $^{14}\eta(t)$. The red points are a direct optical differential measurement $^{15}\eta(t)$, and application of Equation 6.7 (again, using all $\Omega_{O(\text{N})}(t)$ terms) yields $\delta^{15}\text{N}(t)$, which is plotted on the top graph. As expected, precision (calculated by the standard deviation at each interval) improves with increasing signal, and is consistent with the noise analysis in Section 6.4.2. As an example, given $\Delta(\delta^{15}\text{N}) = 17.1 \%_0 \cdot \text{Hz}^{-1/2}$ for 184 ppbv $^{15}$NO, we expect the precision on the last measurement interval (78.5 ppbv $^{15}$NO) to be $\Delta(\delta^{15}\text{N}) = (184 \text{ ppbv})/(78.5 \text{ ppbv}) \times 17.1 \%_0 \cdot \text{Hz}^{-1/2} = 41.1 \%_0 \cdot \text{Hz}^{-1/2}$, which is in good agreement with the measured 42.1 ‰ ∙ Hz$^{-1/2}$. Moreover, the calculation result of $\delta^{15}\text{N}(t)$ is nulled and independent of the sample concentration, an indication that dDM-FRS does not introduce ratiometric artefacts and demonstrates fractionation-free performance.

6.6 Summary of ratiometric methods and future directions
Figure 6.8 depicts a summary of the direct ratiometric method (Chapter 5) and differential ratiometry (Chapter 6). The direct method is shown in Figure 6.8(a) and involves separate measurement of sample and reference signals, followed by application of Equation 5.10 (the definition of $\delta^{15}N(t)$ isotope ratio). Sub-permil precision are demonstrated for $\mu$mol KNO$_3$ injection sample sizes, but is susceptible to systematic errors and calibration time overhead. The differential method devised in this Chapter is intended to overcome these limitations (Section 6.3), and preliminary experimental work validates the mathematical formulation, while demonstrating the efficacy of in-line (real-time) sample referencing (Figures 6.6 and 6.7). The future direction of the dDM-FRS sensor development will integrate active dilution control, whereby the reference peak actively tracks the sample, such that $\Omega_{O(2)}(t) \ll \Omega_{O(1)}(t)$ and the expression given by Equation 6.10 is valid. Using differential spectroscopy, the $\delta^{15}N(t)$ isotope ratio is directly retrieved across the span of a peak, and application of Equation 5.17 (a weighted average of $\delta^{15}N(t)$ by signal strength $[^{14}\tilde{N}]_S$) gives $\delta^{15}N_T$ (total isotopic ratio).

6.7 Concluding remarks

In this Chapter, we have demonstrated a dDM-FRS sensor prototype capable of real-time optical subtraction for in situ sample calibration. The differential measurement is accomplished via retro-reflection which reverses the polarization rotation sense between sample and reference gas paths. Improved polarization optics and low-frequency field modulation eliminate PER and EMI limitations described in Appendix A3, demonstrating a $^{15}$NO MDL of 3.1 ppbv·Hz$^{-1/2}$ ($\Theta_{NEA} = 1.7\times10^{-8}$ rad·Hz$^{-1/2}$) which is 1.9\times the shot-noise limit, and Gaussian-noise limited up to $\sim$ 400 s. The mathematical formalism of differential ratiometry is developed, and validated experimentally. We expect dDM-FRS to improve ratiometric accuracy by ensuring real-time calibration of sample measurements, while reducing the impact of system drift on the final ratiometric result.
References


Chapter 7:
Towards Integrated On-chip Sensing Platforms

Thus far the work in this dissertation has focused on pushing the boundaries of detection sensitivity toward the fundamental shot-noise limit [1-4]. Specifically, Faraday rotation spectroscopy has been particularly effective due to the relative suppression of laser intensity-noise [5, 6], as well as serving as an ideal platform for implementation of balanced-detection [2, 7, 8] and sample modulation techniques [9-11] for baseline removal. True zero-baseline FRS techniques utilizing sample modulation (AC-FRS) however, require significant power budget due to the associated electronics and flow control (audio amplifier, vacuum pump for reduced pressure operation etc.) [1, 6, 10]. Additionally, the inherent susceptibility of FRS to paramagnetic molecules renders it inapplicable for the detection of diamagnetic species. In the remainder of this thesis we investigate alternate sensing modalities in application scenarios where extreme precision is not required; rather, low-power consumption, compact form factors, and scalable production is preferable [12-15] (e.g. large-scale deployment for wide-area sensor networks described in Section 7.3 [15], or integrated on-chip broadband sources, described in Section 7.2 [16, 17]).

7.1 Motivation: miniaturized WSN sensor nodes

Emerging technologies for the construction of compact sensor nodes have enabled utilization of wireless sensor networks (WSN) for distributed monitoring (and feedback control) in applications ranging from threat detection [13, 18] to traffic control [19], structural health [20, 21] and environmental diagnostics [22-24]. In conjunction with network localization algorithms [25], WSNs are capable of providing quantitative spatial trends that are not identifiable using point/extractive sensors alone [26-28]. The application demand of WSNs have accelerated the development of miniature sensing modalities, particularly involving optical technologies such as
micro-cavity resonators for resonant sensitivity enhancement [29-31], broadband on-chip optical sources [32-35], and integrated low-noise detection modules [36, 37] for WSN nodes.

Figure 7.1 shows an example application of a WSN for methane fugitive emissions monitoring on oil well pads (Section 7.3), where individual integrated on-chip sensor nodes are deployed in a wide-area mesh network for spatial resolution of CH$_4$ concentration and source localization. The resulting data is streamed through a remote gateway and uploaded onto a central server, where data analytics is performed (e.g. plume dispersion modeling using wind speed measurements, inversion calculations for leak localization [36]). Upon determination of the presence of a leak within a predefined confidence interval, appropriate enterprise event handling is employed to either seal or otherwise mitigate the effect of such a leak. A vision for such an integrated sensor is given in Section 7.3.7 [15], where a preliminary demonstration of on-chip evanescent field spectroscopy is shown. In Section 7.2, a compact on-chip dual-laser source for multi-heterodyne spectroscopy is investigated, with the goal of scalable broadband sources without opto-mechanical components [16, 17, 34, 35]. Due to the different application space of WSNs (low-cost, compact, and scalable) compared to point/extractive sensors (highly accurate and precise trace-gas monitoring), the development of compact sensor nodes is envisioned here as a complementary technology to point/extractive sensors, and extends the utility of optical spectroscopy to applications requiring spatial as well as concentration information.

7.2 On-chip FP-QCLs for multi-heterodyne spectroscopy

The benefits of compact sensing modalities were discussed above; here we demonstrate a prototype spectrometer utilizing a tunable on-chip source for broadband (> 20 cm$^{-1}$) and high-resolution (3 MHz) multi-heterodyne spectroscopy (MHS) [16, 17, 34, 35]. A dual Fabry-Pérot (FP) QCL source integrated on a single chip is utilized for both line-scanned (12.5 Hz) absorption
(TDLAS) and wavelength-modulated (WMS) MHS of the R18e N₂O transition (1184.385 cm⁻¹), and frequency discrimination is implemented for beat-note frequency stabilization to obtain \((aL)_{\text{min}}^{\text{TDLAS}} = 1.3 \times 10^{-3} \text{ Hz}^{-1/2}\) and \((aL)_{\text{min}}^{\text{WMS}} = 5.0 \times 10^{-4} \text{ Hz}^{-1/2}\) respectively (using a single heterodyne beat-note). The broadband spectral coverage is a function of detector bandwidth (3 dB roll-off DBW = 1 GHz) and difference in laser free-spectral range \((\Delta v_{\text{FSR}} = 160 \text{ MHz, corresponding to } \sim 0.5 \% \text{ fractional QCL length difference})\), which allows up to 12 heterodyne beat-notes using ‘frequency folding’. The principal benefit of MHS is the absence of opto-mechanical components, resulting in greater laser operational stability for multi-species and broadband spectroscopy with scalable production potential.

7.2.1 Application potential of broadband MHS

Broadband, high resolution spectroscopic sources are of particular interest due to their ability to resolve individual analyte transitions in broad multi-species spectra [38, 39]. However, practical trade-offs between spectral breadth and resolution exist; a typical example of the former is the Fourier Transform infrared spectrometer (FTIR) which provides excellent spectral coverage (up to \(10^4 \text{ cm}^{-1}\)) with limited resolution (\(\sim 0.1 \text{ cm}^{-1}\)) [40] due to practical constraints on the maximum interferometer length retardation. On the other hand, a periodic DFB QCL refractive index grating selects a single lasing mode (resolution \(\sim 10^{-4} \text{ cm}^{-1}\)) [39], but with \(\sim 10 \text{ cm}^{-1}\) tuning range [41]. Utilization of the broad QCL gain spectrum (e.g. FWHM \(\sim 300 \text{ cm}^{-1}\) using a bound-to-continuum design [42]) in an external-cavity (EC) configuration enables CW spectral coverage \(> 100 \text{ cm}^{-1}\) [43, 44]. However, the need for high quality AR coatings [45] and actively aligned opto-mechanics renders EC-QCL systems non-scalable [46]. Alternatively, DFB QCL arrays fabricated on a single substrate with varying grating periodicities have demonstrated \(> 200 \text{ cm}^{-1}\) tuning range [45, 47],
although fabrication yield remains low due to the dozens of functioning DFB-QCLs required in a single integrated source [48].

Recently, frequency combs have been implemented in dual-comb spectroscopy [38, 49-52]. In this scenario, two combs with slight FSR difference are mixed on a single photodetector to yield radio-frequency (RF) heterodyne beat-notes (HBN), which provide excellent spectral resolution (~ kHz [52]) and broad coverage (> 100 cm\(^{-1}\) [50]). With the advent of QCL combs, integrated MIR dual-comb sources have become a possibility [53]; however, active mode locking requires careful dispersion engineering to induce four-wave mixing [32]. Alternatively, Khurgin et al. [54] numerically demonstrated passive phase-locking of QCLs through self-frequency modulation due to short (~ ps) upper state lifetimes, thus indicating the possibility of using standard FP QCLs for dual-comb (multi-heterodyne) spectroscopy and avoiding the complexities of actively mode-locked sources. The present Section concerns this latter technique, and provides an experimental demonstration performed in collaboration with J. Westberg and A. Hangauer following the developments of [34] to show implementation of both TDLAS and WMS on a MHS platform using two FP-QCLs integrated on a single chip [16, 17, 35].

7.2.2 Experimental design of a FP-QCL based MHS system

The MHS prototype, displayed in Figure 7.2, is constructed following developments of [34] and [55], and utilizing the lasers described in [34]. Both QCLs (1.23 mm length) are mounted on a single submount for thermal regulation with a single TEC, and the spatial separation of the QCLs on the chip results in beam separation through an AR-coated germanium aspheric collimation lens (Optical Solutions, 4682). One beam (referred as signal, or SIG) passes through the 15 cm sample cell (with an optional bypass for background retrieval), and the other beam (local oscillator, or LO) is mixed with the SIG at the beam-splitter (BS). Part of the optical power is used for (i)
alignment, total power monitoring, and FTIR spectral measurements, and (ii) mixing on a photodetector (Vigo System, PVI-3TE-10.6 with a 3 dB frequency cutoff at 1 GHz DBW), resulting in RF-HBNs whose power is split and directed into a spectrum analyzer (Tektronix RSA5103A) and frequency discriminator to lock the relative positions of the FP-QCLs. Measurement of the RF-HBNs make use of HBN frequency folding to double the spectral coverage within the DBW (positive and negative frequencies are indistinguishable by the photodetector), followed by corresponding ‘unfolding’ prior to data analysis. More specifically, given a FSR difference of $\Delta \nu_{FSR} = 160$ MHz the ‘zeroth’ order RF-HBN is positioned at $\Delta \nu_{FSR}/4 = 40$ MHz, resulting in higher-order BNs occurring at $(2n+1)\Delta \nu_{FSR}/4$, where $n = 1, 3, 5, \ldots$ correspond to ‘negative’ HBN’s, and $n = 2, 4, 6, \ldots$ to ‘positive’ HBN’s. Equidistant HBNs at $\Delta \nu_{FSR}/2$ are thus measured on the SA, and within the 1 GHz DBW, ~ 12 distinct HBNs may be measured in a single spectral scan.

Figure 7.3(a) shows the FTIR (Nicolet 8700) spectrum at 0.125 cm$^{-1}$ resolution of the SIG (red) and LO (black) FP-QCLs, both of which are fixed at 1.03 °C using a single TEC. The SIG and LO pump currents are set at 225.7 mA and 256.2 mA respectively, determined by finding the current/thermal settings that allow stable operating regimes of both lasers. The 0th order HBN corresponds to 1184.385 cm$^{-1}$, near the R18e transition of N$_2$O, whose absorption is demonstrated in the top graph (with/without the SIG optical bypass). Figure 7.3(b) shows the 0th order HBN positioned at $\Delta \nu_{FSR}/4 = 40$ MHz (and stabilized via frequency discrimination), with subsequent HBNs separated by intervals of $\Delta \nu_{FSR}/2 = 80$ MHz. The effect of N$_2$O absorption is to weaken the SIG FP-mode near 1184 cm$^{-1}$, resulting in a HBN attenuation at 40 MHz. The attenuation in the case of pure N$_2$O in the sample cell vs. optical bypass is shown in the inset. Note that the measured HBN width is ~ 3 MHz, acquired through ~ 1 min averaging of the RF spectrum, which
corresponds to $10^4$ cm$^{-1}$ spectral resolution and is sufficient for a variety of high-resolution MIR spectroscopy applications [56, 57]. It is also interesting to observe the presence of inter-HBNs which involve beating between RF-HBN pairs, demonstrating much narrower spectra ($\sim 15$ kHz [16]) and suggesting that frequency jitter between FP-modes of a single QCL are correlated. This observation is consistent with studies of self- frequency modulation of QCLs resulting in passive phase-locked operation [54], opening the possibility of ultra-high resolution spectroscopy in our MHS configuration [56, 57].

7.2.3 MHS experimental results

Below we analyze amplitude and frequency noise of the RF-HBNs, and experimentally demonstrate the efficacy of frequency discrimination for HBN stabilization. TDLAS of N$_2$O is performed using a single RF-HBN, along with a first demonstration of MH-WMS.

(A) Noise spectrum of a single RF-HBN

Figure 7.4 shows the FFT calculation of a both amplitude (orange) and frequency (black) measurement time series, demonstrating strong $1/f$ noise contributions in both cases. Significant improvement ($\sim 30\times$) is expected using either fast laser ramping or phase-sensitive detection beyond 10 kHz, at which $\overline{\sigma_{RIN}} = 1.4\times10^{-4}$ Hz$^{1/2}$. On the other hand, the HBN center frequency instability (black) directly reflects long-term spectral resolution of MHS, and can be mitigated (gray curve) via a discrimination scheme described below to achieve near white-noise performance for averaging times up to $10^3$ s.

(B) Frequency discrimination for RF-HBN stabilization

RF-HBN stabilization is accomplished using a parallel attenuator (Mini-Circuits HAT-20+) and customized RC-filter for frequency dependent response. The resulting outputs are coupled to a gain and phase detector (Analog Devices AD8302) which provides an output proportional to the
logarithm of the input ratio, and is used for active feedback through a PID controller (SRS SIM-960, 100 kHz bandwidth). The discriminator locks the relative positions of the FP-QCLs to ensure the 0th order HBN (used to target the R18e N$_2$O transition at 1184.385 cm$^{-1}$) resides at 40 MHz, and the resulting RF-HBN stability analysis is performed over ~ 10 min. The resulting mitigation of frequency HBN drift is substantial, as seen by the deviations with (black) and without (orange) stabilization (Figure 7.5(a)). Allan deviation for frequency stability analysis is shown in Figure 7.5(b), demonstrating > 2× improvement in short-term (< 10 s) stability and near white-noise averaging up to 200 s, which yields ~ 10 kHz center frequency precision. At short (ms) integration times, the efficacy of the frequency discrimination is also apparent from the inset of Figure 7.5(a), where frequency measurements over ~ 35 ms are displayed.

(C) MH-TDLAS of N$_2$O

As an initial demonstration, multi-heterodyne absorption measurements (MH-TDLAS) were performed using pure N$_2$O sealed at 2 torr in the 15 cm sample chamber. Both lasers (stabilized via frequency discriminator circuit) are scanned at 12.5 Hz across the R18e N$_2$O transition, and the 0th order RF-HBN is acquired with a 25 MHz frequency bandwidth (i.e. 40 MHz ± 12.5 MHz). The resulting trace is acquired over 37.2 ms at 25 MS/s sampling rate using a spectrum analyzer (Tektronix RSA6106A), yielding the raw measurements (gray points, 0.2 µs averaging) shown in Figure 7.6. Averaging at 0.5 ms time bins is shown in orange, and the resulting Voigt profile fit based on HITRAN parameters is displayed in black (showing a peak absorption of ($\alpha L$)$_{\text{peak}}$ ≈ 74.18 % using linear baseline correction). Based on the residual (absorption-peak normalized) standard deviation $\sigma_{\text{stdev}} = 2.28 \times 10^{-2}$ for 0.5 ms time averaging, we follow the convention described in Section 2.1.3 and Appendix A2.2 by averaging the peak absorption SNR over the FWHM ($\Delta \nu_{\text{FWHM}}$ = 73.8 MHz), corresponding to 13.7 bin points (0.5 ms each), resulting in ($\alpha L$)$_{\text{min}} = 1.3 \times 10^{-3}$ Hz$^{-1}$. 

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This calculated minimum fractional absorption is within the expected bounds of TDLAS systems [58], and it is also worth noting that the potential for substantial sensitivity enhancement (∼ 30×) exists by implementing either faster ramping rates or modulation spectroscopy (Figure 7.8), which is investigated in part (D).

(D) MH-WMS of N₂O

Based on the discussion of optimum ramp rate in Appendix A2.1, it is generally desirable to operate near the point where the detection noise floor begins to dominate the total noise contribution. To this end, laser current modulation at \( f_L = 10 \text{ kHz} \) (empirically optimized modulation depth) is performed for both FP-QCLs at the same 12.5 Hz swept current ramp (frequency discrimination enabled). In the presence of wavelength modulation, the frequency location of the RF-HBNs remain unchanged; rather, their amplitudes are modulated in the presence of an absorbing feature, as depicted in Figure 7.7. The resulting demodulation of the HBN amplitude yields WMS harmonic spectra, with spectral noise reduction due to detection above the \( 1/f \) baseband frequency noise. The resulting spectra (\( 2f_L \) harmonic) is shown in Figure 7.8, where the raw modulation signal is shown in gray (background), and software demodulation (as described in Section 2.2.2) is used to retrieve a LMS fit of the harmonic spectra. Based upon the mean normalized spectral residuals (3.01×10⁻² per 0.5 ms time bin), we estimate \( (\alpha L)_{\text{min}} = 5.0 \times 10^{-4} \text{ Hz}^{-\frac{1}{2}} \) in the case of line-locked operation which is ~ 2.6× improved over MH-TDLAS, demonstrating the efficacy of MH-WHM for SNR enhancement.

7.2.4 Concluding remarks

In this Section we provide a preliminary demonstration of multi-heterodyne beat-note spectroscopy using two conventional FP-QCLs integrated on a single chip for broadband (> 20 cm⁻¹) optical spectroscopy. Frequency discrimination is employed for stabilization of HBNs in the
RF domain, which provides near white-noise performance over the ~ 10 min measurement span. TDLAS and WMS techniques are implemented using a single RF-HBN, resulting in \((aL)_{\text{min}} = 1.3 \times 10^{-3} \text{ Hz}^{-1/2}\) and \(5.0 \times 10^{-4} \text{ Hz}^{-1/2}\) respectively. Multi-HBN spectroscopy is generalizable from the present proof-of-concept demonstrations of single HBN measurements [59], validating this technology as a principal component of fully integrated on-chip spectrometers for handheld sensor units and WSN nodes.

7.3 On-chip silicon photonic TDLAS

Following the theme of compact sensing platforms introduced earlier (Section 7.1), along with an example of dual on-chip integrated sources for broadband spectroscopy (MH-TDLAS/WMS) from the previous Section, the work in the present Section is focused on on-chip interaction between light and the sample analyte. Thus far in this dissertation, the spectroscopy of the gas itself (i.e. the sensing region) has involved free-space configurations only; however, such sensors involving discrete optics require active alignment and are limited in scalability. In what follows, a miniaturized on-chip sensing scheme that utilizes passive silicon (Si) waveguides (WGs) for evanescent field TDLAS [15, 36] is investigated. In collaboration with the Silicon Integrated Nanophotonics Group at IBM, NIR detection of methane (CH₄) in the \(2\nu_3\) overtone band near 6057.1 cm⁻¹ is performed, and the sensor (10 cm Si WG) demonstrates Gaussian-noise limited performance up to ~ \(10^3\) s, with < 100 ppmv CH₄ sensitivity attained after \(10^2\) s averaging. Short-term noise analysis yields \((aL)_{\text{min}} = 8.5 \times 10^{-4} \text{ Hz}^{-1/2}\), which is consistent with conventional TDLAS sensor systems [58]. Accuracy of the silicon photonic chip sensor (SiPhCS) is benchmarked with respect to a 10 cm free-space optical path (FSOPS), and correlation of fractional absorption yields an experimental evanescent field exposure (overlap) factor of \(\Gamma_{\text{meas}} = 25.2\%\), in reasonable
agreement with simulated $\Gamma_{\text{meas}} = 28.3\%$. Finally, this Chapter and dissertation is concluded with a vision toward monolithic integration of source, sensing element, and detector on a single chip.

7.3.1 Motivation: integrated methane sensors

Due to the high radiative forcing of CH$_4$ (37× greater than CO$_2$), natural gas leaks pose a significant challenge to the near-term viability of oil and gas extraction [60]. The environmental ramifications are particularly significant given the rapid expansion of oil and gas production in the past few decades [61]; in 2009 alone, CH$_4$ leakage was estimated at ~ $16\times10^9$ m$^3$, corresponding to 2.4% of natural gas production in the United States [60]. For relative perspective, the study from [60] indicates that immediate mitigation of climate effects from passenger cars requires “well-to-wheels” leakage under 1.6%, and 1% in the case of heavy-duty diesel vehicles. Furthermore, official “emission factors” of annual U.S. CH$_4$ release underestimates reports from literature [62], and improved measurement technologies for source attribution are expected to provide better assessment of relative environmental impact of natural gas leaks. Presently, the principal impediment of large scale CH$_4$ measurement is cost, and a technological gap exists for methods of reliable and cost-effective quantification and localization of extraneous CH$_4$ emissions [63].

As mentioned in Section 7.1 (and detailed in Chapters 4 to 6), extractive/point MIR laser spectrometers have demonstrated uniquely well-suited capabilities for crosstalk-free, precision monitoring of trace-gases [1-4, 6, 10]; however, the cost and lack of manufacturing scalability (due to discrete free-space optical components) limits their economic viability in wide-area sensor deployments. For example, CH$_4$ emissions monitoring has previously been conducted using mobile vehicle [26, 64] and aircraft sensors [27, 28, 65] which provide high levels of precision, but cost and resource constraints limit deployment to a small number of sensors at any given time. In this Section, we leverage mainstream silicon photonic (SiPh) technology to demonstrate on-
chip evanescent field TDLAS of CH$_4$ in the 2v$_3$ NIR ro-vibrational overtone band (~6057.1 cm$^{-1}$). Appreciable transverse-magnetic (TM) modal overlap factors ($\Gamma = 25.2 \%$ evanescent field exposure) are accomplished a high-index contrast (HIC) silicon WG design with subwavelength cross-section dimensions, fabricated on a silicon-on-insulator (SOI) substrate, and is a scalable foundry process. The choice of NIR technology is based upon the widespread availability of communication wavelength DFB diode lasers and low-cost InGaAs photodiodes. Toward the end of the Section we discuss a vision of monolithic integration of external-cavity NIR laser, detector, and WG components on a single chip, with the goal of developing low-cost sensor nodes for wide-area deployment.

7.3.2 Design of an on-chip sensor node

The experimental setup is displayed in Figure 7.9(a). Incident light from a $\lambda = 1651$ nm fiber-coupled DFB laser diode is split at a 90:10 power ratio, with the majority power directed to a polarization controller (set to deliver TM mode) and coupled into and out of the SiPh chip sensor (SiPhCS) via lensed fibers (Figure 7.10(c)). The minority power is coupled through a 10 cm free-space open path sensor (FSOPS) which is expected to provide superior performance and is used as a SiPhCS accuracy benchmark. The laser is scanned across the CH$_4$ R4 transition at 6057.08 cm$^{-1}$ via current ramping at 100 Hz, and the optical output from the SiPhCS is measured with an uncooled InGaAs amplified photoreceiver. The FSOPS output is measured using a separate PD for simultaneous spectral acquisition, depicted in Figure 2.3 (Section 2.1.3) whereby the detector analog outputs are digitized through a data acquisition (DAQ) card (NI-USB 6003), followed by spectral fitting algorithms (VLMS/BSDL/DEF-R) described in Chapter 2 and Appendix A5.2. For the purpose of stability and accuracy assessment, both sensors are housed within an environmental chamber for active control of CH$_4$ concentration.
The SiPhCS is comprised of a 10 cm-long silicon-on-insulator (SOI) WG fabricated using deep-UV (DUV) photolithography, with a cross-sectional thickness and width of 250 nm and 430 nm respectively. The former is chosen to maintain consistency with existing fabrication processes for optical interconnect devices, and the latter for near-cutoff propagation of the fundamental TM mode (i.e. an effective index $n_{\text{eff}} = 1.66$ approaching that of the buried oxide (BOx), where $n_{\text{BOx}} = 1.45$) to maximize the evanescent overlap factor $\Gamma$. (Note that the effective optical path $L_{\text{eff}} = \Gamma \cdot L_{\text{physical}}$, and therefore the absorption signal scales with $\Gamma$). Although the TE mode is in principle desirable for compatibility with the laser output mode, significant line-edge roughness (LER) of the WG sidewall limits optical throughput and significantly degrades SNR. Figure 7.10(a) depicts a schematic of the SiPhCS WG, which is fabricated in a spatially efficient “paperclip” geometry with a physical footprint only 16 mm$^2$ for $L_{\text{physical}} = 10$ cm. Numerical modeling predicts a $1/e^2$ cross-section sensing area of 0.08 µm$^2$, which at STP and over $L_{\text{physical}} = 10$ cm results in probing of $4 \times 10^5$ CH$_4$ molecules at 2 ppmv (natural abundance). In addition, $\Gamma_{\text{calc}} = 0.283$, which for a WG $L_{\text{physical}} = 10$ cm, provides $L_{\text{eff}} = 2.83$ cm. This is verified in Figure 7.9(b), which shows the real-time CH$_4$ spectra acquired with both the SiPhCS and FSOPS, while flowing 2.5 % CH$_4$ in a N$_2$ balance into the environmental chamber. Given the identical physical length of the sensors, the ratio of CH$_4$ absorption peaks suggests $\Gamma_{\text{meas}} = 0.254$, which is in agreement with calculations.

Following the method described in [67], wavelength dependent loss measurements (Figure 7.11) are performed by measuring broadband throughput of a semiconductor optical amplifier (SOA) output through three varying WG lengths (3, 6, 10 cm). Linear regression of wavelength dependent losses yields a broadband average TM mode loss (1575 nm to 1750 nm) of 1.88 dB/cm, and 1.72 dB/cm at 1651 nm ($R^2 = 0.994$) with a total insertion (coupling) loss of 11.5 dB. Note that the TE mode yields much higher WG loss (~ 2.5 dB/cm), with substantial modal mismatch.
during coupling which results in > 20 dB total insertion loss at 1651 nm. The measurement noise for TE mode is due to this low coupling efficiency, resulting in measurements near the spectrum analyzer noise-floor. Given the measured TM mode WG losses depicted above, a total of 1.72 dB/cm × 10 cm + 11.5 dB = 28.7 dB loss is expected through the SiPhCS, resulting in ~ 10 µW optical throughput for a laser input power of ~ 10 mW (consistent with typical measurements through the SiPhCS).

Figure 7.10(b) shows HITRAN [66] search results involving spectral interferences of interest; targeting the CH₄ R4 line provides immunity to H₂O crosstalk, while potential exists for multi-species monitoring of CO₂ and H₂S (the latter exhibits immediate danger to life and health, or IDLH at 100 ppmv [68]). For display clarity, CO₂ is shown at 50× natural abundance and H₂S at 10× IDLH levels. Based upon the results of a customized cross-sensitivity software routine for line searching across the entire HITRAN database, multi-species CO₂ and H₂S detection within 5 cm⁻¹ tuning range is possible by targeting the CH₄ R9 line (~ 2× weaker than R4 transition).

### 7.3.3 Demonstration of SiPhCS TDLAS

As described in Appendix A5, sensitivity limitations for on-chip sensors due to spectral baseline structure (e.g. optical etalons) demonstrates the necessity of fringe mitigation methods. In this Section, we utilize 10 cm AR-coated WGs and DEF-R for adaptive etalon reduction, and show initial SiPhCS TDLAS results and long-term (~ 10³ s) stability analysis as a proof-of-concept demonstration of potential for real-time CH₄ monitoring.

#### (A) Fringe mitigation for SiPhCSs

Figure 7.12 shows TM mode spectral acquisition of three WG lengths (3, 6, 10 cm) for two strip WGs fabricated on a 250 nm SOI (3 µm BOx) via standard hardmask (left) and softmask (right) etch respectively. In both cases the cross-section geometries are consistent with that described in
Section 7.3.2 (430 nm width). The standard hardmask etched SiPhCS, used in the remainder of this study for TDLAS results, shows substantial (> 2×) improvement in fringe amplitude after AR-coating for the 3 cm WG (pre-coating shown in Appendix A5.1), while the 10 cm case remains roughly unchanged due to fringe decoherence and mode conversion from distributed backscattering [69]. In Figure 7.12(b), the softmask-etched SiPhCS is subjected to H$_2$ annealing at 900 ºC for 10 mins (at 600 torr), with no AR-coating after processing. Consistent with expectations from prior results, the 3 cm WG demonstrates large ($\alpha L = 10^{-1}$) peak-to-peak fringe amplitude, while for 10 cm, periodic structure appears, likely due to “faceting” that occurs on the WG bends [70]. It is notable that baseline structure occurs regardless of process (similar spectral results are achieved with the “slab” WG geometries, as well as TE mode propagation). In what follows, a combination of AR-coated facets, long (10 cm) WGs for fringe decoherence, and DEF-R for dynamic fringe reduction are simultaneously employed to minimize the impact of optical etalons on TDLAS measurements.

(B) SiPhCS TDLAS in the environmental chamber

Three-stage CH$_4$ flow variation is introduced into the environmental chamber to investigate the utility of the DEF-R spectral retrieval method, and to determine the SiPhCS accuracy with respect to the FSOPS reference (used as an accuracy benchmark). The ~ 1200 s measurement involves (i) zero-gas (ambient laboratory air) up to 400 s, (ii) CH$_4$ flush (2.5 vol. % cylinder CH$_4$) up to 900 s, and (iii) flow arrest and gas-trapping by sealing the environmental chamber.

Figure 7.13(a) depicts a surface plot formed by cascading spectral ramps (horizontal axis) in the vertical direction. Due to initial laser ringing between ramp transitions, 15 % of the initial ramp points and 10 % of ramp endpoints are discarded prior to baseline removal to eliminate systematic normalization artefacts. The presence of consistent baseline structure in this 10 cm WG is evident
in the colormap, showing clear horizontal periodic structure. The horizontal scan time axis accounts for 100× ramp averaging (100 Hz laser current ramp), resulting in a total 1.16 s per vertical measurement unit, and the onset of CH$_4$ in the environmental chamber is visible around 600 s. Figure 7.13(b) empirically validates the effect of DEF-R spectral retrieval by demonstrating significant improvement in spectral contrast through the adaptive removal of fringe drifts. From 0 to ~ 400 s, the consistent fringe structure is essentially eliminated, and the onset of CH$_4$ in the chamber is clearly visible (note the reduced scale range from the color-bar legend).

Figure 7.14(a) shows the retrieved concentration from the DEF-R algorithm applied to the measurements in Figure 7.13(a), with a 5.8 s integration time (5 spectral averages per point). Simultaneous acquisition of FSOPS data is performed (see Figures 2.3 and 7.9), and FSOPS CH$_4$ measurement is shown as a black dashed line. Note the significantly lower measurement noise from the FSOPS, which is used here as a concentration reference measurement due to negligible drift over the ~ 1200 s measurement interval. Slight concentration deviation exists during the CH$_4$ flush interval (400 s to 900 s); however, the sensors are not spatially superimposed and discrepancies due to CH$_4$ gradients are expected during active flow. Note that when the flow is arrested, the SiPhCS measurement converges to the FSOPS result. Using the CH$_4$ flush phase, the linear regression ($R^2 = 0.991$) between the SiPhCS and FSOPS peak absorption (as shown in Figure 7.14(b) after spectral extraction) yields an experimental modal overlap factor of $\Gamma_{\text{meas}} = 25.2 \%$, which is again consistent with simulation results ($\Gamma_{\text{calc}} = 28.3 \%$).

SiPhCS long-term stability is measured using long-term (~ 2400 s) zero-gas (N$_2$ purge) measurement in the chamber as shown in the inset (time-series) of Figure 7.14(c), at 5.8 s integration time (similar to Figure 7.14(a)). Allan stability analysis indicates a sensitivity of 757 ppmv·Hz$^{-1/2}$ (corresponding to $(aL)_{\text{min}}^{\text{SiPhCS}} = 8.5 \times 10^{-4}$ Hz$^{-1/2}$) and a detection limit of ~ 20 ppmv at
10^3 s averaging time. In this scenario, DEF-R improves the short-term precision by ~ 2x, while improving the zero drift time from ~ 10^2 s to > 10^3 s. Similar analysis of the FSOPS sensitivity demonstrates 5 ppmv·Hz^{-1/2} sensitivity with (αL)_{FSOPS}^{FSOPS} = 2.15×10^{-5} Hz^{-1/2}. Note that (αL)_{SiPhCS}^{SiPhCS} / (αL)_{FSOPS}^{FSOPS} = 40 whereas the ratio of sensitivity is 757 ppmv·Hz^{-1/2} / 5 ppmv·Hz^{-1/2} = 151.4, and the ratio 40 / 151.4 = 26.4 % is again consistent with the expected modal overlap. The 40× difference in minimum fractional absorption is primarily due to mechanical noise of the fiber couplers, which is studied in the next Section. Finally, we note that the ~ 150× sensitivity improvement of FSOPS over the SiPhCS validates its use in this experiment as a performance benchmark.

7.3.4 Spectral noise studies of the SiPhCS

In the previous Section, the minimum fractional absorption (αL)_{min} through 10 cm the SiPhCS WG is degraded by ~ 40× compared to FSOPS. To investigate the source of this noise, power normalized FFT calculations are performed on raw time-series traces (1 s total duration, averaged over 20 measurements) for different experimental configurations, shown in Figure 7.15. At high frequencies, all traces are detection noise limited (green), which introduces (αL)_{min} ~ 10^{-6} Hz^{-1/2} contribution to any measurements using the uncooled InGaAs amplified photoreceiver. The red curve represents direct laser-to-detector measurement, demonstrating strong 1/f noise component below ~ 1 kHz, and represents a practical limit of sensing performance. Indeed, spectral density calculations through the FSOPS show excellent agreement between laser and FSOPS RIN, indicating the laser technical noise limits the performance of FSOPS. On the other hand, introduction of fiber couplers (tip-to-tip) between the laser and detector yields an increased low-frequency (< 1 kHz) noise floor, as depicted in Figure 7.15 (gray curve). Further introduction of the SiPhCS WGs demonstrates slight performance degradation in the case where optical
throughput is maximized (termed “good” alignment, shown in blue), whereas sub-optimal power throughput (“bad” alignment, shown in red) exhibits significant low frequency noise peaks > 10× laser RIN for frequencies below 1 kHz, which account for the observed 40× degradation in \((aL)_{\text{min}}\).

Based on the spectral analysis in Figure 7.15, noise convergence occurs above > 1 kHz, indicating the optimum ramp rate to maximize sensitivity, as described in Appendix A2.1. However, the resulting laser frequency ringing at higher ramp rates necessitates wavelength calibration of the acquired spectra (Appendix A4.2), and will be performed in the second generation prototype currently under development. As a final note, we speculate that the origin of low frequency noise peaks is likely mechanical vibrations causing transient coupling instabilities which affect optical throughput. WG coupling further exacerbates the RIN due to the tight alignment tolerances (subwavelength 430 nm × 250 nm cross-section dimensions), and is expected to be resolved through robust optical packaging (e.g. UV curable index matched adhesives, grating couplers, etc.) to bring the SiPhCS performance to par with FSOPS.

7.3.5 Thermal dependence of CH₄ absorption

The SiPhCS measurements thus far have been conducted on a benchtop workspace at room temperature laboratory conditions \((T_{\text{ref}} = 296 \text{ K})\). Deployment of sensor nodes into the open-air environment requires thermal monitoring to account for temperature dependent line-intensity variations \([71, 72]\) due to thermal corrections to the internal partition function \(Q(T)\) and lower state population depletion, as well as the pressure dependent collision linewidth broadening:

\[
S_{\eta \rightarrow \eta'}(T) = S_{\eta \rightarrow \eta'}(T_{\text{ref}}) \cdot \frac{Q(T)}{Q(T_{\text{ref}})} \cdot \frac{\exp(-c_2 \cdot E_{\eta}/T)}{\exp(-c_2 \cdot E_{\eta}/T_{\text{ref}})} \cdot \frac{[1 - \exp(-c_2 \cdot \tilde{\nu}_{\eta \rightarrow \eta'}/T)]}{[1 - \exp(-c_2 \cdot \tilde{\nu}_{\eta \rightarrow \eta'}/T_{\text{ref}})]} \tag{7.1}
\]

\[
\delta \tilde{\nu}_L(p, T) = \left(\frac{T_{\text{ref}}}{T}\right)^n \left[ \text{air} \delta \tilde{\nu}_L(p_{\text{ref}}, T_{\text{ref}}) \cdot (p - p_s) + \text{self} \delta \tilde{\nu}_L(p_{\text{ref}}, T_{\text{ref}}) \cdot p_s \right] \tag{7.2}
\]
In Equation 7.1, $S_{\eta \rightarrow \eta'}(T)$ denotes the temperature dependent linestrength, where $\eta$ and $\eta'$ are the lower and upper transition states respectively. $E_{\eta}$ is the lower energy state, $\tilde{\nu}_{\eta \rightarrow \eta'}$ is the transition center frequency (cm\(^{-1}\)), and $c_2 = 1.439$ cm·K is the second radiation constant. Equation 7.2 follows the notation of Section 2.1.1, where $\delta \nu_L^\text{air}$ and $\delta \nu_L^\text{self}$ denote air- and self-broadened HWHM, $p_s$ is the sample partial pressure and $n$ is the coefficient of temperature dependence ($n = 0.72$ for CH\(_4\) R4 line). The effect of incorporating Equations 7.1 and 7.2 into absorption models described in Chapter 2 is shown in Figure 7.16, which simulates the absorption of the 2ν\(_3\) overtone band over a 100 K temperature range around $T_{\text{ref}}$. From the calculations we note that higher rotational level transitions are significantly less susceptible to thermal variations, with the R9 line demonstrating < 5 % fractional decrease in absorption strength over 100 K temperature range, as shown in Figure 7.16(b), albeit at less than half the line-intensity of the R4 transition. Use of this transition may be particularly suitable in cases where local temperature monitoring is not feasible or undergoes large variations which necessitate frequent sensor calibration. Furthermore, from the HITRAN spectral interference search described in Section 7.3.2, targeting the R9 line multiplet at ~ 6106 cm\(^{-1}\) potentially enables multi-species diagnostics of CH\(_4\), CO\(_2\) and H\(_2\)S within a 5 cm\(^{-1}\) tuning range.

7.3.6 Implementation of modulation techniques

In Section 7.3.4, it was noted that higher ramp rates (> 1 kHz) and robust optical packaging are expected to respectively reduce low frequency 1/f noise contributions from the laser RIN and mechanical instabilities.

Based on Figure 7.15, we note that implementation of WMS (described in Section 2.2) is also expected to significantly improve sensitivity, again at modulation frequencies $f_L > 1$ kHz where the detection noise floor dominates. An added benefit is the substantially relaxed sampling rate requirement of the DAQ card, as analog signals may be directly mixed and filtered to yield the
desired signals, whereas correspondingly high sample rates must be used for TDLAS to ensure sufficient ramp points for DEF-R or VLMS algorithms. Figure 7.17 shows the results of preliminary demonstration of WMS, where an in-line 1% CH\textsubscript{4} reference cell is inserted after the SiPhCS (such that WG noise is measured in the presence of a reference signal to simulate a real CH\textsubscript{4} WMS measurement). The laser is modulated at \( f_L = 10.2 \) kHz and the resulting signal is demodulated at the \( 2f_L \) harmonic (1 ms LIA time constant). Line scanning is accomplished using a 10 Hz current ramp (averaged to 1 s spectra, as displayed in Figure 7.17), and conventional baseline difference is performed by subtracting the spectrum obtained after detaching the CH\textsubscript{4} in-line cell. Based on the standard deviations of the WMS spectral fitting residuals, we estimate a single point SNR = 35.4 (14.7 ms integration time), resulting in a CH\textsubscript{4} detection sensitivity of 46.9 ppmv\cdot Hz\textsuperscript{1/2} or \((aL)_{\text{min}} = 8.3 \times 10^{-5}\) Hz\textsuperscript{1/2}. The approximately 16\( \times \) improvement above TDLAS performance is attributable to reduction of 1/f noise contribution to the measurement. Furthermore, \( 2f_L \) fitting residuals indicate the strong presence of fringe structure, resulting in the presently quoted detection sensitivities underestimating true performance capability of SiPhCS WMS. Moreover, these fringes presently limit the reliability of direct on-chip WMS measurements of CH\textsubscript{4} in the environmental chamber; for example, the drifts observed in Figure 7.13 result from temperature changes during flow measurements, which cause fringe FSR variations. Using a revised prototype design presently underway for the environmental chamber for the next-generation testing platform, we expect to quantify their performance impact on the SiPhCS through standard procedural testing outline in Appendix A6.

7.3.7 Towards integrated SiPhCS nodes

Section 7.3.3 validated SiPhCS performance, demonstrating \((aL)_{\text{min}} = 8.5 \times 10^{-4}\) Hz\textsuperscript{1/2}, which is consistent with conventional TDLAS sensors [58], with and potential near-term sensitivity
improvement achievable through mechanical stabilization (optical packaging) and modulation schemes (Section 7.3.6). Here, we present a long-term vision of an integrated SiPhCS node for deployment in a wide-area sensor network.

The sensor layout is shown in Figure 7.18, complete with a III-V die (laser/detector array) flip-chip assembly to the SiPh substrate [36]. The permanently sealed CH\textsubscript{4} reference cell will be assembled within a formic acid based [73] fluxless solder reflow chamber, modified to introduce CH\textsubscript{4} during the process. The CH\textsubscript{4} reference is expected to be used for periodic recalibration of signal levels, in addition to providing line-locking capability for modulation schemes. Ambient CH\textsubscript{4} is measured through the permeable sample cell membrane (e.g. PTFE [74]) to prevent environmental contamination.

The laser will be constructed in an external-cavity configuration for broadband tunability and multi-species detection [36]. The back/front facets of the gain chip are HR/AR coated respectively [41], with a distributed Bragg reflector (DBR) serving as the output to the sample/reference waveguides. A cavity phase-shift heater aligns the FP resonance to the (tunable) micro-ring filter mode, which ensures single-mode operation by appropriate selection of ring diameter (and therefore FSR).

A control block schematic of the integrated SiPhCS is shown in Figure 7.19, designed for line-locked WMS operation. Coarse wavelength tuning for spectral retrieval is accomplished by table-lookup of thermal set-point biases, and line-locked operation is performed by PID feedback to set the cavity phase shift heater at the CH\textsubscript{4} 3f\textsubscript{L} zero-crossing (measured on PD-1). Thermal dithering of the cavity heater about the bias point results in wavelength modulation sample CH\textsubscript{4} measured by the second detector (PD-2). The resulting digitized PD-2 signal is subjected to direct signal
readout (WMS, line-locked mode) or spectral fitting algorithms (VLMS/BSLD/DEF-R, line-scan mode) for concentration retrieval.

Finally, we note that substantial flexibility exists in the on-chip implementation of the sample cell. This Chapter focuses on evanescent field TDLAS of a linear waveguide; however, alternate schemes have been investigated in literature, including refractive index sensing [75, 76], on-chip balanced detection [77], resonant pathlength enhancement using micro-ring cavities [29, 78] and associated coupling modulation schemes [79]. In addition to SiPhCS TDLAS, active study of on-chip integration of these methods are presently underway as competing techniques for sensitivity enhancement.

7.3.8 Concluding remarks

In this Section, we demonstrated an on-chip silicon photonic evanescent waveguide-based methane trace gas sensor. Sensor characterization shows Gaussian-noise limited performance up to $\sim 10^3$ s, with a sensitivity of $757 \text{ ppmv} \cdot \text{Hz}^{-1/2}$ and minimum fractional absorption $(aL)_{\text{min}} = 8.5 \times 10^{-4}$ Hz$^{-1/2}$, consistent with typical TDLAS sensors [58]. We expect the low-cost and manufacturing scalability of integrated SiPh sensors to enable a next-generation of economical wide-area sensor networks for continuous fugitive emissions monitoring and source localization.
References


[40] Fisher Scientific, “Nicolet 8700 FT-IR spectrometer: state-of-the-art FT-IR capabilities for research scientists,” available online at:


Appendix A1: Derivations

A1.1 Jones matrix calculus for Faraday rotation signals

Using the Jones calculus developed in [1, 2], we write the electric field vector $J_{PD}$ (impinging upon the photodetector) as:

$$J_{PD} = \hat{j}_a \cdot \hat{j}_s \cdot J_i$$  \hspace{1cm} (A1.1)

where the hat notation denotes a matrix operator that acts upon the initial polarized light $J_i$ (prior to the sample, $E_0$ is the initial electric field and $\theta$ is the uncrossing angle relative to the analyzer):

$$J_i = E_0 \cdot \begin{pmatrix} \sin \theta \\ \cos \theta \end{pmatrix}$$  \hspace{1cm} (A1.2)

The operators for the paramagnetic gas sample $\hat{j}_S$ (including MCD and MCB) and analyzer $\hat{j}_a$ is given by the N-matrix formulation devised in [2, 3]:

$$\hat{j}_a = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$  \hspace{1cm} (A1.3)

$$\hat{j}_s = \exp(-\zeta) \cdot \begin{pmatrix} \cosh(\Delta \alpha_{MCD} + i \cdot \Theta_{FRS}) & -i \cdot \sinh(\Delta \alpha_{MCD} + i \cdot \Theta_{FRS}) \\ i \cdot \sinh(\Delta \alpha_{MCD} + i \cdot \Theta_{FRS}) & \cosh(\Delta \alpha_{MCD} + i \cdot \Theta_{FRS}) \end{pmatrix}$$  \hspace{1cm} (A1.4)

$$\Delta \alpha_{MCD} = \frac{\alpha_{LCP} - \alpha_{RCP}}{4} \cdot L, \quad \zeta = \frac{\alpha_{LCP} + \alpha_{RCP}}{4} \cdot L$$  \hspace{1cm} (A1.5)

In Equation A1.5, $\Delta \alpha_{MCD}$ and $\zeta$ accounts for MCD and analyte absorption (resulting in signal attenuation) respectively. Substitution of Equations A1.2 to A1.5 into A1.1 yields:

$$J_{PD} = E_0 \cdot \exp(-\zeta) \cdot \begin{pmatrix} \cosh(\Delta \alpha_{MCD}) \cdot \sin(\theta + \Theta_{FRS}) - i \cdot \sinh(\Delta \alpha_{MCD}) \cdot \cos(\theta + \Theta_{FRS}) \\ \cosh(\Delta \alpha_{MCD}) \cdot \cos(\theta + \Theta_{FRS}) + i \cdot \sinh(\Delta \alpha_{MCD}) \cdot \sin(\theta + \Theta_{FRS}) \end{pmatrix}$$  \hspace{1cm} (A1.6)

The voltage signal on the photodiode (signal and reference refers to extraordinary and ordinary polarizations exiting the analyzer) is given by the square absolute value of the components in Equation A1.6, or $V_{PD} \sim G_V \cdot R_I \cdot J_{PD} \cdot J_{PD}^\dagger$:
\[ V_{\text{sig}} = G_v \cdot R_I \cdot P_0 \cdot \exp(-\zeta) \cdot \left[ \frac{\sin 2\theta \cdot \sin 2\Theta_{\text{FRS}}}{\sinh^2(\Delta\alpha_{\text{MCD}}) + \sin^2\theta \cdot (1 - 2\sin^2\Theta_{\text{FRS}})} \right] \] \hfill (A1.7)

\[ V_{\text{ref}} = G_v \cdot R_I \cdot P_0 \cdot \exp(-\zeta) \cdot \left[ \frac{\sin 2\theta \cdot \sin 2\Theta_{\text{FRS}}}{\cosh^2(\Delta\alpha_{\text{MCD}}) - \sin^2\theta \cdot (1 - 2\sin^2\Theta_{\text{FRS}})} \right] \] \hfill (A1.8)

In Equations A1.7 and A1.8, the initial \(\sin 2\theta \cdot \sin 2\Theta_{\text{FRS}}\) term is the relevant FRS signal of interest, and to first-order we may write:

\[ V_{\text{sig}} = G_v \cdot R_I \cdot P_0 \cdot \exp(-\zeta) \cdot \left[ \sin 2\theta \cdot \Theta_{\text{FRS}} + \sinh^2(\Delta\alpha_{\text{MCD}}) + \sin^2\theta \right] \] \hfill (A1.9)

\[ V_{\text{ref}} = G_v \cdot R_I \cdot P_0 \cdot \exp(-\zeta) \cdot \left[ -\sin 2\theta \cdot \Theta_{\text{FRS}} + \cosh^2(\Delta\alpha_{\text{MCD}}) - \sin^2\theta \right] \] \hfill (A1.10)

Note the identical signal contributions in Equations A1.9 and A1.10; while the latter terms in Equation A1.10 (reference) are much larger than the signal for small \(\theta\). This qualitatively explains the SNR enhancement with smaller \(\theta\), as the same signal is maintained between the signal and reference arms, yet the optical power impinging upon the photodetector is much lower (and therefore contributes less intensity-noise) in the case of Equation A1.9.

In the case of either wavelength or sample modulation, \(\Theta_{\text{FRS}}\) variations are decoupled from the constant offset terms, from which we may derive the three FRS signal cases (corresponding to the 90° method, 45° method, and hybrid-FRS):

\[ V^{90°} = \xi_{90°}(Nf_L) \cdot G_v \cdot R_I \cdot P_0 \cdot \exp(-\zeta) \cdot \sin 2\theta \cdot \Theta_{\text{FRS}} \] \hfill (A1.11)

\[ V^{45°} = 2 \cdot \xi_{45°}(Nf_L) \cdot G_v \cdot R_I \cdot P_0 \cdot \exp(-\zeta) \cdot \sin 2\theta \cdot \Theta_{\text{FRS}} \] \hfill (A1.12)

\[ V^{\text{hybrid}} = \xi_{\text{hybrid}}(Nf_L) \cdot (1 + \gamma) \cdot G_v \cdot R_I \cdot P_0 \cdot \exp(-\zeta) \cdot \sin 2\theta \cdot \Theta_{\text{FRS}} \] \hfill (A1.13)

where we define \(\gamma = \sin^2\theta / \cos^2\theta\) (consistent with the notation in Chapter 4), and \(\xi(Nf_L)\) again denotes the harmonic degradation factor of the FRS signal upon demodulation.
A1.2 Optimization of analyzer uncrossing angle

In the presence of appreciable PER, we use the transformation

\[ P_{\text{sig}} = P_0 \cdot \sin^2 \theta \quad \rightarrow \quad \tilde{P}_{\text{sig}} = P_0 \cdot \lambda(\theta) \]  \hspace{1cm} (A1.14)

where \( \lambda(\theta) = \sin^2 \theta + \varepsilon \cdot \cos^2 \theta \) is the total power (signal and leakage) incident upon the signal photodiode. Following the development in Appendix A1.1, (or simply using Equation 2.12 for the 90° method), we observe a signal transformation by \((1 - \varepsilon)\):

\[ V^{90} = \xi^{90} (N_f) \cdot G_e \cdot R_I \cdot P_0 \cdot \exp(-\zeta) \cdot (1 - \varepsilon) \cdot \sin 2\theta \cdot \Theta_{FRS} \]  \hspace{1cm} (A1.15)

and to first-order the FRS signal remains unchanged. On the other hand, the noise term given by Equation 3.12 becomes:

\[ (\sigma_T)^2 = [\sigma_{RIN} \cdot \lambda(\theta)]^2 + \left( \frac{\sigma_{\text{NEP}}}{P_0} \right)^2 + \left( \frac{2e \cdot \lambda(\theta)}{R_I \cdot P_0} \right) \]  \hspace{1cm} (A1.16)

Combining Equations A1.15 and A1.16 yields a 90° method SNR of:

\[ \text{SNR}^{90}_\text{tot} = \xi^{90} (N_f) \cdot \exp(-\zeta) \cdot (1 - \varepsilon) \cdot \Theta_{FRS} \cdot \varphi(\theta) \]  \hspace{1cm} (A1.17)

where \( \varphi(\theta) \) is the \( \theta \)-dependent SNR contribution given by:

\[ \varphi(\theta) = \sin 2\theta \left[ [\sigma_{RIN} \cdot \sin^2(\theta)]^2 + \left( \frac{\sigma_{\text{NEP}}}{P_0} \right)^2 + \left( \frac{2e \cdot \sin^2(\theta)}{R_I \cdot P_0} \right) \right]^{-1/2} \]  \hspace{1cm} (A1.18)

The SNR maximum occurs at the zero-derivative condition \( d\varphi(\theta)/d\theta = 0 \), which leads to an expression of the form

\[ \left( \frac{\sigma_{\text{NEP}}}{P_0} \right)^2 \cdot \sin^2(\theta) + [\sigma_{RIN} \cdot \sin^2(\theta)]^2 - \Omega_1(\varepsilon) - \Omega_2(\varepsilon^2) \]

\[ \frac{\cos(2\theta)}{\cos(2\theta)} \]  \hspace{1cm} (A1.19)
\[ O_1(\varepsilon^1) = \varepsilon \cdot \frac{2e \cdot \cos^2(\theta)}{R_I \cdot P_0} \cdot \cos^2(\theta) \] (A1.20)

\[ O_2(\varepsilon^2) = [\sigma_{\text{RIN}} \cdot \varepsilon \cdot \cos^2(\theta)]^2 \]

Multiplying both sides of Equation A1.19 by \((G \cdot R_I \cdot P_0)^2\) and using the notation \(\sigma_{\text{sig}}^{P_{\text{int}}}, \sigma_{\text{int}}^{P_{\text{int}}}, \sigma_{\text{int}}^{P_{\text{int}}}, \sigma_{\text{shot}}^{\varepsilon} \) and \(\sigma_{\text{shot}}^{\varepsilon}\) defined in Section 3.3.3 for the intensity- and shot-noise contribution of signal power and leakage power, we may write:

\[
(\sigma_{\text{det}}^2) = \frac{(\sigma_{\text{shot}}^{P_{\text{int}}})^2 \cdot \sin^2(\theta) - (\sigma_{\text{shot}}^{P_{\text{int}}})^2 \cdot \cos^2(\theta)}{\cos(2\theta)} + \frac{(\sigma_{\text{int}}^{P_{\text{int}}})^2 - (\sigma_{\text{int}}^{P_{\text{int}}})^2}{\cos(2\theta)} \] (A1.21)

Which upon rearranging the leakage terms on the RHS gives the result in Equation 3.27, with \(\sigma_{\text{det}}^\text{eff}\) defined in Equation 3.28:

\[
(\sigma_{\text{det}}^\text{eff})^2 = (\sigma_{\text{shot}}^{P_{\text{int}}})^2 \cdot \frac{\sin^2(\theta)}{\cos(2\theta)} + (\sigma_{\text{int}}^{P_{\text{int}}})^2 \cdot \frac{1}{\cos(2\theta)} \] (A1.22)

\(\sigma_{\text{det}}^\text{eff}\) represents an effective detection noise that may be directly measured by completely crossing the analyzer (i.e. \(\sigma_T = \sigma_{\text{det}}^\text{eff}\) at \(\theta = 0^\circ\)). Note that in the special case of negligible \(\varepsilon\) (i.e. good PER), \(\sigma_{\text{det}}^\text{eff} \rightarrow \sigma_{\text{det}}\) consistent with the result in Equation 3.18.

Solution to the optimum uncrossing angle \(\theta_{\text{opt.}}\) is given by solving for \(\theta\) in Equation A1.19. This yields the quadratic equation:

\[
\left( \frac{2e \cdot P_0}{R_I} (1 - \varepsilon) + (\sigma_{\text{RIN}} \cdot P_0)^2 \cdot (1 - \varepsilon^2) \right) \cdot \beta^2 + \\
\left( \sigma_{\text{NEP}}^2 \frac{2e \cdot P_0}{R_I} + (\sigma_{\text{RIN}} \cdot \varepsilon \cdot P_0)^2 \right) \cdot (2\beta - 1) = 0 \] (A1.23)

where we have used \(\beta = \sin^2\theta_{\text{opt.}}\). Application of the quadratic equation on Equation A1.23 yields the analytic solution for \(\beta\) (and thus \(\theta_{\text{opt.}}\)).
\[
\beta = \frac{\sigma_{\text{det}}^{\text{eff}} \cdot (\sigma_{\text{sig}}^{\text{eff}} - \sigma_{\text{det}}^{\text{eff}})}{(\sigma_{\text{sig}}^{\text{eff}})^2 - (\sigma_{\text{det}}^{\text{eff}})^2}
\]  
(A1.24)

In the above, \(\sigma_{\text{sig}}^{P_0}\) denotes the pre-analyzer noise contribution, given by:

\[
\sigma_{\text{sig}}^{P_0} = \sqrt{(\sigma_{\text{det}}^{\text{eff}})^2 + (G_V \cdot \sqrt{2e \cdot R_i \cdot P_0})^2 + (G_V \cdot R_i \cdot \bar{\sigma}_{\text{RIN}} \cdot P_0)^2}
\]  
(A1.25)

Algebraic rearrangement of Equation A1.25 yields the expression given in Equation 3.29, with the special case of negligible \(\epsilon\) given in Equation 3.19.

A1.3 Correspondence between \(\Theta_{\text{NEA}}\) and \((\alpha L)_{\text{min}}\)

Using the developments of Chapter 2, we have the homogeneously broadened Lorentzian absorption (and the corresponding dispersion) lineshape given by Equation 3.33:

\[
\chi_{\text{abs}} (\tilde{v}_d) = \frac{1}{\pi} \cdot \frac{\delta \tilde{v}_L}{\tilde{v}_d^2 + \delta \tilde{v}_L^2}
\]  
(A1.26)

\[
\chi_{\text{disp}} (\tilde{v}_d) = \frac{1}{\pi} \cdot \frac{\tilde{v}_d}{\tilde{v}_d^2 + \delta \tilde{v}_L^2}
\]  
(A1.27)

The absorption peak occurs at \(\chi_{\text{abs}}(\tilde{v}_d = 0) = (\pi \cdot \delta \tilde{v}_L)^{-1}\), which corresponds to a fractional absorption (for optically thin samples) of:

\[
\alpha L = (\mathcal{L} \cdot \frac{T_R}{T} \cdot p \cdot S \cdot C_r) \cdot \frac{L}{\pi \cdot \delta \tilde{v}_L}
\]  
(A1.28)

On the other hand, considering the case of optimum Zeeman splitting for DC-FRS, the maxima/minima of \(\chi_{\text{disp}}(\tilde{v}_d)\) occur at \(d[\chi_{\text{disp}}(\tilde{v}_d)]/d\tilde{v}_d = 0\), or \(\tilde{v}_d \approx \pm \delta \tilde{v}_L\), and thus the relative optical field phase change due to MCB is given by:

\[
\Delta \phi_{\text{max}} = \frac{L}{2} \cdot \frac{T_R}{T} \cdot p \cdot S \cdot C_r \cdot \mathcal{L} \cdot \left| \chi_{\text{disp}} (\tilde{v}_d = +\delta \tilde{v}_L) - \chi_{\text{disp}} (\tilde{v}_d = -\delta \tilde{v}_L) \right|
\]  
(A1.29)

\[
= \frac{1}{2} \cdot (\mathcal{L} \cdot \frac{T_R}{T} \cdot p \cdot S \cdot C_r) \cdot \frac{L}{\pi \cdot \delta \tilde{v}_L}
\]
Presently, we may consider the simple case of DC-FRS (no modulation of sample or laser wavelength), which yields the Faraday rotation angle \( \Theta_{FRS} = \Delta\phi_{\text{max}}/2 \), or:

\[
\Theta_{FRS} = \frac{1}{4} \cdot (L \cdot \frac{T_R}{T} \cdot p \cdot S \cdot C_r) \cdot \frac{L}{\pi \cdot \delta \nu_L}
\]

(A1.30)

Comparing Equations A1.28 and A1.30, we find that for a given concentration \( C_r \) of gas, the fractional absorption \( \alpha L \) is \( 4\times \) greater than the Faraday rotation angle \( \Theta_{FRS} \). In the case where the concentration corresponds to the MDL, i.e. the smallest measurable concentration \( C_{r,\text{min}} \) where the SNR = 1, we have \( \Theta_{FRS} \equiv \Theta_{NEA} \) and \( \alpha L = (\alpha L)_{\text{min}} \). We may therefore write:

\[
\Theta_{NEA} = \frac{1}{4} \cdot (\alpha L)_{\text{min}}
\]

(A1.31)

which concludes the derivation of Equation 3.34.

A1.4 Maximum power limit in hybrid-FRS

In the presence of non-negligible PER, the reference suppression ratio \( \gamma = \sin^2\theta/\cos^2\theta \) undergoes the transformation \( \gamma \rightarrow \gamma + \varepsilon \) (Section 4.6.2). To first order, this yields a hybrid-FRS signal given by:

\[
V_{\text{hybrid}} = \frac{1}{2} \cdot (Nj_L) \cdot (1 + \gamma + \varepsilon) \cdot G_v \cdot R_i \cdot P_0 \cdot \sin 2\theta \cdot \Theta_{FRS}
\]

(A1.32)

Similarly, the noise from the signal is increased by polarization leakage as described in Equation A1.13:

\[
\sigma_f(\theta) = G_v \cdot R_i \cdot P_0 \cdot \left[ \left( \frac{\sigma_{\text{NEP}}}{P_0} \right)^2 + \frac{4e \cdot \lambda(\theta)}{R_i \cdot P_0} + \left[ 10^{\frac{CMRR}{20}} \cdot \sigma_{\text{RIN}} \cdot \lambda(\theta) \right]^2 \right]^{1/2}
\]

(A1.33)

The SNR for the hybrid-FRS leakage case is thus given by:
\[
\text{SNR} = \frac{[\xi(N_f_L) \cdot \Theta_{FRS}] \cdot (1 + \gamma + \varepsilon) \cdot \sin 2\theta}{\left(\frac{\sigma_{\text{NEP}}}{P_0}\right)^2 + \frac{4\varepsilon \cdot \lambda(\theta)}{R_f \cdot P_0} + \left[10^{\frac{CMRR}{20}} \cdot \sigma_{\text{RIN}} \cdot \lambda(\theta)\right]^2}^{1/2}
\]

(A1.34)

Considering a low-power SNR_{LO} case where the FRS signal power dominates over the polarization leakage, Equations 3.20 and 3.21 yield \( \theta_{\text{opt.}} = (P_{\text{sig, opt}}/P_0)^{1/2} \) where \( P_{\text{sig, opt}} = \sigma_{\text{NEP}}/(10^{CMRR/20} \cdot \sigma_{\text{RIN}}) \).

Furthermore, \( \lambda(\theta_{\text{opt.}}) = \sin^2\theta_{\text{opt.}} + \varepsilon \cdot \cos^2\theta_{\text{opt.}} \rightarrow P_{\text{sig, opt}}/P_0 \), and thus

\[
\text{SNR}_{LO} = 2 \cdot \sqrt{P_{\text{sig, opt}}/P_0} \cdot \xi(N_f_L) \cdot G_V \cdot R_f \cdot \Theta_{FRS}
\]

(A1.35)

where \( \sigma_{\text{sig, opt}} = \sigma_T(\theta_{\text{opt.}}) \) and is the total noise due to the signal power at optimum uncrossing. On the other hand, we may consider a high power SNR_{HI} case, where generalizing the trend \( \theta = (P_{\text{sig, opt}}/P_0)^{1/2} \) for high powers where leakage begins to dominate the FRS signal power gives \( \lambda(\theta) \rightarrow \varepsilon \), resulting in:

\[
\text{SNR}_{HI} = 2 \cdot \frac{1 + \varepsilon}{\varepsilon} \cdot \left(10^{\frac{CMRR}{20}} \cdot \sigma_{\text{RIN}}\right)^{-1} \cdot \sqrt{P_{\text{sig, opt}}/P_0} \cdot \xi(N_f_L) \cdot \Theta_{FRS}
\]

(A1.36)

The power above which the SNR no longer improves with \( P_0 \) is well approximated by the intersection point where \( \log(\text{SNR}_{LO}) = \log(\text{SNR}_{HI}) \), as shown in Figure 4.6(b). Equating Equations A1.35 and A1.36 then gives:

\[
G_V \cdot R_f \cdot 10^{\frac{CMRR}{20}} \cdot \sigma_{\text{RIN}} \cdot (\varepsilon P_0) = \sigma_{\text{sig, opt}}
\]

(A1.37)

which is the result in Equation 4.11. Note that the calculation in Equation A1.36 is purely for pedagogical purposes; increasing the power beyond the maximum in Equation A1.37 results in \( P_{\text{sig, opt}} \sim P_0 \), which quickly surpasses the detector saturation limit. Indeed, for small \( \theta \) we may write:
Comparing Equations A1.38 and 4.12, we find that in the case where the saturation power is bounded by

\[ P_{\text{sat}} < P_{\text{sig}}^{\text{opt}} + \sqrt{2 \left(P_{\text{sig}}^{\text{opt}}\right)^2 + \frac{4e \cdot P_{\text{sig}}^{\text{opt}}}{R_T} \cdot \frac{10^{\frac{20}{20}} \cdot \sigma_{\text{RIN}}}{2}} \]  

(A1.39)

then the detector saturation limit is reached before the maximum SNR calculated by Equation 4.12 (and shown in Figure 4.6(b)) is achieved, and defines the practical SNR maximum that is attainable for a given detector.

A1.5  Isotopic ratio calculated from sample peak integration

From Equation 5.16, we have

\[ \delta^{15}N_T = \left( \frac{\left[15^{\text{N}}\hat{N}_s(t)\right]_T}{\left[14^{\text{N}}\hat{N}_s(t)\right]_T} - 1 \right) \times 10^3 \]  

(A1.40)

Based on the definition for \( \delta^{15}N(t) \) given in Equation 5.10, we may write

\[ \left[15^{\text{N}}\hat{N}_s(t)\right] = \frac{\delta^{15}N(t)}{10^3} + 1 \cdot \hat{n}_k \cdot \left[14^{\text{N}}\hat{N}_s(t)\right] \]  

(A1.41)

Substitution of Equation A1.41 into A1.40 gives

\[ \delta^{15}N_T = \frac{\left( \frac{\delta^{15}N(t)}{10^3} + 1 \right) \cdot \left[14^{\text{N}}\hat{N}_s(t)\right]_T \times 10^3}{\left[14^{\text{N}}\hat{N}_s(t)\right]_T} - 10^3 = \frac{\left\langle \delta^{15}N(t) \cdot \left[14^{\text{N}}\hat{N}_s(t)\right]_T \right\rangle}{\left\langle \left[14^{\text{N}}\hat{N}_s(t)\right]_T \right\rangle} \]  

(A1.42)

which demonstrates the result indicated by Equation 5.17. Error propagation of the above may be performed with knowledge of the single point uncertainty \( \Delta \delta^{15}N(t) \):
\[ \delta^{15}N_T \pm \Delta(\delta^{15}N_T) = \frac{\left\langle \left( \delta^{15}N(t) \pm \Delta\delta^{15}N(t) \right) \cdot [^{14}N]_S(t) \right\rangle_T}{\left\langle [^{14}N]_S \cdot (t) \right\rangle_T} \]  
(A1.43)

We note that the time-average of single-point uncertainties \( \Delta\delta^{15}N(t) \) result in propagation of errors in quadrature:

\[ \Delta(\delta^{15}N_T) = \frac{1}{T} \cdot \sqrt{T \int \left[ \Delta\delta^{15}N(t) \cdot [^{14}N]_S(t) \right]^2 \cdot dt} \]  
(A1.44)

Substituting the single-point error \( \Delta\delta^{15}N(t) \) given by Equation 5.12 yields

\[ \Delta(\delta^{15}N_T) = \frac{1}{T} \cdot \sqrt{\int \left[ \frac{\delta^{15}N(t)}{10^3} + 1 \right] \cdot \frac{\Delta[^{15}N]_S}{[^{15}N]_S(t)} \times 10^3 \cdot [^{14}N]_S(t) \cdot dt} \]  
(A1.45)

From Equation 5.10, we have:

\[ \frac{[^{15}N]_S(t)}{[^{14}N]_S(t)} = \tilde{n}_r \cdot \left[ \delta^{15}N(t) \cdot 10^{-3} + 1 \right] \]  
(A1.46)

and substituting Equation A1.46 into A1.45 then gives:

\[ \Delta(\delta^{15}N_T) = \frac{1}{T} \cdot \sqrt{\int \left( \Delta[^{15}N]_S \right)^2 \cdot dt} \times 10^3 \cdot \frac{\Delta[^{15}N]_S}{\sqrt{T}} \]  
(A1.47)

Finally, combining Equation A1.46 and A1.47 results in the integrated peak precision (identical to Equation 5.18):

\[ \Delta(\delta^{15}N_T) = \frac{\Delta[^{15}N]_S}{\sqrt{T}} \cdot \left[ \frac{\delta^{15}N_T}{10^3} + 1 \right] \times 10^3 \]  
(A1.48)
References


Appendix A2: SNR considerations in TDLAS

A2.1 The effect of ramp rate in TDLAS

In comparison to phase-sensitive detection techniques, conventional line-scanned TDLAS typically presents inferior MDL due to large detection ENBW (which includes low-frequency $1/f$ noise). The exact role of the $1/f$ contribution however, depends upon the rate of line-scanning, as the process of baseline normalization linearizes intensity fluctuations on the same time-scale as the ramp. The effect of this linearization is seen in Figure A2.1(a), whereby a simulated 1 s time-series ($10^5$ Sa/s) with both Gaussian ($\sigma_{RIN} = 2\times10^{-5}$ Hz$^{1/2}$) and $(1/f)^2$ noise contribution is shown, and the descending panels show increasing ramp-rate $f_{ramp}$. Baseline normalization of each $1/f_{ramp}$ segment results in the correction of successively higher frequency drifts (the black curve is a 5 ms moving average).

Figure A2.1(b) shows the RIN calculation of $f_{ramp} = 1$ Hz (gray) and 200 Hz (red), where it is apparent that the effect of ramping is to convert spectral noise below $f_{ramp}$ into white-noise like behavior. Integration over the RIN spectrum indicates the total noise of a single point measurement (i.e. $10^{-5}$ s for $10^5$ Sa/s), and can be used to calculated the relative SNR enhancement for increasing $f_{ramp}$:

$$ SNR = \frac{\Delta I}{I_0} \cdot \frac{\zeta(\Delta \tilde{\nu}_{ja} / \Delta \tilde{\nu}_{FWHM})}{\bar{\sigma}_{RIN} \cdot \sqrt{\Delta f_{SR}/2}} \quad (A2.1) $$

Where $\zeta(\Delta \tilde{\nu}_{ja}/\Delta \tilde{\nu}_{FWHM})$ is the simulated SNR decay factor given in Figure A2.3 (Section A2.2), $\Delta f_{SR}$ is the measurement sample rate, and the RMS RIN $\bar{\sigma}_{RIN}$ is defined by Equation 3.5. The result of this calculation is shown in Figure A2.1(c), which displays the normalized SNR average over eight separate simulations (the error bars indicate the maximum/minimum bounds of the eight simulations). The intuitive conclusion of the analysis is that the optimum $f_{ramp}$ for a TDLAS...
measurement occurs at the intersection of the high-frequency white-noise and low-frequency \(1/f\) noise contributions, above which the SNR benefit plateaus. In this particular case, full SNR benefit is achieved at \(f_{\text{ramp}} \approx 500\) Hz, with 90\% of the maximum SNR occurring at \(f_{\text{ramp}} \approx 80\) Hz. It is appropriate to note here that it may be desirable to operate at lower ramping rates to avoid laser.

An experimental demonstration of the sensitivity enhancement with increasing ramp rates is shown in Figure A2.2. A 20 s time-series ASD calculation demonstrates the presence of \(1/f\) RIN, which may be mitigated through the increases in laser ramping frequency. The experimental consequence of increasing \(f_{\text{ramp}}\) for TDLAS through the 10 cm SiPhCS described in Section 7.3 is shown in Figure A2.2(c), where significant short-term SNR improvement is observed (> 10\% for 10 ms measurements), although noise convergence at time intervals > 1 s occurs. We note that the effect of increasing ramp-rate is neutralization of intensity-noise; however, laser frequency jitter (which cause jitter of spectral baseline features) from laser ringing described above is not corrected through this procedure, and is a possible explanation for drifts observed at averaging times > 1 s.

A2.2 The impact of spectral fitting width in TDLAS

In Section 3.1.1 it was noted that the effect of spectral fitting (by rule of thumb) is similar to averaging the maximum SNR at peak absorbance over the FWHM. We may numerically demonstrate this claim by considering a practical TDLAS measurement scenario, where the sample acquisition and ramp rate are kept fixed. Figure A2.3(a) shows a simulated 3.68 ppbv \(^{15}\)NO (1 ppmv \(^{14}\)NO) Q(3/2) TDLAS spectrum at 80 torr (homogeneously broadened lineshape), with peak absorption of \((\alpha L)_{\text{peak}} = 6.47 \times 10^{-7}\) and \(\sigma_{\text{bsl}} = 1.5 \times 10^{-9} \text{ Hz}^{-1/2}\) Gaussian noise baseline. Assuming fixed ramp-rate (1 Hz) and sample-rate (100 Hz or 100 points per ramp), the optimum SNR \((\text{SNR}_{\text{opt}})\) is defined as the hypothetically ideal case where all points are used to measure the absorption peak; i.e. \(\text{SNR}_{\text{opt}} = (\alpha L)_{\text{peak}}/\sigma_{\text{bsl}} = 431.96 \text{ Hz}^{-1/2}\). As the spectral width for the
concentration retrieval is widened (maintaining the same 100 points per ramp), the fractional contribution of the spectral wings becomes dominant, resulting in SNR degradation factor $\zeta(\Delta\tilde{\nu}_{\text{FWHM}}/\Delta\tilde{\nu}_{\text{fit}})$ observed in Figure A2.3(b). The spectral SNRs are computed via $10^3$ s of simulated noisy absorption spectra followed by VLMS retrieval and Allan deviation calculations. The points in Figure A2.3(b) show the result of eight simulation averages using this procedure, and the error bars indicate the maximum/minimum result of the simulations. It is notable that at $\sim 3\times$ FWHM spectral range, the SNR degrades to 50 % of $SNR_{\text{opt}}$, and approximately 25 % of $SNR_{\text{opt}}$ at $\sim 15\times$ FWHM. The assumption of explicit ramp/sample rate does not affect the general result of the calculation, as the SNR normalization accounts for any systematic differences in VLMS retrieval precision. The utility of Figure A2.3(b) can be observed as follows: given an absorption spectrum, VLMS fitting provides the residuals, whose deviation is a measure of $\sigma_{\text{bsl}}$ and enables the calculation of $SNR_{\text{opt}}$. The ratio of the spectral range used for VLMS to the linewidth can then be used to determine $\zeta(\Delta\tilde{\nu}_{\text{fit}}/\Delta\tilde{\nu}_{\text{FWHM}})$, from which the true SNR = $\zeta(\Delta\tilde{\nu}_{\text{fit}}/\Delta\tilde{\nu}_{\text{FWHM}}) SNR_{\text{opt}}$ can be determined. In a practical spectral acquisition scenario, measurement of spectral ranges at or below the FWHM may not be reasonable due to insufficient data for baseline normalization, and therefore a spectral width significantly greater than the orange range in Figure A2.3(a) is required [1, 2]. In the case of a more typical spectral coverage (e.g. the blue highlighted region, or $\sim 15\times$ FWHM) we note that $\zeta(\Delta\tilde{\nu}_{\text{FWHM}}/\Delta\tilde{\nu}_{\text{fit}}) = 25 \%$ of $SNR_{\text{opt}}$ achieved is almost identical to averaging the SNR at the spectral peak over the FWHM and justifies the general rule of thumb outlined in Section 2.1.

References

Appendix A3: 1st-generation dDM-FRS prototype

A3.1 1st-generation dDM-FRS sensor design

In the 1st-generation dDM-FRS prototype (Figure A3.1) [1], key design differences compared to Chapter 6 [2] are the use of a class-H amplifier (Behringer EPQ900) to drive the solenoid (Figure A3.2), reduced pressure operation (35 Torr, Varian IDP3B01) for optimized Zeeman splitting at low B-fields, and MgF$_2$ Rochon polarizers (Foctek RCP5010) [1, 3]. Laser and solenoid (Custom Coils) modulation occurs at $f_L = 50$ kHz, and $f_M = 1.04$ kHz (LC tank configuration; $L = 7.9$ mH and $C = 3$ µF) respectively [1].

Figure A3.2(a) shows the measured axial B-field through both sample and reference paths (4 A at $f_m = 1.04$ kHz), showing a peak field ~ 260 G. Beyond the coil boundary (> 9 in.), field deviations exist due to the asymmetric wiring leads to the audio amplifier.

A3.2 Experimental PER considerations

The PER impact of the retroreflector configuration is investigated in Figure A3.3. RCP1 is continuously varied to transition the incident beam from $s$ to $p$, which undergoes relative phase change upon reflection depending on the RCP1 angle [4], resulting in conversion to elliptical polarization. This is shown in Figure A3.3(b), where the PER experiences local maxima only near $s$ and $p$ states. The green curve is the measured signal maxima for a given RCP1 angle (Malus’ Law [5]), and power normalization is required to obtain PER, as optical suppression is near the detection noise floor. Figure A3.3(b) shows an offset from expected 90º and 180º incidence, which is attributed to polarization rotation due to the tilted/wedged CaF$_2$ windows on the sample/reference gas cells.

The results depicted in Figure A3.3 show PER ~ $10^5$; however, this is an ideal alignment case where sufficient ordinary/extraordinary polarization beams separation is possible. In the
construction of the benchtop system, noise analysis in Figure A3.4 shows crosstalk between the ordinary/extraordinary polarizations (due to ~ 1° separation angle [3] and the TM$_{01}$ transverse laser mode), resulting in poor PER. In this 1st-generation dDM-FRS prototype, we determine $\sigma_{\text{NEP}} = 1.65 \times 10^{-12}$ W·Hz$^{1/2}$, $\bar{\sigma}_{\text{RIN}} = 2.54 \times 10^{-7}$ Hz$^{1/2}$, $P_0 = 4.5$ mW, and $\varepsilon = 1.62 \times 10^{-3}$. This power leakage in an intermediate power case of Equation 3.29 is shown in Figure A3.4(a), where dark color lines are noise plots with respect to useful signal power, i.e. $P_{\text{sig}} = P_0 \cdot \sin^2(\theta)$. The detector-noise (light green) and its effective counterpart ($\text{eff}$ $\sigma_{\text{det}}$, dark green) are shown, where $\text{eff}$ $\sigma_{\text{det}}$ is a result of leakage $(P_0 \cdot \varepsilon = 7.27 \mu$W). Measured noise with associated error bars are shown in gray, and calculations (gray line) are in agreement with experiment. SNR optimization via analyzer uncrossing angle yields $P_{\text{sig}} = 9.99$ µW at $\theta_{\text{opt}} = 2.7^\circ$ and total incident power $P_{\text{sig}} + P_0 \cdot \varepsilon = 17.26$. mW. The impact of leakage is explicitly seen in Figure A3.4(b), where SNRs of various noise limits (i.e. $\sigma_{\text{det}}, \text{eff}$ $\sigma_{\text{det}}, \sigma_{\text{shot}}, \sigma_{\text{int}}$) are displayed. The presence of PER causes increased $\theta_{\text{opt}}$ and reduced SNR$_{\text{tot}}$. Finally, note that the present depolarization is caused by crosstalk between ordinary/extraordinary beams; thus, the effect of SNR degradation from RCP2 leakage is mitigated by using wire-grid polarizers in Section 6.2.

A3.3 EMI baseline removal

The dual-modulation procedure causes the DM-FRS signal to reside in two sidebands centered about the carrier, i.e. $f_+ = 2xf_L + f_M$ and $f_- = 2xf_L - f_M$, and the demodulation process (denoted by operation $D$) for each sideband results in signals $D[f_+]_X, D[f_+]_Y$ and $D[f_-]_X, D[f_-]_Y$, where the $X$ and $Y$ subscripts denote quadrature phases of demodulation, while the + and – indicate $f_+$ and $f_-$ sidebands. Typically, the demodulation phase is adjusted to ensure the signal resides in a single phase quadrature (arbitrarily chosen to be denoted as $X'$), allowing the final DM-FRS signal $V$ to be constructed from $V_{\text{DM-FRS}} = D[f_+]_{X'} + D[f_-]_{X'}$. In principle, the DM-FRS signal is baseline free.
because any spectral background effects (e.g. optical etalons) are observed only in the carrier frequency \( f_L \) and do not enter the sidebands at \( f_+ \) and \( f_- \). Empirically however, in the presence of zero-gas residual spectral features are observed in both the X and Y channels \( (D[f_+]_X \text{ and } D[f_+]_Y \text{ respectively, and } Y' = X' + 90^\circ) \), where \( D[f_+]_X = \Gamma_{XY} \cdot D[f_+]_Y \text{ and } D[f_-]_X = -\Gamma_{XY} \cdot D[f_-]_Y \), \((|\Gamma_{XY}| < 1)\). This may be explained as a result of amplitude modulation of the carrier (e.g. electronic pickup in the laser or detection system) due to EMI, which is more significant than that observed in Chapter 6 [2] due to higher coil modulation frequency \((f_M = 1.04 \text{ kHz vs. } 100 \text{ Hz})\). For this 1st-generation dDM-FRS prototype, we heuristically reduce the impact of EMI by introducing a second term to \( V_{DM-FRS} \) for baseline noise-removal:

\[
V_{DM-FRS} = \{D[f_+]_X \cdot \mp \Gamma_{XY} \cdot D[f_+]_Y\} + \{D[f_-]_X \cdot \pm \Gamma_{XY} \cdot D[f_-]_Y\}
\]

\[
= V_{DM-FRS} - \pm \Gamma_{XY} \cdot D[f_+]_Y \mp \Gamma_{XY} \cdot D[f_-]_Y)
\]

\[
= V_{DM-FRS} - \zeta_{baseline}
\]

(A3.1)

where \( \zeta_{baseline} \) is given by the sum of the out-of-phase components of demodulation. Given that the signal resides in the quadrature component, addition of \( \zeta_{baseline} \) does not affect the signal, but rather eliminates baseline artefacts. Furthermore, this term also increases relative noise contribution given by Equations 3.1 to 3.3; subtraction of \( \zeta_{baseline} \) (Equation A3.1) increases baseline Gaussian-noise, resulting in a degradation in SNR. Nominally, noise in a DM-FRS sensor system is increased by \( \sqrt{2} \) due to dual-sideband demodulation which doubles the EBNW; further addition of the out-of-phase quadrature component using Equation A3.1 results in the quadrature sum of uncorrelated noise terms:

\[
\tilde{\sigma}_{DM-FRS} = \sigma_{DM-FRS} \sqrt{1+\Gamma_{XY}^2}
\]

(A3.2)
Thus a degradation factor \((1+\Gamma_{XY}^2)^{-1/2}\) occurs during baseline removal. In Figure A3.5 and A3.6, simple subtraction using \(\Gamma_{XY} = 1\) yields SNR \(\sqrt{2}\times\) worse than conventional DM-FRS. In general, \(\Gamma_{XY}\) must be customized to optimize baseline rejection. The effectiveness of baseline removal and stability of \(\Gamma_{XY}\) is demonstrated in the next Section.

A3.4 1st-generation dDM-FRS sensor performance

Spectral acquisition (at \(\Delta f = 1\) Hz ENBW per point) is performed by laser current scanning across each isotope (shown in Figure A3.6(a)) using an uncalibrated cylinder with 2 ppmv \(^{14}\)NO and 7.35 ppbv \(^{15}\)NO assuming natural abundance (0.368 \(\%\) \(^{15}\)NO). The bottom graph in Figure A3.6(a) displays the result of current scanning the laser across the \(^{14}\)NO P(19/2)e line with \(N_2\) in the reference and cylinder NO in the sample cell, and the inset (red curve) shows the Q(3/2) line of \(^{15}\)NO. The upper graph is the same measurement for \(^{14}\)NO with \(N_2\) flush in both the sample and reference cells, demonstrating the zero-baseline property of the DM-FRS sensor after successful baseline removal (Section A3.3). Line-locking to the spectral peaks is performed for real-time NO diagnostics, and Allan-deviation stability in the line-locked mode yields white-noise (467.5 nV-Hz\(^{1/2}\)) up to > 400 s at 2.4\(\times\) the quantum shot-noise level (Figure A3.6(b)).

From Figure A3.6(a), the \(^{14}\)NO signal peak is \(V_{sig} = 46.1\) µV, yielding a SNR of 46.1 µV/467.5 nV-Hz\(^{1/2}\) = 98.64 Hz\(^{1/2}\) which corresponds to a \(^{14}\)NO detection limit of 20.3 ppbv-Hz\(^{1/2}\), or \((aL)_{min} = 1.79\times10^{-6}\) Hz\(^{1/2}\) for the major isotope. Similar analysis for the minor isotope (Q(3/2) line of \(^{15}\)NO) yields \((aL)_{min} = 1.10\times10^{-7}\) Hz\(^{1/2}\) and \(\Theta_{NEA} = 1.67\times10^{-8}\) Hz\(^{1/2}\), consistent with measurements in Chapters 5 and 6.

From Figure A3.6(c), we note that the calculated difference \(^{14}\tilde{\eta}_{calc} = \langle [^{15}N]_s >_T - \langle [^{15}N]_r >_T = -1.41\) µV and measured \(^{14}\tilde{\eta}_{meas} = -1.28\) µV are similar, corresponding to a \(^{14}\)R\(_{true}\) = 3.3\(\times\)10\(^{-3}\) or \(^{14}\)CMRR\(_{true}\) = 10\(\times\)log\(^{(^{14}\)R\(_{true})}\) = 24.8 dB. Due to the much lower abundance of \(^{15}\)NO in from the
cylinder source, $^{15}CMRR_{true}$ could not be accurately ascertained within the stability time of the 1st-generation dDM-FRS sensor, and is studied in detail in Section 6.4.2 with the development of the 2nd-generation prototype [2].

A3.5 Single-cell isotope analysis

In addition to differential FRS, the present system is capable of direct isotopic analysis, whereby the analyte of interest is injected into the sample cell while the reference cell is continuously purged with N$_2$. The is useful in a variety of isotope labeling applications not constrained by stringent precision requirements [6-9]. As a demonstration, we follow [10, 11], to establish sensor linearity via IAEA-NO-3 standard measurements ($\delta^{15}$N = 4.7 ‰), by reduction to NO using [12]. Presently, only the sample cell receives NO gas, and the reference is flushed with N$_2$. Five separate KNO$_3$ injections, ranging linearly from 100 to 500 nmol are performed, with isotopes measured separately ($^{14}$NO measurement prior to repeat injections for $^{15}$NO). The N$_2$ carrier gas flow-rate through the sample cell is fixed at 50 sccm, resulting in peak half-width ~ 150 s. The resulting injection peaks are plotted in Figure A3.7(a), where peak maxima of $^{14}$NO are aligned for display clarity. The inset shows corresponding $^{15}$NO peaks. Peak integration is shown in Figure A3.7(b), displaying excellent linearity ($R^2 > 0.995$) with respect to KNO$_3$ injection quantity. The above results demonstrate the utility of the present system for direct isotopic analysis.

Given the peaks measured in Figure A3.7(a), we may estimate the ratiometric precision calculated over the span of an injection peak, by following the development of [13] and Chapter 5. In particular, application of Equation 5.18 using $\Delta[^{15}\text{N}]_s = 560$ nV·Hz$^{-1/2}$ (measurement noise of $^{15}$NO quantified via separate Allan deviation analysis for line-locked $^{15}$NO measurement in N$_2$) and assuming a 500 nmol NO$_3^-$ injection gives:
\[
\Delta(\delta^{15}N_T) = \frac{\Delta[^{15}\text{N}]_S}{\sqrt{T}} \times 10^3 = \frac{560 \text{ nV}/\sqrt{\text{Hz}}}{\sqrt{400 \text{ s}}} \times \frac{1}{6.685 \mu\text{V}} \times 10^3 = 4.19 \% \quad (A3.3)
\]

For time-multiplexed 50 % duty-cycle switching (Section 5.4.1), we expect a degradation factor \(\sqrt{2}\), resulting in a precision \(\Delta(\delta^{15}N) = 5.92 \%\). According to Equation 5.13, this enables sub-permil precisions for sample sizes above ~ 3 μmol. It is instructive here to compare this with the value obtained in Section 5.5.4; for a 5 μmol sample size, we expect 0.592 \% precision, which upon path length normalization is consistent with previous results (Figure 5.9(b)). In the case where high ratiometric precision is required, the line-switched measurement procedure from Section 5.4.1 is adapted to the 2nd-generation prototype in Section 6.5 for real-time in-line ratiometric referencing.
References


Appendix A4: Spectral fitting libraries for TDLAS

A4.1 TDLAS spectral fitting libraries software flow

For the on-chip TDLAS CH₄ measurement in Section 7.3, customized software libraries have been developed for the purpose of (1) sample data acquisition, (2) data format handling and compilation, followed by (3) spectral fitting and noise analysis. The latter is accomplished through HITRAN [1] data parameters for concentration retrieval of the sample analyte of interest.

The TDLAS functional flow chart is depicted in Figure A4.1, where the bracketed numbers are functional code blocks (and associated sub-routines) described in Figure A4.2. The lettered arrows are shown in Figure A4.3, which detail the data format structures for communication between each functional block. It is worth noting that module [0] (parse HITRAN) need only be run once for *.par to *.mat conversion, and all subsequent fitting routines require direct *.mat file read-in from module [3] prior to spectral modeling. Spectral acquisition through module [1] (acq_dspl.m) nominally utilizes a 16-bit NI-USB600X DAQ card at < 50 kS/sec to stream raw sample data which is truncated, averaged, and baseline normalized to 1 s spectral traces prior to VLMS/BSLD/DEF-R fitting routines in [5], and stability analysis in [6].

A4.2 Etalon calibration for time-resolved TDLAS

In collaboration with the Advanced Combustion and Propulsion Laboratory (PI: Yiguang Ju), a demonstration of the etalon calibration routine in module [2] is shown in Figure A4.4, using a photolysis flow reactor for time-resolved formaldehyde (CH₂O) measurements (Figure A4.5) [2]. The necessity of calibration arises due to the high ramp frequency (15 kHz) of the laser required for time-resolved measurements, which induces strong nonlinear oscillations (laser ‘ringing’) near ramp transitions. Due to the Argon balance gas, the broadening coefficients are unknown prior to VLMS fitting; thus wavenumber scaling is required for accurate concentration retrieval. The etalon
calibration is accomplished via peak-search (peak_sort.m) followed by linearization of the etalon period spacing. Extraction of the collision broadening coefficients ($\gamma_{Ar}$) in this pressure broadened limit of CH$_2$O (~ 45 torr), yields $\gamma_{Ar} = 0.117$ cm$^{-1}$·atm$^{-1}$, slightly larger (~ 7%) than the HITRAN [1] air broadening coefficient of $\gamma_{air} = 0.109$ cm$^{-1}$·atm$^{-1}$.

The experimental block diagram is shown in Figure A4.5(a), and involve a DFB-QCL centered near 5.8 µm and ramped at 15 kHz for TDLAS of CH$_2$O (also HO$_2$ at 7.1 µm and OH at 2.8 µm) in the presence of methanol (CH$_3$OH), CH$_4$ or H$_2$ fuel which reacts with O($^1$D) from the UV dissociation of O$_3$ [2]. The production of O$_3$ is independently validated by broadband UV measurements shown in the inset of Figure A4.5(b). Using the broadening $\gamma_{Ar}$ coefficient extracted from the etalon-calibrated VLMS spectral fit, the real-time decay of CH$_2$O after a single UV pulse (10 Hz Q-switched pulse at 266 nm, 1 W average power) is shown in Figure A4.5(b). The present demonstration of CH$_2$O measurements confirms the UV photolysis of O$_3$, and subsequent measurements of HO$_2$ and OH will be performed for comparison with chemical kinetic models.
References


Appendix A5: Fringe reduction for SiPh TDLAS

A5.1 AR coated SiPhCS facets and fringe decoherence

In Section 7.3.3, the presence of baseline fringing was observed in all processes under consideration, and is likely due to both intermediate WG scattering points and facet reflections of the SiPhCS. Due to this significant baseline contribution, methods for fringe mitigation are necessary for accurate CH$_4$ concentration retrieval. A combination of physical and software techniques are implemented toward this goal; the former (AR-coatings and fringe decoherence for long WGs) are demonstrated in this Section, and the latter in Section A5.2.

Figure A5.1(a) shows the spectrum of AR/non-AR-coated WG facets (K Lab Corporation) demonstrating ~ 50% reduction in etalon amplitude (black dashed line). The FFT (top left) is calculated using 10% R4 CH$_4$ transition for wavelength-axis calibration, yielding an etalon FSR corresponding to a ~ 3 cm cavity, as expected from the WG length. The limited efficacy of fringe reduction is expected from imperfect (non-uniform) coating thickness on the 250nm × 430 nm WG facet cross-section.

Figure A5.1(b) shows the 10 cm WG throughput spectrum, demonstrating fringe decoherence described in Section 7.3.3 due to distributed backscattering from the WG LER, which effectively ‘washes’ out the fringe structure (note the lack of spectral peak in the FFT at 10 cm). Due to intermediate scattering dominating the baseline structure, AR coating of longer WGs experience only mild improvement in baseline variation amplitude (compare with Figure 7.12(a)). Nevertheless, given the dominance of fringe drifts on the zero-drift time, the ~ 2× baseline reduction provides appreciable improvement on the accuracy of CH$_4$ concentration retrieval and is used throughout the experimental results in Section 7.3, and the remaining fringe structure is handled via software methods (DEF-R/BSLD).
A5.2 DEF-R for fringe mitigation

In Appendix A2, numerical calculations of short-term precision were shown to vary as a function of the experimental configuration (e.g. ramp rate, spectral width). Long term accuracy however, is typically a function of slow drifts of systematic effects. For example, on-chip TDLAS (Section 7.3) experiences significant spectral baseline structure (which changes over time) due to waveguide back-scattering, as well as absorbing features from adsorbed particulate contaminants. Aside from the nominally used AR-coated facets and fringe decoherence from long WGs, we investigate here an adaptive data processing method, termed the dynamic etalon fitting-routine (DEF-R) for mitigation of these baseline features [1].

Conventional etalon baseline-difference (BSLD, or difference between sample and zero-gas trace) is insufficient for precision trace-gas monitoring, particularly given thermal dependence of fringing which causes slow FSR variations over time. The function of DEF-R is to extend the time where the zero-gas trace remains usable, by introducing fitting parameters to account for time-dependent fringe variation. A heuristic comparison between direct subtraction and DEF-R is shown in Figure A5.2. Conventional etalon subtraction involves a static zero-gas subtracted from a data spectrum, which yields poor fringe-suppression ratio over time due to fringe drifts and contaminant adsorption and desorption. In contrast, the introduction of free-parameters allows the zero-gas trace to remain relevant over longer time periods where environmental factors may result in perturbations to the spectral baseline.

The flow schematic of the DEF-R algorithm is shown in Figure A5.4. We note here that although a total of eight fit parameters can be assigned (3 for VLMS and 5 for DEF-R), typically only three primary parameters (i) $C_g$ for analyte concentration, (ii) $\gamma_t$ for etalon FSR variation, and (iii) $\delta_t$ for fringe shift are required for DEF-R concentration retrieval. The remaining secondary
parameters are given by (iv) $\tilde{b}$ and (v) $\Delta \tilde{\alpha}_{\text{shift}}$ for scan- time to wavenumber conversion and line-center shift respectively, (vi) $\zeta$ is the vertical stretch factor and (vii) $(\lambda_{\text{offset}} \cdot t_{\text{scan}}) + \beta_{\text{offset}}$ involves a slope offset term to account for power fluctuations that result in baseline normalization inaccuracy. The efficacy and dynamic range of baseline removal using DEF-R is shown in Figure A5.3, whereby a 10% CH$_4$ in-line reference cell is measured through the SiPhCS for $> 10^3$ s, which demonstrates the utility of DEF-R for large signal strengths.

The DEF-R algorithm is accomplished in three main stages as depicted in Figure A5.4; first, the user is polled for approximate fit parameter values. This initial stage is optional and may be omitted if the measured zero-gas etalon spectra is similar to the analyte data spectra. In cases where variation may be significant due to environmental factors, coarse alignment (or a lookup table of fit-parameters correlated with environmental parameters) will ensure convergence of the least-mean square (LMS) fitting algorithm. The second stage involves a fine-fit to the average data spectra, which provides a good ansatz for initiating sequential LMS fitting of the spectral data. Finally, the data spectra are successively analyzed and the parameters (generally the analyte concentration being most significant) are retrieved and saved for further analysis.

The above description of DEF-R and Figure A5.4 demonstrates the generalized principle of the dynamic fitting algorithm; that is, the introduction of multiple degrees of freedom on the zero-gas trace enables it to retain relevance over longer time periods where environmental factors may result in perturbations to the zero-gas spectra. Mathematically, we describe the DEF-R algorithm by means of analytic transformations and interpolation on a known zero-gas trace $\varepsilon(t_{\text{scan}})$, resulting in a calculated dynamic spectra given as the product of analyte absorption spectra $\tau$ and transformed zero-gas trace $\Gamma[\varepsilon(t_{\text{scan}})]$:

$$\varphi(t_{\text{scan}}) = \tau(C_g \cdot [t_{\text{scan}} \cdot \tilde{b} + \Delta \tilde{\alpha}_{\text{shift}}]) \times \Gamma[\varepsilon(t_{\text{scan}})] \quad (A5.1)$$
Where the terms in Equation A5.1 follow the preceding definitions above. It is to be noted that in the case of a practical measurement $t_{scan}$ can only be determined in discrete intervals, with intermediate time points requiring interpolation (a cubic spline is used for this purpose). The transformation of the zero-gas (etalon) spectra may be written as:

$$\Gamma[e(t_{scan})] = [\bar{e}(t_{scan} \cdot \frac{1}{\gamma_t} + \delta_t) - \langle e(t_{scan}) \rangle] \times \xi + \langle e(t_{scan}) \rangle + \left[ (\lambda_{offset} \cdot t_{scan} + \beta_{offset}) \right]$$ (A5.2)

In the above, $\bar{e}$ is used to indicate the spline interpolation for spectral interpolation. In the case of small concentration limits, where the etalon contribution dominates beyond any analyte concentration changes, $\delta$ and $\Delta\delta_{shift}$ are fixed by means of measurement of the analyte through a high-concentration reference cell. The remaining parameters $\gamma_t$, $\delta_t$, $\xi$, $\lambda_{offset} \cdot t_{scan} + \beta_{offset}$ are left as free parameters for least-mean-squares (LMS) fitting to an experimentally acquired data spectra given by $D(t_{scan})$. The resulting spectral retrieval is given as:

$$\tau(C_g, \bar{v}) = \frac{D(t_{scan})}{[\bar{e}(t_{scan} \cdot \frac{1}{\gamma_t} + \delta_t) - \langle e(t_{scan}) \rangle] \times \xi + \langle e(t_{scan}) \rangle + \left[ (\lambda_{offset} \cdot t_{scan} + \beta_{offset}) \right]}$$ (A5.3)

and the analyte concentration extraction $C_g$ is the resulting parameter of interest for trace-gas monitoring.

The DEF-R technique is empirically justified in the context of Figure A5.5, where clear accuracy and precision enhancement is observed over a zero-gas line-scanned measurement over 2000 s through a silicon waveguide (see Section 7.3.3 for details). In the case of VLMS, we observe a large initial concentration offset (due to spectral baseline artefacts), followed by a concentration drift over time (corresponding to the etalon drifts). BSLD is capable of removing the initial offset to improve accuracy, but the static nature of subtraction prevents any long-term correction of
baseline drifts resulting in a false concentration deviation. DEF-R eliminates both the initial and long-term inaccuracies, and also tightens the points to enhance short-term precision. The associated Allan-deviation demonstrating Gaussian-noise performance up to $10^3$ seconds, and a short-term precision improvement by $\sim 2\times$.

Figure A5.6 shows a measurement of real time CH$_4$ which again compares DEF-R to BSLD and VLMS using the data presented in Section 7.3.3. The black dashed line in each case corresponds to the FSOPS measurement (utilizing 10 cm path length, in contrast to the $\sim 2.5$ cm optical path length of the SiPhCS). Clear accuracy benefit of DEF-R is demonstrated; in the case of VLMS, initial accuracy deviation is caused by absorption-like etalons, which produce a measurement offset, while for BSLD, initial accuracy is correct due to zero-gas background subtraction, but etalon drifts over time yield poor accuracy for longer measurement intervals. In contrast to the first two techniques, DEF-R is capable of removing the initial offset and maintaining long-term accuracy ($> 10^3$ s). Furthermore, the correlation between the free-space sensor and SiPh chip sensor is plotted in Figure A5.6, yielding reasonable optical confinement factors only in the case where DEF-R is employed (25.2 \%, in good agreement with numerical mode-profile simulations).
References

Appendix A6: SiPhCS test procedures/protocols

In conjunction with the silicon photonics team at IBM Watson, milestones for sensor performance will be quantified through precision [$\sigma_{\text{prec}}$], instrument stability-time [$\tau_{\text{stab}}$] and zero-drift [ZDRFT] defined in Section 3.2, and are empirically analyzed by assessing the SiPhCS with respect to the FSOPS, and cavity ring-down spectrometer (Picarro G2301) [CRDS-G2301]. Absolute sensor accuracy [ACCR] is quantified via five-step CH$_4$ concentration variation using a programmable dilution system, and SiPhCS/FSOPS/CRDS-G2301 signal comparison.

Extreme precision of the CRDS-G2301 system causes signal saturation at 20 ppmv CH$_4$; therefore, a dilution system is utilized for concentration and signal reduction and scaled accordingly for ACCR evaluation. We define the Concentration Retrieval Methods [CRM] to encompass spectral fitting that includes (but is not limited to) VLMS/BSLD/DEF-R/dVLMS algorithms. Testing across a variety of experimental conditions will be conducted, with associated pass/fail evaluation metrics [EM]:

(a) [EM01] $\sigma_{\text{prec}} < 100 \text{ ppmv} \cdot \text{Hz}^{-1/2}$ (SiPhCS)

(b) [EM02] $\tau_{\text{stab}} > 100 \text{ s}$ (SiPhCS)

(c) [EM03] ZDRFT $< 10 \text{ ppmv} \cdot \text{Hz}^{-1/2}$ at $10^3 \text{ s}$ (SiPhCS)

(d) [EM04] ACCR$_i < 3 \cdot (\sigma_{\text{prec}} \text{ SiPhCS})$ for CH$_4$ step $i = 1$ to $5$ using CRM

The itemized list of laboratory equipment for completion of the test matrix is given below.

[I01] SiPhCS characterization setup

[I01a] Microscope objective (5× magnification)

[I01b] Fiber optic illuminator

[I01c] CMOS visible color camera

[I01d] InGaAs short-wave infrared camera ($D^* > 5 \times 10^{12} \text{ cm} \cdot \text{Hz}^{1/2}/\text{W}$) (optional)
[I01e] X/Y/Z piezo actuator stages (< 50 nm resolution, ×3)

[I01f] Associated optical components (AR-coated lenses, diffusors, beamsplitters, dichroic mirrors, diaphragms)

[I01g] Associated optical mechanical elements

[I01h] Thermoelectric cooler for SiPhCS temperature control

[I02] Sealed environmental chamber with flow feedthrough for gas distribution

[I03] Gas handling system for N₂ purge, CH₄ flush

[I03a] Pure N₂ for purge and dilution

[I03b] 2.5 % CH₄ for flush and dilution

[I03c] Gas dilution system for EM04 ACCR metric testing

[I03d] Pressure controller and flow meter (upstream at chamber input port)

[I03b] Associated flow elements (tubing for gas thermalization, ball/needle valves, flow meters, vacuum pump)

[I04] Sensor systems

[I04a] SiPhCS (in packaged/unpackaged form)

[I04b] FSOPS for EM04 ACCR testing

[I05] Laser source components

[I05a] DFB-laser diode/integrated on-chip external cavity laser

[I05b] Laser current driver

[I05c] Thermoelectric controller

[I06] Detectors

[I06a] InGaAs amplified photo-receiver (×2 for SiPhCS and FSOPS)

[I06b] Laser power monitor photodiode
[I07] Associated fiber optical components (fibers, connectors, polarization controllers, splitters, isolators)

[I08] Benchtop equipment (programmable power supplies, oscilloscope, multi-meters, function generators)

[I09] Data acquisition card (×3 channels for SiPhCS, FSOPS, CRDS-G2301)

[I10] CPU/MCU for data analysis

[I11] Spectral recovery algorithms (VLMS, DEF-R, BSLD, dVLMS)

[I12] Dew-point generator for relative humidity control
Appendix A7: DM-FRS instrument operation

A block schematic of components in the transportable DM-FRS prototype is shown in Figure A7.1, which includes the main functional interaction between hardware (optical and flow components), signal generation and recovery, data acquisition, and software control and analysis. Figure A7.2 details the flow control and gas handling components of the instrument. Specific settings of the components with item numbering shown in Figures A7.1 and A7.2 (gray notation) are given in Table A7.1. In what follows, we provide a general outline on the operation and optimization of the instrument in preparation for DM-FRS measurements using a number of predefined procedures [PX], defined in the next Section.

A7.1 Operating procedures

P1  Turn-on procedure

1A  Turn on main power (toggle switch) [item (a1)]

1B  Turn on laser TEC controller output [item (a8), I01] ($T_{set} = 12.5 \, ^\circ C$)

1C  Adjust pre-vacuum needle valve to desired flow conditions (100 sccm nominal)

1D  Pre-check before laser operation:

   i.  pressure controller [item (a4), I05] stabilized at 80 torr

   ii. flow meter [item (a5), I04] stabilized near 100 sccm

   iii. detector TEC ‘lock’ LED indicator green [item (a9)]

   iv.  laser TEC controller [item (a8), I01] stabilized at 12.5 \, ^\circ C, with 1.70 V and 1.21 A TEC output

   v.  all fans (H100i and solenoid cooling fan) are running (Figure A7.9)

1E  Turn on QCL500 laser driver [item (b4), I02] main power (toggle switch)

1F  Turn on QCL500 laser output [item (b4), I02] (toggle switch)
1G Check laser operation:
   i. voltmeter readout: $3.831 \text{ V (383.1 mA laser current)}$
   ii. laser TEC controller [item (a8), I01] at $2.24 \text{ V, 1.70 A TEC output}$

1H Load ziControl.vi, go to “Oscilloscope” tab

1I Check optical alignment:
   i. signal input 1 (FRS detector) $= 320 \text{ mV}$ (at $50 \Omega$ input)
   ii. signal input 2 (ref. detector) $\approx 800 \text{ mV}$ (at $50 \Omega$ input)

1J Run LabVIEW interface for instrument control (Figures A7.6 and A7.7):
   desktop\frs\control\isotope_meas v1.8

1K Select measurement type: (a) line scanning, (b) line-locking, (c) multiplexing

1L Select isotope: (a) Major, (b) Minor

1M Execute measurement (see Procedure P4)

P2 Turn-off procedure

2A Load ziControl.vi, turn off modulation output

2B Turn off QCL500 laser output [item (b4), I02] (toggle switch)

2C Turn off QCL500 laser driver [item (b4), I02] main power (toggle switch)

2D Turn off laser TEC controller output [item (a8), I01]

2E Turn off main power (toggle switch) [item (a1)]

P3 Optical alignment

3A Apply beam-blocks in front of detectors to avoid facet damage

3B Continue from Procedure P1-1G

3C Coarse alignment onto P1 (Figure A7.4(b)), passing through L1

3D load ziControl.vi, go to “Oscilloscope” tab using signal input 1 (FRS signal detector)
3E  Align FRS path (through multi-pass cell)

i.  rotate P1 to the fully open state such that the beam is easily visible on the thermal card

ii. align input beam through upper-half of CaF$_2$ wedge at a downward angle of 4° from horizontal, and adjust M3 and laser steering mirrors such that the beam comes out at the upper-half of CaF$_2$ exit wedge

iii. initially open P2 for maximum transmission; align beam along M4, M5, M6, and M7

iv.  coarse alignment of beam through L2 onto FRS detector

v.  fully cross P2 such that reflected beam impinges upon block (B1)

vi.  unblock FRS detector, open P2 slightly and bring beam into alignment on detector using HF2LI oscilloscope from P3-3D [item (b5), I07]

3F  Go to “Oscilloscope” tab using signal input 2 (ref. detector [item (c4), I07])

3G  Align reference path:

i.  rotate P1 to completely reflect beam

ii.  apply tilt to P1 such that beam is incident upon M1

iii. adjust M1 alignment such that beam is incident upon M2

iv.  adjust M2 (parabolic mirror) to focus coarsely upon facet

v.  remove block, bring beam into alignment with detector. If saturation occurs, rotate P1 to reduce power. If P1 cannot be rotated for further power reduction, misalign M2 to operate under detector saturation

P4  LabVIEW operation
4A Execute LabVIEW interface for instrument control (Figures A7.6 and A7.7):

```
desktop\frs_control\isotope_meas v1.8
```

4B Select measurement type: (1) line measurement, (2) line-locking, (3) multiplexing using selector in [6b.1]

4C Line measurement (Figure A7.6(a)):

i. select major/minor isotope on top edge of interface [6b.2]

ii. in main line-scan tab [6a.1], select voltage bias (line-scanning) parameters [6a.2] (use values in Figure A7.6(a) as default)

iii. select time-per scan point [6a.3]; note that this should be larger than the inverse detection bandwidth that is used in the HF2LI [107]

iv. execute measurement using top right circular toggle [6b.3]

v. when scan reaches completion [6a.4], or user presses ‘STOP SCAN” [6a.4], a pop-up interface queries user for file name and save location

4D Line-locking (Figure A7.6(b))

i. select major/minor isotope on top edge of interface [6b.2]

ii. in line-locking tab [6b.4], select line-scanning parameters [6b.5]

iii. select measurement time constant [6b.6]

iv. select time per point (> inverse bandwidth of measurement) and number of scan points [6b.7]

v. select lock threshold [6b.8], the WMS trough limit such that the null occurs in the following monotonically increasing spectral segment

vi. execute measurement using top right circular toggle [6b.3]
vi. once lock success indicator LEDs illuminate, adjust PID parameters [6b.10] in real-time to minimize residuals in 3f1 WMS signal [6b.11]

vii. when scan reaches completion, or user presses “Stop and Save” [6b.12], a pop-up queries user for file name and save location

4E Multiplexing (Figure A7.7, code layout shown in Figure A7.8)

i. select start biases for both $^{14}\text{NO}$ [7a.1] and $^{15}\text{NO}$ [7a.2]

ii. select time per point [7a.3] (> inverse bandwidth of measurement) and number of scan points [7a.4] per line-switch interval

iii. select lock threshold [7a.5] for both isotopes

iv. execute measurement using top right circular toggle [6b.3]

v. program will consecutively lock to $^{14}\text{NO}$ and $^{15}\text{NO}$ to determine preliminary line-centers [7a.6] for fast switching

vi. once lock success indicator LEDs illuminate, adjust PID parameters [7a.7] in real-time to minimize switch stabilization time [7a.8] [7a.9]

vii. manually switch between isotopes as required for switch speed diagnostics [7a.10]

viii. DM-FRS line switch signal viewed in “line-switch signal” tab [7a.11]

ix. at scan completion, user presses “Stop” [7a.12] to save file

P5 Reference cell refill (Figure A7.3)

5A Remove reference gas cell [item (d5)] from the mount (Figure A7.3(b))

5B Using quick-connectors, connect the reference cell to the gas handling manifold primary inlet (ensure a ball valve is present for flow shut-off)
5C Connect the 2.5 % $^{14}$NO, 1.5 % $^{15}$NO reference gas lecture bottle (make sure ball valve V1 is present) to manifold secondary inlet, and evacuate manifold

5D Close V1 and V2 (at vacuum after P5-5C) prior to gas handling

5E With V3 closed, open V4 to release NO into steel tubing. Close V4, open V3

5F If pressure transducer reads > 760 torr, open metering valve and V2 to vacuum outlet to maintain sub-atmospheric pressure in manifold

5G Open V1 to equilibrate manifold and reference cell pressure

5H Slowly adjust vacuum outlet metering valve to decrease the manifold (and reference cell) pressure to 80 torr

5I Close primary inlet V1 to trap gas in reference cell, and seal cell (take caution to not over tighten the screw seal due to delicate glass threading)

5J Open vacuum outlet V2 and evacuate gas in manifold and associated tubing

5K Disconnect cell and replace in setup; during the first hours of replacement, a fast initial decay of NO is normal. Gas replacement every ~ 2 months is expected

P6 Analyzer angle optimization

6A Continue from P1-1G or P3-3E

6B Load ziControl.vi for HF2LI control and go to “Save” tab (top edge)

6C Manually load either:

desktop\zi_settings\2. zi_major_80torr_100Hz.zicfg

desktop\zi_settings\3. zi_minor_80torr_100Hz.zicfg

depending on isotopologue of interest

6D Load LabVIEW interface desktop\ziExample-HF2-Noise.vi (calculates the bandwidth normalized total noise based on FFT of the input sample data)
6E Block FRS detector to measure detection noise (NEP (in nV), or $\sigma_{NEP} \text{[nV}\cdot\text{Hz}^{-1/2}]$) using Demodulator 2 (+ sideband). Demodulator 3 (- sideband) should give very similar results; it is therefore sufficient to use single-sideband noise.

6F Unblock FRS detector and rotate P2 (analyzer) such that the FRS detector is below saturation (~1.5 V using 50 Ω input impedance). This ensures the noise is dominated by laser intensity fluctuations.

6G Using the “Oscilloscope” tab, measure voltage on FRS detector ($V_{\text{sig}} \text{[mV]}$).

6H Measure single-sideband intensity noise using Demodulator 2, $\sigma_{\text{int}} \text{[nV}\cdot\text{Hz}^{-1/2}]$.

6I Calculate the laser RIN, given by:

$$\bar{\sigma}_{RIN} = \frac{\sigma_{\text{int}} \text{[nV}\cdot\text{Hz}^{-1/2}]}{V_{\text{sig}} \text{[mV]}} \quad \text{(A7.1)}$$

6J Calculate the power $P_{\text{opt}}$ at optimum analyzer uncrossing (Equation 3.21):

$$P_{\text{opt}} \text{[nV]} = \frac{\sigma_{NEP} \text{[nV}\cdot\text{Hz}^{-1/2}]}{\bar{\sigma}_{RIN} \text{[Hz}^{-1/2}]} \quad \text{(A7.2)}$$

Examples of nominal values are $\bar{\sigma}_{RIN} = 2.5 \times 10^{-7} \text{ Hz}^{-1/2}$ and $\sigma_{NEP} = 80 \text{ nV}\cdot\text{Hz}^{-1/2}$, which yields $P_{\text{opt}} = 320 \text{ mV}$ (50 Ω input impedance).

6K Adjust P2 angle ($\theta_{\text{opt.}}$) to achieve $P_{\text{opt}}$ on FRS detector.
Appendix A8: List of publications

Journal Publications


Conferences Abstracts

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Patents / Invention Disclosures

Figure 1.1: Common molecules with linestrengths retrieved from the high-resolution transmission molecular absorption (HITRAN) database. The shaded regions indicate strong water absorption lines to be avoided in atmospheric measurements. Molecules studied in this thesis include: CH$_4$, N$_2$O, NO, and O$_2$. 
Figure 1.2: Distributed feedback QCL characterization (for NO detection in Chapter 6). (a) Lasing spectra for various injection currents, demonstrating a tuning range > 2 cm\(^{-1}\). (b) Surface plot of laser center frequency as a function of laser temperature and current. This particular laser (Alpes) targets the Q(3/2) and P(19/2) lines of \(^{15}\text{NO}\) and \(^{14}\text{NO}\) respectively. A nearby \(\text{H}_2\text{O}\) line is also indicated (1842.3 cm\(^{-1}\)).
Figure 1.3: Developmental timeline of Faraday rotation spectroscopy (FRS). Conventional AC-FRS and DC-FRS were initially demonstrated in the 1900s, prior to research in the PULSe Laboratory. Presently, \((\alpha L)_{\text{min}}\) have reached \(10^{-7} \text{ Hz}^{1/2}\) levels, \(\sim 10^2\times\) better than conventional TDLAS systems [24].
Figure 2.1: TDLAS principle. (a) General schematic of tunable direct laser absorption spectroscopy (TDLAS). Monochromatic laser light impinges upon a detector after passing through an unknown (and to be determined) quantity of analyte. The laser is typically ramped via current injection to tune across the absorption transition for spectral fitting and concentration retrieval. (b) Example of a TDLAS spectrum.
Figure 2.2: Lineshape models and linewidth dependence on pressure. (a) At low pressures, linewidths are dominated by inhomogeneous Doppler broadening leading to Gaussian profiles. Significantly beyond the point where $\delta \nu_D = \delta \nu_L$, Lorentzian profiles serve as an accurate approximation. (b) Lineshape calculations for $^{15}$NO Q(3/2) line in the $^2\Pi_{3/2}$ subsystem, showing the lineshape differences between Gaussian (5 Torr), Lorentzian (45 torr) and Voigt (25 torr) profiles.
Figure 2.3: A data acquisition scheme for TDLAS, representing the measurement system used in Section 7.3 for on-chip evanescent field spectroscopy. In this case, two detectors (chip and free-space reference) are simultaneously sampled, and customized MATLAB software is used for baseline normalization and spectral fitting. Concentration retrieval over long-term measurements yields sensor stability results (Section 3.2), and optional functionality include acquisition of raw time-series traces for spectral density analysis.
Figure 2.4: Calculated lineshapes and signal optimization for wavelength modulation spectroscopy (WMS). (a) The inset shows the concept of WMS, whereby the laser wavelength is modulated across an absorption feature for derivative-like spectroscopy. The demodulated signal is dependent upon the modulation depth \( \tilde{\nu}_m \) with \( 2.2 \times \) the HWHM maximizing the \( 2f \) harmonic signal. (b) Lineshape examples at different modulation depths for the \(^{15}\text{NO} \, Q(3/2)\) line. Beyond the optimum modulation depth, the \( 2f \) lines undergo broadening with noticeable signal degradation, as plotted in (a).
Figure 2.5: The correspondence between absorption and dispersion spectra through the Kramers-Kronig relation. Lineshapes are numerically calculated assuming 1 % CH₄ of the R4 line in the overtone 2ν₃ band.
Figure 2.6: General schematic of a Faraday rotation spectrometer. Incoming light (linearly polarized) can be decomposed into LCP/RCP light, and induced MCB causes polarization rotation (in proportion to the paramagnetic species concentration). Conversion back to optical intensity is accomplished using a second polarizer, called an analyzer, and the resulting FRS signal is measured on the photodiode for demodulation/signal processing.
Figure 2.7: Faraday rotation spectroscopy (FRS) overview. (a) Zeeman split degenerate $\Delta m_J$ transitions for a fixed angular momentum $J$ quantum number is magnetically induced. Each $\Delta m_J = \pm 1$ corresponds to right/left circularly polarized light, and the energy perturbation induces spectral shifts in the absorption and dispersion spectra. (b) For each possible $\Delta m_J = \pm 1$ transition, the associated $g$-factors [23] are used to calculate the Zeeman split magnitude. The resulting Faraday rotation signal (angle) is proportional to the difference in the dispersion spectra, and plotted by a solid black line.
Figure 2.8: Faraday rotation angle calculation for the P, Q, and R branches of $^{14}$NO (includes both $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ subsystems). The calculations were performed at 35 torr with 100 G magnetic field, temperature of 296 K and optical path length of 15 cm. Note the strong FRS angles despite the weakly absorbing Q-branch transitions, which are due to constructive addition of each $\Delta m_J$ transition from identical $g$-factors [23, 24].
Figure 2.9: Wavelength modulation is applied similarly to FRS angle spectra, resulting in a maximum $2f_L$ modulation depth similar to that obtained for WMS. This is particularly useful in the case of balanced-detection DC-FRS, whereby the laser modulation eliminates reduces $1/f$ noise contributions and balanced-detection reduces baseline fringing which is common-mode to both circular polarizations. The inset shows a resulting $2f$ modulation spectrum (red) compared to the original signal angle (blue).
Figure 2.10: Application of sample modulation (magnetic field modulation, or AC-FRS) for baseline removal. (a) The raw DC-FRS signal is modulated in the presence of an oscillating field (black dashed curves), whereas the baseline due to non-paramagnetic contributions does not undergo oscillation. Demodulation therefore retains only the FRS signal of interest, allowing true zero-baseline measurements. (b) Calculation of optimum magnetic field at different pressures for the $^{15}$NO $Q(3/2)$ line. Higher pressures increase the linewidth due to homogeneous collisional broadening, resulting in a greater field required to achieve optimum splitting (occurs at approximately the FWHM).
Figure 2.11: Dual-modulation FRS (DM-FRS) numerical calculations by modulation of both magnetic field and laser wavelength. (a) Optimization of laser modulation depth for range of pressures (at optimum magnetic field for signal maximization). Signals were modeled with $f_M$ magnetic field demodulation and $2f_L$ wavelength demodulation. (b) Examples of DM-FRS spectra compared to AC-FRS. The maximum signal achievable using DM-FRS is 59.5% of AC-FRS; however, the ability to reduce $1/f$ noise contributions render DM-FRS techniques significantly more sensitive.
Figure 2.12: Functional map of FRS techniques. Orange boxes are methods studies in this thesis.

Towards the left, the techniques use AC-FRS (true zero-baseline) for applications where tight tolerances on both precision and accuracy are required. Towards the right of the chart are DC-FRS methods that utilize some form of baseline suppression (typically electronic via balanced-detection) along with wavelength modulation and nearly-crossed polarizers (hybrid-FRS) for SNR enhancement.
Figure 3.1: Allan deviation analysis of simulated noise. (a) simulated Gaussian noise (red curve), Gaussian noise with linear drift (green), and 1/f noise (blue). (b) Corresponding Allan deviation calculations. Gaussian noise follows Hz^{-1/2} averaging improvement, and the linear drift follows the same trend until the drift magnitude overcomes the averaging precision. 1/f noise converges using the Allan deviation, and has a slope of zero. The inset schematic demonstrates the time series data bins in the σ_{ADV} calculation.
Figure 3.2: Noise analysis for analyzer uncrossing angle optimization. (a) Noise measurements yield $\bar{\sigma}_{\text{RIN}} = 2.19 \times 10^{-7}$ Hz$^{-1/2}$ and $\sigma_{\text{NEP}} = 1.25 \times 10^{-12}$ W·Hz$^{-1/2}$ respectively. The intersection of intensity- and detector-noise occurs at $P_{\text{sig}} = 5.7$ μW, corresponding to $\theta_{\text{opt}} = 1.71$° for an analyzer power $P_0 = 6.4$ mW. (b) Normalized signal-to-noise ratio (SNR) curves for each individual noise contribution, along with the total SNR (black curve). The SNR curves are normalized to the maximum SNR of the black curve.
Figure 4.1: Optical layout of the FRS setup in this study. The DFB laser output is attenuated using a NPP (NPP1), and polarized by the GTP prior to entering the MPC. The signal beam exiting the MPC passes through a WP and is detected by the BPD. NPP2 attenuates the reference beam to prevent optical saturation of the reference-photodiode. Abbreviations: DFB: distributed-feedback, GTP: Glan-Thompson polarizer, MPC: multi-pass cell, WP: Wollaston prism, NPP: nano-particle polarizer, BPD: balanced-photodetector.
Figure 4.2: Spectroscopy of $^3P_1(1)$ line and surrounding baseline. 1 °C change corresponds to 1.33 cm$^{-1}$. $2f_L$ harmonic DC-FRS signal with optimized modulation depth. The 36 °C to 37 °C temperature range is shown in the inset, and a $^{16}O^{18}O$ isotopic line is visible at 36.6 °C.
Figure 4.3: Detection limits of BD-FRS measured from baseline noise. (a) Noise characterization with increasing $P_0$. Intensity-noise increases linearly, crossing the shot-noise curve at $P_0 \approx 1.4$ mW, after which negligible SNR improvement occurs. (b) SNR increases rapidly for the low-power shot-noise regime, and increases less rapidly as intensity-dominated regime is approached. Detector saturation occurs at $P_0 = 1.5$ mW for a 2:1 reference-to-signal split ratio.
Figure 4.4: Principle of hybrid-FRS. (a) Malus’ law for the signal- and reference-photodiodes, with a high-power (red curve, hybrid-FRS) and low-power (black curve, 45º method) case. The low-power case ($P_{0,B}$) can be used for conventional balanced-detection when both signal and reference branches are below detector saturation. (b) In conventional balanced-detection using low-power, signal enhancement (black arrow) is achieved by increasing $P_{0,C}$ to $P_{0,B}$ (detector saturation, or intensity- and shot-noise crossover point). In hybrid-FRS, $P_{0,C}$ increases to $P_{0,A}$ (red arrow) with decreasing $\theta$ at constant $P_{\text{sig}}$ (thus constant noise). Signal $\sim 1/\theta$ for small $\theta$, hence SNR $\sim 1/\theta \sim P_0^{1/2}$. Hybrid-FRS avoids saturation and intensity-noise limitations by moving the operating point parallel rather than perpendicular to the $\theta$-axis.
Figure 4.5: Hybrid-FRS and $90^\circ$ method SNR comparison. (a) SNR for $90^\circ$ method at $P_0 = 8$ mW. For small $\theta$, noise $\sim \theta^2$ and signal $\sim \theta$. (b) SNR for hybrid-FRS at the same $P_0$. CMRR suppression of intensity-noise gives significant SNR increase. $V^{90^\circ}$ is normalized to the $V^{\text{hybrid}}$ maximum, $\sigma^{\text{hybrid}}$ is normalized to the $\sigma^{90^\circ}$ maximum, and $\text{SNR}^{90^\circ}$ is normalized to maximum of $\text{SNR}^{\text{hybrid}}$. (c) Multiple SNR plots for $P_0 = 1$ mW, 3 mW, 8 mW and 15 mW. From the curves it is clear that $\text{SNR}^{\text{hybrid}} \geq \text{SNR}^{90^\circ}$. The shaded red regions indicate the disallowed operating regime due to the limitation of detector saturation.
Figure 4.6: Minimum and maximum power limits for hybrid-FRS. (a) Minimum power constraint. Optimum crossing angle $\theta_{opt}$ vs. $P_0$ on the balanced-photodetector. For $P_0 < P_{0,\text{min}} = 1.5 \text{ mW}$ no SNR local maximum exists, and conventional balanced-detection is superior. The red circle is our experimental operating point. (b) Maximum power constraint. Finite polarization extinction ratio will cause light to leak through the nearly-crossed GTP and WP for large $P_0$ and small $\theta$. The leakage optical power introduces more noise than would otherwise be present. Each curve corresponds to traveling along a line of $P_{\text{sig}} = 160 \mu\text{W}$ in Figure 4.5(e), and SNR values are normalized to the maximum SNR at $P_0$ of $10^5 \text{ mW}$ calculated for the ideal polarizers.
Figure 4.7: Hybrid-FRS parameter space and experimental results. (a) Operating regime for hybrid-FRS, where $\theta$ is the crossing angle between the WP and GTP and $P_0$ is the incident power upon the balanced-detector. The shot-noise operating regime is indicated by dashed lines. Each curve corresponds to a line of constant $P_{\text{sig}}$; $P_{\text{sig}} < 20 \mu\text{W}$ in the detector-noise regime, $P_{\text{sig}} > 500 \mu\text{W}$ for detector saturation, and $P_{\text{sig}} > 660 \mu\text{W}$ in intensity-noise regime. The red line defines the power limit of the DFB laser after accounting for optical losses of the system. (b) Calculated signals with measurements superimposed (black points), which lie upon a line of constant $P_{\text{sig}} = 160 \mu\text{W}$ (dashed curve). The inset shows four measured $2f_L$ DC-FRS signals at varying $\theta$. (c) Calculated SNR for hybrid-FRS parameter space. Black points indicate measurements along $P_{\text{sig}} = 160 \mu\text{W}$. An MDL of 0.6 ppmv$\cdot$Hz$^{-1/2}$ is achieved at $\theta = 8.3^\circ$ ($\theta_{\text{opt.}} = 7.5^\circ$), which is 1.4× the shot-noise limit. The inset shows a comparison of measured detection limits and those calculated from the SNR at $P_{\text{sig}} = 160 \mu\text{W}$ (measurement error is indicated by error bars).
Figure 4.8: Summary comparison of DC-FRS methods. Hybrid-FRS uses a combination of both the 45° method (right, blue) and 90° method (left, orange), through concurrent optimization of uncrossing angle and balanced-detection.
Figure 5.1: Spectral schematic of DM-FRS signal frequencies. Laser modulation occurs at $f_L = 50$ kHz, resulting in wavelength modulated carrier frequencies at $N \cdot f_L$ and a corresponding decrease in $1/f$ noise. Further magnetic field modulation ($f_M = 100$ Hz) results in generation of sum and difference frequency sidebands $N \cdot f_L \pm f_M$ (scales in schematic are exaggerated for clarity). In DM-FRS the demodulation bandwidth $\Delta f$ must be considered around each sideband, resulting in $2 \cdot \Delta f$ total noise bandwidth.
Figure 5.2: Integrated sensor schematic. (a) Dual-modulation Faraday rotation spectrometer for NO isotopic analysis. The system is optimized for minor isotope sensitivity ($^{15}$NO Q(3/2) transition, 1842.763 cm$^{-1}$) with a detection limit of 0.36 ppbv·Hz$^{-1/2}$ using a triple-pass gas cell (45 cm optical path length). A reference gas cell (~ 1.5% $^{15}$NO, and ~ 2.5% $^{14}$NO in N$_2$) is utilized as wavelength reference for line-locking. (b) Photograph of spectrometer housed in 12U 19” rack, integrated with a breath sampler. (c) Chemical system for nitrate/nitrite conversion to NO via heated acidic vanadium(III).
Figure 5.3: Noise spectrum about carrier demodulation frequency (2×\(f_L\) = 100 kHz). High frequency field-modulation (\(f_M = 1.554\) kHz) increases electromagnetic interference and transfers wavelength-modulated etalon noise into the DM-FRS signal. This is visible on the right inset, which demonstrates a noise peak at \(f_M\). At low frequency field-modulation (\(f_M = 100\) Hz), EMI is substantially reduced as shown in a separate measurement in the left inset, thus enabling low-noise baseline-free performance.
Figure 5.4: Spectral acquisition and line-switching procedure. (a) Spectra of $^{14}$NO P(19/2)e (blue) and $^{15}$NO Q(3/2) (red) transitions from a G-Cal permeation device. Quasi-simultaneous isotopic analysis via line switching can be performed by alternately locking to the 3/1 WMS zero-crossing each isotope. (b) Zero-gas spectrum using cylinder nitrogen demonstrating near-zero baseline spectra. (c) Measurement of $^{15}$NO spectra using non-certified NO in N$_2$ mixture. Spectral modeling gives $^{15}$NO concentration of 4.56 ppbv, corresponding to 1.24 ppmv $^{14}$NO at natural abundance.
Figure 5.5: Allan deviation stability analysis. (a) Measurement of pure N$_2$ by line-locking to the zero-crossing of the $^{15}$NO 3$f_L$ WMS spectrum. Slight baseline deviation is visible over the ~ 1 hr measurement, indicating EMI influence. (b) Linear baseline correction every ~ 500 s is necessary for liquid sample analysis and similar correction is applied here to demonstrate a practical measurement scenario. (c) Allan deviation of the baseline-corrected measurement, demonstrating white-noise performance up to ~ 1000 s at 2.8× the shot-noise limit. The inset is a typical $^{15}$NO 3$f_L$ WMS spectra used for line-locking.
Figure 5.6: Quasi-simultaneous isotope measurement of 1.24 ppmv $^{14}$NO in N$_2$ mixture diluted using pure N$_2$. Line-switching occurs every 50 s, and polynomial interpolation of $^{14}$NO is used to calculate isotopic ratios (using Equation 5.10, top graph), demonstrating fractionation-free sensor performance. Gray regions denote $^{14}$NO measurements and white denotes $^{15}$NO. A concentration-normalized precision of $\Delta(\delta^{15}N) = 120 \text{‰} \cdot \text{ppmv} \cdot \text{Hz}^{-1/2}$ is determined from a typical measurement segment.
Figure 5.7: Calibration experiments performed using a G-Cal permeation device (Vici Metronics). Two concentrations are used (corresponding to dual flow-rates of 75 sccm for ~ 1 ppmv and 10 sccm for ~ 10 ppmv $^{14}$NO), demonstrating ratiometric analysis independent of sample concentration and flow. Analysis of permil variations demonstrates ratiometric fluctuations of $\sigma_{\permil} = 13.4 \permil \cdot \text{Hz}^{-1/2}$, corresponding to $\sigma_{\text{meas}} = (\sigma_{\permil} \cdot 10^{-3}) \cdot (\Delta [^{15}\text{N}]^R) = 281 \text{ nV} \cdot \text{Hz}^{-1/2}$, approximately consistent with noise in Figure 5.5(c).
Figure 5.8: Precision of time-multiplexed measurements. (a) Real-time measurement of 5 μmol injection of KNO$_3$ (500 μL of 10 mM solution) via line-switching every 15 s at 50 % duty cycle for each isotope. Blue, red and black segments correspond to $^{[14}\overset{\text{N}}{\text{N}}]$s, $^{[15}\overset{\text{N}}{\text{N}}]$s and interpolated $^{[14}\overset{\text{N}}{\text{N}}]$s respectively. The resulting peak has FWHM of ~100 s, obtained in a flow-rate of 64 sccm, and the inset shows three more repeat injections (only $^{[15}\overset{\text{N}}{\text{N}}]$s shown for clarity). Ratiometric curves derived from the quotient of $^{[15}\overset{\text{N}}{\text{N}}]_s(t)$ and interpolated $^{[14}\overset{\text{N}}{\text{N}}]_s$ are plotted above. Clear time dependent curvature is apparent, with maxima occurring at the measurement peak. (b) Calculation of ratiometric precision vs. sample size, using data obtained from (a). Generally, samples $>1$ μmol NO$_3$ are required to ensure sub-permil precision over the peak span.
Figure 5.9: Demonstration of the necessity of line-switching. (a) Separate analysis for $^{14}$NO, $^{15}$NO using a 5 μmol NO$_3$ injection. Ratiometric analysis using alignment of 10 % rise times result in a monotonically increasing fractionation curve and total isotopic ratio of 200.5 ‰ ± 0.18 ‰. Precision is estimated assuming true simultaneous measurement. (b) Similar experiment using line-switching (25 s switching time). Note that using $\sigma_\% = 13.4 \ \%_0 \cdot Hz^{1/2}$ from the calibration measurement in Figure 5.7, we estimate the measurement precision to be $\Delta(\delta^{15}N)_{\text{est.}} = 0.30 \ %_0$, in reasonable agreement with the calculated result of 0.27 ‰.
Figure 5.10: Sequential measurement of ~ 70 nmol reference and sample during a 1000 s measurement window. Note the baseline noise, visible due to ~ 70× signal reduction. Each peak duration is 500 s at a 103 sccm flow-rate. Baseline correction is performed for both isotopes after $^{14}$N interpolation, as the $[^{15}\text{N}]$ variation between sample and reference is similar to baseline variations. For the sample peak, we measure $\delta^{15}\text{N}_{\text{S/R}} = 43.8 \, \text{%} \pm 28.2 \, \text{%}$, which is within one standard deviation of the expected $\delta^{15}\text{N}_{\text{S/R}} = 52.3 \, \text{%}$. 
Figure 5.11: Time-multiplexed measurements in conjunction with gas-trapping. (a) Shows gas trapping of NO from the permeation device. Gas cell leakage (~ 0.05 Torr/s) during the trap period causes signal degradation due to line broadening. Characterization of this decay is shown as the dashed black ($^{15}$NO) and gray ($^{14}$NO) curves, and a relative decay of the measurement to calculated signals may be attributed to loss of NO. (b) Gas trapping of NO from chemical production of NO from NO$_3$-(aq), showing significantly larger relative loss of $^{14}$NO. Normalized NO signals (corrected for leakage) are shown in the inset.
Figure 5.12: Demonstration of ratiometric linearity. (a) Injections of known isotopically labeled references spanning 5 ‰ to 5536 ‰. Plotted in (b) are multiple labeled reference injections (4 points per calculated δ¹⁵N value, and the plot demonstrates excellent linearity (R² = 0.999) with measured δ¹⁵N offset consistent with fractionation observed in Figure 5.8(a). The inset shows the real-time fractionation curve of the most enriched reference injection (δ¹⁵Ncalc = 5536 ‰), demonstrating results similar to those in Section 5.5.4.
Figure 6.1: Schematic of second-generation dDM-FRS prototype integrated with chemistry flow system for nitrate-to-NO conversion using heated acidic vanadium(III). Improvements to the second-generation sensor include lower B-field modulation frequency \( f_M = 100 \text{ Hz} \) and introduction of AR-coated wire grid polarizers to eliminate crosstalk between the ordinary/extraordinary polarizations. An NO reference gas diluted with pure N\(_2\) from a cylinder is used as a known stable isotope reference.
Figure 6.2: Noise analysis for SNR optimization. (a) Measurement of detector and laser noise showing a RIN of $2.89 \times 10^{-7}$ Hz$^{-1/2}$ and NEP = $1.15 \times 10^{-12}$ W·Hz$^{-1/2}$. SNR optimization occurs at the intersection of laser intensity and detector noise, resulting in a signal power $P_{\text{sig}} = 3.81$ µW for an incident analyzer power of $P_0 = 2.0$ mW. (b) Graphical calculation of the analyzer uncrossing angle $\theta_{\text{opt.}} = 2.5^\circ$ at maximum SNR.
Figure 6.3: Spectral acquisition and sensor stability. (a) Measurement of the $^{15}$NO Q(3/2) transition at $\Delta f = 1$ Hz ENBW per point, showing a SNR of $59.4$ Hz$^{-1/2}$ and minimum detection limit of $3.1$ ppbv·Hz$^{-1/2}$. The graph on the top (ambient air) demonstrates the baseline-free nature of the DM-FRS measurement. (b) Allan deviation stability of zero-gas in line-locked mode demonstrating precision at $1.9 \times$ the shot-noise limit, and is Gaussian-noise limited up to $\sim 300$ s. The inset shows the time series of the raw data.
Figure 6.4: Optical subtraction and ratiometric precision. (a) Line-locked measurement of $^{15}$NO from a certified gas cylinder of 50 ppmv $^{14}$NO. Sample, reference, and optical difference are measured sequentially, yielding true $^{15}$CMRR$_{true} = 19.2$ dB. (b) Long-term differential stability of cylinder NO (50 ppmv $^{14}$NO) yielding sub-permil precision at $> 200$ s integration times. For the practical measurement case of μmol level NO, sample injections, $^{14}$NO concentrations are expected to reach $\sim 200$ ppmv, resulting in precision well within sub-permil range for peaks of FWHM $> 100$ s (achievable at reasonable flow rates of $\sim 100$ sccm).
Figure 6.5: Line-switched (50 s intervals) sequential measurement of sample, reference and optical difference signals, used in determination of CMRR for each isotope.
Figure 6.6: Three sequential line-switch measurements of sample (dark blue and red), reference (faded blue and red), and optical subtraction (dashed) superimposed upon a normalized time scale. Optical differences $^{14}\tilde{\eta}(t)$ and $^{15}\tilde{\eta}(t)$ are obtained by flowing identical 50 ppmv $^{14}$NO through sample and reference cells. The resulting permil ratio is shown in the top graph, which is within the expected deviation from null, with standard deviations consistent with noise analysis in Figure 6.4.
Figure 6.7: A five-step dilution process of 50 ppmv cylinder $^{14}$NO, with both the expected signal amplitude ($[^{15}\text{N}]_R$ in blue) and measured optical difference plotted ($^{15}\tilde{\eta}(t)$ in red). $\delta^{15}\text{N}(t)$ is calculated (top graph) from Equation 6.7. Using the $^{14}$NO concentration at each dilution step, the standard deviation is in excellent agreement with stability analysis in Section 6.4.2. In addition, the calculation of $\delta^{15}\text{N}(t)$ demonstrates ratiometric null, independent of sample size indicating fractionation-free dDM-FRS sensor performance.
Figure 6.8: Summary of ratiometric methods devised in Chapters 5 and 6. (a) Direct NO ratiometry via measurement of sample $^{14}\text{N}$S and $^{15}\text{N}$S signals, after a calibration procedure that quantifies a stable isotope standard ($^{14}\text{N}$R and $^{15}\text{N}$R). In this direct scheme, four measurements (two, if using line-switched operation) are required. (b) Differential ratiometry with active dilution tracking ($^{14}\text{N}$R, shown in gray) suppresses the total measured differential signal $^{14}\eta(t)$, such that $\delta^{15}\text{N}(t)$ can be calculated based on measurement of $^{15}\eta(t)$ (we may reasonably assume that $^{15}\text{N}$R of the well-characterized reference standard is known). In dDM-FRS, a single line-switched measurement is required for determination of isotopic ratio.
Figure 7.1: Schematic of WSN implementation using miniature sensors for CH₄ fugitive emissions monitoring. Integrated on-chip spectrometers are deployed in a wide-area mesh network over an oil well pad, and the resulting sensor data is streamed through a remote gateway (concentration readings and leak localization). The outcome of the analytics is used to determine appropriate response.
Figure 7.2: Experimental layout for multi-heterodyne spectroscopy. Two FP-QCLs are separated after collimation, where the ‘signal’ beam passes through a sample (optional bypass for background measurement), and optically heterodyned with the ‘reference’ beam. The resulting RF-HBNs measured by the photodetector are split for measurement with a spectrum analyzer and frequency stabilized using a frequency discriminator. Prior to photodetection, a BS power splits the optical signal for alignment, power, and FTIR measurement. Abbreviations: FM: flip-mirror, M: mirror, BS: beam-splitter.
Figure 7.3: FTIR FP-QCL spectra and RF-HBNs. (a) FP-QCL spectra, showing overlap from ~1175 cm\(^{-1}\) to 1192 cm\(^{-1}\). Both chips are set at 1.03 °C with a single TEC. The top graph shows the SIG probing the R18e N\(_2\)O transition. (b) RF-HBNs from SIG and LO heterodyning in (a). The initial 0\(^{th}\) order HBN is set to 40 MHz, and subsequent HBNs are separated by 80 MHz (160 MHz FSR) due to HBN frequency folding.
Figure 7.4: Spectral density of $0^{th}$ order RF-HBN for both amplitude and frequency. Amplitude noise is shown in orange/yellow (unlocked/locked HBN), demonstrating a strong $1/f$ noise component below 10 kHz ($\text{RIN} = 1.4 \times 10^{-4} \text{ Hz}^{-1/2}$). ASD shown for HBN center frequency (black/gray), demonstrating the efficacy of frequency stabilization of the RF-HBNs using the proposed discrimination scheme.
Figure 7.5: RF-HBN stability improvement using frequency discrimination. (a) 0\textsuperscript{th} order RF-HBN center frequency deviation over ~ 10 min interval with and without frequency stabilization. The inset shows short-term measurement of the same HBN over ~ 35 ms. (b) Allan-deviation calculations show near white-noise performance using the discriminator circuit, yielding frequency precision ~ 10 kHz after ~ 200 s averaging.
Figure 7.6: Multi-heterodyne TDLAS of the R18e N$_2$O transition at ~ 2 torr using the 0$^{th}$ order HBN at 40 MHz. Linear baseline correction is used in conjunction with VLMS fitting to obtain a peak-normalized residual of $2.28 \times 10^{-2}$ per 0.5 ms time bin, resulting in $(aL)_{\text{min}} = 1.3 \times 10^{-3}$ Hz$^{-1/2}$ for a 12.5 Hz ramp.
Figure 7.7: Principle of MH-WMS. Simultaneous modulation of laser injection current for the dual FP-QCL chip converts wavelength modulation in HBN intensity modulation in the presence of an absorption feature. RF-HBN demodulation provides harmonic spectra identical to those expected from WMS.
Figure 7.8: Demonstration of MH-WMS using $2f_L$ harmonic demodulation near optimum ($2.19 \times$ HWHM) modulation depth. Mean normalized residuals show $3.01 \times 10^{-2}$ per 0.5 ms time bin, corresponding to $(aL)_{\text{min}} = 5.0 \times 10^{-4}$ Hz$^{-1/2}$ at 12.5 Hz ramp rate. The gray trace is the raw acquisition of the modulated time-series.
Figure 7.9: Experimental schematic and spectral acquisition. (a) A fiber-coupled DFB laser diode is ramped across the CH$_4$ R4 transition at 6057.08 cm$^{-1}$. The laser output is split with majority power coupled into SiPhCS and minority power directed into the FSOPS (used as an accuracy benchmark). Both sensors are housed within a sealed environmental chamber, and two InGaAs photodiodes are used for simultaneous spectral acquisition from both sensors. The acquisition procedure is detailed in Figure 2.3. (b) Spectral comparison between SiPhCS (using DEF-R) and FSOPS, both with 10 cm physical path length. The absorption ratio is 25.4 $\%$, in good agreement with simulated $\Gamma = 28.3$ $\%$. 
Figure 7.10: Silicon photonic chip sensor (SiPhCS) for CH₄ measurement. (a) SiPhCS “paperclip” 10 cm WG on SOI design for TDLAS. WG engineering provides low-confinement for increased overlap factor. CH₄ molecules in proximity to the WG decrease optical throughput via the Beer-Lambert law. (b) HITRAN [66] search for spectrally interfering molecules near the 2ν₃ CH₄ overtone band, showing the three most significant absorbing species. H₂O absorption should ideally be avoided, whereas CO₂ and H₂S are of potential interest for real-time monitoring. (c) Optical micrograph of coupling between the AR-coated SiPhCS WG facet and lensed fiber, with a measured insertion loss of 11.5 dB (Figure 7.11).
Figure 7.11: Loss measurement by linear regression of fractional losses of an SOA output through 3, 6, and 10 cm WGs. TM mode loss at 1651 nm (near the CH$_4$ R4 transition) yields 1.72 dB/cm ($R^2$ correlation of 0.994) with a total insertion loss of 11.5 dB. TE mode analysis yields much higher insertion loss $>$ 20 dB, with WG losses $\sim$ 2.5 dB/cm at 1651 nm.
Figure 7.12: Spectral acquisition of three WG lengths in two processes: (a) hardmask etch (55 nm silicon nitride passivation above the Si WG), with AR-coatings for reduction of facet reflections. (b) Softmask etch with 900 °C H₂ annealing after processing, demonstrating faceting of the WG bends. For maximal mitigation of fringing, the hardmask etch WG with AR-coating was used together with DEF-R retrieval.
Figure 7.13: Three-stage measurement sequence of CH$_4$ variation in the chamber: 1. zero-gas, 2. CH$_4$ flush, 3. CH$_4$ trap. (a) Surface plot of raw (normalized) spectral compilation, showing laser current ramps cascaded vertically over the three measurement stages totaling ~ 1000 s. The presence of CH$_4$ in the chamber is weakly visible starting at scan 600. (b) Spectral analysis using DEF-R showing the visible enhancement of CH$_4$ spectral absorption. Note the difference in color scale (shown in the color-bar legend), demonstrating the efficacy of fringe noise suppression using DEF-R.
Figure 7.14: SiPhCS real-time CH₄ measurements and Allan-deviation stability analysis. (a) Spectral concentration retrieval (5.8 s averaging) in the presence of varying CH₄ concentration using the data from Figure 7.13. Good agreement is obtained between the SiPhCS and FSOPS. (b) Correlation between SiPhCS and FSOPS peak absorption for a controlled CH₄ release, demonstrating an experimental modal overlap factor of \( \Gamma_{\text{meas}} = 25.2 \% \), consistent with \( \Gamma_{\text{calc}} = 28.3 \% \) from simulations. (c) Zero-gas Allan-deviation stability analysis showing CH₄ sensitivity of 757 ppmv·Hz⁻¹/₂ and \( (\alpha L)_{\text{min}} = 8.5 \times 10^{-4} \) Hz⁻¹/₂ resulting in a detection limit \(~ 20\) ppmv at \( 10^3 \) s. The inset (blue) shows the extracted CH₄ concentration time-series which remains centered around zero (as expected for continuous N₂ purge).
Figure 7.15: Spectral density analysis of optical throughput from the WG, calculated from 20×1 s acquisition time series. The different colors correspond to different measurement configurations. Green is the noise of the detection system, red is the laser intensity-noise directly from the fiber pigtail output. Gray is tip-to-tip coupling between the input/output lensed fibers, and blue/black are through the 6 cm WG and represent aligned/misaligned cases respectively. Misalignment is accomplished by directing the lensed fibers off the WG center (i.e. sub-optimal coupling).
Figure 7.16: Numerical results of the CH$_4$ 2$\nu_3$ overtone band incorporating temperature dependent line intensity and collision broadening. (a) Calculations over a 100 K range indicate that higher rotational transitions demonstrate diminished susceptibility to temperature fluctuations. (b) Peak absorption of the R9 transition, demonstrating < 5 % fractional change over the 100 K span, which is particularly useful in scenarios where frequency thermal calibration is not feasible. Prior study of the R9 transition in Section 7.3.2 also demonstrates potential multi-species detection capability (H$_2$S, CO$_2$).
Figure 7.17: An initial demonstration of on-chip WMS, with an in-line cell inserted after the SiPhCS. Laser modulation at $f_L = 10.2$ kHz followed by demodulation at $2f_L$ yields the measured spectra (red points). Noise is estimated by the standard deviation of WMS fitting residuals resulting in a single point SNR = 35.4 leading to a detection sensitivity of $46.9 \text{ ppmv} \cdot \text{Hz}^{-1/2}$. 

$\sigma_{\text{dev}} = 2.82 \times 10^{-3}$ 

SNR = 35.4 

(single point SNR)

MDL (estimate): $46.9 \text{ ppmv} \cdot \text{Hz}^{-1/2}$

$(\Delta L)_{\text{min}}$ (estimate): $8.3 \times 10^{-5} \text{ Hz}^{-1/2}$

$\sigma_{\text{dev}} = 2.82 \times 10^{-3}$
Figure 7.18: Schematic of an integrated SiPhCS node. The permanently sealed reference cell is used for line-locking and periodic sensor recalibration. The sample cell is covered with permeable membrane for fast CH₄ diffusion while preventing environmental contamination. Numerical labels: (1) III-V chip (gain-detector), (2) Si handle wafer, (3) BOX layer, (4) SiO₂ deposition, (5) micro-ring tunable filter, (6) power splitter, (7) cavity phase-shift heater, (8) micro-ring heater, (9) distributed Bragg-reflector grating, (10) CH₄ reference cell lid, (11) permeable CH₄ cell membrane.
Figure 7.19: Control block schematic for the integrated SiPhCS node, showing the interaction of SiPhCS hardware with the DAQ card and associated feedback loops. Initial thermal setpoints are determined through tabulated calibration values, and WMS is accomplished through line-locking to $3f_L$ zero-crossing of the reference CH$_4$, followed by thermal dithering of the cavity phase-shift heater for wavelength modulation.
Figure A2.1: Effect of ramp rate on TDLAS precision. (a) shows \((1/f)^2\) and white (detector) simulated noise with baseline normalization (10 % wing points) at varying \(f_{\text{ramp}}\). (b) RIN of the time series in (a) for \(f_{\text{ramp}} = 1\) Hz and 200 Hz. The effect of high ramp rates is to linearize low frequency noise below \(f_{\text{ramp}}\). (c) SNR calculation (average over eight simulations) for ramp rates from 1 Hz to 5 kHz frequency oscillations (or laser ‘ringing’) which demand in-line wavelength calibration prior to application of spectral fitting algorithms (Section A4.2).
Figure A2.2: Experimental demonstration of sensitivity enhancement with increasing ramp rate. (a) ASD calculation of optical throughput (20 s) through a 10 cm SiPhCS WG. (b) Calculated vs measured MDL for 100 Hz ENBW. (c) Allan deviation analysis (using DEF-R) from 10 s ramp spectral acquisition through the SiPhCS (Section 7.3). Increasing $f_{\text{ramp}}$ from 100 Hz to 10 kHz provides > 10× enhancement in short-term SNR (consistent with A2.2(b)). Noise convergence beyond 1 s shows medium-term sensor drifts.
Figure A2.3: The effect of spectral fitting width on SNR. (a) A schematic of TDLAS measurement with an idealized white noise baseline. (b) The calculation result of eight averaged simulations of SNR degradation with increasing spectral fitting range. For the calculation, a simulated noise $\sigma = 1.5 \times 10^{-9} \text{ Hz}^{-1/2}$ is used, with 100 points per ramp, resulting in a $\text{SNR}_{\text{opt}} = 431.96 \text{ Hz}^{1/2}$ using the peak absorbance. As the fitting range is increased, the resulting SNR degrades due to fractionally greater sampling of the baseline, which contributes more noise than signal.
Figure A3.1: Schematic of the 1st-generation dDM-FRS prototype. A 5.3 \( \mu \)m QCL \((f_L = 50 \text{ kHz})\) is polarized by a Rochon prism (RCP1), and sequentially enters the reference and sample cell, both at 35 Torr. The B-field is modulated at \( f_M = 1.04 \text{ kHz} \). The analyzer (RCP2) separates extraordinary and ordinary rays, where the latter passes through a \(^{14}\text{N}^{16}\text{O}\) reference for wavelength calibration and line-locking.
Figure A3.2: Sample cell construction and characterization. (a) Field analysis (4 A at $f_m = 1.04 \text{ kHz}$) indicates similar field profiles between sample and reference paths. Slight deviation outside the coil boundary occurs due to the asymmetric wiring to the audio amplifier, and may be the cause of differences in the sample/reference signal (leading to systematic fractional CMRR imperfection described in Section 6.4.2 and Appendix A3.4). (b) Dual sample and reference cell construction within the solenoid.
Figure A3.3: PER study of the retroreflector configuration for dDM-FRS. (a) Power normalized PER for \( p \) and \( s \) polarization states respectively, where normalization is required due to optical suppression near the detection noise floor. (b) PER as a function of incident polarization angle from the RCP1; the maximum measured LIA signal (green) reflects Malus’ Law, and the back-to-back polarizer measurements indicate the necessity of power normalization. The slight offset of \( s \) and \( p \) PER maxima may be attributed to polarization rotation by the CaF\(_2\) wedged windows of the gas cells.
Figure A3.4: Analyzer angle optimization. (a) The effect of leakage due to depolarization from the retroreflector and intermediate optical surfaces between the polarizers. The leakage is treated as effective detector-noise, which requires an increase of the analyzer uncrossing angle. The gray points and line show the measured and calculated noise respectively. Noise analysis yields $\text{RIN} = 2.53 \times 10^{-7} \text{Hz}^{-1/2}$ and $\text{NEP} = 1.65 \times 10^{-12} \text{W}\cdot\text{Hz}^{-1/2}$. (b) Shows the impact of leakage on the SNR, demonstrating an increase in $\theta_{\text{opt}}$ accompanied by SNR degradation at the maximum due to the increased effective detector-noise.
Figure A3.5: Baseline removal. Parts (a) and (b) show positive $f_+$ and negative $f_-$ sidebands in the absence of a field. Parts (b) and (c) show in-phase and out-of-phase quadrature demodulation of the $f_+$ and $f_-$ sidebands. Presently, $\Gamma_{XY} = 1$ is used to yield zero-baseline measurements shown in Figure A3.6.
Figure A3.6: Sensor spectral acquisition, stability and demonstration of optical subtraction of $^{14}$NO. (a) P(19/2)e $^{14}$NO spectra (1842.95 cm$^{-1}$) acquired by laser current scanning, where the inset shows the adjacent Q(3/2) $^{15}$NO line (1842.76 cm$^{-1}$). Measurements are performed at 35 Torr using an uncalibrated 2 ppmv NO cylinder. The top figure shows zero baseline during a zero-gas (N$_2$) flush, using baseline removal described in Section A3.3. (b) Allan deviation via line-locking to the 3f$_l$ zero crossing of 2.5 % $^{14}$NO spectrum. The inset shows the time series data, and the resulting Allan deviation indicates white noise performance up to $\sim 10^3$ s, at 2.4$\times$ the shot-noise limit. (c) Demonstration of optical subtraction by sequential measurement of (i) reference NO, (ii) sample NO, (iii) NO gas in both sample and reference cells, with a retrieved CMRR of 24.8 dB.
Figure A3.7: Sensor linearity with injection of IAEA-NO-3 samples. (a) Five separate injections ranging linearly from 100 to 500 nmol KNO₃ underwent reduction to NO₉, via acidic vanadium(III) upon injection into the reaction vessel. The inset shows temporally separate measurements of ¹⁵NO. Based on the visible 100 nmol injection peak, sample sizes in the ~ 10 nmol range are expected to be measurable. (b) Peak integration is plotted vs. sample size, demonstrating excellent linearity (R² > 0.99). Using the measured system noise from Section A3.2, an expected precision of 0.59 ‰ precision for 5 µmol sample size (used in Chapter 5) is estimated for line-switched quasi-simultaneous isotopic analysis as studied in [2].
Figure A4.1: Functional flow diagram of the library dependencies given in Figure A4.2 for TDLAS data acquisition and spectral fitting. Module [6] is optional post-processing of data for stability analysis or spectral noise density calculations.
Figure A4.2: Libraries for TDLAS spectral retrieval, from Figure A4.1. Modules [0] and [3] to [6] are applicable for general analysis TDLAS measurements and not limited to the acquisition/analysis described in Section 7.3. The fitting functions are given in module [5], which include DEF-R, BSLD, and VLMS routines. An example of the sub-routine etalon_calib.m in [2] is demonstrated in Section A4.2 for time-resolved measurements of formaldehyde in a photolysis flow-reactor.
Figure A4.3: Function data handling between library modules shown in Figure A4.2. A and C are lineshape parameters acquired from the HITRAN [1] database, B and D are data handling and preparation for spectral fitting, which occurs in E and is output as optimum fitting parameter results in F. Further post-processing is available via module [6].
Figure A4.4: Etalon calibration sub-routine from module [2]. (a) Shows the linearization of the etalons, which is applied to linearize the wavenumber scale of the spectral acquisition. (b) Shows the fitted concentration of the acquired trace, using the extracted broadening coefficient of CH$_2$O.
Figure A4.5: Experimental setup and results. (a) Block diagram of the measurement scheme. (b) Time-resolved CH$_2$O measurements at 15 kHz ramp rate (~ 67 µs time resolution). Each scan uses the broadening coefficient determined in Figure A4.4(b) for spectral fitting. The inset shows the clear presence of O$_3$, a necessary constituent for the production of excited O($^1$D) to react with the CH$_3$OH fuel.
Figure A5.1: AR-coating of the SiPhCS WG facets. (a) The bottom figure shows ~ 50% improvement in spectral baseline fringing for the 3 cm WG, and the FFT verifies the facet reflectivity contributes primarily to the fringe structure. (b) Fringe decoherence in the 10 cm WG due to distributed scattering from the WG LER. Only mild improvement in the baseline structure is observed with AR-coating of the 10 cm WG facets.
Figure A5.2: Demonstration of DEF-R for fringe mitigation. The left panel shows an example of conventional etalon subtraction, and the right panel shows the effect of using free-parameters to perturb the zero-gas trace prior to subtraction/ratio calculations.
Figure A5.3: DEF-R fringe reduction for large signal absorptions (10 % in-line CH₄ reference cell). (a) The raw (baseline-normalized) spectral compilation over ~ 10³ s. (b) Spectral compilation after DEF-R, showing the significantly enhanced signal-to-baseline contrast. Over the span of the measurement in (a), the CH₄ concentration (retrieved through VLMS) drifts by almost 0.1 %, whereas DEF-R fitting of the spectra in (b) yields white-noise performance > 300 s.
Figure A5.4: Flow schematic of DEF-R algorithm. The fitting routine is subdivided into three main segments: (1) coarse fitting to average data spectra via user input; (2) fine-LMS fitting using suitable coarse-fit parameters; (3) spectral data fitting with continuous parameter updates for enhanced LMS algorithm efficiency. The full functionality of DEF-R is depicted here, although typically only $C_g$ (analyte concentration), $\gamma_t$ (etalon FSR variation), and $\delta_t$ (fringe shift) are required.
Figure A5.5: Comparison of concentration retrieval methods using (i) direct Voigt fit (VLMS), (ii) conventional baseline difference (BSLD), and (iii) DEF-R. The latter case is the only where both short and long-term inaccuracies are corrected, resulting in precision and accuracy enhancement in the Allan-deviation plots (left).
Figure A5.6: The comparison of CH$_4$ retrieval accuracy between (i) VLMS, (ii) BSLD and (iii) DEF-R method using the data shown in Section 7.3.3. The latter case is the only one yielding agreement with the FSOPS. The bottom right graph depicts the absorption correlation between the FSOPS and SiPhCS, and reasonable confinement factor is achieved only in the case where DEF-R is used.
Figure A6.1: Functional schematic of the experimental test setup. Interconnects are color coded by type.
Figure A7.1: Functional block schematic of the DM-FRS instrument. Component interconnects are color coded according to type: optical (red), electrical (blue), gas flow (green), mechanical (orange). The red labels indicate locations of temperature monitoring using the Pico thermocouples.
Figure A7.2: Flow schematic of the DM-FRS instrument. Two inlets (primary and secondary sample inlets) are selectable through the three-way valve. The downstream pressure controller ensures the sample gas cell is equilibrated at 80 torr at all times. The solenoid valves may be simultaneously toggled for gas trap applications (long-term averaging).
Figure A7.3: Reference cell refill procedure. (a) Shows the gas handling manifold for reference gas refill. Only slight gas (at high pressure) within the steel tubing is required for refill; the gas is equilibrated throughout the manifold and the pressure is brought down to 80 torr using the metering valve. (b) Reference cell construction and mount.
Figure A7.4: Transportable DM-FRS instrument setup. (a) DM-FRS system in a rack-mount, situated on a pneumatic lift table. (b) Top view of the optical layout, showing the optical beam path for alignment (Procedure P3). The white line denotes main beam path, and yellow denotes the reference path.
Figure A7.5: Components of the DM-FRS instrument. (a) front view, (b) rear view, (c) left panel view, (d) right panel view. Parameter settings for important components may be found in Table A7.1.
Figure A7.6: LabVIEW interface for NO measurements. (a) Line-scanning mode, showing the 3/f1 WMS spectrum of 2.5% $^{14}$NO reference gas on the top left panel, and DM-FRS spectrum of 2 ppmv $^{14}$NO in the bottom left. (b) Line-locked mode, showing the DM-FRS $^{14}$NO signals from NO$_3^-$ injections (at 100 ms TC corresponding to 973 MHz measurement bandwidth at 24 dB/octave filter slope). Optional breath analysis output to the Loccioni breath analyzer interface is included as a toggle option.
Figure A7.7: LabVIEW interface for time-multiplexed NO measurements for ratiometry. (a) Line-switching settings panel, showing the switch settings and 3f_L WMS line-locked measurements of $^{14}$NO and $^{15}$NO. (b) Quasi-simultaneous NO DM-FRS signals for isotopic ratiometry. Post-processing for interpolation between switch segments is used for calculation of ratiometric values.
Figure A7.8: LabVIEW code for quasi-simultaneous line-switched isotopic ratiometry. Main functional modules are shown, which include: (i) *.zicfg HF2LI settings file load, (ii) sequential line-lock to $3f_L^{14}$NO and $^{15}$NO to determine initial line-center voltage bias for fast switching, followed by alternating between (iii) $^{15}$NO line-locking and (iv) $^{14}$NO line-locking. Upon the user-determined completion of the line-switch measurements, resulting data is logged to *.bin file, and the interface awaits further user input.
Figure A7.9: Active cooling control of QCL using Corsair h100i cooler. (a) the laser temperature is stepwise incremented over ~ 400 s (black curve), resulting in a corresponding decrease in laser housing backplate temperature (thermal heat sink). (b) The resulting decrease of fan-speed with increasing QCL temperature setpoint. The positive correlation between fan speed and h100i cooler temperature is displayed in the inset, demonstrating real-time fan-speed feedback in response to temperature variations.
Table 1.1: A brief summary of FRS techniques in this thesis. Near shot-noise limits are consistently achievable ($\Lambda$ is the factor above the shot-noise limit, defined in Section 3.3.2), with comparable short-term precision characterized by $\Theta_{\text{NEA}}$ (Section 3.3.4). Generally, true zero-baseline methods via sample modulation (DM-FRS) offer long-term stability, but consume significant power to drive the solenoid. Conversely, permanent magnet solutions and balanced-detection ($45^\circ$ method) offer more power-friendly solutions, and are suitable for low-power handheld/field-deployable applications.

<table>
<thead>
<tr>
<th>Method</th>
<th>short-term precision</th>
<th>long-term accuracy</th>
<th>low-power consumption</th>
<th>$\Lambda$ (1 sec.)</th>
<th>$\Theta_{\text{NEA}}$ [rad·Hz$^{-1/2}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>45º method</td>
<td></td>
<td></td>
<td></td>
<td>2.0</td>
<td>$3.2 \times 10^{-8}$</td>
</tr>
<tr>
<td>Hybrid-FRS</td>
<td></td>
<td></td>
<td></td>
<td>1.4</td>
<td>$1.6 \times 10^{-8}$</td>
</tr>
<tr>
<td>DM-FRS</td>
<td></td>
<td></td>
<td></td>
<td>2.8</td>
<td>$1.3 \times 10^{-8}$</td>
</tr>
<tr>
<td>dDM-FRS</td>
<td></td>
<td></td>
<td></td>
<td>1.9</td>
<td>$1.7 \times 10^{-8}$</td>
</tr>
</tbody>
</table>
Table 4.1: Summary of alternate optical methods for detection of atmospheric O\(_2\). The present hybrid FRS technique demonstrates an order of magnitude improvement over prior technologies. Law, as described in Section 2.1). For higher O\(_2\) concentrations with absorption of > 10 % (in our case corresponding to > 40 % O\(_2\) levels for 6.8 m path length), power normalization of the FRS signal is required, which is easily implemented using the measured DC photodetector signal. Additionally, the current hybrid-FRS system requires < 5 W for operation, making it desirable for field deployable applications.

<table>
<thead>
<tr>
<th>Detection Method</th>
<th>Year, [ref.]</th>
<th>MDL (ppmv)</th>
<th>Averaging Time</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>BD w/ VCSEL</td>
<td>2001, [14]</td>
<td>35</td>
<td>5 mins</td>
<td>~ 50 (\times) shot-noise limit(^1)</td>
</tr>
<tr>
<td>AC-FRS</td>
<td>2010, [28]</td>
<td>30</td>
<td>1 sec</td>
<td>AC-Coils require ~ 30 W</td>
</tr>
<tr>
<td>QEPAS</td>
<td>2010, [20]</td>
<td>13</td>
<td>&gt; 50 sec</td>
<td>~ 1.2 W laser output power 0.21 atm operation</td>
</tr>
<tr>
<td>DC-FRS w/ VCSEL</td>
<td>2012, [26]</td>
<td>6</td>
<td>1 sec</td>
<td>1.3 ppmv @ 60 sec 1.13 (\times) shot-noise limit</td>
</tr>
<tr>
<td>Hybrid-FRS w/ DFB</td>
<td>2013</td>
<td>0.6</td>
<td>1 sec</td>
<td>1.4 (\times) shot-noise limit &lt; 5 W power consumption</td>
</tr>
</tbody>
</table>

\(^1\) Vogel et. al. claim to be 2.7 to 4 times the shot-noise limit, although their results were obtained by comparing shot-noise in 1 sec. with a 5 min. stability measurement. An estimated actual value is shown in the table above.
<table>
<thead>
<tr>
<th>item</th>
<th>item description</th>
<th>part number</th>
<th>settings (laser ON)</th>
<th>notes</th>
</tr>
</thead>
</table>
| I01    | QCL TEC controller                   | Arroyo 5305     | $T_{set} = 12.5 \, ^\circ C$  
2.24 V / 1.79 A  
P: 2.925, I: 0.0245,  
D: 28.4296 | adjust PID settings as necessary |
| I02    | QCL current driver                   | Wavelength Electronics QCL 500 | $I_{set} = 383.1 \, mA$  
$I_{lim} = 400 \, mA$  | current limit set near QCL roll-over |
| I03    | QCL housing fan cooler               | Corsair H100i   | ~ 2000 RPM fan speed                                                              | maintain QCL housing near R.T.            |
| I04    | mass flow meter                      | Alicat M-500SCCM-D | ~ 100 sccm                                                                         | nominal flow; adjust as necessary         |
| I05    | pressure controller                  | Alicat PC3-30PSI-D | $P_{set} = 80 \, torr$                                                            | adjust PID for varying input cond.        |
| I06    | class-D audio amplifier              | Sure Electronics TK2050 | $I_{out} = 3.14 \, A$  
peak-field ~ 200 G          |                                            |
| I07    | HF2LI front-panel settings           | Zurich Instruments HF2LI | AC coupling ON  
2 V input range  
50 $\Omega$ input imp. | default settings in *.zicfg files from …/zi_settings |
| I08    | fun. generator: laser mod.           | Zurich Instruments HF2LI | $\Delta V_{14N} = 60 \, mV$  
$\Delta V_{15N} = 147 \, mV$  
$f_L = 50 \, kHz$  | $^{14}\text{N}^{15}\text{N}$ optimum modulation depths |
| I09    | fun. generator: solenoid mod.        | Zurich Instruments HF2LI | $\Delta V_{coil} = 540 \, mV$  
$f_L = 100 \, Hz$  | modulation voltage input to TK2050       |
| I10    | LIA (DM-FRS / WMS)                   |                  | $BW = 973 \, mHz$  
$TC = 70 \, ms$  
24 dB/oct filter | increase BW for improved time-resolution of meas. |
| I11    | PID controller (line-locking)        |                  | $P = 10$  
$I = 20$  
$D = 0$  | typical starting values; adjust as necessary |
| I12    | breath samples                        | Loccioni SOFIA   | orifice: 15 mL/sec  
aux. range: 100  
aux. unit: ppb   | manual gas calibration necessary         |

Table A7.1: Table of common settings for various components in the DM-FRS sensor. Item numbers correspond to those listed in Figures A7.1 and A7.2.