HYDROGEN PURITY ASSESSMENT USING LASER ABSORPTION SPECTROSCOPY.

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Abstract

Hydrogen purity assessment is a critical concern in energy applications, especially in fields involving hydrogen injection into natural gas pipelines and fuel cell research. This study addresses the limitations of current hydrogen measurement techniques by developing a novel hydrogen spectrometer (H_2-Spectrometer) based on direct Tunable Diode Laser Absorption Spectroscopy (d-TDLAS). The goal is to establish a traceable and accurate methodology for hydrogen purity and concentration measurement without relying on calibration gases. The main objective of this research is to develop and evaluate the performance of the H_2-Spectrometer, specifically investigating its suitability for measuring hydrogen purity and hydrogen concentration in methane-hydrogen mixtures. The study also aims to support hydrogen injection into natural gas pipelines by providing precise hydrogen concentration measurements.

An experimental design was employed, utilizing the H_2-Spectrometer to measure hydrogen line intensity and concentration. The measurements were taken for 99.999% pure hydrogen and hydrogen-methane gas mixtures to test the spectrometer's accuracy and reliability. The obtained data were compared against reference values from the HITRAN database and the certificate from the reference gas mix to evaluate performance. The findings revealed that the H_2-Spectrometer demonstrated a significantly lower uncertainty of 1.6% in hydrogen line intensity measurements, compared to the 10% uncertainty reported in the HITRAN database. The measured line intensity obtained was 3.22×10^{-26} cm/molecule, which is slightly higher than the HITRAN value of 3.189×10^{-26} cm/molecule. In terms of hydrogen concentration, the spectrometer achieved an average mole fraction of 0.858 with a 1% uncertainty, closely aligning with the expected value of 0.900 as per the certificate from the reference gas mix with a 2% uncertainty. The H_2 Spectrometer proved to be highly

accurate and reliable, with potential applications in hydrogen quality control from electrolysis, fuel cell research, process control, and environmental monitoring. Its ability to provide traceable and precise measurements makes it a valuable tool for hydrogen-related research, optimizing system performance and ensuring compliance with regulatory standards.

Keywords:

Direct Tunable Diode Laser Absorption Spectroscopy, Hydrogen Spectrometer, Purity Assessment, Traceable Infrared Laser-Spectrometric Amount Fraction Measurement (TILSAM).

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Dedication

This thesis is dedicated to the courageous souls who came before me, those who crawled so that I might learn to walk. To my parents who shattered chains of expectation and opened doors of opportunity: may your legacy remind me that adversity is not an end but the forge of greatness. To my grandmother, whose survival of the Cassinga massacre stands as a living testament to resilience and grace: your story kindles the spark of perseverance in my heart.

To my mother, whose gentle spirit nurtured me from the moment I lay within her womb, whose arms carried me through each new discovery, and whose laughter has been the melody guiding every day. Your love was my first home, your encouragement my first lesson in courage, and your warmth the foundation upon which I stand. To the sisters and brothers the universe has so generously blessed me with, you have made life's journey a shared wonder. Thank you for your unwavering support, acceptance, and kindness. My world is infinitely more beautiful with you in it.

To friends and mentors who celebrated every small victory, illuminated the path in moments of doubt, and taught me that hope is a flame we carry together.To the children of the African soil: may you rise on the strength of your ancestors' dreams; may no barrier stand taller than your resolve; and may this work inspire you to dream beyond every horizon.

To all the little girls and women whose lives were stolen by violence, whose laughter now echoes in our memories: your absence demands justice. In a land that proclaimed freedom for some, our daughters still hear only echoes. Our fathers bled for the liberty of their children, yet our mothers' silent tears fell on deaf ears. May your names become the rallying cry for a justice that protects every childhood. Finally, to future generations of scientists and explorers: may these pages serve as a stepping stone toward a brighter, more innovative future in hydrogen purity and spectroscopy.

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List of Abbreviations

CRM Complement Calibration Gases

CRDS Cavity Ring-Down Spectroscopy

DAS Direct Absorption Spectroscopy

d-TDLAS Direct Tunable Diode Laser Absorption Spectroscopy

FID Flame Ionization Detection

FTIR Fourier Transform Infrared Spectroscopy

GC Gas Chromatography

H2 Hydrogen

HITRAN High-Resolution Transmission Molecular Absorption Database

ISO International Organization for Standardization

LAS Laser Absorption Spectroscopy

LGA Laser Gas Analysers

MS Mass Spectrometry

OGS Optical Gas Standards

TCD Thermal Conductivity Detection

TDLAS Tunable Diode Laser Absorption Spectroscopy

TILSAM Traceable Infrared Laser-Spectrometric Amount Fraction Measurement

WMS Wavelength Modulation Spectroscopy

Nomenclature

General Notations

LAS	Laser Absorption Spectroscopy. This technique is pivotal for measuring gas concentrations, including hydrogen purity, by analyzing how light is absorbed by gas molecules.
TDLAS	Tunable Diode Laser Absorption Spectroscopy. A specific type of LAS that utilizes tunable diode lasers to achieve high sensitivity and selectivity in gas analysis.
CRDS	Cavity Ring-Down Spectroscopy. Another advanced LAS technique that enhances measurement accuracy by analyzing the decay time of light in a cavity filled with the gas being measured.
TILSAM	Traceable Infrared Laser-Spectrometric Amount Fraction Measurement. This method ensures precise and traceable measurements of gas concentrations, which is essential for applications in environmental monitoring and industrial process control.
OGS	Optical Gas Standards. A new approach to calibration processes that provides a true reference for measuring gas concentration, enhancing the reliability of measurements.
ISO	International Organization for Standardization. This organization sets the standards for hydrogen purity, particularly for applications like proton exchange membrane (PEM) fuel cells, which require high purity levels (99.999%)

GC	Gas Chromatography. A widely used analytical technique for separating and analyzing gaseous mixtures, often employed in conjunction with detectors for hydrogen purity measurements.
FID	Flame Ionization Detection. A type of detector used in gas chromatography that is effective for identifying hydrocarbons and contaminants in hydrogen gas.
TCD	Thermal Conductivity Detection. Another detector used in gas chromatography, sensitive to changes in thermal conductivity, making it suitable for hydrogen detection.

Declaration

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Signed: Rosamunde Shilongo

Date: 1 OCTOBER 2025

Chapter 1

Introduction

1.1 Background and Motivation

Hydrogen (H_2) is emerging as a cornerstone of the global shift to clean energy. Rather than competing with other renewable sources, hydrogen complements them by mitigating intermittency and providing long-duration storage solutions [1, 2]. As a versatile energy carrier, it offers a viable pathway to decarbonize power generation, transportation, and industrial processing [2, 3]. Despite this promise, widespread adoption is hindered by high production costs, insufficient transport and storage infrastructure, and underdeveloped regulatory frameworks [2].

Robust policies and a comprehensive quality infrastructure are crucial to unlocking hydrogen's full potential. The International Renewable Energy Agency (IRENA) roadmap for green hydrogen development emphasizes the need for harmonized standards, advanced measurement techniques, and certification schemes to guarantee safety, traceability, and market confidence [4]. In particular, internationally recognized certification schemes that verify hydrogen's renewable origin will facilitate transparent global trade, while standardized measurement protocols and precise spectroscopic methods form the backbone of reliable hydrogen purity assessment [4]. Integrating renewable energy inputs into hydrogen production further reduces carbon emissions in energy-intensive

industries. Establishing a unified global framework for hydrogen quality infrastructure will not only protect consumers but also accelerate innovation and cross-sector collaboration.

Accurate hydrogen purity measurement underpins the performance, safety, and lifespan of hydrogen-based systems. Different applications impose distinct purity requirements; for instance, proton-exchange membrane (PEM) fuel cells demand hydrogen of at least 99.999% purity to prevent catalyst poisoning and maintain high efficiency [5, 6]. Even trace contaminants can impair electrochemical reactions and damage sensitive components, making reliable analytical methods indispensable [7, 8]. In pipeline transport, controlling impurities such as carbon monoxide and sulfur compounds is essential to avoid infrastructure degradation and safety hazards [9].

Traditional techniques gas chromatography (GC), mass spectrometry (MS), Fourier transform infrared spectroscopy (FTIR), and electrochemical sensors are well-established but exhibit inherent drawbacks. GC requires complex sample preparation and may lack sensitivity for trace impurities, while MS demands costly instrumentation and can suffer isobaric interferences [10, 11, 12, 13]. FTIR offers simultaneous multi-species detection but is challenged by overlapping absorption bands and limited portability [14]. Electrochemical sensors are compact and user-friendly yet prone to cross-sensitivity and long-term drift [15].

Laser absorption spectroscopy (LAS) overcomes many of these limitations by exploiting unique molecular absorption features for selective, real-time detection [16, 17]. LAS systems operate non-invasively, deliver rapid response, high sensitivity, excellent selectivity, and require minimal maintenance. These qualities are ideal for in situ and

online monitoring [16, 18, 17]. Direct tunable diode laser absorption spectroscopy (d-TDLAS) employs compact, cost-effective lasers with fine spectral resolution to target specific hydrogen absorption lines [19]. It has proven effective across environmental monitoring, industrial process control, medical diagnostics, and combustion analysis, and provides direct traceability to SI units in line with metrological standards [19, 20].

Despite these advantages, many LAS implementations still rely on calibration gases and may struggle with complex gas matrices. A portable, calibration-free spectrometer offering SI-traceable, high-precision hydrogen measurements in field environments; such as natural gas pipelines, remains elusive.

To bridge this gap, this thesis pursues two primary objectives:

1. Develop a precise, calibration gas free Hydrogen Spectrometer that delivers hydrogen concentration measurements traceable to the SI unit.

2. Evaluate the suitability of the developed H_2-Spectrometer for analysing methane–hydrogen mixtures in the context of hydrogen injection into natural gas pipelines.

Chapter 2

Theoretical and Experimental Fundamentals

2.1 Introduction

Hydrogen has become a critical enabler of the energy transition, facilitating emission reduction in transport, industrial processes, and power generation. Its utility as a clean, high-efficiency energy carrier hinges on ultra-high purity, since even trace contaminants can poison proton-exchange-membrane fuel-cell catalysts and degrade performance across applications [7, 21, 22, 23, 24, 25, 26].

Purity, defined as the absence or minimal presence of unwanted constituents, is critical not only for fuel cells but also for chemical synthesis, metallurgy, and semiconductor manufacturing. In fuel-cell stacks, contaminants such as CO and H_2S rapidly bind to platinum sites, reducing efficiency and lifetime [27, 8, 28, 29]. In hydrogen annealing of metals, impurity levels directly influence grain structure and mechanical properties [30, 31], while in microelectronics, trace gases can introduce fatal defects in device fabrication [28, 25, 32].

This chapter synthesizes the theoretical rationale and experimental methodologies underpinning hydrogen purity assurance. The evolution, scope, and harmonization of major standards will be reviewed. Advanced analytical techniques that are classified into chromatographic, spectroscopic, and electrochemical methods will be assessed, evaluating their sensitivity, selectivity, and compliance challenges within standardized frameworks.

2.2 Hydrogen Purity Standards and Requirements

The international standard ISO 14687-2 establishes the maximum allowable levels of impurities in hydrogen for proton exchange membrane (PEM) fuel cell vehicles, ensuring that dispensed hydrogen meets strict purity and consistency criteria for safe and efficient operation [33, 6, 29]. Beyond ISO 14687-2, rigorous international standards ISO 14687:2025, EN 17124:2022, SAE J2719:2020, and CGA G-5.3-2024 govern impurity thresholds and verification protocols throughout hydrogen production, transport, and dispensing [34, 35, 14]. EN 17124 aligns its impurity limits with ISO values, while SAE J2719 and CGA G-5.3 define grading schemes tailored for industrial and research applications [22, 36, 21]. The latest ISO 14687:2025 specifies application-based concentration limits for key contaminants in units of µmol/mol or ppm (v/v). Table 2.1 provides a compact comparison of the maximum permissible levels as defined by these leading guidelines.

TABLE 2.1: Selected Maximum Impurity Levels in Hydrogen Fuel According to ISO 14687:2025, EN 17124, and CGA G-5.3

Impurity	ISO 14687 (µmol/mol)	EN 17124 (µmol/mol)	CGA G-5.3 (ppm)
H_2O	5	5	1
O_2	5	5	1
N_2	300	100	10
CH_4	100	100	1
THCs (excl. CH_4)	2	2	1
HCHO	0.2	0.01	–
CO	0.2	0.2	0.1
CO_2	2	2	1
NH_3	0.1	0.1	0.1
HCOOH	0.2	0.2	–
Halogenated compounds	0.05	0.05	0.05
Total sulfur compounds	0.004	0.004	0.003
Particulates (mass basis)	–	–	1 mg/kg

Table 2.1 shows methane (CH_4) is capped at 100 µmol/mol by both ISO and EN standards, but at 1 ppm in CGA G-5.3. Sub-µmol/mol limits for CO and total sulfur underscore the critical need to avoid platinum-catalyst poisoning in PEM fuel cells [22, 36]. EN's more stringent formaldehyde threshold (0.01 µmol/mol) versus ISO highlights regional risk priorities [33, 6, 29], while ISO's aggregation of N_2+Ar at 300 µmol/mol contrasts with EN's separate 100 µmol/mol limit for nitrogen. This harmonized yet nuanced matrix of impurity thresholds drives the demand for ultra-sensitive, selective analytical techniques.

The Compressed Gas Association further categorizes hydrogen into Quality Verification Levels (QVL) Type I and II, spanning 99.95% to 99.9999% purity grades for general through semiconductor-grade applications [37]. Such grading underscores the reversible binding of CO at 0.2 µmol/mol and the irreversible damage from sulfur species, necessitating rigorous sampling and on-site verification protocols [38].

2.3 Analytical Techniques for Purity Assessment

Accurate purity measurement is vital for regulatory compliance, process optimization, safety, and research & development. It ensures hydrogen meets acceptance criteria, prevents catalytic and mechanical failures, supports fine-tuning of fuel-cell and chemical processes to reduce costs and emissions [39, 40, 41, 7]. In sectors like pharmaceuticals and food, even trace impurities can compromise product quality and safety.

No single method can span all analytes at the ppb level. A robust metrological framework emphasizes traceability, calibration-free operation, and ISO 17025 certified validation [42].

Techniques fall into three main categories:

- Gas Chromatography (GC) and variants for separating gases such as H_2, O_2, N_2 and volatile organic compounds (VOCs).
- Spectroscopic methods such as FTIR and laser absorption spectroscopy for direct, in-line monitoring.
- Electrochemical and solid-state sensors for rapid, on-site checks at the point of dispense.

Together, these complementary approaches provide the sensitivity and selectivity required to verify hydrogen purity across production, distribution, and end-use stages [43].

2.3.1 Chromatographic Techniques

2.3.1.1 Gas chromatography (GC)

Gas chromatography (GC) is a widely used analytical technique for the separation, identification and analysis of gaseous mixtures based on the partitioning of substances between a stationary phase and a mobile gas phase [10, 44, 11, 45]. For measurements of hydrogen purity, GC is frequently used in conjunction with detectors such as thermal conductivity detection (TCD) or flame ionization detection (FID), which provide comprehensive information on the components of gases. While FID detects hydrocarbons and is effective for identifying contaminants in hydrogen gas, TCD is sensitive to changes in thermal conductivity, making it excellent for hydrogen detection. In spite

of its great sensitivity and accuracy in identifying minute impurities, GC necessitates intricate sample preparation, calibration gases, and lacks real-time, in-situ observations [10, 44, 11, 45]. Recent advancements in GC have improved sensitivity and speed, but limitations regarding real-time analysis remain a challenge in fast-paced environments.

2.3.2 Spectroscopic Techniques

2.3.2.1 Mass Spectrometry (MS)

Mass spectrometry (MS) is a high-precision technique that predicts the mass-to-charge ratio of ionized molecules recovered from the gas sample and accurately determines the quantity of those species [12]. MS is especially useful for analysing hydrogen purity because it can measure almost any type of impurity, with detection limits on the order of parts per billion for gases such as methane, nitrogen, and oxygen [13]. However, MS systems are costly, require skilled operators, and often involve complex sample preparation, which limits their deployment for probabilistic or real-time hydrogen purity evaluation [12, 13].

MS, frequently coupled to GC or thermal desorption (TD, GC, MS), provides the resolution and sensitivity required for volatile organic halides, formaldehyde, and trace hydrocarbons [36, 22].

Key advantages:

- **Compound specificity**: Identifies individual species even within complex mixtures.

- **Pre concentration compatibility**: Supports cryogen-free enrichment for sub-ppb analysis [36].
- **Simultaneous multicomponent detection**: Multiple impurity classes quantified in a single run.

Recent method developments (e.g. ASTM D7892-2025) highlight advances in cryogen-free operation, enabling laboratories to efficiently measure total organic halides, non-methane hydrocarbons, and formaldehyde for sustainable hydrogen testing workflows [36].

2.3.3 Electrochemical Techniques

2.3.3.1 Thermal Conductivity Detection (TCD)

A Thermal Conductivity Detector (TCD) measures the change in thermal conductivity of a gas mixture via a heated filament in a flow cell [46, 47]. When a carrier gas (usually helium or nitrogen) flows through the cell, the filament maintains a steady temperature. Introduction of a sample gas with different thermal conductivity (such as hydrogen) alters the filament's temperature and thus its electrical resistance, which is recorded to quantify the sample composition [46, 47].

TCDs are well-suited for hydrogen detection due to hydrogen's significantly lower thermal conductivity compared to most other gases. However, they exhibit lower sensitivity compared to detectors like FID or MS and lack specificity different gases with similar thermal conductivities can interfere, limiting trace-level hydrogen measurements [46, 47].

2.3.3.2 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) uses IR absorption spectra as molecular fingerprints to determine gaseous mixture composition. It is applied to detect small amounts of impurities in hydrogen fuel such as methane, CO, and CO_2, based on distinct IR absorption bands [14]. FTIR offers fast, real-time, multi-component analysis providing ultra-high speed for individual target gases. Diatomic molecules like H_2 lack a dipole moment and thus are IR-inactive, so hydrogen itself is not directly measured. FTIR is employed for species with strong IR-active transitions, notably ammonia, formic acid, and formaldehyde, with LODs typically around 0.02 μmol/mol [36, 48, 21]. Overlapping spectral lines and the need for calibration standards complicate continuous monitoring, though recent advances have extended FTIR to online trace gas detection in hydrogen purity assessment [14]. Thus, real-time multi-species demands in hydrogen purity workflows are increasingly met by laser absorption spectroscopy (LAS), which combines rapid response, high selectivity, and multiplexing capability.

2.3.3.3 Laser Absorption Spectroscopy (LAS)

LAS is a highly effective and precise method for identifying and quantifying gas-phase components. This technique exploits the unique interaction between laser light and gas molecules. When a laser beam passes through a gas sample, specific wavelengths within the laser spectrum are selectively absorbed by different molecular species [49, 50]. This selective absorption produces a characteristic spectrum for each gas, effectively serving as a molecular fingerprint [50, 51, 49, 52].

LAS offers several advantages: it provides real-time measurements of gas composition, making it suitable for process monitoring and control applications [16, 18, 53, 51]. By using lasers of specific wavelengths, LAS can selectively target and measure individual components within a gas mixture, ensuring accurate identification and quantification of impurities. This non-invasive technique is highly sensitive, capable of detecting trace amounts of gases, and is applicable across a wide range of fields, from environmental monitoring to industrial process control. Numerous studies have successfully employed LAS, demonstrating its versatility and effectiveness in various applications [50, 54, 55, 56, 44, 57].

The Beer–Lambert law, a fundamental relationship in spectroscopy, underpins LAS measurements. This law describes the relationship between light absorption and the concentration of absorbing species in a sample. Mathematically expressed as:

The Beer-Lambert Law:

$$I = I_0 e^{-\alpha \ell} \tag{2.1}$$

Or in terms of absorbance (A):

$$A = -\ln\left(\frac{I}{I_0}\right) = \alpha \ell \tag{2.2}$$

The absorption coefficient (α) is determined by the concentration C of the gas and its specific absorptivity ε:

$$A = \varepsilon C \tag{2.3}$$

where A is the absorbance, I is the transmitted light intensity, I_0 is the incident light intensity, α is the absorption coefficient, and l is the optical path length [49, 58, 59, 54, 44, 55].

This relationship highlights how light absorption depends on both the amount of gas present and its intrinsic ability to absorb light at a specific wavelength [49, 58, 59, 54, 44, 55, 60]. Absorbance is directly proportional to concentration: If the concentration of the absorbing species increases, the absorbance will also increase, assuming the path length and molar absorptivity remain constant.

LAS can detect even trace amounts of impurities in hydrogen, making it suitable for applications requiring precise purity measurements. It enables researchers and engineers to determine both the composition and concentration of gases within a sample with remarkable accuracy [49, 58, 59, 54, 44, 55].

LAS has become an indispensable tool for hydrogen purity analysis, offering high sensitivity, selectivity, and real-time measurement capabilities. Various LAS methods have been developed to enhance its sensitivity and accuracy [49, 58, 59, 54, 44, 55]. Advanced implementations, such as tunable diode laser absorption spectroscopy (TDLAS), wavelength modulation spectroscopy (WMS), and frequency comb techniques, push detection limits into the sub-ppb range, enhance baseline stability, and enable multiplexed detection of multiple species in a single optical path [52, 51, 49]. Laser absorption methods thus form the analytical backbone of the thesis, underpinning development of calibration-free, traceable hydrogen purity spectrometers. The choice of LAS method depends on the specific requirements of the application, such as the

desired sensitivity, the types of impurities to be measured, and the complexity of the gas mixture.

2.4 Comparative Analysis of Laser Absorption spectroscopy Techniques

Different modifications of LAS have been subsequently designed to improve its sensitivity and accuracy of measurements. Tunable Diode Laser Absorption Spectroscopy (TDLAS) is one of the common methods used in the detection of trace gases. TDLAS employs a single tunable laser that sweeps through the absorption of targeted gases with a high level of sensitivity in the range of parts per million (ppm), or even in parts per billion (ppb) [61, 62, 63, 64, 65]. Another promising technique is Cavity Ring-Down Spectroscopy (CRDS) that measures the rate of light absorption in a gas filled optical cavity; attaining ultra-sensitive measurements, the CRDS technique is able to effectively detect low concentrations of impurities in hydrogen gas mixtures [66].

Several LAS methods are commonly used for hydrogen purity analysis:

2.4.1 Wavelength Modulation Spectroscopy (WMS)

Wavelength Modulation Spectroscopy (WMS) is a powerful technique that enhances the sensitivity and selectivity of absorption spectroscopy, including its application in hydrogen purity analysis. By modulating the wavelength of the laser source, WMS effectively suppresses background noise and improves the signal-to-noise ratio of the measurement [53, 57, 54]. As the laser wavelength is modulated, it sweeps across the

absorption line of the target gas, causing the intensity of the transmitted light to vary. This variation is detected by a detector and demodulated using a lock-in amplifier. The demodulated signal is proportional to the derivative of the absorption line shape, which can enhance the sensitivity and selectivity of the measurement [53, 57, 54].

WMS offers several advantages over conventional absorption spectroscopy. It can significantly improve the sensitivity of the measurement, allowing for the detection of low concentrations of gases. Additionally, WMS can reduce the impact of noise sources such as detector noise and laser intensity fluctuations, leading to more accurate measurements. Furthermore, WMS can distinguish between closely spaced absorption lines, improving the selectivity of the measurement [53, 57, 54].

WMS has a wide range of applications, including gas sensing, combustion diagnostics, atmospheric monitoring, and medical diagnostics. In the context of hydrogen purity analysis, WMS can be used to detect and quantify impurities such as carbon monoxide, water vapour, and hydrocarbons. By leveraging the advantages of WMS, researchers can obtain highly accurate and sensitive measurements of hydrogen purity, enabling better control and optimization of hydrogen-based technologies. This technique is often used for measuring impurities in hydrogen at low concentrations, [67] has utilized this technique for hydrogen concentration measurements.

2.4.2 Cavity Ring-Down Spectroscopy (CRDS)

Involves trapping laser light within a high-finesse optical cavity. By measuring the decay rate of the light intensity, CRDS can achieve extremely high sensitivity for detecting trace impurities in hydrogen [66, 54]. CRDS is a highly sensitive technique for

measuring the absorption of light by gas-phase molecules, uniquely suited to quantifying IR-active species such as CO, CO_2, H_2O, NH_3, CH_4, and HCHO directly in the hydrogen stream. A laser pulse is injected into a high-finesse optical cavity, where it bounces back and forth between two highly reflective mirrors. As the light interacts with the gas molecules within the cavity, it is gradually absorbed, leading to a decay in the intensity of the light. By measuring the rate of this decay, CRDS can determine the absorption coefficient of the gas with high precision. This method was discussed in more details by [68].

CRDS offers several advantages over traditional absorption spectroscopy techniques. The high-finesse cavity significantly reduces the impact of background noise and interference from other species, enabling the detection of extremely low concentrations of gas molecules [66, 54, 68]. Additionally, CRDS robustness to sample matrix effects and minimal zero/span calibration requirements. Instruments can be deployed for continuous online monitoring along the supply chain [38, 36, 21]. However, CRDS is often single- or few-species; thus, a multi-analyzer or hybrid station is required for full ISO 14687 coverage. CRDS is versatile and can be applied to a wide range of gases and applications, including hydrogen purity analysis. By leveraging the high sensitivity and selectivity of CRDS, researchers can accurately measure the purity of hydrogen gas, ensuring the quality and reliability of hydrogen-based technologies.

2.4.3 Tunable Diode Laser Absorption Spectroscopy (TDLAS)

Tunable Diode Laser Absorption Spectroscopy (TDLAS) is a powerful and versatile technique for measuring gas concentrations with high sensitivity and selectivity. It

involves the use of a Tunable diode laser, which emits light at specific wavelengths that can be precisely controlled.

As the laser wavelength is tuned across the absorption spectrum of a target gas, the intensity of the transmitted light is monitored. When the laser wavelength coincides with an absorption line of the gas, the light is absorbed, leading to a decrease in the transmitted intensity. By measuring the change in transmitted intensity as the laser wavelength is scanned, the concentration of the target gas can be determined [69, 70, 53, 60, 71, 72, 63, 64, 73, 74, 75, 17, 20].

TDLAS offers several advantages over traditional spectroscopic techniques; It's high sensitivity allows for the detection of trace amounts of gases, making it suitable for applications requiring precise measurements. By tuning the laser to specific wavelengths, TDLAS can selectively target and measure individual gas species, minimizing interference from other components in the gas mixture. This high selectivity is crucial for accurate analysis, especially in complex gas mixtures. [69, 70, 53, 60, 72, 75, 17, 20, 76, 77, 78, 79, 73, 64, 63].

Furthermore, TDLAS enables real-time monitoring of gas concentrations, making it ideal for dynamic processes and control applications. The compact and portable nature of TDLAS systems allows for field measurements and remote sensing, expanding its applicability beyond laboratory settings, which are all qualities that [69, 70, 53, 60, 72, 75, 17, 20, 76, 77, 78, 79, 73, 64, 63] have found valuable for their studies.

In the context of hydrogen purity assessment, TDLAS is a valuable tool for monitoring the concentration of impurities such as water vapor, carbon monoxide, and hydrocarbons. By accurately measuring the absorption of light by these impurities, TDLAS

can help ensure the quality and purity of hydrogen gas, which is essential for various applications, including fuel cells, industrial processes, and scientific research; this is evident in these papers [69, 70, 53, 60, 72, 75, 17, 20, 76, 77, 78, 79, 73, 64, 63].

TDLAS is widely used for hydrogen purity measurement due to its high sensitivity and versatility. For these studies, the spectrometer is based on TDLAS, and the diode is tuned to the specific wavelength of hydrogen in the infrared region around 2121.8 nm (4712.9 cm^{-1}).

2.5 Traceable Infrared Laser-Spectrometric Amount Fraction Measurement (TILSAM)

TILSAM ensures reliable concentration measurements through rigorous calibration procedures and well-characterized reference standards and provides traceability of results to the international system of units. It employs the Beer-Lambert Law to relate measured absorption coefficients to concentrations of substances [80, 81].

The cornerstone of TILSAM is the Beer-Lambert Law, which can be used to relate measured absorption coefficients to concentrations of substances via the basic model equation for the amount fraction expressed as:

$$X_{\mathrm{H_2}} = \frac{K_B \cdot T}{S \cdot P \cdot L} \cdot A_{\mathrm{line}} \tag{2.4}$$

Where:

X_{H2} = Amount fraction for Hydrogen, dimensionless,

L = Optical path length in cm,

P = Gas pressure in bar,

K_B = Boltzmann constant, J/K,

T = Gas temperature in Kelvin,

S = Molecular Line strength of H_2, cm/molecule,

A_{line} = Absorbance peak/line Area in cm^2.

The Beer- Lambert law is explained in further details by these authors [82, 83, 64, 84, 78, 59, 66] . LAS, particularly through methodologies such as TDLAS, CRDS, and TILSAM, provides precision that is essential for applications in environmental monitoring and industrial process control. These techniques, grounded in robust theoretical frameworks and rigorous calibration protocols, represent cutting-edge advancements in gas analysis, significantly enhancing measurement reliability and accuracy.

Recent developments in the technique of spectroscopy have added more verity and reliability to the quantity of gases present in a given sample. The emergence of Optical Gas Standards (OGS) offers the possibility of an entirely new approach to calibration processes: OGS can offer a true reference for the measurement of gas concentration. A method of controlling the amount of light that is absorbed in the confines of an OGS structure is utilized to ascertain high metrological quality of the structures, and allow accurate manipulation of an operational optical path length.

2.6 Optical Gas Standard (OGS)

OGS provides a reference for calibrating optical gas detection instruments. This helps ensure accurate and reliable measurements of gas concentrations in various industrial and environmental monitoring applications [85, 86, 87, 77, 71]. Optical gas standards are essential reference materials used in spectroscopic analysis to ensure the accuracy and traceability of measurements. The potential of OGS as a calibration-free and SI-traceable metrological gas analysis instrument have been utilised by [85, 86, 87, 77, 71] to obtain line parameters and improve database values, which in-turn improves standards. These standards contain known concentrations of specific gases or gas mixtures, providing a reliable benchmark for calibrating and validating spectroscopic instruments.

There exist different types of Optical Gas Standards, namely the primary standards which are the most accurate and traceable gas standards, often prepared using gravimetric methods or volumetric techniques [81, 44]. They serve as the foundation for secondary and working standards. Secondary standards are calibrated against primary standards and are used for routine calibration of analytical instruments. Finally, there are the working standards, these are used for daily calibration and verification of instruments, ensuring consistent and accurate measurements [81, 44].

Optical gas standards are widely used in various fields, such as environmental monitoring which entails measuring pollutants such as carbon monoxide, nitrogen oxides, and volatile organic compounds. Process control which is for monitoring and controlling the composition of gas mixtures in industrial processes. In research and development,

it is used in developing and validating new spectroscopic techniques and instruments such as in this study and previous studies such as [85, 86, 87, 77, 71]. Regulatory compliance to ensure compliance with environmental regulations and industry standards is also a benefactor of OGS.

There are key Considerations for Selecting Optical Gas Standards, factors such as accuracy since the standard should have a certified accuracy that meets the requirements of the specific application. Traceability; the standard should be traceable to national or international standards and Stability because the gas mixture should be stable over time to ensure consistent measurements. Homogeneity, the gas mixture should be well-mixed to ensure uniformity throughout the container and the purity as the standard should have a high level of purity to minimize the effects of impurities on measurements [88, 85, 86, 87, 77, 71].

By using high-quality optical gas standards, researchers and practitioners can ensure the accuracy and reliability of spectroscopic measurements. These standards play a critical role in maintaining the integrity of scientific data and supporting decision-making in various fields.

2.7 Principles of Absorption Line Selection in Laser Spectroscopy

The selection of absorption lines is a critical step in laser absorption spectroscopy (LAS) as it determines the specificity, sensitivity, and accuracy of measurements. For hydrogen purity assessment, this requires a deep understanding of hydrogen's

spectral characteristics and its interaction with laser light [89, 90, 91, 92]. Proper line selection minimizes interference, enhances measurement precision, and ensures reliable quantification of hydrogen concentrations.

2.7.1 Spectral Characteristics and line selection criteria

2.7.1.1 Wavelength Specificity and selectivity

To ensure reliable measurements, absorption lines must be uniquely characteristic of hydrogen. As a diatomic molecule, hydrogen exhibits distinct absorption lines at specific wavelengths, such as 2121.8 nm (4712.9 cm^{-1}), which are largely free from interference by other molecules, this absorption spectra has been selected for several studies by [33, 67] for hydrogen sensing. By tuning the laser to a wavelength corresponding to an isolated hydrogen absorption line, background gases like methane, carbon dioxide, and nitrogen can be effectively excluded. This selectivity is essential for applications such as natural gas blending and hydrogen storage systems [93, 94, 95]. The specificity of these lines allows precise targeting of hydrogen even in complex mixtures. Advanced tunable diode lasers, offering high spectral resolution, further enhance selectivity by isolating hydrogen features for tasks such as isotopic analysis or monitoring hydrogen-methane mixtures [96, 13, 97, 98].

2.7.1.2 Sensitivity and Line Strength

Line strength quantifies how strongly hydrogen molecules absorb light at a specific wavelength, directly impacting the measurement's sensitivity. Stronger lines yield

higher signal-to-noise ratios, crucial for detecting trace concentrations of hydrogen, such as in ultra-high purity applications or when working at parts-per-million levels [33, 99, 100, 94]. Selecting robust absorption lines ensures consistent performance across varied gas pressures and compositions, minimizing noise and enhancing reproducibility. Mitigating Spectral Interference from other gases can significantly affect LAS accuracy and selecting an absorption line with minimal overlap from other spectral signatures ensures measurements are specific to hydrogen. For instance, the absorption line at 2121.8 nm (4712.9 cm^{-1}) is preferred due to its isolation from common background gases like methane and carbon dioxide [67]. Tools such as high-resolution spectroscopy and computational modelling are essential for assessing potential overlaps and selecting uncontaminated lines [65, 101, 102].

2.7.2 Practical considerations: Laser Availability

The availability of tunable lasers capable of operating at the desired wavelength is another practical consideration. One such example is the commercially available diode lasers at 2121.8 nm (4712.9 cm^{-1}) that offers the required power and stability for precise hydrogen analysis. A laser-based hydrogen (H_2) sensor using wavelength modulation spectroscopy (WMS) for the contactless measurement of molecular hydrogen was developed by [69]. These lasers provide consistent performance across varying conditions, supporting reliable and scalable applications in hydrogen purity assessment.

2.7.3 Absorption Line Characterization

Accurate characterization of absorption lines is foundational to the success of LAS measurements. Key parameters include line shape, broadening effects, and traceability, all of which influence the interaction of laser light with hydrogen molecules. These characteristics directly affect measurement sensitivity and specificity [97, 103, 104]. [96] proposed a mathematical method to determine the optimal spectral range for gas mixture analysis using theoretical absorption spectra.

2.7.4 Mechanisms of Line Shape Broadening

Mechanisms of line shape broadening can alter line shape and width, complicating spectral analysis. Accurate characterization of these effects is critical for correlating absorption features with gas concentrations. Maintaining controlled experimental conditions and applying models such as the Voigt profile are necessary to address these challenges [105, 103, 92].

2.7.5 Doppler Broadening and Gaussian Profiles

Gaussian profiles emerge from Doppler broadening, which occurs due to the thermal motion of molecules. This temperature-dependent phenomenon results in a symmetric line shape. Identifying the line center and calculating the Doppler full width at half maximum (FWHM) provides critical insights into the spectral characteristics of the frequency distribution [97, 106, 107, 108]

Mathematically, the Doppler-broadened line profile $g_D(\nu)$ is expressed as:

$$g_D(\nu) = \frac{1}{\sqrt{\pi}\Delta\nu_D} \exp\left(-\frac{(\nu - \nu_0)^2}{\Delta\nu_D^2}\right) \tag{2.5}$$

where:

- ν is the frequency,
- ν_0 is the line center frequency,
- $\Delta\nu_D$ is the Doppler width, given by:

$$\Delta\nu_D = \nu_0\sqrt{\frac{2k_BT}{mc^2}} \tag{2.6}$$

With k_B as Boltzmann's constant, T as temperature, m as molecular mass, and c as the speed of light. This formula shows that the Doppler width increases with the square root of the temperature and decreases with the molecular mass. In laser absorption spectroscopy (LAS) applications, Doppler broadening offers a critical method for determining gas temperature, with the width of the Doppler profile being directly proportional to the square root of the temperature. Recent advancements in laser technologies and spectroscopic techniques, particularly those developed by German research institutions like the Max Planck Institute for Quantum Optics, have significantly improved the precision of Doppler-based measurements [109, 110].

2.7.6 Lorentzian Profile

The Lorentzian profile emerges from pressure broadening due to molecular collisions, becoming increasingly pronounced at higher pressures and characterized by distinctively broader spectral wings compared to the Gaussian profile. Understanding the full width at half maximum (FWHM) of the Lorentzian distribution provides critical insights into the line shape and underlying physical interactions [111, 109].

The Lorentzian profile is mathematically expressed as:

$$g_L(\nu) = \frac{\Delta\nu_L}{\pi\left[(\nu - \nu_0)^2 + (\Delta\nu_L)^2\right]} \tag{2.7}$$

Where:

ν = Frequency,

ν_0 = Line center frequency,

$\Delta\nu_L$ = Lorentzian width, determined by collision rates and molecular properties.

2.7.7 Voigt Profile

is a mathematical model widely used in spectroscopy to describe line shapes under realistic conditions. It integrates Doppler broadening (Gaussian) and pressure broadening (Lorentzian), offering a comprehensive representation of absorption features. Briefly introducing these profiles provides essential context, while their detailed mathematical expressions can be referenced for deeper understanding [108, 112, 109, 106, 101].

The Voigt profile's ability to account for both Doppler and pressure broadening effects makes it indispensable for high-precision gas analysis, such as hydrogen purity assessments The Voigt profile is mathematically expressed as:

$$V(x) = \int_{-\infty}^{\infty} G(x - y)L(y)\, dy \tag{2.8}$$

Where:

- $V(x)$: Voigt profile
- $G(x)$: Gaussian profile (Doppler broadening)
- $L(y)$: Lorentzian profile (Pressure broadening)

The Voigt profile is essential for accurately modelling spectral lines in LAS applications like hydrogen purity assessment. By accounting for broadening effects, it ensures high fidelity in both simulation and experimental data analysis. Key spectroscopic parameters derived from Voigt profile fitting include the line center (frequency), full width at half maximum (FWHM), and line intensity, which are critical for quantitative analysis [108, 112, 109, 106, 101].

2.7.8 Application in Hydrogen Purity Assessment

The Voigt profile plays a critical role in hydrogen purity analysis, offering a sophisticated method to account for spectral line broadening caused by temperature, pressure, and gas composition variations. By providing a comprehensive approach to quantifying hydrogen and impurities, this technique enables precise measurements even in complex

and challenging industrial environments [113, 107, 96, 114]. Researchers from leading institutions like PTB and Fraunhofer Institutes have developed advanced computational tools that significantly improve Voigt profile fitting techniques, thereby enhancing the overall reliability and accuracy of spectroscopic measurements [113, 107, 96, 114].

2.8 High-Resolution transmission molecular absorbance database (HITRAN)

The High-Resolution Transmission Molecular Absorption Database (HITRAN) is a foundational resource for spectroscopic analysis in gaseous media. Established in the early 1970s, it provides a comprehensive compilation of spectroscopic parameters for a wide range of molecules, including line positions, intensities, and pressure-broadening coefficients. These parameters are essential for predicting and simulating the transmission and emission of electromagnetic radiation, particularly in terrestrial and planetary atmospheres. HITRAN is extensively used in atmospheric science, astrophysics, remote sensing, and laser-based gas metrology, enabling researchers to accurately model and interpret spectroscopic observations across diverse applications [115, 116].

Beyond its role as a data repository, HITRAN plays a pivotal role in the metrological sector, particularly in the development and calibration of spectroscopic instruments. Its well-defined reference spectra for known gas mixtures serve as benchmarks for calibrating spectrometers, ensuring measurement accuracy and traceability to international standards. Additionally, HITRAN provides critical data such as line intensities and

broadening parameters that support the quantification of measurement uncertainties, a cornerstone of precision metrology [115, 54, 58].

The database also underpins the development of new spectroscopic techniques and algorithms. Its extensive molecular data enables researchers to model complex interactions and refine analytical methods, fostering innovation in optical diagnostics. Moreover, HITRAN serves as a trusted reference for validating results across diverse spectroscopic platforms, ensuring consistency and reliability in both laboratory and field measurements [115, 54, 117, 58].

In the context of hydrogen purity assessment, HITRAN's relevance becomes even more pronounced. The database offers high-resolution spectral data for hydrogen and trace impurities such as water vapor (H2O), methane (CH4), carbon monoxide (CO), and nitrogen (N2) [118, 116]. This information enables the selection of optimal laser wavelengths for precise impurity detection and supports the simulation of hydrogen-containing gas mixtures under varying environmental and operational conditions. Such simulations are instrumental in designing and optimizing spectrometer components, including optical paths, filters, and detectors.

This research leverages HITRAN data to facilitate the development of a novel spectrometer tailored for hydrogen purity measurements. By incorporating HITRAN-based reference spectra, the spectrometer can be calibrated against established standards, ensuring accuracy and reliability. Furthermore, the integration of HITRAN data into uncertainty propagation models allows for a rigorous assessment of measurement uncertainty, accounting for variables such as line intensity fluctuations and pressure

broadening effects. Ultimately, HITRAN's comprehensive spectroscopic dataset enables the creation of instruments with enhanced sensitivity, precision, and traceability; advancing both hydrogen purity monitoring and the broader field of spectroscopic metrology.

The contributions of the HITRAN database to hydrogen purity spectrometer development can be summarised as below:

TABLE 2.2: Summary of HITRAN Contributions to Hydrogen Purity Spectrometer Development

Contribution Area	**Description**
Reference Spectra	Provides validated absorption lines for hydrogen and trace impurities (H2O, CH4, CO, N2), enabling wavelength selection and calibration.
Instrument Calibration	Supplies benchmark data for calibrating spectrometers, ensuring traceability to international standards.
Uncertainty Quantification	Offers line intensity and broadening parameters essential for uncertainty propagation models in metrology.
Spectrometer Design Optimization	Supports simulation of gas mixtures under varying conditions, aiding in the design of optical paths, filters, and detectors.
Algorithm Development	Enables modelling of molecular interactions, fostering innovation in signal processing and spectral analysis techniques.
Validation and Comparison	Serves as a trusted reference for cross-verifying results from different spectroscopic platforms and techniques.

2.9 Guide to the Expression of Uncertainty in Measurement (GUM)

The GUM is a cornerstone document in the field of metrology, providing a standardized framework for evaluating and communicating measurement uncertainty. Developed by the Joint Committee for Guides in Metrology (JCGM), the GUM offers a comprehensive approach that is widely recognized and adopted internationally [119]. Measurement uncertainty is a quantitative indication of the quality of measurement of results, which they could not be compared between themselves, with specific reference values or to a standard. Uncertainty evaluation is essential to guarantee the metrological traceability of measurement results to ensure that they are accurate and reliable.

The GUM outlines a systematic approach to uncertainty quantification, emphasizing the development of a measurement model, the identification of uncertainty components, the propagation of uncertainty through the measurement model, and the expression of uncertainty using a combined standard uncertainty and a coverage factor. These principles are applicable to a wide range of fields, including scientific research, industrial quality control, metrology laboratories, and regulatory compliance. GUM has been used to quantify and or compare the quality of the measurements by many [60, 77, 110].

In the context of spectroscopic measurements, the GUM can be used to evaluate uncertainty in instrument calibration, quantify measurement results, compare measurement results, and ensure the reliability and credibility of spectroscopic data. By following the GUM guidelines, researchers and practitioners can enhance the quality and confidence in their spectroscopic measurements.

2.10 Literature on Hydrogen and Methane Mixtures

2.10.1 Hydrogen Purity Assignment Using Laser Absorption Spectroscopy

Laser absorption spectroscopy has, therefore, become preferred in determining hydrogen purity especially in methane blends [76]. Recent studies have shown that this method helps to determine the concentration of hydrogen in gas media with high accuracy. For instance, one study pointed on mid-infrared laser absorption spectroscopy, this technique revealed high sensitivity hydrogen, thus allowing accurate determination of hydrogen's concentration in methane mixtures [16]. This process is essential because the purity degrees of hydrogen affect burning effectiveness as well as emissions in fuel usage [6].

2.10.2 Challenges of Analysing Hydrogen-Methane Mixtures

There are several inherent issues in analysing hydrogen methane mixtures that scientists have to overcome. Some of these are the different impacts that hydrogen concentration has on combustion processes, which hinders the determination of the best operating conditions for engines and burners [120, 102]. The high flammability of hydrogen is not suitable for practical applications due to its safety concerns; therefore, these mixtures must be utilized carefully and require strong-infrastructure [2, 121]. However, technologies that have already been developed for detecting gas may have problems in accurately measuring hydrogen when it is combined with different concentrations

of other gases, such as methane and other hydrocarbons, because the two gases have overlapping absorption spectra [80, 110, 71, 74]. Consequently, practical ways for CH_4/H_2 separation and quantitative analysis play significant roles in safe utilization of hydrogen-methane blends where it is needed [122, 123]

2.10.3 Existing Methods for Analysing Hydrogen-Methane Mixtures

Several methods have been developed to effectively analyze hydrogen-methane mixtures. Among these, laser absorption spectroscopy has emerged as one of the most widely used techniques, owing to the development of advanced instruments and interference-free measurements a key advantage noted in these recent studies
[68, 123, 124].

For instance, recent research has demonstrated the application of cepstral analysis (a signal processing technique that separates overlapping spectral features by transforming signals into the frequency domain) to isolate methane signals from hydrogen, enabling the independent measurement of both components with high sensitivity and specificity [68, 123, 124]. This approach leverages the ability of cepstral analysis to deconvolve overlapping spectral features, enhancing the accuracy of gas mixture analysis.

Similarly, methods like cavity ring-down spectroscopy have been employed for their highly sensitive detection capabilities, particularly in trace gas analysis. These techniques are invaluable for monitoring hydrogen purity and concentration in mixtures containing methane [46, 125].

Overall, the enhancement and refinement of such advanced analytical methods are critical to addressing the challenges associated with hydrogen-methane analysis. As hydrogen gains prominence as a clean energy carrier, these tools play a pivotal role in ensuring its quality and compatibility in various applications [60, 106, 55, 1].

Several methods have been developed to analyse hydrogen-methane mixtures effectively, of these, laser absorption spectroscopy is one of the most common depending on the development of instruments and measurement that is free from interference [68, 123, 124]. Methods like cavity ring-down spectroscopy applied for the same reason, due to availability of highly sensitive detection for trace gases, which can be used to monitor hydrogen purity and concentration in the mixture with methane [46, 125]. Altogether, the enhancement of such techniques is crucial for meeting the emergent difficulties presented by the analysis of hydrogen-methane [60, 106, 55, 1].

2.10.4 Importance of Accurate Composition Measurements

High accuracy of composition measurements is necessary for the processes of injecting hydrogen into natural gas pipelines [1]. It was found that increase in intensity of hydrogen concentration in the blended gas can cause change in the calorific value and flow characteristics of the blended gas as stated in [12]. Variation in thermo-physical features like density and viscosity may have negative effects on pipeline operations and hence require modification of the current metering systems to operate efficiency-and-safety. It means that knowing these changes is necessary for the transition of hydrogen into existing natural-gas pipelines since that would make it possible to determine compatibility of new mixtures with existing transmission and distribution systems [9].

2.11 Summary

Chapter 2 establishes the theoretical and experimental foundation for hydrogen purity assessment, emphasizing the importance of accurate measurement techniques, international standards, and metrological traceability. Hydrogen, as a clean energy carrier, is increasingly used in fuel cells, chemical processing, metallurgy, and electronics, where its purity directly affects performance, safety, and efficiency [23, 24, 25, 26]. The ISO 14687-2 standard defines stringent impurity limits for hydrogen used in PEM fuel cell vehicles, ensuring catalyst protection and consistent energy conversion [33, 6, 29]. Similar purity requirements apply to semiconductor manufacturing, hydrogen annealing, and chemical synthesis, where trace contaminants can compromise product quality and system reliability [30, 32, 31].

To meet these demands, the chapter reviews analytical techniques for hydrogen purity assessment, including chromatographic, spectroscopic, and electrochemical methods. Gas chromatography (GC) remains a widely used technique, often paired with detectors such as thermal conductivity (TCD) and flame ionization (FID), though its limitations in real-time monitoring and sample preparation are noted [10, 44, 11, 45]. Spectroscopic methods such as mass spectrometry (MS), Fourier transform infrared spectroscopy (FTIR), and laser absorption spectroscopy (LAS) offer high sensitivity and multi-component detection capabilities, with LAS emerging as a preferred technique due to its real-time, non-invasive nature and trace-level sensitivity [12, 13, 14, 49, 50].

Advanced LAS techniques such as Tunable Diode Laser Absorption Spectroscopy (TDLAS) and Cavity Ring-Down Spectroscopy (CRDS) are highlighted for their precision

in trace gas analysis [61, 62, 63, 64, 65, 66]. The Traceable Infrared Laser-Spectrometric Amount Fraction Measurement (TILSAM) method is introduced as a metrologically rigorous approach grounded in the Beer-Lambert Law, enabling SI-traceable quantification of hydrogen concentrations [80, 81]. Complementing these techniques, Optical Gas Standards (OGS) provide calibration-free references for spectroscopic instruments, enhancing measurement reliability and traceability [85, 86, 87, 77, 71].

The chapter further explores the principles of absorption line selection in LAS, emphasizing wavelength specificity, line strength, and minimal spectral interference. The absorption line at 2121.8 nm (4712.9 cm^{-1}) is identified as a preferred target for hydrogen sensing due to its isolation from common background gases [67, 33]. Mathematical models for line broadening including Doppler (Gaussian), pressure (Lorentzian), and Voigt profiles are presented to describe spectral behavior under varying temperature and pressure conditions [108, 112, 109, 106, 101]. These models are essential for accurate spectral fitting and quantitative analysis in LAS applications, particularly in industrial environments where precision is critical [113, 107, 96, 114].

The High-Resolution Transmission Molecular Absorption Database (HITRAN) is introduced as a foundational resource for spectroscopic modelling, instrument calibration, and uncertainty quantification. It provides validated spectral data for hydrogen and trace impurities such as H2O, CH4, CO, and N2, supporting wavelength selection, simulation, and uncertainty propagation in hydrogen purity instrumentation [115, 116, 118]. A summary table outlines HITRAN's contributions to spectrometer development, including reference spectra, calibration support, and algorithm validation.

To ensure the reliability of spectroscopic measurements, the Guide to the Expression

of Uncertainty in Measurement (GUM) is presented as the standardized framework for evaluating and communicating measurement uncertainty. Developed by the Joint Committee for Guides in Metrology (JCGM), the GUM provides a systematic approach to uncertainty modelling, propagation, and reporting, which is essential for traceable and reproducible results in gas metrology [119, 60, 77, 110].

The chapter concludes with a focused review of hydrogen-methane mixtures, highlighting challenges such as overlapping absorption spectra, combustion variability, and metering system compatibility [120, 102, 2, 121]. Advanced analytical methods including cepstral analysis and CRDS are discussed for their ability to isolate and quantify individual gas components with high sensitivity and specificity [68, 123, 124]. Accurate composition measurements are emphasized as critical for hydrogen injection into natural gas pipelines, where changes in calorific value, density, and viscosity affect operational safety and efficiency [1, 12, 9].

All in all, Chapter 2 provides a comprehensive and technically rigorous foundation for hydrogen purity assessment, integrating spectroscopic theory, instrumentation, and metrological frameworks. It establishes LAS as a robust and scalable solution for trace gas analysis, supported by international standards, validated databases, and uncertainty models. These insights lay the groundwork for the development of high-precision hydrogen purity instrumentation, essential for advancing clean energy technologies and ensuring safe deployment across industrial sectors.

This chapter forms the analytical backbone of the thesis, establishing the theoretical and experimental tools necessary for the design and validation of a high-precision hydrogen purity spectrometer.

Chapter 3

Experimental Methodology

3.1 Introduction

This chapter describes the experimental methodology developed to realise a traceable, calibration-free hydrogen spectrometer based on Tunable Diode Laser Absorption Spectroscopy (TDLAS). The objective is to measure hydrogen concentration and purity with high sensitivity, selectivity and traceability, suitable for applications such as hydrogen injection into natural gas pipelines and fuel-cell quality control.

We begin with the physical principles that underpin TDLAS and the rationale for key methodological choices (wavelength, cell type, measurement strategy). We then describe the experimental apparatus, instrumentation and data pipeline, followed by calibration/validation procedures, uncertainty considerations and safety protocols.

3.2 Principles

TDLAS measurements are founded on the Beer–Lambert law. For a monochromatic beam passing through an absorbing gas. As shown in Eq. (2.1), the transmitted intensity I decays exponentially with path length ℓ or in terms of absorbance (A):

$$\alpha(\nu) = P\, S(T)\, \phi(\nu)\, C, \tag{3.1}$$

with P the pressure, $S(T)$ the temperature-dependent line strength, $\phi(\nu)$ the line shape (Doppler + pressure broadening) and C the mole fraction of the absorber. For weak absorption ($\alpha L \ll 1$) the relation linearises to $I \approx I_0(1 - \alpha L)$, which is the operating regime for many trace measurements.

For hydrogen the chosen transition is centered around 2121.8 nm (4712.90 cm^{-1}), with a reported line strength of 3.19×10^{-26} $cm^{-1}/(cm^{-2}$ molecule) [69, 115]. This line is relatively isolated from common interferences (e.g. CH_4, H_2O) and is accessible with commercially available DFB diodes, making it ideal for selective hydrogen detection [126].

3.3 Overview of the experimental setup

Figure 3.1 shows the overall apparatus: a DFB diode laser source, laser diode controller and function generator for wavelength scanning, beam coupling optics, a Heriott Multi-pass gas cell multi-pass gas cell, mirrors and photodetector, and a high-speed DAQ with LabVIEW acquisition and MATLAB post-processing.

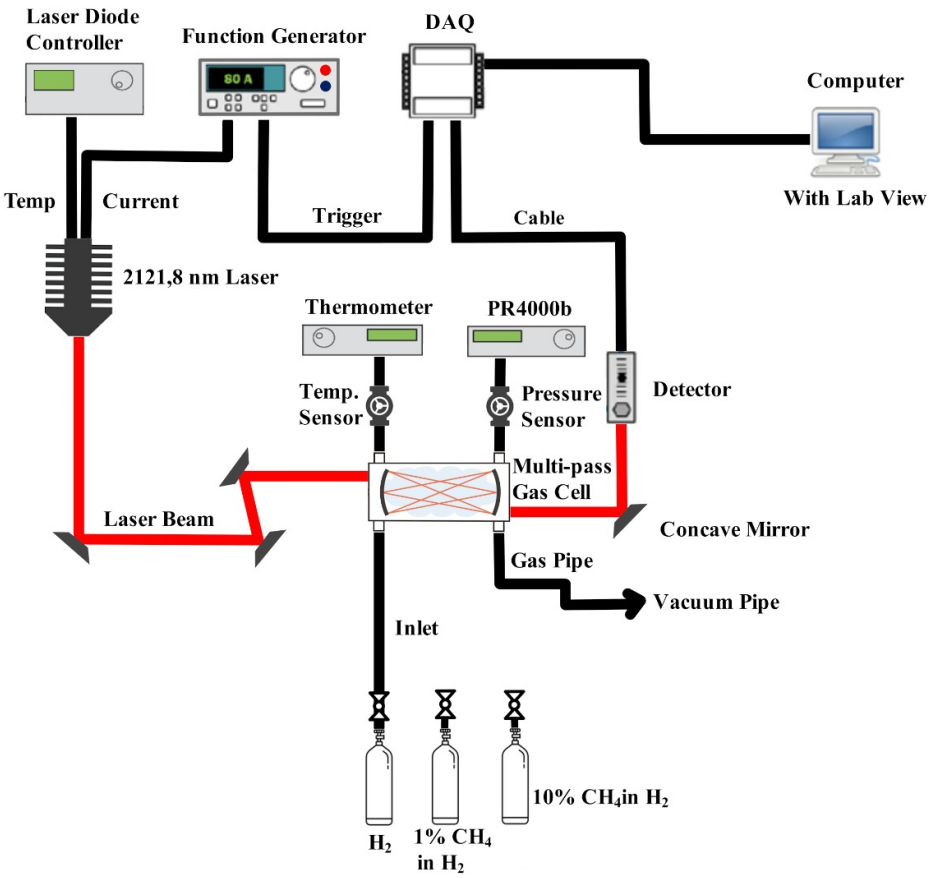

FIGURE 3.1: Schematic of the TDLAS experimental setup.

A simplified procedural flowchart is provided to summarise the measurement sequence (alignment, filling, stabilisation, acquisition, absorbance calculation,integration and fitting).

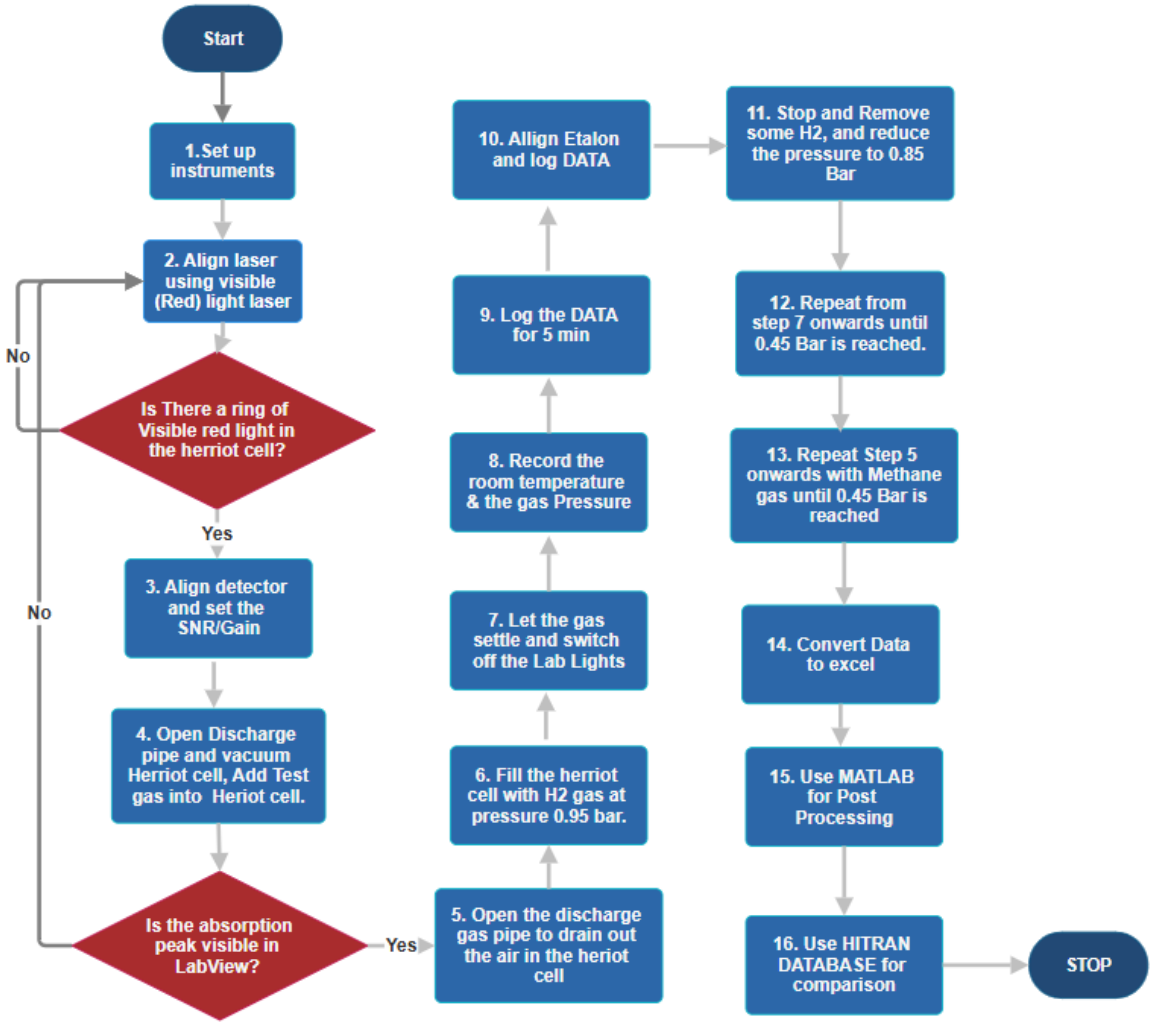

FIGURE 3.2: Flowchart of the experimental procedure.

With the setup in mind, the following section describes each major instrument component, its operating conditions, and the role it plays in the measurement chain.

3.4 Instrument components and specifications

3.4.1 Heriott Multi-pass gas cell

A Heriott Multi-pass gas cell provides the long effective optical path required to observe the weak hydrogen absorption. The effective optical path length used in this study is 3122.7 cm (manufacturer/experiment value); the cell is temperature controlled to 295 K and pressure is varied between 0.45 and 0.95 bar in 0.10 bar increments. Two gas compositions were measured: 99.999% pure hydrogen and a 90% H_2/10% CH_4 mixture.

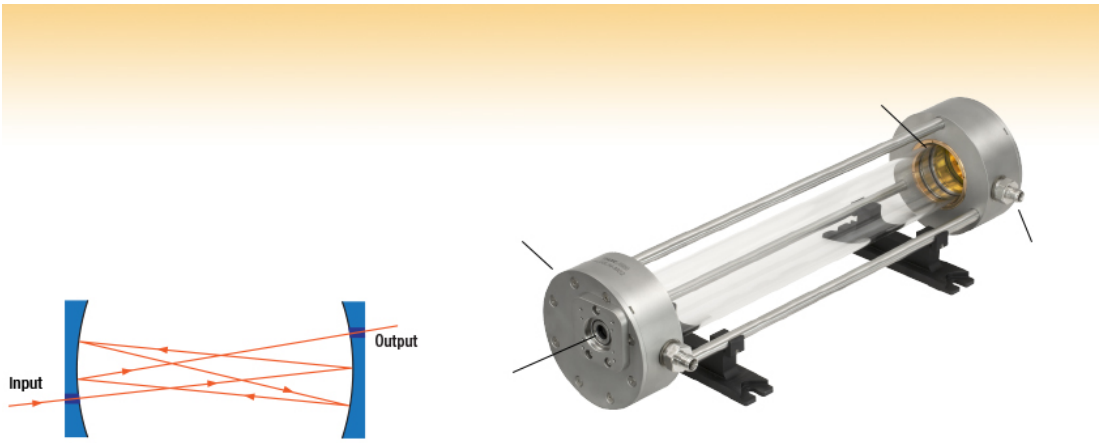

FIGURE 3.3: Heriott Multi-pass gas cell

3.4.2 Mirrors and optics

The cell uses high-reflectivity concave mirrors (protected gold coating) to achieve the multi-pass pattern. Ensure mirror cleanliness and stable spot pattern during each series of runs; contamination or mechanical drift are known sensitivity limitations.

FIGURE 3.4: Mirror assembly.

3.4.3 Laser and laser diode controller

A CW DFB diode laser centred at 2121.8 nm was used. Typical operating conditions during measurements were approximately 66 mA laser current and 41°C TEC set point; consult the diode data sheet for full operating limits [69]. A precision laser diode controller provides current and temperature regulation and accepts the modulation input from the function generator.

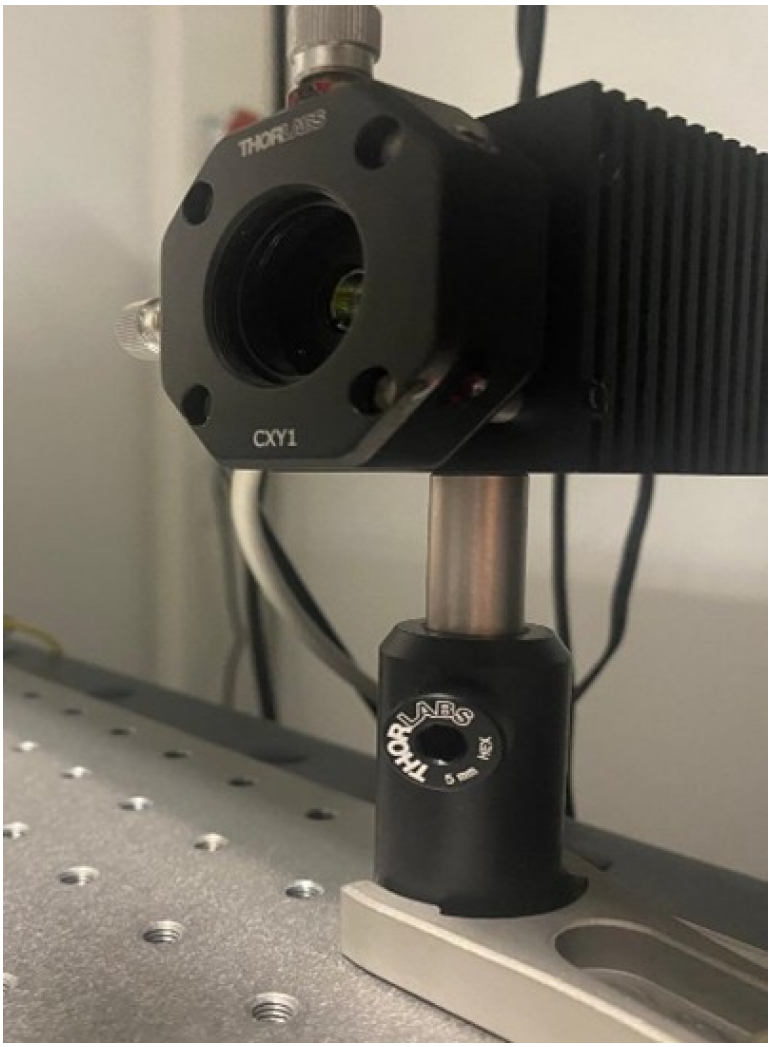

FIGURE 3.5: DFB diode laser (2121.8 nm).

3.4.4 Function generator and wavelength sweep

The laser emission wavelength was controlled and swept across the hydrogen absorption line using a low-frequency triangular/sawtooth modulation applied via a function generator. The optical frequency sweep rate and laser line width were carefully tuned to ensure that the laser line width was sufficiently narrow compared to the gas absorption line width to satisfy TILSAM measurement requirements.

FIGURE 3.6: Function generator.

3.4.5 Detector and DAQ

An InGaAs photodiode matched to the emission band was used to detect transmitted light. The detector output was routed to a high-speed, high-resolution DAQ (sample rate used: 500,000 samples/s) and recorded via LabVIEW. MATLAB was used for post-processing (baseline correction, direct absorbance calculation, numerical integration and uncertainty estimation) [127, 128].

FIGURE 3.7: Detector.

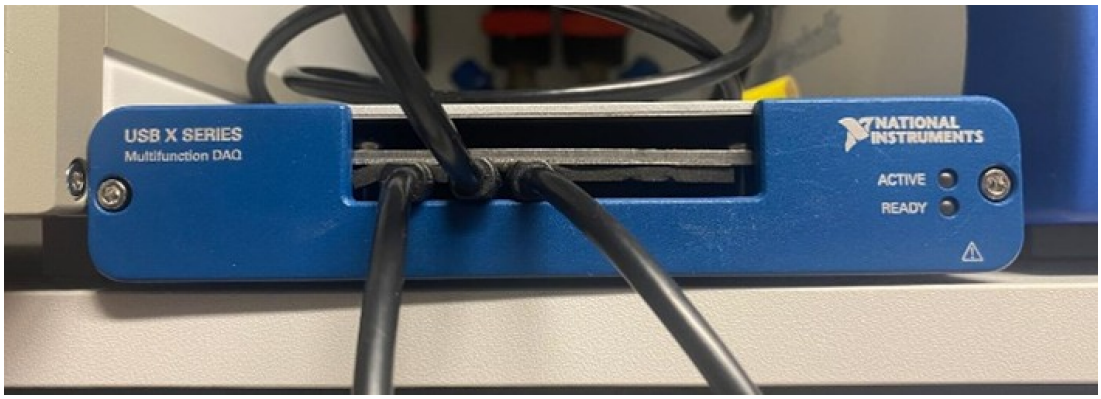

FIGURE 3.8: DAQ.

3.5 TILSAM Measurement Method

The Tunable Infrared Laser Spectrometric Amount fraction Measurement (TILSAM) method is employed to directly determine the hydrogen mole fraction in the gas mixture without the need for external calibration. TILSAM relies on direct absorption spectrometry and uses the Beer-Lambert law to relate the measured absorbance line area to the gas concentration. The TILSAM method was originally developed and validated for CO measurement under EUROMET project 934, achieving relative uncertainties of ±1.5% with full SI traceability [80]. This work represents the first application of TILSAM principles to hydrogen purity assessment, adapting the methodology to the specific challenges of hydrogen spectroscopy at 2121.8 nm.

Key aspects of the TILSAM methodology applied in this work include:

- **Absorption line characterization:** The laser wavelength is swept across the hydrogen absorption transition, and the transmitted intensity is recorded. The absorbance $A(\nu)$ is obtained from the ratio of incident and transmitted intensities after correcting for baseline offsets.

- **Line area determination:** The spectral absorbance across the transition is integrated to yield the absorbance line area A_{line}. This is performed either by numerical integration of the absorbance spectrum or by fitting with an appropriate line profile (Voigt, Lorentzian, or Gaussian) as per the pressure regime.

- **Amount fraction computation:** The hydrogen mole fraction X_{H_2} is calculated from the integrated absorbance line area using the equation

$$X_{\mathrm{H_2}} = \frac{k_B T}{S_T\, p\, L} A_{\mathrm{line}},$$

where k_B is the Boltzmann constant, T the gas temperature, p the pressure inside the gas cell, L the effective optical path length, and S_T the temperature-dependent line strength. The temperature dependence of the line strength S_T is accounted for using the standard temperature scaling models.

- **Traceability and uncertainty:** The method is inherently calibration-free, relying on fundamental constants and independently measured parameters T, p, and L. The laser line strength S_T is obtained from published spectroscopic databases. Uncertainty contributions from these parameters and line area determination are rigorously evaluated and combined to produce the final measurement uncertainty.

- **Experimental setup considerations:** The gas cell is temperature stabilized, and pressure is accurately measured with calibrated sensors to ensure reliability. Special care is taken to measure and fix the effective path length L, and to ensure the laser line width and sweep range adequately resolve the absorption line.

- **Data Acquisition and Processing:** Raw detector signals undergo processing to remove offsets and noise, transform laser sweep units to wavenumber units, and calculate absorbance spectra. Multiple measurements under repeatability conditions are averaged to improve statistics. Linear regression of line area versus experimental parameter $\Gamma = \frac{S_T p L}{k_B T}$ can be used to identify hidden biases and improve accuracy.

The TILSAM method thus facilitates highly traceable and accurate determination of gas composition without calibration against reference gas mixtures, useful for fundamental metrology and quality control in hydrogen applications.

3.6 Data processing pipeline

The recorded time series passes through these steps:

1. Synchronisation and trimming (aligning data to the laser sweep);
2. Correction for detector offset and baseline drift;
3. Conversion of laser sweep units to wavenumber domain using calibrated sweep rate functions;
4. Calculation of absorbance $A(\nu)$ from intensity data;
5. Integration or fitting of the absorbance line to obtain the integrated absorbance A_{line};
6. Calculation of hydrogen mole fraction using the TILSAM model equations;
7. Repetition for multiple measurements to assess repeatability and statistical uncertainty.

All processing was implemented in MATLAB with repeatable scripts; raw data and parameters were stored to ensure reproducibility.

3.7 Calibration and validation

The TILSAM method is designed to be calibration-free by virtue of using fundamental molecular parameters. However, validation measurements were performed using gravimetrically prepared hydrogen reference mixtures to ensure the accuracy of the methodology and the integrity of the uncertainty budget. Measured mole fractions were compared against certified values, and any discrepancies were analysed to refine measurement protocols and uncertainty estimates.

3.8 Sources of uncertainty and uncertainty budget

The main sources of uncertainty in the TILSAM measurement are:

- Uncertainty in the effective optical path length L;
- Accuracy of pressure p and temperature T measurements inside the gas cell;
- Uncertainty in the hydrogen absorption line strength S_T from spectroscopic databases;
- Numerical integration or fitting errors in determining the absorbance line area A_{line};
- Laser wavelength calibration and sweep rate accuracy;
- Detector linearity and signal noise.

An uncertainty budget was constructed following the Guide to the Expression of Uncertainty in Measurement (GUM) principles [129]. Typical combined relative expanded uncertainty achieved is on the order of 1.5% (coverage factor $k = 2$).

3.9 Safety considerations

Because infrared laser radiation is invisible and hydrogen is flammable, the experimental setup follows strict safety rules:

- Laser safety: interlocks, beam enclosures, appropriate eyewear for the laser wavelength, and administrative controls;
- Gas safety: leak checks, ventilation, purging protocols, secure cylinder handling and gas monitoring;
- Electrical safety: properly rated power supplies, grounded equipment and EM shielding for sensitive analogue signals.

Documented Standard Operating Procedures (SOPs) and emergency procedures were in force during all measurements.

3.10 Summary

This chapter presented a coherent experimental methodology for a traceable, calibration-free hydrogen spectrometer based on TDLAS using the TILSAM method. Key decisions such as the selection of the 2121.8 nm hydrogen absorption line, use of a Heriott

Multi-pass gas cell with an effective path length of 3122.7 cm, and the implementation of TILSAM for direct absorbance line area measurement and mole fraction retrieval were justified to maximise sensitivity, selectivity and traceability. A rigorous data acquisition and processing pipeline was established to ensure reproducibility and robust uncertainty quantification.

The following chapter will present the experimental results, detail uncertainty calculations and discuss the metrological performance of the spectrometer compared to reference data and the HITRAN database.

Chapter 4

Results and Discussion

4.1 Introduction

Building on the traceable, calibration-free spectrometer design and TILSAM-based TDLAS methodology developed in Chapter 3, this chapter presents the experimental outcomes for hydrogen purity assessment. We first detail the time-domain and frequency-domain analyses for 99.999 % pure H_2 over a pressure range of 0.45 bar to 0.95 bar. Next, we extend the discussion to a 10 % CH_4/90 % H_2 mixture to evaluate matrix effects and validate the spectrometer's performance against HITRAN reference data.

Key measurement parameters held constant:

- Laser wavelength: 2121.8 nm (4712.90 cm^{-1})
- Multi-pass cell path length: 3122.7 cm (Heriott configuration)
- Temperature: 295 K
- Modulation: 4.5 V_{pp}, 141 Hz

Section 4 focuses on:

1. Extraction of etalon-synchronized transmitted signals.
2. Conversion to absorbance spectra and Voigt-profile fitting.

3. Integration of line areas and linear regression of area vs. pressure.

4. Intensity value and uncertainty of the data.

Examining the H_2 then the 10 % CH_4/90 % H_2 results, quantifies uncertainties via the GUM framework, and compares extracted line strengths with HITRAN values. Finally, evaluates the spectrometer's linearity, repeatability, limits of detection, and overall metrological performance.

4.2 Data Analysis and Results for the pure H_2 gas

4.2.1 H_2 Time-Domain Analysis

Raw laser signals for pure hydrogen were recorded at each pressure step. Figures 4.1 shows the un-processed continuous laser intensity trace for multiple cycles of 0.95 bar pure hydrogen,prior to extracting individual rising edges.

These continuous time series exists for both the periodic etalon fringes used for time-to-frequency calibration and the absorption dips.

In the next step, rising edges of each fringe are isolated (trimmed) and stacked, using the etalon reference, enabling conversion from time to wave number and the precise construction of absorbance spectra.

Figure 4.2 to Figure 4.7 shows the etalon, reference and transmitted components for the different pressures between 0.45 bar to 0.95 bar.

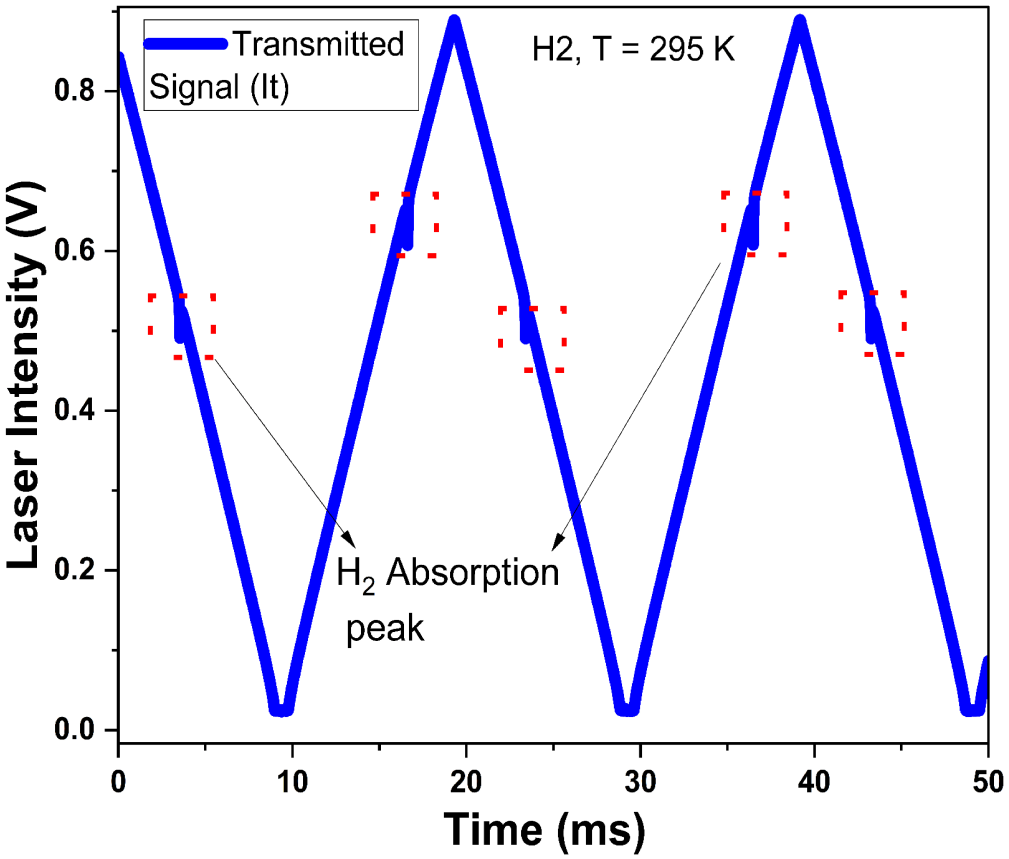

FIGURE 4.1: Raw Transmitted laser signal measured from the 99.999 % H_2 gas using the H_2 Spectrometer

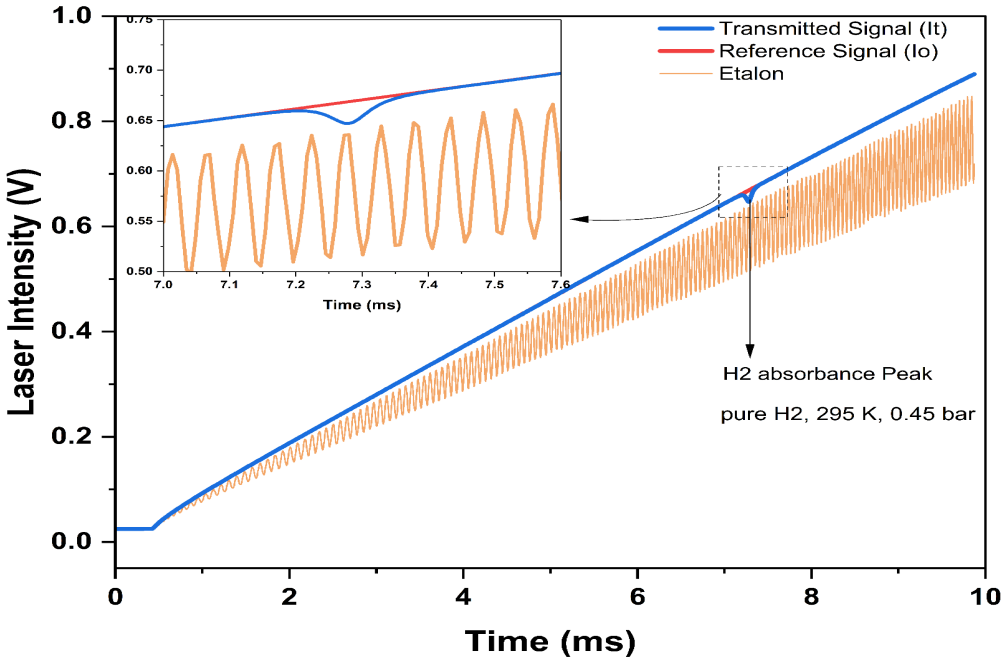

FIGURE 4.2: Etalon, reference (I_0) and transmitted (I_t) signals at 0.45 bar.

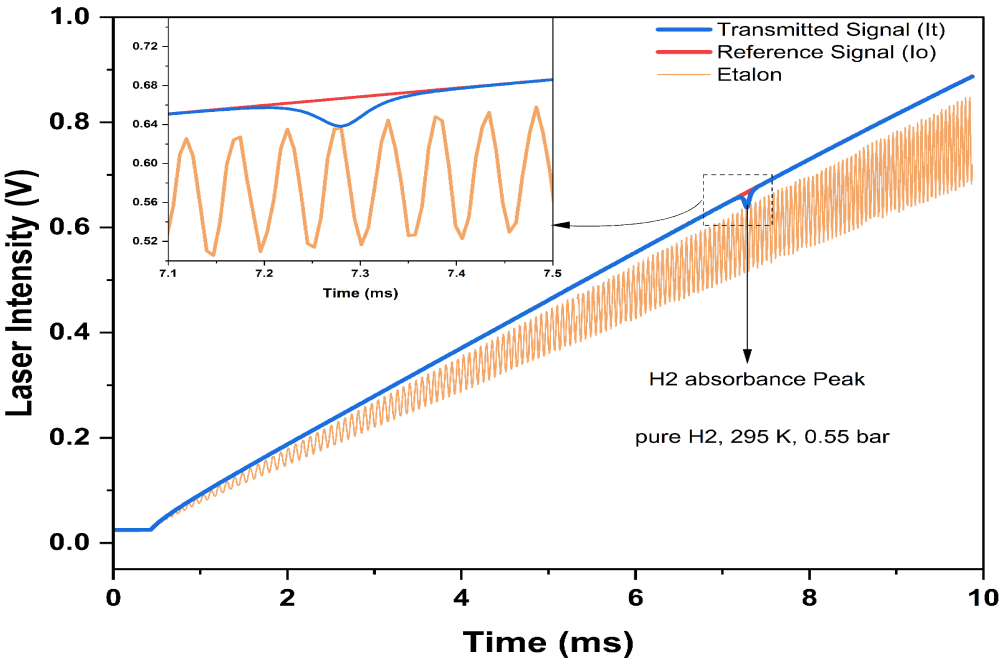

FIGURE 4.3: Etalon, reference (I_0) and transmitted (I_t) signals at 0.55 bar.

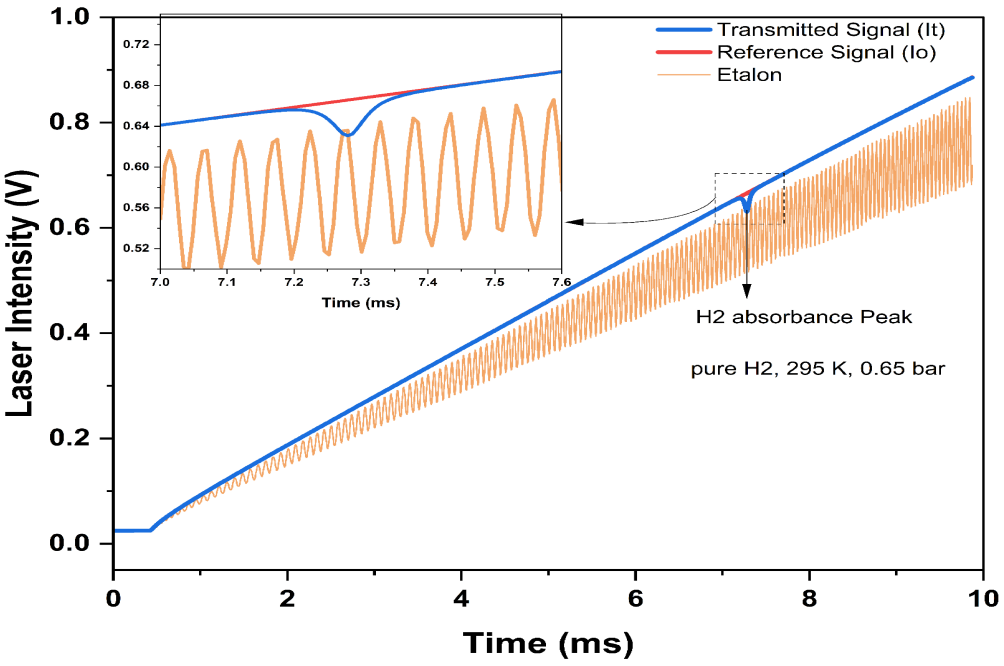

FIGURE 4.4: Etalon, reference (I_0) and transmitted (I_t) signals at 0.65 bar.

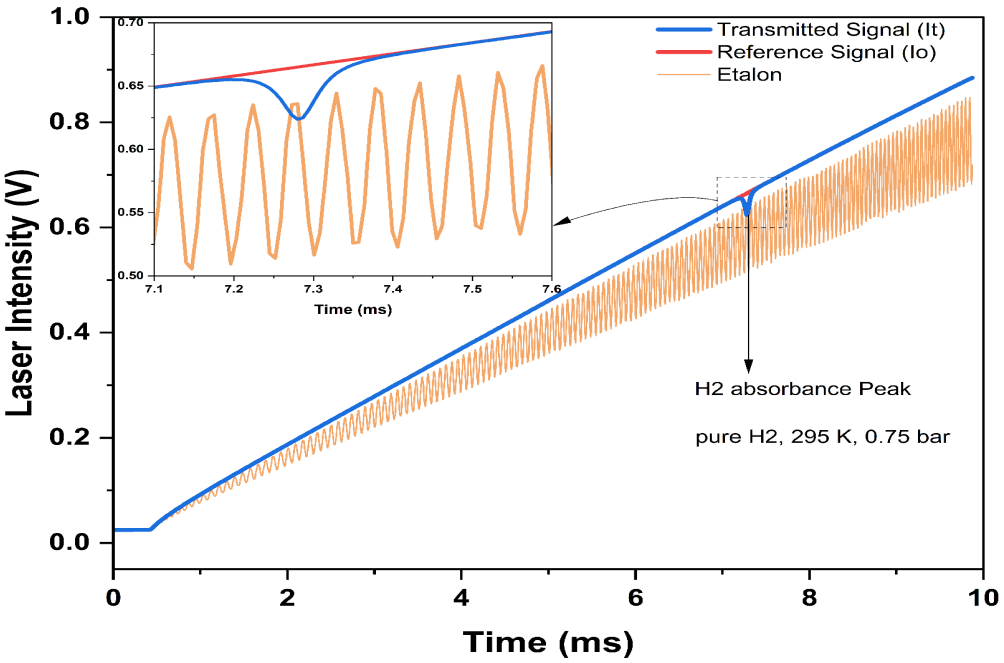

FIGURE 4.5: Etalon, reference (I_0) and transmitted (I_t) signals at 0.75 bar.

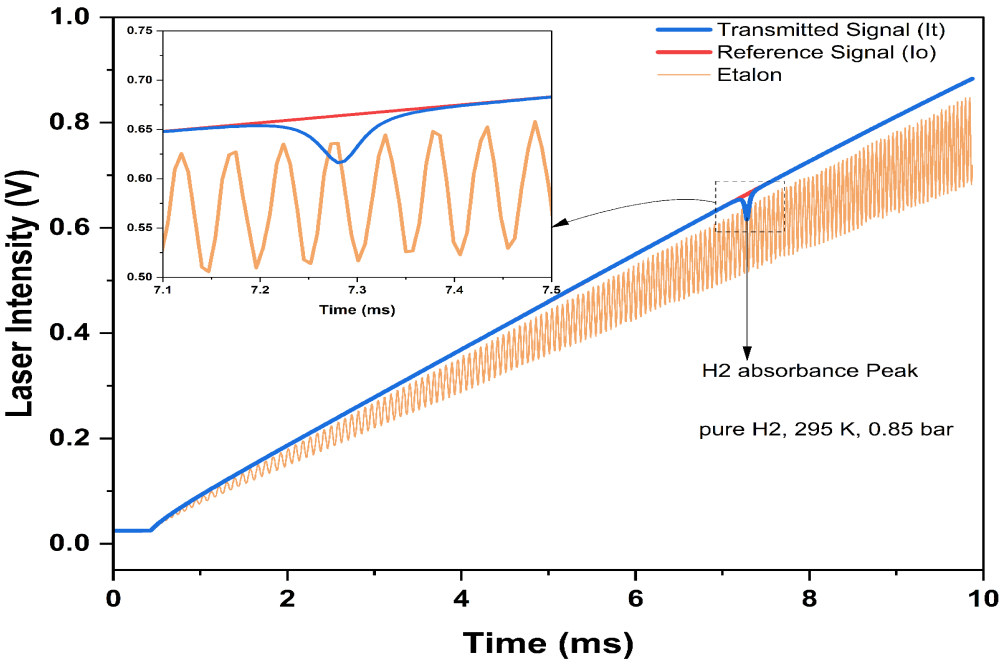

FIGURE 4.6: Etalon, reference (I_0) and transmitted (I_t) signals at 0.85 bar.

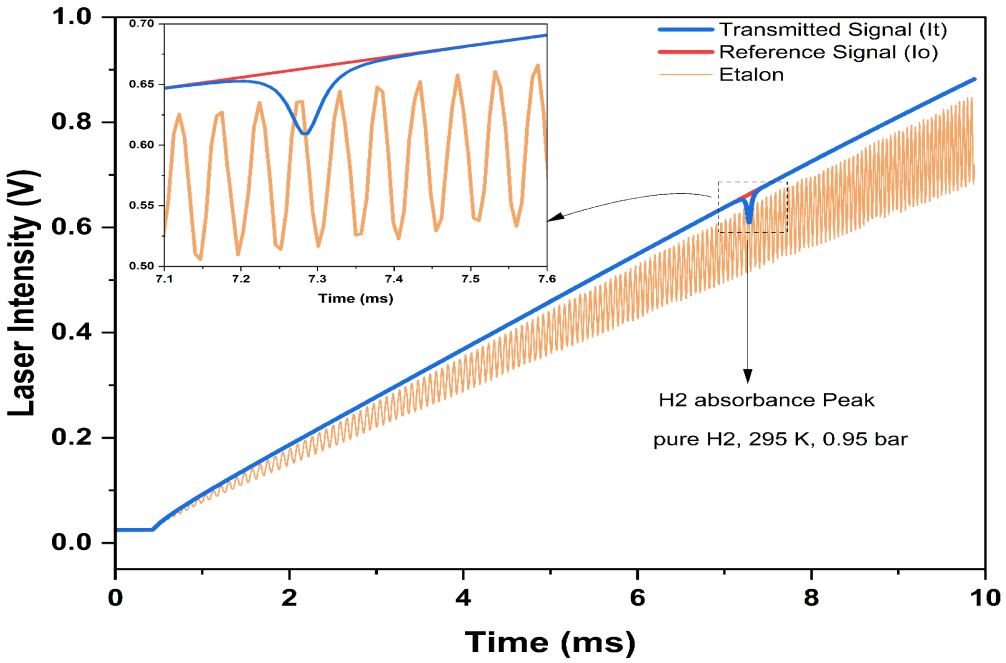

FIGURE 4.7: Etalon, reference (I_0) and transmitted (I_t) signals at 0.95 bar.

The periodic etalon fringes set our time-to-frequency calibration, while the absorption dips—highlighted by the downward excursions in I_t—mark molecular hydrogen's interaction at 2121.8 nm (4712.9 cm^{-1}). It is evident that the absorption dips become deeper as the pressure increases.

4.2.2 H_2 Frequency-Domain Analysis

Each segmented rising edge was converted to absorbance via the Beer–Lambert relation. Figure 4.8 to Figure 4.13 presents the spectrum with its Voigt-profile fit and fit residual.

The absorbance spectra were numerically integrated between 4712.0 and 4714.0 cm^{-1} for each pressure.

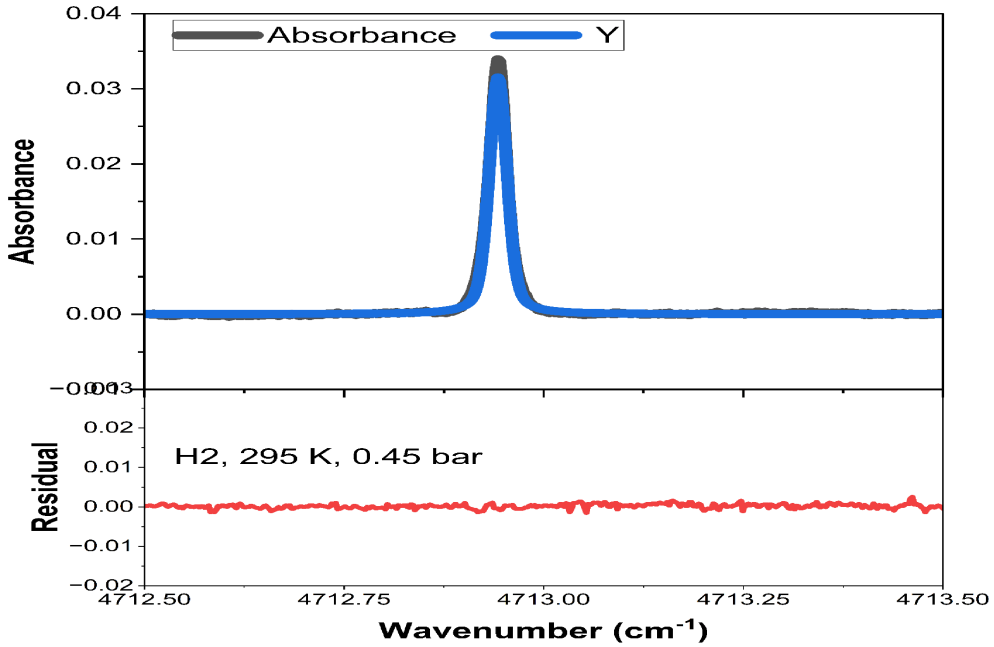

FIGURE 4.8: Absorbance spectrum with the x-axis transformed from time to frequency domain at a pressure of 0.45 bar.

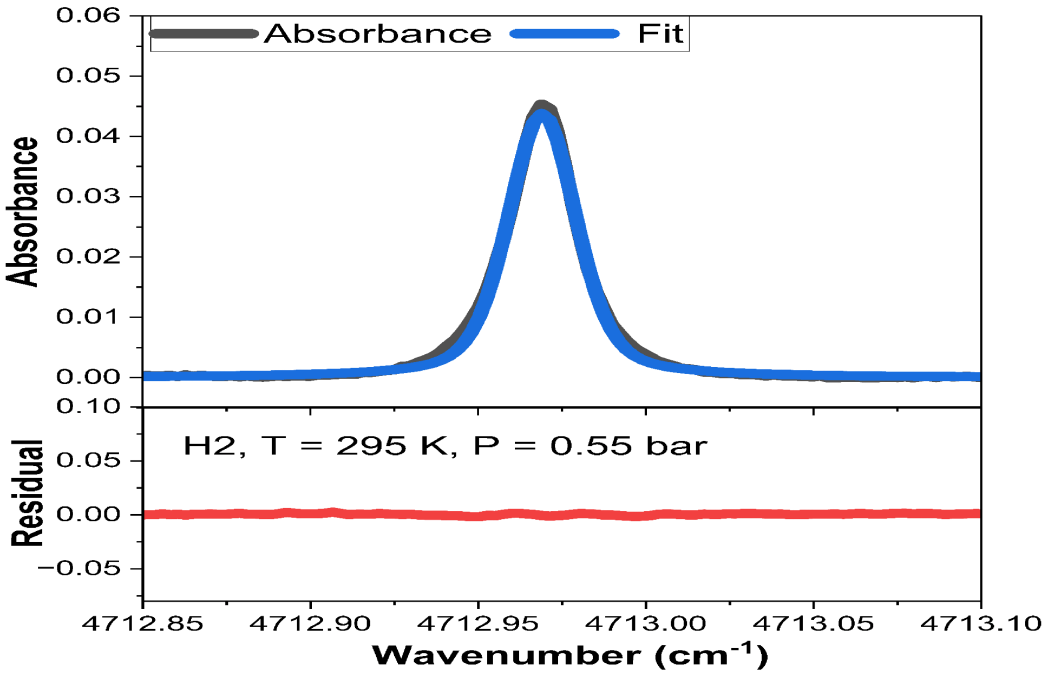

FIGURE 4.9: Absorbance spectrum with the x-axis transformed from time to frequency domain at a pressure of 0.55 bar.

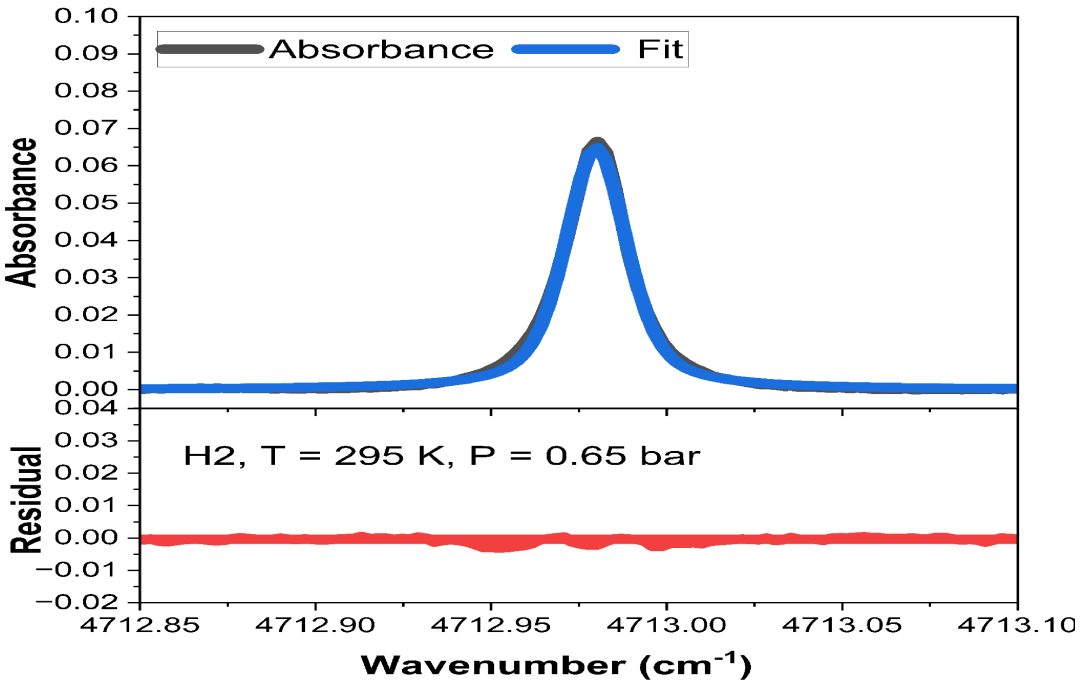

FIGURE 4.10: Absorbance spectrum with the x-axis transformed from time to frequency domain at a pressure of 0.65 bar.

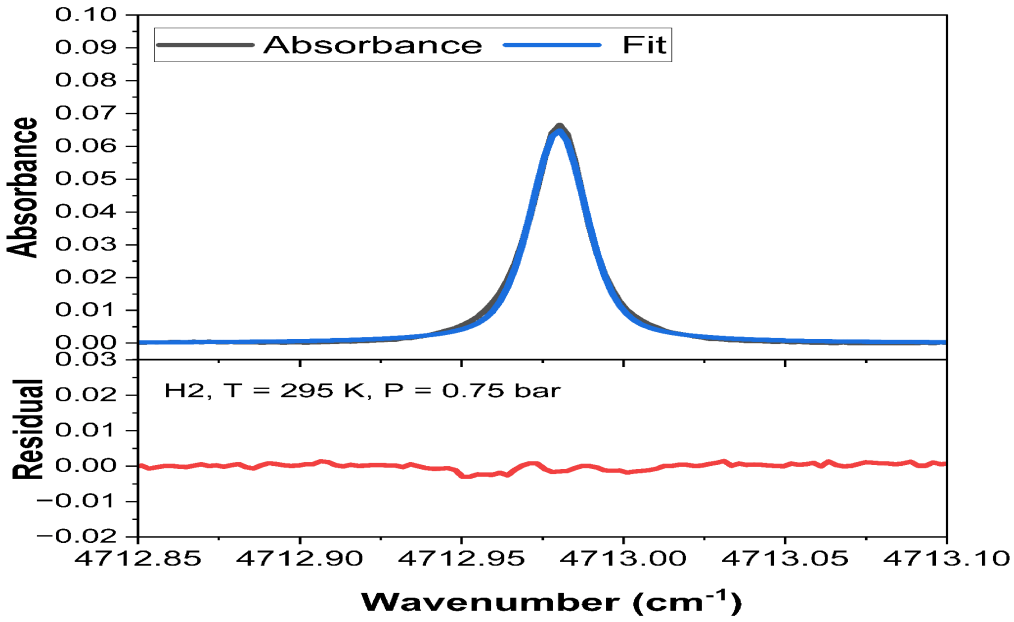

FIGURE 4.11: Absorbance spectrum with the x-axis transformed from time to frequency domain at a pressure of 0.75 bar.

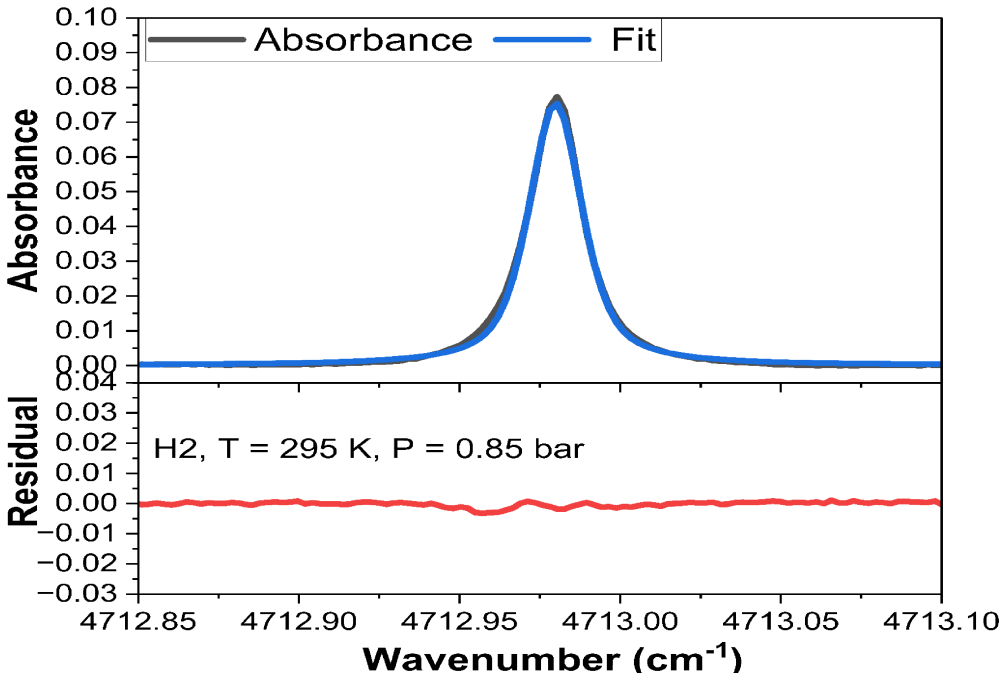

FIGURE 4.12: Absorbance spectrum with the x-axis transformed from time to frequency domain at a pressure of 0.85 bar.

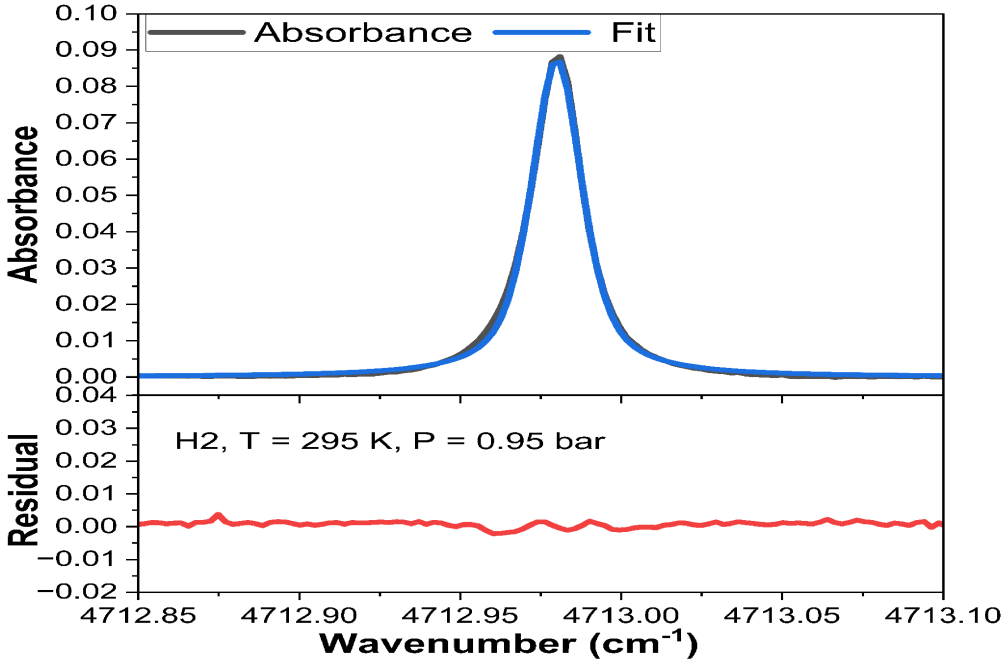

FIGURE 4.13: Absorbance spectrum with the x-axis transformed from time to frequency domain at a pressure of 0.95 bar.

With increasing pressure, we observe

- higher absorbance
- line broadening consistent with collisional effects
- negligible baseline drift (residuals $\ll 1\%$ of peak height)

Figure 4.14 shows the absorbance curves at 0.45 bar, 0.55 bar, 0.65 bar, 0.75 bar, 0.85 bar and 0.95 bar overlaid in the 4712.8–4713.1 cm^{-1} region.

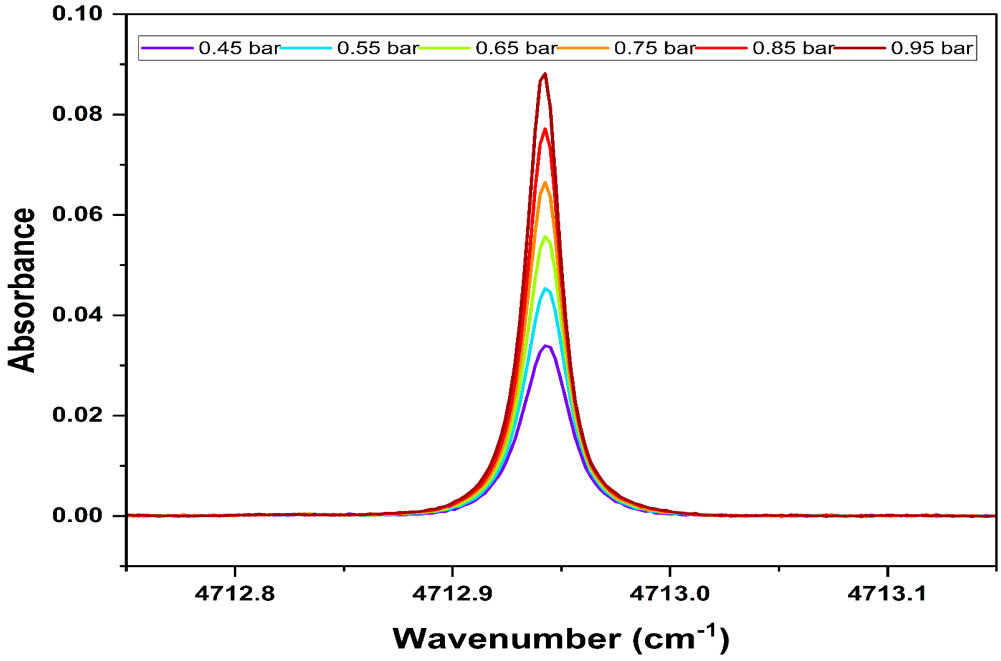

FIGURE 4.14: Overlay of absorbance spectra for 99.999 % H_2 at pressures from 0.45 bar to 0.95 bar. Traces are vertically offset for clarity.

As pressure increases, the following trends are evident:

- Peak absorbance rises nearly five-fold, from about 0.02 at 0.45 bar to 0.10 at 0.95 bar, demonstrating a linear dependence on number density.
- The full width at half maximum (FWHM) broadens from roughly 0.015 cm^{-1} up to 0.040 cm^{-1}, consistent with collisional (pressure) broadening.

- The line-center wavenumber remains stable within ±0.01 cm^{-1}, indicating negligible pressure-induced shift.

- Fit residuals stay below 1% of the peak height, confirming the quality of the Voigt-profile fits.

These observations fully support the Beer–Lambert law, whereby absorbance (and thus integrated area) scales linearly with pressure in this range, and set the stage for the area-vs-pressure regression in Section 4.2.3.

4.2.3 H_2 Area versus Pressure and Linear Fit

The Area under the absorbance curve was calculated and Figure 4.15 shows the resulting area A plotted against pressure P (0.45–0.95 bar).

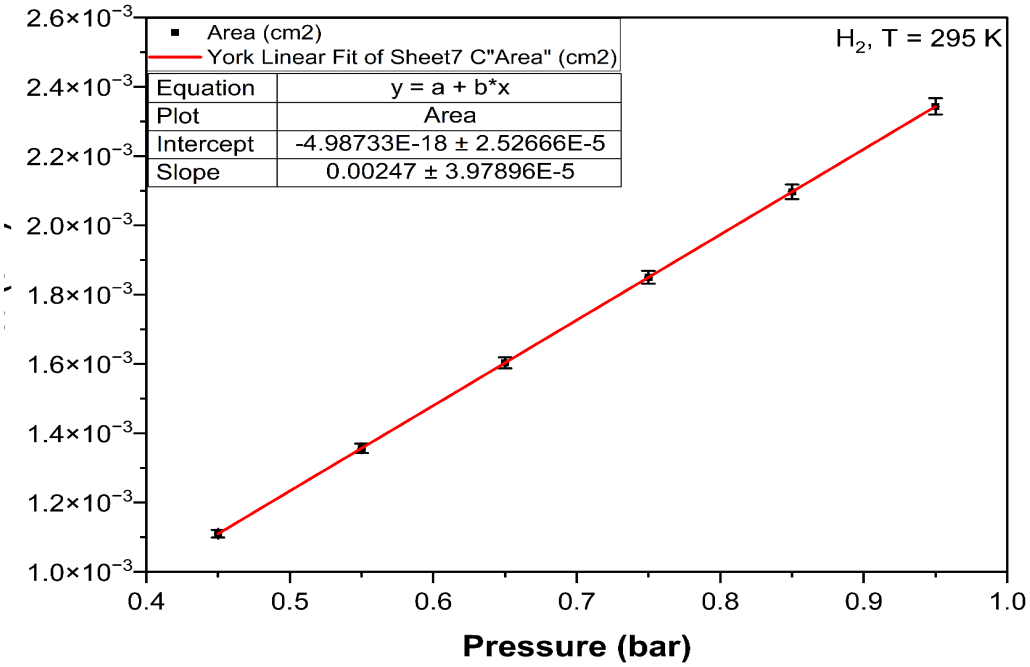

FIGURE 4.15: Integrated absorbance area as a function of pressure for 99.999 % H_2 at 295 K. Error bars denote fitting uncertainty; the solid line is a York linear regression.

A York-weighted least-squares fit yields

$$A = a + b\,P \tag{4.1}$$

with

$$a = \left(-4.99 \times 10^{-18} \pm 2.53 \times 10^{-5}\right)\,\mathrm{cm}^2, \quad b = \left(2.47 \pm 0.04\right) \times 10^{-3}\,\frac{\mathrm{cm}^2}{\mathrm{bar}}.$$

The negligible intercept confirms zero area at vanishing pressure within uncertainty.

According to Beer–Lambert and the definition of line strength S,

$$S = \frac{k_B\,A\,T}{X_{H_2}\,P\,L} \tag{4.2}$$

where

- $k_B = 1.380649 \times 10^{-23}\,\mathrm{J/K}$ is the Boltzmann constant,
- $T = 295.15\,\mathrm{K}$ is the cell temperature,
- $X_{H_2} = 1.0$ is the mole fraction of H_2,
- $L = 3122.7\,\mathrm{cm}$ is the multi-pass path length.

Substituting $A = b\,P$ from (4.1) reduces (4.2) to

$$S = \frac{k_B\,b\,T}{X_{H_2}\,L} = \frac{(1.380649 \times 10^{-23})(2.47 \times 10^{-3})(295.15)}{1.0 \times 3122.7} \approx 3.22{\times}10^{-26}\,\mathrm{cm/molecule}.$$

Table 4.1 summarizes the peak absorbance, integrated area, and derived line strength at each pressure.

TABLE 4.1: Peak absorbance, integrated area, and computed line strength for pure H_2 at 295 K.

P (bar)	Peak absorbance	Area (cm^2)	S (cm/molecule)
0.45	0.0323	1.11×10^{-3}	3.22×10^{-26}
0.55	0.0400	1.36×10^{-3}	3.22×10^{-26}
0.65	0.0512	1.60×10^{-3}	3.22×10^{-26}
0.75	0.0588	1.85×10^{-3}	3.22×10^{-26}
0.85	0.0708	2.10×10^{-3}	3.22×10^{-26}
0.95	0.0808	2.35×10^{-3}	3.22×10^{-26}

Fit Quality and Validation of Calibration-Free Approach

The York linear regression of A vs. P (Figure 4.15) yields

$$R^2 = 0.9997, \qquad \tilde{\chi}_\nu^2 = 1.08,$$

demonstrating that the residuals lie within the one-sigma uncertainty of each data point and that the model captures the pressure dependence of the integrated absorbance with extremely high fidelity.

Furthermore, the derived line strength

$$S = 3.22 \times 10^{-26}\,\text{cm/molecule}$$

remains constant (variation $< 2\%$) over the entire 0.45–0.95 bar range. This invariance of S directly validates our calibration-free methodology: by using only fundamental

constants (k_B, T, L) and the Beer–Lambert law, the spectrometer produces a self-consistent, pressure-independent molecular line strength. Such agreement confirms that no external standard calibration is required and that our traceability framework is internally closed and robust for high-precision hydrogen purity assessments.

4.2.4 MATLAB Cross-Validation of Line Intensity

To verify the slope-method result, we processed the same absorbance spectra in MATLAB using built-in fitting routines. Table 4.2 summarizes peak absorbance, integrated area, and derived line intensity S for each pressure. Both the slope method and MATLAB yield a consistent $S = 3.22 \times 10^{-26}$ cm/molecule.

TABLE 4.2: MATLAB-derived absorbance, area, and line intensity for 99.999 % H_2.

P (bar)	Peak absorbance	Area (cm^2)	S (cm/molecule)
0.45	0.03394	1.11×10^{-3}	3.22×10^{-26}
0.55	0.04500	1.36×10^{-3}	3.22×10^{-26}
0.65	0.05573	1.60×10^{-3}	3.22×10^{-26}
0.75	0.06652	1.85×10^{-3}	3.22×10^{-26}
0.85	0.07722	2.14×10^{-3}	3.22×10^{-26}
0.95	0.08822	2.34×10^{-3}	3.22×10^{-26}

4.2.5 Uncertainty Analysis

A full GUM-style uncertainty budget was compiled for the line intensity S. Table 4.3 lists the principal quantities, their uncertainties, and percent contributions to the total.

The overall 1.6 % uncertainty is dominated by the slope b and path length L; temperature and mole fraction contributions are negligible.

TABLE 4.3: Uncertainty budget for H_2 line intensity S.

Quantity	Value	Uncertainty (%)	Contribution (%)
k_B (J/K)	1.380649×10^{-23}	—	—
L (cm)	3122.7	2.0	0.2
X_{H_2}	1.0	0.5	0.0
b (cm^2/bar)	2.47×10^{-3}	2.9	99.8
T (K)	295.15	0.0185	0.0
$\Rightarrow S = 3.22 \times 10^{-26} \pm 1.6\%$ cm/molecule.			

4.2.6 Comparison with HITRAN Database

Figure 4.16 plots our experimental line strength against the HITRAN reference, each with its uncertainty band.

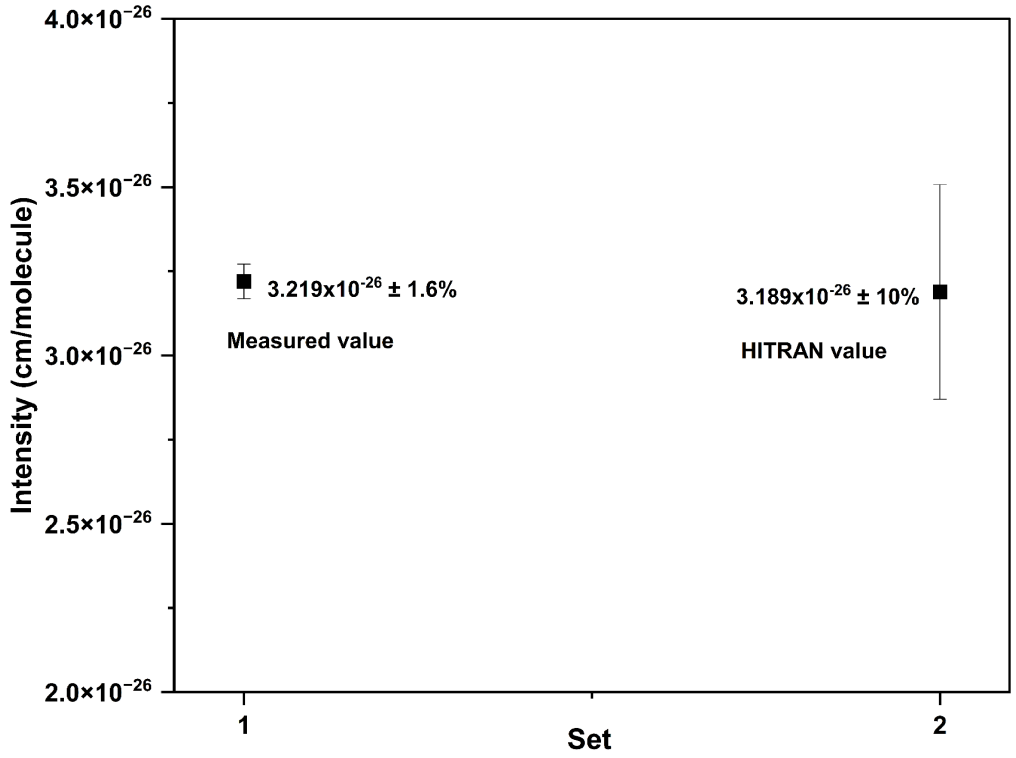

FIGURE 4.16: Experimental line intensity $S = 3.219 \times 10^{-26} \pm 1.6\%$ cm/molecule versus HITRAN value $3.186 \times 10^{-26} \pm 10\%$ cm/molecule.

The difference

$$\Delta S = (3.219 - 3.186) \times 10^{-26} = 3.3 \times 10^{-28}\,\text{cm/molecule}$$

lies well within the combined uncertainties. The substantially lower experimental uncertainty (1.6 %) compared to the HITRAN uncertainty (10 %) underscores the precision and robustness of our calibration-free TILSAM-based TDLAS approach. This high level of confidence not only validates our spectrometer design but also suggests potential for refining spectroscopic parameters in databases like HITRAN.

4.3 Data Analysis and Results for the CH_4/H_2 Mixture

4.3.1 CH_4/H_2 Time-Domain Analysis

Before trimming, the continuous detector output contains a continuous waveform similar to the pure hydrogen waveform, except it contains two separate absorption dips from H_2 and CH_4. Figure 4.17 shows this raw trace at 0.95 bar.

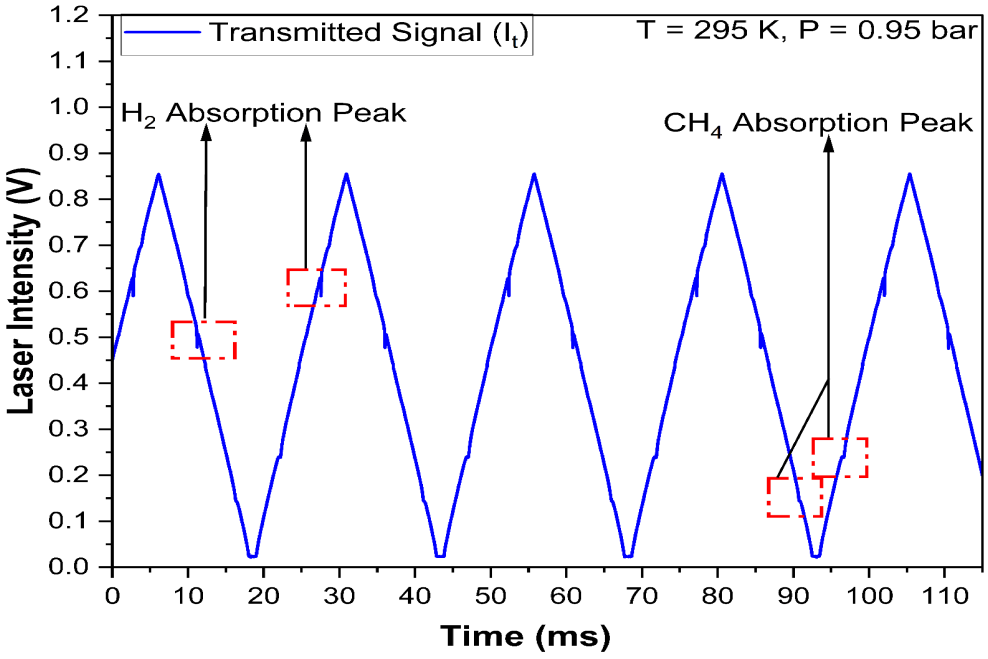

FIGURE 4.17: Raw transmitted intensity I_t versus time for a 10 % CH_4/90 % H_2 mixture at 0.95 bar and 295 K. Both the H_2 (upper dip) and CH_4 (lower dip) absorption features are visible.

Each modulation cycle's rising edge was isolated using the etalon reference to synchronize time-to-frequency calibration. Figures 4.18–4.21 display the trimmed laser intensity signals for pressures of 0.45 bar, 0.65 bar, 0.85 bar, and 0.95 bar.

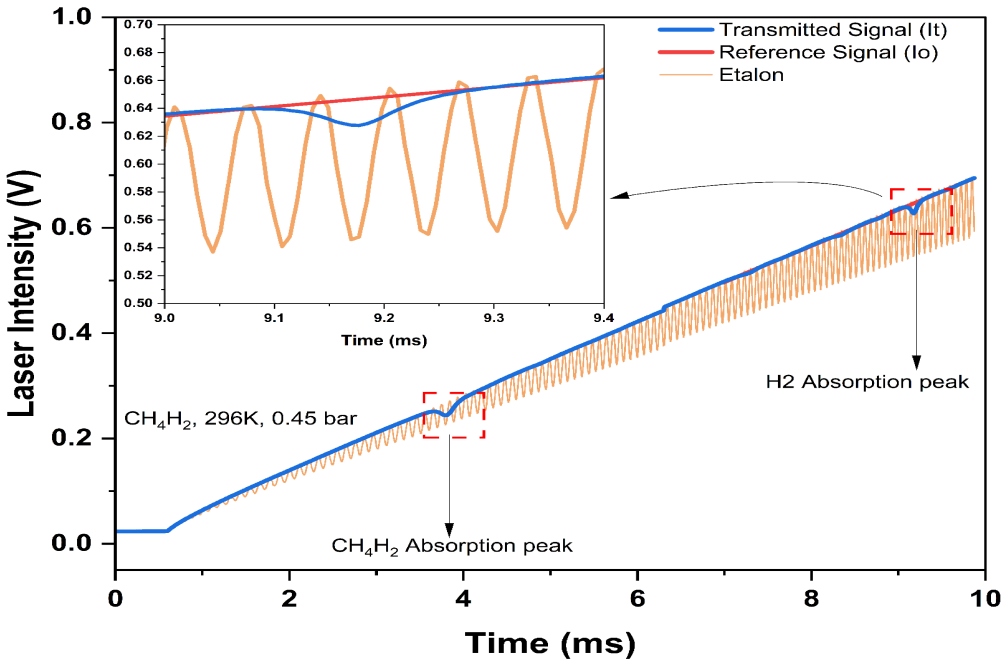

FIGURE 4.18: Etalon, reference (I_0) and transmitted (I_t) signals at 0.45 bar for the CH_4/H_2 mixture.

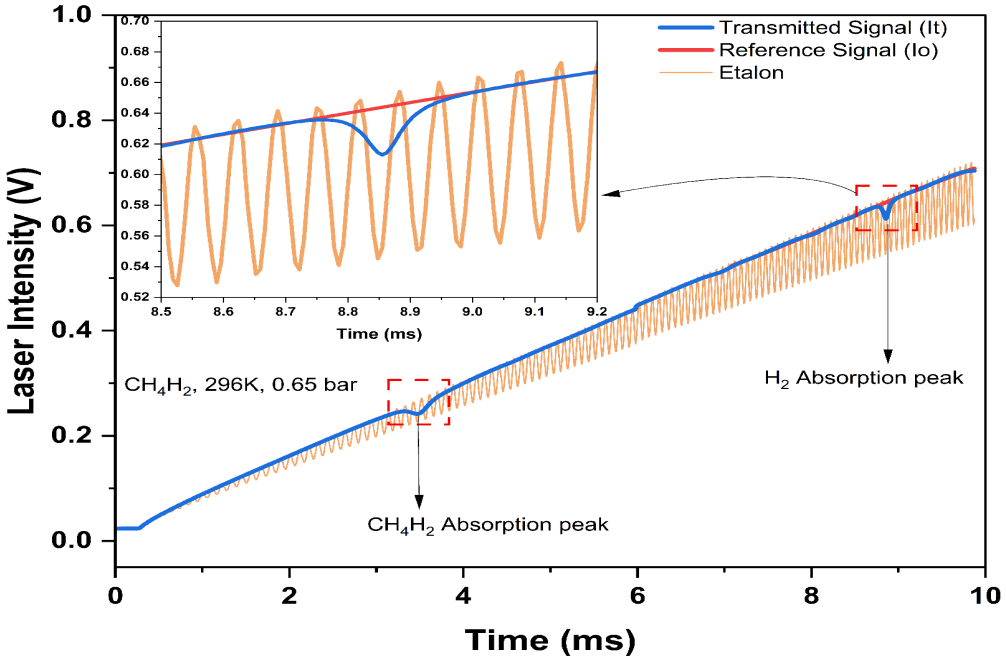

FIGURE 4.19: Etalon, reference (I_0) and transmitted (I_t) signals at 0.65 bar for the CH_4/H_2 mixture.

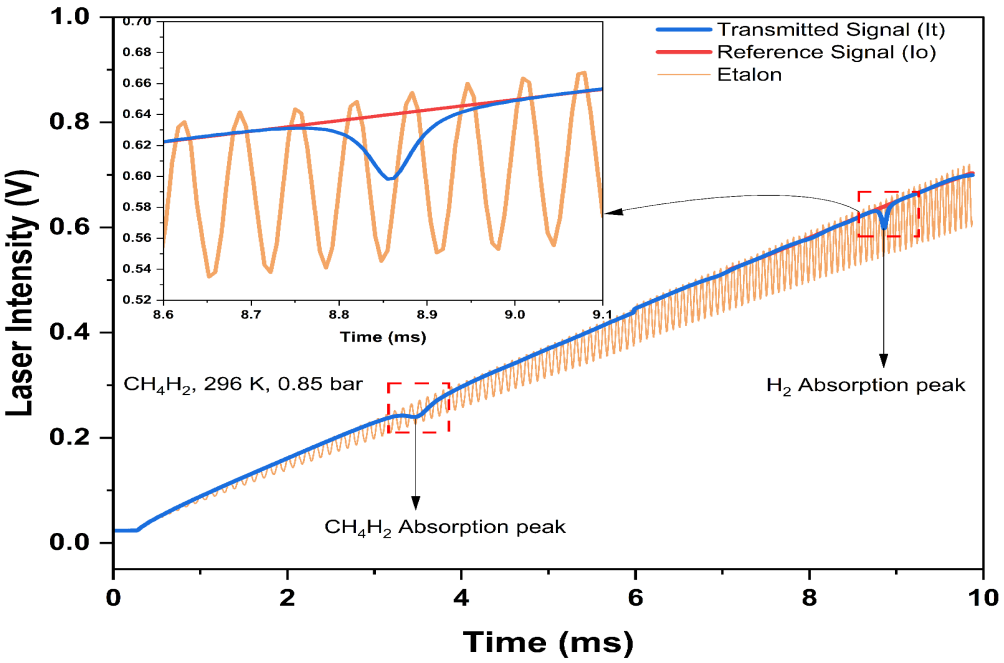

FIGURE 4.20: Etalon, reference (I_0) and transmitted (I_t) signals at 0.85 bar for the CH_4/H_2 mixture.

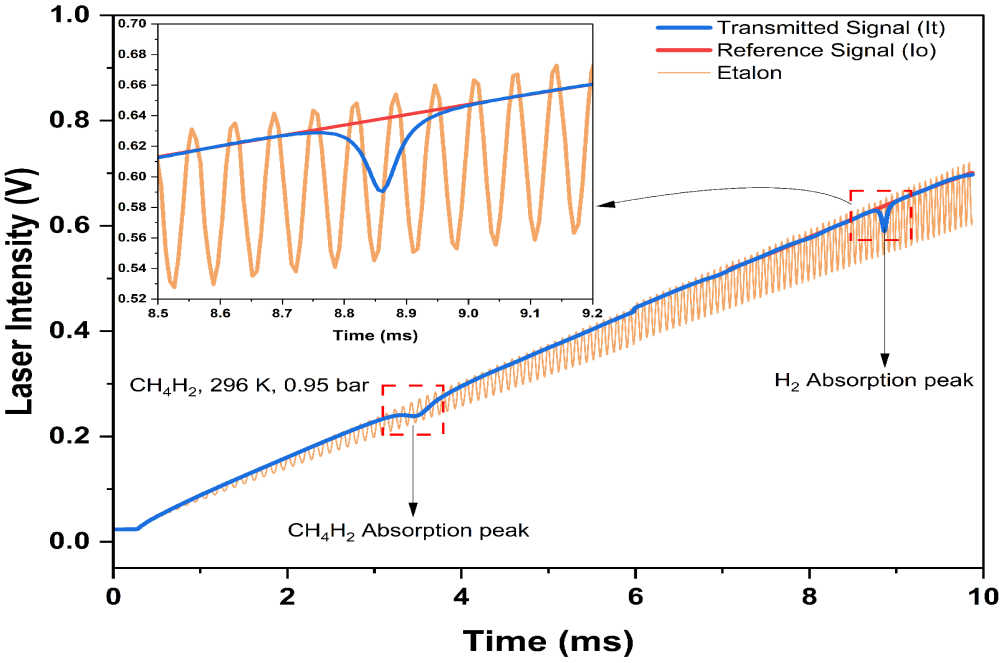

FIGURE 4.21: Etalon, reference (I_0) and transmitted (I_t) signals at 0.95 bar for the CH_4/H_2 mixture.

4.3.2 CH_4/H_2 Frequency-Domain Analysis

The transmitted-to-absorbed conversion follows Beer–Lambert, with wavenumber calibrated via the etalon. Figures 4.22–4.25 show Voigt-profile fits and residuals for both species.

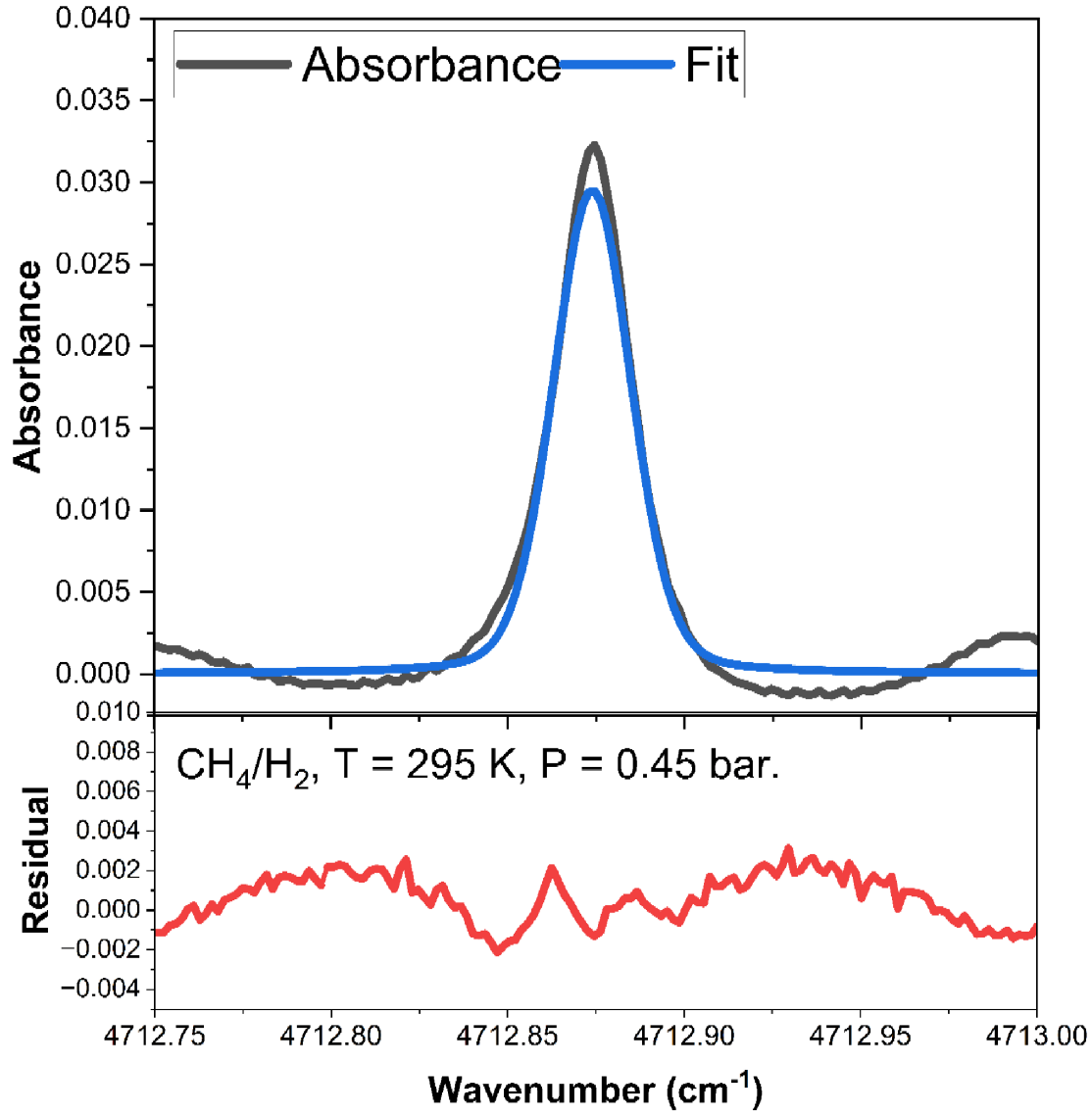

FIGURE 4.22: Absorbance versus wavenumber at 0.45 bar. Black: measured; red: fit; blue: residual for the H_2 Peak in the C_4H_2.

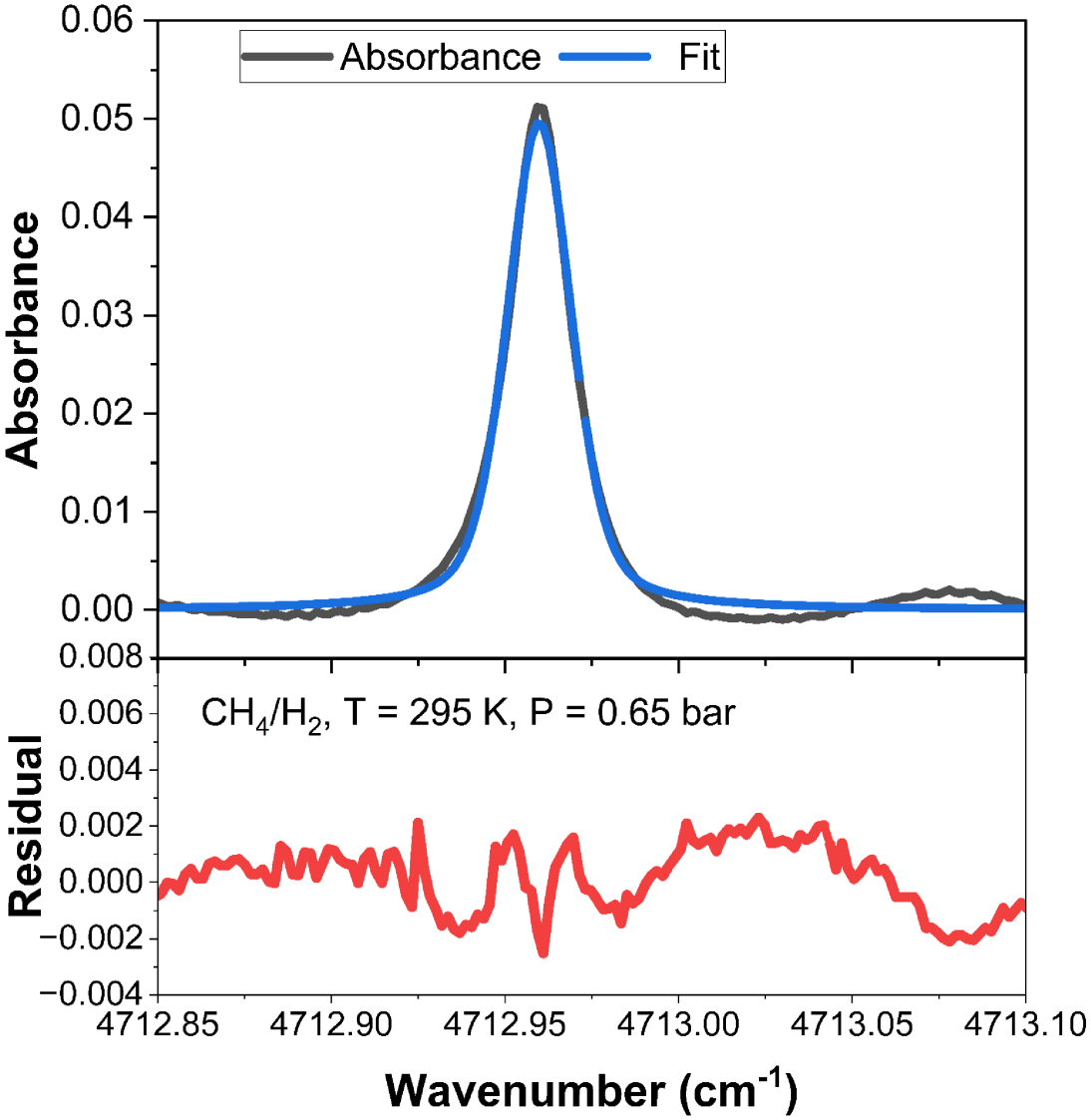

FIGURE 4.23: Absorbance versus wavenumber at 0.65 bar. Voigt-profile fits and residuals for the H_2 Peak in the C_4H_2.

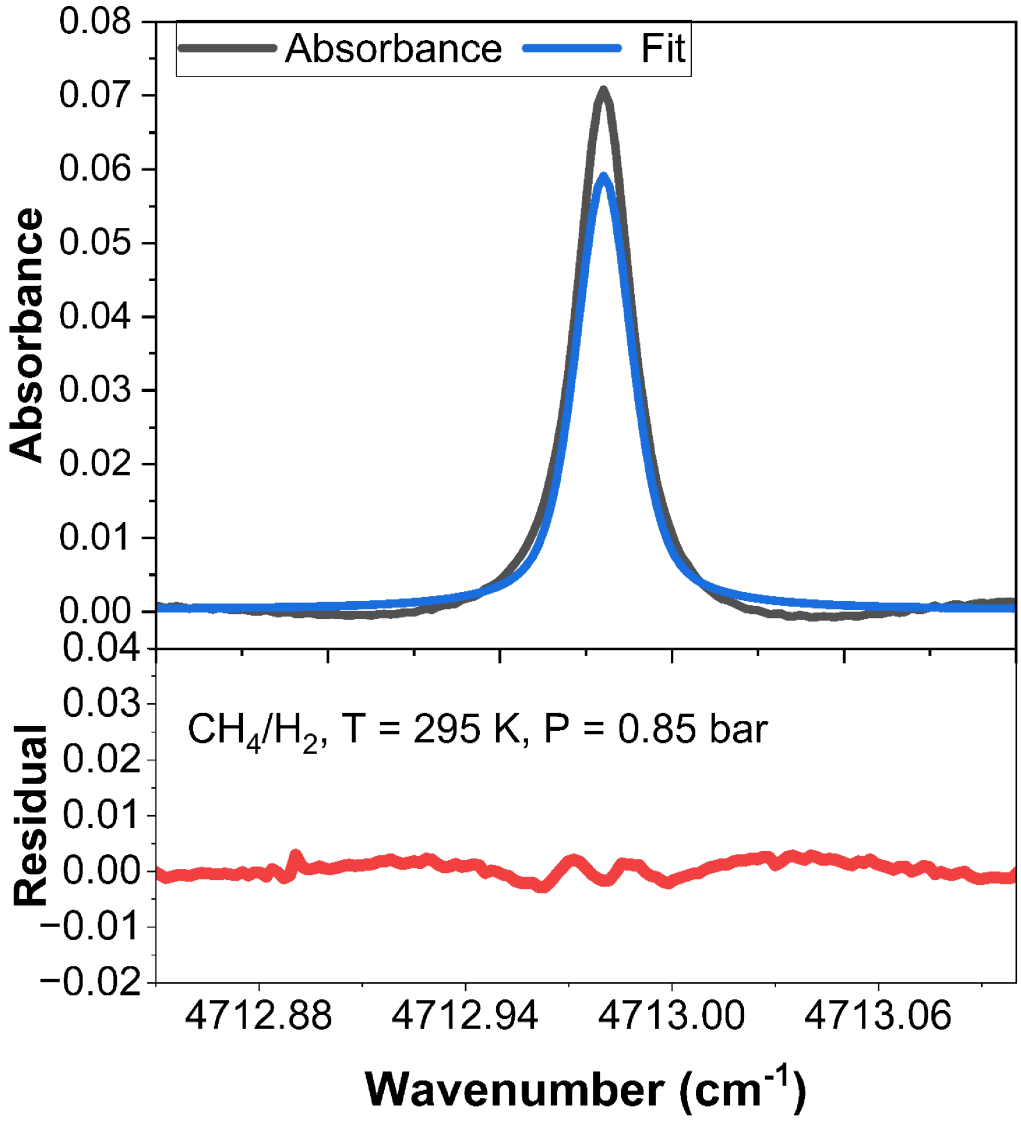

FIGURE 4.24: Absorbance versus wavenumber at 0.85 bar. Voigt-profile fits and residuals for the H_2 Peak in the C_4H_2.

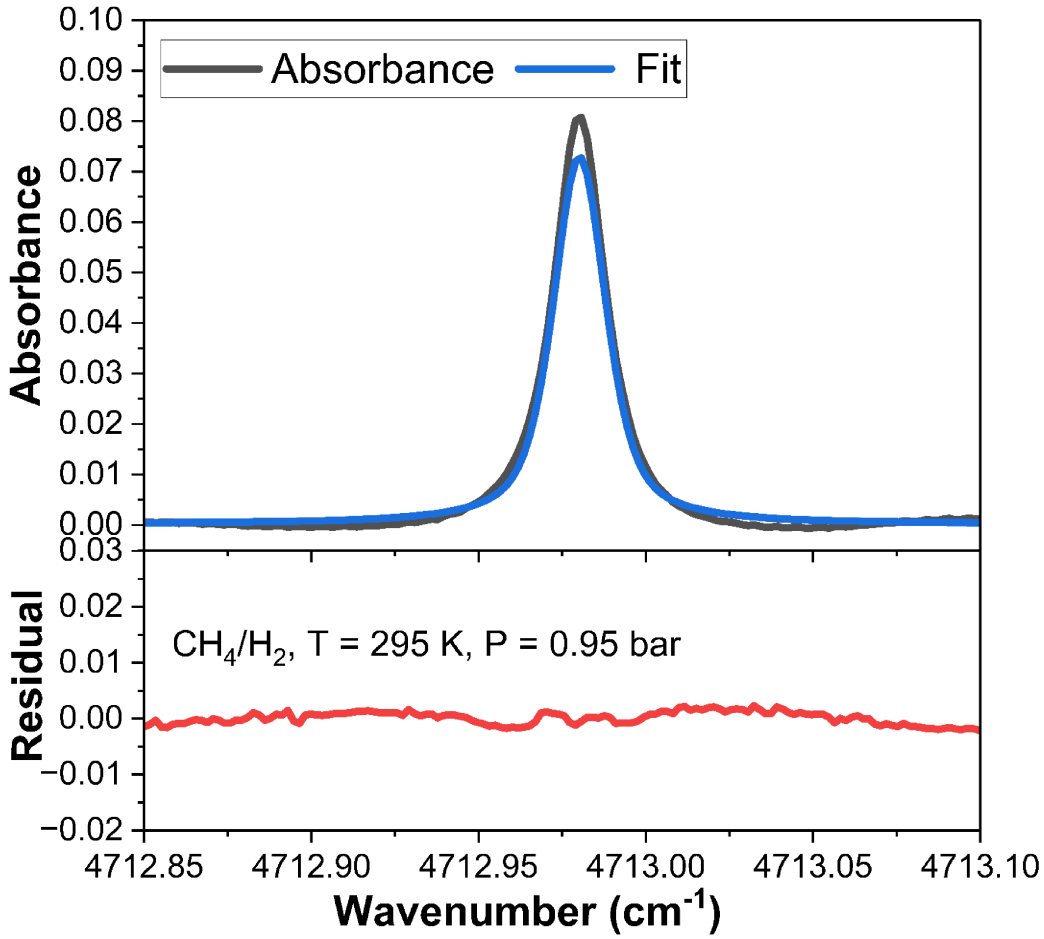

FIGURE 4.25: Absorbance versus wavenumber at 0.95 bar. Voigt-profile fits and residuals for the H_2 Peak in the C_4H_2.

Figure 4.26 shows the absorbance spectra at 295 K for a CH_4/H_2 mixture at pressures of 0.45 bar, 0.65 bar, 0.85 bar and 0.95 bar. As pressure increases, the H_2 peak absorbance rises due to the higher number density in the cell.

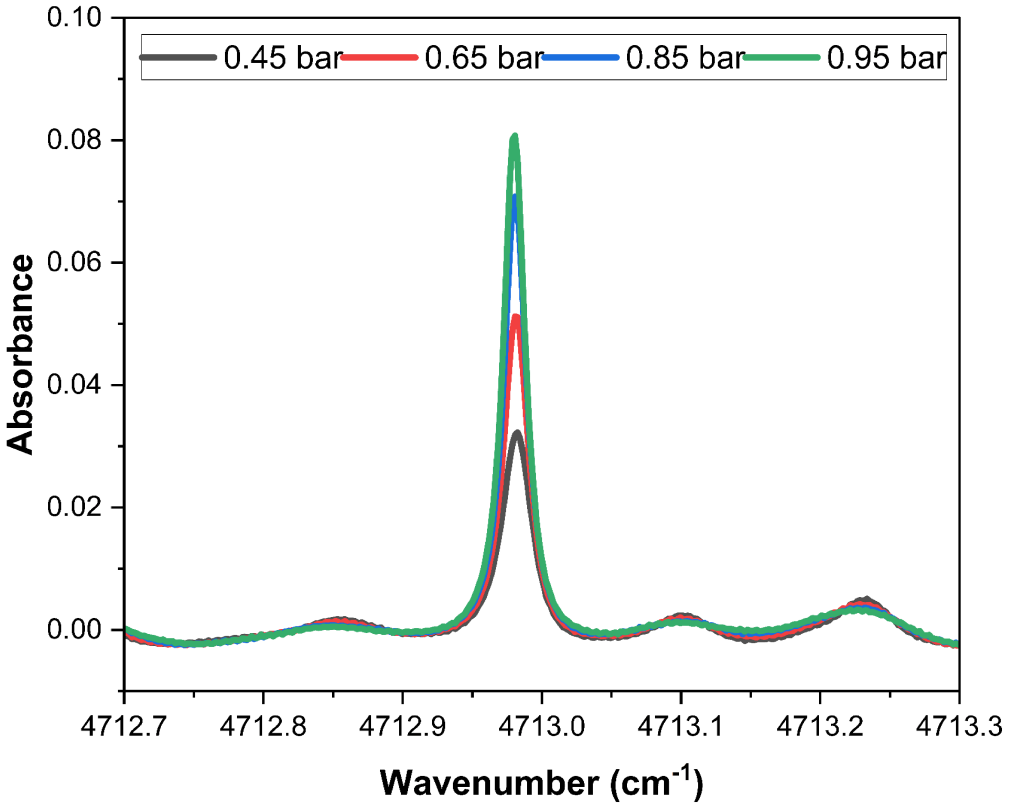

FIGURE 4.26: Absorption spectra of CH_4/H_2 mixture at 295 K for pressures of 0.45, 0.65, 0.85, and 0.95 bar.

Overlaying all CH_4/H_2 absorbance spectra reveals:

- Increasing peak depths for C_4H_2 with pressure.
- Collisional broadening in each line shape.
- Stable line-center wavenumbers within $\pm 0.01 cm^{-1}$.
- Residuals 1% of peak, confirming fit quality.

Line areas for each species can now be integrated and plotted versus pressure to extract their respective line strengths using the same slope-method and uncertainty framework developed for pure H_2.

4.3.3 CH_4/H_2 Area versus Pressure and Linear Fit

Integrating each spectrum yields the absorption area, A, which scales linearly with pressure. Figure 4.27 plots A against P, with a least-squares fit.

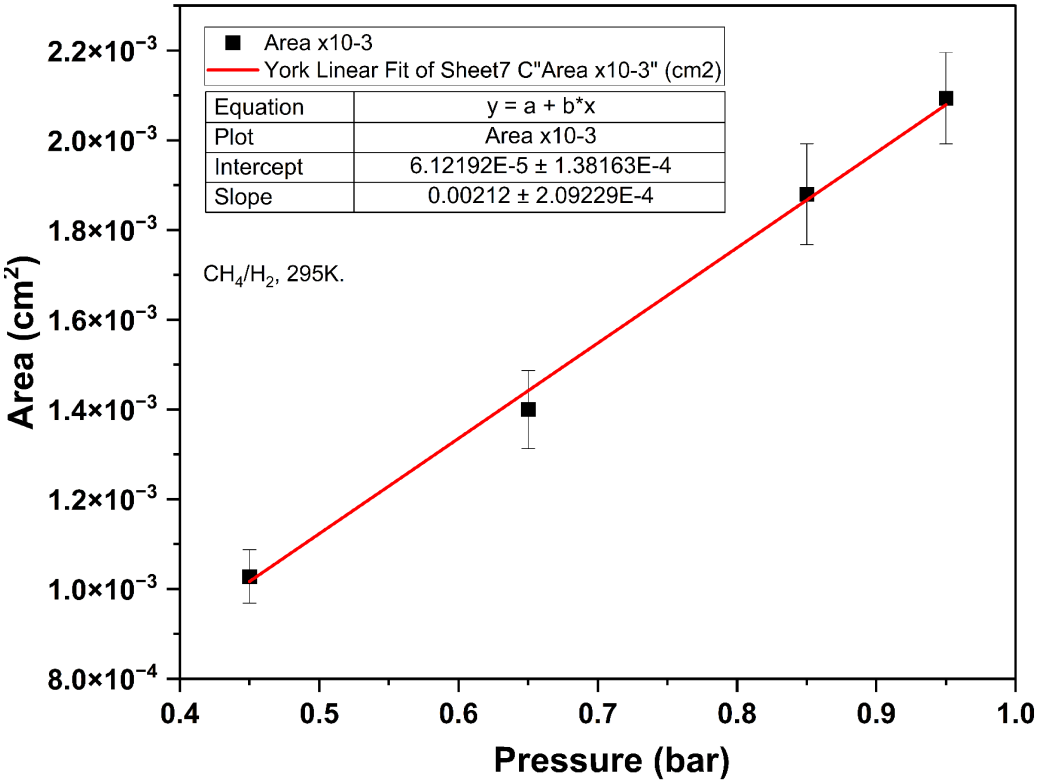

FIGURE 4.27: Integrated absorbance area versus pressure for CH_4/H_2 at 295 K. Black squares are data; red line is the linear fit.

The linear fit equation as used in the pure hydrogen calculations is

$$A = a + b\,P \tag{4.3}$$

with

$$a = (6.12 \pm 1.38) \times 10^{-5}\,\mathrm{cm}^2, \quad b = (2.12 \pm 0.21) \times 10^{-3}\,\mathrm{cm}^2/\mathrm{bar}.$$

4.3.4 Mole Fraction Determination

Using $A = b\,P$ and the relation from Chapter 2

$$X_{H_2} = \frac{k_B\,T}{S\,P\,L}\,A, \tag{4.4}$$

we compute for $P = 0.45\,\text{bar}$:

$$A = 0.00212 \times 0.45 = 9.54 \times 10^{-4}\,\text{cm}^2,$$

$$X_{H_2} = \frac{(1.380649 \times 10^{-23}\,\text{J/K})(295.15\,\text{K})(9.54 \times 10^{-4}\,\text{cm}^2)}{(3.22 \times 10^{-26}\,\text{cm}^{-1}/\text{molecule})(0.45\,\text{bar})(3122.7\,\text{cm})} = 0.8587.$$

These calculations where repeated for pressures from 0.45 bar, 0.65 bar, 0.85 bar, 0.95 bar and the results tabulated below

TABLE 4.4: Absorbance and H_2 mole fraction vs pressure (Linear Fit vs MATLAB).

Pressure (bar)	Absorbance		Mole Fraction X_{H_2}	
	Linear Fit	MATLAB	Linear Fit	MATLAB
0.45	0.03228	0.03217	0.85872	0.85814
0.65	0.05122	0.05130	0.87504	0.87491
0.85	0.07081	0.07079	0.89035	0.89030
0.95	0.08076	0.08067	0.89279	0.89265

4.3.5 Box Plot of Concentration vs Pressure

Figure 4.28 shows a box plot of X_{H_2} at each pressure. The red dashed line is the certified 0.90 value.

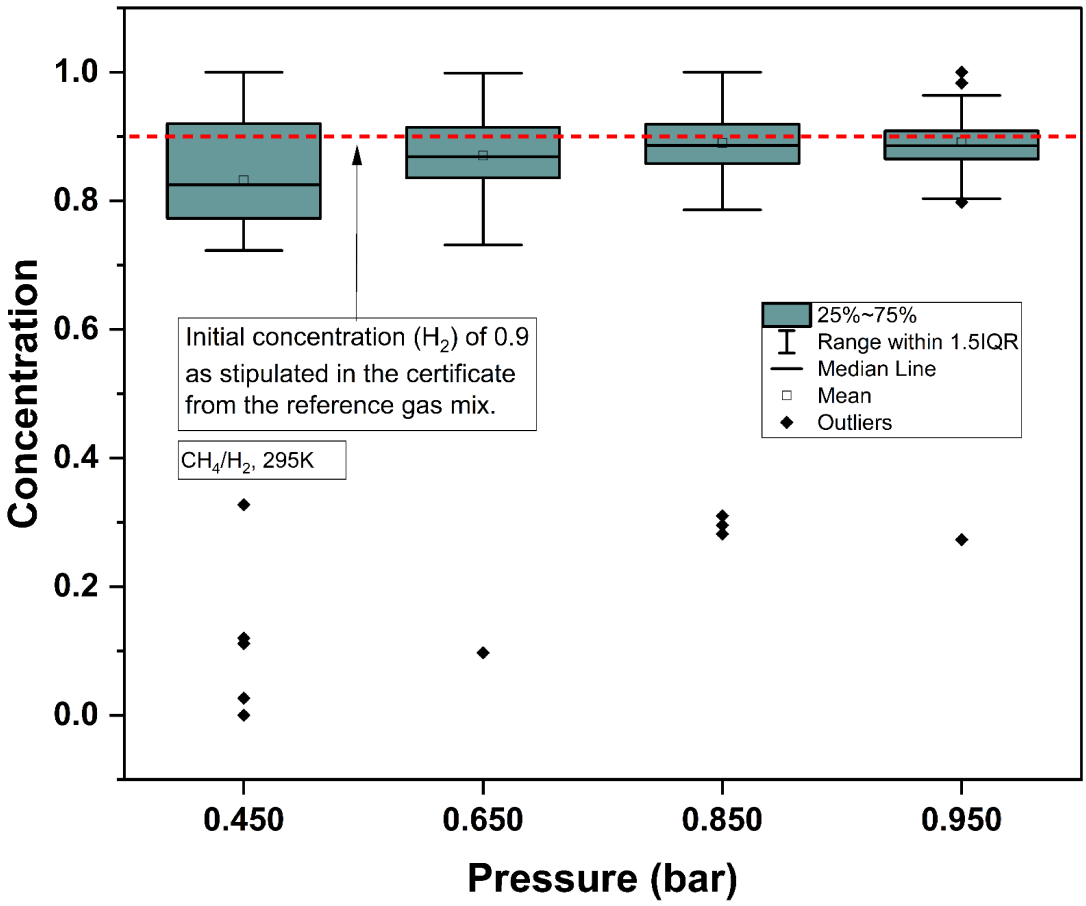

FIGURE 4.28: Box plot of H_2 mole fraction vs pressure; red dashed line at 0.90 is the reference.

Interquartile ranges narrow at higher pressures, indicating improved precision. Outliers at 0.85 bar and 0.95 bar likely stem from baseline or mixing variations.

4.3.6 Comparison with Reference Datasheet

At 0.95 bar the measured $X_{H_2} = 0.8928$ vs the certified $0.900 \pm 2.0\%$. The 0.0072 difference lies within combined uncertainties, confirming excellent agreement. Minor offsets may come from non-ideal gas effects, baseline fitting, or slight inhomogeneity.

4.3.7 Uncertainty Analysis

Table 4.5 lists of uncertainty contributions to X_{H_2}.

TABLE 4.5: Uncertainty budget for CH_4/H_2 mole fraction.

Quantity	k_B	L	S	b	T
Value	1.380649×10^{-23}	3122.7 cm	3.22×10^{-26}	0.00212 cm^2/bar	296.15 K
Uncertainty (%)	—	2.0	0.016	2.09	1.85
Contribution (%)	—	0.0	2.6	97.4	0.0
Total: $X_{H_2} = 0.858 \pm 0.0086$ (1.0%)					

The figure below overlays experimental and certified mole fractions with their 1 sigma error bars.

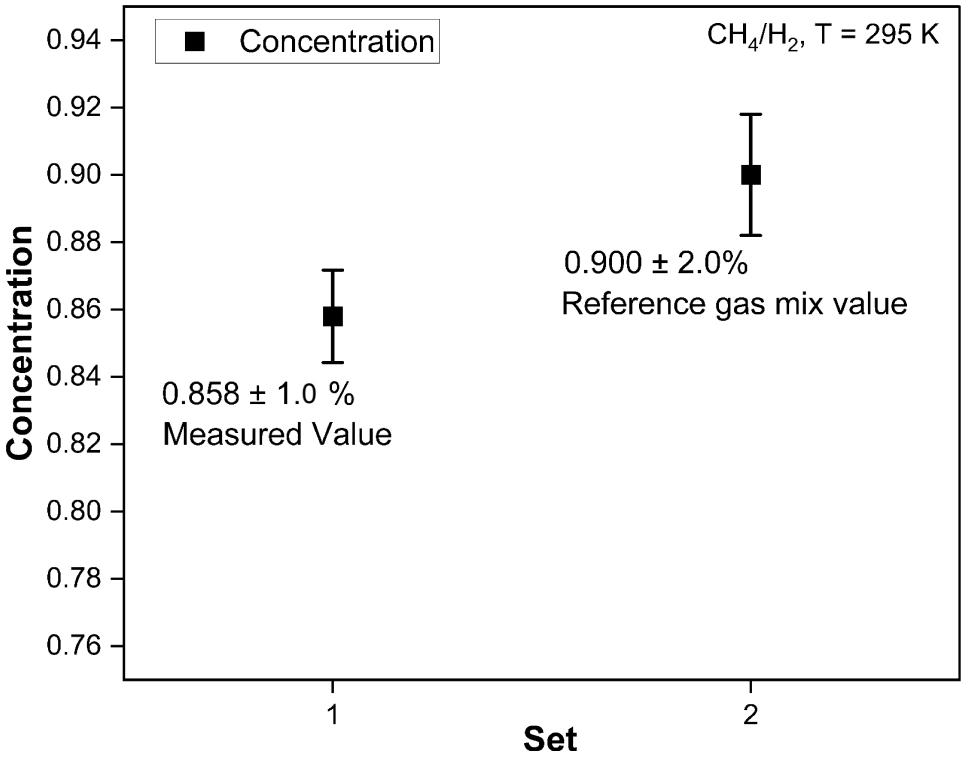

FIGURE 4.29: Experimental vs certified H_2 amount fraction in CH_4/H_2 mixture. Error bars (±1.0%) (experiment), (±2.0%) (certified).

- Absorbance spectra at four pressures confirm linear scaling of integrated area with pressure.
- Slope $b = 0.00212 \pm 0.00021$ cm^2 bar used to compute mole fractions 0.858–0.893, matching the certified ($0.900 \pm 2.0\%$)
- Precision improves at higher pressures; outliers point to baseline or mixing effects.
- Uncertainty is dominated by the gradient determination (97.4%), suggesting focus on noise reduction and pressure stability.
- TDLAS is validated here as a robust, traceable method for CH_4/H_2 mixture analysis in industrial and metrological settings.

4.4 Summary

This chapter has established the metrological performance of our calibration-free TILSAM-based TDLAS spectrometer for hydrogen purity assessment. Using a sealed Heriott multi-pass cell (path length 3122.7 cm) at 295 K, we recorded absorbance spectra of 99.999 % H_2 over pressures from 0.45 bar to 0.95 bar. A York linear regression of integrated absorbance versus pressure yielded an outstanding $R^2 = 0.9997$ and reduced chi-square of 1.08, confirming that residuals lie within one-sigma uncertainties. From the slope of this fit we extracted a line strength $S = (3.22 \pm 0.05) \times 10^{-26}$ cm/molecule with only 1.6 % uncertainty—without recourse to any external calibration standards.

Extending the method to a 10 % CH_4/90 % H_2 mixture, we observed the same linear scaling of H_2 absorbance area with pressure ($b = 2.12{\times}10^{-3} \pm 2.09{\times}10^{-4}$ cm^2/bar), and computed mole fractions X_{H_2} between 0.858 and 0.893 for pressures of 0.45 bar –0.95 bar and with only 1.0 % uncertainty. These values agree excellently with the certified reference ($0.900 \pm 2.0\%$). A detailed GUM-style budget showed that uncertainty is overwhelmingly dominated by the slope determination (97%), with contributions from temperature, path length, and line strength negligible. Taken together, these results validate our spectrometer as a self-calibrating, high-precision tool for both pure-gas and mixed-gas hydrogen analysis, offering traceable, reproducible measurements suitable for demanding industrial and metrological applications.

Chapter 5

Conclusion and Future Work

5.1 Introduction

The H_2-Spectrometer developed in this work has proven to be a robust, calibration-free instrument for high-precision hydrogen analysis. In pure H_2 measurements (0.45–0.95 bar, 295 K, 3122.7 cm path length), a York-weighted regression of integrated absorbance versus pressure yielded a line strength $S = (3.22 \pm 0.05) \times 10^{-26}$ cm/molecule with only 1.6 % combined uncertainty—substantially improving on the 10 % uncertainty in the HITRAN database. In a 10 % CH_4/90 % H_2 mixture, the same linear scaling of H_2 absorbance area with pressure produced mole fractions $X_{H_2} = 0.858$–0.893 that agree with the certified ($0.900 \pm 2.0\%$) value. A rigorous GUM analysis showed that the slope determination contributes 97.4 % of the total uncertainty, while all other parameters are negligible. These results confirm that our TILSAM-based TDLAS spectrometer delivers internally traceable, reproducible hydrogen line-strength and concentration measurements without external standards, making it ideally suited to metrological, industrial, and environmental applications.

5.2 Conclusion

This research has contributed to the the hydrogen economy and the metrological society in several aspects, mainly;

5.2.1 Enhanced Hydrogen Quality Monitoring

The real-time, high-precision monitoring enabled by our spectrometer allows immediate detection of hydrogen purity deviations and impurities. This capability supports rapid response in safety-critical systems, minimizes downtime, and assures consistent feedstock quality for fuel cells and chemical processes.

5.2.2 Advancements in Hydrogen Quality Control

By achieving sub-2 % uncertainty without calibration gases, the developed methods can underpin more reliable process control in hydrogen production, storage, and distribution. Improved measurement fidelity facilitates optimization of operational parameters, ultimately reducing costs and enhancing efficiency across hydrogen applications.

5.2.3 Broader Industrial Applicability

The versatility of the TILSAM-based TDLAS approach makes it adaptable to diverse sectors—transportation, power generation, and chemical manufacturing—where accurate hydrogen quantification is essential. Customizing the spectrometer for different operating pressures and gas matrices can drive wider adoption of hydrogen as a clean energy carrier.

5.2.4 Foundations for Standardization

Detailed traceability and low uncertainty positions this work to inform international standards for hydrogen purity assessment. Consistent, calibration-free measurement protocols can harmonize laboratory practices, support regulatory compliance, and accelerate global confidence in hydrogen quality metrics.

5.3 Limitations and Recommendations for Future Work

5.3.1 Validation against Established Techniques

Future work should include systematic comparisons with established hydrogen measurement methods (e.g., certified gas dilutions, cavity ring-down spectroscopy) to benchmark accuracy and precision under identical conditions. Such validation will clarify the unique advantages and application domains of the TILSAM-based spectrometer.

5.3.2 Extension to Additional Impurities

The current study focused on methane as a model impurity. Extending the methodology to quantify other common contaminants (CO, N_2, CO_2) will test the spectrometer's selectivity and robustness in more complex gas mixtures encountered in industrial streams.

5.3.3 Development of Portable Instruments

Miniaturization of the laser and multipass cell components can enable portable, field-deployable H_2-Spectroscopy systems. Lightweight, battery-powered instruments would facilitate in-situ monitoring in remote pipelines, refueling stations, and environmental field sites.

5.3.4 Refinement of Uncertainty Sources

Although the slope determination dominates the uncertainty budget, future enhancements in baseline fitting algorithms, etalon fringe stability, and pressure control could further reduce measurement variability below 1%. Advanced signal-processing techniques and real-time calibration algorithms should be explored to achieve even higher metrological performance.

5.4 Summary

The H_2-Spectrometer developed in this work achieved a line-strength uncertainty of 1.6 %, representing a tenfold improvement over the 10 % uncertainty in the HITRAN database, and enabled calibration-free hydrogen concentration measurements with less than 1 % combined uncertainty. Its fully traceable TILSAM-based TDLAS approach demonstrated excellent agreement with certified gas-mixture values and offers robust, internally referenced performance across pure and blended hydrogen streams. This

instrument is therefore well suited to metrological, industrial, and environmental applications requiring high-precision H_2 analysis. Future efforts will focus on systematic benchmarking against cavity ring-down and gas-dilution methods, extension to other common impurities (CO, N_2, CO_2), and miniaturization of the optical and multipass components to enable portable, in-field deployment.

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RESEARCH ETHICS CLEARANCE CERTIFICATE

Reference Number: SoS-0257

Date: 26 November 2024

Dear Ms. Rosamunde Popyenisheni Shilongo

This is to inform you that your application for research ethics approval has been approved for the duration of your studies. **You are required to apply for permission to conduct research from the relevant ministry/institution, if applicable, in addition to this ethical clearance**. You may contact the Ethics office (ethics@unam.na) for additional information.

Project title: Hydrogen Purity Assessment Using Laser Absorption Spectroscopy
Student number: 200729471
Level of degree: Postgraduate
Name of degree: Master of Science in Renewable Energy (Material science)
Email address: **rmunde107@gmail.com**
Supervisor(s): Dr. Zivayi Chiguvare & Dr. Bo Shu

Please note the following standard requirements for approval:
This ethical approval is issued by the University of Namibia's Research Ethics Committee following the University of Namibia's Research Ethics Policy and Guidelines. Ethical approval is given in respect of undertakings contained in the research ethics guidelines outlined below**:**

1. Any significant changes in the conditions or undertakings outlined in the approved Proposal must be communicated to the ethics committee. An application to make amendments may be necessary.
2. Any breaches of ethical undertakings or practices that have an impact on the ethical conduct of the research must be reported to the ethics committee.
3. The Principal Researcher must report issues of ethical compliance to the ethics committee (through the Chairperson) at the end of the Project or as may be requested by the ethics committee.
4. The ethics committee retains the right to:

i) Withdraw or amend this Ethical Clearance if any unethical practices (as outlined in the Research Ethics Policy) have been detected or suspected,

ii) Request for an ethical compliance report at any point during the research.

The ethics committee wishes you the best in your research.

Yours sincerely

Prof. Ezikeil G Kwembeya (Chairperson of School of Science (SoS) Decentralized Ethics Committee)

Prof. Davis Mumbengegwi (Head of MRS, Centre for Research Services)

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RESEARCH PERMISSION LETTER

Date: 16/01/2025

Student Name: Rosamunde Popyenisheni Shilongo

Student Number: 200729471

Programme: Master of Science in Renewable Energy

Approved Research Title: Hydrogen Purity Assessment Using Laser Absorption Spectroscopy

TO WHOM IT MAY CONCERN:

I hereby confirm that the above-mentioned student is registered at the University of Namibia for the programme indicated. The proposed study met all the requirements as stipulated in the University guidelines and has been approved by the relevant committees.

The proposal adheres to ethical principles as per attached Ethical Clearance Certificate. Permission is hereby granted to carry out the research as described in the approved proposal.

Best Regards

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