DIODE LASER MEASUREMENTS OF NH₃ AND CO₂ FOR COMBUSTION AND BIOREACTOR APPLICATIONS

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Abstract

Diode laser sensors based on absorption spectroscopy techniques were designed and demonstrated for three applications: 1) in situ NH$_3$ monitoring for combustion emissions using laser sources near 1.5 $\mu$m; 2) in situ CO$_2$ monitoring in combustion zones using lasers near 2 $\mu$m; and 3) field measurements of NH$_3$ and CO$_2$ near 2 $\mu$m in the vent gases of a spacecraft bioreactor at NASA-Johnson Space Center.

Ammonia spectroscopy near 1.5 $\mu$m was investigated to select transitions appropriate for trace ammonia detection in air-quality and combustion emissions-monitoring applications using diode lasers. Six ammonia features were selected for these trace-gas detection applications based on their transition strengths and isolation from interfering species. The strengths, positions, and lower-state energies for the lines in each of these features were measured and compared with values published in the literature, yielding improvements in the spectroscopic database. Ammonia slip was measured in the exhaust above an atmospheric pressure premixed ethylene-air burner to demonstrate the feasibility of the in situ diode laser sensor for Thermal DeNO$_x$ or Selective Catalytic Reduction applications.

High-resolution absorption measurements of CO$_2$ were made in a heated static cell and in the combustion region above a flat-flame burner for the development of an in situ CO$_2$ combustion diagnostic based on a diode laser operating near 2.0 $\mu$m. Calculated absorption spectra of high temperature H$_2$O and CO$_2$ were used to find candidate transitions for CO$_2$ detection, and the R(50) transition at 1.997 $\mu$m ($\nu_1+2\nu_2+\nu_3$ band) was selected based on its linestrength and isolation from interfering high-temperature water absorption. Measurements of spectroscopic parameters such as the linestrength, self-broadening coefficient and line position were made for
the R(50) transition, and an improved value for the linestrength is reported. The combustion product mole fractions of CO$_2$ above a flat-flame burner were determined *in situ* to verify the measured spectroscopic parameters and to demonstrate the feasibility of the diode laser sensor.

Ammonia spectra near 2 $\mu$m were studied with external cavity diode lasers to select appropriate transitions for monitoring trace species concentration in the vent gases of a bioreactor that is being developed at NASA-Johnson Space Center to recycle wastewater aboard manned spacecraft. The $P_P^3(3)_s$ transition of the $\nu_3 + \nu_4$ combination band at 5016.977 cm$^{-1}$ was selected due to its linestrength and isolation from CO$_2$ and H$_2$O absorption. The fundamental spectroscopic parameters of the selected and neighboring transitions were measured to confirm the spectroscopic database using a DFB diode laser. The 2 $\mu$m laser was aligned into a sampling sensor system designed at Rice University to measure NH$_3$ concentration in the vent gases of a ground-test bioreactor at NASA-JSC and to monitor the potential toxicity of space cabin indoor air quality. The same laser probed CO$_2$’s R(50) transition at 5007.787 cm$^{-1}$ to monitor CO$_2$ mole fractions and assess overall bioreactor health and carbon conversion efficiency. The measurements demonstrated the sensor’s ability to track changes in NH$_3$ and CO$_2$ concentration due to different bioreactor events.

All three projects in this work have led to improvements in the published spectroscopic database for NH$_3$ or CO$_2$ for various transitions, and have established the optimum wavelengths to be employed by diode-laser based sensors for different industrial applications.
I would like to thank my wife, Julia, for her unyielding support and dedication to the cause, despite the sacrifices that were required of her; and my daughter Evelyn, for bringing so much joy to our lives.

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Glossary

Acronyms

BWP  Biological Waste Processor or bioreactor
CDT  Central Date Time
DFB  distributed-feedback diode laser
ECDL external-cavity diode laser
FSR  Free-spectral range
FWHM Full-width at half-maximum (halfwidth)
GLS  Gas-Liquid Separator
IR   infrared ($\lambda > 3 \mu m$)
MDA  minimum detectable absorbance
NASA National Aeronautics and Space Administration
NEA  Noise-equivalent absorbance
NIR  near-infrared ($0.76 < \lambda < 3 \mu m$)
SNR  signal-to-noise ratio
TOC  total organic carbon
TWA  Time-weighted average
UV  ultra-violet (λ < 400 nm)

WRS  Advanced Water Recovery System

Symbols

- \( a \)  Voigt parameter that determines relative collisional broadening compared with Doppler broadening
- \( A_0 \)  rotational constant in units of \([\text{cm}^{-1}]\) along a molecule’s figure axis
- \( B_0 \)  rotational constant in units of \([\text{cm}^{-1}]\)
- \( c \)  speed of light in vacuum, \( c = 3.0 \times 10^{10} \text{ cm/sec} \)
- \( E'' \)  Lower-state energy in units of \([\text{cm}^{-1}]\)
- \( h \)  Planck’s constant, \( h = 6.6256 \times 10^{-27} \text{ erg \cdot sec} \)
- \( I_t \)  Transmitted radiation intensity
- \( I_0 \)  Non-absorbed or reference radiation intensity
- \( k \)  Boltzmann’s constant, \( k = 1.38054 \times 10^{-16} \text{ [erg/K]} \)
- \( n_j \)  Concentration of species \( j \)
- \( n \)  Index of refraction
- \( N \)  Broadening temperature exponent
- \( P \)  Pressure
- \( Q(T) \)  Total internal partition function for a molecule at a particular temperature \( T \)
- \( Q_{\text{nuc}} \)  Nuclear partition function
- \( Q_{\text{rot}} \)  Rotational partition function
\( Q_{\text{vib}} \)  \hspace{1em} \text{Vibrational partition function}

\( S_i^* \)  \hspace{1em} \text{Absorption linestrength for a transition } i \text{ in units of } [\text{cm}^{-1}/(\text{mol} \cdot \text{cm}^{-2})] 

\( S_i \)  \hspace{1em} \text{Absorption linestrength for a transition } i \text{ in units of } [\text{cm}^{-2}\text{atm}^{-1}] 

\( V(a, w) \)  \hspace{1em} \text{Voigt function}

\( w \)  \hspace{1em} \text{Voigt non-dimensional frequency parameter}

\( x_j \)  \hspace{1em} \text{Mole fraction of species } j

\( y \)  \hspace{1em} \text{Voigt integral variable}

**Greek Symbols**

\( \alpha \)  \hspace{1em} \text{Absorbance}

\( \gamma \)  \hspace{1em} \text{Collision-broadening coefficient}

\( \Delta \nu_C \)  \hspace{1em} \text{Collisional halfwidth (FWHM)}

\( \Delta \nu_D \)  \hspace{1em} \text{Doppler halfwidth (FWHM)}

\( \nu_i \)  \hspace{1em} \text{ } i^{th} \text{ vibrational mode}

\( \nu_{0,i} \)  \hspace{1em} \text{Linecenter frequency of a spectroscopic transition } i \text{ in units of } [\text{cm}^{-1}] \text{ or } [\text{Hz}]

\( \sigma \)  \hspace{1em} \text{symmetry number: } \sigma = 2 \text{ for CO}_2, \sigma = 3 \text{ for NH}_3

\( \phi \)  \hspace{1em} \text{Lineshape, equivalence ratio}

\( \phi_D \)  \hspace{1em} \text{Gaussian lineshape from Doppler broadening}

\( \phi_C \)  \hspace{1em} \text{Lorentzian lineshape from collisional broadening}

\( \phi_V \)  \hspace{1em} \text{Voigt lineshape}

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Chapter 1

Introduction

1.1 Objectives

The main objective of this work was to design diode-laser based gas sensors with potential for industrial use. Since ammonia (NH$_3$) and carbon dioxide (CO$_2$) are two common gases that play an important role in many chemical processes, sensors that can detect their concentrations accurately in a variety of measurement environments find utility for industrial applications. The goal of this research was to design and demonstrate NH$_3$ and CO$_2$ sensors relevant to the following applications:

NH$_3$ Sensors

1. **Air-quality**: *in situ* monitoring of indoor air quality at facilities such as feedlots, hog farms, and industrial chiller plants, for which NH$_3$ concentrations greater than 25 ppm need to be detected and atmospheric gases such as CO$_2$ and water vapor might interfere with the sensor.

2. **Ammonia-slip**: *in situ* monitoring of NH$_3$ emissions (single-digit ppm concentrations) from large-scale commercial combustors that use Thermal DeNO$_x$ or selective catalytic reduction (SCR), for which hot combustion products might interfere with the sensor.
3. **Bioreactor vent gas analysis**: monitoring of NH$_3$ in bioreactor vent gases for determination of potential spaceboard air toxicity due to NH$_3$ production (< 5 ppm NH$_3$ in a bath gas of N$_2$ and CO$_2$).

**CO$_2$ Sensors**

1. **Combustion**: *in situ* flame monitoring of CO$_2$ concentration (5–15\%) for combustion control applications, for which hot combustion products might interfere with the sensor.

2. **Bioreactor vent gas analysis**: monitoring of CO$_2$ (500 ppm–5\%) in bioreactor vent gases for monitoring wastewater carbon conversion efficiency.

**Design Process**

The design process for these gas sensors included:

1. selecting the best NIR region to probe (i.e. 1.5 or 2.0 $\mu$m).

2. choosing *in situ* or sampling strategies.

3. selection of specific optimum detection wavelengths based on the conditions of the measurements (temperature, pressure, bath gas species, etc.) and the spectroscopy of the interrogated species.

4. high resolution measurements of the pertinent fundamental spectroscopic parameters that were necessary for the application of the sensor.

5. demonstration of the feasibility of the sensor designs.

The design and demonstration process for each application is described in detail in Chapters 5–7.
1.2 Motivation

1.2.1 \textit{In situ} NH\textsubscript{3} Monitoring

Ammonia (NH\textsubscript{3}) is one of the oldest known commercial refrigerants and is used extensively for soil fertilization. Because of the ecological threat posed by freons, the use of ammonia for refrigeration may rise in the future. The petroleum industry employs anhydrous ammonia for neutralizing various acidic constituents of crude oil, while manufacturers employ ammonia for many products, including pharmaceuticals, nylon, and dyes. One of ammonia’s most widespread uses is as a common ingredient in household cleaning agents. Ammonia is a highly reactive gas that is used in many catalytic processes for the production of nitric acid, amides, and nitrides \cite{12}, and the destruction of nitrogen oxides in combustion applications through Selective Non-Catalytic Reduction (SNCR) (also known as Thermal DeNO\textsubscript{x} \cite{48}) or SCR (Selective Catalytic Reduction) systems.

Ammonia exists naturally in the atmosphere at levels less than 10 ppb, but is the primary basic gas and third-most abundant nitrogen-containing compound in the atmosphere, after N\textsubscript{2} and N\textsubscript{2}O. Anthropogenic sources account for approximately 40\% of annual global emissions of NH\textsubscript{3} from domesticated animals and fertilizers \cite{78}. Ammonia gas is also a natural product from urea in mammalian urine. Despite ammonia’s omnipresence, it is a toxic gas, for which a time-weighted average (TWA) exposure limit is 25 parts per million (ppm) \cite{2}. Because ammonia is toxic even in trace quantities and has so many different industrial uses, a need exists to monitor its presence for process optimization and hazard prevention.

Ammonia sensors benefit industrial air-quality by detecting leaks and unhealthy ambient ammonia concentrations before health damage occurs at facilities such as chiller plants and feedlots. SNCR and SCR systems inject ammonia at a specific temperature window downstream of combustion to destroy NO\textsubscript{x} populations. There are approximately 20 new SCR projects built each year in the U.S., 1000 boilers that might be required to reduce NO\textsubscript{x} emissions in 22 states, and up to 10,000 existing boilers nationwide that might be outfitted with SNCR or SCR systems \cite{61}. Sensors
are needed to monitor the emission of excess unconverted ammonia—ammonia slip—that pollutes the environment at Thermal DeNO\textsubscript{x} and SCR sites, and to control the amount of NH\textsubscript{3} that is injected, which can cost $600-$900 per hour. Using sensors to optimize injection amounts can thus save significant expenditures at SNCR/SCR facilities. Because of their capacity for sub-second, sensitive, species-selective, and in situ measurements, diode laser sensors based on absorption spectroscopy offer advantages for monitoring potentially harmful and/or wasteful ammonia concentrations in both the industrial and combustion environments.

**NH\textsubscript{3} Measurement Technologies**

A variety of strategies have been explored for measuring ammonia concentrations, from traditional electrochemical sensors, to sophisticated derivative optical techniques. Many of the published detection strategies, such as optoacoustic, intracavity, and Stark modulation techniques, use sampling systems because of the enhanced sensitivity they offer, with sub-ppm-m detection limits in many cases [6,23,32,42,68,88]. Sampling systems can be very effective for measurement environments that are not hostile and for which NH\textsubscript{3} concentrations vary slowly. For example, at feedlots or hogfarms the ambient NH\textsubscript{3} concentration will buildup throughout the day, rather than through sudden events such as leaks.

However, for hostile or unsteady measurement environments such as flue gases, extractive sampling systems for ammonia detection have several difficulties, including adsorption of NH\textsubscript{3} along the sampling lines, which hinders the sensor’s ability to track quickly-changing concentrations of NH\textsubscript{3}; formation of salts that clog the sampling lines due to reactions between NH\textsubscript{3} and other flue gas constituents; decomposition of NH\textsubscript{3} in the hot metal sampling probes; and gas transport time, which slows down the sensor’s overall time response (these difficulties are well discussed by Hjuler [34] and Kassman [38]). Combining ammonia’s tendency to adsorb with the gas transport delays in the probe system makes extractive sensors inappropriate for flows in which ammonia concentrations vary at sub-minute time-scales or for industrial locations where immediate leak detection is required for safety reasons.
1.2. MOTIVATION

One approach to addressing the difficulty of extractive-sampling in elevated temperature flows that contain NH$_3$ is the inclusion of heated sampling probes and lines that minimize adsorption along the walls of the sampling system, however these systems are often expensive and bulky. These extractive probes also might catalyze heterogeneous reactions in flue gases. Moreover, for environments in which the ammonia is unevenly distributed in the flue gas channel, point measurements from extractive sampling systems might yield values that are much higher or lower than average, whereas the path-averaged nature of line-of-sight measurements are more indicative of the true conditions across the flow.

Sensors that can measure in situ avoid the aforementioned challenges with extractive sampling, but are susceptible to beam-steering caused by gradients in flows and possible spectral interference from ambient constituents and hot combustion products such as CO$_2$ and H$_2$O. In situ optical techniques such as UV or broadband IR absorption, and Photothermal Deflection [11, 22, 52, 60] avoid the species-conversion, time delay, and adsorption problems associated with traditional sampling systems, but often use expensive, bulky or delicate radiation sources that are not suitable for commercialization. Many in situ optical techniques also employ derivative or FM spectroscopy to increase sensitivity, but require calibration gases to provide reference signals and have complicated lineshapes due to the overlapping of multiple NH$_3$ absorption lines in [4, 16, 45]. These reference systems, typically consisting of a static cell with pressure and temperature conditions that are similar to the environment of interest, do not accurately simulate all parameters of the measurement environment. Specifically, reference cells often lack the presence of combustion products, such as H$_2$O and CO$_2$, and thus leave the sensors susceptible to errors induced by lineshape variations that are the result of species-specific interactions, including dipole-dipole and dipole-quadrupole coupling. For example, NH$_3$ dipole-dipole broadening from collisions with water in the flue gases will have different absorption profiles than the dipole-quadrupole broadening profiles that result from interactions with N$_2$ in the reference cell [65, 87], leading to peak-height differences, and therefore detection errors, of up to 50%. Other measurement strategies indirectly measure NH$_3$ by converting it to NO$_x$ or some other species, then measuring the mole fraction of the converted
species via emission or luminescence [15,34]. Because of the difficulties associated with measuring NH$_3$-slip, there currently exists no industry standard for its detection.

Diode laser near-infrared (NIR) *in situ* absorption sensors offer a balance between sensitivity ($< 10$ ppm-m), species-selectiveness, simplicity, and bandwidth; makes absolute and direct measurements of NH$_3$ concentration; and does not require the expensive calibration gases, burdensome reference systems, or complicated lineshape transformations typical of derivative techniques. Diode laser sensors also offer ruggedness, compactness, and affordability, making them suitable for real-world applications. Chapter 5 describes the design of diode-laser based NH$_3$ sensors at 1.5 $\mu$m for air-quality and emissions-monitoring applications and a demonstration of ammonia-slip measurements in a combustion stack.

### 1.2.2 *In situ* Combustion Monitoring of CO$_2$

Carbon dioxide (CO$_2$) is an important atmospheric constituent that exists at an average concentration of approximately 355 ppm [78] and is an important greenhouse gas. As a major product of hydrocarbon combustion, CO$_2$ emissions are an indicator of combustion efficiency and have contributed to a global increase in atmospheric CO$_2$ concentrations to their current levels. Even though these levels are low compared with N$_2$, O$_2$, or H$_2$O concentrations, they play an important role in the global energy balance, and as a result anthropogenic CO$_2$ emissions might be regulated in the future in the form of carbon taxes or otherwise. Measurements of CO$_2$’s presence may prove useful for combustion control applications or might be required for monitoring carbon emissions.

*In situ* sensors for CO$_2$ in combustion environments are advantageous because they yield species mole fraction measurements without intrusive probes that can perturb the flow or combustion environment. In addition, *in situ* methods avoid CO-to-CO$_2$ conversion that can occur inside extractive-sampling probes [54,62,77], and can make rapid measurements at kHz rates and higher that can be used for fast on-line control schemes. Previous combustion control demonstrations have sought to maximize CO$_2$ while minimizing CO, but relied on relatively slow sensors and thus implemented
control at rates of approximately 2 Hz [13].

Previous absorption sensors for CO$_2$ combustion monitoring include diagnostics using relatively weak overtone bands near 1.55 $\mu$m [54, 56, 81], and initial measurements near 2.0 $\mu$m utilizing external-cavity diode lasers (ECDL) [55, 57, 58]. The measurements near 1.55 $\mu$m suffered from weak signal strengths and significant interference from high-temperature water absorption. The latter body of work benefited from CO$_2$’s strong absorption at 2.0 $\mu$m, but was restricted to slow scan rates (< 25 Hz repetition) due to the ECDL’s mechanical operation, and could not access all the isolated CO$_2$ lines in the band. Chapter 6 describes the design and implementation of an in situ CO$_2$ combustion sensor using a distributed-feedback (DFB) diode laser operating near 2 $\mu$m for 125 Hz measurements.

1.2.3 Bioreactor Vent Gas Monitoring of NH$_3$ and CO$_2$

The Crew and Thermal Systems Division at NASA-Johnson Space Center in Houston, TX has been developing an Advanced Water Recovery System (WRS) for implementation aboard manned spacecraft. The WRS will be used to convert wastewater into potable drinking water. NASA is motivated to develop such a system because of the closed nature of spacecraft, which prevents astronauts from simply discarding waste out of the cabin, and because of the expense associated with shipping fresh drinking water to the astronauts.

NASA’s Advanced Water Recovery System is comprised of the feedtank (or waste tank) that holds the wastewater with high total organic carbon (TOC) and ammonium concentrations, the two-stage biological waste processor (BWP), and a post-processing system, as depicted in Figure 1.1 [41]. The feedtank has many fluctuations in TOC and ammonium, depending on the amounts of soap that donors use and how much water each donor drinks. The TOC is comprised of materials such as urea (CO(NH$_2$)$_2$), creatine (C$_4$H$_9$N$_3$O$_2$) and soap, of which soap is the single largest constituent at approximately 40% of the TOC [64]. The ammonium concentration is a result of the urea that is naturally present in mammalian urine, and leads to dissolved ammonia concentrations due to aqueous-phase ammonia/water equilibrium [78].
acidity of the feedtank is adjusted to pH=7.5 by addition of nitric acid as necessary to keep the levels of ammonia low.

The objectives of the two-stage bioreactor are the removal of TOC with the anaerobic packed-bed reactor and nitrification of NH$_3$ as the critical first steps for safe potable H$_2$O recovery. In the process of cleaning the wastewater, gaseous N$_2$, CO$_2$, and trace amounts of NH$_3$ are produced. After the two stages, a gas-liquid separator (GLS) separates the two phases, recirculates the liquid, and vents the gases into the cabin, thereby exposing the astronauts to potentially toxic levels of NH$_3$. NASA is interested in monitoring NH$_3$ during the ground tests to assess the risks associated with venting the bioreactor gases into the cabin. CO$_2$ measurements for the ground tests are valuable as a rough indicator of the packed-bed reactor’s overall health, for which CO$_2$ concentration is approximately related to the reactor’s ability to convert wastewater TOC to bacteria and can be used to track carbon balances.

The vent gases were primarily composed of trace NH$_3$ (10 ppb–15 ppm), CO$_2$ (500 ppm–10%), N$_2$ and saturated water vapor. Chapter 7 describes the process by which a sensor was designed and demonstrated for measuring NH$_3$ and CO$_2$ concentration.
1.2. MOTIVATION

variations in bioreactor vent gases over extended periods at NASA-JSC.

1.2.4 Diode Laser Sensors

Diode laser-based absorption sensors are attractive for many different applications, but especially for those listed above. Because diode lasers are compact, rugged and affordable, they offer utility for any measurement environments that are hostile or that have cost and footprint restrictions. The development of diode laser gas sensors began in the 1970's with lead-salt diode lasers operating in the infrared (IR), and has continued to include modern single-mode distributed feedback (DFB) diode lasers that operate in the near-infrared (NIR). Sensors based on these lasers have been applied at a research level for many applications, including combustion control [25], emissions-monitoring [56], semiconductor process control [18], atmospheric sensing [43] and fuel-leak detection [90]. Recently, industrial and private capital investment in the commercialization of diode laser sensors has surged, providing an end-use for the development of sensors in research laboratories.

Diode lasers in distributed feedback (DFB) and external-cavity (ECDL) configurations have become available at various wavelengths mostly due to their widespread use in the consumer electronics and telecommunications industries. For consumer electronics, visible lasers are often used for CD players and laser printers, while shorter wavelength lasers are being developed and employed for optical storage. The telecommunications applications include DFB lasers in the near infrared (NIR) near 1.3 and 1.55 µm. The benefit of using diode lasers that overlap with these industries is that those lasers are readily available and affordable, with many different manufacturers from which to choose. The main drawback, however, is that the wavelengths for telecommunications and consumer electronics are useful but not ideal for spectroscopic applications. But, since these industries rely even more heavily than before on diode lasers, they have been developing more wavelengths for different applications, including shorter wavelengths for optical storage that go down to the blue and ultraviolet (UV), and longer wavelengths in the NIR for the telecommunications. The blue/UV wavelengths can access some stronger electronic transitions of certain species.
and the longer wavelengths in the NIR can access stronger vibrational transitions of others. Future development of quantum cascade lasers will bring the benefits of diode lasers to the longer wavelengths that are most useful for sensitive gas detection. Section 4.1.1 describes the specific lasers that were employed for this work.

1.3 Scope and Organization of Thesis

1.3.1 Scope

The research in this thesis includes:

1. sensor design for air-quality, combustion and bioreactor applications (selection of NIR regions, wavelengths, and detection strategy).

2. measurements of pertinent fundamental spectroscopic parameters for the sensors.

3. demonstration measurements with the gas sensors to verify feasibility.

Wavelength selections were made by taking into account the measurement conditions (temperature, pressure, pathlength, in situ vs. sampled, bath gas constituents, and time response requirements), and then using measured and calculated absorption spectra to determine the strongest isolated transitions for probing. The following wavelength selections were made:

- 3 ammonia features at 1.5 µm were selected for in situ air-quality monitoring
- 3 ammonia features at 1.5 µm were selected for in situ emissions-monitoring
- 1 ammonia feature at 2.0 µm was selected for bioreactor vent gas analysis
- 1 CO₂ feature at 2 µm was selected for in situ combustion monitoring
- 2 CO₂ features at 2 µm were selected for bioreactor vent gas analysis
Once the wavelengths were selected, high-resolution measurements were made to determine the pertinent fundamental spectroscopic parameters that were necessary for the application of the sensor. In the process of making these measurements, improvements to the published spectroscopic database were made for NH₃ at 1.5 µm and CO₂ at 2.0 µm, and errors in the published partition function for NH₃ were revealed. In addition, the first recorded survey spectra of NH₃ using ECDL’s at 1.5 and 2 µm were published, the first in situ combustion measurements of CO₂ using DFB lasers near 2 µm were made, and the first DFB measurements of NH₃ near 2 µm were recorded. The feasibility for each of the sensor designs was then verified with two different in-lab combustion experiments (emissions-monitoring and flame-monitoring) and field bioreactor experiments.

1.3.2 Organization

This thesis is divided into four main sections:

- **Section 1**: Introduction (Chapter 1)
- **Section 2**: Background Theory & Methodologies (Chapters 2–4)
- **Section 3**: Sensor Design & Demonstration (Chapter 5–7)
- **Section 4**: Conclusions (Chapter 8)

The discussion of background theory and methods includes three chapters. Chapter 2 describes the molecular structure and spectroscopy for NH₃ and CO₂, including vibrations, partition functions, and other issues pertinent to their spectroscopic detection. The general theory of quantitative absorption and lineshapes is presented in Chapter 3, while the methodologies and equipment necessary for high-resolution absorption experiments are summarized in Chapter 4.

The results using diode laser sensors are presented in three chapters. Chapter 5 is devoted to ammonia detection at 1.5 µm for air quality and emissions-monitoring applications. This chapter presents the line selection for these two applications and includes demonstration ammonia-slip measurements. Chapter 6 presents the sensor
design for combustion monitoring of CO$_2$ at 2.0 $\mu$m, including all the necessary background spectroscopic measurements. Chapter 7 describes the bioreactor application and presents field measurements that were made over a 45-hour period on-site at NASA-Johnson Space Center in Houston, TX.

Appendix A describes equilibrium aqueous-phase chemistry analysis that was used to compare NASA’s aqueous-phase ammonia measurements with the diode laser results presented in Chapter 7. Appendix B presents uncertainty analysis for the tabletop spectroscopic measurements, the combustion demonstrations, and the bioreactor field results.
Chapter 2

Polyatomic Near-Infrared Spectroscopy

2.1 Linear Polyatomic Spectroscopy: CO$_2$

2.1.1 CO$_2$ Structure

Linear molecules such as CO$_2$\footnote{All references to CO$_2$ in this work are for $^{12}$C$^{16}$O$_2$} can generally be treated as diatomics with regard to their moments of inertia. The moment of inertia about the A-axis (along the molecule), is approximately zero, $I_A \approx 0$, and the other two moments are equal, $I_B = I_C$. Because the moment of inertia for CO$_2$’s end-over-end rotation is much larger than for diatomics, the rotational constant will be correspondingly smaller (See Table 2.1). The moment of inertia can be related to a molecule’s rotational constant via the following relation,

$$B_0 = \frac{\hbar}{8\pi^2 I_{BC}} \ [cm^{-1}] \quad (2.1)$$

The quantum number for a linear polyatomic molecule’s angular momentum is $J$. Since CO$_2$ is linear and symmetric, it does not have a permanent dipole moment. Thus, CO$_2$ is only spectroscopically active in the IR when a dipole is induced due to...
bending or asymmetric stretching.

2.1.2 Vibrations and Symmetry

Carbon dioxide has four classically-described vibrational modes, of which two bending modes are degenerate, as depicted in the bottom part of Figure 2.1 and listed in Table 2.2. The two stretching modes, asymmetric and antisymmetric, are parallel vibrations, since the vibrations occur parallel to the main symmetry axis, and the bending modes are perpendicular, since they induce changes in the molecule that are perpendicular to the main symmetry axis. Only the vibrations that induce a dipole moment are spectroscopically active in the infrared. The top part of Figure 2.1 shows CO$_2$’s two axes of symmetry, including an infinite number of $C_2$ axes that align through the $C$ atom and perpendicular to the bonds. These axes are two-fold symmetric, thus a rotation of $180^\circ$ produces an indistinguishable change. In addition, CO$_2$ has the $C_\infty$ axis along the molecule, about which an infinite number of rotations produces no distinguishable change in orientation. Because CO$_2$ has an $\infty$-fold axis $C_\infty$ that is perpendicular to an infinite number of planes of symmetry, it belongs to the point group $D_{\infty h}$ and has a symmetry number $\sigma = 2$ [33].

<table>
<thead>
<tr>
<th>Vibration</th>
<th>Frequency [cm$^{-1}$]</th>
<th>Type</th>
<th>Description</th>
<th>IR-active?</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_1$</td>
<td>1333</td>
<td>$\parallel$</td>
<td>Symmetric stretch</td>
<td>No</td>
</tr>
<tr>
<td>$\nu_2$</td>
<td>667</td>
<td>$\perp$</td>
<td>Bending (Degenerate)</td>
<td>Yes</td>
</tr>
<tr>
<td>$\nu_3$</td>
<td>2349</td>
<td>$\parallel$</td>
<td>Asymmetric stretch</td>
<td>Yes</td>
</tr>
</tbody>
</table>
2.1. LINEAR POLYATOMIC SPECTROSCOPY: CO$_2$

Figure 2.1: CO$_2$’s symmetry axes (top panel), and vibrational modes (bottom panel): (a) Symmetric stretch, $\nu_1$, $\parallel$; (b) Bending, $\nu_2$, $\perp$; (c) Antisymmetric stretch, $\nu_3$, $\parallel$

2.1.3 NIR Spectra

CO$_2$ has a center of symmetry, and thus is susceptible to the effects of nuclear spin. Because CO$_2$ is a member of the $D_{\infty h}$ point group, alternate rotational levels have different statistical weights, with odd rotational levels having a zero weight, while even levels have a weight of one. Thus, the odd levels for CO$_2$ are missing. The selection rules for CO$_2$’s rovibrational spectra are that the rotational quantum number can change $\pm 1$, such that $\Delta J = \pm 1$. Standard notation for a transition uses $P$ to denote quantum rotational changes of $\Delta J = -1$, and $R$ for $\Delta J = +1$.

Carbon dioxide’s vibrations contain Fermi resonances ($\nu_1 = 2\nu_2$), and Coriolis coupling. The result of these effects is that the classical notation scheme used by Herzberg and others that describes the vibrational modes breaks down in certain instances. Extended notation schemes have been employed by HITRAN96 and others [71,72] to describe different vibrational bands. HITRAN96 notation uses 5 parameters to distinguish different bands with the following system: $\nu_1\nu_2\ell\nu_3r$, for which $\nu_1$, $\nu_2$, and $\nu_3$ denote the classical vibrations; $\ell$ is the angular momentum of the bending mode; and $r$ is a ranking index that uses the energy level to clarify bands that have similar
CHAPTER 2. POLYATOMIC NEAR-INFRARED SPECTROSCOPY

Figure 2.2: CO$_2$’s NIR spectra with absorption bands labeled using Herzberg notation [33, 72].

Table 2.3: Labeling for the Fermi triad at 2 µm using Herzberg and HITRAN96 notation schemes.

<table>
<thead>
<tr>
<th>Band Center [nm]</th>
<th>Band Center [cm$^{-1}$]</th>
<th>Herzberg</th>
<th>HITRAN96</th>
</tr>
</thead>
<tbody>
<tr>
<td>1957</td>
<td>5109</td>
<td>$2\nu_1 + \nu_3$</td>
<td>20011←00001</td>
</tr>
<tr>
<td>2006</td>
<td>4984</td>
<td>$\nu_1 + 2\nu_2 + \nu_3$</td>
<td>20012←00001</td>
</tr>
<tr>
<td>2057</td>
<td>4861</td>
<td>$4\nu_2 + \nu_3$</td>
<td>20013←00001</td>
</tr>
</tbody>
</table>

quanta.

A plot of CO$_2$’s NIR spectra is shown in Figure 2.2. As the band labels on the plot reveal, the NIR is populated by weak overtone and combination bands. The 2 µm region contains 3 main bands known as the Fermi triad. The labeling for these three bands using Herzberg and HITRAN96 notation are listed in Table 2.3. The band used for CO$_2$ sensors in this thesis is the $\nu_1 + 2\nu_2 + \nu_3$ band centered at 2.006 µm.

2.1.4 Partition Function

The total internal partition function, $Q(T)$, can be described classically as a product of the nuclear, rotational, and vibrational partition functions, $Q_{\text{nuc}}$, $Q_{\text{rot}}$, and $Q_{\text{vib}}$, respectively (Equation 2.2), if the interactions between vibrations and rotations are
neglected [33].

\[ Q(T) = Q_{nuc} Q_{rot} Q_{vib} \]  \hspace{1cm} (2.2)

Because CO\(_2\) is a linear molecule, its rotational partition function can be approximated in similar fashion to a diatomic rigid rotor (RR), namely

\[ Q_{rot} = \frac{kT}{\sigma \hbar c B} \]  \hspace{1cm} (2.3)

where \( \sigma = 2 \) is the symmetry number for CO\(_2\), \( h \) is Planck’s constant, \( k \) is Boltzmann’s constant, \( c \) is the speed of light, and \( B \) is the rotational constant for CO\(_2\) (See Table 2.1).

The nuclear partition function is described by

\[ Q_{nuc} = (2I_C + 1)(2I_O + 1)^2 = 1, \]  \hspace{1cm} (2.4)

where \( I_C = 0 \) and \( I_O = 0 \) are the nuclear spins of the carbon and oxygen atoms, respectively. Thus, accounting for nuclear spin does not affect the overall partition function, but rather affects only the statistics of the different rotational levels, as discussed above.

The simple harmonic oscillator (SHO) model for the vibrational partition function of CO\(_2\) yields

\[ Q_{vib}(T) = \left[ 1 - \exp \left( \frac{-\hbar \nu_1}{kT} \right) \right]^{-1} \left[ 1 - \exp \left( \frac{-\hbar \nu_2}{kT} \right) \right]^{-2} \left[ 1 - \exp \left( \frac{-\hbar \nu_3}{kT} \right) \right]^{-1}, \]  \hspace{1cm} (2.5)

for which the fundamental vibration frequencies are listed in Table 2.2 with double-degeneracy for mode \( \nu_2 \). Thus, the total internal partition function for CO\(_2\), neglecting vibration-rotation coupling, anharmonicities, and non-rigidities, is

\[ Q_{CO_2}(T) = \frac{\frac{kT}{\sigma \hbar c B}}{\left[ 1 - \exp \left( \frac{-\hbar \nu_1}{kT} \right) \right]^{-1} \left[ 1 - \exp \left( \frac{-\hbar \nu_2}{kT} \right) \right]^{-2} \left[ 1 - \exp \left( \frac{-\hbar \nu_3}{kT} \right) \right]^{-1}. \]  \hspace{1cm} (2.6)
Table 2.4: Coefficients of the polynomial expression for $Q(T)$ in Equation 2.7 from Hitran96 [72] for CO$_2$.

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>$70 &lt; T &lt; 500$ K</th>
<th>$500 &lt; T &lt; 1500$ K</th>
<th>$1500 &lt; T &lt; 3005$ K</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>-1.3617</td>
<td>-5.0925e2</td>
<td>-3.4938e4</td>
</tr>
<tr>
<td>b</td>
<td>9.4899e-1</td>
<td>3.2766</td>
<td>66.965</td>
</tr>
<tr>
<td>c</td>
<td>-6.9259e-4</td>
<td>-4.0601e-3</td>
<td>-4.4010e-2</td>
</tr>
<tr>
<td>d</td>
<td>2.5974e-6</td>
<td>4.0907e-6</td>
<td>1.2662e-5</td>
</tr>
</tbody>
</table>

The total internal partition function, $Q(T)$, can also be approximated by a third-order polynomial-fit to a calculated partition function summation (Equation 2.7), for which the coefficients $a$, $b$, $c$, and $d$ are listed in Table 2.4. The classical and polynomial expressions for CO$_2$’s total internal partition function agree within 1.5% in the temperature range 300–1500 K.

$$Q(T) = a + bT + cT^2 + dT^3$$ (2.7)

### 2.2 Symmetric Top Spectroscopy: NH$_3$

#### 2.2.1 NH$_3$ Structure

Ammonia$^2$ has symmetric top structure, with one central $N$-atom above a tripod of three $H$-atoms (See Figure 2.3). The $A$-axis corresponds to the figure axis of a symmetric top, and thus is also the main axis of symmetry. Symmetric tops have two equivalent moments of inertia, both of which are different from the third moment:

$$I_A \neq I_B = I_C$$ (2.8)

$$I_A \neq 0$$ (2.9)

---

$^2$All references to NH$_3$ are for $^{14}$N$^1$H$_3$
2.2. SYMMETRIC TOP SPECTROSCOPY: NH₃

Similar to the description above for linear molecules, the rotational constants are related to the moments of inertia by

\[ A_0 = \frac{\hbar}{8\pi^2 I_{Ac}}, \quad B_0 = \frac{\hbar}{8\pi^2 I_{Bc}}, \quad \text{etc.} \quad [cm^{-1}] \]  \hspace{1cm} (2.10)

Table 2.5 lists the rotational constants for NH₃ along with some other properties of the molecule.

Typically, the equivalent moments of inertia for symmetric top molecules are described simply as \( I_B \), and the main axis moment is \( I_A \). The relative magnitudes of the inertial moments or rotational constants can be used to further distinguish the tops as Prolate or Oblate:

**Prolate:** \( I_A < I_B = I_C \)
\[ A > B = C \]

**Oblate:** \( I_A > I_B = I_C \)
\[ A < B = C \]

Thus, NH₃ is an oblate symmetric top.

Since NH₃ has two main directions of rotation, it has two quantum numbers to describe rotational energy, \( J \) and \( K \), where \( J \) represents the total angular momentum \( (0, 1, 2, \ldots) \), and \( K \) represents the angular momentum about the \( A \)-axis (in other
Table 2.5: Some properties of NH$_3$ [39].

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass</td>
<td>$m = 17$ [amu]</td>
</tr>
<tr>
<td>Bond length</td>
<td>$r_0(NH) = 1.02$ [Å]</td>
</tr>
<tr>
<td>Bond angle</td>
<td>107.8°</td>
</tr>
<tr>
<td>Rotational constants</td>
<td>$A_0 = 6.196$ [cm$^{-1}$]</td>
</tr>
<tr>
<td></td>
<td>$B_0 = 9.944$ [cm$^{-1}$]</td>
</tr>
<tr>
<td></td>
<td>$C_0 = 9.944$ [cm$^{-1}$]</td>
</tr>
<tr>
<td>Symmetry number</td>
<td>$\sigma = 3$</td>
</tr>
<tr>
<td>Dipole moment</td>
<td>$\mu = 1.471$ [D]</td>
</tr>
</tbody>
</table>

words, $K$ represents the orientation and direction of rotation. There are $2J + 1$ possible values of $K$ for each value of $J$, with $K$ restricted to $J, J - 1, \ldots, 1, 0, -1, \ldots, -J$. All non-zero values of $K$ are doubly-degenerate since states that differ only by the sign of $K$ have different directions of motion, but the same energy.

### 2.2.2 Vibrations and Symmetry

Figure 2.3 shows the molecule’s structure as well as its main symmetry axis, which coincides with the figure axis, along which lies the dipole moment. Three rotations of 120° about this axis each produce an indistinguishable change in the molecule. Thus, the main axis is 3-fold symmetric. In addition, NH$_3$ has three planes of symmetry through the molecule at mutual angles of 120°, giving ammonia $c_{3v}$ molecular symmetry.

Ammonia’s four vibrational modes are illustrated in Figure 2.4, and listed in Table 2.6. The two parallel modes, $\nu_1$ and $\nu_2$, are symmetric, while the two perpendicular modes, $\nu_3$ and $\nu_4$, are asymmetric and degenerate. Ammonia also has inversion-doubling due to the motion of the $N$-atom through the $H_3$-atom plane that produces two equilibrium positions for the $N$-atom: the normal pyramidal structure with $N$ above the plane, and an inverted configuration$^3$. Because there are two equilibrium

---

$^3$A result of the inversion motion is that the dipole moment, which lies along the symmetry axis, also moves back and forth. Thus, the value for the dipole moment that is typically quoted in the literature and is listed in Table 2.5, is the inversion-transition moment, not the permanent dipole moment [83].
2.2. SYMMETRIC TOP SPECTROSCOPY: NH$_3$

Table 2.6: Fundamental vibrations, frequencies, types, and description for NH$_3$ [39].

<table>
<thead>
<tr>
<th>Vibration</th>
<th>Frequency [cm$^{-1}$]</th>
<th>Type</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_1$</td>
<td>3357</td>
<td>$\parallel$</td>
<td>Symmetric Stretch</td>
</tr>
<tr>
<td>$\nu_2$</td>
<td>950</td>
<td>$\parallel$</td>
<td>Symmetric Bend</td>
</tr>
<tr>
<td>$\nu_3$</td>
<td>3444</td>
<td>$\perp$</td>
<td>Asymmetric Stretch (Degenerate)</td>
</tr>
<tr>
<td>$\nu_4$</td>
<td>1627</td>
<td>$\perp$</td>
<td>Asymmetric Bend (Degenerate)</td>
</tr>
</tbody>
</table>

positions, the potential energy of NH$_3$ has two minima (See Figure 2.5). Moreover, since the N-atom’s location will invert through the H$_3$-atom plane, that plane serves as another plane of symmetry. Molecules that have a 3-fold axis of symmetry, with 3 vertical planes of symmetry (which is $c_{3v}$), and an additional horizontal plane of symmetry belong to point group $D_{3h}$. Thus, even though the molecule’s structural symmetry is $c_{3v}$, its potential energy has $D_{3h}$ symmetry. For a molecule that is low in the well on one side or the other of the potential barrier, the barrier looks infinitely high and the molecule seems to have two $c_{3v}$ potential wells.

According to classical mechanics, once a particle is in one of the two potential wells
CHAPTER 2. POLYATOMIC NEAR-INFRARED SPECTROSCOPY

Figure 2.5: NH$_3$’s potential energy versus the angle of the $N$-atom relative to the $H_3$-plane [83].

with an energy lower than that of the barrier, it will never go over the barrier into the other well. However, in quantum mechanics, after the passage of some length of time, the particle will statistically be found in the other well as though it had penetrated through the potential hill. This phenomenon is known as the tunnel effect. The result of the inversion-doubling, which produces two potential wells, and the tunnel effect, which allows for resonant energy levels on either side of the potential barrier to interact with each other, is that ammonia’s energy levels become split into those with symmetric and asymmetric wave functions. These split levels are sometimes denoted by $s$ or $+$ for symmetric, and $a$ or $-$ for asymmetric. The energy of the symmetric level is always lower than that of the asymmetric level, and the splitting increases rapidly with vibrational energy. Far above the potential barrier, the splittings occur midway between subsequent levels as if there were one potential well with half the expected spacing between levels. Each of the four vibrational modes adjusts the height of $N$ above the inversion plane, and thus each vibrational mode has some splitting associated with its motion. However the $\nu_2$ bending moment is the most closely coupled to inversion since its motion moves the $N$-atom and $H_3$-plane back and forth with respect to each other, and thus its energy-level splittings are the largest.

The inversion-splitting of energy levels leads to vibration energies and rotational constants that are different for the symmetric and asymmetric states, so the mean values are typically those that are listed in the literature. For example, $\nu_{1s} = 3336.1$
2.2. SYMMETRIC TOP SPECTROSCOPY: NH$_3$

Table 2.7: Assignments for NH$_3$’s NIR spectra, listed roughly in order of contribution to the band.

<table>
<thead>
<tr>
<th>NIR Region</th>
<th>Band Assignment</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5 µm</td>
<td>$\nu_1+\nu_3$, $2\nu_3$, $\nu_3+2\nu_4$, $\nu_1+2\nu_4$, $2\nu_1$</td>
<td>[7, 33, 46, 47, 82]</td>
</tr>
<tr>
<td>1.65 µm</td>
<td>$\nu_2+\nu_3+\nu_4$</td>
<td>[33, 74, 82]</td>
</tr>
<tr>
<td>2.0 µm</td>
<td>$\nu_3+\nu_4$, $\nu_1+\nu_4$, $2\nu_2+\nu_3$, $4\nu_2+\nu_4$, $2\nu_2+2\nu_4$</td>
<td>[14, 33, 75, 76, 82]</td>
</tr>
<tr>
<td>2.3 µm</td>
<td>$\nu_2+\nu_3$, $\nu_2+2\nu_4$, $\nu_1+\nu_2$</td>
<td>[8, 33, 86]</td>
</tr>
</tbody>
</table>

and $\nu_{1a} = 3337.1$ cm$^{-1}$, for which the mean published value is $\nu_1 = 3337$ cm$^{-1}$. The splitting for the symmetric stretch mode is much larger at approximately 36 cm$^{-1}$, for which $\nu_{2s} = 932.4$ and $\nu_{2a} = 968.1$ cm$^{-1}$, and the mean is $\nu_2 = 950$ cm$^{-1}$. The splitting for rotational constants is much smaller, with $B_{0,s} = 9.947$ and $B_{0,a} = 9.942$ cm$^{-1}$.

2.2.3 NIR Spectra

In addition to the inversion-splittings, NH$_3$ spectroscopy is complicated by strong Coriolis effects between $\nu_2$ and $\nu_4$. These splittings, Coriolis effects, and the number of vibrational modes leads to many absorption bands, each of which has thousands of different transitions that are closely spaced and overlapping in many instances (See Figure 2.6). As Figure 2.6 illustrates, NH$_3$ has three main absorption bands in the NIR at 1.5, 2.0, and 2.3 µm respectively. A weak ammonia combination band is also present at 1.65 µm [74, 82], however a detailed listing of line positions and strengths for this region is not currently available. Table 2.7 lists the different bands along with their assignments in approximate order of contribution to the band strength, from largest to smallest. In general, the perpendicular bands predominate in intensity in the NIR.

Because ammonia has two moments of inertia, it has two quantum numbers for angular momentum, $J$ and $K$, as described above in Section 2.2.1. In addition, the symmetry of the quantum level needs to be distinguished as either symmetric or asymmetric. The selection rules for rovibrational transitions allow the vibrational
quantum number $v$ to change in integral units, $\Delta v = +1, +2, \ldots$, for anharmonic vibrations. The accompanying changes in the rotational quantum numbers have different selection rules, depending on whether the band is perpendicular or parallel. For parallel bands, the selection rules are $\Delta J = 0, \pm 1$, and $\Delta K = 0$ since there is no dipole moment for rotation about the $A$-axis. The symmetry restrictions only allow levels of opposite parity to combine with each other. Therefore, the parallel band symmetry selection rules are $+ \leftrightarrow - , + \leftrightarrow + , - \leftrightarrow -$ [31,33]. For perpendicular bands, the allowable transitions are $\Delta J = 0, \pm 1$, $\Delta K = \pm 1$, and $+ \leftrightarrow + , - \leftrightarrow -$ [8,14].

Similar to the notation for linear polyatomics such as CO$_2$, the $P$ branch contains transitions for which $\Delta J = -1$, while the $R$ branch contains those with $\Delta J = +1$. Because NH$_3$ has the allowable transition $\Delta J = 0$, another branch notation must be employed, which is $Q$. The transitions for $K$ are also denoted with $P$, $Q$ and $R$ for changes of $-1$, $0$, and $1$, respectively. The following compact notation can be used to describe a transition:

$$\Delta K \Delta J_{K''}(J'')_\sigma,$$  \hspace{1cm} (2.11)
where $\Delta K = K' - K''$, $\Delta J = J' - J''$, and $\sigma = a$ or $s$, depending on the symmetry of the transition’s lower level. Thus, a transition from $J'' = 3$, $K'' = 0$, and $\sigma'' = s$, to $J' = 2$, $K' = 1$, and $\sigma' = s$ can be summarized as

$$RP_0(3)s.$$

Similarly to CO$_2$, NH$_3$ has a center of symmetry, and thus its rotational statistics are affected by nuclear spin. However, for NH$_3$, the nuclear statistical effects yield alternating rotational level populations rather than levels that are entirely missing. For $c_{3v}$ molecules with a three-fold axis, the levels $K = 0, 3, 6, 9, \ldots$ have twice the statistical weight of the levels $K = 1, 2, 4, 5, 7, 8, \ldots$. The spectrum thus has a series of transitions with alternating intensities _strong, weak, weak, strong, weak, weak,\ldots_ [33].

### 2.2.4 Partition Function

As described above in Section 2.1.4, the total internal partition function, $Q(T)$, can be described by classical means as a product of the nuclear, rotational, and vibrational partition functions, $Q_{\text{nuc}}, Q_{\text{rot}},$ and $Q_{\text{vib}}$, respectively (Equation 2.12), or approximated by a third-order polynomial (Equation 2.13), for which the coefficients $a$, $b$, $c$ and $d$ are listed in Table 2.8.

$$Q(T) = Q_{\text{nuc}}Q_{\text{rot}}Q_{\text{vib}}$$

(2.12)

$$Q(T) = a + bT + cT^2 + dT^3$$

(2.13)

The classical rigid-rotor (RR) partition function for ammonia’s symmetric top structure includes contributions from all three rotational moments in the form

$$Q_{\text{rot}}(T) = \frac{1}{\sigma} \sqrt{\frac{\pi}{ABC}} \left( \frac{kT}{\hbar c} \right)^3,$$

(2.14)

where $\sigma=3$ is the symmetry factor for NH$_3$ and $A$, $B$ and $C$ are the rotational constants listed in Table 2.5.
Table 2.8: Coefficients of the polynomial expression for $Q(T)$ in Equation 2.13 from Hitran96 [72] and Gamache [26].

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Hitran96</th>
<th>Gamache</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$70 &lt; T &lt; 500$ K</td>
<td>$500 &lt; T &lt; 1500$ K</td>
</tr>
<tr>
<td>a</td>
<td>-42.037</td>
<td>-471.39</td>
</tr>
<tr>
<td>b</td>
<td>2.5976</td>
<td>5.4035</td>
</tr>
<tr>
<td>c</td>
<td>0.013073</td>
<td>6.4491e-3</td>
</tr>
<tr>
<td>d</td>
<td>-6.2223e-6</td>
<td>-7.2674e-7</td>
</tr>
</tbody>
</table>

The nuclear partition function is described by

$$Q_{nuc} = (2I_N + 1)(2I_H + 1)^3 = 24,$$  \hspace{1cm} (2.15)

where $I_N = 1$ and $I_H = 1/2$ are the nuclear spins of the nitrogen and hydrogen atoms, respectively. Thus, nuclear spin affects the overall the statistics for individual rotational levels and contributes to the total internal partition function for NH$_3$.

The simple harmonic oscillator (SHO) model for the vibrational partition function of NH$_3$ yields

$$Q_{vib}(T) = \left[1 - \exp\left(-\frac{\hbar \nu_1}{kT}\right)\right]^{-1}\left[1 - \exp\left(-\frac{\hbar \nu_2}{kT}\right)\right]^{-1}$$
$$\times \left[1 - \exp\left(-\frac{\hbar \nu_3}{kT}\right)\right]^{-2}\left[1 - \exp\left(-\frac{\hbar \nu_4}{kT}\right)\right]^{-2},$$  \hspace{1cm} (2.16)

for which the fundamental vibration frequencies are are listed in Table 2.6, with double-degeneracy for modes $\nu_3$ and $\nu_4$. The total internal partition function then becomes

$$Q_{NH_3}(T) = \frac{24}{\sigma} \sqrt{\frac{\pi}{ABC}} \left(\frac{kT}{\hbar c}\right)^3$$
$$\times \left[1 - \exp\left(-\frac{\hbar \nu_1}{kT}\right)\right]^{-1}\left[1 - \exp\left(-\frac{\hbar \nu_2}{kT}\right)\right]^{-1}\left[1 - \exp\left(-\frac{\hbar \nu_3}{kT}\right)\right]^{-2}\left[1 - \exp\left(-\frac{\hbar \nu_4}{kT}\right)\right]^{-2},$$  \hspace{1cm} (2.17)
2.2. SYMMETRIC TOP SPECTROSCOPY: NH$_3$

Figure 2.7: Comparison of the partition function values predicted by HITRAN96 [72], the classical model (RR and SHO), McDowell [50], and Gamache [26].

Figure 2.7 plots the classical partition function (Equation 2.12) and the approximated partition function (Equation 2.13) over a range of temperatures 300–1000 K. The partition function based on polynomial coefficients from HITRAN96 in Table 2.8 underestimates the classically-approximated partition function by $\sim 10\%$ at 500 K and $\sim 40\%$ at 1000 K because it does not include the contributions of the vibrational partition function [26,28]. Using updated coefficients provided by Gamache [26], the polynomial expression and the classical model differ by less than 2\% throughout the temperature range.

Superimposed on the plot is an estimate for the total partition function at 300, 500, and 1000 K, that uses McDowell’s detailed rotational partition function sums, but includes contributions from nitrogen spin (McDowell’s published sums include spin contributions only from the H-atoms) and the vibrational partition function [50]. The values based on McDowell’s calculations agree well with both the classical model and with the polynomial expression using Gamache’s coefficients, confirming the accuracy of the polynomial model with Gamache’s updated values.
Chapter 3

Quantitative Absorption Spectroscopy

3.1 Beer-Lambert Law

The fundamental theory governing absorption spectroscopy is embodied in the Beer-Lambert law, Equation 3.1. The ratio of the transmitted intensity $I_t$ and initial (reference) intensity $I_o$ of monochromatic laser radiation through an absorbing medium at a particular frequency is exponentially related to the absorption transition’s linestrength $S_i$ [cm$^{-2}$atm$^{-1}$], lineshape function $\phi$ [cm], total pressure $P$ [atm] of the medium, mole fraction of the absorbing species $x_j$, and the pathlength $L$ [cm] through which the radiation passes:

$$\frac{I_t}{I_o} = \exp(-S_i\phi P x_j L).$$

(3.1)

The two laser intensities can be converted to absorbance $\alpha(\nu)$ and related to the transition parameters by

$$\alpha(\nu) = -\ln \left( \frac{I_t}{I_o} \right),$$

(3.2)

$$= S_i\phi P x_j L.$$  

(3.3)
Note that absorbance has no units and is the domain for which many spectroscopic lineshapes functions (Gaussian and Lorentzian) are written. Another form of the Beer-Lambert law is

\[
\frac{I_t}{I_o} = \exp(-S^*_i \phi n_j L),
\]

where \( S^*_i \) is the linestrength in number-density units of \([\text{cm}^{-1}/(\text{mol} \cdot \text{cm}^{-2})]\), and \( n_j \) is the number-density of the absorbing species.

### 3.2 Linestrengths

The linestrength of an absorption transition depends on the population in the lower quantum state, which is a function of the Boltzmann fraction, and the probability of the transition, which depends on the specific spectroscopic constants associated with that molecule’s particular transition. As described above, the typical units for linestrengths include a pressure-dependent version, \( S [\text{cm}^{-2}\text{atm}^{-1}] \), and a number-density dependent version used by HITRAN96, \( S^* [\text{cm}^{-1}/(\text{mol} \cdot \text{cm}^{-2})] \). The conversion between \( S \) and \( S^* \) is

\[
S [\text{cm}^{-2}\text{atm}^{-1}] = \frac{S^* [\text{cm}^{-1}/(\text{mol} \cdot \text{cm}^{-2})] \times n [\text{mol}/\text{cc}]}{P [\text{atm}]},
\]

where \( n \) is the number density in \([\text{molecules}/\text{cc}]\) and \( P \) is the pressure in \([\text{atm}]\). Using the ideal gas law and converting pressure units from \([\text{dynes/cm}^2]\) to \([\text{atm}]\) yields the following relationship:

\[
S[\text{cm}^{-2}\text{atm}^{-1}] = \frac{S^* [\text{cm}^{-1}/(\text{mol} \cdot \text{cm}^{-2})] \times 1013250 [\text{dynes}/(\text{cm}^2 \cdot \text{atm})]}{kT},
\]

where \( k = 1.38054 \times 10^{-16} [\text{erg}/\text{K}] \) is the Boltzmann constant and \( T [\text{K}] \) is the temperature at which the conversion is being performed and the linestrength is known.
3.2. LINESTRENTHS

Equation 3.6 reduces to

\[ S = \frac{S^* \times (7.34 \times 10^{21})}{T} \text{ [cm}^{-2}\text{atm}^{-1}]. \]  

(3.7)

For converting room-temperature linestrength \((T = 296K)\), the conversion is

\[ S = S^* \times (2.488 \times 10^{19}) \text{ [cm}^{-2}\text{atm}^{-1}]. \]  

(3.8)

Since the linestrength depends on the Boltzmann fraction of molecules in the absorbing state, the linestrength is a function of temperature. The linestrength \(S_i(T)\) for a particular transition \(i\) at some temperature \(T\) can be determined from the molecule’s reference temperature linestrength \(S_i(T_0)\); the absorbing molecule’s partition function \(Q(T)\); the frequency of the transition, \(\nu_{0,i}\); and the lower-state energy of the transition, \(E''_i\). This relationship is given by

\[
S_i(T) = S_i(T_0) \frac{Q(T_0)}{Q(T)} \left( \frac{T_0}{T} \right) \exp \left[ -\frac{hcE''_i}{k} \left( \frac{1}{T} - \frac{1}{T_0} \right) \right] \\
\times \left[ 1 - \exp \left( \frac{-hc\nu_{0,i}}{kT} \right) \right] \left[ 1 - \exp \left( \frac{-hc\nu_{0,i}}{kT_0} \right) \right]^{-1},
\]

(3.9)

where \(S\) is in units of \([\text{cm}^{-2}\text{atm}^{-1}]\). For units of \([\text{cm}^{-1}/(\text{mol} \cdot \text{cm}^{-2})]\), the following temperature scaling can be used

\[
S^*_i(T) = S^*_i(T_0) \frac{Q(T_0)}{Q(T)} \exp \left[ -\frac{hcE''_i}{k} \left( \frac{1}{T} - \frac{1}{T_0} \right) \right] \\
\times \left[ 1 - \exp \left( \frac{-hc\nu_{0,i}}{kT} \right) \right] \left[ 1 - \exp \left( \frac{-hc\nu_{0,i}}{kT_0} \right) \right]^{-1}.
\]

(3.10)

Thus, a ratio of linestrengths with the different units can be calculated as follows

\[
\frac{S(T)}{S(T_0)} = \frac{S^*_i(T)}{S^*_i(T_0)} \times \frac{T_0}{T}.
\]

(3.11)
3.3 Spectral Lineshapes

The lineshape function $\phi$ reflects the relative variation in the spectral absorption coefficient with frequency. Since it is normalized, the lineshape’s integrated value over frequency is equal to unity.

$$\int_{-\infty}^{+\infty} \phi d\nu = 1$$ (3.12)

A typical lineshape of an isolated absorption line centered at $\nu_0$ is shown in Figure 3.1 as a function of frequency. The lineshape has a maximum value $\phi(\nu_0)$ at a frequency $\nu_0$. The width of the feature, $\Delta\nu$, is defined by the width at half the maximum value (the full width at half maximum, or, FWHM). Note that the half width at half maximum, HWHM, is also used in many references. The integral in Equation 3.12 is defined to have no dimensions. Since the units of $d\nu$ are typically either cm$^{-1}$ or s$^{-1}$, $\phi(\nu)$ will have units of centimeters or seconds respectively.

Broadening of an absorption feature occurs due to phenomena in the medium that perturb the transition’s energy levels or the way in which individual atoms and molecules interact with light. For the measurement conditions that were present for the sensors in this thesis ($\leq 1$ atm, $< 1900$ K), the dominant broadening mechanisms
were from thermal motion (Doppler broadening, inhomogeneous) and collisional effects (collisional broadening, homogeneous), both of which are described below. Other mechanisms such as natural broadening or Dicke narrowing are negligible compared with the magnitudes of the thermal and collisional effects. Line shifting of spectral lineshapes can also be ignored for the pressures and temperatures that are used for these applications.

### 3.3.1 Doppler broadening

When a molecule has a velocity component in the same direction as the propagation of a beam of light, there will be a shift in the frequency at which it will absorb a photon. This effect is called the Doppler shift. The molecules of any gas are in constant motion and the distribution of their random velocities is described by the Maxwellian velocity distribution function. We can consider each group of molecules with the same velocity component to be part of a velocity class. The Maxwellian velocity distribution function tells us what portion of the molecules are in each class. Each velocity class will have its own Doppler shift. Thus the distribution function leads directly to a lineshape function with a Gaussian form:

\[
\phi_D(\nu) = \frac{2}{\Delta\nu_D} \left( \frac{\ln 2}{\pi} \right)^{1/2} \exp \left\{ -4 \ln 2 \left( \frac{\nu - \nu_o}{\Delta\nu_D} \right)^2 \right\}.
\]

(3.13)

The Gaussian lineshape function at linecenter is

\[
\phi_D(\nu_o) = \frac{2}{\Delta\nu_D} \left( \frac{\ln 2}{\pi} \right)^{1/2}.
\]

(3.14)

The Doppler halfwidth (FWHM) \(\Delta\nu_D\) is given by

\[
\Delta\nu_D = \nu_o \left( \frac{8kT \ln 2}{mc^2} \right)^{1/2},
\]

(3.15)
Figure 3.2: Comparison of Doppler widths (FWHM) for \( \text{NH}_3 \) at 6528.76 cm\(^{-1} \) (1.53 \( \mu \)m), \( \text{NH}_3 \) at 5016.977 cm\(^{-1} \) (1.993 \( \mu \)m), and \( \text{CO}_2 \) at 5007.787 cm\(^{-1} \) (1.997 \( \mu \)m) for a range of temperatures.

for which a more convenient form is

\[
\Delta \nu_D = \nu_0 \left( 7.1623 \times 10^{-7} \right) \left( \frac{T}{M} \right)^{1/2},
\]

where \( T \) is in Kelvins and \( M \) is the molecular weight in grams/mole. Figure 3.2 illustrates the increasing Doppler width with higher temperatures for \( \text{NH}_3 \) at 6528.76 cm\(^{-1} \) (1.53 \( \mu \)m), \( \text{NH}_3 \) at 5016.977 cm\(^{-1} \) (1.993 \( \mu \)m), and \( \text{CO}_2 \) at 5007.787 cm\(^{-1} \) (1.997 \( \mu \)m). As can be seen from the figure, thermal broadening affects \( \text{NH}_3 \) much more than \( \text{CO}_2 \) due to the former’s comparatively small mass, and affects shorter wavelengths more than longer wavelengths for the same molecule because of the frequency-dependence of the broadening mechanism.

### 3.3.2 Collisional Broadening

Collisional broadening is the result of perturbations that shorten energy level lifetimes during collisions between two molecules (or atoms) in a gas. According to the Heisenberg uncertainty principle, shortening the lifetime of a molecule in an
energy level leads to greater uncertainty of the molecule’s energy, and thus a broader absorption lineshape. Therefore, the more likely collisions are to occur, the more likely lifetimes are shortened and transitions are broadened. This relationship between collision likelihood and transition breadth is the fundamental mechanism underlying collisional (or pressure) broadening.

The lineshape for collisional broadening takes the form of a Lorentzian function:

$$\phi_C(\nu) = \frac{1}{2\pi} \frac{\Delta \nu_C}{(\nu - \nu_0)^2 + \left(\frac{\Delta \nu_C}{2}\right)^2}. \quad (3.17)$$

The Lorentzian lineshape function at linecenter is:

$$\phi_C(\nu_0) = \frac{2}{\pi \Delta \nu_C}. \quad (3.18)$$

The frequency uncertainty, $\Delta \nu_C$, in Equation 3.17 is the lineshape’s halfwidth (FWHM). This net uncertainty for the interrogated species, $A$, is often modeled as the product of the system pressure and sum of the mole fraction for each perturber species $B$ multiplied with its process-dependent collisional halfwidth $2\gamma_{A-B}$

$$\Delta \nu_C = P \sum_B X_B 2\gamma_{A-B} \quad (3.19)$$

Thus, the collisional width of an absorption transition is directly proportional to pressure. The standard notation for the different broadening coefficients is $2\gamma_{A-B}$, where $A$ is the molecule whose lineshape is being studied and $B$ is the collision partner (or perturber) that interacts with species $A$ to broaden its absorption line. Thus, $2\gamma_{\text{NH}_3-\text{NH}_3}$ is the broadening coefficient for NH$_3$-NH$_3$ collisions (self-broadening, $2\gamma_{\text{self}}$), and $2\gamma_{\text{NH}_3-\text{N}_2}$ is the coefficient for NH$_3$ lineshape broadening due to collisions with N$_2$ (nitrogen-broadening). Mole-fraction-averaged O$_2$ and N$_2$ coefficients are contained in air-broadening coefficients, $2\gamma_{\text{NH}_3-\text{Air}}$. Values of $2\gamma$ are determined experimentally and are published for specific transitions and specific collision partners. Some sample values for $\gamma$ are listed for NH$_3$ and CO$_2$ in Table 3.1; these values reveal the relative magnitude of ammonia’s collisional broadening mechanisms. NH$_3$
coefficients are approximately 50% larger than CO$_2$ coefficients for air-broadening, and about an order of magnitude larger for self-broadening. Thus, NH$_3$’s absorption transitions are typically much broader than CO$_2$’s transitions.

The broadening coefficient $2\gamma$ varies with temperature according to the following expression

$$2\gamma(T) = 2\gamma(T_0)\left(\frac{T_0}{T}\right)^N$$

(3.20)

where $T_0$ is the reference temperature, typically 296 or 300 K, $2\gamma T_0$ is the broadening coefficient at the reference temperature, and $N$ is the temperature exponent, which is less than 1 and typically 0.5. Equation 3.20 scales in a fashion similar to the scaling laws for number density. This scaling result is expected because collisional broadening is dependent on the collision frequency, which scales with number density.

Figure 3.3 compares Gaussian (Doppler) and Lorentzian (collisional) lineshapes that have the same FWHM and the same area. The Gaussian lineshape has a peak value that is about 50% higher than the Lorentzian, but it drops off much faster in the wings. The molecules of each velocity class will also have some finite lifetime and thus some Lorentzian halfwidth. If the Lorentzian halfwidth is much smaller than the Gaussian halfwidth, the Lorentzian component can be ignored, and vice-versa.

### 3.3.3 Voigt Profiles

In the common case for which both Doppler and collisional broadening are significant and neither can be neglected, the appropriate lineshape will be a combination of the two. If we assume that the effects of Doppler and collisional broadening are
decoupled, we can view each velocity class to be collisionally broadened. This combination of effects leads to a lineshape which is a convolution of Doppler and collisional broadening:

$$\phi_V(\nu) = \int_{-\infty}^{+\infty} \phi_D(u) \phi_C(\nu - u) \, du. \quad (3.21)$$

This convolution is called the Voigt function.

The Voigt $a$ parameter indicates the relative significance of Doppler and collisional broadening, with $a$ increasing as the effects of collisional broadening increase:

$$a = \frac{\sqrt{\ln 2} \, \Delta \nu_C}{\Delta \nu_D}. \quad (3.22)$$

The $w$ parameter is a nondimensional measure of the distance from linecenter and is
defined as follows:

\[ w = \frac{2 \sqrt{\ln 2} (\nu - \nu_o)}{\Delta \nu_D}. \]  

(3.23)

Defining an integral variable, \( y \),

\[ y = \frac{2 u \sqrt{\ln 2}}{\Delta \nu_D}, \]  

(3.24)

and using the linecenter Gaussian magnitude, \( \phi_D(\nu_o) \) from Equation 3.13 at \( \nu_0 \) along with the definitions for \( a \) and \( w \) produces

\[ \phi_V(\nu) = \phi_D(\nu_o) \frac{a}{\pi} \int_{-\infty}^{+\infty} \exp(-y^2) \frac{dy}{a^2 + (w - y)^2} \]  

(3.25)

\[ = \phi_D(\nu_o) V(a, w), \]  

(3.26)

where \( V(a, w) \) is the “Voigt function.” The integral can be calculated using standard mathematical routines [36, 93], but it is common to make use of existing tables for this function. At the lincenter, where \( w = 0 \), \( V(a, w) \) reduces to

\[ V(a, 0) = \exp(a^2) \text{erfc}(a), \]  

(3.27)

\[ = \exp(a^2)[1 - \text{erf}(a)]. \]  

(3.28)

### 3.4 Quantitative Mole Fraction Measurements

The species mole fraction \( x_j \) of the absorbing species is directly available from \( S_i, L, P \) and the integrated absorbance area of the lineshape for a transition according to the following relationship:

\[ x_j = \frac{\text{Area}}{S_i P L}. \]  

(3.29)

Therefore, tuning a narrow linewidth diode laser in wavelength over an entire spectroscopic transition obviates the need for thorough lineshape analyses or broadening
3.4. QUANTITATIVE MOLE FRACTION MEASUREMENTS

parameters that determine the lineshape function \( \phi \). However, for fixed-wavelength measurements, species concentration can be deduced from the transition’s peak height if the lineshape is well known, with

\[
x_j = \frac{\alpha_\nu}{S_\nu \phi_\nu PL},
\]

(3.30)

where \( \alpha_\nu \) is the absorbance at the laser’s frequency and \( \phi_\nu \) is the value of the lineshape function at the same frequency. Estimating the lineshape accurately for fixed-wavelength measurements requires knowledge of the gas temperature, concentrations of bath gas constituents, and pressure.

For many spectroscopic applications, trace-gas detection is of interest. Estimates of a transition’s peak height can be used to evaluate the minimum detectivity for a particular wavelength and measurement condition since the peak of an absorption transition will need to be larger than the surrounding noise. Replacing \( \alpha_\nu \) with a reasonable estimate for minimum detectable absorbance (MDA) in equation 3.30 and operating the laser at the absorption feature’s linecenter, \( \nu_0 \), produces the following relationship for minimum detectivity, \( x_{j,\text{min}} \), of a species \( j \):

\[
x_{j,\text{min}} = \frac{\text{MDA}}{S_\nu \phi_\nu PL}.
\]

(3.31)

Typical values for MDA are \( 1 \times 10^{-4} \) for direct absorption techniques, or \( 1 \times 10^{-5} \) for balanced detection, which uses differential absorption with matched detectors to reduce common mode and bit noise [35].

Using Equation 3.28 to estimate the value of the lineshape at linecenter, the minimum detectivity can be calculated for a range of pressures and temperatures. For varying pressures, the lineshape breadth and species concentration will change. For changing temperatures, the lineshape breadth and linestrengths will vary. Figure 3.4 shows the calculated minimum detectivity for the NH\(_3\) transition at 6528.76 cm\(^{-1}\), assuming the MDA = \( 1 \times 10^{-4} \). For variations in calculated detectivity with temperature (top panel), the pressure was held fixed at 1 atmosphere; for variations with
Figure 3.4: Minimum detectivity of the NH$_3$ transition at 6528.76 cm$^{-1}$ as a function of temperature (top panel, $P = 1$ atm) and pressure (bottom panel, $T = 296$ K) with an estimated minimum detectable absorbance of $1 \times 10^{-4}$.

pressure (bottom panel), the temperature was held fixed at 296 K. This figure illustrates that for this particular transition, lower temperatures offer superior sensitivity and that the optimum pressure for detection is near 100 Torr. The shape of the pressure-dependent minimum detectivity curve is determined by the transition from lineshapes that are primarily Doppler-broadened at low pressures ($< 10$ Torr), to lineshapes that are primarily collisionally-broadened ($> 200$ Torr). In the collisional-broadening limit, increased pressure affects only the area of the absorption lineshapes, but not the peak height. The shape of the temperature-dependent minimum detectivity curve is primarily determined by changes in the absorption linestrength.
4.1 General Elements of an Experimental Apparatus

The basic elements of an experiment for measuring absorption spectra include a laser source whose radiation is directed through an absorbing gas medium of known pathlength and monitored with a detector. The laser is wavelength-tuned across the absorption transition, and the transmitted intensity is recorded with the detector and analyzed to determine the integrated area of the absorption lineshape. For high-resolution tabletop absorption measurements that are used to determine fundamental spectroscopic parameters, the pressure, temperature and purity of gas samples that are probed with the laser need to be controlled accurately, and narrow-linewidth, single-mode radiation sources need to be used.

Figure 4.1 shows the basic experimental schematic that was used for all the controlled static cell absorption measurements at a range of wavelengths, pressures, and temperatures. The lasers that were used included a fiber-pigtailed DFB near 2 \( \mu \)m, an ECDL near 2 \( \mu \)m, a fiber-pigtailed DFB near 1.5 \( \mu \)m, and an ECDL near 1.5 \( \mu \)m (See Section 4.1.1 for further discussion). The laser output from the ECDL devices passed through an optical isolator (-30 dB isolation) to prevent back reflections from returning to the laser cavity. Beamsplitters then split the isolated laser output and
Figure 4.1: Experimental schematic for measuring high-resolution absorption spectra of NH$_3$ and CO$_2$ at a range of pressures and temperatures.

directed one path to the IR wavelength meter (Burleigh Wavemeter) for measuring the laser frequency, one path through the solid etalon (FSR=2.01 GHz) for monitoring the wavelength variations during laser tuning, and one path through the static cell to monitor NH$_3$ or CO$_2$ absorption. Low-pass analog filters prevented signal aliasing, and a Nicolet 12-bit digital oscilloscope was used for data acquisition. Since the fiber-pigtailed DFB’s had built-in isolators and required fiber collimators to pitch the radiation into free-space, the isolator in the schematic was replaced with the appropriate collimator whenever a DFB was in use. Transmitted and etalon intensities were monitored with InGaAs photodiodes at 1.5 $\mu$m, and extended wavelength-response InGaAs photodiodes at 2 $\mu$m.

4.1.1 Lasers

The single-mode diode-lasers that were used for spectroscopic measurements (See Table 4.1) consisted of external cavity diode lasers (ECDL’s) and distributed feedback (DFB) diode lasers. The ECDL’s are useful tools for spectroscopic measurements primarily because of their wide tuning ranges that often extend for dozens of nanometers and allow for interrogation of many species and transitions. They also have narrow linewidth (300 kHz typical) that enables high-resolution spectroscopy. Their output powers vary from 1-3 mW, depending on the operating wavelength. Drawbacks to
their use are that the lasers must be scanned at rates less than 300 Hz and have a maximum tuning depth of approximately 1 cm$^{-1}$, thus these lasers are not useful for measurements in quickly-changing flows or for recording absorption features that are very broad. Moreover, ECDL’s have more polarization noise than DFB or other lasers, widely varying transmission power with wavelength (See Figure 4.2), which complicates polynomial baseline estimations, and an output beam that moves in space with the grating position, which can detrimentally affect alignment-sensitive sensors.

In comparison, DFB lasers access a much smaller wavelength range, typically 5 nm over a span of 50 °C, but have deeper tuning ranges within each scan and can tune at rates up to tens of kHz [92]. Figure 4.3 depicts the tuning depth for a Fujitsu DFB operating near 1529 nm (injection current $I_j = 90 \pm 35$ mA) for various modulation frequencies. Even at tuning rates greater than 10 kHz, this particular laser can scan deeper than 1 cm$^{-1}$. Thus, the DFB packages can be used for recording broad spectra and can be applied to interrogate unsteady environments. In contrast with the ECDL’s power variations that are shown in Figure 4.2, the output radiation

Figure 4.2: Tuning range and power variations for the ECDL near 1.5 μm.
intensity of a DFB changes smoothly with wavelength and can be easily approximated with a third-order polynomial. DFB lasers have output linewidths of approximately 10 MHz, which is narrow enough for high-resolution spectroscopy, but is roughly 30 times broader than for the ECDL systems. Moreover, since fiber-pigtailed DFB lasers do not have an external grating and a mechanical tuning system, their package sizes are much smaller than ECDL’s, making them more suitable for field measurements that have space restrictions. Fiber-pigtailed DFB lasers often have output powers near 10 mW in the telecommunications bands at 1.5 µm, and approximately 1 mW at 2 µm. Fiber-coupling offers the convenience of remote detection without atmospheric interferences or a free-space optical path from the laser location to the measurement site.

The specific lasers that were used for the research in this thesis are listed in Table 4.1 and included an ECDL operating in the range 1496–1583 nm (6320–6680 cm$^{-1}$), an ECDL with a tuning range of 1966–2035 nm (4914–5086 cm$^{-1}$), a fiber-pigtailed DFB operating in the 1526–1530 nm (6536–6553 cm$^{-1}$) range, and a fiber-pigtailed DFB operating in the range 1993–1998 nm (5005-5018 cm$^{-1}$). The ECDL’s could be tuned over their entire optical ranges by adjusting the internal grating with
Table 4.1: Manufacturers, configuration and some typical specifications for the lasers used in this work.

<table>
<thead>
<tr>
<th>Range [nm]</th>
<th>Configuration</th>
<th>Manufacturer</th>
<th>Power [mW]</th>
<th>Linewidth</th>
</tr>
</thead>
<tbody>
<tr>
<td>1496–1583</td>
<td>ECDL</td>
<td>New Focus</td>
<td>2</td>
<td>300 kHz</td>
</tr>
<tr>
<td>1526–1530</td>
<td>DFB</td>
<td>Fujitsu</td>
<td>&gt; 10</td>
<td>8 MHz</td>
</tr>
<tr>
<td>1966–2035</td>
<td>ECDL</td>
<td>New Focus</td>
<td>1</td>
<td>300 kHz</td>
</tr>
<tr>
<td>1993–1998</td>
<td>DFB</td>
<td>NEL</td>
<td>2</td>
<td>10 MHz</td>
</tr>
</tbody>
</table>

a piezoelectrically controlled motor. For individual lineshape measurements (approximately 1-cm$^{-1}$ scans), a sawtooth voltage waveform modulated the internal grating with a piezoactuator (typical injection currents: 55 mA, case temperature: 23 °C). The DFB’s were held at a fixed case temperature and scanned by modulating the injection current, typically between 30–150 mA. The case temperature was 22.7 °C for measuring CO$_2$ at 1996 nm, -4.7 °C for measuring NH$_3$ at 1993 nm, and 18.5 °C for measuring NH$_3$ at 1529 nm.

4.1.2 Solid Etalon

The solid etalon that was used to transfer recorded spectra from time spacing into frequency spacing is made of silica glass and is 51.8 mm long. The index of refraction for the etalon varies from 1.44462 at 1.5 µm to 1.43809 at 2.0 µm. The free spectral range (FSR) of the etalon is

$$\text{FSR} = \frac{c}{2nL},$$

where $c$ is the speed of light, $n$ is the index of refraction for the silica, and $L$ is the length of the etalon. Thus, the FSR is approximately 2.005 GHz near 1.5 µm, and 2.014 GHz near 2 µm. Since the actual optical pathlength through the etalon is not known exactly, the FSR was estimated to be 2.01 ± 0.01 GHz for all measurements.

The reflectivity of the solid etalon decreases with longer wavelengths, and as a result, the finesse (or sharpness of the fringes) decreased as well. Figure 4.4 compares the measured etalon transmission at 1.5 µm (top panel) and 2 µm (bottom panel) using DFB lasers. As the plot shows, the finesse at 1.5 µm is approximately $F = 4,$
The finesse is low enough at 2 µm such that the conversion from time spacing into frequency spacing has slightly more uncertainty than comparative processes at 1.5 µm, though frequency spacing uncertainties for both cases are under 1%.

### 4.1.3 Controlled Gas Samples

**Gas Handling**

Controlling gas samples is an important part of measuring fundamental spectroscopic parameters, and carbon dioxide and ammonia have very different requirements for careful handling. Ammonia is a very polar gas that adsorbs to most surfaces. In addition, it is a corrosive gas that is incompatible with many materials and susceptible to heterogeneous dissociation in some instances. Because of its toxicity and the need to maintain sample purity, leaks need to be avoided. In contrast, carbon
4.1. GENERAL ELEMENTS OF AN EXPERIMENTAL APPARATUS

Table 4.2: Materials compatibility with \( \text{NH}_3 \): U for unsatisfactory, S for satisfactory [1,3]

<table>
<thead>
<tr>
<th>Material of Construction</th>
<th>Compatibility</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Metals</strong></td>
<td></td>
</tr>
<tr>
<td>Brass</td>
<td>U</td>
</tr>
<tr>
<td>Stainless Steel</td>
<td>S</td>
</tr>
<tr>
<td>Copper</td>
<td>U</td>
</tr>
<tr>
<td>Monel</td>
<td>S</td>
</tr>
<tr>
<td><strong>Plastics</strong></td>
<td></td>
</tr>
<tr>
<td>Teflon</td>
<td>S</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>U</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>S</td>
</tr>
<tr>
<td><strong>Elastomers</strong></td>
<td></td>
</tr>
<tr>
<td>Viton</td>
<td>U</td>
</tr>
<tr>
<td>Buna-N</td>
<td>S</td>
</tr>
</tbody>
</table>

dioxide is a very stable gas that does not tend to adsorb, corrode, or dissociate in most gas-handling systems.

Table 4.2 lists some different materials and their compatibility with ammonia gas. Satisfactory materials can be exposed to ammonia for long periods of time (days) without negative effects. Unsatisfactory materials show signs of corrosion after short exposure times (hours) to ammonia, leading to impure ammonia samples and materials whose structural integrity has been compromised. Using Table 4.2 as a guide, stainless steel and polypropylene tubing were used exclusively for plumbing, while Buna-N o-rings were used in valves and ultra-torr fittings.

To maintain good leak-tight systems and low ultimate vacuums, stainless-steel ultra-torr fittings and standard plug valves were used whenever possible. Ultimate pressures in static cells were typically 20 mTorr. Mechanical vacuum pumps with ultimate pressures less than 20 mTorr (10–15 mTorr typical) were used to evacuate the gas handling systems for several hours to removed adsorbed room-air water before any gas samples were introduced into the measurement cells. Pure gas samples of CO\(_2\) and \( \text{NH}_3 \) were introduced into and evacuated out of static cells three times before spectra were recorded in order to flush out any room air that remained in the system.
Ammonia’s tendency to adsorb resulted in decreasing pressure after ammonia samples were introduced into test cells. Monitoring the pressure of the system at all times and using 99.99% pure gas (purity specified by Matheson Gas) samples of \( \text{NH}_3 \) instead of calibrated mixtures for the static cell measurements avoided ammonia concentration uncertainty due to this adsorption. Several minutes after filling the cell with \( \text{NH}_3 \), the adsorption would occur slowly enough to permit absorption measurements with an accurate estimate of the ammonia number density in the absorption path. For carbon dioxide, 99.99% pure laser grade gas was used as a source of test samples and since \( \text{CO}_2 \) does not adsorb on the surface of the test cell, measurements could be made immediately without waiting for any settling time.

**Measurement Cells**

Static cells with pure samples were used exclusively for all spectroscopic measurements, while flowing cells with ammonia mixtures were used for some calibration measurements. Room-temperature measurements were made with the heater in Figure 4.1 off and with several different cells and configurations, including a 20 cm quartz cell with double-pass alignment, a 15 cm stainless steel cell in triple- and quintuple-pass alignment, and a single-pass 50 cm quartz cell. Unwanted interference fringes in the transmission path were minimized by mounting 0.5° wedged windows at a 3° (or greater) angle on the cells. Two MKS Baratron pressure gauges with full-scale deflections of 100 Torr and 1000 Torr respectively and accuracies of ±1% were used to monitor the test cell pressure.

For high-temperature static cell measurements, the quartz 20-cm cell was used exclusively to avoid the catalyzed dissociation of \( \text{NH}_3 \) that would occur with heated metal cells [94]. Four type-S thermocouples, equally spaced along the cell axis, were used to monitor the cell temperature. Temperature deviations along the 20-cm cell were determined to be < 2%. Gases were allowed to heat for at least 30 minutes in order to achieve steady and uniform gas temperature inside the cell.

A fast-sampling flow-through multipass cell was used for calibration measurements of flowing ammonia gas mixtures in the lab (with low concentrations of \( \text{NH}_3 \) to avoid damage to the mirror’s coatings with adsorbed \( \text{NH}_3 \)) and for field measurements of
NH$_3$ and CO$_2$ in bioreactor vent gases (See Chapter 7). The multipass cell has two astigmatic mirrors separated by 20 cm that are configured for 182 passes, yielding a total pathlength of 3600 cm in a small volume of 0.3 L [51]. As Equation 3.31 indicates, longer pathlengths can improve a sensor’s minimum detectable concentration, thus the multipass flow through cell is useful for certain trace-gas detection applications. However, low-finesse interference fringes with an approximate magnitude of $5 \times 10^{-4}$ caused by beam overlap within the cell became a limiting factor for sensitive detection when the multipass system was employed.

Since the interference fringes from the cell’s alignment are similar in appearance to absorption spectra, they are difficult to distinguish from small signals, even if FM spectroscopy, averaging, or balanced-detection techniques are used. These fringes are wavelength- and alignment-dependent, and thus cannot be removed with signal averaging over successive scans. Also, since the fringes exist only in the transmission path, auto-balancing techniques such as the Hobb’s circuit [35] cannot remove their
effects. The best approach to remove undesired interference fringes in the multipass cell is to use piezoelectric actuators to translate an alignment mirror at the input of the multipass cell, as described by Chou [17] and Silver, et al. [80]. By translating the mirror position several \( \mu \)m, the angle of alignment into the cell will change slightly and thereby adjust the free-spectral range of the interference fringes. Since the fringes will shift back and forth in frequency space, and thereby in time as the laser scans, they will no longer be coherent and thus can be diminished by averaging. Once the fringes are reduced, other more sensitive techniques can be used also to improve detectivities significantly.

Properly establishing 182 passes for a 36-m pathlength requires careful alignment. In some cases, suboptimal alignment leads to premature “leakage” of some light out the cell before it has traversed the entire pathlength. This leaked radiation is a systematic error that shows up on a detector as an offset of increased intensity, and has the net effect of reducing the effective pathlength of the cell. Previous research calibrated the overall pathlength to be roughly 33 m [54, 56].

By using optically thick absorption, the amount of light “leakage” (or intensity offset) can be quantified and minimized to establish an optimum alignment. The “leakage” is quantified as the amount of intensity measured by the detector at a frequency of 100% absorption. As Figure 4.5 reveals, the transmitted intensity in the wings of an optically-thick absorption feature can be approximately the same for optimal and sub-optimal absorption, but the optimized alignment has much less light “leakage.” Thus, seeking merely to maximize throughput can be misleading. By using a strong absorption feature and monitoring the magnitude of the transmission, optimal alignment can be achieved by seeking to maximize the intensity in the wings of the absorption and minimizing the offset at the location of 100% absorption. Any remaining offset radiation after optimization can be subtracted from transmitted signals before reduction. However, optimum alignments can produce light leakage that is less than 2% of the non-absorbed transmitted intensity, making some subtractions unnecessary in certain instances. After optimizing the alignment and accounting for any remaining offsets, the total pathlength was measured to be 36 m, an improvement over the previous net result of 33 m.
4.2 Measuring Fundamental Parameters

4.2.1 Measuring $S$

The linestrength of an absorption transition is the key parameter for designing absorption-based gas sensors. Though published linestrengths are available for many species, those values are often based on calculations or low-resolution measurements. Thus, high-resolution absorption measurements with controlled gas samples in a lab can be used to improve linestrength estimates. Using a variation of Equation 3.30, the linestrength $S_i$ for a particular transition can be determined from the integrated area of the transition, divided by the partial pressure of the absorbing species $P_j$ and the pathlength $L$.

$$S_i = \frac{\text{Area}}{P_j L} \quad (4.2)$$

To determine the integrated area of absorption features for high-resolution scans, the reference intensity $I_0$ must first be estimated by a polynomial fit to the unattenuated regions of the transmission signal $I_t$ as shown with a dotted line in the top panel of Figure 4.6. Using the free spectral range of the solid etalon (FSR=2.01 Ghz), and the estimation for the reference intensity, the raw etalon and transmitted intensity data can be converted from voltage versus time to absorbance versus frequency, as in the bottom panel of Figure 4.6. Multi-line Voigt fits can be used to extract the integrated absorbance of each individual transition, as shown with dashed lines in the bottom panel of Figure 4.6.

It is important that the pressures and pathlengths for these measurements are selected such that the peak absorption is between 10 and 80%. Signals above 10% are needed to ensure high signal-to-noise ratios (SNR), but peak absorption above 80% approaches the optically-thick regime, for which integrated absorbance is no longer linear with pressure. Pressures need to be used that are low enough to isolate the absorption lines, but high enough to produce the requisite absorption, while pathlengths needs to be employed that are long enough to provide the necessary absorption, but not so long that the features become optically thick. Since CO$_2$
Figure 4.6: The top panel contains raw data traces for the transmitted and etalon intensities of the NH$_3$ feature at 1497 nm along with an estimate for the reference intensity $I_0$. The etalon transmission signal is a series of fringes with a smaller overall intensity than the transmitted signal. The lower panel shows the data after they have been converted to absorbance vs. frequency. The measurement conditions for these panels are $P_{NH_3} = 5.6$ Torr, $L = 40$ cm, and $T = 20 \degree$C.
absorption at 2 \(\mu\)m is generally 2 orders of magnitude weaker than \(\text{NH}_3\)’s absorption, longer pathlengths and higher pressures (up to 120 Torr) were used to study its spectra. For ammonia’s many blended features, low pressures (< 20 Torr) were used to isolate the lines. The SNR for all the recorded spectra that were used to deduce fundamental spectroscopic parameters were at least greater than 75, and typically were greater than 300.

The integrated absorbance area of an individual transition will increase linearly with pressure. Thus, the linestrength can be deduced by performing a linear fit on multiple area measurements at various pressures, as shown in Figure 4.7, and using the slope to measure the linestrength. Since zero pressure corresponds with zero absorbance, the linear fit was restricted to pass through the origin. Typically, linestrength measurements were made with integrated areas from 5–8 different pressure or pathlength conditions. The uncertainty for many of the individual linestrength measurements was estimated to be < 3\% due to measurement uncertainties of 1\% in the total pressure, 1\% in the total pathlength, and 1\% in the area under each Voigt profile. For blended lines, the uncertainty was higher.
4.2.2 Measuring $E''$

By measuring the linestrength over a range of temperatures, the lower-state energy for a transition can be estimated by performing an exponential fit to values for linestrength versus temperature using Equation 3.9. Though a best-fit answer for the lower-state energy can be found with this process, in general, line-assignment techniques are more accurate (7 digits of accuracy) for determining lower-state energies. Thus, the exponential-fitting approach serves as a strategy for confirming the accuracy of a transition’s quantum assignment rather than deducing actual lower-state energy values. For lower-state energy confirmations, integrated absorbance measurements were typically made at a minimum of 5 pressure conditions for each temperature and at 10 different temperatures, yielding at least 50 absorption features for each lower-state energy estimate.

4.2.3 Measuring $\gamma_{\text{self}}$

The self-broadening coefficient, $\gamma_{\text{self}}$, can be measured in a fashion analogous to the linestrength, since the collisional width is linear with pressure (See Equation 3.19). By holding the Doppler width fixed at the appropriate value for the measurement temperature during Voigt fits, the collisional width can be extracted from the overall width of the absorption profile using the measured Voigt $\alpha$ parameter. The broadening coefficient can be determined by performing a linear fit of the measured Lorentzian widths at various pressures, and using the slope to calculate the broadening coefficient. When performing these measurements, a pressure regime must be used for which the collisional widths are larger than the Doppler widths.

Due to the blended nature of NH$_3$’s absorption features, measurements of its self-broadening are very difficult. The higher pressures that are required for the measurement cause the individual transitions to overlap, which complicates efforts to isolate the lineshapes for each transition. Thus, self-broadening measurements were only made for CO$_2$ in this work.
Chapter 5

*In situ* NH$_3$ Monitoring at 1.5 $\mu$m

This research seeks to aid in the design of near-infrared NH$_3$ sensors for air-quality and emissions-monitoring applications by carefully analyzing the absorption band near 1.5 $\mu$m to select isolated NH$_3$ transitions for use with diode laser absorption sensors. Once the appropriate transitions were identified, their fundamental spectroscopic parameters, such as linestrength, line position, and lower-state energy were measured. Sample measurements of NH$_3$-slip were then made in post-combustion exhaust gases to demonstrate the feasibility of the emissions-monitoring sensors and the isolation of the selected NH$_3$ transitions.

5.1 Line Selection

The different environments in which ammonia monitoring is pertinent—air-quality monitoring and leak detection for industrial applications and emissions-monitoring for Thermal DeNO$_x$ and SCR applications—have different conditions and challenges. For air-quality monitoring, the environment is typically a factory floor, a fertilizer facility, or an outdoor stockyard, for which populations of ammonia greater than 25 ppm need to be monitored to prevent health risks. The conditions for these environments are atmospheric pressure and room temperature (0–40 °C), and have potential spectroscopic interferences from atmospheric water. For emissions-monitoring, the environment is typically in a post-combustion exhaust stack, with a pressure slightly
above 1 atm and a temperature range between 300 K and 1250 K. The interfering species for this application are the major products of combustion, namely CO$_2$ and H$_2$O, and the levels of NH$_3$ that need to be monitored are typically < 5 ppm.

NH$_3$ transitions need to be selected that avoid approximately 1–2% of atmospheric water and 250–380 ppm CO$_2$ for the first application, and 10–20% each of hot H$_2$O and CO$_2$ for the latter. Lines suitable for application in an ammonia sensor must avoid these interfering species and have linestrengths that are large enough for sensitive trace-gas detection. For both applications, knowing the temperature sensitivities and linestrengths is required for accurate sensors.

Figure 5.1 depicts the NIR linestrengths of ammonia, water and carbon dioxide from 1.4 to 2.5 µm in wavelength. Three main bands of ammonia are present in this region at 1.5, 2.0, and 2.3 µm respectively. The linestrengths for this figure are from Lundsberg-Nielsen for the 1.5 µm band of NH$_3$ [46,47], and from HITRAN96 for the
2.0 and 2.3 μm bands of ammonia and all the H$_2$O and CO$_2$ bands [72]. A weak ammonia combination band is also present at 1.65 μm [74,82], however a detailed listing of line positions and strengths for this region is not currently available.

Of the three regions, 2.3 and 1.5 μm are the most useful for emissions monitoring of ammonia slip due to the relative scarcity and weakness of the interfering species’ transitions. In contrast, at 2.0 μm H$_2$O and CO$_2$ interferences are substantial, eliminating this region as a viable option for emissions monitoring. All three bands, however, are suitable for air-quality monitoring. The interfering presence of H$_2$O at 1.4 μm tapers off near 1.5 μm and the CO$_2$ linestrengths in this region are fairly weak, allowing for isolated NH$_3$ transitions in post-combustion gases. At 2.3 μm there is almost no CO$_2$ absorption, and the water lines are weaker and less populated, leaving spectral windows available for interference-free NH$_3$ absorption. Though the NH$_3$ linestrengths at 2.3 μm are a few times larger than at 1.5 μm, the commercial availability and field-tested durability of room-temperature diode lasers at the shorter
Table 5.1: Locations of six NH₃ features and their appropriate monitoring applications, along with the Table reference that lists pertinent spectroscopic parameters.

<table>
<thead>
<tr>
<th>Feature</th>
<th>Location [cm⁻¹]</th>
<th>Location [nm]</th>
<th>Application</th>
<th>Spectroscopy</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6528.9</td>
<td>1531.7</td>
<td>Air-quality monitoring</td>
<td>Table 5.2</td>
</tr>
<tr>
<td>2</td>
<td>6548.7</td>
<td>1527.0</td>
<td>Emissions monitoring</td>
<td>Table 5.3</td>
</tr>
<tr>
<td>3</td>
<td>6568.4</td>
<td>1522.4</td>
<td>Air-quality monitoring</td>
<td>Table 5.4</td>
</tr>
<tr>
<td>4</td>
<td>6596.4</td>
<td>1516.0</td>
<td>Emissions monitoring</td>
<td>Table 5.5</td>
</tr>
<tr>
<td>5</td>
<td>6600.0</td>
<td>1515.2</td>
<td>Emissions monitoring</td>
<td>Table 5.6</td>
</tr>
<tr>
<td>6</td>
<td>6678.4</td>
<td>1497.4</td>
<td>Air-quality monitoring</td>
<td>Table 5.7</td>
</tr>
</tbody>
</table>

wavelengths [25] make the 1.5 μm region a superior choice at present for commercial sensor development and application for emissions-monitoring.

Ammonia’s spectroscopy in the near-infrared is complicated, with many strong and overlapping lines that are difficult to resolve. Moreover, spectroscopic databases such as GEISA [37] and HITRAN96 [72] do not contain ammonia’s near-infrared spectra. Though there are many published papers that discuss NH₃ monitoring at 1.5 μm [4,5, 21,23,24,30,63,95,96], and many papers that address fundamental NH₃ spectroscopy at other wavelengths [7–9,14,27,29,44,49,67,75,76,82–84,86,87], few investigate the fundamental spectroscopic parameters at 1.5 μm. However, two papers by Lundsberg-Nielsen are available that extensively catalog the lines, positions, and strengths of NH₃ absorption at 1.5 μm [46,47]. Unfortunately, these works were performed in the optically thick regime, distorting the linestrength measurements for the strongest NH₃ lines and making the features difficult to resolve. Moreover, a recent paper by Modugno and Corsi [59] investigates two regions of the 1.5 μm band (6475–6494 and 6685–6700 cm⁻¹), but does not study the many strong NH₃ lines between these ranges.

Figure 5.2 shows a survey spectrum of ammonia transitions over the range 1492–1550 nm (6450–6700 cm⁻¹) that was recorded with the ECDL. Most of these transitions are a part of the ν₁+ν₃ and 2ν₃ combination and overtone bands, though other bands such as the 2ν₁, ν₁+2ν₄, and ν₃+2ν₄ are also present [7,46] (See Section 2.2.3). By overlaying the measured survey spectra with calculated H₂O and CO₂ absorbance for the two applications, different ammonia features can be identified that are useful for interference-free monitoring. Six NH₃ features are indicated on this survey: three
that are appropriate for emissions-monitoring applications, and three for air-quality monitoring. Table 5.1 lists the feature locations and the applications for which they are useful. Note that each feature contains anywhere from 3 to 9 different transitions. The pertinent spectroscopic parameters for these features are summarized in Tables 5.2–5.7.

The top panel of Figure 5.3 shows three isolated and pressure-broadened NH\textsubscript{3} features that are useful for emissions-monitoring overlaid with the calculated spectral interference of H\textsubscript{2}O and CO\textsubscript{2}. Of the combustion products, H\textsubscript{2}O typically offers the most spectral interference in the NIR. Thus, stoichiometric methane-air combustion product populations (19\% H\textsubscript{2}O, 9.5\% CO\textsubscript{2}) were used to model the interference spectra. The calculated interference was based on HITRAN96 linestrengths at a temperature of T=400 K [72] and stoichiometric methane-air combustion product populations for H\textsubscript{2}O and CO\textsubscript{2}. The bottom panel of Figure 5.3 shows three NH\textsubscript{3} features overlaid with the calculated interference for 85\% standard humidity conditions (X\textsubscript{H\textsubscript{2}O}=2.2\%).

All six features are isolated from interfering species and have linestrengths that are suitable for sensitive detection over 1-m pathlengths at temperatures below 600 K (S\textsubscript{i} > 0.01 cm\textsuperscript{-2}atm\textsuperscript{-1}). Their high-resolution spectra and multi-line Voigt peak fits are shown in Figure 5.4. Of the three suitable air-quality monitoring features, the one at 6528 cm\textsuperscript{-1} offers the best balance between overall feature strength and limited blending, thereby simplifying the peak-fitting process. The lines at 6548 cm\textsuperscript{-1} are the best choice for emissions monitoring because they have the least interference from combustion species, have less blending than the other two features, and are relatively strong, even at elevated temperatures. The latter lines are approximately twice as strong as the best lines identified by Modugno and Corsi [59].

\section{5.2 Spectroscopic Results}

Before an ammonia sensor could be developed, the positions, strengths, and lower-state energies of the absorption lines contained in each of the six aforementioned NH\textsubscript{3} features needed to be verified. The first task was to use high-resolution spectroscopy at room-temperature and low-pressures to determine the number of lines contained
Figure 5.3: Top Panel: Measured ammonia features at 6548, 6596, and 6600 cm\(^{-1}\) overlaid with the calculated absorbances of X\(_{\text{H}_2\text{O}}\)=19\% and X\(_{\text{CO}_2}\)=9.5\% for the products of a stoichiometric methane-air flame. Bottom Panel: Measured ammonia features at 6528, 6568, and 6678 cm\(^{-1}\) overlaid with the absorbance of X\(_{\text{H}_2\text{O}}\)=2.2\% corresponding to 85\% standard atmospheric humidity.
5.2. SPECTROSCOPIC RESULTS

in each NH₃ feature, as well as their individual linestrengths and positions.

As Figures 5.2 and 5.4 demonstrate, the NIR spectrum of NH₃ is very crowded and contains many overlapping transitions. The multitude of lines is a result of ammonia’s inversion-doubling [33], and the coincidence of several harmonic and combination bands at 1.5 µm, including the ν₁+ν₃, 2ν₃, and ν₃+2ν₄ bands [7,47]. Moreover, ammonia’s strong dipole creates broad lineshapes as a result of dipole-dipole interactions during collisions [8,49,65,85,87], causing many of these neighboring lines to overlap.

The six features shown in Figure 5.4 are typical examples of the spectra near 1.5 µm. All six features have several lines close together in frequency, many of which cannot be completely isolated even at low pressures. At the higher pressures that will be prevalent for the monitoring applications, these lines become strongly blended. Determining the spectroscopic parameters of each individual transition within these overlapping features thus requires high-resolution spectroscopy that employs low pressures (1-15 Torr) and longer pathlengths. Typical single-sweep data for these high-resolution scans are shown in Figure 5.4. Because of the blended nature of the features, multi-line Voigt peak fits were needed to extract the integrated area for each individual transition, and thus the linestrength, Sᵢ. These individual fits are illustrated as broken curves for each feature in Figure 5.4.

The uncertainty for many of the individual linestrength measurements was estimated to be < 3% due to measurement uncertainties of 1% in the total pressure, 1% in the total pathlength, and 2% in the area under each Voigt profile. The measurement uncertainty based on spread in the data agreed with the expected uncertainty for strong and isolated lines at room temperature. However, for strong lines that are blended such as those in the feature at 1516 nm, the difficulties in accurately determining the baseline and separating the areas of different transitions increases the uncertainty to 5–6% at room temperature. For lines that are both weak and blended, we estimate the uncertainty is 10–12%. At higher temperatures, “hot lines” emerge, crowding the six spectral features and further increasing the linestrength measurement uncertainties.

Figure 5.5 compares the measured spectra for the six features in Table 5.1 with
Figure 5.4: Recorded high-resolution spectra and multi-line Voigt fits of the six ammonia features selected for monitoring in atmospheric and combustion applications.
(pure NH$_3$, P=5.6 Torr, L=40 cm, T=20°C)
Figure 5.5: Comparison of measured spectra for the six features in Table 5.1 with the calculated spectra based on linestrengths and positions from [46, 47], and broadening coefficients from [49, 65, 85, 87]. (pure NH$_3$, P=5.6 Torr, L=40 cm, T=20°C)
calculated spectra based on the published line positions and strengths in Lundsberg-Nielsen [46, 47], and average published broadening parameters of $\gamma_{\text{NH}_3-\text{NH}_3} = 0.45$ and $\gamma_{\text{NH}_3-N_2} = 0.10 \text{ cm}^{-1}\text{atm}^{-1}$ [49, 65, 85, 87]. In general, the published and measured features agree qualitatively in shape and position. However, there are many differences that emerge regarding the number of lines in each feature, and the specific line positions and linestrengths of the individual lines. The recorded spectra of the six features, as determined by this work, contain 26 transitions (see Tables 5.2–5.7), 5 of which were not listed by Lundsberg-Nielsen. Moreover, Lundsberg-Nielsen lists an additional 14 transitions that were not seen in this research effort.

The biggest differences between the published values and the results in this work occur wherever there are blended features. For isolated transitions of moderate strength (0.005 < $S$ < 0.06), such as the lines at 6548.92, 6568.46 and 6596.53 cm$^{-1}$, the measured line positions and strengths agree with the published values. Features that blend a strong line with a weak line, such as 6548.6, 6568.3, and 6678.3 cm$^{-1}$, are listed by Lundsberg-Nielsen as two equally strong lines. The resolved spectra in this work elucidate the blending and relative linestrengths of these neighboring lines. For the feature at 6596.4 cm$^{-1}$, the previously published work fails to include the two distinct lines at 6596.41 and 6596.43 cm$^{-1}$, instead listing them as one combined line at 6596.42 cm$^{-1}$. Moreover, Lundsberg-Nielsen lists weak lines near 6528.83, 6548.70, 6599.96 and 6678.38 cm$^{-1}$ that were not seen in the recorded spectra in this work. In addition, the linestrengths of the individual strong lines listed in Lundsberg-Nielsen are often underpredicted by 10–20% as compared with the linestrengths measured in this work. Because the room-temperature measurements presented in this work were made in the optically thin regime and with low experimental uncertainty, we consider them to represent improvements over previously published values.

Since ammonia monitoring is pertinent for a range of elevated temperatures, determining how the NH$_3$ linestrengths change as a function of temperature is important. For each feature, the linestrengths were measured at 5–11 temperatures between room temperature and 725 K, with 3–5 different pressures at each temperature. The strongest lines in each of the six NH$_3$ features decreased in strength with increasing temperature, however most features had weak lines that became stronger, and some
had hot lines that were not measurable at room temperature, but then became visible at the elevated temperatures.

Figure 5.6 shows the variations in linestrength with increasing temperature for the lines in the feature near 6548 cm$^{-1}$ (1527 nm). The three strongest room-temperature lines (6548.60, 6548.79, and 6548.92 cm$^{-1}$) decrease in strength with increasing temperature, while the weakest line (6548.64 cm$^{-1}$) gains strength, and a fifth hot line (6548.69 cm$^{-1}$) that was not measured at the lower temperatures emerges at higher temperatures.

Using the data for the measured linestrengths as a function of temperature and Equations 3.9 and 2.7, an exponential fit was performed for each transition to determine the best-fit room temperature reference linestrength $S_o$ and the lower-state energy $E''$. Of the 35 lines in the 6 features, Lundsberg-Nielsen assigned 9 of them to the $\nu_1+\nu_3$ band. Using these assignments and the lower-state energies calculated by Urban, et al. [84] yields the assigned lower-state energies.

The measured lower-state energies in this work were compared with the assigned lower-state energies as a check on the accuracy of the line assignment, and agreed within uncertainty for four of the lines, but disagreed for five of the lines. For the disagreements, the measured values were 20-40% higher than the assigned values. The
disagreements were restricted to the lower-state energy measurements in the features at 1527 and 1516 nm. These differences could be the result of the highly overlapping nature of these features, leading to erroneous high-temperature linestrength measurements or erroneous line assignments. The overlapping lines of these features, especially at high temperature, introduces the possibility of linestrength uncertainties due to the difficulties of accurately determining the baseline and the individual peak areas. In addition, the ground-state combination differences (GSCD) line assignment technique employed by Lundsberg-Nielsen requires thorough knowledge of many lines throughout the band, which is a task complicated by the many blended lines. If lines are missing, as was the case for the published work, then the assignment procedure could include some degree of uncertainty. The source of disagreement is currently not clear.

The lower-state energies and reference linestrengths can be used to predict the minimum ammonia detectivity for in situ combustion monitoring applications. Using a noise equivalent absorbance (NEA) of 1.6e-5, which has been demonstrated for balanced circuit detection schemes [35, 53] and a pathlength L=1 m, the minimum detectivity for the line at $6548.60 \text{ cm}^{-1}$ varies from 1.5 ppm at room-temperature, up to 4 ppm at 700 K for a SNR=1.

Table 5.2 compiles the measured and published spectroscopic parameters for the
first feature in Table 5.1. The measured parameters include line position, line strength, and lower-state energy along with their respective experimental uncertainties. The table also includes published values for comparison, with \( \nu_0 \) and \( S_0 \) from [46], and \( E'' \) from [84], based on the line assignments and symmetry (\( J', K', J'', K'' \), \( \sigma \)) which are from [47]. Lines a, d, and g in Table 5.2 show agreement between the published and measured line positions, but the measured linestrengths yield improved values that are 45–70% stronger than the published values. Lines b, c, and e in the table list transitions from the published literature that were not measured in this work, suggesting that either those transitions do not occur at the specified frequencies, or that the published linestrengths are overpredicted. Line f lists a “hot line” that was not detectable at room temperature, but gains in strength with increasing temperature. Tables 5.3–5.7 summarize the spectroscopic parameters for the other 5 features listed in Table 5.1 in a similar fashion.

While these tables of measured parameters do not comprise a complete atlas of the ammonia spectrum near 1.5 \( \mu \text{m} \), they do provide improved quantitative values for pertinent spectroscopic parameters for the six ammonia features that have been carefully studied with high resolution. Note that Table 5.1 suggests sensor applications that are appropriate for each of the six features.
Table 5.2: Comparison of measured and published parameters for the ammonia feature at 1531 nm (6528 cm$^{-1}$).

<table>
<thead>
<tr>
<th>Feature # 1: Air-Quality Monitoring</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experimental Data</strong></td>
</tr>
<tr>
<td>$\nu_0$</td>
</tr>
<tr>
<td>6528.76</td>
</tr>
<tr>
<td>6528.89</td>
</tr>
<tr>
<td>6529.11</td>
</tr>
<tr>
<td>6529.18</td>
</tr>
</tbody>
</table>

$\nu_0$ Linecenter [cm$^{-1}$]

$S_o$ Linestrength [cm$^{-2}$atm$^{-1}$] at $T_o = 296$ K

$\sigma_s$ Standard deviation of the measured linestrength $S_o$ [cm$^{-2}$atm$^{-1}$]

$S_{o, fit}$ Linestrength [cm$^{-2}$atm$^{-1}$] at $T_o = 296$ K as determined by an exponential fit to $S(T)$ according to Equation 3.9

$E''_{fit}$ Lower-state energy [cm$^{-1}$] as determined by an exponential fit to $S(T)$ according to Equation 3.9

$\sigma_E$ Standard deviation in the fit for measuring $E''_{fit}$ [cm$^{-1}$]

$J', K'$ Upper-state symmetric top rotational quantum numbers

$J'', K''$ Lower-state symmetric top rotational quantum numbers

$\sigma$ Transition symmetry: symmetric (s), or asymmetric (a)

$E''$ Lower-state energy [cm$^{-1}$] based on transition assignment

— Transition is not seen in the measurements or is not listed in the literature

‡ Too weak to measure at room temperature

hot line Transition emerges at higher temperatures

† Unable to determine from exponential fit
5.2. SPECTROSCOPIC RESULTS

Table 5.3: Comparison of measured and published parameters for the ammonia feature at 1527 nm (6548 cm\(^{-1}\)).

<table>
<thead>
<tr>
<th>Experimental Data</th>
<th>Published Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu_0 )</td>
<td>( \nu_0 )</td>
</tr>
<tr>
<td>( S_o )</td>
<td>( S_o )</td>
</tr>
<tr>
<td>( \sigma_e )</td>
<td>( \sigma_e )</td>
</tr>
<tr>
<td>( S_{o,fit} )</td>
<td>( J' )</td>
</tr>
<tr>
<td>( \sigma_{E_{fit}} )</td>
<td>( K' )</td>
</tr>
<tr>
<td>( E''_{fit} )</td>
<td>( J'' )</td>
</tr>
<tr>
<td>( \sigma_{E''} )</td>
<td>( K'' )</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>( \sigma )</td>
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<td>( \sigma_e )</td>
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<td>( S_{o,fit} )</td>
<td>( J' )</td>
</tr>
<tr>
<td>( \sigma_{E_{fit}} )</td>
<td>( K' )</td>
</tr>
<tr>
<td>( E''_{fit} )</td>
<td>( J'' )</td>
</tr>
<tr>
<td>( \sigma_{E''} )</td>
<td>( K'' )</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>( \sigma )</td>
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</tbody>
</table>

Table 5.4: Comparison of measured and published parameters for the ammonia feature at 1522 nm (6568 cm\(^{-1}\)).

<table>
<thead>
<tr>
<th>Experimental Data</th>
<th>Published Data</th>
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</thead>
<tbody>
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<tr>
<td>( \sigma_e )</td>
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<tr>
<td>( S_{o,fit} )</td>
<td>( J' )</td>
</tr>
<tr>
<td>( \sigma_{E_{fit}} )</td>
<td>( K' )</td>
</tr>
<tr>
<td>( E''_{fit} )</td>
<td>( J'' )</td>
</tr>
<tr>
<td>( \sigma_{E''} )</td>
<td>( K'' )</td>
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<tr>
<td>( \sigma )</td>
<td>( \sigma )</td>
</tr>
<tr>
<td>( \nu_0 )</td>
<td>( \nu_0 )</td>
</tr>
<tr>
<td>( S_o )</td>
<td>( S_o )</td>
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<tr>
<td>( \sigma_e )</td>
<td>( \sigma_e )</td>
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<tr>
<td>( S_{o,fit} )</td>
<td>( J' )</td>
</tr>
<tr>
<td>( \sigma_{E_{fit}} )</td>
<td>( K' )</td>
</tr>
<tr>
<td>( E''_{fit} )</td>
<td>( J'' )</td>
</tr>
<tr>
<td>( \sigma_{E''} )</td>
<td>( K'' )</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>( \sigma )</td>
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</tbody>
</table>
Table 5.5: Comparison of measured and published parameters for the ammonia feature at 1516 nm (6596 cm$^{-1}$).

<table>
<thead>
<tr>
<th>Feature # 4: Emissions Monitoring</th>
<th>Published Data</th>
</tr>
</thead>
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<tr>
<td><strong>ν$_0$</strong></td>
<td><strong>S$_0$</strong></td>
</tr>
<tr>
<td>6596.20</td>
<td>0.0015</td>
</tr>
<tr>
<td>6596.29</td>
<td>0.0179</td>
</tr>
<tr>
<td>6596.34</td>
<td>0.0125</td>
</tr>
<tr>
<td>6596.38</td>
<td>0.0175</td>
</tr>
<tr>
<td>6596.41</td>
<td>0.0161</td>
</tr>
<tr>
<td>6596.43</td>
<td>0.0108</td>
</tr>
<tr>
<td>6596.53</td>
<td>0.0053</td>
</tr>
<tr>
<td>6596.68</td>
<td>†</td>
</tr>
<tr>
<td>6596.79</td>
<td>†</td>
</tr>
</tbody>
</table>

Table 5.6: Comparison of measured and published parameters for the ammonia feature at 1515 nm (6600 cm$^{-1}$).

<table>
<thead>
<tr>
<th>Feature # 5: Emissions Monitoring</th>
<th>Published Data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>ν$_0$</strong></td>
<td><strong>S$_0$</strong></td>
</tr>
<tr>
<td>6599.81</td>
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</tr>
<tr>
<td>6599.89</td>
<td>0.0330</td>
</tr>
<tr>
<td>6599.95</td>
<td>†</td>
</tr>
<tr>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>6600.03</td>
<td>0.0019</td>
</tr>
<tr>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>6600.08</td>
<td>0.0061</td>
</tr>
<tr>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>6600.18</td>
<td>0.0310</td>
</tr>
<tr>
<td>6600.25</td>
<td>†</td>
</tr>
</tbody>
</table>
5.3. NH₃-SLIP SENSOR DEMONSTRATION

Using the spectroscopic information listed above, a sensor was developed and tested to demonstrate the feasibility of interference-free NH₃-slip monitoring in combustion applications using the absorption feature near 6548 cm⁻¹. The experimental schematic is shown in Figure 5.8. The combustor consisted of a lean premixed ethylene-air flat-flame atmospheric pressure burner operating at an equivalence ratio of $\phi \approx 0.7$, a vertical exhaust stack, and a 120-cm long horizontal stack section 79 cm above the burner. Windows at the ends of the 3.8-cm diameter horizontal section permitted optical access for the absorption measurements. The gas temperature along the horizontal section decreased linearly from 530 to 410 K, as measured with a type-T thermocouple at 12 locations along the stack.

Gaseous NH₃ was injected into the exhaust 18 cm above the burner to simulate typical Thermal DeNOₓ and SCR applications, for which NH₃ is injected downstream of the combustion and then allowed to mix with and destroy the NOₓ population. The temperature of the exhaust gases at the injection location was approximately
Figure 5.8: Schematic for the ammonia slip experiment. Measurements of NH$_3$ slip in the exhaust of a premixed ethylene-air-ammonia flame are made in a horizontal stack 79 cm above the burner.
5.3. NH₃-SLIP SENSOR DEMONSTRATION

Figure 5.9: Measured absorbance data for NH₃ feature #2 near 6548 cm⁻¹ (1527 nm) in the post-flame gases above an ethylene-air-ammonia premixed flame (P=1 atm, L=240 cm, T=465 K). A CO₂ feature is shown near 6548.3 cm⁻¹.

850 K. In general, methane-air premixed combustion produces the greatest amount of spectral interference because of the large quantities of hot H₂O in the exhaust. However, for the feature at 6548 cm⁻¹, CO₂ interference is prominent. Therefore, for this experiment, ethylene (C₂H₄) was chosen as the fuel to produce greater amounts of CO₂ and to provide a stricter test of the diode laser sensor.

The optical system consisted of a fiber-coupled DFB at 1527 nm to probe ammonia feature #2, a flipper mirror and solid etalon to measure the laser’s frequency variation during tuning, and a two-pass configuration through the exhaust stack for a total pathlength of 240 cm. For the stack measurements, the DFB was scanned at 1250 Hz and 20-sweep averages were used to reduce high-frequency noise, yielding a measurement bandwidth of 62.5 Hz (16 ms measurement time) and an MDA of 4 × 10⁻⁵, corresponding to 5 ppm-m minimum detectivity for a SNR=1.

Figure 5.9 shows the measured results for in situ monitoring of NH₃ in the exhaust gases into which NH₃ had been seeded. The data correspond to ammonia
mole fractions in the range of 22–144 ppm, as inferred from Voigt fits to the absorbance signals. Figure 5.10 shows the absorbance data for the condition at which the mole fraction is measured to be 40 ppm. A CO$_2$ feature at 6548.3 cm$^{-1}$ is shown on the same plot, demonstrating the ammonia feature’s avoidance of the spectral interference. Moreover, the areas of the NH$_3$ features decrease linearly with NH$_3$ concentration, indicating that there are no hidden H$_2$O or CO$_2$ transitions buried underneath the NH$_3$ feature. Using frequency modulation [79] or auto-balancing circuit techniques [35] should improve the SNR by another order of magnitude, potentially yielding sub-ppm sensitivities for the \textit{in situ} sensor. In addition, longer pathlengths can be employed at industrial-scale combustor stacks, which will also improve the sensor’s minimum detectivity. Therefore, the validity of a diode-laser based NH$_3$-slip absorption sensor near 1.5 $\mu$m capable of measuring ppm concentrations has been demonstrated.
5.4 Conclusions

The spectroscopy of ammonia near 1.5 $\mu$m has been thoroughly investigated to select appropriate absorption transitions for in situ ammonia monitoring in air-quality and combustion emissions applications using diode laser sensors. Six features were identified that offer a good balance of sensitivity and interference-free detection: 3 features for air-quality monitoring, and 3 features for emissions-monitoring.

Survey spectra were recorded in a static cell by tuning an ECDL over its entire range (1496–1582 nm). High resolution absorption measurements of the six selected features were made by scanning the ECDL approximately 1 cm$^{-1}$ over individual features. Fundamental spectroscopic parameters for the six NH$_3$ features, including line positions, linestrengths, and lower-state energies, were measured in room-temperature and heated static cells. These measured parameters were compared with previously published data and many discrepancies in the number and strengths of lines were noted. Unlike previously published measurements, the results reported here were obtained in optically thin conditions. Thus, we expect these results are an improvement on the pertinent parameters for the six selected features.

A measurement application was used to demonstrate the capacity for interference-free NH$_3$ monitoring with diode laser sensors in the combustion gases above a pre-mixed ethylene-air flame with NH$_3$ injection. Over a 2.4 m pathlength, interference-free measurements of 22–144 ppm of NH$_3$ are demonstrated with a noise equivalent absorbance (NEA) of $4 \times 10^{-5}$ that corresponds to a 5 ppm-m minimum detectivity at a SNR=1, verifying the feasibility of the diode laser sensor near 1.5 $\mu$m for in situ monitoring of single-digit ppm concentrations of NH$_3$-slip.
Chapter 6

*In situ* Flame Monitoring of CO$_2$ at 2.0 \( \mu m \)

The objective of the present research is to develop an *in situ* CO$_2$ diagnostic for combustion applications based on recently available DFB diode lasers operating near 2.0 \( \mu m \), which offers access to CO$_2$’s strong absorption band near 2.0 \( \mu m \). To meet the objective of this research, a candidate CO$_2$ absorption transition was selected (the R(50) line at 1.997 \( \mu m \)), its fundamental spectroscopic parameters were investigated, and measurements of CO$_2$’s presence in a combustion zone using the candidate transition were made to demonstrate the viability of the sensor and to verify the spectroscopic measurements.

### 6.1 Line Selection

Figure 6.1 graphically depicts the near-infrared (NIR) linestrengths of carbon dioxide and water over a range of wavelengths from 1 to 3 \( \mu m \) at a temperature of 1500 K [72]. The absorption bands near 1.55 \( \mu m \) overlap conveniently with commercially-available telecommunications diode lasers and thus have been used for previous measurements of CO$_2$. However, as can be seen by Figure 6.1, sensors at 2.0 \( \mu m \) can access linestrengths that are approximately 2 orders of magnitude larger than at 1.55 \( \mu m \). Thus, diagnostics that employ these longer wavelengths offer greater sensitivity.
CHAPTER 6. IN SITU FLAME MONITORING OF CO\textsubscript{2} AT 2.0 µM

Figure 6.1: Calculated water and carbon dioxide linestrengths in the near infrared at 1500 K [72].

Figure 6.2: Calculated spectra of 10% CO\textsubscript{2} and 10% H\textsubscript{2}O near 1.997 µm at combustion conditions ($L = 10$ cm, $P = 1$ atm, $T = 1500$ K). The R(50) and R(56) transitions of the $\nu_1 + 2\nu_2 + \nu_3$ band at 5007.787 and 5010.035 cm$^{-1}$, respectively, are partially isolated from high-temperature water interference.
6.2. SPECTROSCOPIC RESULTS

Calculated absorption spectra based on the Hitran96\(^1\) database near 2.0 \(\mu m\) were compared for combustion conditions (\(T=1500\) K, 10% H\(_2\)O, 10% CO\(_2\), balance air, \(P=1\) atm, \(L=10\) cm) and used to find isolated CO\(_2\) transitions. As can be seen in Figure 6.2, both the R(56) and R(50) transitions are relatively isolated and thus are candidate lines for use with a diode laser absorption sensor. Previous measurements of CO\(_2\) near 2.0 \(\mu m\) employed a research-grade ECDL and were restricted to interrogating the R(56) line at 5010.035 \(cm^{-1}\) for combustion monitoring [55,57]. However, this transition’s absorption records were affected by non-negligible spectral interference from neighboring high-temperature H\(_2\)O lines and required complicated 7-line Voigt fits to extract the partial pressure of CO\(_2\). The R(50) transition offers stronger absorption and superior isolation from high-temperature H\(_2\)O spectra in combustion environments than the R(56) line, and thus was selected for the diode laser sensor in this work.

6.2 Spectroscopic Results

An understanding of the linestrength and lineshape variations with pressure and temperature aids in the development of CO\(_2\) sensors for combustion environments. Figure 6.3 shows the results of pressure broadening at room temperature near 5008 \(cm^{-1}\) for pure CO\(_2\). At elevated pressures and moderate temperatures, neighboring CO\(_2\) transitions can overlap due to strong collisional broadening. Moreover, the linestrengths and broadening (and thus the overlap) will change with temperature. Therefore, measurements of the fundamental spectroscopic parameters are important for developing accurate sensors.

Figure 6.4 shows a typical static-cell absorption lineshape overlaid with a best-fit Voigt profile. The peak-normalized residual is less than 2% with a standard deviation of 0.5%, yielding a signal-to-noise ratio (SNR) of approximately 200, and has no structure, indicating that the Voigt profile adequately models the absorption lineshape. The high-frequency component in the residual is likely the result of an accidental

\(^1\)Hitran96 was used instead of Hitemp for these simulations because the Hitemp database was found to have many errors at 2 \(\mu m\) for high temperature CO\(_2\) linestrengths. [57]
Figure 6.3: Absorbance of pure CO$_2$ for various pressures near 5008 cm$^{-1}$ ($T = 294$ K, $L = 40$ cm).

Figure 6.4: Sample lineshape for static cell measurements of CO$_2$ absorbance at 5007.787 cm$^{-1}$ (R(50) transition, $P = 68.1$ Torr, $L = 40$ cm, $T = 294$ K).
6.2. SPECTROSCOPIC RESULTS

Figure 6.5: Measured integrated absorbance area vs. CO$_2$ pressure at $T = 294$ K for the R(50) line at $\nu_0 = 5007.787$ cm$^{-1}$. The linestrength for this transition is inferred from the slope to be 0.001355 cm$^{-2}$atm$^{-1}$.

The linestrengths at a given temperature were determined from the slopes to linear fits on the integrated areas at various pressures, as described in Section 4.2.1 (See Figure 6.5). The total uncertainty for the individual linestrength measurements was estimated to be approximately 3%, resulting from measurement uncertainties of 1% in the total pressure, and 2% in the area under each Voigt profile. The room-temperature (294 K) linestrength of the R(50) transition was measured to be 0.001355 cm$^{-2}$atm$^{-1}$, which is approximately 7% higher than the linestrength calculated by Rothman, et al. [70] and listed in HITRAN96 (0.001268 cm$^{-2}$atm$^{-1}$). Since the total experimental uncertainty is approximately 3%, compared with 5% for the value in HITRAN96, and the lower measured value is consistent with other published linestrengths of CO$_2$ near 2 $\mu$m that are lower than HITRAN96 [20, 57, 58], we consider this measured linestrength to be an improvement over the published intensity.

The linestrength of the R(50) transition was determined for a range of elevated temperatures, as displayed in Figure 6.6. As described in Section 4.2.2, an exponential fit to the measured linestrengths at various temperatures was performed to infer the lower-state energy $E''$ and to check the accuracy of the transition’s quantum
assignment (the fit is overlaid in Figure 6.6 as a solid line). The lower-state energy was inferred to be $992 \pm 5$ cm$^{-1}$, which agrees with the value from HITRAN96 of $994.1913$ cm$^{-1}$ and thereby confirms the line assignment. The measured linestrengths are uniformly 7% higher than the values calculated in HITRAN96, which are overlaid as a broken line in the graph.

The estimated detectivity of the R(50) transition at a combustion temperature of 1500 K and atmospheric pressure is approximately 200 ppm-m, assuming a noise-equivalent absorbance of $1 \times 10^{-4}$. At a typical exhaust temperature of 500 K, the detectivity is approximately 50 ppm-m. Other transitions in the 2.0 $\mu$m band are more suitable for trace-gas detection at cooler temperatures.

The self-broadening coefficient was measured in a fashion analogous to the linestrength in the process described in Section 4.2.3. Room-temperature absorption measurements were made between 150 and 500 Torr, a pressure regime in which the collisional width is larger than the Doppler width, and thus collisional width estimates are of higher quality. For the R(50) transition, the room-temperature self-broadening coefficient was found to be $2\gamma_{\text{self}} = 0.149 \pm 0.004$ cm$^{-1}$ atm$^{-1}$, approximately 4% higher than

![Figure 6.6: Linestrength versus temperature for the R(50) transition at 5007.787 cm$^{-1}$.](image)
6.2. SPECTROSCOPIC RESULTS

Figure 6.7: Measured collisional widths vs. CO$_2$ pressure at T=294 K for the R(50) line at $\nu_0=5007.787$ cm$^{-1}$. The self-broadening coefficient for this transition is inferred from the slope to be 0.149 cm$^{-1}$atm$^{-1}$.

the value listed in Hitran96 (0.1436 cm$^{-1}$atm$^{-1}$) and 1.5% lower than the published calculation of 0.1514 cm$^{-1}$atm$^{-1}$ [69], both of which are within our experimental uncertainty. Self-broadening coefficients for the R(50) transition were determined for temperatures up to 1400 K, yielding a temperature exponent of $N = 0.521$, which is about 1.5% lower than the calculated value of 0.529 from Rosenmann, et al. [69]. The total uncertainty for the individual broadening coefficient measurements was estimated to be approximately 4% due to measurement uncertainties of 1% in the total pressure, and 3% in the Lorentzian width extracted from each broadened Voigt profile.

Measurements of room-temperature linestrength and self-broadening coefficients were also performed for the neighboring CO$_2$ transitions between 5007 and 5008.6 cm$^{-1}$. These spectroscopic parameters are summarized in Table 6.1 along with the published values for comparison. Since these results were obtained with only 3% experimental uncertainty for linestrength and 4% for broadening coefficients, it is expected that they are an improvement over the values listed in Hitran96, which have uncertainties between 5–10% for the linestrengths, and 10–20% for the broadening coefficients. Since the discrepancy between the measured and published values is not uniform for the different transitions that were investigated in this work, we do
not draw any conclusions about the overtone bandstrength in general. Note that the measured line positions for each of these transitions agreed with Hitran96 within the precision of the IR wavelength meter (0.01 cm$^{-1}$).

Table 6.1: Comparison of measured and published parameters for the CO$_2$ transitions neighboring 5007.787 cm$^{-1}$.

<table>
<thead>
<tr>
<th>$\nu_0$</th>
<th>Trans</th>
<th>$S_{0,M}$</th>
<th>$S_{0,H}$</th>
<th>$2\gamma_M$</th>
<th>$2\gamma_H$</th>
<th>$E_{S,M}$</th>
<th>$E_{S,H}$</th>
<th>$E_{\gamma,M}$</th>
<th>$E_{\gamma,H}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5006.979</td>
<td>R(48)</td>
<td>0.001892</td>
<td>0.001780</td>
<td>0.157</td>
<td>0.1462</td>
<td>3%</td>
<td>5%</td>
<td>4%</td>
<td>20%</td>
</tr>
<tr>
<td>5007.363</td>
<td>R(22)</td>
<td>0.000143</td>
<td>0.000160</td>
<td>0.174</td>
<td>0.1892</td>
<td>3%</td>
<td>10%</td>
<td>4%</td>
<td>10%</td>
</tr>
<tr>
<td>5007.787</td>
<td>R(50)</td>
<td>0.001355</td>
<td>0.001268</td>
<td>0.149</td>
<td>0.1436</td>
<td>3%</td>
<td>5%</td>
<td>4%</td>
<td>20%</td>
</tr>
<tr>
<td>5008.566</td>
<td>R(52)</td>
<td>0.000901</td>
<td>0.000888</td>
<td>0.146</td>
<td>0.1412</td>
<td>3%</td>
<td>5%</td>
<td>4%</td>
<td>20%</td>
</tr>
<tr>
<td>5008.580</td>
<td>R(24)</td>
<td>0.000148</td>
<td>0.000145</td>
<td>0.188</td>
<td>0.1852</td>
<td>3%</td>
<td>10%</td>
<td>4%</td>
<td>10%</td>
</tr>
</tbody>
</table>

$\nu_0$ Line center [cm$^{-1}$] from Hitran96

Trans Transition notation (branch, P or R; and lower-state rotational quantum number, $J''$)

$S_{0,M}$ Measured linestrength [cm$^{-2}$atm$^{-1}$] at $T_0 = 294$ K

$S_{0,H}$ Linestrength from Hitran96 [cm$^{-2}$atm$^{-1}$] at $T_0 = 294$ K

$2\gamma_M$ Measured self-broadening coefficient [cm$^{-1}$atm$^{-1}$] at $T_0 = 294$ K

$2\gamma_H$ Self-broadening coefficient from Hitran96 [cm$^{-1}$atm$^{-1}$] at $T_0 = 294$ K

$E_{S,M}$ Uncertainty for the measured room-temperature linestrength

$E_{S,H}$ Uncertainty for the room-temperature linestrength from Hitran96

$E_{\gamma,M}$ Uncertainty for the measured room-temperature broadening coefficient

$E_{\gamma,H}$ Uncertainty for the room-temperature broadening coefficient from Hitran96
6.3 Combustion Measurements

Figure 6.8 shows the experimental setup for the measurements of CO$_2$ concentration in the combustion region above a flat-flame burner. The 6-cm diameter flat-flame burner operated on premixed ethylene and air and used a shroud flow of N$_2$ to flatten the horizontal flame sheet, stabilize the flame’s outer edges, and minimize the entrainment of ambient air into the combustion region near the burner’s surface [66] (See Figure 6.9). The flows of ethylene and air were metered with calibrated rotameters. Fixing the air flow rate (30.9 L/min) and varying the ethylene flow rate (1.35–3.1 L/min) produced a range of equivalence ratios $\phi=0.6–1.44$ (limited by the burner, not the sensor). Uncertainty in the fuel flow rate, and thus the equivalence ratio, was approximately 2%. The temperature was uniform to within 8% variation across the plateau as measured by traversing a type-S thermocouple across the combustion region. A screen was placed horizontally roughly 5 cm above the flame to minimize the effects of a 10-Hz instability.

The diode laser system consisted of multiplexed lasers operating at 1.343, 1.392, 1.799 and 1.997 $\mu$m. The output beams from all four lasers were combined into one multimode optical fiber (50 $\mu$m core diameter, multimode, low-OH silica) and
CHAPTER 6. IN SITU FLAME MONITORING OF CO$_2$ AT 2.0 µM

Figure 6.9: Experimental schematic of the McKenna flat-flame burner [66].

directed through the combustion region using a collimating lens for simultaneous measurements of H$_2$O, CO$_2$, and gas temperature along a single optical path (24 cm nominal pathlength, four passes) 1.5 cm above the burner surface. The beam was demultiplexed after the combustion region with a diffraction grating (830 grooves/mm, 1.25-µm blaze angle), so that the transmitted intensity from each laser could be monitored independently. Standard and extended-wavelength InGaAs detectors (2-mm detector diameter, 300-kHz bandwidth) were used to record the transmitted beam intensities.

The width of the flame at each equivalence ratio was determined by traversing the thermocouple across the burner at the measurement height of 1.5 cm above the burner surface. The width of the flame was taken to be the distance between the points in the temperature distribution at which the temperatures were at least 95% of the core temperature, as shown in Figure 6.10. The optical pathlength at each equivalence ratio is 4 times the flame width, since 4 passes of the laser beam were used. Measurements of flame width were made at several equivalence ratios, and then a polynomial fit was used to estimate the pathlength at other equivalence ratios (See Figure 6.11). As the figure shows, pathlengths decreased with equivalence ratio.

The lasers were wavelength-scanned at 1250 Hz (800 µs per single sweep, 800 points per scan), to minimize beam-steering effects and low frequency (1/f) noise.
Figure 6.10: Temperature across the burner at the measurement height of 1.5 cm above the burner surface, as measured with a thermocouple. The width of the flame is shown on the plot as the distance between the locations where the temperature is at least 95% of the core temperature.

Figure 6.11: Pathlength across the burner (4 passes) as determined by temperature profiles measured with traversed thermocouples.
Detector voltages were sampled at 1 MHz with a 12-bit digital oscilloscope. Signals due to flame emission were typically less than 3% of the laser intensity and were subtracted from the transmission signals before analysis of the absorption spectra. The spectroscopic details of the water and temperature diagnostic are discussed in Sanders, et al. [73].

The recorded CO$_2$ mole fractions in the combustion region are displayed in Figure 6.12 and overlaid with the equilibrium values at the measured temperatures for equivalence ratios between 0.7 and 1.4. The measured concentrations agree within 10% of the equilibrium values throughout the lean and rich regimes. Temperature fluctuations and edge effects in the flame (especially in lean conditions) led to uncertainties in the effective pathlength (5%), which when combined with the uncertainty in the temperature measurement (3%), and uncertainty in the linestrengths (3%), produces an overall uncertainty of approximately 10%. Though this agreement is not suitable for fundamental flame studies, it is useful for tracking trends in CO$_2$ concentration for on-line control applications.

Figure 6.13 shows a sample data trace of a recorded CO$_2$ absorption lineshape.
6.4 Conclusions

A CO\textsubscript{2} sensor for combustion environments using diode laser absorption techniques has been developed and demonstrated. Calculated high-temperature absorption spectra of CO\textsubscript{2} and H\textsubscript{2}O were overlaid to find suitable transitions for \textit{in situ} monitoring,
yielding two candidates: the R(50) transition at 5007.787 cm\(^{-1}\) and the R(56) transition at 5010.035 cm\(^{-1}\). The R(50) transition was selected for the CO\(_2\) diagnostic based on its linestrength and isolation from water interference at combustion temperatures. Pertinent spectroscopic parameters \((S, \nu_0, E''', 2\gamma_{\text{self}})\) for this transition were measured and compared with the literature, resulting in an improved value for room-temperature linestrength with an uncertainty of 3\% and self-broadening coefficient with an uncertainty of 4\%. Measurements of CO\(_2\) concentration in the combustion region above a flat-flame burner at atmospheric pressure were made to verify the fundamental spectroscopic parameters and to demonstrate the capacity for \textit{in situ} monitoring using diode laser sensors near 2.0 \(\mu\text{m}\).
Chapter 7

Field Measurements of NH₃ and CO₂ in a Bioreactor at 2.0 µm

This chapter describes the process by which a sensor was designed and demonstrated for measuring NH₃ and CO₂ concentration concentrations in bioreactor vent gases over many hours at NASA-JSC. The sensor design needs to record trace (< 5 ppm) NH₃ and varying mole fractions of CO₂ over extended measurement periods to assess the bioreactor vent gas toxicity and general bioreactor efficiency.

7.1 Line Selection

Designing a laser-based sensor for NH₃ and CO₂ in the bioreactor vent gases requires careful selection of optimum transitions that offer adequate sensitivity over the range of expected mole fractions and isolation from potential interfering species. The main constituents of the bioreactor vent gases include N₂, 10 ppb – 15 ppm NH₃, 500 ppm–10% CO₂, and saturated water vapor. Trace amounts (< 10 ppb) each of NO₃ and NO₂ might also be present. Thus, for sensitive NH₃ detection, the strongest available and isolated transitions need to be selected. For CO₂ detection, a transition needs to be employed that offers sufficient signal at the low concentration end (500 ppm), yet is not optically thick for high concentrations (10%). Moreover, NH₃ transitions need to be chosen that are isolated from saturated water vapor and
Figure 7.1: Calculated H$_2$O, NH$_3$ and CO$_2$ linestrengths in the near infrared at 296 K [46,47,72].

CO$_2$, while CO$_2$ transitions need to be chosen that are isolated from saturated water vapor and NH$_3$.

Figure 7.1 shows the linestrengths of H$_2$O, NH$_3$, and CO$_2$ in the near-infrared between 1.4 and 2.5 $\mu$m. Similarly to the previous discussion in Chapters 5 and 6, the linestrengths in the 2.0 $\mu$m region are approximately 100 times stronger for CO$_2$ as compared with the telecomm wavelengths near 1.6 $\mu$m and the NH$_3$ linestrengths are approximately 3 times stronger than at 1.5 $\mu$m. Thus, using DFB diode lasers at the longer wavelengths offers the opportunity for more sensitive detection.

For the ammonia slip monitoring application described in Chapter 5, the 2.0 $\mu$m band is not appropriate due to the interference from high-temperature H$_2$O and CO$_2$. But for monitoring bioreactor vent gases, the 2.0 $\mu$m band is suitable because less water is present (less than 2% saturated water vapor in the vent gases compared with 10% water vapor in combustion exhaust); the temperatures are lower than for combustion emissions applications, and thus the H$_2$O interferences are diminished; and lower pressures are used, allowing for NH$_3$ transitions to be selected that are
isolated from CO$_2$ interference. The 2 $\mu$m band is also the best NIR choice for CO$_2$ monitoring because of the numerous strong and isolated lines that are available for the bioreactor vent gases.

Using an ECDL at 2 $\mu$m, survey spectra were recorded for NH$_3$ from 4900–5100 cm$^{-1}$ (1960–2040 nm), as shown in Figure 7.2. By overlaying the measured survey spectra of NH$_3$ with calculated populations of CO$_2$, candidate NH$_3$ transitions could be determined. The best choice for sensitive NH$_3$ monitoring in the presence of CO$_2$ and H$_2$O is the $^P$P$_3$(3)$_s$ transition at 5016.977 cm$^{-1}$. This transition is part of a doublet that offers the third strongest absorption in the measured survey spectra at 2 $\mu$m, but as figure 7.3 illustrates, is also isolated from H$_2$O interference. The selected feature does have some overlap in the wings from the P(32) transition of CO$_2$ at 5017.030 cm$^{-1}$ for large concentrations. This slight overlap enables a single scan to yield measurements of NH$_3$ and CO$_2$ simultaneously for instances during which the CO$_2$ concentration is greater than approximately 3%.

For bioreactor gas samples containing smaller amounts of CO$_2$ (< 3%), the R(50) line at 5007.787 cm$^{-1}$ employed for flame monitoring in Chapter 6 is also useful. Figure 7.4 shows the peak absorption for the R(50) and P(32) transitions at 5007.787
and 5017.030 cm$^{-1}$, respectively, for the sampling cell conditions over the range of expected CO$_2$ concentrations in the bioreactor gas samples (500 ppm–10%). By operating the DFB at different temperatures, both transitions are accessible with a single laser. The peak absorption of the P(32) varies from approximately 0.3% at $X_{CO_2} = 3\%$ up to 0.8% for $X_{CO_2} = 10\%$. The peak absorption for the R(50) transition varies from roughly 1% at $X_{CO_2} = 500$ ppm to 80% at $X_{CO_2} = 8\%$, thus it offers the dynamic range necessary to track the varying concentrations without being optically thick at the high end nor undetectable at the low end. Moreover, the transition is isolated from H$_2$O and NH$_3$ and offers the added simplicity of being a single Voigt line, in contrast with other transitions of CO$_2$ in the 2 $\mu$m band that overlap with CO$_2$ isotope transitions, and thus require multi-line fits.

Absorption from a flowing gas mixture of 9 ppm NH$_3$ (as inferred from the integrated absorbance area of the absorption transitions), 14 Torr CO$_2$, and a balance of N$_2$ through the 3600 cm multipass cell was measured with a single sweep of the laser from 5016.7 to 5017.1 cm$^{-1}$ (See Figure 7.5). The absorption spectra show five

Figure 7.3: Calculated spectra near 5017 cm$^{-1}$ for 1 ppm NH$_3$, 5% CO$_2$, and 2% H$_2$O (standard humidity).
7.2 Spectroscopic Results

Using the process described in Section 4.2, the linestrengths, positions and lower-state energy for the five NH$_3$ features near 5017 cm$^{-1}$ were determined, since these transitions blend into one feature even at sub-atmospheric pressures. A high-resolution image of the five absorption features measured in a static cell is depicted in Figure 7.6. Four of the five transitions in Figure 7.6 have been assigned to the $^P P_1(2)$ and $^P P_3(3)$ doublets, while the fifth feature has been assigned as the $^R Q_3(7)_s$ transition, all from the $\nu_3 + \nu_4$ perpendicular combination band [14,72,75,76].

The integrated area vs. pressure for the transition at 5016.977 cm$^{-1}$ is shown in
Figure 7.5: Demonstration measurements confirming NH$_3$'s isolation from interfering H$_2$O and CO$_2$ absorption at 5016.977 cm$^{-1}$ and the capacity to measure NH$_3$ and CO$_2$ simultaneously with a single laser sweep.
7.2. SPECTROSCOPIC RESULTS

Figure 7.6: High-resolution measurement of the NH$_3$ transitions near 5017 cm$^{-1}$.

Figure 7.7. The slope of the linear fit to the integrated area measurements yields the linestrength. The same process was performed to measure the linestrength of all five transitions near 5017 cm$^{-1}$, the results of which are summarized in Table 7.1. The measured linestrengths agreed with the published values at best within 0.9% for the transition at 5016.471 cm$^{-1}$, and at worst within 3.4% for the transition at 5016.665 cm$^{-1}$, both of which are well within the combined uncertainty from the measurements (±3%) and published values (5–10%). Since these high-resolution measurements had smaller uncertainty than those listed in Hitran96, we consider the measured values to be an improvement.

Measurements of linestrength at various temperatures are shown in Figure 7.8. The individual data points are overlaid with a solid line that indicates predicted values based on the measured room-temperature value and the corrected partition function as described in Chapter 2. The measured and predicted values agree within the measurement uncertainty, and thereby confirm the line assignment and lower-state energy of this particular transition. The same agreement was determined for the other four features near 5017 cm$^{-1}$. 
Figure 7.7: Integrated area vs. pressure for the $^3P_3(3)_s$ NH$_3$ transition at 5016.977 cm$^{-1}$. The slope of the linear fit yields a deduced room-temperature linestrength of 0.2160 cm$^{-2}$ atm$^{-1}$.

Figure 7.8: Measured linestrengths at various temperatures for the $^3P_3(3)_a$ NH$_3$ feature at 5016.802 cm$^{-1}$ overlaid with predicted values.
7.2. SPECTROSCOPIC RESULTS

The published line strengths, positions, and lower-state energy values are summarized in Table 7.1 for the five NH$_3$ features, along with measured line strengths for comparison. All the measured line positions agreed with Hitran96 values within the experimental uncertainty, and the published lower-state energies were consistent with the line strength versus temperature results presented here.

Table 7.1: Comparison of measured and published parameters for the ammonia transitions near 5017 cm$^{-1}$ (1993 nm).

<table>
<thead>
<tr>
<th>$\nu_0$</th>
<th>Linecenter from Hitran96 [cm$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transition</td>
<td>Standard spectroscopic transition notation: $\Delta K \Delta J_{K''}(J'')_{\sigma}$</td>
</tr>
<tr>
<td>$J', K'$</td>
<td>Upper-state symmetric top rotational quantum numbers</td>
</tr>
<tr>
<td>$J'', K''$</td>
<td>Lower-state symmetric top rotational quantum numbers</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Transition symmetry: symmetric (s), or asymmetric (a)</td>
</tr>
<tr>
<td>$E''$</td>
<td>Lower-state energy [cm$^{-1}$]</td>
</tr>
<tr>
<td>$S_{0,H}$</td>
<td>Linestrength from Hitran96 [cm$^{-2}$atm$^{-1}$] at $T_o = 293$ K</td>
</tr>
<tr>
<td>$S_{0,M}$</td>
<td>Measured Linestrength [cm$^{-2}$atm$^{-1}$] at $T_o = 293$ K</td>
</tr>
<tr>
<td>$\sigma_s$</td>
<td>Standard deviation of the measured linestrength $S_{0,M}$ [cm$^{-2}$atm$^{-1}$]</td>
</tr>
<tr>
<td>$\Delta S_0$</td>
<td>Difference between the Hitran96 and measured linestrengths [%]</td>
</tr>
</tbody>
</table>

Using the measured linestrengths, lower-state energy and Hitran96’s broadening coefficients, the minimum detectivity for the feature at 5016.977 cm$^{-1}$ is predicted for
Figure 7.9: Minimum detectivity for the NH$_3$ feature at 5016.977 cm$^{-1}$ for varying pressure conditions.

Varying pressures at 296 K in Figure 7.9. As the graph reveals, 100 Torr is the optimum pressure for sensitive detection (See Section 3.4 for a detailed description of the minimum detectivity calculations). At higher pressures, the NH$_3$ population increases and the neighboring lines become blended, but the peak signal remains roughly the same, so higher pressures do not offer increased ability to distinguish absorption signals from background noise. At lower pressures, the population of NH$_3$ molecules decreases, giving less overall signal. The minimum detectivity at 100 Torr and 296 K is roughly 0.25 ppm for NH$_3$ at 5016.977 cm$^{-1}$, assuming a minimum detectable absorbance, MDA=$5 \times 10^{-4}$, limited by the presence of interference fringes in the multipass cell. Overlaid on the graph is the minimum detectivity of the transition at 1531 nm for comparison, revealing a factor of three improvement in signal by using the longer wavelengths at 2 $\mu$m. The minimum detectivity for CO$_2$’s P(32) transition at 5007.787 cm$^{-1}$ is based on the measured data in Figure 7.12, and is estimated to be 40 ppm.

7.3 Experimental Setup

The experimental schematic for the sensor system developed by Rice University is shown in Figure 7.10. A 5 m polypropylene vent line from the GLS in the BWP
brought bioreactor vent gases to the Rice sensor system at a flow rate between 10–50 cc/min, yielding gas transport times from the vent to the multipass cell between 3 and 15 minutes. A water trap midway through the sampling line allowed for any condensate to be separated from the gases, leaving $N_2$, $CO_2$, $NH_3$, and remaining water vapor to be transported to the sensor. The laser source, drivers and detector system were changed in the Rice sensor to make it suitable for $2 \mu m$ detection of $NH_3$ and $CO_2$.

The sensor was comprised of a 0.3-$L$ multipass cell with 36-m optical pathlength and gas residence times between 6 and 30 minutes, as described in Section 4.1.3. Valves at the entry and exit of the cell in combination with a miniature vacuum pump controlled the cell pressure and flow rate. An operational pressure of 100 Torr was implemented for optimum $NH_3$ detectivity, as shown in Figure 7.9. An MKS Baratron pressure gauge monitored the cell pressure at all times. A heat jacket was wrapped around the cell and operated at a steady temperature of approximately $38^\circ C$, as monitored with two thermocouples at each end of the cell. This operational temperature was selected because it is hot enough to prevent water condensation on the walls and mirrors in the cell, but low enough to prevent thermal damage to the cell’s seals and optical components and to prevent significant reduction in linesstrength.

Radiation from a fiber-pigtailed DFB operating at 1993 nm for $NH_3$ measurements
and 1997 nm for CO₂ measurements was coupled into the multipass cell for a 36-m alignment, then focused onto an extended-wavelength response InGaAs detector using a parabolic mirror. The detector used a battery power supply to reduce electrical noise and was connected directly to the data acquisition system of a laptop computer. The laptop computer collected spectra once per minute during the data-collection window. The DFB laser was scanned at a 125 Hz repetition rate and was collected at an 87,500 Hz sampling frequency to provide 500 data points per sweep. One thousand consecutive averages were used to reduce electrical noise for NH₃ detection, yielding an overall measurement time of 8 seconds; 500 averages were used to detect CO₂, yielding a 4 second measurement time. Large interference fringes (roughly $5 \times 10^{-4}$ in magnitude, see Section 4.1.3), were the limiting factor for sensitivity.

### 7.4 Bioreactor Measurements

#### 7.4.1 2 µm Diode Laser Sensor Results

Using the Rice sensor system and 2 µm detection, measurements of NH₃ and CO₂ concentration were made over a 45-hour period at NASA-JSC, starting near 9:00 Central Date Time (CDT) on August 30, 2000 and ending near 6:00 CDT on September 1, 2000. Sample measurements of NH₃ and CO₂ concentration are illustrated in Figures 7.11 and 7.12. For the first 23 hours, measurements of NH₃ concentration were made every minute (See Figure 7.13), with exception of one 2.5-hour and one 6-hour window during which the sensor software locked up. The 23 hours of NH₃ measurements were followed by 6 hours of CO₂ measurements, with one small window during which adjustments to the software were made. NH₃ monitoring resumed for another 16 hours after the CO₂ collection time ended.

Figure 7.13 reveals the sensor’s ability to operate successfully for automated long-term and remote monitoring of sampled gases. The laser demonstrated very little frequency drift or power variation and operated reliably over the 45-hour measurement window, during which it scanned continuously. The concentration trends in this figure show the sensor’s capacity to track bioreactor events. Three of these events are listed
Figure 7.11: Sample measurement of 3.7 ppm NH$_3$ in the bioreactor vent gases.

Figure 7.12: Sample measurement of 540 ppm CO$_2$ in the bioreactor vent gases.
on the plot at the time of occurrence. First, the bioreactor was switched into a recycle mode at 14:00 CDT on the first measurement day, during which fresh samples of wastewater were not added to the system. Approximately 4 hours later, the NH$_3$ concentration began a steady decline. At approximately 21:00 CDT, nitric acid was added to lower the pH of the bioreactor and thereby reduce NH$_3$ concentration. The NH$_3$ concentration in the vent gases continues to drop, but whether that drop is due to the lower pH, the recycling, or both is difficult to discern.

At 8:00 CDT on the second measurement day, a fresh 1-L sample of wastewater was added to the bioreactor to replace a sample that had been removed for analysis. The CO$_2$ measurements indicate a slight rise in concentration within 2 hours of that sample addition, which is consistent with the increased TOC conversion underway in the BWP. The resumed NH$_3$ measurements at 14:00 CDT on the second day show NH$_3$ concentration at the limit of detectability, indicating that NH$_3$ levels continued to drop during the CO$_2$ measurement window.

Figure 7.13: Concentration measurements of CO$_2$ and NH$_3$ versus time over a 45-hour period.
Figure 7.14: NH₃ mole fraction records over a one-hour period overlaid with a 15-minute running average that corresponds to half the gas residence time in the cell. The standard deviation of the measurements during this period is less than 0.1 ppm.

From the bioreactor test data we infer the NH₃ sensor is quite stable. With the long residence time of sample fluids in the water recovery system, bioreactor events produce variation in the vent gases with a time constant of several hours. Gas residence times for the multipass cell are between 6 and 30 minutes, as described before. Thus, variations over shorter timeframes are indicative of sensor performance. Figure 7.14 shows the NH₃ mole fraction measurements over a one-hour period on August 30, 2000, with statistical variations about a mean of 4.2 ppm. Overlaid on the minute-by-minute measurements is a 15-minute running average, which is half the gas residence time for the slowest flow rates that were used. The typical variation from one measurement to the next is 3%, while the largest variation is less than 7%. The standard deviation of the measurements over this hour is 0.1 ppm. Thus, we conclude that oscillations in measured NH₃ mole fraction between 1 and 6 ppm during the first day of data collection are the result of real variations in the gas contents, rather than drift in the sensor system.
7.4.2 Comparison Measurements

1.5 µm Diode Laser Sensor Measurements

Measurements with diode laser sensors at 1531 nm were performed in the days prior and subsequent to the results in this work and are presented by Claps, et al. [19]. The measurements using lasers near 1.5 µm were not made simultaneously with the 2.0 µm measurements presented here; thus, a direct comparison cannot be made. However, the results from the shorter-wavelength measurements do provide a “rough” estimate for the order of magnitude concentrations that could be expected in the vent gases. For several days before the beginning of the 2.0 µm detection and for 1 week thereafter, the NH₃ concentrations in the bioreactor vent gases oscillated between 0 and 5.6 ppm. A similar oscillation is evident in Figure 7.13 in Day 1 between 10:00 and 18:00 CDT. The remainder of the NH₃ data in this work is dominated by the switch of the reactor to recycle mode and the change in pH. The subsequent Rice data beginning September 1, 2000 show similarly low concentrations of NH₃ mole fraction before the bioreactor was switched on again and the oscillations in NH₃ mole fraction resumed. That the results of the 2 µm laser sensor smoothly fit the overall time sequence of Rice data further suggests comparable sensor performance.

Aqueous Phase Measurements

In addition to the 1.5 µm diode laser results, measurements of aqueous ammonia concentrations in the packed-bed reactor were made once daily by the Advanced Water Recovery System research team at NASA-Johnson Space Center in the mornings using standard wet-chemistry techniques. These concentrations, in units of mg/L, can be converted to gas-phase equilibrium concentrations via Henry’s law, as explained in Appendix A. Table 7.2 summarizes the values for the days of the measurements in addition to one preceding and following day. Because these measurements were made at one instant in the day and in the packed-bed reactor, they serve only as a rough indicator of the order of magnitude concentration that can be expected in the bioreactor vent gases. These concentrations varied from just over 8 ppm down to 2.4 ppm over the 5-day period including the measurement window. A distinct reduction
Figure 7.15: Concentration measurements of NH$_3$ over time in the bioreactor vent gases using a laser at 1531 nm. [19]
Table 7.2: Aqueous-phase measurements of NH$_3$ concentration in the bioreactor and their corresponding equilibrium gas-phase NH$_3$ concentrations ($T = 291$ K, $P = 25$ psig).

<table>
<thead>
<tr>
<th>Date</th>
<th>[NH$_3$(Aq)] (mg/L)</th>
<th>$X_{\text{NH}_3}$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>29-Aug</td>
<td>20.7</td>
<td>8.3</td>
</tr>
<tr>
<td>30-Aug</td>
<td>19.9</td>
<td>8.0</td>
</tr>
<tr>
<td>31-Aug</td>
<td>10</td>
<td>4.0</td>
</tr>
<tr>
<td>1-Sep</td>
<td>14.5</td>
<td>5.8</td>
</tr>
<tr>
<td>2-Sep</td>
<td>6.1</td>
<td>2.4</td>
</tr>
</tbody>
</table>

in NH$_3$ concentration from 8.0 ppm on August 30, 2000, to 4.0 ppm August 31, 2000 is consistent with the results from the Stanford diode laser sensor, which shows a diminishing NH$_3$ population in the vent gases beginning at 18:00 on August 30 and continuing through midday August 31.

7.5 Conclusions

Sensors were designed for detection of trace NH$_3$ and varying concentrations of CO$_2$ in the vent gases of a bioreactor. A DFB laser operating near 2 µm offered significant gains in accessible absorption intensities, so the optimum transitions in that region were selected for use with the Rice sensor system. The Rice sensor system employed a multipass cell, which increased sensitivities and allowed for low-pressure operation to isolate the different absorption transitions. The Rice sensor system was adapted for operation at 2 µm and operated over a 45-hour period for quasi-continuous measurements of NH$_3$ and CO$_2$ concentration. Measurements of NH$_3$ concentration agreed roughly with values recorded by a 1.5 µm system in the days preceding and following the 2 µm measurements, and with once daily aqueous-phase measurements of ammonia. Trends in NH$_3$ and CO$_2$ concentration were consistent with different bioreactor events during the measurement period. A minimum detectivity of 0.25 ppm for NH$_3$ and 40 ppm for CO$_2$ was achieved using direct absorption and a 36-m multipass cell at 100 Torr.
Chapter 8

Conclusions

This thesis has described the preliminary design and demonstration of diode-laser based gas sensors for three industrial applications: 1) *in situ* ammonia-slip monitoring for combustion systems that employ Thermal DeNO\(_x\) and SCR; 2) *in situ* carbon dioxide sensing for combustion control applications; and 3) vent gas monitoring of ammonia and carbon dioxide for bioreactor ground tests. The design process has included selection of overall strategy (*in situ* versus extractive sampling) and determination of optimum sensor wavelengths with consideration for the conditions of the measurement environment (pressure, temperature, bath gas constituents) and the sensitivity needs of the sensor. Two in-lab combustion experiments and one set of field measurements were used to verify the feasibility of the different sensors. The successful implementation of these sensors for systems with different requirements has demonstrated the versatility of diode laser sensors for a range of detection needs and a variety of applications.

8.1 Summary

8.1.1 NH\(_3\) Monitoring at 1.5 \(\mu\)m

Diode laser absorption sensors to monitor air-quality and ammonia emissions were designed by investigating the spectroscopy of ammonia near 1.5 \(\mu\)m to select the
optimum transitions to interrogate. Six features were identified that offer a balance of sensitivity and interference-free detection: 3 features for air-quality monitoring, and 3 features for emissions-monitoring. Survey spectra of ammonia’s band near 1.5 µm were recorded in a static cell by tuning an ECDL over its entire range (1496–1582 nm), and high-resolution spectra were recorded by tuning over the six features that were selected for incorporation with the sensors. Fundamental spectroscopic parameters for the six NH$_3$ features, including line positions, linestrengths, and lower-state energies, were measured, yielding improvements to the published spectroscopic database.

Interference-free NH$_3$ monitoring was demonstrated with diode laser sensors that monitored the combustion gases above a premixed ethylene-air flame with NH$_3$ injection. Over a 2.4 m pathlength, measurements of 22–144 ppm of NH$_3$ were made using direct absorption with a minimum detectivity of 5 ppm-m. These demonstration measurements verify the feasibility of the diode laser sensor near 1.5 µm for in situ monitoring of single-digit ppm concentrations of NH$_3$-slip.

### 8.1.2 CO$_2$ Flame Monitoring at 2.0 µm

A CO$_2$ sensor for combustion environments using diode laser absorption techniques has been developed and demonstrated. Using calculated absorption spectra of CO$_2$ and H$_2$O, CO$_2$‘s R(50) absorption line at 5007.787 cm$^{-1}$ was determined to be the optimum transition to probe with a diode laser sensor, based on its linestrength and isolation from water interferences at combustion temperatures and populations. Pertinent spectroscopic parameters ($S$, $\nu_o$, $E''$, $2\gamma_{self}$) for this transition were measured and compared with the literature, resulting in an improved value for room-temperature linestrength and self-broadening coefficient. CO$_2$ mole fractions in the combustion region above a flat-flame burner at atmospheric pressure was measured with the sensors for a range of equivalence ratios, and measured values agreed within 10% with expected equilibrium levels. These measurements demonstrate the capacity for in situ CO$_2$ monitoring in combustion environments using diode laser sensors near 2.0 µm.
8.1.3 NH$_3$ and CO$_2$ Monitoring at 2.0 $\mu$m in Bioreactor Vent Gases

Sensors were designed for detection of trace NH$_3$ and varying mole fractions of CO$_2$ in the vent gases of a bioreactor during ground-testing. The sensor was comprised of a multipass flow-through sampling system developed at Rice University and a DFB laser near 2 $\mu$m. NH$_3$’s $P_P(3)_3$ transition of the $\nu_3 + \nu_4$ combination band at 5016.977 cm$^{-1}$ was selected due to its relative line strength and isolation from CO$_2$ and H$_2$O absorption. The R(50) and P(32) transitions of CO$_2$ at 5007.787 and 5017.030 cm$^{-1}$, respectively, were selected due to their isolation from NH$_3$ and H$_2$O and capacity for tracking CO$_2$ for a range of concentrations from 500 ppm to 10% without being optically thick for high concentrations and with sufficient signal for low concentrations. The fundamental spectroscopic parameters of the selected and neighboring transitions for NH$_3$ were measured to confirm the spectroscopic database and line assignments.

Quasi-continuous field measurements of NH$_3$ concentration were made at NASA-JSC over a 45-hour period, during which ammonia levels varied between 0–6 ppm. CO$_2$ concentrations were also monitored over 6 hours during the 45-hour measurement period using the same laser to probe CO$_2$’s R(50) transition, and population variations between 500–800 ppm were recorded. Measurements of NH$_3$ concentration agreed roughly with values recorded by a 1.5 $\mu$m system in the days preceding and following the 2 $\mu$m measurements, and with once daily aqueous-phase measurements of ammonia. A minimum detectivity of 0.25 ppm for NH$_3$ and 40 ppm for CO$_2$ was achieved using direct absorption and a 36-m multipass cell at 100 Torr. The measurements demonstrated the sensor’s ability to track changes in NH$_3$ and CO$_2$ concentration due to different bioreactor events.

8.2 Recommendations for Future Work

Many avenues of further research remain for extending the current work, four of which are suggested and described below.
8.2.1 Improvements to the NIR Spectroscopic Database for NH$_3$

An accurate atlas of absorption transitions for NH$_3$'s bands at 1.5 and 1.65 $\mu$m has not been compiled as of yet, so a need exists to fulfill that knowledge gap. Such a compendium of line positions and strengths can readily be accomplished at room temperature using ECDL's that are commercially-available for those wavelengths. Once a thorough listing of lines, positions, and transition strengths are available, spectroscopists can use that information to assign the transitions using a ground-state combinational difference technique. Since both bands overlap with lasers for telecommunications applications, they will continue to be attractive for sensing applications due to the availability of laser sources at those wavelengths, but first the spectroscopy needs to be known.

Measurements of NH$_3$ at the injection point for Thermal DeNO$_x$ or SCR might be valuable for on-line control control systems that need short time-response. However, such measurements are difficult because at the injection location the temperatures (approximately 1200 K) are higher than at the exhaust stack. These higher temperatures lead to correspondingly higher interference from water absorption and to weaker NH$_3$ transitions. The lines selected in this work at 1.5 $\mu$m for ammonia emissions-monitoring are unsuitable for in situ NH$_3$ detection at those higher temperatures due to the increased water interference. However, water absorption, even at high temperatures, is weak at 1.65 $\mu$m. Thus, NH$_3$'s 1.65 $\mu$m band might prove valuable for measurements of ammonia at the injection point, even though it is weaker than the 1.5 $\mu$m band. Because the NH$_3$ mole fractions at the injection point will be much higher than at the exit of the stack (hundreds of ppm instead of ppm), the transition strengths at 1.65 $\mu$m might be suitable for the application’s detection needs. Such a sensor cannot be developed, however, until NH$_3$’s spectroscopy at 1.65 $\mu$m has been thoroughly studied.
8.2.2 CO\textsubscript{2} Flame Sensing

One extension of the CO\textsubscript{2} detection work includes applying the sensor as a part of a multi-parameter combustion monitor for feedback control. Combustion measurements of H\textsubscript{2}O, CO\textsubscript{2}, CO and temperature have already been demonstrated [91]. Obtaining these parameters simultaneously and on-line enables combustion control applications that would seek to maximize T, CO\textsubscript{2}, and H\textsubscript{2}O, while minimizing CO emissions.

Another topic to explore includes measuring the concentration profile of CO\textsubscript{2} across combustion flows to improve the accuracy of line-of-sight CO\textsubscript{2} sensors. One of the difficulties with absorption sensors is their susceptibility to errors from non-uniformity in the optical path. For the CO\textsubscript{2} flame monitoring sensor described in Chapter 6, understanding the effective pathlength required careful measurement with thermocouples that had been traversed across the flame. However, thermocouples provide only a record of temperature uniformity, and for path-averaged CO\textsubscript{2} measurements, an understanding of the CO\textsubscript{2} concentration profile would be more valuable. The CO\textsubscript{2} profile can be determined using novel IR-PLIF imaging techniques, developed by Kirby and Hanson [40]. These images can be used for determining CO\textsubscript{2} profiles as a precursor to absorption measurements. Once these profiles are accurately known, the effective detection pathlength can be determined, thereby potentially reducing a large component of experimental uncertainty for the sensor.

8.2.3 NH\textsubscript{3} Detection in Bioreactor Vent Gases

Now that the feasibility for detecting NH\textsubscript{3} in bioreactor vent gases has been demonstrated for ground-testing, the next step is to improve the sensitivity. Because the limiting factor in this work for sensitivity was the presence of large interference fringes in the transmission path through the multipass cell, FM and auto-balanced detection do not offer much advantage. Instead, avoiding the fringes entirely by optimizing alignment or removing the fringes using piezoactuators as described in Section 4.1.3 can improve the sensitivity dramatically. In addition, other sensitive techniques such as photoacoustic spectroscopy can be used with diode lasers and resonant cells [23] to improve detection limits for sampling systems.
CHAPTER 8. CONCLUSIONS

8.2.4 Alternate Techniques for Sensitive Detection

All of the work in this thesis used direct absorption. Direct absorption is useful because it is simple and absolute. However, other techniques exist that offer advantages for sensitive detection, some of which are appropriate for use with the three sensing applications described in this thesis.

Balanced detection uses two well-matched detectors and differential absorption to remove common-mode noise such as laser fluctuations. This technique has been widely applied for many in situ and sampling sensors and would be useful for the in situ applications described in this thesis. Using balanced detection can often improve detection limits by an order of magnitude, but has the drawback that it is limited to operation at low bandwidth (e.g. less than 50 Hz), and thus cannot track quick changes in the measurement environment.

Frequency-modulation spectroscopy (FM Spectroscopy), uses a high-frequency dither in addition to the ramp-modulation used for direct absorption. This dither effectively moves the measurement bandwidth to higher frequencies, which reduces the amount of background 1/f noise. Looking at the second harmonic of the dither, i.e. the 2f signal, is akin to monitoring the derivative of the standard lineshape. Thus, instead of looking for small changes in big signals, which is the method for direct absorption, FM spectroscopy changes the sensor to look for small changes in small signals, and is thus potentially much more sensitive. The disadvantage of this technique is that the lineshapes become quite complicated and are no longer absolute indicators of the absorption signal, but rather need to be calibrated against reference lineshapes. Creating reference cells that accurately simulate the measurement environment in temperature, pressure, and constituent species can be difficult. FM spectroscopy also does not eliminate the effects of interference fringes, which are often the limiting factor for sensitivity.

Cavity ringdown spectroscopy (CRDS) is a very sensitive technique that uses high-reflectivity mirrors and accurate alignment to yield hundreds or thousands of passes similar to a laser resonator and with the measurement location between the mirrors (i.e. in the cavity). These multiple passes produce pathlengths that are up to kilometers long. The ringdown, or exponential time constant of the radiation signal’s
decay due to losses at the mirrors, gets shortened when absorbing molecules are in the optical path. By comparing the exponential decay time constants for ringdown with and without the test gas present yields an estimate for the mole fraction of the absorbing species. This technique is sensitive due to its long optical pathlength, but is a calibrated technique and requires high-reflectivity mirrors. The latter requirement prevents the use of CRDS for *in situ* measurements in combustion flows, where dirt and soot might detrimentally affect the mirrors, and for which the use of windows would affect the alignment of the resonator cavity. CRDS is applicable mostly for clean measurement environments, such as for the bioreactor application, and can potentially yield 10 ppb detection limits.

Photoacoustic spectroscopy uses the effect that radiation absorbed by the target species will be converted into heat and then pressure waves, which create small acoustic signals that can be detected with very sensitive microphones. The advantage of this technique is that no signal exists for isolated transitions unless the absorbing species is present (i.e. it is a zero-baseline technique), it is not affected detrimentally by etalons, and very sensitive microphones are commercially-available. The drawbacks are that this technique cannot be implemented for *in situ* monitoring. Photoacoustic spectroscopy, similarly to CRDS, can potentially yield 10 ppb detection limits, and would be useful for the bioreactor application.

Digital filtering can be used to improve the signal-to-noise ratio for each of the above measurement techniques, and is an under-explored area of laser diagnostics. Digital signal processing (DSP) uses the frequency components of measured signals to adaptively match a reference signal to the data, thereby removing undesired signal components. Since computers with processing speeds that are high enough to implement DSP strategies are now affordable, this area of study may grow in the future.
Appendix A

Mixed-Phase Equilibrium for Aqueous Solutions

Measurements of equilibrium aqueous phase NH$_3$ can be related to gas-phase NH$_3$ through Henry’s law [78],

\[ [A(aq)] = H_A \ p_A \]  \hspace{1cm} (A.1)

where $p_A$ is the partial pressure of species A in the gas phase with units of atmospheres, $[A(aq)]$ is the aqueous-phase concentration of A [mol · L$^{-1}$] that has equilibrated with $p_A$, and $H_A$ is the Henry’s law coefficient in units of mol · L$^{-1}$ · atm$^{-1}$. Note that Henry’s law only applies for ideal dilute solutions. For the relationship as written in Equation A.1, larger Henry’s coefficients indicate higher solubility. The Henry’s coefficients for O$_2$, CO$_2$ and NH$_3$ are listed in Table A.1, and reveal that NH$_3$ is a very soluble gas. This relationship only describes the physical solubility of the gas without regard to any subsequent dissociation or acid-base equilibration that occurs in the solution.

Solubility, and therefore the Henry’s law coefficient, is very temperature-dependent, with solubility increasing as temperature decreases. Therefore, even small temperature changes can lead to substantially different equilibrium partitioning between the aqueous and gas-phase concentrations of a particular species. The van’t Hoff equation
Table A.1: Henry’s law coefficients for some standard gases [78].

<table>
<thead>
<tr>
<th>Species</th>
<th>$H \text{ [mol} \cdot \text{L}^{-1} \cdot \text{atm}^{-1}]$ at 298 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{O}_2$</td>
<td>$1.3 \times 10^{-3}$</td>
</tr>
<tr>
<td>$\text{CO}_2$</td>
<td>$3.4 \times 10^{-2}$</td>
</tr>
<tr>
<td>$\text{NH}_3$</td>
<td>62</td>
</tr>
</tbody>
</table>

Table A.2: Henry’s law coefficients for $\text{NH}_3$ at several temperatures.

<table>
<thead>
<tr>
<th>$H \text{ [mol} \cdot \text{L}^{-1} \cdot \text{atm}^{-1}]$</th>
<th>$T \text{ [K]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>86.4</td>
<td>291</td>
</tr>
<tr>
<td>62.0</td>
<td>298</td>
</tr>
<tr>
<td>45.2</td>
<td>305</td>
</tr>
</tbody>
</table>

gives the temperature dependence of the Henry’s law coefficient,

$$\frac{d \ln H_A}{dT} = \frac{\Delta H_A}{RT^2},$$  \hspace{1cm} (A.2)

where $R$ is the universal gas constant, and $\Delta H_A$ is the reaction enthalpy at constant temperature and pressure. For small temperature ranges, over which $\Delta H_A$ is approximately constant, the van’t Hoff equation can be integrated with respect to temperature, yielding

$$H_A(T_2) = H_A(T_1) \exp \left( \frac{\Delta H_A}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \right).$$  \hspace{1cm} (A.3)

Using $R = 1.9873 \times 10^{-3} \text{ [kcal/mole} \cdot \text{K]}$, $\Delta H_A = -8.17 \text{ [kcal/mole]}$ for temperatures near 298 K [78], a reference temperature $T_1 = 298 \text{ K}$ and the Henry’s law coefficient for ammonia from Table A.1, the solubility of $\text{NH}_3$ in water at different temperatures can be determined. Sample values are listed in Table A.2.

Table A.3 shows the $\text{NH}_3$ concentration conversion from aqueous- to gas-phase for measurements over a 5-day period performed at NASA.
Table A.3: Aqueous-phase measurements of NH$_3$ concentration in the biorector and their corresponding equilibrium gas-phase NH$_3$ concentrations ($T = 291 \, [\text{K}], \, P = 25 \, [\text{psig}]$).

<table>
<thead>
<tr>
<th>Date</th>
<th>[NH$_3$(Aq)] (mg/L)</th>
<th>$X_{\text{NH}_3}$ (ppm)</th>
</tr>
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<tbody>
<tr>
<td>29-Aug</td>
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<td>14.5</td>
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</tr>
<tr>
<td>2-Sep</td>
<td>6.1</td>
<td>2.4</td>
</tr>
</tbody>
</table>
Appendix B

Uncertainty Analysis

Understanding the experimental uncertainty for various optical measurements is important for determining the precision of the results that have been obtained. This appendix describes the general error propagation equation and its application for estimating uncertainties in measurements of absorption linestrengths and concentrations for NH$_3$ and CO$_2$.

B.1 Error Propagation

When a measured quantity, $x$, is dependent on variables $u, v, \ldots$,

$$x = f(u, v, \ldots),$$

then the propagation of uncertainty in each of the variables produces an overall uncertainty for $x$. If the independent variables are also uncorrelated, then the error propagation equation for $x$ is given by [10]

$$\sigma_x \approx \sqrt{\sigma_u^2 \left( \frac{\partial x}{\partial u} \right)^2 + \sigma_v^2 \left( \frac{\partial x}{\partial v} \right)^2 + \cdots},$$

(B.2)

where $\sigma_x$ is the uncertainty in $x$, $\sigma_u$ is the uncertainty in $u$, etc.
B.2 Linestrength Measurements

For measurements of the room-temperature absorption linestrength in controlled lab experiments, the typical experimental uncertainty is < 3%. As described previously, the linestrength can be found from the Beer-Lambert law in the following form:

\[ S_i = \frac{\text{Area}}{P x_j L}, \]  

(B.3)

where the integrated area is

\[ \text{Area} = \int_{\nu}^{\nu_0} \frac{I_t}{I_0} d\nu. \]  

(B.4)

Thus, the uncertainty in the linestrength is described by

\[ \sigma_S = \sqrt{\sigma_{\text{Area}}^2 + \sigma_P^2 + \sigma_{x_j}^2 + \sigma_L^2} \]  

(B.5)

The uncertainty in pressure, \( P \), is a result of the precision of the MKS Baratrons, which was less than 1% for pressures below 10 Torr, and less than 0.5% for pressures above 10 Torr. The concentration uncertainty, \( \sigma_{x_j} \), was a result of the purity of the gas source (Matheson gas supplies with a 99.99% specified purity were used for all linestrength measurements of NH\(_3\) and CO\(_2\)); whether any gas decomposition had occurred in the system; and whether room air had accidentally been introduced into the gas sample. For NH\(_3\) and CO\(_2\), gas decomposition is very slight at room temperature, thus the gas purity was limited by how well room air had been evacuated from the cells before measurements began. For static cells, the ultimate pressure of the system was typically 0.02 Torr and pure CO\(_2\) or NH\(_3\) had been flushed through the cell several times, yielding an expected pressure of undesired room air in the cell to be less than 0.01 Torr. For CO\(_2\) linestrength measurements, pressures greater than 20 Torr were used, yielding uncertainty in gas purity of less than 0.05%. For NH\(_3\), pressures as low as 1 Torr were used, yielding an uncertainty in gas purity of less than 1%. The pathlengths for all experiments were known with an uncertainty less than
Table B.1: Sample uncertainties for variables related to room temperature linestrength measurements of strong, slightly blended NH$_3$ lines at 1.5 $\mu$m and strong, isolated CO$_2$ lines at 2.0 $\mu$m.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Symbol</th>
<th>NH$_3$ Uncertainty [%]</th>
<th>CO$_2$ Uncertainty [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>$\sigma_P$</td>
<td>$&lt; 1$</td>
<td>$&lt; 0.5$</td>
</tr>
<tr>
<td>Concentration</td>
<td>$\sigma_x$</td>
<td>$&lt; 1$</td>
<td>$&lt; 0.05$</td>
</tr>
<tr>
<td>Pathlength</td>
<td>$\sigma_L$</td>
<td>$&lt; 0.5$</td>
<td>$&lt; 1$</td>
</tr>
<tr>
<td></td>
<td>$\sigma_{I_0}$</td>
<td>$&lt; 0.25$</td>
<td>$&lt; 0.25$</td>
</tr>
<tr>
<td></td>
<td>$\sigma_{d\nu}$</td>
<td>$&lt; 0.5$</td>
<td>$&lt; 0.75$</td>
</tr>
<tr>
<td></td>
<td>$\sigma_{\text{integral}}$</td>
<td>$&lt; 1.5$</td>
<td>$&lt; 1$</td>
</tr>
<tr>
<td>Area</td>
<td>$\sigma_{\text{Area}}$</td>
<td>$&lt; 2.6$</td>
<td>$&lt; 1.5$</td>
</tr>
<tr>
<td>Linestrength</td>
<td>$\sigma_S$</td>
<td>$\approx 3$</td>
<td>$\approx 2$</td>
</tr>
</tbody>
</table>

1% (typically 0.5% for single-pass measurements).

The integrated area of the absorption transition can be typically determined with $< 2\%$ uncertainty for isolated transitions, and is dependent on the uncertainties of the transmitted intensity, non-absorbed reference intensity, frequency spacing and integral or Voigt fit. The transmitted intensity can be determined with very high precision, limited by any offset voltages from dark current or scattered radiation. These offsets are typically 2–5 mV out of signals that are greater than 2 V for tabletop experiments, yielding an uncertainty in $I_t$ that is less than 0.25%. Polynomial curvefits to the wings of absorption features to estimate the non-absorbed baselines, $I_0$, yields an uncertainty of approximately 1–2%, depending on the specific laser that was used, the signal to noise of the measurement, and how far away from linecenter the scan was made. For NH$_3$ measurements that were made at 1.5 $\mu$m with the ECDL, the uncertainty in $I_0$ is approximately 2% due to the limited tuning range of the ECDL, the difficulty in using polynomial fits to approximate the unabsorbed laser intensity, and the breadth of the absorption features. For measurements made at 2 $\mu$m with the DFB laser, the uncertainty in $I_0$ is closer to 1%, since the laser could tune farther, is more closely approximated by polynomials, and both the NH$_3$ and CO$_2$ spectra were more isolated.

The numerical Voigt routine that is used to approximate the lineshapes has less
Table B.2: Overall linestrength uncertainties of strong, isolated transitions at room temperature and elevated temperature for NH$_3$ and CO$_2$ at 1.5 and 2 µm.

<table>
<thead>
<tr>
<th></th>
<th>NH$_3$ at 1.5 µm</th>
<th>NH$_3$ at 2 µm</th>
<th>CO$_2$ at 2 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Room Temperature</td>
<td>&lt; 3%</td>
<td>&lt; 2%</td>
<td>&lt; 2%</td>
</tr>
<tr>
<td>Elevated Temperature</td>
<td>&lt; 4%</td>
<td>&lt; 3%</td>
<td>&lt; 3%</td>
</tr>
</tbody>
</table>

than 1% uncertainty [36]. For strong lines that are slightly blended, the uncertainty increases to approximately 1.5%. The uncertainty of the frequency spacing is a function of how well the FSR of the solid etalon is known (±0.5%), and how well the peak location of the fringes can be determined. At 1.5 µm, the finesse of the fringes is such that the fringe locations can precisely be determined, and thus the frequency spacing is limited to the precision of the etalon, or 0.5%. At 2 µm, the finesse of the fringes is lower, and thus the location of their peaks is less certain, increasing the overall uncertainty in the frequency spacing to approximately 0.75%.

The overall integrated area uncertainty for NH$_3$ lines that are strong and slightly blended and measured with the ECDL at 1.5 µm is thus a little larger than 2.6%. The uncertainty for strong and isolated CO$_2$ lines that were measured with the DFB at 2 µm is approximately 1.5%. Thus, the overall room-temperature linestrength uncertainties are approximately 3% for NH$_3$ at 1.5 µm and 2% for CO$_2$ at 2 µm. Table B.1 lists sample values for uncertainties of individual variables and overall linestrength measurements of NH$_3$ at 1.5 µm and CO$_2$ at 2 µm.

For NH$_3$ at 1.5 µm, some of the strong transitions were highly blended with other strong lines, such as for the 7 transitions near 1516 nm (Feature # 4). For these transitions, the extent of the blending limited the precision of the unabsorbed radiation intensity approximation, $I_0$, and the Voigt fitting routines, producing an overall uncertainty of 5–6% at room temperature. For the lines that were blended and weak, the uncertainty in linestrength approximations was as high as 10–12% at room temperature. For elevated temperature measurements, the linestrength uncertainties increase by approximately 1–2% due to the emergence of “hot lines” that crowd the spectrum, thereby complicating the polynomial baseline fits and multi-line Voigt fits, and the increased risk of gas dissociation. For CO$_2$, increased temperature raises the
linestrength uncertainty to approximately 3%.

### B.3 Concentration Measurements

For measurements of concentration in the ammonia-slip, flame and bioreactor experiments, the uncertainties were typically greater than for the well-controlled tabletop linestrength measurements. As described previously, the concentration of a species, $j$, can be measured according to

$$x_j = \frac{\text{Area}}{S_i P L}.$$  \hspace{1cm} (B.6)

Thus, the uncertainty in the concentration is described by

$$\sigma_{x_j} = \sqrt{\sigma_{\text{Area}}^2 + \sigma_P^2 + \sigma_{S_i}^2 + \sigma_L^2}.$$  \hspace{1cm} (B.7)

The linestrength is temperature-dependent ($S_i = f(T)$), thus uncertainties in temperature will also affect the overall uncertainty. The uncertainty in linestrength at a particular temperature, $\sigma_{S_i}$, has been described in the previous section (See Table B.2).

The uncertainties for the different parameters depends on the conditions for each particular experiment. For the combustion experiments, the pressure was atmospheric, and thus was known quite well, with an uncertainty of less than 0.5% (limited by the precision of the MKS Baratron). For the bioreactor measurements, the multipass cell was not actively controlled to maintain 100 Torr, so the pressure varied by a few Torr throughout the day as the flow conditions changed, yielding a pressure uncertainty of 2%. For the bioreactor and ammonia-slip experiments, the uncertainty in temperature was approximately 1%, while for the flame measurements of CO$_2$, the temperature uncertainty was < 3%. The pathlength for the ammonia-slip measurements was known with an uncertainty of less than 1%, while for the flame measurements, the pathlength was known only with an uncertainty of 5%. For the bioreactor measurements, the pathlength through the cell was known with an uncertainty of less than 2%. The integrated areas were known to an uncertainty less
Table B.3: Overall uncertainties for concentration measurements in three experiments.

<table>
<thead>
<tr>
<th>Variable</th>
<th>NH₃-Slip</th>
<th>CO₂ Flame</th>
<th>Bioreactor (NH₃ &amp; CO₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>σₚ</td>
<td>0.5%</td>
<td>0.5%</td>
<td>2%</td>
</tr>
<tr>
<td>σₜ</td>
<td>1%</td>
<td>3%</td>
<td>1%</td>
</tr>
<tr>
<td>σₛ</td>
<td>4%</td>
<td>3%</td>
<td>2%</td>
</tr>
<tr>
<td>σₗ</td>
<td>1%</td>
<td>5%</td>
<td>2%</td>
</tr>
<tr>
<td>σₐrea</td>
<td>4%</td>
<td>3%</td>
<td>3%</td>
</tr>
<tr>
<td>σₓ,j</td>
<td>≈ 6%</td>
<td>≈ 7%</td>
<td>&lt; 5%</td>
</tr>
</tbody>
</table>

than 3% for the isolated lines in the flame and bioreactor measurements, but for the blended features in the ammonia-slip demonstration, less than 4%.

Table B.3 lists the overall concentration uncertainties for the three experiments. For the bioreactor measurements, concentrations were determined with uncertainties less than 5% for both NH₃ and CO₂. For the ammonia-slip measurements, the uncertainty was approximately 6%, primarily limited by the precision of the spectroscopy and the ability to extract the integrated area from individual transitions. For the flame measurements of CO₂, the largest uncertainty was in the pathlength, producing an overall uncertainty of approximately 7%. However, for the flame measurements, the pathlength and temperature were not truly decoupled, and thus the error propagation equation (Equation B.2) breaks down as an approximation. More realistically, the uncertainty for the CO₂ measurements is approximately 10%, which agrees with the accuracy of the measurements when compared with equilibrium calculations.
Bibliography


