Development of a high-resolution mid-infrared spectroscopy apparatus for the study of methane and other astrochemical molecules.

S M Shah Riyadh
University of Louisville

Follow this and additional works at: https://ir.library.louisville.edu/etd

Part of the Atomic, Molecular and Optical Physics Commons, Optics Commons, Physical Chemistry Commons, and the Quantum Physics Commons

Recommended Citation

This Doctoral Dissertation is brought to you for free and open access by ThinkIR: The University of Louisville's Institutional Repository. It has been accepted for inclusion in Electronic Theses and Dissertations by an authorized administrator of ThinkIR: The University of Louisville's Institutional Repository. This title appears here courtesy of the author, who has retained all other copyrights. For more information, please contact thinkir@louisville.edu.
DEVELOPMENT OF A HIGH-RESOLUTION MID-INFRARED SPECTROSCOPY APPARATUS FOR THE STUDY OF METHANE AND OTHER ASTROCHEMICAL MOLECULES

By
S M Shah Riyadh

B.S., Shahjalal University of Science & Technology, Bangladesh, 2016
M.S., University of Dhaka, Bangladesh, 2018
M.S., University of Louisville, USA, 2020

A Dissertation
Submitted to the Faculty of the
College of Art and Science at the University of Louisville
In Partial Fulfilment of the Requirement
for the Degree of

Doctor of Philosophy in Physics

Department of Physics and Astronomy
University of Louisville
Louisville, Kentucky

May 2024
DEVELOPMENT OF A HIGH-RESOLUTION MID-INFRARED SPECTROSCOPY APPARATUS FOR THE STUDY OF METHANE AND OTHER ASTROCHEMICAL MOLECULES

By

S M Shah Riyadh

B.S., Shahjalal University of Science & Technology, Bangladesh, 2016
M.S., University of Dhaka, Bangladesh, 2018
M.S., University of Louisville, USA, 2020

A Dissertation Approved on
April 4th, 2024
By the Following Dissertation Committee:

Dr. Jinjun Liu (Dissertation Director)

Dr. Gamini Sumanasekera

Dr. Sergio B. Mendes

Dr. Ming Yu

Dr. Richard J. Wittebort
DEDICATION

This dissertation is dedicated to

My parents
Mr. Shah Suja, Mrs. Azmiri Begum
and my lovely wife
Sharmin Akter

who have always given me constant love, strength, and encouragement toward the successful completion of my Ph.D.
ACKNOWLEDGEMENTS

As I reflect upon the many challenges and triumphs of my PhD journey, I am deeply aware that this voyage has not been a solitary one. It is with immense gratitude that I recognize the individuals who have contributed to my academic, personal, and professional development during this pivotal chapter of my life.

At the forefront of this cohort is my supervisor, Dr. Jinjun Liu, whose guidance and unwavering support have been nothing short of transformational. Dr. Liu, your insight and steadfast encouragement have been the bedrock upon which I have built my research and academic confidence. Your mentorship has been a beacon, guiding me through the complexities of my PhD with patience and profound wisdom.

To my distinguished advisors, Dr. Gamini Sumanasekera, Dr. Sergio B. Mendes, Dr. Ming Yu, and Dr. Richard J. Wittebort, I extend my profound appreciation for your invaluable guidance and expertise. Your collective wisdom has significantly shaped both the direction and caliber of my research. Your thoughtful feedback and unwavering high standards have pushed me to achieve more than I thought possible.

I am also grateful to my lab mates, Ian Jones, Rajan Lamichhane, and Touhidul Islam. Your friendship, collaborative spirit, and shared passion for research have greatly
enriched my daily lab experience. Our mutual support and camaraderie have turned daunting tasks into memorable and enjoyable endeavors.

Special thanks are due to Hamzeh Telfah, my postdoc. Your tutelage and the clarity of your guidance have been instrumental in my development as a scientist. The knowledge and skill you have imparted will be enduring tools in my future career.

I must also thank Steve and Josh for their instrumental support. Your expertise and readiness to assist with the equipment have been vital to the success of my experimental work. Your contributions have been an essential component of my research progress.

Finally, my gratitude extends to all those who have contributed directly or indirectly to my research and well-being throughout this PhD journey. Your roles have been varied, but each has been significant, helping to compose the symphony of this transformative experience.

Thank you all for your support, without which this dissertation would not have been possible.
ABSTRACT

DEVELOPMENT OF A HIGH-RESOLUTION MID-INFRARED SPECTROSCOPY APPARATUS FOR THE STUDY OF METHANE AND OTHER ASTROCHEMICAL MOLECULES

S M Shah Riyadh

April 4th, 2024

The present dissertation reports the first steps toward a novel spectroscopic apparatus for investigating methane and other molecules with astrochemical interests. These molecules are known for their complex ro-vibrational (rotational-vibrational) energy levels due to their high symmetry and strong intramolecular interactions. Especially, in the high-energy region of the vibrational spectra, combination bands and “polyad” render the perturbative treatment often adopted by molecular spectroscopy inefficient or ineffective. In addition, spectra from high-temperature regions of space contain hot transitions from vibrationally excited levels. To facilitate the acquisition and analysis of high-resolution vibrational spectra of astrochemicals in near or mid-infrared, we have been developing a cavity-enhanced two-photon, or “double-resonance” (CEDR), spectroscopic technique. The first photon uses a continuous-wave optical parametric oscillator (CW-OPO) as the
light source, whose frequency is locked to a Doppler-free saturation absorption line. It excites the target molecule from the vibrational ground level to a judiciously selected vibrational excited level, usually a CH-stretch mode for its convenience and the possibility of accessing vibrational levels of various symmetries from this intermediate level. The second photon detects a transition from the intermediate level to a higher vibrational level, addressing a limited number of rotational levels allowed by selection rules. To increase sensitivity and selectivity, the first transition may be enhanced by locking the absorption cavity to the CW-OPO, while the CW cavity ring-down (CRD) technique is used as the detection method. Here we report progress toward the research goal, including the principles and specifics of optical and electronic devices, spectroscopic techniques, and analysis of spectroscopic data. In particular, we report the first wide-range Doppler-free saturation absorption spectrum of the Q branch of the $\nu_3 = 1$ band (asymmetric-stretch mode) of CH$_4$, providing significantly improved frequency accuracy compared to lines in existing spectroscopic databases and yielding an average linewidth of 4.5 MHz (FWHM). Absolute frequency calibration was anchored to established optical frequency comb-referenced transition frequencies, with an etalon facilitating relative calibration. Improved accuracy of 3 MHz for 12 transitions is documented. By adopting more advanced mid-infrared light sources and improving the frequency-calibration system, the frequency accuracy may be further improved by a few orders of magnitude. Frequency stabilization of the CW-OPO, a prerequisite of the future CEDR system, has also been achieved and included in the present dissertation. Also reported is the development of the CW-CRD system and proof-of-principle spectra of atmospheric water (H$_2$O). Finally, the general scheme and technical details of the envisioned CEDR spectroscopy apparatus are reported.
The expected mid-infrared CEDR spectroscopic apparatus will have proven a uniquely capable system for the study of astrochemical molecules, supporting observations of the James Webb Space Telescope (JWST). Moreover, high-precision spectroscopic constants extracted from simulating and fitting future high-resolution single-photon mid-infrared spectra can be used to predict pure rotational spectra with precision comparable to or surpassing those of ground-based radio frequency telescopes such as the Green Bank Telescope and ALMA, and hence, guide their observations. From a fundamental point of view, future CEDR spectroscopy will significantly simplify the ro-vibrational spectra, selecting a few rotational levels in each vibrational state. Such a simplification will enable theoretical analysis and quantitative understanding of polyad structures and ro-vibrational interactions such as anharmonicity, the Coriolis interaction, and the Fermi resonance.
TABLE OF CONTENTS

DEDICATION ........................................................................................................ iii

ACKNOWLEDGEMENTS ................................................................................... iv

ABSTRACT ........................................................................................................ vi

LIST OF TABLES .................................................................................................. xiii

LIST OF FIGURES ............................................................................................. xiv

1. INTRODUCTION ............................................................................................. 1

1.1. Background and Motivation......................................................................... 1

1.2. Significance and Applications of Infrared Spectroscopy .............................. 7

1.3. Research Objectives and Methodology....................................................... 10

1.4. Dissertation Overview.................................................................................. 14

2. THEORETICAL BACKGROUND .................................................................... 15

2.1. Principles of Interactions between Electromagnetic Radiation and Molecules ........................................................................................................ 15

2.2. Principles of Nonlinear Optics and Optical Parametric Oscillator .......... 18

2.3. Lineshapes and Line Broadening Mechanisms.............................................. 27

2.3.1. Natural Broadening.................................................................................. 31

2.3.2. Pressure Broadening .............................................................................. 31
2.3.3. Doppler Broadening ........................................................................................................ 32

2.3.4. Power Broadening ........................................................................................................ 34

2.4. Principles of Doppler-Free Spectroscopy Techniques ................................................... 35

2.5. Principles of Cavity-Ring-Down Spectroscopy ................................................................. 41

2.6. Principles of Frequency Locking ....................................................................................... 45

3. OVERVIEW OF THE MID-INFRARED DOPPLER-FREE SATURATION
ABSORPTION SPECTROSCOPY SETUP .............................................................................. 49

3.1. Components of the Mid-Infrared Doppler-Free Setup ................................................... 49

3.2. Continuous-Wave Optical Parametric Oscillator (CW-OPO) as a Light Source
for Mid-Infrared Spectroscopy ............................................................................................... 50

3.2.1. The Optical System of the CW-OPO ........................................................................... 50

3.2.2. The Automation and Wavelength Tuning ................................................................... 62

3.3. Sample Cells and Gas Delivery System .......................................................................... 69

3.4. Acousto-Optic Modulator (AOM) and It’s Cooling System ............................................ 72

3.5. Polarization Components ............................................................................................... 78

3.6. Detection and Amplification ............................................................................................ 80

3.8. Optical Setup .................................................................................................................. 87

4. DATA ACQUISITION AND SPECTRAL CALIBRATION .................................................... 91

4.1. Signal Amplification ........................................................................................................ 91

4.2. DAQ Card and Scan Speed ............................................................................................ 93
7.2.2. CW-CRDS sample Cell ............................................................................ 137
7.2.3. Mode Matching ....................................................................................... 141
7.2.4. Optical Design ....................................................................................... 144
7.2.5. Detection System and Electronic components ...................................... 147
7.3. Time Synchronization Spectroscopy scan system ................................... 150
7.4. Room Temperature CW-CRDS of Water .............................................. 152

8. SUMMARY AND FUTURE DIRECTION ......................................................... 154

REFERENCES .................................................................................................... 157
APPENDIX A .................................................................................................... 163
APPENDIX B .................................................................................................... 166
CURRICULUM VITAE ....................................................................................... 177
LIST OF TABLES

Table 1: TOPO motor calibration table: .............................................................. 65

Table 2: List of Transition frequencies (in cm$^{-1}$) determined in the present work in comparison with the HITRAN database. ................................................................. 118

Table 3: Transitions with improved frequency accuracy in the Q branch of the ν3=1 band of CH4 in comparison with the calculated transition frequencies in the HITRAN database. .................................................................................................................... 122
# LIST OF FIGURES

Figure 1: The complexity of methane's spectrum is depicted through horizontal lines, which signify the levels of vibrational energy. The black curve illustrates the quantity of vibrational sublevels within each polyad, with names indicating the distinct absorption bands. Various spectral regions are showcased through images and spectra: a simulated spectrum for lower polyads is presented in pink, while an example of the spectra captured on Titan by the Huygens probe is highlighted in red. ©NASA/JPL/Space Science Institute[1, 2] .......................................................... 5

Figure 2: Closely packed transition lines creating indistinguishable spectrum .......... 10

Figure 3: Excitation schemes of the Two-photon Double Resonance spectroscopy spectroscopic technique. ........................................................................................................ 12

Figure 4: Dipole under strong Electric field. .............................................................. 19

Figure 5: Gain of a signal for a material with length $\ell$ .......................................... 25

Figure 6: Change in Ring-down-time with an absorber present (Yellow), compare to the absence of absorber (orange) ...................................................................................................... 43

Figure 7: Components of the Mid-Infrared Doppler-Free Setup. ............................. 49

Figure 8: Connection configuration of the TOPO based laser system .................... 50

Figure 9: Schematic diagram for a working CW-OPO system ............................... 57
Figure 10: Output Power of the TOPO ................................................................. 59

Figure 11: Power drift of the TOPO ................................................................. 60

Figure 12: OPO table generation process ....................................................... 63

Figure 13: CW-OPO wavelength tuning process ........................................... 68

Figure 14: First sample Cell used for doppler-free scan .............................. 69

Figure 15: Second Sample Cell used for OPO locking ................................... 70

Figure 16: Schematic Diagram of the AOM Cooling System .......................... 75

Figure 17: Change in polarization by periscope orientation ............................ 78

Figure 18: Pre-amplifiers for InSb (left) & MCT (Right) detectors .................. 81

Figure 19: Home-built Fabry-Perot Cavity ....................................................... 84

Figure 20: Fabry-Pérot Cavity (Etalon) Trace .............................................. 85

Figure 21: Schematic diagram of the doppler free saturation absorption spectroscopy .. 89

Figure 22: Front panel of the custom LabVIEW ......................................... 94

Figure 23: Initial scan parameters in the LabVIEW .................................... 95

Figure 24: TOPO control section of the LabVIEW front panel ...................... 97

Figure 25: Spectral Calibration ................................................................. 99

Figure 26: A section of the scan chosen for calibration ................................ 100

Figure 27: Peak-to-Peak distance (step no.) prior calibration ...................... 101

Figure 28: FSR fluctuation in order of 10^{-10} MHz .................................. 102
Figure 29: Spectral calibration algorithm.............................................................. 103

Figure 30: Comparison between doppler-free and doppler-broaden signal from the setup. ........................................................................................................................................................................................................... 111

Figure 31: FWHM of the Doppler-free signal.......................................................... 112

Figure 32: (Top) Doppler-free saturation absorption spectrum of Q-branch transitions of the v3=1 band of CH4 (b) compared to those in the HITRAN database (a). (Bottom) a portion of the Doppler-free spectrum (d) compared to previous transition frequency measurements using frequency combs for absolute frequency calibration (c). Asterisked transitions are those not reported in the comb-calibrated measurements. Panel (e) shows etalon fringes for relative frequency calibration.......................................................... 114

Figure 33: Figure Details of Doppler-free lineshapes of the asterisked transitions...... 115

Figure 34: Signal deviation from frequency comb measurement............................ 116

Figure 35: Fluctuation in FSR.................................................................................. 123

Figure 36: Creating population in the intermediate state by laser locking............... 125

Figure 37: Electronic schematic of the CW-OPO locking........................................ 126

Figure 38: Lamb-dip signal for frequency lock-in.................................................... 127

Figure 39: Error signal Generation........................................................................... 128

Figure 40: Schematic Diagram of PID Lock-in......................................................... 130

Figure 41: Front panel of Digilock control during a successful lamb-dip lock........... 131

Figure 42: A sample parameter for locking the CW-OPO........................................ 132
Figure 43: CW-CRDS sample cell

Figure 44: Assembly of the Piezoelectric Transducer (PZT) Side Mirror Mount. The left panel shows a cut view highlighting the internal configuration with key components color-coded for clarity: PZT housing and flexible tube (red), optical window mount (blue), PZT extension (light brown), PZT retainer (dark yellow), and the optical window (grey blue). The right panel presents an external view of the assembled mount, showcasing the integration of these components along with the spacer flange (yellow green).

Figure 45: Mirror mount assembly for the non PZT side.

Figure 46: Schematic diagram of CW-CRDS with M2 ring laser.

Figure 47: Schematic diagram of CW-CRDS with the ECDL.

Figure 48: Electronic Signal configuration of CW-CRDS.

Figure 49: Time Synchronization of the CW-CRDS.

Figure 50: CW-CRS spectrum of water(red) compared to the HITRAN database(blue)

Figure 51: Proposed Two Photon Spectroscopy setup.

Figure 52: TOPO Cavity.
1. INTRODUCTION

1.1. Background and Motivation

At the core of modern spectroscopy lies the quest to elucidate molecular structures and dynamics through their spectral fingerprints. The mid-IR spectrum, in particular, is rich with vibrational transitions characteristic of molecular bonds, offering a window into the molecular world. However, the spectral resolution required to discern closely spaced molecular transitions often clashes with the need for high sensitivity to detect species at trace levels. This project seeks to reconcile these demands by harnessing the precision of Doppler-free spectroscopy to resolve narrow molecular transitions, alongside the unparalleled sensitivity of CW-CRDS, capable of detecting species down to parts-per-trillion levels.

The fingerprint region (2800-3300 cm\(^{-1}\)) of the infrared spectrum is crucial for molecular spectroscopy, enabling the differentiation of hydrocarbons (alkanes, alkenes, alkynes) through C-H bond stretching vibrations. Essential for chemical analysis, this range helps in identifying molecular structures and compositions, pivotal in organic chemistry, petrochemical analysis, and environmental monitoring. Liu (2021) emphasizes its significance in organic chemistry for distinguishing hydrocarbon types by the precise stretching positions of the C-H bond[3, 4].
The fingerprint region's complexity, marked by the presence of overtones and combination bands, gives rise to polyads, a phenomenon that significantly enriches the field of molecular spectroscopy[5]. Polyads are essentially clusters of vibrational energy levels that are closely packed together. These clusters form as a result of the molecule absorbing energy, leading to an excited state where multiple vibrational modes can be simultaneously active. The energy levels within a polyad are so closely spaced that they often overlap, particularly as the molecule's energy approaches or exceeds that of its ground state. This overlap creates broad, complex spectral features that are challenging to dissect and analyze due to their density and the blending of numerous vibrational signatures[6].

As shown in Figure 1, molecules exhibiting high symmetry, such as methane (CH₄), the study of polyads becomes particularly insightful. Methane's tetrahedral (Tₐ) structure allows for a variety of vibrational modes that can combine or harmonize to form polyads[7]. Resolving these polyads, or distinguishing the individual energy levels within them, unveils detailed information about the molecule's vibrational behavior. This information is crucial for understanding how energy is distributed and transferred within the molecule, offering a deeper insight into its molecular dynamics and interactions[8]. Such an understanding is not only pivotal in predicting and interpreting the chemical behavior of molecules like methane but also in designing experiments and technologies that rely on precise molecular interactions.

Astrochemistry and spectroscopy have long been affixed, serving as fundamental tools for exploring the molecular composition of interstellar and circumstellar environments. The analysis of electromagnetic radiation, which traverses vast cosmic distances to reach Earth,
provides crucial insights into these environments. Traditionally, observations have predominantly focused on the ultraviolet to visible spectrum, with instruments like the Hubble Space Telescope operating within a 0.1 to 2.5-micron range. However, the launch of the James Webb Space Telescope (JWST) in December 2022 marked a significant shift toward exploring the infrared spectrum, which ranges from 0.6 to 28 microns. This spectrum includes the fingerprint region [9, 10].

The JWST's capabilities extend into the near and mid-infrared regions, where molecular spectra exhibit polyads. By studying these polyads, we can gain insights into the processes that govern molecular formation and behavior in space, contributing to our understanding of the chemical evolution of the universe. This knowledge is instrumental in exploring fundamental questions about the origins of life and the nature of the cosmos [11].

However, analyzing the fingerprint region presents several challenges, including the effects of Fermi resonance, Coriolis coupling, and the high density of rotational levels at elevated temperatures, which obscure the rotational structure in experimental spectra[12, 13]. Recent advancements in spectroscopic methodologies, particularly in laser spectroscopy, have been crucial in overcoming these obstacles. Developments in tunable lasers and nonlinear optical techniques have significantly improved the resolution and analysis of complex molecular spectra [14, 15].

The importance of the fingerprint region is also highlighted in environmental monitoring and petrochemical analysis, where the identification of hydrocarbons can inform pollution studies and the optimization of fuel production processes [16]. Furthermore, the study of
polyads in high-symmetry molecules like methane not only advances our understanding of basic molecular physics but also has implications for energy research, where methane is a key component [17].

In the broader context of molecular spectroscopy, the fingerprint region serves as a window into the molecular world, offering unparalleled insights into molecular structures and dynamics. This understanding is crucial for a wide range of applications, from chemical synthesis to the exploration of cosmic phenomena.
Rotational analysis in the NIR and Mid-IR region is complicated by phenomena such as Fermi resonance and Coriolis coupling. At higher temperatures, where the thermal energy significantly exceeds the rotational constant \((kT >> B)\), the spectra are further complicated by a high rotational partition function, resulting in a dense population of rotational levels and a congested rotational structure in experimental spectra. Hot-band transitions, originating from vibrationally excited levels, add another layer of complexity. Additionally, Doppler broadening, proportional to temperature, affects the spectral
resolution, challenging the detailed rotational analysis in direct absorption spectroscopy at ambient conditions [5][6]. In addition to this complication, thermochemical analysis indicates that under temperatures below approximately 1,000 K and across various plausible atmospheric compositions, methane (CH$_4$) is expected to be the predominant carbon-containing species. This phenomenon is observed in the planets within our solar system and has been verified in the atmospheres of brown dwarfs and self-luminous exoplanets[18], drastically increasing the likelihood of hot bands, not all of which will be excitations to states directly accessible from the ground state. On Saturn's moon Titan, it serves a function akin to that of water on Earth, resulting in a diverse and intricate chemical environment. As the energy increases, the number of levels within each polyad expands, leading to methane's extensive absorption bands. This phenomenon is depicted in Figure 1, which features an image of Saturn captured by the Cassini spacecraft, highlighting dark zones where light is absorbed in regions of highly excited polyads. Such light absorption by methane also contributes to the opacity of Titan's atmosphere[1].

These challenges underscore the need for advanced spectroscopic methodologies capable of high-resolution and sensitive detection in the NIR and Mid-IR region. The development of lasers with extensive tunability, facilitated by recent nonlinear optical techniques, offers promising avenues for addressing these spectroscopic challenges. Such technological advancements hold the potential to significantly enhance our understanding of molecular dynamics in space, contributing to the broader field of astrochemistry [7][8].
1.2. Significance and Applications of Infrared Spectroscopy

Infrared spectroscopy, particularly in the mid-infrared range, stands at the forefront of analytical science, offering a non-invasive, high-resolution window into molecular structures and dynamics. Its significance spans across multiple disciplines, harnessing the unique ability to probe the vibrational states of molecules, which is invaluable for both fundamental research and practical applications.

**Astrochemistry and Astrophysics:** The exploration of astrochemical molecules, such as methane, in the interstellar medium underscores the profound utility of mid-infrared spectroscopy. It facilitates the study of molecular clouds, planetary atmospheres, and cometary comas, providing insights into the chemical processes that occur in these environments.[19] This research is instrumental in advancing our understanding of cosmic phenomena, including star formation, planetary system development, and the potential for life in the universe. The precise analysis of vibrational spectra allows for the identification and quantification of molecules, even in the extreme conditions of space, supporting observations from telescopes and space missions.
**Environmental Science**: Mid-infrared spectroscopy plays a pivotal role in monitoring atmospheric pollutants and tracing greenhouse gas emissions. The technique’s sensitivity to the vibrational signatures of molecules like carbon dioxide and methane makes it indispensable for assessing air quality, studying climate change, and developing strategies for environmental protection.[20]

**Chemical and Petrochemical Industries**: In the realm of chemical analysis, the capability to distinguish between different hydrocarbon structures through their C-H bond vibrations opens up vast possibilities. This precision is critical for identifying compounds, determining molecular configurations, and analyzing reaction outcomes, which are essential for product development, quality assurance, and regulatory compliance in the chemical and petrochemical sectors.[21, 22]

**Biomedical Research and Diagnostics**: The ability of infrared spectroscopy to detect specific molecular bonds and functional groups without the need for labels or dyes renders it a powerful tool for biomedical applications. It is used in diagnosing diseases, analyzing tissue samples, and investigating biomolecular structures, contributing to the development of therapeutic strategies and medical technologies.[23]

**Technological Innovation and Method Development**: The advancement of high-resolution mid-infrared spectroscopic techniques, such as the development of cavity-enhanced or two-photon spectroscopy, underscores the ongoing innovation in this field. These improvements not only enhance the sensitivity and selectivity of molecular detection but also pave the way for new applications in scientific research and industry.[24]
In sum, infrared spectroscopy, with its unparalleled analytical capabilities, continues to be a cornerstone of modern science and technology. Its applications, from deciphering the mysteries of the cosmos to safeguarding our environment and advancing health sciences, underscore its indispensable role in addressing some of the most pressing challenges of our time.
1.3. Research Objectives and Methodology

Doppler-free spectroscopy addresses the challenge of spectral line overlap in molecular spectra, particularly when distinguishing closely packed rovibrational levels. Traditional spectroscopic methods often suffer from Doppler broadening, where the motion of molecules blurs the spectral lines, making it difficult to resolve individual transitions. As illustrated in the Figure 2, two energy levels that are typically indistinguishable due to their proximity and the broadening effects can be clearly separated using Doppler-free techniques. This method utilizes counter-propagating laser beams to interact exclusively with molecules having minimal or no velocity along the beam's axis, thereby eliminating the Doppler effect. This selective interaction allows for the precise resolution of rovibrational levels, offering a clearer understanding of molecular structures and dynamics.

Schawlow's Nobel lecture in 1982 laid the foundational principles of laser spectroscopy, including Doppler-free techniques, highlighting their critical role in unveiling the quantum mechanical nature of molecules [25]. This was followed by Kiermeier et al.'s 1986 exploration of Doppler-free saturation spectroscopy in polyatomic...
molecules, specifically investigating photochemical hole burning in gas-phase s-tetrazine, showcasing the technique's utility in dissecting complex molecular systems[26]. Bylicki et al. in 1989, and Meijer et al. in 1987, further expanded the technique's applicability through saturation spectroscopy and optical-optical double resonance (OODR) methods, respectively, enabling detailed studies of molecular dynamics and structures in various experimental settings, including collimated molecular beams [27, 28]. Advancements continued into the 21st century, with Huang et al. in 2013 applying Doppler-free spectroscopy to the precise measurement of iodine hyperfine transitions at 671 nm, achieving high precision in studying molecular iodine's hyperfine structure[29]. Most recently, Bartalini et al. in 2009 demonstrated the integration of Doppler-free polarization spectroscopy with quantum cascade laser technology at 4.3 μm, marking a significant milestone in high-resolution spectroscopy in the mid-infrared spectrum[30]. Together, these contributions underscore the evolution of Doppler-free spectroscopy from its theoretical underpinnings to its practical applications across a spectrum of molecular systems, promising to unveil new dimensions in the quantum mechanical exploration of molecules.

Doppler-free spectroscopy offers a powerful solution for resolving the complex spectra of methane (CH₄). Understanding methane (CH₄) is crucial due to its significant role in astrochemistry, atmospheric science, and combustion processes. Methane, a potent greenhouse gas, plays a pivotal role in Earth's climate system and is a primary component of natural gas, making it essential for energy production [31]. In astrochemistry, methane's presence on other planets and moons provides clues about extraterrestrial chemistry and
potential habitability \cite{32, 33}. High-resolution Doppler-free spectroscopy offers a powerful tool for resolving the complex rovibrational levels of methane, enabling precise measurements of its spectral lines \cite{34}. This capability is vital for accurately modeling methane's atmospheric chemistry, understanding its role in planetary atmospheres, and improving combustion efficiency in energy applications \cite{35}. The technique's ability to eliminate Doppler broadening allows for the detailed study of methane's quantum mechanical behavior, providing insights into its molecular structure and dynamics that are critical for various scientific and industrial applications \cite{34}.

In Two-photon Double Resonance spectroscopy, we access highly excited vibrational levels in a two-photon excitation method: a $|1\rangle \leftrightarrow |0\rangle$ "pump" transition followed by a $|2\rangle \leftrightarrow |1\rangle$ "repump" transition, as shown in Figure 3. The probability of achieving multi-photon excitations is typically low, especially with continuous wave (CW) lasers. To improve the signal-to-noise ratio (S/N), the pump transition is enhanced using a high-finesse optical cavity, and the repump transition is detected with the cavity ring-down (CRD) technique. The frequency of the pump laser is set to a specific ro-vibrational transition identified from the Doppler-free absorption spectrum by laser lock-in technique, while the repump laser's frequency is varied to explore the energy levels of the target state. The CEDR
method aims to significantly increase the S/N by using cavity enhancement. Selecting the right intermediate state (|1⟩), allows access to new quantum states, including higher polyads and vibrational levels close to the dissociation limit. The spectra from double-resonance have a simpler rotational structure since only one rotational level of the intermediate state is excited. This simplification helps in rotational simulation and vibronic assignment.

Previous attempt on CH₄ was successful in recording double resonance spectra but was limited by the linewidth.[36, 37]. A low-resolution survey of CH₄ in the NIR and visible regions has been reported previously, which will be used to guide the future two-photon spectroscopy measurements[38].
1.4. Dissertation Overview

This study aims to develop a novel spectroscopic apparatus for high-resolution analysis of methane and other molecules of astrochemical interest. These molecules present complex ro-vibrational energy levels due to their high symmetry and strong intramolecular interactions, which are challenging to analyze with traditional spectroscopic methods, especially in the vibrational spectra’s high-energy regions. Initially the research focuses on developing a Doppler-free saturation absorption spectroscopy apparatus using a continuous-wave optical parametric oscillator (CW-OPO) to scan the Mid-IR region with high precision and high speed. This is followed by a locking system to lock the laser source (CW-OPO) to a single ro-vibrational level. This step is the beginning of a two-photon or "double-resonance" spectroscopic technique. In this technique, the CW-OPO is used to move the target molecule from the vibrational ground level to a chosen ro-vibrational excited level. Then, a highly sensitive continuous-wave cavity ring-down (CW-CRDS) spectroscopy setup is used to detect transitions to higher vibrational levels. This method aims to enhance sensitivity and selectivity in spectroscopic measurements. The ultimate goal is to facilitate the acquisition and analysis of high-resolution vibrational spectra of astrochemical molecules in the near or mid-infrared, significantly improving frequency accuracy compared to existing spectroscopic databases and enabling a deeper understanding of molecular dynamics in space.
2. THEORETICAL BACKGROUND

2.1. Principles of Interactions between Electromagnetic Radiation and Molecules

The interaction between electromagnetic radiation and molecules is a cornerstone of molecular spectroscopy, enabling the determination of molecular structure, dynamics, and environment. This interaction is governed by the quantum mechanical principles of absorption, emission, and scattering of photons by molecules. The energy of an incident photon can be absorbed by a molecule if it matches the energy difference between two quantum states, leading to electronic, vibrational, or rotational transitions. This process can be described by the equation:

\[ E_{\text{photon}} = h \nu = E_f - E_i \]  \hspace{1cm} (2.1)

where \( E_{\text{photon}} \) is the energy of the photon, \( h \) is Planck's constant, \( \nu \) is the frequency of the electromagnetic radiation, and \( E_f \) and \( E_i \) are the energies of the final and initial states, respectively.

If we consider a system composed of \( N \) two-level molecules, each capable of existing in one of two energy states, with the system maintained at a constant temperature \( T \) and immersed in broadband electromagnetic (EM) radiation with density \( \rho(\nu) \). At thermal equilibrium, the ratio of the number of molecules in the final state \( N_f \) to those in the initial
state $N_i$, where the total number of molecules $N = N_f + N_i$, follows the Boltzmann distribution:

$$\frac{N_i}{N} = e^{-\frac{h\nu_{if}}{kT}}$$  \hfill (2.2)

Here, $h\nu_{if} = E_f - E_i$ represents the energy difference between the two states, encapsulating the Boltzmann expression for equilibrium between distinct, nondegenerate energy levels.

The interaction between these molecules and EM radiation manifests through three primary processes: absorption, spontaneous emission, and stimulated emission. Each process alters the state of a molecule between $E_i$ and $E_f$.

**Absorption:** Occurs when a molecule in the initial energy state $E_i$ absorbs a photon with energy $h\nu_{if}$, corresponding to the energy gap to the final state $E_f$, transitioning to that higher energy state. The rate of absorption can be expressed as:

$$\frac{dN_f}{dt} = B_{f\rightarrow i}\rho(v_{if})N_i$$  \hfill (2.3)

Where, $B_{f\rightarrow i}$ is the coefficient for absorption.
**Spontaneous Emission:** A molecule in the final energy state $E_f$ can spontaneously emit a photon and transition to the initial energy state $E_i$, independent of the external EM field. This emission rate is described by:

$$\frac{dN_f}{dt} = -A_{f\rightarrow i}N_f$$

(2.4)

Where, $A_{f\rightarrow i}$ is the spontaneous emission coefficient.

**Stimulated Emission:** Similar to absorption but in reverse, when a molecule in the final state $E_f$ encounters a photon of energy $\hbar \nu_{if}$, it can be stimulated to emit an identical photon and transition to the initial state $E_i$. The rate of stimulated emission is given by:

$$\frac{dN_f}{dt} = -B_{f\rightarrow i}\rho(\nu_{if})N_f$$

(2.5)

Where, $B_{f\rightarrow i}$ is the coefficient for stimulated emission.

Equilibrium conditions dictate that the rates of absorption and emission processes are balanced. Given that the Boltzmann distribution describes the population ratio between the energy states, the radiation density $\rho(\nu_{if})$ responsible for these transitions aligns with the Planck radiation law:

$$\rho(\nu_{if}) = \frac{8\pi\hbar^3\nu_{if}^3}{c^3} \left( \frac{1}{e^{\hbar\nu_{if}/kT} - 1} \right)$$

(2.6)
This relationship between absorption, spontaneous emission, and stimulated emission processes illustrates the intricate balance that governs the interaction between electromagnetic radiation and molecules. The coefficients for absorption \( (B_{f\rightarrow i}) \) and stimulated emission \( (B_{f\rightarrow i}) \) are shown to be equivalent, signifying a fundamental symmetry in the processes of energy absorption and emission. Furthermore, the spontaneous emission coefficient \( (A_{f\rightarrow i}) \) can be derived from these relationships, highlighting the quantum mechanical underpinning of these interactions.[39-41]

### 2.2. Principles of Nonlinear Optics and Optical Parametric Oscillator

When light, or an electromagnetic wave, comes into contact with a dielectric material, it causes the electrons to shift relative to their nuclei, creating a polarization, or a dipole moment per unit volume. This interaction can lead to the material emitting light waves, with the energy and wavelength of these waves depending on the dipole moment and its oscillation frequency. In situations where the incoming electric field is weak, the material's induced polarization changes linearly with the field's strength, described by the equation:

\[
P = \varepsilon_0 \chi^{(1)} E,
\]  

(2.7)
Where, \((P)\) and \((E)\) represent the polarization and electric field vectors, respectively, \((\chi^{(1)})\) is the linear susceptibility, and \((\varepsilon_0)\) is the vacuum permittivity. This scenario falls under linear optics, where both the dipole's oscillation and the resulting optical wave match the input field's frequency.

However, when the electric field's strength increases significantly, the relationship between dipole displacement and the electric field becomes nonlinear, marking the domain of nonlinear optics. As shown in Figure 4 due to a strong electric field, the dipole vibrates at multiple frequencies, not just the original input frequency, thereby producing new wavelengths of light. The general expression for induced polarization then becomes:

\[
P = \varepsilon_0 \chi^{(1)}E + \varepsilon_0 \chi^{(2)}E^2 + \varepsilon_0 \chi^{(3)}E^3 + \cdots \quad (2.8)
\]

incorporating higher-order nonlinear susceptibilities like \((\chi^{(2)}), (\chi^{(3)}), \) etc. Non-centrosymmetric materials exhibit even-order nonlinear effects, while both centrosymmetric and non-centrosymmetric materials can display odd-order nonlinearities. Achieving such nonlinear optical effects typically requires the high optical intensities only lasers can provide.[42, 43]
Second-order nonlinear optical effects occur in non-centrosymmetric materials when subjected to strong electromagnetic fields. These effects arise due to the second-order term in the expansion of the material's polarization response to an applied electric field. Some key second-order nonlinear effects are:

1. **Second Harmonic Generation (SHG):** This effect involves the conversion of two photons of a given frequency \((\omega)\) into a single photon with twice the frequency \((2\omega)\), effectively doubling the frequency of the incident light. SHG is widely used for frequency doubling of laser light, enabling the generation of new wavelengths that are not directly accessible with available laser sources.

2. **Sum Frequency Generation (SFG):** In SFG, two photons of different frequencies \((\omega_1)\) and \((\omega_2)\) combine to produce a photon with a frequency equal to the sum of the two initial frequencies \((\omega_1 + \omega_2)\). SFG is useful for spectroscopy and in generating light at frequencies that are not easily accessible by direct methods.

3. **Difference Frequency Generation (DFG):** DFG is the opposite of SFG, where a photon of frequency \((\omega_3)\) is generated by mixing two photons of higher frequencies \((\omega_1)\) and \((\omega_2)\) such that \((\omega_3 = \omega_1 - \omega_2)\). This process is used to produce tunable infrared radiation.

4. **Optical Parametric Amplification (OPA) and Optical Parametric Oscillation (OPO):** These processes involve the amplification of a signal beam and the generation of an idler beam through the nonlinear interaction of a pump beam with a nonlinear optical material. OPAs and OPOs are used to generate widely tunable coherent radiation.
5. Electric Field Induced Second Harmonic Generation (EFISHG): This phenomenon occurs when an external electric field is applied to a material, enhancing its nonlinear optical response, including the generation of second harmonic signals. It's used for electric field sensing and studying the electronic properties of materials.

6. Pockels Effect: Also known as the linear electro-optic effect, this is where the refractive index of a material changes linearly with an applied electric field, leading to modulation of the phase of the transmitted light. It's utilized in electro-optic modulators for controlling light in optical communication systems.

These second-order nonlinear effects play crucial roles in modern optics and photonics, enabling a range of applications from laser technology and light generation to spectroscopy and optical communication. [44-46]
Continuous-wave optical Parametric Oscillators (CW-OPOs) represent a frontier in the domain of nonlinear optics, offering a coherent and tunable light source across diverse wavelength ranges. Unlike their pulsed counterparts, which emit in temporal bursts, CW-OPOs operate in a steady, continuous mode, granting them enhanced stability and narrower spectral line widths. This continuous emission emerges through a process wherein a photon from a pump wave is converted into two distinct photons, termed the signal and the idler, in a nonlinear optical medium. The principle underpinning this conversion is phase matching, ensuring efficient energy transfer. Due to their unique properties, CW-OPOs have carved a niche in numerous scientific applications, ranging from precision spectroscopy to quantum information science. [40, 41]

I. Energy Conservation:

The energy of the pump photon is divided between the signal and idler photons.

\[ \hbar \omega_p = \hbar \omega_s + \hbar \omega_i \]  \hspace{1cm} (2.9)

Where:

- \( \hbar \) is the reduced Planck constant.
- \( \omega_p, \omega_s, \) and \( \omega_i \) are the angular frequencies of the pump, signal, and idler waves, respectively.
II. Momentum (or Phase) Matching:

For efficient energy transfer, the momentum of the pump photon should match the combined momentum of the signal and idler photons.

\[ k_p = k_s + k_i \]  \hspace{2cm} (2.10)

Where:

- \( k_p, k_s, \) and \( k_i \) are the wave vectors of the pump, signal, and idler, respectively.

In the ideal scenario of perfect phase matching \( \Delta k = 0 \), the dipoles within the medium align such that their emissions reinforce one another in the forward direction, allowing the field amplitude to increase linearly as it travels through the medium. This ideal alignment results from the uniform phase velocity of all interacting waves, a condition not typically met due to the natural dispersion within nonlinear media that causes different optical waves to travel at varying phase velocities, leading to a nonzero \( \Delta k \). As a consequence, the coherence of the wave interaction diminishes beyond a certain distance, known as the coherence length, \( l_c = \frac{2\pi}{\Delta k} \) where the phase relationship between the waves shifts by 180 degrees. This causes the waves to periodically align and misalign as they propagate, resulting in a cyclic exchange of energy.

To overcome this challenge and achieve effective phase matching, two principal techniques are employed: birefringent phase matching (BPM) and quasi-phase matching (QPM). BPM exploits the natural birefringence of certain crystals to match the phase velocities of the
interacting waves by aligning the crystal such that the refractive index for one wave matches the effective refractive index for the other wave. On the other hand, QPM involves artificially modulating the sign of the nonlinear coefficient along the propagation direction to maintain the phase alignment, effectively allowing for a controlled interaction despite the phase mismatch.

III. Oscillation Threshold:

For a CW-OPO to start oscillating, the parametric gain must exceed the round-trip losses in the resonator. The threshold condition can be represented as:

\[ G(\omega_s, \omega_i) > L \]

Where:

- \( G(\omega_s, \omega_i) \) is the parametric gain for signal and idler frequencies.
- \( L \) is the round-trip loss in the OPO cavity.
IV. Parametric Gain:

The single-pass parametric gain within a nonlinear crystal with length $\ell$ is defined as:

$$G_s(L) = \frac{I_s(l)}{I_s(0)} - 1 = \frac{\Gamma^2 l^2 \sinh^2 \left( \sqrt{\Gamma^2 l^2 - \left(\frac{\Delta k l}{2}\right)^2} \right)}{\Gamma^2 l^2 - \left(\frac{\Delta k l}{2}\right)^2}$$  \hspace{1cm} (2.12)

where $I_s$ represents the signal field intensity and $\Gamma$ is the gain factor, calculated by:

$$\Gamma^2 = \frac{8\pi^2 d_{eff}^2}{c \varepsilon_0 n_p n_s n_i \lambda_p \lambda_s \lambda_i} I_p(0)$$  \hspace{1cm} (2.13)

In this formula, $I_p$ is the pump intensity, and $n_p, n_s,$ and $n_i$ are the refractive indices of the pump, signal, and idler at their respective wavelengths $\lambda_p, \lambda_s,$ and $\lambda_i$.

For perfect phase matching condition, $\Delta k = k_p - k_s - k_i = 0$:

$$G_s(L) = \sinh^2(\Gamma l)$$  \hspace{1cm} (2.14)

*Figure 5: Gain of a signal for a material with length $\ell$*
For low gains ($\Gamma l < 1$), this can be approximated to:

$$G_s(l) \approx \Gamma^2 l^2 \quad (2.15)$$

And for high gains ($\Gamma l > 1$), it simplifies to an exponential increase:

$$G_s(l) \approx \frac{1}{4} e^{2\Gamma l} \quad (2.16)$$

Thus, under phase-matching conditions, the signal gain initially shows a quadratic dependency on $\Gamma$ in the low-gain scenario and transitions to an exponential growth with $2\Gamma$ in the high-gain scenario.[42]
2.3. Lineshapes and Line Broadening Mechanisms

In spectroscopy, the broadening of spectral lines can be categorized into two main types based on their causes: inhomogeneous and homogeneous broadening. These broadening mechanisms affect the observed line shapes (the appearance of spectral lines) in distinct ways.

**Homogeneous Broadening**

Homogeneous broadening occurs when all the emitters (atoms, molecules, ions) within a sample contribute equally to the broadening of a spectral line. This means that the broadening effect applies uniformly across the entire sample, affecting each emitter in the same way regardless of its location or environment. Homogeneous broadening leads to a symmetric line shape, often Lorentzian, around the central frequency. The primary causes of homogeneous broadening include:

- **Natural Broadening**
- **Pressure Broadening (Collisional Broadening)**
- **Power Broadening**
Inhomogeneous Broadening

Inhomogeneous broadening arises from variations in the local environment of each emitter within the sample, causing differences in the frequency of the emitted or absorbed radiation. This type of broadening results in an asymmetric or non-uniform line shape and is not characterized by a single mechanism affecting all emitters equally. Inhomogeneous broadening can be caused by:

- Doppler Broadening
- Stark Broadening
- Zeeman Broadening

Comparison and Impact on Spectroscopy

The key difference between homogeneous and inhomogeneous broadening lies in their cause and effect on the spectral line shape:

- Homogeneous broadening affects all emitters equally, leading to symmetric line shapes, typically Lorentzian.

- Inhomogeneous broadening results from variations in the local environments or conditions experienced by the emitters, causing asymmetric or non-uniform line shapes, often Gaussian for Doppler broadening.
When a transition possesses a natural homogeneous lineshape $g_H(v - v_0)$, centered around $(v_0)$, and an inhomogeneous distribution function $g_I(v_0 - v_0)$, with its center at $(v_0)$, the overall lineshape function $g(v - v_0)$ mathematically expressed as:

$$
 g(v - v_0) = \int_{-\infty}^{\infty} g_I(v' - v_0) g_H(v - v_0') \, dv_0' 
$$

(2.17)

Here, the function $g_I(v' - v_0)$ denotes the likelihood of a system resonating within the frequency range $(v_0')$ to $(v_0' + dv_0')$, formalized as:

$$
 dp = g_I(v' - v_0) \, dv_0'. 
$$

(2.18)

This equation is recognized mathematically as a convolution between $(g_I)$ & $(g_H)$.

Typically, the homogeneous lineshape function $(g_H)$ adopts a Lorentzian profile, whereas the inhomogeneous function $(g_I)$ follows a Gaussian distribution. The convolution of these two yields what is known as a Voigt lineshape function.

If the width of the inhomogeneous part is much larger than the width of the homogeneous part, meaning $(\Delta v_l \gg \Delta v_H)$, then the homogeneous lineshape $(g_H(v - v_0))$ can be treated like a very sharp peak at $(v = v_0)$. This leads to:

$$
 g(v - v_0) = \int_{-\infty}^{\infty} g_I(v' - v_0) \delta(v - v_0') \, dv_0'. 
$$

(2.19)
which simplifies to:

\[ g(\nu - \nu_0) = g_l(\nu - \nu_0). \]  \hspace{1cm} (2.20)

On the other hand, if the width of the inhomogeneous part is much smaller than that of the homogeneous part, or \((\Delta \nu_l \ll \Delta \nu_H)\), then the inhomogeneous lineshape \(g_l(\nu'_0 - \nu_0)\) can be treated like a very sharp peak as well, and the overall lineshape turns into:

\[ g(\nu - \nu_0) = g_H(\nu - \nu_0). \]  \hspace{1cm} (2.21)

This shows whether the inhomogeneous or homogeneous broadening shapes the overall appearance of the spectral line, depending on which one is wider. [39]
2.3.1. Natural Broadening

Natural broadening arises from the intrinsic uncertainty in the energy levels of molecules, as described by Heisenberg's uncertainty principle. The lifetime of an excited state ($\tau$) imposes a limit on the precision with which the energy (and therefore the frequency) of the transition can be defined, resulting in a Lorentzian lineshape with a full width at half maximum (FWHM) given by:

$$\Delta \nu = \frac{1}{2\pi \tau}$$  \hspace{1cm} (2.22)

2.3.2. Pressure Broadening

Pressure broadening, or collisional broadening, occurs due to interactions between molecules in a gas phase, which alter the energy levels and phase of the emitting or absorbing molecule. This mechanism is more pronounced at higher pressures where collisions are frequent. The broadening effect is also modeled by a Lorentzian distribution, and its width is proportional to the pressure of the gas.
2.3.3. Doppler Broadening

When an atom moves with velocity $\mathbf{v}$ and interacts with a plane electromagnetic wave characterized by a wave vector $\mathbf{k}$, the frequency of the wave as perceived by the atom is subject to the Doppler effect, depending on the alignment of $\mathbf{v}$ and $\mathbf{k}$. Specifically, the observed frequency ($\nu'$) shifts according to the equation:

$$
\nu' = \nu \left(1 - \frac{\mathbf{v} \cdot \mathbf{k}}{c|\mathbf{k}|}\right)
$$

(2.23)

where ($c$) is the speed of light, and ($\mathbf{v} \cdot \mathbf{k}$) represents the component of the velocity along the direction of ($\mathbf{k}$), allowing for the more general expression of the Doppler shift.

This phenomenon can be understood from two perspectives. In the atom's reference frame, the electromagnetic wave's frequency is shifted, whereas in the laboratory frame, it is the resonance frequency ($\nu_0$) that shifts due to motion, represented by:

$$
\nu'_0 = \frac{\nu_0}{1 \pm \nu/c}
$$

(2.24)
To derive the Doppler lineshape function, one must account for the velocity distribution of atoms in a gas, which follows the Maxwell-Boltzmann distribution:

\[
p_v dv = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv^2/(2kT)} dv
\]

where \( m \) is the atomic mass, \( T \) the temperature, and \( k \) the Boltzmann constant. By integrating this distribution and considering the differential relation \( dv = \left(\frac{c}{v_0}\right) dv_0' \), we arrive at the inhomogeneous Doppler lineshape function:

\[
g_D(v - v_0) = \frac{1}{v_0} \left(\frac{mc^2}{2\pi kT}\right)^{1/2} e^{-mc^2(v - v_0)^2/(2kTv_0^2)}.
\]

The full width at half maximum (FWHM) of this lineshape, \( \Delta v_D \), is:

\[
\Delta v_D = 2v_0 \sqrt{\frac{2kT\ln(2)}{mc^2}},
\]

Conveniently reformulated for quick estimations of Doppler broadening in spectroscopy, especially when working with frequencies in wavenumbers (\( \text{cm}^{-1} \)):

\[
\Delta \bar{v}_D = 7.2 \times 10^{-7} \bar{v}_0 \sqrt{\frac{T}{M}}.
\]

Here, \( T \) is in Kelvin (K), \( M \) in atomic mass units (u), and both \( (\bar{v}_0) \) & \( (\Delta v_D) \) in the same frequency units, typically cm\(^{-1}\). This equation allows for a straightforward calculation
of Doppler broadening across different frequency units, aligning the units of \((\Delta \nu_D)\) with those used for \(\nu_0\).

The Doppler lineshape function, considering the FWHM, is expressed as:

\[
g_D(v - \nu_0) = \frac{2}{\Delta \nu_D} \sqrt{\ln(2) \over \pi} e^{-4 \ln(2) \left(\frac{v - \nu_0}{\Delta \nu_D}\right)^2}
\]  

(2.29)

This equation represents the Doppler lineshape in terms of its FWHM, capturing the effect of thermal motion on spectral line broadening.[39]

### 2.3.4. Power Broadening

Power broadening results from the saturation of a molecular transition at high intensities of the incident radiation. As the intensity increases, the difference in population between the lower and upper energy levels decreases, leading to a broadening and flattening of the absorption line. The width of the power-broadened line can be described by:

\[
\Delta \nu_{\text{power}} = \Delta \nu_0 \sqrt{1 + \frac{I}{I_{\text{sat}}}}
\]

(2.30)

where \(\Delta \nu_0\) is the natural linewidth, \(I\) is the intensity of the light, and \(I_{\text{sat}}\) is the saturation intensity.
2.4. Principles of Doppler-Free Spectroscopy Techniques

In experimental spectroscopy at room temperature, the effects of pressure and power broadening can be minimized by maintaining the gas system at low pressures and using low-intensity light sources. Under such conditions, Doppler broadening emerges as the predominant broadening mechanism. To acquire a Doppler-free spectrum, specialized experimental techniques are necessary. These techniques are designed to eliminate the Doppler effect and provide a clearer insight into the intrinsic properties of the spectral lines. Doppler broadening is a consequence of the distribution of velocities of molecules or atoms in a gas, which leads to a broadening of spectral lines due to the variation in the observed frequency of radiation, according to the Doppler effect. This broadening can obscure fine details of spectral lines, making it difficult to achieve high precision in measurements of atomic and molecular transitions. The principles underlying Doppler-free spectroscopy are crucial for applications requiring high spectral resolution, such as fundamental physics experiments, precise determinations of atomic and molecular structures, and tests of theoretical predictions.

To overcome this broadening, Doppler-free techniques use two counter-propagating beams with identical frequencies. Because the beams are traveling in opposite directions, their Doppler shifts due to the motion of the molecules cancel each other out for molecules with zero velocity along the beam axis. As a result, the spectral lines associated with these "stationary" molecules are not broadened by the Doppler effect. This allows for the observation of very narrow spectral features, which correspond to the actual molecular transitions without any Doppler broadening. These features can be extremely narrow,
limited only by the natural linewidth of the transition or other broadening mechanisms such as pressure or power broadening.

The fundamental equation for the Doppler shift of a molecular transition observed in the laboratory frame is given by:

$$\nu' \approx \nu_0 \left(1 \pm \frac{v_z}{c}\right)$$

(2.31)

Here:

- $\nu'_0$ is the observed frequency of the molecular transition.
- $\nu_0$ is the rest frequency of the molecular transition (true frequency without any motion).
- $v_z$ is the velocity component of the molecule along the direction of the light beam.
- $c$ is the speed of light.

For Doppler-free spectroscopy, molecules with $v_z=0$ (i.e., no velocity component along the direction of the light beam) will have $\nu'_0 = \nu_0$, meaning the observed frequency will be the true transition frequency without any Doppler shift. Techniques like saturation spectroscopy or two-photon spectroscopy exploit this principle to achieve very high spectral resolution.
Techniques for Achieving Doppler-Free Spectroscopy

I. **Saturated Absorption Spectroscopy**: This technique uses two counter-propagating laser beams, where one beam saturates the transition at its center frequency for atoms with zero velocity along the beam direction. The other beam, when scanned across the transition, can interact with the same zero-velocity group, resulting in a sharp dip in absorption at the center of the Doppler-broadened profile. This dip is free from Doppler broadening and allows precise measurement of the transition frequency.[47]

II. **Two-Photon Spectroscopy**: In this method, two photons are absorbed simultaneously by an atom or molecule to make a transition. If the two photons come from opposite directions, the Doppler shifts can cancel each other out, making the process Doppler-free. This technique is particularly useful for transitions that are forbidden or weak in single-photon processes.[48]

III. **Lamb-Dip Spectroscopy**: Lamb-dip spectroscopy is performed with a single beam. At high intensities, the center of the Doppler-broadened line is saturated, leading to a dip in the absorption profile known as the Lamb dip. This method provides a way to measure the natural linewidth and, by extension, the true frequency of a transition.[49]

IV. **Optical Ramsey Fringes in a Molecular Beam**: This technique involves splitting a laser beam into two spatially separated beams that interact with a molecular beam at different points. The phase coherence between the two interactions leads to
interference fringes that are insensitive to the first-order Doppler effect, allowing precise spectroscopic measurements.[50-54]

Mathematical Description of Doppler-Free Techniques

The effectiveness of Doppler-free techniques can be quantified by comparing the linewidths of transitions measured with and without these methods. For saturated absorption spectroscopy, the linewidth of the Doppler-free feature ($\Delta\nu_{DF}$) can be significantly narrower than the Dopplerbroadened linewidth ($\Delta\nu_D$) given by the equation (2.7), typically on the order of the natural linewidth ($\Delta\nu_{nat}$) of the transition:

$$\Delta\nu_{DF} \approx \Delta\nu_{nat} \ll \Delta\nu_D$$

(2.32)

For two-photon spectroscopy, the condition for Doppler-free spectroscopy can be described when the momentum imparted by the two photons cancels out, which is mathematically expressed as:

$$\Delta\nu_{DF} = 0, \text{ when } \overrightarrow{k_1} + \overrightarrow{k_2} = 0$$

(2.33)

where $\overrightarrow{k_1}$ and $\overrightarrow{k_2}$ are the wave vectors of the two photons involved in the transition.

Counter-Propagating Beam Configuration: The effectiveness of this configuration in eliminating Doppler broadening is predicated on the fact that the Doppler shifts from the
pump and probe beams exactly cancel for atoms or molecules with a velocity component along the beam direction. This results in a sharp absorption feature (Lamb dip) at the transition frequency for stationary or zero-velocity class atoms/molecules.

**Saturated Absorption Spectroscopy Condition:** For the counter-propagating pump and probe beams, the condition for observing a Lamb dip (Doppler-free peak) in the absorption profile can be described by the saturation condition, where the intensity of the pump beam \( I_{\text{pump}} \) is sufficient to saturate the transition. The width of the Lamb dip \( \Delta \nu_L \) can be expressed as a function of the saturation parameter, \( S \), and the natural linewidth \( \Delta \nu_{\text{nat}} \):

\[
\Delta \nu_L \approx \sqrt{S} \Delta \nu_{\text{nat}}
\]

(2.34)

Where, \( S \) is defined as the ratio of the pump beam intensity to the saturation intensity \( I_{\text{sat}} \) of the transition:

\[
S = \frac{I_{\text{pump}}}{I_{\text{sat}}}
\]

(2.35)
The saturation intensity \((I_{sat})\) itself is related to the transition properties and can be calculated from:

\[
I_{sat} = \frac{\hbar \omega_0 \Gamma}{2\sigma}
\]  

(2.36)

where:

- \(\hbar\) is the reduced Planck's constant,
- \(\omega_0\) is the angular frequency of the transition,
- \(\Gamma\) is the decay rate of the excited state,
- \(\sigma\) is the cross-section of the transition.
2.5. Principles of Cavity-Ring-Down Spectroscopy

Cavity Ring-Down Spectroscopy (CRDS), first pioneered in 1988 by O’Keefe and Deacon[55]. While Jun Ye, Long-Sheng Ma, and John L. Hall pioneered Continuous Wave Cavity Ring-Down Spectroscopy (CW-CRDS) in 1998[56]. Later, Kevin K. Lehmann et al. provides an in-depth framework for CRDS, significantly enhancing the understanding and application of this spectroscopic technique.[57-60]

This technique refines absorption spectroscopy to achieve ultra-high detection sensitivities, ranging from parts-per-billion ($10^{-9}$) to parts-per-trillion ($10^{-10}$), by enhancing light-matter interaction through an optical cavity that follows the Beer-Lambert law,

$$I_{\text{out}} = I_{\text{in}} \exp\left[-\alpha L\right]$$

(2.37)

where $I_{\text{in}}$ & $I_{\text{out}}$ denote incident and transmitted light intensities, $\alpha$ the absorption coefficient, and $(L)$ the path length, CRDS effectively addresses the sensitivity challenges in measuring gaseous samples with low absorption coefficients. It amplifies the interaction within a small volume, significantly improving the signal-to-noise ratio even with low milliwatt laser sources and is unaffected by laser intensity fluctuations due to its time-domain measurement approach.

In a general CRDS optical cavity setup, it comprises two mirrors with exceptional reflectivity, at least exceeding 99.95%. This configuration's stability hinges on geometrical prerequisites, particularly the curvature ($r_l$) of the mirrors and their interspatial distance $(L)$. The cavity's stability criterion is captured by the equation:
$0 < g_1 g_2 < 1 \quad (2.38)$

where each mirror's stability parameter, $(g_i)$, is articulated as

$$g_i = 1 - \frac{L}{r_i} \quad (2.39)$$

For effective light confinement within the cavity, it must resonate with wavelengths satisfying the condition for a standing wave:

$$n\lambda = 2L \quad (2.40)$$

This ensures amplification of the light's intensity inside the cavity until the excitation light is halted by an acoustic-optical modulator (AOM), leading to a reduction in internal light intensity.
Without any sample, the leaked intensity \( I_{\text{out}} \) as a function of time can be expressed as

\[
I_{\text{out}} = I_{\text{in}} \exp \left[ - \left( \frac{\text{number of reflections}}{\text{per round trip}} \right) \left( \frac{\text{intensity loss}}{\text{per reflection}} \right) \left( \frac{\text{total number of}}{\text{round trips}} \right) \right]
\]

\[
= I_{\text{in}} \exp \left[ -(2)(1 - R)(tc/2L) \right]
\]

\[
= I_{\text{in}} \exp \left[ -t/\tau_0 \right]; \quad \text{(2.41)}
\]

Where ring-down time \( \tau_0 \),

\[
\tau_0 = \frac{L}{(1 - R)c} \quad \text{(2.42)}
\]
Now, consider a sample inside the cavity with absorption coefficient $\alpha$ while laser-radiation is in resonance with the absorption feature of the sample. In the presence of sample, the intensity leaking from the cavity takes the form:

$$I_{\text{out}} = I_{\text{in}} \exp \left[ - \left\{ \frac{(1 - R) c}{L} t + \left( \text{absorption loss for sample per round trip} \right) \left( \text{total number of round trips} \right) \right\} \right]$$

$$= I_{\text{in}} \exp \left[ - \left\{ \frac{(1 - R) c}{L} t + (2\alpha d) \left( \frac{tc}{2L} \right) \right\} \right]$$

$$= I_{\text{in}} \exp \left[ - \frac{tc}{L} (1 - R) + (\alpha d) \right]$$

$$= I_{\text{in}} \exp \left[ - \frac{t}{\tau} \right].$$ \hspace{1cm} (2.43)

Here ring-down time due to absorption $\tau$,

$$\tau = \frac{L}{[(1 - R) + \alpha d] c}. \hspace{1cm} (2.44)$$

Here $d = L$ for gas. So, the absorption coefficient:

$$\alpha = \frac{1}{c} \left[ \frac{1}{\tau} - \frac{1}{\tau_0} \right] = \frac{\Delta k}{c}, \hspace{1cm} (2.45)$$

where $\Delta k$ represents the change of decay rate due to the sample. \cite{61, 62}

The absorption coefficient is directly derived from $\tau$ and $\tau_0$ measurements, which depend solely on mirror reflectivity and cavity length, unaffected by laser intensity.
The optical cavity functions as a Fabry-Perot resonator, selectively transmitting only those longitudinal frequencies, known as cavity modes, that complete a round-trip inside the cavity with a total phase change that is an integral multiple of \(2\pi\). The frequency gap \(v_{\text{FSR}}\) between adjacent cavity modes, or the free-spectral-range (FSR), is defined by:

\[
v_{\text{FSR}} = \frac{c}{2L}.
\] (2.46)

The cavity mode's full width at half-maximum \(\Delta v_{\text{cavity}}\), or the cavity mode-width, depends on the cavity's finesse \((F)\), a measure influenced solely by the reflectivity \((R)\) of the cavity mirrors. The finesse is calculated as

\[
F = \frac{\pi \sqrt{R}}{1 - R}
\] (2.47)

and the relationship between the cavity mode-width and the finesse is given by:

\[
\Delta v_{\text{cavity}} = \frac{v_{\text{FSR}}}{F}.
\] (2.48)

Thus, higher mirror reflectivity \((R)\) leads to higher finesse \((F)\), which in turn results in a narrower cavity mode-width \(\Delta v_{\text{cavity}}\). A narrower mode-width indicates a higher power buildup inside the cavity, leading to a longer ring-down time.

\section*{2.6. Principles of Frequency Locking}

One effective method for achieving stable laser operation is through locking amplifier-based frequency locking techniques. This approach leverages the sensitivity and selectivity
of locking amplifiers to maintain the laser frequency within a narrow bandwidth, ensuring high stability and accuracy.

Locking amplifier-based frequency locking operates on the principle of converting frequency fluctuations into amplitude variations that can be reliably detected and used as a feedback signal to correct the frequency. The process involves modulating the laser frequency with a stable reference signal and detecting the resulting amplitude variations using a lock-in amplifier. The output of the locking amplifier, which corresponds to the error signal, is then fed back to the laser's frequency control input to correct any deviations from stable reference signal.

The mathematical representation of the error signal $S$ can be expressed as:

$$S = A \sin(\omega t + \phi)$$  \hspace{1cm} (2.49)

where $A$ is the amplitude of the modulation, $\omega$ is the modulation frequency, and $\phi$ is the phase shift introduced by the frequency deviation from the set point. The error signal is then used to adjust the laser frequency to minimize $\phi$, thereby stabilizing the laser frequency. [63, 64]

**PID Locking Technique**

For a PID (Proportional-Integral-Derivative) based laser frequency locking system, where the laser is locked to an atomic or molecular transition frequency instead of a cavity resonance. This method is somewhat different from locking to a cavity and typically
involves using a spectroscopic signal from an atomic or molecular transition as the reference for locking the laser frequency.

In a PID-based locking system, the laser frequency is stabilized by locking it to a specific atomic or molecular transition frequency. This is achieved by monitoring the absorption or dispersion signal associated with the transition as the laser frequency is scanned. The deviation of the laser frequency from the center of the transition is used to generate an error signal, which is then fed into a PID controller. The PID controller adjusts the laser frequency to minimize this error, effectively locking the laser to the transition.

The error signal in a PID-based locking system can be derived from the spectroscopic signal of the atomic or molecular transition. For a simple absorption-based system, the error signal, $S$, as a function of the laser frequency, $\omega$, can be approximated by the derivative of the absorption profile, $A(\omega)$, with respect to frequency:

$$S(\omega) = \frac{dA(\omega)}{d\omega}$$  \hspace{1cm} (2.50)

The PID controller uses this error signal to adjust the laser frequency by applying a correction that is a combination of the proportional ($P$), integral (I), and derivative (D) components of the error signal:

$$\text{Correction} = K_p S(\omega) + K_i \int S(\omega)dt + K_d \frac{dS(\omega)}{dt}$$  \hspace{1cm} (2.51)

where $K_p$, $K_i$, and $K_d$ are the proportional, integral, and derivative gains, respectively.
Implementing a PID-based frequency locking system requires careful design to ensure stability and robustness. The choice of the PID gains ($K_p, K_v, K_d$) is critical and requires tuning based on the specific characteristics of the laser and the spectroscopic transition. Additionally, the system must be designed to minimize noise and drift in the error signal, which can arise from fluctuations in the laser intensity, changes in the atomic or molecular sample, and environmental factors.[65]
3. OVERVIEW OF THE MID-INFRARED DOPPLER-FREE SATURATION ABSORPTION SPECTROSCOPY SETUP

3.1. Components of the Mid-Infrared Doppler-Free Setup

![Diagram of mid-infrared Doppler-free setup]

*Figure 7: Components of the Mid-Infrared Doppler-Free Setup.*

The mid-infrared Doppler-free spectroscopy setup includes a laser source (OPO), a sample cell, detection and amplification apparatus, data acquisition components, and finally, the data analysis and calibration segment. Laser scanning, detection, and data acquisition were synchronized and automatically controlled by our LabVIEW system (Figure 7).
3.2. Continuous-Wave Optical Parametric Oscillator (CW-OPO) as a Light Source for Mid-Infrared Spectroscopy

3.2.1. The Optical System of the CW-OPO

The OPO system indicated in Figure 7 is consists of several optical and electronic parts as shown in Figure 8.

![Figure 8: Connection configuration of the TOPO based laser system.](image)
**Distributed Feedback Diode Laser (DFB):**

A DFB laser incorporates a periodic structure operating along the optical path of its active medium, usually integrated within or adjacent to the laser diode's waveguide. This grating provides distributed feedback directly into the laser cavity, which is essential for its operation.

The grating in a DFB laser acts as a distributed mirror. It reflects a specific wavelength of light back into the active medium while allowing other wavelengths to pass through or be attenuated. This selective feedback enhances the amplification of the chosen wavelength (the Bragg wavelength), determined by the grating's period (the distance between the grating lines), leading to stable, single-mode operation.[66]

The Bragg wavelength — the specific wavelength that is efficiently reflected and thus amplified by the grating — is determined by the grating period and the refractive index of the laser medium. By designing the grating with a precise period, the DFB laser can be tailored to emit light at a desired wavelength. This wavelength can be finely tuned further by adjusting the temperature of the laser diode or by applying a current, which affects the refractive index of the waveguide.[67]

The output of a DFB laser is characterized by a narrow linewidth, typically in the order of a few MHz or less, which is a direct consequence of the single-mode operation enforced by the grating. This narrow linewidth is crucial for applications requiring high spectral resolution, such as spectroscopy, sensing, and communication.
In operation, when current is applied to the DFB laser, the active region emits light. Due to the distributed feedback provided by the grating, only the light matching the Bragg condition is efficiently amplified and dominates the laser output. This process ensures that the laser emits a stable, narrow linewidth light at the designed wavelength, which can be slightly adjusted through external controls.[68]

We utilized the Toptica DFB PRO BFY_33192 laser model, which is specifically engineered for applications requiring precise wavelength control, narrow linewidth, and stable output. This particular model has been instrumental in our experiments, offering the precision and reliability needed for sophisticated optical applications.

**Specifications of Toptica DFB PRO BFY_33192:**

- **Wavelength Range:** 1062.5 to 1066 nm
- **Linewidth:** 2 MHz
- **Temperature Range:** $T_{\text{min}} = 2.8^\circ\text{C}$, $T_{\text{max}} = 48^\circ\text{C}$
- **Scan Range:** 24 GHz
- **Current Modulation:** 20mA at 0.1 Hz
- **Output Power:** 30 mW (attenuated to 3-5 mW for our use)
- **Frequency Modulation Modes:** DC coupled, AC coupled
**Fiber Amplifier:**

Fiber amplifiers utilize a doped optical fiber as the gain medium to amplify an optical signal through the process of stimulated emission. The core of the optical fiber is doped with rare-earth elements such as erbium (Er), ytterbium (Yb), or neodymium (Nd), which can absorb pump light at one wavelength and emit it at another, facilitating amplification.

**Operational Principle:**

- **Doping:** The optical fiber's core is infused with dopant atoms that possess unique optical properties suitable for amplification.

- **Pumping:** A pump laser emits light into the doped fiber, exciting the dopant atoms to a higher energy level.

- **Signal Amplification:** As the optical signal travels through the doped fiber, it interacts with the excited atoms. These atoms release their stored energy as photons at the signal wavelength when they return to their ground state, amplifying the original signal.

- **Output:** The result is an amplified version of the input signal, emerging at the end of the fiber with significantly increased power.

This process enables fiber amplifiers to efficiently boost the power of optical signals without converting the signal back to the electrical domain, maintaining the integrity and quality of the signal throughout the amplification.[69]
Amplification and Output:

As shown in Figure 8, the DFB laser's output, adjusted to 2.5-5 mW, was amplified by the YAR-10K-1064-LP-SF, which utilizes an ytterbium-doped fiber core. The amplified light, now at up to 10 W, was subsequently fed into the OPO system as the pump source, facilitating broad-spectrum tunable output.

Specifications of IPG Photonics YAR-10K-1064-LP-SF:

- **Manufacturer**: IPG Photonics
- **Model**: YAR-10K-1064-LP-SF
- **Wavelength**: 1064 nm
- **Output Power**: 10 W (operated in APC mode)
- **Amplification Type**: Ytterbium-doped fiber amplifier
- **Polarization**: Linear
- **Operation Mode**: Single-Frequency
- **Pump Method**: Diode
- **Control Modes**: ACC (Automatic Current Control) & APC (Automatic Power Control)
- **Operational Mode Used**: APC at 10W
This approach ensures the high-power, coherent light necessary for effective OPO operation, demonstrating the integrated system’s capability to produce tunable laser output for precision applications.
Wavemeter

The pump and signal wavelengths ($\lambda_p$ and $\lambda_s$) are measured by a wavelength meter (HighFiness WS/6-200-Vis/IR) with nominal absolute accuracies of 150 and 120 MHz for the pump and signal wavelength, respectively. The idler wavelength ($\lambda_i$) is determined from the former two with an experimentally confirmed accuracy of $\sim$30 MHz at $\sim$3 μm.

The pump and signal beams were coupled to an optical fiber using two couplers with 5 degree of freedom and sent to an optical switch. An optical fiber from the optical switch carries the two beams to the wavemeter.

It is important to note that both the pump and signal beams were attenuated to avoid oversaturation into the wavemeters. Depending on the coupling efficiency, the alignment was adjusted to maintain a response time of 1ms-10ms. Due to the OPO beam drift, the optical coupling also needs to be readjusted for scanning over a large wavelength range.
Continuous-Wave Optical Parametric Oscillator (CW-OPO)

For our application, an Optical Parametric Oscillator (OPO) that has a wide tuning range, high resolution, fast tuning speed, narrow linewidth, and high output power is required. As an example, we can use something with the following configuration:

In the depicted Optical Parametric Oscillator (OPO) system on Figure 9, light from the pump laser, after being shaped by a phase-matching lens, is directed into the cavity and encounters a series of optical components that facilitate the generation of signal and idler beams. The pump beam is initially transmitted through mirror M1, a dichroic element, which steers the beam into a nonlinear crystal positioned between mirrors M1 and M2. This crystal is fundamental to the OPO process, wherein the pump photon is down-converted into two photons of lower energy. Adjacent to the nonlinear crystal are thermal pads, indicative of a temperature control mechanism to maintain the phase-matching conditions.
conditions essential for the efficiency of the OPO process. The resonator cavity, composed of mirrors M1, M2, M3, and M4, defines the optical path for the generated beams. Mirror M3 is distinct as it is mounted on a piezoelectric transducer (PZT), which provides fine adjustments to the cavity length and, thus, the phase-matching conditions, enabling precise control over the wavelengths of the signal and idler photons. An etalon is introduced into the beam path within the cavity to enhance spectral purity, functioning as a wavelength-selective filter and thereby enforcing single-mode operation. The system's design facilitates the emission of two distinct beams from the nonlinear crystal: the idler and signal beams.

We utilized a Toptica TOPO in our setup due to its configuration that aligns closely with our depicted OPO system. Among other capabilities, it has a wide tuning range and high resolution. This choice was driven by the TOPO's ability to deliver a versatile and precise output, essential for our experimental demands. [70, 71]

The TOPO system from Toptica is characterized by its fully automated, continuous-wave operation and its capacity for high-resolution spectroscopy across a wide mid-infrared spectrum. The TOPO is specifically engineered to operate within a wavelength range of 1.45 to 4.0 µm. It supports a mode-hop-free tuning range up to 300 GHz, coupled with a narrow linewidth of 2 MHz, facilitating the observation of comprehensive spectroscopic signatures without the need for manual adjustments or module exchanges.
Key specifications of the Toptica TOPO include:

- **Coarse tuning range**: 1.45 - 2.07 µm for the signal and 2.19 - 4.00 µm for the idler.

- **Output Power**: 2 W for the signal and 1 W for the idler, ensuring sufficient power across its operational spectrum. Figure 10 depicts the output power characteristics of the TOPO.

![Figure 10: Output Power of the TOPO.](image)

- **Linewidth**: Below 100 kHz for the signal and 2 MHz for the idler, providing exceptional spectral purity.

- **Mode hop-free tuning range**: Less than 1 GHz for fine adjustments, extending up to 300 GHz, depending on the output wavelength.

- **Beam Quality Factor M²**: Below 1.2, indicative of high beam quality.
• **Frequency modulation and lock:** Includes PZT modulation for both signal and idler, with additional pump frequency modulation, ensuring stability and precision.

• **Control interfaces:** Equipped with DLC pro touchscreen, PC software, Ethernet, USB, and analog remote control, offering versatile control options.

![Power drift of the TOPO](image)

*Figure 11: Power drift of the TOPO.*

• **Warm-up time:** Typically, 30 minutes.

• **Power consumption:** Typically, < 250 W, emphasizing its efficiency.

• **PC Interface:** Includes Ethernet, USB, and analog control for comprehensive connectivity options.

• **Environment temperature:** Operating between 15 - 30 °C and storage from 0 - 40 °C.
Figure 8 illustrates the connection configuration of the laser system for our experiment. In the experimental setup, control of the Toptica Distributed Feedback Diode Laser (DFB-Pro) is managed by the Toptica Digital Laser Controller (DLC-Pro) through temperature and current control mechanisms. The DFB-Pro laser features an optical fiber interface, providing an output of approximately 30 mW. This output undergoes attenuation via an optical fiber attenuator and an Optical Isolator (OI), the latter being crucial for blocking back reflections. Eliminating back reflections is essential to maintain the continuity of the wavelength scanning process. After attenuation, the laser output is reduced to below 5 mW. This attenuated signal is then input to a Fiber Amplifier, resulting in a single-mode output of 10 W. This amplified output is then directed to the Tunable Optical Parametric Oscillator (TOPO) through a high-power optical fiber.

Control of the TOPO is facilitated through multiple Ethernet and electronic connections from the DLC-Pro, which adjust various parameters including the piezoelectric transducer (PZT) settings, the temperature of the crystal and its housing, and current control, among others.

For system integration and control, a PC was connected to the DLC-Pro using either a serial port or an Ethernet connection, with Ethernet being preferred for its higher speed and reliability. A custom LabVIEW program is utilized to synchronize and manage the parameters of the DFB, DLC, and TOPO during scanning or while generating optical parametric oscillator (OPO) tables. Furthermore, the DLC-Pro includes an in-built data acquisition system, which has been used periodically for system optimization.
3.2.2. The Automation and Wavelength Tuning

OPO Table Generation

The process for generating the Optical Parametric Oscillator (OPO) table through a custom LabVIEW program involves several carefully sequenced steps as presented in Figure 12 aimed at automating this aspect of the CW-OPO system's operation. The procedure is as follows:

I. Initialization of Parameters: The LabVIEW program is initiated by setting the starting positions for the OPO etalon and the crystal motor. Along with these positions, the step size for the scanning process is also defined. These initial settings are crucial for outlining the boundaries of the scanning operation.

II. Temperature Stabilization: Before commencing the scan, the program ensures the stabilization of the crystal's temperature and that of its housing. This step is vital for maintaining consistent environmental conditions, which directly influence the accuracy of wavelength measurements.

III. Scanning Sequence Begins: The scanning process starts at the predetermined initial positions. The motor systematically moves from start to finish in the set steps, thoroughly covering the specified range. This movement is critical for capturing detailed data across the entire operational range.
IV. **Data Acquisition**: As the motor executes its scanning sequence, the wavemeter continuously measures the output wavelengths. Simultaneously, an integrated power meter within the TOPO setup assesses the pump's depletion at every step. This concurrent measurement is essential for evaluating the efficiency of the parametric conversion process.

V. **Cycle Completion and Etalon Adjustment**: Upon reaching the end position, the motor returns to the starting point. Then, the etalon is incrementally advanced by a predefined step size, and the scanning sequence is initiated once more. This cycle repeats until the etalon completes all its steps from start to finish, ensuring a comprehensive examination of the CW-OPO's tuning range.

VI. **Data Compilation and Processing**:

The collected data, including etalon position, motor position, wavelength, and
power measurements, forms a preliminary table. This table reflects the relationship between the OPO's physical adjustments and its optical output.

VII. **Refinement of Data**: The raw table undergoes a sorting process to isolate points of maximum idler output or minimum pump depletion. This refined table highlights the most efficient operational points, guiding the OPO's tuning for optimized performance.

Before Generation of the OPO table the following pre-determined **table 1** was used to have an educated guess for finding the initial conditions. The table generation initial conditions were found with the aid of manual adjustment of motor-position, etalon-position and the motor calibration table.
Table 1: TOPO motor calibration table:

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1500</td>
<td>3665</td>
<td>4.66</td>
<td>31.0</td>
</tr>
<tr>
<td>1550</td>
<td>3400</td>
<td>8.01</td>
<td>31.0</td>
</tr>
<tr>
<td>1600</td>
<td>3180</td>
<td>10.51</td>
<td>31.0</td>
</tr>
<tr>
<td>1650</td>
<td>3000</td>
<td>12.36</td>
<td>31.0</td>
</tr>
<tr>
<td>1700</td>
<td>2840</td>
<td>13.73</td>
<td>31.0</td>
</tr>
<tr>
<td>1750</td>
<td>2715</td>
<td>14.70</td>
<td>31.0</td>
</tr>
<tr>
<td>1800</td>
<td>2610</td>
<td>15.43</td>
<td>31.0</td>
</tr>
<tr>
<td>1850</td>
<td>2505</td>
<td>16.01</td>
<td>31.0</td>
</tr>
<tr>
<td>1900</td>
<td>2420</td>
<td>16.41</td>
<td>31.0</td>
</tr>
<tr>
<td>1950</td>
<td>2335</td>
<td>16.47</td>
<td>10.0</td>
</tr>
<tr>
<td>2000</td>
<td>2265</td>
<td>16.39</td>
<td>7.0</td>
</tr>
</tbody>
</table>


Wavelength Tuning

The scanning as shown in Figure 13, for the Optical Parametric Oscillator (OPO) using a LabVIEW program involves several streamlined steps, combining user inputs with automated procedures:

I. Initial Setup from User Inputs:

The user inputs define the scanning range by setting the start and end points along with the step size for the scan’s progression.

II. Finding the Starting Reference Point:

Based on these inputs, the program searches the pre-generated table for a reference point near the scan's intended start. This step positions the laser accurately by adjusting the etalon and motor to the table's specified settings.

III. Temperature and Wavelength Adjustment:

The program then adjusts the DFB laser's temperature to steer the system towards the target starting wavelength. This automatic adjustment ensures the scan begins at the correct wavelength.
IV. **Beginning Data Acquisition:**

As the system aligns closely with the target wavelength, the program starts collecting data. The speed of this process is regulated by the step size and ramping constants predefined by the user for capturing the data methodically across the scan range.

V. **Mode Hop Management:**

Upon encountering a mode hop, the program pauses to select a new reference point from the table close to this new position and reinitiates the scanning process from there. This ensures continuous data collection without manual reset.

VI. **Continuation Until Scan Completion:**

This loop repeats, with the program moving through the scan range automatically, until it either completes the user-defined range or is manually stopped.

The optical parametric oscillator (OPO) requires regular alignment of its cavity to maintain optimal power output over time. In the event of total power loss, removal of the OPO etalon is necessary to perform a foundational alignment. The procedural steps for etalon removal and cavity alignment are detailed in Appendix A.
Figure 13: CW-OPO wavelength tuning process.
3.3. Sample Cells and Gas Delivery System

In the experimental setup, two distinct sample cells were utilized to accommodate various aspects of the experiment. Each cell was designed with specific features to meet the unique requirements of the spectroscopic measurements being conducted.

The first sample cell, extending nearly 85 cm in length, was equipped with Brewster-angled windows on both ends. These windows, crafted from calcium fluoride (CaF$_2$), are known for their high transparency in the infrared region, minimizing reflection losses for light polarized in the plane of incidence. This design feature is crucial for enhancing the optical path's efficiency within the cell. Additionally, the cell included two Swagelok gas connections: one dedicated to attaching a pressure sensor and the other serving a dual purpose for gas delivery and vacuum connection. The pressure within this cell was controlled, ranging from $2 \times 10^{-2}$ torr to $5 \times 10^{-2}$ torr. This pressure regime was selected to mitigate pressure broadening effects, ensuring that spectral lines remained sharp and well-defined for accurate analysis.

*Figure 14: First sample Cell used for doppler-free scan*

The first sample cell in Figure 14, extending nearly 85 cm in length, was equipped with Brewster-angled windows on both ends. These windows, crafted from calcium fluoride (CaF$_2$), are known for their high transparency in the infrared region, minimizing reflection losses for light polarized in the plane of incidence. This design feature is crucial for enhancing the optical path's efficiency within the cell. Additionally, the cell included two Swagelok gas connections: one dedicated to attaching a pressure sensor and the other serving a dual purpose for gas delivery and vacuum connection. The pressure within this cell was controlled, ranging from $2 \times 10^{-2}$ torr to $5 \times 10^{-2}$ torr. This pressure regime was selected to mitigate pressure broadening effects, ensuring that spectral lines remained sharp and well-defined for accurate analysis.
The second sample cell, Figure 15, has a modular design, and its length can be adjusted from 0.25 meters up to 1 meter. This adjustment was facilitated by adding or removing full nipples, allowing for the cell's length to be tailored to the specific needs of the experiment. The cell was also equipped with a butterfly valve for vacuum pump connectivity and a separate feedthrough ConFlat (CF) flange for the gas delivery system. For the optical windows, calcium fluoride (CaF2) was again the material of choice, mounted using Thorlabs VC23FL window holders. These holders are compatible with 2.75” CF flanges designed for 1.5” optics, providing a secure and stable window installation while maintaining the vacuum. Unlike the first cell, this modular cell did not utilize Brewster-
angled windows but, due to its adjustable length, it was ideal for the OPO laser locking system. In our locking system we focused the beam at different distances for strong lamb-dip signal acquisition which required these adjustments in cell length.

Each cell's design and features were thoughtfully selected to optimize the conditions for spectroscopic measurements, considering factors such as optical transmission, pressure control, and the physical dimensions of the experimental apparatus.
3.4. Acousto-Optic Modulator (AOM) and It’s Cooling System

The Acousto-Optic Modulator (AOM) is a crucial device for precise control of laser frequency and amplitude. It relies on acousto-optic interactions occurring within a crystalline material. By using an RF transducer, the AOM generates high-frequency sound waves in this crystal. As these sound waves travel, they create periodic changes in how the crystal affects light. When a laser beam enters this dynamic environment, it interacts with the sound waves, causing laser light to change direction. This interaction, known as laser beam diffraction, is central to adjusting laser properties in real-time. **Frequency Modulation (FM):** The frequency modulation (FM) of the laser beam is governed by the following equation:

\[ \Delta f = f_{RF} \frac{\lambda}{v} \sin(\Delta \theta) \]  

(3.1)

Where:

- \( \Delta f \) : The frequency shift of the laser beam.
- \( f_{RF} \) : The applied RF frequency to the AOM.
- \( \lambda \) : The wavelength of the incident laser light.
- \( v \) : The acoustic wave velocity within the crystal.
- \( \Delta \theta \) : The angle of diffraction.
**Amplitude Modulation (AM):** The degree of AM can be quantified by the following expression:

\[
\text{Modulation Depth}(\%) = \frac{A_{\text{acoustic}}}{I_{\text{beam}}} \times 100\% \quad (3.2)
\]

Where:

- **Modulation Depth:** The extent of intensity modulation, expressed as a percentage.
- **\( A_{\text{acoustic}} \):** The amplitude of the acoustic wave.
- **\( I_{\text{beam}} \):** The intensity of the incident laser beam.

In our experimental configuration, we utilized the BRIMROSE GEF-100-20-3000-WC Acousto-Optic Modulator (AOM) along with fix frequency RF driver BRIMROSE FF-100-B2-V7 for the precise modulation of the pump frequency \( f_{RF} = 100 \) MHz. The intensity modulation was capitalized for the amplification of the doppler-free signal. This particular AOM model is designed for free-space applications within the infrared (IR) optical range and features water cooling to maintain stable operation under high-power conditions. The AOM is equipped with a Germanium substrate, optimized for a wavelength operation around 3000 nm, with a tolerance of \( \pm 1000 \) nm, making it ideal for mid-IR applications.

The AOM's integration into the system was achieved using an XYZ mount combined with an XY angular mount, affording the setup five degrees of freedom. This level of adjustability is critical for aligning the laser beam to the optimal Bragg angle, ensuring
maximum power conversion into the first order modulated beam. The specifications of the AOM, such as a center frequency of 40 MHz with a frequency shift range of 10 MHz and an active aperture of 1 mm, underline its capability to efficiently modulate laser beams within its operational parameters. Additionally, the device boasts a high optical transmission (>85%) and diffraction efficiency (~70%), with an optical damage threshold of 5 W/mm².

The system's ability to finely tune the alignment, courtesy of the five degrees of freedom, allows for precise control over the beam's interaction with the AOM, achieving an optimal Bragg angle for efficient first-order diffraction. The output coupler lens within the OPO system is utilized to focus the beam, ensuring the proper spot size within the AOM for effective modulation. Specifications such as the rise time of 120 ns and an extinction ratio greater than 1000:1 further demonstrate the AOM's suitability for high-resolution spectroscopic applications.

The AOM is driven by a variable frequency RF driver (Model # VF-40-10-V-B2-V10), capable of operating across a frequency range of 35 to 45 MHz. This driver allows for fine-tuning of the modulation frequency through a 0 - 10V analog input, with TTL compatible modulation up to 20 MHz. Such features ensure that the AOM can be precisely controlled to match the experimental requirements, enhancing the modulation quality and, consequently, the spectroscopy's resolution.
In house AOM Cooling system:

The cooling system depicted in Figure 16 is engineered to maintain the Acousto-Optic Modulator (AOM) at a stable temperature during operation. This system is vital to prevent thermal drifts that can affect the AOM's performance, especially during prolonged experiments.

Figure 16: Schematic Diagram of the AOM Cooling System
Here's a description of the cooling system for the BRIMROSE GEF-100-20-3000-WC AOM used in the setup:

I. **Cooling Bath:** The system includes a cooling bath set at 5°C, ensuring that the coolant remains at a consistent low temperature. The bath is connected to stainless steel tubing that allows for efficient heat exchange.

II. **Distilled Water Reservoir:** Distilled water is used as the primary coolant because of the availability and sufficient purity for thermal management purposes.

III. **Stainless Steel Tubing:** 3/16” outer diameter stainless steel tubing transports the coolant from the reservoir to the AOM and back. This material is chosen for its durability and excellent thermal conductivity.

IV. **Pump:** A pump propels the distilled water through the system, ensuring a continuous flow of coolant around the AOM. This component is crucial for maintaining an adequate flow rate, as indicated by the valve settings.

V. **Valve (Flow Regulator):** A valve is included to regulate the flow of coolant, allowing for precise control over the cooling rate. This regulation is necessary to match the cooling requirements of the AOM during various operational intensities.

VI. **Pressure Reducer:** To safeguard the AOM and the tubing from high pressure, a pressure reducer is installed downstream of the pump. This device ensures that the coolant pressure remains within safe limits.
VII. **Connection to AOM:** The coolant is delivered to the AOM via barbed fittings that ensure a secure and leak-free connection. The AOM's design includes a water-cooled housing that directly cools the active crystal, effectively dissipating the heat generated during RF power absorption and acoustic wave generation.

VIII. **Return Path:** After passing through the AOM, the heated coolant is carried away from the modulator and back into the cooling bath, where it releases its absorbed heat before recirculation.

This closed-loop cooling system is designed to ensure that the AOM operates within its optimal temperature range, maintaining high diffraction efficiency and consistent acoustic velocity, which are crucial for reliable frequency modulation in the spectroscopy experiment. The system's design takes into account the AOM's specific heat dissipation needs, indicated by the 10 W RF power specification and the 5 W/mm² optical damage threshold.
3.5. Polarization Components

The idler output of the Optical Parametric Oscillator (OPO) is initially in a state of horizontal polarization. To adjust the vertical positioning and polarization state of the beams, a pair of periscopes are employed. A 180-degree periscope is used to alter the height of the probe beam without changing its horizontal polarization. Conversely, a 90-degree periscope is utilized to rotate the polarization of the pump beam by 90 degrees, effectively changing it from horizontal to vertical (Figure 17). This polarization manipulation is essential for the subsequent optical processes, allowing for the overlap of the pump and probe beams with the polarizing elements of the setup.

Figure 17: Change in polarization by periscope orientation.
Wire Grid Polarizer:

The Thorlabs Ultra Broadband Wire Grid Polarizer, model WP25M-UB, which operates effectively over a wide range of wavelengths from 250 nm to 4 µm, was utilized in the setup to differentiate between the pump and probe beams based on their polarization states. This polarizer, designed with a grid of metallic wires, is critical in allowing the polarized probe beam to transmit while reflecting the orthogonally polarized pump beam, thereby enabling the perfect overlap of these two components for the experiment's requirements.
3.6. Detection and Amplification

3.6.1. IR Detectors

In the spectroscopic setup, two identical InSb detectors, Infrared Associates, model number 449-INSB-1.0-SL8, with a diameter of 1.0 mm and an active area of 7.85×10−3 cm2, are employed, operating effectively at a cryogenic temperature of 77 K to ensure low noise levels. The detectors are encapsulated in a dewar model KR-321 with a sapphire window, which supports a field of view (FOV) of 15 degrees.

These detectors are characterized by a rise time of 120 ns, making them highly responsive to changes in incident radiation, which is crucial for capturing rapid transient signals in Doppler-free spectroscopy. The noise level, measured in terms of RMS voltage per square root bandwidth, is 466.07 nV/√Hz, indicating the detectors' ability to perform with minimal background interference.

3.6.2. Lock-in amplifiers

For the locking mechanism in our experiment, we utilized Mercury Cadmium Telluride (MCT) detectors from Kolmar Technologies, model KV104-0.1-1-E/11. These detectors operate with a bandwidth exceeding 500 MHz, suitable for high-speed applications. Their spectral response peaks at 10.5 µm, with a cutoff wavelength greater than 11.5 µm. The small detector size of 0.1 x 0.1 mm facilitates a rapid response, critical for the experiment's precision. The MCT detectors demonstrate a responsivity greater than 4 Amps/Watt and a detectivity (D*) above 3×10^10 Jones, ensuring high sensitivity in the infrared range.
These specifications highlight the MCT detectors' capability to provide fast and sensitive detection.

### 3.6.3. Pre-amplifiers

For initial optimization, the setup included three custom-built preamplifiers designed for two InSb detectors and one MCT detector. The InSb preamplifiers, identified as INSB-1000 (left), feature a frequency response range from 1.5 Hz to 200 kHz. The MCT preamplifier (right), PVMCT-1000, covers a frequency range from 1.5 Hz to 150 kHz. Both types provide a low-gain DC output and a high-gain AC output.

![Pre-amplifiers for InSb (left) & MCT (Right) detectors.](image)

These preamplifiers operate as current-mode trans-resistance amplifiers with a secondary gain stage. The initial stage is a current mode operational amplifier (op-amp) with the detector connected to the inverting input. A low-noise DC voltage is applied to this input to supply the majority of the bias current. The non-inverting input connects to an adjustable DC voltage from the bias supply, allowing the first stage to operate in closed loop with the
bias current. The bias supply is configured to keep the first stage op-amp at a quiescent current of 0 amps, supporting up to +/- 20 mA for signal current. This setup permits bias voltage adjustments without affecting the first stage's 0V DC output level.

Negative feedback converts changes in detector bias current into voltage. The first stage has a voltage gain of 10-15 V/V and a trans-impedance gain of 500 to 1000 Volts/Amp. The output from the first stage passes through a 100 µF non-polar capacitor to the second stage, introducing a 1.5 Hz low frequency roll-on pole to eliminate DC drift. The AC coupling can be disabled for DC operation.

The second stage is a voltage amplifier with an adjustable gain from 5 to 120 and a 50 ohms output impedance. It is designed to connect directly to test equipment without needing impedance matching. The preamplifier's noise performance is below 1 nV/Hz\(^{1/2}\), ensuring detector noise-limited performance. Connecting the dewar ground to the preamp case's ground improves noise reduction.
3.7. Fabry-Perot Cavity

The Fabry-Perot etalon in our setup is a critical component for high-resolution spectroscopy. It operates based on the principle of multiple beam interference between two parallel, highly reflective mirrors. The Free Spectral Range (FSR) is a fundamental characteristic of the etalon, indicating the frequency interval between successive transmission peaks, which is crucial for resolving closely spaced spectral lines. FSR is determined by:

\[
FSR = \frac{c}{2nL \cos \theta}
\]

(3.3)

where \( c \) is the speed of light, \( n \) is the index of refraction of the medium in the etalon, in our case, air, \( L \) is the length of the etalon, and \( \theta \) is the incident angle of the laser beam, the following factors can affect the stability of the FSR:
In constructing our Fabry-Pérot Cavity (Etalon) (Figure 19), we used four Invar rods for the framework, ensuring that the overall length of the cavity was held constant at 0.90 meters. The stability in length is key to maintaining the precision of our etalon's Free Spectral Range (FSR), which is the spacing between its resonant frequencies. The rods are held in place and reinforced by Invar plates located between the mirror mounts.

*Figure 19: Home-built Fabry-Perot Cavity.*
The mirrors at the ends of the etalon are secured using Thorlabs KC1-S mounts. These mounts have SM1 threading, making them suitable for integration with 30 mm cage systems, and they provide the necessary adjustments for alignment. The use of Invar, a material chosen for its minimal expansion with temperature changes, is crucial in maintaining a stable FSR as the etalon operates. The support provided by the Invar plates ensures the structure keeps its shape and the mirrors remain precisely aligned, which is essential for the etalon to enhance the desired light frequencies effectively through constructive interference.

Figure 20: Fabry-Pérot Cavity (Etalon) Trace.

Avg. FSR = 166.38 MHz
FWHM = ~ 19 MHz
For our Fabry-Pérot Cavity (Etalon) we used 2 flat mirrors with 85% reflectivity around 3.3 µm wavelength. Which resulted in a full width half maximum (FWHM) of ~19 MHz and an average FSR of 166.38 MHz.

Initially we were using free space beam coupling into the Fabry-Pérot Cavity. But due to the beam drift of the OPO idler output for long range scan the FSR was changing, resulting in a change in the incident angle $\theta$ (equation 3.3). To resolve this issue, we used an optical fiber-based coupling system to eliminate the beam drift effect into the cavity. A chopper was used to modulate the beam intensity and a lock-in amplifier was used to amplify the modulated signal as shown in Figure 21.
3.8. Optical Setup

In our experimental setup for Doppler-free saturation absorption spectroscopy, the system is anchored by an Optical Parametric Oscillator (OPO) with three distinct outputs: pump, idler, and signal. Initially, the pump and signal beams are directed through a beam splitter. A portion of these beams is then routed into optical fibers for wavelength measurement by a wavemeter, achieving a 30 MHz accuracy for determining the idler wavelength. The remaining parts of these beams are safely terminated using beam dumps.

The idler beam is processed through a beam collimation lens, which is fine-tuned to focus the beam within the Acousto-Optic Modulator (AOM). At the outset, the idler passes through a periscope setup that includes a beam sampler. This setup directs a fraction of the beam into a single-mode optical fiber leading towards a Fabry-Perot cavity. Before this fiber entry, the beam is modulated by passing through an optical chopper equipped with a frequency control system. The bulk of the idler beam is then split by a coated CaF2 beamsplitter in a 60/40 ratio, considering its horizontal polarization—60% for the pump path and 40% for the probe path.

For the pump beam's path, after its initial horizontal polarization, it is focused into the AOM where the generation of sidebands is optimized, particularly enhancing the first order to a 70% conversion efficiency. This process is governed by the AOM RF driver, modulated by the lock-in amplifier set to an internal frequency of 102 kHz. Subsequently, the first order modulated beam is rerouted through a 90-degree periscope, altering its polarization to vertical. This vertically polarized pump beam is then collimated and
directed through a series of pinholes, ensuring its precise overlap with the HeNe laser for alignment before reflection by the wire grid polarizer into the sample cell. The pump's power is finely adjusted through the AOM RF driver's amplitude control.

Conversely, the probe beam undergoes a similar collimation process and is height-adjusted while maintaining its horizontal polarization via a 180-degree periscope. Its power is modulated using a variable neutral density filter. This preparation ensures that the probe beam, guided through the same pinhole as the pump, perfectly overlaps within the sample cell. Due to its polarization, the probe beam passes through the wire grid polarizer and is focused onto the InSb detector for subsequent analysis.
Figure 21: Schematic diagram of the doppler free saturation absorption spectroscopy.
Upon the probe beam's detection, its signal is sent to a lock-in amplifier for signal enhancement. This step is pivotal as the pump beam is modulated using the lock-in amplifier's internal reference, allowing only the signal that is modulated via the pump beam's interaction with the molecules to be amplified. This ensures the selective amplification of the Doppler-free signal.

Additionally, the output from the beam sampler, after its journey through the optical fiber, is collimated and steered toward our Fabry-Perot cavity, referred to as an etalon. The transmitted light through this etalon is then captured by another InSb detector and its signal is amplified using another lock-in amplifier. This particular lock-in amplifier uses the frequency from the chopper, introduced before the optical fiber, as a modulation reference.

The amplified signals from both the probe and etalon are then fed into the first and second channels of a Data Acquisition (DAQ) card, respectively. A LabVIEW program controls the wavelength scanning and data collection from the DAQ card, also enabling the display of in-situ data graphs for real-time analysis.
4. DATA ACQUISITION AND SPECTRAL CALIBRATION

4.1. Signal Amplification

In the experimental configuration designed for Doppler-free spectrum detection, signal amplification was systematically approached using two distinct lock-in amplifiers from Stanford Research Systems: the SR810 and the SR530. The SR810 lock-in amplifier was dedicated to amplifying signals from the Doppler-free spectrum, whereas the SR530 was utilized for signals emanating from the etalon. Modulation of the Acousto-Optic Modulator (AOM) was achieved by harnessing the SR810's internal reference signal, which was set to a frequency of 102 kHz.

Signal from the InSb detector was directed to the SR810's Channel A input. Employing its internal reference signal, the SR810 lock-in amplifier selectively amplified only the Doppler-free component of the signal. A specific time constant of 30 ms was selected to align with the scanning step increment of 0.5 MHz, ensuring that the amplified Doppler-free signal retained its symmetry during the acquisition process. Moreover, to comprehensively document spectral transitions across various intensity levels, three discrete sensitivity settings were used to collect three complete scan of the whole Q-branch of CH$_4$, each tailored to different intensity segments of the spectrum. The operational mode for this part of the experiment included DC output coupling and a standard dynamic reserve setting.
For the etalon signals, the SR530 lock-in amplifier was configured with a fixed sensitivity of 50 mV and a low dynamic reserve setting. A time constant of 300 ms was established, guided by the external trigger sourced from the chopper frequency (~ 101Hz). This setup ensured synchronized amplification with the modulation frequency, and periodic phase adjustments were made to maximize the clarity and accuracy of the etalon signal output.

The methodologies applied for signal amplification, characterized by the strategic use of lock-in amplifiers SR810 and SR530, facilitated precise enhancement of signals pertinent to both the Doppler-free spectrum and the etalon. Modulation frequencies, sensitivity settings, and time constants were chosen to align with the experimental objectives, ensuring the symmetry of the Doppler-free signal and the integrity of the etalon signal.
4.2. DAQ Card and Scan Speed

In our experimental design, the Measurement Computing PCI-DAS4020/12 DAQ card was integral for data collection. Configured to operate within a ±5 V input range, this setting was chosen to align with anticipated signal amplitudes from our measurements. The DAQ card features:

**Four high-speed 12-bit analog input channels**, allowing for the capture of multiple signals concurrently. The input range flexibility is critical for accommodating signals of varying strengths, ensuring accurate data capture without saturation or signal loss.

**Sampling Rate**: The card offers a maximum sampling rate of 20 MHz. However, when utilizing multiple channels, this maximum rate is divided among the active channels, impacting the temporal resolution of data acquisition. For instance, activating two channels effectively reduces the sampling rate to 10 MHz per channel, necessitating adjustments in the experimental design to balance between temporal resolution and the number of signals monitored simultaneously.

For our specific data collection needs, Channel 0 was dedicated to the primary experimental signal, capturing the Doppler-free spectrum. Channel 2 was allocated for signals derived from the Fabry-Perot cavity, allowing for simultaneous capture of complementary data streams. This dual-channel utilization necessitated a recalibration of the expected sampling rate per channel to ensure that the data integrity was maintained across both channels.
4.3. LabVIEW Synchronization

The DAQ card's operation, including triggering and sample rate adjustments, was controlled through a custom-developed LabVIEW interface. This programmatic control allowed for dynamic adjustments to the data acquisition process, including the initiation of data capture through a rising slope trigger set at a 1 V threshold. This trigger mechanism ensured synchronized start times for data collection across all active channels.
Additionally, baseline and gating parameters were dynamically adjusted within the LabVIEW program, providing a flexible framework for signal processing directly tied to the experimental conditions. Connectivity between the DAQ card and the experimental apparatus was established using BNC cables, selected for their 50-ohm impedance, which is standard for minimizing signal reflection and attenuation over the transmission path.

Signal and etalon traces are plotted in real-time, as depicted in Figure 22. Generating plots with extensive data at each step may considerably lengthen processing time, thus reducing scan speed. To mitigate this issue, an option to bypass real-time graphing on each iteration has been implemented, allowing for a more expedited scanning process.

The top right interface as shown in Figure 23 is designed for configuring laser scan parameters within the LabVIEW program. It provides options to set the mode to Continuous Wave (CW) and to input the scan parameters, including the start and end points with a customizable step size, which can be measured in units of nanometers, megahertz, or wavenumbers. The acquisition method can be chosen as either analog or digital, and the

Figure 23: Initial scan parameters in the LabVIEW.
corresponding acquisition instrument can be selected from multiple options provided in the interface.

At the bottom, the interface offers data saving configurations, including the specification of a file path for saving the scan results. There are also multiple data saving options that allow for flexibility in how and when the data is stored, such as saving to the hard disk drive, post-scan, after mode hops, or after a set number of data points. A field is provided for the entry of variable conditions which can be associated with specific experiment parameters. These settings are integral as they influence the scanning process's efficiency, potentially affecting the scan duration depending on the frequency and method of data saving chosen.

The TOPO control section of the LabVIEW interface in Figure 24 displays controls and indicators for a Toptica OPO system. The top left includes pump source selectors with status indicators and IP configuration for USB and TCP connections. Termination controls such as "End this scan" and "Stop current stitch" are present for operational control. The program path indicates a file directory for the calibration table.
Displayed laser parameters include Pump Wavelength, Signal Wavelength, and Idler wavelength are updated from the wavemeter reading. Parameters for the scan include a Stitch Wait Time of 10 ms and a Scan Waiting Time set to zero, with a mode hop detection threshold of 1 GHz.

The frequency change per volt ($\frac{d\nu}{dV}$) for the current scan is 0.378 GHz/V, and the frequency change per degree celsius ($\frac{d\nu}{dT}$) for the temperature scan is 20.8 GHz/K. Which was pre-measured for the OPO prior to the scan. Although, during the scan these values are not constant but represented by a second order polynomial we used the constant

Figure 24: TOPO control section of the LabVIEW front panel.
value that closely follow the polynomial because we will use our separate and more accurate wavelength calibration program after the data collection process. The maximum voltage 'Max V' is shown as 140 V and the minimum 'Min V' as 0 V. Similarly, 'Max C' (max current) is 90 mA and 'Min C' (min current) is 50 mA, while for temperature, 'Max T' is 48 K and 'Min T' is 5 K.

Gauges indicate the set temperature and DFB current with red indicators showing the real-time values in relation to the minimum and maximum. The bottom portion of the interface shows actual values for DFB Current and DFB Temperature. Controls for setting the pump wavelength and stitching parameters are also included, with input fields for Look-Up Table values and scan range adjustments. A status bar on the top right indicates the stitch wait status and scan progression.
4.4. Spectral Calibration

A system of Python based data analysis program was developed for spectral calibration. The process begins with the identification of peaks within both the signal and the etalon data. If peaks are missing, parameters are adjusted for better detection. The system then calculates the number of Free Spectral Range (FSR) intervals between two calibration peaks, using frequency comb data to determine the FSR. This step is critical for ensuring the accuracy of the wavelength measurements.

\[ N_{\text{etalon peaks}} = \frac{A1}{E1} + \text{No. of integer etalon Peaks between } P_i \text{ and } P_f + \frac{A2}{E2} \]  

(4.1)

\[ \text{Free Spectral Range (FSR)} = \frac{f_2 - f_1}{N_{\text{etalon peaks}}} \]  

(4.2)

Next, the data is linearized using cubic-spline interpolation to create a smooth and continuous data set. This linearized data is then compared with reference peaks to adjust any offsets, ensuring that the data matches the known standards.

Figure 25: Spectral Calibration.
The final steps involve creating a new dataset with the linearized and adjusted data, which is then saved. Afterwards, the Root Mean Square (RMS) and Standard Deviation (STD) in relation to the frequency comb data is calculated.

Figure 26 presents a data set from an uncalibrated experimental setup, highlighting two prominent signal peaks at the extremes of the spectrum: the leftmost peak ($P_i$), and the rightmost peak ($P_f$). These peaks signify transitions that have been previously characterized with high precision using a frequency comb technique. The python code outlined in Appendix B, section 1 uses equation 4.1 to determine the number of etalon peaks ($N_{\text{etalon peaks}}$) by using the number of data points within A1, E1, A2, and E2 as shown in Figure 25. Subsequently, the script calculates the Free Spectral Range (FSR) using Equation 4.2, which incorporates $f_1$ and $f_2$, the precise frequency comb measurements associated with the $P_i$ and $P_f$ transitions, respectively.
To linearize the data, the code identifies the positions of the etalon peaks. Initially, it plots the peak-to-peak distances of these etalon positions to identify any significant discrepancies, as illustrated in Figure 27. Subsequently, utilizing the newly calculated Free Spectral Range (FSR), the Python code linearizes the etalon positions using cubic spline interpolation. Following this, the program generates a plot of the corrected peak-to-peak distances to verify the effectiveness of the linearization process.

Figure 27: Peak-to-Peak distance (step no.) prior calibration.

Figure 28 displays the fluctuations in peak-to-peak distances post-linearization, which are on the order of $10^{-10}$ MHz, essentially negligible for the purposes of our experiment. This indicates that the linearization process has successfully standardized the etalon peak positions, ensuring that any experimental errors associated with non-linear data are minimized.
For absolute frequency calibration, the Python code described in Appendix B, Section 2 is employed. This code takes the relatively calibrated data and inputs it into the absolute calibration routine to determine the absolute frequency shift of the spectrum. The procedure involves comparing the frequency comb position of the leftmost peak \((P_i)\) in the experimental data with the corresponding frequency comb data \((f_i)\). The program then adjusts the entire dataset by this difference to complete the calibration process.

Due to the 1st order beam shift of 50 MHz introduced by the Acousto-Optic Modulator (AOM), the absolute calibration is found to be close to this value.

Figure 29 further elaborates the combine algorithm used for the relative and absolute frequency calibration.
Figure 29: Spectral calibration algorithm.
4.5. Error Analysis

Mechanical instability of the Invar frame of the etalon: \(-1.5\text{KHz}/\mu\text{m}\)

Thermal expansion of the Invar frame, which is very small for this material: \(-0.1\text{KHz}/\text{C}\)

Thermal drift of the index of refraction of the air: \(-0.5\text{KHz}/\text{C}\)

Fluctuation of the index of refraction of the air caused by the air flow in the lab. This was reduced to negligible by inserting a plastic covering between the mirrors.

Incident angle. Initially the OPO beam drifting resulted on significant change in \(\theta\) to impact and change the FSR by a standard deviation of 0.0688 MHz. By introducing optical fiber system from etalon beam propagation this error was eliminated.

Uncertainty of the peak finding

The magnitude of the uncertainty of picking the peaks depends on the line shape, number of data in the peak, and signal-noise ratio of the experimental traces, data averaging in the peak finding algorithm. We used local maxima for finding the peak and our step size was 0.5 MHz.

In assessing the precision of peak identification within our spectral data, the peak finding error, \(\sigma_{\text{peak}}\), was calculated based on the experimental parameters: a step size (\(\Delta\nu\)) of 0.5MHz, peak full width at half maximum (FWHM) of 4.5MHz, and a signal-to-noise ratio (SNR) of approximately 100. The peak finding error is determined by the formula:
\[ \sigma_{\text{peak}} = \frac{\text{FWHM}}{2 \sqrt{2 \ln(2)}} \times \frac{1}{\text{SNR}} \]  

(4.3)

Substituting the given values into this equation yields:

\[ \sigma_{\text{peak}} \approx 0.0191 \text{MHz} \]  

(4.4)

This value represents the standard deviation of the peak position due to the inherent noise and measurement resolution, indicating the limit to the accuracy with which we can determine the central frequency of each spectral peak under the specified conditions.
5. Doppler-Free Saturation Absorption Spectra of Methane (CH$_4$) $v_3 = 1$ Band

5.1. Introduction

Methane (CH$_4$) has a long-standing interest in multiple research fields. In spite of its prominence and significance, the study of the methane molecule is complicated by a number of challenges posed by its molecular structure and properties. Methane has a high level of symmetry ($T_d$) that translates to a wealth of near-degenerate vibrational states that form strongly perturbed groups known as polyads. Understanding these collections of structures requires highly accurate theoretical calculations and high-resolution, high-precision spectroscopic measurements. Multiple linelists of CH$_4$ developed for and accessible through the databases ExoMol[72] and TheoReTS [73] have been determined via ab initio calculations, which require experimental measurements to verify their accuracy and to check the theoretical spectra developed from the linelists.

One section of the mid-infrared region of particular significance, the 3.0-3.5 μm region, covers most of the pentad of CH$_4$ and contains 9 vibrational sublevels. Of the sublevels of CH$_4$ that can be reached from the ground vibrational level using this range of wavelengths, the most prominent is the $v_3=1$ asymmetric-stretch band, whose P, Q, and R branches have been scanned individually in multiple prior experiments.[74] Methane transitions in this region can be used to calibrate transition frequencies of other molecules in the mid-infrared, especially those of X-H stretch bands. The region also serves as an effective range for the pump transition in double-resonance spectroscopy measurements using an optical
parametric oscillator (OPO) as the pump source, while a diode laser can be used to reach the triacontad and tetracontad from this range.[75]

In the present work, the saturation absorption spectroscopy technique is used to record the Doppler-free spectrum of the Q branch of the ν3=1 band of CH4 with the idler beam of a continuous-wave (CW) OPO as the mid-infrared light source. Transition frequency calibrated using optical frequency combs in previously reported CH4 spectra are used for absolute frequency calibration, while fringes in the transmission of a Fabry-Pérot etalon are used for the relative frequency calibration. Transition frequencies with improved accuracy compared to HITRAN values [74] are reported.
5.2. Experimental Setup

Our Doppler-free saturation absorption spectroscopy setup as described on section 3.8 and Figure 21, uses the conventional counter-propagating pump-probe scheme.[76] The light source is the idler beam of a CW OPO. Its technical details have been provided in section 3.2. Briefly, the 1064 nm output from a distributed feedback (DFB) diode laser (Toptica, DFB Pro BFY) is amplified in a fiber amplifier (IPG, YAR-10K-1064-LP-SF) to ~10 W and used as the pump beam of the OPO. The output of the DFB is attenuated to 3.5 mW before being fed into the fiber amplifier. Its wavelength is tunable over a range of ~4 nm (35 cm\(^{-1}\)). The OPO uses a fan-out Periodically Poled Lithium Niobate (PPLN) crystal in a singly-resonant cavity. The OPO system is capable of covering the wavelength range of 1.45-4.0 μm (2500-6900 cm\(^{-1}\)) with a degeneracy gap between 2.07-2.19 μm. The pump and signal wavelengths (\(\lambda_P\) and \(\lambda_S\)) are measured by a wavelength meter (HighFiness WS/6-200-Vis/IR) with nominal absolute accuracy of 150 and 120 MHz for the pump and signal wavelength, respectively. The idler wavelength (\(\lambda_i\)) is determined from the former two with an experimentally confirmed accuracy of ~30 MHz at ~3 μm. The linewidth of the idler was measured to be \(\lesssim 2\) MHz (7\(\times 10^{-5}\) cm\(^{-1}\)) in this wavelength region, which can be further improved by using a continuously tunable diode laser (CTL) as the seed for the fiber amplifier. The idler output (2.19-4.0 μm) has >1 W power.

A large change in the idler wavelength is achieved by changing the PPLN crystal motor position. The idler wavelength can also be conveniently and rapidly tuned by temperature-tuning (up to 25 GH/s) or current-tuning (up to MHz frequencies between the set current points) the DFB laser, i.e., tuning the pump wavelength. Alternatively, \(\lambda_i\) can be tuned by
adjusting the voltage applied to a piezoelectric transducer (PZT) driving one mirror of the OPO cavity, i.e., tuning the signal wavelength. In the present work, the signal wavelength is fixed, while the DFB wavelength is temperature-tuned to achieve large mode-hop-free (MHF) ranges (typically 50-100 GHz in the 3 μm region). Prior to a spectral scan, a “look-up” table was prepared as described in section 3.2.2 to identify the optimal PPLN crystal motor position and the position of the motor driving the mode-selecting intracavity etalon in the OPO cavity to maximize the idler beam power for each idler frequency. During the spectral scan, the method explained in Section 3.2.2 and Figure 13 was used.

The idler beam of the OPO is split into two by a CaF$_2$ beamsplitter. The reflected beam is attenuated by a variable neutral density filter to 1-2 mW and used as the probe beam of the saturation absorption measurement. The transmission of ~500 mW idler beam is modulated by the AOM. The square-wave modulation voltage (102 kHz repetition rate with a 50% duty cycle) is provided by the reference signal of a lock-in amplifier (SRS SR810) sent to the AOM driver (Brimrose, FF-100-B2-V7). The modulated first-order sideband has an average power of ~175 mW. Its polarization is rotated from horizontal to vertical by a 90° periscope. Another CaF$_2$ beamsplitter is used to reflect a small portion of the first sideband (≤10 mW), which is used for relative frequency calibration. The transmission, used as the pump beam of the saturation absorption measurement, is attenuated to 50-70 mW and overlapped with the probe beam in the absorption cell using a wire-grid polarizer. The frequency-calibration beam is sent through an etalon [free spectral range, FSR=166(7) MHz, finesse~10]. The high-reflectivity mirrors of the etalon (LayerTech) are mounted in
an Invar frame to reduce thermal expansion and improve the stability of its FSR. (Section 4.1.5)

The probe beam of the saturation absorption measurement and the transmission of the frequency-calibration beam through the etalon are detected with liquid-N$_2$-cooled InSb (Infrared Associates, 449-INSB-1.0-SL8) and MCT detectors (Kolmar Technologies, KV104-0.1-E1/KA5) photovoltaic detectors, lock-in amplified (SRS SR810 and SR530, respectively), and sent to a DAQ card (MCC, PCI-DAS-4020/12, 20 MHz sample rate). The LabVIEW program developed was used for producing the look-up table for changing the idler wavelength of the OPO, its automatic wavelength scan, and the data acquisition process. In this work, a step size of 0.5 MHz and a scan speed of 1 GHz/min (2,000 data points/min) were used without data averaging at each wavelength.
In our experimental setup, the pump is modulated, which ensures that the Doppler-free Lamb dip signal is modulated from the pump through the molecule to the probe. This modulation allows the lock-in amplifier to selectively amplify only the Doppler-free component within our counter-propagating pump-probe configuration. Consequently, we achieved a signal-to-noise ratio of approximately 20. Figure 30 portrays a comparison between our doppler-free signal with the doppler-broaden signal. The doppler-broaden signal was also collected using our experimental setup without the presence of pump or lock-in amplification.
The absorption cell no. 1 with the Brewster-angled windows (section 3.3, Figure 14) with a CH$_4$ pressure of $\leq$0.5 Torr was used. Therefore, the pressure broadening makes a less significant contribution to the overall linewidth of the saturation absorption spectrum than the combined linewidth of the pump and probe beams ($\leq 2 \times \sqrt{2} \approx 2.8$ MHz and the power broadening. The average FWHM of CH$_4$ transitions recorded in the present work is $\sim 4.5$ MHz (Figure 31).

Figure 31: FWHM of the Doppler-free signal.
5.3. Spectrum of ν3 = 1 band of CH₄

We scanned the wavelength region of ca. 3310-3325 nm (ca. 3008-3020 cm⁻¹) covering the Q branch of the ν₃=1 band of CH₄. Figure 33(b) presents the Doppler-free spectrum, which is compared with molecular transitions cataloged in the HITRAN database shown in Figure 32(a). Additionally, Figure 32(d) displays a specific segment of the Doppler-free spectrum, illustrating weaker high-J transitions, which is juxtaposed with previous transition frequency measurements using frequency combs for absolute frequency calibration shown in Figure 32(c).

In Figure 32(c), red lines identify the locations of two frequency comb measurements used for the calibration process as detailed in Section 4.4. This calibration is crucial for achieving absolute frequency accuracy and is depicted alongside the etalon fringe trace used for relative frequency calibration in Figure 32(e). Transitions not included in prior comb-calibrated measurements are marked with asterisks, emphasizing the enhancements in measurement accuracy introduced by this study.
Figure 32: (Top) Doppler-free saturation absorption spectrum of Q-branch transitions of the ν3=1 band of CH4 (b) compared to those in the HITRAN database (a). (Bottom) a portion of the Doppler-free spectrum (d) compared to previous transition frequency measurements using frequency combs for absolute frequency calibration (c). Asterisked transitions are those not reported in the comb-calibrated measurements. Panel (e) shows etalon fringes for relative frequency calibration.
Details of four transition lines in this region are shown in Figure 33. The line at 3010.7513 cm\(^{-1}\) demonstrates a linewidth of 2.2 MHz, dominated by the OPO linewidth, while the others are significantly power-broadened.

*Figure 33: Figure Details of Doppler-free lineshapes of the asterisked transitions.*
Absolute frequency calibration of the CH$_4$ lines was done using previously reported high-accuracy transition frequencies ($\sigma_\nu \approx$2 or 3 kHz) measured using optical frequency combs [77, 78]. The Python program described on section 4.4 was used for frequency calibration. First, the program determines the FSR of the etalon using comb-calibrated transition frequencies of selected CH$_4$ lines (referred to as the “reference transitions”). They are selected for their large transition intensities and are typically separated by 1-2 cm$^{-1}$.

![Figure 34: Signal deviation from frequency comb measurement.](image)
The FSR is calculated by the python code describe in section 4.4; and equation 4.2 and 4.2. The FSR values determined are FSR=166.37(4) MHz. A cubic spline interpolation is then used for frequency linearization, and the reference transitions are used to determine the absolute frequencies. The calibrated transition frequencies (excluding the reference transitions) are compared to the comb-calibrated values given in Refs. [77, 78], yielding a mean deviation of -0.48 MHz and a standard deviation of 1.036 MHz (Figure 34). In comparison, the standard deviation of transition frequencies read by the wavelength meter is ~30 MHz.
5.4. Improvement of the HITRAN Database transition accuracy

The full list of calibrated CH\textsubscript{4} lines recorded in the work is given in the Table 2. The error code used are from the standard error code definition from HITRAN [79].

Table 2: List of Transition frequencies (in cm\textsuperscript{-1}) determined in the present work in comparison with the HITRAN database.

<table>
<thead>
<tr>
<th>This Work</th>
<th>HITRAN</th>
<th>Error code</th>
<th>Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>3008.849035</td>
<td>3008.849035\textsuperscript{a}</td>
<td>7</td>
<td>0.00E+00</td>
</tr>
<tr>
<td>3008.849414</td>
<td>3008.849399</td>
<td>7</td>
<td>-1.55E-05</td>
</tr>
<tr>
<td>3009.011367</td>
<td>3009.011406</td>
<td>7</td>
<td>3.94E-05</td>
</tr>
<tr>
<td>3009.533316</td>
<td>3009.533</td>
<td>4</td>
<td>-3.16E-04</td>
</tr>
<tr>
<td>3009.606294</td>
<td>3009.605398</td>
<td>4</td>
<td>-8.96E-04</td>
</tr>
<tr>
<td>3009.669854</td>
<td>3009.669556</td>
<td>4</td>
<td>-2.98E-04</td>
</tr>
<tr>
<td>3009.679939</td>
<td>3009.679401</td>
<td>4</td>
<td>-5.38E-04</td>
</tr>
<tr>
<td>3010.177852</td>
<td>3010.177841</td>
<td>7</td>
<td>-1.12E-05</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>------</td>
<td>------------</td>
<td>------------</td>
<td>-----</td>
</tr>
<tr>
<td>3010.178226</td>
<td>3010.178258</td>
<td>3010.178282</td>
<td>7</td>
</tr>
<tr>
<td>3010.599665</td>
<td>3010.599241</td>
<td>3010.599421</td>
<td>4</td>
</tr>
<tr>
<td>3010.670274</td>
<td>3010.670274a</td>
<td>3010.670274</td>
<td>7</td>
</tr>
<tr>
<td>3010.736177</td>
<td>3010.736445</td>
<td>3010.736445</td>
<td>4</td>
</tr>
<tr>
<td>3010.751242</td>
<td>3010.751617</td>
<td>3010.751617</td>
<td>4</td>
</tr>
<tr>
<td>3010.804506</td>
<td>3010.80413</td>
<td>3010.80413</td>
<td>3</td>
</tr>
<tr>
<td>3010.880354</td>
<td>3010.879916</td>
<td>3010.879916</td>
<td>4</td>
</tr>
<tr>
<td>3010.883117</td>
<td>3010.88304</td>
<td>3010.88304</td>
<td>3</td>
</tr>
<tr>
<td>3010.892709</td>
<td>3010.892699</td>
<td>3010.892699</td>
<td>7</td>
</tr>
<tr>
<td>3010.911498</td>
<td>3010.911498a</td>
<td>3010.911498a</td>
<td>7</td>
</tr>
<tr>
<td>3011.240853</td>
<td>3011.240277</td>
<td>3011.240277</td>
<td>4</td>
</tr>
<tr>
<td>3011.43358</td>
<td>3011.433641</td>
<td>3011.433641</td>
<td>7</td>
</tr>
</tbody>
</table>
This frequency comb measurement was used as a standard for the calibration of a scan. In the scanned wavelength region, there are 9 relatively weak transitions that were not reported in the comb-calibrated measurements in Refs. [77, 78] but have been observed in our Doppler-free measurement. The accuracy of their transition frequencies from theoretical calculations is reported as $10^{-3}$-$10^{-2}$ cm$^{-1}$ (error code 3) or $10^{-4}$-$10^{-3}$ cm$^{-1}$ (error code 4) in HITRAN. [6, 8, 80] Therefore, the Doppler-free measurement reported here...
improved the frequency accuracy of these transitions by a factor of up to 100. The calibrated transition frequencies of these improved transitions are given in Table 3 in comparison with those reported in HITRAN.
Table 3: Transitions with improved frequency accuracy in the Q branch of the ν3=1 band of CH4 in comparison with the calculated transition frequencies in the HITRAN database.

<table>
<thead>
<tr>
<th>This Work</th>
<th>HITRAN</th>
<th>Ref.</th>
<th>Error code</th>
<th>J”</th>
<th>Sym.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3009.66985</td>
<td>3009.66956</td>
<td>[80]</td>
<td>4</td>
<td>14</td>
<td>F1-F2</td>
</tr>
<tr>
<td>3009.67994</td>
<td>3009.67940</td>
<td>[80]</td>
<td>4</td>
<td>14</td>
<td>F2-F1</td>
</tr>
<tr>
<td>3010.75128</td>
<td>3010.75162</td>
<td>[80]</td>
<td>4</td>
<td>14</td>
<td>F2-F1</td>
</tr>
<tr>
<td>3010.80451</td>
<td>3010.80413</td>
<td>[80]</td>
<td>3</td>
<td>14</td>
<td>A1-F2</td>
</tr>
<tr>
<td>3010.88038</td>
<td>3010.87992</td>
<td>[80]</td>
<td>4</td>
<td>15</td>
<td>A1-A2</td>
</tr>
<tr>
<td>3010.88311</td>
<td>3010.88304</td>
<td>[80]</td>
<td>3</td>
<td>13</td>
<td>E-E</td>
</tr>
<tr>
<td>3011.24090</td>
<td>3011.24028</td>
<td>[80]</td>
<td>4</td>
<td>14</td>
<td>F1-F2</td>
</tr>
<tr>
<td>3011.80140</td>
<td>3011.80115</td>
<td>[8]</td>
<td>3</td>
<td>14</td>
<td>F1-F2</td>
</tr>
<tr>
<td>3011.82046a</td>
<td>3011.82036</td>
<td>[80]</td>
<td>4</td>
<td>13</td>
<td>F2-F1</td>
</tr>
</tbody>
</table>

aThis transition is assigned to R(13) of the ν2+ν4 band.
5.5. Conclusion

A high fluctuation in the FSR was observed in the initial data without the introduction of the optical fiber due to drift in the Idler beam of the OPO during scan. After introducing the optical fiber based beam delivery system to the etalon the standard deviation was reduced to 0.04139 MHz with a mean of 166.379 MHz.(Figure 35). The relative frequency calibration may be further improved by stabilizing the etalon FSR by, for example, locking it to frequency combs [81, 82] or a polarization-stabilized He-Ne laser.

In summary, we have demonstrated the viability of a rapid (2,000 data points/min), high-resolution, high-frequency-accuracy spectroscopy setup with a CW OPO by recording the $\nu_3=1$ band of CH$_4$. Compared to previously reported spectra of CH$_4$ transitions in the same region using a CW OPO (see, for example, Refs. [83, 84]), we have combined wide
tunability, rapid scan speed, and an improved spectral resolution in a Doppler-free saturation absorption spectroscopy system. Combining the narrow linewidth with absolute and relative frequency calibration, we report transition frequencies with improved accuracy ($\sigma_\nu \approx 1$ MHz) for 9 transitions.

A reference beam and a differential detection scheme can be used to further improve the sensitivity of the saturation absorption spectroscopy system. Also, an updated version of the CW OPO with higher output power (>2 W in the 3 μm region) is now commercially available, which may be used to further improve the signal-to-noise ratio (S/N) of weak transitions. The linewidth of the OPO can be further reduced by using a continuously tunable diode laser (CTL) as the seed of the OPO. Indeed, a linewidth of less than 2 MHz for the CH$_4$ Doppler-free spectrum was achieved in our lab using a CTL (Toptica, CTL 1050). To further reduce the output linewidth, one can lock the OPO cavity to a seed laser,[85] a molecular transition,[75] or an external frequency reference, e.g., an ultra-low expansion cavity and frequency combs.[86] In the present work, most transitions are significantly power-broadened. One can attenuate the pump and probe beam powers for the saturation absorption spectroscopy measurements to reduce the spectral linewidth, although data averaging at each wavelength may be necessary to maintain the S/N.
6. LOCKING OF THE CW-OPO TO A DOPPLER-FREE LINE

6.1. Introduction

To construct the apparatus for two-photon spectroscopy, the subsequent phase involves developing a laser locking system. This system will stabilize our continuous-wave optical parametric oscillator (CW-OPO) to a specific methane (CH4) transition, previously identified using the Doppler-free saturation absorption apparatus described in Chapter 5. This configuration will serve as the initial excitation source, promoting molecules to an intermediate energy state. From this state, it will be feasible to probe higher excited states, thus advancing our understanding of molecular dynamics (Figure 36).

In order to seamlessly transition from Doppler-free scanning to Doppler-free locking, modifications are required to adapt the scanning system into a locking system. To maintain the system's modularity, facilitating easy switches between scanning and locking modes, we devised a scheme that allows most of the apparatus to remain in similar positions while implementing only minor adjustments. This strategic approach ensures that the core setup remains largely unchanged, enhancing the system's versatility without necessitating extensive reconfiguration.

Figure 36: Creating population in the intermediate state by laser locking.
6.2. Experimental Design

In our experimental setup for PID locking of the Optical Parametric Oscillator (OPO) to a specific Doppler-free transition, we utilized an MCT detector (model KV104-0.1-1-E/11) due to its high bandwidth exceeding 500 MHz (Details of section 4.1.4), essential for the fast detection necessary in laser lock-in systems. Fast detection is critical to promptly identify deviations from the target frequency, enabling the system to quickly adjust and maintain the lock.

Figure 37: Electronic schematic of the CW-OPO locking.
The electronic configuration (Figure 37) for error signal generation and feedback control utilized the Toptica Digilock 110. In this arrangement, the MCT photodiode was connected to the Digilock's main input for processing the detected optical signal. The Digilock 110, with its dual-output capability, facilitated both rapid and gradual frequency modulation. The auxiliary output of the Digilock, designed for fast dither corrections, was directly connected to the DFB-Pro's AC current modulation input. Conversely, the main output of the Digilock, intended for slower frequency modulation, was connected to the DLC-Pro. This allowed for modulation of the laser's operating parameters, such as current, temperature, or piezo adjustments, based on the feedback signal from the Digilock.

To lock the Optical Parametric Oscillator (OPO) to a Doppler-free transition, our procedure started with applying slow modulation to capture the Doppler absorption peak. This initial phase aimed at identifying the peak within the broadened absorption spectrum.
Following this, adjustments in scanning frequency, voltage offset, and modulation amplitude were precisely made to focus on the Lamb dip signal, situated at the bottom of the Doppler profile. As Figure 38 illustrates, this Lamb dip appeared approximately 50 MHz away from the central peak due to the frequency shift from using the first-order sideband of the Acousto-Optic Modulator (AOM) for the pump. This offset led to the hole burning not being centered on the distribution.

After narrowing down to the Lamb dip signal, fast dither modulation was implemented directly on the DFB-Pro to generate a lock-in based error signal. Upon generating a distinct error signal, as shown in Figure 39, we fine-tuned the PID controller's parameters to achieve a stable lock at the peak of the Lamb dip.

*Figure 39: Error signal Generation.*
6.3. Integration of PID Locking with Mid-Infrared Doppler-Free Setup

In our optical setup designed for versatility between Doppler-free scanning and lock-in stabilization, minimal changes were made to ensure modularity. As shown in the Figure 40, to enhance the system, two flipping lenses were strategically positioned on either side of the absorption cell. These lenses concentrated the beam at the cell's center, amplifying the power-broadened Doppler-free signal.

For the transition from a Doppler-free scanning setup to lock-in stabilization, the detector output was rerouted from the lock-in amplifier to the Digilock, facilitating error signal processing and feedback control for frequency stabilization. In exploring the system's compatibility with different laser sources, both Distributed Feedback (DFB) and Continuous Wave Tunable Laser (CTL) sources were evaluated. The experimentation with these sources resulted in successful lock-in stabilization of the OPO frequency.

Notably, the CTL source demonstrated superior stability and efficiency, attributable to its enhanced capability for high-frequency modulation of the internal piezoelectric component. This characteristic of the CTL made it particularly effective for achieving precise frequency control, underscoring its suitability for applications demanding high stabilization accuracy.
Figure 40: Schematic Diagram of PID Lock-in.
6.4. Achieving Stable and Accurate Laser Frequency Lock

CTL Locking to Doppler-Free Line:

When locking the CTL to a Doppler-free line with an approximate linewidth of 5 MHz, we aimed for an accuracy of about 500 kHz, anticipating a 10% reduction in linewidth due to the locking mechanism's stabilization effect. The CTL's internal piezo provided fine-tuning capabilities, facilitating stable long-term locking through simultaneous fast (current modulation) and slow (piezo adjustment) dither mechanisms.

Figure 41: Front panel of Digilock control during a successful lamb-dip lock.
DFB Locking to a Doppler-Free line:

Successful stable lock was achieved by the Distributed Feedback (DFB) laser to a Doppler-free spectral line. This required extensive and rigorous optimization of Proportional-Integral-Derivative (PID) parameters. Utilizing a dual-PID setup—one for the main output and another for the auxiliary output—as illustrated in Figure 41, we managed to maintain the lock with an accuracy of around 500 kHz.

Figure 42 presents a set of samples PID parameters that were used in securing a successful lock. This configuration underscores the critical role of precise PID tuning in overcoming the initial challenges faced with DFB laser locking. Through meticulous adjustment and optimization of the control parameters, the DFB laser's performance was significantly enhanced, allowing for stable, long-term locking (~15 mins) to the Doppler-free line.

![Figure 42: A sample parameter for locking the CW-OPO.](image)
**OPO Locking limitations:**

Explorations into using the OPO's piezo for locking encountered significant hurdles. Initiation of slow dithering led to mode hopping in the OPO signal, undermining the stability and accuracy of the lock. The slow drift of the OPO frequency also impeded a longer lock than 15 minutes. Although an offset voltage was implemented to reduce the impact, the drift moved the frequency beyond the capability of the offset range of Digi lock sometimes.

**Modulation Parameters:**

Slow Scan Modulation: Adjustments were made at 10 Hz, 3 Hz, and notably at 1 Hz, focusing on isolating the Doppler-free signal as the sole threshold.

Fast Dither Modulation: Frequencies of 50 KHz, 120 kHz, 560 kHz, and 720 kHz were explored, with lock-in based adjustments proving critical for achieving a stable lock and error signal generation.

To accommodate the requirements for precise wavelength targeting, a combination of TOPAS and TOPTICA control programs was utilized. This dual-software approach enabled fine-tuned control over the experimental setup, ensuring that the desired wavelength was accurately achieved and maintained throughout the locking process.
6.5. Conclusion

A stable laser lock with an accuracy of 500 kHz is a crucial milestone for our two-photon spectroscopy setup aimed at studying methane (CH\textsubscript{4}) molecules. This precise locking serves as the pump mechanism, effectively exciting CH\textsubscript{4} molecules to the desired v3=1 transition state. Such a level of control and precision enables us to selectively target specific transitions, adhering to selection rules, and subsequently probe CH4 to higher polyads using the highly sensitive Continuous Wave-Cavity Ring-Down Spectroscopy (CW-CRDS) technique. This strategic approach significantly enhances our experimental capacity to conduct targeted spectroscopic investigations, opening new avenues for detailed exploration of molecular dynamics and interactions.
7. CONTINUOUS-WAVE CAVITY RING DOWN SPECTROSCOPY (CW-CRDS)

7.1. Introduction

Our goal was to enhance the capabilities of two-photon spectroscopy by introducing a system capable of detecting very small numbers of molecules following an initial transition. To achieve this, we developed a Continuous-Wave Cavity Ring-Down Spectroscopy (CW-CRDS) setup known for its exceptional sensitivity, capable of detecting molecules at ppm levels. This high level of sensitivity is crucial for our two-photon spectroscopy experiments, where the number of molecules available after the first transition is significantly reduced.

The CW-CRDS system we built is both automated and robust, designed to streamline the experimental process and ensure consistent, reliable results. After thorough testing, the system demonstrated its ability to function effectively, confirming its readiness to be integrated into the two-photon spectroscopy setup.

This integration is a pivotal step forward, which will allow us to probe the second transition with the high sensitivity required for our experiments. The successful development and testing of the CW-CRDS system mark a significant advancement in our spectroscopic analysis capabilities, setting the stage for deeper insights into molecular behaviors through two-photon spectroscopy.
7.2. Experimental Setup Overview

7.2.1. Laser source:

In our study, we configured a Continuous Wave Cavity Ring-Down Spectroscopy (CW-CRDS) setup utilizing an M Squared Ultra Narrow Linewidth CW Ti:Sapphire Laser (Sols TiS 10W SRX-XF + ECD-X), equipped with a frequency doubling unit. The system was powered by a CW Coherent Verdi-V10 (532 nm) laser, featuring vertical polarization, as its pump source. This setup boasted a 25 GHz mode-hop-free scanning capability and was complemented by a tera scan program capable of scanning the THz wavelength range without detectable mode hops through simultaneous optical adjustments. The laser produced a horizontally polarized output beam in the TEM$_{00}$ spatial mode. Our configuration offered a tuning range between 700 to 1000 nm, an ultra-narrow linewidth of less than 50 kHz, and output power levels up to 6 W for the Ring system and 2.5 W for the Second Harmonic Generation (SHG) unit.

Upon achieving satisfactory CW-CRDS spectra with the Ring laser, we transitioned to a New Focus Tunable Diode Laser (Model 6324) for probing lower polyads, covering a wavelength span of 1277-1342 nm. For our CRDS measurements, we developed a custom LabVIEW program to manage the scanning and data acquisition process.
7.2.2. CW-CRDS sample Cell

The sample cell integrates a Swagelok fitting with a ConFlat (CF) flange for the gas inlet, ensuring compatibility with high-vacuum environments. At the center of the cell, a CF full nipple facilitates connections within the vacuum system. The cell incorporates two custom-made mirror mounts, each equipped with windows for optical experiments. One of the mounts includes a piezoelectric transducer (PZT) for precise optical path length adjustments. This configuration allows for controlled gas flow into the cell while supporting detailed optical measurements and adjustments necessary for experiments demanding high precision and stability in both gas environment and optical path. A butterfly valve was used for Vacuum pump connections. A roughing mechanical pump was used for pumping the cell down to $10^{-3}$ torr. A Pfeiffer vacuum gauge was used for vacuum measurement.

Figure 43: CW-CRDS sample cell.
Figure provides an intricate view of the mirror mount assembly that includes a piezoelectric transducer (PZT) for precise optical cavity length adjustments. The figure is divided into two parts: a cut view illustrating the internal arrangement of components (left) and an external view showing the complete assembly (right). The components are color-coded to enhance clarity and understanding of the assembly structure.

Figure 44: Assembly of the Piezoelectric Transducer (PZT) Side Mirror Mount. The left panel shows a cut view highlighting the internal configuration with key components color-coded for clarity: PZT housing and flexible tube (red), optical window mount (blue), PZT extension (light brown), PZT retainer (dark yellow), and the optical window (grey blue). The right panel presents an external view of the assembled mount, showcasing the integration of these components along with the spacer flange (yellow green).
- **PZT Housing (Red):** The foundational structure housing the PZT combines a standard component and a custom-fabricated piece. This red-coded housing in the figure is central to the assembly, securing the PZT transducer and enabling adjustments to the optical cavity's length.

- **Flexible Tube (Red):** A flexible linkage, connects the housing to the optical window mount. This adaptation allows for versatile positioning of the assembly components.

- **Optical Window Mount (Blue):** Fabricated from scratch, this mount secures the optical window, ensuring an unobstructed path for laser beams within the cavity.

- **PZT Extension (Light Brown):** A custom-engineered, aluminum extension reduces the load on the PZT transducer, facilitating its adjustment capabilities within the assembly.

- **PZT Retainer (Dark Yellow):** This component, depicted in dark yellow in the figure, ensures the PZT transducer and its extension are securely positioned within the housing.

- **Optical Window:** A pre-manufactured optical window is mounted onto the assembly. It serves as a transparent medium for laser transmission, critical for the assembly's optical and vacuum functionality.
- **Spacer Flange**: This flange, highlighted in yellow green, assists in aligning and attaching the optical window and mirror mount. Its modification ensures precise positioning of the optical components.

- **Mirror Mounts**: These mounts are designed to hold high-reflectivity mirrors, fundamental in forming the optical cavity. Customized to fit mirrors of various sizes, these mounts are essential but not color-coded in the figure for simplicity.

- **Retaining Rings**: Custom-fabricated rings secure the mirrors within their mounts. While critical for maintaining optical alignment.

Figure depicts the components and assembly of the mirror mount designed for high-reflectivity optical mirror with no PZT in our experiments. The mirror mount, machined from a 2.75" double-sided ConFlat flange, is shown in blue. This mount is specifically modified to accommodate a 1" ring-down mirror, which is represented in light yellow. Adjacent to the mount, the mirror mount ring, tailored to the dimensions of the mount, is illustrated in black. A CF window on the outside of the mirror mount was installed to keep the vacuum intact.

*Figure 45: Mirror mount assembly for the non PZT side.*
7.2.3. Mode Matching

Achieving optimal mode matching in Continuous Wave Cavity Ring-Down Spectroscopy (CW-CRDS) is essential for maximizing the sensitivity and accuracy of the measurements. The objective of mode matching is to maximize the overlap between the laser beam's transverse electric field distribution and that of the cavity mode. For Gaussian beams, this involves matching the beam waist ($\omega_0$) of the incoming laser beam to the waist of the cavity mode, as well as ensuring that the beam's radius of curvature matches that of the cavity at the coupling point.

The propagation of a Gaussian beam through a lens system can be described by the complex beam parameter $q(z)$:

$$q(z) = z + z_R i$$

where $(z)$ is the longitudinal position along the beam's propagation direction, and $(z_R)$ is the Rayleigh range, defined as $(z_R = \frac{\pi \omega_0}{\lambda})$, with $(\omega_0)$ being the beam waist and $(\lambda)$ the wavelength of the light.

When a Gaussian beam passes through a lens of focal length $(f)$, its complex beam parameter transforms according to the lensmaker's equation:

$$\frac{1}{q'} = \frac{1}{q} - \frac{1}{f}$$

where $(q')$ is the transformed complex beam parameter after passing through the lens.
The ABCD matrix method is a powerful tool for analyzing the propagation of light through optical systems. For a system consisting of two lenses before the cavity, the overall ABCD matrix can be constructed by multiplying the matrices representing each optical element and the spaces between them:

\[ M = M_{\text{space}_2} \cdot M_{\text{lens}_2} \cdot M_{\text{space}_1} \cdot M_{\text{lens}_1} \]

where \((M_{\text{space}})\) & \((M_{\text{lens}})\) represent the matrices for free-space propagation and lens transformation, respectively. Each matrix has the form similar to:

\[
M_{\text{space}} = \begin{pmatrix} 1 & d \\ 0 & 1 \end{pmatrix}, \quad M_{\text{lens}} = \begin{pmatrix} 1 & 0 \\ -\frac{1}{f} & 1 \end{pmatrix}
\]

with \((d)\) representing the distance of free-space propagation and \((f)\) the focal length of the lens.

To achieve mode matching, the beam parameters at the cavity input \((q_{\text{in}})\) must match the cavity's eigenmode parameters \((q_{\text{cavity}})\). This can be expressed as:

\[ q_{\text{in}} = q_{\text{cavity}} \]

By adjusting the distances \((d)\) between lenses and the cavity, as well as selecting appropriate focal lengths \((f)\), the incoming beam can be shaped to meet this condition.

To determine the optimal positions of the lenses and the cavity mirrors, we developed a Python program that utilizes the ABCD matrix method for optical systems. This
computational approach allowed for the pre-calculation of the lens positions, facilitating a theoretical understanding of how the laser beam would propagate through the optical setup.

For the Cavity Ring-Down Spectroscopy (CRDS) setup, mode matching was achieved to ensure the laser beam was optimally coupled into the cavity modes, two plano-convex lenses with focal lengths of 30 mm and 25 mm were positioned before the cavity. The arrangement and positioning of these lenses were critical for matching the Gaussian laser beam profile to the cavity’s mode structure.
7.2.4. Optical Design

Figure 46: Schematic diagram of CW-CRDS with M2 ring laser.
Figure 47: Schematic diagram of CW-CRDS with the ECDL.
In our CW-CRDS configuration, laser output first passes through an optical isolator to block back reflections. This beam is then focused to an Acousto-Optic Modulator (AOM) that is precisely adjustable in six degrees of freedom, ensuring detailed control of the beam's first-order diffraction. A portion of the 1st order diffracted beam, after passing through the AOM, is diverted to a Fabry-Perot cavity for relative frequency calibration. The beam's alignment is further refined by overlaying it with a He-Ne laser beam through specific alignment optics consists of flipping mirror, guaranteeing accurate system alignment. The laser beam, thus aligned, navigates through mode selection optics to synchronize with the optical cavity's mode structure before it enters the sample cell. Following interaction with the sample, the beam is directed onto a detector via a telescope arrangement, optimizing signal detection for CW-CRDS analysis. This approach ensures high-precision measurements of gas-phase samples.

Figure 46 illustrates the optical setup for M2 ring laser with a Verdi-10 pump. The Ring laser system was controlled through our LabVIEW program for step scans.

Figure 47 depicts the ongoing effort to replicate the results from the ring laser but to the 1277-1342 nm region. So that, we can access the lower polyads.
7.2.5. Detection System and Electronic components

Waveform Generator and PZT Control

A waveform generator is used to produce a triangular wave, which is applied to the control system of a piezoelectric transducer (PZT). This setup is utilized to dither the cavity length, achieved by slightly adjusting the PZT-mounted mirror. The objective of dithering is to scan the cavity resonance across the laser frequency. When the cavity is on resonance, the intracavity power builds up to a maximum.

Detector, Comparator, and Triggering

For the M2 system we used Thorlabs PDA10A, Si-based fixed gain detector. It has a bandwidth of 150 MHz. this was used along with the Hamamatsu pre-amplifier for signal amplification.

As the intracavity power reaches a maximum, indicating optimal resonance, the detected signal correspondingly reaches a high threshold. At this point, a detector monitoring the cavity output sends the signal to a fast comparator. Once the signal exceeds the predefined threshold, indicating a successful coupling of the laser into the cavity mode, the comparator triggers a signal. This comparator, characterized by a rapid response time (e.g., 4.5 ns), is crucial for timely and accurate detection of resonance conditions.
Delay Generator (DG) and AOM Control

The trigger signal from the comparator activates the delay generator (DG), which then performs two critical functions. First, it sends a TTL signal to the data acquisition (DAQ) card on the PC, marking the start of data collection for the ring-down event. This allows for the precise timing of the measurement relative to the detected resonance condition. Second, the DG sends an inverted TTL signal to the Acousto-Optic Modulator (AOM) driver. This signal instructs the AOM to quickly shut off the first-order laser beam, effectively ceasing the laser input into the cavity and initiating the ring-down process.

Figure 48: Electronic Signal configuration of CW-CRDS
Ring-Down Measurement

With the laser abruptly turned off by the AOM, the light intensity inside the cavity begins to decay exponentially. The decay time, or ring-down time, is measured by the detector and recorded by the DAQ system. This decay is indicative of the cavity losses, including those caused by absorption and scattering by the sample within the cavity. Figure 48 illustrates the electronic process of acquiring Ring-down measurements. The sequence begins with the comparator, which triggers a delay generator (DG). Following this, the DG is responsible for shutting off the Acousto-Optic Modulator (AOM) while simultaneously triggering the Data Acquisition System (DAQ) to begin data acquisition. This setup ensures synchronized control over the measurement components, facilitating precise data collection.
7.3. Time Synchronization Spectroscopy scan system

The automation of the Continuous Wave Cavity Ring-Down Spectroscopy (CW-CRDS) setup is enhanced by a custom LabVIEW program, designed to manage the laser scanning process and data acquisition with high precision. As depicted in the accompanying figure illustrating the time sequence, the program meticulously scans the laser across a specified wavelength range, pausing at each step to await the triggering of data acquisition through the Measurement Computing PCI-DAS4020/12 DAQ card, as detailed in section 4.2.

For each laser wavelength step, the program is configured to collect data for a user-defined number of averages, ensuring robust signal-to-noise ratio improvement and measurement reliability. This averaging process is critical for mitigating the impact of random fluctuations in the ring-down signal, thereby enhancing the overall quality of the spectroscopic data.

Figure 49: Time Synchronization of the CW-CRDS.
In the depicted time synchronization Figure 49 of the CW-CRDS system, a waveform generator applies a triangular voltage to the PZT, dynamically tuning the optical cavity's length. During this modulation, when the resonance condition within the cavity is achieved, the intracavity power increases. This event is detected by a photodiode, which, upon reaching a pre-set power threshold, triggers a comparator. The comparator, in turn, activates a delay generator.

The delay generator performs a dual function; it sends one signal to deactivate the Acousto-Optic Modulator (AOM), ceasing the laser input into the cavity, and another signal to the data acquisition system to commence recording. The result is the observation of a cavity ring-down signal, characterized by an exponential decay function representing the loss of light within the cavity. This decay is captured by the data acquisition card.

Furthermore, the LabVIEW program is equipped with real-time data processing capabilities, automatically calculating the absorption coefficient from the ring-down time at each step. This feature enables the live display of the absorption spectrum, allowing any necessary adjustments in situ. Manual configuration of the gates for ring-down data acquisition is also facilitated within the LabVIEW program, granting the experimenter fine control over the timing and duration of the signal capture. The LabVIEW automation with the specified data acquisition system underscores the setup's capability to conduct CW-CRDS experiments with precision and efficiency. By combining automated scanning and data acquisition with live data analysis and spectrum display, the system offers a comprehensive solution for conducting high-resolution gas-phase spectroscopic analysis.
7.4. Room Temperature CW-CRDS of Waters

In assessing the functionality of our Continuous Wave Cavity Ring-Down Spectroscopy (CW-CRDS) system, we focused on the spectroscopic analysis of water vapor as a test gas. The experimental cell was saturated with H₂O and operated under a low pressure of 10⁻³ torr to facilitate the conditions conducive for detailed spectral analysis. The CW-CRDS technique was employed across a narrow wavelength range from 969 to 971 nm.

The resulting spectrum (red), as depicted in the Figure 50, showcases a series of absorption features characteristic of water vapor within this spectral window. Notably, the observed
spectrum aligns with the spectral data available from the HITRAN database (blue), serving as a benchmark for comparison. This concordance between our experimental findings and the established spectral database unequivocally demonstrates the system's accuracy and reliability in capturing the spectral signatures of gasses molecule.

The successful observation of the water spectrum, with its distinctive absorption lines, confirms the operational integrity and precision of our CW-CRDS setup. Moreover, this achievement validates the system's capability to serve as a probe in a two-photon spectroscopy setup, where accurate and sensitive detection of spectral lines is paramount. The perfect match with the HITRAN database not only underscores the system's functionality but also its readiness for deployment in next step of the two-photon spectroscopy.
8. SUMMARY AND FUTURE DIRECTION

The culmination of this dissertation saw the establishment of a rapid-scanning Doppler-free saturation absorption spectroscopy apparatus, designed for high-fidelity investigations into molecular spectroscopy. The precision engineering involved the integration of an OPO idler output into a calibration etalon via optical fiber, enhancing the system's accuracy and stability for frequency measurements.

Focusing on the Q branch of the CH$_4$ ν3=1 vibrational band, the study achieved meticulous frequency calibration, a step forward in the spectroscopic characterization of methane. The modular nature of the setup proved invaluable, facilitating a transition to an OPO-locking mechanism that broadened the range of investigable spectroscopic phenomena.

Initial experiments with the CRDS system yielded data that confirmed the system’s potential for high-resolution spectral analysis. Moreover, these preliminary findings have paved the way for extended research into a wider array of Mid-IR astrochemical molecules.

Future endeavors will aim to synthesize the OPO-locking and CRDS systems, targeting the acquisition of two-photon double-resonance spectra as shown in Figure 51. This work will include precise line shape measurements, exploring phenomena such as pressure broadening and shifts, which are crucial for understanding the underlying physics of molecular interactions.
The anticipated integration with slit-jet expansion techniques is expected to refine spectral resolution further, thereby enhancing the detection of subtle spectroscopic features. The advancements detailed herein not only serve the immediate academic community but also project a pathway for subsequent inquiry into the intricate spectra of molecules relevant to astrochemistry and beyond.
Figure 51: Proposed Two Photon Spectroscopy setup.
REFERENCES


42. Devi, K., Continuous-wave optical parametric oscillators and frequency conversion sources from the ultraviolet to the mid-infrared. 2013.


APPENDIX A

OPO Etalon Replacement and Cavity Alignment

The etalon removal process from the OPO cavity is executed with precision and care to avoid contamination and damage. The procedure begins by donning gloves to ensure a clean environment is maintained. The cavity lid is then opened to reveal the interior components of the laser system. The etalon servo is adjusted to a setting of 4000, positioning the etalon horizontally. A 1.5 mm Allen key is used to loosen the screw located at the base of the etalon mount without fully removing the screw. The etalon is then carefully slid out in the direction specified by the arrow, by holding it from the top fin. Once removed, the etalon should only be handled by the top fin and stored in a pre-designated, secure, and clean location until it is to be re-inserted. The re-insertion of the etalon into the laser cavity is carried out by reversing the steps taken during its removal.

The laser cavity consists of four mirrors designated RM1, RM2, RM3, and RM4, forming an optical resonator (Figure 52). The procedure commences with ensuring the nonlinear crystal is centrally located along its operational range, specifically between 8 and 12 millimeters, to enable optimal interaction with the laser beam.

The laser pump, which is a fiber amplifier, is then set to emit a power output of 2 watts. A narrow card, with dimensions similar to that of a bisected business card, approximately 0.5 inches in width, is placed anterior to the mirror RM4. This arrangement is expected to
produce two distinct green emissions, which are indicative of second harmonic generation occurring within the nonlinear crystal. The first emission is a forward-propagating beam following the trajectory RM2 to RM3 to RM4 to RM1, while the second is a retroreflected beam emanating from the crystal surface.

Subsequent adjustments involve the alignment of mirror RM1 to achieve the coalescence of both beams on the RM4 surface, which is critical for constructive interference and enhanced beam intensity. The card is then repositioned in front of RM3, and mirror RM4 is fine-tuned until the green emissions converge on the RM3 surface.

Upon successful alignment, the pump power is escalated to 10 watts. If the laser system begins to oscillate, as evidenced by substantial red light within the cavity, further power optimization is pursued in accordance with the operating manual. Should the system fail to

Figure 52: TOPO Cavity.
oscillate, the power is reverted to 2 watts, mirror RM2 is minutely adjusted, and the alignment process is reiterated.

Once oscillation is established and the output power aligns with the specifications detailed in the datasheet, the pump power is reduced to zero, and the etalon is reinserted into the system. The pump power is then restored to 10 watts, and the final alignment is conducted.
APPENDIX B

Python program for data analysis

SECTION 1

***** RELATIVE CALIBRATION******

#!/usr/bin/env python3
#
# _*- coding: utf-8 -*_
#---------------------------------------------------
# Created Date: 05/26/2022
# All Right Reserved
# version = '1.0'
#---------------------------------------------------
import numpy as np
import matplotlib.pyplot as plt
from scipy.signal import find_peaks
from scipy.interpolate import CubicSpline
#file= str(input("filename:"))
data = np.loadtxt("exp_orange.txt",skiprows=1)
fsr=166.48978239445358
step = data[:,0]
wavelengthNm= data[:,1]
signal = data[:,2]+0.5
etalon = data[:,3]
cml_origin = data[:,4]
plt.figure(figsize = (25,8))
peaks, _ = find_peaks(signal, height=0.4, threshold=None, distance=50)
print("doppler free peaks list: ", peaks)
print(cml_origin[peaks])
print("no. of dfree peaks=", len(peaks))
```python
# print(10000000/wavelengthNm[peaks])
# print(29979.2458*(10000000/wavelengthNm[peaks]))
plt.plot(etalon)
plt.plot(signal)
plt.show()
plt.figure(figsize = (25,8))

plt.plot(etalon)
plt.plot(signal)
plt.xlim(0,10000)
plt.show()
no_data=peaks[-1]-peaks[0]
print(no_data)

peak_etalon, _ = find_peaks(etalon, height=0.2, threshold=None, distance=150)
# print(peak_etalon)
print("no. of etalon peaks=", len(peak_etalon))
no_data_etalon=peak_etalon[31]-peak_etalon[30]
print(no_data_etalon)
no_peaks=no_data/347
print(no_peaks)
```
# Calculating difference list

diff_list = []

for i in range(1, len(peak_etalon)):
    diff_list.append(peak_etalon[i] - peak_etalon[i-1])

# printing difference list

plt.figure(figsize = (25,8))
plt.plot(diff_list)
plt.show()

# print ("difference list: ", str(diff_list))

# fsr calculator

'''no of fsr'''

# print(peaks)

# print(peak_etalon)
a=[]

def myFunc(x):
    if peaks[0] < x < peaks[-1]:
        return True
    else:
        return False

inside_peaks = filter(myFunc, peak_etalon)

for x in inside_peaks:
    a.append(x)

# print(a)
print(len(a))

b=list(peak_etalon)

m=b.index(a[0])
idx_etalonBefore_signal=m-1
etalonBefore_signal = b[idx_etalonBefore_signal]

n = b.index(a[-1])
idx_etalonAfter_signal = n + 1
etalonAfter_signal = b[idx_etalonAfter_signal]

# print(etalon_before_signal, etalonAfter_signal)
# print(peaks[0], peaks[-1])
# print(a[0], a[-1])

x_peak_left = (a[0] - peaks[0]) / (a[0] - etalonBefore_signal)
print(x_peak_left)

x_peak_right = (peaks[-1] - a[-1]) / (etalonAfter_signal - a[-1])
print(x_peak_right)
total_no_peak = len(a) + x_peak_left + x_peak_right
print("total no. of peaks = " + str(total_no_peak))

# fsr determinaiton
ref_first_value = 90376685.3938000
ref_last_value = 90393517.8759000

fsr_test = (ref_last_value - ref_first_value) / (total_no_peak - 1)
print("estimated fsr = " + str(fsr_test))

peaks, _ = find_peaks(etalon, height=0.25, threshold=None, distance=150)

plt.figure(figsize = (25,8))
plt.plot(etalon)

plt.plot(peaks, etalon[peaks], "x")
# plt.xlim(80000,100000)
# print("no. of peaks = ", len(peaks))
print(peaks)
plt.show()

plt.figure(figsize = (25,8))
plt.plot(etalon)
plt.plot(peaks, etalon[peaks], "x")
plt.xlim(-100, 2000)
print("no. of peaks=", len(peaks))
plt.show()

# Calculating difference list
diff_list = []
for i in range(1, len(peaks)):
    diff_list.append(peaks[i] - peaks[i-1])

# printing difference list
plt.figure(figsize = (25,8))
plt.plot(diff_list)
plt.show()
# print("difference list: ", str(diff_list))

from scipy.interpolate import CubicSpline
x = peaks
print(np.shape(x))
y = np.arange(0, fsr*len(peaks), fsr)
# print(y)
print(np.shape(y))
# use bc_type = 'natural' adds the constraints as we described above
f = CubicSpline(x, y, bc_type='natural')
x_new = np.linspace(peaks[0], peaks[-1], (peaks[-1]-peaks[0]+1))
y_new = f(x_new)

plt.figure(figsize = (20,8))
plt.plot(x_new, y_new, 'bo')
plt.plot(x, y, 'ro')
j=2
k=int(len(peaks)/2)

plt.xlim(peaks[j],peaks[k])
plt.ylim(y[j],y[k])
# print(y_new)

plt.title('Cubic Spline Interpolation')
plt.xlabel('x')
plt.ylabel('y')
plt.show()

'''with open('b.txt', 'w') as f:  
  for i in y_new:  
    f.write("[10]\n".format(round(i,5)))'''
colA= y_new
colB=wavelengthNm[peaks[0]+0:]
colC=signal[peaks[0]+0:]
colD=etalon[peaks[0]+0:]

filename= "fsr_"+str(fsr)+"_"+str(colB[0])+"nm__to__"+str(colB[-1])+"nm).txt"

with open(filename, 'w+') as f:  
  for i,j,k,l in zip(colA,colB,colC,colD):  
    f.write("{0}\t{1}\t{2}\t{3}\n".format(round(i,12),round(j,12),round(k,12),round(l,12)))

new_data = np.loadtxt(fname=filename)
new_step = new_data[:,0]
new_wavelengthNm= new_data[:,1]
new_signal = new_data[:,2]
new_etalon = new_data [:,3]
plt.figure(figsize = (25,8))
plt.plot(new_step,new_etalon)
new_peaks= find_peaks(new_etalon, height=0.2, distance=150)
peak_pos = new_step[new_peaks[0]]
print(peak_pos)

# Calculating difference list
diff_list2 = []

for i in range(1, len(peak_pos)):
    diff_list2.append(peak_pos[i] - peak_pos[i-1])

# printing difference list

plt.figure(figsize = (25,8))
diff_list2_plot=diff_list2[1:-1]
plt.plot(diff_list2_plot)
# plt.ylim(170,171.71)
# plt.xlim(0,1000)
plt.show()
# print("difference list: ", str(diff_list2))

new_cm1=10000000/new_wavelengthNm

plt.figure(figsize = (25,8))
plt.plot(new_step,new_signal)
plt.plot(step,signal)
# import numpy as np
import matplotlib.pyplot as plt
from scipy.signal import find_peaks

japan=np.loadtxt("fre_comb_3008.84903_3010.178442.txt", usecols=(-4,-3,-1,))
# print(japan)
japan_MHz=japan[:,0]
japan_cm1=japan[:,1]
japan_intensity=japan[:,2]
data = np.loadtxt("fsr_166.42733598965563_(3323.543741nm)__to__(3322.037661nm).txt")
step = data[:,0]
wavelengthNm= data[:,1]
    cm1=10000000/wavelengthNm
signal = data[:,2]+.5
etalon = data[:,3]

# print(cm1[0])
MHZ_0=cm1[0]*29979.2458
# print(MHZ_0)
correction=55.714924439787865
step_calib=step+MHZ_0+correction
# print(step_calib)
# plt.figure(figsize = (6,4))
# plt.plot(cm1,signal)
plt.figure(figsize = (25,8))
peaks, _ = find_peaks(signal, height=1, threshold=None, distance=15)
print(peaks)
print("our peaks"+str(step_calib[peaks]))

plt.figure(figsize = (25,8))
plt.plot(step_calib,signal)
plt.plot(japan_MHz,japan_intensity,"ro")
for x,y in zip(japan_MHz,japan_intensity):
    label = "{:.2f}".format(x)
    plt.annotate(label,
                  (x,y),
                  textcoords="offset points",
                  xytext=(0,10),
                  ha='center',
                  size = 25)
plt.bar(japan_MHz,japan_intensity,width=50,color="red")
#plt.xlim(90242800,90242890)
plt.ylim(.4,1)
plt.yticks(fontsize=25)
plt.xticks(fontsize=25)

print(japan_MHz[0]-step_calib[peaks[0]],japan_MHz[-1]-step_calib[peaks[-1]])
'''first peak'''

```python
plt.plot(japan_MHz, japan_intensity, "ro")
for x, y in zip(japan_MHz, japan_intensity):
    label = "{:2f}".format(x)
    plt.annotate(label, 
                 (x, y), 
                 textcoords="offset points", 
                 xytext=(0, 10), 
                 ha='center', 
                 size=25)
plt.bar(japan_MHz, japan_intensity, width=1, color="red")
plt.xlim(japan_MHz[0] - 100, japan_MHz[0] + 100)
plt.ylim(-.5, 4)
plt.yticks(fontsize=25)
plt.xticks(fontsize=25)
```

'''last peak'''

```python
plt.figure(figsize=(25, 8))
plt.plot(step_calib, signal)
plt.plot(japan_MHz, japan_intensity, "ro")
for x, y in zip(japan_MHz, japan_intensity):
    label = "{:2f}".format(x)
    plt.annotate(label, 
                 (x, y), 
                 textcoords="offset points", 
                 xytext=(0, 10), 
                 ha='center', 
                 size=25)
plt.bar(japan_MHz, japan_intensity, width=1, color="red")
```
plt.xlim(japan_MHz[-1]-100,japan_MHz[-1]+100)
plt.ylim(-.5,6)
plt.yticks(fontsize=25)
plt.xticks(fontsize=25)
print("japan"+str(japan_MHz))

filename="test.txt"
with open(filename, 'w+') as f:
    for i,j in zip(step_calib,signal):
        f.write("{:.14} {:.14}\n".format(round(i,14),round(j,14)))

data=np.loadtxt("test.txt")
step = data[:,0]
signal = data[:,1]
plt.figure(figsize = (25,8))
plt.plot(step,signal)
plt.bar(japan_MHz,japan_intensity,width=10,color="red")
plt.xlim(step[15000],step[17000])
CURRICULUM VITAE

S M Shah Riyadh
689 Lynn St, Apt 1, Louisville, KY, USA -40217
s0riya01@louisville.edu | https://sites.google.com/view/smshahriyadh/home | +1 (502)716-2420
U.S. Permanent Resident (Green Card)

PROFESSIONAL PROFILE

• 5+ years of experience in building scientific apparatus including design and development of optical and optoelectrical system, Lasers, Laser Systems, optomechanical systems, optical alignment (mode matching, beam path analysis), Fiber coupling, cavity mode matching, optical metrology and free space optics, Vacuum system design, troubleshooting, equipment repair, etc.

• Strong experimental skills and hands-on experience with a variety of laser spectroscopic techniques (Doppler-free spectroscopy, Laser locking, CW & Pulsed Cavity Ring-down Spectroscopy (CRDS), tunable diode laser absorption spectroscopy (TDLAS), two-photon spectroscopy, Laser-induced Fluorescence (LIF)/ Dispersed Fluorescence (DF), Ultrafast Spectroscopy (pump-probe), Furrier-transform Infrared (FTIR), etc.

• Solid understanding of fundamentals of physics, Photonics and optics i.e., concept of quantum physics, matrix mechanics, laser material interaction, ro-vibronic energy structure, diffraction, interference, dispersion, aberration, polarizations, Beam quality, etc.

• Experienced with Data Acquisition & Analysis system development using DAQ, LabVIEW and Python for laser-based spectroscopic apparatus.

• Hands-on experience with novel and nano-material synthesis techniques such as Chemical Vapor Deposition (CVD), Chemical etching, hot water treatment, Ion-Bombardment, etc. with Knowledge and experience with scanning electron microscope (SEM), Energy Dispersive x-ray Spectroscopy (EDX), transmission electron microscopy (TEM), Raman Spectroscopy, microscope, etc.

• Extensive experience with molecular beam, Vacuum system design, Jet expansion cooling, signal processing, numerical analysis, signal broadening, Thermal effects, pressure broadening, vibrational effect etc.

• Experienced with working in a diverse team or individual project with polished technical writing and presentation skills.

EDUCATION

University of Louisville, Louisville, KY
PhD, Physics and Astronomy
April 2024

University of Louisville, Louisville, KY
Master of Science, Physics and Astronomy, GPA: 3.75
Aug 2020

University of Dhaka, Dhaka, Bangladesh
Master of Science, Renewable Energy Technology GPA: 3.75
Aug 2018

Shahjalal University of Science and Technology, Sylhet, Bangladesh
Bachelor of Science, Physics, GPA: 3.17
Dec 2014

TECHNICAL SKILLS

• Optics, lasers, and other optical systems: Cavity Ring-down Spectroscopy (CRDS), Optical Parametric Oscillator (OPO), Tunable Diode Laser (TDL), Distributed-feedback laser (DFB), Fiber Amplifier, Acousto-Optic Modulator (AOM), polarizer, Electro-Optic modulator (EOM), Detector selection, Laser locking system, YAG laser, DYE laser, Ring laser (solid and dye), Fiber optics (coupler, connectors, cleavers, splicers, attenuators, single and multi-mode, etc.) Excimer lasers, Raman shifting, Difference-frequency mixing, Auto tracker, etc.

• Electronics and optoelectronics: Delay/pulse generators, Lock-in amplifiers, Box-car integrators, Oscilloscope, Data Acquisition (DAQ), PMT, Photodiode, CCD cameras, Spectrographs, Spectrum analyzers, thermopile, etc.

• Ultra-high vacuum techniques: Mass flow system, Swagelok fittings, Vacuum system leak tests

• Program: Python, LabView, Origin, Mathcad, MATLAB, SolidWorks, SigmaPlot, Gaussian, GaussView, and Microsoft Office products, etc.
EXPERIENCE

Graduate Research Assistant (2020-2023)
UofL Laser Lab, Department of Chemistry, University of Louisville, KY (Team Leader)

  - Designed and built specialized experimental equipment using TDL, OPO, ECDL for precise two-photon cavity-enhanced double-resonance spectroscopy of astrochemical molecules by combining absorption spectroscopy and CW-CRDS.
  - Engineered a meticulously controlled vacuum system, ensuring a stable environment for accurate experimentation.
  - Devised and seamlessly integrated an advanced laser locking system, guaranteeing exceptional spectral precision and consistent outcomes.
  - Took a leadership role in designing and constructing the experimental setup, optimizing components to achieve high-precision absorption measurements.
  - Developed a comprehensive data acquisition system using LabVIEW, and data analysis program using Python capturing spectroscopic data with exceptional accuracy.
  - Led the creation of a robust data analysis program, facilitating efficient interpretation and extraction of key absorption features.

Graduate Teaching Assistant (2018-2020)
Department of Chemistry, University of Louisville, KY

- **Combined Experimental and Computational Study on the Transition of the Calcium Isopropoxide Radical as a Candidate for Direct Laser Cooling** (2022)
  - Optimized and troubleshoot setups for Laser-Induced Fluorescence (LIF) and Dispersed Fluorescence (DF) techniques, enhancing experimental efficiency.
  - Managed data acquisition processes and performed Gaussian data analysis for precise insights.
  - Instructed undergraduate chemistry laboratory sessions and provided personalized tutoring.

Department of Physics and Astronomy, University of Louisville, KY

  - Managed Chemical Vapor Deposition (CVD) processes to grow materials for in-depth analysis.
  - Instructed undergraduate physics laboratory sessions and conducted private tutoring.

Research Student (2018)
Bangladesh Atomic Energy Commission, Dhaka, Bangladesh

  - Orchestrated Chemical Vapor Deposition (CVD) processes to cultivate semiconductor materials critical for solar cell research.
  - Conducted comprehensive characterization using Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDX) techniques.
SELECTED PUBLICATIONS & CONFERENCE PRESENTATIONS

Google Scholar: https://scholar.google.com/citations?user=Tza3NG8AAAAJ&hl=en


- Manthila Rajapakse, Bhupendra Karki, Usman O Abu, Sahar Pishgar, Md Rajib Khan Musa, SM Shah Riyadh, Ming Yu, Gamini Sumanasekera, Jacek B Jasinski “Intercalation as a versatile tool for fabrication, property tuning, and phase transitions in 2D materials” npj 2D Materials and Applications, 5.1 (2021): 30. [Link]

- Bhupendra Karki, Byron Freelon, Manthila Rajapakse, Rajib Musa, SM Shah Riyadh, Blake Morris, Usman Abu, Ming Yu, Gamini Sumanasekera, Jacek B Jasinski, “Strain-induced vibrational properties of few layer black phosphorus and MoTe2 via Raman spectroscopy” Nanotechnology, 31.42 (2020): 425707. [Link]

Professional Achievements

- DEI Student Leader Award, 2023 [Link]
  For contributions to UofL’s goals for advancing diversity, equity, and inclusion including efforts to build an anti-racist campus community.

- Introduction to Vacuum Science & System Design Physical Vapor Deposition & Thin Film Growth Models
  Nov 14th, 2019, by Kurt J. Lesker

- Graduate school PLAN Workshop award, 2023 [Link]

- Completion of Student Organization Advisory Board Leadership Series, 2022

- GSC Research Grant, University of Louisville, 2019

- UofL Laser lab Laser Safety training

- Industrial battery and solar assembly line management at Rahim Afroz Solar Factory, Savar Union, Dhaka, 2018

- 1st Runner Up, Bangladesh Mathematical Olympiad, 2008

- Merit Scholarship by Intermediate and Secondary Education Board, Bangladesh, 2006

Volunteer Services

- Bangladesh Student Association, University of Louisville
  President 2022 -
  Lead the organization, Fund raising and organizing cultural programs.

- SHIKORH, SUST
  Publication Secretary 2012 - 2014
  Worked closely with hundreds of people to publish quarterly magazines.

- Copernicus Astronomical Memorial of SUST (CAM-SUST)
  General Secretary 2011 - 2012
  Lead a large group of astronomers, provided free education on science for school and high school in the area.