Development of a Tunable Diode Laser Absorption Spectroscopy System for
Quantification of Transient Emissions from Liquid Hydrocarbon Storage Tanks

by

Fraser Kirby

A thesis submitted to The Faculty of Graduate Studies and Research
in partial fulfilment of the degree requirements of

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in
Mechanical Engineering

Ottawa-Carleton Institute for
Mechanical and Aerospace Engineering

Department of Mechanical and Aerospace Engineering

Carleton University

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the Faculty of Graduate Studies and Research

acceptance of the thesis

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Dr. Matthew Johnson, Thesis Supervisor

Dr. Ronald Miller, Chair, Department of Mechanical and Aerospace Engineering

Carleton University

2023-07-21
Abstract

Fixed-roof atmospheric storage tanks are used throughout the oil and gas sector to store liquid hydrocarbons and are a key source of volatile organic compound (VOC) emissions. Despite their prevalence, vented emissions from these tanks are rarely monitored and remain poorly understood. This thesis presents a non-intrusive, inline optical measurement system to quantify oxygen fraction (which can be used to infer VOC fraction) in the vent line of an uncontrolled tank. The sensor utilizes tunable diode laser absorption spectroscopy with wavelength modulation to target near infrared absorption bands of diatomic oxygen ingested into the tanks during diurnal tank breathing processes and is compact, robust, and compliant with CSA zoning standards. Lab characterizations of two variants of the system are presented. Over the full-scale (0 – 20.95% O₂) measurement range, the optical variant had a long-term precision of < 0.72% absolute (at 95% confidence) while the detector variant improved this to < 0.31% absolute.
Acknowledgements

I would like to thank my supervisor Matthew Johnson for his help in revising my thesis. Your passion, drive and interest in pursuing the technology of tomorrow is fantastic and I look to see where it leads.

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To Scott Seymour, thank you for your help early on into my start at EERL and for your introduction to ‘Canal-basics 101’. This project couldn’t have gotten to where it is without a few impromptu troubleshooting projects along the way. It was an honor to learn alongside you.

To Dillion Mazerolle, thank you for your help with branching this project and working as an intermediary to initialize the system in Devon, AB.

A special thank you to Kevin Sangster for your invaluable help on the manufacturing front, and for your input and willingness to share tips and suggestions along the design iterations of my project. To Kevin, Nick and Alex; thank you for your support and for the chats that always stemmed from a visit to the shop – you guys’ rock!

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## Nomenclature

<table>
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<th>Symbol</th>
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<th>First usage Equation</th>
<th>First usage Pg.</th>
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<td>[Hz]</td>
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<td>$2f$ or $2f_{\text{mod}}$</td>
<td>2nd Harmonic at twice the mod. frequency</td>
<td>[Hz]</td>
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<td>$2f/1f$</td>
<td>Calibration ‘free’ normalized WMS</td>
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<td>$\alpha$</td>
<td>Absorption</td>
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<td>$a_{\text{mod}}$</td>
<td>Amplitude of frequency modulation</td>
<td>[cm$^{-1}$]</td>
<td>(2.6)</td>
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<td>$\omega$</td>
<td>Angular frequency, $\omega = 2\pi f_{\text{mod}} t$</td>
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<td>(2.7)</td>
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<td>$c$</td>
<td>Speed of light in a vacuum, $c = 299,792,458$ [m/s]</td>
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<td>(3.1)</td>
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<td>$C_{2+}$</td>
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<td>$d$</td>
<td>Length of fiber ring resonator</td>
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<td>[Hz]</td>
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<td>$H_{k}$</td>
<td>k$^{\text{th}}$ Fourier Coefficient</td>
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<td>$\Delta v$</td>
<td>Change in wavelength, free-spectral range</td>
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<td>$g$</td>
<td>Transition line shape</td>
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<td>(2.2)</td>
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<td>$i_0$</td>
<td>Linear laser intensity modulation $\bar{I}_o$</td>
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<td>[m]</td>
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<td>Fiber effective refractive index</td>
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<td>Natural Number</td>
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<td>$\sigma_{\nu_c}$</td>
<td>Absorption cross-section evaluated at $\nu_c$</td>
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<td>(2.2)</td>
<td>31</td>
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<td>$\sigma_{\nu_{c,i,j}}$</td>
<td>Absorption cross-section of the $i^{th}$ absorption line center of the $j^{th}$ gas species evaluated at $\nu_c$</td>
<td>[cm$^2$/molecule]</td>
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<td>$R_{nf}$</td>
<td>Resulting $n^{th}$ harmonic signal, root sum square of $X_{nf}$ and $Y_{nf}$</td>
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<td>37</td>
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<td>$S$</td>
<td>Transition line strength</td>
<td>[cm/molecule]</td>
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<td>Optical transmissivity at $\nu_c$</td>
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<td>$\bar{\nu}$</td>
<td>Average (center) wavenumber</td>
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<td>$x_{vapour}$</td>
<td>Mole fraction of hydrocarbon vapours</td>
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<td>$x_{O_2,\infty}$</td>
<td>Mole fraction of oxygen in ambient air</td>
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<td>$x_{O_2,v}$</td>
<td>Mole fraction of oxygen in vented stream</td>
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<td>Hydrogen sulfide</td>
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<td>InGaAs</td>
<td>Indium gallium arsenide</td>
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<tr>
<td>N₂</td>
<td>Nitrogen</td>
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<tr>
<td>NOx</td>
<td>Nitrous Oxide</td>
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<td>O₂</td>
<td>Oxygen</td>
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<td>Si</td>
<td>Silicon</td>
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<th>Description</th>
<th>First use Pg.</th>
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<td>Anti-reflective</td>
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<td>AWG</td>
<td>American Wire Gauge</td>
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<tr>
<td>(B)HFS</td>
<td>(Bacharach®) Hi-Flow Sampler</td>
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<td>BNC</td>
<td>Bayonet Neill–Concelman</td>
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<td>BTEX-H</td>
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<td>Canadian Association of Petroleum Producers</td>
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<td>Collision Induced Absorption</td>
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<td>CIB</td>
<td>Collision Induced Broadening</td>
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<td>CPU</td>
<td>Central Processing Unit</td>
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<td>DA</td>
<td>Direct Absorption</td>
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<td>Acronyms</td>
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<td>DC</td>
<td>Direct Current</td>
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<td>DCS</td>
<td>Device Characterization Summary</td>
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<tr>
<td>DFB</td>
<td>Distributed Feed-back</td>
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<td>DIAL</td>
<td>Differential absorption light detection and ranging</td>
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<td>Discrete Mode</td>
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<td>Energy and Emissions Research Laboratory</td>
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<td>EPA</td>
<td>Environmental Protection Agency</td>
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<td>FC/APC</td>
<td>Ferule Connector / Angled Physical Contact</td>
<td>49</td>
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<tr>
<td>FGEN</td>
<td>Frequency Generator</td>
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<tr>
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<td>Frequency Modulation Spectroscopy</td>
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<tr>
<td>FNPT</td>
<td>Female National Pipe (Thread) Tapered</td>
<td>51</td>
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<tr>
<td>FRR</td>
<td>Fiber Ring Resonator</td>
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</tr>
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<td>FSR</td>
<td>Free-spectral Range</td>
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<td>Gas Sniffing</td>
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<td>High-Resolution Transmission Molecular Absorption Database</td>
<td>31</td>
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<td>HWHM</td>
<td>Half-width Half-max</td>
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<td>I/O</td>
<td>Input/Output</td>
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<tr>
<td>ICL</td>
<td>Interband Cascade Laser</td>
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<td>LD</td>
<td>Laser Diode</td>
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<td>LUT</td>
<td>Look-up Table</td>
<td>63</td>
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<tr>
<td>MFC</td>
<td>Mass Flow Controller</td>
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<td>MM</td>
<td>Multi-mode</td>
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<tr>
<td>Acronyms</td>
<td>Description</td>
<td>First use Pg.</td>
</tr>
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<td>----------</td>
<td>--------------------------------------------------</td>
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<td>Manual for Petroleum Monitoring Standards</td>
<td>24</td>
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<td>National Instruments</td>
<td>57</td>
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<td>National Pollutant Release Inventory</td>
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<td>National Pipe Thread</td>
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<td>OD</td>
<td>Outer Diameter</td>
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<td>(Q)OGI</td>
<td>(Quantitative) Optical Gas Imaging</td>
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<tr>
<td>QCL</td>
<td>Quantum Cascade Laser</td>
<td>39</td>
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<tr>
<td>RAM</td>
<td>Random Access Memory</td>
<td>57</td>
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<tr>
<td>RTD</td>
<td>Resistive Temperature Device</td>
<td>58</td>
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<td>SI</td>
<td>Sweep Integration</td>
<td>33</td>
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<td>Single-mode</td>
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<tr>
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<td>Signal to noise ratio</td>
<td>41</td>
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<td>SRS</td>
<td>Stanford Research Systems</td>
<td>52</td>
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<tr>
<td>TDL</td>
<td>Tuneable Diode Laser</td>
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<td>TDLAS</td>
<td>Tunable Diode Laser Absorption Spectroscopy</td>
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<tr>
<td>TEC</td>
<td>Thermal Electric Cooler</td>
<td>32</td>
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<tr>
<td>UV-NIR</td>
<td>Ultraviolet to Near-infrared region</td>
<td>41</td>
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<tr>
<td>VI</td>
<td>Virtual Instrument</td>
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<tr>
<td>VMR</td>
<td>Volume Mixing Ratio</td>
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<tr>
<td>VOC</td>
<td>Volatile Organic Compound</td>
<td>19</td>
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<td>WMS</td>
<td>Wavelength Modulation Spectroscopy</td>
<td>34</td>
</tr>
<tr>
<td>WRFA</td>
<td>Width ratio of fringe to absorption</td>
<td>40</td>
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Chapter 1  Introduction

1.1 Background

Liquid storage tanks are used throughout the oil and gas industry to store hydrocarbon liquids at upstream production sites as well as at downstream processing plants and refineries. Despite their commonality and use, emissions of volatile organic compounds (VOCs) and greenhouse gases (GHGs) from these tanks are generally not actively monitored and remain poorly understood. VOCs are a subset of organic molecules that have a high vapour pressure (i.e., volatile) and low water solubility. They may be emitted by a wide array of products at both the commercial and industrial scale through the emission of noxious vapours. While biogenic emitters of VOCs do occur in the environment, the most prevalent VOC emitters are attributed to anthropogenic sources in which a significant contribution is linked to petrochemical activities in the oil and gas sector (Chan et al., 2020; Pinthong et al., 2022; Roveda et al., 2020). In Canada, 241,660 tonnes of VOC emissions were reported to the National Pollutant Release Inventory (NPRI) in 2019, 52% of which were emitted by the oil and gas sector (Government of Canada, 2021).

Benzene, toluene, ethylbenzene, xylenes, and n-hexanes (BTEX-H) are VOCs that are found in crude oil. They are known precursors linked to localized (ground-level) ozone formation (Edie et al., 2020) and fine-particulate matter which are the main constituents of smog (Government of Canada, 2022). BTEX-H are associated with an assortment of short- and long-term adverse health impacts in humans including 1) being carcinogenic, 2) contributing to cell apoptosis and tissue damage, 3) increased developmental risk of asthma and 4) anemia from prolonged exposure (Lawrence et al., 2022; Leusch & Bartkow, 2010; Pinthong et al., 2022; Queensland, 2012; Roveda et al., 2020). Methane (CH₄), ethane (C₂H₆), and propane (C₃H₈) are the main compounds of natural gas which may often remain dissolved in crude oil samples after separation and consequentially are released alongside vented VOCs. In addition to degrading air quality, these hydrocarbons can be especially
damaging to the environment as they undergo photochemical reactions with nitrogen oxides (NOx) and other compounds in the troposphere, resulting in the production of thermal trapping GHGs which can influence weather patterns and severe weather events, and contribute to climate change through global warming (Cho et al., 2021).

A review by Allen (2016) suggested that storage tanks are a dominant source of VOC emissions from oil and gas sector operations. Helicopter-based infrared surveys of over 8000 oil and gas well pads in the U.S. by Lyon et al. (2016) attributed more than 90% of 500 detected sources to tank vents and hatches, further concluding that tank controls often underperform and that these sources represented a key mitigation opportunity for reducing VOCs and associated emissions from the industry. Downwind ground-based measurements at U.S. natural gas gathering and processing facilities by Mitchell et al. (2015) found substantial tank venting at 20% of sites, further noting that these sites had 4x greater emissions than similar sites without substantial tank venting.

Likewise in Canada, field surveys using a range of techniques have implicated production tanks as a significant source of oil and gas sector VOC and methane emissions. Chambers et al. (2008) used differential absorption light detection and ranging (DIAL) to measure hydrocarbon emissions from a refinery site in Alberta and found storage tanks accounted for over 50% of the sites total C_2+ hydrocarbons and benzene emissions. More recently, Tyner and Johnson, (2021) analyzed aerial gas mapping lidar measurements (Bridger Photonics, 2021; Conrad, Tyner, & Johnson, 2023) at oil and gas facilities in British Columbia and identified tanks as the largest source of methane emissions in the sector and a key factor behind actual emissions being 1.6-2.2x greater than official federal inventory estimates. Subsequent measurement work in both British Columbia and neighboring Alberta confirmed tanks as the first or second largest methane source in each province (Conrad, Tyner, Li, et al., 2023; Johnson et al., 2023).

To the author’s knowledge only two recent studies have reported direct measurements from tanks and only one specifically attempted to deduce VOC emissions. Clearstone Engineering Ltd. (2019a) conducted root cause analysis of tank venting for a sample of 47 tanks in British Columbia and Alberta using available measurement
schematics, stored liquid type, vapour samples, and separator operating conditions in conjunction with qualitative infrared camera video. Emissions were primarily estimated using simulation and correlations. Measured tank venting (obtained using an ultrasonic flowmeter) was only reported for a single site. Picard and Johnson (2011) attempted to measure VOC emissions from an underground storage tank at a retail gasoline station in Northwest Calgary. They instrumented the vent line of the tank with an electrochemical oxygen sensor and flow meter to provide simultaneous oxygen concentration and flow velocity data. The oxygen sensor was intended to measure the air fraction in the vent gas (assuming no oxygen originated in the stored liquid and the oxygen-nitrogen ratio in ambient air is fixed) and the VOC fraction was then estimated by difference. While findings indicated significantly higher than predicted emission on comparison with AP-42 estimates, the study ultimately suffered from poor accuracy of the oxygen measurements in application. These issues were attributed to the electrochemical sensor, which in general can be sensitive to cross-contamination from other species, experience time-dependent sensitivity degradation, and have narrow temperature stability ranges – all of which can significantly affect measurements. The ultimate goal of the current work is to develop a suitable oxygen sensor that could be used in place of the electrochemical sensor, enabling accurate measurement of tank VOC emissions following an approach similar to Picard and Johnson (2011).

1.2 Production Storage Tanks

Production tanks serve a key role across oil and gas operations by providing high-density storage for extracted or refined resources prior to end-user delivery. Two main types of storage tanks are used in the oil and gas sector: floating-roof and fixed-roof tanks. Floating-roof tanks feature a free-floating lid equipped with an adaptive rim seal which rises and falls with the changing of internal liquid levels. This floating-roof is designed to reduce evaporative losses associated with stored liquids within the tanks. However, due to their complexity and costs, floating roof tanks are generally only found at larger gas processing plants and distribution centers (Clearstone Engineering Ltd., 2019a).
Within the upstream oil and gas sector, most production sites use fixed-roof, atmospheric pressure tanks for hydrocarbon storage (AER, 2020; Clearstone Engineering Ltd., 2019a). These tanks may be “controlled” or “uncontrolled”. Controlled tanks are integrated with emission mitigation technology (such as vapour recovery units) that are intended to collect and reduce vapour emissions such that they do not escape into the atmosphere. By contrast, uncontrolled tanks are designed to vent vapours directly to atmosphere.

Uncontrolled fixed-roof tanks are enclosed vessels which are maintained at atmospheric pressure via a breathing vent at the top of the tank, as shown in the schematic below from AP-42 of the U.S. Environmental Protection Agency (EPA) organic liquid storage tanks report (U.S. EPA, 2020). This vent permits the tank head space (i.e., vapour space above the liquid in the tank) to ‘breath’ freely, either exhausting vapours to the surroundings or drawing in fresh air under varying environmental conditions and daily operational routines. Fixed-roof tank designs have the lowest construction cost and are generally considered the minimum acceptable equipment standard for the storage of hydrocarbons and organic liquids within the oil and gas industry (U.S. EPA, 2020). Emissions from uncontrolled fixed-roof tanks are generally not actively monitored; consequently, the resulting exhausts from associated venting behaviour remain poorly characterized and less-so understood. The present work is motivated by the goal of improving monitoring of losses associated with uncontrolled fixed-roof tanks, which are further discussed below.
Figure 1.1: Typical fixed-roof tank design [adapted from U.S. EPA (2020)].

Vapour emissions from uncontrolled fixed-roof tanks occur through three main processes: standing losses, working losses, and flashing losses. Standing losses, also known as ‘breathing’ losses, occur as vapours in the head spaces of the tank expand or contract with temperature changes (commonly driven by diurnal temperature cycles) or changes in barometric pressure. As the gas in the tank expands, hydrocarbon vapours are forced out through the breathing vent and are emitted to atmosphere. Conversely, as temperature and/or barometric pressure changes cause the internal tank gases to cool, fresh air is drawn into the tank which restarts the evaporation process until equilibrium is re-established. Notably, breathing losses occur without changes to the liquid level within the tank.

Working losses are driven by changes in liquid level as the tank is filled or drained. The addition of new liquid displaces vapours within the tank which are expelled through the tank breathing vent. Alternatively, during liquid draining operations, fresh air is drawn into the tank which restarts the evaporation process. The combination of standing and working losses are often referred to as evaporative losses.

Flashing losses, also known as ‘solution gas’ losses, occur when there is a pressure differential between the injected liquid and the tank. Specifically, when higher pressure liquid enters the lower pressure tank, dissolved gases in the liquid rapidly flash (boil) out – pushing vapours up and out through the tank vent. These losses differ distinctly from
evaporative losses and are typically only encountered in upstream oil and gas operations. In situations where flashing losses are present, however, they generally tend to dominate emissions and obscure the prior two loss types in terms of emitted vapours (CAPP, 2002).

1.2.1 Emission Estimation Standards for Fixed Roof Tanks

VOC emissions from tanks are commonly estimated using a set of semi-empirical equations published by the U.S. EPA and contained within Chapter 7 of AP-42 (U.S. EPA, 2020). These relations were initially developed and patented by the American Petroleum Institute (API) in 1962, which continues to publish its own set of revised estimation models in Chapter 19 of its *Manual for Petroleum Monitoring Standards* (MPMS) (API, 2017). These empirical relations comprise various emissions factors\(^1\), liquid composition and geographical data, and specific tank-based information which are combined to estimate annual breathing and working losses. Although these equations have been used over the last half-century as the best available means for evaporative emission estimation, they are highly sensitive to inputted values and are considered precise only when generalized across large tank populations (U.S. EPA, 2006). Considering that the real-world behaviour of tanks may vary substantially over time (Brantley et al., 2014; Golston et al., 2018), this limits the predictive ability of these relations to significantly deviate from actual emissions in application. If estimates over shorter temporal windows or for smaller tank populations are desired, the accuracy degrades such that errors can “span over an order of magnitude or more [despite use of otherwise correct factors and data]” (US EPA, 2006). Ultimately, methods from AP-42 are limited due to imperfect validation capabilities at the time they were established and the fact that the field measurements used to develop these relations were collected over a short-term basis. As a result, longer averaging times are required to settle out inherent discrepancies and associated assumptions and thus these only provide general insight into tank behaviour.

Another industry estimation method relies on use of a gas-in-solution (GIS) factor which is multiplied with the present flow volumes to estimate vented emissions due to

\(^1\) Due to limited validation and supporting data however, reliance on published industry values may be required in instances where measurements are not otherwise possible.
flashing. This methodology is based on Henry’s law² and commonly used by the Alberta Energy Regulator (AER) as standard for estimating flashing losses as outlined in their Manual 015 and Directives 017 and 060 (AER, 2020, 2022). The GIS factor may be developed based on periodic lab testing of pressurized field samples. In situations where sampling is not feasible, the Vazquez and Beggs³ relationship or “rule of thumb” factors are deemed acceptable for industry purposes (AER, 2022). While use of the GIS factor aims to provide a faster method for estimating associated losses, its precision is limited (Lasater, 1958) and it is subject to error due to changing geographical composition or pressures affecting the amount of dissolved gas in the liquid delivered to the tank. However, measurement methods facilitating time-sensitive collection of both VOC fraction and flow rate information could significantly improve the accuracy of tank venting estimates.

1.2.1.1 General monitoring methods

Several methods are used to monitor for unintentional releases of hydrocarbons (referred to as “fugitive emissions”) that could result from malfunctioning equipment or leaks within an oil and gas facility. Common qualitative approaches include gas sniffing (GS), i.e., using handheld detectors to monitor for readings exceeding nominal screening values, or optical gas imaging (OGI) to visualize sources. Neither offers quantitative information on emission rates and there is a weak correlation between VOC detection and leak size (Kangas, 2017). OGI is dependent on operator competence and is impacted by an assortment of real-world variables including temperature, distance-to-source, and thermal background, which hinder broader application and reliability (Zeng & Morris, 2019). Quantitative OGI (QOGI) attempts to estimate source rates through supplemental software interpretation of emissions; however, similar disadvantages and operator dependencies

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² Pertaining to the amount of gas in a saturated substance that will evolve as it undergoes a pressure drop.
³ The Vazquez and Beggs relation (Vazquez; & Beggs, 1980; Vazquez & Beggs, 1977), known as the ‘bubble point pressure correlation’, is based on regression of experimentally determined bubble-points for a variety of crude oil systems initially established by Standing (Standing, 1947) and Lasater (Lasater, 1958). The relations proposed by Vazquez and Beggs aim to address ambiguities with the prior findings and provide refined GIS factor estimates by segmenting regression correlations based on “lower” and “higher” density fittings of crude oils specimens.
have been noted in field applications (Festa-Bianchet, Milani, et al., 2023; Festa-Bianchet, Tyner, et al., 2023; O’Neill, 2020b, 2020a; SRC, 2018) which can significantly influence the interpretation of results varying them by orders of magnitude.

Hi-flow samplers (HFS) quantify leaks using a portable vacuum system that attempts to suck the entire leak volume plus surrounding air through the device which measures gas concentration and total volume of air flow. Launched in 2001, the Bacharach® Hi-Flow Sampler (BHFS) was standardized for use in natural gas (NG) screening up to 2020. Through this process leaks were isolated and suctioned through a catalytic flow cell for sampling and species recognition. While for a time the BHFS was the industry standard for NG monitoring, it has since been discontinued after academic review (Connolly et al., 2019; Howard et al., 2015) identified significant discrepancies and instrument failures resulting in underreporting of emission values often leading to insensitive results in application. Other devices such as the SEMTECH® HI-FLOW 2, HETEK® Flow-Sampler, and AddGlobe® Gas Flow Meter have since been proposed for adoption with promises of refined performance, however, these devices are still in early stage of implementation and intended more so to fill the market-gap left by the BHFS for minor leak quantification (Zimmerle et al., 2022).

Ultimately, the aforementioned devices provide point source identification methods for minor leaks and losses from operational equipment. They rely heavily on operator skill and are mainly intended for use in accessible ground-level facilities. As a result, significant potential exists to overlook attributed loses at elevated or otherwise inaccessible places around operating sites. Furthermore, the short timeframe for which these devices are active limits their versatility surrounding transient sources, namely vented emissions. Presently however, there are no industry standardized detection technologies for field-use implementation to measure vented emission estimates from active storage tanks.

Affiliated research within the Energy and Emission Research Laboratory (EERL) has recently developed a novel flux sensor to quantify methane emissions from vent sources (Festa-Bianchet et al., 2022; Seymour et al., 2022). This system has been successfully used to measure casing gas venting at heavy oil production sites (Festa-Bianchet, Tyner, et al.,
methane venting from storage tanks (Festa-Bianchet, Milani, et al., 2023) but is designed to measure methane and total gas flow rates and cannot measure VOC emissions. Given the assortment of VOC and other molecules that may be present in venting media of a tank, it is not practical and likely not possible to attempt to quantify individual VOC species. Instead, it is proposed to measured total VOC emissions as the difference between the total gas flow rate and the fraction of air in the stream similar to the approach attempted by Picard and Johnson (2011). Specifically, diatomic oxygen (O₂) which is ingested during diurnal tank breathing and occurs at fixed proportion in air can be measured and used to determine the fraction of air in a vent stream of a tank. The balance of the vented gas from the tank can then be assumed to contain VOCs as further discussed in Chapter 2.

To the author’s knowledge there is now one commercially available O₂ measurement technology intended for direct integration into industrial process monitoring, the GPro 500 TDL (Mettler Toledo, 2020). While not explicitly advertised for vent gas monitoring, the GPro 500 is a tunable diode laser-based system advertised as compatible in a variety of process operations (including vent headers). First introduced in 2016 and proposed as a favorable alternative to traditional extractive and paramagnetic sensors technologies, the GPro 500 is advertised to enable for faster responses, simpler process installation, and user-specified detection between several different species of gases (Mettler Toledo, 2016). Manufacturer-reported specifications suggest the sensor is capable of measuring 0-100% O₂ at an accuracy of 1% of measurement or 100 ppm O₂ (whichever is greater) with 1 s sampling rate and T₉₀⁴ response of < 2 s (Mettler Toledo, 2015, 2018). While these specifications suggest it could be used as part of a tank monitoring experiment, to the author’s knowledge the GPro 500 has not been adopted by any governmental research agencies, regulations, or industry partners since its introduction. It is also unclear if this system could/would be approved for use at the Natural Resource Canada CanMET Energy pilot plant facility in Devon, AB, which is the ultimate intended user of the sensor being developed in this thesis.

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⁴ i.e., Time to achieve reading equivalent to 90% of flow concentration
A key challenge for any instrumentation to be used to measure tank emissions is the necessity of operating in a restricted hazardous (flammable gas) environment. In Canada, equipment used in these environments is regulated by the Canadian Standards Association (CSA) who designate different zones of protection. Limitation is placed on the use of any electronics or potential spark inducing sources within these areas based on the type of operating equipment and zone classification (i.e., anticipated presence of flammable gases or vapours over time) as shown in Table 1.1. Areas subject to a continual presence of gases or fumes, including the immediate vicinity of tank vents, are characterized as Class I Zone 0 environments and are the most stringent operating environments in application. Within these zones, only simple voltage and current limited electronics that are separately protected by Zener or galvanic isolation barriers may be deployed.

<table>
<thead>
<tr>
<th>Zones</th>
<th>Typical Definition of Zones (for guidance only)</th>
<th>ATEX Minimum Permissible Equipment Category for Zone</th>
<th>Minimum Equipment Integrity Requirements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gases and Vapour Zones</td>
<td>Explosive atmosphere is present continuously, for long period or frequently</td>
<td>1</td>
<td>Equipment must be safe under normal operation, expected and rare malfunction</td>
</tr>
<tr>
<td>Dust</td>
<td>Explosive atmosphere is likely to occur under normal operation, occasionally</td>
<td>2</td>
<td>Equipment must be safe under normal operation, expected malfunction</td>
</tr>
<tr>
<td>0 20</td>
<td>Explosive atmosphere may occur under abnormal operation and persist for a short period only</td>
<td>3</td>
<td>Equipment must be safe under normal operation</td>
</tr>
</tbody>
</table>

The higher the probability of an explosive atmosphere occurring and persisting, the lower the allowable potential risk of ignition and the higher the safety integrity requirements of the equipment to be installed. The relationship between zones and equipment categories can be varied following a complete risk assessment.

1.3 Thesis Motivation and Objective

There exist significant discrepancies between reported national GHG inventories and actual observed emissions resulting from the oil and gas sector despite the existence of point source monitoring and estimation methods – including those previously discussed. The purpose of this thesis is to develop a sensor capable of continuous monitoring of the VOC volume fraction in vented gas streams from fixed roof-storage tanks. Measurements
will be inferred from the transmission of light from a laser diode (LD) selectively targeting diatomic oxygen. Absorption of light in this range will correspond to the mass fraction of oxygen present in the flow and provide indication of the remaining composition of venting gases present in the exhaust line. This work aims to supplement currently available monitoring technologies and provide improved insight into transient behaviour of commercial tanks in the field.

An optical recoupling system has been proposed for inline installation at the venting outlet of these production tanks to overcome the challenges posed by the CSA Class I, Zone 0 environment – termed as the cross-pipe measurement cell. The system is non-intrusive and has been developed to be compact, weather and moisture resilient, and in accordance with CSA zoning standards. The sensor is designed to be installed along the exhaust line of the production tanks with minimal contribution to pressure or head losses in the line. This thesis will present quantitative calibration and controlled lab performance of the developed system to examine its suitability for field application (and subsequent findings). In application, the cross-pipe measurement cell will be used in combination with zone rated equipment and flow-metering to evaluate and monitor transient flux from an instrumented research tank in Western Canada. Ultimately, results could be used to assess and re-evaluate current monitoring prediction standards for improved monitoring and quantification purposes for inventory reporting. This project aims to supplement currently available monitoring technologies and provide better insight and indication regarding contributing emissions from production tank sources and their inherent behaviour.

1.4 Thesis Outline

Chapter 2 summarizes the theory and processing techniques used in Tunable Diode Laser Absorption Spectroscopy and its application to the cross-pipe measurement cell project. Chapter 3 details the experimental apparatus, including required fiber optical equipment, digital acquisition hardware, and relevant subsystems and subsequent cell variations. Chapter 4 presents lab performance and testing results and discusses relevant findings. Finally, Chapter 5 concludes the thesis and summarizes key findings and recommendations for future extensions of this work.
Chapter 2  Species Concentration using Tunable Diode Laser Absorption Spectroscopy

The developed sensor uses Tunable Diode Laser Absorption Spectroscopy (TDLAS) to determine the oxygen fraction in the vented gas flows. In TDLAS, a narrow-bandwidth laser selectively excites a target molecule in a gas mixture with narrow-band radiation, resulting in elevation to higher energy states as energy is preferentially absorbed from passing photons. The transmission of light through the medium is directly related to the number density of absorbing species. If the wavelength can be selected such that it is only absorbed by a single target species of interest at a known temperature and pressure, then the transmission of light may be directly related to the volume fraction of that species.

2.1 Spectroscopic Absorption Measurement of Light by Targeted Molecules

TDLAS relies on the fact that different compounds will absorb energy from light at differing wavelengths – often referred to as absorption bands – which may vary in location and intensity depending on the species being probed and its rotational-vibrational interactions with the irradiating light source. This quality may be used to isolate specific species within a flow by tuning the source wavelength to match the corresponding resonance frequencies of target compounds.

![Diagram of TDLAS process](image)

Figure 2.1: Simplified depiction of TDLAS process through sample medium containing wavelength absorption media, the attenuated light signal is interpreted as a dip in intensity across the corresponding absorption band.
Absorption spectroscopy measurements are governed by the Beer-Lambert-Bouguer law, shown below, which relates the incident optical intensity, $I_0$ [V], to the transmitted intensity, $I$ [V], for a ray of light passing through an absorbing medium:

$$\tau_{\nu_c} = \frac{I}{I_0} = \exp \left( -\frac{qpL}{k_bT} \right) \sigma_{\nu_c}(p,T,q,v)$$

(2.1)

where $\tau_{\nu_c}$ [-] is the optical transmissivity evaluated at some wave center frequency, $\nu_c$ [cm$^{-1}$ – wavenumber], for external parameters including pressure, $p$ [Pa], temperature, $T$ [K], and optical path length, $L$ [m], of the absorbing gas species of interest at some volume mixing ratio, $q$ [-]. $k_b$ is the Boltzmann’s constant [1.380649-$10^{-23}$ J/K] and $\sigma_{\nu_c}$ [cm$^2$/molecule] is the absorption cross-section evaluated at $\nu_c$. The absorption cross-section for a single spectral peak centered at $\nu_c$ can be further decomposed as:

$$\sigma_{\nu_c}(p,T,q,\nu_c) = S(T,\nu_c)g(p,T,q,\nu-v_c)$$

(2.2)

where $S(T,\nu_c)$ [cm/molecule] is the transition line strength and $g(p,T,q,\nu-v_c)$ [cm] is the transition line shape. For a single species, the absorption cross-section can be computed from the line shape and line strength parameters using empirically tabulated values compiled in a spectral database such as the High-Resolution Transmission molecular absorption database (HITRAN) (Gordon et al., 2022; Rothman et al., 2009). This database is commonly used to simulate atmospheric absorption and emission phenomena.

To accurately describe transmittance of radiation, all spectral transitions from relevant species neighbouring the wavenumber of interest must also be considered (Gordley et al., 1994). The Beer-Lambert-Bouguer law can thus be generalized to account for absorption from multiple species according to:

$$\tau_{\nu_c} = \frac{I}{I_0} = \exp \left( -\sum_j \sum_l \left( \frac{q_jpL}{k_bT} \right) \sigma_{\nu_c,l}(p,T,q_j,\nu) \right)$$

(2.3)
where $\sigma_{v_{i,j}}$ is the cross-section of the $i^{th}$ absorption line center of the $j^{th}$ gas species. Assuming negligible scattering effects\(^5\) of the incident irradiating beam, the remaining portion of light which is not transmitted must be absorbed by the intermediate medium of interest, defined as absorption, $\alpha$.

$$\alpha(v) = 1 - \tau(v) \quad (2.4)$$

The volume mixing ratio (VMR) of selected species of interest can thus be determined through spectroscopic measurement of transmitted (or absorbed) light at a given wavelength. Information regarding how the laser is spectrally tuned and techniques of varying its emission may be found in Section 2.2. Discussion of relevant prior application of TDLAS can be found Section 2.3. Further discussion of the selected target species, atmospheric oxygen ($O_2$), may be found in Section 2.4 – including selection of the specific wavenumber corresponding to the targeted absorption feature (described in Section 2.4.1).

### 2.2 Tunable Diode Laser Absorption Spectroscopy

TDLAS utilizes narrow-bandwidth light to selectively excite isolated absorption bands of targeted molecules. However, it requires that the emitted wavelength of light match the absorption band of the desired monitoring species. The output wavenumber of the laser diode may be tuned to match the target absorption band by regulating the laser diode temperature and driving current. Thermal tuning is generally achieved through use of a thermoelectric cooler (TEC) utilizing the Peltier effect\(^6\) which provides coarse control ($\sim 100$ cm\(^{-1}\)) of the laser output through expansion or contraction of the diode crystal but has slow frequency responses ($< 1$Hz) due to delayed bulk heating and cooling effects. By contrast, regulation of the diode driving current provides high frequency control ($> $ kHz) of the emitted wavelength through subtle changes in the crystal’s width but is generally limited to narrow spectral tuning ranges (1-2 cm\(^{-1}\)) due to limited expansion effects.

\(^5\) Scattering occurs when light interacts with molecules and/or particles and is redirected from its original direction of propagation. Light scattering is inversely proportional to the fourth power of its wavelength and depends on the size of the impeding molecule. At the operating wavelengths, Rayleigh scattering is most relevant where the particles are much smaller than the wavelength of incident irradiation (Carn, 2013). As such, shorter wavelengths (e.g., ultraviolet) demonstrate greater scattering than the longer wavelengths (e.g., NIR) utilized in this project.

\(^6\) Through which heat is emitted or absorbed as a result of passing an electronic current across a junction between two dissimilar conductors in a circuit.
associated with joule heating alone. Common implementations of TDLAS differ by how the laser is spectrally tuned during a measurement; these are further discussed in the following sections.

2.2.1 Direct Absorption Spectroscopy

Direct absorption (DA) is the simplest method for measuring absorption via laser spectroscopy. In DA, a specific absorption band is targeted by fixing the temperature and current of the laser diode, resulting in a fixed emission at a constant wavelength. The return signal intensity after absorption is compared to a reference absorption free intensity measurement (i.e., through a non-absorbing medium without the target species of interest) using the Beer-Lambert-Bouguer law. While the simplest method for direct VMR measurements, DA methods can be susceptible to greater measurement scatter and lower accuracy in application. In particular, DA can be affected by stability of the laser diode in readings over longer periods of time and can require meticulous retuning to re-center the wavelength of emission.

2.2.2 Sweep Integration Spectroscopy

In sweep integration (SI) the laser wavelength is continuously varied back and forth over a target center corresponding to a known absorption wavelength for a specified compound of interest. This is achieved by regulating the temperature of the diode through use of a laser diode controller. A selected low frequency (typically < 100 Hz) signal such as a ramp, saw-tooth, or sinusoid is used to sweep ($f_{\text{sweep}}$) the diode current while maintaining a fixed temperature setpoint. The resulting laser emission is a slow oscillating wavelength pattern above and below the centering frequency setpoint. As the emitted light’s wavelength traverses through the absorption peak region, a portion of the emitted energy is subsequently absorbed resulting in a dip in the return signal intensity. By comparing the resulting return signal with the initial absorption free signal intensity, the portion of transmitted light can be used to deduce the total absorption that has occurred and hence the species VMR via the Beer-Lambert-Bouguer law.

By tuning the wavelength of emitted light, greater precision and accuracy of spectroscopy measurements can be obtained over DA with the trade-off of greater signal processing requirements needed for post-processing of results. SI additionally benefits from visualization of absorption feature as the diode is swept across its tunable range, enabling full or partial measurement of absorption peaks depending on the specified sweep parameters. As the laser is
tuned, absorption bands reduce the transmitted light (i.e., cause a dip in the measured return intensity). However, SI spectroscopy is susceptible to optical and/or electrical noise which can be further mitigated using wavelength modulation spectroscopy.

2.2.3 Wavelength Modulation Spectroscopy

Wavelength modulation spectroscopy (WMS) extends the SI method by superimposing a secondary high frequency sinusoidal function ($f_{\text{mod}}$) onto the slower swept signal that drives the current provided to the tunable diode laser (TDL). This results in a shift in the absorption information to a higher frequency, which may subsequently be extracted at the harmonics of $f_{\text{mod}}$ using digital lock-in filters during post-processing. This method is desirable because it shifts the absorption signal away from lower frequency ($1/f$) interference and AC noise sources, providing significantly improved signal-to-noise ratios and measurement sensitivity.

An important distinction must be made between WMS and a secondary modulation technique known as frequency modulation spectroscopy (FMS). Specifically, while FMS is likewise concerned with imposing a modulating frequency onto a slower swept feature, the frequency of such modulation is much faster (100 MHz to GHz range) than WMS (kHz to sub-MHz range). Classification between these two methods is thus determined by the ratio of the frequency of modulation to the half-width at half-max (HWHM) of the chosen absorption feature. A ratio less than unity indicates the WMS regime, while a ratio greater or equal to unity represents the FMS regime (Bomse et al., 1992). While FMS measurements operate effectively free of laser noise, such systems require acquisition hardware and filtering not considered practical for the intended field-deployable system. This study exclusively considered WMS utilizing a phase-insensitive measurement approach as further elaborated below.

WMS can prove especially useful for measuring species such as oxygen which have narrow spectral absorption windows (lasting only a few cm$^{-1}$). Absorption information is extracted at harmonics of the original sinusoidal frequency, $f_{\text{mod}}$, by using digital lock-in amplifiers\textsuperscript{7}, which consist of a low-pass filter and mixer. Second harmonic detection, in which components are extracted at twice the modulation frequency ($2f_{\text{mod}}$), is most commonly used (K. H. Lyle et al.,

\textsuperscript{7} Lock-in amplifiers extract signals around a reference $f_{\text{mod}}$ while efficiently rejecting all other frequency components through filtering (Zurich Instruments, 2016).
2007; Rojas et al., 1997; Schoonbaert et al., 2015; Sun et al., 2013) for WMS systems. Extraction of the first harmonic (1f_{mod}) has also been used to normalize the 2f signal to account for variations in laser intensity including scattering and unintentional beam steering caused by vibrations (Rieker et al., 2009; Sun et al., 2013; Upadhyay & Chakraborty, 2015). This 2f/1f normalization is sometimes referred to as “calibration free” WMS; however, this process is typically limited to optically thin (α < 0.05) regimes beyond which decreasing values of the 1f signal lead to increased uncertainty in peak features and meaningless measurements (Hosseinzadeh Salati & Khorsandi, 2014).

As a result of modulating the injection-current provided to the laser, both the frequency and intensity of the emitted light are modulated with some phase difference between them. When describing this intensity and wavelength variation, the slower sweeping component is often neglected as it has minimal impact on the line shape of the measured second harmonic feature (Olson et al., 1980). These modulated signals can subsequently be described by:

\[
I_o(t) = \bar{I}_o (1 + i_o \cos(2\pi f_{mod} t + \psi_1) + i_2 \cos(4\pi f_{mod} t + \psi_2))
\]  \hspace{1cm} (2.5)

\[
v(t) = \bar{v} + a_{mod} \cos(2\pi f_{mod} t)
\]  \hspace{1cm} (2.6)

where \(\bar{I}_o\) [V] is the mean laser intensity, \(i_o\) and \(i_2\) are the amplitudes of the linear and first order term of the nonlinear laser intensity modulation, and \(\psi_1\) and \(\psi_2\) are the phase shifts between the laser intensity and frequency for the linear and nonlinear intensity modulation, respectively. \(\bar{v}\) is the average (center) wavenumber [cm\(^{-1}\)] and \(a_{mod}\) [cm\(^{-1}\)] is the amplitude of frequency modulation.

Through substitution of Equations (2.5) and (2.6) into the general transmissivity equation (2.3) and rearranging, an expression for the post absorption laser intensity can then be defined for the modulated system:
\[ I(t) = I_0(t) \cdot \tau_{v_c} \]
\[ = I_0(t) \cdot \exp \left( - \sum_j \sum_i \left( \frac{q_j p_j L}{k_B T} \right) \sigma_{v_c,i,j}(p,T,q_j,\tilde{v} + a_{mod} \cos(\omega)) \right) \]  

(2.7)

where the angular frequency \( \omega = 2\pi f_{mod} t \) is used to simplify representation. Recognizing that the transmittance term of Equation (2.7) is a periodically even function, it may be expanded into a Fourier cosine series. The notation used here is based on Rieker (2009), where transmittance is rewritten as:

\[ \tau(v(t)) = \sum_{k=0}^{k=+\infty} H_k(\tilde{v}, a_{mod}) \cos(k\omega) \]  

(2.8)

and where the Fourier coefficients, \( H_k \), are defined as:

\[ H_0(\tilde{v}, a_{mod}) = \frac{1}{2\pi} \int_{-\pi}^{\pi} \tau(\tilde{v} + a_{mod} \cos(\omega)) \, d\omega \]  

(2.9)

\[ H_b(\tilde{v}, a_{mod}) = \frac{1}{\pi} \int_{-\pi}^{\pi} \tau(\tilde{v} + a_{mod} \cos(\omega)) \cdot \cos(b\omega) \, d\omega, b \in \mathbb{N} \]  

(2.10)

By combining the Fourier components for transmissivity with the output laser intensity, a theoretical representation of the detected signal can be achieved. To obtain the second harmonic signal for the phase-insensitive approach, this may be multiplied by \( \cos(2\omega) \) and \( \sin(2\omega) \) to isolate the in-phase, \( X_{2f} \), and quadrature, \( Y_{2f} \), components of the simulated \( 2f \) signal, namely:
\[ X_{2f} = \frac{1}{2\pi} \int_{-\pi}^{\pi} I_o(\omega) \cdot \tau(v(\omega)) \cdot \cos(2\omega) d\omega \]

\[ = \frac{I_o}{2} \left[ H_2 + \frac{i_o}{2} (H_1 + H_3) \cos \psi_1 + i_2 \left( H_0 + \frac{H_4}{2} \right) \cos \psi_2 \right] \]  

(2.11)

\[ Y_{2f} = \frac{1}{2\pi} \int_{-\pi}^{\pi} I_o(\omega) \cdot \tau(v(\omega)) \cdot \sin(2\omega) d\omega \]

\[ = -\frac{I_o}{2} \left[ \frac{i_o}{2} (H_1 - H_3) \sin \psi_1 + i_2 \left( H_0 - \frac{H_4}{2} \right) \sin \psi_2 \right] \]  

(2.12)

Likewise, the respective first harmonic components may be obtained through multiplication by \( \cos(\omega) \) and \( \sin(\omega) \), which takes the final form of:

\[ X_{1f} = \frac{I_o}{2} \left[ H_1 + i_o \left( H_0 + \frac{H_2}{2} \right) \cos \psi_1 + \frac{i_2}{2} (H_1 + H_3) \cos \psi_2 \right] \]  

(2.13)

\[ Y_{1f} = -\frac{I_o}{2} \left[ i_o \left( H_0 - \frac{H_2}{2} \right) \sin \psi_1 + \frac{i_2}{2} (H_1 - H_3) \sin \psi_2 \right] \]  

(2.14)

Both the in-phase and quadrature components are required to account for the phase misalignment between the laser intensity and wavelength. The phase-insensitive lock-in approach takes advantage of the orthogonality of the sinusoidal modulation to extract these two signals; however, the parameters \( i_o, i_2, \psi_1 \) and \( \psi_2 \) are laser specific and must be measured in a lab environment prior to application – this process is described further in Chapter 3. The theoretical \( n_f \) amplitude (where \( n = 1, 2, \ldots \)) may be calculated by taking the root sum square of the \( X \) and \( Y \) components (in a conversion from cartesian to polar coordinates).

\[ R_{n_f} = \sqrt{X_{n_f}^2 + Y_{n_f}^2} \]  

(2.15)

Experimentally, the \( n_f \) signal is digitally acquired through use of a digital lock-in amplifier – which effectively duplicates the above process with an analog signal by isolating its in-phase and
quadrature components (termed as demodulation) to determine the peak amplitude. The measured $2f$ peak height (and corresponding $1f$ feature) may be compared to a theoretical look-up table of peak heights for a set of environmental conditions to obtain the species VMR. Scaling and/or normalization of the $2f$ signal by the mean DC component is used in comparison with the look-up table to accommodate for changes in transmissivity through the system that may arise from fouling or deposits on the mirrors within the cell.

### 2.3 Previous Applications and literature review summary

TDLAS has been successfully used in a wide range of applications including environmental trace detection, process control and performance monitoring, and clinical species recognition of biomarkers in human-beings (Hosseinzadeh Salati & Khorsandi, 2014; Khorsandi & Ghavami Sabouri, 2020; Michel et al., 2016; Schwarm et al., 2020; Xia et al., 2019) as further summarized in Appendix A. Table 2.1 summarizes relevant TDLAS studies that have targeted oxygen fractions in a flowing stream or pipe.
## Table 2.1: Summary Details of Previous Oxygen and Cross-pipe TDLAS Systems.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Detection Technique</th>
<th>Application</th>
<th>Target Species</th>
<th>Laser Type / Optical Power [mW]</th>
<th>Detector Type / Integrated?</th>
<th>Targeted Wavelength (nm)</th>
<th>Optical Path Length (m)</th>
<th>Modulation Frequency (Hz)</th>
<th>Integration Time (s)</th>
<th>Absorption</th>
<th>Reported Sensitivity (+/- % or sigma variance)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Philippe &amp; Hanson, 1991)</td>
<td>WMS</td>
<td>Shock tube - Air-based flux sensor for high-speed air flows</td>
<td>Oxygen</td>
<td>AlGaAs Laser/3</td>
<td>Si/No</td>
<td>759.7</td>
<td>0.143 and 0.165</td>
<td>Fs=10k Fs=10M</td>
<td>0.5ms</td>
<td>0.2-0.9%</td>
<td>N/A, 10% relative</td>
</tr>
<tr>
<td>(Philippe &amp; Hanson, 1993)</td>
<td>WMS - 2f</td>
<td>Shock tube - Air based flux sensor for P, T, V, Vel detection in transient flows</td>
<td>Oxygen</td>
<td>AlGaAs Laser/3</td>
<td>Si/No</td>
<td>759.7</td>
<td>0.143 and 0.165</td>
<td>Fs=10k Fs=10M</td>
<td>0.5ms</td>
<td>0.1-1%</td>
<td>-</td>
</tr>
<tr>
<td>(Neethu et al., 2014)</td>
<td>WMS - 2f, 2f/4f, 2f/1f</td>
<td>Multi-pass optical gas cell for process validation</td>
<td>Oxygen</td>
<td>DFB/3</td>
<td>Si/No</td>
<td>760.241</td>
<td>0.56</td>
<td>Fs=200 Fs=10k</td>
<td>N/R</td>
<td>0-100%</td>
<td>-</td>
</tr>
<tr>
<td>(K. Lyle, 2005)</td>
<td>DA, WMS - rf (1 &lt; n &lt; 6)</td>
<td>Jet turbine bell mouth for flux measurements</td>
<td>Oxygen</td>
<td>DFB/3</td>
<td>Si/Yes</td>
<td>763.28</td>
<td>1.505</td>
<td>Fs=50-100 Fs=20-40k</td>
<td>1s</td>
<td>20.5-20.54%</td>
<td>0.76% absolute</td>
</tr>
<tr>
<td>(Xiong et al., 2015)</td>
<td>WMS - 2f</td>
<td>Open path monitoring of oxygen as a proof of concept</td>
<td>Oxygen</td>
<td>VCSEL/3</td>
<td>Si/No</td>
<td>760.445</td>
<td>0.32</td>
<td>Fs=10 Fs=12k</td>
<td>2.6s</td>
<td>1%</td>
<td>120ppm</td>
</tr>
<tr>
<td>(Liu et al., 2023)</td>
<td>WMS - 2f, 2f/1f</td>
<td>Detection of oxygen in airliner fuselages</td>
<td>Oxygen</td>
<td>DFB/40</td>
<td>InGaAs/Yes</td>
<td>760.241</td>
<td>2.5</td>
<td>Fs=100 Fs=10k</td>
<td>NR**</td>
<td>0-3%</td>
<td>relative 2.3-5% 1.7-3%</td>
</tr>
<tr>
<td>(Verma et al., 2012)</td>
<td>WMS - 2f/1f</td>
<td>Single pass cell as a proof of concept</td>
<td>Oxygen</td>
<td>DFB/10</td>
<td>NR**/No</td>
<td>760.236</td>
<td>0.3</td>
<td>Fs=200 Fs=10k</td>
<td>NR**</td>
<td>0-100%</td>
<td>7% relative</td>
</tr>
<tr>
<td>(Chang et al., 2022)</td>
<td>WMS - 2f/1f</td>
<td>Oxygen TDLAS Herriott style cell for proof of concept</td>
<td>Oxygen</td>
<td>DFB/6</td>
<td>InGaAs/No</td>
<td>760.89</td>
<td>3.3</td>
<td>Fs=2 Fs=1k</td>
<td>1s</td>
<td>5-20%</td>
<td>0.25% absolute</td>
</tr>
<tr>
<td>(Jatana et al., 2019)</td>
<td>SI</td>
<td>Volume ratio, moisture, temperature and pressure detection in internal combustion engines exhaust</td>
<td>Oxygen Water vapour</td>
<td>DM/10</td>
<td>InGaAs/Yes</td>
<td>759.95 1388.18</td>
<td>4.3</td>
<td>Fs=5k Fs=N/A</td>
<td>0.2ms</td>
<td>0-2% O2</td>
<td>&lt; 2% relative</td>
</tr>
<tr>
<td>(Wang et al., 2019)</td>
<td>SI</td>
<td>Dual volume ratio and pressure detection in ultraviolet range as proof of concept</td>
<td>Oxygen</td>
<td>N/A *Deuterium lamp</td>
<td>FFT-CCD/No</td>
<td>186-196</td>
<td>0.4</td>
<td>Fs=4 Fs=N/A</td>
<td>25s</td>
<td>0-3%</td>
<td>&lt; 0.021% absolute</td>
</tr>
<tr>
<td>(Zhou et al., 2017)</td>
<td>WMS - 2f</td>
<td>Oxygen detection using diffused integrating cavity absorption cell</td>
<td>Oxygen</td>
<td>VCSEL/0.3</td>
<td>Bi-Alkali/No **Photomultiplier tube</td>
<td>764.38</td>
<td>6</td>
<td>Fs=10 Fs=6k</td>
<td>100s</td>
<td>0.1-3%</td>
<td>&lt; 2 % relative</td>
</tr>
</tbody>
</table>


* - reported literature utilized incoherent deuterium bulb source for emission spectra

** - reported literature utilized photomultiplier (PMT) for detection/spectral recapture purposes

NR**/(·) - not reported in publishing
Lyle (K. Lyle, 2005) developed a real-time oxygen measurement WMS system for quantification of oxygen flux (velocity and volume fraction) through the bell-mouth inlet of a commercial jet airliner. The ultimate end-design of their oxygen system featured two collimated lasers aimed at opposing angles across the bell-mouth at two opposing photodetectors 1.505 m away. While the study focused on velocity measurements via Doppler shift, oxygen fractions were measured using a direct absorption technique. Measurements had a relative accuracy of 1% of the ambient value (20.5-20.54% O\textsubscript{2}) at 1 Hz sampling rate and had an associated standard deviation of 0.76% relative to the mean detected value. At an increased one-hour integration time, the relative error was improved to 0.6%. A variety of physical and mechanical challenges such as available instrumentation locations and beam angle, inability to purge the optical areas or isolate for velocity effects, non-uniform flow and swirl flow effects, and mechanical vibrational inducing beam steering and optical-misalignment contributed to lower than anticipated performance of the system.

Figure 2.2: Schematic of Oxygen Flux system and laser installation in the bell mouth as viewed a) from side, and b) from front [adapted from K. Lyle (2005)].

Xiong et al. (2015) demonstrated a ‘width ratio of fringe to absorption’ (WRFA) methodology for selecting an optimized modulation index (m) to reduce associated optical fringe effects in WMS readings (namely 2/f/1f) at low VMR. Testing was conducted through a 32 cm open-path cell through which a 1% oxygen mixture was continuously flowed. Improved detection precision of 120 ppm was obtained at m=4.1 versus the 150 ppm obtained at the “traditional” index value of m=2.2. Long-term fluctuation monitoring
found a nearly 8x reduction in fluctuation (2.2x10³ ppm versus 1.7x10⁴ ppm, respectively), which was attributed to suppression of dominant optical fringes.

Jatana et al. (2019) developed a multi-purpose sensor which utilized a ~4.3 m Herriott cell for analyzing the exhaust line of an internal combustion engine. The system used sweep-integration TDLAS to monitor VMR of oxygen and water-vapour, as well as temperature and pressure variation of the internal combustion engine (installed in a laboratory environment) exhaust line during various stages of operation. Oxygen dilutions between 0.2–2% were synthesized and monitored, for which the relative error was < 10% for VMR above 0.6%. A detection limit of ~1000 ppm was reported at an SNR = 1, however, issues with window fouling (as a result of oil deposits) were ultimately found to be performance limiting in application.

Zhou et al. (2017) developed a WMS oxygen detection system using a diffuse integrating cavity with an effective pathlength of 6 m. The study aimed to create a more effective alternative to electrochemical and amperometric cells (chemical reaction cells which are susceptible to component aging and cross-contamination) while providing an inexpensive method for increased detection sensitivity of oxygen VMR. Unlike other summarized literature, light within the diffuse cavity was captured using a photomultiplier tube (a vacuum phototube which amplifies [~10⁸] current from UV-NIR electromagnetic radiation to provide sensitive detection capabilities) instead of a traditional photodetector. Oxygen volume fractions between 0.1 – 3% were tested in which < 2% relative deviation was observed. The detection limit was reported as 350 ppm (at an SNR = 1). Subsequent research by Wang et al. (2019) recognized the large cavity volume was ultimately limiting in the design in both terms of portability and response time (> 100 s) – instead opting to shift to Schumann-Runge bands (185-200 nm) of oxygen, use a 40 cm long single-pass cell, and a simplified SI logic for a dual VMR and pressure sensing system. Measured VMR had absolute uncertainties < 0.021% and a reported detection sensitivity of 150 ppm (at an SNR = 3).

Liu et al. (2023) developed an airborne oxygen sensor for monitoring the VMR of oxygen in the ullage of aircraft fuselages in the presence of an onboard inert gas generation
system (i.e., continual N₂ purge gas supply used to inert the vapours within the fuselage and reduce flammability/ignition risks). This research considered laboratory measurement deviations as a result of pressure changes, vibrational disturbances, and laser intensity attenuation. The former issue was addressed using a 2\textsuperscript{nd} order polynomial pressure compensation coefficient, and the latter two issues were addressed using a calibration-free WMS (2f/1f) approach. Pressure compensation over a range of 0.1-1 bar was found to reduce relative error to within 1% of the setpoint reading. The 1f normalization of the 2f harmonic achieved relative errors of < 3% when measuring of O₂ fractions between 1-3% (versus < 5% relative error for traditional 2f measurements) and improved accuracy by minimizing impacts of vibrational related beam-steering and beam-scattering from condensation. A minimum detection limit of 3.03 ppm (based on background response) and detection accuracy of 9.6 ppm were reported. Despite the intended installation area, no indication of zoning certification or compatibility was provided.

2.4 Absorption Species Measurement and Selection

The measurement system presented in this thesis is designed to measure the oxygen fraction in the gases/vapours entering and exiting a hydrocarbon storage tank through its breathing vent. This takes advantage of the presence of ambient oxygen involved in the tank breathing process and indirectly enables monitoring of vapours emitted from the tank. Since the only oxygen in the system can be assumed to originate from the ambient air (i.e., the stored hydrocarbons contain negligible oxygen) where it occurs in a fixed ratio with nitrogen and argon, the measured oxygen fraction can be used to deduce the fraction of non-air vapours passing through the tank vent.

As fresh air is drawn into the tank, some of the stored hydrocarbon products will be induced to evaporate until new saturation conditions are reached. As standing or working losses are encountered as a result of temperature variations or refilling operations, a change in the available vapour space will result in the expulsion of an equivalent volume of the gas-vapour mixture to the atmosphere through the breathing vent. The volume fraction of oxygen within this mixture relative to ambient concentrations can be used to determine the remaining fraction of hydrocarbons vented, according to Equation (2.16):
where $x_{\text{vapour}}$ is the mole fraction of hydrocarbon vapours [%], $x_{O_2,\infty}$ is the mole fraction of oxygen in ambient air [mol %], and $x_{O_2,v}$ is the measured mole fraction of oxygen present in the vented tank emissions [mol %]. This relation assumes a fixed mixing ratio of oxygen to nitrogen in ambient air across the full range of atmospheric conditions (Drouin et al., 2017) and that the only source of oxygen within the vapour-space is from atmospheric air previously ingested into the tank. Through this process, inferred bulk concentration monitoring of vented hydrocarbons can be made. Should further compositional data be desired, sample bagging and post-processing by means of gas chromatography (GC) can be used as a fairly common and well-established procedure for species recognition as is typically done with similar oil and gas field samples.

2.4.1 Absorption Peak Selection

A strong, isolated, and well-defined absorption peak is preferred to ensure a robust measurement. As plotted in Figure 2.3a, the atmospheric A-band of oxygen near 760 nm (i.e., in the near-infrared (NIR) region of the visible light spectrum) has several unique, discrete, and narrow absorption features that are well-isolated from other known potentially interfering molecules (shown in Figure 2.3b). Data in these figures were calculated using spectral data from the HITRAN2020 database (Goldenstein et al., 2017; Gordon et al., 2017, 2022; Rothman et al., 2013) for ambient conditions at 25°C, 1 atm, and a 4.03 m long pathlength, and are plotted over the wavenumber range of 13120 cm$^{-1}$ to 13160 cm$^{-1}$ (759.2 – 762.8 nm).
Absorption by H$_2$O and CO$_2$ at maximum expected concentrations of 20000 ppm and 412 ppm, respectively, is multiple orders of magnitude weaker than comparable absorption by oxygen. Furthermore, the two most common molecules composing ~92% of natural gas, CH$_4$ and C$_2$H$_6$, have no observed absorption bands in this region, nor does H$_2$S, a common natural gas contaminant. The presented measurement system targets the strongest oxygen absorption feature in this region, at 13146.6 cm$^{-1}$ (760.65 nm), which is also distinct from notable H$_2$O and CO$_2$ absorption features.
Chapter 3  Experimental Setup

3.1 System Overview

Figure 3.1 shows a schematic of the developed oxygen sensor which separates the laser control and analysis components (base station) from the cross-pipe measurement cell, such that the latter can be located in a flammable gas environment (hazardous area). The base station components are housed within a single Pelican case for simplified transportation and setup. The laser diode and fiber network were housed in a thermally regulated enclosure to hold their temperature stable during operation. As discussed in Section 3.2, two variants of the cross-pipe measurement cell were designed and tested: an optical variant, in which signals to and from the sensor were transmitted optically through armoured fiber optic cables; and a detector variant, in which light exiting the multi-pass cell directly irradiates a photodetector whose electrical signal is transmitted back to the main base station via an intrinsically safe Zener barrier.

Figure 3.1: Schematic overview of the oxygen measurement system which separates a base station (located in a safe area) from the cross-pipe measurement cell (which can be safely located in a flammable gas hazardous environment). Both variants (optical and detector) of the cross-pipe measurement cell are shown. The laser diode and coupler network are maintained within a thermally regulated enclosure.
3.2 Cross-Pipe Measurement Cell

Figure 3.2 shows a labelled cross-sectional view of the cross-pipe measurement cell designed to make non-intrusive optical measurements of oxygen volume fraction over the cross-sectional area of a pipe. The key component of this apparatus is the multi-pass optical cell (IRcell) shown in gold and further described in Section 3.2.1. Two variants of the system were designed and constructed: an optical variant, in which laser light passing through the IRcell was captured into a fiber optical cable via an optical collimator (Figure 3.2a); and a detector variant, in which light passing through the IRcell was focused directly onto a photodiode detector (Figure 3.2b) whose signal was transmitted electrically back to the base station. The main components of the system are separately detailed in the sections that follow.

![Figure 3.2: Side sectional view of assembled cross-pipe measurement cell (a) optically recoupled and (b) direct detector cell variants.](image)

A custom-designed enclosure composed of three main components was built to house the IRcell as shown in Figure 3.3. The mounting plate (used to hold the adjustable collimator mounts), spacing block (surrounding the IRcell), and the top flange (used for the N₂ purge line) were fastened together using ¼” socket head bolts. Recessed grooves in the flange and mounting block held 3/32” dash-153 o-rings and cord stock to seal the cell from weather-events and moisture. The mounting holes for the kinematic-mount and collimator standoffs were positioned to meet alignment constraints of the multi-pass cell (Section 3.2.1) while maintaining compact sizing of the overall enclosure. The alignment screws of the collimator kinematic-mounts could be accessed through a removable cover.
plate (top and bottom of Figure 3.2) that was attached using M4 screws and sealed using a 1/16” gasket material.

Figure 3.3: Exploded view of IRcell housing showing mounting plate, spacing block, top flange and cover plate components. Angled collimator mounting position shown in red.

3.2.1 Multi-pass Cell

A multi-pass cell from IRsweep (Model: IRcell-S4) was used to maximize the pathlength of the laser beam as it traversed the gas to be measured in the pipe. The cell is made from a gold coated copper substrate and consists of an array of radially segmented mirrors with 5-mm aperture inlet and outlet “viewing windows”. In its intended application by the manufacturer, the cell has top and bottom cover plates (which enclose the left and right sides of the gold cell shown in Figure 3.3) to form a low volume (31 ml) sample cell. Sample gases can be drawn into the cell through ports in the cover plates. In a typical laboratory application, the IRcell is mounted on an optical table using rigorous alignment setups and immobilizers. The goal of this project was to attempt to adapt this cell for inline sampling of a pipe flow as part of a compact flow-through vent gas monitoring system.

The multi-pass cell has four optical path length configurations – adjustable by varying which mirror is first targeted within the cell by the entry beam of light. This project used the maximum 4.03 m pathlength which required targeting of the 2nd counter clockwise mirror relative to the input aperture to achieve the desired beam-configuration shown in Figure 3.4. This required fixing the collimators at a 3.75° angle relative to the inlet/outlet aperture, which was made possible through angled specification of fixturing points on the
mounting plate (as shown in Figure 3.3). Fine positioning of the collimator beam was possible using fine-adjustment of the hex-bolts on the kinematic mounts to direct the laser onto the central region of the targeted mirror.

![Figure 3.4: Traversed path of laser beam through the IRcell-S4 to achieve the full 4.03m beam-pattern configuration](image)

Laser light was directed into the IRcell as a 2-mm beam created using a reflective collimator (Thorlabs – Model: RC02APC-P01) positioned using a ½” kinematic mount (Thorlabs – Model: POLARIS-K05S2). The kinematic mount included two hex adjuster screws with locking nuts which were used to enable bi-directional control and angling of the emitted beam. Wedged anti-reflective (AR) coated windows from Thorlabs (Model: WW10530-B) were used on the outer surface at both aperture ports of the IRcell in conjunction with o-rings to seal the measurement region within the pipe. The wedged windows were used to minimize reflective fringe patterns within the return signal. At wavelengths between 650–1050 nm, the broadband antireflection coating used by Thorlabs was reported to reduce reflective losses to < 0.5% per surface (vs. 4% for similar uncoated windows) at incident angles between 0-30°.

3.2.1.1 Optically Recoupled Variant

The optically recoupled variant of the measurement system used the same reflective collimator and kinematic-mount as the launch optics to recapture the light into multi-mode (MM) fiber (OM6 Technologies – Model: FCA-259-FCA-35M-E204) that delivered the measured optical signal back to a remotely located detector and data acquisition system.
The fiber used FC/APC\(^8\) end connections to minimize back reflections. A large core diameter (62.5 \(\mu\)m) MM fiber was selected over a smaller single-mode (SM) fiber (5 \(\mu\)m diameter) for easier and more reliable alignment and optical recoupling. While a SM fiber would be preferred to avoid intermodal dispersion within the fiber (see Section 3.3.3), sustained alignment would be impractical as a result of system vibration and beam steering effects in the intended field application. The MM fiber was wrapped in a protective armoured sleeve (5 mm OD) for field deployment and a weather and moisture insulating gland was used at the cross-pipe measurement enclosure to seal around the MM fiber. The optically recoupled signal was routed to a remotely located PDA36A photodetector. While this method provided a reliable method for recapturing the transmitted signal in a laboratory environment, the signal integrity was observed to be sensitive to vibrational effects and physical disturbance affecting the routed fibers, leading to interest in a detector-variant of the measurement system.

3.2.1.2 Detector Recapture Variant

The detector variant of the cross-pipe measurement cell used a directly irradiated photodetector (described in Section 3.3.2) employed within the collimator cavity in order to capture the return intensity of the probing beam and relay it back to the host computer using shielded 24 AWG industrial cable (South Wire – Spec: 49022). A mating 4-pin M12 connector (TE Connectivity – Model: T4111012041-000) was used to connect the 24 AWG cable directly to the diode enclosure (through a moisture insulating gland (LAPP Worldwide – Model: 53112014)) for routing back to the host computer.

While seemingly complicating design implementation, directly integrated detectors have been used in field applications (Festa-Bianchet et al., 2022; Miller et al., 1996) with notable improvements over fiber-recoupled variants and reduced susceptibility to beam steering effects from vibrational disturbances. However, to permit operation in a flammable gas environment, the photodetectors must be unamplified (i.e., such that it

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\(^8\) All fiber connections were made using polished face-center/angle physical contact (FC/APC) connections, which although more expensive and less robust than traditional plastic connections used in the telecommunication industry, significantly limit back-reflectance of light and can provide sustained mating performance without optical return loss degradation (Ahluwalia, 2020).
qualifies as a “simple device” under relevant regulations (CSA C22.1:21 Appx. F.4.2.3)) and must be isolated from over-voltages from the unregulated (“safe”) area.

For the present system, the photocurrent from the diode was relayed through an intermediate Zener barrier from Pepperl+Fuchs (Model: Z757) which served as an associated apparatus to regulate and limit unsafe back-voltages to the cell which are regulated in field applications according to CSA 22.1 standards. This approach overcame signal stability limitations of the optical fiber-based system, although the weak signal of the unamplified photodiode meant it was important to shield the cable from electrical interference and limited the maximum distance between the cross-pipe measurement cell and the base station.

3.2.2 Collimator and Detector Enclosures

The launch collimator (and receiver collimator in the optical variant) and detector (for the detector variant) were housed in enclosures shown in Figure 3.5a and b, respectively. These enclosures were attached to the measurement cell, as shown at the top and bottom of Figure 3.2. A cover plate (not shown in Figure 3.5) and 1/16” thick gasket material (McMaster-Carr – Model: 95665K92) sealed the top of the enclosure but could be removed for easy access to adjust the collimator positioning and configure the digital or fiber connections.

![Collimator and Detector Enclosures](image)

Figure 3.5: Close up view of the (a) collimator enclosure and (b) detector enclosure (for the detector variant) within the cross-pipe measurement cell.
The optical fiber or electrical cable entered the enclosure through a pipe stub and sealing gland assembly connected to a 1” NPT port on the side of the enclosure. This gland sealed out moisture and protected the connections within the enclosure, i.e., the fiber boot (rigid end of the fiber) or electrical M12 connector. The gland assembly comprised of a 3/8” Skintop MS NPT gland from LAPP Worldwide (Model: 53112014), connected to threaded pipe fittings (assorted from McMaster-Carr – Models: 2161K33, 51205K216, 5120K229, 46755K126), and attached to the mounting plate (Figure 3.3) using M4 fasteners through a custom FNPT face-plate (which included a recessed 1/16” dash-025 o-ring groove for sealing).

For the optical collimator enclosures specifically, a separate 1/4” NPT female port in the top flange enabled optional continual nitrogen purging of the enclosure cavity. Nitrogen purging is a commonly employed technique (Norooz Oliaeet al., 2022; Rieker et al., 2009; Seymour & Johnson, 2019) to minimizing unwanted background absorption signals that occur outside the desired measurement volume (e.g., the space between collimator and aperture window) and increase the linearity of the optical response. In the present lab application, the collimator enclosures were purged with a regulated low-pressure (< 6 inH₂O) supply of nitrogen gas. Preliminary experiments considered both purged and non-purged measurements made in the laboratory environment, which demonstrated a strong linearity in signal response in both cases. However, using the nitrogen purge improved a slight linear offset of the calibrated signal due to the inevitable presence of some amount of oxygen in the enclosure. In field applications, use of the purged cavity remains desirable to maintain a positive pressure differential between the cavity and its surroundings to mitigate tarnishing of the collimators or ingress of oxygen, moisture, or other contaminants due to unintended leaks over time. For the enclosed photodiode variant, the N₂ purge port was removed due to a significant reduction in the free beam space to the detector surface and limited ability to further purge this remaining volume.

For the detector enclosure, the photodiode was seated in place using an epoxy resin seal and was inclined at a 10° angle to mitigate reflective or resonance/etalon interference surfaces that could otherwise form and interfere with the detected signal. The photocurrent
signal was relayed to the host computer through an interfacing M12 faceplate (Phoenix Contact – Model: SACC-SQ-M12FS-4CON-20/0,5) on the diode enclosure which was integrated with an IP67 rated gasket seal. A 7/16” pressure fitting with gasket from McMaster-Carr (Model: 50925K431) was used to seal the main access port once internal electrical connections had been configured. The detector signal was routed to the host computer through the intermediate Zener barrier junction.

3.3 Optical Setup

The optical setup of the oxygen measurement system can be categorized into four main subsections. The laser diode and laser diode controller (Section 3.3.1) were used to regulate and control sweeping operation of the emitted wavelength of the probing beam. The fiber network (Section 3.3.3) was used to split the emitted beam source for simultaneous sampling and characterization. The measurement cell (previously discussed in Section 3.2.1) was used to increase the effective pathlength traversed by the beam through the interrogation region and refine measurement capabilities. Finally, the data acquisition system (Section 3.4) was used to receive and process cell information to determine the anticipated species volume ratio.

3.3.1 Laser Diode and Controller

A discrete mode laser diode from Eblana Photonics (Model: EP761-0-DM-B06-FM) with an output power of 6 mW and a tunable center frequency near 760 nm was used to probe flow conditions within the pipe. The laser diode was supplied in a 14-pin butterfly mount configuration with an integrated TEC for temperature stabilization and included an internal single stage optical isolator to prevent unwanted back-reflection and limit propagation of feedback interference back to the diode. The laser output was coupled into a single mode 5/125 fiber terminated with an FC/APC end connection.

The laser diode was mounted into an ILX lightwave diode mount (Model: LDM-4980) and housed within a thermally regulated enclosure stored alongside the host computer in a conditioned indoor environment. The laser diode was tuned using a Stanford Research Systems (SRS) laser diode controller (Model: LDC 501) which regulated the diode’s emitted wavelength via control of both the temperature (using the integrated TEC)
and current supplied to the laser diode. The laser controller was pre-programmed using tuning parameters provided by the laser diode supplier, which may be entered directly through the controller front panel or through a USB interface connection with the host computer. An external modulation signal for the laser diode controller was delivered via a BNC connection on the front panel and provided a varying voltage signal that controlled the variation of the injection-current provided to the laser diode. For the desired WMS system, a low frequency sweep was combined with a high-frequency sinusoid through the MFLI lock-in amplifier (Section 3.4) prior to being passed to the current modulation input on the laser diode controller.

3.3.2 Photo Detectors

Silicon semiconductor photo-detectors were used for both variants of the measurement cell. The fiber-recoupled variant used amplified switchable gain detectors (Thorlabs – Model: PDA36A) with a wavelength range of 350 – 1100 nm and a responsivity of approximately 0.48 A/W at the targeted measurement wavelength of ~760 nm. A notable advantage of these photo-detectors is the large 3.6×3.6 mm detector surface area, which simplified alignment to detect the ~1.8-mm diameter recoupled beam. Attachable FC/APC fiber connection faceplates (Thorlabs – Model: SM1FCA) were used to attach the return fiber end to illuminate the detectors. These faceplates thread directly onto the PDA36A detector through integrated SM1 (1.035”-40) threads. For the detector variant of the measurement cell a different, unamplified silicon photo-detector (Thorlabs – Model: FDS100) was selected. While its responsivity (0.48 A/W) and detection area (3.6 x 3.6 mm) were similar to the PDA36A photo-detector, the FDS100 was notably smaller to facilitate direct integration into the measurement cell.

3.3.3 Single mode Fiber Splitter Assembly

The fiber-coupled output of the laser was fed into a custom-built single mode (SM) fiber network (Oz Optics – Model: SMJ-3A3A-633-4/125-5A-35) with various fiber optic taps to split off fixed fractions of the laser light to enable simultaneous monitoring and measurement of various optical reference signals (shown in Figure 3.6). The fiber network was constructed using single mode fibers which limit propagation of light in the fiber to a
single mode which avoids potential for intermodal dispersion\(^9\) and allows for transmission over longer distances. Separate optical taps and fiber components were fused together to form a single optical network which minimizes optical losses and reflections that would otherwise be introduced by using individual optical couplers. The end connections of the tapped assembly all used FC/APC connections.

Figure 3.6: Fused 760 nm SM fiber network for splitting off fractions of the laser signal to be directed to a laser reference detector, an oxygen reference cell, and a fiber ring resonator.

The laser signal entering the fiber network was split into four lines. An initial 95/5 tap directed 5% of the incoming signal onto a PDA36A detector to monitor the absorption-free laser intensity. A second 95/5 tap directed 5% of the remaining signal into a fiber-coupled oxygen reference cell (Wavelength References – Model: O2-H[16.5]-740-FCAPC-760nm). This cell contained pure oxygen at a nominal pressure of 740 Torr with a 16.5 cm long optical pathlength accessed via single mode FC/APC connections. The reference cell was initially used to monitor performance of the laser diode and ensure that the center wavelength remained centered on the targeted oxygen absorption feature. The transmitted light through the reference cell was routed to a PDA36A photo-amplifier and read in as secondary signal using an Oscilloscope card. The oxygen reference cell was not used in the final WMS system.

The third tap of the fiber network was connected to a fiber ring resonator (further described in Section 3.3.3.1) which was used for wavelength characterization and to determine laser parameters as outlined in Section 3.6.2. The remaining main line leaving the fiber optic network was routed to the cross-pipe measurement cell using a 40 m long

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\(^9\) In which the transmitted signal may become spread in time as a result of varying propagation velocities across multiple modes for an optical signal (FED Stnd 1037C).
single mode fiber (OzOptics – Model: SMJ-3A4A-633-4/125-5A-40). This fiber was protected by a 5 mm OD armoured sheath and similarly had FC/APC end connections to minimize optical noise and reflections.

### 3.3.3.1 Fiber Ring Resonator

The fiber ring resonator (FRR) was used to characterize the wavelength and laser parameters of the phase-insensitive WMS approach. It was constructed from two 50/50 coupler segments using SM fiber and connected to the optical network via a fused connection to the third 95/5 coupler as shown in Figure 3.6. The output of the FRR is an interference pattern with predictable spacing that occurs as a result of constructive/destructive interactions of the inputted light as it interacts with itself as it travels through the ring. The fringe pattern generated by the FRR can be used to accurately measure relative changes in wavelength over time through quantification of its free-spectral range (FSR). The FSR describes the optical frequency shift between any neighbouring fringes in the FRR signal and is a fixed value described by Equation (3.1) from Urquhart (1987);

$$\Delta \nu = \frac{c}{2n_e d}$$  \hspace{1cm} (3.1)

where $\Delta \nu$ is the change in wavelength (i.e., FSR) [Hz], $c$ is the speed of light in a vacuum [$3 \times 10^8$ m/s], $n_e$ [-] is the fiber effective refractive index, and $d$ is the physical length [m] of the fiber in the ring.

The FRR length was intended to have a small radius (i.e., small length $d$) such that the FSR had multiple, discernable interference peaks when used in the intended wavelength range. However, because the FRR was made by a third party from individual spliced components of relatively inaccurate lengths, the FSR had to be experimentally measured. This was done by sweeping the laser diode over a sufficiently wide wavelength range to capture two neighboring oxygen absorption features of known wavenumber. By observing and counting the number of optical fringes that occurred between these two known wavenumber peaks, the FSR of the FRR could be determined. This process was repeated
across multiple neighbouring oxygen peaks within the available tuning range of the Eblana Photonics diode to provide a refined FSR value of ~0.414 GHz (0.01380 cm⁻¹). Figure 3.7 shows an example scan between two neighbouring absorption features at 13160.33 cm⁻¹ and 13160.8 cm⁻¹.

![Figure 3.7: Sample plot of laser Intensity exiting the FRR as the laser is swept between 13160.33 cm⁻¹ and 13160.8 cm⁻¹. The number of interference peaks (grey markings) between two characterized absorption bands of known wavenumber – represented as a dip in the interpreted laser intensity – were used to determine the respective FSR of the FRR.]

3.3.4 Optical System Thermal Enclosure

An insulated, temperature stabilized enclosure housed the fiber network and associated detectors, the oxygen reference cell, the laser diode and laser mount, and the remote optical detectors for the fiber variant of the cross-pipe measurement cell. The temperature within the box was stabilized at 28°C using a thermometric heater/cooler (TE Technology – Model: CP-040HT) whose setpoint was controlled and monitored remotely through an RS232 connection using a temperature controller (Model: TC-36-25-R232) and thermistor, also from TE Technology. To ensure proper convective circulation, two small 24 VDC circulating fans (Newark – Model: 99Y7372) were placed within the enclosure. All heat generating components were housed at the bottom of the box with the cold plate of the thermoelectric cooler installed on the opposing top surface to maximize cooling effects. In application, the thermal enclosure is housed alongside the host computer in a conditioned indoor environment.
3.4 Ancillary Data Acquisition (DAQ) and Control System

The data acquisition and control system consisted of a National Instruments PXI chassis (Model: PXIe-1071) and controller (Model: PXIe-8840) with separately installed data acquisition cards plus a separate digital lock-in amplifier (Zurich Instruments – Model: MFLI with MF-MD and MF-DIG software upgrades). The NI PXIe-8840 controller used an Intel Core i7-5700EQ (at 2.6GHz Quad-core processor) CPU, 8 Gb of RAM, 285 Gb hard-drive disk, and Windows 10 Pro (x64 bit) operating system running LabVIEW software (LabVIEW 2019 SP1). The NI PXIe-1071 chassis enabled the controller to communicate with up to 3 PXI compatible expansion cards over a 3 Gb/s high-bandwidth backplane with 10 and 100 MHz reference clocks. In the tested configuration, a NI PXI-5406 frequency generator, NI PXI-6238 Multifunctional I/O Module, and NI PXI-5922 Oscilloscope were installed in the chassis, all synchronized using a common reference trigger from the PXI-5406. The controller integrated chassis (alongside relevant expansion cards) took the form of what is referred to as the ‘host computer’.

The PXI-5406 arbitrary function generator (FGEN) was used to generate a triangular waveform to slowly (20 Hz) sweep the wavelength of the emitted light from the diode over the target oxygen absorption feature. The resulting waveform passed over the absorption feature twice in a single sweep. For WMS measurements, the triangular waveform from the FGEN was routed through the auxiliary input of the Zurich MFLI lock-in amplifier which superimposed a high-frequency (20 kHz) sinusoid modulation. This modulated signal was then sent to the laser diode controller via a BNC connection. The return signal from the photodiode was read-in through the main-line voltage input of the MFLI and subsequently filtered and demodulated to extract the desired harmonics components of the signal as described in Chapter 2, Section 2.2.3. The MF-MD add-on was enabled to allow simultaneous recording of 0f (DC), 1f, and 2f harmonics including phase and quadrature components.

The MF-DIG software upgrade was also enabled to allow the Zurich MFLI to serve as a 2-channel digital oscilloscope when using the native LabOne MFLI ‘SCOPE’ interface. This functionality was used to acquire simultaneous voltage and current inputs for laser characterization and to measure the intensity versus wavelength response when
using the FRR. The NI PXI-5922 oscilloscope card was only used during the initial system
development. Finally, the NI PXI-6238 multifunction DAQ (with TB-2341 terminal block
mount) was used to log the 4 – 20 mA signals from the temperature and pressure
transducers. Conversion from the analog signal to the corresponding digital reading was
done natively within LabVIEW using the NI-DAQmx current utility by applying the
appropriate scaling factors. These signals were initially read at 16-bit resolution at 100 Hz
and immediately averaged to give an effective sample rate of 1 Hz.

3.5 Ancillary Pressure and Temperature Measurement

Separate transducers were mounted via ¼” NPT ports to the cross-pipe
measurement cell to record temperature and pressure data used in the calculation of oxygen
volume fraction. These transducers were used to compensate for temperature and pressure
effects within the cell and were mounted adjacent to the flow path through the enclosure
as shown in Figure 3.8.

![Resistive Temperature Detector](image1.png)

![Pressure Transducer](image2.png)

Figure 3.8: Installation location of the ancillary temperature (RTD) and pressure transducers relative to
optical interrogation region in (a) initial laboratory setup and (b) proposed field installation with
custom reduction fitting.

Absolute pressure was measured using an intrinsically safe, non-incendive pressure
sensor (Ashcroft Inc. – Model: A4WAM0242C630#A) with a pre-calibrated manufacturer-
rated accuracy of < 0.25% full scale over its 0–30 psia operating range. Temperature was
measured using a 4-wire resistance temperature device (RTD) probe (Omega Engineering
– Model: PR-25AP-1/10-0200-1/4-M12) which had a configurable temperature range
between −50 to 250°C and 1/10 DIN\textsuperscript{10} resistive tolerancing/accuracy. The M12 connections to the probe were wired through an intrinsically safe temperature transmitter (WIKA Instruments – Model: T15). Both the pressure and temperature readings were transmitted as 4–20 mA signals which were logged by data acquisition system. To enable safe operation in Class I, Zone 0 hazardous locations (where flammable gases are expected during normal operation), both devices were isolated from the DAQ using a CSA approved transparent repeater (PR Electronics – Model: 9106B). The 9106B is a 2-channel isolated 1:1 repeater which may be used to provide high galvanic isolation (2.6 kVAC) between Zone 0, 1, or 2 hazardous location environments and safe areas. The 4–20 mA transducer signals were read-in through the hazardous side terminals of this barrier and relayed to the safe side connections which could then be sampled by a multifunctional data acquisition on the host computer. A 180 W power supply (Traco-Power – Model: TSP-180-124EX) provided 24 VDC power to the 9106B barrier which in turn powered the pressure transducer and RTD transmitter. The same power supply was to provide power for the 24 VDC circulating fans within the thermal enclosure as discussed in Section 3.3.4. Mass Flow Controllers

Two digital mass flow controllers (MFC) with maximum flow outputs of 100 SLPM were used to create controllable mixtures of air and pure nitrogen (N\textsubscript{2}) (with oxygen fractions ranging from 0-20.95%) which could be delivered to the cross-pipe measurement cell for system calibration and testing. The identical Bronkhorst EL-FLOW\textsuperscript{®} Select Series MFCs (Model: F-202AV) were digitally controlled via a RS232 connection with the host computer. The MFCs had integrated thermal mass flow sensors\textsuperscript{11} and were calibrated in a controlled environment using a 100 SLPM DryCal\textsuperscript{®} (Mesa Labs – Model: 200-800-75) which has a standardized flow accuracy of ±0.15%.

\textsuperscript{10} 1/10 DIN is a divided value tolerancing that is not constant over the whole of the measuring range. It is defined as ±0.03°C at 0°C and is amongst the highest commercially available accuracy standard for RTD related sensing element measurements.

\textsuperscript{11} Through which thermal differences are monitored across two regions of a thin capillary tube aside from the main flow line which is instrumented with a small heater between the two temperature probes. Following energy retention laws, the thermal differences between these two probes as a result of flow (as fluid carries away heat) can be directly related to mass flow which is regulated by an associated solenoid controller feedback-loop system.
3.6 System Characterization

3.6.1 Absorption Peak Characterization

Prior to use in spectroscopy measurements, the available tuning range of the laser diode and corresponding absorption peak frequency(s) had to be determined. The laser diode manufacturer provided a set of laser specific parameters as a Device Characterization Summary (DCS). These included device tuning parameters and threshold information (to prevent damaging of the diode), as well as spectral characteristics pertaining to the center wavelength of emission at a nominal temperature and current setpoint.

For the DDU2708 diode from Eblana Photonics, the center wavelength of 760.92 nm was achieved at laser diode controller setpoints of 35°C and 80 mA. The range of potentially detectable oxygen absorption peaks was investigated by narrowly sweeping the injection-current while varying the laser diode thermal setpoint. The laser beam was passed through a 160 cm pathlength sample cell filled with ambient air and onto a photodiode detector. Observed dips in the measured intensity were recorded and compared with corresponding absorption peak strengths tabulated from the HITRAN spectral database to confirm corresponding wavelengths. As shown in Figure 3.9, the DDU2708 diode was found to have an effective thermal tuning range of 13127-13166 cm\(^{-1}\) when the temperature was tuned between 15–49.5°C. Within this range, the 13146.6 cm\(^{-1}\) (760.65 nm) absorption feature (within the atmospheric A-band of oxygen) was selected for measurement as previously discussed in Section 2.4.

Figure 3.9: (a) Tunable spectral range of the DDU2708 laser diode and (b) corresponding absorption bands for oxygen in ambient air (300 K, 1 atm) measured over a 160 cm path length and computed from HITRAN2020 database using Spectraplot. The selected operating wavelength is outlined in red.
3.6.2 Laser Intensity and Phase Characterization

As discussed in Section 2.2.3 computation of the theoretical $2f$ features used to evaluate species volume mixing ratio required knowledge of the amplitudes $i_o$ and $i_2$ and phases $\psi_1$ and $\psi_2$ of the absorption free signal, in addition to the average laser intensity, $\bar{I}_o$. These values were inferred by acquiring the FRR and reference line signals with only the modulation waveform driving the laser injection-current. The laser parameters for the DDU2708 Eblana diode at the operating modulation frequency are shown in Table 3.1.

Table 3.1: Resulting laser characterization parameters for DDU2708 diode used for computing theoretical harmonics signals at 20 kHz operating frequency.

<table>
<thead>
<tr>
<th>Modulation Frequency [Hz]</th>
<th>Modulation Voltage [V]</th>
<th>$i_o$ [-]</th>
<th>$\psi_1$ [deg]</th>
<th>$i_2$ [-]</th>
<th>$\psi_2$ [deg]</th>
<th>$a$ [cm$^{-1}$]</th>
<th>$a_2$ [cm$^{-1}$]</th>
<th>$\phi_2$ [deg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>20000</td>
<td>0.03</td>
<td>0.01278373</td>
<td>212.52</td>
<td>5.2243E-05</td>
<td>131.04</td>
<td>0.1113</td>
<td>0.000233</td>
<td>681.89</td>
</tr>
</tbody>
</table>

The methodology to extract the reference $i_o$, $i_2$, $\psi_1$ and $\psi_2$ information from the FRR and reference laser signals followed logic presented in (Festa-bianchet & Seymour, 2020), which is included in the appendices of this document. Through this process, peak values were extracted from the normalized FRR signal which were spaced out according to the previously characterized FSR (0.01380 cm$^{-1}$) and fitted using the non-linear curve fit VI, with model $(d + (a \times \cos(w \times x + p) + a_2 \times \cos(w_2 \times x + p_2))$, where $d$ is a constant value to account for the non-symmetric wavelength curve, $x$ is the time-step, $a$, $a_2$ are the amplitudes, $w$, $w_2$ are the frequencies, and $p$, $p_2$ are the phases. A similar process was repeated (excluding the constant $d$) to fit intensity data, with the mean value subtracted from the dataset prior to fitting. A sample depiction of this fitting process is shown below in Figure 3.10.
3.6.2.1 Optimization of the Chosen Laser Modulation Amplitude

To maximize the signal to noise ratio (SNR) of the WMS measurements, the modulation voltage provided from the MFLI was selected based on literature describing the optimized modulation index which maximizes the $2f$ signal. The modulation index is a dimensionless parameter which may be used across a variety line shapes to characterize modulation amplitude relative to the width of an individual absorption feature. Rieker et al. (2009) describes the modulation index as:

$$m = \frac{a_{mod}}{\Delta \nu_{HWHM}}$$  \hspace{1cm} (3.2)

where $m$ [-] is the modulation index, $a_{mod}$ is the amplitude of modulation [cm$^{-1}$], and $\Delta \nu_{HWHM}$ [cm$^{-1}$] is the half width at half maximum (HWHM) of the particular absorption feature of interest. By increasing or decreasing the modulation voltage, a wider or more narrow modulation amplitude may be achieved. For a wide variety of line shapes, maximization of the $2f$ signal has been reported to occur around a modulation index of 2.2 (Reid & Labrie, 1981). As seen in Table 3.1, at the operating modulation frequency of 20 kHz and modulation voltage of 30 mV, the resulting amplitude of modulation from fitting was determined to be 0.1113 cm$^{-1}$. For the 13146.6 cm$^{-1}$ absorption feature, the HWHM is 0.051760 cm$^{-1}$ (such that $m \approx 2.15$). Maximization of the $2f$ feature was subsequently checked by varying the modulation voltages from the MFLI, as shown in Figure 3.11, in which the optimized modulation voltage was found to occur around
~45 mV. Despite the potential for a small addition in peak amplitude, feasibility of the 30-mV modulation voltage was found to provide sufficient SNR and was not modified such to maintain direct comparability with previous system results.

Figure 3.11: Modulation amplitude and resulting $2f$ peak height. Significant reduction in the $2f$ height was observed at <25 mV modulation voltages. Overmodulation (> 45 mV) of the $f_{mod}$ signal results in broadening of the $2f$ feature and side-bands and a gradual reduction in the overall $2f$ amplitude. Note that the mean signal intensity is not impacted by the amplitude of modulation.

3.7 Data Processing for Volume Mixing Ratio Measurements

Volume mixing ratios (VMRs) were obtained following a methodology adapted from (Schoonbaert, 2015) in which a four-dimensional look-up table (LUT) was used to compare measured and theoretical $2f$ peak heights for various temperatures, pressures, and corresponding oxygen mixing ratios as discussed in Section 2.2.3. For each measurement, the temperature and pressure from the cross-pipe cell were used to linearly interpolate the LUT to obtain a two-dimensional dataset of theoretical $2f$ peak heights and oxygen VMR. The corresponding oxygen ratio for the measured $2f$ peak-height was then linearly interpolated from this two-dimensional table to produce a predicted VMR measurement. Predicted values were subsequently compared with known flow concentrations from controlled gas mixtures when initializing the system to develop relevant calibration parameters – further detailed in Chapter 4.

Processing time and overall precision of this method depended on the resolution of the look-up table. While smaller step-sizes were desirable to increase precision and measurement sensitivity, they greatly increased computational processing times and
memory requirements for the host computer. Hence, the frequency and step-size intervals at which the LUT were updated were tailored to enable the host-computer to maintain real-time measurements while ensuring small enough step-sizes to benefit from the finite measured values from the installed sensors. For each sweep period, two\textsuperscript{12} independent measurements were made corresponding to the rising and falling segments of the sweep ($f_{\text{sweep}}$) signal. Both the leading and lagging absorption segments were collected and processed separately prior to being averaged to obtain a VMR reading. A linear calibration was applied to the average value, as further described in Chapter 4, to correct for differences between predicted and real-world values in application.

\textsuperscript{12} The period of time in which the voltage is increasing is referred to as the ‘leading’ section of the sweep whereas the second half-period where the voltage is decreasing is referred to as the ‘lagging’ section of the sweep.
Chapter 4  Results and Discussion

The two variants of the oxygen measurement system were tested under laboratory conditions using digital mass flow controllers (MFCs) to flow a range of controlled oxygen mixtures through the cross-pipe measurement cell. As further detailed in Sections 4.1 and 4.2, systematic experiments were completed to quantify anticipated measurement uncertainties and calibration stability, in which both variants demonstrated fast, linear responses to changes in the oxygen volume fraction. The optical variant of the system was briefly deployed for initial field trials as summarized in Section 4.3. Finally, subsequent investigation to improve system performance in future field trials is summarized in Section 4.4. The VMR presented are expressed as either an absolute precision (i.e., raw or ‘absolute’ ± difference from a mean value) or as a relative error (i.e., this same difference expressed as a percent to an expected value).

4.1 Laboratory Testing of the Optical Recoupling Variant of the O₂ Measurement System

WMS measurements used 2f or 2f/1f harmonic components – as outlined in Chapter 2 – to measure the volume mixing ratio (VMR) of oxygen within the cross-pipe measurement cell. When computing the VMR via 2f WMS, the mean DC signal intensity (i.e., mean 0f component through the cross-pipe system) was used to scale theoretical values contained within a 4d LUT (previously described in Chapter 3). Conversely, when computing the VMR via 2f/1f WMS, the intensity dominated 1f component was used to normalize the 2f component (Hosseinzadeh Salati & Khorsandi, 2014; Sun et al., 2013). This scaling and/or normalization of the 2f signal by the mean DC component accommodated for changes in transmissivity through the system that may arise as a result of fouling or deposits on the mirrors within the cell probing the gaseous flows.
4.1.1 Allan-Werle/Temporal averaging performance

To assess measurement precision as a function of averaging time, tests were completed to create an Allan-Werle\textsuperscript{13} deviation plot as shown in Figure 4.1 for the all-optical cell variant. A fixed mixture of 80% air/N\textsubscript{2} (16.76% O\textsubscript{2}) was continually flowed through the absorption cell as measurements were made at different averaging times between 0.05 – 250 s. The results suggest precision error is minimized at 1-second averaging, where the oxygen fraction in the cell can be measured with an absolute precision ±0.016%. Notably, however, this precision degrades to ±0.12% (absolute) as the averaging time is further increased beyond 10 s. This degraded stability is attributed to sensitivity of the return fibers to subtle disturbances which were ultimately found to be implementation limiting in the optical design variant. As short-term response was the desirable quality for monitoring capabilities in the sensor, further tests considered a 0.5 s integration time which implies an absolute VMR precision of < 0.026%. Although not displayed temporally, the system quickly responded to changing oxygen dilutions, which were observed in the immediate signal but otherwise were not explicitly characterized.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4_1.png}
\caption{Measurement precision of optical 2f and 2f/1f signals over progressively longer averaging periods. Note the increased variation at averaging times greater than 1 s, which is attributed to system sensitivity to external disturbances of the return fibers in the recoupled variant.}
\end{figure}

\textsuperscript{13} Allan-Werle plots are a statistical tool used to summarize measurement precision in terms of expected standard deviation at increased sampling averaging times. They are intended to identify noise types in signals, and to provide insight into the averaging time which minimizes noise.
4.1.2 Oxygen Volume Mixing Ratio Calibration and Calibration Stability

The system was calibrated using controlled mixtures of dry-air and pure nitrogen, producing mole fractions of oxygen between 0 – 20.95% at 11 discrete setpoint increments. During calibration, each setpoint was stabilized for 75 s, after which 0.5-second averaged WMS samples were acquired. Figure 4.2 shows a typical oxygen fraction response of the optical cell variant before (blue) and after (orange) calibration using the 2f (Figure 4.2a) and 2f/1f (Figure 4.2b) processing methods. A strong linear correlation ($R^2 > 0.99$) between the measured oxygen VMR and that specified from the MFCs was observed for both methodologies, which required a slope and offset correction. Over the 0 – 20.95% O$_2$ range, the optically recoupled system measured oxygen VMR within ±0.38% (absolute) using the 2f method and ±0.29% (absolute) using the 2f/1f method, both at 95% confidence as indicated by the plotted prediction intervals.

Calibrations were repeated intermittently over a 2-month span between May 13$^\text{th}$ and July 12$^\text{th}$, 2022 (leading up to initial deployment of the optical system further described in Section 4.3) to characterize system stability. Within this period, fiber connections were carefully disconnected, cleaned, and reconnected on June 6$^\text{th}$ and July 4$^\text{th}$ (indicated by vertical dashed lines in Figure 4.3), otherwise the sensor connections were not disturbed. Calibrations for Figure 4.3a were performed with both the launch and receive collimator enclosure plates left open, such that the collimator enclosures were filled with ambient air. By contrast, for the calibrations plotted in Figure 4.3b, both collimator cover plates were temporarily attached, and the collimator enclosure purged with nitrogen. The purpose of
these “purged tests” was to assess the influence of air/oxygen within the collimator enclosures on the measurements. Immediately after each set of purged tests was completed, the cover plates were removed such that the enclosures were again open to the surrounding air.

As shown in Figure 4.3, the calibration slopes using either the $2f$ and $2f/1f$ methods were stable (blue and grey dots/crosses) over the 2-month span with less than 3% relative difference from their mean values. There was also no significant difference in calibration slopes whether the collimator enclosures were purged with nitrogen or not. By contrast, the $2f$ and $2f/1f$ calibration offsets varied by up to ±80% of their mean value. Although the magnitudes of the calibration offsets were approximately halved when the collimator enclosures were purged with nitrogen, the range of values obtained during the two-month test period appears to be no less variable. Such drift behaviour is not uncommon with traditional sensors, but this does imply a need to re-zero the instrument on a regular basis. While undesirable, the offset factor was nevertheless maintained within a relatively narrow range compared to the full-scale (20.95% O$_2$) range of the sensor and is not anticipated to significantly affect measurement performance. Therefore, the oxygen mixing ratio measurements could be performed with an averaged or assumed offset parameter but would further benefit from refined values for improved accuracy in the field. The potential impact of this level of calibration drift on measurement accuracy is explored further in the next section.
4.1.3 Anticipated Long-term Performance of the Optical Variant System

Using the mean calibration slope and offset parameters from Figure 4.3a as the reference calibration, the test data over the 2-month span were used to derive prediction intervals at 95% confidence of the measured oxygen mixing ratio for the optically recoupled cross-pipe measurement system, as shown in Figure 4.4. As expected, the 2-month prediction intervals were larger than the post-calibration prediction intervals shown in Figure 4.2, but still similarly narrow for both methods. For measurements of 0 – 20.95% oxygen volume fraction, the anticipated absolute margin of error was approximately ±0.72% for the 2f (Figure 4.4a) and ±0.70% for the 2f/1f (Figure 4.4b) measurements as plotted.

Figure 4.4: Two-month prediction interval and associated relative error for the optical variant system using (a) 2f signal and (b) 2f/1f signals collected over a 2-month monitoring interval. Absolute errors in measured oxygen fraction were approximately constant over the 0–20.95% measurement range at 0.72% and 0.70% for the 2f and 2f/1f methods.

Across the 6.3 – 20.95% O2 range, relative errors were less than 8% for both the 2f and 2f/1f methods. At lower oxygen fractions, however, increased variability in readings resulted in relative errors upwards of 25%. This was attributed to the sensitivity of the return fiber in the optical variant which resulted in lower a SNR from inherent background noise at low dilutions. The 0% setpoint (i.e., background signal) was excluded from plotting for relative error; however, observations saw this value shifted to a negative reading when the correction parameters were applied (attributed to the earlier mentioned linear offset factor).
4.2 Laboratory Testing of Detector Recaptured Variant of the O₂ Measurement System

4.2.1 Allan-Werle/Temporal averaging performance

Figure 4.5 plots the Allan-Werle deviation of the detector variant (solid) superimposed on the previously summarized result for the optical variant (dotted). In contrast to the optical variant, the precision uncertainty of the detector variant steadily improved with increased averaging time, achieving a minimum absolute precision of ±0.009% oxygen volume fraction at an averaging time of 10 s. While the short-term precision (i.e., averaged over 0.05 – 1 s) measurements were comparable to that of the optical variant, ~10x improved stability (< 0.01% absolute versus 0.1%) was achieved at longer averaging times. At the selected 0.5-second integration time (intended to maximize transient response in a field application), Figure 4.5 suggests that the detector variant should achieve an absolute precision of ±0.020%.

![Figure 4.5: Allan-Werle temporal deviation of 2f and 2f/1f signal comparison between the Detector (solid) and Optical (dotted) cell variants. Due to system behavioural differences in which the 1f signal would cross the zero-axis in the rebuilt detector variant, the 2f/1f signal was replaced with a 2f with background suppression (2f (B)) method in subsequent trials. Note the inherent response of the 2f (B) signal is identical and does not change from the 2f response, background suppression was used to observe for potential improvements at lower oxygen VMR as expanded on below.](image)

4.2.2 Oxygen Volume Mixing Ratio Calibration and Calibration Stability

Subsequent testing of the detector recaptured variant was performed using a rebuilt acquisition system and installation enclosure. Due to system behavioural differences impacting the 2f/1f measurement (in which the 1f signal would cross the zero-axis), signals...
from the detector version used $2f$ and $2f$ with background subtraction ($2f(B)$) measurement logic. The mean DC signal was used to scale the 4d LUT in both methods. For the $2f(B)$ method, a 5 s averaged background $2f$ signal (i.e., harmonic components captured at 100% $N_2$ condition acquired separately at the start of the interval described in Section 4.2.2) was subtracted from subsequent $2f$ readings to evaluate stability and any performance differences from the standard $2f$ approach. Both the $2f$ and $2f(B)$ methods were tested with non-purged and purged collimator enclosures.

Example calibrations for the detector variant of the oxygen measurement system are shown in Figure 4.6. Similar to the optical variant, the system response was strongly linear ($R^2 > 0.99$), although the calibration offset term was lower with the detector variant. A slight reduction in this offset factor was further attained in the $2f(B)$ method, but otherwise both methods displayed similar behaviour and resolution capabilities. Plotted prediction intervals for the calibration suggest that oxygen volume fraction uncertainties of $\pm 0.24\%$ (absolute) can be expected following calibration for both the $2f$ and $2f(B)$ methods at 95% confidence.

![Graphs showing calibration profiles](image)

**Figure 4.6: Sample Calibration Profile for Detector variant (a) $2f$ and (b) $2f(B)$ signals from December 20th, 2022. Respective prediction interval for the final calibration (at 95% confidence) indicated by the solid black lines.**

To assess calibration stability, calibrations were repeated intermittently over a 1.5-month span between December 12th, 2022, and January 31st, 2023, as summarized in Figure 4.7. For results shown in Figure 4.7a, the cover plates were left open and exposed to ambient air. For tests plotted in Figure 4.7b, the launch collimator was purged with nitrogen similar to the tests described in Section 4.1.2, but the corresponding detector enclosure (which had a much smaller volume than the collimator enclosure used in the
optical variant) was not. The SM fiber connection was carefully disconnected, cleaned and reconnected on Jan 2\textsuperscript{nd} and Jan 18\textsuperscript{th} (indicated by the vertical dashed line on the figures); otherwise, during this period the sensor connection were not disturbed. The calibration slope varied by less than 3\% from the mean value over the 1.5-month span for both the 2f and 2f (B) methods (which was similar to the variation in calibration slope seen with the optical variant) as shown in Figure 4.3. However, the calibration offset was much more stable with the detector variant. Comparing values without N\textsubscript{2} purging, the mean calibration offset for the detector variant was \textasciitilde0.15\% and \textasciitilde0.09\% with the 2f and 2f (B) methods and varied by less than \textasciitilde16\% and \textasciitilde22\% respectively, versus \textasciitilde0.53\% for the 2f optical variant (Figure 4.3a) with a variation of \textasciitilde65\%.

![Figure 4.7: Detector variation in calibration parameters between December – February. Absolute magnitude of calibration parameters for (a) non-purged and (b) purged collimator cavities. Note a significant reduction in linear offset value and deviation was observed over the sampling period compared to the optical variant.](image)

Purging of the collimator cavity did not appreciably change the mean offset value of the 2f (B) method (\textasciitilde0.09\% versus \textasciitilde0.082\%); however, purging did reduce the offset for the 2f method by half (from \textasciitilde0.15\% to \textasciitilde0.076\%). Relative variability from their mean value was comparable for both methods at less than \textasciitilde20\%. Findings suggest use of a static background subtracted signal is most desirable in circumstances where cavity purging is not possible; however, may otherwise be avoided.

### 4.2.3 Anticipated Long-term Performance of the Detector Variant System

Using the calibration test data collected over a 1.5-month space as summarized in Figure 4.7, long term prediction intervals for the detector variant system (without N\textsubscript{2} purging) were derived as plotted in Figure 4.8a and b for the 2f and 2f (B) volume fraction methods, respectively. Over the target operation range of 0 – 20.95\% O\textsubscript{2}, similar
anticipated uncertainties in the oxygen volume fraction of ±0.29% and ±0.31% were achieved for the 2f and 2f (B) methods, respectively. This is significantly better than the ±0.70% uncertainty achieved with the optical variant of the system.

For oxygen fractions between 6.3 – 20.95% O₂, relative errors were similar for the 2f and 2f (B) methods at less than 4%. This is approximately 2x better than measurement error obtained using the optical cell variant. As expected, the background subtraction was found to favorably reduce errors at lower oxygen ratios by suppressing interfering noise in the signal. At lower dilutions, relative errors upwards of 15% and 9% for the 2f and 2f (B) methods, respectively, were observed. Overall, the predicted VMR from detector variant showed consistent and repeatable performance with gradual improvement over the optically recoupled cell.

4.3 Initial Field deployment

4.3.1 System Deployment Devon, AB

The optical variant of the oxygen measurement system was installed for initial testing at the CanMET Devon research facility in Devon, AB in the Summer of 2022. This facility includes two connected fixed-roof storage tanks filled with pentane (C₅H₁₂) (Figure 4.9a). Pumping equipment between the two tanks permits controlled cycling of the liquid levels to simulate working losses. The measurement system was installed on the tank shown in
the right of Figure 4.9a, directly downstream of the vent port (Figure 4.9b). The vent line was subsequently routed to an ultrasonic flow meter (GE Sensing – SO#: 501010133884) and paramagnetic oxygen gas analyzer (Servomex® – Model: 01910001B) for independent O2 fraction and flow rate measurement (Figure 4.9c). The paramagnetic analyzer (SERVOTOUGH) continually extracts small volumes from the main flow line to evaluate the mole fraction of oxygen at a reported accuracy of < 0.05% oxygen (intrinsic error based on 95% confidence limits) (Servomex, 2009). Due to initial site access restrictions and approval processes, the optical system was installed; however, ancillary temperature and pressure measurements had to be referenced from pre-instrumented sensors near the top of the pentane tank venting port.

![Figure 4.9: CanMET Devon FROTTH Plant Facilities displaying (a) pentane tank set, (b) installed optical system variant and associated solenoid (yellow) for isolating tank exhaust with air/N2 line, and (c) exhaust line setup and associated monitoring devices.](image)

The paramagnetic sensor has a $T_{90}$ sampling response time of approximately 6 s (i.e., characterized as time to achieve reading equivalent to 90% of flow concentration at a sample rate of 1 L min$^{-1}$ following a step change from 0 to 0.5% oxygen) (Servomex, 2009)
and is installed at the end of the pentane tank exhaust line. Thus, the paramagnetic sensor is the first to experience air-intake events, but demonstrates a slower, more gradual response to changing $O_2$ conditions. By contrast the cross-pipe system responds instantaneously (within the 0.5 s sampling rate as demonstrated previously in a controlled environment) to changes in the oxygen fraction in its measurement cell and is also first to respond to venting events. Once initialized, the optical system was set to monitor working losses from the tank. Figure 4.10 provides a 49-hour summary of the measured oxygen fraction from the optical variant of the presently developed measurement system ($2f$ (red), $2f/1f$ (green)) and the reference paramagnetic sensor (blue). The acquisition rate of the cross-pipe measurement system was timed with respect to the paramagnetic sensor such that one 5-second time averaged sample was saved every 60 s. The $2f$ signal was subject to drift (apparent when comparing signals near 4:08 on August 31), which may be due to disturbances of the fibers or possibly also due to beam steering due to index of refraction gradients in the measurement cell impacting the mean signal intensity of the system. However, the $2f/1f$ signal was observed to be resilient to these drifting qualities (attributed to the intensity dominated $1f$ signal normalization) and provided more consistent behaviour over the testing interval.

![Figure 4.10](image)

**Figure 4.10:** Comparison of measured oxygen fraction in the vent line of the test pentane tank at the CanMET-Devon facility. Measurements using the $2f$ (red), $2f/1f$ (green), and paramagnetic (blue) sensors are plotted over a 2-day span. Note the drifting observed in $2f$ signal between 3 and 9 am on August 31, 2022.
While conducting working loss studies, discrepancies were observed between the oxygen fraction reported by the WMS cross-pipe measurement cell and the paramagnetic sensor that appeared to be proportional to oxygen VMR. The difference between readings grew as the oxygen fraction decreased, presumably corresponding to an increase of the VOC fraction. Notably, the offset between readings appeared repeatable and would clear upon fresh intake of air. To troubleshoot this, subsequent testing was conducted in which the exhaust line was isolated and controlled dry-air and N\textsubscript{2} mixtures were flowed – shown in Figure 4.11. Under these conditions, measured oxygen fractions by the two instruments agreed, ruling out a potential issue with calibration of the cross-pipe system. While photoinduced isomerization of radical pentane molecules by visible wavelength light has been previously demonstrated (Dolivo et al., 1986), the presence of free radical pentane molecules is not considered to be significant enough in and of itself to cause such interference in absorption signals. Upon return (and rebuilding) of a detector variant system, effort was focused to investigate and identify this issue. Further discussion of this can be found in the following section.

![Figure 4.11: Comparison of oxygen fractions measured by the cross-pipe measurement cell and the SERVOTOUGH sensor for controlled air/N\textsubscript{2} mixtures in 5% step intervals. Blue line represents a 1:1 correlation.](image)
4.4 Subsequent testing with Detector Variant

4.4.1 Lab testing with air and different diluent gases

As pentane is a liquid at standard temperature and pressure, direct investigation was difficult without the ability to flow controlled amounts of vapourized pentane in the laboratory. While the EERL facilities include a flare-gas vaporizer system (capable of infusing low quantities of pentane into active gas-flows), it uses methane as a carrier gas whose affects were unknown and was not readily adjustable. Therefore, controlled testing was first completed using the 160 cm absorption tube, which was filled with various air/CH₄ dilutions and analyzed using a simplified sweep integration TDLAS logic. Following a typical dry-air/N₂ calibration, the N₂ MFC was substituted with CH₄ MFC and randomized setpoint intervals were then repeated between 0 – 100% CH₄ mixtures (Figure 4.12a). Results plotted in Figure 4.12a demonstrated a similar discrepancy in the predicted VMR as the field-testing observations. Unlike prior calibrations, correlation better approached a non-linear (‘bowed’) 2nd order polynomial, with relative errors demonstrating a logarithmic appearance (away from the 0% O₂ setpoint) as seen in Figure 4.12b. Such effects showed that the observed behaviour was not necessarily as a result of a specific gas contaminant.

Experiments were subsequently completed using the detector variant of the cross-pipe WMS system to measure oxygen fraction in various mixtures of air and CH₄, C₂H₆, or CO₂ in comparison to the typical air/N₂ calibration as shown in Figure 4.13 (for both vertical (V) and horizontal (H) cell orientations). Irrespective of orientation, the predicted
VMR erred to a varying extent depending on the dilution gas but likewise demonstrated a bowed appearance with a maximum deviation at intermediate volume fractions. Notably none of the individual considered gases absorb light at the operating wavelength, but the findings suggest their presence with air nevertheless affects the measured absorption signal. These effects were ultimately attributed to species-dependent phenomena known as ‘collision-induced absorption’ and ‘collision-induced broadening’.

Figure 4.13: Corresponding air/N₂ calibrated signal and resulting impact with differing dilution gases on associated VMR in horizontal (H) and vertical (V) cell orientations. Notably, a significant discrepancy is observed for comparatively low dilution mixtures of CO₂ and air.

4.4.1.1 Collision Induced Absorption and Broadening and their Implications in TDLAS

Collision-induced absorption (CIA) results from intermolecular interactions between colliding molecules and subsequent effect on transmission properties (Lothar, 1993). While conventional molecular spectra typically arise from transitions occurring between ro-vibrational energy states (i.e., spectra arising from rotational and vibrational motion as a result of energy absorption from passing photons), collision-induced absorption produces diffuse, continuous transitional spectra as a result of induced dipole moments between molecules. Notably, even though individual molecules may not be spectrally active at a given infrared wavelength (i.e., do not absorb light), their presence can lead to combined molecule interactions via collision with other molecules whose translational motion will
generally be infrared active (i.e., demonstrate absorption). These combined molecule interactions possess absorption spectra of their own, which are more than the sum of the individual interacting molecules spectrum (Lothar, 1993). While historically some effort has been made to describe such interactions (Gallagher & Holstein, 1977; Kenkichi, Okada; Kajikawa, Tomoyoshi; Yamamoto, 1968; Lothar, 1993), the topic has received limited consideration and available spectral databases such as HITRAN only consider collision partners found in ambient air.

Collision-induced broadening (CIB), also known as ‘pressure broadening’, likewise arises from collisions between molecules and affects natural emission processes. A few recent studies have introduced collision induced broadening parameters to enable more accurate line-shape modeling for spectroscopic based sensors and measurements (e.g., Tan et al. (2019), who considered H₂O interactions on atmospheric gases including CO₂, CH₄ and O₂ and Tan et al. (2022) who also considered interactions with H₂, He, and CO₂ for a variety of additional gases including N₂O, CO, H₂CO, and H₂S) for improved interpretation of spectra broadening in the HITRAN 2020 database (Gordon et al., 2022; HITRAN, 2023). However, there is a dearth of available data for C₂⁺ hydrocarbons and other compounds that are commonly found in venting and oil and gas extractions activities. As demonstrated in Figure 4.13, broadening effects can be significant even for low partial pressures of the colliding molecule (such as air-CO₂ interaction at the operating wavelength). The CIA and CIB effects result in dampening of the 2f feature and peak height, resulting in a diminished VMR prediction. The corresponding impact on 2f peak-heights at 50% of air and for various gas mixtures are shown in Figure 4.14.
Figure 4.14: Impact on 2f Signal for mixtures of 50% by volume air and other gas species.

The implication such phenomena have on the ultimate goal of the cross-pipe measurement cell project will vary depending on the extent that the composition of VOC mixtures can be deduced in application. Figure 4.13 suggests, for binary systems these effects can be readily addressed through direct calibration of the measurement cell. However, for more complicated (ternary, quaternary, etc.) compositions and variable compositions (as might be anticipated from upstream oil and gas deposits), further correction factors, sequenced gas monitoring, or post-processing of results would be required to refine the accuracy capabilities of the system. For the future field measurements on pentane tanks at the CanMET facility in Devon, it is proposed to complete an in-situ calibration using the reference paramagnetic sensor, after which the cross-pipe measurement cell can be used as a fast-response oxygen sensor during tank venting measurements.
Chapter 5  Conclusion

An intrinsically safe, tunable diode laser absorption spectroscopy oxygen measurement system was developed for use in monitoring of transient vented emissions from fixed-roof liquid hydrocarbon storage tanks. The sensor targets the atmospheric absorption band of oxygen at 760 nm and utilizes wavelength modulation spectroscopy and associated harmonic components to determine the transient volume mixing ratio of oxygen at up to 2 Hz. The sensor was developed to be compact, weather and moisture resilient, and in compliance with CSA zoning restriction for installation in hazardous oil and gas operating environments.

The cross-pipe measurement system utilized a multi-pass optical cell composed of radially segmented mirrors for an effective pathlength of 4.03 m. The system was designed to be installed in-line with venting media without disrupting the natural breathing phenomena or inducing significant head loss or back-pressures within the line. Two variants of the system were demonstrated: an optically recoupled variant (in which the laser beam exiting the multi-pass cell was recaptured into a multi-mode fiber and relayed to a remotely deployed detector), and a direct-to-detector variant (in which the light leaving the multi-pass cell was aimed directly onto a photodetector integrated within the cross-pipe enclosure).

Oxygen volume mixing ratios were calculated by comparing 2f or 2f/1f normalized peak heights with precomputed values in a lookup table and subsequently applying an empirical calibration. Allan-Werle deviation of the optical variant demonstrated a measurement precision of ±0.026% oxygen volume fraction at a 0.5-second integration time. In lab tests using mixtures of air diluted with nitrogen spanning oxygen fractions of 0 – 20.95%, prediction intervals immediately following calibration indicated absolute margins of error of ±0.38% and ±0.29% for the 2f and 2f/1f measurement methods, respectively. However, the optically recoupled system was sensitive to physical disturbances of the return fiber which affected long-term calibration parameter stability. For tests over a two-month period, the measurement uncertainty increased to ±0.72% and
±0.70% at 95% confidence relative to a mean calibration for the 2f and 2f/1f measurement methods, respectively. This corresponds to relative errors of less than 8% for both the 2f and 2f/1f methods, respectively, for oxygen volume fractions ranging between 6.3 – 20.95%.

The detector variant demonstrated improved performance, achieving an Allan-Werle precision of ±0.020% oxygen volume fraction at 0.5-second integration time which fell to a minimum of ±0.009% at an averaging time of 10 s. Post-calibration accuracy (defined as the 95% prediction interval) was ±0.24% oxygen volume fraction over a range of 0 – 20.95% O2 for both the 2f and 2f (B) methods. The longer-term stability was also notably improved; for tests over a 1.5-month period, a ±0.29% and ±0.31% oxygen volume fraction uncertainty was achieved relative to a single mean calibration for the 2f and 2f (B) measurement methods, respectively. Using the mean parameters from this time period, relative errors for oxygen dilutions between 6.3 – 20.95% were less than 4% for both the 2f and 2f (B) methods.

Following initial laboratory testing, the optically recoupled variant was installed on a test tank at the CanmetENERGY research facility in Devon, AB and briefly used to monitor working losses over a 49-hour period during simulated filling and draining activities. While measured oxygen fractions agreed well with an independent paramagnetic sensor when flowing controlled air/N2 dilutions, oxygen fractions reported by the optical system appeared to be biased low during instances of active VOC venting. Further testing to recreate these effects in a controlled setting attributed this to secondary collision-induced absorption and collision-induced broadening due to the presence of gas species (i.e., pentane) not present during calibration and not considered in the HITRAN database. In the future these effects may be best addressed by using in-situ calibrations.

5.1 Future Considerations

Although the present system is able to monitor transient compositions of oxygen in a controlled environment, it was unable to accurately quantify oxygen volume fractions in the presence of interfering compounds beyond those considered in standard HITRAN broadening parameters (air, N2, self). For the intended experiments on pentane-filled tanks
at the CanmentENERGY facility in Devon, AB, secondary collision effects may be easiest accounted through in-situ calibration of the currently installed system. Potential applications on tanks containing additional species or mixture would be more challenging but depending on the range of mixtures, empirical calibrations could still be performed in conjunction with sample collection and gas chromatography.

Temperature stability testing of the system is recommended, ideally in an environmental chamber where both temperature and humidity can be controlled. Such testing would establish the susceptibility of the system to measurement drift related to any potential beam-steering effects from contraction of the enclosure or mounting block. Finally, further refinement of the acquisition system could be explored such that it might be scaled down and moved closer to the cross-pipe system (e.g., within an explosion-proof enclosure). This would greatly simplify field deployment in future studies.
References


consumer-commercial/overview.html


HITRAN. (2023). Collision-Induced Absorption (CIA) cross-sections in HITRAN.


Rothman, L. S., Gordon, I. E., Barbe, A., Benner, D. C., Bernath, P. F., Birk, M.,


Appendix A: Literature Review

A.1 Additional TDLAS Studies in relation to Gas monitoring

A variety of studies have utilized TDLAS for recognition of other compounds or for trace detection purposes. While these studies may operate at differing wavelengths or involve separate processing methodologies than those presented, they provide useful insight into avenues for further improvement on TDLAS and for potential refinement techniques of the cross-pipe sensor in future applications. In addition to those contained within Chapter 3, this section summarizes some supplementary applications and reported findings from other previous TDLAS studies monitoring other gases.
## Table A-1: Details and Characteristics of other past TDLAS Systems.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Detection Technique</th>
<th>Application</th>
<th>Target Species</th>
<th>Laser Type / Optical Power [mW]</th>
<th>Detector Type / Integrated?</th>
<th>Targeted Wavelength (nm)</th>
<th>Optical Path Length (m)</th>
<th>Modulation Frequency (Hz)</th>
<th>Integration/Time (s)</th>
<th>Absorption</th>
<th>Reported Sensitivity (+/- % or sigma variance)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sun et al - 2013</td>
<td>WMS</td>
<td>Absorption Tube for process validation</td>
<td>Water in Air</td>
<td>DFB/20</td>
<td>InGaAs/Yes</td>
<td>1392</td>
<td>1.005</td>
<td>Fs=25, Fm=10k</td>
<td>-</td>
<td>0.75%</td>
<td>-</td>
</tr>
<tr>
<td>Norooz Oliaee et al - 2022</td>
<td>SI WMS - 2f/1f, 2f-0f;</td>
<td>Multi-pass Herriott style cell for fugitive emission monitoring</td>
<td>Methane in Air</td>
<td>GaSb DFB/1.5</td>
<td>HgCdTe/Yes</td>
<td>3270.4</td>
<td>6.804</td>
<td>Fs=25, Fm=10k</td>
<td>1s 44.4s</td>
<td>0.0015-0.004% (40 ppm)</td>
<td>DAS: 7% rel WMS: 0.97ppb; 0.225 ppb</td>
</tr>
<tr>
<td>Rojas et al - 1997</td>
<td>WMS</td>
<td>Free-space flow atomizer for optical density observation</td>
<td>Rubidium in Air/acyetylene flame</td>
<td>-</td>
<td>-</td>
<td>780</td>
<td>0.1</td>
<td>Fs=1, Fm=10/1k</td>
<td>-</td>
<td>0-100%</td>
<td>-</td>
</tr>
<tr>
<td>Khorsandi et al - 2020</td>
<td>WMS - apodized 2f/1f</td>
<td>Coal-combustion through free-space glass tube, CO/CO2 in air</td>
<td>Carbon monoxide and Carbon dioxide in air</td>
<td>DFB/5</td>
<td>InGaAs/No</td>
<td>1573.0, 1572.87 and 1572.66</td>
<td>8</td>
<td>Fs=NR**, Fm=3k</td>
<td>-</td>
<td>1-11%</td>
<td>4.00E-04</td>
</tr>
<tr>
<td>Salati et al - 2014</td>
<td>WMS - apodized 2f/1f</td>
<td>Single pass flow tube experiment</td>
<td>Carbon Monoxide in Air</td>
<td>DFB/3</td>
<td>InGaAs/Yes</td>
<td>2328.486</td>
<td>0.15</td>
<td>Fs=NR**, Fm=3k</td>
<td>30ms**</td>
<td>0-88%</td>
<td>-</td>
</tr>
<tr>
<td>Gao et al - 2018</td>
<td>WMS - 2f/1f</td>
<td>Herriott Gas cell for ppm measurement of ethanol</td>
<td>Ethanol</td>
<td>ICL/3.5</td>
<td>HgCdTe/No</td>
<td>3345</td>
<td>10.5</td>
<td>Fs=NR**, Fm=5k</td>
<td>&lt; 0.6s</td>
<td>0-3ppm</td>
<td>28 ppb</td>
</tr>
<tr>
<td>Cassidy et al - 1982</td>
<td>WMS - 2f</td>
<td>Open path monitoring of trace-gases in the atmosphere</td>
<td>Nitrous Oxide</td>
<td>-</td>
<td>-</td>
<td>8731.1</td>
<td>250 m (1-600 m variable)</td>
<td>Fs=NR**, Fm=1k</td>
<td>-</td>
<td>-</td>
<td>0.01%</td>
</tr>
</tbody>
</table>
Table A-1: Details and Characteristics of Past TDLAS Systems (continued).

<table>
<thead>
<tr>
<th>Reference</th>
<th>Detection Technique</th>
<th>Application</th>
<th>Target Species</th>
<th>Laser Type / Optical Power [mW]</th>
<th>Detector Type / Integrated?</th>
<th>Targeted Wavelength (nm)</th>
<th>Optical Path Length (m)</th>
<th>Modulation Frequency (Hz)</th>
<th>Integration/Time (s)</th>
<th>Absorption</th>
<th>Reported Sensitivity (+/- % or sigma variance)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fang et al - 2018</td>
<td>WMS - 2f</td>
<td>Multipass optical gas cell for sub-ppm methane detection</td>
<td>Methane</td>
<td>ICL/3.5</td>
<td>MCT/Yes</td>
<td>3291.1</td>
<td>16</td>
<td>Fm=2k</td>
<td>2s</td>
<td>0-10ppm</td>
<td>13.07ppb</td>
</tr>
<tr>
<td>Davis et al - 2016</td>
<td>SI</td>
<td>Integrating sphere compared with single-pass absorption tube</td>
<td>Methane</td>
<td>ICL/3</td>
<td>Cooled MCT/Yes</td>
<td>3313</td>
<td>0.1 0.545</td>
<td>Fm=N/A</td>
<td>1s</td>
<td>0-1010ppm</td>
<td>2.2ppm 1.0ppm</td>
</tr>
<tr>
<td>Wavelength - 2022</td>
<td>WMS - 2f</td>
<td>Absorption Tube for process validation</td>
<td>Carbon Monoxide in Air</td>
<td>DFB/10</td>
<td>Ge/Yes</td>
<td>1566.64</td>
<td>1</td>
<td>Fm=4k</td>
<td>-</td>
<td>2.50%</td>
<td>RSME &lt;0.37%</td>
</tr>
<tr>
<td>Tian et al - 2021</td>
<td>SI (with NN) WMS - 2f</td>
<td>Multi-pass Herriott absorption cell for Neural Network (NN) process validation</td>
<td>Methane</td>
<td>DFB/10</td>
<td>InGaAs/No</td>
<td>1653.723 1532.830</td>
<td>3</td>
<td>Fm=2k</td>
<td>-</td>
<td>0-1000ppm 0-500ppm</td>
<td>.5783%; .6826% .5871%; 6081% relative</td>
</tr>
<tr>
<td>Montori et al - 2015</td>
<td>CIDAS</td>
<td>Variable open path length cell for theory validation</td>
<td>Methane</td>
<td>DFB/15</td>
<td>InGaAs/No</td>
<td>1650.7 1557.8</td>
<td>1.61-5.62</td>
<td>N/A</td>
<td>-</td>
<td>-</td>
<td>20ppm</td>
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<tr>
<td>Li et al - 2006</td>
<td>WMS</td>
<td>Absorption Tube for theory validation</td>
<td>Water in Air</td>
<td>DFB/10</td>
<td>InGaAs/Yes</td>
<td>1387.86</td>
<td>1.05</td>
<td>Fm=50k</td>
<td>-</td>
<td>0.1-1%</td>
<td>-</td>
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<tr>
<td>Nwaboh et al - 2013</td>
<td>SI</td>
<td>Hallow Tube for setup validation</td>
<td>Carbon dioxide in Nitrogen</td>
<td>DFB/2</td>
<td>InGaAs/No</td>
<td>2005.09</td>
<td>5.27</td>
<td>Fm=N/A</td>
<td>No averaging (single scan)</td>
<td>59 ppm</td>
<td>2% relative</td>
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## Table A-1: Details and Characteristics of Past TDLAS Systems (continued).

<table>
<thead>
<tr>
<th>Reference</th>
<th>Detection Technique</th>
<th>Application</th>
<th>Target Species</th>
<th>Laser Type / Optical Power [mW]</th>
<th>Detector Type / Integrated?</th>
<th>Targeted Wavelength (nm)</th>
<th>Optical Path Length (m)</th>
<th>Modulation Frequency (Hz)</th>
<th>Integration/Time (s)</th>
<th>Absorption</th>
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</thead>
<tbody>
<tr>
<td>Wu et al - 2020</td>
<td>WMS - 2f</td>
<td>Hallow Waveguide for atmospheric species detection</td>
<td>Carbon dioxide Water in N2</td>
<td>DFB/11.2</td>
<td>Cooled HgCdTe/No</td>
<td>2729.36</td>
<td>3663.04</td>
<td>Fs=30 Fm=4k</td>
<td>1s</td>
<td>0-4000ppm 2.3%</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>26.9ppm .014%</td>
</tr>
<tr>
<td>Hanson and Philippe - 1993</td>
<td>WMS - 2f</td>
<td>Shock tube - Air based flux sensor for P, T, Vel detection in transient flows</td>
<td>Oxygen</td>
<td>AlGaAs Laser/3</td>
<td>Si/No</td>
<td>759.7</td>
<td>0.143 and 0.165</td>
<td>Fs= 10k Fm=10M</td>
<td>0.5ms</td>
<td>0.1-1%</td>
</tr>
<tr>
<td></td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>Dong et al - 2015</td>
<td>DA WMS - 2f</td>
<td>Multipass optical gas cell</td>
<td>Formaldehyde</td>
<td>ICL/3.8</td>
<td>MCT/Yes</td>
<td>3483.1</td>
<td>54.6</td>
<td>Fs_d= 500 Fs_w= 5 Fm= 43k</td>
<td>0.5s 1.5s</td>
<td>0-220ppb 0-45ppb</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.25ppb 0.58ppb</td>
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<tr>
<td>Miller et al - 2014</td>
<td>WMS - 2f</td>
<td>Herriott Gas cell for atmospheric ammonia measurements</td>
<td>Ammonia</td>
<td>QCL/NR** (HP)</td>
<td>HgCdTe/Yes</td>
<td>9060</td>
<td>30-60</td>
<td>Fs=50 Fm=15k</td>
<td>0.1</td>
<td>&lt; 25ppm 0.15ppb</td>
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<tr>
<td>Shcherbakova et al - 2021</td>
<td>SI</td>
<td>Herriott Gas cell for multi species biomarker recognition</td>
<td>Acetone Ethanol</td>
<td>QCL/20</td>
<td>MCT/Yes</td>
<td>5500-10000</td>
<td>76</td>
<td>Fs=20 Fm=N/A</td>
<td>&lt; 1s</td>
<td>2-100 ppm 10-50ppb</td>
</tr>
<tr>
<td>Liang et al - 2018</td>
<td>WMS - fringe suppression</td>
<td>Free path for trace CH4 detection</td>
<td>Methane</td>
<td>DFB/NR**</td>
<td>-</td>
<td>1653.72</td>
<td>1.45</td>
<td>Fs=NR** Fm=NR**</td>
<td>1s</td>
<td>&lt; 75 ppm 90ppb</td>
</tr>
<tr>
<td>Krempek et al - 2013</td>
<td>WMS - 2f</td>
<td>Spherical mirrored cell (for cell validation purposes)</td>
<td>Ethane in Nitrogen</td>
<td>DFB/1.75</td>
<td>MCT/Yes</td>
<td>3359.2</td>
<td>57.6</td>
<td>Fs=50 Fm=16k</td>
<td>1s</td>
<td>5-100ppb 0.74ppb</td>
</tr>
<tr>
<td>Reference</td>
<td>Detection Technique</td>
<td>Application</td>
<td>Target Species</td>
<td>Laser Type / Optical Power [mW]</td>
<td>Detector Type / integrated?</td>
<td>Targeted Wavelength (nm)</td>
<td>Optical Path Length (m)</td>
<td>Modulation Frequency (Hz)</td>
<td>Integration/Tim e (s)</td>
<td>Absorption</td>
</tr>
<tr>
<td>-------------------</td>
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<td>-------------------</td>
</tr>
<tr>
<td>Schwarm et al - 2020</td>
<td>WMS - 2f/1f</td>
<td>Ketogenic diet application of astigmatic multi-pass cell for trace detection of acetone in human breath samples</td>
<td>Acetone</td>
<td>DFB QCL/&lt;10</td>
<td>HgCdTe/Yes</td>
<td>8196.72</td>
<td>76</td>
<td>Fs=100 Fm=100k</td>
<td>1s</td>
<td>0.5-20ppm</td>
</tr>
<tr>
<td>Xia et al - 2019</td>
<td>WMS - 2f</td>
<td>Trace analysis of human breath samples using Herriott multi-pass cell</td>
<td>Acetone</td>
<td>DFB ICL/10</td>
<td>HgCdTe/Yes</td>
<td>3367</td>
<td>15.8</td>
<td>Fs=1 Fm=10k</td>
<td>1s</td>
<td>0-200ppm</td>
</tr>
<tr>
<td>Michel et al - 2016</td>
<td>WMS - 2f</td>
<td>Path integrated trace detection of methane in field/harsh environments through long free-paths</td>
<td>Methane</td>
<td>QCL/40</td>
<td>Cooled MCT/Yes</td>
<td>8000</td>
<td>458</td>
<td>Fs=100 Fm=40k</td>
<td>1s</td>
<td>0-2ppm</td>
</tr>
<tr>
<td>Xia et al - 2019</td>
<td>WMS - 2f</td>
<td>Open path monitoring of ambient GHG concentrations over extended lengths</td>
<td>Methane Carbon Dioxide</td>
<td>DFB/10</td>
<td>InGaAs/Yes</td>
<td>1654 1602</td>
<td>1300</td>
<td>Fs=2 Fm=20k</td>
<td>1s 20s</td>
<td>2-3.5ppm</td>
</tr>
</tbody>
</table>

Montori et al. (2015) demonstrated improved SI concentration measurements through a Constant Intensity Direct Absorption Spectroscopy (CIDAS) approach in which constant power\textsuperscript{14} from a sweeping laser source was directed through varying interrogation lengths. Results demonstrated improved sensitivity and detection in controlled CO\textsubscript{2} and CH\textsubscript{4} species test using CIDAS, whereas traditional DA approaches were either unable to detect absorption features (due to the large variation in laser power) or demonstrated poor SNR. Acquisition sensitivity of 1.651 μm CH\textsubscript{4} absorption feature through 1.61-5.62 m pathlengths showed a 40x better minimum detectable absorption of CIDAS compared to DA sweeps, with further recognition that longer pathlength were required for traditional DA measurements. In addition to improved sensitivity requiring smaller pathlength, the CIDAS approach benefits from immediately visible absorption signals which can assist with ease in alignment and laser tuning. Such method may expand utility or be used to develop simplified sensors for monitoring of other compounds (i.e., sequenced monitoring) in relation to the cross-pipe sensor in order to refine measurements.

Davis et al. (2016) presented a novel SI instrument which utilized a 10 cm diameter integrating sphere (effective pathlength 54.5 cm) approach as a multi-pass cell for probing of the 3.3 μm CH\textsubscript{4} absorption lines. The integrating sphere interior was gold coated and diffusely reflective, with the added quality that they are tolerant to misalignment and do not suffer from interference fringes (Tranchart et al., 1996) unlike traditional optical cells. Results were compared with a more typical single-pass cell design (effective pathlength 25 cm) in which concentrations dilutions between 0-1010 ppm CH\textsubscript{4} were tested in a controlled laboratory setting to compare quantitative performance. Detection limits of 1.0 and 2.2 ppm were reported for the integrating sphere and single-pass cell, respectively, with concluding remarks describing the desirability of the integrating sphere design over traditional TDLAS in vibrationally sensitive applications such as in-situ field environments.

\textsuperscript{14} Acousto-Optic Modulator (AOM) was used to deflect a fraction of the inputted laser beam through circuitry stabilization and automated monitoring of the driving radiofrequency to maintain a constant probing power.
Tian et al. (2021) implemented a DA based system utilizing a Harriott cell (with 3 m effective pathlength) which used neural networks (NN) and deep learning for species recognition and concentration measurements of CH$_4$ and C$_2$H$_2$. The study compared a custom deep NN SI subroutine to traditional WMS based measurement, as well as three other typical machine learning algorithms (decision tree regression, adaptive boosted decision tree regression, and K-nearest neighbor) for concentration mixtures ranging between 0-1000 ppm and 0-500 ppm of CH$_4$ and C$_2$H$_2$, respectively. The custom routine was integrated with a transfer learning protocol (Wilcoxon signed-rank test) which enabled successive training of the algorithm when provided with only a small initial training set of data, and was found to consistently outperform the other mentioned routines by multiple orders of magnitude. Interestingly, the deep learning protocol was found to provide comparable or better levels of accuracy to traditional WMS measurements, with absolute mean errors of 1.1794 ppm and 1.3827 ppm versus 1.2843 ppm and 1.4083 ppm (CH$_4$ and C$_2$H$_2$, respectively) for the NN SI routine and WMS system, respectively, over the full-scale range of testing. The results demonstrate promising application for further NN integration into trace gas diagnosis of TDLAS measurements, with added recognition benefits of blended absorption features and separation inherently integrated into the fully automated system. In application to the cross-pipe system, utilization of NN assisted peak searching routines may prove beneficial to accommodate ternary, quaternary, etc. effects as a result of contaminants in the vented streams. Similar to the information contained within Tian et al. (2021), however, such method would require (pre-)training of the post-processing script to interpret secondary collision effects of known compounds in relation to characterized oxygen absorption peaks. While such method could eventually be employed on harmonics of the WMS signal, initial testing can be performed on SI signal for simplicity and proof-of-concept moving forwards.

Sun et al. (2013) introduced a novel approach of calibration free WMS which utilized the 1f harmonic signal (which is intensity dominated due to injection-current-modulated TDL) to normalize the 2f harmonic measurement without the need for a zero-absorption baseline. Demonstration targeting 0.75% H$_2$O in air through a 1.005 m pathlength showed good agreement with the targeted absorption feature of interest. While desirable, Sun recognized the applicability of such method was limited to the optically thin
region ($\alpha < 0.045$), beyond which decreasing amplitude towards zero ($0$) in the crossover point from the $1f$ signal can result in erroneous results in the normalized signal (Chang et al., 2022). Hosseinzadeh Salati & Khorsandi (2014) proposed an apodized $2f/1f$ method to address this issue, which aims to suppress negative wings in the harmonic signals to further accent the peak height and location. This approach was demonstrated in a controlled experiment probing the $2.328 \mu m$ CO absorption feature through a $15 cm$ absorption tube for volume fractions between 0-88%, with readings demonstrating good correlation beyond the optical thin limit. Khorsandi & Ghavami Sabouri (2020) further visited this method in 2020 concerning industrial monitoring of CO and CO$_2$ levels through which controlled lab coal-combustion experiments and supplemental experiment on a recuperator channel of a gas-powered furnace (through an 8 m multi-pass instrument) were presented. Varying excess air amounts were provided in the lab between 60-80%, with fast response of the system to observe anticipated effects of increased CO and CO$_2$ production from 5-11% and 3-8%, respectively. An industrial field test demonstrated CO and CO$_2$ concentrations VMRs of $< 1\%$ and $< 9.5\%$, respectively, which agreed with automated concentrations monitoring reports provided through daily SMPP$^{15}$ protocols. While initial testing using $2f/1f$ was briefly considered using the optical variant, it was discontinued in the later rebuild of the system after initialization of the new diode found issue with the $1f$ signal response. Further consideration of this method maybe beneficial. As noted in Sun et al. (2013), in situation where the $1f$ signal experiences cross-over, an averaged $1f^*$ feature may be used instead without greatly sacrificing inherent intensity dominated components within the $1f$ feature.

$^{15}$ Short Message Peer-to-Peer – an industrial standardized protocol used for reporting and relaying data communications to and from associated mobile devices.
Appendix B: Modulation Characterization

B.1 Eblana Diode Characterization Report

Prepared by Simon Festa-Bianchet
Data collected by Scott Seymour
Edited by Fraser Kirby

Energy & Emissions Research Lab.
Carleton University

26/03/2020

• Introduction
The following results were collected from characterization tests done on an Eblana diode to measure the intensity vs wavelength response. Both sweep and modulation were tested. Sweep signals (sinusoid) were collected at 938kHz for 524,288 points, while modulation signals were collected at 60 MHz for 262,144 points. This higher sampling frequency was required to resolve the fiber ring resonator during modulation. Data were collected using a single MFLI lock-in, with the MD-DIG option installed so that both the voltage and current inputs could be sampled simultaneously. The collected signals were:
Ch1: Eagle board voltage from FRR

Ch2: Current measurement from bare photodiode for intensity reference

The laser was operating at 7.7 °C and 59.34mA.

The LabView VI is titled “Laser Intensity parameters.vi”

- **Processing Steps**

All signals (intensity and FRR) were decimated by a factor to allow for faster processing, this factor is included in the attached screen grabs and data. The fiber ring resonator (FRR) signal was normalized by its maximum and then the Labview Peak Finder VI was used to identify the peaks. These peaks were then spaced out by the FSR of the FRR (0.001153 cm⁻¹) and fit using the non-linear curve fit VI, with model \( (d + a\cos(wx + p) + a_2\cos(w_2x + p_2)) \) where \( a/a_2 \) are the amplitudes, \( w/w_2 \) are the frequencies, \( p/p_2 \) the phases, \( d \) is a constant value to account for the wavelength curve not being symmetric about 0, and \( x \) is time step. Note that the second frequency is not usually included in wavelength models and was only used here as it produced a better fit. This same model was also used to fit the intensity data, but without the constant \( d \). The average intensity was removed before the fit by subtracting the mean value from the data set. Note that all intensity data is in [A], or the direct photodiode current. The figures below for modulation incorrectly display it as [V]. This error does not affect interpretation since these values are normalized by the mean intensity (see below). The phase is also incorrectly labeled as [Hz] instead of [deg] in the modulation screenshots. The phase of the principal frequency of the wavelength curve was set to 0 and the other phases adjusted to reference this zero. This was done to follow the established nomenclature in literature where the frequency is given with no phase and the intensity’s phase is with respect to the wavelength.

**Note that in the above model the linear and non-linear modulation amplitudes, \( a \) and \( a_2 \), are the amplitudes normalized by \( d \). This is not the case for the amplitudes identified in the Labview code, so these values must be normalized by \( d \) before using them in the model.**
• Results

• Modulation

  File: \Phase Shift FRR\Signals\Mod_5kHz_025V\meas_scope_20200228_113229.txt

  File: \Phase Shift FRR\Signals\Mod_10kHz_025V\meas_scope_20200228_112650.txt
Modulation Results

With a driving voltage of 0.25V here are the characteristics of this diode’s response:

<table>
<thead>
<tr>
<th>Mod Freq</th>
<th>$i_0$ [-]</th>
<th>$\psi_1$ [deg]</th>
<th>$i_2$ [-]</th>
<th>$\psi_2$ [rad]</th>
<th>$a$ [cm$^{-1}$]</th>
<th>$a_2$ [cm$^{-1}$]</th>
<th>$\phi_2$ [rad]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5000</td>
<td>1.339E-01</td>
<td>190.69</td>
<td>3.36E-04</td>
<td>292.75</td>
<td>0.1925</td>
<td>0.003363</td>
<td>288.02</td>
</tr>
<tr>
<td>10000</td>
<td>1.340E-01</td>
<td>192.79</td>
<td>3.25E-04</td>
<td>287.68</td>
<td>0.1792</td>
<td>0.003145</td>
<td>287.55</td>
</tr>
<tr>
<td>20000</td>
<td>1.342E-01</td>
<td>196.26</td>
<td>3.28E-04</td>
<td>279.04</td>
<td>0.1657</td>
<td>0.002935</td>
<td>286.02</td>
</tr>
</tbody>
</table>

It is assumed that the above amplitudes are linearly dependent on the driving voltage, and so can be adjusted based on the selected modulation voltage. Ideally data should be collected at the modulation voltage which is to be used in flux measurements. In case they are required, here were the values for the mean intensity (removed before fit and used to normalized amplitudes):

<table>
<thead>
<tr>
<th>Mod Freq</th>
<th>$I_{bar}$ [A]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5000</td>
<td>0.000669841</td>
</tr>
<tr>
<td>10000</td>
<td>0.000670388</td>
</tr>
<tr>
<td>20000</td>
<td>0.00067071</td>
</tr>
</tbody>
</table>
- **Sweep**
  - File: \Sweep_sine10Hz\_07V\meas\_scope\_20200228\_123713.txt
  ![Sweep sine 10Hz plot](image1)

- File: \Sweep_sine20Hz\_07V\meas\_scope\_20200228\_114104.txt
  ![Sweep sine 20Hz plot](image2)

- File: \Sweep_sine40Hz\_07V\meas\_scope\_20200228\_124132.txt
  ![Sweep sine 40Hz plot](image3)
• File: \Sweep_sine50Hz_07V\meas_scope_20200228_123443.txt

• Sweep Results

With a driving voltage of 0.7V here are the characteristics of this diode’s response:

<table>
<thead>
<tr>
<th>Sweep Freq</th>
<th>$i_0$ [-]</th>
<th>$\psi_1$ [deg]</th>
<th>$i_2$ [-]</th>
<th>$\psi_2$ [rad]</th>
<th>$a$ [cm$^{-1}$]</th>
<th>$a_2$ [cm$^{-1}$]</th>
<th>$\phi_2$ [rad]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>3.676E-01</td>
<td>181.07</td>
<td>2.08E-03</td>
<td>195.26</td>
<td>0.7755</td>
<td>0.039045</td>
<td>200.76</td>
</tr>
<tr>
<td>20</td>
<td>3.696E-01</td>
<td>181.41</td>
<td>2.33E-03</td>
<td>200.52</td>
<td>0.7711</td>
<td>0.038722</td>
<td>201.19</td>
</tr>
<tr>
<td>40</td>
<td>3.723E-01</td>
<td>182.10</td>
<td>2.27E-03</td>
<td>204.06</td>
<td>0.7641</td>
<td>0.038254</td>
<td>200.72</td>
</tr>
<tr>
<td>50</td>
<td>3.716E-01</td>
<td>182.38</td>
<td>2.27E-03</td>
<td>203.74</td>
<td>0.7611</td>
<td>0.038047</td>
<td>200.85</td>
</tr>
</tbody>
</table>

With average intensities:

<table>
<thead>
<tr>
<th>Sweep Freq [Hz]</th>
<th>$I_{bar}$ [A]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.000675433</td>
</tr>
<tr>
<td>20</td>
<td>0.000672003</td>
</tr>
<tr>
<td>40</td>
<td>0.000668133</td>
</tr>
<tr>
<td>50</td>
<td>0.000669341</td>
</tr>
</tbody>
</table>

For the purposes of the velocity algorithm and the conversion between sweep amplitude in volts from the FGEN to wavelength amplitude in cm$^{-1}$ output by the diode:
B.2 DCN2341 Diode Tuning and Resulting Modulation Characterization

Similar characterization was performed on the initial diode (DCN2341) from Eblana photonics as described in Chapter 3. The resulting tuning range is shown in Figure B.1.

Modulation parameters for five separate modulation frequencies the resulting laser characterization is shown in Table B-1, the 20 kHz signal modulation was ultimately used.

<table>
<thead>
<tr>
<th>Modulation Frequency [Hz]</th>
<th>Modulation Voltage [V]</th>
<th>$i_0$ [-]</th>
<th>$\psi_1$ [deg]</th>
<th>$i_2$ [-]</th>
<th>$\psi_2$ [deg]</th>
<th>$a_1$ [cm$^{-1}$]</th>
<th>$a_2$ [cm$^{-1}$]</th>
<th>$\phi_2$ [deg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>0.125</td>
<td>6.4389E-02</td>
<td>189.01</td>
<td>1.9629E-04</td>
<td>129.95</td>
<td>0.1011</td>
<td>0.000442</td>
<td>244.58</td>
</tr>
<tr>
<td>5000</td>
<td>0.22</td>
<td>1.0359E-01</td>
<td>190.67</td>
<td>2.3304E-04</td>
<td>73.13</td>
<td>0.1216</td>
<td>0.000486</td>
<td>214.85</td>
</tr>
<tr>
<td>10000</td>
<td>0.3</td>
<td>1.1482E-01</td>
<td>191.69</td>
<td>3.7155E-04</td>
<td>148.40</td>
<td>0.1242</td>
<td>0.000714</td>
<td>176.09</td>
</tr>
<tr>
<td>20000</td>
<td>0.45</td>
<td>1.1207E-01</td>
<td>193.02</td>
<td>4.0677E-04</td>
<td>203.05</td>
<td>0.1114</td>
<td>0.000725</td>
<td>140.14</td>
</tr>
<tr>
<td>50000</td>
<td>1.2</td>
<td>1.3385E-01</td>
<td>196.65</td>
<td>6.0463E-04</td>
<td>247.65</td>
<td>0.1177</td>
<td>0.000813</td>
<td>129.30</td>
</tr>
</tbody>
</table>
Appendix C: Cross-pipe cell - IRcell Enclosure Schematics

CAD Schematics for references purposes only. All components manufactured from 316 SS unless otherwise specified.

CAD Files available at: https://1drv.ms/f/s!AoG753QP5F290n9mu3fFE5Dxr-ec
C.1 Optical Variant

Figure C.1: Top Flange.
Figure C.2: Spacer Block.

Spacer Plate - Fraser Kirby
ALL DIMS IN INCHES
Date: 2020-11-27
Figure C.3: Mounting Plate with added modifications.
Figure C.4: Instrumentation Cover.
Figure C.5: Instrumentation Fitting.
Figure C.6: Optical Block for Fiber Connections.
C.2 Revised Detector Variant

Figure C.7: Optical Block for Diode Connection.
Figure C.8: Diode Enclosure.
Figure C.9: Viewing Window.
Figure C.10: Revised Mounting Plate.
Figure C.11: Revised Spacer Block.
Figure C.12: Revised Top Flange.
Figure C.13: Revised Instrumentation Cover.
Figure C.14: Revised Instrumentation/Reduction Fitting.