

Laser-Induced Breakdown Spectroscopy for Analysis of High Density Methane-Oxygen Mixtures

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Abstract

The applicability of laser-induced breakdown spectroscopy (LIBS) toward greater than atmospheric density combustion diagnostics is examined. Specifically, this involves ascertaining the feasibility of measuring chemical equivalence ratios directly from atomic emission spectra at high density. The need for such measurement arises from the desire to quantify real time, localized combustion performance in weakly mixed flows. Insufficiently mixed flows generally result in unwanted byproducts, possess the propensity for overall combustion instability, and are increasingly likely to experience localized flame extinction.

We simulate methane/oxygen combustion in ambient pressures ranging 1 to 4 atmospheres, demonstrating these results to be analogous to what would be obtained under combustion conditions at pressures roughly 10 times greater. Given that LIBS measurements are independent of the sample's initial state, we introduce a reaction quenching species (neon) at large mole fraction into the mixture, thereby eliminating any chance of ignition and thus many experimental difficulties associated with observing high density atomic spectra.

Table of Contents

1	Introduction	1
1.1	LIBS as a technique	3
1.2	Experimental methodology	4
2	Background on the Laser-Induced Spark	7
2.1	Development of the spark	7
2.2	Spectral emission of the plasma	11
2.2.1	Radiative processes and transition probabilities	11
2.2.2	Spectral line broadening	12
2.3	Local thermodynamic equilibrium	16
3	Combustion Chemistry	18
4	Experimental Setup and Spectral Line Choices	22
4.1	Apparatus	22
4.1.1	Some details on the Nd:YAG	25
4.2	C and O line selection	25
5	Results and Analysis	28
5.1	Determination of a high-density C/O to equivalence ratio relationship	32

5.1.1	Line and continuum intensity variation	35
5.2	Electron number density calculation	37
6	Summary	41
	Bibliography	43
	Vita	49

List of Figures

2.1	Shadowgraphs of laser-induced spark decay in air, between 5 and 500 μs after termination of the laser pulse, initiated by 75 mJ of Nd:YAG 1064 nm radiation. Beam propagation is from left to right.	10
3.1	Mole fraction versus equivalence ratio for the CH_4/O_2 reaction at 4 atm. Calculated with NASA-CEA code.	21
3.2	CEA calculated combustion temperature versus equivalence ratio for the CH_4/O_2 reaction over the ambient pressure range 0.5 to 4 atm. .	21
4.1	Experimental setup includes elements native to a LIBS detection apparatus: a laser, a detection system, and a sample.	24
4.2	Photograph of the high pressure sample vessel with the spectrometer slit in the background.	24
4.3	Plot of Quanta-Ray DCR Nd:YAG energy per pulse and optical pulse width versus Q-switch delay. Note “0 ns” Q-switch delay is defined as minimum. Energy measurement error < 0.5%.	26
4.4	Plot of calculated relative intensities for potential O, C and H spectral lines. Computed for 15000 K using Payling and Larkins software [37].	27
5.1	Sample 2-D stoichiometric ($\phi = 1$) C-O spectra at 1 and 4 atm, for 3.5 μs delay.	29

5.2	Integrated C-O spectra between 1 and 4 atm, for $\phi = 0.25$ and $\phi = 0.5$.	30
5.3	Integrated C-O spectra between 1 and 4 atm, for $\phi = 1$ and $\phi = 2$. . .	31
5.4	Plot demonstrating typical means of continuum subtraction prior to calculation of C/O ratios and Stark widths - the continuum is fit with a high order polynomial.	32
5.5	Calibration plot of measured C/O ratio versus equivalence ratio, ϕ , for varying pressures. ~ 165 mJ YAG energy	33
5.6	Non-flowing sample - C/O ratio versus ϕ for varying incident laser energies. Presented for comparison with Figure 5.5.	34
5.7	Plot of measured C 193 / Continuum versus equivalence ratio for varying pressures.	36
5.8	Plot of measured O 777 / Continuum versus equivalence ratio for varying pressures.	36
5.9	Plot of continuum at 767 nm versus equivalence ratio for varying pressures.	37
5.10	Plot of n_e v. P derived from Stark FWHM of C 193 nm at time $3.5 \mu s$. $\phi = 0.5$	40

Chapter 1

Introduction

Perhaps no single technological advancement has had a greater impact on human development than the mastery of fire, or more specifically combustion. To define it generally, combustion is the oxidation of a material through a series of rapid exothermic chemical reactions, releasing energy and various chemical products. Anthropologists have presented evidence suggesting that *Homo erectus* made use of controlled fire at least 400,000 years ago for cooking, illumination, a source of warmth, and as a means to ward off predators [1]. Much more recently during the Industrial Revolution of the 18th and 19th centuries, the transportation and manufacturing innovations of the time, particularly those based on the steam engine, widely utilized the burning of lumber and coal as energy sources. Modern civilization continues to rely heavily upon combustion to provide energy for everything from electricity generation (through the burning of fossil fuels) to advanced forms of propulsion.

Given combustion's overwhelming importance to contemporary society, there have been numerous efforts to improve upon the various applications by making them efficient and economically viable. One such progression was the development of the internal combustion (IC) engine from the external combustion (EC) engine. The

very nature of the IC engine exploits the expansion of high temperature and pressure chemically reacting fluids to do mechanical work. The high density reaction environment of IC engines provides for greater efficiency, greater power-to-weight ratio, less machinery complexity, quicker startup times, and cheaper initial cost [2]. Considering these advantages and the potential for continued development and refinement, the need to develop a deeper understanding of the details of high density combustion dynamics quickly becomes apparent.

Under high density combustion the chemical reaction rate increases drastically as a result of an increased probability of species collision (reduced mean free path), leading to an increased likelihood of turbulent flow, which in turn improves the homogeneity of the reactant mixture. More complete mixing leads to improved thermodynamic efficiency and more usable energy. Additionally, the intensified reaction rate allows for increased stability under more fuel-lean conditions, thereby improving fuel efficiency and limiting undesirable reaction byproducts.

When discussing combustion, one must consider both premixed and non-premixed regimes. Non-premixed flames possess burning rates that are predominantly limited by the rate of mixing of the fuel and oxidizer (due to diffusion and turbulence) and are typical for diesel engines, many gas turbine combustors, as well as most liquid or gas-fueled rockets. For premixed flames the local burning rate is controlled not only by diffusion but also by the chemical reactions themselves [3]. Premixed turbulent flames are typical for spark ignition engines as well as solid fueled rockets.

A high pressure combustor best suited to obtaining experimental calibration data should possess a premixed flow to more easily determine details of the reaction chemistry. However the majority of real combustors exhibit flows that are quite different from the premixed approximation, and thus the homogeneity of the reactant mixture can vary radically with temporal and spatial variation. Insufficient mixing produces

undesired byproducts and general combustion instability. Thus, the need arises to quantify the extent of mixing in combustors via the measurement of localized fuel-to-oxidizer ratios. The primary focus of this thesis is to demonstrate a method for accomplishing that very measurement.

1.1 LIBS as a technique

Observations of laser-induced optical breakdown of gases were first reported by Maker et al. [4] and by Meyerand and Haught in 1963 [5]. Extensive research has been conducted on the subject since that time, covering a wide range of gas mixtures, pressures, and laser configurations. At present the mechanisms leading to breakdown, as well as the influence of various parameters such as laser wavelength, focal length, focal diameter, pressure, pulse length, and material on the creation of the spark are well known. Cremers and Radziemski thoroughly outline the emergence of spectroscopic analysis of the laser-induced spark as an accepted technique [6].

Laser-induced breakdown can be defined as the generation, by the end of the incident laser pulse, of a near-completely ionized accumulation of matter (a plasma) in the focal region. More quantitative definitions involve the measurement of attenuation of the laser beam by the plasma and the level of total ionization. Observationally, the breakdown is characterized by the presence of an intense flash or glow in the focal region [7]. The laser pulse must be of sufficient irradiance, which is typically in the range of $GW \cdot cm^{-2}$ [8] to initiate ionization, and the exact breakdown threshold is specific to the sample composition and density.

Laser-induced breakdown spectroscopy (LIBS) as a technique is widely used for real-time in-situ analysis of samples in every phase of matter and is especially useful in hazardous environments [9]. Recently, LIBS has been demonstrated as an effective

means of determining combustion characteristics inside a chemically reacting flame. Specifically, quantitative measurements of atomic species concentrations can be obtained directly from the spectra and applied toward combustion equivalence ratio determination [10] [11] [12] [13] [14].

1.2 Experimental methodology

We will demonstrate the suitability of the LIBS process for measurement of chemical equivalence ratios under high density combustion. Since modern combustion applications make use of a wide range of fuels and oxidizers and our goal is to demonstrate the effectiveness of a measurement process, we will reduce some of the reaction complexities by considering one of the simpler cases: the reaction of gaseous methane CH_4 with oxygen O_2 .

Our primary concern is the determination of local equivalence ratios from the fuel-to-oxidizer F/O ratio, which we define by the intensity ratio of neutral atomic carbon to oxygen spectral lines, or $F/O = C/O$. Significant obstacles exist for high density LIBS measurements, most notably a reduction of the overall spectral peak-to-noise ratio due to increased background continuum and both collisional quenching and broadening of atomic and ionic emission lines.

The obvious experimental means by which to measure the C/O ratio would be to apply LIBS to an actively reacting high density combustion environment. However, the high temperatures, pressures and large flow rates make performing such an experiment with highly flammable mixtures extremely complex to implement in a university laboratory setting. The various reaction products can further compound experimental difficulties, especially in the case of carbon soot for fuel-rich mixtures. Additionally, we can not simply look at the reactants without combustion because the

laser-induced spark will actually initiate the combustion process, thereby disrupting the presumed symmetry of the flow [15] (introducing the need for a second laser to conduct the actual LIBS measurement).

So, recall the previously stated fundamental property of LIBS: by its very nature, the LIBS process completely atomizes a sample. Thus the entire spectroscopic signal of an atomic species can be measured regardless of the species' original state. Consequently, when applying LIBS to chemical reactions it matters not whether the sample is derived from the reactants or the products; the same measurement will result. So therefore we can simulate the measurement of combustion conditions without actually observing any chemical reaction.

To prevent initiation of a reaction, the gas sample will include a non-reacting diluent species, neon, at significant enough mole fraction to quench any possibility of combustion. Neon safely eliminates the possibility of ignition as long as the sum proportion of methane and oxygen remains less than approximately 15 percent of the total gas mixture (extrapolated from Lewis and von Elbe [16]).

The simplest means to house this newly non-combusting sample would be a static high pressure vessel. However, probing such a static sample gives rise to a new problem: the sample is given insufficient relaxation time between laser shots to return to its initial state [15] [17] [18]. In effect, each subsequent probing laser shot would be looking at atomic metastable levels persisting from the preceding shots. This problem is solved by simply flowing the sample through the focal volume at sufficient velocity to refresh it between laser shots.

To summarize, the primary focus of this thesis is the analysis of the feasibility of applying LIBS toward high density combustion diagnostics, specifically toward the measurement of fuel-to-oxidizer ratios directly from the spectra. In an effort to accomplish the above stated goal we subject various high density mixtures of a

specific combustible mixture, methane and oxygen, to spectroscopic analysis via laser-induced spark. To simplify the experimental process and eliminate any possibility of combustion, we introduce a noble, non-reacting gas (neon) in large mole fraction with respect to the reactants into the sample.

Chapter 2

Background on the Laser-Induced Spark

2.1 Development of the spark

Let us begin with a discussion on the evolution of the laser-induced spark. Morgan identifies four distinct stages covering the transformation from neutral gas into hot plasma and its subsequent extinction: initiation, formative growth, plasma development accompanied by shockwave generation and propagation into the surrounding gas, and finally extinction [19].

The initiation stage spans the time between the arrival of the laser radiation in the focal volume, until the release of a free electron and subsequent growth of the free electron and ion concentrations in the gas. Ionization and the optical breakdown itself come about as a result of two primary processes: electron impacts and multi-photon absorption.

Electron impact ionization (Equation 2.1) requires the presence of an initial electron, which can be introduced by multi-photon ionization (MPI), thermionic emission

from a large particle, or the tunnel effect [7]. In most cases the electron is easily generated via MPI through the use of laser radiation with sufficiently short wavelength and large irradiance. For longer wavelengths, however, MPI often can not furnish the necessary electrons. Large particles can be heated by the incident radiation, and eventually this releases electrons via thermionic emission. Given a sufficiently strong electric field, outer shell electrons can be knocked from their orbits via the tunnel effect as well. Regardless of the origin of the seed electron, e^- impact ionization increases the electron density exponentially with time.



Described by the process in Equation 2.2, multi-photon ionization involves the simultaneous absorption by an atom or molecule of a sufficient number of photons to cause ionization. The ionization rate due to MPI within a laser beam of irradiance I is proportional to I^m , where m is the number of photons required. Thus, assuming constant irradiance, the degree of ionization due to MPI increases linearly with time. In general the degree and rate of ionization of the laser-induced spark depends heavily upon both e^- impact and multi-photon ionization. The two work in conjunction to effect a sort of “cascade”-type ionization.

The formative growth stage is the subsequent period of time during which magnification of the number of free electrons and ions takes place until the state of “breakdown” is reached. Arbitrarily defined, “breakdown” implies an electron number density of at least 10^{13} cm^{-3} , or a degree of fractional ionization of the gas atoms which is sufficient to cause significant absorption and scattering of incident laser ra-

diation [20].

Once the characteristic conditions of the breakdown exist, and if the laser pulse continues to deposit energy into the gas, a highly ionized, conducting, and hot plasma will form. The plasma continues to evolve throughout the remaining duration of laser irradiation, becoming optically thick and absorbing nearly all of the incoming radiation while expanding in a direction opposite that of laser propagation [15] [21]. The resulting large electron number density ($\gtrsim 10^{15} \text{ cm}^{-3}$) enhances the absorption of laser beam energy and results in increased ionization, higher temperatures, and plasma expansion. A supersonic shockwave also begins to propagate radially outward from the plasma kernel within the first few microseconds.

Figure 2.1 presents shadowgraphs that show the spatial evolution of a laser-induced air plasma between 5 and 500 μs after termination of the laser pulse. The shockwave is clearly visible in the shadowgraphs. Behind the shockwave the gas expands rapidly, even to the point of overexpansion, thus giving rise to a spatially varying particle velocity distribution [15] [18]. The pressure of the high temperature inner-gas diminishes until it can overcome the expansive momentum of the outer traveling particles. The subsequent opposing velocity gradients produce toroidal flow vortices, which in turn create the irregular kernel shape visible at late times [22].

Following the conclusion of the laser pulse, in what can be called the extinction phase, the plasma gradually diminishes until thermodynamic equilibrium is restored with the surrounding environment. The electron density decays through recombination, diffusion and attachment; and the energy in the plasma kernel decays through heat conduction, the continued expansion of the shockwave, and radiative transfer.

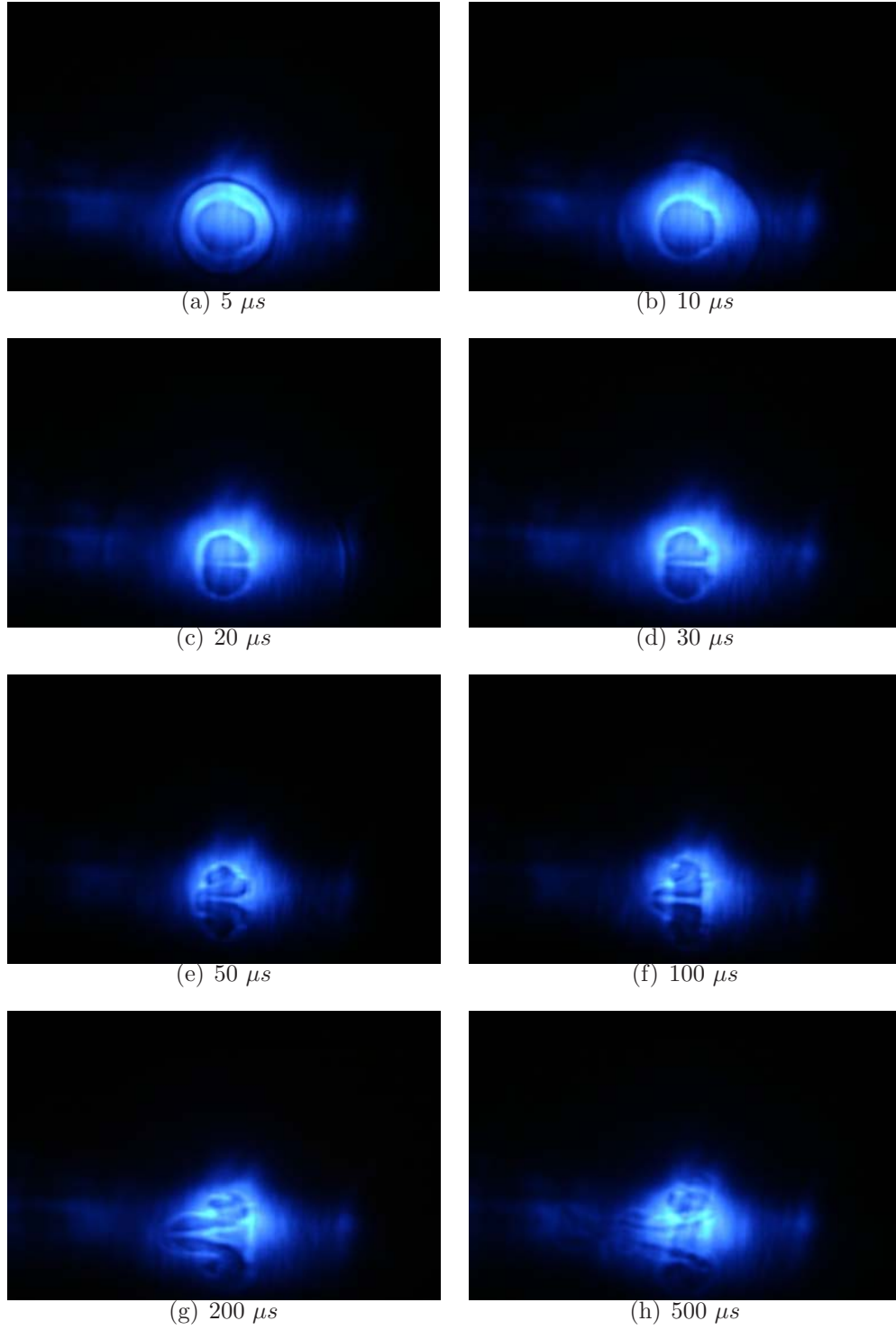


Figure 2.1: Shadowgraphs of laser-induced spark decay in air, between 5 and 500 μs after termination of the laser pulse, initiated by 75 mJ of Nd:YAG 1064 nm radiation. Beam propagation is from left to right.

2.2 Spectral emission of the plasma

Now let us briefly discuss some details about spectral emission of the laser-induced plasma, beginning with a discussion of the electron-ion blackbody continuum and followed by a review of radiative processes and transition probabilities.

Plasma spectral emission is dominated by electron-ion recombination continuum radiation when plasma temperatures are greatest, shortly after the termination of the laser pulse ($\lesssim 100$ ns). The spectral radiance I ($W \cdot sr^{-1} \cdot m^{-3}$) can be approximated by a blackbody curve according to Planck's law

$$I(\lambda, T) = \frac{2hc^2}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1}, \quad (2.3)$$

where λ is the wavelength, T is the temperature in Kelvin, h is Planck's constant, k is the Boltzmann constant, and c is the speed of light. Individual spectral lines emerge as the continuum diminishes over time. Ionic spectra begin to appear within the first few hundred nanoseconds after the onset of optical breakdown, atomic spectra by 0.5 - 1.5 microseconds, and molecular spectra shortly thereafter [22] [23].

2.2.1 Radiative processes and transition probabilities

This section will review the various radiative transfer processes and their associated transition probabilities. Consider spontaneous emission: a quantum system in an excited state $|n\rangle$ spontaneously radiates a photon as it de-excites into a lower energy state $|m\rangle$. The process can be expressed in terms of the Einstein transition probability $A_{nm}(s^{-1})$, which gives the rate that a system in state $|n\rangle$ will undergo spontaneous transitions to state $|m\rangle$. The radiative lifetime $\tau_{nm}(s)$ for the decay of $|n\rangle$ to $|m\rangle$ is defined as the reciprocal of the transition probability $\tau_{nm} \equiv 1/A_{nm}$. The spectral

radiance I_{nm} ($W \cdot sr^{-1} \cdot m^{-3}$) due to emission of a particular atomic or ionic line is given by

$$I_{nm} = n_n A_{nm} g_n \frac{1}{4\pi} \frac{hc}{\lambda} \frac{1}{U(T)} e^{-(E_n/kT)}, \quad (2.4)$$

where n_n is the species number density, g_n is the statistical weight of the upper state $|n\rangle$, and $U(T)$ is the partition function [24].

If the system is immersed in a radiation field of frequency ν , then two other processes are also possible. Assuming the system is in the lower state $|m\rangle$, the radiation field can effect the transition from $|m\rangle$ to $|n\rangle$ through the absorption of a photon of energy $h\nu$. The probability of such an event is $B_{mn}\rho(\nu)$, where B_{mn} is the Einstein absorption coefficient and $\rho(\nu)$ is the spectral energy density of the radiation field. The second process involving an external radiation field occurs for systems initially in the upper state $|n\rangle$. The radiation field can stimulate the transition from $|n\rangle$ to $|m\rangle$ with a probability given by $B_{nm}\rho(\nu)$, where B_{nm} represents the Einstein stimulated-emission coefficient [25].

The aforementioned processes constitute the essential means by which the plasma emits radiation over its lifetime, from initiation to laser-heating and finally to decay. The overall spectroscopic history of the spark persists considerably longer than both the radiative lifetime of the emitting species and the typical laser pulse length, suggesting the profound importance of electron impact excitation to the emission process.

2.2.2 Spectral line broadening

If we represent an atom (or molecule) by a simple harmonic oscillator with resonant frequency ω_0 , and suddenly perturb it from equilibrium, then the atom will radiate electromagnetic energy for a time τ determined by either the radiation damping

constant or by collisional decay. The lifetime-limited line profile function is given by the Lorentzian [25]

$$L(\omega) = \frac{1}{\pi} \cdot \frac{1/\tau}{(\omega_0 - \omega)^2 + (1/\tau)^2}. \quad (2.5)$$

In the case of natural broadening, the radiative lifetime typically has a value of about $\tau_{Nat} \approx 10^{-8} \text{ s}$ for atomic resonance lines, with angular frequency HWHM (Half-Width at Half-Maximum) $\Delta\omega_{Nat} = 1/\tau_{Nat} \approx 10^8 \text{ rad/s}$ or $\Delta\nu_{Nat} \approx \frac{10^8}{2\pi} \text{ s}^{-1}$. Since

$$c = \lambda\nu, \quad (2.6)$$

the natural linewidth is

$$\Delta\lambda_{Nat} = \frac{\lambda^2}{c} \Delta\nu_{Nat}. \quad (2.7)$$

Additional broadening occurs when collisions reduce the lifetime of the excited state. Included in this category is broadening due to the Stark effect, or the perturbation of atomic energy levels by the free electron generated electric field. Also included is the dipole-dipole interaction described by Van der Waals broadening. The line profile resulting from collisional broadening again takes the Lorentzian form

$$L_c(\omega) = \frac{1}{\pi} \cdot \frac{1/\tau_c}{(\omega_0 - \omega)^2 + (1/\tau_c)^2}. \quad (2.8)$$

If a radiating atom (or molecule) possesses a velocity component $\vec{v}$ in the direction of the observer, then the observed frequency ω is Doppler-shifted with respect to the rest-frame frequency ω_0 :

$$\omega = \omega_0 (1 \pm |\vec{v}|/c). \quad (2.9)$$

If the plasma or gas exhibits a Maxwellian velocity distribution, then the probability

that an emitter will have a velocity component in the $\vec{v}$ direction is

$$f(\vec{v})d\vec{v} = \left\{ \frac{m}{2\pi kT} \right\}^{1/2} e^{-mv^2/2kT} d\vec{v}. \quad (2.10)$$

Combining Equations 2.9 and 2.10 gives the probability that a photon will be observed with frequency in the interval $(\omega, \omega + d\omega)$:

$$G(\omega) = \frac{1}{\beta\pi^{1/2}} e^{-(\omega-\omega_0)^2/\beta^2}, \quad (2.11)$$

where $\beta = \left\{ \frac{2kT\omega_0^2}{mc^2} \right\}^{1/2}$. Note that thermal motion produces a Gaussian line profile. The FWHM wavelength $\Delta\lambda_{Doppler}$ for the Doppler-broadened spectral line is [26]

$$\Delta\lambda_{Doppler} = 2\lambda(2kT \ln 2/mc^2)^{1/2}. \quad (2.12)$$

To account for both collisional and Doppler (thermal) broadening effects, the convolution of the Lorentzian and Gaussian profiles, Equations 2.5 and 2.11, respectively, are convolved to yield the Voigt profile:

$$\begin{aligned} V(\omega) &= \int_{-\infty}^{\infty} G(\omega^*)L(\omega - \omega^*)d\omega^* \\ &= \frac{1}{\beta\tau\pi^{3/2}} \int_{-\infty}^{\infty} \frac{d\omega^*}{(\omega_0 - \omega + \omega^*)^2 + (1/\tau)^2} e^{-(\omega^* - \omega_0)^2/\beta^2}. \end{aligned} \quad (2.13)$$

Introducing the substitutions $y \equiv (\omega^* - \omega_0)/\beta$, $u \equiv (2\omega^* - \omega)/\beta$, and $a \equiv 1/\beta\tau$ simplifies the above expression to:

$$V(u) = \frac{a}{\beta\pi^{3/2}} \int_{-\infty}^{\infty} \frac{dy}{(u - y)^2 + a^2} e^{-y^2} \quad (2.14)$$

Despite the overall line profile being susceptible to change from any number of

broadening effects, the presence of high temperatures and large electron densities in LIBS plasmas effectively limits the primary contribution to the spectral line width to the Stark effect [27]. This makes spectrally isolated, broadened emission lines quite useful for calculation of electron number densities due to Stark effect broadening.

The total Stark broadening (FWHM) $\Delta\lambda_{Stark}$ in nanometers of a spectral line is given by [8]

$$\Delta\lambda_{Stark} = 2w \left\{ \frac{n_e}{10^{16}} \right\} + 3.5wA \left\{ \frac{n_e}{10^{16}} \right\}^{5/4} \left[1 - BN_D^{-1/3} \right], \quad (2.15)$$

where w (nm) is the electron impact parameter, n_e (cm^{-3}) is the electron number density, A is the ion broadening parameter, and B is either equal to 1.2 or 0.75 for ionic or neutral lines, respectively. Values for w and A are easily found in the literature, with Griem [28] being a standard source for w . The first term on the right side comes from the electron interaction, while the second term is generated from the ion interaction. N_D is the number of particles in the Debye sphere

$$N_D = 1.72 \times 10^9 \frac{T^{3/2}}{n_e^{1/2}}, \quad (2.16)$$

where T is the temperature in Kelvin. Electron density determination through use of this mechanism is a well-established and reliable technique for the range 10^{14} - 10^{18} cm^{-3} . For typical LIBS conditions, the contribution of the ions to the total Stark broadening is negligible compared to that of the electrons. The enhanced influence of electron impacts is a result of the large free electron densities typical in LIBS plasmas [29]. Equation 2.15 thus reduces to

$$\Delta\lambda_{Stark} \approx 2w \frac{n_e}{10^{16}}. \quad (2.17)$$

2.3 Local thermodynamic equilibrium

A plasma under strict thermodynamic equilibrium possesses a uniform electron temperature and emits an isotropic and homogenous radiation field according to the Planck distribution. However, real plasmas are subject to strong electromagnetic field gradients and are not so simply characterized. In an attempt to resolve this we apply the assumption of local thermodynamic equilibrium (LTE); i.e., all thermodynamic properties are the same as they would be under strict equilibrium properties, but at the local temperature and density. Moderate gradients of temperature and density can be present (as in a quasi-stationary plasma), but if that variation magnifies then the distribution of atomic states will be affected [30] [31]. LTE primarily applies in the presence of large number densities, where collisional ionization dominates radiative recombination [32].

Given that a particle requires a certain number of collisions to equilibrate with its surroundings, if the number density is insufficiently large for the particle to interact with a reasonable number of nearby particles before it leaves the vicinity, then in effect local equilibrium can never be achieved. Furthermore without equilibrium, the temperature, which is proportional to the average internal energy of a system in equilibrium, would become locally undefined.

Under LTE conditions, the relative population of excited levels in an atom/ion can be described by the Boltzmann distribution:

$$\frac{n_i}{n_{total}} = \frac{g_i}{U(T)} e^{-E_i/kT}, \quad (2.18)$$

where n_i (cm^{-3}), E_i (J) and g_i are the population, energy and degeneracy of the quantum level i , n_{total} (cm^{-3}) is the total number density of the species involved, and

$U(T)$ is the partition function at temperature T in Kelvin:

$$U(T) = \sum_i g_i e^{-E_i/kT}. \quad (2.19)$$

The LTE requirement that atomic and ionic states should vary in population as a result of electron collisions, rather than by radiation, demands an electron density which is sufficient to provide a high collision rate. The McWhirter [33] criterion gives the lower bound for such an electron number density:

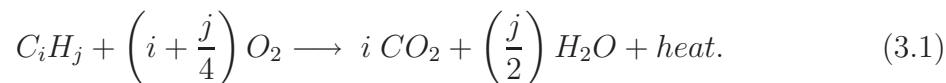
$$n_e(cm^{-3}) \geq 1.6 \times 10^{12} T^{1/2}(\Delta E)^3, \quad (2.20)$$

where ΔE in electron-Volts is the energy difference between the upper and lower levels of the atomic transition. Note however that the criterion was only derived for optically thin and homogeneous and stationary plasmas, and clearly since laser-induced plasmas may not satisfy these conditions, the criterion only serves as a necessary, but not sufficient prerequisite for LTE [34]. However, Radziemski et al. [23] found in one experiment from chemical analysis that the low temperatures ($kT_e \approx 1-2$ eV) and dense conditions ($n_e \approx 10^{16}cm^{-3}$) typical to LIBS plasmas justifies the use of the LTE approximation.

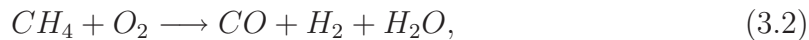
Chapter 3

Combustion Chemistry

Recall that combustion is a sequence of exothermic chemical reactions occurring between a fuel and an oxidizer. Under ideal conditions, a generic hydrocarbon C_iH_j (where $i, j \in \mathbb{Z}^+$) will completely combust with oxygen to produce carbon dioxide and water, along with additional heat:



We consider the combustion of gaseous methane with oxygen. The intermediate reactions begin with a production of CO via oxidative pyrolysis



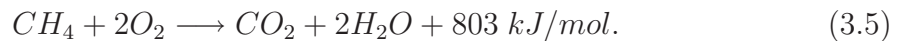
followed by the oxidation of H_2 to form H_2O and the release of heat



Finally the CO oxidizes to produce CO_2 and releases additional heat



The result is a reduction of Equation 3.1 to account for the stoichiometric reaction of methane and oxygen into gaseous CO_2 and H_2O :



For future reference, we define the equivalence ratio [35] of the actual fuel-to-oxidizer F/O concentration to the stoichiometric fuel-to-oxidizer $(F/O)_{stoich}$ concentration

$$\phi \equiv \frac{F/O}{(F/O)_{stoich}}, \quad (3.6)$$

where $\phi = 1$ corresponds to a stoichiometric mixture, and $\phi < 1$ and $\phi > 1$ denote fuel lean and fuel rich mixtures, respectively. Given the stoichiometric reaction for a methane-oxygen mixture in Equation 3.5, the equivalence ratio becomes

$$\phi = \frac{F/O}{0.5}. \quad (3.7)$$

Note that here the ratio F/O is based upon molar mass, rather than atomic mass.

Complete combustion is never fully achieved under real conditions. Applying the NASA chemical equilibrium code authored by Gordon and McBride [36] to the CH_4/O_2 reaction gives us a theoretical prediction of the expected product mole fractions and temperatures based on input fuel-to-oxidizer mixtures and ambient pressure. Figure 3.1 indicates the most observable products for a stoichiometric mixture to be H_2O CO CO_2 and OH . Hydrogen gas and carbon soot are predominant when insuf-

ficient oxygen is present to completely oxidize the fuel ($\phi \gg 1$), or when the process is quenched by a heat-sink. Conversely, when there is an excess of oxygen ($\phi \ll 1$) the products are mostly H_2O , CO_2 and OH .

Figure 3.2 demonstrates the effect of varying ambient pressure on the combustion temperature; variation is most notable in the range $0.25 \lesssim \phi \lesssim 2.0$ and for the very fuel rich cases. For the near order of magnitude increase in pressure between 0.5 and 4 atmospheres, the temperature only enhances by $\sim 12\%$ for $\phi \approx 1$, $\sim 20\%$ for $\phi \approx 4$, and at a dramatically increased rate at greater equivalence ratios. Overall temperatures peak for the stoichiometric condition and rapidly fall off with deviation from $\phi = 1$.

The simulated results produced by the code suggest that measured data varies by roughly a factor of 10 from combustion conditions. Therefore measurements at 4 atm and 300 K are comparable to that which would be obtained at 40 atm and 3000 K under combustion conditions.

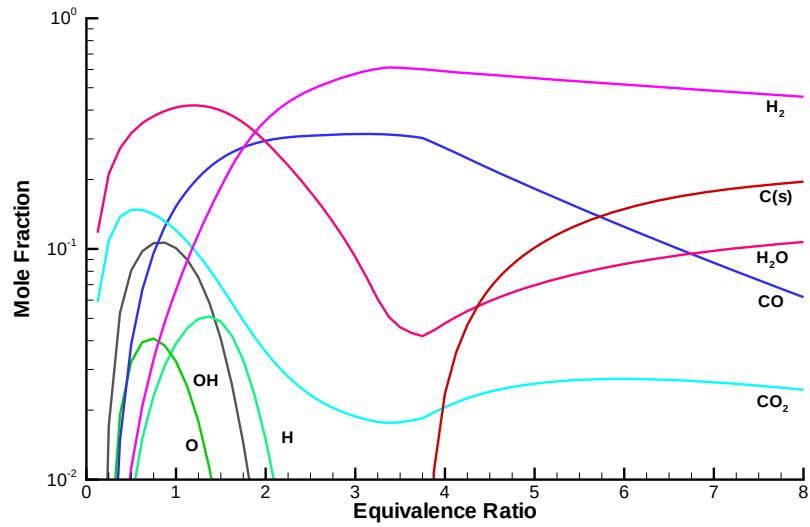


Figure 3.1: Mole fraction versus equivalence ratio for the CH_4/O_2 reaction at 4 atm. Calculated with NASA-CEA code.

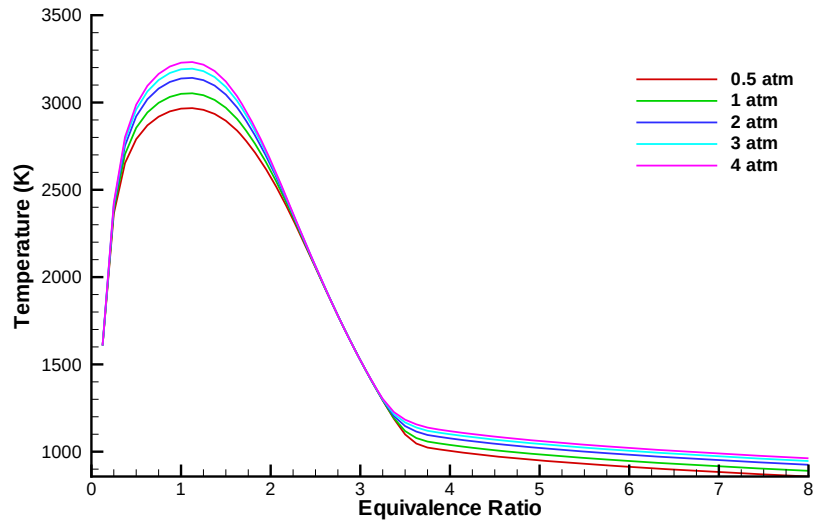


Figure 3.2: CEA calculated combustion temperature versus equivalence ratio for the CH_4/O_2 reaction over the ambient pressure range 0.5 to 4 atm.

Chapter 4

Experimental Setup and Spectral Line Choices

4.1 Apparatus

The physical components employed for measurement of spectra are typical to a LIBS detection system. These include a nanosecond-pulsed laser, an intensified detection apparatus coupled to a spectrometer, and a sample. We use a Quanta-Ray DCR Q-switched Nd:YAG laser operating at 10 Hz and emitting fundamental 1064 nm radiation as the excitation source. For detection, an EG&G Princeton Applied Research two-dimensional intensified CCD detector is coupled to an Acton Research Corporation SpectraPro-500 Czerny-Turner type spectrometer, equipped with a 1200 groove per millimeter grating (blazed for 750 nm). The slit width is set to 10 μm . The nominal spectrometer reciprocal linear dispersion is 1.7 nm/mm. The effective resolution at the CCD is 0.015 mm/pixel in the spatial dimension, and when equipped with the narrowest grating the spectral resolution is about 0.03 nm/pixel. The smallest resolvable line feature is about 0.2 nm.

A high pressure lecture bottle is filled with the desired ratio of sample gases by partial pressure, and the subsequent mixtures are leaked into a homemade aluminum high pressure test vessel. The test vessel (referred to as the “cell”) consists of three intersecting 2 cm diameter cylindrical chambers, giving rise to eight entrance/exit ports at the ends. The ends are O-ring sealed with 0.25 cm thick optical quality quartz windows. A mass flow controller is attached to the cell along an exhaust line to maintain a relatively constant yet sufficient flow speed to refresh the sample between laser shots. The entire system is evacuated of ambient air prior to experimentation through the use of an attached vacuum system, which includes a mechanical roughing pump and an oil diffusion pump.

Laser pulse durations are measured via diffuse reflection to a Thorlabs DET10A/M Si biased detector (rise time about 1 ns) with peak sensitivity in the vicinity of 700 nm. The signal provided by the diode is displayed on a Tektronix TDS3054 500 MHz oscilloscope. Pulse energies are determined from a Thorlabs S314C power meter ($\pm 3\%$ uncertainty at 1064 nm) interfaced with a personal computer.

Figure 4.1 gives an overall depiction of the apparatus. The laser beam cross section is enlarged via an inverted telescope, comprised of a plano-concave and a bi-convex lens with focal lengths -100 and $+300$ mm. The Nd:YAG beam is then focused into the center of the cell using a biconvex $+100$ mm lens. The resulting plasma spectral emissions are collected and focused onto the spectrometer slit via a pair of lenses with focal lengths of 75.6 and 150 mm, sequentially. All of the lenses have a diameter of 2.5 cm. As such, the F-number of the final collection lens is set to match that of the spectrometer as closely as possible. A photograph of the high pressure cell and the spectrometer slit in the background is shown in Figure 4.2.

Measurements occur typically with 160-170 mJ per pulse, giving rise to spark dimensions of about 8 mm in length and 2 mm in width (as visible to the naked

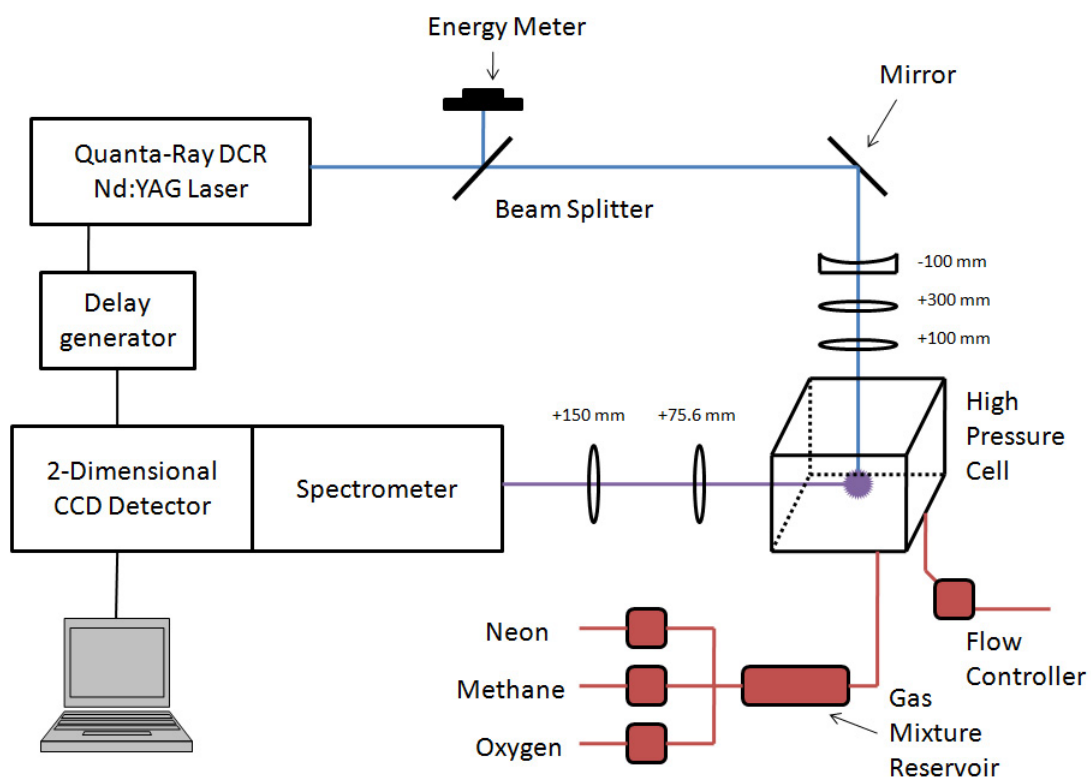


Figure 4.1: Experimental setup includes elements native to a LIBS detection apparatus: a laser, a detection system, and a sample.



Figure 4.2: Photograph of the high pressure sample vessel with the spectrometer slit in the background.

eye). Given the aforementioned laser and optical components, the focal spot diameter and length are estimated to be about 10.5 and 231 μm , respectively. Spectra are wavelength calibrated through the application of several Oriel low pressure Pen-Ray line sources (mercury, xenon, krypton, and neon filled lamps are used).

4.1.1 Some details on the Nd:YAG

Some information on the typical performance of the Quanta-Ray DCR Nd:YAG laser is given as follows. Operating at 10 Hz, the circular “donut” -shaped beam profile of approximate diameter 0.8 cm exhibits a divergence of about 1.15 mrad, as measured across a 7.6 m distance. The output energy per pulse varies by $< 0.5\%$. The maximum power is about 2.20 W while running with the Q-switch delay minimized and both the oscillator and lamp at the recommended maximum output (70 J/pulse). Note for all of these measurements that the frequency doubling crystal is in the optical path; the second harmonic 532 nm output is merely minimized.

A plot of pulse energy and duration versus Q-switch delay is given in Figure 4.3 for typical operating conditions (both oscillator and amplifier are set for 60 J/pulse). As desired, pulse energy is at a maximum when pulse width is at a minimum. The error bars on the pulse width are governed by the jitter; as the Q-switch delay is increased, the peak-to-peak jitter magnifies dramatically. Pulse duration measurement becomes untenable beyond 200 ns Q-switch delay; the error exceeds the measured value.

4.2 C and O line selection

The identification of which constituent atomic elements of the CH_4/O_2 reaction are ideal for measurement of the equivalence ratio is entirely dependent upon the spectral region of interest, and hence the quality of spectral lines available. Figure 4.4 presents

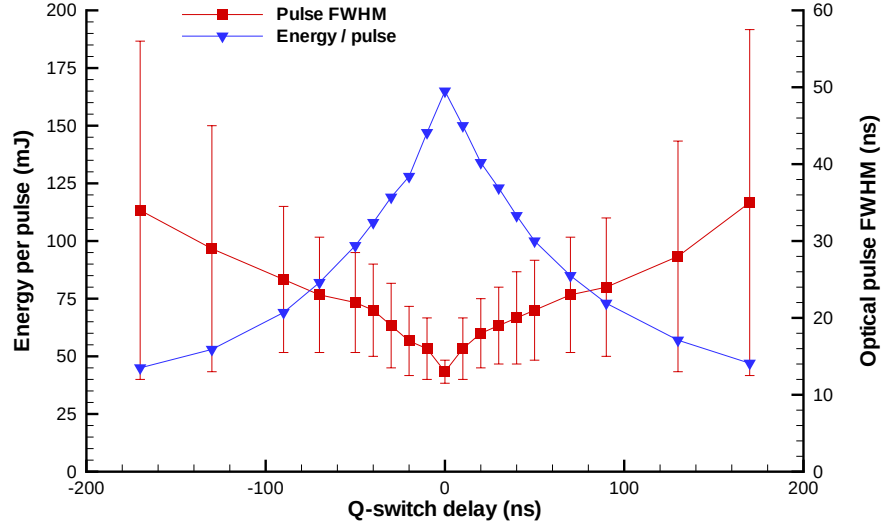


Figure 4.3: Plot of Quanta-Ray DCR Nd:YAG energy per pulse and optical pulse width versus Q-switch delay. Note “0 ns” Q-switch delay is defined as minimum. Energy measurement error $< 0.5\%$.

calculated intensities for potential line sources as computed by the Paying and Larkins software [37]. Clearly the oxidizer must be quantified from oxygen spectra, but this still leaves the need for a fuel source. Considering the possibilities, C and H , and the availability of clean lineshapes in the presence of an oxygen source, we choose C as our spectral fuel source. Thus measurements herein of the equivalence ratio are determined from the intensity ratio $F/O = C/O$. Note, however, that Phuoc and White [10] and Stavropoulos et al. [13] use $H\text{-}\alpha$ at 656.3 nm.

As for specific spectral line sources, the atomic oxygen triplet at 777 nm is an obvious choice due to its relative intensity and continued definition at high density. As for carbon, we choose the deep-ultraviolet line at 193 nm, appearing at 772 nm as fourth order on the spectrometer in use. No neon is present in the vicinity of either the C nor the O line.

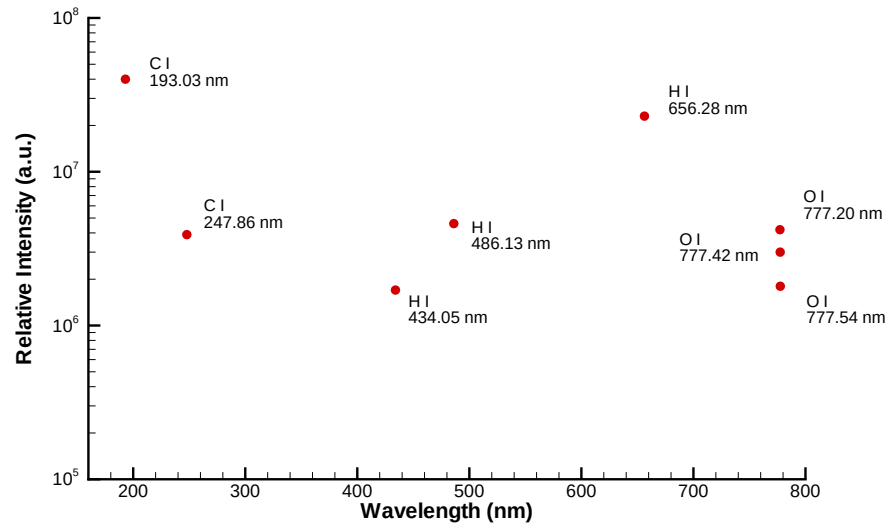


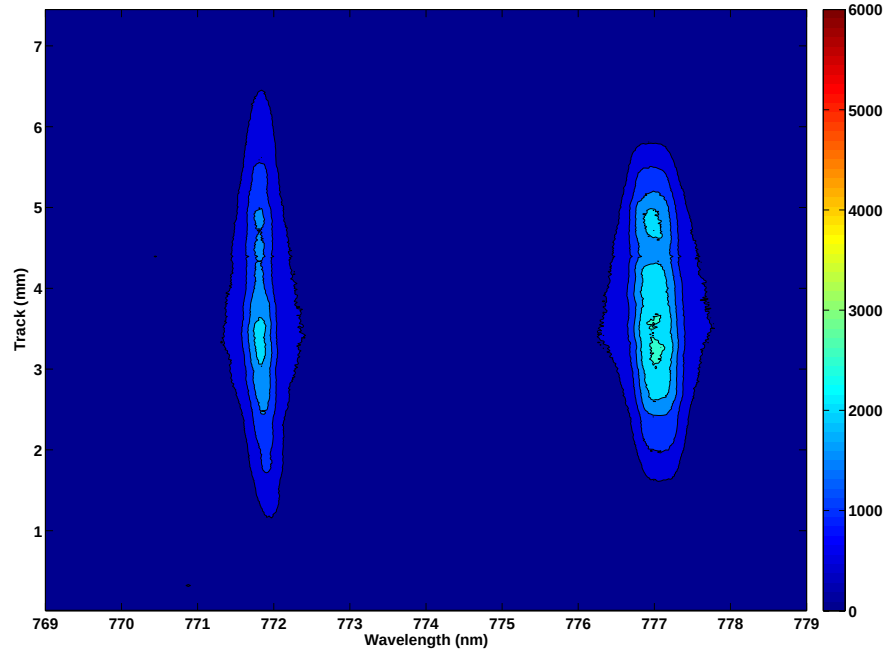
Figure 4.4: Plot of calculated relative intensities for potential O, C and H spectral lines. Computed for 15000 K using Payling and Larkins software [37].

Chapter 5

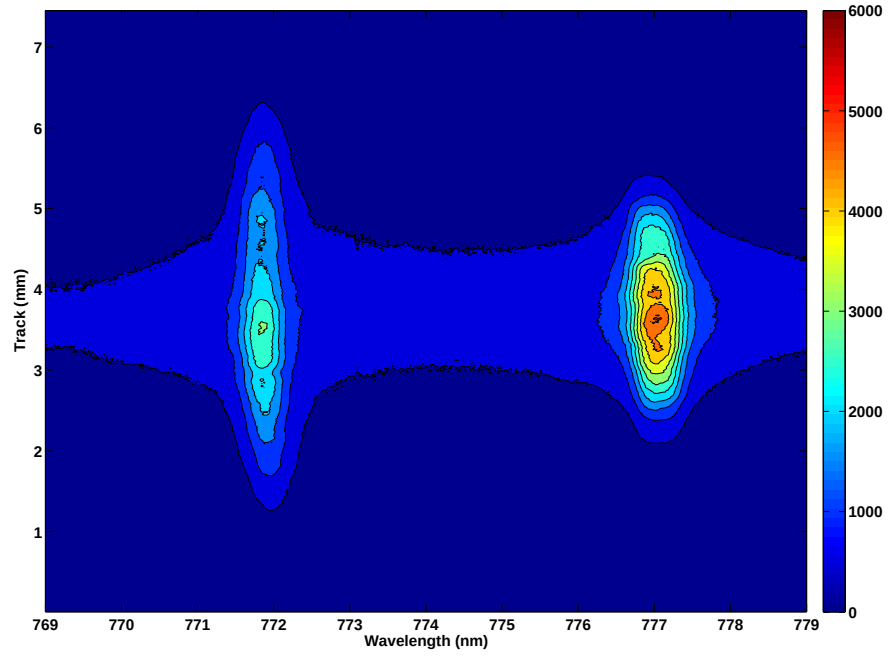
Results and Analysis

A collection of three separate spectra is collected for each condition desired, including every combination of absolute pressure ranging from 1 to 4 atmospheres and CH_4/O_2 equivalence ratio from $\phi = 0.25$ to 4, suspended in a balance of 85 percent neon. The individual spectra are then analyzed through the application of a MatLab routine written by the author of this thesis. Incident laser power is kept constant (within the laser's inherent variation of $< 0.5\%$) while pressure and mixtures are varied. Spectra are accumulated over a $0.5 \mu s$ gate for each of 200 laser shots, beginning at $3.5 \mu s$ after optical breakdown. In principle, plasma decay occurs during a finite time, and thus measured quantities represent average values.

The general appearance of the spectral lines varies with pressure, most notably in terms of wavelength broadening and apparent intensity growth (see Figure 5.1 for sample 2-D spectra, Figures 5.2 and 5.3 for integrated spectra). The continuum background also becomes more prevalent with greater pressure. Spatially, the spectra possess a bit of non-uniformity (or 'hot spots'), likely a result of imperfect optics and/or variation of the laser beam's modal structure.

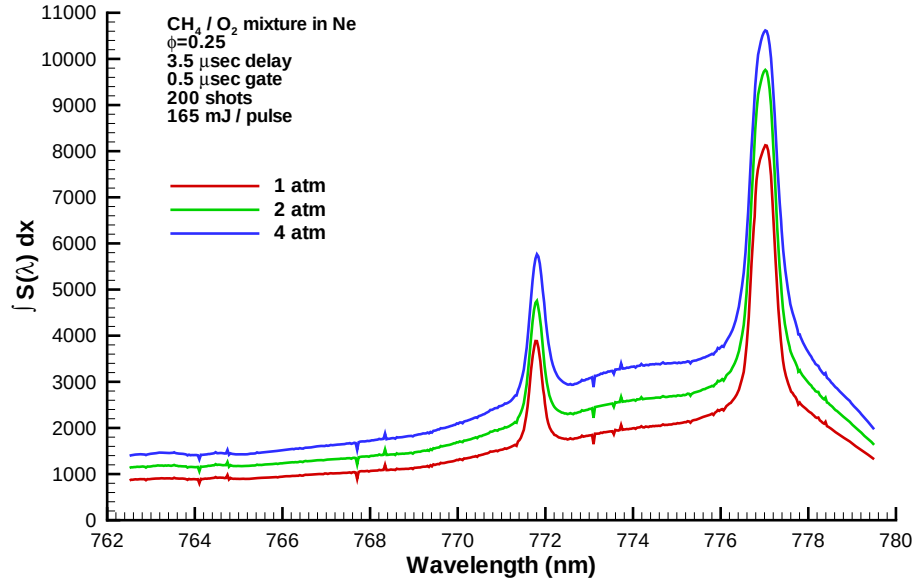


(a) 1 atm

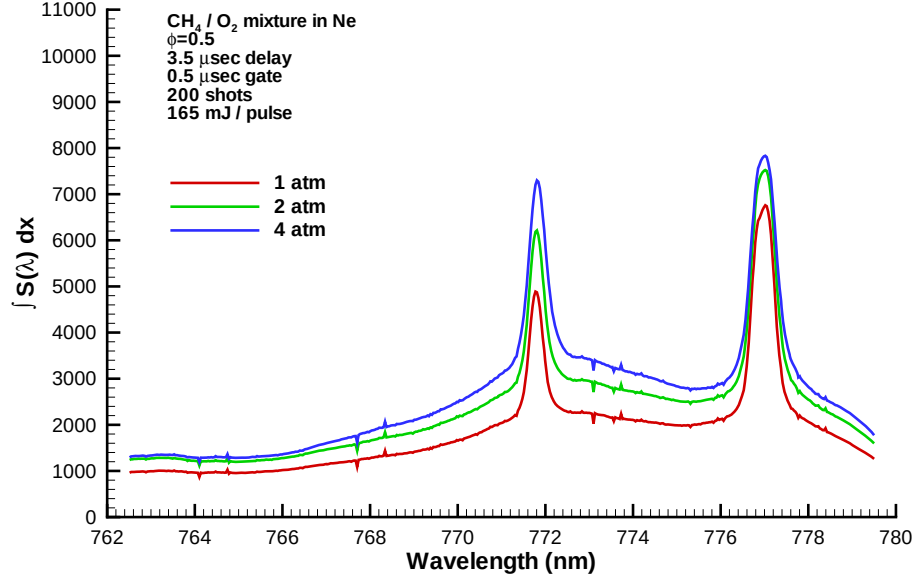


(b) 4 atm

Figure 5.1: Sample 2-D stoichiometric ($\phi = 1$) C-O spectra at 1 and 4 atm, for $3.5 \mu s$ delay.

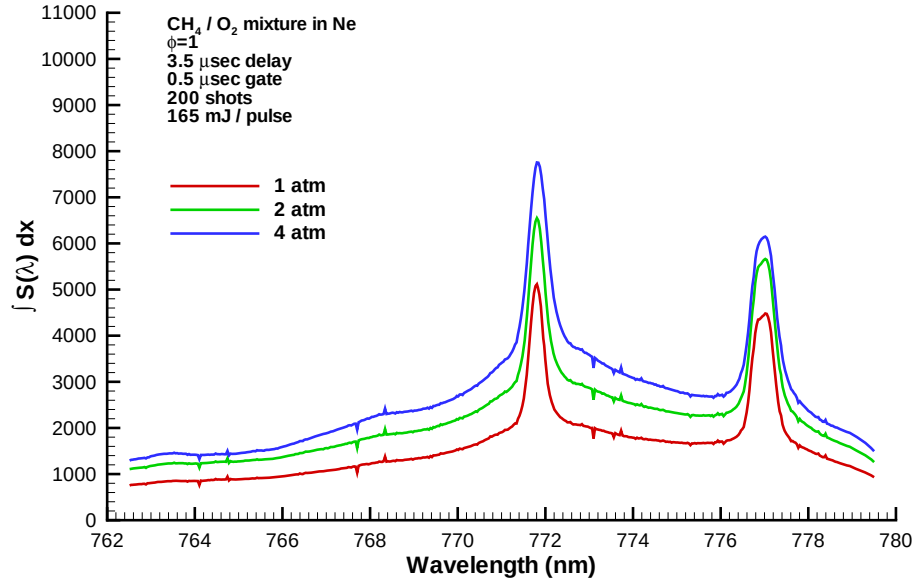


(a) $\phi = 0.25$

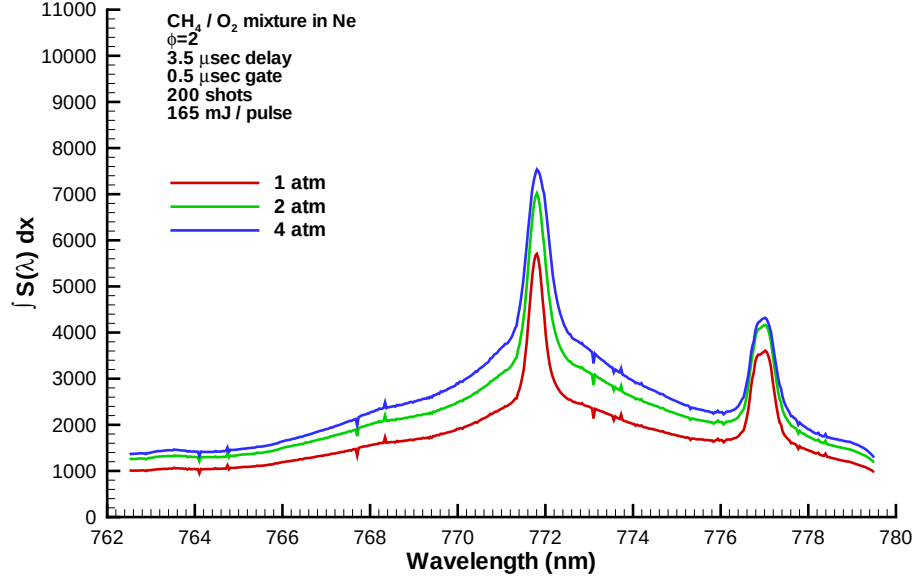


(b) $\phi = 0.5$

Figure 5.2: Integrated C-O spectra between 1 and 4 atm, for $\phi = 0.25$ and $\phi = 0.5$.



(a) $\phi = 1$



(b) $\phi = 2$

Figure 5.3: Integrated C-O spectra between 1 and 4 atm, for $\phi = 1$ and $\phi = 2$.

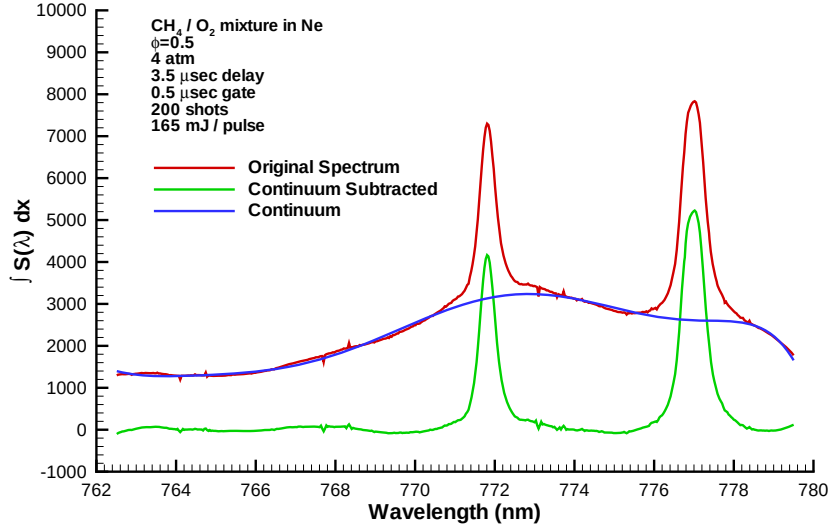


Figure 5.4: Plot demonstrating typical means of continuum subtraction prior to calculation of C/O ratios and Stark widths - the continuum is fit with a high order polynomial.

5.1 Determination of a high-density C/O to equivalence ratio relationship

As has been discussed previously, atomic emission spectroscopy of desired species can be used to ascertain the combustion equivalence ratio [13] [14]. Before this can be accomplished however, one must be able to relate the measured line intensities to the desired equivalence ratios through the use of a calibration relationship. When considering fuel-to-oxidizer to equivalence ratio calibrations across varying ambient physical conditions, those conditions must be shown to exert only a minimal (if any) effect upon the calibrations.

Our chosen neutral atomic carbon and oxygen emission lines at 193 and 777 nm, respectively, are spectrally and spatially integrated at pressures ranging from 1 to 4 atm and input CH_4/O_2 mixtures ranging from $\phi = 0.25$ to 4. The carbon 193 nm

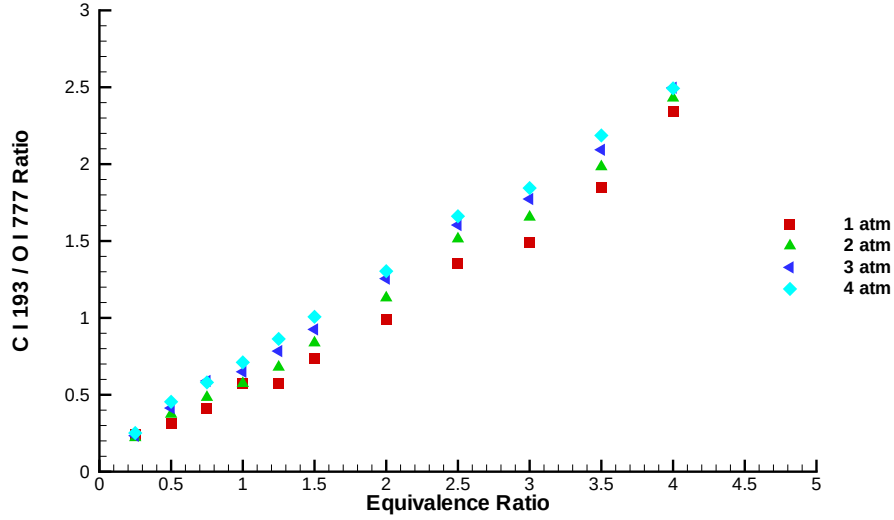


Figure 5.5: Calibration plot of measured C/O ratio versus equivalence ratio, ϕ , for varying pressures. ~ 165 mJ YAG energy

line is visible to fourth order at 772 nm on the spectrometer, making simultaneous measurement of the carbon and oxygen lines quite feasible with standard gratings. Note that ideally one should determine relative intensities for the lines, especially since the detection system is not UV intensified and the carbon line appears at first order in the deep UV. Such a calibration, though, is not mandatory in this case because it would only alter the magnitude of the C/O ratio; a C/O to equivalence ratio relationship is still computable.

Figure 5.5 displays the desired relationship between measured C/O and equivalence ratio which can be used as a means of achieving the aforementioned calibration. As a straight-forward extension to findings in other works [10] [13] [14] at low density, the relationship seems to follow near direct proportionality across all fuel-to-oxidizer mixtures. There is minimal C/O variation over the factor of four increase in pressure, while laser energy is held constant.

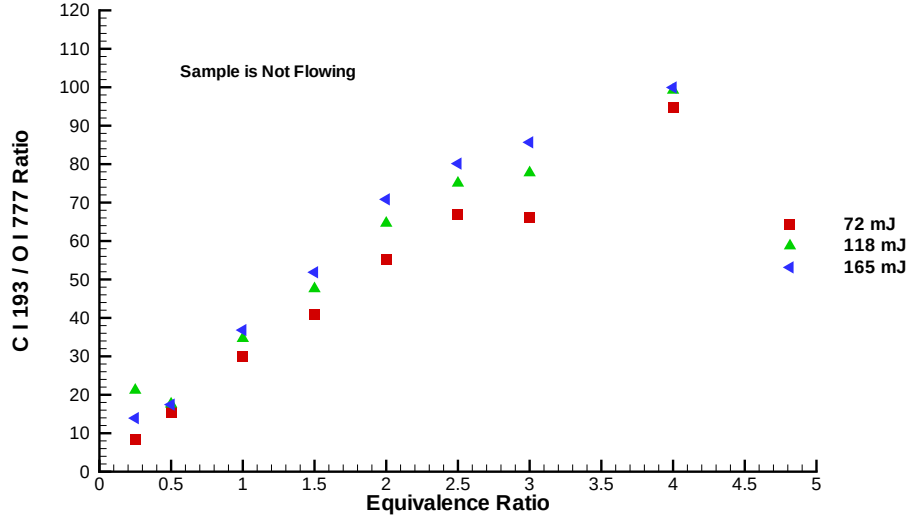


Figure 5.6: Non-flowing sample - C/O ratio versus ϕ for varying incident laser energies. Presented for comparison with Figure 5.5.

Figure 5.6 presents a similar C/O v. ϕ relationship for varying incident laser energies, but note that in this case the sample mixture is completely static (i.e. no flow). One can see immediately by comparison of Figures 5.5 and 5.6 that the C/O ratio begins to stray from linearity with progressively fuel-rich mixtures beyond $\phi \approx 2$. Additionally, C/O values for the static sample are about a factor of 10 greater than those for the flowing case, a trend likely indicative of long-lasting metastable atomic levels skewing the line measurement. In agreement with Phuoc and White [10], Figure 5.6 does, however, indicate relative independence of C/O ratio measurements with respect to laser energy. This of course assumes sufficient power density to fully ionize the sample.

5.1.1 Line and continuum intensity variation

Though emission signal is typically very large at early times after the onset of optical breakdown, the signal-to-background (or continuum) ratio can be unacceptably small. As a result large uncertainty can come about in the measurement of spectral lines. Therefore in general one endeavors to obtain data for large signal-to-background ratios with large signal and at times such that spectra have not diminished as a result of plasma cooling and recombination. Accordingly we have chosen to examine emissions at substantially later times, commencing $3.5 \mu s$ after breakdown.

Let us consider for the moment one-dimensional spectra near the center of the plasma. Figures 5.7 and 5.8 indicate both C and O line intensities remaining at least 2-3 times greater than the underlying continuum radiation. As expected the C 193 line possesses the smallest signal-to-background ratio when mixtures are fuel lean ($\phi < 1$), growing progressively stronger as the carbon content increases. The converse is true for the O 777 line. Interestingly, the O line S-to-B ratio falls off rapidly with greater fuel content, a trend which seems to be an almost preferential O-quenching effect – the carbon S-to-B ratio falls off at a much lesser rate as ϕ gets small. A likely justification for this would be self-absorption. Additionally, the line to continuum relationships remain rather independent of changes in ambient pressure. The slight rise in both C and O S-to-B ratios for $\phi = 3$ and 4 would seem to be a result of the dip in continuum background for those mixtures. Since the continuum is approximated to be the same for both C and O, C/O ratios remain unaffected. The continuum background is shown to steadily increase with pressure in Figure 5.9, while remaining relatively constant (if not slightly increasing) under equivalence ratio variation.

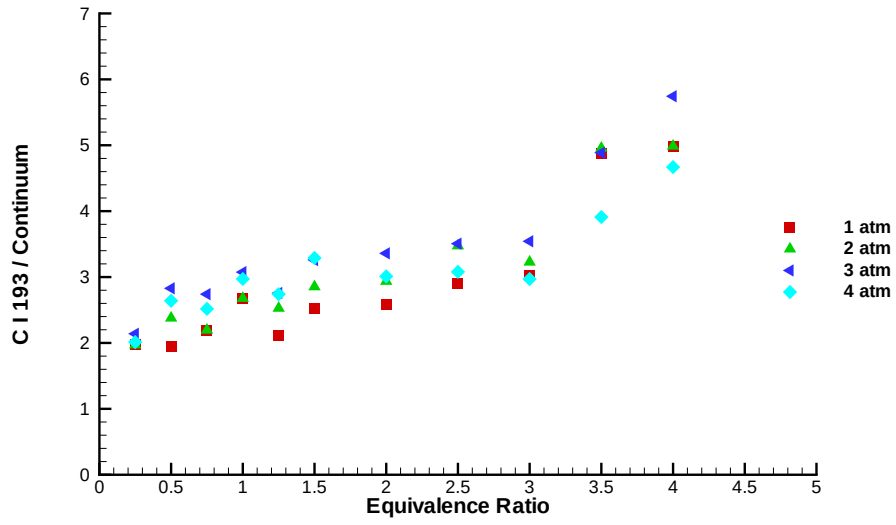


Figure 5.7: Plot of measured C I 193 / Continuum versus equivalence ratio for varying pressures.

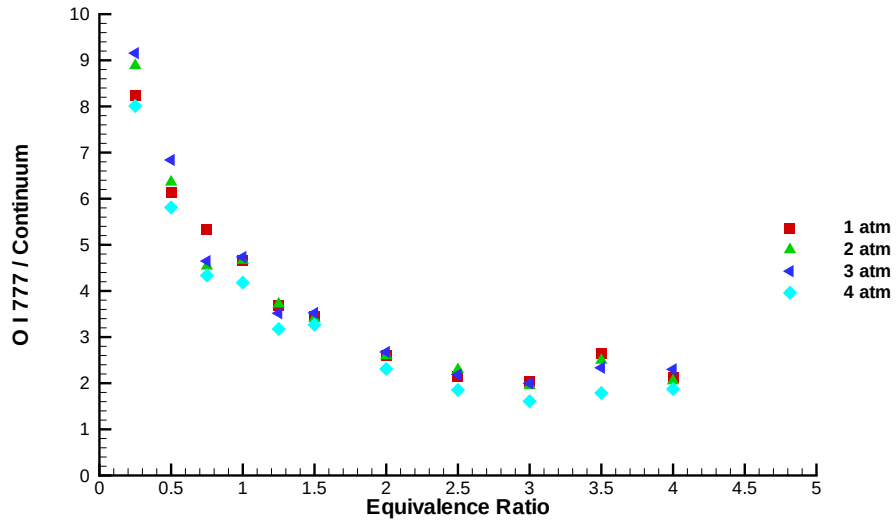


Figure 5.8: Plot of measured O I 777 / Continuum versus equivalence ratio for varying pressures.

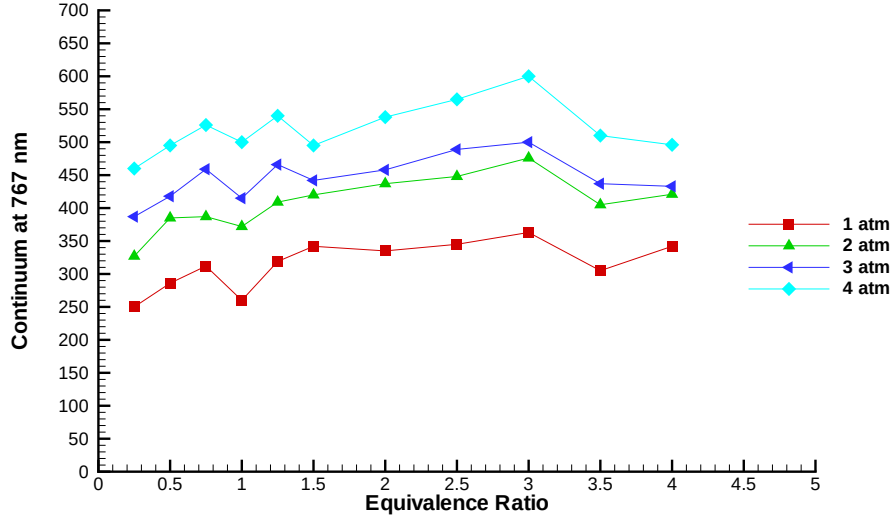


Figure 5.9: Plot of continuum at 767 nm versus equivalence ratio for varying pressures.

5.2 Electron number density calculation

One of two spectroscopic techniques is commonly employed for measurement of the electron number density in laser-induced plasmas. The first requires measurement of the population ratio of two successive ionization states of the same element and subsequent application of the Saha equation, and the second makes use of Stark-effect broadening of emission lines (see Section 2.2.2).

Electron number densities herein are inferred from the Stark broadening of the atomic carbon emission line ($2s^22p^2 \rightarrow 2s^22p3s$) centered at 193.09 nm , with energy level separation $\Delta E \approx 6.42 \text{ eV} \approx k(74.5 \times 10^3 \text{ K})$. Given an anticipated electron temperature range of 5000 to 15000 Kelvin, we calculate the minimum electron number density n_e necessary to support the assumption of local thermodynamic equilibrium (LTE) by applying Equation 2.20 (the McWhirter criterion). The resulting minimum number density range is $3.0 \times 10^{16} \text{ cm}^{-3} \lesssim n_e \lesssim 5.2 \times 10^{16} \text{ cm}^{-3}$, depending upon

temperature.

Number densities, $n_e(\text{cm}^{-3})$, are calculated from Equation 2.17:

$$\Delta\lambda_{\text{Stark}} \approx 2w \frac{n_e}{10^{16}}, \quad (2.17 \text{ revisited})$$

where $\Delta\lambda_{\text{Stark}}(\text{nm})$ is the Stark FWHM of the emission line, and the electron impact parameter, $w \approx 0.0238 \text{ nm}$, is extrapolated from Griem [28]. Determination of n_e by this method is entirely independent of any requirements regarding local thermodynamic equilibrium [8]. However, it is quite acceptable to utilize Stark broadening tables and/or empirical formulae [38] for determination of electron density. Stark widths are calculated by deconvolving only instrumental broadening from the measured line widths, since all other broadening effects are assumed to be minimal (see Section 2.2.2). The instrumental broadening resulting from the finite resolving power of the collection system at 193 nm is estimated from low pressure ($\sim 0.2 \text{ atm}$) CO_2 spectra to be $\sim 0.29 \text{ nm}$. Applying the relation $\Delta\lambda_{\text{Stark}} \approx (\Delta\lambda_{\text{meas}}^2 - \Delta\lambda_{\text{instr}}^2)^{1/2}$ gives the deconvolved Stark width from the measured $\Delta\lambda_{\text{meas}}$ and instrumental broadening $\Delta\lambda_{\text{instr}}$ widths. A multiplicative factor of 0.95 is applied to the widths as measured at 772 nm to scale toward the actual line location at 193 nm.

Values for n_e are given in Table 5.1, with a plot of n_e v. ambient pressure in Figure 5.10. Measured values for n_e do indeed exceed the minimum required for LTE, if only slightly for the upper estimate at 15000 K. Note that electron densities are derived from only the $\phi = 0.5$ condition. There is a monotonically increasing relationship between n_e and P , approaching linear, but obviously this can not be the overall trend since n_e must go to zero as pressure goes to zero. Nakimana et al. present a similar n_e trend for an Al plasma, though at sub-atmospheric pressure [39]. Of course n_e is dependent on the initial number density of the sample, but the relationship can also

Table 5.1: Measured Stark line widths and inferred electron number densities for pressures ranging 1 to 4 atm at time 3.5 μsec after breakdown. $\phi = 0.5$

Pressure(atm)	Stark FWHM(nm)	$n_e(10^{16} \text{ cm}^{-3})$
1.0	0.27 ± 0.03	5.7 ± 0.2
2.0	0.31 ± 0.01	6.4 ± 0.1
3.0	0.35 ± 0.03	7.3 ± 0.2
4.0	0.39 ± 0.02	8.1 ± 0.1

be attributed to the fact that as ambient pressure increases, the plasma experiences a more intense confinement force from the surrounding gas and thus n_e increases.

Let us now compare our electron number density values to previous measurements derived from hydrogen- α , - β , and - γ Stark widths in a high pressure methane flow [40]. The methane data give at time 2 μs after breakdown and pressure ~ 2.7 atm a number density on the order of $5 \times 10^{16} \text{ cm}^{-3}$, which is within reasonable proximity to our measurement of $7.3 \times 10^{16} \text{ cm}^{-3}$ at 3 atm and 3.5 μs . Use of a Nd:YAG laser of less energy per pulse (approximately 75 mJ) and an earlier measurement time in the previous work are plausible explanations for the higher number density measurements across comparable pressures. Self-absorption can cause systematic errors for higher than atmospheric density measurements; however, the extent of self-absorption has not been further investigated in this thesis.

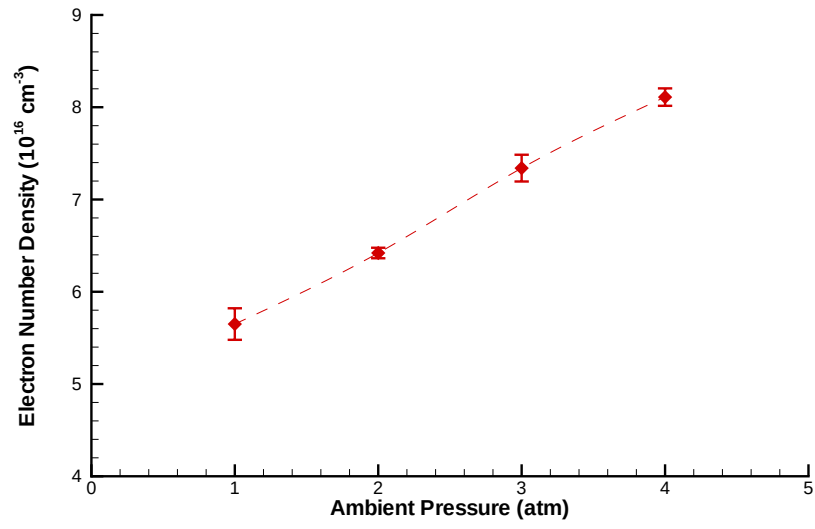


Figure 5.10: Plot of n_e v. P derived from Stark FWHM of C 193 nm at time $3.5 \mu\text{s}$. $\phi = 0.5$

Chapter 6

Summary

Laser-induced breakdown spectroscopy has been applied to greater than atmospheric density methane-oxygen mixtures in an effort to verify the feasibility of applying LIBS toward the measurement of high density combustion equivalence ratios. Relying upon an elementary tenet of LIBS that the entire sample is ionized in the formation of the plasma, we have assumed for the purpose of our analysis that the chemical reactants, CH_4 and O_2 , are equivalent to the products of their reaction. This assumption precluded us from any need to observe an actual chemical reaction.

The addition at significant mole fraction of a reaction-quenching species, namely neon, into the methane/oxygen mixture provided us with a non-combusting environment at high density suitable for LIBS analysis. By measuring carbon and oxygen emission lines at 193 and 777 nm, respectively, we have successfully determined a calibration relationship between the measured fuel-to-oxidizer ratio and input equivalence ratio. We have presented results indicating the invariance of the calibration to both greater than atmospheric densities, and also laser excitation energy. The spectral lines seem subject to selective quenching in their respective species' lean mixtures. For further exploration of this phenomenon, experimental studies are sug-

gested to evaluate the effect of self-absorption and the associated optical thickness of the laser-induced plasma. But we have indeed shown that LIBS is applicable for localized high density combustion diagnostics.

Our success could be the first step toward the development of real time *in situ* high density combustion-health monitoring devices based on the LIBS technique. But in reality this work was a mere simulation, and the next clear step would be to apply LIBS toward an actively combusting high density environment, should a suitable testing facility be developed.

Selecting the carbon 193 nm line for equivalence ratio measurements also allowed us to infer electron number densities from Stark broadening. We found number densities to monotonically increase with respect to ambient pressure, but self-absorption may be an issue. We were able to demonstrate the validity of LTE in the plasma by applying the McWhirter criterion. This would have obvious importance in future efforts that include a measurement of electron temperature.

Bibliography

- [1] Weiner S, Xu Q, Goldberg P, Liu J, Bar-Yosef O. “Evidence for the Use of Fire at Zhoukoudian, China.” Science **281** (1998) 251-253.
- [2] McAllister S, Chen J-Y, Fernandez-Pello AC. Fundamentals of Combustion Processes. New York: Springer Science, 2011.
- [3] Lipatnikov A. Fundamentals of Premixed Turbulent Combustion. Boca Raton: CRC Press, 2013.
- [4] Maker PD, Terhune RW, Savage CM. Proceedings of the 3rd International Conference on Quantum Electronics, Paris (1963). New York: Columbia University, 1964.
- [5] Meyerand RG, Haught AF. “Gas Breakdown at Optical Frequencies.” Physical Review Letters **11** (1963) 401-403.
- [6] Radziemski LJ, Cremers DA. “Laser plasmas for chemical analysis,” in Radziemski LJ, Solarz RW, Paisner JA (Eds.), Laser Spectroscopy and its Applications. New York: Marcel Dekker Inc., 1987.
- [7] Weyl GM. “Physics of Laser-induced Breakdown: An Update” in Radziemski LJ, Cremers DA (Eds.) Laser-induced Plasmas and Applications. New York: Marcel Dekker Inc., 1989.
- [8] Tognoni E, Palleschi V, Corsi M, Cristoforetti G, Omenetto N, Gornushkin I, Smith BW, Winefordner JD. “From sample to signal in laser-induced break-

down spectroscopy: a complex route to quantitative analysis,” in Miziolek AW, Palleschi V, Schechter I. Laser Induced Breakdown Spectroscopy. New York: Cambridge University Press, 2006.

- [9] Buckley SG, Johnsen HA, Hencken KR, Hahn DW. “Implementation of laser-induced breakdown spectroscopy as a continuous emissions monitor for toxic metals.” Waste Management **20** (2000) 455-462.
- [10] Phuoc TX, White FP. “Laser-induced spark for measurements of the fuel-to-air ratio of a combustible mixture.” Fuel **81** (2002) 1761-1765.
- [11] Ferioli F, Puzinauskas PV, Buckley SG. “Laser-induced breakdown spectroscopy for on-line engine equivalence ratio measurements.” Applied Spectroscopy **57** (2003) 1183-1189.
- [12] Sturm V, Noll R. “Laser-induced breakdown spectroscopy of gas mixtures of air, CO_2 , N_2 , and C_3H_8 for simultaneous C, H, O, and N measurement.” Applied Optics **42** (2003) 6221-6225.
- [13] Stavropoulos P, Michalakou A, Skevis G, Couris S. “Quantitative local equivalence ratio determination in laminar premixed methane-air flames by laser-induced breakdown spectroscopy.” Chemical Physics Letters **404** (2005) 309-314.
- [14] Stavropoulos P, Michalakou A, Skevis G, Couris S. “Laser-induced breakdown spectroscopy as an analytical tool for equivalence ratio measurement in methane-air premixed flames.” Spectrochimica Acta Part B **60** (2005) 1092-1097.
- [15] Chen YLA. “Laser-Induced Gas Breakdown and Ignition.” Ph.D. Dissertation, The University of Tennessee, 1998.

- [16] Lewis B, von Elbe G. Combustion, Flames, and Explosion of Gases. Orlando: Academic Press, 1987.
- [17] Plemmons DH. "Laser-Spark Ignition and the NH Radical." Ph.D. Dissertation, The University of Tennessee, 1996.
- [18] Dors IG. "Laser Spark Ignition Modeling." Ph.D. Dissertation, The University of Tennessee, 2000.
- [19] Morgan, CG. "Laser-induced breakdown of gases." Reports on Progress in Physics **38** (1975) 621-665.
- [20] Young M, Hercher M. "Dynamics of Laser-Induced Breakdown in Gases." Journal of Applied Physics **38** (1967) 4393-4400.
- [21] Chen YL, Lewis JWL, Parigger C. "Spatial and temporal profiles of pulsed laser-induced air plasma emissions." Journal of Quantitative Spectroscopy & Radiative Transfer **67** (2000) 91-103.
- [22] Parigger CG. "Laser-induced breakdown in gases: experiments and simulation," in Miziolek AW, Palleschi V, Schechter I. Laser Induced Breakdown Spectroscopy. New York: Cambridge University Press, 2006.
- [23] Radziemski LJ, Loree TR, Cremers DA, Hoffman NM. "Time-resolved laser-induced breakdown spectroscopy of aerosols." Analytical Chemistry **55** (1983) 1246-1252.
- [24] Hamed SS. "Spectroscopic Determination of Excitation Temperature and Electron Density in Premixed Laminar Flame." Egyptian Journal of Solids **28** (2005) 349-357.

- [25] Measures RM. Laser Remote Sensing: Fundamentals and Applications. New York: John Wiley & Sons, 1984.
- [26] Shaikh NM, Rashid B, Hafeez S, Jamil Y, Baig MA. "Measurement of electron density and temperature of a laser-induced zinc plasma." Journal of Physics D: Applied Physics **39** (2006) 1384-1391.
- [27] Gornushkin IB, King LA, Smith BW, Omenetto N, Winefordner JD. "Line broadening mechanisms in the low pressure laser-induced plasma." Spectrochimica Acta Part B **54** (1999) 1207-1217.
- [28] Griem, HR. Spectral Line Broadening by Plasmas. New York: Academic Press, 1974.
- [29] Thakur SN. "Atomic Emission Spectroscopy," in Singh JP and Thakur SN. Laser-Induced Breakdown Spectroscopy. Amsterdam: Elsevier, 2007.
- [30] Van der Mullen JAM. "On the atomic state distribution function in inductively coupled plasmas - I. Thermodynamic equilibrium considered on the elementary level." Spectrochimica Acta Part B **44** (1989) 1067-1080.
- [31] Van der Mullen JAM. "Excitation equilibria in plasmas." Physics Reports **191** (1990) 109-220.
- [32] Gauthier JC. "Spectroscopy and atomic physics," in Hooper, MB. Laser-Plasma Interactions 4: Proceedings of the Thirty-fifth Scottish Universities Summer School in Physics. Taylor & Francis, Inc., 1989.
- [33] McWhirter RWP in Eds. Huddleston RH, Leonard SL. Plasma Diagnostic Techniques. New York: Academic Press, 1965.

- [34] Cristoforetti G, Giacomo AD, Dell’Aglio M, Legnaioli S, Tognoni E, Palleschi V, Omenetto N. “Local Thermodynamic Equilibrium in Laser-Induced Breakdown Spectroscopy: Beyond the McWhirter Criterion.” Spectrochimica Acta Part B **65** (2010) 86-95.
- [35] Strehlow R. Combustion Fundamentals. New York: McGraw-Hill, 1984.
- [36] Gordon S, McBride B. “Computation program for calculation of complex equilibrium compositions, rocket performance, incident and reflected shocks, and Chapman-Jouguet detonations.” Interim Revision NASA Report SP-273, NASA Lewis Research Center, 1976.
- [37] Payling R, Larkins P. Optical Emission Lines of the Elements. New York: John Wiley & Sons, 2000.
- [38] Parigger CG. “Atomic and Molecular Emissions in Laser-Induced Breakdown Spectroscopy.” Spectrochimica Acta Part B **79-80** (2013) 4-16.
- [39] Nakimana A, Haiyan T, Xun G, Zuoqiang H, Jingquan L. “Effects of ambient conditions on femtosecond laser-induced breakdown spectroscopy of Al.” Journal of Physics D: Applied Physics **46** (2013) 285204.
- [40] Parigger CG, Dackman M, Hornkohl JO. “Time-resolved spectroscopy measurements of hydrogen-alpha, -beta, and -gamma emissions.” Applied Optics **47** (2008) G1-G6.

Vita

Matthew Dackman was born in Baltimore, Maryland in 1983. He graduated from Pikesville High School in the Baltimore suburb of Pikesville, Maryland in 2001. He earned a Bachelor of Science degree with a double major in physics and mathematics from Dickinson College in May 2005. While at Dickinson, he acquired a great deal of interest in the field of physics and decided to continue his education at the graduate level. He completed a Master of Science degree at the University of Tennessee Space Institute in 2014.