Chirped Laser Dispersion Spectroscopy: Fundamentals and Applications

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Abstract

The subject of this thesis is the fundamentals, implementation, and applications of Chirped Laser Dispersion Spectroscopy (CLaDS), an alternative dispersion spectroscopy technique that aims to overcome some limitations of absorption-based sensing. CLaDS preserves many of the benefits of dispersion sensing, namely baseline-free operation, immunity to received intensity, and linearity with sample concentration, and is fairly easy to implement without the need for stabilized interferometers, mode-locked lasers, and complex optical configurations required by many other dispersion-based sensors.

First an introduction to CLaDS and a derivation of the spectroscopic signals are provided, highlighting fundamental similarities and differences to absorption-based sensing. Next the fundamental limit of CLaDS is investigated through analysis of the shot-noise limited performance under ideal operating conditions. This in turn allows for a theoretical and direct comparison to the shot-noise-limited performance of direct laser absorption spectroscopy (DLAS). This investigation shows that when full spectral scan fitting of realistic unknown parameters for each technique is used, both techniques demonstrate the same efficiency of parameter extraction. Following this theoretical investigation of ideal CLaDS performance, the technical details, methods of implementation, and component-introduced limitations of real-world CLaDS systems are discussed. Also included is a discussion of the first demonstration of an optical heterodyne enhanced CLaDS technique (HE-CLaDS). To overcome some of the
technical limitations imposed by system instability, a modulation based technique (CM-CLaDS) was developed; the theory, optimization and noise characteristics of which are detailed. Finally, several applications of CLaDS are provided. These include atmospheric sensing, distributed sensor networks, and fiber dispersion characterization, all of which aim at demonstrating the technical advantages of the CLaDS technique.
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Chapter 1: Introduction

1.1. Motivation

Spectroscopic instrumentation is the backbone of most fundamental investigations of atomic and molecular structures [1], and continued development of laser-based spectroscopic sensors has allowed the application of such techniques to quantitative analysis in areas such as atmospheric science [2], medical diagnostics [3], industrial monitoring [4], combustion diagnostics [5], and planetary science [6]. As the applications vary, so do the sensing configurations required for efficient information extraction. For metrology applications, point sensors in laboratory environments are expected, while studies of global trends of atmospheric gases require large-scale measurement platforms. Therefore the choice of spectroscopic technique for a given application is dependent on the sensitivity requirements and desired sensing configuration. This thesis describes the fundamentals, characterization, and implementation of Chirped Laser Dispersion Spectroscopy (CLaDS) as a sensing tool for chemical detection in atmospheric, industrial, and sensor network applications. To serve as a backdrop for the development of this technique, this chapter will review some of the standard spectroscopic techniques in this field, as well as provide an overview of existing dispersion measurement methods. To conclude, an outline of the thesis topics will be provided.

1.2. Direct Laser Absorption Spectroscopy

The physical mechanism that governs all absorption-based spectroscopic sensors is the Beer-Lambert law, which describes the attenuation of transmitted light through a medium due to
absorption. This section includes a derivation of the law, a discussion of spectral lineshapes, and examples of alternative absorption-based techniques.

**Figure 1.1.** Schematic of a typical DLAS sensor.

In Direct Laser Absorption Spectroscopy (DLAS), also referred to as Tunable Laser Absorption Spectroscopy (TDLAS), light from a single-mode laser is transmitted through a gaseous sample containing the molecules of interest, as shown in Fig.1.1. The laser wavelength is then ramped, by a modulation of the injection current, over the molecular transition of interest. Due to absorption by the molecules in the sample, the transmitted light will be attenuated when the wavelength of the laser coincides with a molecular transition. This is shown in the illustration of transmitted intensity, \( I \), as a function of time in Fig.1.1. Due to the tuning characteristics of the laser, a modulation of the injection current results in a change in both the output wavelength and intensity. This in turn produces a baseline on top of which the change in intensity (i.e. the absorption) is measured. For trace measurements, where this relative change in intensity is particularly small, strong baseline effects, such as high non-linearity, can make it technically challenging to accurately determine the gas parameters from the absorption scan. A discussion of
the role of baseline in parameter extraction through curve fitting for absorption systems will be
discussed in Chapter 3.

1.2.1. Beer-Lambert’s Law

To derive the Beer-Lambert Law, the molecular sample will be modeled as the two level system,
shown in Fig.1.2. Light with flux \( F_o = I_o / h \nu \) (units: photons m\(^{-2}\) s\(^{-1}\)) is incident on the medium.
Assuming only absorption \((E_o \rightarrow E_i)\) and stimulated emission \((E_i \rightarrow E_o)\) in the two level system,
the rate of change in the excited state is given by

\[
\frac{dN_i}{dt} = -B_{i\rightarrow 0} \cdot \rho \cdot N_i + B_{i\rightarrow 0} \cdot \rho \cdot N_0,
\]

where \( B_{i\rightarrow 0} \) is a rate constant known as the Einstein B coefficient (also the Einstein absorption
coefficient), \( B_{i\rightarrow 0} \) is the stimulated emission coefficient, \( \rho = I / c = h \nu F / c \), and \( N_{0,1} \) represents
the number of molecules per cubic meters in the ground and excited state, respectively [7].

Figure 1.2. a) Two level system and b) interaction schematic used to derive Beer-
Lambert’s Law. Adapted from [7].

Eq. (1.1) can be written in terms of the absorption cross section, \( \sigma \) (units m\(^{-2}\)), which represents
the “physical area” seen by the absorbing molecules.
\[
\frac{dN_1}{dt} = \sigma \cdot F (N_0 - N_1) \quad (1.2)
\]

where

\[
\sigma = \frac{2\pi^2 \mu_0^2}{3\varepsilon_0hc} \cdot \omega \cdot g(\omega - \omega_0) \quad (1.3)
\]

Here \( \mu_{10} \) is the transition dipole moment (debye), \( \varepsilon_0 \) is the permittivity in vacuum (F\cdot m\(^{-1}\)), \( h \) is Planck’s constant (J\cdot s), \( c \) is the speed of light (m/s), \( \omega \) is the laser frequency (rad\cdot s\(^{-1}\)), and \( g(\omega - \omega_0) \) is the area normalized lineshape function (rad\(^{-1}\)\cdot s).

If the light is incident on an infinitesimally small portion of the material, with thickness \( dx \) and a cross sectional area of 1 m\(^2\) (see Fig. 1.2b), then the change in flux induced by interaction with the material can be written as

\[
dF = -\sigma F (N_0 - N_1) dx. \quad (1.4)
\]

To investigate the effect of the entire medium (often referred to as “path integrated absorption”), Eq. (1.4) must be integrated over the sample length yielding

\[
\int_{x_0}^{x} \frac{dF}{F} = -\sigma (N_0 - N_1) \int_{0}^{L} dx
\]

\[
\ln \left( \frac{F}{F_0} \right) = \ln \left( \frac{I}{I_0} \right) = -\sigma (N_0 - N_1) L. \quad (1.5)
\]

This last equation can be rewritten in a common form of Beer-Lambert’s Law,

\[
I = I_0 \exp(-\alpha(\omega) \cdot L) \quad (1.6)
\]
where $\alpha(\omega) = \sigma (N_0 - N_1)$ is defined as the absorption coefficient [7, 8]. Physically speaking, the absorptive effect described by Beer-Lambert’s law is the result of destructive interference between the external radiation and the oscillations induced by the induced dipole moments [9]. This, however, is a finite excitation, the lifetime of which defines the natural lifetime broadening of the absorption spectrum. A further discussion of spectral broadening and lineshapes is included in the next section. Also from Eq. (1.6), the exponential nature of absorption can be seen, which for high absorbance results in a non-linearity in the final measurement of transmission. This non-linearity introduces dynamic range limitations when the same instrument is used to measure both optically thin (low absorption) and optically thick (high absorption) samples. This concept and a comparison to the CLaDS response are discussed further in Chapter 4.

### 1.3. Spectral Modeling

Laser light that is tuned to a molecular transition not only experiences attenuation, $\alpha(\omega)$, used in Beer-Lambert’s law to describe absorption, but also undergoes a phase shift related to the wavenumber, $k(\omega)$. These two phenomena are described by the complex wave number, $\tilde{k}(\omega)$,

$$
\tilde{k}(\omega) = k(\omega) - i \frac{\alpha(\omega)}{2}.
$$

(1.7)

Assuming that $k(\omega) = \frac{\omega}{c} n(\omega)$, where $c$ is the speed of light in a vacuum, Eq. (1.7) can be rewritten in terms of the refractive index, $n(\omega)$.

$$
\tilde{k}(\omega) = \frac{\omega}{c} n(\omega) - \frac{i \alpha(\omega)}{2}.
$$

(1.8)
The real and imaginary components of the complex wavenumber can be related using the Kramers-Kronig relation [8], allowing the real part, \( n(\omega) \), to be derived from the imaginary part, \( \alpha(\omega) \), resulting in the following expression.

\[
n(\omega) = 1 + \frac{C}{\pi} \int_{0}^{\infty} \frac{\alpha(\omega')}{\omega'^2 - \omega^2} d\omega'
\]

Using this relation, existing models that simulate molecular absorption can be modified to calculate the respective dispersion introduced by the sample. An example of this is shown in Fig.1.3.

![Diagram](image)

**Figure 1.3.** Absorption coefficient, \( \alpha(\omega) \), and wavenumber, \( k(\omega) \), as a function of angular frequency. The peak absorption coefficient and change in wavenumber are denoted as \( \alpha_c \) and \( \Delta k \), respectively.

Under dilute-medium conditions (i.e. low loss), it can be assumed that the peak absorbance, \( \alpha_c \), is approximately equal to the change in wavenumber, \( \Delta k \) (or \( \Delta n \cdot \omega / c \)). In addition, the full width half maximum (FWHM) of the absorption coefficient corresponds to the peak-to-trough width of the refractive index curve, a feature that will be important in Section 2.4 when the optimization of the CLaDS amplitude is discussed.
The following sections detail common broadening mechanisms that in turn dictate the spectral lineshape profile used to accurately simulate or fit measured data, formulization for two lineshape profiles, and signal formulas for DLAS. The analogous expression for the CLaDS technique will be provided in the next chapter.

1.3.1. Broadening Mechanisms

Broadening mechanisms result from non-ideal energy level distributions and can be categorized into two general categories: homogeneous and inhomogeneous. Homogeneous broadening occurs when all the molecules in the sample exhibit the same lineshape, while inhomogeneous broadening is the result of subgroups within the sample having different probabilities of transition. As mentioned previously, the natural linewidth of a given transition results from the relaxation from the excited state to the lower state energy via spontaneous emission (described by the Einstein A coefficient [7]). This homogenous phenomenon can be modelled as a damped harmonic oscillator, resulting in a Lorentzian lineshape profile [8]. The natural linewidth, however, is often masked by other broadening mechanisms which cause significantly larger linewidths. Collisions between molecules randomizes the phase of the emission, resulting in collisional (or pressure) broadening. This homogeneous broadening is also described with a Lorentzian profile. Thermal motion of the molecules results in inhomogeneous Doppler broadening, modeled as a Gaussian profile; and is a significant contributor to the total spectral linewidth. Detailed consideration of the thermal broadening cannot be described by a Gaussian only, but rather requires a line profile which is the convolution of the Gaussian (thermal effect) and Lorentzian (natural, pressure broadening) lineshapes. This combined lineshape, called the Voigt profile, more accurately predicts the spectral wing shape under these conditions, which is crucial to extraction of temperature and pressure information from spectroscopic measurements.
Additional broadening mechanisms exist, such as Stark broadening in charged gases, Dicke narrowing [10], as well as lineshapes for soft and hard collisions (i.e. Galatry and Rautain profiles) [11, 12]. Instrumental effects such as transit-time, saturation, and power broadening may also exist and require attention is the development of spectral models [8]. However, for the molecules and applications presented in this thesis, the Lorentzian and Voigt line profiles are sufficient.

1.3.2. Spectral Lineshapes

1.3.2.1. Lorentzian Model

For conditions that warrant the use of a Lorentzian lineshape function, the complex wavenumber expression in Eq.(1.8) can be expressed as

$$\vec{k}(\omega) = \frac{\omega}{c_o} - i \frac{\alpha_c}{2} \left( \frac{\omega_L}{\omega_L + i(\omega - \omega_c)} \right), \quad (1.10)$$

where $\omega$ is the laser frequency (rad/s), $c_o$ is the speed of light in vacuum (m/s), $\alpha_c$ is the peak absorption coefficient (cm$^{-1}$), $\omega_L$ is the Lorentzian halfwidth (rad/s), and $\omega_c$ is the line center (rad/s). By separating out the real and imaginary components of Eq.(1.10), $k(\omega)$ and $\alpha(\omega)$ become:

$$\alpha(\omega) = \alpha_c \left( \frac{\omega_L^2}{\omega_L^2 + (\omega - \omega_c)^2} \right)$$

$$k(\omega) = \frac{\omega}{c_o} - \frac{\alpha_c}{2} \left( \frac{\omega_L(\omega - \omega_c)}{\omega_L^2 + (\omega - \omega_c)^2} \right). \quad (1.11)$$

Using the expression for $\alpha(\omega)$ and Beer-Lambert’s Law (Eq.(1.6)), the DLAS signal for a Lorentzian lineshape profile is given by Eq.(1.12).
The real part of the complex wavenumber, $k(\omega)$, describes the phase change induced by the interaction with the sample; the mechanism under investigation in the dispersion spectroscopy techniques discussed later in this chapter. The provided expressions for $k(\omega)$ will be utilized in the next chapter to derive the CLaDS signal shapes.

### 1.3.2.2. Voigt Model

Unlike the Lorentzian profile, the Voigt profile cannot be computed analytically, but rather requires a numerical model. The Faddeeva function (also known as the complex error function), $W(x+iy)$ [13, 14], was developed to rapidly calculate the convolution of the Gaussian and Lorentzian profiles. With a method to evaluate $W(x+iy)$, the absorption and dispersion spectra can be calculated with the following formulization. For a Voigt profile, the complex wavenumber is given by

$$\tilde{k}(\omega) = \frac{\omega}{c_o} - i \frac{\alpha_c}{2} \left( \frac{W(x+iy)}{W(iy)} \right), \quad (1.13)$$

where the real and imaginary inputs to the Faddeeva function are given by

$$x = \sqrt{\ln 2} \frac{\omega - \omega_c}{\omega_G} \quad y = \sqrt{\ln 2} \frac{\omega_L}{\omega_G}. \quad (1.14)$$

Here $\omega_L$ and $\omega_G$ represent the Lorentzian and Gaussian halfwidths (rad/s), respectively. It then follows that the absorbance and dispersion spectra can be expressed as:
\[ \alpha(\omega) = \alpha_c \text{Re} \left\{ \frac{W(x + iy)}{W(iy)} \right\} \]
\[ k(\omega) = \frac{\omega}{c_o} - \frac{\alpha_c}{2} \text{Im} \left\{ \frac{W(x + iy)}{W(iy)} \right\}. \]  

(1.15)

The absorption spectrum, with a peak absorbance, \( \alpha_c \), is then described by the following expression.

\[ I = I_o \exp \left\{ -\alpha_c \text{Re} \left\{ \frac{W(x + iy)}{W(iy)} \right\} \cdot L \right\}. \]  

(1.16)

Figure 1.4. Area-normalization absorbance lineshape functions for the Voigt and Lorentzian profiles. If the pressure-broadening term (\( \gamma_P \)) dominates the Doppler broadening term (\( \gamma_D \)), the Voigt lineshape can be approximated as a Lorentzian.

At higher pressures, such as atmospheric pressure, many molecules exhibit spectral profiles that can be modeled by a Lorentzian (i.e limited contribution from Doppler broadening). In these cases, the broadening due to collision of the molecules dominates (i.e. pressure broadening).
Figure 1.4 illustrates this result. Similarly to the Lorentzian case, the formulation for $k(\omega)$ assuming a Voigt lineshape will be used to calculate the CLaDS signal in Chapter 2.

1.3.3. Alternative Absorption-based systems

Several alternative absorption-based sensor architectures have been developed to overcome technical limitations of DLAS systems. A widely used technique, Wavelength Modulation Spectroscopy (WMS), a type of derivative spectroscopy [15], utilizes a sinusoidal modulation of the injection current (on the order of kHz), producing a corresponding modulation of the laser wavelength. This transfers the spectral information to a higher operating frequency, such that noise sources close to DC (e.g. a $1/f$ intensity noise from the laser) are avoided. The signal is then extracted through phase sensitive detection (i.e. with a lock-in amplifier) at a harmonic of current modulation frequency. This technique has been widely studied [16, 17], and has been demonstrated to yield high sensitivities [18], however, the signal dependence on intensity requires power normalization procedures [19].

While WMS, along with other techniques, focus mostly on reducing the noise in the detection system, another class of techniques aims at enhancing the signal amplitude. This enhancement is achieved through use of an optical cavity, where the resonant nature of the configuration allows for long interaction length (i.e. long optical path) with the sample under test. Cavity Ring-Down Spectroscopy (CRDS) is the most widely used and sensitive cavity-enhanced technique and has become a benchmark technique in the field such as chemistry, atmospheric and environmental science, and combustion diagnostics [20, 21]. The instrumental configuration of such systems is often rather complex, requiring high quality optical mirrors, sophisticated feedback techniques to lock the laser wavelength to the cavity, and is often limited to extractive based sensing.
1.4. Dispersion Spectroscopy Methods

As mentioned in Section 1.3, transmission of laser radiation through a molecular sample not only results in absorption of a portion of the input light, but also a phase shift resulting from the perturbation of the induced dipole moments. This time-dispersed polarization density (i.e. dispersion) is the mechanism under study in phase sensitive instrumentation. Dispersion spectroscopy techniques are of interest for chemical detection due to the inherently linear response and baseline free nature of the physical mechanism they probe; two features which absorption-based techniques do not possess and therefore often impose technical limits on the sensor performance. These techniques probe the real part of the complex wavenumber (see $k(\omega)$ in Eq.(1.11) and Eq.(1.15)) describing the light’s interaction with the sample. Light dispersion in gaseous samples was investigated in 1901 [22], and has since been developed into several standard spectroscopic techniques. This section will provide an overview of existing dispersion spectroscopy techniques, ranging from the Hook method first developed in 1912 [23], to frequency comb spectroscopy systems that utilize the laser technology that was awarded the Nobel Prize in 2005 [24, 25]. This overview of existing techniques serves to provide context and to the highlight the novelty of the work presented in this thesis.

1.4.1. Hook Method

The hook method, or hakenmethode in the original German, was developed by Roschdestwensky in 1912 [23], however, it was rarely used by English-speaking researchers until a review of the method was published by W.C. Marlow in *Applied Optics* in 1967 [26]. The method, which combines a spectrometer with an interferometer, was used originally used to measure oscillator strengths of atomic and molecular transitions. The optical setup provided in that 1967 review paper is shown in Fig.1.5. A broadband, white-light source is coupled to a Mach-Zehnder
interferometer, in which one arm contains the sample under test. Interference between the two arms is captured using a stigmatic spectrograph, producing a spectrally dispersed two-dimensional interference pattern.

![Diagram of interferometer setup](image)

**Figure 1.5.** Hook system for measurement of optical dispersion. The broadband source ($S_1$) is coupled into a Mach-Zehnder interferometer, where the sample ($T_1$) is placed in one of the arms. Phase compensating windows ($C_1, C_2$) are placed in the other arm. Light exiting the interferometer is analyzed using a grating ($G_1$) after passing through a filter ($F_1$). A fringe pattern is generated on the observation screen ($P_3$). Reprinted with permission from [26].

If no dispersive sample is present and the paths are of equal length, a near horizontal fringe will be generated (see Fig.1.6a). If a dispersive element is introduced into one of the interferometer arms, the change in refractive index in the vicinity of the line center will cause the fringe pattern to distort.

If the fringe pattern is then made oblique by introducing a path length difference between the two arms, “hooks” are formed in the interference pattern (see Fig.1.6b). The hook separation, i.e. the dispersion induced by the transition, can then be used to calculate the oscillator strength, often called $f$ values, using the developed theory [26, 27].
Figure 1.6. Fringe pattern obtained using the hook method with a) equal and b) unequal optics paths in the interferometer. Reprinted with permission from [26].

The hooks, which correspond to the minima and maxima of the fringe pattern, are shown for a doublet is shown in Fig.1.7. The fringe intensity as a function of height on the spectrograph and wavelength can be modelled, from which the hook locations can be determined by differentiating the fringe height with respect to wavelength and setting the result to zero.

Figure 1.7. Fringe profile in the vicinity of a doublet line for a) separate line features and b) features with more significant overlap. Reprinted with permission from [26].

While an accurate method to determine the anomalous dispersion around a molecular transition, the hook method measures a relatively small effect, and is often restricted to the measurement of strong spectral lines or requires long sample tubes that can introduce non-uniformities[27]. Variations of the hook method have also been developed to incorporate fringe shift and slope analysis to provide more sensitivity by utilizing more features of the interference pattern for information extraction [27]. Since the overall sensitivity of the technique is limited by the quality
of the interferogram (i.e. fringe contrast), much of the development surrounding this technique has focused on the stability of the optical setup [28], as well as improved data extraction through use of low-noise cameras (part of the spectrograph) and subsequent digital signal processing [29]. Lasers were later incorporated into “hook”-like systems, resulting in a transfer of the wavelength resolution from the detector (i.e. the spectrograph) to the source (i.e. a narrow linewidth laser) and allowing for an overall improvement in fringe sensitivity [28, 30]. Lasers as sources also allow for use of single elements for detection. For example, a Fabry-Perot etalon and a photodiode were used to function as a spectrum analyzer in [31], and a spatial filter and single photodetector element were used to capture the spatial variation of the fringe pattern in [30]. Interferometric holography techniques were also incorporated into fringe-shift measurement systems as an alternative detection scheme [32].

The hook method and its derivatives provide an accurate method for measurement of the optical dispersion induced by a molecular sample. In addition to probing a mechanism that is inherently baseline-free and directly proportional to concentration, the techniques assume that phase contributions from thermal and optical noise sources would be identical between the two arms of the interferometer, and are therefore canceled out through the differential measurement. This, however, is only true if the interferometer arms are stabilized and the phase introduced by the sample cell is compensated for in the other arm (see mirrors C1,C2 in Fig.1.5). The requirement for optical-mechanical stabilization and phase compensation, while achievable in a laboratory setting, makes implementation of these techniques for field-deployable systems unrealistic. Sophisticated electronic systems and real-time feedback would be required to maintain the performance of these phase-sensitive systems, making the overall instrument more complex and costly. In addition, the structure of these sensing systems requires that the sample be placed in
one arm of an interferometer, which implies an extractive sensing configuration. As a result, open-path detection is highly impractical in these systems.

1.4.2. Other Interferometric Techniques

In addition to the hook method described in the previous section, other interferometric techniques have been developed for molecular dispersion measurements. An alternative fringe-shift method was developed that utilizes a difference measurement between two Fabry-Perot (FP) resonators. In this method the sample is placed in one FP resonator and the other is left in open air. The fringe pattern for each resonator is captured separately and the two signals are subtracted either electronically or in post processing. Assuming the FP resonators are identical, the refractive index change introduced by the gas will distort the fringe in comparison to the “zero-gas” pattern produced from the empty resonator. Therefore the dispersion of the gas is measured by subtracting the two fringe signals [33]. The accuracy of this technique relies upon the “empty” resonator being truly purged of the targeted species (CO₂ in the case of Ref. [33]) and the cross stability of the two resonators. Similarly to the hook-method, this technique is extractive in nature and does not lend itself to open-path measurement configurations.

More recently, a dual-frequency interferometric technique was developed to measure the fringe-shift induced by the presence of the sample for the application of hydrogen plasma diagnostics. In this method, called resonant heterodyne interferometer (RHI), two wavelengths are used in a interferometric configuration to measure the difference between the fringe pattern near the transition center and the pattern several linewdths away. The subtraction of the two interferometer signals is then directly proportional is the change in refractive index (as well as state densities) [34]. To probe the transition, the online wavelength was swept over the spectral region of interest using a tunable diode laser around 656.3nm. A HeNe laser was then used for
the fixed-frequency, offline measurement. Heterodyne detection was performance through the introduction of an acousto-optic modulator (AOM) which generates a frequency shifted beam, which serves as the reference channel. The un-shifted beam interacts with the sample and is then recombined with the reference channel and captured by two wavelength selective avalanche photodiodes. The phase difference of the resulting beatnote frequencies is then used to calculate the change in refractive index. In a similar manner to the other interferometric techniques, the path lengths of the two arms must be equal and stable with respect to one another in order to accurately and precisely measure the optical dispersion.

1.4.3. Frequency Modulation Spectroscopy

Another spectroscopic technique that can probe dispersion is frequency modulation spectroscopy (FMS). In FMS, an external phase modulator is used to generate sidebands around the laser frequency (see Fig.1.8). The driving frequency of the modulator is chosen to be comparable or even much larger than the linewidth of the targeted transition, such that a single frequency component (of the carrier and two sideband set) probes the transition (see Fig.1.9) [35].

![Diagram](image)

**Figure 1.8.** Typical optical setup for a FMS system. Reprinted with permission from [35].

The power spectrum of this is illustrated in Fig.1.9. The power in the sidebands is ideally equal; however, the sidebands are π radians out of phase with respect to each other (a result of the phase
modulation). Therefore, when there is no sample (i.e. absorption or dispersion), the amplitude in sidebands remains unchanged and in quadrature phase.

![Figure 1.9](image)

**Figure 1.9.** Frequency domain picture for FMS illustrating the large sideband spacing with respect to the linewidth of the probed transition. Reprinted with permission from [35].

This in turn results in destructive interference of the two frequencies on the photodetector and no beatnote signal. If, however, a sample introduces loss and a phase shift to one of the sidebands, the symmetry between the sidebands is broken and a beatnote signal is generated. The in-phase component of the beatnote signal is proportional to the absorption mismatch between the sidebands, assuming the second sideband experiences no loss. Similarly, the quadrature component is proportional to difference in phase and provides information about the dispersion. The phase adjuster in Fig.1.8 can then be used to choose between measurement of absorption or dispersion.

While fundamentally similar to wavelength modulation spectroscopy (WMS), the main distinction between WMS and FMS is the magnitude of modulation frequency with respect to the linewidth of the probed transition. If the modulation frequency is significantly smaller than the linewidth, the sidebands probe essentially the same spectral point on the transition, and
wavelength modulation is performed. If the modulation frequency is large compared to the linewidth and a small modulation index (~1) is used, the transition can then be probed by a single sideband, resulting in frequency modulation operation [16]. Another difference between the two techniques is the implementation of the applied modulation. In WMS, a sinusoidal component is added to the bias injection current of the laser, creating small frequency (and amplitude) modulation of the output laser radiation. In FMS, the modulation frequencies are large enough that an external modulator is often required to generate the sidebands.

Co-propagation of the multi-frequency probe beam in FMS mitigates many of the stabilization issues in the interferometers required for systems employing the hook-method (as well as other interferometric techniques). In addition, the modulation transfers the signal to a higher frequency where $1/f$ laser amplitude noise is lower and approaches the quantum limit [16]. The main limitation in FMS sensors is residual amplitude modulation (RAM) from the phase modulation, which introduces a small amplitude (or phase) mismatch between the sidebands. As a result, the beatnote signal contains a small non-zero signal even when no signal is present, introducing a non-zero baseline. In addition, the RAM is modulated by intensity noise of the laser, introducing additional noise into the output signal [36]. The effects of RAM can be reduced through sample-modulation methods [37], as well as employing active feedback of the bias to the phase modulator [38]. Two-tone FMS techniques have also been developed where the phase is modulated with two frequencies, creating an additional set of sidebands on the laser carrier (see Fig.1.10).
Figure 1.10. Spectral components of single tone and two-tone frequency modulation spectroscopy. Reprinted with permission from [39].

After interaction with the sample, a beatnote signal at the difference frequency between the two sideband pairs is generated and therefore does not require a high speed detector. In addition, RAM can be reduced by operating at a frequency difference larger than the highest frequency component of the RAM noise [39, 40]. Similarly to RAM, etalon fringes (i.e. parasitic reflections from parallel optical surfaces), can also limit the sensitivity; an effect that can be minimized through careful design of the optical layout and components.

Since FMS has been shown to operate at near quantum-limited performance [37], further development in the area has focused on methods to enhance the signal using cavity-enhanced configurations. By combining FMS with cavity-enhanced spectroscopy, noise-immune cavity enhanced heterodyne molecular spectroscopy, or NICE-OHMS, was created [41]. In NICE-OHMS, the three-frequencies (carrier and two sidebands generated by a phase modulator) are coupled to the adjacent axial modes of a cavity with matched free spectral range (FSR).

The cavity equally alters the amplitude and phase of all the frequencies, such that the influence of the cavity does not distort the balance of the transmitted signals. In this way, the measurement
is immune to any residual laser frequency noise (how it gets the name “noise-immune”). Under the influence of intracavity dispersion (due to the molecules), the central frequency component will be pulled due to the change in refractive index, resulting in an unbalance of the phase and the generation of a RF beatnote, just as in FMS. Thus a standard FMS detection scheme can be utilized while the signal is enhanced by the increased interaction length provided by the cavity [42, 43]. The laser is locked to the cavity through use of a second EOM modulated at a lower frequency (see Fig.1.11). The reflection of this signal from the cavity is then used to create an error signal to provide feedback to the laser (see Chapter 6 in Ref. [43] for a detailed explanation of laser frequency stabilization in NICE-OHMS). To capture spectral lineshapes, the cavity FSR is swept (along with the locked laser) using a piezoelectric transducer (PZT in Fig.1.11) on one of the cavity mirrors to scan over the transition of interest. Etalon effects can also be mitigated by placing the optical components at “etalon immune distances”, such that produced fringes would have an FSR equal to an integer multiple of the phase modulation frequency [44].

**Figure 1.11.** General schematic of NICE-OHMS sensor (left) and frequency spectrum and detection method through frequency pulling (right). Reprinted with permission from [42].

NICE-OHMS is a sophisticated spectroscopic technique that combines shot noise limited detection with cavity enhancement, and yields some of the best detection limits for spectroscopic
detection \((2.6 \cdot 10^{-13} \text{ cm}^{-1} \text{ Hz}^{-1/2})\) for laboratory-based measurements. The complexity of the instrument, however, makes such a technique incompatible with field deployable systems where thermal stability is often an issue and open-path or remote sensing is desired.

### 1.4.4. Frequency Comb Spectroscopy

The development of stabilized frequency combs, originally developed for optical frequency metrology [24, 25], was later applied to spectroscopic detection. The comb acts as broadband source which probes the sample with many \((> 10^5)\) narrow, phase-locked optical frequencies over the hundreds of nanometer bandwidth of the output radiation [46]. To capture and extract information from all of the comb teeth individually, a dual-comb approach is often used. In this method two combs are stabilization with respect to one another and operate at slightly different repetition rates. This results in a slightly different FSR for each comb, with a difference in the RF range. When the two combs are heterodyne mixed on a photodetector, each pair of comb modes is down-converted to a different frequency in the RF photodetector signal (see Fig.1.12), and can be processed using standard RF techniques.

![Figure 1.12](image)

**Figure 1.12.** Detection scheme for dual-comb spectroscopy. Reprinted with permission from [46].
Due to the phase-lock between the two combs, both the attenuation of the amplitude (i.e. absorption) and the induced phase shift (i.e. dispersion) can be extracted over the entire bandwidth of the comb [46, 47].

Dual-comb technology has also been used for open-path measurement of atmospheric constituents over kilometer path lengths with precisions suitable for studies of atmospheric trends [48]. To reduce the effect of phase noise introduced by atmospheric turbulence both combs were sent out over the open-path, which in turn results in attenuation of both their amplitudes. A later work aimed to overcome this loss in amplitude, and correspondingly the heterodyne gain in the down-conversion, by only transmitting one comb through the open path and using the second as a strong local oscillator. The phase noise was then reduced through adaptive compensation, possible due to the well-defined intrinsic phase of the comb and the fast sampling rate of the individual spectra [49].

Frequency comb technology allows for broadband, high accuracy and high precision sensing of molecular absorption and dispersion [50], however, the cost and complexity of the stabilized, passively mode-locked lasers that produce the comb radiation make this technology incompatible with sensing needs where cost is a limiting factor. Alternative, and potentially lower cost, “comb-like” sources have also been investigated using telecommunication based components in the near-IR [51, 52], as well as mid-infrared, quantum cascade lasers [53-55].

1.5. This Work

This thesis describes an alternative dispersion spectroscopy technique that aims to overcome some of the fundamental limitations of absorption-based sensing, without the needed for stabilized interferometers, mode-locked lasers, and complex optical configurations required by
many other dispersion-based sensors. Chirped Laser Dispersion Spectroscopy, or CLaDS, preserves the benefits of dispersion sensing, is compatible with commercially available optical components operating in multiple spectral regions, and is well suited for remote, open-path sensing configurations. In Chapter 2 of this thesis, the CLaDS technique will be introduced and the CLaDS signal will be derived. Chapter 3 presents a study of the fundamental limits of the technique through analysis of the shot-noise limited performance under ideal operating conditions; a work that then allows for a theoretical comparison of CLaDS to the more conventional absorption techniques in spectroscopy. The technical details, methods of implementation, and component-introduced limitations of CLaDS are discussed in Chapter 4. A modulation based CLaDS technique is presented in Chapter 5, and several applications and demonstrations of technical advantages of CLaDS are outlined in Chapter 6. Finally, Chapter 7 presents an outlook about the future of CLaDS for real-world sensing applications.
Chapter 2: Fundamentals of Chirped Laser Dispersion Spectroscopy

2.1. Introduction

Laser-based spectroscopic sensors are powerful tools for chemical detection applications. Many techniques probe the absorption that results from the interaction of the targeted molecules with light tuned to the wavelength of a molecular transition. While the physics of these techniques are well understood, many real world applications require sensing environments that are not conducive to intensity based measurement schemes. For example, remote sensing systems are often desired for the investigation of large scale phenomenon, such as spatial variations of greenhouse gases \[56\] or security applications where standoff detection is desired \[57\]. When the sample is outside the well-controlled environment of the instrument, intensity based techniques face additional challenges because the desired signal is encoded in the amplitude of the received light. As a result, any non-signal variations of the intensity directly introduce noise into the measurement. In addition to intensity noise issues, molecular absorption is measured as a relative change in optical power incident on a photodetector. Due to the non-idealities of the tuning behavior of most laser sources, the absorption signal is measured on top of a strong baseline which needs to be removed before an accurate determination of the spectral response can be made. Baseline issues can additionally lead to limits of the sensor’s dynamic range.
To mitigate these technical challenges, dispersion measurement systems have been investigated as an alternative sensing method, and such is the motivation for Chirped Laser Dispersion Spectroscopy (CLaDS). In CLaDS systems, the light probes the dispersion, instead of the absorption, induced by the light-matter interaction. When the spectroscopic signal is encoded in the phase or frequency of the received light, the signal itself is independent of the received intensity, making these systems well suited for open-path sensing applications. This feature has been experimentally verified and will be discussed in Section 6.2. The baseline free nature of the CLaDS measurements also allows for high dynamic range with one instrument, a result that will be detailed in Section 4.1.1.1. This chapter will outline the fundamentals of the CLaDS technique through derivations of the spectral signal, and also include details about the developed models and signal optimization. Specifics about the implementation of the technique, noise characteristics, and example applications will follow in subsequent chapters.

2.2. Chirped Laser Dispersion Spectroscopy

In DLAS, a single laser frequency is tuned across the targeted molecular transition, and the attenuation of light is used to extract the sample parameters. In CLaDS, the dispersion induced by the sample is extracted through the use of a multi-frequency beam with known frequency spacing. The ideal system, containing two frequency components of known spacing and equal amplitudes, is shown in Fig 2.1.
Figure 2.1. Dual-frequency beam, with a fixed frequency spacing of $\Omega$, used in the CLaDS technique. Methods of generating this signal as well as the use of multiple frequencies ($>2$) are addressed in Chapter 4. In an idealized system, all frequency components are of equal amplitude, here denoted as $A_0$.

The configuration of a typical CLaDS system is shown in Figure 2.2. Since the molecular sample introduces a frequency dependent perturbation in refractive index, each frequency component of the probe beam will experience a different index of refraction and therefore travel at different speeds towards the photodetector. The dispersion information describing the sample is encoded in the time-dependent phase difference between the two co-propagating signals. In the CLaDS technique, this information is extracted by mixing the two waves on the photodetector and frequency demodulating the beatnote current at the original frequency spacing, $\Omega$. The frequency demodulation process takes the time derivative of the differential phase signal retrieved through heterodyne detection. Therefore, there is a direct enhancement of the retrieved instantaneous beatnote frequency the faster the laser frequency is scanned with respect to time, i.e. larger chirp rate. In CLaDS, the output signal is directly proportional to the chirp rate, allowing for a certain level of flexibility when designing a CLaDS system. Further implications of the chirp rate will be discussed in a later chapter discussing noise considerations.
Figure 2.2. System configuration for a typical CLaDS system. A multi-frequency probe beam, shown here as generated by an intensity modulator/frequency shifter, interacts with the sample. The transmitted light is mixed on the photodetector and the dispersion profile is extracted through the frequency demodulation of the heterodyne beatnote.

The theory describing the CLaDS technique can be derived in several ways, two of which are presented here. The first is a time domain picture, which was presented in the first paper detailing the fundamental of CLaDS, and analyzes the propagation delay each frequency component experiences as it is travels through the sample [58]. The second is a complimentary frequency domain picture [59]. More information about the technical details of implementing this technique will be provided Chapter 4.

2.3.1. Time Domain Derivation

The analysis presented here follows the original derivation of the CLaDS technique developed by Wysocki and Weidmann as detailed in Ref. [58]. It investigates the phase and amplitude distortion two electromagnetic wave experience as they propagate through a medium. The two frequency components, as illustrated in Fig.2.1 can be described as two propagating electric fields, $E_1$ and $E_2$. 
\[ E_1(t) = A_1 \cos(\omega_1 t + \phi_1) \]
\[ E_2(t) = A_2 \cos(\omega_2 t + \phi_2) \]  

In this analysis, the two optical waves can be modeled as propagating through two different media with index of refraction profiles, \( n_1(\omega) \) and \( n_2(\omega) \), as shown in Fig.2.3. The difference in accumulated phase between the two signals is directly related to the refractive index difference of the two media. In the CLaDS case, the two refractive index profiles, \( n_1(\omega) \) and \( n_2(\omega) \), represent the same medium but are probed at different optical frequencies, i.e. \( n(\omega_1) \) and \( n(\omega_2) \). Therefore information about \( n(\omega) \), and the sample properties, can be extracted through this differential phase measurement.

**Figure 2.3.** Scheme used to model the CLaDS signal through the propagation delay through the sample of each frequency component, here shown the interaction with two different samples. In reality, each frequency component interacts with the same sample, however each interaction can be modeled as two refractive index curves that are shifted.
in time with respect to one another. The differential between these two dispersion curves is frequency demodulated (i.e. time derivative) to reveal the CLaDS signal.

Independent of whether a sample is present or not, when these two optical fields fall on a photodetector, a square-law device, a photocurrent, \( I \) (units = A), is produced, and is proportional to the average power of the superimposed fields on the detector surface,

\[
I = r \cdot |E_1 + E_2|^2 = r \cdot |A_1 \cos(\omega_1 t + \phi_1) + A_2 \cos(\omega_2 t + \phi_2)|^2
\]  

(2.2)

where \( r \) is the responsivity of the photodetector in [A/W]. Expansion of this expression yields the following.

\[
I = r \cdot \left(A_1^2 + A_2^2\right) + 2r \cdot A_1 \cdot A_2 \left(\cos\left((\omega_1 - \omega_2)t + (\phi_1 - \phi_2)\right)\right)
\]

\[= r \cdot \left(A_1^2 + A_2^2\right) + 2r \cdot A_1 \cdot A_2 \left(\cos(\phi(t))\right)
\]  

(2.3)

Note that the sum term at \( \omega_1 + \omega_2 \) is in the optical frequency range and is therefore outside the bandwidth of the photodetector. As a result, it was neglected in Eq.(2.3). It is clear that RF term at \( \omega_1 - \omega_2 \) contains both amplitude and phase information about the sample. To extract the phase information, a chirp of the laser frequency is applied. Assuming an ideal linear response of the laser, the chirp rate can be modelled as a constant, \( S = \frac{\partial \omega}{\partial t} \), resulting in an instantaneous optical frequency of

\[
\omega(t) = \omega_o + S \cdot t,
\]  

(2.4)

where \( S \) is the chirp rate in units of rad/s^2. The resulting electric field under this frequency chirp is given by
\[ E_i = A_i \cos \left( \omega_i t + \frac{1}{2} S \cdot \tau_i^2 \right). \]  \hspace{1cm} (2.5)

Assuming now that a sample is present (see the configuration outlined in Fig.2.2), each optical signal will experience a propagation delay, \( \Delta t_{i,2} \), due to the dispersive medium.

\[ \Delta t_{i,2} = \frac{L \cdot (n(\omega_{i,2}) - 1)}{c}. \]  \hspace{1cm} (2.6)

As defined in Fig.2.1, the frequency spacing between the electric fields is defined to be \( \Omega \), making \( \omega_2 = \omega_1 + \Omega \). Therefore the fields present at the photodetector can be written as

\[
E_1(t) = A_1 \cos \left( \omega_1 \cdot (t - \Delta t_1) + \frac{1}{2} S \cdot (t - \Delta t_1)^2 \right)
\]

\[
E_2(t) = A_2 \cos \left( \omega_1 \cdot (t - \Delta t_2) + \frac{1}{2} S \cdot (t - \Delta t_2)^2 - \Omega \cdot (t - \Delta t_2) \right). \hspace{1cm} (2.7)
\]

According to Eq. (2.3), the beat-note phase becomes

\[
\varphi(t) = (\Omega + S \cdot (\Delta t_2 - \Delta t_1)) t - \Omega \cdot \Delta t_2 + \omega_1 \cdot (\Delta t_2 - \Delta t_1) - \frac{1}{2} S \cdot (\Delta t_2^2 - \Delta t_1^2). \hspace{1cm} (2.8)
\]

This beatnote signal is subsequently frequency demodulated; a process that outputs the instantaneous beatnote frequency (i.e. the frequency change as a function of time) by taking the time derivative of the phase signal, \( f(t) = \frac{1}{2\pi} \frac{d\varphi}{dt} \). For the phase given in Eq. (2.8), this yields the following instantaneous frequency.
Spectral models are typically built using the fundamental interaction of the light with the sample and thus it is useful to convert the above expression to one that is a function of optical frequencies, rather than time. This can be done using the chirp rate,

\[ t = \frac{\omega - \omega_0}{S}. \]  

(2.10)

The time derivative in Eq. (2.9) can also be converted to optical frequency units as shown below.

\[ \frac{d}{dt} (\Delta t) = \frac{L}{c} \frac{dn_{1,2}}{dt} = \frac{L}{c} \frac{dn}{d\omega} \cdot \frac{d\omega}{dn^{1,2}} = \frac{S \cdot L}{c} \frac{dn}{d\omega^{1,2}} \]  

(2.11)

Using Eqs. (2.6) and (2.11) with the assumption that the optical frequency is much greater than the frequency spacing between the two fields (\( \omega \gg \Omega \)), Eq. (2.9) becomes

\[ f(\omega) = \frac{1}{2\pi} \left\{ \Omega - \frac{S \cdot L}{c} \cdot \omega \left[ \frac{dn}{d\omega} \bigg|_{\omega=\Omega} - \frac{dn}{d\omega} \bigg|_{\omega=\omega} \right] + \frac{S \cdot L}{c} \cdot (n(\omega-\Omega) - n(\omega)) \right\}. \]

(2.12)

The last term in (2.12) can be replaced with the first order Taylor expansion coefficient

\[ n(\omega-\Omega) - n(\omega) = -\Omega \frac{dn}{d\omega} \bigg|_{\omega=\omega}. \]

Again with the assumption that \( \omega \gg \Omega \), the expression becomes

\[ f(\omega) = \frac{1}{2\pi} \left\{ \Omega - \frac{S \cdot L}{c} \cdot \omega \left[ \frac{dn}{d\omega} \bigg|_{\omega=\Omega} - \frac{dn}{d\omega} \bigg|_{\omega=\omega} \right] \right\}. \]

(2.13)
In a practical implementation, the frequency demodulation will be calculated as the deviation around a given frequency, and if that constant frequency is set to $\Omega$, then the expression is reduced to

$$f(\omega) = \frac{S \cdot L}{2\pi \cdot c} \cdot \omega \cdot \left(\frac{dn}{d\omega}_{\text{lo}-\Omega} - \frac{dn}{d\omega}_{\text{lo}}\right).$$

(2.14)

The amplitude of the beatnote signal also provides spectral information about the sample under test due to molecular absorption. The amplitudes in Eq. (2.7) can be expanded to include the influence of the gas sample as a function of optical frequency, given by

$$A_{1,2}(\omega) = A_{\alpha,2} \exp\left(-\frac{\alpha(\omega_{1,2}) \cdot L}{2}\right).$$

(2.15)

Through amplitude demodulation of the RF beatnote photocurrent, the absorption information from

$$A(\omega) = 2A_1 \cdot A_2 \exp\left(-\left(\frac{\alpha(\omega) \cdot L}{2} + \frac{\alpha(\omega-\Omega) \cdot L}{2}\right)\right),$$

(2.16)

can be extracted through similar analysis to that of direct laser absorption spectroscopy. However, unlike the frequency demodulated signal, the amplitude signal does not depend on the chirp rate and is susceptible to intensity baseline issues.

### 2.2.2 Frequency Domain Derivation

As a compliment to the time domain analysis presented above, a frequency domain picture can also be used to derive the CLaDS signal. The material presented here is modified from the derivation found in [59] by Hangauer et al. Assuming again the ideal case of two co-propagating
optical fields \((E_1, E_2)\) of equal amplitude probing the sample, as illustrated in Fig. 2.1, the electric field amplitude, \(E_D\), after propagating through the sample can be modeled as

\[
E_D = E_o H(\omega),
\]

(2.17)

where \(H(\omega)\) is the transfer function of the sample and represents the distortion (i.e. absorption and dispersion) introduced by the presence of the target molecules. Assuming an optical path length of \(L\), the transfer function can be expressed as

\[
H(\omega) = e^{-i\tilde{k}(\omega)L}.
\]

(2.18)

Here \(\tilde{k}(\omega)\) is the complex wavenumber (introduced in Chapter 1). After interaction with the gas and mixing on the photodetector, the beatnote signal is given by

\[
P_{\text{beat}} = 2E_2E_1^*H(\omega_1 + \Omega)H^*(\omega_1).
\]

(2.19)

Assuming for simplicity that \(E_1 = E_2 = 1\), \(\omega = \omega_1\), and plugging Eq. (2.18) into (2.19), the beatnote signal becomes

\[
P_{\text{beat}} = 2e^{-i\tilde{k}(\omega + \Omega)L}e^{i\tilde{k}^*(\omega)L}.
\]

(2.20)

To extract the dispersion information, the received signal is frequency demodulated according to

\[
f(t) = \frac{1}{2\pi} \frac{dP}{dt} = \frac{1}{2\pi} \text{Im} \left\{ \frac{dP_{\text{beat}}}{dt} \frac{1}{P_{\text{beat}}} \right\}.
\]

(2.21)

The derivative of Eq. (2.20) which respect to optical frequency is given by
\[
\frac{dP_{\text{beat}}}{d\omega} = 2i \cdot L \cdot e^{-i(\omega+\Omega)k} \cdot e^{i\tilde{k}(\omega)L} \cdot \left( \frac{\tilde{d}k^*}{d\omega} \bigg|_{\omega} \right. - \left. \frac{d\tilde{k}}{d\omega} \bigg|_{\omega+\Omega} \right).
\]  

(2.22)

Using the chirp rate, \( S = \frac{d\omega}{dt} \), to convert Eq. (2.22) to a time derivative and dividing it by the original beatnote signal, \( P_{\text{beat}} \), yields,

\[
f(\omega) = \frac{1}{2\pi} \text{Im} \left\{ 2i \cdot L \cdot S \cdot \left( \frac{\tilde{d}k^*}{d\omega} \bigg|_{\omega} \right. - \left. \frac{d\tilde{k}}{d\omega} \bigg|_{\omega+\Omega} \right) \right\}.
\]  

(2.23)

Evaluation of Eq.(2.23) gives,

\[
f(\omega) = \frac{S \cdot L}{2\pi} \left( \frac{\tilde{d}k}{d\omega} \bigg|_{\omega} \right. - \left. \frac{d\tilde{k}}{d\omega} \bigg|_{\omega+\Omega} \right).
\]  

(2.24)

With the approximation that \( \frac{d\tilde{k}}{d\omega} = \frac{\omega}{c} \frac{dn}{d\omega} \), Eq. (2.24) agrees with the time-domain result from section 2.2.1, Eq. (2.14). As in the time domain method, a similar procedure can be followed to calculate the amplitude response under the same optical conditions.

2.3 Modeling

Using the formulas provided in the previous sections, the CLaDS signal can be modeled using existing methods to calculate molecular lineshapes. The complex wavenumber (or similarly, the complex refractive index) was introduced in Chapter 1 as describing the light-matter interaction from which absorption and dispersion are observed. Also in Chapter 1, the signal models for DLAS were derived from the imaginary part of \( \tilde{k}(\omega) \). Here, the real part of \( \tilde{k}(\omega) \) will be used to generate analogous signal models for CLaDS. Two common lineshape functions for the complex
wavenumber, Lorentzian and Voigt, are used in the conjunction with the CLaDS theory to develop models suitable for simulation and fitting algorithms.

2.3.3. Lorentzian Calculation of CLaDS Spectra

Under pressure broadening-limited conditions, a Lorentzian lineshape function may be a sufficient model to calculate the molecular spectra. In a practical sense this is rather advantageous because the corresponding absorption and dispersion signal can be calculated analytically, allowing for potentially fast fitting and analysis routines. Assuming a Lorentzian lineshape function, the complex wavenumber (see Eq.(1.10)), can be rewritten as:

$$\tilde{k}_L(\omega) = \frac{\omega}{c} + i \frac{\alpha_c}{2} \cdot \left( \frac{1}{\omega_L} - \frac{1}{1 + i \left( \frac{\omega - \omega_o}{\omega_L} \right)^2} \right), \quad (2.25)$$

where $\omega_o$ and $\omega_L$ are the line center frequency and halfwidth, respectively, in optical frequency units (rad/s), $\alpha_c$ is the peak absorbance coefficient (cm$^{-1}$), and the term in the brackets represents the lineshape function. The above equation holds for the assumption that $|\omega - \omega_o| \gg \omega_c$, that is the optical frequency is the vicinity of the line center. A more detailed derivation of this expression can be found in Ref. [8]. After solving for real part of Eq. (2.25), the corresponding wavenumber expression (see Eq. (1.11)) becomes
Using Eq. (2.26), the CLaDS signal can be calculated with Eq. (2.24). Note that $k(\omega)$ can be transformed into an expression for $n(\omega)$, permitting the use of Eq. (2.14) in CLaDS calculations. For computational simplicity, a normalized frequency variable is introduced, $x=(\omega-\omega_c)/\omega_L$. The frequency spacing can also be represented in this normalized form where $D=\Omega/\omega_L$. By taking the derivative of Eq. (2.26) and plugging the result into (2.24), the expression for the CLaDS signal in these normalized frequency units becomes

$$f_{\text{CLaDS}} = \frac{1}{2\pi} \cdot S \cdot \frac{\alpha_c}{2\omega_L} \left( \frac{x^2 - 1}{(1 + x^2)^2} - \frac{(x + D)^2 - 1}{(1 + (x + D)^2)^2} \right).$$

(2.27)

If the sensing conditions and molecular parameters allow for it, use of this analytical model of the CLaDS signal can allow for fast parameter extraction through curve fitting algorithms. However, if the target species cannot be accurately described using a Lorentzian lineshape (i.e. is not limited by pressured-broadening), other lineshapes must be used for reliable extraction of the sample parameters. In the next section another common lineshape function, the Voigt function, will be used to model the CLaDS spectra.

### 2.3.2 Voigt Calculation

While a Lorentzian lineshape model may be used for the pressure-broadening limited case, many real world sensing conditions require a lineshape that takes into account the collisional/pressure broadening mechanism (Lorentzian), as well as the effects of the thermal motion of the
molecules, known as Doppler broadening. This latter broadening mechanism is described using a Gaussian lineshape. Therefore many sensing conditions require a lineshape function that takes into account both the Lorentzian and Gaussian models for broadening. To address this need, the Voigt lineshape was developed and is defined as the convolution between the Lorentzian and Gaussian functions. The Voigt profile is given by

\[ P(x, y) = \frac{1}{\omega_G} \left( \frac{\ln 2}{\pi} \right)^{1/2} K(x, y), \]  

(2.28)

where \( K(x, y) \) is the Voigt function given by

\[ K(x, y) = \frac{y}{\pi} \int_{-\infty}^{\infty} \frac{e^{-a^2}}{y^2 + (x-a)^2} da. \]  

(2.29)

The normalized units in Eqs.(2.28)-(2.29) are defined as

\[ y = \frac{\omega_L}{\omega_G} \sqrt{\ln 2}, \]

\[ x = \frac{\omega - \omega_L}{\omega_G} \sqrt{\ln 2}. \]  

(2.30)

Here \( \omega_L, \omega_G, \) and \( \omega_o \) represent the Lorentzian halfwidth, the Gaussian halfwidth, and the line center, respectively [60]. The Voigt profile, \( P(x, y) \), is normalized to an area of 1 and assumes that the pressure and Doppler broadening mechanisms are independent. Unlike in the Lorentzian case, the Voigt function does not have an analytical solution, and therefore needs to be calculated numerically through the usage of the Faddeeva function (also sometimes called the plasma dispersion function), \( W(z) \). The Faddeeva function is closely related to the complex error function and is defined as
\[ W(z) = \frac{i}{\pi} \int_{-\infty}^{\infty} \frac{e^{-z^2}}{z-t} \, dt \]  
(2.31)

where \( z = x+iy \). With a numerical method for \( W(z) \) [14, 61], the complex wavenumber can be computed using Eq.(1.13), the real part of which is given by

\[ k(\omega) = \frac{\omega}{c_0} - \frac{\alpha_c}{2} \text{Im} \left\{ \frac{W(x+iy)}{W(iy)} \right\}. \]  
(2.32)

Note that the wavenumber expression, \( k(\omega) \), can easily be converted to a refractive index expression, \( n(\omega) \), by multiplying by \( c/\omega \). The derivative of the Faddeeva function is given by

\[ W'(z) = 2i / \sqrt{\pi} - 2zW(z) \]  
[62]. By using this derivative relation in conjunction with Eqs. (2.32) and (2.24), the CLaDS signal using a Voigt lineshape function becomes

\[ f_{\text{CLaDS}} = \left( \frac{1}{2\pi} \right) (S \cdot L \cdot \alpha_c) \times \ldots \times \text{Im} \left\{ \frac{(x+iy)W(x+iy)-(x+x_\Omega+i y)W(x+x_\Omega+i y)}{W(iy) \cdot (\omega_c / \sqrt{\ln 2})} \right\}. \]  
(2.33)

Here \( x_\Omega \) represents the second frequency component shift by frequency \( \Omega \). Just as in the Lorentzian case, Eq. (2.33) can be used to model and fit CLaDS spectra for parameter extraction.

### 2.4 CLaDS Signal Optimization

Due to the differential nature of the CLaDS technique, there exists an optimum frequency spacing, \( \Omega \), for a given set of molecular parameters (line strength, broadening coefficients, etc.) and sensing conditions (temperature, pressure). The maximum CLaDS signal is produced when the frequency spacing matches that of the inflection point (the point where a change in curvature...
occurs) of the absorption coefficient curve. The peak CLaDS signal as a function of frequency spacing is shown in Fig.2.4.

Three variations of lineshapes are shown in Fig.2.4. The frequency spacing axis is normalized to the total absorption coefficient linewidth (HWHM), denoted here as \( \omega_T \), to highlight the relationship between \( \Omega \) and \( \omega_T \). First, for a Lorentzian lineshape (black curve in Fig.2.4), the maximum occurs at \( \Omega = \sqrt{3} \cdot \omega_T \), which is in accordance with the literature for Lorentzian models [8]. For the Voigt lineshape two scenarios are considered. First is the case where the Lorentzian linewidth is large compared to the Gaussian width \( \omega_L \gg \omega_G \). Under these conditions, the Voigt profile approaches that of the Lorentzian, and results in an optimum spacing of \( \Omega \approx 1.8 \omega_T \), which is comparable the Lorentzian case. The other Voigt case shown in Fig.2.4 is where the Lorentzian and Gaussian linewidths are comparable. In this case a maximum at \( \Omega \approx 2 \omega_T \) is observed. Due to the derivate nature of the CLaDS technique, careful examination of the expected line profile and width is required to choose the optimum frequency spacing to be in accordance with the inflection points of the transition profile.
Figure 2.4 CLaDS amplitude as a function of frequency spacing, $\Omega$, for Lorentzian and Voigt lineshapes. Unlike for the Lorentzian model, the Voigt linewidth cannot be determined analytically, and therefore requires an empirical model for the linewidth, such as the one found in Ref. [63]. For $\Omega \gg 2\omega_r$, the signals from each frequency component making up the total CLaDS signal are fully separated, making the CLaDS amplitude independent of $\Omega$.

2.5 Discussion

This chapter has outlined the fundamentals of the CLaDS technique, detailed the various methods to model CLaDS spectra, and discussed the optimization of the frequency spacing. In the above analysis, an ideal dual-frequency (single-sideband modulation, SSB) optical spectrum was assumed. Continuing with this assumption, the noise characteristics of the CLaDS technique will be examined in the next chapter, allowing for theoretical comparison of CLaDS to existing techniques. Technical details about the implementation and non-idealities of CLaDS will be discussed in Chapter 4, while several applications for the technique are covered in Chapter 6.
Chapter 3: Fundamental Noise Characteristics

3.1. Introduction

In this chapter the fundamental noise limits of CLaDS will be investigated. To perform this study, operation under “shot-noise limited” conditions will be assumed. Shot noise, is defined as a white noise, which is the fundamental noise in photo-detection systems resulting from the discrete nature of electron generation in optical receivers [64]. Other noise such as relative intensity noise (RIN) or detector thermal noise represent technical limitations, while shot noise is the fundamental barrier to system sensitivities [65]. In this chapter, the output noise characteristics for an ideal CLaDS receiver will be derived assuming shot noise limited photodetection. The influence of the carrier-to-noise ratio, chirp rate, averaging, and low frequency phase noise will also be investigated. The model developed here will also allow for the comparison of fundamental limits for CLaDS to the well-established technique, Direct Laser Absorption Spectroscopy.

3.2. Noise Model

The model used for noise propagation in an ideal CLaDS sensor is shown in Fig.3.1. The formulization of the fundamental noise characteristics is derived assuming a dual-frequency optical beam (SSB, with equal power in each component) falls onto a photodetector producing a heterodyne beatnote photocurrent.
Figure 3.1. Block diagram of noise propagation through a) a CLaDS frequency

demodulation process ($\xi = 0$ is assumed), and b) a DLAS system.

Due to the square-law behavior of the detector, the dual-frequency optical signal is heterodyne

mixed, resulting in a beatnote photocurrent given by

$$i_{\text{beat}}(t) = A(t) \cdot \cos(\Omega \cdot t + \phi(t) + \xi(t)) + N(t)$$

(3.1)

where $A(t)$ is the instantaneous amplitude (units [A]), $\Omega$ is the frequency spacing of the optical

signals (units [rad/s]), and $\phi(t)$ is the instantaneous phase (units [rad]). The symbols $N$ and $\xi$

represent the random processes of optical intensity noise and RF carrier noise, respectively. For

this analysis, the phase noise, $\xi$, is the combined result of RF oscillator and down-conversion

noise. The phase term $\phi(t)$ contains the sample’s dispersion information and is extracted through

frequency demodulation of the beatnote photocurrent. In this analysis, an ideal frequency

demodulator is assumed, but the process is broken into two steps, intermediate frequency
filtering and ideal phase detection and time differentiation (called “Ideal FM detector” in Fig.3.1). The latter process is governed by the equation

\[ f(t) = \frac{1}{2\pi} \frac{d\phi(t)}{dt}, \]  

(3.2)

and represents the instantaneous beatnote frequency from which the dispersion information (i.e. the CLaDS signal) is extracted.

In order to evaluate the fundamental limit of CLaDS, shot noise is assumed to be the dominant noise source of the photodetector signal. This is illustrated in Fig.3.1, where the single-sided noise spectral density after photodetection is spectrally flat with an amplitude equal to \( N_i \) [A²/Hz]. The carrier to noise ratio (CNR) at this point is defined as the signal to noise ratio after demodulation around \( \Omega \) and is given by

\[ CNR = \frac{A^2}{2N_i B}, \]  

(3.3)

where \( B \) is the intermediate frequency (i-f) bandwidth. The SNR of the in-phase (and similarly out-of-phase) component is given by \( \frac{A^2}{(N_i B)} \), i.e. twice the CNR. In the limit of high CNR (\( CNR \gg 1 \)), the one-sided noise spectral density \( S_o(f) \) (units [Hz²/Hz]) is as follows

\[ S_o(f) = \frac{N_i}{A^2} f^2 + f^2 S_\xi(f), \quad \text{for} \; 0 \leq f < B. \]  

(3.4)

The first term in Eq. (3.4) originates from the intensity noise present in the beatnote signal (see Eq.(3.1)), and the second term is the noise contribution from the phase noise, \( \xi \). In this study, these two noise sources are assumed to be independent, a reasonable assumption given the different physical sources of the noise. This noise source, \( \xi \), can be modeled as having an RF
oscillator linewidth with a Lorentzian shape and a half-width at half-maximum of $\pi f_0$. This random noise, which is independent of chirp rate (i.e. constant after frequency demodulation), is unavoidable in real-world systems. In addition to random phase noise, low-frequency noise from the driving circuitry can be combined into this constant noise contribution. Assuming a Brownian motion type of behavior, $S_\xi(f) \sim 1/f^2$, the two-sided frequency noise spectral density becomes

$$S_\xi(f) = \frac{N_i}{A^2} f^2 + f_0, \quad \text{for } 0 \leq f < B. \quad (3.5)$$

The constant, $f_0$, quantifies the Brownian motion type phase noise, or, after demodulation, white frequency noise. In a previous analysis of the CLaDS noise, this low-frequency noise component (referred to as DC noise in that work) was experimentally observed and verified as a constant in the CLaDS signal [66]. The effects of this noise source will be discussed later in section 3.4.1. For the investigation into fundamental limits, the contribution of phase noise is neglected ($\xi = 0$, $f_0 = 0$). Unlike this purely technical noise, the conversion of intensity shot noise to frequency noise through the demodulation process is a fundamental limit.

When the carrier power is comparable to the noise ($\text{CNR} \approx 1$) the demodulation process cannot accurately distinguish the phase signal from that of the noise, resulting in significantly higher output noise. The CNR capture effect in FM demodulators has been observed by the communication community [67], and is presented pictorially in Fig.3.2. Significant degradation of the phase detection procedure is typically observed at a threshold of $\text{CNR} \approx 1$, and causes a drastic increase in the output noise of the FM demodulator [67].
Figure 3.2. Noise in phase detection with high CNR (≫1, left figure) and low CNR (≈1, right figure). For high CNR, the uniform distribution of the phase noise, $\xi$, coverages to $\phi$. In the low CNR case, as the phase noise varies from $-\pi$ (at $t_1$) to $+\pi$ (at $t_2$), the vector sum of the carrier and noise signals results in an average phase of zero. This indicates the noise “captured” the signal, as shown by the disk (gray dashed line) representing the noise.

This threshold effect has been observed in CLaDS systems as a significant decrease in sensor precision when the CNR drops below a certain value (discussed further in section 6.2.2). While extraction of spectroscopic data is still possible below this threshold, most applications require sensitivities and fast reporting windows that make operation below the CNR threshold unrealistic. As a result, significant effort into the development of the optical layout (ex. minimizing loss through the optical modulators with anti-reflective coatings) is done to guarantee operation in the high-CNR regime. Accordingly, further analysis in this chapter will assume a sufficiently high CNR.
Under the assumptions stated above as well as ideal (rectangular shaped) low-pass filters, the CLaDS output noise power (variance) is calculated by integrating the noise spectral density, $S_o(f)$ over the demodulation bandwidth (again for $f_o = 0$).

$$\sigma_{\text{CLaDS}}^2 = \int_0^B S_o(f) \, df = \frac{1}{3} \frac{N_i}{A^2} B^3.\quad (3.6)$$

This can be conveniently written as a function of $\text{CNR}$.

$$\sigma_{\text{CLaDS}} = \sqrt{\frac{N_i \cdot B^3}{3A^2}} = \sqrt{\frac{1}{6 \cdot \text{CNR}} \cdot B^2} \quad (3.7)$$

The $\text{CNR}$ term is proportional to $1/B$, such that the total CLaDS output noise scales as $B^{3/2}$.

The fundamental limit for the intensity noise is given by shot noise, therefore models for the noise and carrier power under these conditions, in conjunction with Eq. (3.7), can be used to calculate the output CLaDS noise under shot-noise conditions. In this case, the noise is given by

$$N_i = N_{\text{shot}} = 2e \cdot I_{\text{avg}} = 2e \cdot r \cdot P_T\quad (3.8)$$

where $e$, $I_{\text{avg}}$, $r$, and $P_T$ represent the elementary charge [As], the average photocurrent [A], the responsivity [A/W], and the average power on the photodetector [W], respectively. Under these conditions, the carrier amplitude can be expressed as

$$A = \eta_{\text{het}} \cdot r \cdot P_T \quad (3.9)$$

where $\eta_{\text{het}}$ is the heterodyne efficiency (max value of 1). This efficiency encompasses the effects of wavefront distortions between the optical beams and the frequency response of the detector. In Eq. (3.9) it is assumed that two optical frequencies of identical powers equal to one half the total
power, $P_T$, generate the beatnote signal (see Fig.3.1). Using Eq. (3.8) and (3.9), the CNR under shot noise conditions can be modeled

$$\text{CNR}_{\text{shot}} = \frac{\eta_{\text{net}}^2 \cdot r \cdot P_T}{4e \cdot B},$$

(3.10)

which can be used to calculate the shot noise limited CLaDS noise:

$$\sigma_{\text{CLaDS–shot}} = \frac{1}{\eta_{\text{net}}} \sqrt{\frac{2e \cdot B^3}{3r \cdot P_T}}.$$

(3.11)

This formulization will be the backbone to the study of fundamental limits of the CLaDS technique; however, first numerical verification of these models is presented in the following section. In DLAS the noise propagation is relatively straightforward as shown in Fig.3.1b. The acquisition bandwidth, $B$, determines the amplitude noise power at the output of the DLAS receiver, which can be calculated as:

$$\sigma_{\text{DLAS}}^2 = \int_0^B N_i df = N_i B,$$

(3.12)

and in shot-noise limited case can be expressed as

$$\sigma_{\text{DLAS–shot}} = \sqrt{2e \cdot r \cdot P_T \cdot B}.$$

(3.13)

### 3.2.1. Model Verification

To test the developed noise model, the analytical expressions in the previous section were compared to simulations of an ideal frequency demodulation. For given detection parameters (i.e. CNR), a sine wave with the appropriate carrier amplitude (Eq.(3.9)) and additive random
noise corresponding to the shot noise level described by Eq.(3.8) was simulated. The demodulation bandwidth \( B \) in Eq.(3.3), was then varied to investigate the dependence of the output noise on bandwidth. For the case of an ideal sine wave, an acquisition bandwidth corresponding to half the sampling rate was used. More information about bandwidth considerations for spectroscopic systems as opposed to sine waves is discussed in a section 3.3.

To eliminate any additive noise due to the numerical approximation of the sine wave or the filtering process, an additional carrier signal was generated, but with no added noise. After undergoing the same analysis with the noise-free signal, the demodulated signals were subtracted to reveal the true FM demodulation noise due to only shot noise at the input. The results of this analysis in comparison to the analytical expression derived above for the same detection parameters are detailed in Fig.3.3. This verification of our analytical model for the noise allows us to use this method to provide an accurate comparison to direct absorption spectroscopy.

![Image](image.png)

**Figure 3.3.** The comparison of simulated (red dots) and analytical (black line) analysis of shot-noise-limited frequency demodulation noise as a function of
bandwidth, \( B \). Also demonstrated here is the \( B^{3/2} \) nature of the demodulation noise.

### 3.3. Bandwidth Considerations

As the previous section illustrates, higher detection bandwidths result in higher output noise. Therefore, in an effort to have the lowest detection limit, the optimum bandwidth for the given sensing conditions must be determined. This is such that the spectroscopic signal is not filtered out but also that no unnecessary noise is added to the measurement. For CLaDS, where the noise dependence on bandwidth has an order greater than that of DLAS, this is particularly important.

To determine this optimum bandwidth, the spectrum of the transmission signal was analyzed to determine the frequency within which the signal is contained. For CLaDS this transmission signal is the phase change induced by interaction of the multi-frequency beam with the targeted species. The model for this signal can be extrapolated from the derivations in Chapter 2. Assuming a Voigt lineshape [13, 60], the expression for the CLaDS phase signal is given by

\[
\phi_{\text{CLaDS}} = -\left( \frac{\Omega \cdot L}{c_0} + \frac{\alpha_c \cdot L}{2W(iy)} \right) \text{Im}\left\{ W(x + iy) - W(x + x_\Omega + iy) \right\}. \quad (3.14)
\]

While the magnitude of the phase signal does not depend on the chirp rate (\( S \)), it does determine the time in which the signal is captured (\( \phi_{\text{CLaDS}} \) is a function of time, \( \phi_{\text{CLaDS}}(t) \)). To investigate this relationship, the bandwidth that fully contains the phase signal power was simulated as a function of different chirp rates, and the results are shown in Fig. 3.4.
**Figure 3.4.** Calculation of optimum bandwidth for CLaDS and DLAS; (a) Phase and absorption spectra calculated with a chirp rate of $5 \times 10^{14}$ Hz/s. The bandwidth containing 90% of the signal power is shown by the dotted line. For accurate calculation of the signal bandwidth, the DC component of each time domain signal was removed; (b) The 90% bandwidths as a function of chirp rate showing a linear relationship.

Figure 3.4 also shows that both modulating signals (absorption and dispersion) yield the same 90% signal bandwidth, which is not intuitive based on their different line-shapes, but fundamentally quite obvious since they are derived from the real and imaginary part of the same complex function connected through Kramers-Kronig relations. As expected, the relationship between bandwidth and chirp is linear, however, the simulations in Fig.3.4 assume a trace measurement (i.e. a low absorbance level). Strictly speaking, for a CLaDS system the peak frequency deviation must also be considered in the FM demodulation bandwidth term ($B_{CLaDS} = f_{mod} + f_{dev}$). This later term, $f_{dev}$, is very small in a trace measurement compared to the modulating signal, and therefore has little influence in the CLaDS bandwidth. Of course, for high level measurements this term may have some effect, but this analysis focuses on trace, low level measurements, as the goal is to investigate fundamental limits. Some of the results in the following sections will be presented in terms of a normalized bandwidth ($B_{norm} = B \cdot T_o$), which
for a fixed scan time ($T_o$, [s]) and a fixed scan range (12 HWHMS) provides an easy way to compare between the two spectroscopic methods capturing the same integrated signal power.

3.4. Single Point, Shot-noise limited SNR

The physical mechanism that generates the CLaDS signal (i.e. the change in refractive index due to a molecular transition) is coupled to the interaction affecting transmission that is the basis of Direct Laser Absorption Spectroscopy (DLAS). This relationship between absorbance and dispersion through the complex wavenumber was introduced in Chapter 1, along with models to describe DLAS spectral signals for both Lorentzian and Voigt lineshapes. The corresponding signal models for CLaDS were provided earlier in Chapter 2.

In order to compare the performance of CLaDS to that of DLAS, a normalized figure of merit must be established to ensure a fair comparison. To do this, the shot noise limited signal-to-noise ratio (SNR) of both techniques will be calculated assuming the same spectroscopic sample and identical acquisition parameters (i.e. sampling rate, scanning rate, number of samples averaged, etc.) and detection parameters (i.e. average optical power, noise at the output of the photodetector, etc.). For each technique optimum operating parameters, such as bandwidth and frequency spacing in the case of CLaDS, will be assumed.

3.4.1. CLaDS Single Spectral Point SNR

The model for noise propagation in a CLaDS detection system was detailed in section 3.2, and summarized by Fig.3.1. Assuming white noise at the input to the frequency demodulator, the output noise in the CLaDS signal is described by Eq.(3.7) and is proportional to $B^{3/2}$, where $B$ is the demodulation bandwidth. To develop a model for the SNR under shot noise limited conditions, a single-sideband (SSB) probe signal containing two optical frequencies at optimum
spacing for the given transition (see Section 2.4 for more information on optimum $\Omega$) is assumed to interact with the sample. The transmitted light is captured by the photodetector (PD). The phase of the received beatnote signal as function of time is calculated, from which the optimum bandwidth, $B$ (see Section 3.3), is determined. Using this as the demodulation bandwidth, the photodetector signal is frequency demodulated, which equates to taking the time derivative of the phase signal. A generic expression for the CLaDS single point SNR can be written as

$$ SNR_{\text{CLaDS}} = \frac{f_{\text{CLaDS}}^{\text{max}}}{\sigma_{\text{CLaDS}} \sqrt{1/K}}, $$

(3.15)

where the models for $f_{\text{CLaDS}}$ developed in Chapter 2 can be used to calculate the CLaDS signal amplitude, and $K$ is the number of averages.

The model presented in section 3.2 does not explicitly take into account the role of averaging on the total output noise. Under white noise dominated conditions, the instrument noise reduces as $\sqrt{K}$. For a given reporting window (ex. 1 data point every 1 sec), the chirp rate (i.e scan rate) determines the number of scans that can be averaged with that window (assuming there is no restriction imposed by the processing unit). Intuitively speaking, sensor performance should only be dependent on the total time that was used to obtain a single scan. Recording raw spectral scans at a high rate and subsequent averaging should yield the same noise performance as a single, slow scan that takes the same time.

Unlike in absorption spectroscopy, an advantage of the CLaDS technique in this regard is that the signal also scales with the chirp rate. Thus, a larger chirp rate results in a larger signal and higher noise (according to Eq.(3.7)), but also allows for a shorter scan time, and therefore permits more averaging to occur (i.e. $S \propto B \propto K$). If an optimized system is assumed (where the chirp rate
determines the optimum bandwidth and the maximum number of scans averaged), the $SNR_{CLaDS}$ in the random intensity noise dominated regime will be independent of the chirp rate. This has been previously shown by Daghestani et al. [68].

If the noise power density containing the low frequency noise term is used (Eq. (3.5)), the SNR will show chirp dependence at low chirp rates where intensity noise term is comparable to low frequency noise term. By chirping the laser faster, the useful signal is spread over a larger frequency range, and thus the near-DC corruption shows decreasing impact. The smallest chirp rate that is able to overcome the influence of this low-frequency component depends on the magnitude of the noise source. Fig.3.5 shows a simulation of SNR as a function of chirp rate for $f_0$ ranging from 0 to 1Hz. It is clear that for higher $f_0$, a higher chirp rate is required to achieve maximum SNR. Moreover if the number of averages $K$ is not adjusted properly, or just kept constant, the SNR as a function of chirp-rate will exhibit a characteristic maximum at optimum chirp rate beyond which a steady decrease is observed. The same is true for a single scan which is shown in Fig.3.5 as dash-dotted curve. This is consistent with empirical studies in the previous work by Nikodem et al. [66], which used a constant number of 500 averages at all chirp rates, and the resulting curves showed similar shape with a local maximum. The black curve in Fig.3.5 represents the purely random intensity noise limited case (Eq.(3.7)), and at high chirp rates the SNR asymptotically approaches this constant value. For realistic systems where this low-frequency noise cannot be avoided, tuning the chirp rate (and simultaneously the number of averages) allows the user to overcome effects of this noise contribution.

At higher chirp rates, the chirp spreads the measurement over a larger frequency range, and thus the near-DC noise once again becomes negligible. The smallest chirp rate that is able to overcome the influence of this LF component depends on the magnitude of the noise source. In
Fig.3.5, with a low frequency noise component of only $f_0=0.1$Hz, a relatively small increase in the chirp rate results in maximum SNR (no-LF component). However, if the noise is larger at 5Hz, a larger chirp rate is required to reach maximum performance. If a large enough chirp rate is used the system can be analyzed as though there is no LF noise component present. For realistic systems where this LF noise cannot be avoided, increasing the chirp rate (and simultaneously the number of averages) allows the user to overcome effects of this noise contribution.

**Figure 3.5.** The effect of chirp-independent, low-frequency noise on the CLaDS SNR. Smaller noise contributions from these sources can be quickly overcome with smaller chirp rates. Larger noise sources, however, require larger chirp rates.

Assuming a sufficiently high chirp rate to overcome the influence of the LF-noise, the CLaDS single point SNR can be written using the formulas for $f_{CLaDS}$ from Chapter 2 and the noise model developed here. With the Lorentzian expression for the CLaDS signal in Eq.(2.27) and the shot noise limited CLaDS noise given by Eq.(3.11), the CLaDS shot noise limited SNR can be expressed as
\[
SNR_{\text{CLaDS--shot}} = \frac{f_{\text{CLaDS}}^{\text{max}}}{\sigma_{\text{CLaDS--shot}} \cdot \sqrt{1 / k}} = \frac{1}{2\pi} \frac{S \cdot L \cdot \alpha_c}{2\omega_L} \cdot (1.12)
\]

Here the factor of 1.12 represents the maximum of the normalized CLaDS shape shown in brackets in Eq.(2.27) for a frequency spacing \( D = 2 \). It is important to note that in this analysis, \( f_{\text{CLaDS}} \) represents the peak signal amplitude, not the peak-to-trough value. This form was used in this analysis since the output noise expression represents an amplitude value, and therefore sets the minimum detectable level. A similar expression for SNR will be developed for DLAS in the next section.

### 3.4.2. DLAS Single Point SNR

The signal in DLAS is the fractional absorption recorded as a function of optical frequency for the given spectroscopic parameters. Under the assumption of a trace-gas measurement, the exponential term in Beer-Lambert’s Law (see Section 1.2.1) can be approximated as

\[
A_{\text{DLAS}} = \alpha_c \cdot L \cdot r \cdot P_T
\]

where \( \alpha_c \) is the peak absorbance, and the signal is transformed to the same units as the noise [A]. Using the shot noise limited formula for DLAS given by Eq.(3.13), an analogous expression to (3.16) can be developed for the shot-noise-limited SNR for a DLAS system.

\[
SNR_{\text{DLAS--shot}} = \frac{A_{\text{DLAS}}}{\sigma_{\text{DLAS--shot}} \cdot \sqrt{1 / k}} = \frac{\alpha_c \cdot L \cdot r \cdot P_T}{\sqrt{2e \cdot r \cdot P_T \cdot B \cdot \sqrt{1 / k}}}.
\]

Using Eqs. (3.16) and (3.17), the performance of CLaDS and DLAS are directly compared in the next section.
3.4.3. Single Spectral Point SNR Comparison

With the SNR expression presented in the previous sections, the shot noise limited performance of each technique can be compared on the basis of single spectral point detection. Single spectral point detection is an idealized scenario of system operation that could be used for continuous signal acquisition at the center of absorption line provided there is no baseline and baseline drifts in the spectroscopic system. Although such an idealized approach is unrealistic for real-world systems, the ultimate SNR in this limit represents an upper bound of SNR achievable in perfect conditions.

Through the analysis detailed in the previous sections we demonstrated that at a given chirp (scanning) rate, the optimum detection bandwidth for CLaDS and DLAS is the same. We also showed that at high chirp rates the CLaDS SNR is independent of chirp rate. Given these results, accurate, analytical expressions for single point SNR values for both CLaDS and DLAS were obtained. If the intensity noise at the output of the photodetector, $N_i$, the ratio of SNRs for both techniques yields:

$$\frac{SNR_{DLAS}}{SNR_{CLaDS}} = \frac{A_{DLAS}^{\text{max}}}{\sigma_{DLAS}^{\text{max}}} / \frac{A_{CLaDS}^{\text{max}}}{\sigma_{CLaDS}^{\text{max}}}.$$  \hspace{1cm} (3.18)

Using Eq.(3.18), the SNR values for both techniques, as well as their ratio can be directly calculated for given spectroscopic and detection parameters. This direct SNR comparison is shown in Fig.3.6 as a function of normalized bandwidth, for a scan time of $T_0 = 1$ms, a chirp rate of $S = \omega_L \times 12/T_0$ (i.e. the width of the spectral scan is 12 HWHMs), a Lorentzian linewidth of $\omega_L = 2\pi \times 2$ GHz, a peak absorbance of $\alpha_c \cdot L = 2 \times 10^{-4}$, a detector noise density with a magnitude of $N_i = 10^{-14}$ A$^2$/Hz, and a CLaDS frequency spacing of $\Omega = 2\omega_L$. 

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Figure 3.6. The SNR of DLAS and CLaDS and the ratio of both versus the filtering bandwidth. Data from normalized bandwidths less than 11 (99.995% of signal power) are not considered in this analysis because the signal for both techniques is partially filtered out, making concentration extraction difficult. The dotted lines show the reference case chosen for comparison of a single point analysis scheme detailed in the previous sections.

Due to the fundamental relationship between absorption and dispersion, using the Lorentzian formulization for both DLAS and CLaDS (Eq.(1.12) and Eq.(2.27), and the shot noise models given by Eq.(3.13) and Eq.(3.11), the shot noise limited SNR ratio can be written as:

\[
\frac{SNR_{DLAS\text{-}shot}}{SNR_{CLaDS\text{-}shot}} = \frac{\alpha_c \cdot L \cdot r \cdot P_T / \sqrt{2e \cdot r \cdot P_T \cdot B}}{\frac{1}{2\pi} S \cdot L \cdot \frac{\alpha_c (1.12)}{2\omega_L} / \left( \frac{1}{\eta_{het}} \sqrt{\frac{2e \cdot B^3}{3r \cdot P_T}} \right)}, \tag{3.19}
\]

Again, here the factor of 1.12 represents the maximum of the normalized CLaDS shape shown in brackets in Eq.(2.27) for a frequency spacing \( D = 2 \). In addition, weak absorption is assumed such the values for peak absorption and absorbance are equivalent. The chirp rate can be expressed in terms of the range of the frequency chirp and the total measurement time, \( S = \omega_L^* \).
\( \omega_R / T_0 \), where \( \omega_R \) is the scan range in terms of halfwidths. For this calculation a scan range of 12 halfwidths is used (justification for this value will be included in the next section 3.5.2). Using a value for the normalized bandwidth, the chirp rate can be expressed in terms of bandwidth. With this relation and \( B_{\text{norm}} = B \cdot T_0 \), Eq.(3.19) can be rewritten and further simplified to

\[
\frac{\text{SNR}_{\text{DLAS shot}}}{\text{SNR}_{\text{CLADS shot}}} = \frac{\alpha_c \cdot L \cdot r \cdot P_T / \sqrt{2e \cdot r \cdot P_T \cdot B}}{1 \cdot \frac{\omega_L \cdot \omega_R \cdot B}{B_{\text{norm}}}} \cdot \frac{1}{\frac{\omega_L}{2 \omega_L}} \cdot \frac{1}{\frac{2 \cdot B^3}{3r \cdot P_T}} = \frac{4\pi \sqrt{1/3}}{(1.12)\eta_{\text{het}} \omega_R / B_{\text{norm}}}.
\]

Using Eq. (3.20) and \( \omega_R = 12, B_{\text{norm}} = 11, \) and \( \eta_{\text{het}} = 1, \) the SNR ratio is 5.93. This result agrees with the calculations presented in Fig.3.6 for the given normalized bandwidth. The results shown in this section indicate that the SNR for DLAS is \( \sim6x \) higher than that of CLaDS under the same conditions. More information about results obtained via fitting, instead of a single-point peak analysis, is presented in the next section.

### 3.5. SNR for Full Spectral Scan

The previous section showed that the single spectral point SNR between DLAS and CLaDS differs; however, a single-point analysis does not represent the method a real spectrometer would use to extract spectroscopic information from the measured data. Rather, a spectral scan followed by a fitting algorithm would be employed. Thus both methods will be compared based on full spectral scan mode, which should take into account all the subtleties of the signal, noise, and baseline.
The CLaDS technique generates a non-white noise spectrum in which a $f^2$ noise spectral density causes the SNR (which captures the noise integrated over the entire bandwidth) to appear much worse (as compared to DLAS where the noise is white). This can be seen in Fig.3.7, where relative noise is lower for the DLAS spectrum (Fig.3.7b), but the in the CLaDS spectrum (Fig.3.7a) the signal and high-noise regions do not significantly overlap.

Figure 3.7. Signal and noise power spectral densities for a) CLaDS and b) DLAS using identical system parameters.

Therefore an appropriate fitting algorithm which takes into account the different distribution of noise and signal in the frequency domain is required to efficiently extract information from the CLaDS spectra. To investigate this idea, the behavior of nonlinear regression (or curve fitting) of DLAS and CLaDS spectra are analyzed when appropriate noise models are used in the fitting algorithm.

For a given spectral fit, there is some uncertainty on the retrieved absorbance value, denoted by $\sigma(\alpha_c \cdot L)$. This standard error can be obtained by analyzing the Jacobian matrix of the model function used to perform the fit [69]. Similar error values can be extracted for other fit parameters, however in this analysis the extraction of the gas absorbance (or concentration) will
be the main focus. To assess the efficiency of parameter extraction through various curve fitting routines, the uncertainty of the retrieved absorbance is normalized to an ideal system precision (free of experimental imperfections), given by

$$\sigma((\alpha_c \cdot L)_{ideal}) = \frac{\sqrt{N_i \cdot B}}{r \cdot P_T}. \quad (3.21)$$

The ratio $\sigma(\alpha_c \cdot L) / \sigma((\alpha_c \cdot L)_{ideal})$ is a figure of merit termed the Observation Factor in Ref. [70]. An introduction to this method for curve fitting assessment is presented in the next section.

### 3.5.1. Observation Factor

The Observation Factor represents a normalized error on a retrieved fit parameter, and is independent of line strength and laser power noise amplitude. The ratio $\sigma(\alpha_c \cdot L) / \sigma((\alpha_c \cdot L)_{ideal})$ enables a fair comparison of different laser-based spectroscopic methods and reduces the complexity of the assessment by removing the influence of spectroscopic and detection parameters. Another advantage of this assessment method is that this ratio can be easily computed from the Jacobian matrix, $F$, of the model used in the nonlinear regression [70]. Since the noise on the CLaDS spectrum is non-white the generalized least squares method, an extension of the (ordinary) least squares method, must be used.

In generalized least squares, the error function is given by

$$L(x, \theta) = (y - f(x, \theta))^T A^{-1} (y - f(x, \theta)) \quad (3.22)$$

where $y$ is the vector of measurements, $x$ is the vector of abscissa points, $\theta$ is the vector of the unknown model parameters, $A$ is the covariance matrix, and $f$ is the model function [71]. For the
ordinary least squares, \( A = I \), where \( I \) is the identity matrix, corresponding to the assumption of white noise.

For the generalized least squares model, the observation factor is given by the following expression (see 4.3 in [71] and [72] for the errors on estimated parameters for generalized and nonlinear least squares:

\[
\frac{\sigma(\alpha_c \cdot L)}{\sigma((\alpha_c \cdot L)_{\text{ideal}})} = \sqrt{(F^T A^{-1} F)^{-1} F^T A^{-1} W A^{-1} F(F^T A^{-1} F)^{-1})_{11} n} \tag{3.23}
\]

where \( W \) is the covariance matrix of the noise. The elements of the matrix \( W \) are related to the noise spectral density, \( S_0 \), on the spectrum by (see eq. 3.84 in [70])

\[
(W)_{ij} = \frac{1}{\sqrt{2}} \int_0^{1/2} S_0(\tau n / T_0) \cos(2\pi f |i - j| \tau) d\tau \tag{3.24}
\]

with \( n/T_0 \) is the sampling rate of the measured signal, and \( n \) is the number of points for one spectral scan.

For white noise \( A = W = I \), in which case the known formula \( \sqrt{(F^T F)^{-1}_{11} N} \) is obtained. The covariance matrix, \( W \), of the noise is calculated from the noise spectral density on the spectrum using Eq.(3.24) and will be different for CLaDS and DLAS analysis. For DLAS, white noise is assumed, therefore \( A = I \) is used. For CLaDS, where the measurement noise is the derivative of white noise (i.e. violet noise), \( A = \text{tridiag}(-0.5,1,-0.5) \) (i.e. the tridiagonal matrix with 1 on the main diagonal and -0.5 on the diagonal above and below the main diagonal) is used. This
covariance matrix is obtained from calculation of the finite difference of white noise, which represents the derivative that governs the frequency demodulation process. Note that although Eq.(3.23) is only valid asymptotically for the case of “low noise”, this is not a constriction in the real world, since the nonlinear curve fit would not give very high performance if the noise level exceeds a certain limit (e.g. convergence problems) [70].

From a more physical standpoint, the observation factor represents how much the error in the parameter extraction deviates from an idealized system error where only the peak of the absorption curve is measured (i.e absorbance noise on a single point). This corresponds to a fit of only the peak absorbance while all other parameters are known apriori, and resulting in an observation factor equal to 1 [73]. This case, along with others, is shown in Fig.3.8, where the observation factor for a DLAS system as a function of normalized bandwidth is plotted for several fitting routines consisting of varying fit parameters.

![Figure 3.8](image)

**Figure 3.8.** Observation Factor as a function of normalized bandwidth for several fits with different unknown parameters. In all but the dark blue case, a spectral scan range
of xR = 12 HWHMs was used (the choice of this value will be discussed in the next section).

Shown in Fig.3.8 is that for sufficient measurement bandwidths \((B \cdot T_0 > 11)\) there is negligible bandwidth dependence of the observation factor. At lower bandwidths, however, the spectral information is filtered out, making the parameter extraction highly inefficient. As the number of fit parameters is decreased, the values start to approach the limit of 1, corresponding to a fit of only the peak absorbance with a reduced scan range \((xR = 1 \text{ HWHM})\). This latter case represents an idealized and technically difficult case of measurement of a single point at the peak of the absorption curve with no baseline or drift effects.

### 3.5.2. Fitting Comparison Results

In the comparison presented here, a Lorentzian lineshape is assumed with the following parameters: time for one scan \(T_0 = 1\text{ms}\), Chirp rate \(S = \omega_L \cdot 12/T_0\) (i.e. the width of the spectral scan is 12 HWHMs), Lorentzian linewidth \(\omega_L = 2\pi \cdot (2 \text{ GHz})\), peak absorbance \(\alpha_c \cdot L = 0.03\), detector noise density \(N_i = 10^{-14} \text{ A}^2/\text{Hz}\). For CLaDS a frequency spacing of \(\Omega = 3\omega_L = 2\pi \cdot (6 \text{ GHz})\) is used. In the DLAS signal a quadratic baseline of \(1+0.1x-0.05x^2\) with \(x = (t-T_0/2)/T_0\) was chosen to mimic the power variation of a typical diode laser scan.
Figure 3.9. Spectral shapes and illustration of fit parameters used for the comparison of CLaDS to DLAS.

Note that \( \Omega = 3\omega_L \) is larger than the optimum value found in section 2.4; however, this increase in \( \Omega \) allows for more efficient parameter extraction during the fitting process due to the full separation of the two features that make up the overall CLaDS shape. Unlike in DLAS, the full separation of the two features in CLaDS provides a built-in relative frequency reference which permits the model to fit for both the transition linewidth and the chirp rate without significant cross-talk. Despite the increase in frequency spacing, the change is signal bandwidth (and therefore noise) is negligible, allowing for use of the same noise models as detailed previously.

The five unknowns in the CLaDS spectrum are \( \alpha_c \cdot L, \omega_L, S, \) line center and a offset. For direct absorption the fit parameters are: \( \alpha_c \cdot L, \omega_L, \) line center and the three polynomial coefficients for the baseline. These parameters are illustrated in Fig.3.9. Note that for direct absorption the line width and chirp rate cannot be fit simultaneously since both parameters scale the spectrum horizontally. This is a well-established issue in single absorption line methods where the wavenumber scale cannot be inferred from the spectrum itself. For CLaDS the modulation frequency, \( \Omega \), is ideally known and therefore the separation of the two CLaDS peaks can be used
to infer a relative wavenumber scale without the need for additional calibration. In this analysis the impact of bandwidth was achieved by implementing a discrete Fourier transform (DFT) based filtering scheme.

**Figure 3.10.** Observation Factor as a function of normalized bandwidth for different scan ranges (given in HWHMs) in DLAS (left) and CLaDS (right). In DLAS, scan ranges (xR) less than 12 HWHMs result in a loss of system precision because the fit cannot efficiently decouple the baseline from the gas signature. In CLaDS, there is only an spectral offset, which does not result in this same coupling effect. Therefore, low scan ranges result in lower noise in a CLaDS system. For the sake of a fair comparison, a scan range of 12 HWHMs was chosen for use in both techniques.

The scan range of 12 HWHMs was chosen to minimize the error in both techniques that results from the amount of wings captured in the spectrum. For DLAS, enough of the wings must be captured to decouple the influence of the baseline from the spectral fit and depends on the polynomial order required to fit the baseline. In CLaDS, the more of the wing that is captured,
the fewer the points are used to fit the signal (assuming a constant number of captured points) and therefore the error increases (see Fig.3.10). A scan range of 12 HWHMs was empirically found to be the lowest scan range that accurately represents the baseline in the DLAS fit.

Using this set scan range and the fit parameters stated previously, the observation factor for DLAS and CLaDS can be calculated as a function of normalized bandwidth. For the DLAS analysis, white noise and an ordinary least squares algorithm were analyzed. For CLaDS, an analogous situation to the DLAS case (white noise, ordinary least squares) was simulated. In addition, a generalized least squares method assuming a violent noise model was also examined for CLaDS. This latter case more closely matches the noise characteristics in a CLaDS spectrum. The results of this analysis are shown in Fig.3.11, and show that when the appropriate noise model for each technique is utilized in the curve fitting routine, comparable parameter extraction is observed.

![Figure 3.11](image.png)

**Figure 3.11.** The noise performance for DLAS (green trace) and CLaDS. CLaDS with the fit assuming white noise on the spectrum (i.e. ordinary least squares, $A=I$, red
trace) and a fit correct $f^2$ noise density (generalized least squares, $A=$tridiag(-0.5,1,-0.5),
blue trace) is shown. For the red trace, CLaDS detection has an optimum bandwidth,
while, as expected for the correctly specified covariance matrix the CLaDS fitting is
independent of the bandwidth. If the bandwidth is too low the noise performance
dramatically worsens, because the signal content is removed by the low-pass filtering.

With a proper noise model the CLaDS performance becomes independent of the detection
bandwidth, which is not the case if ordinary least squares fitting is considered (red curve in
Fig.3.11). Hence, the generalized least squares fitting not only provides a sensitive evaluation
method for CLaDS signals, it also makes the detection less sensitive on the selected bandwidth
(provided the noise is low enough that the nonlinear fit exhibits no convergence problems).

An analogous concept to the process of matching the noise model used in spectral fitting to that
of the signal is the method of pre-emphasis and de-emphasis used in frequency modulated (FM)
communication systems. Received FM signals used for communication are known to have a
parabolic noise spectrum, introducing more noise at higher frequencies. To mitigate this effect,
the message signal is pre-emphasized to amplify higher frequencies in a complimentary fashion.
A de-emphasis filter is then employed to compensate for this predetermined distortion,
essentially removing the frequency dependency of the noise [67]. In the spectroscopic systems
presented here there is no way to pre-emphasize the signal (since it is generated by the
interaction of the laser light with the gas), however, the method used to extract the spectroscopic
information can be modified to match the noise characteristics of the received signals, allowing
for efficient information retrieval.
3.6. Discussion

This chapter has discussed a model for the output noise in a CLaDS instrument as function of its detection parameters. The role of the demodulation bandwidth and chirp rate was also investigated, showing a linear relationship between chirp rate and optimum bandwidth. A chirp-independent SNR is achieved when 100% duty cycle averaging is employed. Technical noise in CLaDS systems was studied in other works which examined the influence of fringe noise [66], as well the non-ideal chirp rate [68], in addition to other noise sources. The noise models developed here, in conjunction with the signal models presented in Chapter 2, allowed for a theoretical study comparing the fundamental limits of the CLaDS technique is comparison to Direct Laser Absorption Spectroscopy to be conducted.

The presented investigation into the sensitivities of both CLaDS and DLAS provides a direct comparison between the two techniques under the fundamental limits of white noise on the photodetector signal. Analysis of the single point SNR for DLAS under shot noise conditions is rather straightforward; however, CLaDS analysis requires extra care due to the fact that both the signal amplitude and noise depend on the chirp rate of the laser. As a result, averaging and bandwidth considerations must be addressed. Under simulations of a trace measurement, the presented model was simulated and yielded a discrepancy of a factor of ~6 between the single point SNR for the two techniques, in the favor of DLAS. However, when the correlation of noise in the CLaDS spectrum, resulting from the frequency demodulation process, is considered in a generalized least squares fitting routine, this discrepancy is removed and both techniques show the same performance. This is in part due to the simplified baseline of the CLaDS signal, which can often be represented as a simple vertical offset, as compared to the often non-linear baseline
on the DLAS spectra. Further investigations are needed to analyze the fundamental performance of chirp-modulated CLaDS (see Chapter 5), in addition to sensing of optically thick samples.
Chapter 4: CLaDS Implementation: Signal Generation and Detection Schemes

4.1. Implementation of CLaDS

This chapter provides practical information about the implementation of the CLaDS technique using various optical technologies operating in both the near and mid-infrared. The CLaDS technique under ideal conditions and irrespective of spectral region was outlined in Chapter 2, while here the technique details and practicalities of the multi-frequency signal generation and detection schemes are discussed. Implications of non-idealities of implementation are also included.

4.1.1. Single Sideband Operation

CLaDS was originally envisioned as a dual frequency technique where a single sideband was generated with respect to the original laser frequency [58]. The derivations shown in Chapter 2 assume this single sideband approach. Pure single-sideband (SSB) operation has been achieved using an acousto-optic modulator (AOM) functioning as a frequency shifter; a configuration that has been demonstrated in the mid-infrared (section 4.1.1.1). Quasi-single sideband operation (qSSB) has been realized in the near-infrared using electro-optic modulators (section 4.1.1.2) and in the mid-infrared using a direct laser modulation technique (section 4.1.1.3).
4.1.1.1. AOM Implementation

CLaDS systems implemented using an acousto-optic modulator (AOM) operating in the mid-infrared have been featured in a number of publications [58, 66, 74-77]. The AOM, shown in the system configuration in Fig.4.1, is driven by an external sinusoidal signal. Governed by the acousto-optic effect, an AOM (sometimes called a Bragg cell), uses the interaction of a sound, or acoustic, wave with an optically isotropic medium to generate a propagating sound wave which in turn generates a dynamic graded-index material. The interaction of the light with this periodic index material results in Bragg diffraction of the incoming light, causing both a spatial diffraction and frequency shift determined by the acoustic frequency [9, 78], denoted here as $\Omega$. The frequency shifted signals are diffracted at different angles, therefore the 0th order (un-shifted) and 1st order ($+\Omega$) beams can be spatially isolated and recombined into one collinear beam, resulting in a pure single-sideband probe beam.
**Figure 4.1.** Setup for a SSB CLaDS system implemented using an acousto-optic modulator (AOM); (QCL – quantum cascade laser, M – mirror, BS – beam splitter, PD – photodetector).

In addition to the fairly straightforward physics of SSB CLaDS (only two co-propagating wave interfere to create the signal), systems utilizing this technique exhibit perfect signal linearity with the target concentration. This is in contrast to absorption based systems where, due to the exponential in Beer-Lambert’s Law, a non-linear response with concentration is expected for sample absorptions greater than \(~10\%\). As a result of this non-linear behavior, it is technically challenging to use one instrument for optically thin (low absorption) and thick (high absorption) samples without the additional complexity of targeting multiple molecular transitions of varying strengths [79]. Dispersion, while often more challenging to measure due to the fact that the information is encoded in the phase of the received light, is directly proportional to absorbance and therefore linear with species concentration. CLaDS, a measure of dispersion, therefore has the potential for a truly linear response. This linearity was demonstrated experimentally by Nikodem et al. in Ref. [77], where an AOM based, SSB-CLaDS system (Fig.4.2) probed an N\textsubscript{2}O sample of varying concentrations from tens of parts-per-million by volume (ppmv) to 2500ppmv. The resulting fractional absorption therefore ranged from single percent value up to values around 90\%. CLaDS spectra over the range of sample concentrations and the extracted CLaDS amplitudes as a function of N\textsubscript{2}O concentration is shown in Fig.4.2. A linear fit \((y=a*x)\) of the CLaDS amplitude vs. concentration curve yielded a \(R^2\) value of 0.9999, illustrating a perfectly linear response.
Figure 4.2. Top: Experimental configuration (M – mirror, BS – beam splitter); Bottom Left: CLaDS signals for several different concentrations of N$_2$O. All the spectra are vertically scaled for aid in an easy comparison between spectra; Bottom Right: CLaDS amplitude as a function of N$_2$O concentration. Reprinted with permission from [77].

Also demonstrated by Nikodem et al. in Ref. [77] was the same linear response for a variant of CLaDS called Chirp-Modulated (CM) CLaDS, a technique that will be discussed in detail in Chapter 5. In a subsequent section, signal linearity with concentration for the dual-sideband CLaDS approach will be examined.

While there are advantages for utilizing an AOM to generate the multi-frequency signal required for the CLaDS technique, there are also some technical details that may limit the overall performance of the instrument. First, the beams emerge from the AOM at different angles, and
while this feature allows for spatial isolation of the beams resulting in pure single-sideband operation, this spatial separation requires additional optics to recombine the beams, consequently increasing the complexity of the system and reducing the opto-mechanical stability. In addition, the two beams travel separate paths until they are recombined. Any path length difference between will produce an offset in the CLaDS spectra [58]. A model used to investigate the effect of this path length difference is shown in Fig.4.3, where one path is delayed by an amount, $\Delta L$.

![Model of CLaDS spectra](image)

**Figure 4.3.** Model used to study the effect of a path length offset between the two optical waves at $\omega_1,2$. $L$ is the geometric length of the gas cell, $L_{total}$ is the free-space length, and $\Delta L$ represents the path length mismatch. Adapted from Fig.2b in [58].

The path length difference results in a constant frequency offset equal to $S \cdot \Delta L / c$. This effect can be added to the equations derived in Chapter 2 (Eq. 2.13) to yield a more complete model of the CLaDS spectra,

$$f(\omega) = \frac{1}{2\pi} \left( \Omega + \frac{S \cdot \Delta L}{c} - \frac{S \cdot L}{c} \cdot \Omega \cdot \left( \frac{dn}{d\omega_{\omega-\Omega}} - \frac{dn}{d\omega_{\omega}} \right) \right),$$  \hspace{1cm} (4.1)

While this effect can be modeled, the need for additional optical components to perform the spatial recombination not only increases the complexity of the instrument, but also reduces the
stability of the optical alignment, an issue that becomes of increased importance in field-deployable systems. To overcome this technical limitation, a variant of the CLaDS technique, Chirp-Modulated (CM) CLaDS, was developed and utilizes a harmonic detection to eliminate the effect of this frequency offset [74]. More about this technique will be discussed in Chapter 5.

Additionally, commercially available mid-infrared AOM technologies are often limited to frequency shifts on the order of 100MHz, while larger shifts are only possible at shorter wavelengths. As introduced in Chapter 2, the optimum frequency spacing (i.e. to yield the largest signal amplitude) corresponds to the linewidth of the targeted transition. For open-path sensing applications, pressure-broaden transitions of common atmospheric species are on the order of GHz. Thus, the frequency spacing provided by mid-infrared AOM devices result in sub-optimal CLaDS spectra. Efforts to generate GHz frequency shifts using mid-infrared technologies using direct modulation schemes are presented in the next section.

4.1.1.2. qSSB with near-infrared EOMs

While to date SSB emission is not achievable through direct modulation of a diode laser, qSSB emission in the near-infrared is possible through the use of external electro-optic modulators (EOMs) [80]. To test the feasibility of this concept in a CLaDS sensor, a system operating at 1.55 μm to target hydrogen cyanide (HCN) was developed (see Fig.4.4). To generate a qSSB optical spectrum, a dual-parallel Mach-Zehnder modulator (DPMZM) was used. An electro-optic device with two MZMs embedded into the parallel branches of a third MZM, the DPMZM was driven with orthogonal sinusoidal inputs. With appropriate selection of the three bias voltages, signification suppression of one of the sidebands can be achieved.
**Figure 4.4.** CLaDS system with DPMZM for dual-color beam (SSB spectrum) generation. 3dB hybrid coupler is used to drive modulator with two orthogonal signals; (LD – laser diode, SG – signal generator, PC – polarization controller, PD – photodetector, OS – optical spectrum) [81].

With the configuration presented in Fig.4.4, an optical spectrum analyzer was used to measure the sideband suppression, which for these tests was 17dB. While further suppression is desired (usually >25dB), the laser and DPMZM system was used to measure the CLaDS spectra for the 15553.755 nm transition in the $2\nu_3$ ro-vibrational band of HCN. The qSSB optical spectrum and the resulting CLaDS spectra are shown in Fig.4.5. For this experiment, a 5.5 cm sealed cell at 25 Torr was used, along with a chirp rate of $S = 250$ MHz/ns and a frequency shift, $\Omega$, of 1.5 GHz.

This proof of concept experiment showed that the CLaDS technique can be performed using EOM technology to generate a qSSB optical spectrum in the near-infrared. Further discussion of the implications of the non-ideal spectrum on system performance will be provided in the conclusion.
Figure 4.5. a) Normalized transmission spectrum of the target HCN transition and b) a quasi SSB spectrum at the output of DPMZM when driven at 1.5 GHz, both measured with high-resolution spectrum analyzer; c) CLaDS spectrum of the P15 transition of HCN recorded using SSB modulation with spacing of $\Omega = 1.45$ GHz. Frequency axes show detuning of the laser frequency from the center of the P15 transition at 1553.755 nm (~193.86 THz). Spectrum in c) is normalized by the chirp rate to facilitate comparison with DSB-based signals recorded at different chirp rate [81].

4.1.1.3. qSSB with Direct Modulation of a QCL

To overcome the limitations of AOM technology commercially available in the mid-infrared, Hangauer et al. investigated the high frequency modulation of a QCL with the intention to generate single-sideband emission [82]. Tuning of the optical frequency of a semiconductor laser through modulation of the injection current is typically caused by two effects: a low frequencies joule heating induces a change in refractive index (i.e. thermal tuning), and at high frequencies light-carrier interactions cause a change in refractive index (i.e. electronic tuning) [83]. Due to the tuning behavior of the laser, modulation of the injection current changes both the output
optical frequency as well as the intensity. The modulation indices to describe this behavior are given by the Intensity Modulation (IM) index \( (m = \frac{\Delta I}{I_0}) \) and the Frequency Modulation (FM) index \( (\beta = \frac{\Delta f}{f_m}) \). In Ref. [82], they found that the unique FM and IM characteristics of QCLs allow for optical quasi-single-sideband emission through direct current modulation. By keeping the internal laser temperature constant, the direct effects of carrier injection were separated from secondary thermal effects. Through accurate measurement of the sideband ratio, \( SR \), and FM/IM phase shift, \( \theta \), for frequencies ranging from 300 Hz – 1.7 GHz, qSSB operation (i.e. significant suppression of one of the sidebands, ideally \( SR = 0 \) and \( \beta/m = 1/2 \) ) was observed for \( \theta \sim 18^\circ \) and \( SR = -16 \) dB for 200 MHz – 1 GHz. This qSSB approach cannot be translated to diode laser approaching in the near-infrared due to a difference the intrinsic linewidth enhancement factor (see [82, 84-86] for more information). In a separate experiment, qSSB emission from a directly modulated QCL was used to successfully perform spectroscopic detection of ammonia (NH\(_3\)) at 9.618 \( \mu \)m using the CLaDS technique [59].

4.1.2. Dual Sideband Operation

While initially proposed and developed as a two-frequency, single-sideband method, CLaDS can be extended to a multi-frequency technique. Under the assumption of ideal intensity modulation with fully coherent sidebands, and with negligible absorption effects introduced by the sample, a CLaDS spectrum can be generated by a triple-color, dual sideband (DSB) beam, as shown in Fig.4.6. In this idealized case, two beatnotes are generated by the photodetector, one at the difference frequency between the carrier and the upper sideband (0\(^{\text{th}}\) and +1\(^{\text{st}}\) order) and one at the difference frequency between the carrier and the lower sideband (0\(^{\text{th}}\) and -1\(^{\text{st}}\) order), both at \( \Omega \).
Figure 4.6. Three frequency beam with fixed frequency spacing used in dual-sideband CLaDS.

Assuming that the beatnote amplitudes are equal, the resulting signal would represent the average of the individual phase signals. Thus, the DSB CLaDS spectrum can be expressed as

\[
f_{\text{DSB}}(\omega) = \frac{1}{2\pi} \left[ \Omega + \omega \cdot \frac{1}{2} \cdot \frac{S \cdot L}{c} \left( \frac{dn}{d\omega_{\omega+\Omega}} - \frac{dn}{d\omega_{\omega}} \right) \right] + \ldots
\]

\[
... + (\omega - \Omega) \frac{1}{2} \cdot \frac{S \cdot L}{c} \left( \frac{dn}{d\omega_{\omega}} - \frac{dn}{d\omega_{\omega-\Omega}} \right) \].

Assuming that \( \omega \gg \Omega \), the formulation for the CLaDS signal reduces to

\[
f_{\text{DSB}}(\omega) = \frac{1}{2\pi} \left[ \Omega + \omega \cdot \frac{1}{2} \cdot \frac{S \cdot L}{c} \left( \frac{dn}{d\omega_{\omega+\Omega}} - \frac{dn}{d\omega_{\omega-\Omega}} \right) \right].
\]

Comparing Eq. (4.3) to Eq.(2.13), using the DSB configuration the spectra at \( 2\Omega \) is encoded in the averaged beatnote at \( \Omega \), however, the signal amplitude is decreased by half. Despite the reduction in signal amplitude, the potential to optimally probing the targeted molecular transition at half the linewidth may result in an overall system improvement due to availability and
performance of high bandwidth photodetectors and digitization systems. In the next two sections the implementation of DSB CLaDS in both the near- and mid-infrared will be discussed.

4.1.2.1. DSB CLaDS with EOMs

To generate a dual-sideband optical spectrum to be used in a CLaDS instrument, a standard Mach-Zehnder modulator (MZM) can be used. Currently these electro-optic devices are only available in the shorter wavelength region; however, many interesting molecules such as CH$_4$ have overtone transitions in the near-infrared (see Chapter 6 for more discussion of applications).

![Figure 4.7. CLaDS system with MZM for triple-color beam (DSB spectrum) generation](image)

Use of these fairly simplistic devices may be advantageous when the cost or complexity of DPMZMs eliminate them as realistic options. As a proof of concept demonstration of DSB CLaDS, a sensor was developed to target HCN at 1553.755 nm, a wavelength that is well within the specifications of most commercially available MZMs. The developed system is shown in Fig.4.7 [81].

Operating as an intensity modulator, the MZM in Fig.4.7 is driven sinusodially. The operating principle of the MZM is shown in Fig.4.8, where the input modulation is converted to intensity modulation by the transfer function of the MZM device. The bias of the MZM was chosen to
position the input modulation along the approximately linear portion of the curve. Selection of
the modulation amplitude was then chosen to maximize the response without over modulating
which would introduce higher harmonics (i.e. more significant, higher harmonic sidebands) into
the output signal. In addition, the MZM is a phase-sensitive device, so an external polarization
controller (PC) was used to align the input polarization to that of the device.

![Diagram of T(V) curve]

**Figure 4.8.** Transmission curve \((T(V))\) of a MZM showing the conversion of voltage
modulation \((V_M)\) to intensity variation around the quadrature point \((V_B)\).

Using the sensor illustrated in Fig.4.7, CLaDS spectra of HCN were collected for various MZM
modulation frequencies (i.e. frequency spacing of the triple-color beam, \(\Omega\)). The results of these
tests are shown in Fig.4.9, where a clear amplitude dependence on \(\Omega\) is shown, as well as
excellent agreement with the model given by Eq. (4.3).
Figure 4.9. Experimental CLaDS spectra recorded using the DSB CLaDS setup shown in Fig. 7 for three different modulation frequencies (spectra are shifted vertically and horizontally for viewing purposes only). The measured spectra are in good agreement with the developed models [81].

To investigate the loss in signal amplitude in this DSB approach, the signals captured with the sensor described here were compared to those captured the qSSB sensor built around a DPMZM (detailed in section 4.1.1.2) for the same molecular transition of HCN. The CLaDS amplitudes as a function of frequency spacing, $\Omega$, for both instruments are shown in Fig. 4.10 in the range of 100 MHz to 2.3 GHz. As expected the optimum spacing for the DSB instrument occurs at $\Omega \approx 0.73$ GHz, which is half of the SSB value of $\Omega \approx 1.46$ GHz. In addition, the corresponding maximum amplitudes differ by a factor of two as predicated by Eq.(4.3). Operation in a DSB configuration allows for flexibility of the CLaDS technique to probe a molecular transition with the optimum frequency spacing with half the modulation frequency as compared to SSB.
Figure 4.10. The amplitude of the CLaDS signal as a function of modulation frequencies Ω obtained with SSB modulator shown in Fig.4.4 and DSB modulator in Fig.4.7. Excellent agreement with the model is observed [81].

4.1.2.2. DSB CLaDS with Direction Modulation

Generation of a DSB optical spectrum is also possible through direct modulation of the injection current to a laser. This was demonstrated recently in the mid-infrared by Hangauer et al. in their investigation of high frequency modulation of QCLs [82]. As discussed in section 4.1.1.3, the phase (θ) and ratio of the frequency modulation (FM) and intensity modulation (IM) indices (β and m, respectively) that result from modulation of the injection current can be varied by changing the DC bias current and TEC temperature for given modulation parameters (current amplitude and frequency). For SSB operation, where a sideband ratio of SR = 0 is desired, they showed the intensity and frequency modulation should be in phase (θ = 0) and the FM/IM ratio should be equal to $\frac{1}{2}$ ($\beta/m = \frac{1}{2}$). To achieve DSB emission, the DC current and TEC temperature can be adjusted to achieve a sideband ratio SR = 1 and no frequency modulation ($\beta = 0$), which
indicates pure intensity modulation. This is analogous to the case where an external EOM is used to generate pure intensity modulation as discussed in section 4.1.2.1.

4.1.3. Other Configurations

Alternative implementations of the CLaDS technique to the ones presented above have also been investigated to address various technical limitations, namely the unavailability of high speed modulators in the mid-infrared and the effect of multiple sidebands (i.e. more than two) on the CLaDS signal. The lack of high-speed modulators in the mid-infrared results in the generation of sub-optimal CLaDS spectra. To take advantage of high-speed electro-optic modulators available in the near-infrared, a differential frequency generation (DFG) source was utilized to convert the multi-color beam generated at 1.55 μm to the mid-infrared regime at 3.4 μm [87]. The developed system is presented in Fig.4.11, where the triple-color beam at 1.55 μm is amplified using a Er-doped fiber amplifier (EDFA) and combined with light from a pump laser at 1 μm. The two beams are then focused on a periodically poled lithium niobate (PPLN) crystal, where the $\chi^{(2)}$ nonlinearity of the material results in the generation of radiation at the difference frequency between the two input signal. More information about DFG can be found in Ref. [88].

Figure 4.11. DFG CLaDS system configuration. (DFB LD – distributed feedback laser diode; PD – photodetector; EDFA – Er-doped fiber amplifier; YDFA – Yb-doped fiber}
amplifier; PPLN – periodically poled lithium niobtate crystal). Reprinted with permission from [87].

After the generation of the mid-infrared radiation, a Ge filter was used to filter out any residual near-infrared light. The inherent baseline free nature of CLaDS allows this system to mitigate issues resulting from fluctuations of the baseline due to variations in the DFG efficiency and temperature drifts, which impose limitations on spectroscopic systems using DFG sources. Further investigation of this technique will require long-term analysis of system stability and accuracy.

In another work by Nikodem et al., the effect of modulation amplitude and bias voltage on signal shape and strength in CLaDS systems implemented using electro-optical modulators was studied [89]. The work detailed in section 4.1.2.1 about DSB CLaDS using EOM technology assumes a simple model where only three electromagnetic waves are taken into account, the carrier and the first order, upper and lower sidebands. This is achieved when the EOM (intensity modulator) is biased in the center of the quasi-linear region of the device’s transfer function, and is driven using a fairly weak RF input signal. In Ref. [89], they further investigate the influence of higher order sidebands on the CLaDS signal. For traditional CLaDS analysis at $\Omega$, they found that the modulator should be biased around the quadrature points such that there is limited signal dependence on bias voltage. Biasing the device at either the maximum or minimum of the transmission curve results in low RF output power, and therefore high noise. Second, they found that higher RF driving powers produce additional sidebands in the optical spectrum, the beatnotes of which constructively contribute to an enhancement of the CLaDS amplitude. Demodulation at $2\Omega$ yielded different conclusions, namely that modulator should be biased at either the maximum or minimum of the transmission curve to efficiently generate the second
harmonic. When the modulator is biased at the minimum of the transmission curve, the signal amplitude can be enhanced by increasing the RF driving power to generate additional sidebands that add constructively. Retrieval of the CLaDS signal through analysis of the $2\Omega$ beatnote, has potential for higher signal amplitudes and therefore lower detection limits, however, additional complexity is added to the system as the RF driving signal and bias voltage need to be monitored and stabilized due to drifts present in LiNbO$_2$ modulators.

4.2. Detection Schemes

In most of the CLaDS instruments detailed in this thesis, detection of the sample’s dispersion information is extracted through detection of the instantaneous frequency using a high-speed photodetector. While this is the most straightforward approach to signal detection using CLaDS, alternate detection architectures have been investigated to overcome limitations or enhance the performance of this standard detection scheme. In this chapter, the original detection procedure used in this thesis will be discussed, followed by works by other researchers aimed at reducing the noise in the measurement through down-conversion techniques and finally a new detection scheme proposed in this thesis provides a boost of the carrier power at the input to demodulator.

4.2.1. Standard High-Speed Detection

A standard CLaDS detection system is illustrated in Fig.4.12, where a multi-color beam (with frequency spacing $\Omega$) falls incident on the photodetector and is heterodyne mixed, generating a photocurrent at the beatnote frequency, $\Omega$. To extract the instantaneous frequency as a function of time, the resulting photocurrent is electronically mixed with both in-phase (I) and in quadrature (Q) local oscillator (LO) reference signals with frequencies equal to $\Omega$. This shifts the electronic signal down to DC. After they are low pass filtered, the bandwidth of which
determines the overall demodulation bandwidth. The importance of this bandwidth on noise characteristics was discussed in detail in Chapter 3. After filtering, the signal phase is extracted by determining the phase relationship between the I and Q signals. The frequency information is subsequently calculated by taking the time derivative of the phase signal.

Figure 4.12. Standard CLaDS Detection Scheme. The RF photocurrent generated by the photodetector (PD) undergoes IQ (in-phase and quadrature) demodulation at $\Omega$, after which the signals are low-pass filtered (LPF). The phase is extracted from the IQ data, and the derivative of the phase reveals the CLaDS signal.

The standard detection scheme provides a fairly straight-forward approach to spectroscopic detection with processing that is very similar to the standard FM detector used in radios. Drawbacks of this approach stem from the fact that the CLaDS signal is encoded on a MHz-GHz RF carrier, thus requiring high-speed photodetectors. Depending on the spectra range of interest, there may be limitations on detector bandwidth availability or overall performance (i.e. responsivity, NEP, etc.). The next section discusses methods developed to use low-speed and low-bandwidth detection of high frequency signals.
4.2.2. Down-Conversion Techniques

While CLaDS is considered a high frequency technique, it does not require the full bandwidth from DC to the detector bandwidth. Instead the signal is encoded in a potentially small region around the carrier frequency, $\Omega$. This relatively small bandwidth around a high frequency carrier makes it possible for the use of down conversion techniques to either electrically, optically, or electro-optically convert the high-frequency signal to a lower operating frequency for detection with low-speed and low-bandwidth detectors. This section details several investigations into down-conversion techniques implemented in CLaDS systems.

4.2.2.1. Electro-optic Heterodyne Down-Conversion

Martin-Mateos et al. sought to mitigate the need for high-speed detectors by developing a CLaDS system that utilized an additional optical intensity modulator to provide electro-optic preprocessing of the multi-frequency optical spectrum [90]. The system they built, shown in Fig.4.13, includes a second EOM with frequency, $\Omega_2$, which slightly different from the first EOM frequency, $\Omega_1$.

Operation with a low modulation index for both modulators allows for negligible generation of higher harmonics. The resulting optical spectrum after the second demodulator then includes five frequencies, the original carrier and two sidebands at $\omega_0 \pm \Omega_1$, which experience both attenuation and dispersion due to the gas, and the two additional sidebands at $\omega_0 \pm \Omega_2$. The five optical signals are then captured using a photodetector with a bandwidth slightly larger than the frequency offset $\Omega_1 - \Omega_2$. 


The photodetector, a square-law device, generates sum and difference frequencies of all the input components, however, the only frequencies that fall within the detector bandwidth are the beatnotes between the two lower sidebands ($\omega_o - \Omega_1$, $\omega_o - \Omega_2$) and the upper sidebands ($\omega_o + \Omega_1$, $\omega_o + \Omega_2$). Each of these beatnotes occur at $\Omega_1 - \Omega_2$, and assuming that the amplitudes are equal and weak absorption, the resulting phase and frequency signals are simply the average of the two signals. In this way the resulting CLaDS signal is analogous to the DSB CLaDS approach detailed in section 4.1.2.1, however, in their work the high frequency signal is captured using a low-speed detector. This proof of concept work demonstrated the feasibility of electro-optic down-conversion of the CLaDS spectra to a lower RF frequency regime, however, a further investigation on the loss in carrier power and the total detection CNR would be required to accurately compare the SNR capabilities of this technique to that of a standard detection system.

4.2.2.2. Electrical, Parametric Down-conversion

While the technique summarized in the previous section externally changed the overall responsivity of the CLaDS detection system through use of an additional electro-optic modulator before the detector, a work by Hangauer et al. investigated the feasibility of intrinsic responsivity
changes of the CLaDS detector to perform high-speed detection at low-bandwidth and low-noise [91]. The intrinsic response, \( r \), of both an InGaAs avalanche photodiode (APD) operating at 1.6 \( \mu \)m and a mid-infrared HgCdTe (MCT) detector were modulated. This was achieved either by electronically changing the reverse bias voltage, or by induced detector saturation through the use of a second high-power laser. The latter method was only tested for the MCT detection system. The non-linearity due to the modulation of \( r \) results in parametric down-conversion of the high-frequency signal, making it possible to capture with a low-speed, and potentially low-noise detector.

Assuming ideal and full modulation of the detector responsivity, they found a theoretical conversion efficiency of 25%, where 100\% is assumed for direct detection. Experimental results differed slightly from this theoretical limit, as an efficiency of 13\% was measured for optical modulation of the MCT responsivity. For electronic tuning of the MCT bias voltage, an efficiency of 20\% was realized. Similarly, a 20\% conversion efficiency was measured when the bias voltage of the APD was modulated and compared to the maximum direct detection response. For the two detectors tested in this work, the MCT under electronic modulation of \( r \) yielded comparable SNR results to direct detection. For the APD down-conversion results, however, a factor of 10 improvement in SNR was observed compared to the direct detection measurements. Optimization and the choice of a direct or down-conversion technique ultimately would depend on the bandwidth and noise parameters of the detector electronics and the noise characteristics at the desired demodulation frequency.
4.2.3. Heterodyne-Enhanced CLaDS Detection

Noise in the CLaDS spectra is determined by the carrier-to-noise ratio (CNR) at the input to the FM demodulator (see Section 3.2 for more information). The techniques discussed in Section 4.2.2 aim at reducing the noise floor in the CLaDS detection system through the use of low-speed detectors, which in turn decrease the detector bandwidth. In contrast, the work presented in this section aims at boosting the carrier power through the addition of a strong optical local-oscillator.

In a standard CLaDS sensor, as well as in other dispersion spectroscopy techniques [48, 52], the phase signal is extracted from co-propagating electromagnetic (EM) waves. External phase noise is common mode and therefore rejected through this differential measurement. As a result of this co-transmission, all the EM wave amplitudes are attenuated, effectively eliminating the heterodyne gain (in terms of amplitude) of the photo-detection process, and resulting in a relatively low CNR at the input to the frequency demodulator.

As a reminder, the heterodyne detection of two EM waves with amplitudes $A_1$, $A_2$, frequencies $\omega_1$, $\omega_2$, and phases $\phi_1$, $\phi_2$, produces a beatnote photocurrent that is proportional to:

$$ I \propto A_1^2 + A_2^2 + 2A_1A_2 \cos((\omega_1 - \omega_2)t - (\phi_1 - \phi_2)) + ... $$

$$ ... + 2A_1A_2 \cos((\omega_1 + \omega_2)t - (\phi_1 + \phi_2)). $$

(4.4)

To overcome this CNR limitation in the previous CLaDS systems, while still preserving the high phase-noise rejection, an additional LO channel has been incorporated into the system (see Fig.4.14) in conjunction with additional frequency mixing of the received RF beatnote signal to extract the CLaDS spectra (outlined in Fig.4.16). In Fig.4.14, the optical configuration for the Heterodyne-Enhanced (HE-) CLaDS is detailed. The output from a chirped laser is split using a
beam splitter (BS) into two arms, a local oscillator channel and a sample channel. The sample channel follows the original CLaDS system configuration where an intensity modulator or frequency shifter is used to generate a multi-frequency beam with known frequency spacing, \( \Omega \). These co-propagating frequencies interact with the sample under test where the sample’s dispersion profile is encoded into the time-varying frequency spacing of the multi-frequency signal. In the LO channel, the original laser frequency is shifted by a known amount, \( \Omega_{LO} \). The two channels are then recombined using a beam combiner (BC) and heterodyne mixed on the photodetector (PD).

**Figure 4.14.** System configuration for the modified HE-CLaDS system to incorporate a LO channel. A beam splitter (BS) is used to split the laser radiation into two channels. In the local oscillator channel, a frequency shifter is used to shift the laser frequency by \( \Omega_{LO} \). In the sample channel, a frequency shift or intensity modulator is used to generate addition sidebands (one or two) at \( \Omega \) around the laser carrier frequency. This multi-frequency probe beam interacts with the sample under test and then in recombined using a beam combiner (BC) before the total optical signals are captured by the photodetector (PD) and are processed in the electronic domain.
The resulting photocurrent now contains the beatnote between the multiple frequencies in the sample channel as well as the beatnote between each of those sample frequencies and the LO. Due to the bandwidth of the photodetector, only difference frequencies will be present in the signal after the square-law detection performed by the photodetector. The LO shift, $\Omega_{LO}$, can be chosen (within the constraints of the technology used) to be either larger or smaller than the original frequency offset, $\Omega$. If the LO shift is greater than original frequency shift ($\Omega_{LO} > \Omega$), then noise of each frequency component with respect to the LO is correlated. In contrast, if the LO shift is smaller than original frequency shift ($\Omega_{LO} < \Omega$), then noise between each frequency component and the LO is anti-correlated. This is shown pictorially in Fig.4.15.

**Figure 4.15.** a) Single-sideband CLaDS optical spectrum (left) with an LO frequency shift, $\Omega_{LO}$, greater than the original frequency offset, $\Omega$, and the resulting RF beatnote spectrum (right) after square law detection by the photodetector; b) Single-sideband CLaDS optical spectrum (left) with an LO frequency shift, $\Omega_{LO}$, less than the original frequency offset, $\Omega$, and the resulting RF beatnote spectrum (right) after square law
detection by the photodetector. The sum frequencies generated by the frequency mixing are filtered out by the bandwidth of the photodetector which typically operates in the RF range.

As seen in Fig.4.15, depending on the relationship between the values of $\Omega_{LO}$ and $\Omega$, the LO-beatnotes (i.e. beatnotes at $\Omega_{LO} \pm \Omega$ and $\Omega_{LO}$) are either correlated (for $\Omega_{LO} > \Omega$) or anti-correlated (for $\Omega_{LO} < \Omega$). To extract spectroscopic data in either configuration, the procedure outline in Fig.4.16 is executed, either with analog RF electronics or with digital processing.

**Figure 4.16.** Processing steps using a digital (scheme 1) and an analog (scheme 2) approach. Grey blocks indicate analog components, while white blocks represent digital processes. In the analog approach, the RF signal from the photodetector (PD) is notch
filtered to remove the original CLaDS beatnote at $\Omega$, then frequency doubled using a frequency multiplier, then the desired frequency demodulated. In the digital approach, the RF signal from the PD is mixed down to lower frequency by an electronic LO at $2\Omega$, after which the signal is digitized using an analog-to-digital converter (ADC). The digital data is then filtered to remove the original CLaDS beatnote, frequency doubled (achieved by taking the square of the signal), and subsequently frequency demodulated.

In either the analog or digital domain, the heterodyne beatnote generated by the photodetector is first notch filtered to remove the original beatnote at $\Omega$. Then the signal is frequency doubled to yield a second mixing to extract both the sum and difference frequencies. In the case that $\Omega_{LO} > \Omega$, the difference frequency at $\Omega$ is filtered and frequency demodulated. For $\Omega_{LO} > \Omega$, the sum frequency at $\Omega$ is filtered and frequency demodulated to yield the CLaDS spectra.

It is important to note that while procedure has been outlined for a single-sideband (SSB) CLaDS configuration with only two frequencies, this methodology holds for a dual-sideband (DSB) CLaDS configuration with three frequencies (carrier and two sidebands), and multi-heterodyne systems as well. This technique was experimentally verified using a modified CLaDS system used to target methane (CH$_4$) in the near-infrared.

In fiber-coupled systems electro-optic modulators (EOM) can be used to generate the multi-frequency probe beam, while an AOM generates the LO frequency shift. In addition, a simple delay line in fiber can also be used to create a frequency shift based on the difference in propagation delay. Both of these implementations are illustrated in Fig.4.17.
Figure 4.17. Examples of the implementation of the HE-CLaDS technique in a fiber-coupled system architecture with a) and AOM used as a frequency shifter, and b) a fiber delay used to generate an effective frequency shift. In both configurations, fiber-couplers (FCs) are used to split and recombine the signals.

In addition to the CLaDS technique detailed above, this invention could be incorporated into other phase-sensitive spectroscopic techniques. For example, Chirp-Modulated (CM) CLaDS, a technique where additional modulation of the laser chirp allows for harmonic detection resulting in reduced detection bandwidths and therefore reduced noise [74], can also be modified to include this heterodyne-enhancement.

The system detailed above has been tested in a fiber-coupled system as illustrated in Fig.4.17b. A distributed feedback diode laser operating around 1650nm was used to target the R4 transition in $2\nu_3$ overtone band of methane. A ~4 m difference in fiber length between the LO and signal
channels generated a frequency shift of $\Omega_{LO} \approx 12$MHz. The signal channel operated using dual-sideband (DSB) operation [81], generating by driving an EOM with an RF signal at $\Omega = 1GHz$. The resulting frequency spectrums, analogous to those in Fig.4.15, for this DSB setup with $\Omega_{LO} < \Omega$ are shown in Fig.4.18.

**Figure 4.18.** Optical spectrum using DSB CLaDS and an LO frequency shift less than the frequency offset ($\Omega_{LO} < \Omega$). The resulting difference frequency spectrum after mixing on the photodetector is shown (while sum frequencies are filtered out by the photodetector). The anti-correlated signals at $\Omega - \Omega_{LO}$ and $\Omega + \Omega_{LO}$ are used in further analysis to extract spectroscopic information from the sample.

To mitigate the external phase noise in the system, the sum frequency of the LO and sideband beatnotes ($\Omega - \Omega_{LO}$ and $\Omega - \Omega_{LO}$) was used for spectral analysis since those beatnotes are anti-correlated (as shown in Fig.4.18). Operation in the DSB configuration is also possible with a LO frequency shift greater than the original offset (i.e. $\Omega_{LO} > \Omega$).
Figure 4.19. Preliminary results using DSB CLaDS, with $\Omega_{\text{LO}} \approx 12$ MHz, $\Omega = 1$ GHz, $\Omega_{\text{DC}} = 1$ GHz. The circled letters in the process diagram correspond to the experimental data shown in the figures.

Processing of this RF beatnote spectrum was captured using the down conversion and digitization approach outlined in Fig. 4.16. A benchtop spectrum analyzer (Tektronix RSA5103A) was used to perform the down conversion and subsequent digitization, the spectrum of which is shown in Fig. 4.19a.

After digitization, the down-converted signal was high pass filtered to remove beatnote at DC (original at 1 GHz before down-conversion), the results of which are shown in Fig. 4.19b. To extract the sum frequency of the remaining beatnotes, the time domain signal was frequency doubled, yielding a spectrum as shown in Fig. 4.19c. The resulting signal was then frequency demodulated, producing the CLaDS signals shown in Fig. 4.19d. Through this analysis, the feasibility of CLaDS spectra being captured through heterodyne-enhanced detection has been experimentally verified.
HE-CLaDS was also tested using an AOM as a frequency shifter as detailed in Fig.4.17a. The local oscillator shift was fixed at $\Omega_{LO} = 200$ MHz, which was outside the bandwidth of the spectrum analyzer used for analog down-conversion in the previous test. As a result, the analog mixing method shown in Fig.4.16, Scheme 2 was employed using $\Omega = 910$ MHz, a narrowband notch filter centered around 910 MHz (Micro-Tronics, BRC50722) and a frequency doubler (Mini-Circuits, ZX90-2-11+). The photodetector spectrum with the beatnotes around 910 MHz and the frequency doubled spectrum (after notch filtering) are shown in Fig.4.20.

Figure 4.20. Detector spectrum (top) showing the conventional CLaDS beatnote at $\Omega = 910$ MHz and the local oscillator beatnotes at $\Omega \pm 200$ MHz; the frequency doubled spectrum (bottom) at $2\Omega = 1820$ MHz showing an improvement in CNR for the given noise.

The periodic structure seen in Fig.4.20 is optical feedback resulting from parasitic reflections from the 2:1 (50/50) fiber splitter used to combine the sample and LO channels. Under these
noise conditions (i.e. the fringe), the conventional CLaDS beatnote at $\Omega = 910$ MHz has a CNR of approximately 13dB. In comparison, the HE-CLaDS beatnote at $2\Omega = 1820$ MHz sees an increased CNR of around 27dB, demonstrating the potential for this technique to act as a sensitivity booster by utilizing a strong optical local oscillator in the CLaDS receiver. Next steps in this comparison will involve mitigation of the optical fringe and a CNR comparison with the conventional CLaDS technique where there is no influence from the LO channel (i.e. no fringe).

Future work on this method will also involve quantitative measurement of the CLaDS SNR, both in the standard detection scheme and the heterodyne-enhanced system, as well as an investigation into alternative techniques to generate the LO frequency shift, modeling of the noise propagation through the system, and optimization of the system parameters.

4.2.4. Time Domain Fitting

In the conventional CLaDS technique concentration information is usually extracted through a spectral fitting routine, as described in Section 3.5. In this method, a frequency demodulator is used to extract the instantaneous beatnote frequency (i.e. the CLaDS signal), and the resulting signals are analyzed in the fit. In addition, the instantaneous frequency can also be extracted through a fit of the raw beatnote signal. The signal generated by the photodetector contains both amplitude and dispersion information, shown for an optically thick sample in Fig.4.21. The amplitude of the carrier signal (at frequency $\Omega$) is attenuated due to the gas absorption, and the frequency of the signal is distorted due to induced dispersion.
Figure 4.21. Example time-dependent beatnote signal showing amplitude attenuation and frequency change due to the influence of a high absorbance sample. The time scan considered here represents a period of the laser ramp frequency.

With an appropriate model for the beatnote signal (see Section 2.3), this signal can be fit to extract the concentration of the sample. In the simplest implementation, both the raw beatnote photocurrent is fit with a model taking into account both absorption and dispersion. While there may be some benefit in using both physical mechanisms in the fitting routine, the analysis of amplitude will most likely be susceptible to the same absorption-based issue as a standard fitting routine, which is the impact of non-linear baselines and saturation effects. To investigate if this time-domain fit of the beatnote signal can be extended to only fit the influence of dispersion, a digital amplitude limiter was introduced. The impact of the limiter is shown in Fig.4.22, where a threshold is set to eliminate any variations in amplitude, after which the signal is low-pass filters to remove higher order terms introduced by thresholding. This process preserves the dispersion information because it is measured through change in frequency, which is unaffected by the ideal amplitude limiting [92].
Figure 4.22. Amplitude limiting scheme and corresponding time domain signal. The envelope of beatnote signal right after the photodetector was chosen to mimic a 2nd order absorption baseline.

A subsequent fit of the red curve in Fig.4.22 with to the following equation for the time-dependent beatnote signal, $b(t)$, along with a model for the CLaDS signal, $f_{\text{CLaDS}}$, allows for determination of the sample concentration.

$$b(t) = A \cdot \sin(2\pi \cdot f_{\text{CLaDS}} \cdot t + \phi_o)$$  \hspace{1cm} (4.5)

Here $A$ represents a constant, arbitrary amplitude, and $\phi_o$ is a constant phase offset. Beatnote signal with additive white noise were simulated, and analyzed using the method presented in Fig.4.22. Results of the beatnote fit are shown in Fig.4.23, along with a comparison of the input CLaDS signal to the CLaDS signal recreated using the parameters extracted from the time-domain fit. These results suggest that sample concentration can be accurately determined through analysis of the frequency of the time-dependent beatnote signal.
Fit of the amplitude limited beatnote signal along with the corresponding residuals. The simulated CLaDS spectra and in the CLaDS signal recreated using the parameters extracted from the fit.

This proof of concept work shows that a model for the CLaDS spectra can be extended to the analysis of the raw beatnote signal produced by the photodetector, eliminating the need for the frequency demodulator. Preliminary analysis of this detection scheme suggest that the benefits of the CLaDS technique, namely immunity to intensity variations, are preserved, however, the linearity with concentration has yet to be examined. In addition, the influence of determining the phase offset ($\phi_o$ in Eq. (4.5)) under noisy conditions and the possible advantages of analyzing an ideal white noise dominated signal have yet to be explored.

4.3. Discussion

Detailed in this chapter were the various configurations and methods of implementation for the CLaDS technique. Optical signal generation in both the near- and mid-infrared was discussed, along with technical advantages and limitations of existing optics components, such as electro-
optic modulators and acousto-optic frequency shifters, utilized in these systems. One of the major advantages of the CLaDS technique is the inherent linearity with sample concentration [77]. However, for DSB and qSSB CLaDS systems deviation from this linearity occurs for high absorbance signal. For weak absorbance ($|\alpha \cdot L| \ll 1$), frequency dependency of the gas attenuation can be neglected. As a result, the phase information can be extracted assuming equal power in each of the sidebands. However, at high absorbance conditions, the frequency-dependency of the gas attenuation (i.e. absorption) becomes significant enough to affect the ratio of the sideband amplitudes. As a result, absorption-dependent terms are introduced into the CLaDS signal. The non-linearity of these absorption terms in turn results in a non-linearity of the CLaDS amplitude at higher concentrations. This effect, however, is significantly smaller than the non-linearity present in absorption-based system where deviation begins around 0.2 absorbance level. The deviation from a linear trend becomes more pronounced the further the configuration is from pure SSB, but for the qSSB system developed in Ref. [59], the linear response region was extended by 5 times, resulting in a 10% deviation from a true linear response at an absorbance level of 1. The formulization to model this behavior can also be found in Ref. [59].

The standard approach to the CLaDS detection system was outlined, and included a discussion of the drawbacks of high-frequency detection. Several proof of concept down-conversion studies with the aim to lessen the requirement for high-speed photodetectors were also summarized. In addition, an alternative configuration where an optical local oscillator is used to boost the carrier power of the heterodyne detection process was introduced. Continued work on the implementation of the CLaDS technique will evolve with the development of new optical components, such as electro-optic devices and waveguides in the mid-infrared, improved photodetection devices, or multi-mode sources.
Chapter 5: Chirped-Modulated CLaDS

5.1. Introduction

Direct techniques such as DLAS and CLaDS are powerful tools for spectroscopic detection; however, limitations of system components often inhibit the overall sensor performance. To overcome technique limitations modulation techniques are often employed to overcome these technical limitations. For example, $1/f$ noise present in many laser systems often motivates the use of WMS. Similar is the original motivation for FMS which was developed to overcome the high intensity noise of dye lasers [17]. For CLaDS, the investigation into additional modulation schemes resulted from several technical challenges found in the initial CLaDS systems. The first CLaDS sensor was developed in the mid-infrared and utilized an acousto-optic modulator (AOM), also called a frequency shifter, to generate a second frequency component [58]. As detailed in section 4.1.1.1, the recombination of separate beams from the AOM into one collinear beam in free space requires precise optical alignment; a trait that may limit the robustness and dynamic range of a CLaDS sensor. In addition, as outlined in Chapter 3, the noise in a CLaDS measurement is directly related to the measurement bandwidth (Eq.3.7). With the Chirp-Modulated (CM) CLaDS technique described in this chapter, the measurement bandwidth can be further reduced using a line-locking configuration, and the sensitivity to opto-mechanical stability can be mitigated. The derivation of CM-CLaDS signals, mathematical models for verification and simulation, as well as a noise model are provided in the subsequent sections.
5.2. CM-CLaDS Signal Model

Similar to the relationship between DLAS and WMS, a CM-CLaDS signal is achieved by modulating the wavelength (or frequency) of the laser radiation. However, unlike in WMS, the frequency modulation results in a simultaneous modulation of the chirp rate. In either technique, an applied sinusoidal modulation of the laser frequency (or wavelength) yields a time dependent frequency that can be modeled as

\[ \omega(t) = \omega_o + \omega_d \cdot \cos(2\pi f_m t). \]  \hspace{1cm} (5.1)

Here \( \omega_o \) is the center frequency and \( \omega_d \) is the modulation depth in units of angular frequency. For WMS, the sinusoidal modulation causes modulation of the optical frequency according to Eq. (5.1), resulting in a time dependent intensity given by

\[ I(\omega_o, t) = I_o \exp\left(-\alpha(\omega_o + \omega_d \cos(2\pi f_m t)) \cdot L\right), \]  \hspace{1cm} (5.2)

where \( I_o \) and \( \alpha(\omega) \) are the input optical intensity and absorption coefficient, respectively. Harmonic detection of the in-phase component of the time-varying photodetector signal according to (5.3) results in the WMS signal for the given harmonic.

\[ H_{n}^{\text{WMS}}(\omega_o) = 2f_m \int_{0}^{\frac{1}{f_m}} I(\omega_o, t) \cos(2\pi nf_m t) dt \]  \hspace{1cm} (5.3)

In CM-CLaDS the influence of current modulation is more complex. A typical CM-CLaDS system is illustrated in Fig.5.1.
The major differences between a CM-CLaDS system and that of the CLaDS systems presented in the previous chapters is the addition of sinusoidal modulation of the laser current and lock-in detection following the frequency demodulation process.

The derivation of the CM-CLaDS signal presented here follows the formulization originally presented by Nikodem et al. in Ref. [74]. In a conventional CLaDS system based on a free-space AOM configuration, the signal is given by

\[ f(\omega) = \frac{S}{2\pi c} \left[ \Delta L - L \cdot \omega \left( \frac{dn}{d\omega} \bigg|_{\omega=\Omega} - \frac{dn}{d\omega} \bigg|_{\omega=\omega_o} \right) \right] \] (5.4)

where \( \Delta L \) represents the path length mismatch between the two frequency components. Applying a sinusoidal modulation to the laser frequency (or wavelength) yields a time dependent frequency (described by Eq. (5.1)), and therefore a chirp modulation rate given by

\[ S = \frac{d\omega}{dt} = S_o \sin(2\pi f_m t), \] (5.5)
where \( S_o = f_m \omega_d \). Applying this frequency and chirp modulation to Eq.(5.4), and assuming that the center frequency is much greater than the modulation depth \((\omega_o \gg \omega_d)\) yields a beatnote signal of

\[
f(\omega_o, t) = \frac{S_o \Delta L}{2\pi c} - \frac{S_o L\omega_o}{2\pi c} \times ... \times \sin(2\pi f_m t) \left( \frac{dn}{d\omega} \bigg|_{\omega_o + \omega_d \cos(2\pi f_m t) - \Omega} - \frac{dn}{d\omega} \bigg|_{\omega_o + \omega_d \cos(2\pi f_m t)} \right).
\]

(5.6)

Harmonic detection (i.e. phase-sensitive detection) is then performed to extract the in-phase and quadrature component of the Fourier coefficients. For the \( n \)th component, the harmonic detection produces the following signals

\[
a_n(\omega_o) = 2f_m \int_0^{1/f_m} f(\omega_o, t) \cos(2\pi nf_m t) dt
\]

(5.7)

\[
b_n(\omega_o) = 2f_m \int_0^{1/f_m} f(\omega_o, t) \sin(2\pi nf_m t) dt
\]

(5.8)

where \( a_n \) and \( b_n \) are the in-phase and quadrature components, respectively. The influence of the chirp modulation causes the signal shapes to differ from that of the derivative-like behavior found in WMS systems; a topic covered in the next section. As mentioned in Chapter 4, a technical limitation of the AOM-based, mid-infrared system is the potential path length difference between the two beams, resulting in a DC offset of the CLaDS spectra. Fluctuations of this offset through opto-mechanical instability can impact the accuracy and dynamic range of the measurement. With this chirp-modulated approach and subsequent phase-sensitive detection, this offset is eliminated for \( n \geq 2 \) [74]. In fiber-based system or those based on direct-modulation of the laser, the path length difference is no longer an issue. In either case, the instantaneous beatnote signal can be simplified to
Using Eqs. (5.7) and (5.8), the Fourier components can be calculated using the expression for the instantaneous beatnote frequency. With this model, which will be mathematically verified in a later section, CM-CLaDS system performance can be simulated and optimized for various system parameters.

5.3. Explanation of Signal Formation

Under sinusoidal modulation of the laser current, the resulting CM-CLaDS signal shape can be thought of as the product of two effects, which in turn explains why CM-CLaDS signals do not follow the derivative-like shape of those in WMS. First, amplitude modulation results from the change in frequency induced by the current modulation. This effect is modelled by the differential term in parenthesis is Eq. (5.6), and is analogous to the operation of WMS. In CM-CLaDS, however, the spectral shape under modulation is not an absorption profile, but rather the CLaDS spectra (see the “CLaDS Signal” curves is Fig.5.2). When biased at the peak of the spectrum undergoing frequency modulation (Fig.5.2a), modulation of the laser frequency results in an amplitude modulation with approximately twice the frequency of the applied modulation. In WMS, this would correspond to the peak of the 2f signal. Along regions of the spectrum that are approximately straight lines (Fig.5.2b), the frequency modulation results in amplitude modulation that closely mimics the applied signal and is scaled by the slope of the line (i.e. at 1f).
Figure 5.2. Evolution of CM-CLaDS signal shapes at a) the peak of the CLaDS signal, b) the line center, and c) after the full scan. The multiplication of two, out of phase effects (frequency to amplitude modulation and chirp modulation) result in signal shapes that differ from the expected derivative-like shapes.

Second, the influence of the chirp rate is taken into account. As stated in Eq.(5.5), the chirp rate is the rate of change of the laser frequency over time \( \frac{\partial \omega}{\partial t} \), and therefore the chirp rate is \( \pi \) radians out of phase with the frequency modulation. In addition, the chirp does not depend on the bias point of the modulation. The final output shape (i.e. the input to the lock-in amplifier in Fig.5.1) is however the multiplication of this chirp variation and frequency to amplitude modulation (as seen in Eq.(5.6)). At the peak of the CLaDS shape (Fig.5.2a), the frequency to amplitude conversion produces a 1f signal with an offset, and when this is multiplied by the 1f chirp rate modulation, an approximate 1f signal is generated. At the line center (Fig.5.2b), the
frequency to amplitude signal most closely represents the original modulation (a cosine), which
after multiplication by the chirp rate signal (a sine), produces a 2f signal. The full scan of the 1f,
2f CM-CLaDS is presented in Fig. 5.2c. The influence of the chirp rate, a constant throughout the
scan of the spectrum, provides an additional modulation of the signal that causes the harmonic
shapes to differ from the simple derivative-like analysis found in WMS or other derivative
spectroscopy techniques.

5.4. Model Verification

Due to the derivative-like nature of CM-CLaDS and WMS, higher harmonics (resultant from
non-negligible modulation depths) contain information about the transmission signal. Therefore
higher harmonics can be used to correct the \( n^{th} \) harmonic to recreate the \( n^{th} \) derivative of the
transmission signal \([70]\). As a result, use of multiple harmonics serves as a means of verification
for the developed signal models assuming an accurate model for the transmission (absorption
and dispersion) through the gas is used. In WMS, the 2\(^{nd}\) derivative of the transmission
absorption signal, \( T_a''(\omega) \), can be reconstructed from the 2\(^{nd}\) harmonic WMS signal by
considering higher harmonics according to

\[
\omega_d^2 \cdot T_a' (\omega) = \sum_{even} \frac{n^2}{n!} H_{n}^{\text{WMS}} (\omega) \cdot (-1)^{n/2+1}.
\]  

More information about this methodology can be found in section 3.3.1 of [70]. A similar
analysis can be utilized in the CM-CLaDS case. Here, however, the transmission signal is phase,
\( T_\varphi''(\omega) \), rather than absorption. Following the formulations similar to those used in WMS, the
CLaDS harmonic spectra can be modelled using derivatives of the transmission signal, which is
our case is phase, \( \varphi(\omega) \), rather than absorption. Using similar analysis as to that found in [70], the
second derivative of the phase signal can be reconstructed by correcting the $2f$ harmonic spectrum with higher harmonic signals. This method can therefore be used to verify the numerical model used to simulate the CM-CLaDS signals in this chapter. The major difference between this formulation and that used for WMS is the extra consideration of the time derivative used in CLaDS to perform frequency demodulation (which encompasses the influence of the chirp rate). In the Fourier domain, a time derivative corresponds to a multiplication by $j2\pi n f_m$, which is taken into account here in Eq.(5.11). Using the harmonic components calculated from the formulation in Section 5.2, the second harmonic signal can be corrected to produce the second derivative of the phase (i.e. transmission signal).

$$\omega_a^2 \phi''(\omega) = \frac{2\pi}{f_m \text{even}} \sum_{n} n \cdot H_n^\phi(\omega) \cdot (-1)^{(n/2)+1}$$ (5.11)

Two examples of this analysis are shown in Fig.5.3, where the second derivative of the phase signal, $\phi''(\omega)$, is compared to the corrected 2nd harmonic CM-CLaDS signal for an under-modulated and over-modulated case. In Fig.5.3.a, a modulation depth of 0.1 times the frequency spacing, $\Omega$, is simulated, representing the under-modulated instance. For these conditions, only one harmonic signal, $H_2^\phi(\omega)$, is needed to accurately reproduce the derivative shape. In the over-modulated example, Fig.5.3b, a modulation depth that is 1.5 times the frequency spacing is calculated, and was found to require 3 additional harmonic spectra ($H_n^\phi(\omega)$, where $n = 2,4,6,8$) to reconstruct the transmission signal.
Figure 5.3. Verification of the CM-CLaDS signals using the derivative of the transmission (i.e. phase) signal for an under-modulated case (left) and an over-modulated case (right).

Mathematical verification of the signal model allows for use of the calculated signal strengths to accurately represent the harmonic spectra of the CLaDS signals in our signal to noise calculations in Section 5.8.

5.5. Convolution-based CM-CLaDS Calculation

The fundamental mechanism probed in CLaDS is derived from the same interaction as that of absorption, and thus it follows that similar mathematical tools may be used to calculate the expected CM-CLaDS signal. Like in WMS, the CM-CLaDS can be modeled as a convolution of the CLaDS signal (derivative of the phase) with a convolution kernel. The derivation of this expression is presented here and follows the methodology used for WMS in Ref. [70, 93]. This alternative form of calculating the CM-CLaDS spectra allows for additional insight into the phenomenon as a filter response and may allow for faster calculations and spectral fits.
In CM-CLaDS, under sinusoidal modulation of the laser wavelength \((\omega + \omega_d \cos(z))\) the harmonic spectrum, \(H_n(\omega, \omega_d)\), can be expressed as the Fourier series decomposition presented in Eq. (5.12).

\[
H_n(\omega, \omega_d) = \frac{\varepsilon_n}{2\pi} \int_{-\pi}^{\pi} \left[ T_\varphi(\omega + \omega_d \cos(z)) \right] \cdot \sin(nz) dz
\]  

(5.12)

In this case, the modulated signal is the derivative of the transmitted phase, \(T_\varphi(\omega)\), \(\varepsilon_n\) is equal to 2 for \(n = 0\), and 1 for \(n = 1, 2, 3, \ldots\), and the lock-in detection is calculated in phase with the chirp rate (i.e. \(\sin(nz)\)). Expanding the derivative term illustrates the role of the chirp rate.

\[
H_n(\omega, \omega_d) = \frac{\varepsilon_n}{2\pi} \int_{-\pi}^{\pi} \omega_d \sin(z) \cdot T_\varphi'(\omega + \omega_d \cos(z)) \cdot \sin(nz) dz
\]  

(5.13)

To transform Eq. (5.13) into a convolution expression, a new variable is defined, \(\eta = -\omega_d \cos(z)\).

\[
\frac{d\eta}{dz} = \omega_d \cdot \sin(z) = \omega_d \sqrt{1 - \cos^2(z)} = \sqrt{\omega_d^2 - \eta^2}
\]  

(5.14)

The lock-in term, \(\sin(nz)\), can be represented as

\[
\sin(nz) = \sqrt{1 - \frac{\eta^2}{\omega_d^2}} \cdot U_{n-1}\left( \frac{\eta}{\omega_d} \right)
\]  

(5.15)

Where \(U_n(x)\) is the Chebyshev polynomial of the second kind. Using Eqs. (5.14) and (5.15), Eq. (5.13) becomes a clear convolution expression.

\[
H_n(\omega, \omega_d) = \frac{\varepsilon_n}{\omega_d \cdot 2\pi} \int_{-\pi}^{\pi} T_\varphi'(\omega - \eta) \cdot \sqrt{\omega_d^2 - \eta^2} \cdot U_{n-1}\left( \frac{\eta}{\omega_d} \right) d\eta
\]  

(5.16)

Eq.(5.16) can be rewritten as the convolution of the CLaDS signal with a kernel.
\[ H_n(\omega, \omega_d) = T(\omega) \otimes K_{\text{CLaDS}}(\eta, \omega_d) \] (5.17)

where

\[ K_{\text{CLaDS}}(\eta, \omega_d) = \begin{cases} 
(-1)^{(n+1)/2} \cdot \frac{\varepsilon_n}{\omega_d \pi} \cdot U_{n-1} \left( \frac{\eta}{\omega_d} \right) ; & \text{n odd} \\
(-1)^{n/2} \cdot \frac{\varepsilon_n}{\omega_d \pi} \cdot U_{n-1} \left( \frac{\eta}{\omega_d} \right) ; & \text{n even}
\end{cases} \]

Presentation of the CM-CLaDS signal composition as a convolution not only allows for the potential of fast calculations, but also provides an alternative way of viewing harmonic detection schemes as the convolution of the un-modulated signal with a fixed filter. Further discussion of this interpretation as it pertains to WMS can be found in section 3.2.2 of Ref. [70].

5.6. Signal Optimization

Optimization of the signal strength as a function of system parameters involves a two-dimensional analysis of the modulation depth, \( \omega_d \), and the frequency spacing, \( \Omega \). In WMS, only the modulation depth is optimized, making the analysis less complex and analytical in the case of Lorentzian lineshapes [94]. Here we numerically simulate the CM-CLaDS signal using Eq.(5.7)-(5.9) and vary both of the free parameters. The optimized modulation depth for a Lorentzian lineshape differs from the WMS case (\( \omega_d = 2.2 \cdot \omega_L \) [17, 94]) because of the influence of the other free parameters, \( \Omega \). The modulation depth that yields the strongest signal is coupled to the linewidth of the probed spectrum. However, in the case of CLaDS, the effective linewidth of the spectrum can be altered by changing the frequency spacing. For larger \( \Omega \) values, a larger \( \omega_D \) is used to fully modulate the signal, and as Eq. (5.5) shows, \( S \) subsequently increases. This increase in chirp rate corresponds to an increase in the output signal strength. Using a Lorentzian
lineshape, the results of this optimization is show in Fig. 5.4. The parameters are normalized to the linewidth of the transitions, allowing for comparison across varying spectroscopic conditions.

**Figure 5.4.** (a) Simultaneous optimization of frequency spacing and modulation depth; (b) Maximum along the modulation depth axis; (c) Maximum along the frequency spacing axis. The maximum CM-CLaDS signal occurs at normalized values of $\Omega/\omega_L = 3.5$ with $\omega_D/\omega_L = 2.8$. This analysis also demonstrates how the optimization of both parameters is highly coupled.

Taking the maximum along each parameter dimension allows for easy viewing of the optimum frequency spacing and modulation depth pair. From this analysis, the maximum CM-CLaDS signal occurs at a frequency spacing, $\Omega$, of $3.5 \cdot \omega_L$ with a modulation depth of $2.8 \cdot \omega_L$. Calculation of these signals can also be modeled using the convolution based method outlined in section 5.5, which will yield identical results but provides faster computation.

An additional benefit of CM-CLaDS comes in the form of baseline suppression. The technique is a differential measure of dispersion and is therefore baseline free. However, if a dispersive background is present, for example due to fiber dispersion or and offset between the RF modulation and detection frequencies, the effect is eliminated by utilizing detection at higher harmonics. If these dispersive backgrounds can be represented by a first order polynomial or
less, measurement at the second harmonic removes these baseline effects. This was demonstrated in Ref. [74] with the remove of an offset in the data due to path length difference between the two frequency components with $2f$ detection. The baseline free nature of CM-CLaDS also allows for operation in a line-locked mode without introducing concerns about accuracy. Due to the complicated baselines in absorption spectroscopy, this cannot always be said for wavelength modulation spectroscopy.

5.7. Noise Analysis

Assuming white noise (i.e. random) at the output of the photodetector, the noise propagation follows a very similar chain to that of conventional CLaDS (see Chapter 3). However, the sinusoidal variation of the laser injection current modulates the signal into harmonics of the modulation frequency, which can then be extracted through phase-sensitive detection. Therefore, the additional processing step of lock-in detection needs to be considered in the noise model. For WMS, the noise propagation is fairly straightforward and is determined by the noise spectral density, $N_i$ (units $A^2/Hz$), at the output of the detector and the detection bandwidth:

$$\sigma_{WMS} = \sqrt{N_i \cdot B_{\text{lock-in}}}$$

(5.18)

where $B_{\text{lock-in}}$ (units Hz) is the equivalent noise bandwidth associated with the lock-in amplifier time constant.

The noise propagation through an ideal CM-CLaDS receiver is illustrated in Fig.5.5. Optimized operation of CLaDS is achieved when two probe frequencies ($f_o$, $f_o+\Omega$) of equal optical power are heterodyne mixed on the photodetector. The noise in the resultant photocurrent is assumed to be random with a power spectral density of $N_i$ (units $A^2/Hz$). In the frequency demodulator, an
intermediate frequency (i-f) filter first determines the demodulation bandwidth \( B \). Then the instantaneous frequency is extracted through a derivative process which results in an \( f^2 \) behavior of the noise power spectral density [67]. At this point in conventional CLaDS, the total output noise is extracted by integrating \( N_{FM}(f) \) over the entire demodulation bandwidth. However, in CM-CLaDS a lock-in amplifier is needed to extract the signals. In addition to signal detection, the lock-in amplifier limits the noise in the signal output by acting as a narrowband, band-pass filter around the modulation frequency, \( f_{m} \). 

As seen in Fig. 5.5, the output noise in CLaDS follows a non-linear dependence with the demodulation bandwidth, and is proportional to \( BW^{3/2} \) (see Chapter 3). This behavior is due to the time derivative involved in the frequency demodulation process. For conventional CLaDS, the total output noise contains all the contributions of noise from DC up to the demodulation bandwidth frequency. In a line-locked CM-CLaDS mode, the analyzed signal is the amplitude of single-frequency (or tone) which has a bandwidth related to the time constant of the lock-in

**Figure 5.5.** Noise propagation in an ideal CM-CLaDS detector. PD – photodetector, \( P_T \) – total optical power (W), \( f_o \) – optical frequency (Hz), \( \Omega \) – frequency spacing (Hz), \( N_i \) – noise power spectral density \( (A^2/Hz) \), \( B \) – demodulation bandwidth (Hz), \( C \) – carrier amplitude (A), \( f_m \) – modulation frequency (Hz).
amplifier. As a result of this reduction in bandwidth, the noise in the CLaDS signal is also reduced, an example of which is shown in Fig. 5.6.

The output noise in CM-CLaDS can be modeled by Eq. (5.19), and is function of the noise power spectral density, $N_i$, at the output of the photodetector, the beatnote carrier amplitude, $C$, the modulation frequency, $f_m$, and the bandwidth associated with the harmonic detection, $B$.

$$n_{CM-CLaDS} = \sqrt{\frac{1}{3} \frac{N_i}{C^2} \left( \left( \frac{f_m + B}{2} \right)^3 - \left( \frac{f_m - B}{2} \right)^3 \right)}$$  \hspace{1cm} (5.19)

When operated in a scanned mode, an entire harmonic spectrum is captured rather than a single point. Each point the retrieved spectrum carries with it the noise detailed in Eq. (5.19), and therefore the total noise in the measurement is increased. Subsequent spectral fitting may reduce some of this noise, but not to the level of the single-point detection achieved through line-locking.

**Figure 5.6.** Output noise power spectral density of the CLaDS detection system for an input noise of $N_i = 10^{-7}$ A/Hz$^{-1/2}$ and CNR = 1. The gray shaded region represents the total noise contribution from all the frequencies within a direct CLaDS demodulation.
bandwidth of 150kHz. The black region represents to the total output noise for a CM-CLaDS system with a modulation frequency of 100kHz.

5.8. Signal to Noise Ratio

The signal and noise models presented in the previous section allows for calculation of the expected SNR for a given set of spectroscopic and detection parameters. In Chapter 3, similar SNR models were developed, permitting a theoretical comparison of the techniques (DLAS, CLaDS, WMS, CM-CLaDS). The parameters used in this study are presented in Table 5.1 and were chosen to be representative of realistic sensing conditions and detection capabilities.

Table 5.1. Detection and Spectroscopic Parameters for Sensitivity Calculations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Input Noise Spectral</td>
<td>Nᵢ</td>
<td>2e-5</td>
<td>A/Hz⁻¹⁄₂</td>
</tr>
<tr>
<td>Density</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heterodyne efficiency</td>
<td>η₁</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>Absorbance</td>
<td>αc·L</td>
<td>0.03</td>
<td>-</td>
</tr>
<tr>
<td>HWHM</td>
<td>ωᴸ</td>
<td>2e9</td>
<td>rad/s</td>
</tr>
<tr>
<td>Measurement time</td>
<td>Tₒ</td>
<td>1</td>
<td>ms</td>
</tr>
<tr>
<td>Averaging Time</td>
<td>T_Total</td>
<td>1</td>
<td>s</td>
</tr>
<tr>
<td>Number of scans</td>
<td>k</td>
<td>1/Tₒ</td>
<td>-</td>
</tr>
<tr>
<td>Lock-in Bandwidth</td>
<td>B_Lock-in</td>
<td>1</td>
<td>Hz</td>
</tr>
</tbody>
</table>
The optimum frequency spacing, $\Omega$, in the conventional CLaDS technique is approximately equal to the FWHM of the molecular transition (see Section 2.4), while the optimum $\Omega$ for CM-CLaDS was determined in Section 5.6. Both values are include in Table 5.2 which details the scan and modulation parameters used in the conventional CLaDS and CM-CLaDS simulations, respectively. In the case of CM-CLaDS and WMS, only a single-point detection scheme that mimics operation in a line-locked mode was analyzed. The results of this theoretical comparison are shown in Table 5.4.

Practical implementation of the WMS technique requires additional power normalization due to the dependence of the WMS signal on the average incident laser intensity. One of the most widely used methods to address this power-dependency is $2f/1f$ normalization [19, 95-97]. In this technique the value of the first harmonic signal at the line center, which for optically thin samples is assumed to be directly proportional to the incident laser intensity, is used to cancel the dependence on intensity in the ratio of the $2f$ and $1f$ signals. Under ideal laser modulation (i.e no power variation as a function of current), the value of the $1f$ signal at the line center is zero, however, the slope of a real laser IV curve results in a non-zero offset. Furthermore, non-linearity of the laser current-voltage (IV) curve produces residual amplitude modulation (RAM) in the $2f$ signal, often requiring background subtraction to remove this signal [96]. In order to provide a fair comparison of the techniques, the noise introduced by these additional processes must be taken into account. In this analysis the determination of the $2f$ RAM background signal is assumed to be noiseless, however, deviation from this characterized value lead to issues with accuracy.
Table 5.2. Modulation and Scan Parameters for Sensitivity Calculations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>Units</th>
<th>Normalized Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scan Range (CLaDS)</td>
<td>( x_R )</td>
<td>12</td>
<td>HWM</td>
<td>( x_R/\omega_L = 12 )</td>
</tr>
<tr>
<td>Chirp Rate (CLaDS only)</td>
<td>( S )</td>
<td>2.4e13</td>
<td>rad/s²</td>
<td>( x_R\cdot \omega_L/T_o )</td>
</tr>
<tr>
<td>Frequency Spacing</td>
<td>( \Omega_{CM-CLaDS} )</td>
<td>7e9</td>
<td>rad/s</td>
<td>( \Omega/\omega_L = 3.5 )</td>
</tr>
<tr>
<td></td>
<td>( \Omega_{CLaDS} )</td>
<td>3.5e9</td>
<td></td>
<td>( \Omega/\omega_L = 1.73 )</td>
</tr>
<tr>
<td>Modulation depth (CM-CLaDS)</td>
<td>( \omega_{d,CM-CLaDS} )</td>
<td>5.6e9</td>
<td>rad/s</td>
<td>( \omega_D/\omega_L = 2.8 )</td>
</tr>
<tr>
<td>Modulation depth (WMS)</td>
<td>( \omega_{d,WMS} )</td>
<td>4.4e9</td>
<td>rad/s</td>
<td>( \omega_D/\omega_L = 2.2 )</td>
</tr>
<tr>
<td>Modulation Frequency</td>
<td>( f_m )</td>
<td>50</td>
<td>kHz</td>
<td>-</td>
</tr>
</tbody>
</table>

The signal in many systems employing 2f/1f normalization is calculated as the magnitude of the in-phase (X) and quadrature (Y) components of lock-in detection to eliminate the dependence on the signal phase. The signal (S) X and Y component are additionally normalized by the 1f signal and the corresponding background (BG) signal is subtracted (see Eq.(5.20)).
Calculation of the magnitude using components with identical noise results in an increase in noise by a factor of \( \sqrt{2} \); however, if the noise was uncorrelated there would be no increase in noise. The \( 2f \) and \( 1f \) values in Eq. (5.20) are calculated from the same photodetector signal, and therefore the same noise (i.e. highly correlated) is present on each value (again under the assumption of white noise). Therefore, calculation of the magnitude instead adjusting the phase to rotation the signal into a single channel decreases the SNR by a factor of \( \sqrt{2} \).

The \( 1f \) signal is created due to the non-ideal tuning characteristics of a typical laser. To simulate this effect a representative tuning curve was determined using the parameters for the intensity modulation of a typical DFB diode laser provided in Ref. [96]. The following expression for intensity as function of wavenumber was calculated from the values for intensity traces and normalized linear and quadratic modulation coefficients found in Fig. 4-6 in Ref. [96].

\[
I(\tilde{\nu}) = 0.066\tilde{\nu}^2 + 0.846\tilde{\nu} + 0.875
\]  
(5.21)

Since the ratio of two noisy signals changes the relative noise of the output (according to Eq. (5.22), where \( \sigma_{X_{2f}R_{1f}} \) is the covariance of the random variables \( X_{2f}, R_{1f} \)).

\[
\sigma \left( \frac{X_{2f}}{R_{1f}} \right) = \left( \frac{X_{2f}}{R_{1f}} \right) \sqrt{\frac{\sigma_{X_{2f}}}{X_{2f}} + \frac{\sigma_{R_{1f}}}{R_{1f}}} - \frac{\sigma_{X_{2f}R_{1f}}}{X_{2f}R_{1f}}
\]  
(5.22)
Using the representative intensity modulation mentioned above and the parameters detailed in Table 5.1 and Table 5.2, the values for the $2f$ and $1f$ values for the X component were calculated; the results of which are summarized in Table 5.3.

Using the calculated values in Table 5.3 and Eq.(5.22) for a given noise amplitude (ex. $\sigma_{x_{2f}} = 1 \times 10^{-6}$ A$/\sqrt{\text{Hz}}$), the noise on the ratio is calculated. After taking into account the noise added by the magnitude calculation and assuming the background signal is noiseless, the SNR of the $2f/1f$ signal is $1.3 \times$ worse than the SNR using a signal channel with no normalization and the same noise amplitude (i.e. the ideal case). The value suggests that the correlation of the noise in the $2f/1f$ signal slightly reduces the noise added by the magnitude calculation ($\sqrt{2} \approx 1.4142$); however, if the noise on the $2f$, $1f$ signals is uncorrelated or not of equal amplitudes (as would be the case under the presence of $1/f$ noise), the noise would increase and the SNR of the $2f/1f$ would decrease. The analysis presented here assumes the ideal case of white noise; however, further work on this comparison would require a study of the influence of $1/f$ noise on the signal precision.

<table>
<thead>
<tr>
<th>Table 5.3. Calculated Harmonic Values</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Signal</strong></td>
</tr>
<tr>
<td>$X_{2f,S}$</td>
</tr>
<tr>
<td>$X_{2f,BG}$</td>
</tr>
<tr>
<td>$R_{1f}$</td>
</tr>
</tbody>
</table>

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Considering the signal and noise models detailed thus far in this thesis, a summary of the SNR values for the various techniques assuming the same sample and detection parameters is provided in Table 5.4. The comparison of single spectral point detection of DLAS to CLaDS agrees with the study outlined in Chapter 3, where DLAS outperforms CLaDS by a factor of \( \sim 6.2 \).

In the comparison between the direct and modulation techniques, Table 5.4 suggests that conventional CLaDS slightly outperforms CM-CLaDS when only a single point is analyzed. However, single point detection with conventional CLaDS is a hypothetical situation where only the peak is captured within a 1 Hz bandwidth. In CM-CLaDS and WMS this detection scheme can be implemented using line-locking techniques. A more realistic comparison of the techniques would rather relate the scan SNR of conventional CLaDS to that of the line-locked value of CM-CLaDS, which favors CM-CLaDS due to the reduction in bandwidth.

Table 5.4. Signal to Noise Ratio Comparison

<table>
<thead>
<tr>
<th>Technique</th>
<th>Single Point SNR</th>
<th>Scanned SNR</th>
</tr>
</thead>
<tbody>
<tr>
<td>DLAS</td>
<td>1488</td>
<td>14.1</td>
</tr>
<tr>
<td>CLaDS</td>
<td>240</td>
<td>2.3</td>
</tr>
<tr>
<td>CM-CLaDS</td>
<td>157</td>
<td>-</td>
</tr>
<tr>
<td>WMS (ideal)</td>
<td>510</td>
<td>-</td>
</tr>
<tr>
<td>WMS (2f/1f)</td>
<td>392</td>
<td>-</td>
</tr>
</tbody>
</table>
It is also important to note that the calculations above assume white noise limited performance. Use of a different model, such as that of $1/f$ (pink) noise, may alter the results. The major benefit of the CM-CLaDS, beyond the ability to implement single point detection, is the reduction in detection bandwidth. Due to the non-linear relationship between output noise and bandwidth in CLaDS, lower operating bandwidths have a significant impact on the overall sensor performance. In WMS, accurate line-locking is contingent on the successful removal of the 2f RAM signal through calibration; an issue that is lessened in CM-CLaDS due to the simplified baseline of the CLaDS signal.

5.9. Discussion

In this chapter the fundamentals of Chirp-Modulated (CM) CLaDS were introduced and the corresponding signal models were verified mathematically. A discussion of the signal shape was included to qualitatively illustrate the influence of the chirp modulation, an effect that is not found in other modulation techniques such as wavelength modulation spectroscopy. Optimization of the modulation parameters (i.e. frequency spacing and modulation depth) was explored and showed how these effects are coupled through the chirp modulation. Lastly, a model of the SNR in CM-CLaDS system was developed, allowing for a theoretical comparison of the technique to a conventional CLaDS system.
Chapter 6: Applications

6.1. Introduction

The choice of appropriate sensing technology for a given application depends upon the sensing requirements (i.e. sensitivity, response time, etc.) as well as the sensing environment (i.e. open-path, harsh conditions, etc.). The nature of the CLaDS technique, as a measure of optical dispersion through analysis of transmitted phase rather than intensity, makes it particularly well suited for many sensing applications. Several key advantages of the CLaDS technique along with references to experimental verifications are summarized in the table below.

Table 6.1. Advantages of the CLaDS technique

<table>
<thead>
<tr>
<th>Feature</th>
<th>Experimental Verification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Signal immunity to intensity fluctuations</td>
<td>Fig. 6.4</td>
</tr>
<tr>
<td>Linearity with concentration</td>
<td>Fig. 4.2</td>
</tr>
<tr>
<td>Simplified baseline (ideally baseline-free)</td>
<td>Ref. [58]</td>
</tr>
<tr>
<td>Potential for ranging information extraction</td>
<td>Ref. [98] and Fig. 6.33</td>
</tr>
<tr>
<td>Signal independent of detector technology/parameters</td>
<td>Fig. 6.6</td>
</tr>
</tbody>
</table>
Demonstrations of sensing applications that utilize the features listed in Table 6.1 are detailed in the rest of this chapter, and include an investigation of large-scale methane trends of atmospheric methane (section 6.2), fiber dispersion characterization (section 6.4), and distributed sensing network (section 6.3). Applications investigated by others will be included in the conclusion.

6.2. Atmospheric Sensing of Methane

Methane (CH₄) is a potent greenhouse gas that is very effective at trapping heat within the earth’s atmosphere. Compared to carbon dioxide (CO₂), methane has a 25 times greater global warming potential, with a shorter lifetime (12 years versus 100 for CO₂) [99]. The potency and relatively short lifetime make methane a particularly interesting gas in discussions of climate change. Despite this interest, the localized sources of methane are still not well quantified, in part due to the limitations of current sensing technology. Many methane sensors for atmospheric sensing applications are based on extractive or multi-pass cells designs which provide highly accurate and precise data, but do so for a relatively small spatial footprint. To investigate larger scales trends with these sensing systems, many sensor nodes are needed. Such a sensing configuration may be costly as well as include additional system complexity such as the communication between the nodes as well as issues with cross-calibration and stability of many, independent nodes [100]. To facilitate the investigation of larger scale methane trends, a remote, multi-path methane sensor based on the CLaDS technique was developed, characterized, and tested in the field. Utilizing one central system to multiple sensing paths distributes the cost of the sensor over a larger spatial area. In addition, use of the same central sensor provides increased robustness (i.e. calibration, noise performance, etc.) over multiple paths. In this section, the design, development, and characterization of this instrument will be provided [101], along with details and findings from its first field test [102].
6.2.1. Sensor Design

Building off the work of the DSB CLaDS technique implemented in the near-IR with EOMs found in Section 4.1.2.1 (which targeted the $2\nu_3$ ro-vibrational band of Hydrogen Cyanide (HCN) at 1553.755 nm [81]), an instrument targeting methane ($\text{CH}_4$) in the 1650 nm wavelength range was developed. Initial exploration of the transitions in the region is presented in Fig. 6.1, where the simulated CLaDS signals for methane, water vapor ($\text{H}_2\text{O}$), and carbon dioxide ($\text{CO}_2$) show small spectral overlap in the 1653 nm ($\sim$6047 cm$^{-1}$) region. In atmospheric sensing, cross talk from adjacent water vapor lines often poses a large problem due the high variability and abundance of water vapor in the atmosphere.

![Figure 6.1. CLaDS signals for methane (black), water vapor (red), and carbon dioxide (blue) mixtures balanced with $\text{N}_2$ for atmospheric conditions (i.e. 297 K, 1 atm); normalized to the CLaDS methane signal [101].](image)

To probe the desired methane transition, a CM-CLaDS system was developed around a distributed feedback diode laser (DFB) emitting in the 1653 nm wavelength region; a diagram
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and picture of which are shown in Fig. 6.2. See Chapter 5 for more information about the CM-CLaDS technique. To generate the dual-sideband spectrum, a Mach-Zehnder EOM (Covega LN56S) was driven at 1.2GHz to probe the methane line with an effective frequency spacing between the sidebands of 2.4GHz.

**Figure 6.2.** System Configuration of the prototype CH₄ CLaDS sensor. OC – optical coupler, MZM – Mach-Zehnder modulator, RR – retro-reflector, PD – photodetector, LIA – lock-in amplifier, PI – proportional integral. Reprinted with permission from [101].

While operation in the near-IR probes weaker molecular transitions than those in the mid-IR, the availability of high-speed modulators allows for the generation of optimum sideband spacing for atmospherically broaden molecules such as methane. Additionally, the strength of mid-IR transitions may result in saturation over long interaction lengths. Use of dual-sideband CLaDS (i.e. carrier frequency and two sidebands) probes the molecular transition at twice the modulation frequency, allowing for use detectors that are readily available in this wavelength region. The optimum frequency spacing for the given transition was found to be ~1.4GHz [101], by due the limited bandwidth of the photodetector (Menlo System FPD310-F) used in this instrument (3dB
bandwidth of 1GHz), a slightly lower modulation frequency of 1.2 GHz was used instead. This provided an improved detector response with very little degradation to the signal amplitude (< 10%).

The multi-frequency beam was launched into free-space using a fiber coupled collimator (Thorlabs RC08APC-P01), and the light was directed using a motorized mirror (Newmark Systems, GM-6) to a corner-cube retroreflector (Newport Broadband Hollow Retroreflector). Light returned by the retro-reflector was collected using a commercial Newtonian telescope (Celestron 127EQ) and focused onto the fast photodetector. The resulting photocurrent was subsequently frequency demodulated using a spectrum analyzer (Tektronix RSA5106A) to measure the deviation of the heterodyne beatnote around $\Omega = 1.2$GHz. Not shown in Fig.6.2 is a second reference cell that was placed after the EOM for the purpose of calibration. A 99:1 coupler was used to deliver 1% of the multi-frequency probe power to a seal reference cell (20% CH$_4$ in N$_2$ at 755 Torr, Wavelength References) and a separate photodetector. This calibration channel was periodically probed using a RF switch which allowed the same spectrum analyzer to be used for analysis of both the calibration and sample channels.

In this prototype instrument, CM-CLaDS was used to continuously monitor the methane concentration, a technique that was discussed in detail in Chapter 5. The injection current to the DFB-diode laser was modulated with a sinusoid at 80kHz. As illustrated in Fig.6.2, a 99:1 coupler was used to couple 1% of the laser light to a sealed reference cell and additional photodetector for line-locking using this WMS signal. A PID controller, operating with only the proportional and integral components engaged, was used to create an error signal that was then fed back to the laser to lock the laser wavelength to the line center. In the sample channel, the second harmonic signal ($2f$) was retrieved through harmonic detection (i.e. phase sensitive
detection) of the FM demodulated CLaDS signal. Due to the baseline-free nature of CLaDS, the amplitude of the CM-CLaDS signal is directly proportional to the sample’s concentration. This makes the conversion CM-CLaDS to concentration straightforward through use of the calibration signal.

Due to the timescales of the processes under investigation in studies of atmospheric methane, a 1s instrument response time is desired. To match this need, the prototype instrument reported a single data point every 1 second. To determine the $2f$ component with this interval, 150ms of the frequency demodulated signal was collected and read by a LabVIEW program for subsequent harmonic detection, which represents a 12.5% overall duty cycle. The effect of operating with a reduced duty cycle is shown in Fig.6.3, where the Allan Deviation plots for data captured and analyzed for a 100% and 15% duty cycles. Allan Deviation analysis is a graphical method to identify sources of noise and drift for a given instrument, and assesses the overall sensor stability. Upon averaging, a white noise limited system would show a reduction of noise as a function of $\sqrt{N}$, where $N$ is the number of averages, which on the log-log scale of a Allan Deviation plot would show a slope of $-1/2$. More information about Allan Deviation can be found in Ref. [103].

For the random-noise limited system used in this analysis, an increase in the duty cycle (i.e. averaging capacity), shows a clear improvement of the instrument’s detection limit.
Figure 6.3. Allan deviation for 100% (black) and 15% (red) duty cycle operation. The 100% duty cycle data was captured using the ‘FastSave’ mode the Tektronix spectrum analyzer (RSA5103A); a feature that stores raw data that was subsequently analyzed in post-processing.

Operation with a reduced duty cycle is the result of insufficient processing capabilities of the onboard computer; a limitation that can be overcome through the development of a custom, and dedicated processing unit.

6.2.2. Sensor Characterization

To characterize the performance of the developed prototype, several tests were carried out to assess the system’s response to power variations, long-term stability, comparison to existing technology, and use of alternative hard targets [101]. As discussed previously, CLaDS is a measure of received phase, and is therefore highly immune to intensity fluctuations [58]. To test this feature in the developed methane instrument, a constant concentration sample (3cm long gas cell filled with 20% CH\textsubscript{4} in N\textsubscript{2} at 755 Torr) was introduced into the system and the optical losses
between the modulator and detector were varied to generate different RF beatnote powers. The resulting CLaDS spectra under these varying power conditions is shown in Fig.6.4.

**Figure 6.4.** CLaDS spectra for different received beatnote powers using a 3 cm gas cell containing 20% CH$_4$ in N$_2$ at 740 Torr and 1000 frames averaged. Loss was introduced between the EOM and the photodetector to generate different CNR values. Results for -10dBm, -30dBm, and -50dBm were artificially offset by 1 kHz for easy viewing [101].

According to the results in Fig.6.4, the amplitude of the CLaDS spectra remain constant despite a 50dBm change in RF signal power. From 0dBm to -20dBm power, the noise is the signal remains relatively constant, while after a decrease of 30dB or more, the noise in the signal shows a steady increase. This steady increase of noise at low received powers is the result of the thresholding effect present in the frequency demodulation process and was discussed in Chapter 3. This test indicates that for the developed instrument, power fluctuations that produce changes in the RF power above -20dBm should not introduce changes in the noise characteristics of the instrument. For significant power reduction, resulting in RF powers around -50dBm, an increase in instrument noise is expected. Independent of RF beatnote power, the signal remains
unaffected. In instances where a large power reduction occurs, and when the application and timing constraints allow for it, the precision of the measurement can be partially recovered through further averaging.

In the developed system, corner-cube retroreflectors (Newport, Broadband Hollow Retroreflector) were used as hard targets. While retro-reflecting targets return the majority of the light (> 90%) back to the sensor and result in higher CNR values, the targets themselves are rather expensive and require that the target locations be predetermined and in accessible locations. Other, less-expensive reflector targets in addition to diffusely scattered targets such as walls could potentially be used. To see if these alternative targets would be suitable for the developed instrument, several targets were tested in a scattering target configuration. In Fig.6.5, the instrument noise is plotted as a function received beatnote power for tests with the retroreflector target and several inexpensive reflectors. The tested targets included a reflective aluminum traffic sign (McMaster Carr), two molded plastic reflectors (such as those used as bicycle reflectors), and reflective tape (3M). With the retro-reflectors, lower return powers were achieved by partially blocking a part of the beam.

While these alternative targets follow the same noise trend as the retroreflector system (i.e. no additional noise is added through use of these diffuse reflectors), the return powers achieved with these reflectors place the system in a regime where the noise is dominated by the frequency demodulation process. As a result, the precision of the instrument becomes highly dependent on the received optical power, which could make it difficult to accurately compare data captured during periods with different return powers.
Figure 6.5. CLaDS noise a function of received beatnote power (i.e. CNR) for several retroreflecting and diffusely scattering targets. Two clear noise regions exist, one dominated by fringe noise and the other my demodulation noise [101].

In addition, the relatively high noise values require longer averaging times, which with a 12.5% duty cycle would require a response time that is longer than the 1 second reporting window desired for investigations of transient methane events. As a result of these tests, high quality retroreflector targets were used in the first field deployment of this instrument.

In another test, the amplified photodetector (Menlo Systems, FPD310-F) in the signal channel was replaced with a biased photodiode (EOT, ET-3000). Using a 35m open path in the laboratory to probe ambient levels of methane in the air (~1.8ppmv), the CLaDS signal was measured with both detectors, the results of which are shown in Fig.6.6.
Figure 6.6. The 2f CLaDS spectra for ambient level of methane over a 35m optical path for two different detector, an amplified photodetector (Menlo System, FPD310-F) and a biased photodiode (EOT, ET-3000). Consistent CLaDS amplitudes are achieved despite the significantly detector technologies and parameters. Reprinted with permission from [101].

Despite the change in photodetector, each with significantly different detection parameters, the CLaDS amplitudes are nearly identical. Noise produced with each detector is in fact different, but the consistency of CLaDS signal amplitude exemplifies this technique’s immunity to electrical drifts, detector aging, or detection technology.

To examine the long-term stability of the developed instrument, two sensing configurations were analyzed, one with online analysis of a gas cell filled with a stable concentration and one with offline analysis of a 35m open-path within the laboratory. For online analysis, 1% CH₄ in N₂ at 500 Torr was continuously flowed through a 23mm gas cell using a dilution system (Envirionics 4040 diluter) for more than 24 hours (Fig.6.7.a). These parameters were chosen to mimic the
path-integrated dispersion profile of atmospheric methane levels over 100m of optical path. The resulting Allan Deviation for this test is shown in Fig.6.7.b.

**Figure 6.7.** (a) Line-locked CLaDS signal as a function of time for a stable methane concentration generated using a dilution system; (b) Allan Deviation plot of the time series in (a) as well as without active line-locking [101].

The Allan Deviation analysis in Fig.6.7.b shows that, with the implementation of line-locking, random noise dominates the sensor performance for integration time up to 300s. After ~300s the instrument begins to drift but does not exceed 600ppb-m for the integration times tested here. Without line-locking, laser drift causes a decrease in the noise performance for integration times larger than 100s. Although this test allows for online analysis of the system performance, it does not address potential noise contributions from the open-path optics such as the telescope, detector, and reflectors. To investigate the influence of the remote-sensing portion of the system, an Allan Deviation analysis was performed using an open-path configuration similar to that which will be deployed in the field, that is a ~35m total optical path using a retroreflector target. However, in this test the sample (i.e. the laboratory air) is an uncontrollable environment. To reduce the influence of changes in methane level within the laboratory, an offline analysis was
performed where the laser frequency was detuned from the line center of any methane, water vapor, or carbon dioxide transitions; the results of which are shown in Fig.6.8.

Figure 6.8. Allan Deviation plot for an off-line measurement performed using the full prototype system in the remote sensing configuration [101].

The remote-sensing data shows a local minimum at ~200s, 100s shorter than the gas cell measurements, and a stabilized detection limit of 700ppb-m at longer integration times. Comparing the results of these two tests show that the main source of long-term drift are the remote-sensing optics, mostly likely from parasitic scattering between the telescope body and the photodetector window. From the remote-sensing Allan Deviation analysis, a path length and bandwidth normalized detection limit for the instrument was determined to be 1.3ppm-m-Hz$^{1/2}$.

The developed prototype performance was also compared to an existing open-path methane sensor called the Remote Methane Leak Detector (RMLD). The RMLD, developed by Physical Sciences Inc., utilizes Wavelength Modulation Spectroscopy (WMS) in the same spectral region to quantify the methane levels with a nominal precision of $\leq$ 10ppm-m for paths greater than 15m in a scattering configuration (from targets such as walls) [104]. For this comparison, both
instruments were placed outside and probed the same retroreflector placed 43m away. The instruments were placed as close together as possible in an attempt to overlap the optical paths of each sensor. With methane leak detection as the main application for the RMLD technology, methane was released from a gas cylinder to mimic gas plumes released from a leaking pipeline. The response of each sensor as a function of time is presented in Fig.6.9.

![Figure 6.9](image)

**Figure 6.9.** Cross comparison of the CLaDS instrument and the RMLD with released methane plumes and a high concentration cell inserted into the optical path [101].

At around 250s into the test, a large diameter gas cell containing a high concentration of methane was placed in front of the retroreflector to guarantee that each instrument probed the same sample. In general, there was good agreement between the responses of the two instruments. Small discrepancies in the amplitude and timing of the measured methane spikes can be attributed to differences in the actual optical paths between the two sensors as the released methane plumes diffused through the region under test. Furthermore, the RMLD’s use of WMS, while a well understood technique requiring fairly simple detection electronics, involves power normalization, often a 2f/1f normalization procedure introduced in Ref. [19]. The CLaDS
instrument instead requires more sophisticated RF detection electronics, but is highly immunity to the intensity variations that are to be expected in a remote-sensing configuration and does not require power normalization protocols. After the characterization detailed in this section, the developed prototype was transferred to a weatherized enclosure and tested under field conditions. Details and results from this first field test are provided in the next section.

6.2.3. Field Deployment

The prototype instrument described in the previous section was deployed at Sallies’ Fen Environmental Station (SFES), located in Barrington, NH (43°12.5′ N, 71°3.5′ W), for several months starting in June 2013. As emphasized in the introduction to this section, methane is a potent greenhouse gas. Work by researchers at the University of New Hampshire has led to monitored methane emissions at SFES for more than two decades [105-108]. Natural sources are spatially heterogeneous [109], making them particularly challenging to identify and understand using point-sensor technology. To address this need, a remote, multi-path sensor was designed, characterized, and deployed in the field [102]. The results of this first field test illustrate the capability of this sensing technology and areas that are in need of further development.

After further consideration of the atmospheric conditions to be expected in the fen, namely the influence of water vapor, the operating wavelength for the deployed instrument was adjusted to probe a different methane transitions than that discussed in section 6.2.1. The in-laboratory system operated around 6046 cm\(^{-1}\) (1653nm) to probe the R3 transition in the 2\(\nu_3\) overtone band of methane. In an open-path sensing system, the presence of water vapor is uncontrolled and can vary significantly. To investigate this influence, the CLaDS spectra of two methane lines (R3 and
R4) were simulated under varying water vapor conditions (see Fig.6.10). Spectral parameters for CH₄, H₂O, and CO₂ were based on data from the HITRAN 2008 database [110].

![Graph showing influence of water vapor concentration on two methane lines.](image)

**Figure 6.10.** Influence of water vapor concentration on two methane lines. Both lines have similar linewidths and are simulated for a double sideband (DSB) with Ω = 1.2 GHz [102].

Due to more significant spectral overlap, the methane transition at 6046 cm⁻¹ shows larger cross-talk with water vapor. As a result of these simulations, the transition at 6057 cm⁻¹ (1651 nm; R4 in the 2ν₃ overtone band) was selected for the sensor deployment. This change in operation wavelength was achieved by changing the temperature of the laser to 5°C instead of the 25°C used during the laboratory experiments.

**6.2.3.1. System Integration and Sensing Configuration**

Prior to deployment, the prototype methane instrument was installed inside a weatherized, temperature-controlled cabinet (DDB Unlimited) as shown in Fig.6.11. The laser radiation was launched through a sealed polycarbonate window at the top of the cabinet and a gimbal mounted mirror (Newmark Systems, GM-6) directed the light to retroreflectors mounted in a ring around
the centralized system. A 10×10 foot canopy was installed over the instrument to prevent direct exposure to rain and sunlight.

**Figure 6.11.** CLaDS instrument in the weatherized cabinet installed at SFES. The inset shows a close up of the optical port and gimbal mounted mirror for directing the laser radiation to several targets [102].

Within the fen the sensor was placed on a platform in a central location and six retroreflectors were mounted on posts about 20 m away from the instrument (see Fig.6.12). The location and distance of each target were chosen to probe emissions from specific plant species. It’s important to note that a target distance of 20 m is not a limitation of the sensor, but was rather chosen to examine certain areas. The optical path length for each target was accurately measured prior to sensor operation, and the values were stored for later use when calculating the path-averaged concentration for each target. At each target, 2 minutes of data (at 1Hz) was collected, and then
the position of the motorized mirror was changed to probe the next target. This process then continued for the length of the deployment, with calibration using the onboard reference cell performed once an hour.

Figure 6.12. Sensing configuration at SFES. The yellow rectangle, red circles, and blue square represent the sensor platform, the location of the six retroreflectors, and the weather station, respectively [102].

Each retroreflector was anchored to the fen surface on an aluminum fence post. The relatively unstable wetland surface caused both the retroreflector mountings and the sensor platform to change position slightly depending on the fen’s water table and other external influences (such as researchers walking on the site’s boardwalk). To account for this movement, an active alignment system was developed. Both initial alignment and re-alignment procedures were implemented using a raster-scanning algorithm of the gimbal motor positions (see Fig.6.13). For initial alignment between the sensor optics and the targets, the procedure outline in Fig.6.13.b. was employed. For each target a large raster grid and step size (11×11, 100 counts) was used for
rough alignment, after which the maximum value from the scan was used to perform a subsequent raster scan on a smaller grid and step size (7×7, 50 counts). Fine tuning of the gimbal position (5×5, 20 counts) was then performed and the motor positions for each target were stored.

![Rastering algorithm for optimizing the position of the mirror position for maximum return power.](image)

**Figure 6.13.** Rastering algorithm for optimizing the position of the mirror position for maximum return power. (a) Searching algorithm configuration; (b) Results of consecutive raster scans of decreasing grid size (11×11, 7×7, 5×5) and step size (100, 50, 20 counts). Lighter regions indicate higher received powers [102].

If during the measurement cycle the return optical power (inferred by the RF beatnote power) dropped below a predetermined value, an additional raster scan procedure was initiated to try to recover the alignment between the instrument and the retroreflector. After a small scan was performed (5×5, 20 counts), if the power threshold was not meet, a larger raster was initiated (11×11, 100 counts). If this larger scan did not localize the target, the path was flagged within the software as needing attention by a human operator.

To accompany the methane data, a weather station (Davis Vantage Pro2) provided meteorological data (temperature, relative humidity, wind speed and direction). Data collection for this test began in late July 2013 and continued until mid-October, with a 3-week break in August when the gimbal mount was sent out for repairs.
6.2.3.2. Signal Calibration and Precision in Field Conditions

During the measurement cycle the onboard calibration channel was periodically probed to ensure the system accuracy remained consistent throughout the deployment. The calibration channel contained a seal gas cell (Wavelength References, 3 cm) filled with 19.4% methane in nitrogen at 740 Torr. Ideally, the temperature controlled environment of the sensor cabinet would keep the calibration cell under stable conditions; however, the onboard air conditioner had limited cooling capacity (4000 BTU) and no heating capabilities. As a result, the cabinet environment experienced large temperature swings (greater than 7ºC) causing the calibration signal to show a clear dependence on temperature (Fig.6.14.a).

![Figure 6.14.](image)

**Figure 6.14.** (a) Observed temperature dependence of the raw calibration data (black squares) and temperature-independent signal after correction (red circles); (b) Calibration signals for 19 days of the campaign both before (black squares) and after (red circles) temperature correction procedure [102].

The observed temperature effects are the result of two temperature dependent processes. First, the line strength of the molecular transition depends on temperature [111]. Second a change in
cell temperature will induce a pressure change assuming isovolumetric conditions according to
the ideal gas law. The cabinet temperature was recorded using the Davis Vantage Pro2 console
sensor, and the corresponding data was used to suppress the influence of the temperature
variations. To correct for the line strength’s dependence of temperature, the following expression
was used,

\[ S(T) = S(T_{ref}) \frac{Q(T_{ref})}{Q(t)} \exp \left( -\frac{c_2 E_q}{T} \right) \left[ 1 - \exp \left( -\frac{c_2 v_{qq'}}{T} \right) \right], \]  

(6.1)

where \( T \) is temperature (K), \( S(T) \) is the spectral line intensity (cm\(^{-1}\)/[molecule cm\(^{-2}\)]), \( Q(T) \) is the
total internal partition function, \( c_2 \) is the second radiation constant (1.4388 cm\( \cdot \)K), \( E_q \) is the lower
state energy of the transition (cm\(^{-1}\)), and \( v_{qq'} \) is the line frequency (cm\(^{-1}\)) [111]. Using Eq. (6.1)
and a reference temperature of \( T_{ref} = 296 \text{K} \), the measured temperature data was used to scale the
raw calibration data. Similarly, the change in pressure was scaled using the following relation

\[ p = \frac{T}{T_o} p_o \]  

(6.2)

where \( p \) and \( T \) are the measured pressure (atm) and temperature (K) in the cell and \( p_o \) and \( T_o \) are
the values provided by the manufactures of the sealed cell. Using the temperature and pressure
within the sensor cabinet, the pressure broadened halfwidth (cm\(^{-1}\)/atm) can be modeled using Eq.
(6.3), where \( \gamma_{air} \) is the air-broadened HWHM (cm\(^{-1}\)/atm), \( \gamma_{self} \) is the self-broadened HWHM (cm\(^{-1}\)/atm), \( p_s \) is the partial pressure (atm), and \( n \) is the coefficient of temperature dependence.

\[ \gamma(p, T) = \left( \frac{T_{ref}}{T} \right)^n \left( \gamma_{air}(p, T_{ref})(p - p_s) + \gamma_{self}(p, T_{ref}) p_s \right) \]  

(6.3)
Using Eqs. (6.1)-(6.3), the CM-CLaDS spectra under varying temperature conditions can be modeled with spectral parameters from the HITRAN 2008 database [110]. For this specific methane transition, spectral parameters were taken from Ref [112]. These temperature dependent model were then used to correct the raw calibration data, the results of which are shown in Fig.6.14.b.

In addition to the influence on the calibration signal, temperature variations within the sensor cabinet also affected the main source of drift in the system; parasitic reflections between the telescope body and the window of the photodetector. The telescope body expands and contracts in a temperature varying environment, and thus the fringe between the telescope and the photodetector was amplified. The instrument precision was characterized as 1.7ppm-m-Hz$^{-1/2}$ prior to deployment. It should be noted here that this number is corrected for the operating duty cycle (15%). Under the influence of an unstable environment, the precision was estimated (from the standard deviation of the measured data) as 0.2 ppm over 40m in 1s. This corresponds to about a 5x degradation in sensor performance (or ~2x if the value is not correct for duty cycle). Despite this increase in fringe noise, the measured signals were large enough (due to the path length) to investigate the instrument’s ability to probe interesting and meaningful methane trends in this open, multi-path sensing configuration.

6.2.3.3. Observed Atmospheric Methane Trends

6.2.3.3.1. Diurnal Cycles

During this first field test, several methane trends were investigated using the remote, multi-path methane sensor; the first of which was the occurrence of diurnal cycles. Changes in the concentration of methane close to the vegetation floor are expected due to the breakdown of the
turbulent mixing layer during the night hours. During this time, the cooler temperatures and lower wind speeds cause a reduction in the height of this layer, preventing the transport of emissions from the vegetation floor to higher portions of the atmosphere. As a result, there are higher observed concentrations during the night hours under calm conditions [113]. To investigate this phenomenon in the fen, data from the CLaDS instrument was compared to that of an autochamber system collocated in the area. The autochamber system for the CH₄ flux measurements was operated by the University of New Hampshire (UNH) and consisted of sampling chambers placed on the vegetation floor in locations throughout the fen [106, 114].

Figure 6.15. (a) Diurnal cycle measured by the CLaDS instrument (black triangles representing each 2 minute intervals) and the UNH autochamber system (blue squares) on 31 July 2013; (b) Concentration measurement for path #3 of the CLaDS measurement for four consecutive days showing clear diurnal peaks in the night hours [102].

Each chamber has a pneumatic lid and probed only one at a time. A tubing system then transferred the accumulated emissions to a centralized spectrometer (Aerodyne Research,
Quantum Cascade Laser Trace Gas Monitor) for analysis. Figure 6.15.a shows both data sets for 31 July 2013.

The CLaDS system sampled the ambient methane levels at a height of 2m above the fen surface. In contrast, the autochamber system measured directly on the surface. This difference in sampling height explains why both instruments see a diurnal peak, but the autochamber system shows a larger peak (~6ppmv) compared to the CLaDS instrument (~3ppmv). The scatter in methane values for the CLaDS sensor is partially due to the measurement of multiple paths; however, the thermal instability of the sensor cabinet resulted in an overall degradation of sensor performance. This reduction in sensitivity is discussed later in this section and accounts for the occurrence of the unrealistic values below 1.8 ppm. To show variations in diurnal peaks, four days of measurements of a single path from the CLaDS system are shown in Fig.6.15b.

6.2.3.3.2. Multi-path Measurements

Unique to this multi-path measurement configuration is the ability to measure several open, optical paths with the same instrument. With this type of configuration, spatial variations of the methane levels can be investigated. The first trends that were examined were those under low-wind conditions (i.e. wind speed < 0.45 m/s, or 1 mph). Assuming negligible transport due to wind, statistical differences between various paths can be measured. When each path-averaged methane measurement is path-normalized, observed differences indicate different emission rates most likely related to the different plant species under each optical path.

Daily averages for data acquired in low-wind conditions of the first 17 days of the campaign are shown in Fig.6.16. Under the assumption that the measured methane levels correspond to the emission of plants directly under the line of sight of each path, clear trends are visible for some
paths. For example, paths 3 and 6 show higher daily averages and are located in areas with majority sedges. In contrast, paths 4 and 5 are located in non-sedge regions and show consistently lower daily average. The observation of higher methane levels in sedge dominated regions is consistent with previous measurement at this site which showed that sedges are direct conduits of methane from the subsurface to the atmosphere [107]. These types of multi-path measurements can provide further insight into the emission difference between various plant species, and the role they play in larger methane trends.

**Figure 6.16.** Path-normalized, daily average concentration of low-wind data over 17 consecutive days, illustrating clear path dependent emission rate trends. On day 9, a rain and thunderstorm event caused a spike in methane levels throughout the fen [102].

In contrast to low-wind regimes, in higher wind conditions ( > 0.45 m/s), the assumption that the open-path measurement directly correlates to the emissions from plants directly below the light of sight is no longer valid. Instead, the wind transports the methane in accordance with the wind speed and direction. Under steady wind conditions, the horizontal winds and direction can
provide insight into large-scale emission trends using this multi-path configuration. In addition, there may be a possibility of source localization using this sensing technique.

**Figure 6.17.** Observed mixing event due to the breakup of the nocturnal boundary layer. The red vector indicates the direction and magnitude of the wind, while the blue stars indicated the magnitude of the methane concentration. The green numbers show the path number and position of each path on this 360 grid [102].

In Fig.6.17, the CLaDS sensing system was used to observe mixing effects due to the breakup of the nocturnal boundary layer. During the night hours (04:12) a slight peak of > 2ppmv is observed, which is consistent with the diurnal cycle trend described previously in this section. At around 09:00, the first significant winds of the day cause mixing that allows the accumulated methane to dilute upward into the atmosphere. Due to the fact that the fen is a net emitter of
methane, there is a decrease in the path-normalized methane concentration since movement of air masses from outside of the fen would expectedly contain less methane. Using this type of multi-path sensing configuration allows for investigations of the spatial and temporal variations from event such as the breakup of the nocturnal boundary layer and other large-scale, transient methane events.

The results of this first field test revealed areas where the developed system requires improvement (such as customized electronics for increased operational duty cycled and more robust free-space optics), but also highlighted the capability for large-area, multi-path measurements using the CLaDS technique.

6.3. Distributed, Multi-Path Sensing

Spectroscopic sensor networks have a large variety of applications, from atmospheric sensing, energy and industrial monitoring, to safety and security applications. Important in these networks is a sufficient number sensor nodes to extract the desired information, but also important is the accuracy, precision, and stability of the nodes such that the measurements are reliable. Additionally, maintenance and cost considerations must be taken into account. Many existing networks are made up of individual spectrometers that run independently of other sensor nodes. While these types of networks have the potential for providing high precision measurements, issues with accuracy and drift between sensors may limit the overall performance of the network. Also some applications, like leak detection of a natural gas pipeline or other potentially explosive or harsh environments, require completely passive sensor nodes, eliminating the use of any active sensor node technology (for sensing, communication, etc.). For such applications, a centralized analysis unit that serves many passive sensor nodes is the ideal architecture.
As demonstrated in Section 6.2, use of a centralized instrument to sense multiple sampling locations has a number of advantages, the main one being that each path (or “node”) shares the same system parameters (i.e. calibration, instrument noise, drifts, etc.). The instrument detailed in that section was designed for long, open-path measurements to investigate atmospheric methane trends. The technology can be readily applied to other sensing configurations as well. One example is a distributed sensing network implemented as part of a fiber network. This takes advantage of the robustness, cost, and availability of fiber components originally intended for the telecommunications industry. In the spectral region with high transmission through standard silica fiber, methane sensing of the R branch of the $2\nu_3$ overtone band (1620-1660nm [112]) is of particular interest for applications such as pipeline health, fracking monitoring, and coal-mining warning alarms. Given that methane is explosive at 5% concentration in a given volume, for warning alarm systems the threshold is set to $\frac{1}{4}$ the explosive limit. Accordingly, the sensor networks described in this section aim to achieve a detection limit below 1.25% CH$_4$ per volume.

The CLaDS technique is particularly well suited for remote sensing via fiber optic cable because the measurement is one of received phase, rather than intensity. As a result, the SNR of the measurement is less dependent on fiber length (i.e. attenuation due to loss of the fiber). This phenomenon is illustrated in Fig.6.18, where the CLaDS signal is plotted for various sensor locations (i.e. the length of the fiber). Despite an almost 4 km difference in optical fiber in the system, the SNR for each CLaDS spectra remained unchanged.
Figure 6.18. Comparison of SNR using no “remote” fiber (black), only a collection fiber (red, 2.26km), and both delivery and collection fibers (blue, 1.645km + 2.26km) [115].

With the potential to probe multiple paths of varying lengths with comparable noise performance, a centralized spectrometer based on the CLaDS technique is particularly interesting for sensor network architectures. To address multiple nodes with a single spectrometer, the input from each sensor must be multiplexed in some fashion. The two methods that will be discussed here are a time-multiplexed approached, where the propagation delay through the fiber spaces out the return signals in the time domain (section 6.3.1), and a frequency-multiplexed configuration which is unique to the CLaDS technique (section 6.3.2).

6.3.1. Time Domain Approach

To demonstrate time-multiplexed distributed sensing with CLaDS, a two-node system was built. For the application of methane leak detection, one centralized unit (i.e. laser, detector, electronics, processing, etc.) served two passive sensor nodes. A generic single node CLaDS system is illustrated in Fig.6.19 and a simplified schematic of the proof of concept multi-node
system is shown in Fig.6.20. The transmitter block (Tx) contains the laser, EOM, and driving electronics, while the receiver (Rx) contains the photodetector and processing electronics, which in these tests was a spectrum analyzer (Tektronix, RSA5103A). In this configuration the light is transmitted and returned to the centralized unit (Tx and Rx) through the use of circulators that only allow light propagation in designated directions. The nodes (sealed, high-concentration 3 cm gas cells) were separated by 19km of fiber optic cable.

**Figure 6.19.** A fiber-based CLaDS system. The transmitter section generates the optical signal that probes the sample (passive sensor node, gas cell), which is connected to the receiver via fiber optical cable.

**Figure 6.20.** The proof-of-concept two node distributed sensing configuration.

To distinguish the return signal from each of the sensor nodes, the output from the transmitter was pulsed. Each sensor node path contains different lengths of fiber and therefore has varying propagation time from the transmitter to the receiver. As a result of the difference in pulse delay, the returns signals from each node are spaced out in time, such that each node can be analyzed.
separately. Discussed further in Section 6.4, the CLaDS technique provides a measure of non-resonant dispersion, such as background fiber dispersion, as well as resonant phenomena such as molecular transitions. Shown in Fig.6.21 are CLaDS spectra measured with longer fiber optic links than the ones shown in Fig.6.18. Here the signature of the methane signal has a variable frequency offset depending on the fiber length (from the intrinsic fiber dispersion). With the models developed in Section 6.4, this baseline due to the fiber dispersion can be characterized and removed from the spectroscopic data. In this time-gated, multi-node system presented here, the offsets in the CLaDS spectra were measured and corrected for using a simple baseline removal procedure.

**Figure 6.21.** CLaDS spectra measured using different fiber link lengths showing a clear offset due to accumulated fiber dispersion.

For the proof of concept system, several pulse widths were used to characterize the system performance. The received amplitude signals for pulse widths ranging from 100-20μs are shown in Fig.6.22. Use of shorter pulse widths allows for the potential to more closely pack the sensor nodes, however, the shorter timescales result in higher chirp rates which in turn require larger detection bandwidths (see Chapter 3). Given ideal processing capabilities, this larger bandwidth
could be overcome through averaging (i.e. 100% duty cycle), however, technical challenges may impose limits on processing capabilities. While not investigated in this work, pulse width constraints could potentially be overcome by adding additional fiber the sensor nodes to artificially generate longer delays to further separate this return signals in time.

For a given network, the ultimate sensitivity will be determined by the number of nodes (determining how the power from the transmitter is shared), the minimum sensor spacing (propagation delay), and the required response rate (how much averaging can be performed). For the system under test, sensor node 2 expectedly shows lower return amplitudes caused by the additional fiber loss in that sensor channel. Due to the lower return intensities, this far node was be used for assessment of the system’s detection limit within a 1 Hz reporting window.

![Figure 6.22.](image)

**Figure 6.22.** Received intensity signals as a function of time from the two nodes for a variety of pulse widths

The CLaDS spectra for sensor node 2 for varying pulse widths are shown in Fig.6.23. As expected, shorter pulse widths require larger chirp rates to cover the same wavelength range in less amount of time, and therefore resulting in larger CLaDS amplitudes for shorter pulse widths.
Figure 6.23. The corresponding CLaDS signals for the far node.

For both the shortest and longest pulse widths tested here, the CLaDS spectra were fit to extract the corresponding concentration, while the residuals were analyzed to determine the path length and bandwidth normalized detection limits (see Fig.6.24). For the CLaDS signal captured with a 100μs pulse width, the system performance was determined to be 82 ppm-m-Hz$^{-1/2}$, while for the 20μs pulse the system performance was similar at 84 ppm-m-Hz$^{-1/2}$. While sealed cells were used in this test, the detection limits could be translated to a more realistic sensing configuration for leak detection applications. Assuming a 3cm open path was used as the sensing element, sensitivities of 0.28% CH$_4$ in air in 1 second could be achieved with this system. A value which is well within the 1.25% concentration requirement for leak detection alarms.

Figure 6.24. CLaDS spectral fit and residuals for a 100μs pulse (left) and a 20μs (right).
It is important to note that this time-multiplexed approach could also be performed using absorption based techniques, such as Direct Laser Absorption Spectroscopy (DLAS). The use of wavelength modulation spectroscopy in this type of sensing configuration would run into challenges due to the fast ramp rates. Typical WMS systems operate with kHz sinusoidal modulation of the laser current superimposed with slow ramp rates on the order of Hz. In this configuration, the ramps rates are on the order of kHz, which would require even faster wavelength modulation, which may be beyond the capabilities of many laser driver electronic systems and begins to encroach on the frequency modulation regime of operation. An investigation into the potential of DLAS for time-multiplexed distributed sensing is detailed in the next subsection in a discussion of an overlay of the leak detection system on an existing fiber network.

6.3.2. Frequency Domain Approach

For many applications, continuous wave (CW) measurements are desired for the best sensitives and response times, however, this feature also requires that the technique used be truly simultaneous in nature. While a time-multiplexed distributed sensing approach is feasible with CLaDS as well as DLAS, the measurement of optical dispersion allows for the CLaDS technique to also be translated to a frequency-multiplexed sensing network, allowing for CW operation.

Recently, CLaDS was extended to a range-resolved technique where both the path-integrated sample concentration and the range information can be extracted from one beatnote signal. Through a method that is similar to FMCW radar, the range-resolved signal is extracted by introducing a chirp to the modulation frequency, $\Omega$ (often referred to as a frequency spacing). First demonstrated in free-space, this technique can be considered the combination of FMCW
ranging and optical spectroscopy [98]. This technique was then implemented in a fiber system, with a configuration shown in Fig.6.26 [116].

The important difference between the system here and the time-multiplexed system, besides the parallel connection of the sensor nodes, is the additional chirp of the carrier frequency, $\Omega$ ($\Delta \Omega / \Delta t = 299.8 \text{MHz}$). Using this carrier chirp in addition to the difference in fiber dispersion that results from the difference in fiber lengths, both the distance and gas information from multiple nodes can be extracted simultaneously. For this two node system, the received amplitude signal (Fig.6.27.a) clearly shows the interferometric pattern resulting from the interference of the two paths. Extracting information from this signal would be rather difficult, however, in the frequency domain these two signals are clearly distinguishable (Fig.6.27.b).

With a frequency shift equal to $(\Delta \Omega / \Delta t) \tau_g$, where $\tau_g$ is the total group delay, the 8km of fiber in the path of gas cell 2 results in a shift of 12kHz, while the 16km of fiber seen by gas cell 1

**Figure 6.26.** Simplified sensing configuration; EOM – electro-optical modulator, 50/50 – coupler, PD – photodetector, Gas Cells – 3cm fiber coupled cells (Wavelength References). The proposed multi-range CLaDS method is able to separate the spectroscopic signals from both paths (8km and 16km of fiber which corresponds to ~12km and ~24km of effective optical path) even though both are continuously probed and the light is passing through both cells with unknown intensity ratio.
provides double the shift at 24kHz, as shown in Fig.6.27.b. To extract the CLaDS spectra from these signals, the desired frequency region (corresponding to the sensor node of interest), is down-converted, low-pass filtered, and subsequently frequency demodulated. This process for gas cell 1 is shown in Fig.6.28.

**Figure 6.27.** (a) Raw time-domain signal observed at the detector output resulting from the combination of light from the two measurement paths; (b) RF spectrum of the raw signal clearly shows the two sensor signals separated in frequency domain.

**Figure 6.28.** (a) RF spectrum of the filtered and down-converted signal originating from gas cell 1 (at 25 kHz) and (b) its AM and FM demodulated traces showing features due to gas absorption and dispersion.
While both the amplitude and frequency demodulated signal can be extracted using this technique, the range information is present only in the CLaDS signal as an offset in the instantaneous beatnote frequency (which is directly translated to sensor distance). In Fig.6.28.b the difference in offset sign is due to the difference in chirp rate direction (i.e. up-chirp or down-chirp). To prove that there is no cross-talk between the two nodes, this same analysis was performed with the other cell (cell 2) physically disconnected from the system (blue curves in Fig.6.28.b). In both cases, the same gas signal was measured, although there is a slight difference in the noise.

This proof of concept system demonstrates truly simultaneous detection of methane from two parallel sensor nodes. The minimum spacing required between two adjacent sensor nodes (i.e. the spatial resolution) was not examined in this study, but is most likely limited by the filter bandwidth used in the demodulation procedure. In addition to examining this fundamental or technical limit, future work on this technique will involve an investigation into more efficient processing algorithms and optimization of the optical layout to minimize loss and distortions throughout the system.

6.4. Fiber Dispersion Measurement

In CLaDS, optical dispersion is measured through the interaction of multiple, coherent, co-propagating electromagnetic waves with the sample under test. As a result, CLaDS is capable of measuring not just resonant phenomena such as molecular transitions, but all dispersive effects, such as non-resonant fiber dispersion. Often a limiting factor in communication systems, fiber dispersion is the wavelength dependence of the group velocity (group velocity dispersion, GVD) and is caused by intrinsic material effects and properties of the waveguide structure. With the
development of novel waveguide structures (i.e. hollow core, mid-IR fibers, etc.), straightforward and simple dispersion characterization may become of increased importance [117].

Existing technologies used to characterize fiber dispersion often require separate instrumentation and offline analysis. Pulse delay techniques measure the delay of optical pulses at different wavelengths to determine the group velocity, from which the dispersion parameter, $D$ [ps/(nm-km)], can be calculated with numerical differentiation [118]. This method requires a separate, complex experimental configuration, including precise timing electronics. Alternate schemes employ modulation phase shift methods which measure the phase change of a modulated signal between the device under test and a reference, or calibration, path [119, 120]. From this phase change the group delay is calculated and differentiated to calculate the dispersion parameter, $D$. Other systems measure the group delay using interferometric methods with tunable laser sources [121], broadband optical sources [122], or supercontinuum sources [117]. In addition to the extra step of numerical differentiation, interferometric configurations may involve one path traveling through the fiber and another traveling through the air and thus require precise and stable optical alignment to avoid phase noise. In the case of [122], the use of an asymmetric Sagnac interferometer eliminates the need for a reference channel.

Another category of measurement techniques utilize intensity modulators to generate sidebands, and a subsequent investigation into phase or intensity variations of those sidebands is employed to quantify the fiber dispersion. For example, in the base-band AM response method a frequency swept signal modulates the optical signal. The AM modulation response is retrieved through comparison of the transmitted and input swept signals. The frequencies corresponding to minima of the AM response are used to calculate the dispersion parameter for each probe laser
wavelength [123]. Most similar to the method presented here is a phase response technique that directly measures the phase difference between the modulating and the demodulation signal through use of a local oscillator laser to measure frequency changes of the received signal. The phase information is retrieved using slow laser scan rates (~10s ramp) with a tuning range of 5.5 GHz [124]. In this section an alternative method to measure the fiber dispersion parameter utilizing the Chirped Laser Dispersion Spectroscopy (CLaDS) technique is developed. In CLaDS, a fast chirp of the laser frequency allows for direct measurement of dispersion profile without the need for additional laser sources or reference channels.

![Figure 6.29](image-url)  

Figure 6.29. Schematic of measurement system. DFB – distributed feedback diode laser (NEL); PD – photodetector; EOM – electro-optic modulator.

To utilize the CLaDS technique for fiber characterization, the fiber under test simply replaces the gas sample (gas cell or open path) in previous instruments. The configuration for this measurement is shown in Fig.6.29, where the sample is a single mode fiber (Corning SMF-28) of a known length. An electro-optic modulator (EOM) is used to generate sidebands with a fixed frequency spacing, \( \Omega \), around the laser carrier frequency. As the light interacts with the sample, each frequency (the carrier and two sidebands) experiences a different index of refraction according to the dispersion profile of the sample. At the photodetector, a square law device, the
multiple frequencies are mixed, and the subsequent beatnote photocurrent is frequency
demodulated. When the laser frequency is chirped, with chirp rate $S$ (rad/s$^2$), changes in the
frequency of beatnote signal around the original frequency spacing, $\Omega$, are directly related to the
dispersion present in the sample. For the double-sideband spectrum generated using a single
EOM as shown in Fig. 6.29, the frequency deviation is given by

$$f_{DSB} = \frac{S \cdot L}{4\pi} \left( \left. \frac{\partial k}{\partial \omega} \right|_{\omega-\Omega} - \left. \frac{\partial k}{\partial \omega} \right|_{\omega+\Omega} \right),$$

(6.4)

where $S = d\omega/dt$ (rad/s$^2$), $L$ (m) is the length of the sample, and $k$ (m$^{-1}$) is the wavenumber. The
group velocity dispersion (GVD) of a sample is given by the second derivative of the
wavenumber with respect to angular frequency. In the telecommunications community the figure
of merit to described the GVD is the dispersion parameter, $D$ (ps/[nm·km]), which provides the
same information in more convenient units for discussions of different fiber lengths (given in
km) and different pulse widths (given in nm). The dispersion parameter, $D$, is related to the GVD
through Eq. (6.5).

$$D = -\frac{\omega}{2\pi c} \frac{\partial^2 k}{\partial \omega^2}.$$  

(6.5)

Given that the fiber dispersion is a broadband effect, it can be assumed that the group velocity
changes linearly in the relatively small frequency range from $\omega-\Omega$ to $\omega+\Omega$. Therefore,

$$\left. \frac{\partial k}{\partial \omega} \right|_{\omega-\Omega} - \left. \frac{\partial k}{\partial \omega} \right|_{\omega+\Omega} \approx 2\Omega \frac{\partial^2 k}{\partial \omega^2},$$

(6.6)
that is the finite difference in Eq. (6.4) can be approximated by the second derivative of $k$. Using this relation, Eq. (6.4) can be solved for the second derivative terms and plugged into Eq. (6.5) to yield

$$D = -\frac{2\omega^2}{c} \frac{f_{DSB}}{S \cdot L \cdot 2\Omega}. \quad (6.7)$$

Eq. (6.7) shows that the CLaDS signal, $f_{DSB}$, can be used to directly calculate the dispersion parameter. The $2\Omega$ in the denominator is the result of using the DSB CLaDS approach; that is the dispersion profile is probed at a frequency spacing that is twice that of the EOM modulation frequency. If a single-sideband configuration was used instead, the factor would be just $\Omega$. When implemented as a technique for the measurement of fiber dispersion, CLaDS demonstrates all the same benefits as demonstrated for characterization of molecular dispersion; that is signal immunity to intensity changes and linearity with path length and chirp rate. CLaDS measurements for different fiber lengths, chirp rates, and optical powers are shown in Fig.6.30, to demonstrate these benefits.

Knowledge of the chirp rate, $S$, as seen in Eq. (6.7), is needed to accurately calculate the dispersion parameter. The chirp rate is in term determined by the applied current modulation to the laser and the laser’s tuning behavior. The conversion of applied current modulation to wavelength tuning is often not a linear relationship, but rather a complex process involving thermal and carrier effects.
Figure 6.30. (a) CLaDS signals collected for applied ramps of 10kHz and 2kHz as well as for 20km and 10km length of fiber, demonstrating the signals proportionality with both chirp rate (red vs blue or black vs cyan) and optical path length (red vs black or blue vs cyan). (b) CLaDS signals collected for 0dB and 10dB of signal attenuation indicating the immunity of the retrieved dispersion signal to optical power (only the noise increases due to decrease in the total photon flux).

The shape of the scans in Fig.6.30 is the result of chirp rate variations during the scan of the laser wavelength. A typical relationship between the applied current modulation and resulting chirp rate is shown in Fig.6.31. Under current modulation, a typical semiconductor laser shows transient regions primarily affect by slow thermal effects resulting high, non-linear chirp rates in these regions. While it is possible to characterize the chirp rate profile in these regions, the overall precision of the measurement may be negatively affected. As a result, for the measurements discussed here, the stable regions (i.e. regions of slowly varying chirp) were used for the dispersion analysis.
Figure 6.31. A typical frequency tuning process of a semiconductor laser. $I_{\text{ideal}}(t)$ is the applied current to the laser which in ideal case should cause frequency tuning with similar waveform $\omega(t)$. The corresponding chirp-rate ($\partial \omega / \partial t$) vs time plot should resemble a rectangular waveform, but the lower plot shows the actual resultant $S(t)$ plot.

For analysis in this work, only stable regions indicated with green shading are utilized.

Empirically determined tuning coefficients are often provided by the laser manufacturer, however the conditions (modulation rate, current amplitude, etc.) under which this coefficient is determined may be different from the parameters used in a given system. In the case where the tuning coefficient of the laser, $C$, is precisely known and dynamic effects can be excluded, the chirp rate is given by $S = C \cdot \partial I / \partial t$. Another method to characterize the chirp rate involves use of an etalon to create an interferometric pattern, from which the location of fringe peaks can be used to calibrate the wavelength tuning of the laser with the applied current modulation. This latter technique is particularly simple to realize with a fiber loop interferometer.
In this work, spectroscopic knowledge of a molecular species with a transition in the wavelength region of interest was used as an alternative method to characterize the chirp rate. To perform this calibration, a gas cell containing a known gas was introduced into the measurement path (instead of the fiber under test as shown in Fig.6.29). First the gas parameters (i.e. absorbance and line-width) were extracted using conventional direct laser absorption spectroscopy. Then several CLaDS spectra were captured with the line center moved throughout the scanning window; an effect achieved by slowly changing the temperature of the laser submount. From these CLaDS spectra and in conjunction with the knowledge of the molecular parameters from the absorption analysis, a model of the CLaDS spectra was used to extract the chirp rate for each spectra (recall that the CLaDS signal amplitude is directly proportional to the $S$). The results of this characterization are shown in Fig.6.32, where a clear non-linear trend of the chirp rate can be seen.

Figure 6.32. Characterization of the chirp rate using spectroscopic signals. The molecular transition was used to extract the chirp rate as a function of time (black diamonds, right y-axis).
After initial quantification of the chirp rate, achieved using any method, the stable regions of the CLaDS signal (corresponding to the green regions in Fig. 6.31) were used to directly calculate the dispersion parameter, $D$, with Eq. (6.7). A simple linear fit of the later part of the scan is shown in Fig. 6.33 for a fiber length of $L = 20$ km and a frequency spacing of $2\Omega = 2.4$ GHz.

![Figure 6.33](image)

**Figure 6.33.** Linear fit of the end portion of the CLaDS signal used to directly calculate the dispersion parameter, $D$. The time variable (x-axis) directly relates to the optical frequency of the laser. Here the sweep corresponds to a 45GHz deviation around 181.6THz. Here the center frequency and chirp rate are $1.14e15$ rad/s and $1.64e16$ rad/s$^2$, respectively. Chirp rate fit parameters presented here: $f_{CLaDS}(t) = 7.7 \times 10^6 \times t + 1986; R^2 = 0.9548$.

Using Eq. (6.7) along with the measurements shown in Fig. 6.22, a $D_{\text{avg}}$ of 22.39 ps/(nm·km) with a 1σ of 0.0982 ps/(nm·km) was calculated. This average value is consistent with the data in Ref. [125] indicating $D \approx 23.0$ ps/(nm·km) at 1650nm and with the documentation for this fiber (data sheet of Corning SMF-28 fiber specifies $D \leq 22.0$ ps/(nm·km) at 1625 nm, which is expected to be slightly higher at 1650nm).
Unlike other methods that rely on numerical differentiation to calculate the wavelength dependence of the refractive index curve, the CLaDS technique provides a direct measurement of this phenomenon. In addition, the simple optical setup does not require an interferometer with a separate reference path or sophisticated timing circuits, but rather straightforward amplitude-modulation and frequency-demodulation processing. With the technique presented here, coverage of a large wavelength range would require the use of multiple lasers and the precision of the method requires careful characterization of the laser chirp rate. Here, the generation of the frequency chirp is the result of direct modulation of the laser current; however, external modulation methods could be utilized to provide a highly linear and stable frequency chirp, such as those used in Frequency-modulation Continuous wave (FMCW) Ladars [126, 127].

By analyzing the frequency of the received signal, instead of amplitude, the CLaDS method for fiber characterization is highly immune to intensity variations and non-dispersive baselines that introduce noise into the measurement. By directly measuring the frequency deviation of a carrier wave and one or two sidebands, the CLaDS technique allows for a simple and robust fiber characterization method. This technique also allows for simultaneous integration into sensing system for continuous monitoring applications. Finally, knowledge of this background fiber dispersion measured using CLaDS plays an important role in the execution of the distributed, fiber-based sensor networks described in the previous section.

6.5. Discussion

The applications discussed in this chapter highlight some of the important features of the CLaDS technique and indicate areas where there is need for further development. In addition to the study of atmospheric methane shown in Section 6.2, other CLaDS systems were developed to target
methane [68], as well as other important constituents such as nitrous oxide [75] and hydrogen sulfide [128]. Much of the work in developing sensor networks has focused on creating many sensor nodes [129], however, with the CLaDS technique nodes linked by fiber-optic cable open up the possibility of distributed multi-path sensing (section 6.3). While molecular transitions in the near-IR are significantly weaker than those in the mid-IR, near-IR instrumentation remains of interest due to the relatively low cost, robustness, and availability of telecommunication components. In addition, use of the existing fiber-to-the-home infrastructure potentially provides a very cost-effective platform to perform real-time, distributed natural gas leak detection. In an additional work the operation of a distributed, two-node gas sensing network overlaid on a passive optical network (PON) was demonstrated. The communication network, a hybrid time-division multiplexed (TDM) and wavelength-division multiplexed (WDM) PON, operating with 10Gb/s Ethernet traffic transmission, was modified to incorporate several sensing nodes [130]. In this test DLAS was employed; however, for the small pulse widths used it was technically challenging to measure an adequate amount of the baseline to perform spectral fitting. Instead a 2nd order time-domain differential analysis was employed to measure the curvature the received amplitude signal, allowing for a threshold detection system where, through previous calibration, a threshold amplitude could be set to correspond to 1.25% CH₄. In contrast to this DLAS approach, the CLaDS measurement scheme (shown in Section 6.3) permits full quantitative information about the sample through spectral fitting even at small pulse widths due to the simplified signal baseline.

Future applications of the CLaDS technique may include industrial monitoring of smoke stack emissions where the harsh and turbulent environment requires a robust sensing technology and fence-line or pipeline monitoring where the potential for simultaneous concentration and range
information would facilitate leak localization procedures. Also, fiber dispersion characterization using the CLaDS technique may become of increased importance with the development of novel waveguide materials and structures, both used for sensing and communication applications.
Chapter 7: Conclusion and Outlook

7.1. Conclusion

This thesis has discussed the signal generation, noise characteristics, various implementation methods and detection schemes, and demonstrated applications of Chirped Laser Dispersion Spectroscopy. Derived from the same physical interaction as Direct Laser Absorption Spectroscopy, CLaDS probes optical dispersion induced by the interaction of the laser light with the targeted molecules. This makes the signal inherently independent of intensity, baseline-free, and linear with respect to concentration; all features that are advantageous in many field-deployable sensor applications. Analysis of the performance and efficiency of signal extraction under the fundamental limit of shot-noise shows the CLaDS spectra contains that same amount of information as DLAS. This assumes ideal operating conditions for both techniques, which does not take into account various technical limitations; however, this study of fundamental limits is still significant because many technical limitations are eventually eliminated through further development of optical components and detection algorithms. Existing experimental demonstrations of CLaDS systems highlight the technique’s application toward atmospheric open-path sensing, distributed sensor networks, and as a general dispersion characterization tool beyond molecular analysis.
7.2. Future Outlook

While considerable development has been made on the functionality, implementation, and performance of the CLaDS technique since it was originally proposed in 2010 [58], there is still room for further investigations into technical limitations, incorporation into new configurations, and expansion towards new applications. As the name suggests, the chirp of the laser frequency is a crucial component to the functionality of the technique. Lasers, however, are not ideal devices, and exhibit (sometimes highly) non-linear chirps depending on the device and modulation parameters. This non-linearity of the chirp translates into a distortion of both the frequency axis and the CLaDS amplitude, making careful characterization of the chirp necessary for accurate parameter extraction, especially in conventional CLaDS systems. To make the sensing systems more robust, real-time characterization of the chirp profile, methods to linearize the chirp, or ways to mitigate the effects of non-linearity may be necessary. Further development of the range resolved CLaDS technique may also require attention be paid to the chirp profile [98]. Mitigating this chirp non-linearity may also play an important role in the development of multi-heterodyne system employing the CLaDS technique, since the chirp variation across the multi-mode structure or over time may introduce significant phase distortion to the extracted signal.

To make the CLaDS technique more applicable to remote sensing applications, the use of scattering targets, as opposed to the retro-reflector targets used in [101, 102], must be implemented. The issue with scattering targets is the low return optical powers received by the instrument. Since the CLaDS output noise, and therefore short term precision, is dependent on the carrier to noise ratio of the measured beatnote signal, low return power translate to low carrier powers and higher noise (see Chapter 3). Investigations into down-conversion techniques
to lower the noise and the heterodyne architecture to boost the carrier power (see Chapter 4), this restriction for high optical return power (i.e. requiring retro-reflector targets) has the potential to be overcome. The effect of speckle noise, a limiting factor in most coherent, remote sensing systems [57], requires attention in standoff detection configuration. Experimental verification of these techniques in a remote sensing setup with a scattering target must be performed to truly assess the potential of this technique for remote sensing application. After a successful demonstration of this, there is potential for the application of the CLaDS technique to airborne and space borne instrumentation. The Remote Methane Sensing Mission (MERLIN) is set to launch a minisatellite in 2020 which aims to investigate spatial and temporal variations of atmospheric methane. The onboard instrument is an Integrated Path Differential Absorption (IPDA) LIDAR (Light Radar), which launches pulses at two wavelengths; one on or near the center of the probed methane transition (around 1.65μm) and one offline. From the ratio of the return powers for these two wavelengths, the differential atmospheric optical depth (DAOD) can be determined [131, 132]. In this technique, methane concentration is determined through the ratio of two return signals, both of which are significantly attenuated by propagation through the Earth’s atmosphere. Upon maturity of the Heterodyne-Enhanced CLaDS technique (see Chapter 4), this attenuation due to long propagation distances may be overcome through the addition of a strong local oscillator. The linear system response with concentration of CLaDS may also prove to be beneficial for parameter extraction in these column integrated measurements, however, the optical layouts of existing CLaDS systems has not reach the stage in development required for flight readiness. Additional potential applications for the CLaDS technique include those with harsh sensing environments, such as smoke stacks or combustion systems, where the technique’s immunity to intensity may also prove to be beneficial.
Much of the development surrounding the CLaDS technique has focused on generation of the optical probe signal and efficient detection methods, while enhancement of the CLaDS signal amplitude through use of resonant cavities has yet to be explored. This is in part due to the fact that CLaDS requires a fast chirp of the laser frequency, which needs to be coupled to the resonant cavity. The linewidth of the cavity modes, often very narrow, requires that the laser be locked to these modes. Transmission of a multi-frequency signal through adjacent axial modes of the cavity has been demonstrated in NICE-OHMS [42], however the scan of the laser frequency is achieved by applying a modulation of the cavity length (using a PZT attached to one of the cavity mirrors) for relatively slow scans (up to ~100Hz for sub-Doppler detection) [43]. These chirp rates are too low for CLaDS systems, where the signal amplitude is directly proportional to the chirp rate. Pound Drever Hall (PDH) locking modules (see Ref. [133] for more info on PDH) are available with bandwidths around 100MHZ [134], however the lock of the laser frequency to the cavity requires a fast PZT be attached to one of the mirrors. The response time of the PZT (after taking into account the weight of the mirror and mount) would most likely dictate the maximum frequency at which the laser could be chirped. The enhancement of the signal amplitude due to the resonant cavity may potentially overcome limitations imposed by slower chirp rates, and modulation techniques, such as CM-CLaDS, may also prove to be applicable. Thus, further investigation into methods and component specifications to chirp the locked-laser frequency in a cavity configuration is required to demonstrate cavity-enhanced CLaDS.
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