

**Application of Resonant and Non-Resonant Laser-Induced
Plasmas for Quantitative Fuel-to-Air Ratio and Gas-Phase
Temperature Measurements**

**A Dissertation Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville**

**Mark Gragston
December 2018**

ACKNOWLEDGEMENTS

During my time at the University of Tennessee I have had the pleasure of meeting and working with many kind, helpful, and resourceful people. This includes the administrative staff, lab members, and friends. I am very thankful for all the assistance and efforts from these fantastic people.

Furthermore, I am fortunate to have had a great advisor and friend in Dr. Zhili Zhang, who provided many excellent opportunities and resources critical to success not only in the Ph.D. program, but for my professional efforts going forward.

I would also like to thank my friend and former labmate Yue (Derek) Wu. He was not only a great mentor during my first year in the lab, but a good friend.

Finally, I would like to thank my committee members, Dr. Hans DeSmidt, Dr. Christian Parigger, and Dr. John Schmisser, for their help in my development as a researcher and for their participation in my pursuit of the doctoral degree.

ABSTRACT

In this work, two laser-induced plasma techniques are used for gas-phase chemical and temperature measurements. The first technique, laser-induced breakdown spectroscopy (LIBS) is applied for fuel-to-air ratio (FAR) measurements in a well calibrated Hencken flame. In Chapter I, relevant technical and background information for each technique is provided. In Chapter II, measurements are first performed for high-pressure (1-11 Bar) methane-air flames, for which calibration curves are generated using the emission ratio of hydrogen at 656 nm and ionic nitrogen at 568 nm. The effect of pressure on the sensitivity and precision of the resulting calibrated curves is evaluated. Results indicate a degradation of measurement precision as environmental pressure increases, with data indicating that fluctuations of the plasma play a major part in this behavior. Expanding upon this work with LIBS, a comparison of FAR calibration curve results for atmospheric methane-air Hencken flame using three different laser pulse widths, femto-, pico-, and nanosecond regimes, is done in Chapter III. The results are discussed in the context of potential advantages for high-pressure LIBS-based FAR measurements. Results indicate that while nanosecond duration pulses provide better precision at 1 Bar conditions, femtosecond duration pulses might be better suited for high-pressure measurements.

In Chapter IV, the radar REMPI technique, which uses microwave scattering from a plasma created by selective multiphoton ionization of molecular oxygen, is used for gas-phase temperature measurements through the wall of ceramic-enclosed environments. Specifically, measurements are done through the wall of a heated laboratory flow reactor and through the wall of a ceramic well-stirred reactor. Results show good agreement with thermocouple and/or computational modeling and the effectiveness of radar REMPI for through-the-wall measurements.

In Chapter V, a new technique is discussed, namely acoustic REMPI, which utilizes the pressure wave generated from the creation of the REMPI plasma for

diagnostics. The acoustic emission from the plasma is characterized and used for gas-phase temperature measurements. Comparison, with radar REMPI shows a high-level of agreement.

Finally, in Chapter VI, a summary of the work in this dissertation is provided along with a discussion of potential for work in the future.

TABLE OF CONTENTS

CHAPTER I General Introductory Material.....	1
Laser-Based Diagnostics.....	2
Laser-Induced Breakdown.....	3
Resonance Enhanced Multiphoton Ionization	7
Radar REMPI.....	13
References	17
CHAPTER II Equivalence Ratio Measurements in Methane-AIR Flame at 1-11 Bar Using Nanosecond Laser Induced Breakdown Spectroscopy	21
Abstract.....	22
Introduction	23
Experiment Setup	25
Results of LIBS Measurement at High Pressure	26
Analysis of Pressure Dependence.....	33
Summary and Conclusions.....	39
References	43
CHAPTER III Comparison Study of Time-gated Nano-, Pico-, and femtosecond laser-induced breakdown spectroscopy for fuel-to-air ratio measurements in methane-air flames.....	46
Abstract.....	47
Introduction	47
Experiment Setup	49
Results and Discussion	49
Emission Spectra and Temporal Characteristics	49
Equivalence Ratio Determination	57
Summary and Conclusions.....	63
Acknowledgements.....	63
References	64

CHAPTER IV See-through-wall molecular oxygen rotational temperature measurement in a flow reactor and well-stirred reactor	66
Abstract.....	67
Introduction	68
Experiment Setup	71
Flow Reactor	71
Well-Stirred Reactor	75
Rotational Temperature Measurements of Molecular Oxygen	79
Experiment Results.....	81
Flow Reactor	81
Well-Stirred Reactor	88
Summary and Conclusions	95
Acknowledgements.....	96
References	97
CHAPTER V Acoustic Detection of Resonance-Enhanced Multiphoton Ionization for spatially resolved temperature measurements	100
Abstract.....	101
Introduction	102
Experiment Setup	104
Results	106
Summary and Conclusions	116
References	118
CHAPTER VI Summary and Potential For Future Work	121
References	125
VITA.....	126

LIST OF TABLES

Table 2.1: Mean value and <i>RSD</i> of H/N value obtained from optimized ns-LIBS measurements presented in Fig. 2.6.....	41
Table 4.1: Selected rotational lines of S_{21} for used temperature measurements.....	82
Table 4.2: Summary of average temperatures calculated from the slopes presented in Fig. 10 and comparison to thermocouple measurements at the same position.	93
Table 5.1: Selected rotational lines of S_{21} used for temperature determination from the spectrum in Fig. 6.	114

LIST OF FIGURES

Figure 1.1: Level diagram for the (2+1) multiphoton excitation process.....	9
Figure 1.2: Homodyne microwave scattering circuit.....	16
Figure 2.1: Schematic view of experimental setup for LIBS measurements of F/A ratio in a high-pressure combustion chamber. SHG: second-harmonic generator; $\lambda/2$: half-wave plate; PBS: polarized beam splitter; BD: beam dump; f1, f2: convex lenses.	27
Figure 2.2: LIBS spectra obtained in laminar flame with $\phi = 1$ at 1 bar, 6 bar, and 11 bar using laser energy of 50 mJ/pulse and 150 mJ/pulse.....	28
Figure 2.3: Peak-intensity ratio of H_{656}/N_{568} as function of T_{delay} for laser energies of (a) 50 mJ/pulse and (b) 150 mJ/pulse. For each condition 100 data points are presented. Methane-air flame was set at equivalence ratio of $\phi = 1$. Error bar represents one standard deviation.....	31
Figure 2.4: Peak-intensity ratio of H/N as a function of laser pulse energy for pressure of 1, 6, and 11 bar. Data were obtained using T_{delay} of 40 ns (a) and 80 ns (b). Methane-air flame was set at equivalence ratio of $\phi = 1$. Error bar represents one standard deviation.....	32
Figure 2.5: Fluctuation of LIBS F/A-ratio measurements at a given input laser energy and T_{delay} for pressures of 1, 6, and 11 bar. Methane-air flame was set at equivalence ratio of $\phi = 1$. Relative standard deviation (<i>RSD</i>) = standard deviation/mean.....	34
Figure 2.6: Correlation of H_{656}/N_{568} as a function of ϕ measurement at a time delay of 80 ns and laser energies of 150 mJ/pulse, 100 mJ/pulse, and 50 mJ/pulse for pressures of 1, 6, and 11 bar, respectively. Symbols denote experimental measurements; solid lines are linear fits. Error bar represents one standard deviation.....	35
Figure 2.7: Effect of pressure on the Hencken flame.....	37
Figure 2.8: Ten consecutive single-shot images of atomic N_{II} emission from ns-LIB at $P = 1$ bar and 11 bar taken at $T_{\text{delay}} = 40$ ns. Laser energy used for	

LIB was 100 mJ/pulse. Methane-air flame was set at equivalence ratio of $\phi = 1$	38
Figure 2.9: H/N peak-intensity ratio as a function of pressure with input energies of 50 mJ/pulse and 150 mJ/pulse. Data were obtained using T_{delay} of 40 ns (a) and 80 ns (b). Methane-air flame was set at equivalence ratio of $\phi = 1$	40
Figure 3.1. Generalized model of the experimental setup for local equivalence ratio determination with ns-, ps-, and fs-LIBS.	50
Figure 3.2: Time resolved spectra of LIBS in a methane-air flame with $\Phi = 1$ (normalized by 656 nm emission). (a) Nanosecond LIBS using Nd:YAG 532 nm output with pulse width of 10 ns and laser energy 150 mJ/pulse. (b) Picosecond LIBS using 532 nm output and pulse width of 100 ps and 45 mJ/pulse. (c) Femtosecond LIBS using Ti:Sapphire 800 nm output with 100 fs pulse width and 4.5 mJ/pulse. ($\Phi = 1$).	53
Figure 3.3: Background subtracted peak emission intensities (normalized) of $H\alpha$ (656 nm), NII (568 nm), and OI (777 nm) for various time delays. (a) Nanosecond LIBS using Nd:YAG 532 nm output with pulse width 10 ns and laser energy 150 mJ/pulse. (b) Picosecond LIBS using 532 nm output and pulse width 100 ps. (c) Femtosecond LIBS using Ti:Sapphire 800 nm output with 100 fs pulse width and 4.5 mJ/pulse. ($\Phi = 1$).	54
Figure 3.4: Electron temperatures for ns-, ps-, and fs-LIBS in a methane-air flame ($\Phi = 1$). Calculated with the line ratio method given Eq. 3.1 using the nitrogen ion emission lines at NII (568 nm) and NII (594 nm). Typical errors for this method are about 10%. Note that the assumption that similar lineshapes for the two spectral lines was used, so that peak intensities could be used instead of spectrally integrated intensities.	56
Figure 3.5: Time evolution of $H\alpha$ (656 nm)/ NII (568 nm) and $H\alpha$ (656 nm)/ OI (777 nm) for ns-, ps-, and fs-LIBS. ($\Phi = 1$).	58

Figure 3.6: Emission spectra (each by normalized $H_{\alpha}(656 \text{ nm})$ peak intensity) for various equivalence ratios. (a) ns-LIBS with time delay of 80 ns, and laser energy 150 mJ/pulse, and gate width of 20 ns (b) ps-LIBS with time delay of 30 ns, laser energy of 45 mJ/pulse, and gate width of 10 ns (c) fs-LIBS with time delay of 15 ns, laser energy of 4.5 mJ/pulse, and gate width 10 ns.....59

Figure 3.7: Calibration curves for obtaining the local equivalence ratio from emission line ratios. (a) Nanosecond LIBS using Nd:YAG 532 nm output with pulse width 10 ns and laser energy 150 mJ/pulse. (b) Picosecond LIBS using 532 nm output and pulse width of 100 ps. (c) Femtosecond LIBS using Ti:Sapphire 800 nm output with 100 fs pulse width and 4.5 mJ/pulse. Error bars are shown along with curve fit results (dotted line). 100 shots were used for each data point.60

Figure 3.8: Relative standard deviation of emission ratios versus equivalence ratio for each laser case. Note that the best results from Fig. 7 were used, $H_{\alpha}(656 \text{ nm})/N_{II}(568 \text{ nm})$ for ns-LIBS and $H_{\alpha}(656 \text{ nm})/O_I(777 \text{ nm})$ for ps- and fs-LIBS.....62

Figure 4.1: Experimental setup for see-through-wall temperature measurement of molecular oxygen in a flow reactor. Ceramic insulation (white) covers the heating coils, which allow for temperature adjustments within the reactor. .72

Figure 4.2: The computational result of the flow reactor heated by a cylindrical heater. The black dots indicate the test points for temperature measurements in both axial and radial directions.74

Figure 4.3: (Left) Schematic of the well-stirred reactor used in the experiment. (Right) A cross-section of the well-stirred reactor showing the laser entry point (exhaust stack not shown). Temperature measurements were performed at 0.1, 0.15, 0.2, 0.3, and 0.4 inches from the bottom of the toroid.76

Figure 4.4: (Left) Basic model of the experiment setup showing the relative location of the horn to the well-stirred reactor. (Right) Picture of the experimental setup viewing from the UVT table. UV laser beam was bent

down and reflected upward into the WSR. Microwave detecting horn is measuring REMPI plasma through the ceramic WSR wall. The ceramic exhaust stack was present during data collection.	78
Figure 4.5: The loss tangent of various ceramics as a function of temperature for various microwave frequencies. The plot was generated using data from references [23-25].	84
Figure 4.6: (a) Transparency test of ½” thick alumina ceramic used in the flow reactor, showing less than 10% loss. (b) Spectra of molecular oxygen obtained at room temperature and elevated temperature conditions (i.e., heated air in a flow reactor) by using 2+1 REMPI process.	86
Figure 4.7: Boltzmann plots for oxygen temperature determination by rotational lines of $S_{21}(J'' = 9-25)$. Six testing points (Pos. 1 – Pos. 6 shown in Fig. 4.2) in axial direction have been set for temperature measurements.	87
Figure 4.8: The spatial distribution of O_2 rotational temperature in the flow reactor in both axial and radial directions.	89
Figure 4.9: Normalized REMPI spectra of molecular oxygen from each of the vertical positions in the well-stirred reactor. Figure progression is from top to bottom and left to right.	90
Figure 4.10: Boltzmann plots from the S_{21} branch REMPI spectra of molecular oxygen from Fig. 4.9. X-axis is the line position of the rotational branches. Y-axis is the normalized microwave signal by laser intensity and rotational line strength. A linear fitting is given to obtain the rotational temperatures at various heights in the WSR. Figure progression is from top to bottom and left to right.	92
Figure 4.11: Graph of the results in Table 4.2 showing the difference between radar REMPI and thermocouple measurements of the temperature.	94
Figure 5.1: Schematic of the setup used for simultaneous acoustic and radar REMPI measurements. Since the measurement point is totally invisible, probe volume is highlighted with an artificial mark in the figure.	105

Figure 5.2: Comparison of acoustic and microwave signals from REMPI of O ₂ in air.	107
Figure 5.3: (left) Variation of the delay time with distance between the photoacoustic source and the microphone; the speed of sound calculated from the time delay of the signal.	108
Figure 5.4: Fitted curve of the distance dependence of the acoustic signal, showing approximately 1/r dependence.....	109
Figure 5.5: Laser energy dependence of (a) photoacoustic and (b) radar REMPI signals.	110
Figure 5.6: Spectra obtained from simultaneous photoacoustic and radar REMPI measurements. Markers denote locations chosen for analysis.	112
Figure 5.7: Boltzmann plots for photoacoustic and radar REMPI signals in Fig. 5.6 generated using Eq. 3 along with the data in Table 1.	115
Figure 5.8: Ultrasonic emission was also detected from the REMPI plasma (300 kHz).	117

CHAPTER I
GENERAL INTRODUCTORY MATERIAL

Laser-Based Diagnostics

Engineering design and analysis has been revolutionized by advances in the computer industry. Significant information regarding complicated processes can now be obtained by modeling processes such as fluid flow and heat transfer. For example, the aviation industry uses several models to aid in the design of various components of aerospace vehicles, including propulsion related components. Furthermore, modern aviation is beginning to utilize the available modeling and computational resources to create digital twins of aircrafts, which can help predict critical design issues and log performance. However, accurate models require precise and reliable data for realistic and accurate predictions. In kind, high-quality data requires accurate and sensitive measurements. Some traditional measurement techniques too greatly affect the system under investigation, which is particularly true for combustion and aerospace measurements. For example, in reacting flow such as combustion, the presence of a thermocouple can significantly affect the system, or be insensitive to high-speed fluctuations of temperature. Yet another example can be made of wind tunnel measurements, where instrumentation placed in the tunnel for measurement purposes can lead to inconsistent or unreliable data.

Laser diagnostics seeks to use lasers as tools for making precise measurements, while minimally disturbing the system. Because of the unique properties of light, high-fidelity information can generally be obtained, and with the development of burst mode lasers and high-speed camera systems, high-speed information can also be obtained, which is important for turbulent systems.

In aerospace systems, parameters that are important to model development include local temperature, species concentrations, and flow velocities. In combustion processes, heat release rate, fuel properties (fuel spray break-up, local equivalence ratio), and ignition properties are also of interest. These parameters can all be found using traditional and novel laser diagnostics [1, 2]. Species and temperature can be measured quite accurately using techniques like Raman

scattering [1, 3], radar REMPI [4, 5], and laser-induced fluorescence (LIF) [2], while fuel-to-air ratio can be measured with laser-induced breakdown spectroscopy (LIBS) [6-8], Raman scattering [1, 2], and LIF. A variety of other laser diagnostic techniques exist and have been successful in modern aerospace applications, including for hypersonic flight development [9]. This dissertation will focus on the use of LIBS and radar REMPI for equivalence ratio and temperature detection respectively. Both parameters are critical to aerothermodynamic design and performance. Local temperature has implications for reaction rates, boundary layer-material interaction, and thermal stress loads, whereas fuel-to-air ratio is important for combustion chemistry, combustion performance, and emission reduction.

Laser-Induced Breakdown

Laser-induced breakdown (LIB) refers to the creation of plasma from the focusing of laser radiation to sufficiently high-intensity, specifically beyond the optical breakdown threshold. This threshold is not well-defined due to the intermittent and stochastic nature of the breakdown process. Thus, the threshold is defined as the intensity such that breakdown occurs 50% of the time. Furthermore, the breakdown threshold is dependent on factors like number density, laser wavelength, and pulse duration. For example, the breakdown thresholds in STP air are approximately 2.5×10^{12} W/cm² and 2.0×10^{10} W/cm² respectively for 532 nm and 1064 nm laser radiation with a pulse width of 8 ns [10]. The breakdown threshold is also reduced if the laser wavelength is tuned to a resonance wavelength of the medium [11, 12]. The resonance basically allows electrons to be liberated more easily, and results in extra energy available for the electron avalanching process. However, non-resonant LIB is far more common since it is much simpler to setup and provides nearly identical measurement quality.

The creation of the LIB plasma starts with the generation of seed electrons from multiphoton ionization. For laser pulses that are a few hundred picoseconds

or longer, the initial seed electrons are energized by the remaining laser field and go on to cause more ionization. This process is termed avalanche breakdown. Within the avalanching process is another process, inverse-bremsstrahlung, which causes electrons to gain energy from photons via three body collisions processes with atoms of molecules. For shorter pulses, multiphoton ionization is the driving force for plasma production due to the electron collision frequency being much too short when considering the laser pulse width; hence, no avalanching can occur. Since the avalanching mechanism is not present in this scenario, it is not truly considered breakdown, but is usually grouped with it nonetheless.

Due to the rapid accumulation of free electrons and ions, the laser plasma rapidly expands, creating a shockwave with speeds much greater than the speed of sound [13]. The initial electron temperature and density of the plasma start off very high and decay very quickly as the plasma expansion occurs [10, 14]. Since these two properties are very important to the characteristics of any plasma, it is reasonable that the plasma emission properties also change rather quickly throughout the LIB plasma lifetime. Within hundreds of nanoseconds after initial plasma formation (i.e. after the laser pulse has expired), significant continuum emissions are present, a key characteristic of the free-free, free-bound, and bound-free energy transitions occurring within the still energetic plasma [11, 15]. As the electron density and temperature decrease, the continuum emissions begin to decay away and atomic and ionic emission lines begin to emerge and dominate. Note, the continuum emissions are usually regarded as background and are avoided by adjusting the gate delay of the collection camera. Furthermore, a few microseconds after the initial plasma formation, molecular lines can be observed [16].

Under the condition of local thermodynamic equilibrium, discussed later, the number of atoms in the plasma of species m in an excited state f is given by the Boltzmann distribution:

$$N_m^{(f)} = N_m^{(0)} \frac{g_m^{(f)}}{Z(T)} e^{-\frac{E_m^{(f)}}{k_B T}} \quad (1.1)$$

Here, $N_m^{(f)}$ denotes the excited state population of species m , $N_m^{(0)}$ denotes the ground state, $g_m^{(f)}$ is the degeneracy of energy state $E_m^{(f)}$, and k_B is the Boltzmann constant. For species m , the number of photons, $N_{\gamma,m,\lambda}$, emitted at wavelength λ from transitions from state E_f to lower state E_i during time Δt is approximately:

$$N_{\gamma,m,\lambda} = N_m^{(f)} A_m^{(f)} \Delta t = A_m^{(f)} N_m^{(0)} \Delta t \frac{g_m^{(f)}}{Z(T)} e^{-\frac{E_m^{(f)}}{k_B T}} \quad (1.2)$$

$A_m^{(f)}$ is the spontaneous Einstein emission coefficient for species m transitioning from state f to a lower state, producing the radiation at wavelength λ . Since the energy of the emitted photon is $E_\gamma = \frac{hc}{\lambda}$, the average emitted power from the plasma at wavelength λ corresponding to species m is:

$$P_{m,\lambda} = N_m^{(0)} \frac{hc A_m^{(f)}}{\lambda} \frac{g_m^{(f)}}{Z(T)} e^{-\frac{E_m^{(f)}}{k_B T}} \quad (1.3)$$

Hence, the associated emission intensity, $I_{m,\lambda}$, is proportional to the above:

$$I_{m,\lambda} \propto N_m^{(0)} \frac{hc A_m^{(f)}}{\lambda} \frac{g_m^{(f)}}{Z(T)} e^{-\frac{E_m^{(f)}}{k_B T}} \quad (1.4)$$

Eq. 1.4 is valid only under the conditions of local thermodynamics equilibrium (LTE), in which the temperature of the plasma can be characterized by a single temperature (i.e. the electron temperature approximately equal to the ion temperature). An exact definition of the criteria which must be met for LTE to be guaranteed is generally not easy to measure due to the complex nature of laser

plasma (inhomogeneous, transient, *etc.*), especially when multiple species are involved [17]. Generally, the McWhirter criterion is used to justify an analysis that assumes LTE, though many authors merely assume LTE conditions [17]. The McWhirter criterion is defined as [11, 17]:

$$n_e(cm^{-3}) > 1.6 \times 10^{12} \sqrt{T_e} (\Delta E)^3 \quad (1.5)$$

ΔE is the largest energy transition between two adjacent energy levels. Eq. 1.5 assumes that self-absorption is negligible in the plasma [17]. Note that physically LTE corresponds to the primary energy transition between plasma elements being dominated by collision rather than radiative processes. These collisions allow the velocity and energy distributions to be described by Maxwell-Boltzmann distributions. Consequently, a single temperature is sufficient to describe the system. While the McWhirter criterion will always be fulfilled when LTE is achieved, it is not necessarily a sufficient condition to ensure LTE [11, 17]. In general, one can guarantee the LTE exists if the temperature from a Boltzmann analysis matches that predicted by the Saha equation; however, this is considered experimentally tedious.

In order to find the electron temperature of the LIBS plasma using a Boltzmann analysis, Eq. 1.4 can be arranged into the following form [7, 10, 11]:

$$\ln \left(\frac{I_{m,\lambda} \lambda}{hc A_m^{(f)} g_m^{(f)}} \right) = - \frac{E_m^{(f)}}{k_B T} + \ln \left(\frac{N_m^{(0)}}{Z(T)} K \right) \quad (1.6)$$

Here, K is the constant of proportionality for Eq. 4. Under local thermodynamic equilibrium, the temperature Eq. 6 yields is equal to the electron temperature, T_e . If not, then Eq. 6 yields the ion temperature. In the event that only two points are used for the Boltzmann analysis, Eq. 6 reduces to the ratio of the two emission lines, with the assumption that the shape of the emission lines is similar [11].

Electron density is also a critical parameter for plasma characterization, as shown its presence in the McWhirter criterion. The electron density of a laser-induced plasma can be found spectroscopically by considering the Stark broadening of atomic emission lines [11, 15, 16, 18-20]. Typical elements used for gaseous laser-induced breakdown plasmas are nitrogen and hydrogen. If available, hydrogen is considered the best option for Stark broadening analysis due to it having a linear Stark effect response. For gas phase breakdown, typical electron densities reach about $1 \times 10^{18} \text{ cm}^{-3}$ [14]. Empirical formulas using H-alpha (656 nm) and H-beta (486 nm) emission lines have been shown to be effective for electron density estimation [16, 19-22]. Other means of electron density analysis include emission line-to-continuum ratios [23], continuum emission analysis [15], and the Saha equation [15].

Equation 1.4 suggests that a linear relationship between fuel-to-air ratio and LIB plasma emission ratios for a proper choice of elemental species. Specifically, if $I_{a,\lambda} \propto N_a^{(0)}$ is the emission intensity from chemical species a from a fuel component and $I_{b,\lambda'} \propto N_b^{(0)}$ is the emission intensity from a chemical species b from the oxidizer, then the ratio of the two yields a relationship to the fuel-to-air ratio (or equivalence ratio ϕ):

$$\frac{I_{a,\lambda}}{I_{b,\lambda'}} \propto \frac{N_a^{(0)}}{N_b^{(0)}} \propto \phi \quad (1.7)$$

Resonance Enhanced Multiphoton Ionization

The previous section dealt with laser-plasma generation via non-resonant coupling of laser light with atoms and plasma formation via the electron avalanche mechanism. Resonance-Enhanced Multiphoton Ionization (REMPI) uses highly focused light tuned to a resonant wavelength to ionize atoms or molecules through a multiphoton process. The ionization results in the formation of a very weak, short-lived plasma that is much different from the breakdown plasma. The REMPI

plasma typically produced no sound detectable by human ears and no optical emissions detectable by the eye. The plasma is much smaller than the LIB plasma, and is very precisely located at the focus due to intensity needed to commence the multiphoton process. While much lower energies are used for REMPI experiments, the tuning of the laser wavelength is necessary. Note that excessive energy can lead to resonant LIB.

REMPI can be thought of as consisting of two major parts, the ionization process and the multiphoton excitation process. Since this dissertation will utilize a (2+1) process, that is two photons for excitation and one photon for ionization, consider the (2+1) excitation-ionization scheme shown in Figure 1.1.

The first process is the excitation of an electron to the n level. This process is completely described by time-dependent perturbation theory. Consider an interaction Hamiltonian given by:

$$V_{mg} = -\mu_{mg}(Ee^{-i\omega t} + E^*e^{i\omega t}) \quad (1.8)$$

Since two-photon absorption is a second-order process, the first-order and second-order terms must be calculated. According to perturbation theory [24], N^{th} -order correction coefficients are given by:

$$\frac{da_m^{(N)}}{dt} = \frac{1}{i\hbar} \sum_l a_l^{(N-1)} V_{ml} e^{-i\omega_{lm}t} \quad (1.9)$$

The first-order process ($N = 1$) is represented physically by single photon absorption, and is given by:

$$\frac{da_m^{(1)}}{dt} = \frac{1}{i\hbar} \sum_l a_l^{(0)} [-\mu_{ml}(Ee^{-i\omega t} + E^*e^{i\omega t})e^{-i\omega_{lm}t}] \quad (1.10)$$

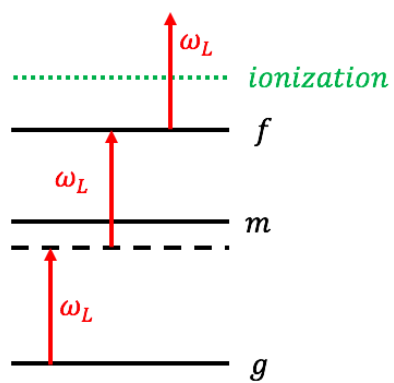


Figure 1.1: Level diagram for the (2+1) multiphoton excitation process.

with initial conditions $a_g^{(0)}(t) = 1$ and $a_l^{(0)}(t) = 0$ for $l \neq g$. These conditions simply state that prior to the perturbation provided by the electromagnetic wave, only the ground state is populated. Applying these conditions to Eq. 1.10 yields,

$$\frac{da_m^{(1)}}{dt} = -\frac{\mu_{mg}}{i\hbar} (E e^{i(\omega_{mg}-\omega)t} + E^* e^{i(\omega_{mg}+\omega)t}) \quad (1.11)$$

Direct integration of this equation gives:

$$\begin{aligned} a_m^{(1)} &= -\frac{\mu_{mg}}{i\hbar} \int_0^t (E e^{i(\omega_{mg}-\omega)t} + E^* e^{i(\omega_{mg}+\omega)t}) dt \\ &= \mu_{mg} \left(\frac{E e^{i(\omega_{mg}-\omega)t} - 1}{\hbar(\omega_{mg} - \omega)} + \frac{E^* e^{i(\omega_{mg}+\omega)t} - 1}{\hbar(\omega_{mg} + \omega)} \right) \end{aligned} \quad (1.12)$$

The rotating wave approximation (RWA) allows for the second term in Eq. 1.12 to be neglected [24]. Therefore,

$$a_m^{(1)} = \frac{\mu_{mg} E}{\hbar} \frac{e^{i(\omega_{mg}-\omega)t} - 1}{(\omega_{mg} - \omega)} \quad (1.13)$$

Omitting E^* term in the interaction potential due to the RWA, the second-order equation is:

$$\begin{aligned} \frac{da_f^{(2)}}{dt} &= \frac{1}{i\hbar} \sum_m \frac{\mu_{mg} E}{\hbar} \frac{e^{i(\omega_{mg}-\omega)t} - 1}{(\omega_{mg} - \omega)} [-\mu_{fm} E e^{-i\omega t} e^{-i\omega_{mf}t}] \\ &= -\frac{1}{i} \sum_m \frac{\mu_{mg} \mu_{fm} E^2}{\hbar^2 (\omega_{mg} - \omega)} [e^{i(\omega_{fg}-2\omega)t} - e^{i(\omega_{fm}-\omega)t}] \end{aligned} \quad (1.14)$$

The second term in the brackets can be neglected since it does not contribute to two-photon absorption, and Eq. 1.14 can be integrated to give:

$$a_f^{(2)} = \sum_m \frac{\mu_{mg}\mu_{fm}E^2}{\hbar^2(\omega_{mg} - \omega)} \left[\frac{e^{i(\omega_{fg}-2\omega)t} - 1}{\omega_{fg} - 2\omega} \right] \quad (1.15)$$

The probability for occupancy of the level f is then:

$$p_f^{(2)}(t) = |a_f^{(2)}(t)|^2 = \left| \sum_m \frac{\mu_{mg}\mu_{fm}E^2}{\hbar^2(\omega_{mg} - \omega)} \right|^2 \left| \frac{e^{i(\omega_{fg}-2\omega)t} - 1}{\omega_{fg} - 2\omega} \right|^2 \quad (1.16)$$

For large t , Eq. 1.16 becomes:

$$p_f^{(2)}(t) = \left| \sum_m \frac{\mu_{mg}\mu_{fm}E^2}{\hbar^2(\omega_{mg} - \omega)} \right|^2 2\pi t \delta(\omega_{fg} - 2\omega) \quad (1.17)$$

Note that the transition rate $R_{fg}^{(2)}$ from ground state to final state is defined as to $R_{fg}^{(2)} \equiv p_f^{(2)}(t)/t$ and the cross-section for a two-photon process is $\sigma_{fg}^2(\omega) = R_{fg}^{(2)}/I^2$ where I is the intensity. Then the two-photon excitation cross-section is given by:

$$\sigma_{fg}^2(\omega_L) = K \left| \sum_m \frac{\mu_{fm}\mu_{mg}}{\hbar^2(\omega_{mg} - \omega_L)} \right|^2 S(2\omega_L) \quad (1.18)$$

Here K is a proportionality constant, ω_L is the laser wavelength, and S is the lineshape profile of the laser.

The previous formalism completely describes the two-photon excitation part of the (2+1) REMPI. By considering energy level population dynamics, the

ionization part of the process can be incorporated. The time evolution of level f is given by [25, 26]:

$$\frac{dn_f}{dt} = -A_f n_f - Q_f n_f - \left(\frac{I}{\hbar \omega_L} \right) \sigma^i n_f + \left(\frac{I}{\hbar \omega_L} \right)^2 \sigma_{fg}^2(\omega_L) n_g \quad (1.19)$$

Here, n_f is the number density of level f , A_f is spontaneous emission Einstein coefficient for level f , Q_f is the quenching rate for level f , and n_g is the ground state number density. Furthermore, the number density of liberated electrons, n_e , due to the (2+1) REMPI process is [25, 26]:

$$\frac{dn_e}{dt} = -R n_e + \left(\frac{I}{\hbar \omega_L} \right) \sigma^i n_f \quad (1.20)$$

Here, R is a rate constant associated with electron loss (recombination, etc.) and σ^i is the single photon ionization cross-section for level f . Under steady state conditions, $\frac{dn_e}{dt} = \frac{dn_f}{dt} = 0$, Eq. 1.19 and Eq. 1.20 can be combined to give the free electron number density:

$$n_e = \frac{\left(\frac{I}{\hbar \omega_L} \right)^3 \sigma^i \sigma_{fg}^2}{R \left[A_2 + Q_2 + \sigma^i \left(\frac{I}{\hbar \omega_L} \right) \right]} n_g \quad (1.21)$$

A key aspect in this level dynamics model is lack of any information about the intermediate level, level m , in the two-photon process. This is due to the assumption that the level is virtual rather than real, and the energy-time uncertainty relation restricts the lifetime of virtual levels to being very short. Thus, the two-photon excitation is considered instantaneous.

An important property of REMPI is the dependence on laser energy (i.e. intensity). This is often used as a standard in experiments to verify multiphoton processes are occurring and that the desired excitation processes is contributing to the measured signal. Eq. 1.21 for (2+1) REMPI gives two extremes in terms of laser intensity dependence. First, consider the case in which $\sigma^i \left(\frac{I}{\hbar\omega_L} \right)$ dominates the denominator. Then $n_e \propto I^2 n_g$, which means the plasma creation is dominated by the two-photon process. The second extreme is when any of the other terms in the denominator dominate, which gives a cubic dependence on intensity. Hence, generally, the process will be somewhere between those two cases.

Radar REMPI

Radar REMPI uses coherent scattering of microwave off the plasma produced from the REMPI process. In general, incoherent microwave will have a net scattered amplitude that is reduced due to phase interferences, whereas, the coherent case avoids this amplitude reduction in net scattered electric field amplitude. Another condition necessary for coherent scattering is that the microwave wavelength is much greater than the plasma length, which is taken to be about Rayleigh range length [25, 27]. Furthermore, it can be assumed that the quasi-neutral plasma can be modeled as an oscillator with driving force coming from the microwave perturbation. Of interest are the free electrons in the REMPI plasma, given that the excited molecule is much more massive and can be regarded as stationary; thus, the electron will provide the strongest response to the microwave perturbation. The displacement, $x(t)$, of an electron in the plasma due to the microwave is then [28]:

$$\frac{d^2 x(t)}{dt^2} + \nu_{en} \frac{dx(t)}{dt} + \omega_p^2 x = \frac{-e E_{MW} \cos(\omega_m t)}{m_e} \quad (1.22)$$

Here, ν_{en} is the electron-neutral collision frequency, E_{MW} is the amplitude of the microwave electric field, ω is the microwave frequency. The plasma frequency, ω_p , is given by:

$$\omega_p^2 = \frac{n_e e^2}{\epsilon_0 m_e} \quad (1.23)$$

The plasma frequency is very important for light-plasma interaction. Specifically, the plasma will be transparent to any light with frequency higher than the plasma frequency [28, 29]. Furthermore, if the probe microwave frequency is too small, there will be an exponential attenuation, which is define by the plasma skin depth [28]:

$$\delta^2 = \frac{2\epsilon_0 c^2 m_e \nu_{en}}{\omega_m e^2 n_e} \quad (1.24)$$

This skin depth places an important criterion on the plasma length for the microwave scattering; specifically, the skin depth should satisfy: $\delta \gg L_{plasma}$ [25, 27, 30]. If the skin depth is smaller than the characteristic scale of the plasma (again, taken to be about the Rayleigh range), then a portion of the plasma will be shielded from the probing microwaves.

Eq. 1.22 can now be solved to yield the displacement [28]:

$$x(t) = \frac{eE_{MW}}{m_e \sqrt{(\omega_p^2 - \omega_m^2)^2 + \nu_{en}^2 \omega_m^2}} \cos(\omega_m t + \phi_S) \quad (1.25)$$

Here ϕ_S is a phase shift due to the plasma. Since the electron-plasma system will act like a dipole oscillator, the radiation field intensity will be given by the typical dipole formula [31, 32]:

$$I_{Scatter} = \frac{e^2 \omega_m^4 d^2}{32\pi^2 \epsilon_0 c^3} \frac{\sin^2(\theta)}{r^2} \quad (1.26)$$

In Eq. 26, $d = -en_e Vx$ is the dipole moment with volume given by V . Thus, Eq. 1.25 and Eq. 1.26 together with assumption of a collision dominated plasma with $\nu_{en} \gg \omega_m \gg \omega_p$ yields:

$$I_{Scatter} \propto \frac{n_e^2 \omega_m^2 V^2 E_{MW}^2}{\nu_{en}^2} \frac{\sin^2(\theta)}{r^2} \quad (1.27)$$

Since $I_{Scatter} \propto |E_{Scatter}|^2$, the scattered electric field magnitude is:

$$E_{Scatter} \propto \frac{n_e V \omega E_{MW}}{\nu_{en}} \frac{\sin(\theta)}{r} \quad (1.28)$$

Thus, the scattered microwave signal is related to the total number of electrons, $N_e = n_e V$, within the probe volume assuming Rayleigh scattering conditions are met and that the skin depth is larger than the plasma length scale. Furthermore, Eq. 1.28 states that the scattering signal is also proportional to the electric field strength of the pre-scattered microwave.

A homodyne microwave detection system is used for microwave scattering on the REMPI plasma. This system has been used successfully in previous works [4, 5, 12, 27, 30, 33], and a circuit schematic is shown in Fig. 1.2.

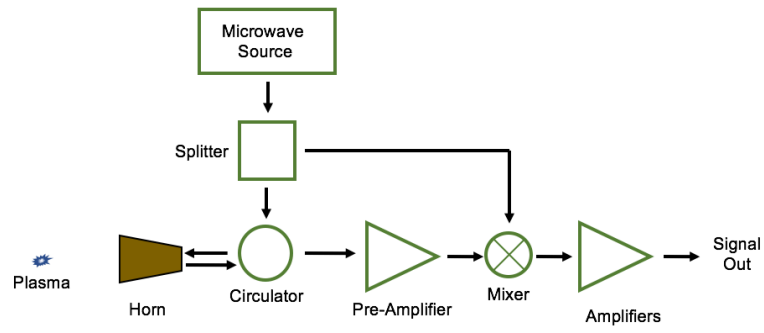


Figure 1.2: Homodyne microwave scattering circuit.

References

1. A. C. Eckbreth, *Laser Diagnostics for Combustion Temperature and Species*, Combustion science and technology book series (Taylor & Francis, 1996).
2. K. Kohse-Höinghaus, *Applied Combustion Diagnostics* (CRC Press, 2002).
3. N. Jiang, P. S. Hsu, J. G. Mance, Y. Wu, M. Gragston, Z. Zhang, J. D. Miller, J. R. Gord, and S. Roy, "High-speed 2D Raman imaging at elevated pressures," *Opt. Lett.* **42**, 3678-3681 (2017).
4. Y. Wu, J. Sawyer, Z. Zhang, and S. F. Adams, "Flame temperature measurements by radar resonance-enhanced multiphoton ionization of molecular oxygen," *Appl. Opt.* **51**, 6864-6869 (2012).
5. Y. Wu and Z. Zhang, "Two-dimensional quantitative measurements of methyl radicals in methane/air flame," *Appl. Opt.* **54**, 157-162 (2015).
6. H. Do and C. Carter, "Hydrocarbon fuel concentration measurement in reacting flows using short-gated emission spectra of laser induced plasma," *Combustion and Flame* **160**, 601-609 (2013).
7. T. X. Phuoc, "Laser-induced spark for simultaneous ignition and fuel-to-air ratio measurements," *Optics and Lasers in Engineering* **44**, 520-534 (2006).
8. A. Michalakou, P. Stavropoulos, and S. Couris, "Laser-induced breakdown spectroscopy in reactive flows of hydrocarbon-air mixtures," *Applied Physics Letters* **92**, 081501 (2008).
9. P. M. B. Danehy, Brett F.; Johansen, Craig T.; Cutler, Andrew D.; Hurley, Samantha, "Spectroscopic Measurement Techniques for Aerospace Flows," NASA, ed. (NASA, 2014).
10. A. W. Miziolek, V. Palleschi, and I. Schechter, *Laser Induced Breakdown Spectroscopy* (Cambridge University Press, 2006).
11. J. P. Singh and S. N. Thakur, *Laser-Induced Breakdown Spectroscopy* (Elsevier Science, 2007).

12. Y. Wu, Z. Zhang, N. Jiang, S. Roy, and J. R. Gord, "Resonant- and avalanche-ionization amplification of laser-induced plasma in air," *Journal of Applied Physics* **116**, 143304 (2014).
13. I. Dors, C. Parigger, and J. Lewis, "Fluid dynamics effects following laser-induced optical breakdown," in *38th Aerospace Sciences Meeting and Exhibit* (American Institute of Aeronautics and Astronautics, 2000).
14. V. Hohreiter, J. E. Carranza, and D. W. Hahn, "Temporal analysis of laser-induced plasma properties as related to laser-induced breakdown spectroscopy," *Spectrochimica Acta Part B: Atomic Spectroscopy* **59**, 327-333 (2004).
15. H. R. Griem, *Principles of Plasma Spectroscopy*, Cambridge Monographs on Plasma Physics (Cambridge University Press, 2005).
16. C. G. Parigger, "Atomic and molecular emissions in laser-induced breakdown spectroscopy," *Spectrochimica Acta Part B: Atomic Spectroscopy* **79-80**, 4-16 (2013).
17. G. Cristoforetti, A. De Giacomo, M. Dell'Aglio, S. Legnaioli, E. Tognoni, V. Palleschi, and N. Omenetto, "Local Thermodynamic Equilibrium in Laser-Induced Breakdown Spectroscopy: Beyond the McWhirter criterion," *Spectrochimica Acta Part B: Atomic Spectroscopy* **65**, 86-95 (2010).
18. L. Pardini, S. Legnaioli, G. Lorenzetti, V. Palleschi, R. Gaudiuso, A. De Giacomo, D. M. Diaz Pace, F. Anabitarte Garcia, G. de Holanda Cavalcanti, and C. Parigger, "On the determination of plasma electron number density from Stark broadened hydrogen Balmer series lines in Laser-Induced Breakdown Spectroscopy experiments," *Spectrochimica Acta Part B: Atomic Spectroscopy* **88**, 98-103 (2013).
19. C. G. Parigger, M. Dackman, and J. O. Hornkohl, "Time-resolved spectroscopy measurements of hydrogen-alpha, -beta, and -gamma emissions," *Appl. Opt.* **47**, G1-G6 (2008).

20. C. G. Parigger, D. H. Plemmons, and E. Oks, "Balmer series H β measurements in a laser-induced hydrogen plasma," *Appl. Opt.* **42**, 5992-6000 (2003).
21. M. A. Gigosos, M. Á. González, and V. n. Cardeñoso, "Computer simulated Balmer-alpha, -beta and -gamma Stark line profiles for non-equilibrium plasmas diagnostics," *Spectrochimica Acta Part B: Atomic Spectroscopy* **58**, 1489-1504 (2003).
22. N. Konjević, M. Ivković, and N. Sakan, "Hydrogen Balmer lines for low electron number density plasma diagnostics," *Spectrochimica Acta Part B: Atomic Spectroscopy* **76**, 16-26 (2012).
23. A. Sola, M. D. Calzada, and A. Gamero, "On the use of the line-to-continuum intensity ratio for determining the electron temperature in a high-pressure argon surface-microwave discharge," *Journal of Physics D: Applied Physics* **28**, 1099 (1995).
24. R. Shankar, *Principles of Quantum Mechanics* (Springer US, 2012).
25. S. D. McGuire, "Stand-Off Gas Phase Diagnostics by Microwave Detection of Laser Generated Ionization," (Princeton University, Princeton University, 2015).
26. T. L. Chng, "Remote Detection of Trace Species for Combustion and Atmospheric Magnetometry," (Princeton University, Princeton University, 2017).
27. J. C. Sawyer, "Generation and Microwave Scattering Diagnostics of Small Volume Plasmas," (Trace: Tennessee Research and Creative Exchange, 2016).
28. Y. P. Raizer, V. I. Kisin, and J. E. Allen, *Gas Discharge Physics* (Springer Berlin Heidelberg, 2011).
29. F. F. Chen, *Introduction to Plasma Physics and Controlled Fusion: Volume 1: Plasma Physics* (Springer US, 2013).

30. Y. Wu, J. C. Sawyer, L. Su, and Z. Zhang, "Quantitative measurement of electron number in nanosecond and picosecond laser-induced air breakdown," *Journal of Applied Physics* **119**, 173303 (2016).
31. J. J. David, *Classical Electrodynamics* (Wiley Eastern Limited, 1975).
32. D. J. Griffiths, *Introduction to Electrodynamics* (Cambridge University Press, 2017).
33. Y. Wu, "Measurements of Methyl Radicals and Temperatures by using Coherent Microwave Rayleigh Scattering from Resonance Enhanced Multiphoton Ionization," (Trace: Tennessee Research and Creative Exchange, 2015).

CHAPTER II

**EQUIVALENCE RATIO MEASUREMENTS IN METHANE-AIR
FLAME AT 1-11 BAR USING NANOSECOND LASER INDUCED
BREAKDOWN SPECTROSCOPY**

Versions of this chapter were originally published by Mark Gragston, Yue Wu, Zhili Zhang, Paul Hsu, Anil Patnaik, Sukesh Roy, and James R. Gord:

Mark Gragston¹, Yue Wu¹, Zhili Zhang¹, Paul Hsu², Anil Patnaik², Sukesh Roy², James R. Gord³. "Sensitivity, Stability, and Precision of Quantitative ns-LIBS-Based Fuel-Air Ratio Measurements for High Pressure Methane-Air Flames." *55th AIAA Aerospace Science Meeting, AIAA SciTech Forum*, (AIAA-2017-0384), (2017).

Paul Hsu², Mark Gragston¹, Yue Wu¹, Zhili Zhang¹, Anil Patnaik², Sukesh Roy², James R. Gord³. "Sensitivity, Stability, and Precision of Quantitative ns-LIBS-Based Fuel-Air Ratio Measurements for High Pressure Methane-Air Flames." *Applied Optics*, 55, 28, (8042-8048). (2016).

Author Affiliations:

¹Department of Mechanical, Aerospace, and Biomedical Engineering, University of Tennessee, Knoxville, TN 37996 USA

²Spectral Energies LLC, Dayton, OH 45431 USA

³Air Force Research Laboratory, Aerospace Systems Directorate, Wright-Patterson AFB, OH 45433, USA

Abstract

Nanosecond-laser-based laser-induced breakdown spectroscopy (ns-LIBS) is employed for quantitative local fuel-air (F/A) ratio (i.e., ratio of actual fuel-to-oxidizer mass over ratio of fuel-to-oxidizer mass at stoichiometry) measurements in well-characterized methane-air flames at pressures of 1 – 11 bars. Nitrogen and hydrogen atomic-emission lines at 568 nm and 656 nm, respectively, are selected to establish a correlation between the line intensities and the F/A ratio. The effects of laser-pulse energy, camera gate delay, and pressure

on the sensitivity, stability, and precision of the quantitative ns-LIBS F/A ratio measurements are investigated. The optimal laser energy and camera gate delay are determined for each pressure condition. It is found that measurement stability and precision are degraded with an increase in pressure. Primary limitations of the F/A ratio measurement employing ns-LIBS at elevated pressures are identified as instabilities caused by the laser-induced dense plasma and the presence of high-level soot. Potential improvements are suggested.

Introduction

Laser-induced breakdown spectroscopy (LIBS) is a relatively straightforward and yet a powerful technique that has been widely used for elemental-composition measurements in all forms of matter [1]. In a LIBS measurement, a focused high-energy laser beam is used to induce ionization, dissociation, and optical breakdown of a target medium for producing plasma at the probe volume; the spectroscopic analysis of light emitted from the plasma is employed for determining chemical components.

During the past decade, several groups have explored applications of LIBS in combustion diagnostics for fuel-air (F/A) ratio measurements in premixed combustion systems [2-8] and practical engines [9-14]. Real-time measurements of local and global F/A ratios provide significant advantages with regard to combustion monitoring and control, which can aid in improving engine performance while reducing combustion instability, blow-off, flashback, and pollutant emission [1,15]. Additionally, knowledge of the localized F/A ratio provides a way for combustion modelers to explore the underlying physics that govern combustion instability and, hence, improve engine design [16]. LIBS measurements of the local F/A ratio are conducted through empirical correlation of the ratios of the intensities of the atomic spectral lines of H, C, CN, N, and O, that are emitted from a laser-induced spark in the gaseous mixture. The major advantages of LIBS-based F/A ratio measurement in practical combustion facilities are: (1) ease of experimental setup with single-beam approach, (2) elimination of

invasive fuel additives or seeding, (3) single-ended detection capability, and (4) high spatial resolution.

Several studies have demonstrated that the ratios of the peaks of emission lines can be used to correlate and quantify the F/A ratio, including H_{γ} (656 nm) / N_{II} (568 nm) lines [8], H_{γ} (656 nm) / N_I (500 nm) lines [16], H_{β} (486 nm) / N_I (746 nm) lines [11], H_{γ} (656 nm) / O_I (844 nm and 777 nm) lines [2, 4, 12, 16], H_{γ} (656 nm) / N_I (742-746 nm) lines [2, 3], C_I (711 nm) / N_I (740–750 nm) lines [9], C_I (711 nm) / O_I (776 nm) lines [9], C_I (711 nm) / N_I (746 nm) + O_I (776 nm) lines [5], CN (707-734 nm) / N (740-750 nm) lines [9], and CN (707-734 nm) / O_I (776 nm) lines [9]. In most of the LIBS F/A ratio experiments, time-gated detection was employed to avoid sampling of the initial intense continuum emission from laser-induced plasma and improve the signal-to-background ratio [1-14]. This also aided in eliminating the stray light, Rayleigh scattering, and chemiluminescence. Additionally, for the short-gated LIBS measurement, gate width and delay of approximately tens of nanoseconds (ns) were required for high-speed reacting flows [8]. Generally, the camera gate width and delay time ranging from 0.04 microsecond (μ s) to many microseconds were employed for recording LIBS emission spectra. Some recent studies have shown that ungated detection with an appropriate blocking of the scattered beam can also be used for LIBS F/A ratio measurements [16-19].

For most of the previous measurements of F/A ratio, ns-duration laser pulses were employed for generating the optical breakdown. In typical ns-LIBS initial free electrons are generated through non-resonant and multi-photon ionizations by the front end of the high-intensity pulse. Subsequently, the free electrons are accelerated by the inverse Bremsstrahlung process with the remainder of the same pulse. Those accelerated electrons ionize and dissociate other molecules by collisions, generating secondary electrons; and such cascaded ionization or avalanche ionization processes produce dense plasma at the probe volume and in its vicinity. Since at atmospheric pressure the electron-molecule collision timescale is on the order of picoseconds (ps) [20–22], the ns-duration laser pulse is sufficiently long for cascaded electron generation and interaction of

the energetic electrons with the neutral molecules, leading to expanded plasma. Since the plasma generation via avalanche ionization is a stochastic process, small variations in plasma density and electron kinetic energy can cause a large fluctuation in LIBS emission signals, thereby affecting the sensitivity, stability, and precision of the quantitative F/A ratio measurements. Additionally, the presence of soot further complicates the LIBS measurement, particularly in elevated-pressure conditions, because it causes variations in plasma parameters, which results in variation in elemental-line emission intensity and ratios [12]. The temporal behavior of emission decay from the excited atomic species depends on the thermal expansion, plasma-quenching processes, and radical/atom-recombination reactions. Thus, LIBS measurement is strongly affected by flow conditions (such as gas composition and pressure) and laser parameters (such as pulse duration and energy). Recently, Ferioli and Buckely [5] and Do and Carter [8] studied the stability of ns-LIBS for fuel-concentration measurements in atmospheric-pressure, laminar, premixed hydrocarbon flames. Their studies indicated that optimization of camera-gate delay and input pulse energy can minimize measurement fluctuation.

In the present paper, quantitative analysis of the sensitivity, stability, and precision of the 10-Hz, ns-LIBS measurements are presented for the F/A ratio in methane-air flames at *elevated pressures* (up to 11 bar). The effects of the camera-gate delay, laser energy, and pressure on the LIBS measurements were investigated in detail. The H γ (656-nm) and N $_{II}$ (568-nm) lines were selected for F/A ratio measurements. The N $_{II}$ line has higher selectivity in the signal compared to other prominent lines such as N I (740–750 nm) and O I (776 nm and 844 nm) lines because breakdown is the only source for generating the N $_{II}$ signal, unlike in the other two ions.

Experiment Setup

The experimental setup is shown in Figure 2.1. The second harmonic of the Nd:YAG laser (PowerliteTM DLS, Continuum) generated 10-ns-duration laser

pulses with maximum energy of 200 mJ/pulse at a 10-Hz repetition rate. The laser pulse energy for generation of optical breakdown was controlled with a half-wave plate and a polarizer. A Hencken burner was placed inside a stainless-steel high-pressure chamber. The laser beam was focused at the center of the Hencken burner using a spherical lens with a focal length of $f = 50$ mm. The focal spot was located at 27.5 mm above the burner surface. The beam waist at the focal point was measured by a beam profiler; the typical beam waist at the focus was ~ 50 μm . LIBS signals were collected outside the chamber using a spherical lens with a focal length of $f = 150$ mm and then coupled to a 0.25-m spectrometer that was equipped with a 150-grooves/mm grating blazed at 800 nm (SpectraPro 2300i, Princeton Instruments). A time-gated, intensified CCD camera (PI-MAX4, Princeton Instruments) with a 1024×512 pixel array was employed for the acquisition of single-shot LIB emission spectra. Air was used as the buffer gas for the high-pressure experiments. To prevent condensation of water on the chamber windows, cold and dry air was used to purge the windows continuously during the measurements.

Results of LIBS Measurement at High Pressure

The stability, sensitivity, and precision of LIBS-based F/A- ratio measurements for well-premixed, laminar methane-air flames at pressures in the range 1 – 11 bar were investigated. To achieve the most stable and reliable LIBS F/A ratio measurements at elevated pressures, the experimental parameters, including camera gate delay (hereafter referred to as T_{delay}) and input laser energy, were optimized at each pressure condition.

The LIBS measurement is strongly dependent on the temporal evolution of the emission spectrum from the laser-induced optical breakdown. Figure 2.2 shows the temporal evolution of the plasma emission spectra from LIBS at three different pressures--1 bar, 6 bar, and 11 bar--with input laser energy of 50 mJ/pulse and 150 mJ/pulse. The spectra presented in Fig. 2.2 were collected with a gate width of 20 ns for each of T_{delay} . Each spectrum was averaged over 100 laser

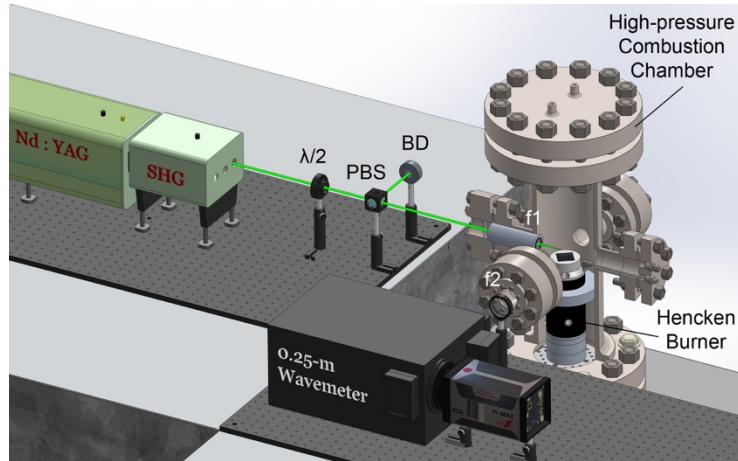


Figure 2.1: Schematic view of experimental setup for LIBS measurements of F/A ratio in a high-pressure combustion chamber. SHG: second-harmonic generator; $\lambda/2$: half-wave plate; PBS: polarized beam splitter; BD: beam dump; f_1 , f_2 : convex lenses.

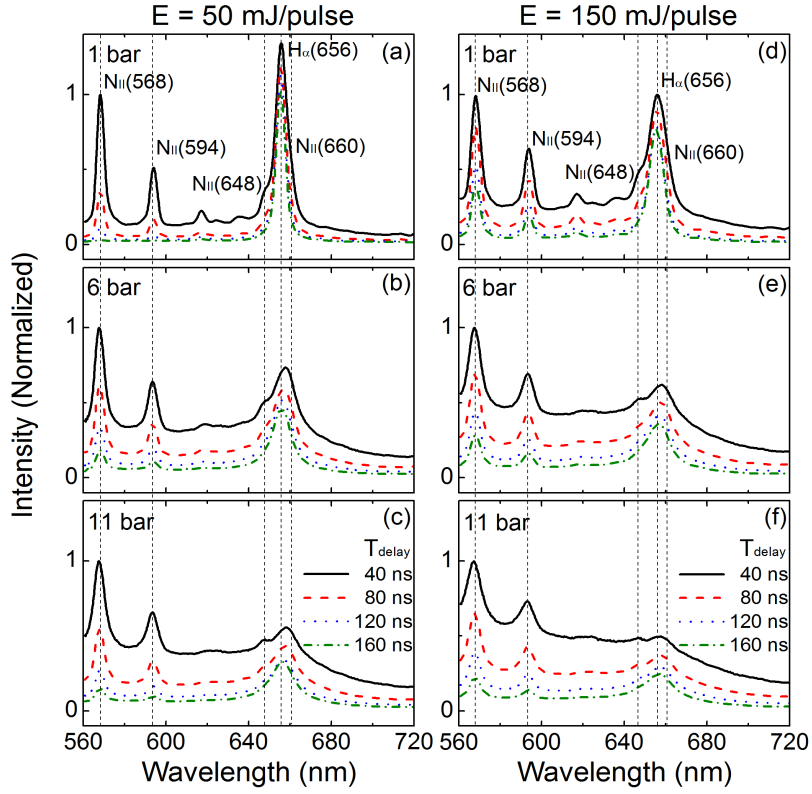


Figure 2.2: LIBS spectra obtained in laminar flame with $\phi = 1$ at 1 bar, 6 bar, and 11 bar using laser energy of 50 mJ/pulse and 150 mJ/pulse.

shots. Because of higher selectivity of the N_{II} line in the signal, compared to the N_I or O_I lines, the N_{II} (568-nm) and $H\gamma$ (656-nm) lines were selected for F/A ratio measurements. Note that the primary source of doubly ionized N (i.e., N_{II}) is gas breakdown, unlike in the case of the other two ions that could be produced by varieties of other dynamic processes. For example, ionization, electron recombination, and plasma quenching can contribute to N_I and O_I signals. Furthermore, the longer lifetime atomic and ionic lines are affected by multiple physical processes that are primarily stochastic in nature and, hence, are difficult to interpret for quantitative measurement.

Clearly, the emission spectra varied considerably with input laser energy, T_{delay} , and pressure. The spectra shown in Fig. 2.2 indicate that the overall intensity of the plasma emission decreases with an increase in T_{delay} . Therefore, the use of a short T_{delay} is advantageous for achieving a higher signal. Also, note that the signal is generated from the emission of atomic and molecular species; however, to uniquely assign the observed spectroscopic signal to any one of the various competing processes is not straightforward. Hence, to minimize the effect of the number of processes that affect the signal, the spectroscopic measurement at earlier delays is more suitable for accurate determination of concentrations, as observed in Fig. 2.2 for short T_{delay} . Nevertheless, T_{delay} must be optimized to avoid the broadband thermal radiation from plasma and permit the atomic emission lines to be extracted. Additionally, Fig. 2.2 shows that the $H\gamma$ (656 nm) lineshape is asymmetric at early delays. These results are from the overlapping of the nearby N_{II} emission lines at 648 nm and 660 nm. At higher pressure the effect is even more pronounced. It can be observed that the lineshape returns to being symmetric at $T_{\text{delay}} \sim 80$ ns. Therefore, to minimize the unwanted optical interference to the H line, a T_{delay} after 80 ns is preferred. Note that the background broadband emission is much larger for the high-pressure condition.

The LIBS emission signals vary with input laser energy and T_{delay} ; therefore, to reduce the fluctuations in the H/N ratio and optimize the stability of the measurement, the effects of laser energy and T_{delay} on the H/N ratio were

investigated. The LIBS experiment was performed at laser energies of 50, 75, 100, and 150 mJ per pulse for pressures of 1 bar, 6 bar, and 11 bar. Figure 2.3 shows the effect of laser energy and T_{delay} on the stability of the H/N value for the 1-bar and 11-bar cases. Each dot in the plot corresponds to single-shot data of the H/N ratio for a specific T_{delay} , pressure, and laser energy. Note that the plotted H_{λ} (656 nm) and N_{II} (568 nm) line peak intensities are corrected from the background, i.e., the contribution of the continuum from the broadband plasma emission at the selected atomic emission line is removed.

The data show a large spread of single-shot data at 1 bar, with 50-mJ laser energy indicating that the energy is insufficient to provide stable optical breakdown for LIBS at atmospheric pressure. The observed high fluctuation for the 50-mJ/pulse case after an 80-ns delay is attributed to extremely weak nitrogen emission. Hence, at atmospheric pressure, higher energy is preferred to provide stable F/A ratio measurements. In contrast, measurement stability decreases with an increase in input energy for high-pressure conditions. Such higher instability with higher laser energy could result from dense plasma generation and a high soot level at higher pressure (see Sect. 4 for a detailed discussion). Therefore, at high-pressure conditions, lower laser energy is preferable for stable and precise F/A ratio measurements. Note that a shorter gate delay T_{delay} produces higher stability in the H/N ratio.

The effects of laser pulse energy on the H/N peak intensity ratio at elevated pressure are shown in Fig. 2.4. For the measurements in atmospheric pressure with $T_{\text{delay}} \sim 40$ ns, the H/N peak intensity ratio becomes nearly constant when the laser energy exceeds 100 mJ/pulse. Such saturation-like behavior of the H/N ratio is also observed for the 80-ns T_{delay} in Fig. 2.4(b). Furthermore, it is observed that at higher pressure, the ratio is less sensitive to the laser pulse energy, particularly at longer T_{delay} . However, the fluctuation of the ratio increases with T_{delay} because of the short emission lifetime of the N_{II} line.

For determination of the optimal laser energy and T_{delay} parameters for stable LIBS F/A ratio measurements at each pressure, the fluctuation of the H/N

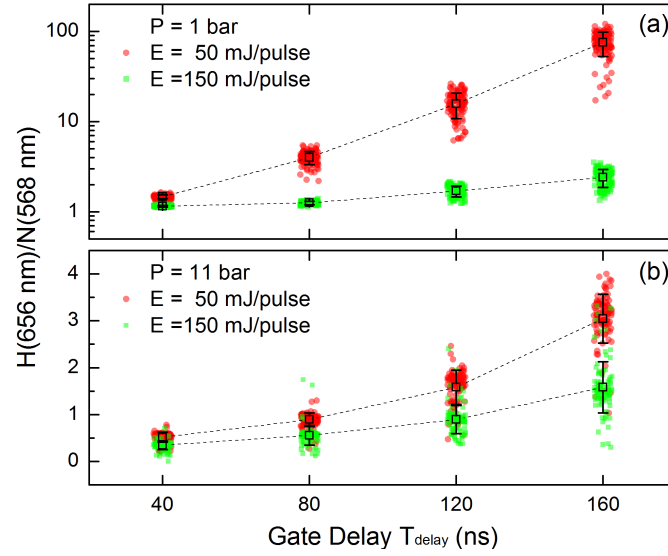


Figure 2.3: Peak-intensity ratio of H_{656}/N_{568} as function of T_{delay} for laser energies of (a) 50 mJ/pulse and (b) 150 mJ/pulse. For each condition 100 data points are presented. Methane-air flame was set at equivalence ratio of $\phi = 1$. Error bar represents one standard deviation.

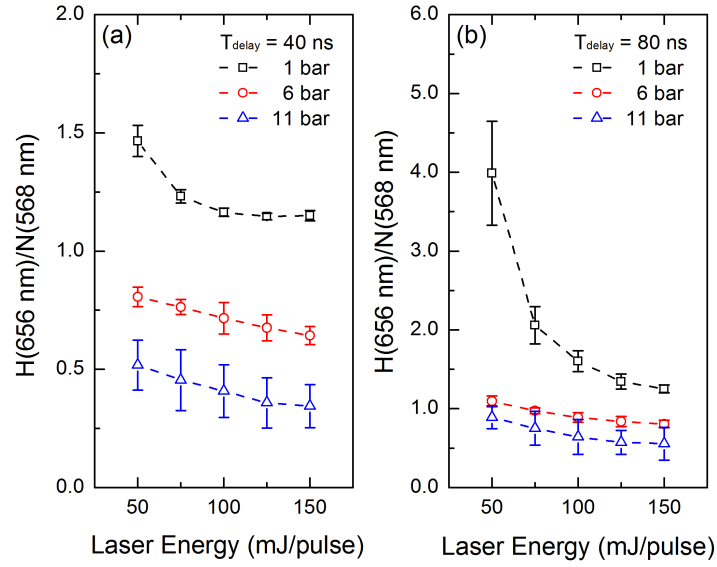


Figure 2.4: Peak-intensity ratio of H/N as a function of laser pulse energy for pressure of 1, 6, and 11 bar. Data were obtained using T_{delay} of 40 ns (a) and 80 ns (b). Methane-air flame was set at equivalence ratio of $\phi = 1$. Error bar represents one standard deviation.

peak intensity for all of the cases is shown in Fig. 2.5. The results indicate that the optimal laser energies for stable LIBS measurements (for 50-mm focal lens) at pressures of 1, 6, and 11 bars are 150 mJ/pulse, 100mJ/pulse, and 50 mJ/pulse, respectively. The optimal T_{delay} for all of the pressure cases is ~ 80 ns. Again, the measurement precision is better for high (low) laser energy in low- (high-) pressure conditions. An 80-ns T_{delay} is preferred to avoid the aforementioned optical interference in the H γ line at early delay.

Based on the above parametric studies for stable LIBS-based F/A ratio measurements, we selected the optimal laser energy and T_{delay} parameters for methane-air flames at each pressure; the calibration curve for H/N as a function of equivalence ratio ϕ is shown in Fig. 2.6. Although higher signal stability and improved precision were achieved with the use of optimal parameters, fluctuations were still higher at elevated-pressure conditions, which could result from denser plasma, higher soot levels at high pressure, and overheating of the medium. For methane-air flames, soot concentration is proportional to (pressure)ⁿ, where n is $\sim 1.7 \pm 0.7$ within the pressure range 1–10 bar [23]. In Fig. 2.6 it can also be observed that the fluctuation increases with equivalence ratio, which may be due to the soot levels being high in the fuel-rich conditions. When optimal laser energy and T_{delay} for the atmospheric-pressure condition were used, both measurement sensitivity and precision significantly decreased with an increase in pressure. Such pressure-dependent test conditions for optimal sensitivity and precision could be problematic for measurements in gas-pressure-varying combustion facilities such as Otto four-stroke engines.

Analysis of Pressure Dependence

All results presented in the previous section clearly indicate that the stability, sensitivity, and precision of N/H ratio is strongly dependent on the pressure condition. Therefore, further study is required for analyzing the pressure dependence. Physically, the higher the pressure, the smaller the mean free path between the molecular species in the target volume, which increases collision

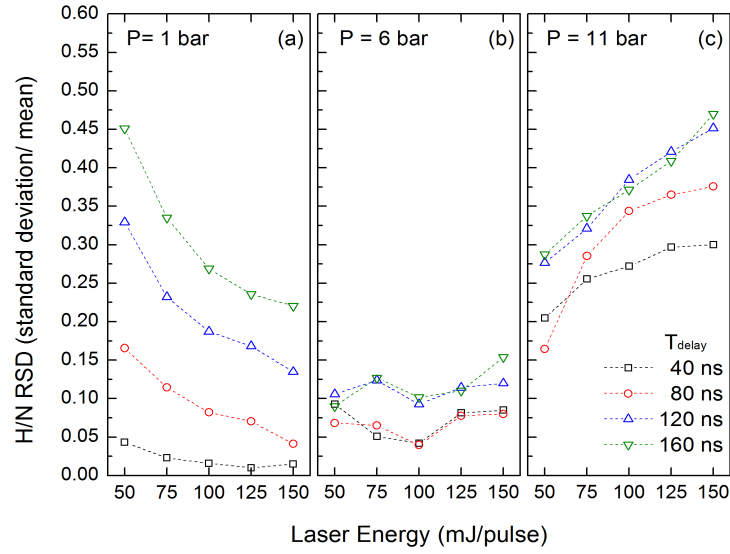


Figure 2.5: Fluctuation of LIBS F/A-ratio measurements at a given input laser energy and T_{delay} for pressures of 1, 6, and 11 bar. Methane-air flame was set at equivalence ratio of $\phi = 1$. Relative standard deviation (RSD) = standard deviation/mean.

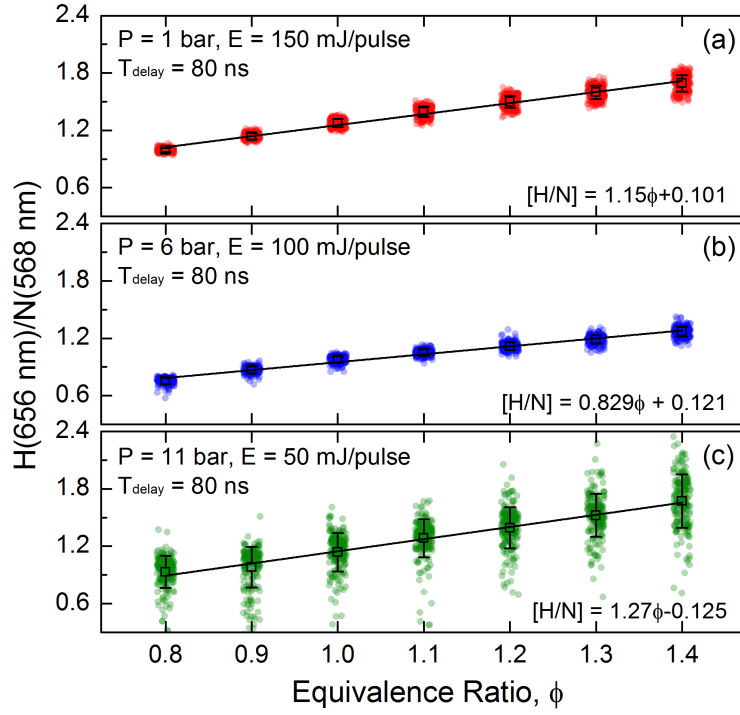


Figure 2.6: Correlation of H_{656}/N_{568} as a function of ϕ measurement at a time delay of 80 ns and laser energies of 150 mJ/pulse, 100 mJ/pulse, and 50 mJ/pulse for pressures of 1, 6, and 11 bar, respectively. Symbols denote experimental measurements; solid lines are linear fits. Error bar represents one standard deviation.

frequency between the electrons and molecules. Hence, in a high-pressure condition, the initial multiphoton-ionization-generated seed electrons are being accelerated by the laser pulse to generate the cascade or avalanche ionization through collisions with even lower pulse energies than those used in the atmospheric condition. This leads to a lower threshold for laser-induced breakdown at elevated pressures and increased instability due to the stochastic avalanche ionization [24, 25]. Therefore, further analysis of optimization of the laser and detection parameters is necessary for different pressure conditions. In this section the focus is on the effect of pressure for all of the test conditions and how it affects the sensitivity, stability, and precision of F/A ratio measurements.

To aid the understanding of the gas breakdown and plasma emission at different pressures, 10 consecutive single-shot images of N II (568 nm) are plotted in Fig. 2.7(a) and Fig. 2.7(b) at 1 bar and 11 bar, respectively, for the same laser energy. Clearly, at 1 bar the shot-to-shot stability was very high compared to that for the 11-bar condition. When the pressure was increased, the inverse-bremsstrahlung process likely benefits from the increases number local number density, resulting in a more efficient avalanching process. Additionally, the presence of a high level of soot lowered the breakdown threshold and altered the laser-induced plasma property. For example, an increase in pressure by one order of magnitude increased the soot concentration by almost two orders of magnitude. This excess soot production is shown by the transient of the flame towards yellow emission wavelengths in Fig. 2.7.

This led to a higher level of background emission [see, for example, Fig. 2.2(c) and 2.2(f)]. Additionally, this caused enhanced avalanche ionization and, hence, expanded the breakdown region well beyond the width both in the longitudinal and the transverse directions of the laser beam at the focal point [Rayleigh length $\sim 150\ \mu\text{m}$ (longitudinal) and beam waist $\sim 50\ \mu\text{m}$ (transverse)]. Thus, at higher pressures the plasma became rather unstable, and the size and shape of the plasma distribution varied significantly from shot to shot. Note that the emission signals for both pressure conditions are normalized in Fig. 2.8.



Figure 2.7: Effect of pressure on the Hencken flame.

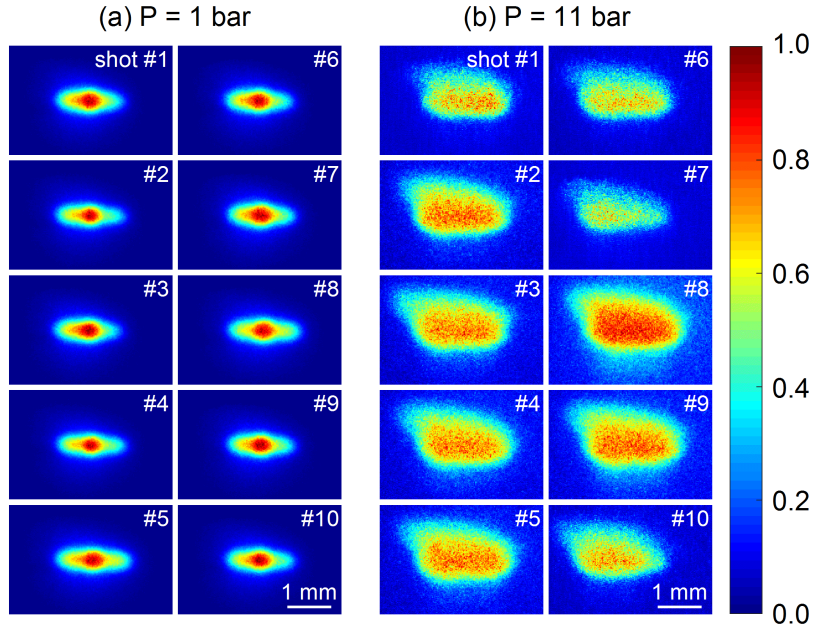


Figure 2.8: Ten consecutive single-shot images of atomic N_{II} emission from ns-LIB at P= 1 bar and 11 bar taken at $T_{\text{delay}} = 40$ ns. Laser energy used for LIB was 100 mJ/pulse. Methane-air flame was set at equivalence ratio of $\phi = 1$.

As observed in Fig. 2.4, the H/N ratio increases by several fold with one-order-of-magnitude increase in pressure because the chosen lines H_{656} and N_{568} have distinctly different pressure dependencies. As shown in Fig. 2.2, the $H_{\lambda}(656)$ line is strong at 1 bar but highly susceptible at elevated pressure conditions, whereas the $N_{II}(568)$ line retains a higher value even at high pressures. These asymmetric responses to the pressure for the two lines are key to the stability, sensitivity, and precision of the F/A ratio measurement at high-pressure conditions. To obtain a pressure scaling, the peak of the H/N ratio as a function of pressure was plotted in Fig. 2.9. The H/N ratio decreases two to three times with an-order-of-magnitude increase in pressure for $T_{\text{delay}} = 40$ ns. A similar trend is observed at higher density (not shown here), but at lower pressure the fluctuation is higher than that for $T_{\text{delay}} = 40$ ns. It is concluded that with proper calibration, this method may be useful for measuring pressure.

To finally consolidate the findings of the quantitative study of the stability and precision of the ns-LIBS-based F/A ratio measurements, the mean value and RSDs of the H/N ratio data were tabulated in Table 2.1 for different pressure and equivalence-ratio conditions. Clearly, at atmospheric pressure the F/A ratio results in higher precision for low ϕ and at higher pressure no specific trend in the precision is observed. The ns-LIBS-based F/A ratio measurement results are precise within 2 to 5% for atmospheric conditions and vary within 15 to 22% for elevated pressure at 11 bar.

Summary and Conclusions

The sensitivity, stability, and precision of ns-LIBS-based F/A ratio measurement in well-premixed, laminar methane-air flames under pressure conditions varying from 1 bar to 11 bar were studied. A parametric study for a variety of equivalence ratios, laser energies, and camera gate delays was conducted to determine the optimal conditions for different pressures.

Specifically, the findings can be summarized as follows:

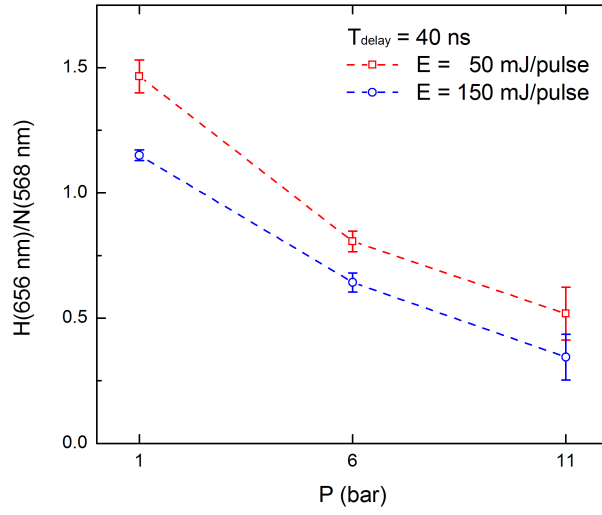


Figure 2.9: H/N peak-intensity ratio as a function of pressure with input energies of 50 mJ/pulse and 150 mJ/pulse. Data were obtained using T_{delay} of 40 ns (a) and 80 ns (b). Methane-air flame was set at equivalence ratio of $\phi = 1$.

Table 2.1: Mean value and *RSD* of H/N value obtained from optimized ns-LIBS measurements presented in Fig. 2.6.

ϕ	P = 1 bar		P = 6 bar		P = 11 bar	
	Mean	<i>RSD</i> [%]	Mean	<i>RSD</i> [%]	Mean	<i>RSD</i> [%]
0.8	1.00	2.1	0.76	4.4	0.93	18.0
0.9	1.14	2.8	0.87	4.0	0.98	21.8
1.0	1.28	3.2	0.98	3.6	1.14	17.7
1.1	1.39	3.9	1.05	3.0	1.28	15.5
1.2	1.50	4.3	1.12	3.7	1.39	15.5
1.3	1.60	4.5	1.19	3.8	1.52	14.8
1.4	1.69	5.1	1.27	4.2	1.67	16.7

1. The optimal gate delay for all the pressure cases is ~ 80 ns, which precludes optical interferences from broadband plasma emissions and N_{II} (648) and N_{II} (660) lines and maintains high stability in the H/N ratio.
2. The measurement precision is better for high (low) laser energy in low- (high-) pressure conditions, which balances plasma stability at different pressures with emission intensities.
3. The optimal laser energies for F/A ratio measurements using H_{656}/N_{568} as a function of ϕ measurement at a time delay of 80 ns are 150 mJ/pulse, 100 mJ/pulse, and 50 mJ/pulse with a lens of 100-mm focal length for pressures of 1, 6, and 11 bar, respectively.
4. Both the stability and the precision of ns-LIBS measurements of the F/A ratio decrease with an increase in pressure.
5. The H/N ratio value can be also used to determine pressure with a proper calibration.

The primary cause of greater instability at elevated pressure is the longer interaction by the ns lasers, which causes the unstable avalanche process and the presence of a higher concentration of soot particulates. Since the avalanche breakdown process dominates the ns-LIBS signal, the H/N measurement is relatively unstable. However, if a shorter laser pulse were used in the target volume, the inverse-Bremsstrahlung-mediated cascaded collisions would be reduced [24, 25] and, hence, the stability of the H/N measurement increased. Hence, shorter-pulse-duration LIBS measurement may be more suitable in increasing the stability of F/A ratio measurements.

References

1. S. Musazzi and U. Perini (Eds.), *Laser-Induced Breakdown Spectroscopy*, (Springer-Verlag, Berlin Heidelberg 2014).
2. T. X. Phuoc and F. P. White, "Laser-induced spark for measurements of the fuel-to-air ratio of a combustible mixture," *Fuel* **81**, 1761-1765 (2002).
3. P. Stavropoulos, A. Michalakou, G. Skevis, and S. Couris, "Laser-induced breakdown spectroscopy as an analytical tool for equivalence ratio measurement in methane–air premixed flames," *Spectrochim. Acta Part B* **60**, 1092-1097 (2005).
4. P. Stavropoulos, A. Michalakou, G. Skevis, and S. Couris, "Quantitative local equivalence ratio determination in laminar premixed methane-air flames by laser induced breakdown spectroscopy (LIBS)," *Chem. Phys. Lett.* **404**, 309-314 (2005).
5. F. Ferioli, S. and G. Buckley, "Measurements of hydrocarbons using laser-induced breakdown spectroscopy," *Combust. Flame* **144**, 435-447 (2006).
6. T. X. Phuoc, "Laser-induced spark for simultaneous ignition and fuel-to-air ratio measurements," *Opt. Lasers Eng.* **44**, 520-534 (2006).
7. A. Michalakou, P. Stavropoulos, and S. Couris, "Laser-induced breakdown spectroscopy in reactive flows of hydrocarbon–air mixtures," *Appl. Phys. Lett.* **92**, 081501 (2008).
8. H. Do and C. Carter, "Hydrocarbon fuel concentration measurement in reacting flows using short-gated emission spectra of laser induced plasma," *Combust. Flame* **160**, 601-609 (2013).
9. F. Ferioli, P. V. Puzinauskas, and S. G. Buckley, "Laser-induced breakdown spectroscopy for online engine equivalence ratio measurements," *Appl. Spectrosc.* **57**(9), 1183-1189 (2003).
10. L. Zimmer and S. Tachibana, "Laser induced plasma spectroscopy for local equivalence ratio measurements in an oscillating combustion environment," *Proc. Combust. Inst.* **31**, 737-745 (2007).

11. L. Zimmer, K. Okai, and Y. Kurosawa, "Combined laser induced ignition and plasma spectroscopy: fundamentals and application to a hydrogen-air combustor," *Spectrochim. Acta B* **62**, 1484-1495 (2007).
12. S. Joshi, D. B. Olsen, C. Dumitrescu, P. V. Puzinauskas, and A. P. Yalin, "Laser-induced breakdown spectroscopy for in-cylinder equivalence ratio measurements in laser-ignited natural gas engines," *Appl. Spectrosc.* **63**, 549-554 (2009).
13. M. Buschbeck, F. Buchler, T. Halfmann, and S. Arndt, "Laser-induced breakdown spectroscopy for lambda quantification in a direct-injection engine," *Spectrochim. Acta B* **74-75**, 103-108 (2012).
14. S. B. Han and Y. J. Chung, "The influence of air-fuel ratio on combustion stability of a gasoline engine at idle," SAE paper 1999-01-1488 (1999).
15. T. Lieuwen and V. Yang, *Combustion Instabilities in Gas Turbine Engines, Progress in Astronautics and Aeronautics, Vol. 210* (American Institute of Aeronautics and Astronautics, Reston, VA, 2005).
16. M. M. Tripathi, K. K. Srinivasan, S. R. Krishnan, F. Y. Yueh, and J. P. Singh, "A comparison of multivariate LIBS and chemiluminescence-based local equivalence ratio measurements in premixed atmospheric methane-air flames," *Fuel* **106**, 318-326 (2013).
17. J. Kiefer, J. W. Tröger, Z. S. Li, and M. Aldén, "Laser-induced plasma in methane and dimethylether for flame ignition and combustion diagnostics," *Appl. Phys. B* **103**, 229-236 (2011).
18. J. Kiefer, J. W. Tröger, Z. S. Li, M. Aldén, and A. Leipertz, "Laser-induced breakdown flame thermometry," *Combust. Flame* **159**, 3576-3582 (2012).
19. J. Kiefer, B. Zhou, Z. S. Li, and M. Aldén, "Impact of plasma dynamics on equivalence ratio measurements by laser-induced breakdown spectroscopy," *Appl. Opt.* **54**, 4221 (2015).
20. H. L. Xu, A. Azarm, J. Bernhardt, Y. Kamali, and S. L. Chin, "The mechanism of nitrogen fluorescence inside a femtosecond laser filament in air," *Chem. Phys.* **360**, 171-175 (2009).

21. S. L. Chin, T. J. Wang, C. Marceau, J. Wu, J. S. Liu, O. Kosareva, N. Panov, Y. P. Chen, J. F. Daigle, S. Yuan, A. Azarm, W. W. Liu, T. Seideman, H. P. Zeng, M. Richardson, R. Li, and Z. Z. Xu, "Advances in intense femtosecond laser filamentation in air," *Laser Phys.* **22**, 1-53 (2011).
22. S. L. Chin, "From multiphoton to tunnel ionization," in *Advances in Multiphoton Processes and Spectroscopy* (S. H. Lin, A. A. Villaeys, and Y. Fujimura, Eds.), (World Scientific, Singapore, 2004), Vol. 16, pp. 273-306.
23. L. M. Miller and H. G. Maahs, "High-pressure flame systems for pollutions studies with results for methane-air diffusion flames," TN D-8407, NASA 2007.
24. H. L. Xu and S. L. Chin, "Review: remtosecond laser filamentation for atmospheric sensing," *Sensors* **11**, 32-53 (2011).
25. Y. Wu, J. C. Sawyer, L. Su, and Z. Zhang, "Quantitative measurement of electron number in nanosecond and picosecond laser-induced air breakdown," *Journal of Applied Physics* **119**, 173303 (2016).

CHAPTER III
COMPARISON STUDY OF TIME-GATED NANO-, PICO-, AND
FEMTOSECOND LASER-INDUCED BREAKDOWN
SPECTROCOPY FOR FUEL-TO-AIR RATIO MEASUREMENTS IN
METHANE-AIR FLAMES

Abstract

Laser-induced breakdown spectroscopy (LIBS) with various laser pulses is used for local equivalence ratio measurements in an atmospheric methane-air Hencken flame. The goal is to determine if any significant advantage exists for ultrashort pulses when applied to high-pressure combustion measurements. Results indicate that while nanosecond duration pulses give the best sensitivity and precision for equivalence ratio determination, femtosecond pulses provide similar precision and sensitivity, but the femtosecond spectra have less continuum background emission, which is a favorable trait for high-pressure conditions. Picosecond pulses are also found to provide the worst sensitivity and precision of the three types of pulses investigated.

Introduction

Laser induced breakdown spectroscopy (LIBS) is a simple and straightforward technique that makes use of light focused onto a small sample or probe volume to create a plasma, which has an emission spectrum that gives detailed information about the elemental composition of the sample. Furthermore, LIBS is a highly favored technique for applied spectroscopy due to its relatively simple setup and strong signal.

Because of its strong signal, LIBS has become a common tool for combustion analysis, particularly for local fuel-to-air ratio (FAR) measurements [1-4]. Several studies have shown that various elemental emission ratios (e.g. H/N, H/O, C/N) have a linear relationship with the fuel to air ratio in laminar flames [3, 5, 6]. Many of these studies use camera gate and delay times on the order of microseconds to allow the continuum radiation of the plasma to subside and increase the signal to noise ratio [7]. It is also necessary to allow enough time for the laser induced plasma to achieve local thermodynamic equilibrium (LTE), so that Boltzmann statistics and the Saha equation are suitable for describing plasma [8-10]. However, short gated LIBS, which uses measurements in the nanosecond

domain, has been successful for fuel to air ratio measurements in methane flames [1, 2].

Most of the previous work done with LIBS for fuel-to-air ratio measurements has been conducted with pulse lasers operating with nanosecond pulse widths. However, the advancement of laser technology has made picosecond and femtosecond pulsed lasers more widely available. It is then necessary to understand how FAR measurements with LIBS are impacted by the laser pulse width. Work done by Kotzagianni and Couris [11, 12] has already shown that it is possible to extract information about fuel mole fractions in flames using femtosecond lasers.

For nanosecond pulsed lasers, focused laser light generates seed electrons through multiphoton ionization [13]. The seed electrons are then energized by through inverse-bremsstrahlung and liberate other bound electrons via collisions, which are also then energized by inverse-bremsstrahlung. This ionization process, electron avalanching, continues until a plasma forms, which will then expand and cool. For a typical ns pulse, most of the breakdown process is complete before the end of the pulse and the remaining portion of the pulse simply contributes to heating the plasma. If the laser pulse is shorter than the mean collision time between free electrons and bound electrons, then the avalanching process cannot proceed. Thus, for shorter pulses (i.e. picosecond and femtosecond), electron avalanching is reduced and a cooler plasma is produced. The effects of pulse width and laser wavelength on LIBS have been well documented, showing that shorter pulses do indeed reduce the total free electron number of the LIBS plasma [14, 15]. The reduction of the pulse width may be favorable for equivalence ratio measurements in sooty flames.

In this work, the linearity and precision of equivalence ratio determination from select elemental ratios is discussed for nano-, pico-, and femtosecond laser pulses. It is shown that the availability and background to signal ratio of elemental emission lines around the optical range is drastically different for short pulses (specifically fs-pulses) compared to nanosecond pulses, and thus a different

elemental emission line ratio is needed for each setup. The N_{II} (568 nm), H_{α} (656 nm), and O_I (777 nm) emission lines are given explicit attention since they are frequently used in literature for the equivalence ratio determination from LIBS.

Experiment Setup

A general rendering of the experiment setup is shown in Fig. 3.1. For the nanosecond laser induced breakdown experiments, a Nd:YAG laser (Spectra Physics 290) with pulse width of 10 ns operating at 532 nm with 10 Hz repetition rate was used. Laser energy was controlled via polarizing filter and was set to 150 mJ/pulse. The beam spot size was approximately ~9 mm. A 100 mm plano convex lens was used to focus the beam about 3.5 cm above the surface of a Hencken burner. The flow rate of the fuel and air, totaling to 9 SLPM, was controlled using a flow controller. LIBS emission spectra were collected using a 100 mm spherical lens to collimate the light and another 100 mm spherical lens to focus the light into a spectrometer (Princeton Instruments). A PI-Max4 ICCD was used to collect images of the spectra from the spectrometer. For picosecond LIBS, a Nd:YAG (Positive Light) laser with pulse width 100 ps and wavelength 532 nm at 10 Hz repetition rate was used. The energy was set to 45 mJ/pulse. The spot size of this laser was measured as ~8 mm. The femtosecond LIBS was done using a Ti:Sapphire (Astrella F1K) laser with pulse width of 100 fs, wavelength 800 nm, and with 1 kHz repetition rate. The laser energy was set to 4.5 mJ/pulse and the spot size was ~10 mm. A gate width of 20 ns was used for ns-LIBS, while 10 ns was used for ps- and fs-LIBS. This change in gate width for the shorter pulses accounts for the fact that the corresponding plasmas have much quicker emission decay times, which is shown in this work.

Results and Discussion

Emission Spectra and Temporal Characteristics

Because of the relatively long pulse width of nanosecond lasers, the

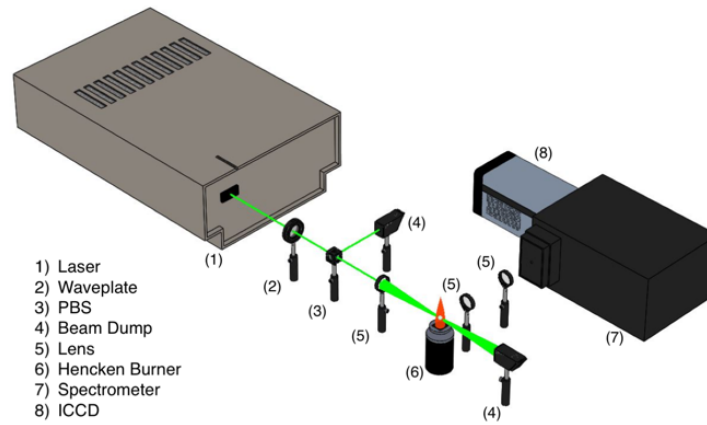


Figure 3.1. Generalized model of the experimental setup for local equivalence ratio determination with ns-, ps-, and fs-LIBS.

resulting LIBS plasma emission is very bright, with a considerable amount of continuum radiation at early times after breakdown. This is reflected in Fig. 3.2(a), which shows the emission spectra of the ns-LIBS plasma for various time delays between laser breakdown and data collection. For the nanosecond LIBS, the $N_{II}(568 \text{ nm})$ emission is very prominent at early times, while the hydrogen emission is convoluted by emission lines $N_{II}(648 \text{ nm})$ and $N_{II}(661 \text{ nm})$ on either side. $N_{II}(568 \text{ nm})$, $N_{II}(648 \text{ nm})$, and $N_{II}(661 \text{ nm})$, are all ionic emission lines and will cease fairly quickly as the plasma expands and cools. Furthermore, the $O_I(777 \text{ nm})$ emission shown in Fig. 3.2(a) has a very poor line to continuum ratio at nearly all time delays shown. Therefore, one would expect $H_\alpha(656 \text{ nm})/O_I(777 \text{ nm})$ to have large shot to shot variation due to the difficulty in subtracting the background emission near such a small peak, suggesting that $H_\alpha(656 \text{ nm})/N_{II}(568 \text{ nm})$ is better suited for equivalence ratio determination in the nanosecond case for short time delay measurements.

For ps-LIBS, $H_\alpha(656 \text{ nm})$ and $N_{II}(568 \text{ nm})$ are present, but $O_I(777 \text{ nm})$ is convoluted by continuum radiation and nearby lines as shown in Fig. 3.2(b). As in the nanosecond case, the $N_{II}(568 \text{ nm})$ and $H_\alpha(656 \text{ nm})$ emissions are very strong. Furthermore, $N_{II}(568 \text{ nm})$ again decays much quicker than the hydrogen 656 nm emission. Thus, $H_\alpha(656 \text{ nm})/N_{II}(568 \text{ nm})$ again seems better suited for extracting information about the equivalence ratio due to the strong signals of those two emission lines and the amount of continuum emission near the $O_I(777 \text{ nm})$ emission line. Note in general the continuum emission is much weaker than that seen in the nanosecond case.

The femtosecond spectrum shown in Fig. 3.2(c) drastically differs from the nanosecond and picosecond spectrum. Note that even for early delay times between breakdown and data collection, much less continuum radiation is present than for the nanosecond and picosecond case, which is likely due to the pulse being too short to cause an electron avalanche process. Therefore, the fs-LIBS plasma is likely a much cooler plasma. The lack of strong nitrogen ion emission

lines (e.g. $N_{II}(568 \text{ nm})$) also confirms the plasma is much cooler than the ns- and ps-LIBS plasma. Typically, the free electrons accelerated by the laser field aid in the production of ions inside the plasma through collision processes; however, the femtosecond laser pulse is too short for this process to occur. Furthermore, the fs-LIBS spectrum also has much less background around the $O_I(777 \text{ nm})$ emission line. Because of the extremely low $N_{II}(568 \text{ nm})$ emission, $H_{\alpha}(656 \text{ nm})/O_I(777 \text{ nm})$ seems best for the equivalence ratio determination with fs-pulse LIBS.

It is well documented that pulse width has a drastic effect on the lifetime of the LIBS plasma emission lines [8, 16]. The time resolved emissions of $N_{II}(568 \text{ nm})$, $H_{\alpha}(656 \text{ nm})$, and $O_I(777 \text{ nm})$ are explicitly shown in Fig. 3.3. For each case, the $H_{\alpha}(656 \text{ nm})$ emission decays more slowly than the $O_I(777 \text{ nm})$ and $N_{II}(568 \text{ nm})$ emissions. However, the nitrogen emission is considerably different for each of the pulse widths. In the nanosecond case, the $N_{II}(568 \text{ nm})$ emission intensity is reduced by a factor of two around 220 ns, whereas in the picosecond and femtosecond cases this occurs at 40 ns and 15 ns respectively. Note that Fig. 3.3 is consistent with the previous conclusion that the $H_{\alpha}(656 \text{ nm})/N_{II}(568 \text{ nm})$ emission line ratio is suitable for nanosecond and picosecond LIBS, while $H_{\alpha}(656 \text{ nm})/O_I(777 \text{ nm})$ is better for femtosecond LIBS. Specifically, in the nanosecond and picosecond cases, the nitrogen line emission is still strong before 100 ns, but in the femtosecond case, the nitrogen emission is considerably less after just 5 ns. The differences in the decay time of the $N_{II}(568 \text{ nm})$ emission are likely due to the contrasting electron densities and electron temperatures in each of the laser induced plasmas. If LTE conditions are valid, the electron temperature T_e is equal to the excitation temperature and can be estimated using the ratio of two emission lines from the same atomic species [10, 17]:

$$\frac{I_2}{I_1} = \frac{\lambda_1 g_2 A_2}{\lambda_2 g_1 A_1} \exp\left(-\frac{E_2 - E_1}{k_B T_e}\right) \quad (3.1)$$

I represents the emission intensity, λ is the peak wavelength of the emission line,

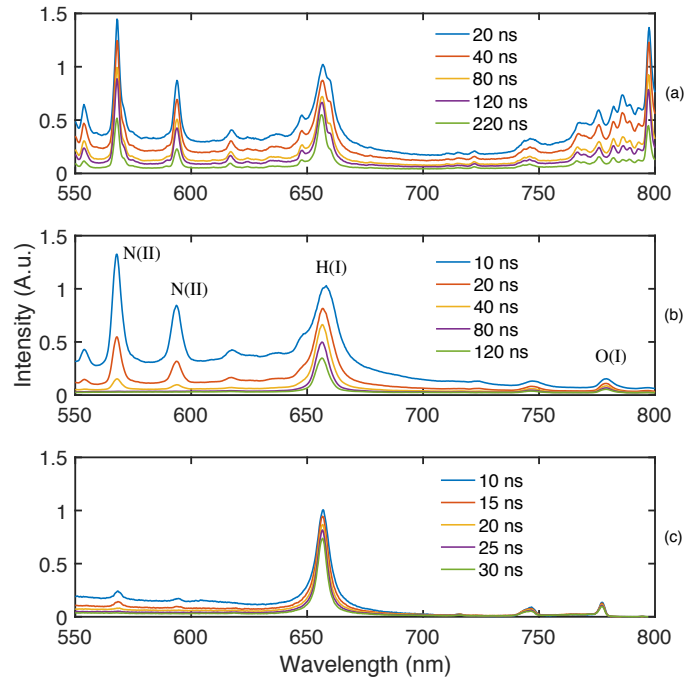


Figure 3.2: Time resolved spectra of LIBS in a methane-air flame with $\Phi = 1$ (normalized by 656 nm emission). (a) Nanosecond LIBS using Nd:YAG 532 nm output with pulse width of 10 ns and laser energy 150 mJ/pulse. (b) Picosecond LIBS using 532 nm output and pulse width of 100 ps and 45 mJ/pulse. (c) Femtosecond LIBS using Ti:Sapphire 800 nm output with 100 fs pulse width and 4.5 mJ/pulse. ($\Phi = 1$).

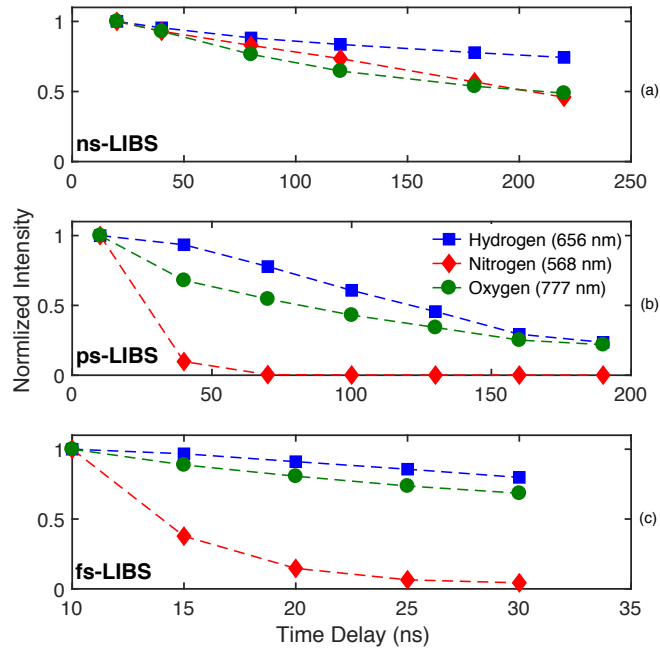


Figure 3.3: Background subtracted peak emission intensities (normalized) of $H\alpha$ (656 nm), NII (568 nm), and OI (777 nm) for various time delays. (a) Nanosecond LIBS using Nd:YAG 532 nm output with pulse width 10 ns and laser energy 150 mJ/pulse. (b) Picosecond LIBS using 532 nm output and pulse width 100 ps. (c) Femtosecond LIBS using Ti:Sapphire 800 nm output with 100 fs pulse width and 4.5 mJ/pulse. ($\Phi = 1$).

g is the degeneracy, A is the spontaneous Einstein emission coefficient, E is the energy of the excited state, and k_B is the Boltzmann constant. Typical errors for this method are about 10%.

The nitrogen ion emissions $N_{II}(568 \text{ nm})$ and $N_{II}(594 \text{ nm})$ were chosen for the electron temperature calculation, since they are present for the fs-LIBS spectrum at 10 ns. Figure 3.4 shows the results for the electron temperature calculation using Eq. 3.1. Note that compared to the nanosecond case, the picosecond and femtosecond plasmas are much cooler. Since the average kinetic energy of an electron can be taken to be proportional to T_e for LTE conditions, Fig. 3.4 shows that electrons in the ns-LIBS plasma are much more energetic than the electrons in the ps- and fs-LIBS plasma, which is likely due to inverse-bremsstrahlung interaction with the long laser pulse. Thus, the electrons in the LIBS plasma are more likely to create ionic species through collisions. Furthermore, the lack of nitrogen ion emission lines in the fs-spectrum can be explained by the relatively low temperature of the fs-LIBS plasma. Specifically, in LTE conditions the populations are distributed per Boltzmann statistics, and the probability P of an energy state E being populated is proportional to the Boltzmann factor, $P \propto \exp(-E/k_B T_e)$. Therefore, using the maximum electron temperatures in Fig. 3.4, the relative probabilities for the population of the excited state for the $N_{II}(568 \text{ nm})$ emission line are $P_{ns}/P_{fs} = 35.2$ and $P_{ps}/P_{fs} = 2.0$. Note, the LIBS peak emission intensity at LTE for a specific wavelength is approximately given by [3, 17, 18]:

$$I = N \frac{hcgA}{4\pi\lambda Z(T_e)} \exp\left(-\frac{E_{excited}}{k_B T_e}\right) \quad (3.2)$$

Here, h is Planck's constant, c is the speed of light in a vacuum, and $Z(T_e)$ is the partition function. Thus, Eq. 3.2 suggests that I_{fs} is about 35.2 times smaller than I_{ns} and 2.0 times smaller than I_{ps} for the $N_{II}(568 \text{ nm})$ emission line.

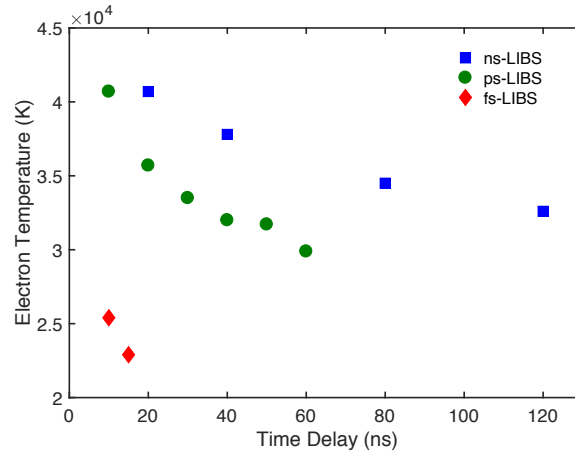


Figure 3.4: Electron temperatures for ns-, ps-, and fs-LIBS in a methane-air flame ($\Phi = 1$). Calculated with the line ratio method given Eq. 3.1 using the nitrogen ion emission lines at NII(568 nm) and NII(594 nm). Typical errors for this method are about 10%. Note that the assumption that similar lineshapes for the two spectral lines was used, so that peak intensities could be used instead of spectrally integrated intensities.

Therefore, because of the weakness of $N_{II}(568 \text{ nm})$ emission, for femtosecond LIBS measurements we expect $H_{\alpha}(656 \text{ nm})/O_I(777 \text{ nm})$ to give better calibration curve results, while for ps- and ns-LIBS we expect $H_{\alpha}(656 \text{ nm})/N_{II}(568 \text{ nm})$ to be more useful due to the strong intensity of the corresponding emissions. Figure 3.3 also suggests that shorter delay times are better for all three cases, especially for picosecond and femtosecond LIBS because of the rapid decay of emission intensity.

Finally, to choose an optimal time delay for each measurement, the time evolution of $H_{\alpha}(656 \text{ nm})/N_{II}(568 \text{ nm})$ and $H_{\alpha}(656 \text{ nm})/O_I(777 \text{ nm})$ were studied, as shown in Fig. 3.5. The goal was to determine a time such that the ratios would be less susceptible to jitter, while also having reasonable signal. Note that for the nanosecond case, $H_{\alpha}(656 \text{ nm})/N_{II}(568 \text{ nm})$ seems to be stable early, while $H_{\alpha}(656 \text{ nm})/O_I(777 \text{ nm})$ doesn't seem to plateau at any time. For ps-LIBS, earlier times seem favorable for $H_{\alpha}(656 \text{ nm})/N_{II}(568 \text{ nm})$ and $H_{\alpha}(656 \text{ nm})/O_I(777 \text{ nm})$. At time delays greater than 50 ns, the first ratio becomes very large due to the weakening of $N_{II}(568 \text{ nm})$ emission. This is consistent with the spectra in Fig. 3.2. Finally, for the femtosecond case, the $H_{\alpha}(656 \text{ nm})/N_{II}(568 \text{ nm})$ ratio is best measured early and $H_{\alpha}(656 \text{ nm})/O_I(777 \text{ nm})$ seems to be stable for all explored time delays. Again, this is consistent with the observed spectra in Fig. 3.2. Furthermore, since fs-LIBS has little to no continuum radiation, earlier time delays can be used to maximize signal to noise ratio. Thus, the time delays used for the measurements were 80 ns, 20 ns, and 10 ns for ns-, ps-, and fs-LIBS respectively.

Equivalence Ratio Determination

For all LIBS cases, it is expected that as the fuel to air ratio is increased, intensity of the $H_{\alpha}(656 \text{ nm})$ should increase with relative to $N_{II}(568 \text{ nm})$ emission intensity, and $O_I(777 \text{ nm})$ peak emission intensity. Figure 3.6 shows the effect of equivalence ratio on the spectra in each LIBS setup, while Fig. 3.7 shows the results for equivalence ratio determination from the line ratios. Again, the chosen

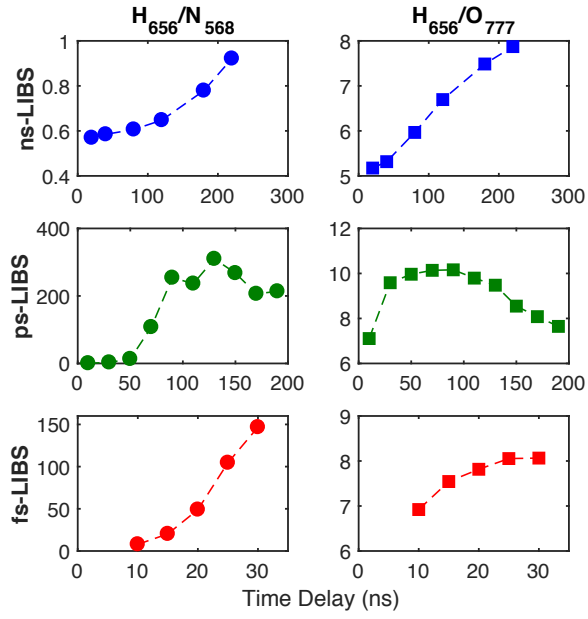


Figure 3.5: Time evolution of $H\alpha(656 \text{ nm})/NII(568 \text{ nm})$ and $H\alpha(656 \text{ nm})/OI(777 \text{ nm})$ for ns-, ps-, and fs-LIBS. ($\Phi = 1$).

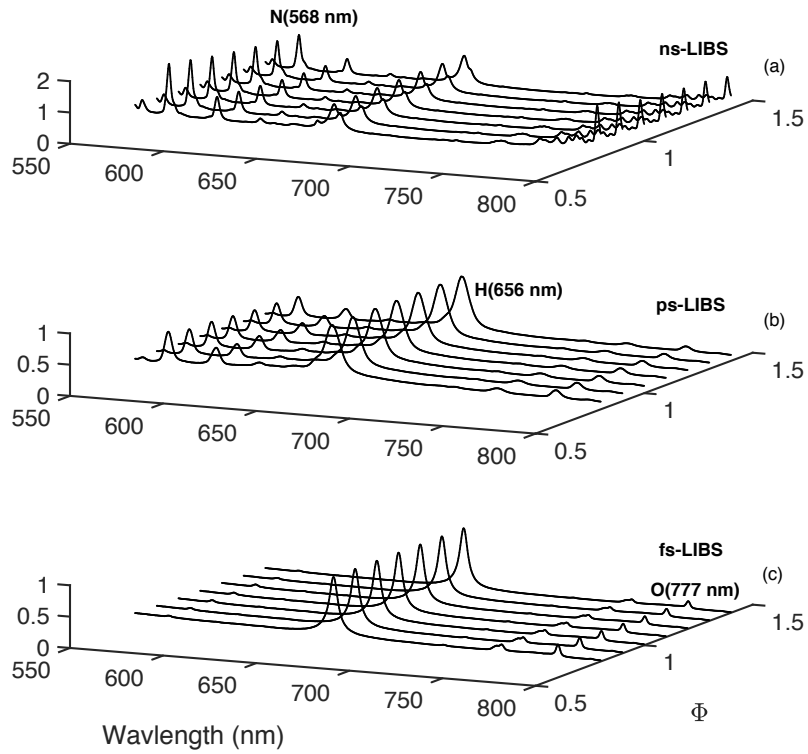


Figure 3.6: Emission spectra (each by normalized H α (656 nm) peak intensity) for various equivalence ratios. (a) ns-LIBS with time delay of 80 ns, and laser energy 150 mJ/pulse, and gate width of 20 ns (b) ps-LIBS with time delay of 30 ns , laser energy of 45 mJ/pulse, and gate width of 10 ns (c) fs-LIBS with time delay of 15 ns, laser energy of 4.5 mJ/pulse, and gate width 10 ns.

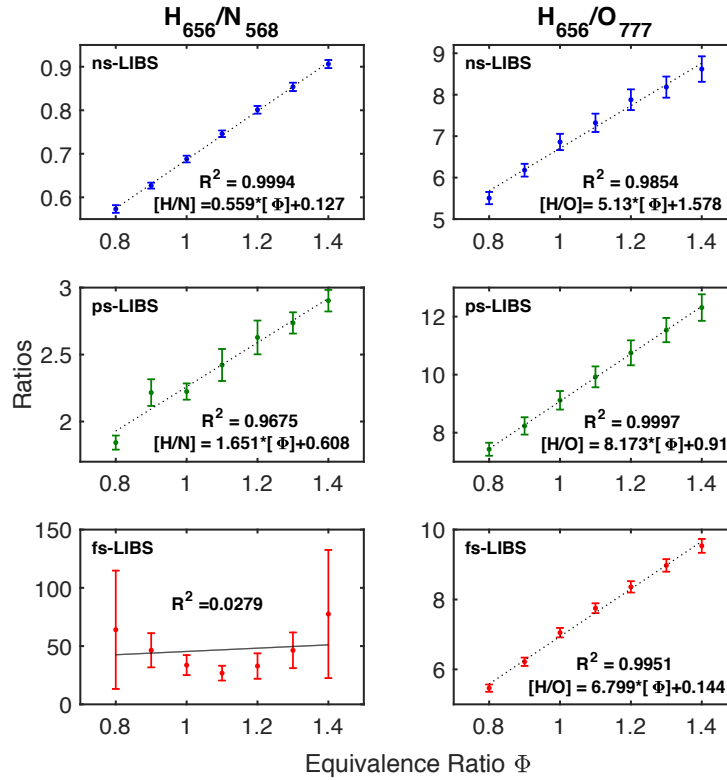


Figure 3.7: Calibration curves for obtaining the local equivalence ratio from emission line ratios. (a) Nanosecond LIBS using Nd:YAG 532 nm output with pulse width 10 ns and laser energy 150 mJ/pulse. (b) Picosecond LIBS using 532 nm output and pulse width of 100 ps. (c) Femtosecond LIBS using Ti:Sapphire 800 nm output with 100 fs pulse width and 4.5 mJ/pulse. Error bars are shown along with curve fit results (dotted line). 100 shots were used for each data point.

time delays for the measurements were 80 ns, 20 ns, and 10 ns for ns-, ps-, and fs-LIBS respectively. The gate widths were 20 ns for ns-LIBS and 10 ns for ps- and fs-LIBS. The delay times were chosen by considering the times in Fig. 3.2 that were associated with high signal to continuum ratio and times where the continuum was essentially stable. Furthermore, early times are chosen due to the strong dependence of the LIBS plasma emission lifetime on pulse width. As it was shown in Fig. 3.3, the emission lifetimes of the picosecond and femtosecond LIBS plasma are much shorter than the nanosecond case.

All experiments yielded at least one calibration curve with an excellent R-squared value. Picosecond LIBS gave the most linear data, but the error bars are larger than those shown for ns-LIBS and fs-LIBS, implying that error on the slope and intercept coefficient would be larger too. Furthermore, in all three cases the $H_{\alpha}(656 \text{ nm})/O_I(777 \text{ nm})$ gave a reasonable calibration curve, whereas the $H_{\alpha}(656 \text{ nm})/N_{II}(568 \text{ nm})$ ratio was only useful in ns- and ps-LIBS.

One key point of interest was to determine if changes in laser pulse width would offer any advantage for fuel rich conditions, since these conditions correspond to more soot production. Using the best calibration curves for each case, the relative standard deviation of the applied emission ratio was studied versus equivalence ratio, as shown in Fig. 3.8. In these terms, ns-LIBS generally offered the most accurate measurements, including for fuel rich conditions. Femtosecond gave the next best results and picosecond LIBS gave the least consistent results. For ns-LIBS, the $H_{\alpha}(656 \text{ nm})$ and $N_{II}(568 \text{ nm})$ emission lines are very strong compared to the background, which likely contributes to its accuracy. For pico- and femtosecond LIBS however, the $O_I(777 \text{ nm})$ emission is generally closer to the continuum background, which gives higher error. This is supported by the fact that the $H_{\alpha}(656 \text{ nm})/O_I(777 \text{ nm})$ has much larger error bars in Fig. 3.7, which is due to the smallness of the $O_I(777 \text{ nm})$ emission, as can be seen in Fig. 3.2.

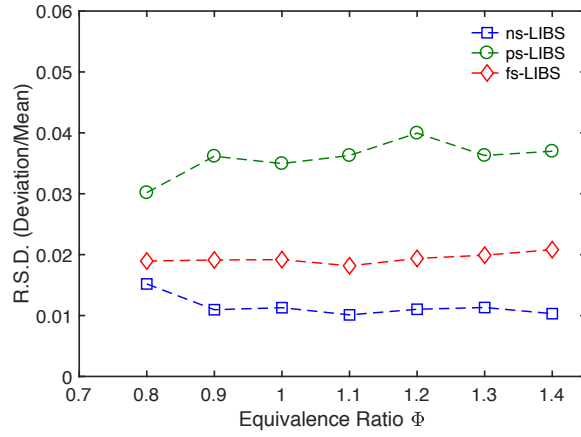


Figure 3.8: Relative standard deviation of emission ratios versus equivalence ratio for each laser case. Note that the best results from Fig. 7 were used, $H_{\alpha}(656 \text{ nm})/N_{II}(568 \text{ nm})$ for ns-LIBS and $H_{\alpha}(656 \text{ nm})/O_I(777 \text{ nm})$ for ps- and fs-LIBS.

Summary and Conclusions

In summary, nanosecond, picosecond, and femtosecond LIBS were shown to be capable of very accurate local equivalence ratio measurements using emission lines near the optical range. The emission spectra of ns- and ps-LIBS in methane air flame at standard pressure was shown to be very similar for nanosecond delay times over the range of 550 - 800 nm. However, fs-LIBS had much less continuum and was generally void of ionic nitrogen emission lines. It was shown that the differences in plasma electron temperature could be responsible for the lack of ion emissions. This conclusion is consistent with physical effects of pulse width on the breakdown dynamics. Though not demonstrated here, the lack of nitrogen ion emission lines could be advantageous in certain scenarios, such as high-pressure combustion diagnostics, where nitrogen ion lines can greatly interfere with the H_{α} (656 nm) emission; therefore, even though ns-LIBS gave the best linear trend, fs-LIBS is still promising for such applications, especially considering the associated lack of continuum radiation.

Acknowledgements

This work has been approved for public release by AFRL: (No. 88ABW-2017-5859).

References

1. H. Do and C. Carter, "Hydrocarbon fuel concentration measurement in reacting flows using short-gated emission spectra of laser induced plasma," *Combustion and Flame* **160**, 601-609 (2013).
2. P. S. Hsu, M. Gragston, Y. Wu, Z. Zhang, A. K. Patnaik, J. Kiefer, S. Roy, and J. R. Gord, "Sensitivity, stability, and precision of quantitative Ns-LIBS-based fuel-air-ratio measurements for methane-air flames at 1–11 bar," *Appl. Opt.* **55**, 8042-8048 (2016).
3. T. X. Phuoc, "Laser-induced spark for simultaneous ignition and fuel-to-air ratio measurements," *Optics and Lasers in Engineering* **44**, 520-534 (2006).
4. J. W. Lewis, Y.-L. Chen, J. O. Hornkohl, and C. Parigger, "Laser-induced Optical Breakdown Measurements to Evaluate Fuel/Oxygen Mixing," in *Laser Applications to Chemical, Security and Environmental Analysis*, Technical Digest (Optical Society of America, 2006), PDP_10.
5. J. Kiefer, J. W. Tröger, Z. Li, T. Seeger, A. Leipertz, and M. Alden, "Laser-induced Breakdown Spectroscopy: A Simple but Versatile Tool for Combustion Diagnostics," in *Lasers, Sources, and Related Photonic Devices*, OSA Technical Digest (CD) (Optical Society of America, 2012), LM5B.2.
6. J. Kiefer, J. W. Tröger, Z. S. Li, and M. Aldén, "Laser-induced plasma in methane and dimethyl ether for flame ignition and combustion diagnostics," *Applied Physics B* **103**, 229-236 (2011).
7. J. Kiefer, B. Zhou, Z. Li, and M. Aldén, "Impact of plasma dynamics on equivalence ratio measurements by laser-induced breakdown spectroscopy," *Appl. Opt.* **54**, 4221-4226 (2015).
8. D. W. Hahn and N. Omenetto, "Laser-Induced Breakdown Spectroscopy (LIBS), Part I: Review of Basic Diagnostics and Plasma–Particle Interactions: Still-Challenging Issues Within the Analytical Plasma Community," *Appl. Spectrosc.* **64**, 335A-366A (2010).

9. C. Aragón and J. A. Aguilera, "Characterization of laser induced plasmas by optical emission spectroscopy: A review of experiments and methods," *Spectrochimica Acta Part B: Atomic Spectroscopy* **63**, 893-916 (2008).
10. G. Cristoforetti, A. De Giacomo, M. Dell'Aglio, S. Legnaioli, E. Tognoni, V. Palleschi, and N. Omenetto, "Local Thermodynamic Equilibrium in Laser-Induced Breakdown Spectroscopy: Beyond the McWhirter criterion," *Spectrochimica Acta Part B: Atomic Spectroscopy* **65**, 86-95 (2010).
11. M. Kotzagianni and S. Couris, "Femtosecond laser induced breakdown for combustion diagnostics," *Applied Physics Letters* **100**, 264104 (2012).
12. S. Couris, M. Kotzagianni, A. Baskevicius, T. Bartulevicius, and V. Sirutkaitis, "Combustion Diagnostics with Femtosecond Laser Radiation," *Journal of Physics: Conference Series* **548**, 012056 (2014).
13. C. G. Morgan, "Laser-induced breakdown of gases," *Reports on Progress in Physics* **38**, 621 (1975).
14. Y. Wu, J. C. Sawyer, L. Su, and Z. Zhang, "Quantitative measurement of electron number in nanosecond and picosecond laser-induced air breakdown," *Journal of Applied Physics* **119**, 173303 (2016).
15. R. Tambay and R. K. Thareja, "Laser-induced breakdown studies of laboratory air at 0.266, 0.355, 0.532, and 1.06 μm ," *Journal of Applied Physics* **70**, 2890-2892 (1991).
16. M. Sabsabi, "Chapter 7 - Femtosecond LIBS A2 - SINGH, JAGDISH P," in *Laser-Induced Breakdown Spectroscopy*, S. N. Thakur, ed. (Elsevier, Amsterdam, 2007), pp. 151-171.
17. H. R. Griem, *Principles of Plasma Spectroscopy*, Cambridge Monographs in Plasma Physics (Cambridge University Press, 2005, 2005), p. 366.
18. V. N. Rai and S. N. Thakur, "Chapter 4 - Physics of Plasma in Laser-Induced Breakdown Spectroscopy," in *Laser-Induced Breakdown Spectroscopy* (Elsevier, Amsterdam, 2007), pp. 83-111.

CHAPTER IV
SEE-THROUGH-WALL MOLECULAR OXYGEN ROTATIONAL
TEMPERATURE MEASUREMENT IN A FLOW REACTOR AND
WELL-STIRRED REACTOR

Versions of this chapter were originally published by Mark Gragston, Yue Wu, Zhili Zhang, Joseph Miller, Robert D. Stachler, Scott Stouffer, and Joshua Heyne:

Mark Gragston¹, Yue Wu¹, Zhili Zhang¹, Robert D. Stachler², Joshua Heyne², Scott D. Stouffer³, and Joseph D. Miller⁴. “See-through-wall Radar REMPI for Spatially Localized Temperature Measurements in a Well-Stirred Reactor.” 55th *AIAA Aerospace Sciences Meeting, AIAA SciTech Forum*, (AIAA 2017-0384)

Yue Wu¹, Mark Gragston¹, Zhili Zhang¹, and Joseph Miller⁴, “Spatially Localized, See-through-wall Temperature Measurements in a Flow Reactor using Radar REMPI,” *Optics Letters* 42 (2017): 53-56.

Author Affiliations:

¹Department of Mechanical, Aerospace, and Biomedical Engineering, University of Tennessee, Knoxville, TN 37996 USA

²Department of Mechanical and Aerospace Engineering, University of Dayton, Dayton, OH 45469

³Energy and Environmental Engineering Division, University of Dayton Research Institute, Dayton OH 45469 USA

⁴Air Force Research Laboratory, Aerospace Systems Directorate, Wright-Patterson AFB, OH 45433, USA

Abstract

“See-through-wall” coherent microwave scattering from Resonance Enhanced Multiphoton Ionization (REMPI) for rotational temperature measurements of molecular oxygen has been developed and demonstrated in a flow reactor at atmospheric pressure. Through limited, single-ended optical

access, a laser beam was focused to generate local ionization of molecular oxygen in a heated quartz flow reactor enclosed by ceramic heating elements. Coherent microwaves were transmitted, and the subsequent scattering off the laser-induced plasma was received, through the optically opaque ceramic heater walls and used to acquire rotational spectra of molecular oxygen and to determine temperature. Both axial and radial air-temperature profiles were obtained in the flow reactor with an accuracy of ± 20 K ($\pm 5\%$). The experimental results show good agreement with a steady-state computational heat transfer model. Furthermore, spatially localized measurements of temperature are demonstrated through the wall of a ceramic toroidal well-stirred reactor (WSR) using resonance enhanced multiphoton ionization (Radar REMPI). The WSR, which is used to study the emissions and combustion stability of realistic fuels, is constructed of ceramic SiO_2 and is optically opaque. Traditionally, in-situ non-intrusive optical diagnostic methods have not been utilized in the WSR due to harsh operating conditions and non-existing optical access. In this work, a single optical port on the bottom of the reactor was used to introduce a focused laser beam which generated REMPI plasma from molecular oxygen inside the WSR. Boltzmann plots from the resulting molecular oxygen REMPI spectra were analyzed to yield local gas temperatures. Temperature measurements were made at multiple positions, from the centerline of the WSR to the bottom of the reactor. The Radar REMPI temperature measurements were within ± 10 K of thermocouple measurements obtained simultaneously at each corresponding location. This suggests that Radar REMPI is a viable non-intrusive, *in-situ* diagnostic technique for temperature, and potentially, species measurements through microwave-transparent materials.

Introduction

Flow reactors are often used for chemical kinetics experiments because of their simplified thermodynamic, hydrodynamic, and geometric boundary conditions [1]. Usually zero-dimensional (0D) or one-dimensional (1D) assumptions of thermal and chemical uniformity are used to develop and simplify kinetic models

in which tens of thousands of reactions may be involved. Although reactors are well designed and optimized for uniform temperature and species profiles, non-uniform flow patterns exist in all laboratory reactors, especially near the boundary layer where heat transfer is highly dependent on fluid convection and reactor surface radiation. In order to provide useful data for experimental validation and reduction of model uncertainty, experimental non-uniformity must be quantified with high fidelity measurements [2].

To maintain nearly uniform temperature, pressure and chemistry, consistent with 0D or 1D assumptions, most reactors exhibit very limited or even non-existent optical access. Intrusive thermocouples are typically used for temperature measurements and can perturb the flow and promote catalytic surface reactions, requiring detailed corrections to the measured temperature. Mass spectroscopy (MS), gas chromatography (GC), and/or Fourier-transform infrared (FTIR) spectroscopy used for species measurements require extractive sampling and are typically limited to stable products. Radical and intermediate species are generally not measured due to their high reactivity and limited lifetime in the reacting flow, although they can play major roles in combustion. In general, there is limited knowledge of the local temperature, heat release, and radical and intermediate species concentrations inside reactors used for chemical kinetics experiments.

JET-stirred reactors (JSR) are also used in the combustion community to quantify gaseous and particulate emissions [3, 4] develop and assess chemical kinetics mechanisms [5, 6] and determine rich and lean combustion stability limits of both simple and complex fuels [6-8] JSR devices can provide chemical kinetics data that is complementary to data from shock tubes and flow reactors, but with the advantage that reactions in JSR devices are in theory zero-dimensional, *i.e.* homogenous in time and space. This allows for simplified analysis of combustion emissions and chemical mechanisms as a function of global thermodynamic parameters (temperature, pressure) and bulk fluid residence time. While many designs exist, the toroidal well-stirred-reactor design (WSR) of Nenniger [9] has been used extensively for measuring combustion emissions, particulate matter,

and rich and lean stability limits of conventional, alternative, and surrogate aviation fuels under thermodynamic conditions relevant to gas turbine combustors [3, 4, 9, 10]. Despite significant use of the WSR design for combustion analysis, limited optical access has prevented application of non-intrusive optical and laser diagnostics measurement methods necessary to verify zero-dimensional operation. In general, spatially resolved measurements of mean and fluctuating temperature and species concentration are required to assess the degree to which physical WSR devices imitate theoretical perfectly stirred reactor models.

Laser diagnostic measurement methods have had tremendous success when applied to combustion processes. Many parameters important to understanding combustion processes such as temperature, species concentration, velocity, and fuel to air ratio, can now be obtained using methods such as tunable diode laser absorption spectroscopy (TDLAS), spontaneous or coherent Raman scattering, laser induced fluorescence, and laser-induced breakdown spectroscopy [11-14]. Though there are many optical diagnostic techniques available for combustion studies, most of them require more than one optical access port; one for laser entry and one for signal collection. Furthermore, in practical combustion applications optical access may be restricted for various reasons such as reducing heat loss, increasing operating pressure, and safety. In the current WSR design, there are no optical ports embedded in the design to ensure homogeneous heating and turbulent mixing of the fuel/air in the WSR. No previous attempts at implementing optical diagnostics have been conducted due to the harsh operating conditions and/or limited optical access ports.

In this work, a single-ended optical diagnostic utilizing microwave detection, radar REMPI, was demonstrated for *in-situ* temperature measurements *through* a ceramic flow reactor and WSR. Microwaves are capable of penetrating through a number of materials, including ceramics and dielectric materials such as Al_2O_3 , SiO_2 , and SiC . Therefore, radar REMPI, which uses microwaves for detection, is suitable for studying combustion environments that are enclosed by ceramic materials such as well-stirred and jet-stirred reactors and advanced gas-turbine

combustors. In this paper, the experimental setup for temperature measurements in a ceramic-covered flow reactor and a ceramic well-stirred reactor and radar REMPI measurement are described first. Theory for O₂ rotational temperature is then presented, followed by experimental results, conclusions, and future efforts.

Experiment Setup

Flow Reactor

The experimental setup, shown in Fig. 4.1, is similar to previous applications of Radar REMPI for gas-phase temperature measurements of molecular oxygen [15-17]. The acronym Radar REMPI stands for coherent microwave Rayleigh scattering from Resonance-Enhanced Multi-Photon Ionization. The microwave Rayleigh scattering signal from the (2+1) REMPI produced plasma of molecular oxygen ($C^3\Pi_g(v' = 2) \leftarrow X^3\Sigma_g^-(v'' = 0)$) is proportional to the total number of electrons inside the plasma, which is also proportional to the number of O₂ molecules. Hence the temperature information can be inferred from the Boltzmann distribution. A pulsed, ultraviolet (UV) laser beam was generated via second harmonic generation of an Nd:YAG-pumped tunable dye laser with pulse repetition rate of 10 Hz. The wavelength was continuously tunable from 284–289 nm with linewidth of 1 cm⁻¹. Automatic tracking (“autotracking”) was used with second harmonic generation to ensure maximum conversion efficiency and minimal spatial movement as the wavelength was scanned. The UV beam was focused by a +150-mm spherical lens to a volume with diameter of 100 μm (estimated beam waist) and length of ~2 mm. The size of the Radar REMPI measurement volume is significantly smaller than the internal dimensions of the flow reactor enabling temperature and species measurements in both radial and axial directions. The axial and radial spatial resolution is estimated as 2 mm and 100 μm, respectively, and can be varied by changing the focal length of the lens or the diameter of the laser beam on the lens. The microwave horn shown in Fig. 4.1 was used to transmit and receive microwaves scattered from the ionized oxygen through the

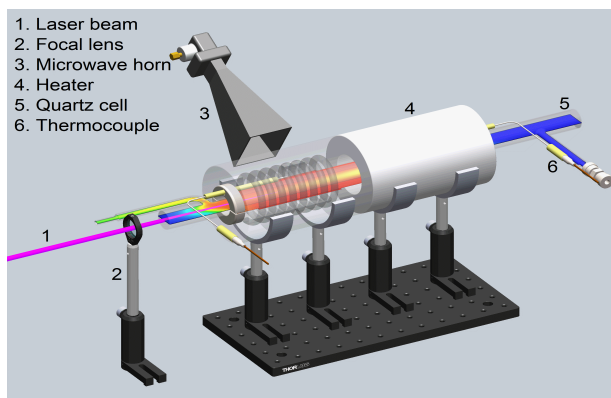


Figure 4.1: Experimental setup for see-through-wall temperature measurement of molecular oxygen in a flow reactor. Ceramic insulation (white) covers the heating coils, which allow for temperature adjustments within the reactor.

ceramic heater without optical access. A detailed description of the homodyne detection system can be found in our previous publications [15-17]. In addition to the unique “see-through-wall” characteristic of the current method, the overall experimental setup is simple to align and robust to operate because the spatially localized measurement resolution is controlled by focusing a single laser beam.

The flow reactor is constructed of a fused-silica cylinder with inner diameter of 23.4 mm and length of 500 mm and polished windows on each end. Two cylindrical heater components provide stable resistive heating sources for the reactor using a helically wound wire embedded in high purity alumina ceramic fiber insulation (only one heater is visible in Fig. 4.1). The heater temperature was set at 675 K with fluctuations of less than 1 K. A numerical simulation of temperature distribution inside the heated flow reactor is shown in Fig. 4.2. Air at 298 K radially enters the reactor, is heated by convection, and radially exits the reactor. Flow is from right to left in Figs. 4.1 and 4.2 and the laser beam propagates opposite the flow direction (from left to right). The air flow rate was set at 2 standard liters per minute (SLPM) and the flow was simulated under laminar conditions. Consistent with thermocouple measurements on the quartz flow reactor, the heating elements were modeled with constant temperature boundary conditions of 675 K.

Temperature measurements were performed at six axial positions (Pos. 1–6 in Fig. 4.2) at distances of 215.9 mm, 190.5 mm, 165.1 mm, 139.7 mm, 114.3 mm, and 63.5 mm, respectively, from the laser entrance window with computed variation of ≈ 20 K between positions. These positions were selected to test the temperature sensitivity of the Radar REMPI technique within 20 K, which is comparable to temperature differences of interest in chemical flow reactors. Temperature measurements were also performed in the radial direction at Position 2 as a sensitive test of the spatial resolution for capturing temperature gradients. The measurement position was changed in both the axial and radial directions by moving the focusing lens to ensure a consistent optical geometry.

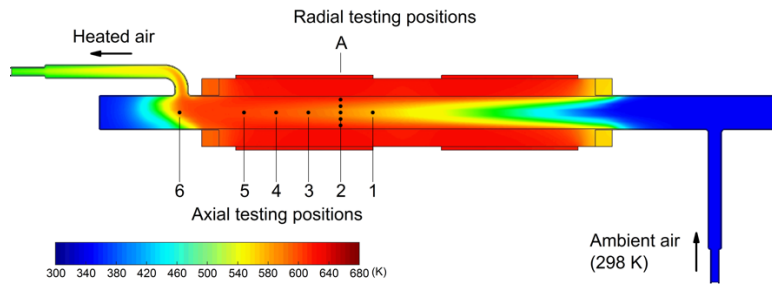


Figure 4.2: The computational result of the flow reactor heated by a cylindrical heater. The black dots indicate the test points for temperature measurements in both axial and radial directions.

Well-Stirred Reactor

The well-stirred reactor used in this work has been used in previous studies for quantifying combustion emissions and lean and rich blowoff limits of conventional, alternative, and surrogate fuels [4, 10]. Briefly, vaporized-liquid or gaseous fuels are premixed with air in the jet ring manifold as shown in Fig. 4.3. To ensure all fuel is vaporized and to minimize potential thermal decomposition of the fuel before combustion in the reactor, the temperature of the mixture is held at ≈ 505 K. The mixture is injected into the toroidal reactor through multiple 1-mm-diameter jets with Mach number of ~ 0.8 . The bulk residence time for non-reacting flow is ≈ 28 ms and ≈ 6 ms when the reactor is operating because of gas expansion. Recently, the reactor has been used for measurements of ignition probability as a function of residence time and equivalence ratio. In this case, the temperature profile in the reactor before ignition is a critical initial boundary condition for the ignition process. While measurement of the temperature profile can be made by physically scanning a Type-K thermocouple across the diameter of the toroidal reactor, the physical probe may perturb the flow and, therefore, the temperature profile. Additionally, a thermocouple will measure total temperature of the flow which will deviate from the static temperature of the flow near the middle of the toroid because the inlet jets have a Mach number of 0.8. Accurate, non-invasive measurement of the static temperature distribution is critical for providing high-fidelity boundary conditions for modeling of ignition events in the reactor.

For this proof-of-principle demonstration, radar REMPI is used to measure the temperature profile in the WSR for constant temperature inlet conditions. The reactor was heated exclusively by flowing heated air through the system, and fuel was not used in the characterization experiments. Data collection commenced once the system was near thermal equilibrium as measured by a thermocouple inserted into the reactor. For this work, the reactor was operated with an air flow rate of 500 SLPM and an inflowing air temperature of 477 K. The temperature of the reactor at thermal equilibrium was ≈ 450 K. The reactor halves were

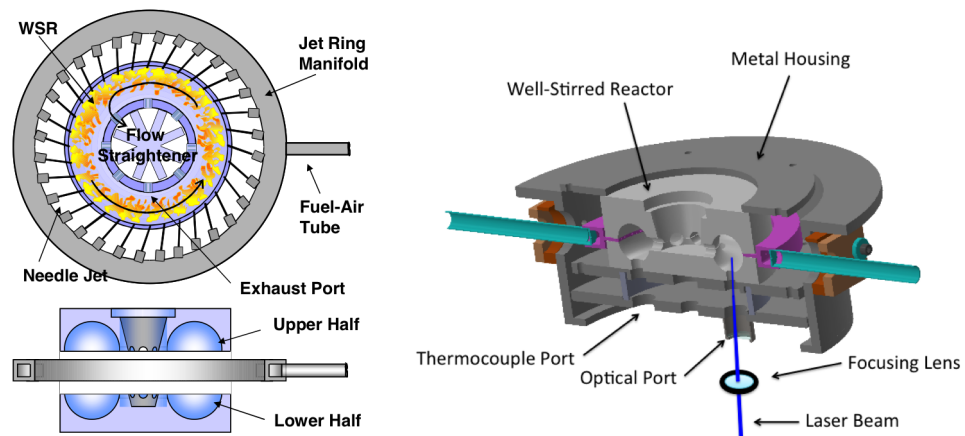


Figure 4.3: (Left) Schematic of the well-stirred reactor used in the experiment. (Right) A cross-section of the well-stirred reactor showing the laser entry point (exhaust stack not shown). Temperature measurements were performed at 0.1, 0.15, 0.2, 0.3, and 0.4 inches from the bottom of the toroid.

constructed from silicon dioxide (Rescor 750), SiO_2 , and clamped together using an outer metal casing. As shown in Fig. 4.3, the two access ports used for introduction of the thermocouple and laser beam into the reactor are separated by 180 degrees along the bottom of the toroid. The optical port is covered by a quartz window at the metal housing while the thermocouple port is completely sealed. The thermocouple was moved vertically within the reactor flow field in conjunction with the radar REMPI focusing lens to provide temperature values at the same height for comparison of the two temperature measurement techniques.

The measurement setup is shown in Fig. 4.4. An Nd:YAG laser (Spectra Physics Pro-290) at wavelength of 532 nm was used to pump a Sirah dye laser (PRSC-D-24) to produce laser light that was then frequency doubled and pulse energy was automatically tracked and optimized using a Continuum UVT. The input wavelengths for the measurements were automatically swept between 276 and 287 nm with a rate of 0.02 nm per second. Mirrors guided this laser beam to the bottom of the well-stirred reactor, where the beam was directed upward by the second mirror. Before entering the well-stirred reactor, a positive 100-mm spherical focusing lens was used to focus the upward beam through a fused silica window, as shown in Fig. 4.3. The focused beam generated REMPI plasma inside the reactor flow field through multiphoton ionization of O_2 . The focusing lens was moved vertically using a translation stage so that measurements could be taken at multiple positions within the reactor.

The REMPI plasma was quantified using microwave scatter with a homodyne detection system. A 12 dBm tunable microwave source (HP 8350B sweep oscillator) was separated into two channels. One channel was used to illuminate the plasma using the microwave horn (WR75, 15 dB gain) and to collect microwaves scattered by the plasma. The microwave scatter from the plasma that was received by the horn then passed through a microwave circulator, which amplified the signal by 30 dB using a preamplifier (at ~10 GHz). After the frequency was converted down in the mixer, two other amplifiers with bandwidth of 2.5 kHz

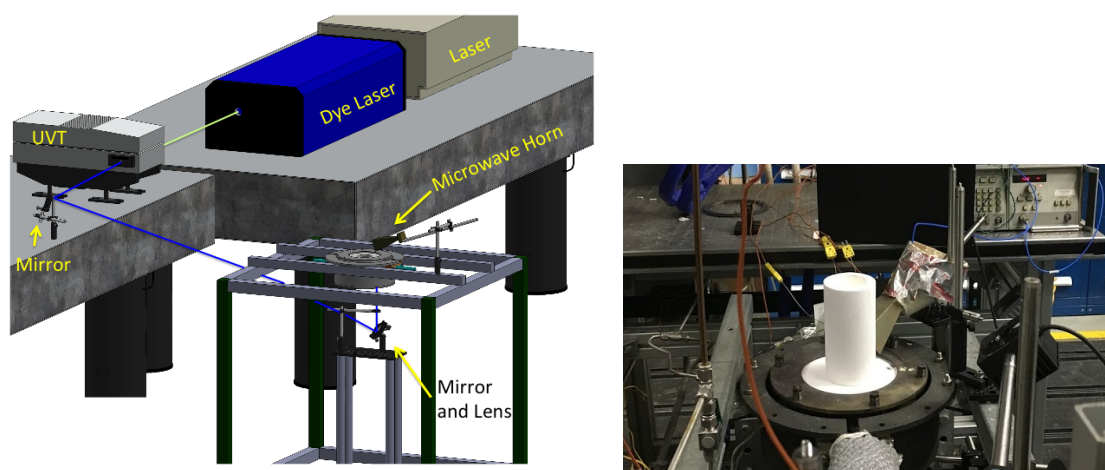


Figure 4.4: (Left) Basic model of the experiment setup showing the relative location of the horn to the well-stirred reactor. (Right) Picture of the experimental setup viewing from the UVT table. UV laser beam was bent down and reflected upward into the WSR. Microwave detecting horn is measuring REMPI plasma through the ceramic WSR wall. The ceramic exhaust stack was present during data collection.

to 1.0 GHz amplified the signal by 60 dB. The signal was then monitored and recorded by an oscilloscope. A photodiode monitoring the ultraviolet beam out of the UVT was also monitored and recorded by the same oscilloscope. The microwave horn was placed between the metal housing and the exhaust stack. The orientation of the microwave horn was chosen to maximize the scattered signal from the REMPI plasma while accounting for the geometry of dipole radiation. During the experiment, the microwave frequency was ≈ 10 GHz, but was adjusted to maximize the signal prior to each data collection. Because microwave radiation at 10 GHz is only slightly attenuated by SiO_2 , the microwave transmission and detection was performed *through* the ceramic reactor without the need for optical accessibility. This significantly reduces experimental complexities associated with windows in combustion environments and minimizes heat loss in the reactor.

Rotational Temperature Measurements of Molecular Oxygen

Radar REMPI has been used successfully for temperature measurements in reacting and non-reacting environments [15, 17-19]. The method uses microwave scattering from electrons freed from molecules or atoms by photonic absorption. In this work, electrons are liberated using a (2+1) multiphoton excitation process. The ground state of molecular oxygen, $\text{O}_2(X^3\Sigma)$, is suitably described by Hund's case (b) [19, 20]. As a result of hyperfine splitting, the ground state is a triplet with rotational energies:

$$G_1 = B_v J(J+1) - D_v J^2(J+1)^2 + (2J+3)B_v - L - \sqrt{(2J+3)^2 B_v^2 + L^2 - 2LB_v} + G(J+1)$$

$$G_2 = B_v J(J+1) - D_v J^2(J+1)^2 \quad (4.1)$$

$$G_3 = B_v J(J+1) - D_v J^2(J+1)^2 + (2J+1)B_v - L - \sqrt{(2J-1)^2 B_v^2 + L^2 - 2LB_v} + GJ$$

where B_v is the rotational energy constant, D_v is the distortional energy constant. For this work, the excited state used is $O_2(C^3\Pi(v = 2))$, which follows Hund's case (a). Hyperfine splitting results in energy levels given by Eq. 4.2 [17].

$$\begin{aligned}
 F_1(\Omega = 0) &= n_{01} + B_{\text{eff}1}J(J + 1) - D_{v1}J^2(J + 1)^2 \\
 F_2(\Omega = 1) &= n_{02} + B_{\text{eff}2}J(J + 1) - D_{v2}J^2(J + 1)^2 \\
 F_3(\Omega = 2) &= n_{03} + B_{\text{eff}3}J(J + 1) - D_{v3}J^2(J + 1)^2
 \end{aligned} \tag{4.2}$$

The constants n_0 , B_{eff} , and D_v in Eq. 4.1 are available in literature [17, 21, 22].

Because of the hyperfine structure of REMPI spectra, each branch (O, P, Q, R and S) has multiple lines. The two-photon transition line strength, $S_{fg}^{(2)}$, between the excited state $C^3\Pi$ and the ground state $X^3\Sigma$ is [16,18]:

$$\begin{aligned}
 S_{fg}^{(2)} &= \sum_{k=0,2} \frac{|\beta_k^{(2)}|^2}{2k+1} (2J+1)(2J'+1)(2N'+1) \\
 &\quad \times \left[\begin{matrix} J' & S & N' \\ \Lambda' + \Sigma & -\Sigma & -\Lambda' \end{matrix} \right]^2 \left[\begin{matrix} J & k & J' \\ \Omega & -\Delta\Lambda & -\Lambda' - \Sigma \end{matrix} \right]^2
 \end{aligned} \tag{4.3}$$

where $\beta_k^{(2)}$ is the polarization coefficient, J is the rotational quantum number, and the brackets, [...], denote the Wigner 3-j symbol. Note that for the ground state, $X^3\Sigma$, $\Lambda' = 0$ and $\Sigma' = \pm 1, 0$ and for the excited state, $C^3\Pi$, $\Lambda = 1$, $\Sigma = \pm 1, 0$, and $\Omega = 0, 1, 2$. For linearly polarized light $\beta_k^{(2)} = \frac{\sqrt{10}}{3}$, and for circular polarization $\beta_k^{(2)} = \sqrt{5}$. Furthermore, for circular polarization only the $k = 2$ term contributes. As in previous work using radar REMPI for O_2 rotational temperature measurements, the S_{21} branch will be used, which is suitable for temperatures less than 700 K [17].

The wavelengths, rotational ground state energies, and line strengths calculate using Eq. 4.1-4.3 for the S_{21} branch lines used in the work can be found in Table 4.1.

As previously stated, radar REMPI uses microwave scattering on electrons liberated through photonic excitation of atoms or molecules. The signal E_{MW} from the scattering of microwaves on the plasma is proportional to electron density, N_e , which is related to the number of molecules completing the (2+1) ionization process, as shown in Eq. 4.

$$E_{MW} \propto N_e = N_0 S_{fg}^{(2)} I^3 \sigma_i \exp\left(-\frac{E_g}{k_B T}\right) \quad (4.4)$$

Note that in Eq. 4.4, I is the laser intensity, σ_i is the ionization cross-section from the excited state, E_g is the ground state energy, T is temperature, and k_B is the Boltzmann constant. Since multiple emission lines are available, Eq. 4.4 can be arranged so that the temperature can be found from a linear plot of the data with the assumption that $S_{fg}^{(2)}$ is constant over the scanning wavelength range.

$$\ln\left(\frac{E_{MW}}{I^3 S_{fg}^{(2)}}\right) \propto -\frac{E_g}{k_B T} \quad (4.5)$$

Experiment Results

Flow Reactor

The novel aspect of the current work is the ability to detect ionization of molecular oxygen, and therefore make spatially localized temperature measurements, through ceramic walls without the need for optical access. This “see-through-wall” detection is enabled by using microwave radiation with a

Table 4.1: Selected rotational lines of S_{21} for used temperature measurements.

Wavelength (nm)	J'	G_1 (cm⁻¹)	$S_{fg}^{(2)}$
286.65	17	440.49	10.72
286.78	15	345.79	9.72
286.88	13	262.54	8.71
286.99	11	190.74	7.70
287.09	9	130.42	6.69
287.18	7	81.57	5.66
287.26	5	44.20	4.62
287.34	3	18.33	3.50

frequency of 10 GHz. Many ceramic materials commonly used for flow reactor insulation and high-temperature combustor components, including aluminum oxide (Al_2O_3), silica dioxide (SiO_2) and silicon carbide (SiC), exhibit high transmission in this range [23, 24]. In general, Beer's law describes the loss of power due to absorption of an electromagnetic wave traveling through a medium:

$$P(z) = P_0 e^{-k\delta z} \quad (4.6)$$

where k is the wavenumber for the electromagnetic wave in the medium, z is the distance traveled within the medium, and δ is the argument of the loss tangent, which is the ratio of the real and complex parts of the dielectric constant for the medium. The loss tangent is generally dependent on material thickness, microwave frequency, metallic content, and temperature [23-25]. Though a detailed discussion of the effect of these parameters is outside the scope of this paper, Fig. 4.5 shows the effect of temperature on the loss tangent of several ceramics.

If the loss tangent is small, the small angle approximation allows δ to be taken as approximately the loss tangent. Thus, Fig. 4.5 and Eq. 4.6 suggest that the power loss will increase with increasing temperature. For example, for sintered alumina at 35 GHz microwave frequency, Eq. 4.6 gives that 1% power will be lost at 296 K (room temperature) and 5% power will be lost at 1273 K for a traversed length of 1 cm within the alumina. Figure 4.5 also shows that the loss tangent is smaller for lower frequencies; thus, the absorption loss would also be smaller. Note that Beer's law describes absorption loss, but power loss will also come from reflection and transmission considerations of the incident microwave radiation, which depends on the index of refraction and geometry of the material.

The detected microwave scatter through a 1/2-inch-thick sample of the alumina ceramic used in the flow reactor is shown in Figure 4.6(a). For comparison, a single-shot microwave scattering signal is also shown without the ceramic material between the transmitter/receiver and the ionization volume. A

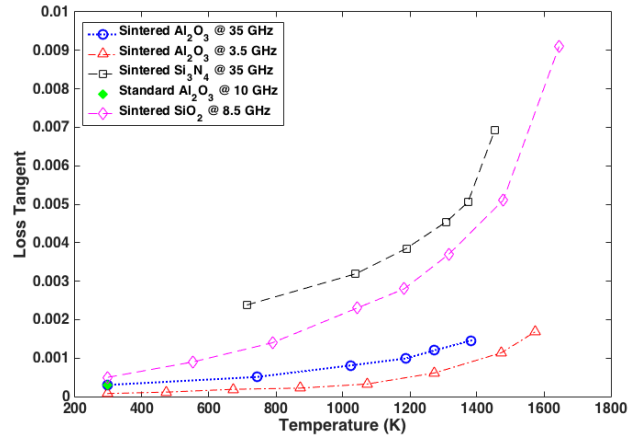


Figure 4.5: The loss tangent of various ceramics as a function of temperature for various microwave frequencies. The plot was generated using data from references [23-25].

decrease in microwave scattering of less than 10% was observed for the ½-inch-thick sample and increases to ≈30% for a thickness of 2 inches. While only aluminium oxide was demonstrated here, transmission will vary for other ceramic materials because of variations in their dielectric constants as previously noted.

Experimental Radar REMPI spectra of molecular oxygen in the flow reactor are shown as black lines in Figure 4.6(b) from ≈300–1100 K. Each spectrum was acquired by scanning the excitation wavelength of the ionization laser and recording the magnitude of the scattered microwave signal. Each point in the spectrum is the average of 20 laser shots. Transmission and detection of the microwave signal through the ceramic flow reactor may impact the REMPI spectrum in two ways: biasing the spectral shape because of frequency-dependent microwave transmission, and increasing noise because of reduced signal transmission. The first issue is addressed by optimizing the microwave frequency for transmission to account for material thickness and geometry, and then maintaining a constant frequency between 9 and 11 GHz. This ensures that the spectrum remains unbiased from frequency-dependent variations in transmission. The second issue is addressed by increasing the number of laser shots acquired at a given point in the spectrum. Qualitatively, the experimental and model spectra shown in Fig. 4.6(b) agree well and no systematic bias is observed because of detection through the ceramic flow reactor. Although some minor discrepancies exist between the experimental and model spectra, the evaluated temperatures are within 27 K of the steady-state thermocouple measurements from ≈300–1100 K (<10% difference).

Figure 4.7(a–f) shows experimental Boltzmann plots of the S_{21} branch of the rotational molecular oxygen spectra corresponding to the six axial locations, Positions 1–6, indicated in Figure 4.2. Excellent fits ($R^2 \sim 99\%$) are achieved for all six locations.

S_{21} represents the S branch which originates from ground state (G_2) and transits to excited state (F_1). The ground-state rotational levels including 9, 13–25

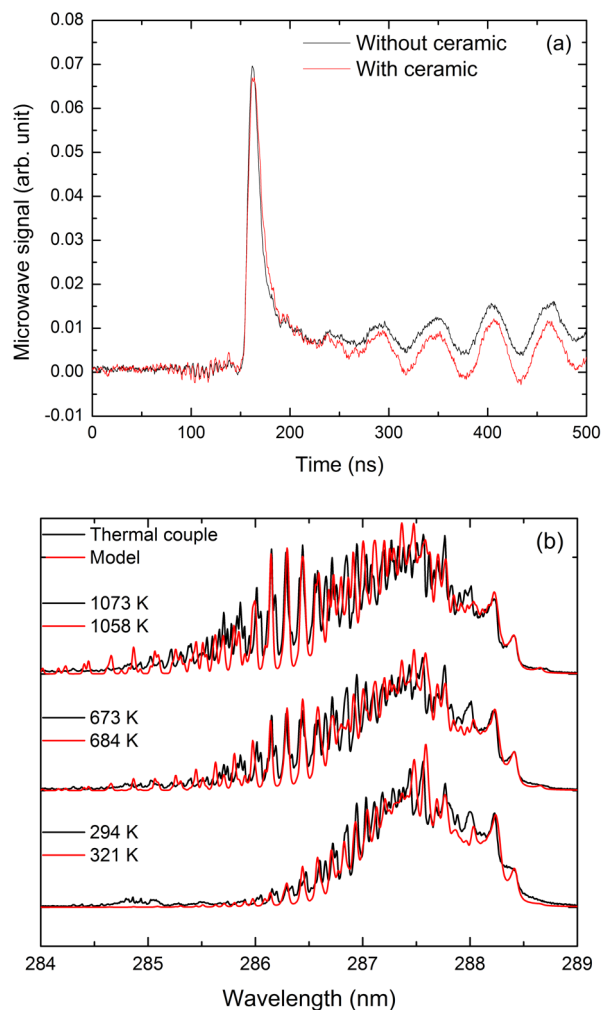


Figure 4.6: (a) Transparency test of $\frac{1}{2}$ " thick alumina ceramic used in the flow reactor, showing less than 10% loss. (b) Spectra of molecular oxygen obtained at room temperature and elevated temperature conditions (i.e., heated air in a flow reactor) by using 2+1 REMPI process.

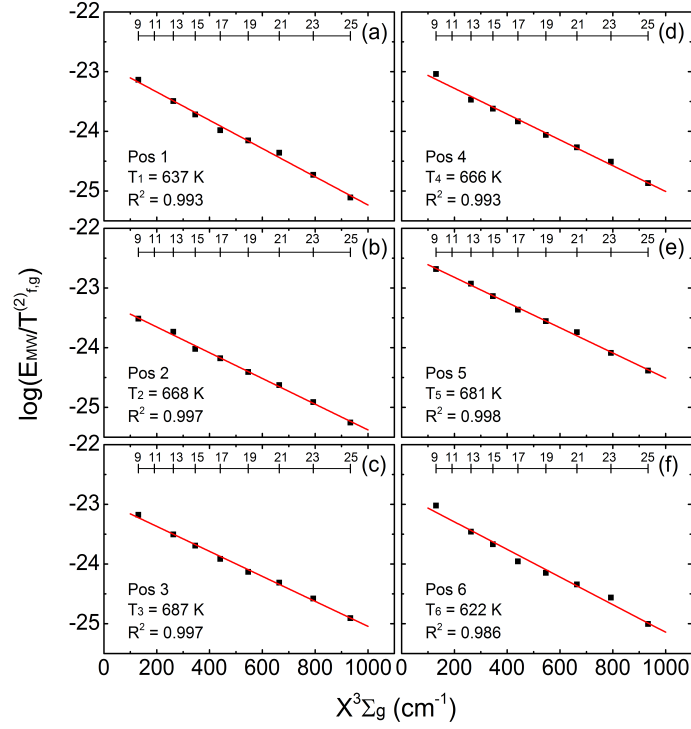


Figure 4.7: Boltzmann plots for oxygen temperature determination by rotational lines of $S_{21}(J'' = 9-25)$. Six testing points (Pos. 1 – Pos. 6 shown in Fig. 4.2) in axial direction have been set for temperature measurements.

have been used in the Boltzmann plot while $S_{21}(J'' = 11)$ has been omitted due to relative low temperature sensitivity. The corresponding temperatures calculated from the slope of the Boltzmann plots are listed in each panel.

The computed temperatures are plotted as stars in Fig. 4.8(a) for the axial direction and in Fig. 4.8(b) for the radial direction. The solid and dashed lines in Fig. 4.8 are results using a computational heat transfer model in Solidworks Flow Simulation module. The heat conduction, convection, and radiation between solids and air were considered in the simulation with applied adiabatic boundary conditions between the furnace and environment. The solid line is the computed temperature distribution along the centerline of the flow reactor and indicates the existence of a small temperature gradient along the axial direction (≈ 0.5 K/mm). The dashed and dotted lines are the computed temperatures at ± 0.2 -inch offsets from the centerline. Overall, the see-through-wall Radar REMPI temperature measurements agree well with the simulated results condition near the inner surface of the flow reactor with 5 K absolute differences. Close to the surface the air temperature is heated by surface conduction and radiation, reaching the temperature set point of 675 K. However, in the center of the flow reactor only convection plays a significant role, leading to lower air temperatures. This temperature distribution is captured by both the simulation and experimental measurements. Figure 4.8(b) also highlights the sub-mm spatial resolution of the Radar REMPI technique, which is sufficient to capture the ≈ 5 K/mm gradient in the radial direction.

Well-Stirred Reactor

Figure 4.9 shows normalized REMPI spectra of molecular oxygen at various heights within the WSR. Each spectrum has been averaged over two scans to achieve better SNR. The baselines of the all spectra were obtained at off-resonant wavelengths. The spectra were normalized by the maximum observed signal. Fairly consistent spectral measurements have been obtained for locations in the lower half of the toroid. Accurate measurements were not achieved in the upper

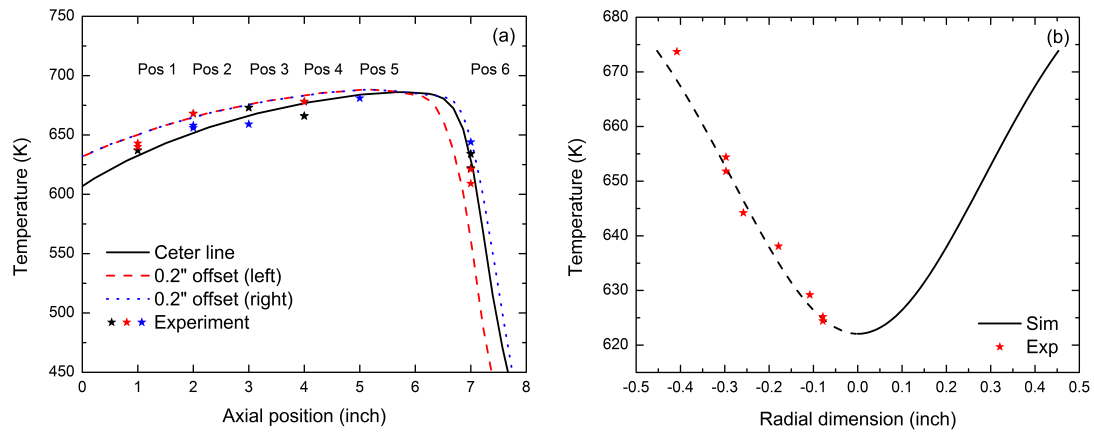


Figure 4.8: The spatial distribution of O_2 rotational temperature in the flow reactor in both axial and radial directions.

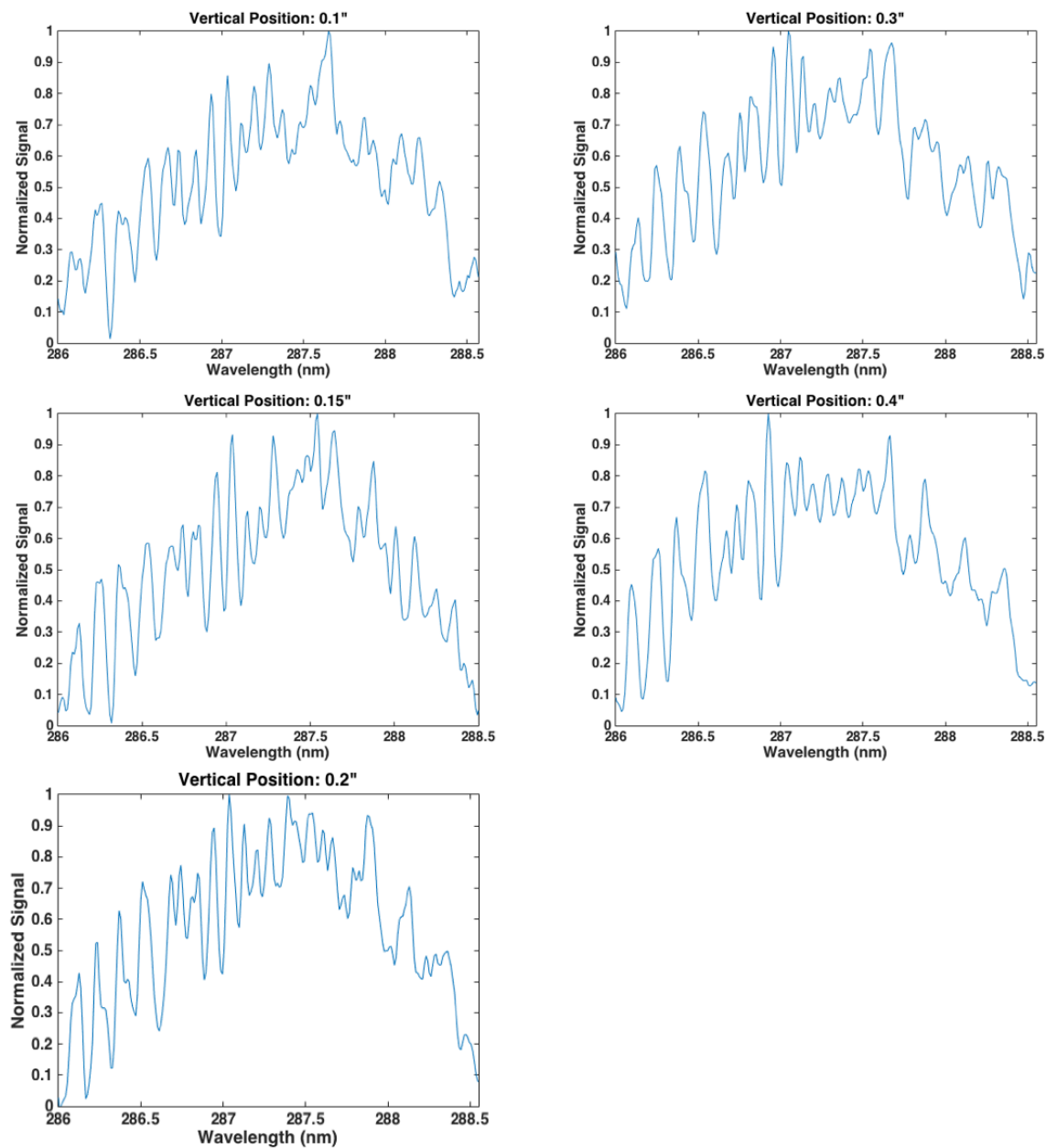


Figure 4.9: Normalized REMPI spectra of molecular oxygen from each of the vertical positions in the well-stirred reactor. Figure progression is from top to bottom and left to right.

half of the toroid because of competition between limited optical focal lengths required to avoid breakdown on the upper wall in the toroid and stronger signal of molecular oxygen plasma in the WSR. Breakdown can be identified as an abnormal increase of a few points in the spectra, which essentially sets the limits of the focusing lens and laser energy. No ceramic ablation was found on the reactor after the measurements, indicating the breakdown was entirely due to interactions with the heated air.

Figure 4.10 shows the Boltzmann plots of molecular oxygen REMPI spectra at various heights inside the WSR. Microwave signals at various S_{21} rotational branches of molecular oxygen were identified from Figure 4.9. The line position of S_{21} branches is denoted along the x-axis and the signal normalized by rotational line strength and laser intensity is shown as the y-axis. A linear fit of the data yields rotational temperature as suggested via Eq. 4.5. In general, sufficient linear fits have been achieved with R^2 at $\approx 90\%$. During the experiment, the signal-to-noise ratio increased as the height in the reactor was increased. This is reflected in Fig. 4.10 by the generally better R^2 values for vertical positions 0.3 and 0.4 inches. This is probably due to less absorption of the microwave scattering by the lower wall. While increasing the absorption of the microwave scatter reduces the overall signal strength, the relative features of the spectra remain unchanged.

The comparison of temperatures obtained from the optical measurements and thermocouple is summarized in Table 4.2 and plotted in Figure 4.11. Agreement between the radar REMPI measurement values for the temperature and thermocouple measurements is quite good with difference of less than 2%, and generally becomes better for increasing height, which may reflect the increasing signal to noise ratio with increasing height. However, a substantial temperature gradient is expected near the wall which is not captured by the thermocouple measurements but may be indicated by the rapid decrease in temperature at 0.1 inches as measured using radar REMPI. Also, while a relatively flat profile is measured by the thermocouple, the radar REMPI measurements indicate a possible decrease in temperature towards the middle of the reactor

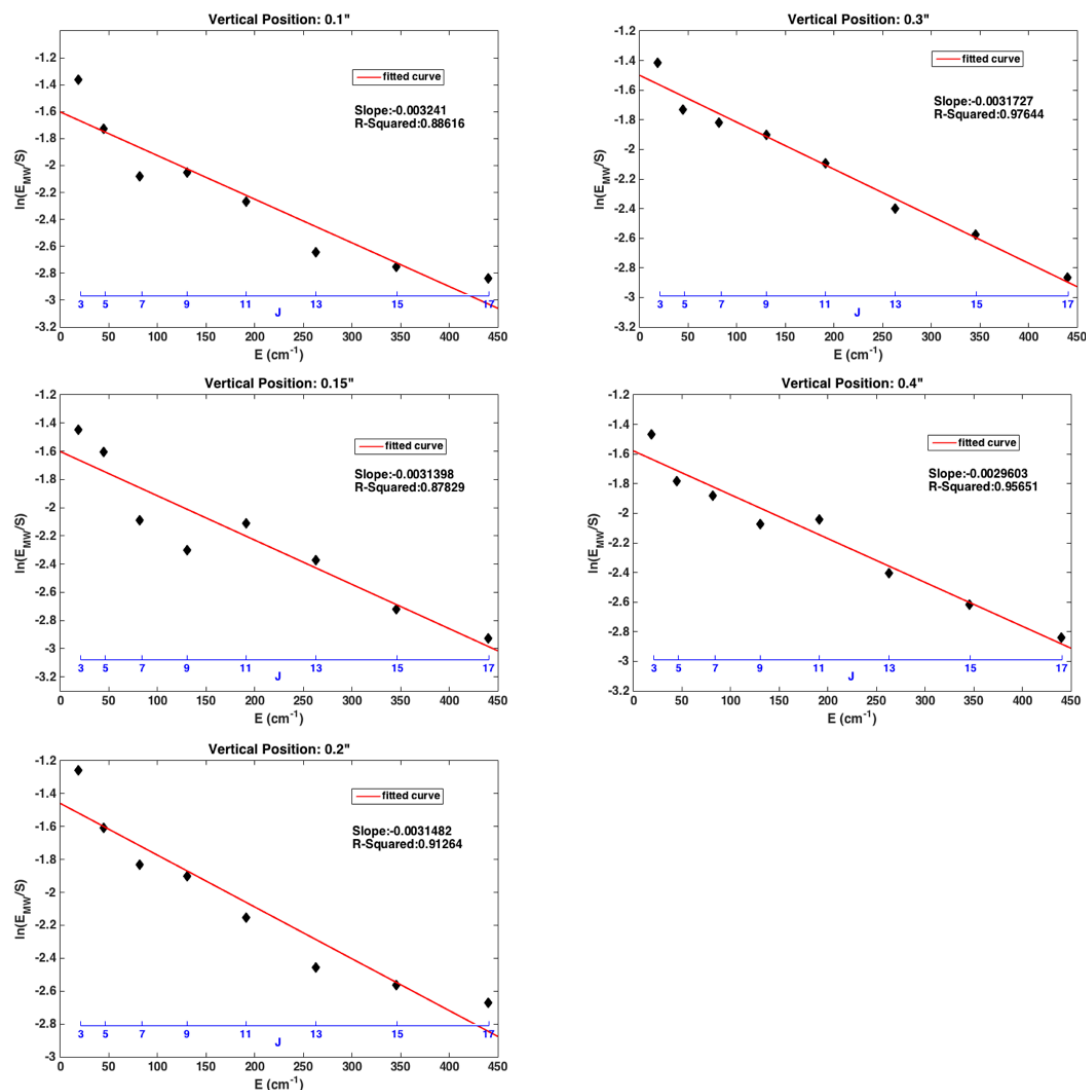


Figure 4.10: Boltzmann plots from the S_{21} branch REMPI spectra of molecular oxygen from Fig. 4.9. X-axis is the line position of the rotational branches. Y-axis is the normalized microwave signal by laser intensity and rotational line strength. A linear fitting is given to obtain the rotational temperatures at various heights in the WSR. Figure progression is from top to bottom and left to right.

Table 4.2: Summary of average temperatures calculated from the slopes presented in Fig. 10 and comparison to thermocouple measurements at the same position.

Vert. Position (in.)	T_{REMPI} (K)	$T_{Thermocouple}$ (K)	% Difference
0.1	444.0	452.7	1.9
0.15	458.3	452.5	1.3
0.2	457.0	452.1	1.1
0.3	453.5	451.5	0.4
0.4	452.1	451.3	0.2

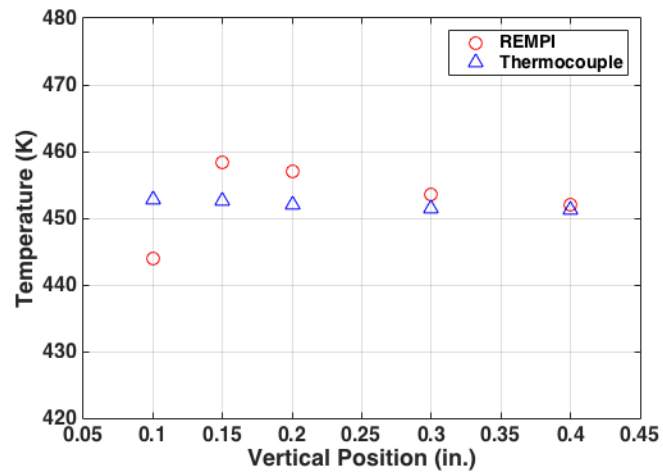


Figure 4.11: Graph of the results in Table 4.2 showing the difference between radar REMPI and thermocouple measurements of the temperature.

which would be consistent with the decrease in static temperature associated with the Mach 0.8 jets along the centerline. This would not be expected to have an impact on the thermocouple measurements since they measure total temperature, not static temperature.

It should be noted that this difference in temperature measurements at various locations in the WSR might also indicate a setup difference. Since the radar REMPI measurement required optical access for the laser beam, a 1-inch diameter quartz window, with about a 0.7 inch clearance in the center was mounted at the bottom of the WSR. The thermocouple was mounted symmetrically on the other side of the toroid, which was completely sealed. A difference in heat transfer may have resulted in a slightly lower temperature near the optical port. Of course, the lower signal to noise ratio on the lower portion might exaggerate the difference as well.

Summary and Conclusions

In conclusion, O₂ rotational temperature measurements of heated air at 450 K were successfully demonstrated *through* the walls of a ceramic covered, heated flow reactor and a ceramic well-stirred reactor using Radar REMPI. For the flow reactor, temperature results agree very well with computer simulation results. For the WSR, the measured temperatures show good agreement (± 10 K) with time-averaged temperatures measured using a thermocouple, and suggest that radar REMPI is a reliable technique for obtaining temperature information through microwave transparent media with minimal optical access. The demonstration of the optical measurement and characterization of the ceramic reactor provides significant promise for further quantification of the temperature and species concentration distributions inside the well-stirred reactor. This information is critical for accurately assessing chemical mechanisms, emissions, and combustion stability of conventional, alternative, and surrogate aviation fuels.

Acknowledgements

This work/material is approved for public release by AFRL (88ABW-2016-5904 and 88ABW-2016-5558).

References

1. F. L. Dryer, F. M. Haas, J. Santner, T. I. Farouk, and M. Chaos, "Interpreting chemical kinetics from complex reaction–advection–diffusion systems: Modeling of flow reactors and related experiments," *Progress in Energy and Combustion Science* **44**, 19-39 (2014).
2. H. Wang and D. A. Sheen, "Combustion kinetic model uncertainty quantification, propagation and minimization," *Progress in Energy and Combustion Science* **47**, 1-31 (2015).
3. J. Blust, D. Ballal, G. Sturgess, J. Blust, D. Ballal, and G. Sturgess, "Emissions characteristics of liquid hydrocarbons in a well stirred reactor," in *33rd Joint Propulsion Conference and Exhibit* (American Institute of Aeronautics and Astronautics, 1997).
4. S. Stouffer, R. Striebich, J. Zelina, and C. Frayne, "Combustion Particulates Mitigation Investigation Using a Well-Stirred Reactor," in *38th AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit* (American Institute of Aeronautics and Astronautics, 2002).
5. P. Dagaut, M. Reuillon, and M. Cathonnet, "Experimental study of the oxidation of n-heptane in a jet stirred reactor from low to high temperature and pressures up to 40 atm," *Combustion and Flame* **101**, 132-140 (1995).
6. M. F. Karalus, K. B. Fackler, I. V. Novosselov, J. C. Kramlich, and P. C. Malte, "A Skeletal Mechanism for the Reactive Flow Simulation of Methane Combustion," V01BT04A065 (2013).
7. M. F. Karalus, "An Investigation of Lean Blowout of Gaseous Fuel Alternatives to Natural Gas," (University of Washington, 2013).
8. D. L. Blunck, S. Zeppieri, J. T. Gross, S. Stouffer, and M. B. Colket, "Hydrocarbon Emissions from a WSR Near Lean Blow-Off," in *53rd AIAA Aerospace Sciences Meeting* (American Institute of Aeronautics and Astronautics, 2015).

9. J. E. Nenniger, A. Kridiotis, J. Chomiak, J. P. Longwell, and A. F. Sarofim, "Characterization of a toroidal well stirred reactor," Symposium (International) on Combustion **20**, 473-479 (1985).
10. S. Stouffer, R. Pawlik, J. Zelina, and D. Ballal, "Combustion Performance and Emissions Characteristics for a Well Stirred Reactor for Low Volatility Hydrocarbon Fuels," in *43rd AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit* (American Institute of Aeronautics and Astronautics, 2007).
11. A. C. Eckbreth, *Laser Diagnostics for Combustion Temperature and Species*, Combustion science and technology book series (Taylor & Francis, 1996).
12. C. E. Dedic, J. D. Miller, and T. R. Meyer, "Dual-pump vibrational/rotational femtosecond/picosecond coherent anti-Stokes Raman scattering temperature and species measurements," Opt. Lett. **39**, 6608-6611 (2014).
13. H. Do and C. Carter, "Hydrocarbon fuel concentration measurement in reacting flows using short-gated emission spectra of laser induced plasma," Combustion and Flame **160**, 601-609 (2013).
14. J. Kiefer, J. W. Tröger, Z. Li, T. Seeger, M. Alden, and A. Leipertz, "Laser-induced breakdown flame thermometry," Combustion and Flame **159**, 3576-3582 (2012).
15. S. F. Adams, Y. Wu, and Z. Zhang, "Oxygen Rotational Temperature Determination Using Empirical Analyses of $C3\Pi(v' = 2) \leftarrow X3\Sigma(v'' = 0)$ Transitions," Appl. Spectrosc. **69**, 1036-1041 (2015).
16. J. Sawyer, Y. Wu, Z. Zhang, and S. F. Adams, "O₂ rotational temperature measurements in an atmospheric air microdischarge by radar resonance-enhanced multiphoton ionization," Journal of Applied Physics **113**, 233304 (2013).
17. Y. Wu, J. Sawyer, Z. Zhang, and S. F. Adams, "Flame temperature measurements by radar resonance-enhanced multiphoton ionization of molecular oxygen," Appl. Opt. **51**, 6864-6869 (2012).

18. Y. Wu, Z. Zhang, and S. Adams, "Temperature Measurements by Radar REMPI in methane/air flames at atmospheric pressure," in *51st AIAA Aerospace Sciences Meeting including the New Horizons Forum and Aerospace Exposition* (American Institute of Aeronautics and Astronautics, 2013).
19. Y. Wu, Z. Zhang, and S. F. Adams, "O₂ rotational temperature measurements by coherent microwave scattering from REMPI," *Chemical Physics Letters* **513**, 191-194 (2011).
20. C. Mañinos, "Multiphoton rotational line strength in diatomic molecules and for states with Hund's case-(a) or case-(b) coupling," *Physical Review A* **33**, 3983-3992 (1986).
21. A. Sur, C. V. Ramana, W. A. Chupka, and S. D. Colson, "Rydberg–valence interactions in the Π_g states of O₂," *The Journal of Chemical Physics* **84**, 69-72 (1986).
22. A. Sur, C. V. Ramana, and S. D. Colson, "Optical spectra of the lowest Π_g Rydberg states in O₂," *The Journal of Chemical Physics* **83**, 904-905 (1985).
23. F. Cardarelli, *Materials Handbook: A Concise Desktop Reference* (Springer London, 2013).
24. W. W. Ho, Gyrotrons, and C. Rockwell International. Science, *Millimeter Wave Dielectric Property Measurement of Gyrotron Window Materials, Technical Report for the Period January 26, 1983 Through February 29, 1984* (Rockwell International Science Center, 1984).
25. W. B. Westphal and A. Sils, *Dielectric Constant and Loss Data*, Technical report (Air Force Materials Laboratory (U.S.)) (Air Force Materials Laboratory, Air Force Systems Command, 1972).

CHAPTER V

**ACOUSTIC DETECTION OF RESONANCE-ENHANCED
MULTIPHOTON IONIZATION FOR SPATIALLY RESOLVED
TEMPERATURE MEASUREMENTS**

A version of this chapter was originally published by Mark Gragston, Yue Wu, and Zhili Zhang:

Mark Gragston, Yue Wu, and Zhili Zhang. "Acoustic Measurement of O₂ REMPI in Air." 2018 AIAA Aerospace Sciences Meeting *Optics Letters* 221 (2018): 102-105.

Yue Wu, Mark Gragston, and Zhili Zhang. "Acoustic Detection of Resonance Enhanced Multiphoton Ionization for Spatially Resolved Temperature Measurements." *Optics Letters* 42 (2017): 3415-3418.

Author Affiliations:

Department of Mechanical, Aerospace, and Biomedical Engineering, University of Tennessee, Knoxville, TN 37996 USA

Abstract

In this work, acoustic detection of resonance-enhanced multiphoton ionization (A-REMPI) is characterized and used to measure spatially-resolved O₂ rotational temperature in air. The acoustic signal is generated using O₂ REMPI in air and is detected by a single microphone operating within the audible range. Compared to electron number measurements by coherent microwave scattering, nonlinear light absorption and subsequent local pressure perturbation are captured by the microphone. Typical acoustic cycle of compression and rarefaction of the acoustic wave is observed in the A-REMPI. Since the pressure perturbation can be regarded as close to thermodynamic equilibrium, the rotational temperature measured by A-REMPI is lower and closer to the realistic condition.

Introduction

Just before the 20th century, Alexander Graham Bell took notice of acoustic signal production from certain wavelengths of light interacting with matter, which he called the photoacoustic effect. Later, this effect was combined with laser technology, and the technique of photoacoustic spectroscopy (PAS) was developed. In this technique, local heating from light interacting with matter, such as photonic absorption, laser plasma formation, and photo thermal expansion, produces a pressure wave (i.e. acoustic wave). The sound wave can then be used for diagnostic purposes by observing changes of the phase, propagation speed, and amplitude in various materials [1]. There are several advantages of PAS compared to typical laser diagnostic methods. Acoustic detectors are generally much cheaper than modern imaging equipment and tomographic methods can be readily applied with microphone arrays to obtain three-dimensional information. Acoustic waves can penetrate liquid and solid materials with little attenuation compared to light and electromagnetic waves. Thus PAS has been applied to open-end trace gas analysis [2-4] non-invasive in-vivo biomedical imaging [5, 6] and combustion diagnostics [7-9].

Specifically, temperature measurements by PAS were conducted using time of arrival of the laser-induced acoustics wave, which is based on the temperature dependence of the speed of sound in an ideal gas [10, 11]. However, there are two key limitations. Most experiments used laser-induced breakdown (LIB) or non-resonance enhanced laser absorption to generate acoustic waves, which is highly inefficient and might generate shock waves to perturb the flow. Additionally, this technique can only extract a path-averaged temperature from probe volume to the detector.

Resonance-enhanced multiphoton ionization (REMPI) uses resonant photons to excite and subsequently ionize atoms or molecules. In a (2+1) REMPI process, two-photon absorption is used to excite a molecule and a third photon is used for ionization. Compared to traditional single photon methods for molecules,

REMPI can provide accurate information about rotational states, especially in combination with wavelength scanning [12, 13]. The radar REMPI technique has been employed to accurately measure species concentrations and temperatures in flames [13-15]. Furthermore, the dynamics of the REMPI plasma and its effects on inert gaseous surroundings have been investigated by Shneider et al, who showed that acoustic waves with speed close to the speed of sound are generated due to gas heating from frictional and recombination processes [16, 17].

Here, detection of REMPI with a microphone, acoustic detection of resonance-enhanced multiphoton ionization (A-REMPI) of O_2 in air, is demonstrated and analyzed. Resonance enhanced light absorption/ionization and subsequent weak pressure perturbation are measured using a microphone operating within the audible range, so that only one laser beam is needed. Using a spectrum obtained from this measurement, O_2 rotational temperature is calculated. For comparison, radar REMPI measurements are taken simultaneously. Rotational temperatures are obtained based on Boltzmann analyses of S_{21} bands of O_2 spectra by both microphone and microwave measurements. Compared to Radar REMPI, A-REMPI is more economical and allows for multiple phase measurements and easier transition to an array detection system.

Several models of the photoacoustics have been developed, with varying levels of precisions [1, 18]. Here, the photoacoustic theory is combined with REMPI of molecular oxygen to obtain rotational temperatures. The photoacoustic pressure Δp is linearly related to the absorbed laser energy for a temporally and spatially Gaussian beam [18]:

$$E_{PA} \propto \Delta p \propto \frac{E_{abs}}{\sqrt{r}} \quad (5.1)$$

where E_{PA} is the acoustic signal obtained from the microphone, E_{abs} is the absorbed laser energy, and r is the distance from the source to the detector. In (2+1) REMPI only the ionization photon will impart kinetic energy on the liberated

electron. So $E_{abs} \propto N^* \sigma^i I$, where N^* is the number of excited molecules, σ^i is the ionization cross-section, and I is the laser intensity. The acoustic signal can be expressed as [15, 19, 20]:

$$E_{PA} \propto \frac{N^* \sigma^i I}{\sqrt{r}} \propto N_0 T_{f,g}^{(2)} I^3 \sigma^i \exp\left(\frac{E_g}{k_B T}\right) / \sqrt{r} \quad (5.2)$$

where N_0 is the number density of molecular oxygen at the ground state, $T_{f,g}^{(2)}$ is the two-photon line strength, E_g the ground state energy, and k_B the Boltzmann constant. Similar to Radar REMPI, the rotational temperature T can then be obtained using a Boltzmann plot from A-REMPI, as described by:

$$\ln\left(\frac{E_{PA}}{I^3 T_{f,g}^{(2)}}\right) \propto -\frac{E_g}{k_B T} \quad (5.3)$$

Experiment Setup

For comparison, both A-REMPI and Radar REMPI were set up simultaneously, as shown in Fig. 5.1. A dye laser (Continuum ND 6000) pumped by an Nd:YAG laser (Surelite SL-10) with a pulse width of 8 ns and repetition rate of 10 Hz was used to generate a UV beam that was UVT tracked for scanning between 284 – 289 nm (1 cm^{-1} linewidth). The UV beam was focused by a 100 mm lens. The beam created a weak plasma through (2+1) REMPI of molecular oxygen ($C^3\Pi_g(v' = 2) \leftarrow X^3\Sigma_g^-(v'' = 0)$) in air, which was used as the acoustic source. A microphone (Adafruit MAX 4466) for acoustic detection was placed 2 cm away from the focal point and directly across from the microwave horn used for radar REMPI. It should be noted that the microphone used here is similar to those in modern smartphones, which means the acoustic measurements of REMPI processes can be conducted by a phone.

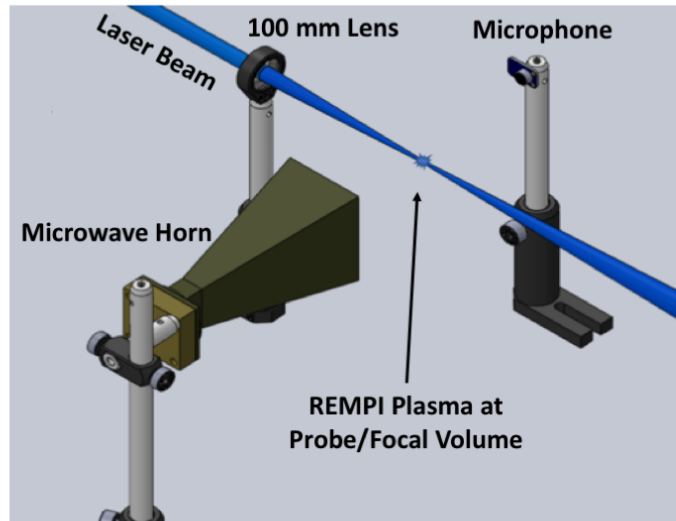


Figure 5.1: Schematic of the setup used for simultaneous acoustic and radar REMPI measurements. Since the measurement point is totally invisible, probe volume is highlighted with an artificial mark in the figure.

Results

Figure 5.2 shows examples of the acoustic and coherent microwave scattering signals collected from O₂ REMPI during the experiment. As expected, coherent microwave signal follows the generation of free electrons, which is on the order of tens of nanoseconds. The acoustic signal is on a much longer time scale (hundreds of microseconds) than the microwave signal since speeds of light and of sound differ by several orders of magnitude. Note that the shape of the A-REMPI signal matches theoretical descriptions of photoacoustic signals from literature [7, 21]: a compression and a rarefaction. The acoustic signal is broadband, ranging from audible to ultrasound frequencies. Compared to LIB, however, the bandwidth is significantly narrower.

Furthermore, the time between the peak acoustic signal and the laser pulse can be used to extrapolate the average speed of sound along the acoustic wave path from the source to the microphone. As shown in Fig. 5.3, the acoustic wave propagation speeds calculated from A-REMPI of O₂ in air are consistent with the speed of sound at standard conditions, about 345 m/s. This can be used as a new diagnostic tool for speed of sound measurements in multiphase flows. Fig. 5.4 shows the change in photoacoustic signal amplitude as the distance between the source and microphone is increased. A power law fit shows that the signal approximately decreases as $r^{-1/2}$, which is exactly the behavior predicted for a cylindrical wave.

Figure 5.5 shows the dependence of both the A-REMPI and radar REMPI signal amplitudes on laser intensity. Equation 5.2 gives the laser intensity dependence of the photoacoustic signal. Since, this is a (2+1) process, the absorbed energy should approximately depend on I^3 ; however, previous work with this REMPI excitation process has shown that I^2 is a better approximation [14, 15]. This discrepancy in theory and experiment can be easily accounted for by considering quenching and other background effects, while also noting that the final photon gives a significant amount of its energy to the liberated electron. Both

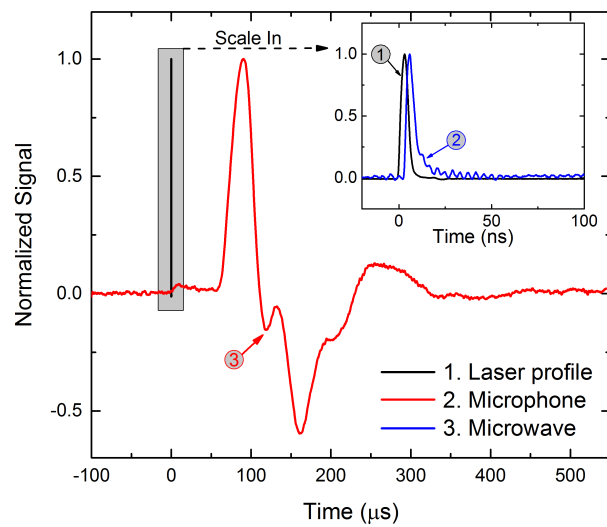


Figure 5.2: Comparison of acoustic and microwave signals from REMPI of O_2 in air.

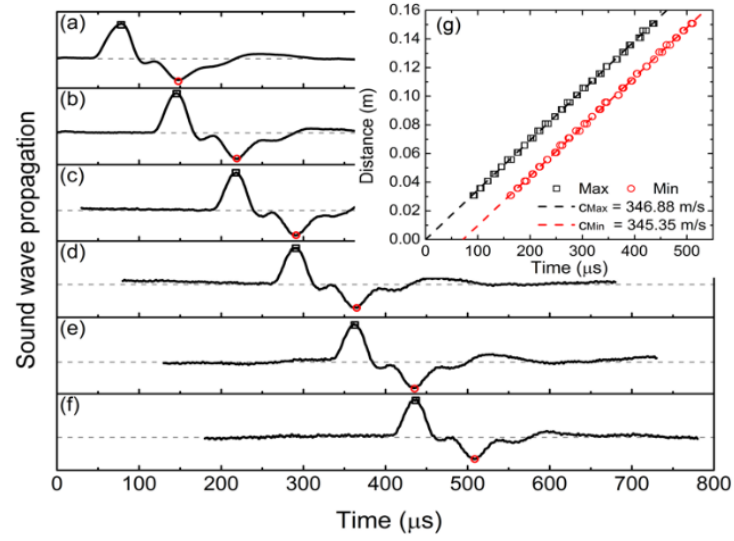


Figure 5.3: (left) Variation of the delay time with distance between the photoacoustic source and the microphone; the speed of sound calculated from the time delay of the signal.

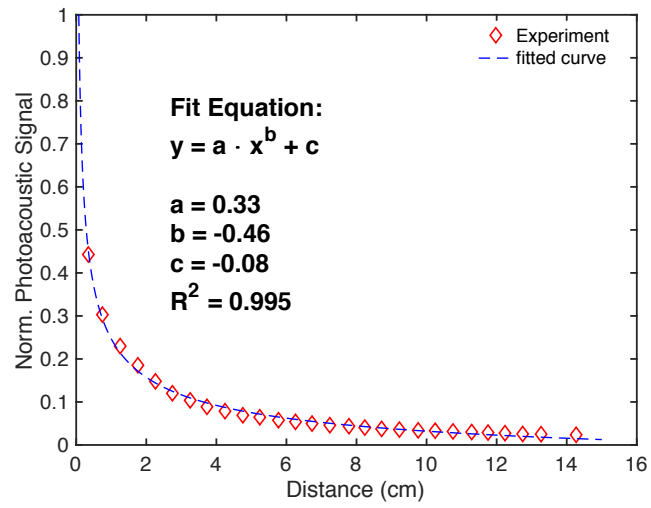


Figure 5.4: Fitted curve of the distance dependence of the acoustic signal, showing approximately $1/\sqrt{r}$ dependence.

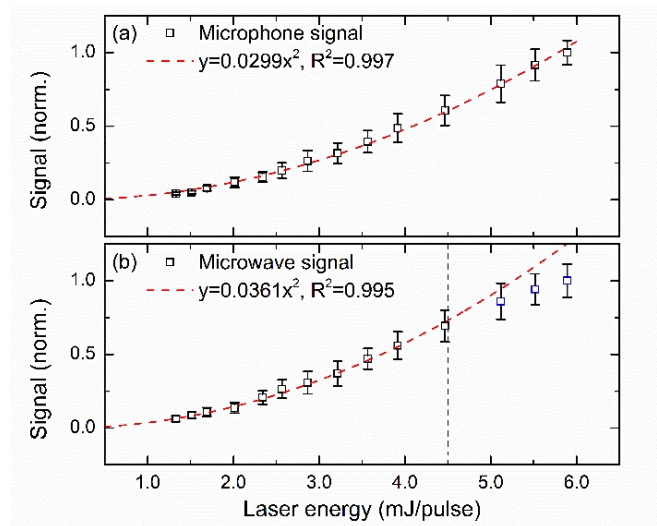


Figure 5.5: Laser energy dependence of (a) photoacoustic and (b) radar REMPI signals.

measurements show good agreement with the expected I^2 dependence. Note that the deviation in the microwave signal at higher pulse energies is due to the occurrence of photodissociation of molecular oxygen instead of generating photoelectrons. A-REMPI seems to be insensitive to this deviation, which is reasonable since photodissociation is accompanied by heat release, which in turn results in pressure wave creation.

Figure 5.6 shows rotational molecular oxygen REMPI spectra simultaneously obtained from A-REMPI and radar REMPI for the wavelength scans. Both REMPI spectra are quite similar, showing all major ro-vibrational lines. There are some differences in relative strengths of various lines, particularly on the lower wavelength side. Normalized by the band head (~ 288 nm) of O_2 spectra, strengths of higher rotational levels in A-REMPI spectrum are weaker than those in Radar REMPI spectrum. The differences between the two spectra between 286- 287.5 nm are due to radar REMPI actively measuring photoelectrons and acoustic detection passively measuring pressure perturbations. The microwaves utilized for the measurement use their own energy to directly measure the photoelectrons of the REMPI produced plasma, which gives the technique a high level of sensitivity of REMPI processes. The A-REMPI measurement indirectly infers the spectrum from the mechanical processes produced by the plasma, and thus, utilize energy taken out of the measurement region. Acoustic detection is heavily reliant on the microphone sensitivity. Since at shorter wavelengths, the states are less populated due to the relatively low temperature of ambient air, and therefore, less electrons will be liberated for plasma formation. The resulting weak absorption can then be expected to generate a relatively weak acoustic wave. The longer wavelengths in Fig. 5.6 correspond to energetically favorable configurations and result in a plasma that generates a stronger acoustic signal. Additionally, energy deposit by laser pulses are not negligible at nanosecond scales by microwave detection. When acoustic signal is detected at 100-200 μ S, the deposit energy has been dissipated into the surrounding and the probed volume should be very close to thermal equilibrium. Thus, the laser heating effects should be less in A-REMPI.

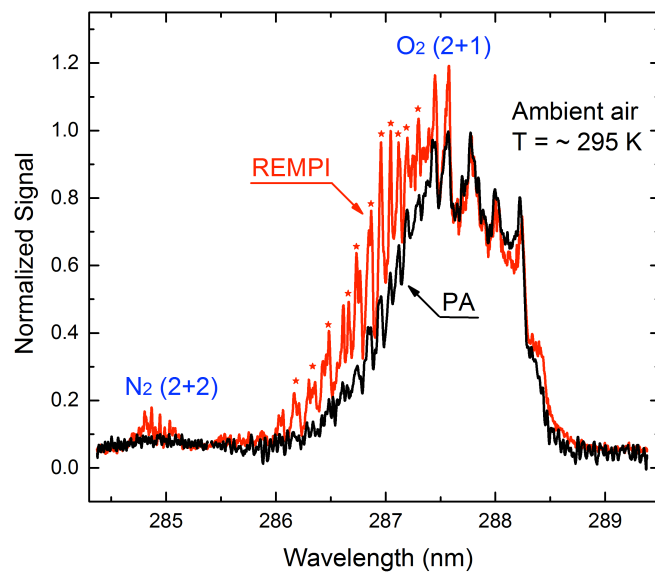


Figure 5.6: Spectra obtained from simultaneous photoacoustic and radar REMPI measurements. Markers denote locations chosen for analysis.

Another striking difference seen in Fig. 5.6 is the lack of N₂ signal detected by the photoacoustic system. The (2+2) REMPI process for N₂ is several orders of magnitude weaker than the (2+1) process for O₂. Therefore, the generated acoustic wave is very weak, and is below the detection limit of the acoustic system used in this work. This is also another example of the loss of signal due to conversion of energy to mechanical energy (i.e. pressure wave generation).

Based on the rotational spectra of molecular oxygen, Boltzmann plots are shown in Figure 5.7. Rotational temperatures are thus calculated based on Eq. 5.3. Previous works have shown that the prominent S branch transition ($\Delta J = \pm 2$) yields the most accurate results for room temperature [14, 15]. Thus, the S₂₁ rotational lines chosen are given in Table 5.1. The line strengths have been calculated by Mainos [22]. Since the relative strengths of various bands exist in the spectra, two fitted lines are shown in Figure 5.7. Both the radar REMPI and A-REMPI measurements give highly linear results, yielding r-squared values of > 0.98. It means that the methods of active or passive detections do not alter the relative populations of O₂ rotational levels. Temperature measurements should be similar. The A-REMPI measurement gave a slightly more agreeable temperature value, 293±10 K, than the radar REMPI temperature value of 301±10 K. In both cases, laser pulse energy is nonlinearly absorbed into the probed volume. The flow is unavoidably heated by the laser. Since the absorbed pulse energy (a few mJ/pulse) is relatively small, the probed volume is only slightly heated. Photoelectrons are almost instantaneously detected by microwave scattering, as shown in Figure 5.2. It shows slightly elevated temperature. Since the pressure perturbation at 100µS can be regarded as close to thermodynamic equilibrium, temperature measurements by A-REMPI is lower and closer to the realistic conditions.

It is worth mentioning that the detected signal used in the work was in the human audible range, 20 Hz to 20 kHz. No interference was observed since the oscilloscope used for the signal collection was triggered by a photodiode monitoring the laser output. However, some potential measurement environments

Table 5.1: Selected rotational lines of S_{21} used for temperature determination from the spectrum in Fig. 6.

Wavelength (nm)	J''	G_1 (cm⁻¹)	$T_{f,g}^{(2)}$
286.25	23	793.08	13.73
286.38	21	664.15	12.73
286.52	19	546.62	11.72
286.65	17	440.49	10.72
286.78	15	345.79	9.72
286.88	13	262.54	8.71
286.99	11	190.74	7.70
287.09	9	130.42	6.69
287.18	7	81.57	5.66
287.26	5	44.20	4.62
287.34	3	18.33	3.50

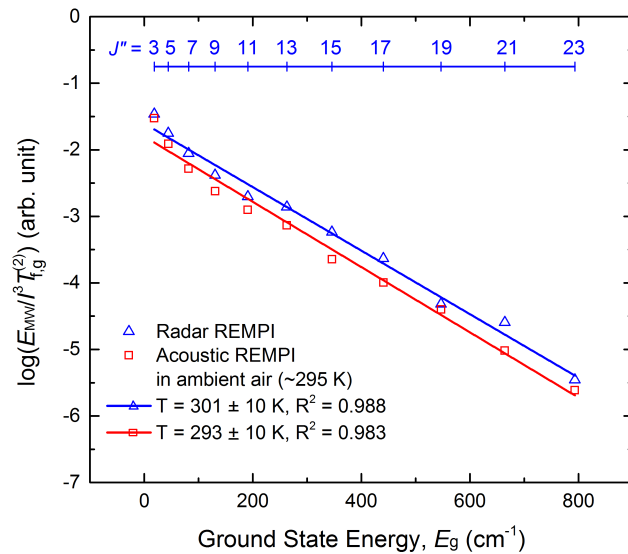


Figure 5.7: Boltzmann plots for photoacoustic and radar REMPI signals in Fig. 5.6 generated using Eq. 3 along with the data in Table 1.

may be subject various noise, with this being especially prevalent in the combustion and aerospace research communities. Previous work with acoustic emissions from laser-induced plasmas has shown that acoustic emissions in the ultrasonic regime do occur and are more prevalent for shorter laser pulse durations [23]. The same work postulated that the shift in acoustic emission of laser-induced plasmas towards ultrasonic frequencies with pulse duration is related to the reduction of the electron avalanching mechanism typical of breakdown plasmas. Since the REMPI plasma is produced through multiphoton ionization alone, it too should have ultrasonic acoustic emissions. Figure 5.8 shows the acoustic wave detected using a 300 kHz acoustic transducer, which can be seen to have a similar shape to the acoustic signal in Fig. 5.2. Therefore, ultrasonic detection for acoustic REMPI is feasible for measurements of temperature or species too.

Summary and Conclusions

In summary, acoustic detection of resonance enhanced multiphoton ionization (A-REMPI) is demonstrated and characterized for molecular oxygen. A-REMPI signal has a typical characteristic compression and rarefaction cycle. The time of flight of the acoustic signal can be used for speed of sound measurements in multi-phase media. Rotational spectra of molecular oxygen obtained by A-REMPI can be used to spatially-resolved determine rotational temperature with an accuracy comparable to radar REMPI. Since the 2+1 REMPI process not only produces sound at audible frequencies, but also at ultrasonic frequencies as well. Thus, the technique can be applicable even in noisy environments by choosing to work with an ultrasonic microphone or transducer. Since acoustic waves can easily propagate through multiple phases of matter, this technique could prove useful for multiphase diagnostics.

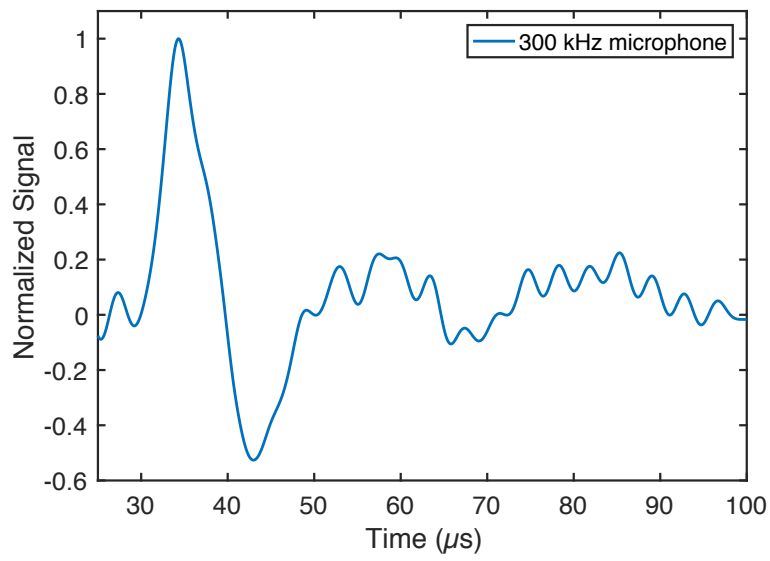


Figure 5.8: Ultrasonic emission was also detected from the REMPI plasma (300 kHz).

References

1. Tam, A. C. "Applications of photoacoustic sensing techniques," *Reviews of Modern Physics* Vol. 58, No. 2, 1986, pp. 381-431.
2. Besson, J.-P., Schilt, S., and Thévenaz, L. "Multi-gas sensing based on photoacoustic spectroscopy using tunable laser diodes," *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* Vol. 60, No. 14, 2004, pp. 3449-3456.
3. Wynn, C. M. P., S.; Clark, M. L.; Kunz, R. R. "Dynamic photoacoustic spectroscopy for trace gas detection," *Applied Physics Letters* Vol. 101, No. 18, 2012, p. 184103.
4. Sullenberger, R. M., Clark, M. L., Kunz, R. R., Samuels, A. C., Emge, D. K., Ellzy, M. W., and Wynn, C. M. "Trace aerosol detection and identification by dynamic photoacoustic spectroscopy," *Optics Express* Vol. 22, No. S7, 2014, pp. A1810-A1817.
5. Wang, L. V. "Photoacoustic imaging and spectroscopy." CRC Press, 2009.
6. Hai, P., Zhou, Y., Gong, L., and Wang, L. V. "Quantitative photoacoustic elastography in humans," *Journal of Biomedical Optics* Vol. 21, No. 6, 2016, pp. 066011-066011.
7. Rose, A., Pyrum, J. D., Salamo, G. J., and Gupta, R. "Photoacoustic detection of OH molecules in a methane–air flame," *Applied Optics* Vol. 23, No. 10, 1984, pp. 1573-1579.
8. Stenberg, J., Hernberg, R., and Vattulainen, J. "Analysis of pollutant chemistry in combustion by in situ pulsed photoacoustic laser diagnostics," *Applied Optics* Vol. 34, No. 36, 1995, pp. 8400-8408.
9. Humphries, G. S., Dunn, J., Hossain, M. M., Lengden, M., Burns, I. S., and Black, J. D. "A simple photoacoustic method for the in situ study of soot distribution in flames," *Applied Physics B* Vol. 119, No. 4, 2015, pp. 709-715.

10. Grosjean, D. F., Sarka, B., and Goss, L. P. "Time-resolved temperature measurements in a laboratory flame using the optoacoustic beam-deflection method," *Optics Letters* Vol. 10, No. 7, 1985, pp. 324-326.
11. Zapka, W., Pokrowsky, P., and Tam, A. C. "Noncontact optoacoustic monitoring of flame temperature profiles," *Optics Letters* Vol. 7, No. 10, 1982, pp. 477-479.
12. Demtröder, W. "Applications of Laser Spectroscopy," *Laser Spectroscopy 2: Experimental Techniques*. Springer Berlin Heidelberg, Berlin, Heidelberg, 2015, pp. 589-650.
13. Wu, Y., Bottom, A., Zhang, Z., Ombrello, T. M., and Katta, V. R. "Direct measurement of methyl radicals in a methane/air flame at atmospheric pressure by radar REMPI," *Optics express* Vol. 19, No. 24, 2011, pp. 23997-24004.
14. Wu, Y., Gragston, M., Zhang, Z., and Miller, J. D. "Spatially localized, see-through-wall temperature measurements in a flow reactor using radar REMPI," *Optics Letters* Vol. 42, No. 1, 2017, pp. 53-56.
15. Wu, Y., Sawyer, J., Zhang, Z., and Adams, S. F. "Flame temperature measurements by radar resonance-enhanced multiphoton ionization of molecular oxygen," *Applied optics* Vol. 51, No. 28, 2012, pp. 6864-6869.
16. Shneider, M. N., Zhang, Z., and Miles, R. B. "Simultaneous resonant enhanced multiphoton ionization and electron avalanche ionization in gas mixtures," *Journal of Applied Physics* Vol. 104, No. 2, 2008, p. 023302.
17. Shneider, M. N., Zhang, Z., and Miles, R. B. "Plasma induced by resonance enhanced multiphoton ionization in inert gas," *Journal of Applied Physics* Vol. 102, No. 12, 2007, p. 123103.
18. Lai, H. M., and Young, K. "Theory of the pulsed optoacoustic technique," *The Journal of the Acoustical Society of America* Vol. 72, No. 6, 1982, pp. 2000-2007.

19. Sawyer, J., Wu, Y., Zhang, Z., and Adams, S. F. "O₂ rotational temperature measurements in an atmospheric air microdischarge by Radar REMPI," *Journal of Applied Physics* Vol. 113, 2013, p. 233304.
20. Wu, Y., Zhang, Z., and Adams, S. F. "O-2 rotational temperature measurements by coherent microwave scattering from REMPI," *Chemical Physics Letters* Vol. 513, No. 4-6, 2011, pp. 191-194.
21. Rabasović, M. D., Markushev, D. D., and Jovanović-Kurepa, J. "Pulsed photoacoustic system calibration for highly excited molecules," *Measurement Science and Technology* Vol. 17, No. 7, 2006, p. 1826.
22. Mañnos, C. "Multiphoton rotational line strength in diatomic molecules and for states with Hund's case-(a) or case-(b) coupling," *Physical Review A* Vol. 33, No. 6, 1986, pp. 3983-3992.
23. Manikanta, E., Kumar, L. Vinoth, Venkatechwarlu, P, Leela, Ch, Kiran, P. Prem. "Effect of pulse duration on the acoustic frequency emission during the laser-induced breakdown of atmospheric air," *Applied Optics* Vol. 55, No. 3, 2016, pp. 548-555.

CHAPTER VI

SUMMARY AND POTENTIAL FOR FUTURE WORK

The work presented in this dissertation has shown the effectiveness of two techniques, laser-induced breakdown spectroscopy and radar REMPI for gas phase chemical analysis and temperature measurement respectively. Specifically, the results in Chapters II and III show that fuel-to-air ratio calibration curves generated from the H/N and H/O emission ratios are generally linear, but are also sensitive to time delay between plasma creation and measurement, laser energy, laser pulse width, and environmental pressure. Results from Chapter II suggest that at higher pressure conditions, an instability in plasma generation occurs which in turn affects measurement precision negatively. One contribution to this oscillation in plasma position is the increased production of soot at higher pressures and the general lower of the breakdown threshold, which results in the plasma forming slightly before true focus depending on laser energy fluctuations. Furthermore, increased continuum emissions associated with the higher-pressure conditions add to measurement error, particularly in the process of background removal.

To understand if any advantage in using shorter laser pulses for FAR measurements at higher pressure conditions, femto-, pico-, and nanosecond laser pulses were used in Chapter III for measurements of equivalence ratio in a Hencken flame at atmospheric pressure. Results suggests that femtosecond laser pulses could be beneficial for high-pressure conditions due to the decreased continuum radiation. This decrease is due to the lack of avalanching occurring for the femtosecond pulse case.

Despite the thoroughness of the results present here, there are still questions needing to be answered with regards to LIBS-based FAR measurements at higher-pressures. One such question is the impact that self-absorption has on the measurement. Various research has shown that self-absorption effects associated with the hydrogen emission at 656 nm are present at higher pressure conditions [1,2], and suggest the need for accounting for these effects. This work should be done with femto-, pico-, and nanosecond LIBS.

Furthermore, spectroscopic calculation of the shot-to-shot electron density fluctuations should be done to gain quantitative insight into the shot-to-shot consistency of the plasma and how environmental pressure and soot production affects plasma creation. The results could be compared with simultaneous microwave scattering results such as those in [3,4]. However, this sort of work is directly impacted by the study of self-absorption effects, since not accounting for the phenomenon will lead to inaccurate electron density values.

Chapter III results should also be applied to high-pressure combustion, just as in Chapter II. While the results in Chapter II suggest femtosecond laser pulse duration could work best for LIBS-based fuel-to-air ratio measurements at higher-pressure conditions, effects such as beam attenuation from nonlinear laser-matter processes prior to true focus could affect signal quality. Further, work should be expanded for various wavelengths and not just the 532 nm and 800 nm results shown here.

The later portion of this dissertation, Chapters IV and V moved away from the non-resonant LIBS technique and instead utilized the radar REMPI technique for gas phase temperature determination. While LIBS is fantastic for chemical analysis and for measurements such as FAR, radar REMPI is able to measure temperature very accurately. It was shown that measurement of temperature using (2+1) REMPI on molecular oxygen was possible through microwave transparent materials. Specifically, temperature measurements in a flow reactor and a well-stirred reactor showed good agreement with computational and thermocouple results respectively. This technique can be improved by first determining the parameters optimal for microwave measurements through the specific material. The system used in this work was built for 9-12 GHz microwave emission/detection. However, certain wavelengths may give better signal through materials. Once the system is optimized, application for species and temperature measurements in more extreme enclosed environments (such as a reacting low in the well-stirred reactor) can be made.

Finally, Chapter V explicitly showed that acoustic emission from the REMPI plasma creation can be used for gas-phase diagnostics. The acoustic emission was characterized in terms of spatial and temporal properties, and temperature measurements agreed well with results for radar REMPI. It was also shown that ultrasonic frequencies are emitted from the plasma, which could prove useful for measurements in environments with lots of audible noise pollution. Further work, should be done to see what exact bandwidth of acoustic emission results from the REMPI plasma creation and if higher-order processes such as (2+2) REMPI on nitrogen has similar properties and usefulness. Also, using a better pressure transducer, detection of the acoustic emission for temperature measurements in combusting environments could be done in the future. This of course will have to take into account acoustic shadowing effects.

In summary, the work presented in the dissertation provides useful laser diagnostics techniques and insight for aerothermodynamic related measurements. Specifically, emission spectroscopy for non-resonant laser-induced breakdown plasma was used for fuel-to-air ratio measurement and radar and acoustic REMPI techniques were expanded upon and created respectively for temperature gas phase temperature measurements.

References

1. C. G. Parigger, D. M. Surmick, and G. Gautam, "Self-absorption characteristics of measured laser-induced plasma line shapes," *Journal of Physics: Conference Series* **810**, 012012 (2017).
2. C. G. Parigger, L. D. Swafford, D. M. Surmick, M. J. Witte, A. C. Woods, and G. Gautam, "Hydrogen Alpha Self-Absorption Effects in Laser-Induced Air Plasma," *Journal of Physics: Conference Series* **548**, 012043 (2014).
3. A. K. Patnaik, P. S. Hsu, Y. Wu, M. Gragston, Z. Zhang, J. R. Gord, and S. Roy, "Ultrafast Laser-Induced-Breakdown Spectroscopy (LIBS) for F/A-Ratio Measurement of Hydrocarbon Flames," in *2018 AIAA Aerospace Sciences Meeting* (American Institute of Aeronautics and Astronautics, 2018).
4. A. K. Patnaik, Y. Wu, P. S. Hsu, M. Gragston, Z. Zhang, J. R. Gord, and S. Roy, "Simultaneous LIBS signal and plasma density measurement for quantitative insight into signal instability at elevated pressure," *Opt. Express* **26**, 25750-25760 (2018).

VITA

Mark T. Gragston did his undergraduate studies at Louisiana Tech University in Ruston, LA with a double major in physics and mathematics and also completed his master's in engineering with work in mechanical engineering and biomedical engineering. In 2015, Mark enrolled in the mechanical engineering Ph.D. program at The University of Tennessee in Knoxville, TN. During the program, Mark was awarded a NASA sponsored Tennessee Space Grant Consortium Graduate Fellowship, a Best Student Paper Award in Aerospace Measurement Technology at AIAA SciTech 2018 for acoustic detection of REMPI, and a U.S. provisional patent for the application of Radar REMPI for through-the-wall gas-phase temperature measurements.