Influences of alumina particles on hydroxyl macrostate estimates in a high-speed, reacting flow

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INFLUENCES OF ALUMINA PARTICLES ON HYDROXYL MACROSTATE ESTIMATES IN
A HIGH-SPEED, REACTING FLOW

A Dissertation
presented in partial fulfillment of requirements
for the degree of Doctor of Philosophy
in the Department of Physics and Astronomy
The University of Mississippi

by

JONATHAN HERLAN

May 2021
ABSTRACT

Line-of-sight spectral observations in the near ultraviolet regime are made of the high-speed afterburning exhaust plume from a lab-scale rocket simulator which reacts gaseous H$_2$ with gaseous O$_2$. In the plume, afterburning results from energetic, unspent fuel (H$_2$) reacting with the external Air. Hydroxyl (OH) is a dominant intermediate product in the reaction zone and is probed using broadband, near UV absorption spectroscopy to estimate the macrostate parameters of the exhaust plume. Molecular energy transition data from the HITRAN online database is used to model the absorption spectra as a bivariate function of the macrostate parameters temperature, $T$, and molecular column density, $N_l$. The reported macrostate builds the model spectrum which has the maximum probability in the posterior of a Bayesian estimator. Aluminum oxide (Al$_2$O$_3$) particles of nominal effective diameter 0.3 $\mu$m are injected into the rocket combustion chamber through the H$_2$ fuel line with relatively low mass-loading and are carried along with the flow into the exhaust plume. The presence of these particles has a clearly broadband extinction effect on the transmission spectra. Separating this effect from the molecular absorption in a spectrum is achieved without any prior knowledge of the particle size distribution, provided the scattering spectrum has been characterized experimentally without any other spectral effects involved. In this way, broad band spectral measurements can be used to estimate the plume macrostate whether or not interstitial particulate is present. A bench top experiment with a vapor reference cell containing Oxygen gas (O$_2$) at a known pressure and temperature is used to validate this procedure.
DEDICATION

To my parents, Wes and Patty Herlan. There’s no question that, in your love for me, you put more work into setting me up for this kind of success in life than I put into this dissertation. Thank you for your love.

“And God said, Let there be light: and there was light.”

Genesis 1:3 KJV

“And the light shineth in darkness; and the darkness comprehended it not.”

John 1:5 KJV

“But if we walk in the light, as he is in the light, we have fellowship one with another, and the blood of Jesus Christ his Son cleanseth us from all sin.”

1 John 1:7 KJV

“Let your light so shine before men, that they may see your good works, and glorify your Father which is in heaven.”

Matthew 5:16 KJV
LIST OF ABBREVIATIONS AND SYMBOLS

Acronyms

bb as a subscript, represents blackbody
CFD Computational Fluid Dynamics
DC Direct Current
EM Empirical Method
HITEMP High-temperature molecular spectroscopic database
HITRAN High-resolution TRANsmission molecular absorption database
ns as a subscript, represents seed-off or “no-seed”
PIV Particle Image Velocimetry
RM Repository Method
rms Root Mean Square
s as a subscript, represents seed-on
so as a subscript, represents seed-only
SRM Solid Rocket Motor
UV Ultra Violet
WB the set of wavelength bins used to optical depths

Latin Letters

a a discrete set of physical parameters
$ a_1 $ and $ a_2 $ empirical constant coefficients for the empirical method
$ a_\alpha $ the first of two outward scattering coefficients from Mie scattering
Al$_2$O$_3$ chemical symbol for aluminum oxide
b normalization factor for the spectrometer slit function in Equation 2.31
an empirical constant coefficient

the second of two outward scattering coefficients from Mie scattering

a constant coefficient in Equation 3.5

speed of light in a vacuum

a constant coefficient in Equation 2.28

chamber pressure

a constant coefficient in Equation 3.5

scattering extinction coefficient

particle size-weighted-average of the scattering extinction coefficient

a set of experimental data

effective particle diameter

diameter of lens

diameter of nozzle

energy

inter-molecular force constant in connection to Equation 2.20

focal length in relation to optics

F-number of an optical system

spectrometer slit function at wavenumber \( \nu^{(i)} \)

density of states (degeneracy)

a mathematical model for a physical processes

Planck’s constant

outward-going spherical Bessel functions of the third kind

chemical symbol for gaseous Hydrogen, diatomic molecules

chemical symbol for water
\( \text{H}_2\text{O}_2 \) \hspace{0.5cm} \text{chemical symbol for hydrogen peroxide} \\
\( J \) \hspace{0.5cm} \text{prior information} \\
\( \mathcal{J} \) \hspace{0.5cm} \text{the moment of inertia for the molecule} \\
\( I \) \hspace{0.5cm} \text{transmitted radiative intensity} \\
\( I_0 \) \hspace{0.5cm} \text{incident radiative intensity} \\
j \hspace{0.5cm} \text{coefficient of radiative emission} \\
\( j_\alpha(x) \) \hspace{0.5cm} \text{spherical bessel functions of the first kind} \\
k \hspace{0.5cm} \text{Boltzmann’s constant} \\
k \hspace{0.5cm} \text{wavevector of radiation in Mie theory} \\
k \hspace{0.5cm} \text{a constant coefficient for scattering using the empirical method} \\
K \hspace{0.5cm} \text{coefficient of radiative absorption} \\
l \hspace{0.5cm} \text{length scale of dominant turbulent eddies in Chapter 1} \\
l \hspace{0.5cm} \text{path length through the measurement volume} \\
l(a|d) \hspace{0.5cm} \text{likelihood function of the Bayesian estimator} \\
m \hspace{0.5cm} \text{the ratio of wavevectors in Equations 2.36 and 2.37} \\
m \hspace{0.5cm} \text{mass of } \uparrow \\
M \hspace{0.5cm} \text{molar mass of the molecule} \\
M \hspace{0.5cm} \text{(in Equation 2.19) the total mass of the molecule} \\
\text{MgF}_2 \hspace{0.5cm} \text{chemical symbol for magnesium fluoride} \\
n \hspace{0.5cm} \text{index of refraction} \\
n \hspace{0.5cm} \text{uncertainty in a physical model} \\
n_{\text{air}} \hspace{0.5cm} \text{temperature component for the air-broadened half-width at half-maximum} \\
N_A \hspace{0.5cm} \text{number of particles in Chapter 1} \\
N_A \hspace{0.5cm} \text{Avogadro’s number in Equation 2.26}
$N$ number density of molecules

$N$ (in Section 3.3.3.1) the total number of available samples

$N$ absolute number of molecules

$N_s$ number density of particles

$N_l$ (considered as a single term) the column density of molecules

$O_2$ chemical symbol for gaseous Oxygen diatomic molecules

$OH$ chemical symbol for hydroxyl radical molecules

$p(a|d,J)$ posterior distribution function

$P$ pressure

$P_{amb}$ ambient pressure

$Q$ molecular partition function values for integer values of temperature

$\mathbb{R}$ set of real numbers

$s(a|J)$ prior distribution function

$S$ (in relation to Equation 2.22) total electronic spin angular momentum

$S_j(T)$ line strength of the $j^{th}$ transition at temperature, $T$

$St$ Stoke’s number

$T$ temperature

$u$ rms fluid velocity

$\mathcal{V}$ volume of the system under consideration

$V_A$ volume of a single particle

$V_{tot}$ total volume occupied by fluid and particles

$W(a)$ weighting function

$x$ ratio of half-widths in Equation 2.28

$x$ the particle size parameter in relation to Mie theory
stream-wise spatial coordinate

optical thickness as a random variable in Section 3.3.3.1

true mean of the optical thickness in Section 3.3.3.1

position in wavenumber space for Whiting’s Voigt profile

cross-stream spatial coordinate

Voigt line shape profile

Greek Letters

half-width at half-maximum of the spectrometer instrument function

air-broadened Lorentzian half-width at half-maximum

Doppler half-width at half-maximum

Lorentzian half-width at half-maximum

the spatial half-width at half-maximum of the spectrometer instrument function

Voigt half-width at half-maximum

dissipation rate of turbulent kinetic energy

center wavenumber in an array, rounded to the nearest integer

polar coordinate in spherical coordinates

wavelength

reduced mass of the molecule in relation to Equation 2.20

cos \theta in relation to Equations 2.36 and 2.37

kinematic viscosity of the fluid in Chapter 1

inverse wavelength ("wavenumber")

normalization factor for the Bayesian posterior

particle density

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\( \sigma \) standard deviation in Equation 2.25 and Section 3.3.3.1

\( \sigma_s \) coefficient of radiative scattering

\( \tau_A \) or \( \tau_p \) relaxation time of the particle

\( \tau_F \) or \( \tau_e \) characteristic time of the vortex motion

\( \tau_K \) Kolmogorov time scale

\( \tau_{\text{exp}} \) experimental data of transmissivity

\( \tau_{\text{mod}} \) theoretical model of transmissivity

\( \phi \) fuel equivalence ratio

\( \Phi_p \) volume fraction of particles in the fluid

\( \omega \) angular frequency of a harmonic oscillator

**Notation**

▲ a placeholder for various terms

\( \hat{\varepsilon} \) unit vector for the coordinate ▲

\( \langle \varepsilon \rangle \) ensemble average of ▲

\( \tilde{\varepsilon} \) non-normalized form of the function ▲

\( \text{distance AB} \) distance from point A to point B
ACKNOWLEDGEMENTS

The environment of people I have been around during graduate school has been a nutritious soil in which I could grow not only as a scientist but also as a man. There are many people to whom I owe a debt of gratitude. However, I will do my best to avoid perfectionism and keep these formal acknowledgments focused on those who have played a particularly influential role in my success as a graduate student.

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Now, for a kid like I was—who could hardly sit still or pay attention to school ever since the beginning of my education—to have made it through twenty three years of school seems like an impossible feat. Nevertheless, I am here and I know that God has been at work in my life at each step of the way. He brought me this far for a reason even though I was not always faithful to seek his direction and often made my accomplishments about winning the favor of other people. With whatever I have to give here now and in the years to come, I pray that “Now I will praise the Lord” (Genesis 29:35).
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CHAPTER 1

INTRODUCTION

Electromagnetic radiation passing through a multi-phase flow experiences extinction due to a combination of radiative absorption and scattering. The spectral characteristics of these extinction effects carry information about the constituents of the flow. While all matter has both an absorption and a scattering effect on radiation, sometimes one or the other effect is negligible, as is the case for our system. In this study, we consider a spectral region where the diatomic molecule Hydroxyl (OH) is the primary absorber and causes negligible scattering while a fine cloud of aluminum oxide (Al$_2$O$_3$) predominantly scatterers radiation and contributes negligible absorption. The aim of this study has been to use transmission spectra to estimate the macrostate parameters, temperature and number density, of the OH in a rocket exhaust plume while solid particulate is present, complicating the measurement. Achieving this goal first requires consideration of the question answered in this dissertation: how does the presence of micron-scale alumina particles in a high-speed, reacting flow influence near-UV spectroscopic estimates of the hydroxyl radical macrostate? For this study, we take advantage of the fact that the alumina particles have a log-normal size distribution with a mean effective diameter of 0.28 $\mu$m and that polydisperse particulate scattering, according to Mie theory, has a flattened*, broad band influence on radiative transmission. Meanwhile, OH is the only strong absorber among the species present in the measurement volume, having active features in the spectral band of interest from 294 nm–331 nm. These features are distinct and discretely organized within the band, allowing the solid-phase scattering effect on the spectrum to be distinguished from the gas-phase absorption, influencing the transmissivity even in bands where the OH has no absorptive effects.

*For a polydispersion of particles, the total scattering coefficient is the weighted average of the scattering coefficients from each representative particle size, thereby the total coefficient is flattened as compared to the coefficients of individual particles as will be shown in Chapter 2.
If the absorption spectra are found to change significantly with the presence of the particles, then the cause must be the transfer of energy from the fluid to the particles or vice versa since the oxidized aluminum particles do not directly participate in the chemical reaction which produces the OH. So then, a difference observed in the absorption spectra of OH may give a clue about the energy exchange that occurs between the particulate and the fluid in the multiphase flow.

1.1 Survey of Relevant Literature

Multiphase flow scenarios span a broad range, including such scenarios as pollen transport in air\(^1,2\), aerosolized transmission of infectious diseases\(^3\), vascular flows\(^4\), sediment transport in water\(^5\), coal-driven power plant exhaust\(^6,7\), liquid-fueled gas combustors\(^7\), rocket exhaust plumes\(^8\), and PIV flow-visualization\(^9,10\). The experimental system used in this study simulates the multiphase, high-speed reacting flow of a solid rocket motor (SRM) exhaust plume. The following is an overview of studies related to multiphase, reacting flows and SRM plume behavior.

1.1.1 Three-Way Interaction

A given sample volume of a rocket exhaust plume shear layer exhibits energy in a smörgåsbord of forms: mechanically, thermally, chemically, radiatively, and acoustically. It is in the shear layer where unspent fuel or combustion products interact with the atmospheric gases, causing afterburning, and where the formation of turbulent structures occurs, generating jet noise.\(^{11}\) The exhaust gasses of the rocket, the exhaust particulate, and the entrained atmospheric air are the materials which exhibit these energy transfer mechanisms. The bulk of the energy contained in the system lives in the exhaust gas and the particulate which exchange energy between each other and each individually contributes to the chemical reaction taking place in the shear layer. For set atmospheric conditions, the three way interaction between the fluid, the particles and the chemistry can be illustrated as in Figure 1.1. The particle-fluid interaction and the fluid-chemistry interaction are covered in the following sections. The particle-chemistry interaction involves the particles participating in the reaction process; however, aluminum oxide, having already been oxidized, does
Figure 1.1: An illustration of three-way exchange of energy in a multi-phase, reacting flow.

not play an active role in the combustion reaction considered here. Thus, if the particle loading is to influence the chemistry in the present system, it must do so indirectly by energy exchange first with the fluid. Mechanisms for this interaction include the energy the fluid imparts to the particles to move them around and the wake generated by flow past the particle.

1.1.1.1 Fluid-Particle Interaction

In 1985 Dash et al. had begun to look for answers to questions about high-speed, two-phase, reacting flows. In particular, they were seeking to address the diminished turbulence levels, the decreased jet width, and the reduced centerline decay rates in a rocket exhaust plume. If a gas is enlisted to carry around solid particles then it must donate some of its energy to moving these particles. In 2014, Vié et al. demonstrated with CFD simulations that a Lagrangian formalism provides faithful results in the low Stokes number regime, where the number of particles involved actually influences the particle-turbulence interactions.

Several experimental studies in low-speed flows have considered the effect that particle loading has on the energy in a fluid. Models are provided in the literature which attempt to describe both the behavior of particles in turbulence and the response of turbulence to the particles. It has been found that different sized particles exhibit different behaviors in a turbulent flow.
Experimental evidence suggests that merely treating the particles as a gaseous species using Fick’s law of diffusion is insufficient for non-isotropic turbulence.\(^7\) In 1985, Crowe et al. used prior data and a numerical model to explain that the dispersion of particles in large-scale turbulence can be roughly estimated with a ratio between the relaxation time of the particle, $\tau_A$, and the characteristic time of the vortex motion, $\tau_F$.\(^7\) This ratio is called the Stoke’s number,

$$\text{St} = \frac{\tau_A}{\tau_F}. \quad (1.1)$$

The response time of the particle is found by:

$$\tau_A = \frac{\rho_A d_A^2}{18\mu_g} \quad (1.2)$$

where $\mu_g$ is the dynamic viscosity of the gas while $\rho_A$ and $d_A$ are the particle density and effective diameter, respectively. The characteristic time scale of the flow, $\tau_F$, must be chosen according to the eddy length scales present,

$$\tau_F = \frac{l}{u} \quad (1.3)$$

where $l$ is the length scale of the dominant eddies and $u$ is the rms fluid velocity. For a Stokes number much smaller than one, the particle moves along with the fluid, dispersing with the mixing layer. For a ratio near one, an effect called eddy tossing is observed in which the particle gets captured by a vortex and then gets thrown from the edges of these large scale eddies by means of inertia. This tossing enhances the process of particle dispersion and explains the finding by Dash that the particulate in a jet diffuses more rapidly than does the fluid.\(^{16}\) For a ratio much larger than one, the particles disperse minimally, traveling with little regard for the surrounding flow behavior. At the turn of the century, a Large Eddy Simulation (LES) study at a Mach number of 0.27 with varying particle sizes supported Crowe’s findings that the behavior of entrained particles depends on the relaxation time scale of the entrained particles.\(^7,17,16\) Eddy tossing was also confirmed in
this study.

Elghobashi in 1994 published a diagram which summarizes the regimes of interaction between particles and fluid, see Fig. 1.2. In the diagram,

\[ \tau_p = \tau_A \text{ from Eq. 1.2} \]

\[ \tau_K = \left( \frac{\nu}{\epsilon} \right)^{1/2}, \text{ the Kolmogorov time scale} \]

\( \epsilon \): the dissipation rate of turbulence kinetic energy

\[ \tau_e = \tau_f \text{ from Eq. 1.3} \]

\[ \Phi_p = \frac{N_A V_A}{V_{\text{tot}}}, \text{ the volume fraction of particles} \]

\( N_A \): the number of particles

\( V_A \): the volume of a single particle

\( V_{\text{tot}} \): the total volume occupied by fluid and particles.

For volume fractions below \( 10^{-6} \), the fluid influences the particles but the presence of the particles has negligible influence on the fluid. This regime therefore contains one-way coupling and includes many of the multiphase flow scenarios encountered in everyday life. In the second dilute suspension case, for volume fractions from \( 10^{-6} \) to \( 10^{-3} \), there is a two-way coupling in which the fluid begins to see an effect from momentum transfer with the entrained particles. For a given volume fraction, a smaller time scale ratio results in a larger exposed surface area of the particles which acts to enhance the dissipation of the turbulence. This is the case, for example, when the particle diameter is small. When the time scale ratio is larger, for example in the case of smaller eddy length scales, the Reynold's number of the particles is higher, leading to vortex shedding off the particles which enhances turbulence production. In between these two regions is where the Stoke's number is roughly unity and where Crowe predicted the eddy tossing occurs. These two regions contain the flow scenarios of most solid rocket motor plumes. In dense suspensions where \( \Phi_p > 10^{-3} \), particles frequently interact with each other, resulting in a so-called four-way coupling. As the
Figure 1.2: Particle-fluid interaction regimes. An illustration of the three types of coupling in the interactions between a fluid and the entrained particles within it taken from Elghobashi (1994).\textsuperscript{18}
volume fraction passes 0.5, the particles dominate the volume and as the volume fraction approaches 1, the result is a granular flow.

Every multiphase flow involves redistributing energy, taking some away from the carrier fluid. However, not all multiphase flows exhibit a strong difference in fluid energy with the addition of particles. The change depends on the attributes of the flow and the particles as well as on how many particles are present. Adding a chemical reaction to this equation has its own role to play in redistributing the energy in a fluid.

1.1.1.2 Turbulence-Chemistry Interaction

Both molecular diffusion and heat transfer are required for a combustion reaction to survive.\textsuperscript{19} By extension, turbulence—being a diffusive mechanism—can aid the combustion process. Gaydon and Wolfhard explain that the various length scales of turbulent structures will play different roles in the combustion process. Large coherent structures extract energy from the gas flow but eventually decay, getting smaller and contributing more to material and energy transport. Ultimately these structures return energy to the gas through heating by viscous effects.\textsuperscript{19}

There can also be an influence from the flame to the turbulence. For example, thermal expansion from the combustion reaction produces spatial inhomogeneities.\textsuperscript{20} Since turbulence depends on such quantities as the gas density, a modulation in these parameters has a corresponding influence on the turbulence in the fluid. The primary point here being that the turbulence and the chemical reaction processes are linked just as the particle and fluid energies are linked. These effects can be observed in studies of SRM plumes.

1.1.2 Present Application: A Rocket Exhaust Plume

From the terrestrial launch pad to the vacuum of space, rockets interact with their altitude-dependent environment in a manner that is evidenced by the luminous exhaust plume of the rocket. Whether fueled by liquid, solid, or gas propellant, conventional rockets rely on chemical combustion for thrust such that the plume carries information about the rocket motor because it contains the products of the combustion. When these heterogeneous combustion products from the combustion
chamber exit the rocket nozzle they enter the potential core of the plume, encounter shocks where the flow decelerates through high pressure regions and ultimately diffuse into the atmosphere. Along the edge of the plume a turbulent shear layer forms between the rocket exhaust and the external atmosphere. Here the exhaust products with ample kinetic energy are introduced to atmospheric gases, causing secondary combustion or “afterburning”.*

In a solid propellant motor, non-uniform burning of the fuel as well as inhomogeneities added to the propellant grain leave the combustion process in various stages of completion along the propellant surface, allowing grains of the solid fuel to break away from the bulk.8 Furthermore, the particulate exhibits a delayed response to heat and acceleration as compared to the surrounding fluid, having a size-dependent behavior, altering flow patterns, and even—for some types of particulate—reacting with the chemical species in the flow.13 Solid propellant is often enhanced with aluminum powder so that aluminum oxide (or alumina, Al₂O₃) is found among the combustion products. Aluminum often constitutes up to 20% by mass of a solid propellant grain while alumina particulate accounts for around 30% of the mass flow rate in the inner core of the exhaust plume.21 With a melting temperature around 3000 K, alumina particulate is typically molten as it exits the nozzle, cooling and condensing with increased distance from the exit plane.21 These loose particles get carried along with the flow, melting, aggregating, and breaking up so that the particles have sizes ranging from 0.1 µm to 20 µm depending on the location within the exhaust flow path.8,21

Pandey et al. (2018) presents a summary of studies conducted since 1964 on the radiative emission of solid rocket motor exhaust plumes along with key findings from studies of alumina particle properties. Particulate plays the strongest role in plume thermal emissions and this emission is characterized by the particle properties. Therefore, it is a challenge to accurately model these plumes if these properties are neither known nor measurable.21 The most basic numerical models consider the plume to be a homogeneous, isotropic, axisymmetric cone radiating as a gray-body from its surface while more intricate models break the cone up into discrete patches or even model it as a collection of numerous radiative pseudo-particles. Each model comes with its limitations,

*The mode of afterburning for a rocket is different in nature from and not providing additional thrust as in the afterburners in high-performance combat aircraft.
but the greatest hindrance to improving these models is the lack of predictability for the radiative properties of the alumina particulate.\textsuperscript{21,22,23,24} Even still, while a full representation of these plume characteristics remains elusive, many of these numerical models have seen meaningful success when compared with full-scale flight test data.

The properties of aluminum oxide (Al\textsubscript{2}O\textsubscript{3}) have been the subject of numerous studies with the conclusion that the temperature, size, shape, crystalline structure, and the number of particles present all have an influence on the spectral characteristics of the particles whether for emission, absorption or scattering. As a result, there are several different models giving varying results for the temperature-dependent, spectrally-varying complex index of refraction for the alumina\textsuperscript{23}, which plays a crucial role in any expression for the radiative properties of the particulate. For the present scenario, the refractive index matters for looking at the scattering behavior.

The simplest scattering model, Mie scattering, assumes the particles are spherical which only gives a first order approximation of the more complex scattering behavior of non-spherical particles. The model for the size distribution of the particles in the exhaust flow is also a matter of debate\textsuperscript{21}, and the shapes and size distributions change between the combustion chamber, the nozzle, and various distances from the nozzle exit in the exhaust plume. Experimentally, samples of the particles have been collected from rocket motor exhaust plumes by various means\textsuperscript{*} and in different locations along the exhaust flow path. Subsequently these samples were analyzed to ascertain the time-averaged particle size distributions. Non-intrusive diagnostics such as light scattering techniques provide time-resolved information about the particle size distribution integrated along a line-of-sight, but do not usually give spatial resolution in the flow field. Furthermore, in most realistic solid rocket motor plume scenarios, the flow field is too opaque to use radiative transfer to probe the inner structure of the plume where important information about the radiative properties of the plume are hidden.\textsuperscript{21} Therefore, most efforts to understand the radiative properties of SRM plumes come from computational studies.

In 2015, Kuzmin \textit{et al.} published a numerical parametric study evaluating how the particle

\*One notable method involved collecting particles by shooting darts through the SRM plumes.\textsuperscript{25}
size distribution, the particle temperature, the gas temperature, and the mass fraction of the particles in the flow influence the optical properties and radiation characteristics of a rocket plume model. They used a one dimensional model of the plume, applying a constant temperature and pressure to the combustion products and a fixed composition of the seven gaseous species included in the model. The integro-differential radiative transfer equation is used, taking into consideration all radiative features of the flow. A procedure for modeling all of these terms is described. They confirmed that the parameters of the particles have a significant influence on the thermal radiation in the plume. Furthermore, it was observed with this model that the measured radiation from the plume exceeds that which is expected of an absolute black body at the local temperature of the plume and, because of the gas phase presence adding spectral features to the radiation, a gray-body approximation of the radiation leads to significant errors. While the particulate is the dominant thermal emitter, the spectral features of the gas cannot be omitted. Practical measurements of SRM plumes lack the ability to identify the properties of plume constituents from simple spectral measurements.

Without a full understanding of the material parameters of the particulate in a given plume, modeling the plume is an inverse problem which is often approached through trial and error, finding the assumptions which produce a faithful numerical reproduction of the experimentally observed data. Therefore, gathering further experimental information about the behavior of these plumes remains important.

In the lab, it is possible to control the characteristics of model rockets, eliminating various complications in order to emphasize the study of a particular aspect of the plume flow field. The present work considers a rocket exhaust plume under low alumina volume fraction \( \Phi_p \sim 10^{-7} \) conditions so that the reactions within the afterburning plume can be evaluated without a thick cloud of intervening particulate. This also means that the influence of the particulate on the fluid energy in the plume, and therefore the plume macrostate, is expected to be negligible. Estimating the macrostate of a gas using spectrometry while particulate scatterers are present

\[ \text{This estimate comes from a back-of-the-envelope calculation based on the measured scattering spectra and the modeled Mie-scattering extinction coefficient of the particulate.} \]
requires either *a priori* knowledge of the particle properties and a model of the scattering, a secondary measurement to determine the particle properties and model the scattering, or a means of removing the spectral scattering features from the measured spectrum. While knowledge of a full set of the particle properties remains difficult to acquire and optical access as well as equipment availability complicate the addition of a second measurement, the removal of the scattering part of
the spectrum by empirically determined means is still possible and is a relatively common practice in the fields of astronomy, material and food science, and medicine, for example.

1.1.3 Scattering Removal

The procedures for removing scattering vary depending on the features of the scattering medium and the desired parameter to measure. Several procedures involve assuming a simple, constant with respect to wavelength scattering spectrum, thereby utilizing a multiplicative correction to the spectra in order to obtain the spectral features of the chemicals of interest.\textsuperscript{26,27,28,29} Astronomers also have a systematic process to account for atmospheric extinction in spectrophotometric measurements. They take images of cataloged or well classified stars and repeat these measurements under different atmospheric conditions in order to construct a model of the local atmospheric features so that those features can be removed in future scientific measurements.\textsuperscript{30} A basic understanding of the scattering features of a system informs the construction of a model for that scattering in order to isolate the desired non-scattering spectral features.

The size, shape, temperature, material properties, angles of incoming and outgoing radiation, and number of particles present all have a role to play in deciding the spectral behavior of the scattering. The radiative transfer model used in this study already contains two unknowns for the macrostate of the absorbing molecule. To incorporate scattering into the radiative transfer model would involve more than doubling the number of parameters in an already computationally heavy* fitting algorithm. For this reason it is more favorable to altogether remove the scattering part of the transmission spectrum without any knowledge of the parameters of the particles present. While

\*On a 64-bit Windows 7, desktop PC with 16 GB of RAM and a four core, 3.21 GHz processor, it takes 1.5 hours to run the Bayesian analysis of one spectrum.
this may not be possible in all situations, certain circumstances lend themselves to this possibility, as will be shown in this study.
CHAPTER 2

THEORETICAL DEVELOPMENT

This chapter focuses on reviewing the theory involved in predicting how radiation will be extinguished by a multiphase target volume. Taken independently, the spectral absorption of the volume depends nonlinearly on two macrostate parameters of the gaseous constituents while the spectral scattering is related to the composition and effective size distribution of the bulk particulate (“seed”). Each effect has an associated term in the radiative transfer model.

The macrostate parameters considered in the molecular absorption are the temperature, $T$, and number density, $N$, of the molecule. For simplification of discussion these shall be jointly referred to as the macrostate of the system. Using statistical mechanics and well documented data of the spectral absorption characteristics of hydroxyl (OH), a Bayesian Inversion spectral fitting algorithm is designed to estimate the macrostate parameters of the gas from an experimental transmissivity spectrum. Then a brief treatment of Mie scattering is given to lay out some expectations for the spectral features of the particulate scattering.

2.1 Radiative Transfer

A radiative transfer model describes the transmission of radiation through a given volume, accounting for the emission, absorption, and scattering of radiation which takes place in the volume. A proper derivation of the radiative transfer formalism can be found in Radiative Heat Transfer by Michael Modest. Only a summary of the key pieces in development of the analytic model will be discussed here.

The primary quantity for consideration in the study of radiative transfer is the radiative intensity, $I$, with SI units of W/m². Small changes in intensity, $dI$, are related to the infinitesimal
path length, $dl$, over which radiation travels through the medium, and to a coefficient which is derived from the physical properties of the matter involved. The three processes are described as follows:

1. **Factors of extinction**
   - Absorption:
     \[
     dI(\nu) = -K(\nu)I(\nu)dl
     \]  
   - Scattering:
     \[
     dI(\nu) = -\sigma_s(\nu)I(\nu)dl
     \]

2. **Factors of augmentation**
   - Emission:
     \[
     dI(\nu) = j(\nu)dl
     \]
• In-Scattering (into the $\hat{e}_l$-direction):

$$dI(\nu, \hat{e}_l) = dI \left( \sigma_s(\nu) \frac{d\Omega}{4\pi} \int I(\nu, \hat{e}_{li})\Phi(\nu, \hat{e}_{li}, \hat{e}_l)d\Omega_i \right).$$ (2.4)

Where $K$ and $\sigma_s$ are the wavenumber-dependent absorption and scattering coefficients, respectively and $\nu$ is the wavenumber, $\nu = 1/\lambda$ where $\lambda$ is the wavelength. The form for both extinction mechanisms is identical apart from the values of the coefficients. For emission, $j(\nu)$ is the emitted intensity which, for thermal emission, becomes $K(\nu)I_{bb}(\nu, T)$ when the system is at Local Thermodynamic Equilibrium (LTE) at a temperature, $T$, where $I_{bb}$ represents the emitted intensity of a blackbody at temperature $T$ (Eq. 2.5). Observe that the LTE constant of proportionality for emission is the same as the constant of proportionality for absorption since, at LTE, absorptivity equals emissivity. Thermal emission has a broadband effect described by the Planck equation, also referred to as the intensity of Blackbody emission:

$$I_{bb}(\nu, T) = \frac{2hc\nu^3}{e^{hc\nu/kT} - 1}$$ (2.5)

where $h$ is Planck’s constant and $k$ is the Boltzmann constant.

In-scattering is the process by which off-axis radiation gets scattered into the beam of measured radiation (“on-axis”). This can occur from any angle at which radiation is incident, so every angle of possible in-scattering is taken into consideration by integration over all solid angles, $\Omega$. The term $\Phi(\nu, \hat{e}_{li}, \hat{e}_l)$ is called the scattering phase function and represents the probability that a ray from $\hat{e}_{li}$ will be scattered into the direction $\hat{e}_l$. In the case of equal amounts of radiation being scattered in all directions, the phase function equals unity*. This is called isotropic scattering.

*Other well documented but non-constant forms of the phase function can be obtained from various scattering theories, such as the Mie solution to Maxwell’s equations.
Brought together, the difference in intensity between points \( l \) and \( l + dl \) is given by:

\[
I(\nu, l + dl, \hat{e}_l, t + dt) - I(\nu, l, \hat{e}_l, t) = \\
j(\nu, l, t) dl - [K(\nu) + \sigma_s(\nu)] I(\nu, l, \hat{e}_l, t) dl + \frac{\sigma_s(\nu)}{4\pi} \int_{4\pi} I(\nu, \hat{e}_{ll}) \Phi(\nu, \hat{e}_{ll}, \hat{e}_l) dl \ d\Omega_i. \tag{2.6}
\]

If we assume that the medium is homogeneous and that its flow velocity, \( u \), is much smaller than the speed of light, \( u \ll c \), that the medium is non-polarizing, that the state of polarization can be neglected, and that the medium has constant index of refraction, then we can expand the first term in Equation 2.6 by a Taylor series of two-variables about \( dl = dt = 0 \),

\[
I(\nu, l + dl, \hat{e}_l, t + dt) \approx I(\nu, l, \hat{e}_l, t) + dt \frac{\partial I(\nu)}{\partial t} + dl \frac{\partial I(\nu)}{\partial l}.
\]

Notice, higher orders are zero by the fact that \( dt^n = dl^n \rightarrow 0 \) for \( n \geq 2 \). Dividing by \( dl \), the equation becomes:

\[
1 c \frac{\partial I(\nu)}{\partial t} + \frac{\partial I(\nu)}{\partial l} = \\
j(\nu, l, t) - [K(\nu) + \sigma_s(\nu)] I(\nu, l, \hat{e}_l, t) + \frac{\sigma_s(\nu)}{4\pi} \int_{4\pi} I(\nu, \hat{e}_{ll}) \Phi(\nu, \hat{e}_{ll}, \hat{e}_l) \ d\Omega_i. \tag{2.7}
\]

Despite the simplifying assumptions applied to arrive at this expression, it is valid whether or not the medium is at thermodynamic equilibrium. Since \( 1/c \ll 1 \) the time derivative vanishes except in cases where \( \partial I/\partial t \gg 1 \), such as in extreme heating or when using short-pulse lasers. The most commonly used form of the radiative transfer equation is:

\[
\frac{dI(\nu)}{dl} = j(\nu, l, t) - [K(\nu) + \sigma_s(\nu)] I(\nu, l, \hat{e}_l, t) + \frac{\sigma_s(\nu)}{4\pi} \int_{4\pi} I(\nu, \hat{e}_{ll}) \Phi(\nu, \hat{e}_{ll}, \hat{e}_l) \ d\Omega_i. \tag{2.8}
\]

With this in hand, the task becomes finding an expression for each of the physical factors. Strictly speaking, any medium participates with incident radiation via all three processes\(^{32} \), but these
processes influence the transmitted radiation differently according to the specific wavelength band considered. For the wavelength band of interest here, absorbers are distinguished from scatterers and the two factors of augmentation are neglected. Emission is neglected on the basis that the thermal emission is not strong enough in the near UV while the in-scattering is neglected on the assumption that the solid angle of radiation incident on the measurement volume is too small to have a meaningful effect.

2.2 Absorption: Diatomic Gas

In this section a procedure is outlined for modeling the spectrum associated with the diatomic molecule OH, Hydroxyl. Since the strength and shape of the spectral lines depends on the temperature and the number of molecules present in a measurement volume, the model spectrum built here can be compared with empirical spectra to estimate these macrostate parameters.

2.2.1 Beer-Lambert Law

Molecular absorption spectroscopy makes a reference measurement of a light source and then considers how that reference is influenced as a function of wavelength after passing through an absorbing medium. The work of J. H. Lambert in the mid 1700s led to the development of the theory* that explains how the absorptivity of light relates to the path length, $l$, through the absorbing medium. In 1852 August Beer reported on an experiment in which he related the absorbance of the medium to the concentration of absorbing material contained within. Together, these form the expression which describes the transmitted intensity of radiation through a homogeneous, absorbing medium, commonly known as the Beer-Lambert law:

$$I(\nu) = I_0(\nu)e^{-K(\nu)l}.$$  \hspace{1cm} (2.9)

*While J. H. Lambert is given credit for this development, his analytical model was published in 1760 built on the empirical relationships described in words 31 years earlier in an article published by P. Bouguer.\textsuperscript{13}
Notice that this expression is the direct result of solving for \( I \) in Equation 2.1. The transmissivity is then defined as

\[
\tau(\nu) = \frac{I(\nu)}{I_0} = e^{-K(\nu)l}.
\]

(2.10)

If the medium is not homogeneous so that the absorbance varies with the distance traveled through the medium, then the argument of the exponential term remains an integral across the path:

\[
- \int_0^l K(\nu; l')\, dl'.
\]

For a more careful development of this model from first principles, consider the work of Swinehart in the *Journal of Chemical Education*.\(^{34}\)

### 2.2.2 Energy states of a diatomic molecule

Molecules contain a certain hierarchy of energy states according to their composition. If a molecule receives energy from its environment this energy can both alter the kinetic energy of the molecule and give energy to another degree of freedom. However, transitions in these other degrees of freedom only occur if the input energy matches the energy needed to make the transition to a new state. This process is called spontaneous absorption because it involves the absorption of energy from a photon. The amount of energy in the photon is equal to the difference in energy, \( \Delta E \), between the two states of the transition. The photon has a wavelength,

\[
\lambda = \frac{hc}{\Delta E}.
\]

(2.11)

It is worth noting that spectroscopists usually work in terms of the “wavenumber”, \( \nu = 1/\lambda \), which is directly proportional to the change in energy.

The energy states in a molecule are associated with more degrees of freedom than are observed in the energy states of an atom. Where an atom can take on kinetic and electronic
Figure 2.2: An illustration of the energy levels in an arbitrary diatomic molecule. $\Delta s$ represents the interatomic separation distance.
energy*, molecules can take on kinetic and electronic as well as rotational and vibrational energy. Just as the electronic shells have quantized energies, so also the rotations and vibrations have quantized energies. This idea of numerous energy states should paint the picture of a discretized energy ladder structure such as seen in Figure 2.2, in which there are numerous options for energy transition and, therefore, numerous possible wavelengths of photons which may be emitted or absorbed. The larger energy transitions are associated with shorter wavelengths while the smaller energy transitions are associated with longer wavelengths. Thus, the energy ladder translates to a radiation absorption spectrum†.

The distribution of occupied energy states for any molecular species depends both on its number density and on the equilibrium temperature between the collection of molecules and their environment. Together these parameters define the macrostate of the system, that is the bulk properties of the molecular gas, or the statistical distribution of available energy states. As has already been explained, a transition between these energy states is associated with the wavelength of the photon absorbed or emitted to make the transition. For example, Figure 2.3 shows that more photons with \( \lambda = 311.3 \text{ nm} \) and the associated energy \( E = \frac{hc}{\lambda} = 6.4 \times 10^{-5} \text{ J} \) are absorbed by OH at \( T = 2700 \text{ K} \) than are absorbed at \( T = 3200 \text{ K} \). Also, a cloud of OH absorbs more photons of this energy with \( N = 1.8 \times 10^{16} \text{ molec./cm}^3 \) than with \( N = 9.0 \times 10^{15} \text{ molec./cm}^3 \). Increasing the number density decreases the transmissivity across the entire spectrum while increasing the temperature changes the shape of the transmissivity landscape. This behavior begins to make sense when considering Equation 2.14, but will become more clear in later discussion.

In general, a transmission spectrum for a molecular gas is uniquely defined by its macrostate. For this reason it is not necessary to take into account the entire spectrum in order to determine the macrostate of the gas. Transmission spectra can be collected over a narrow band of wavelengths\(^{35}\) or even at select wavelengths\(^{36}\) and still provide meaningful results. In the case of a heterogeneous gas each molecular species present displays its own transmission spectrum. This causes trouble for analysis when the spectrum of one molecule overlaps that of another molecule. Nevertheless,

*Atoms also have a fine energy-level structure as a result of spin angular momentum in the nucleus or the electron.
†The energy ladder is the same for spontaneous emission, so it could also be described as an emission spectrum.
Figure 2.3: Demonstration of $T$ and $N$ influences on OH spectra. Transmissivity spectra of OH calculated using (Top) two different number densities and (Bottom) two different temperatures, holding the temperature and number density constant, respectively. In each figure, the baseline spectrum from Fig. 2.4 is shown for reference.

it is also possible to find spectral bands where only one of the molecules has transition lines, as is explained next.
2.2.3 The Reaction Mechanisms

Chemical kinetics mechanisms attempt to describe each step involved in the process of a reaction, including the intermediary reactions in which temporary products react again before arriving at a final product. For the present study, the reactions considered are between diatomic Hydrogen (H$_2$) and the diatomic Oxygen (O$_2$) within Air (23.14 \% by weight) under two different mixture ratios. For a listing of the species produced in the process of these reactions, see Table 2.1. In a stoichiometric mixture the final product of reaction will be water vapor (H$_2$O),

\[ 2H_2 + O_2 \rightarrow 2H_2O. \] (2.12)

Intermediate products of this reaction appear in the region where the reaction is occurring*. One of the prominent intermediate species in an H$_2$-Air reaction is the neutral, diatomic hydroxyl radical, OH.$^{37}$ A consideration of the spectral lines for each of the species involved in the kinetics models for the above mentioned reactions reveals that, of these species, OH is the only molecule with transition energies related to the wavelength band between 306–313 nm (see Figure 2.4). Furthermore, the most abundant hydroxyl molecule with eight neutrons in the Oxygen nucleus and one neutron in the Hydrogen nucleus, $^{16}$OH, is the only isotopologue of OH with strong transitions in this band. This affords the opportunity to consider the spectral behavior of a single molecular species in isolation. The following discussion focuses on the energy states of diatomic molecules in general but with the aim of studying Hydroxyl specifically.

2.2.4 Data from the HITRAN Database

The crux for extracting physically significant information from a transmission spectrum is the absorption coefficient (as shown in Equation 2.1). It bridges the divide between macroscopic observations of radiation transmission and the statistical mechanics of the absorbing medium. It will be shown in section 2.2.1 that the absorption coefficient is used to construct model spectra

*These intermediate products, especially OH, may also form by dissociation in regions of high energy, such as in the normal shock of a rocket plume.
Table 2.1: Possible molecules present based on two chemical kinetics models.

<table>
<thead>
<tr>
<th>Species</th>
<th>$H_2-O_2^{38}$</th>
<th>$H_2-Air^{37}$</th>
<th>HITRAN$^{39}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1</td>
<td>1</td>
<td>0 $^a$</td>
</tr>
<tr>
<td>O</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$H_2$</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$O_2$</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$N_2$</td>
<td>1 $^b$</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
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<td>1</td>
<td>1</td>
</tr>
<tr>
<td>NO</td>
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<td>1</td>
<td>1</td>
</tr>
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<td>1</td>
<td>1</td>
</tr>
<tr>
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<td>1</td>
<td>1</td>
</tr>
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<td>$HN=O$</td>
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<td>1</td>
<td>0</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>H$_2$O$_2$</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

A listing of species in the chemical kinetics models for $H_2-O_2$ and $H_2-Air$ reactions alongside an indicator showing whether or not the spectral characteristics of that species are in the HITRAN database. $^a$: Although this data is not available in HITRAN it is well documented in the NIST Atomic Spectra Database.$^{40}$ $^b$: $N_2$ will have some participation in the reaction mechanism if the reaction takes place in an $N_2$ bath.

corresponding to varying macrostates. Focusing on the absorption coefficient or “absorbance” for now, it takes the form:

$$K_j(\nu; T, N) = NS_j(T)Y(\nu - \nu_j)$$  \hspace{1cm} (2.13)

or,

$$K^{(i)}_j(T, N) = NS_j(T)Y^{(i)}_j.$$  \hspace{1cm} (2.14)

The second expression is written in discrete form by indicating the $i^{th}$ value of wavenumber, $\nu^{(i)}$, corresponding to the measured spectral data which are sampled at distinct wavelength “bins”, or pixels. The $j$ indicates a quantity associated with the $j^{th}$ transition which occurs at a wavenumber, $\nu_j$. All of these terms will be revealed in the following discussion except the thermodynamic temperature, $T$ with units Kelvin, and molecular number density, $N$ with units number of molecules per cubic centimeter. These two quantities will be estimated by fitting spectra to data. The line
Figure 2.4: Transmission spectrum of OH at standard temperature and pressure. Transmissivity calculated at $T = 294$ K, $N = 1.0 \times 10^{16}$ molec./cm$^3$, $P = 1$ atm. and $l = 1$ cm.

strength, $S_{j}$, described in section 2.2.5, can be obtained from a database where it is tabulated. The Voigt distribution function, $Y_{j}^{(i)}$, brings shape to each spectral line through various spectral broadening effects and will be explained in detail later, in section 2.2.6.

The open electronic source used in this study is the HIGH-resolution TRANsmission molecular absorption database, known by the abbreviation HITRAN$^{39}$, which catalogs tables from multiple sources for multiple scientifically relevant molecules and their isotopologues. Some of the available molecules are listed in Table 2.1. The following data were downloaded from the HITRAN database for the dominant isotopologue of hydroxyl (OH):

$M$: Molar mass of the molecule in [g mol$^{-1}$]
$Q(T)$: Molecular partition function values for integer values of temperature, $T$

$S_j(T_0)$: Line strength in [cm$^{-1}$ molec.$^{-1}$ cm$^2$] for the $j^{th}$ transition at the reference temperature, $T_0 = 296$ K

$\nu_j$: Center wavenumber in [cm$^{-1}$] of the $j^{th}$ transition

$n_{\text{air}}$: Temperature exponent for the air-broadened half-width at half-maximum

$\gamma_{\text{air}}$: Air-broadened Lorentzian half-width at half-maximum in [cm$^{-1}$ atm$^{-1}$] at 1 atm pressure and the reference temperature

$E_j$: Energy in [cm$^{-1}$] of the lower state in the $j^{th}$ absorption transition

The data conforms to the cgs system of units, the values with a subscript $j$ are vectors organized according to increasing transition wavenumber, $\nu_j$, and the values which depend on temperature are vectors organized according to increasing temperature, $\{T \in \mathbb{Z} \mid 1 \leq T \leq 9000\}$ K. In the database there are 192 transitions in the wavenumber band of interest, where $\{\nu_j \in \mathbb{R} \mid 31948.0 \leq \nu_j \leq 32681.0\}$ cm$^{-1}$ (i.e. roughly 313–306 nm).

Now, to make a comparison between empirical spectra and a model spectrum built from the tabulated data of HITRAN, both spectra are arranged in the form of transmissivities. For the empirical data this is simply:

$$\tau_{\text{emp}}^{(i)} = \frac{I^{(i)}}{I_0^{(i)}}. \quad (2.15)$$

The model transmissivity spectrum, $\tau_{\text{mod}}^{(i)}$, is constructed from the HITRAN data following from Equation 2.10 but in the absence of explicit intensities:

$$\tilde{\tau}_{\text{mod}}^{(i)}(T, N) = e^{-\sum_{j=1}^{\kappa} K_j^{(i)}(T, N)} = \prod_{j=1}^{\kappa} e^{-K_j^{(i)}(T, N)}. \quad (2.16)$$

The full transmissivity is the result of a product of the transmissivities due to all $\kappa$ energy transitions considered. In other words, the total absorption coefficient is the sum of absorption coefficients
from each transition: $K^{(i)}(T, N) = \sum_j K^{(i)}_j(T, N)$.

Since the path length, $l$, through the absorptive volume is not adequately known, it will be multiplied by $N$ to get the column density, $Nl$, so that the model fitting parameters are $T$ and $Nl$. Finally, this model is convolved with an instrument function which will be described in section 2.2.7 and then a comparison is made between the model and the data.

2.2.5 Line Strength

The line strength, $S(T)$, contains the majority of the statistical mechanics in the absorbance. This connection is made clearer in the following discussion. A diatomic molecule possesses energy from four degrees of freedom:

1. Translational
2. Electronic
3. Vibrational
4. Rotational

In an ideal case the molecules behave as rigid-rotators and harmonic oscillators. Non-ideal behavior includes vibrations inducing a time-dependent moment of inertia for the rotational energy, rotation altering the equilibrium bond length for vibrational energy via centrifugal stretching, and higher vibrational states taking large excursions from equilibrium such that the restoring force can no longer be approximated as quadratic in displacement. For now, we consider an ideal, single-species gas with $N$ non-interacting, diatomic molecules in thermodynamic equilibrium at a temperature $T$. The key feature of statistical mechanics that appears in the expression for the line strength is the total partition function, $Q_{\text{tot}}$, which effectively counts the number of states available to the system at energy $E_\kappa$:

$$Q_{\text{tot}}(T) = \sum_{\text{all microstates}} g(E_\kappa) e^{-E_\kappa/kT}$$  \hspace{1cm} (2.17)

*This refers specifically to the electronic states of the electron(s) shared between the atoms of the molecule.
where \( g(E) \) is called the density of states or the degeneracy of energy state \( E \) and it represents the number of configurations of the system at which the total energy of the system is still \( E \). The assumption that the energy modes are independent degrees of freedom allows for a simplification. The total partition function can be re-written as the product of individual partition functions corresponding to the individual degrees of freedom.

\[
Q_{\text{tot}}(T) = Q_t(T)Q_v(T)Q_r(T)Q_e(T) \\
= \left( \sum \sum \sum \sum g_t e^{-E_t/kT} \right) \left( \sum g_v e^{-E_v/kT} \right) \left( \sum g_r e^{-E_r/kT} \right) \left( \sum g_e e^{-E_e/kT} \right). \tag{2.18}
\]

It can be shown\(^4\) that the individual partition functions are

\[
Q_t(T) = \frac{1}{N!} \left[ V \left( \frac{2Mk\pi T}{h^2} \right)^{3/2} \right]^N \tag{2.19}
\]

\[
Q_v(T) = \frac{e^{-hc\omega/2kT}}{1 - e^{-hc\omega/2kT}} \tag{2.20}
\]

\[
Q_r(T) = \frac{8\pi^2 f kT}{h^2} \quad \text{for } T > 300K \tag{2.21}
\]

\[
Q_e(T) = \sum g_e e^{-(E_n - E_0)/kT} \tag{2.22}
\]

For the expressions above, the terms are defined as

- \( V \) the volume of the system under consideration
- \( M \) the total mass of the diatomic molecule
- \( h \) Planck’s constant
- \( f \) the inter-molecular force constant
- \( \omega = \frac{1}{2\pi c} \sqrt{f} \) the frequency of a harmonic oscillator
• $\mu$ the reduced mass of the molecule

• $I$ the moment of inertia for the molecule

• $g_e = (2S + 1)$ when no component of the electronic orbital angular momentum lies along the internuclear axis but $g_e = 2(2S + 1)$ otherwise

• $S$ the total electronic spin angular momentum

• $E_0$ is the ground state electronic energy

The rigid-rotator, harmonic oscillator approximation fails to fully take into account the electronic energy levels. If it did, then the vibrational and rotational partition functions would have explicit dependence on the electronic energy level. However, it turns out there are simple corrections that can be made to the model to account for the nonlinear effects in most cases. A discussion of these effects can be found in the works of Davidson\textsuperscript{41} and Lucht\textsuperscript{42}.

Conveniently, the statistical mechanics can be seen in the partition function that is contained in the line strength,

$$S_j(T) = \frac{S_j(T_0)Q(T_0) e^{\frac{-hcE_j}{kT}} \left(1 - e^{\frac{-hc\nu_j}{kT}}\right)}{Q(T) e^{\frac{-hcE_j}{kT_0}} \left(1 - e^{\frac{-hc\nu_j}{kT_0}}\right)}$$

(2.23)

which is calculated from tabulated values in the HITRAN database.

2.2.6 Broadening Effects

The Voigt distribution, $Y(\nu - \nu_j)$, in Equation 2.14 incorporates spectral broadening factors into the transition. A true spectrum is more than simply a collection of dirac-delta style lines with their intensities. Various influences on the gas and on the transmission of radiation give width to the lines, broadening or distorting them. Consequently, the shapes of these lines communicate what is happening in the gas at the molecular level. These effects include:

1. Natural broadening

2. Doppler broadening
Figure 2.5: A demonstration the spectral broadening profiles.
3. Pressure broadening.

Together, these mechanisms have a convolution effect on the absorbance. The shape of a spectral line due to an energy transition of a molecule in a vacuum is a consequence of the energy being quantized, in other words, in the form of a photon. A photon parcels the energy up in the form of a wavepacket with finite extent. The natural spectral content of the photon is not a single wavelength, but a distribution with a peak at a particular wavelength. This gives spectral lines an initial Lorentz distribution profile (see Figure 2.5). The Lorentz profile is

\[ \tilde{Y}_L(\nu - \nu_j) = \frac{\gamma_L}{\pi (\gamma_L^2 + (\nu - \nu_j)^2)} \] (2.24)

where \( \gamma_L \) is the half-width at half-max (HWHM) of the distribution. The HWHM of the natural broadened profile is most often very small compared to pressure broadening—as is the case here—so natural broadening is neglected.

Doppler broadening arises from the random motion of particles in a gas giving the macroscopic gas the quality of thermal energy. At the moment a molecule of the gas absorbs a photon, the velocity of the molecule might have had a component of motion parallel to the path of the photon. If it was moving towards the oncoming photon, the Doppler effect dictates that the frequency of the photon will be slightly higher in the reference frame of the molecule than it is in the lab frame. Because there is a normal distribution of velocities at thermodynamic equilibrium, resulting in more or less speed towards or away from the photon, the effect of doppler broadening is to give the spectral lines a Gaussian profile (see Figure 2.5):

\[ \tilde{Y}_D(\nu - \nu_j) = \frac{e^{-(\nu - \nu_j)^2/2\sigma^2}}{\sqrt{2\pi \sigma}} \] (2.25)

where \( \sigma \) is the standard deviation of the distribution. The half-width at half-maximum is given by
\[ \gamma_D = \sqrt{2 \ln 2} \sigma \text{ or } \]
\[ \gamma_D = \frac{v_j}{c} \left( \frac{2N_A k T \ln 2}{M} \right)^{1/2} \quad (2.26) \]

where \( N_A \) is Avogadro’s number.

Pressure broadening, also called collisional broadening, convolves the spectral lines with a Lorentz distribution (Equation 2.24) having a width due both to the natural decay rate of the molecule from an excited state to a lower state via spontaneous emission of a photon and the ensemble-averaged rate of collisions taking place between molecules. In other words, if inter-molecular collisions become more frequent in a gas than the natural rate of spontaneous emission for the gas molecules then the collisions can induce an early photon emission, broadening the spectral content of the wavepacket by shortening its temporal extent. The half-width at half-maximum\(^{*}\) is given by:

\[ \gamma_L = \gamma_{air} P_{amb} \left[ \frac{T_0}{T} \right]^{n_{air}}. \quad (2.27) \]

At higher pressures, the peak of the line is known to skew, or even shift, but these effects are negligible for the spectral resolution of our system.

The resulting distribution from these combined broadening effects is called a Voigt distribution, \( Y_j^{(i)} \), and is the profile used in constructing the model spectra for this study (see Figure 2.5). It is simply the convolution of a Gaussian with a Lorentzian distribution. To save computational effort, the convolution calculation can be approximated using Whiting’s empirical expression\(^{43}\) for each value of \( v_j \):

\[ \tilde{Y}_j^{(i)} \approx \frac{1}{2 \gamma \left( c_1 + c_2 x + c_3 x^2 \right)} \left( 1 - x \right) e^{-c_4 y^2} + \frac{x}{1 + y^2} + c_5 (1 - x) x \left[ e^{-c_6 y^{9/4}} - \frac{1}{1 + c_7 y^{9/4}} \right] \quad (2.28) \]

where

\(^{*}\)When the self-broadened half width of the target gas is different from the air-broadened half width, then this expression gains a self-broadening term.\(^{39}\)
\[ x = \gamma_L / \gamma_V \]
\[ y = |v^{(i)} - v_j| / \gamma_V \]
\[ \gamma_V \approx 0.5346 \gamma_L + (0.2166 \gamma_L^2 + \gamma_D^2)^{1/2}; \] the Voigt half-width at half maximum.

and Table 2.2 lists the values of the constants.

**Table 2.2:** The assignment of constant values for Equation 2.28.

<table>
<thead>
<tr>
<th>#</th>
<th>c#</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.065</td>
</tr>
<tr>
<td>2</td>
<td>0.447</td>
</tr>
<tr>
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<tr>
<td>4</td>
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</tr>
<tr>
<td>5</td>
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</tr>
<tr>
<td>6</td>
<td>0.0841</td>
</tr>
<tr>
<td>7</td>
<td>0.0210</td>
</tr>
</tbody>
</table>

Before being included in the absorption coefficient, the distribution should be normalized so that \( \int Y_j(\nu) \, d\nu = 1 \). Thus,

\[ Y_j(\nu^{(i)}) = \frac{\tilde{Y}_j(\nu^{(i)})}{\int_{-\infty}^{\infty} \tilde{Y}_j(\nu) \, d\nu}. \]  \hspace{1cm} (2.29)

2.2.7 The Instrument Function

The instrument function or instrumental bandpass, along with the spectral resolution, restrict how well an instrument can discriminate between nearby spectral lines. It is a collection of features from the entrance optics, the entrance slit, the spectrometer optics, and the detector. All of these influences are convolved together with the real spectrum to obtain the measured spectrum. The most dominant of these factors is the entrance slit function. It is also the only factor considered in this analysis. The image of the slit is projected through the spectrometer optics onto the detector without any magnification. As a result, the measured spectrum is actually a collection of slit images, one for each wavelength of light constituting the radiation impinging on the spectrometer. The finite width of the slit results in the spectrum being smeared out. Mathematically this is the
Figure 2.6: Examples of slit functions. An example of two common instrument (or “slit”) functions and the result of applying them to a spectral line.

Figure 2.7: Demonstration of a slit function applied to an OH transmission spectrum. Applying a box-car slit function to the general spectrum in Fig. 2.4 and generated for a slit with width 0.18 mm, as used in the experiments here.
convolution of the real spectrum with the distribution of radiation intensity across the entrance slit (for example, consider Fig. 2.6). This normalized distribution is the slit function.

It is common to use a standard normal distribution or a box-car function to model the slit function (refer to Fig. 2.6). The instrument function can also be directly determined by considering either the intensity distribution of the spectrum at zeroth order* or the profile of an isolated spectral line, for example, from the mercury emission calibration source. In principle then, the instrument function would then be the deconvolution of the theoretical emission line from the measured emission line. However, for a discretized selection of data, the process of deconvolving the slit function from the data is challenging. It is easier to convolve a theoretical spectrum with a calculated instrument function. This is where the normal distribution or box-car functions come in.

For a finite domain, the instrument function is built centered in the domain. With no magnification in the spectrometer the full-width at half-max of the instrument function distribution, $2\gamma_S$, is equal to the slit width, $s_S$. This width in space can then be converted to wavelength using the spectral resolution in units of nm/mm. So, for a slit width of $s_S$, this corresponds to a change in wavelength, $\Delta \lambda = s_S \times (m/d_p)$ where $m$ is the resolution of the spectrometer in units of nm/pixel and $d_p$ is the width of a pixel in mm. In an ideal scenario, slit width would be zero, giving a dirac-delta distribution so that the spectral lines remain unaltered by the instrument through which they pass. In the analysis conducted presently, a box-car slit function is chosen:

$$f_s(\nu^{(i)}) = \begin{cases} \frac{1}{\beta} & \text{if } |\nu^{(i)} - \eta| \leq \beta \\ 0 & \text{if } |\nu^{(i)} - \eta| > \beta \end{cases}$$

(2.30)

here we have used as placeholders: $\eta$ which is at the midpoint of the wavenumber array $\nu^{(i)}$ such that, if $A$ is the length of the array, $\eta = \text{round}\{(\nu^{(A)} + \nu^{(1)})/2\}$, and $\beta$ which is the half-width at half-

*Zeroth order for the spectrometer is at a wavelength of 0 nm, where the grating is rotated to the angle at which radiation from the slit comes directly through the spectrometer, that is, it is reflected by the grating without undergoing diffraction.
maximum of the box-car function, $\beta = \gamma_S / \Delta \lambda$. The raw slit function, $f_s(\nu)$, must be normalized, giving $f_s(\nu(i))$ where $b = \int f_s(\nu) \, d\nu$. Now, convolving the box-car function with the absorptivity, the result is converted into a model transmissivity which can be compared to the data (for example, consider the red curve in Fig. 2.7). The discrete form of this model is

$$1 - \tau_{mod}^{(i)}(T, NL) = \sum_{q=1}^{2560} [1 - \tau_{mod}^{(q)}(\nu(q), T, NL)] f_s(\nu(i-q+1))$$

(2.31)

As given in MATLAB documentation for the convolution function\textsuperscript{45}, with the spectral band truncated to that of the data. With the ability to construct a model spectrum at selected values of temperature and number density the process of fitting the model to the data to estimate $T$ and $NL$ can begin.

### 2.2.8 Spectra Fitting Algorithm

#### 2.2.8.1 Bayesian Inversion Fitting Scheme

Bayesian inversion seeks to take measured data and estimate the physical parameters of the system which generated the data. It is an inverse problem, hence the “inversion.” To perform Bayesian inversion, the following information is needed:

1. A discrete set of physical parameters: $\mathbf{a}$.

2. Experimental data: $\mathbf{d}$.

3. The physical theory: $\mathbf{g}$. This operates on the physical parameters and, with uncertainty, $\mathbf{n}$, produces the data: $\mathbf{d} = \mathbf{g}(\mathbf{a}) + \mathbf{n}$

4. Prior information: $I$. This provides constraints on the physical parameters, forming the prior distribution, $s(\mathbf{a}|I)$. 
The outcome of Bayesian inversion is a posterior distribution that is the normalized product of the prior distribution and the likelihood function:

\[ p(\mathbf{a} | \mathbf{d}) = \xi \cdot s(\mathbf{a} | \mathcal{J}) \cdot l(\mathbf{a} | \mathbf{d}) \]  

(2.32)

where \( \xi \) is the normalization factor obtained by integrating \( s(\mathbf{a} | \mathcal{J}) \cdot l(\mathbf{a} | \mathbf{d}) \) over the entire parameter space and \( l(\mathbf{a} | \mathbf{d}) \) is the likelihood distribution built according to the problem considered. The integration for the normalization factor can get quite tricky for numerous parameters but various simplification methods exist. For the two physical parameters considered in this study, the integration is computationally manageable.

As stated before, the two physical parameters considered here are the temperature, \( T \), and the molecular column density, \( Nl \). As a result, \( \mathbf{a} = \{ T, Nl \} \). The physical model is \( \tau_{\text{mod}} \) as has been discussed already, so \( g(\mathbf{a}) = \tau_{\text{mod}}(\lambda; T, Nl) \). The prior information organizes the possible values which can be taken by \( T \) and \( Nl \), weighted according to their probability. Here, based on prior experience fitting models to this data, the parameter values are chosen to fall in the ranges \( \{ T \in \mathbb{Z} \mid 1000 \leq T \leq 5000 \} \) and \( \{ Nl \in \mathbb{R} \mid 4.52 \times 10^{15} \leq Nl \leq 5.483 \times 10^{17} \} \). For \( Nl \), the discrete values chosen in the prescribed range are logarithmically spaced, dividing the range into 3474 parts. The prior distributions for these two parameters are chosen to be Gaussian-normal distributions, \( s(T | \mathcal{J}) \) and \( s(Nl | \mathcal{J}) \). The mean of the temperature prior for the rich cases is 2967 K and the standard deviation is chosen to be rather broad, at 4120 K. For the column density in the rich cases, the mean of the prior is \( 4.192 \times 10^{16} \) with a standard deviation chosen to be \( 1.4234 \times 10^{17} \).

In the stoichiometric cases the temperature prior has a mean of 3662 K and a standard deviation of 2131 K while the column density prior is \( 1.006 \times 10^{17} \) with a standard deviation of \( 1.927 \times 10^{16} \). These parameters are determined according to results from earlier spectral fitting analysis. Because these priors are guesses at the solution, we leave the distributions broad so as not to strongly favor a solution which is incorrect. Alternatively, these could be chosen to have a constant value over all values in the range. Regardless of the choice of distribution, the full prior is \( n \)-dimensional for \( n \)
Figure 2.8: An example of a spectral model fit to experimental data using Bayesian statistics. Comparison of an empirical spectrum and the curve of best fit built using $T = 2715$ K and $Nl = 3.700 \times 10^{16}$ molec./cm$^2$. In the lower plot, the percent difference residual between the model and the data is shown.
An example prior distribution for the Bayesian inversion fitting routine. Prior distribution built from a Gaussian distribution in the two independent variables, $T$ and $Nl$. The red star indicates the final location of the posterior maximum, the blue circle indicates the location of overall maximum for the present distribution quantity.

Physical parameters considered in the model. The full prior is the matrix product of the individual distributions,

$$s(a|\mathcal{J}) = s(T|\mathcal{J})^t s(Nl|\mathcal{J})$$  \hspace{1cm} (2.33)

where $t$ represents the transpose. See Figure 2.9 for a graphical representation of this prior distribution.

For the likelihood distribution (Figure 2.10, right), we use a product of Gaussians from each
point considered in the wavelength space. For each pair of \( T \) and \( Nl \) the distribution is

\[
\ln\{l(T, Nl|d)\} = - \sum_{i=1}^{497} \frac{[\tau_{\text{mod}}(\lambda^{(i)}; T, Nl) - \tau_{\text{exp}}(\lambda^{(i)}; T_{\text{exp}}, Nl_{\text{exp}})]^2}{2(\sigma_{\text{exp}}^{(i)})^2}.
\]

Here the sum is over all pixels corresponding to values of \( \lambda \) within the active spectral range of OH absorption. The expression is the sum of the square of the standard, Euclidean distance between each of the corresponding points of the model and the data. It is the same sum that is minimized in a least-squares fitting scheme. To verify that the model and the data match correctly along the wavelength axis, the cross covariance between the two is computed. If there is an offset, the model is shifted in order to make a direct comparison between the spectra. Offsets can be caused by the convolution of the slit function with the model spectrum or by inaccuracies in the wavelength calibration for the spectrometer, such as making a poor selection of the center wavelength for an emission line.

The exponential term of the likelihood is given in Figure 2.10 on the left. The standard deviation in the denominator is the standard deviation of the experimental transmissivity at each value of wavelength.

Lastly, the normalization factor, \( \xi \), is calculated by integration over the entire parameter space. In this case, the parameter space is discrete, so trapezoidal sums are used instead. Let \( F(T, Nl) = s(T, Nl|d) l(T, Nl|d) \), then

\[
\frac{1}{\xi} \approx \frac{5.483 \times 10^{17}}{4.52 \times 10^{15}} \int_{4000}^{5000} \int_{1000}^{5000} F(T, Nl) \, dT \, dNl
\]

\[
\approx \sum_{\alpha=2}^{4000} \sum_{\beta=2}^{3474} \frac{4 \Delta T \cdot \Delta Nl^{(\alpha)}}{4} \left[ F(T^{(\alpha)}, Nl^{(\beta)}) + F(T^{(\alpha)}, Nl^{(\beta-1)}) + F(T^{(\alpha-1)}, Nl^{(\beta-1)}) + F(T^{(\alpha-1)}, Nl^{(\beta-1)}) \right].
\]

Now the posterior distribution is obtained as in Equation 2.32 and as shown in Figure 2.11. The peak value in the posterior is the most likely point in the parameter space and considered to be the solution to the inverse problem. Thus the solution gives the parameters which build the
Figure 2.10: The sum of squared differences and the resulting likelihood distribution for the Bayesian inversion fitting routine. (Left) The distribution composed solely of the sum of squared differences, used in the least squares fitting approach and applied in the exponent of the likelihood distribution. Here, we are looking for the parameters which form the curve that is the shortest Euclidean distance from the data. (Right) The likelihood distribution obtained from comparing the model within the explored parameter space to the synthetic data. In both figures, the red star indicates the final location of the posterior maximum, the blue circle indicates the location of overall maximum for the given distribution quantity.

spectrum most closely matched to the data, shown in Figure 2.8.

In the event that multiple spectral effects influence the spectrum, the model can be expanded to include the added effects or the added effects can be removed before the fitting procedure is conducted. For the present case of transmission spectra with combined effects of molecular absorption and particulate scattering, the scattering part will be removed before conducting the absorption spectrum fitting procedure.

2.2.8.2 Estimating Uncertainty in Fitted Parameters

The posterior distribution represents a bi-variate probability distribution or a joint probability distribution function, jpdf. Isometric lines through the maximum along each dimension of the distribution function are not Gaussian so the metric chosen to indicate the uncertainty of the fitted parameters is the half-width-at-half-max for the upper and lower wings of the distribution.
Figure 2.11: The posterior distribution for the Bayesian inversion fitting routine. The posterior distribution at whose peak the model spectrum from Figure 2.8 is built.

Figure 2.12: The isometric curves along each dimension through the posterior maximum. The red dashed lines in each figure show the width of the uncertainty estimate using the HWHM of the distribution.
2.3 Scattering: Non-Gaseous Particles

In essence, the process of scattering electromagnetic radiation by any object or cloud of particles is a solution to Maxwell’s equations given the boundary conditions of the object or cloud. The solution by Mie is the most noteworthy of the solutions for scattering by spherical particles. The full form takes into account the size and shape of the particles and the polarization of radiation as well as the wavelength. This is necessary when the size of the particles is comparable to the wavelength of radiation being scattered. For particles which are adequately small compared to the wavelength, simplifications can be applied, leading to Rayleigh scattering. Given a particle size, scattering is particularly prominent with shorter wavelengths and, over all bands, the scattering varies slowly with wavelength as compared to the discrete spectral features of molecular emission or absorption. This solution is designed for a single particle or for a collection of particles spaced sufficiently far apart. It becomes more complicated for a cluster of particles not sufficiently far apart. Since the development of Mie scattering, techniques to model more complicated systems have been developed. These take into consideration both different shapes and sizes of particles while also expanding the Mie solution to include the possibility of multiple particles in a cluster. A noteworthy solution and computer code for predicting the scattering from a cluster of different sized particles is the T-Matrix method.

The particles considered in this study have a nominal diameter of 0.30 µm which is right at the operating wavelength for this study. As a result, the shapes of the particles and the polarization of the radiation have an important influence on the scattered radiation. It will be shown that the present procedure side steps the need to know these various complications by simply using empirical results to model the scattering without knowing the parameters of the particles.

Bohren and Huffman present a thorough derivation of the scattering coefficients which come out of Mie Theory. The reader is referred to that text for the rigorous derivation. Here we consider the results which are most useful in generating models of scattering. The scattering
coefficient, $\sigma_s$, from Equation 2.8 takes the form

$$\sigma_s(\nu) = N_s \nu^2 \sum_{\alpha=1}^{\infty} (2\alpha + 1) \text{Re}\{a_\alpha + b_\alpha\}. \quad (2.35)$$

Where $a_\alpha$ and $b_\alpha$ are the outward scattering coefficients given by

$$a_\alpha = \frac{\mu m^2 j_\alpha(mx)[xj_\alpha(x)]' - \mu_1 j_\alpha(x)[mxj_\alpha(mx)]'}{\mu m^2 j_\alpha(mx)[xh_\alpha^{(1)}(x)]' - \mu_1 h_\alpha^{(1)}(x)[mxj_\alpha(mx)]'} \quad (2.36)$$

$$b_\alpha = \frac{\mu_1 j_\alpha(mx)[xj_\alpha(x)]' - \mu j_\alpha(x)[mxj_\alpha(mx)]'}{\mu_1 j_\alpha(mx)[xh_\alpha^{(1)}(x)]' - \mu h_\alpha^{(1)}(x)[mxj_\alpha(mx)]'}. \quad (2.37)$$

Here $\mu = \cos \theta$, $\theta$ is the polar angle from the spherical coordinates of the particle, and $m = \frac{k_1}{k} = \frac{n}{n_1}$ where $k$ is the wavevector in the surrounding medium and $k_1$ is the wavevector inside the particle while $n$ is the refractive index in the surrounding medium and $n_1$ is the refractive index in the particle. Being primarily air, the surrounding medium has an index of refraction roughly around 1. For the particle, the index of refraction changes not only with wavelength but also with temperature, $T$. There are two parts to the refractive index, the real part which is related to the scattering properties of the material and the imaginary part which is related to the absorptive properties of the material.\(^{23,22}\) For now, we neglect the absorption by the particles and consider only the scattering part because the complex part of the refractive index is three orders of magnitude smaller than the real part of the refractive index. Due to the prominence of alumina particulate in solid rocket exhaust plumes several different studies have been conducted through the years with the aim of describing the complex refractive index of the particulate at high temperatures, from 1500 K to 3000 K.\(^{23}\) Because these studies have been conducted under different conditions, there are several different expressions to describe the wavelength and temperature dependence of the refractive index.\(^{23}\) We use the model for the real part of the refractive index developed by Kuzmin et al.\(^{22}\)

$$n = 1.747 + 0.0066\lambda - 0.0068\lambda^2 + 0.00003T. \quad (2.38)$$

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Returning again to Eqs. 2.36 and 2.37, \( x = ka \) with \( a \) equal to the radius of the spherical particle. The \( j_\alpha(x) \) are the spherical Bessel Functions of the first kind. Meanwhile the \( h^{(1)}_\alpha(x) \) are the outward-going spherical Bessel Functions of the third kind. The terms in square brackets with a prime, for example \( [\cdot]' \), represent differentiation of the term inside the brackets with respect to the argument of the Bessel function. So, for example,

\[
[ mxj_\alpha(mx) ]' = \frac{\partial}{\partial(mx)} [ mxj_\alpha(mx) ].
\] (2.39)

Since it is not practical or feasible with a finite system to generate an infinity of terms in the sum for Equation 2.35, Bohren and Huffman proposed an approximation using \( \max(x) + 4\max(x)^{(1/3)} + 2 \) as the number of terms, giving the scattering coefficient plus or minus a small error equal to the sum of all the neglected terms.

Now, for ease of notation, we call everything besides the number density of particles, \( N_s \), in Equation 2.35 the extinction coefficient so that, \( C_{ext}(a) = \nu^2 \sum_{\alpha=1}^{\infty} (2\alpha + 1)\text{Re}\{a_{\alpha} + b_{\alpha}\} \). Each particle size has its own extinction coefficient associated with it. For a polydispersion of particle sizes in a volume, the extinction coefficient is then the weighted average of extinction coefficients according to the probability distribution of the particle sizes.

A LS Instruments Dynamic Light Scattering instrument on campus at the University of Mississippi was used to find the particle size distribution of the particular lot of alumina used in making the scattering measurements. A log-normal fit was applied to the dominant peak of the size distribution, the distribution was normalized for integration along the particle diameter axis, and then twenty points from this curve were chosen with ten points on either side of the peak. The area under these twenty points accounts for roughly 80\% of the actual distribution. The distribution is truncated and discretized in order to optimize computational time. Now, rather than calculating the weighted average using an integral, it is calculated using the statistical weight of these twenty points. With the weighting function, \( W(a) \), where \( \sum_{i=1}^{20} W(a_i) = 1 \), the weighted average for the
The measured particle size distribution. The particle size distribution measured by a light scattering instrument, giving a mean diameter of 0.28 \( \mu \text{m} \).

The extinction coefficient is:

\[
C_{\text{tot}}(\nu; a) = \sum_{i=1}^{20} W(a_i)C_{\text{ext}}(a_i).
\] (2.40)

The process of averaging the extinction coefficients together like this results in an aggregate coefficient which is smoothed out compared to the individual coefficients.\(^{32}\) For the 0.30 \( \mu \text{m} \) nominal diameter polydispersion of particles used in this study, it is observed that the aggregate scattering coefficient is nearly constant over the band of interest. This implies that the transmissivity due to scattering by this particulate dispersion might be considered a constant over wavelength.

For reference, the scattering coefficient over a band from 200 nm to 3000 nm is plotted in Figure 2.14. It can be seen that the coefficient reaches a local maximum around 300 nm and is rather flat in the 306–313 nm range being considered in this study.

2.4 Assumptions and Simplifications

The experimental system considered in this study involves a high-temperature, reacting, moving gas with scattering and absorbing characteristics. A summary of the assumptions made to
Figure 2.14: The particulate scattering coefficient. (a) A broad-band look at the behavior of the scattering coefficient, computed for a particle temperature of 2900 K. The red line indicates the total scattering coefficient. The gray lines indicate the individual scattering coefficients for each of the particle sizes. The darker the gray line, the stronger it contributes to the weighting function, $W(a)$. (b) The scattering coefficient in the band of interest for this study.

simplify the problem include:

1. Homogeneous volume: The properties of the gas do not change from one end of the exhaust plume to the other, along the line of sight. This also means that the radiation is not refracted by the presence of the plume, so, under this homogeneity assumption there are no density gradients in the plume to have a lens effect on the radiation.

2. Slow flow with respect to speed of light

3. Non-polarizing medium

4. Polarization independent: The radiative transfer is the same regardless of the polarization of the incident light.

5. Constant index of refraction: The index of refraction does not change throughout the measurement volume.

6. Local Thermodynamic Equilibrium: Spectra constructed for a given temperature assume the temperature of the system has already stabilized. This assumption is valid provided the
volume is not being probed at a rate near or below the sub micro-second time scales it takes for the temperature to stabilize.\textsuperscript{47,48}

7. Independent energy modes: The rigid-rotator harmonic oscillator model with corrections applied.

8. The thermal emission from the flame is negligible in the wavelength band being considered

9. The in-scattering is negligible: The solid angle of incident radiation is narrow enough to neglect this term and the cloud of particles is sparse enough that single scattering will not direct radiation into the beam path.

Assumptions 1–6 are standard assumptions in the field of radiative transfer, assumption 7 is often used for the development of molecular absorption theory. The final two assumptions are made here with good reason and for simplification of the theory.

Now, from Equation 2.8, the remaining expression is

\[
\frac{dI(\nu)}{dl} = -[K(\nu) + \sigma_s(\nu)] I(\nu)
\]

where the notation is simplified and the path length and time dependence of $I$ have been dropped for ease of notation. This expression can be immediately solved, giving

\[
I(\nu) = I_0 e^{-\int \sigma_s(\nu) dl} e^{-\int K(\nu) dl}.
\] (2.41)

This expression leaves open the possibility that the scattering and absorption coefficients depend on the location in the path through the plume. The uniform volume assumption simplifies the expression so that only the total distance, $l$, across the measurement volume is needed

\[
I(\nu) = I_0 e^{-l\sigma_s(\nu)} e^{-lK(\nu)}.
\] (2.42)
The basis of data analysis in the present work has now been established. Statistical mechanics provides a model for the transmissivity of a gas of OH. Assuming that the OH is in thermodynamic equilibrium within the measurement volume, we can use the model to estimate the macrostate of the gas. The Mie solution to Maxwell’s equations provides a description of the particle extinction coefficient which is smoothed out over wavelength due to averaging among the various coefficients produced by the polydispersion of particle sizes. As a result, it is shown that the expected scattering coefficient for the 0.30 µm nominal diameter particles is nearly constant across the spectral range of interest.
CHAPTER 3

STUDIES IN A LAB-SCALE ROCKET EXHAUST PLUME

The experimental system involves a sub-scale, static, rocket simulator which reacts gaseous H\textsubscript{2} with gaseous O\textsubscript{2} in a combustion chamber and produces a high speed, reacting exhaust plume. Broad band radiation is passed through the plume and the transmission spectrum is measured. By adjusting the fuel and oxidizer flow rates, a fuel equivalence ratio

$$\phi = \frac{m_{\text{H}_2}/m_{\text{O}_2}}{(m_{\text{H}_2}/m_{\text{O}_2})_{\text{st}}}$$

(3.1)
can be specified. Here $m_{\text{H}_2}$ is the mass of hydrogen and $m_{\text{O}_2}$ is the mass of oxygen entering the combustion chamber. The subscript $st$ represents the the ratio of the masses at stoichiometric conditions. Spectral measurements are made for two fuel equivalence ratios: stoichiometric ($\phi \approx 1$) and rich ($\phi \approx 2$).

Solid* aluminum oxide particles are injected into the combustion chamber of the rocket, causing radiative scattering in the plume. The details of this setup and procedure are described in this chapter.

3.1 Materials and Methods

A spectral transmission measurement begins with the radiation source. The radiation is focused to a measurement volume where the radiation extinction is measured and then refocused onto the entrance slit of a spectrometer. The spectrometer distributes the incident radiation into

*They are solid when they are injected into the combustion chamber although they may be molten when they exit the combustion chamber.
Figure 3.1: Illustration of the radiation path for the static rocket experiment.

Spectral components and a camera at the spectrometer exit receives and digitizes that spectrum. Figure 3.1 illustrates this measurement system.

3.1.1 Light Source

Studying broad band radiative absorption requires a radiation source whose luminosity is greater than that of the flame and whose spectrum in the band of interest is, or can be, relatively broad.\textsuperscript{42} A PerkinElmer FX-1160 Xenon flashlamp with a PerkinElmer FYD-1150 Lite-Pac trigger module was chosen for the radiation source. The arc lamp produces short-duration, bright, white light with spectral content from the near UV and going to the near IR. The timing of the flashlamp excitation and the camera image acquisition were coordinated using a BNC 575 series pulse generator.
The reference intensity, $I_0$, was measured by the spectrometer without the plume present. The transmitted intensity, $I$, was obtained in the same way as $I_0$ except that a reacting flow was present in the measurement volume, causing spectral extinction in a manner characteristic of the constituents in the flow. It is assumed the only differences between $I$ and $I_0$ are the effects caused by the test gas in the measurement volume.

3.1.2 Spectrometer

The spectrometer is an Acton Spectra Pro 2750, 750 mm focal length, Czerny-turner spectrometer ($f/9.7$) equipped with a planar, 600 grooves/mm, 300 nm-blaze grating. At the focal plane is positioned a pco.edge monochromatic sCMOS camera which records the spectra digitally to a computer.

3.1.2.1 Spectrometer Calibration

Wavelength calibration was conducted using an Oriel 6035 Mercury Pen-Ray lamp as the radiation source. The mapping from wavelength to position across the spectrometer exit plane is nonlinear, but this doesn’t become dramatically evident until considered over a large wavelength band. To do this requires that the grating turret rotate to a different angle. Holding the turret stationary at one band reduces calibration errors that would result from the motor slipping, but it limits the range of wavelengths that can be used in a study. Since the band of interest here, $306 - 313$ nm, covers only 7 nm, it was only necessary to calibrate the spectrometer at a single turret position, spanning a 36 nm spectral range. The wavelengths used for calibration were from the lines of first ionization of Mercury, centered at 296.7283 nm, 302.1504 nm, 312.5674 nm, 313.1555 nm, and 313.1844 nm. The last two center wavelengths are lines which are very close together. The distance between these two is too small for the resolution of our system so they appear as one peak. These two peaks are given slightly different relative intensities in the NIST Basic Atomic Spectroscopic Database, so we take the peak observed through the spectrometer to be the weighted average of these two peaks, assuming that the transmissivity of the spectrometer is constant over this small wavelength interval.
Figure 3.2: Time history of Xenon arc lamp emission. Fitted oscilloscope data of silicon PIN photo diode response to Xe arc lamp flash. \( V(t) = ae^{-t/b} \), where \( a = 6.6633 \) V, and the time constant \( b = 179.53 \) \( \mu \)s.

3.1.3 Detector

The pco.edge mono (“pco”) camera uses a monochromatic, scientific CMOS chip with a 2160\( \times \)2560 array of square pixels, each 6.5 \( \mu \)m on a side. Of the available pixels, a region of interest containing 256\( \times \)2560 pixels constrains the total height of the measurement images to roughly the height of the entire beam at the spectrometer output. The 16.6 mm wide chip restricts the lateral extent and therefore the captured wavelength band of the measurement. A single row from a single spectrum snapshot represents a spectrum, 1 by 2560 pixels. Thus, there are 2560 wavelength bins with a combined spectrometer-camera system spectral resolution of roughly 0.0142 nm/pixel, with a full operation band of 36 nm from 295 nm to 331 nm. Other industry standard detectors such as
the PI-MAX capture a broader band of wavelengths but have a larger pixel size compared to the pco.edge, therefore the pco.edge provides a marked improvement in spectral resolution. While the pco.edge is not designed for use in the UV, it has a non-zero (between 5–10%), linearly increasing quantum efficiency in the spectral range from 300–350 nm, enabling its use provided the optical system throughput is strong enough. For the plume measurements the camera used a global shutter with an exposure time of 1 ms. However, it was determined after the plume measurements that the majority of the flash lamp emission occurs over the course of 444.6 $\mu$s, as determined by the time during which the emission signal is above 10% of the peak, assuming a linear rise to the peak (see Fig. 3.2). Since this emission lifetime coincides with the detected signal, the exposure time is effectively the 444.6 $\mu$s of the flash lamp emission. There is negligible emission from any other sources in the spectral range of interest so there is no more voltage accumulated on the detector for the remainder of the camera exposure. There was no programmed timing delay between the timing generator and the camera exposure trigger; however, the flash lamp was given a delay of 3 ms to account for the initialization time of the detector. The timing generator pulse period was therefore 4 ms and both channel outputs were on an identical duty cycle of 1 on, 4 off, giving 16 ms of no triggers to account for the readout time after each acquisition even though the pixel rate was 95 MHz. As a result, the total time interval from the start of one frame and the start of the next frame was 20 ms.

3.1.4 Lab-Scale Rocket Experiment

The rocket simulator was fixed to a stand built from 80-20 rail. The optics before the turning mirror are mounted to a vertical 80-20 rail so that the optics hang horizontally, creating a vertical beam path. The support spine for these optics along with the remaining optics and the spectrometer are mounted to an optics bread board, raised on legs. This stand was carefully positioned so that the beam waist occurs at the face-on center of the exhaust plume.

The beam path elements were:

$X$: Xenon arc lamp
Figure 3.3: Photograph of the static rocket experiment. In this image the spectrometer entrance slit is blocked by a dust cover.
\(A_1\): Circular iris aperture

\(L_1\): Fused silica bi-convex lens with \(f = 90\, \text{mm}\) and \(D = 46\, \text{mm}\) giving \(f/1.96\)

\(\mathcal{R}\): Rocket simulator reacting exhaust plume

\(M\): UV anti-reflective coated turning mirror angled at \(45^\circ\) with respect to the beam path.

\(L_2\): Fused silica bi-convex lens with \(f = 150\, \text{mm}\) and \(D = 46\, \text{mm}\) giving \(f/3.26\)

\(A_2\): Slit aperture

\(S\): Spectrometer entrance slit, \(s_S = 0.180 \pm 0.005\, \text{mm}\).

Note that the aperture opening sizes were not directly recorded, but all needed values can be obtained by working backwards from the detector to the measurement volume.

3.1.4.1 Distances

For all data series, the stream-wise distance from the nozzle exit to the point of measurement was \(2.00 \pm 0.1\, \text{in.}\) and the beam path was approximately centered on the nozzle (\(\pm 0.1\, \text{in.}\)). The cross-stream length of the beam at the focus was measured to be \(0.16 \pm 0.04\, \text{in.}\) with the stream-wise width of the beam being approximately \(0.04 \pm 0.04\, \text{in.}\). This informs the estimation of the path length through the plume as explained in Section 3.1.4.2.

For reference, the distances along the path between the centers of the optical elements are given in Table 3.1. The optics were adjusted slightly for the seed-on measurements, improving the signal strength of the optical system by nearly 40\%. Nevertheless, the beam was focused to the same neighborhood in the exhaust plume. Since the transmissivity is a ratio of intensities and the only part of the optical system that changes between the reference intensity spectrum and the transmitted intensity spectrum is the presence of the plume, all the spectral losses from the optical system drop out. Optimizing the throughput of the system improves the signal to noise ratio, it doesn’t change the actual spectral behavior.
Table 3.1: Distances between optical elements for the spectral measurements.

<table>
<thead>
<tr>
<th></th>
<th>Seed-off</th>
<th>Seed-on</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X A_1$</td>
<td>$102 \pm 2$ mm</td>
<td>$101 \pm 1$ mm</td>
</tr>
<tr>
<td>$A_1 L_1$</td>
<td>$25 \pm 2$ mm</td>
<td>$25 \pm 2$ mm</td>
</tr>
<tr>
<td>$L_1 R$</td>
<td>$317 \pm 2$ mm</td>
<td>$334 \pm 2$ mm</td>
</tr>
<tr>
<td>$RM$</td>
<td>$317 \pm 2$ mm</td>
<td>$301 \pm 2$ mm</td>
</tr>
<tr>
<td>$ML_2$</td>
<td>$54 \pm 1$ mm</td>
<td>$71 \pm 2$ mm</td>
</tr>
<tr>
<td>$L_2 A_2$</td>
<td>$137 \pm 1$ mm</td>
<td>$129 \pm 1$ mm</td>
</tr>
<tr>
<td>$A_2 S$</td>
<td>$101 \pm 1$ mm</td>
<td>$101 \pm 1$ mm</td>
</tr>
</tbody>
</table>

3.1.4.2 The Measurement Volume

The absorption spectroscopy setup used here is a single point measurement in that it probes the reacting flow within a narrow solid angle as viewed from the spectrometer. This measurement can also be described as a line-of-sight measurement because everything along a ray traced from the light source, through the optical system, to the detector can have an influence on the radiation which takes that path (see Section 2.1). Given the spectral transmission of the optics in the beam path, the transmissivity of these elements is dropped when dividing $I$ by $I_0$ since the transmissivity of the optics is the same for both measurements. The only effect considered is that of the reacting flow. Furthermore, this measurement is described as line-of-sight because the estimated parameters are the line-integrated values of the measurement volume.

The actual volume of the reacting flow which is taken into consideration for a measurement is called the measurement volume. Determining the measurement volume entails an understanding of the optics that direct the probe beam into the spectrometer and what part of that beam is actually considered in the data. We’ll start by considering the detector. The detector and slit orientation was set up such that each row of pixels corresponds to a slightly different location along the long-axis of the slit and, correspondingly, a slightly different location across the stream in the measurement volume. With the $x$-axis along the streamwise direction and the $z$-axis oriented toward the ceiling, a decrease in pixel row number (moving closer to the top of the image) corresponds to a change in the probing location along the negative $y$-axis in the measurement volume. Thus, the pixel height and number of pixel rows used in a spectrum set the span-wise extent of the measurement.
volume. Similarly, the spectrometer slit width constrains the measurement volume in the streamwise
direction provided the slit aperture is fully illuminated by the incident beam.

Because the probe beam has been focused in the measurement volume and is focused
again onto the spectrometer entrance slit, the distances across the beam at the detector are roughly
translated into distances across the beam in the measurement volume using the inverse of the linear
magnification of the second focusing lens, $|M| = 0.6415$. Thus, the second lens demagnifies
the image, producing a smaller image on the entrance slit than the image in the plume. The
measurement area per pixel row can be calculated as follows for each pixel row:

\[
\text{Detected Area} = \text{Pixel Height} \times \text{Slit Width} = (6.5 \times 10^{-3} \text{ mm}) \times (0.180 \text{ mm}) \approx 1 \times 10^{-3} \text{ mm}^2 \tag{3.2}
\]

\[
\text{Measurement Area} = \frac{\text{Detected Area}}{|\text{Magnification}|^2} = \frac{1.17 \times 10^{-3} \text{ mm}^2}{(0.6415)^2} \approx 3 \times 10^{-3} \text{ mm}^2. \tag{3.3}
\]

Thus we have the cross-sectional area in the measurement volume corresponding to one row of
pixels used for spectra. The data used here involve the average of 41 rows of data, as will be
discussed in Section 3.3.3.2. So the functional area of the focus in the plume from one row of
pixels is roughly 0.1 mm$^2$. To properly obtain the full measurement volume, we would need to
know the geometric intersection between the plume and the part of the beam which passes through
our specified measurement area. This involves the path length through the plume, the distance
from the first lens to the plume and then to the second lens, as well as a more careful analysis of
the convergence and divergence of the probe beam. If we make the simplification that the beam is
a rectangular cuboid, we can estimate the minimum volume using the product of the path length
through the plume and the cross-sectional area.

The path length through the plume can be estimated by looking at the profile of the rocket
plume in an image taken from the lab camera footage. The computer software, Image J, is used to
analyze footage from a 5 megapixel, NHD-865MSB Swann security camera used as our laboratory
monitoring camera. Images from the lab camera used to estimate the path lengths are given in
Figures 3.4 and 3.5. For the seed off data sets, the camera angle results in a perspective projection of the system. The ratio of the rocket base plate width to the height is used to calculate the azimuthal angle from the plume axis to the center of the field of view for the camera and this angle is used to correct the apparent lengths, projected onto the lab camera detector plane. A scale is applied to the image using the known diameter of the rocket body. For each set of data the distance from the rocket exit plane to the center of the measurement beam is also known because it was measured and recorded each day of experimentation, see Section 3.1.4.1. The mean distance across the plume, $l$, and across the cloud of particulate, $l_s$, in the neighborhood of the measurement beam are estimated for each spectral measurement.

Additionally, we look at CFD simulations which have been conducted for a separate study of the same system. By considering the regions where the OH is present in the plume in a cross-sectional slice at the center of the plume we can estimate the path length through the absorbing media. All of the length estimates are given in Table 3.2. For each measurement, the OH component of the plume is considered to be that part of the plume which exhibits either optical emission as seen in the lab camera or the distance along the OH mass fraction profile which exceeds $1/8$ of the peak mass fraction as obtained from the CFD results. The Particle component of the lab camera images is the white cloud which surrounds the afterburning shear layer of the plume. There were no CFD results from comparable seed-on cases used to obtain path length estimates. The seed-off path lengths estimated from the lab camera agree well with the corresponding estimate from the CFD data.

Notice in Figure 3.4 that the emission pattern of the plume is different for the two equivalence ratios. This emission is often referred to as the blue or continuous radiation, extending from roughly 220 nm to 600 nm with a peak emission around 440 nm with various fine structure elements, and constitutes a significant portion of the visible radiation in hydrogen flames.\textsuperscript{50} Although the source of this radiation remains under investigation, evidence suggests it has a connection to the presence of Hydroxyl with a possible model being the chemiluminescence produced by a reaction between two OH molecules, creating excited hydrogen peroxide ($\text{H}_2\text{O}_2$).\textsuperscript{50} Regardless of the model, the
Figure 3.4: Lab camera images, seed-off. Image from the laboratory camera during a (top) stoichiometric and a (bottom) rich equivalence ratio combustion process. Alumina particulate seeding is turned off. Notice that the angle of the camera with respect to the rocket model means that the apparent distances in the image are perspective projections of the actual distances.
Figure 3.5: Lab camera images, seed-on. Image from the laboratory camera during a (top) stoichiometric and a (bottom) rich equivalence ratio combustion process. Alumina particulate seeding is turned on.
Figure 3.6: Examples of rich plume image. (Top) Reynolds Averaged Navier Stokes CFD results for the rich burn case, showing the mass fraction of OH. (Bottom) Mean In-Band Radiance of the rich burn case flow field as imaged by an infrared camera. The white line at $x/D_n = 4.00$ represents the line of sight for the measurement in the plume. In both cases, the plume exits the rocket model into the high-speed flow of a wind tunnel, whereas, for the data considered in the present experiment, the model is outside the wind tunnel and there is only a low speed co-flow across the model.
Figure 3.7: Examples of rich plume image. (Top) Reynolds Averaged Navier Stokes CFD results for the stoichiometric burn case, showing the mass fraction of OH. (Bottom) Mean In-Band Radiance of the stoichiometric burn case flow field as imaged by an infrared camera. The white line at $x/D_n = 4.00$ represents the line of sight for the measurement in the plume. In both cases, the plume exits the rocket model into the high-speed flow of a wind tunnel, whereas, for the data considered in the present experiment, the model is outside the wind tunnel and there is only a low speed co-flow across the model.
Table 3.2: Path length and measurement volume estimates.

<table>
<thead>
<tr>
<th>Seed</th>
<th>Burn Component</th>
<th>Lab Camera [cm]</th>
<th>CFD [cm]</th>
<th>Min. Volume [cm³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Off</td>
<td>Stoich. OH</td>
<td>1.4</td>
<td>1.5</td>
<td>$1.4 \times 10^{-3}$</td>
</tr>
<tr>
<td>Off</td>
<td>Rich OH</td>
<td>0.86</td>
<td>0.86</td>
<td>$0.86 \times 10^{-3}$</td>
</tr>
<tr>
<td>On</td>
<td>Stoich. OH</td>
<td>1.3</td>
<td>-</td>
<td>$1.6 \times 10^{-3}$</td>
</tr>
<tr>
<td>On</td>
<td>Stoich. Particle</td>
<td>2.5</td>
<td>-</td>
<td>$2.8 \times 10^{-3}$</td>
</tr>
<tr>
<td>On</td>
<td>Rich OH</td>
<td>*</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>On</td>
<td>Rich Particle</td>
<td>2.7</td>
<td>-</td>
<td>$3.0 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

Estimates of path length through the exhaust plume and the corresponding minimum measurement volume given the cross-sectional area of 0.001 cm². (-): Measurement unavailable. (*): The emission region in the plume cannot be distinguished in the seed on, rich, gaseous component of the plume because the relevant 1.7 cm path across the plume fully contains overloaded pixels but is comparable to the 1.8 cm path across the full plume in the rich, seed-off case.

proposed mechanisms for the blue radiation strongly favor the involvement of OH and so this radiation serves as a marker for the presence of OH in the flame. Turning again to Figure 3.4, the emission pattern of the rich case follows the shear layer, where afterburning takes place, but the emission for the stoichiometric case occurs most strongly at the vicinity of the normal shock cells, occurring in the shear layer with less intensity. In a perfect stoichiometric reaction, there is no Hydrogen in the exhaust flow, only water vapor (recall Eq. 2.12), reducing the likelihood of forming OH with the oxygen introduced by the entrained atmosphere in the shear layer. The OH present in the stoichiometric plume is most likely due to shock-heated, thermal dissociation of water vapor in the plume and not a consequence of energy input to the molecules through chemical reaction.51,52 Therefore, the information carried in the stoichiometric spectra is more related to the energy in the shock cells than the afterburning shear layer although the spectra will carry a convolution of information from both regions of the plume. Changes in the rich plume spectra resulting from the addition of particulate will more clearly tell a story about the chemical reaction in the shear layer while changes in the stoichiometric spectra due to the addition of particulate will require more investigation to distinguish the shear layer contribution from the core contribution since the current measurement only provides line-integrated spectra.

Holding the assumption that the observed emission demonstrates the presence of Hydroxyl,
we can estimate the path length traversed by the measurement beam through the Hydroxyl in the plume. The measurement volumes then range from $0.75 \times 10^{-3}$ cm$^3$ for the rich, seed-off gas measurement to $2.8 \times 10^{-3}$ cm$^3$ for the stoichiometric, seed-on particle cloud measurement.

### 3.1.4.3 Run Sequence

The run profile of the static rocket experiment involves initially opening the hydrogen and oxygen valves slowly and at different rates, allowing more fuel to fill the combustion chamber to initiate the reaction. After ignition, the two gases level out at the specified pressures to achieve the desired equivalence ratio. When the run ends, the program closes the fuel and oxidizer lines and nitrogen gas is opened intermittantly to purge the lines and cool off the combustion chamber in
Figure 3.9: Flow seeding system. Left: An illustration of the apparatus used to seed the fuel gas flow with Alumina particulate. Triangle slice demonstrates an internal view of the hopper with particulate present. Right: Image from the lab camera, showing the rocket setup, the seeder hopper and the three-way valve used to direct the fuel gas to flow through the seeder hopper or to bypass the seeder hopper.

preparation for the next run.

The spectral measurements are initiated before rocket start up and continue until 512 samples are collected, that is 10.24 s. Rocket run times were set for 10 s in the case of the seed-off measurements and set for 6 s in the case of the seed-on measurements since the whole 10 s were deemed unnecessary.

3.1.4.4 Seeding the flow

Aluminum oxide (Al₂O₃) particles with a mean diameter 0.28 µm are picked up by the gas in the H₂ fuel line, carried into the combustion chamber, and ejected with the reaction products into the plume. A hopper for holding seed particulate was piped into the hydrogen line via a three-way valve with a three-way check valve downstream so that the hydrogen could be allowed to flow through the hopper before flowing to the combustion chamber or chosen to bypass the hopper and flow directly to the rocket combustion chamber. The hopper consisted of schedule 160 steel pipe
with inside diameter 3/4 in., capped on both ends and accessed via two Swagelok pipe fittings, one in a tapped hole through the top and the other in a tapped hole through the side of the pipe, near the top. The total inside length was roughly 7.5 in. The hopper was built in order to hold high pressure hydrogen and prevent failure in the event the hopper experiences full pressure from the supply bottle. Stainless steel tubing was inserted through the fittings to provide inflow and outflow from the hopper. The inlet was at the top, having an inverted L-shaped neck with adjustable height—or, equivalently, adjustable depth into the hopper. The operating principle for the hopper is that the high pressure air entering the hopper would agitate the seed in the hopper, picking some of the seed up and carrying it along, into the combustion chamber. In practice, this design does not easily lend itself to control of the seed efflux. From studies that were done to evaluate the performance of the rocket at different combustion conditions and higher particulate mass loadings, the following factors were observed to influence the effectiveness of seeding:

1. How tightly the particulate is packed in the hopper: loosely packed particles are more easily picked up by the stirring effect of the gas in the hopper.

2. The distance between the top of the seed and the bottom of the inlet neck: it was observed, although not carefully quantified, that there was a “sweet spot” for this distance which produced a greater initial efflux of particulate for a given mass and packing of particulate in the hopper. Furthermore, beyond a certain level, the lower the level of seed was at the start of a run the less the efflux of seed that was produced.

3. The mass flow rate of gas: the flow rate influences the flow behavior within the hopper and thereby influences how well the particulate is picked up.

4. The molecular mass of gas: in tests which flowed air through the seed hopper rather than hydrogen, there was a marginal increase in total mass efflux from the seed hopper over the course of a run.

It was also observed that seed continues to flow out of the lines at the end of a run while purging the lines with nitrogen even though the seeder hopper is bypassed. This leads to the
inference that particulate gets trapped in the gas line and in the combustion chamber so that, although it was recorded, a measurement made to determine the change in mass of seed inside the seed hopper during each run does not adequately represent the mass flow of seed through the combustion chamber. Instead,

\[ \Delta m_{\text{Al}_2\text{O}_3} = m_{\text{(stuck in line)}} + m_{\text{(in flow)}}. \]  

(3.4)

Here, \( m_{\text{(●)}} \) is the mass of alumina associated with the seed that is (●=) stuck in the line or in the flow. The mass of seed that enters the flow and the mass of seed that gets stuck in the line have not been separately measured. The average \( \Delta m \) recorded over 10 runs is 3.532 g. For these tests, the hopper was filled with seed at each run until the top of the seed pile reached 4.375 in. below the top of the inlet spout of the hopper. During each run, some of the seed was carried along with the fuel gas while some was left in the hopper, having been packed tighter at the bottom rather than picked up by the stream of gas entering the hopper. As runs progressed, \( \Delta m \) grew smaller. After four runs, the hopper was taken to be cleaned out, emptying it completely of seed, and then it was refilled to the specified height, resetting the trend of \( \Delta m \) for the next four runs.

3.2 Results

Here we look at the results from three different data series. The first data series will be called “seed-off” because the alumina seed is not being added to the flow, only OH absorption is present in the transmission spectra. The mean absorption varies depending on the two equivalence ratios used. The term “stoichiometric” refers to \( \phi \approx 1 \) while “rich” refers to \( \phi \approx 2 \). The second data series, “seed-only,” contains one event. For this event, seed is added to the flow, the rocket is run with oxygen and hydrogen pressures set to the conditions specified for rich equivalence ratio runs, but the glow plug in the combustion chamber is not turned on so that no reaction takes place. This gives a cold jet with particulate present and ensures that only particulate scattering influences the transmission spectrum. The third data series records transmission spectra which
3.2.1 Seed-off

The spectral behavior resulting from the start-up can be identified in the spectrograms from each event in the seed-off series. This is shown for each burn case in Figure 3.10. An ensemble average of all the spectra snapshots taken during the steady-state phase of the run produces spectra such as those shown in Figure 3.11. Immediately it is evident that the stoichiometric reaction results in more OH absorption than does the rich reaction since the transmissivity is lower in the stoichiometric case. As compared to the rich case, this translates to a greater path length through the stoichiometric plume, a higher species concentration, a higher temperature, or a mixture of the three.

3.2.2 Seed-only

Figure 3.12 gives an overview of the seed-only data set. The only dominant gases present in the plume are the oxidizer and fuel gases. The glow plug which activates the reaction was turned off in order to conduct a measurement without the OH absorption so that the particulate scattering have the combined effect of OH absorption and particulate scattering. This series will be called “seed-on” by comparison to the first series, because now combustion takes place inside the rocket model and alumina seed is added to the flow.
Figure 3.11: Ensemble averaged transmissivities, seed-off. Spectra at two burn conditions for the seed-off case with the static rocket experiment.
Figure 3.12: Seed-only spectrogram and single-wavelength time history. (Left) Spectrogram of the transmissivity for the seed-only case. The extinction is caused by scattering due to the presence of particulate since no reaction is taking place to generate OH absorption. (Right) The time trace of transmissivity at one wavelength which has been identified by the red dotted line in the spectrogram on the left.

can be studied in isolation from the molecular absorption spectrum. The broad band particulate scattering manifests itself as tall dark lines in the spectrogram of Figure 3.12. During the run, the optical thickness of the particulate cloud varied with time, coming out in sometimes thicker and sometimes thinner clouds, corresponding to varying mass flow rates of particulate. This explains the varying levels of transmissivity at all wavelengths. For example, consider the single-wavelength ($\lambda = 312.8347$ nm) time history in Figure 3.12. The transmissivity makes a sharp drop at around 0.5 s, indicating the start of the flow through the rocket. By 2.5 s, the transmissivity begins to make its way back towards unity, indicating a decrease in particulate flow rate. Soon after 6 s passes, the run ends and then there is another sharp transmissivity drop. This secondary drop is momentary and caused by the sudden onset of nitrogen gas used for the post run purge, clearing particulate out of the gas lines. Again, the transmissivity trends toward unity as the purge gas continues. With this gradient of scattering levels available, it is possible to select samples whose average produces a spectrum at nearly any depth between a transmissivity of 0.3 and 1.0. This will be demonstrated in Section 3.3.
Figure 3.13: Seed-on spectrograms. Spectrograms of the transmissivity for the seed-on case. Left: Stoichiometric, $\phi \approx 1$; Right: Rich, $\phi \approx 2$.

Figure 3.14: Ensemble averaged transmissivities, seed-on. Spectra from the stoichiometric and rich equivalence ratios, taken while alumina particulate is present.
3.2.3 Seed-on

Observe that the spectrograms for the seed-on (Figure 3.13) case demonstrate both the broad band, transient behavior seen in the seed-only spectrograms (Figure 3.12) in addition to the more steady absorption features of the seed-off spectrograms (Figure 3.10). The irregularity of the broadband extinction agrees with lab camera images, showing that the seeding in the plume reaches a stable state only briefly. The seeding diminishes significantly early in the run and strengthens again during the nitrogen purge of the combustion chamber, after the rocket shuts down. Both spectrograms exhibit this sudden burst of transmission loss subsequent to the end of the longer-duration absorption features. As a result of the seeding irregularity, obtaining an ensemble averaged spectrum for the seed-on case is not as straightforward as in the seed-off case. There is only a short time window of about 0.5 s (25 elements) containing strong scattering for the two measurement events considered. Using only these 25 elements, a rough ensemble average of the seeded spectra, $\langle \tau_s \rangle$, can be built, as shown in Figure 3.14.

Comparing the spectra in Fig. 3.14 to those in Fig. 3.11, three features stand out. First, the seed-on spectra contain the obvious features of the OH absorption. Second, the seed-on spectra are diminished overall so that the baseline is well below unity, whereas the seed-off spectra have a baseline near 1 especially in the band below 306.1 nm. Third, this broadband extinction of the seed-on spectra is not merely a constant multiple offset of the seed-off spectra. The baseline exhibits an overall decrease in transmission with increasing wavelength for the seed-on spectra.

3.3 Analysis

3.3.1 The Repository Method

Returning to the seed-only data, Figure 3.15 gives a histogram of the transmissivity depths at $\lambda = 312.8347$ nm for all recorded time. Four selections of samples, each with a different number of samples and from different transmissivity depths, are used to produce the four distinct scattering spectra shown in Figure 3.16. The color coding of the sample selections from the histogram in Figure 3.15 corresponds with the spectra in Figure 3.16. There are different procedures for making
Figure 3.15: Histogram of seed-only data. The distribution of available transmissivities for spectra at one line of pixels and at one wavelength.

Figure 3.16: Scattering spectra built from seed-only data. Scattering transmissivity spectra constructed by the repository method for three different selected ranges of optical depth. The dashed black line identifies $\lambda = 312.8347$ nm and the dotted black line identifies $\lambda = 306.7441$ nm.
the sample selection. For the first spectrum, the time window during the strongest extinction, from 0.70 s to 2.06 s, is chosen. The maximum and minimum within this window are chosen as bounds for the transmissivity at this wavelength. Then all of the 81 samples for which the transmissivity at \( \lambda = 312.8347 \) nm falls within this range are averaged to build a spectrum. The next two spectra result from first specifying upper and lower limits of transmissivity depth and then finding all of the samples for which the transmissivity at \( \lambda = 312.8347 \) nm falls within these limits. The fourth spectrum was built in a similar manner as the previous two, except the samples selected were those for which the transmissivity at \( \lambda = 306.7441 \) nm falls within the specified limits. It will also be noted that, while the specified range of transmissivities at \( \lambda = 306.7441 \) nm was 0.81 to 0.89, the same selection of samples corresponds to transmissivities at 312.8347 nm within a range from 0.6964 to 0.9916 with a mean of 0.8742. In effect, this fourth spectrum demonstrates the use of select samples to build a spectrum instead of utilizing all available samples within a range. Both the number of samples and the range of transmissivities can be selected in order to tune the construction of a model particulate scattering spectrum using this repository of scattering data. This provides a means of removing scattering spectra from the data. We will call this method the repository method (RM).

3.3.2 The Empirical Method

An important observation from the spectra in Figure 3.16 is that each of these seed-only transmissivities, \( \langle \tau_{so}(\lambda) \rangle \), have the imprint of the emission source spectrum, \( I_0(\lambda) \). This can be most clearly seen when comparing the absorptivity to the incident intensity in the same plot with each curve along a different scale such as in Figure 3.17. Here the absorptivity is used instead of transmissivity to make a better qualitative comparison between the spectral features. A simple proportional relationship between \( I_{so} \) and \( I_0 \) does not, therefore, exist since their ratio, \( \tau_{so}(\lambda) \), is not a constant with respect to wavelength. Spectral features are retained in the ratio. The relationship
Figure 3.17: Comparison of scattering absorptivity with the incident intensity of the light source.

more closely follows a linear relationship*:

\[ \langle I_{so}(\lambda) \rangle = C \langle I_0(\lambda) \rangle + B \]  

(3.5)

where the empirical coefficients \( B \) and \( C \) are constants with respect to wavelength but have some dependence on the optical thickness and where division by \( \langle I_0(\lambda) \rangle \) leaves the spectral content of the reference intensity in the denominator of the transmissivity. To ascertain the value of \( B \) and \( C \), each of the transmitted intensities, \( I_{so} \), from the four scattering spectra built in Figure 3.16 are related to the incident intensity through the inverse of Equation 3.5.

\[ \langle I_0(\lambda) \rangle = k \langle I_{so}(\lambda) \rangle + b. \]  

(3.6)

Here \( k \) is selected to be the difference of \( \langle I_0(\lambda) \rangle \) between two wavelength bins divided by the difference of \( \langle I_{so}(\lambda) \rangle \) between the same two wavelength bins. The value of \( b \) is then determined using Equation 3.6 and the values of \( \langle I_{so}(\lambda) \rangle \) and \( \langle I_0(\lambda) \rangle \) at a given wavelength. Since these coefficients are calculated using individual bins of data which inherently contains noise, the accuracy of these

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*In conversation with Aric Ruosso from Lawrence Livermore National Lab, he suggested this behavior might indicate that these particles behave as a neutral density filter.
Figure 3.18: Transformations from $I_{so}$ to $I_0$. Using a linear transformation the scattering spectra built from the seed-only data can be returned to the incident intensity spectrum. The solid lines represent scattering spectra, the dotted lines represent the transformation of the corresponding data.
Figure 3.19: Linear fit of the transform coefficients for the empirical method. A linear fit to the transformation coefficients $B$ and $C$ used in Equation 3.5 gives $C = -0.00289B + 0.99881$. 
two coefficients is improved by then scaling them by the mean across all wavelength bins of the ratio between $\langle I_0(\lambda) \rangle$ and $k \langle I_{so}(\lambda) \rangle + b$. As a result, the new coefficients ensure that the transform of $\langle I_{so}(\lambda) \rangle$ now has an average ratio to $\langle I_0(\lambda) \rangle$ equal to unity. Upon conducting this procedure for transmitted spectra with different optical depths and obtaining coefficients with which to transform the incident intensity to an equivalent scattering intensity by Equation 3.5, a regular relationship emerges between $B$ and $C$ as shown in Figure 3.19. Two additional points were added to these values, extrapolating from the known behavior of Equation 3.5. First, in order for the relationship to hold when $B = 0$ it must be true that $C = 1$. Second, when $C = 0$, $B$ must equal whatever value the detector reads when no radiation is incident on the detector. The average noise floor reading for the detector was determined to be 349.37. The relationship between these six values of $B$ and $C$ has a linear form. Without the two extrapolated points bookmarking either end of these samples, the points appear to follow a broad, quadratic polynomial. Nevertheless, the four measured points fit the linear model with an average percent difference of 13.1% while they fit the quadratic model with an average percent difference of 14.7%. Therefore, the linear relationship is retained, claiming that

$$C = a_1 B + a_2$$

(3.7)

where $a_1 = -0.00289$ and $a_2 = 0.99881$. This reduces the relationship in Eq. 3.5 to one unknown coefficient. As a result, for a selected incident intensity, $I_0$, and a related transmitted intensity, $I_{so}$, we can prescribe one coefficient to relate the two using these empirically determined constants:

$$B = \frac{[\langle I_{so}(\lambda_i) \rangle - 0.9981 \langle I_0(\lambda_i) \rangle]}{[1 - 0.00289 \langle I_0(\lambda_i) \rangle]}$$

(3.8)

where $i$ indicates a single element of $\lambda$ is chosen in order to calculate $B$. In practice, twenty-five values of $B$ are obtained and then averaged. This defines a procedure for building a model of scattering using empirically defined coefficients. It will be called the empirical method (EM).

With two procedures in hand for modeling the particulate scattering, we turn to the seed-off
and seed-on data in order to make a comparison between the OH macrostate of the two burn conditions in each case.

3.3.3 Data Selection

In order to make a fair comparison between the exhaust plume conditions with the seed-off to the exhaust plume conditions with the seed-on, the combustion chamber conditions recorded by the rocket control computer and the ignition time should be compared for each run. Most of the scattering for the seed-on runs occurs near the end of start-up phase and ends near the onset of a steady chamber pressure, $c_p$, see Figure 3.20. The actual chamber pressures are intentionally obscured in these plots by dividing all chamber pressure values by the average of all four chamber pressure time-histories, $\bar{c}_p$. Ideally, the data would come entirely from the steady run conditions but minimal scattering is observed at these times, recall Figure 3.13. To make sure the OH macrostate estimates are comparable, the phase of the rocket run being considered in each case should be comparable. First, the moment of ignition is identified in the chamber pressure time histories. Likewise, the moment of ignition is identified in the spectral data. Then the difference in time for the chamber pressure to go from ignition to $c_p/\bar{c}_p > 0.75$ in all cases is measured, allowing comparable regions in the chamber pressure between the two run types to be compared. Using the ignition times from each data set as a reference, the time window of the useful 25 samples of seed-on spectral data is related to the chamber pressure curve for the corresponding run. Then, comparable regions of the chamber pressure are identified for the seed-off runs and this time window is related back to the seed-off spectra, providing 25 samples of each seed-off data set for making comparison to the seed-on data. The chamber pressure time histories and the single-wavelength spectra time-histories are shown in Figure 3.20 along with the corresponding 25-element time windows.

In order to include more samples in the data, 41 rows of transmission spectra are selected for each data set, providing a total of 1025 spectra before removing outliers, as discussed in Section 3.3.3.2.
Figure 3.20: Relating spectra from the seed-on runs to spectra taken during the seed-off runs. Time histories of the rocket chamber pressure in normalized units for the (a) stoichiometric conditions and (b) rich conditions. Time histories of the plume transmissivity at one wavelength for the (c) stoichiometric conditions and (d) rich conditions.
3.3.3.1 Verifying the Random Variable is Gaussian

Making conclusions about the flow field using the ensemble averaged extinction data assumes that enough samples have been included for the mean to be a proper estimator of the true mean. Furthermore, it assumes that the Gaussian statistical mean adequately represents the behavior of the data. Here we briefly set out to validate this assumption for the present data set.

Taking the optical thickness to be a random variable, \(-\ln(I/\langle I_0 \rangle) = x\), collected from a stationary stochastic process, the mean can be tracked as a function of the number of samples used to construct the mean. Rather than look at a single mean for each given number of samples, the mean becomes a random variable of its own and the mean of block means is reported. The Central Limit Theorem submits that, as the number of samples used grows, the mean of the samples behaves as a new random variable, \(X_{ji}\), with a Gaussian distribution about the true mean, \(X\). Thus, calculating the mean of the block means, \(X_i\), gives a better estimate of the true mean. Furthermore, each distribution, \(X_{ji}\), has a variance equal to the true variance of \(x\), divided by the number of samples, \(\sigma_i^2 = \sigma^2/n_i\). For the present case, five random samples of the variable were selected, the mean, \(X_{ji}\), was calculated for the block of samples, and then this was repeated 50 distinct times, randomly selecting from the available data each time. The record is built by doing this again at many different block sizes, \(n_i\), incrementing in steps of five samples up to the total number of available samples, explained in Section 3.3.3.2. This ultimately produces a mean of block means as a function of block size, for an example see Figure 3.21. Each wavelength bin in the spectrum has its own behavior in convergence to its mean value, only the value at one wavelength (319.8937 nm) for a single measurement event is given as a demonstration.

The standard deviation of the sample means behaves according to the full sample standard deviation, divided by the square root of the number of samples considered, implying that the data set is normally distributed. As a result, we can work with the classical statistical quantities in the analysis of the data. Notice that the standard deviation does not exactly follow \(\sigma/\sqrt{n_i}\), this is a consequence of using pseudo random data. Since there are only \(N\) available samples and we evaluate the process out to \(N\), the repetition of data is taken into consideration by including a
Figure 3.21: Convergence of a single mean of block means. A record of the calculated mean of 50 block means according to the number of samples used in the blocks. Considering the record of optical thickness, \(-\ln(I/\langle I_0 \rangle)\), at \(\lambda = 319.8937\) nm for the seed-off, stoichiometric burn spectra.
Figure 3.22: Convergence of the mean of block 95% confidence intervals. A record of the calculated mean of 95% confidence intervals according to the number of samples used in the blocks.

It can be shown that the variance of the data also converges to a small value. This is demonstrated here using the 95% confidence level at half the number of samples, 515, for the wavelength bin having the greatest variance. The confidence intervals of all wavelengths are shown in Figure 3.22.

3.3.3.2 Ensemble Averaged Values

Having confidence that we can use standard statistics to gather meaningful information about the flow field, we can carefully define the parameters for averaging the data. As already mentioned, a data matrix, $I$, contains a pixel intensity related to detector voltage for each active
pixel in the region of interest on the detector array, 256 × 2560 pixels. The third dimension is time, containing 512 individual snapshots. There are two ways to average the spectra: over time and along pixels, row-wise. Practically speaking, the time-averages are a manner of approximating the ensemble average at a point. Averaging the spectra row-wise involves conducting a spatial average in the measurement volume. Nevertheless, the spatial average is used to improve the signal to noise ratio and so shall be included in the ensemble averaging process.

Not all 512 snapshots were captured during stable conditions of the rocket burn. Furthermore, a single spectrum has an unfavorably low signal to noise ratio due in large part to the poor quantum efficiency of the detector in the spectral range of interest as well as to the fluctuations in the Xenon radiation source. The signal to noise ratio is improved, in keeping with the limitations of the present system, by using an ensemble average of the subset of snapshots from the event which contain stable conditions in the measurement volume. For the seed-on measurements, the particulate seeding is intermittent and so a select number of samples out of those collected during the stable rocket conditions are used in the average, amounting to 25 snapshots for each burn condition. For the seed-off measurements, there are roughly 380 samples of steady conditions to average in each case. However, 25 seed-off snapshots from a comparable time window as the 25 seed-on samples are chosen for temporal averaging in order to make a fair comparison between the seed-off and seed-on data. From each snapshot, 41 rows were selected for the spatial averaging, giving a total of 1025 transmission spectra for composing averages. Transmission spectra, rather than intensities, are averaged in order to reduce the variance in the averages since the intensity is non-uniform across the entrance slit and between the pixel rows. Holding to the homogeneous measurement volume assumption, the change in macrostate properties is small over short distances radially across the measurement volume, perpendicular to the probe beam. Some of the data sets contain outliers, living beyond 2.5 standard deviations from the rest of the data. This reduces the number of available samples for each data set to no less than 984, which is still plenty of samples to produce a reliable mean spectrum.

It is important here to distinguish what quantities are being averaged. Since the incident
intensity, $I_0$, measurements were recorded in separate events from the transmitted intensity recordings, the ensemble average of all 512 samples is used in all instances of the incident intensity. This treats the reference intensity as a stationary spectrum during each data collection event. Each time-dependent transmitted intensity spectrum, $I(t)$, is then divided by a corresponding, constant-in-time incident intensity spectrum, $\langle I_0 \rangle$, to obtain the transmissivity. Each data set is then organized into a $1025 \times 2560$ array of transmissivities from the 41 rows and 25 snapshots. Rather than working directly with an average of these transmission spectra, it is more informative to compute the average of the exponential terms since the extinction terms live in the exponent of the transmissivity. The ensemble average is thus applied to the natural logarithm of the transmissivity, giving,

$$\left< \ln \left( \frac{I}{\langle I_0 \rangle} \right) \right> = -\langle \int_{-\infty}^{\infty} (\sigma_s + K_2) dl \rangle \approx -\langle \sigma_s l_s \rangle - \langle K_2 l \rangle. \quad (3.9)$$

Now a distinction can be made between the average of the scattering coefficient and the average of the absorption coefficient.

The long exposure time in addition to using ensemble averaged spectra preclude the reporting of instantaneous dynamics of the plume parameters. As it is for the present experiment, the process of working with time-averaged data assumes the plume parameters are statistically stationary in time, which is valid given the repeatability of the system run conditions. This is a necessary assumption not only for averaging samples together, but also for addressing the fact that the exposure time of the detector entails multiple flow through times in the measurement volume. The effective 444.6 $\mu$s exposure time for a spectrum sample along with the stream-wise measurement length of 0.281 mm means that, for the flow to have one flow-through time it would have a speed of 0.632 m/s. For our high speed flow, where the Mach number exceeds 1, there are more than 490 flow-through times in a given spectrum acquisition. Thus, many molecules pass through the measurement volume during a single exposure. An analysis of the dynamics in this system would therefore require a light source and a detector which can operate in the sub-microsecond range.
Figure 3.23: Bayesian fit results for the seed-off spectra. The Bayesian inversion fitting results for the seed-off, (left) rich, $\phi \approx 2$, and (right) stoichiometric, $\phi \approx 1$, combustion mixtures. The spectrum with the most likely pair of temperature and column density values are plotted over the experimental spectrum. Below each plot, the percent difference residual between the model and the data is shown.

3.3.4 Initial Seed-off Macrostate Estimates

With 984 samples in the rich case and 1008 samples in the stoichiometric case, the Bayesian inversion fit described in Chapter 2 is used to estimate the macrostate of the OH in the seed-off plumes. The results are shown in Figure 3.23 for both burn cases. The most likely pair of macrostate parameters for the rich case are reported as $T = 2613$ K and $Nl = 3.426 \times 10^{16}$ molec./cm$^2$ and for the stoichiometric case are reported as $T = 4047$ K and $Nl = 12.49 \times 10^{16}$ molec./cm$^2$. These results are reported along with the associated half-max error estimates in Table 3.3. The wavelength band used for the fit is 306–313 nm because the OH is not a strong absorber over the rest of the recorded band.

Two observations can be made about these fit results. First of all, both the rich and the stoichiometric data curves demonstrate an excursion from a value of 1 in the region to the far left in both figures, around 306.1 nm. Without any other factors causing extinction, since the OH is
Figure 3.24: Bayesian fit results for the seed-off spectra after baseline adjustment. The Bayesian inversion fitting results for the seed-off, (left) rich, $\phi \approx 2$, and (right) stoichiometric, $\phi \approx 1$, combustion mixtures after the baseline has been adjusted. The spectrum with the most likely pair of temperature and column density values are plotted over the experimental spectrum. Below each plot, the percent difference residual between the model and the data is shown.

Negligibly active in this region, transmission curves should equal unity there, as demonstrated by the model spectra. The second observation is that the best fit stoichiometric model has an average absolute percent difference from the data which is twice that of the average percent difference between the model and data for the rich case.

To see what effect the DC offset in the baseline of the data has on the fits, the offset was removed by finding the average of the transmissivity over 25 wavelength bins below 306.1 nm and dividing this from the whole transmissivity. This is done in each burn case and the resulting spectra are fit to a model spectrum with the Bayesian fitting scheme. The resulting fits are shown in Figure 3.24. Now the most likely pair of macrostate parameters for the rich case are reported as $T = 2440$ K and $Nl = 2.947 \times 10^{16}$ molec./cm$^2$ and for the stoichiometric case are reported as $T = 3777$ K and $Nl = 9.709 \times 10^{16}$ molec./cm$^2$. The results come out lower than they did before. Furthermore, these fits show only a marginal decrease in the percent difference residuals from fits.
Figure 3.25: Comparison of transmission spectra for the rich data. (Left) Spectra from the rich, seed-on event ($s$) compared with models for the scattering part of the spectrum determined by building a scattering model by the repository method (RM) or the empirical method (EM). (Right) Absorption spectrum from the rich, seed-off event ($ns$) compared to the effective absorption spectrum obtained by dividing the seed-on spectrum by the models in the left figure.

of the un-altered data. Table 3.3 provides a summary of the results along with the upper and lower half-width at half-max error estimates from each posterior distribution.

3.3.5 Scattering Removal

A scattering model is claimed to match the scattering part of a seed-on spectrum when the model meets the spectrum in the spectral band $\{\lambda \in \mathbb{R} | 294.7 \text{ nm} < \lambda < 306.1 \text{ nm}\}$. This is equivalent to claiming that a transmission spectrum for the seed-on data equals a transmission spectrum from the seed-only data, $\tau_s \approx \tau_{so}$, within the spectral region where the OH is weakly absorbing.

For the repository method, finding an appropriate model entails averaging the seed-on transmission spectrum over 25 wavelength bins, from 305.7011 nm to 306.0412 nm. For simplicity, this particular collection of wavelength bins shall be referred to as WB. Then a scattering transmissivity spectrum is built from the repository of seed-only data, ensuring that the average of this spectrum over WB matches that of the seed-on spectrum.

The empirical method involves only the data collected in the seed-on data set, having already determined the spectral behavior of scattering for the seed in this system. Taking the average of
Figure 3.26: Comparison of the transmission spectra for the stoichiometric data. (Left) Spectra from the stoichiometric, seed-on event (s) compared with models for the scattering part of the spectrum determined by building a scattering model by the repository method (RM) or the empirical method (EM). (Right) Absorption spectrum from the stoichiometric, seed-off event (ns) compared to the effective absorption spectrum obtained by dividing the seed-on spectrum by the models in the left figure.

A comparison between the seed-on transmissivities and the two scattering models are shown in Figures 3.25 and 3.26. When the seed-on spectrum is divided by either of these two estimated scattering-only spectra, the result is an estimate for the absorption part of the seed-on transmissivity spectrum. The estimated absorption spectra compared with the absorption spectrum from the seed-off events are also shown in Figures 3.25 and 3.26. For notation, the following conventions are used:

\[
\tau_{RM} = \exp[- \int \sigma_{RM} dl] \approx \exp[-\sigma_{RM} l_s] \tag{3.10}
\]

and, similarly,

\[
\tau_{EM} = \exp[- \int \sigma_{EM} dl] \approx \exp[-\sigma_{EM} l_s]. \tag{3.11}
\]
Additionally, letting $\tau_{\text{RM}}$ equal either RM or EM,

$$
\frac{\tau_s}{\tau_{\text{RM}}} = \exp[-\int (K_s + \sigma_s - \sigma_{\text{RM}}) \, dl] \approx \exp[-K_s l - (\sigma_s - \sigma_{\text{RM}})l_s]
$$

(3.12)

and we define

$$
K_{\text{RM}} l := K_s l + \sigma_s l_s - \sigma_{\text{RM}} l_s.
$$

(3.13)

Both of the estimated absorption spectra can now be run through the Bayesian inversion fitting routine to estimate the macrostate parameters of the OH in the seed-on runs. The most likely pairs of macrostate parameters are summarized along with their associated error estimates in Table 3.3. In all cases, the removal of the scattering spectrum brings the baseline of the absorption spectrum to unity below 306.1 nm since the scattering spectrum was fit to the seed-on spectrum in this region for each case. Furthermore, the stoichiometric models again have a larger average absolute percent difference from the data than the rich models have to the corresponding data.

3.4 Discussion

Table 3.3 summarizes the macrostate estimates obtained for the two burn cases, the two seeding conditions for each case, and the two scattering removal techniques for each seed-on condition as well as the two alternate seed-off spectra in which the baseline is adjusted. This makes a total of eight macrostate estimate pairs.

As a broad stroke comparison of these macrostate estimates, it is evident that the OH conditions in the plume resulting from a stoichiometric reaction have a higher temperature than do the OH conditions in the plume resulting from the fuel rich combustion reaction.

For both the rich and the stoichiometric case, although the most likely temperatures for the seed-on cases are lower than that for either of the seed-off options, the RM estimates are within one error estimate from both of the seed-off options while the EM estimate is lower than all of the other options but only a little more than one error estimate from maximum likely seed-off temperature. Furthermore, the column density estimates for the alternative seed-off measurement as well as the
Figure 3.27: Bayesian fit results for the rich seeded data. The Bayesian Inversion Fitting results to the absorption part of a rich, seed-on spectrum where the scattering part of the spectrum has been removed through the (Left) repository method and the (Right) empirical method. The spectrum with the most likely pair of temperature and column density values are plotted over the experimental spectrum.

Table 3.3: Summary of spectral fitting results.

<table>
<thead>
<tr>
<th>nominal φ</th>
<th>Parameter</th>
<th>$K_{\text{n}_2}$</th>
<th>$K_{\text{n}_2,\text{alt}}$</th>
<th>$K_{\text{RM}}$</th>
<th>$K_{\text{EM}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$T$ [K]</td>
<td>4047$^{+162}_{-155}$</td>
<td>3777$^{+181}_{-173}$</td>
<td>3761$^{+301}_{-281}$</td>
<td>3598$^{+261}_{-245}$</td>
</tr>
<tr>
<td>1</td>
<td>$N_l$ [$\times 10^{16}$ molec./cm$^2$]</td>
<td>12.49$^{+0.546}_{-0.540}$</td>
<td>9.709$^{+0.481}_{-0.471}$</td>
<td>9.302$^{+0.748}_{-0.740}$</td>
<td>8.802$^{+0.617}_{-0.610}$</td>
</tr>
<tr>
<td>2</td>
<td>$T$ [K]</td>
<td>2613$^{+289}_{-268}$</td>
<td>2440$^{+312}_{-288}$</td>
<td>2332$^{+493}_{-434}$</td>
<td>2200$^{+407}_{-365}$</td>
</tr>
<tr>
<td>2</td>
<td>$N_l$ [$\times 10^{16}$ molec./cm$^2$]</td>
<td>3.426$^{+0.306}_{-0.303}$</td>
<td>2.947$^{+0.264}_{-0.261}$</td>
<td>2.935$^{+0.412}_{-0.403}$</td>
<td>2.796$^{+0.327}_{-0.320}$</td>
</tr>
</tbody>
</table>

List of macrostate estimates for all of the OH molecular absorption spectra considered, the seed-off data along with the seed-on data after the scattering has been removed by the repository method or by the empirical method.
Figure 3.28: Bayesian fit results for the stoichiometric seeded data. The Bayesian Inversion Fitting results to the absorption part of a stoichiometric, seed-on spectrum where the scattering part of the spectrum has been removed through the (Left) repository method and the (Right) empirical method. The spectrum with the most likely pair of temperature and column density values are plotted over the experimental spectrum.
Figure 3.29: Summary plot of OH macrostate estimates using number density and temperature. A summary of the macrostate estimates for the stoichiometric (a) and rich (b) burn case can be given with the estimated path length through the plume being used to obtain number densities. The error bars represent the upper and lower half-width estimates of the Temperature and column density as reported in Table 3.3. The marker shapes represent: (square) $K_{ns}$, (circle) $K_{ns,alt}$, (diamond) $K_{RM}$, and (triangle) $K_{EM}$.

two seed-on options fall within less than an error estimate of each other while the column density estimate from the original seed-off measurement falls outside one error estimate from any of the other column density estimates. This suggests that the column density of OH, and therefore the OH production, may not be strongly influenced by the present particulate loading. According to the trend of the mean reported estimates, it is possible that the temperature and column density of OH decrease with the addition of seed however any change in the present case for the rich burn has negligible effect given the random error of the system.

Aggregating the column density estimates with the path length estimates from Section 3.1.4.2 provides for estimates of the average OH number density in the volume. With the large uncertainties in $K_{ns,alt}$, $K_{RM}$, and $K_{EM}$, given macrostate estimates are too close to make a confident distinction between them. On the other hand, the macrostate estimates produced by the original seed-off spectrum, $K_{ns}$, lie almost entirely out of the estimated errors of any of the other estimates. Again, it is suggested that this original spectrum contains an erroneous baseline shift which provides misleading macrostate estimates.

For the stoichiometric data, there are two primary ways that the model spectra differ from the experimental data. First of all, the broadband offset of the spectrum, below unity suggests there is a broadband source of extinction influencing the spectrum. This may be explained by the fact
that the measurement beam passes through the exhaust plume slightly off of the center so that the sharp gradients in the fluid properties as well as possible passage through a reflected shock would cause the beam to be deflected and so altering the part of the beam illuminating the spectrometer entrance slit. Secondly, just below 308 nm there is a clear disparity between the model and the data. The reason for this is that the HITRAN database was designed to work for scenarios at standard terrestrial atmospheric temperatures and neglects a large number of transitions which are more likely to occur at higher temperatures. During most of this work the authors were not aware that the HITEMP database, in connection to the HITRAN database, was built specifically for higher energy environments. An example of constructing a model with the HITEMP data and fitting it to the experimental alternate stoichiometric data is given in Figure 3.30. The most likely macrostate parameters given are $T = 3986^{+205}_{-195}$ K and $Nl = 9.510^{+0.4574}_{-0.4489} \times 10^{16}$. While there are still a few instances where the percent difference residual is still near 2%, there is an obvious improvement in the fit using the HITEMP parameters and this data is therefore recommended for future spectral studies of high temperature gases.

Radiation passing through the plume will be refracted due to the change in gas parameters between the atmosphere and the plume. It was assumed that there would be no refraction if the probe beam passed directly through the center of the plume. A minor offset from the center could re-direct the beam slightly, leading to a slight shift of the beam location on the chip. This could explain the broadband extinction being observed in the original seed-off data.

3.4.1 The Empirical Method Scattering Model

Some observations can be made from the residual in Figure 3.18. First, the absolute average residual from the transmitted spectrum with the overall lowest transmissivity is the greatest among the four considered transmitted intensities. The lower the transmitted intensity, the greater the scaling factor that needs to be applied to that spectrum in order to get the spectrum to match the incident intensity, therefore, the more the noise is amplified even though the transmitted spectra are rather clearly resolved with minimal noise. For the residual with the greatest noise, intensity 1, the
Figure 3.30: Bayesian fit result using HITEMP data for the seed-off, stoichiometric spectrum after baseline adjustment. The Bayesian inversion fitting result using the HITEMP database matches the seed-off, stoichiometric combustion mixture after baseline adjustment better than the model built with data from the HITRAN database fit the data. The spectrum with the most likely pair of temperature and column density values is plotted over the experimental spectrum. Below the plot, the percent difference residual between the model and the data is shown.
distribution of values is nearly Gaussian with a standard deviation of roughly 4.5%. The inverse of Equation 3.5 is used to produce these spectra and generate the scattering model.

We also notice that there is a trend upwards from 295 nm to 330 nm for the residuals of the second and third spectra, in a pattern similar to the shape of the Xenon emission spectrum. The residuals for the second and fourth spectra fall within ±5%.

3.4.2 The Influence of Micron-Scale Alumina

The present results demonstrate that the introduction of aluminum oxide in a reacting flow alters spectroscopic measurements by inscribing a broadband decrease in transmissivity over the spectral characteristics of the chemical species being studied. The overall extinction varies with the optical thickness of the particulate cloud. Therefore, while this procedure works well for the low mass-loadings considered in this problem, it would not work at higher mass loadings when the particulate cloud is too optically thick to transmit radiation.

For the aluminum oxide particles with a mean particle diameter near the wavelengths being considered, the scattering spectrum predicted by Mie theory is nearly constant across the spectral band of interest. Furthermore, the spectral features of OH provide a small window where the molecule is weakly absorbing and the broadband features of scattering can be distinctly accessed. A scattering spectrum can therefore be fit to this region of the spectrum and then removed so that the absorptive features of OH can be used to obtain estimates of the gas macrostate.

It is found that the low mass-loading of particulate has little to no influence on the thermochemical properties of the flow. Returning to Elghobashi’s fluid-particle interaction regimes, the observed behavior of the OH macrostate after the addition of particulate agrees with the estimated volume fraction of $\Phi_p \sim 10^{-7}$ used in this study where, at this volume fraction, the particles have no influence on the fluid. If the particles took out a large amount of energy from the fluid, the combustion reaction rates would be expected to decrease and this would be evidenced by the decrease in OH production. Without any demonstrable change in OH number density, the effect of particulate on the OH macrostate is negligible.
The advantage of this procedure is that it does not require *a priori* knowledge about the particulate parameters. This procedure can be easily implemented provided

1. the spectral scattering behavior of the particulate can be measured independently and

2. there is a spectral band being measured over which the chemical species of interest is not spectrally active.

Although this procedure works in the present system with scattering caused by alumina oxide with nominal diameter 0.3 \( \mu \)m, a study involving different optics setups and different particle parameters would be necessary to elucidate the physical mechanism which enables this type of analysis.
CHAPTER 4

VALIDATION AND CONCLUSIONS

Thus far, estimates of the OH macrostate in a high-speed, multiphase reacting flow have been given by fitting spectral models to experimental data. To give credence to these results, the estimate procedure was applied to a system of known gas concentration and temperature. In this chapter, the validation experiment and the resulting data will be discussed. Then, conclusions from the entire thesis study and thoughts for future work will be given.

4.1 Bench Top Validation Experiment

Gas cells are common tools for spectra calibration or frequency standard references and are generally used with a laser passing through the cell in free space or through fiber-optic coupling. These cells can, in principle, be filled with any stable gas, pure or mixed, to a desired pressure. Using the ideal gas law, the number density of gas molecules, \( N \), present in the cell is directly proportional to the pressure of the gas, \( P \):

\[
N = \frac{N}{V} = \frac{P}{kT}
\]

where \( N \) is the absolute number of molecules present in the volume \( V \), \( k \) is the Boltzmann constant, and \( T \) is the temperature at which the cell was filled to the specified pressure. Nevertheless, a gas cell can be used to validate the macrostate estimation technique proposed in this dissertation.

Using much of the instrumentation and optics from the exhaust plume studies, a bench top experiment was set up using a 300 W, 120 V incandescent light bulb as the light source and an \( \text{O}_2 \) gas reference cell as the target volume. The tungsten filament in the light bulb serves as a near black body emitter, giving a broadband, slowly varying spectrum in the upper visible region. The voltage
Figure 4.1: Photograph of the bench top experiment setup.
to the bulb is adjusted using a Variac, variable transformer. For the experiments conducted here, the voltage of the Variac was set to 90 V. Molecular absorption is applied using a glass, Wavelength References free space gas cell with a 40 cm path length containing pure Oxygen gas (O$_2$) at 740 torr. The windows on either end of the cell are Magnesium Fluoride (MgF$_2$) with a thickness of 2 mm, an outer diameter of 25 mm, and a wedge angle of 0.5 degrees, installed at an angle of 3 degrees.

Furthermore, the windows were installed with the thicker side of the windows 180 ± 20° apart from each other, with respect to rotation about the center of the cell. Both the wedge and the tilt of the windows led to difficulties for the present measurement. In principle, the windows would be installed so that any influence the first window has on the transmitted beam would be undone by the influence the second window has on the beam. The benefit of such a setup would be reducing internal reflections and fringe patterns. However, slight misalignments result in both a redirection of the beam and a change in phase across the wavefront of the beam. Both the wedge and the tilt of the windows alter the beam, but the wedge has the most influence. The immediate result is that the beam arrives at the spectrometer slit in a slightly different location than it did without the windows present, causing a spurious relationship between the reference intensity measurement and the transmitted intensity measurement. In an attempt to counteract these differences, a cell blank was constructed using two MgF$_2$ windows identical to the ones used in the vapor cell and mounted in rotating optics mounts which were held to an angle iron. The windows were spaced 40.3 ± 0.3 cm apart to replicate the window spacing in the reference cell and turned counter to each other about the vertical axis. The first window was turned until the normal was roughly 1.6° off of the beam axis and the second window was turned the opposite direction until the normal was 2.3° off of the beam axis. These turns were measured after the spectra had been collected. It would have been better to orient the windows in a manner that matched the tilt of the vapor cell. Regardless, too many degrees of freedom make it difficult to confidently reproduce the outgoing beam from the vapor cell. Instead, a multiplicative factor was applied to the spectra to scale the measured O$_2$ transmission features in a manner that gives a baseline of one. This is comparable to the process
Figure 4.2: Illustration of bench top experiment setup.

used in Chapter 3 to obtain the “alternate” seed-off spectra.

The beam path elements were:

\( \mathcal{I} \): Tungsten filament light bulb

\( \mathcal{A}_1 \): Slit aperture opened to 1.28 mm with a height of approximately 4 mm

\( \mathcal{A}_2 \): Circular iris aperture with open diameter \(13/64 \pm 1/64\) in. with a circular plate serving as a beam block outside of the aperture

\( \mathcal{L}_1 \): Fused silica bi-convex lens with \( f = 150 \text{ mm} \) and \( D = 46 \text{ mm} \) giving \( f/3.26 \)

\( \mathcal{V} \): Measurement volume into which the gas cell is placed
**Table 4.1:** Distances between optical elements for the validation experiment.

<table>
<thead>
<tr>
<th>Element</th>
<th>Distance (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T A₁</td>
<td>64 ± 1 mm</td>
</tr>
<tr>
<td>A₁ A₂</td>
<td>233 ± 1 mm</td>
</tr>
<tr>
<td>A₂ L₁</td>
<td>63 ± 1 mm</td>
</tr>
<tr>
<td>L₁ A₃</td>
<td>531 ± 1 mm</td>
</tr>
<tr>
<td>A₃ L₂</td>
<td>47 ± 1 mm</td>
</tr>
<tr>
<td>L₂ S</td>
<td>125 ± 1 mm</td>
</tr>
</tbody>
</table>

A₃: The narrow aperture of a rectangular box-cutting razor blade serving as a beam block, with an aperture width of 2.5 ± 0.1 mm and a height of 6.3 ± 0.1 mm.

L₂: Fused silica bi-convex lens with \( f = 90 \) mm and \( D = 46 \) mm giving \( f/1.96 \)

S: Spectrometer entrance slit, \( s_S = 0.140 ± 0.005 \) mm.

These optics were set up to focus the beam in the middle of the measurement volume and defocus the beam on the spectrometer entrance slit in order to achieve a nearly uniform intensity along the slit.

The distances along the path, between the centers of the elements, were measured by a metric ruler and reported as given in Table 4.1.

At each spectral measurement, the temperature of the air next to the vapor cell was measured using a K-Type thermocouple and an ExTech handheld digital thermocouple reader. This gave the temperature of the reference gas in the cell since it is at thermodynamic equilibrium with the room environment. One reading was recorded per spectral measurement. Additionally, a photo diode was set up facing the light bulb, near the same elevation as the center of the bulb filament, and with a standoff distance of 26.2 cm from the filament. The photodiode is an Electro-Optics Technology, Inc. biased silicone detector ET-2020. A digital multimeter connected to the photodiode displayed the DC voltage accumulated on the diode. Again, one reading was recorded per spectral measurement. The charge on the diode remained stable at 24.48 V for each measurement.
4.1.1 Procedure

For each set of spectral measurements, the reference intensity, \( I_0 \), was recorded first, after allowing time for the light bulb to reach a stable temperature. The reference intensity refers to the intensity transmitted through the cell blank. Then the cell blank is removed and the vapor reference cell is installed in the measurement volume. The transmitted intensity, \( I \), is recorded. Then the vapor cell is removed and again the cell blank is installed. Then the next set of measurements is recorded.

4.1.2 Analysis

Analysis of the vapor cell data is not as simple as analysis of a free gas. Recall that the Beer-Lambert law relates the radiative intensity transmitted through a volume to the radiative intensity incident on the volume, \( I_i \). If the intensity transmitted through the cell blank is used as a reference intensity, \( I_0 \), instead of the incident intensity then careful consideration must be made about what changes in the measurement volume when adding the vapor cell. Symbolically, this works out to accounting for the transmissivity terms left in \( \ln(I/I_0) \) when \( I \) and \( I_0 \) both follow a form of the Beer-Lambert law:

\[
I_0 = I_i \exp\left[ - \int_{-\infty}^{\infty} (K_{b, \text{Air}} + K_{b, \text{MgF}_2} + K_{\text{optics}}) \, dl \right]
\]

\[
I = I_i \exp\left[ - \int_{-\infty}^{\infty} (K_{c, \text{O}_2} + K_{c, \text{MgF}_2} + K_{\text{optics}}) \, dl \right]
\]

where each \( K \) term represents the path-dependent, exponential extinction term of the corresponding element in the beam path after the first lens, \( L_1 \). In each case, the extinction due to the optics from the second lens to the detector is present so the optics term drops out in the ratio of the two intensities. The subscript \( b \) signifies terms from the cell blank measurement while the subscript \( c \) signifies terms from the vapor cell measurement. The extinction term for the air is a sum of extinction terms for all of the constituents in the air. Using measurements of the ambient temperature, relative humidity, and pressure along with the standard mass fractions of air constituents, the atmospheric
Figure 4.3: Transmission spectrum of moist air. Transmission spectrum through a 40 cm column of moist air at sea level and a temperature of 22.4°C, a relative humidity of 42.2%, a dew point of 9.1°C, and an atmospheric pressure of 14.46 psia. A boxcar instrument function for a slit width of 0.14 mm has been applied. Displayed are the transmission spectra for the four strongest spectral absorbers in air for the present wavelength band of observation and the resulting total transmissivity.

The transmission spectrum is calculated and shown in Figure 4.3. The absolute humidity of the air was estimated using the ambient conditions and the NOAA Air Resources Laboratory READY Moisture Calculator. The spectra are built using the HITRAN database for the air molecules along with all of the associated isotopologues which have the greatest line strength in the relevant spectral band. It is evident from Figure 4.3 that the strongest contributor to the transmission loss in air over this spectral band is diatomic oxygen with a total number density of $5.339 \times 10^{18}$ molecules/cm$^3$.

As a result, in the spectral range $\{\lambda|750 \leq \lambda \leq 780\}$ nm, we must account not only for the
oxygen in the cell, but also the transmission loss due to the air between the windows of the cell blank. Assuming all terms are constant with respect to the corresponding path length through the element, then
\[
\ln \left( \frac{I}{I_0} \right) \approx -lK_{c,O_2} - l_wK_{c,MgF_2} + lK_{b,Air} + l_wK_{b,MgF_2}
\]  
(4.2)
Here \( l = 40 \pm 0.1 \) cm, the path length through the cell, and \( l_w = 2 \pm 0.1 \) mm is the width of the windows. The extinction terms for the windows have been kept in the expression above since the windows of the cell blank and of the reference cell both influence the spectrum in yet undetermined ways which complicate the analysis.

4.1.3 Results

An analysis procedure similar to that used before was applied to the table top experiment data. The lamp emission was steady throughout the data collection process, as evidenced by negligible change in a spectrum of the emission source measured after the data collection compared with a similar spectrum measured before the data collection process. This is further supported by the stable voltage measured by the photo diode at each spectrum collection event. Despite the steady spectrum, 41 rows and 25 randomly selected elements were chosen for each measurement. The 41 rows were chosen to be centered on the middle of the incident probe beam, the location of which varied depending on what elements were placed in the beam path. The total 1025 samples of data for each measurement were then evaluated for normal statistical behavior, see Figure 4.4. Since all of the transmitted spectra involve stationary processes, the distributions should be normal. However, the measurements for transmissivity are complicated because the recorded spectra contain features which are probably a consequence of the windows and not any molecular absorption.

In Figure 4.4, a wavelength bin just below the active band of \( O_2 \) absorption was selected and then a histogram constructed using all 1025 samples of tranmissivity at this wavelength for both sets of transmission measurements. The mean of the two distributions is slightly different because the orientation of the cells was slightly different between the two sets and the scaling factor was not
Figure 4.4: Distributions of samples for reference cell transmission spectra. The distribution of selected samples for the vapor reference cell transmissivities at a single wavelength. The associated Guassian distribution is drawn along with the histograms for reference.
yet applied to the data. While the distribution from the second set of data is already Gaussian, the data from the first set was not normally distributed initially so the outliers were removed to obtain more normally distributed data before conducting the analysis. The improved histogram is shown for Set 1 in Figure 4.4.

After averaging the extinction coefficients the experimental transmissivities are built. The average transmission in a band from 758.49 nm to 758.81 nm, immediately below the active band of oxygen absorption, was used as a scaling factor for both transmissivities to bring the baseline of the oxygen spectral features to unity. Next, the spectra are multiplied by the atmospheric transmissivity at the ambient conditions of the room in order to isolate the spectral effects due to the Oxygen only. This results in the spectra shown in Figure 4.5. When compared with the hydroxyl spectra from the

Figure 4.5: Transmission spectra for the two sets of reference cell measurements.
rocket exhaust plume, the oxygen signal is barely distinguishable within the noise of the system. From left to right, the pattern of the absorption involves a somewhat broad dip followed by a series of relatively narrow dips. See the model in Figure 4.6 for a trace of the O\textsubscript{2} spectrum.

The transmissivities are fit with an oxygen spectrum using the Bayesian inversion scheme. For qualitative comparison, the scale of the figure matches the scale of the fit results from Chapter 3. Compared with the OH absorption in the exhaust plume studies, the O\textsubscript{2} absorption in the current band and at the measured temperature is quite weak even with a higher number density and path length. The relative weakness of the signal leads to high uncertainty in the macrostate estimates. This can be reduced with a good prior distribution. However, since the temperature and number density of the O\textsubscript{2} in the cell are well known, a uniform distribution over the entire parameter space with \( \{ T \in \mathbb{Z} \mid 100 \leq T \leq 1000 \} \) K and \( \{ N \in \mathbb{R} \mid 1 \times 10^{17} \leq N \leq 1 \times 10^{20} \} \) molecules/cm\textsuperscript{3} was used for the prior distribution so as not to bias the outcome of the fit. The number density range is distributed into 1000 logarithmically spaced intervals while the temperature grid uses every integer in the range.

The weakness of the absorption signal leads to high uncertainty in the measurements, particularly with regard to the selection of temperature. Higher temperatures tend to fit the data better than the lower temperatures. This is evidenced by the broad distribution of the posterior from the fit results for the second set of reference cell spectra. Figures 4.7 and 4.8 demonstrate how the probability distribution favors the upper end of the temperature range, leading to an error estimate which has a broader range above the peak probability than below it. Additionally, the left plot in Figure 4.8, the line of constant number density which passes through the most likely macrostate, shows that the distribution involves discontinuities. The authors suspect this is a consequence of the weak signal since this behavior was not observed with the rocket exhaust plume data where the absorption signal is notably stronger. Therefore, while the macrostate estimate does fall within the estimated error from the true macrostate, see Table 4.2, the broad distribution of possible values renders this procedure useful for only rough estimates of the macrostate parameters. The macrostate estimates for only the second set of transmission data are given in Table 4.2. The fit
Figure 4.6: Bayesian fit results for the vapor reference cell measurement. The spectrum with the most likely pair of temperature and number density values are plotted over the experimental spectrum. The y-axis scale of the figure mirrors that of the spectral fit results from the prior chapter for comparison.
Figure 4.7: Posterior of the spectral fit for the vapor reference cell measurement. Unlike the posteriors for the earlier hydroxyl data, this one has discontinuities along the temperature axis, parallel to the number density axis.

conducted with the first set of data resulted in undetermined estimated errors in temperature. The posterior distribution was too broad along the temperature axis for the half maximum to appear within the temperature range provided in the parameter space. In the table, the uncertainty reported for the actual temperature of the cell comes from the random error of the instrument being used to measure the present temperature. The uncertainty reported for the actual number density of oxygen in the cell was determined by assuming an initial temperature of $20 \pm 5^\circ C$ and calculating the error generated in Equation 4.1 due to the uncertainty in initial temperature at which the cell was filled to the specified pressure of 740 torr.
**Figure 4.8:** Profiles of the posterior distribution at the point of maximum likelihood. (Left) The profile of constant number density. (Right) The profile of constant temperature.

**Table 4.2:** Summary of spectral fitting results for the reference cell experiment.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$K_{\text{actual}}$</th>
<th>$K_{\text{meas.}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T$ [K]</td>
<td>294.3 ± 0.3</td>
<td>$273^{+271}_{-95}$</td>
</tr>
<tr>
<td>$N$ [$\times 10^{19}$ molec./cm$^3$]</td>
<td>2.44 ± 0.04</td>
<td>$2.14^{+0.721}_{-0.717}$</td>
</tr>
</tbody>
</table>

The known macrostate of the reference cell gas is compared with the macrostate estimated by the fitting of a spectral model to the data.
4.2 Conclusion

A procedure has been developed to study the thermodynamics of a rocket motor exhaust plume with entrained solid-phase particulate. No *a priori* knowledge of the particle size distribution is necessary for this procedure. Instead, the particle scattering behavior is classified in a separate measurement so that it can be removed from a spectrum as if it were another optical element. This is similar to the way a professional astronomer would calibrate a ground-based telescope to eliminate atmospheric extinction so that more faithful quantitative spectral measurements of cosmic objects can be obtained. Two methods are explored for removing the scattering effect. The first, called the repository method, works directly with existing data of the particulate scattering to build a model of the scattering effect in the plume. The second method, called the empirical method, takes the scattering data already collected and builds a model that fits the preexisting scattering data and can, in principle, be used to model scattering at any level of extinction. Then, transmission spectra containing both particulate scattering and molecular absorption can be processed so that only the absorption part of the spectrum remains and can be used for analysis of the macrostate, and therefore the thermodynamics, of the plume gas. Understanding how the particles influence the chemistry of the reacting plume is an important foundation to lay in order to explore additional questions about this system such as: “what does the particle effect on the spectra communicate about the turbulence in the flow field?”

4.2.1 Future Improvements

Refinement of the technique presented in this study could start with a detector optimized for operation in the near UV regime. This would enhance the signal-to-noise ratio of the data and enable shorter exposure times, ideally providing an exposure time less than half of a microsecond so that approximately one flow through time occurs during the span of the exposure. This could allow the analysis of instantaneous spectra so that the flow dynamics can be taken into consideration. This would be further strengthened by the incorporation of a form of radiation output monitor. Ideally, this would entail sending part of the incident radiation intensity into the spectrometer, arriving at the
Figure 4.9: Illustration of traversing optical system concept.

detector to enter the same measurement as the transmitted intensity. This way the incident intensity is also instantaneous rather than averaged and correlated to the transmitted intensity measurement, further reducing ambiguities in the spectra.

These improvements could be taken a step deeper by making more careful distance measurements of the plume profile in order to reduce the uncertainty in the path length estimates. In fact, if a proper model can be built of the OH temperature and number density as a function of the path taken through the plume, then line-of-sight measurements would contain more information about the structure of the plume, acting more like a tree-core sample than as a line-integrated value.

Furthermore, spatially resolved spectra from the plume would greatly enhance the quality of this study, giving more information than the current line averaged approximation. Preliminary steps in this direction can be achieved by installing the front end of the optics system on a traversing platform and using the second lens to collimate the beam, sending it to a third lens which refocuses the beam onto the spectrometer slit which is held at a fixed location. An illustration in Figure 4.9 demonstrates this concept. This could probe the plume at select stations along the plume axis.

The spectral fitting routine can also be improved. Since the posterior distribution was
smoothly varying in most cases with a unique global maximum probability. Therefore, it would be advantageous to conduct the spectral fitting using a non-linear, least squares levenberg-marquardt algorithm which works quickly for finding curves of best fit provided the global maximum of the parameter space is the same as the local maximum. This is also the industry standard procedure for spectral fitting. However, this fact was not known to the author at the outset of this project and a Bayesian fitting approach was recommended to ensure that the global maximum is selected by the fitting algorithm.

Farther reaching goals for the probe system would involve the use of tunable diode laser absorption spectroscopy (TDLAS) to interrogate points in the measurement volume. This would be an easy way to improve the temporal and spectral resolution of the measurements and is an industry standard technique\textsuperscript{35,54}. One problem with TDLAS is that a tunable laser for the UV, to look at a similar spectral band as considered in the present study, comes with a rather high price tag. This may not be an issue depending on the molecular species available to study. A more spatially resolved, laser-based technique entails a hyperspectral laser split into multiple beam paths in order to conduct tomographic measurements of the flow field cross section.\textsuperscript{55} A general overview of spatially and temporally resolved spectral measurement techniques for combusting flows is given in the 2011 review paper by Alden \textit{et al.}\textsuperscript{56}

Another thrust for the improvement of this experiment would be the particle loading and detection. A major complication with the current data is that the scattering is inconsistent. It would be desirable to measure the particulate scattering at varying mass flow rates. This has been done in a high speed jet system using an alternative approach to the seeding, by suspending the alumina in a pH-balanced ethanol solution before injecting the particles into the flow. Both systems appear to provide consistent streams of particulate. In fact, extinction measurements within the jet plume seeded by this solution provided particulate scattering data which could be used to estimate the mass loading of the particles in the flow provided the seed size distribution is known. Therefore, the scattering part of combined spectra may be useful for future determination of some particle loading features. The amount of information which can be obtained will likely remain limited
Additional questions which have been opened by this study open are:

1. How well does the present particulate scattering spectrum identification procedure work with different particle sizes, materials, and mass loadings?

2. How much particulate mass loading is necessary before the reaction chemistry begins to exhibit significant changes in the macrostate parameters?

3. What can be said about the particle-fluid interaction based on changes in the macrostate estimates when particulate is present?

Particle loading in high speed flows continues to gain attention as interest expands with hypersonic reentry vehicles, supersonic flows in extraterrestrial atmospheres, and solid rocket motor exhaust plumes. Meanwhile, particle analysis within these high speed flows remains a formidable challenge. A diverse set of tools including those explored in this thesis can help develop a more complete experimental understanding of the problem. The spectral behavior of molecules have been long understood and the prediction of particulate scattering behavior, although difficult to measure, is relatively well developed theoretically. Spectral measurements in which both absorption and scattering play an active role are not new, but making use of the available techniques in the field of high-speed reacting flows is advantageous for handling the complex experimental problems currently being explored.
LIST OF REFERENCES


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Education

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Academic Employment

2012 - 2015 – Research Assistant, Dept. of Physics and Astronomy, Middle Tennessee State University: Cultivated critical reasoning, experimentation, and data analysis skills under William Robertson, PhD.

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