DEVELOPMENT OF FAST-SAMPLED SPECIES AND LAMINAR FLAME SPEED MEASUREMENT TECHNIQUES IN A SHOCK TUBE

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Abstract

This dissertation focuses on the development of two experimental approaches for the study of low-temperature combustion kinetics in a shock tube: a combined laser absorption spectroscopy-gas chromatography (LAS-GC), fast-sampling speciation diagnostic, and a method for measuring laminar flame speeds in a shock tube at previously unexplored temperature conditions.

The combined LAS-GC diagnostic was developed in three phases, with each phase increasing in complexity. First, the endwall of a conventional shock tube was modified to allow for the extraction of a single gas sample at the end of each shock experiment, thereby allowing for the determination of species yield values after the reacting gas at the core of the tube has been quenched by the arrival of an expansion wave. This single-sample, post-expansion-fan, combined laser absorption-GC sampling technique was validated through a study of ethylene pyrolysis (1% ethylene/argon) at 5 atm, 1200-1900 K. Across the entire temperature range, laser- and GC-based measurements of ethylene showed close agreement, thereby bolstering confidence in the accuracy of both experimental techniques and confirming the efficacy of using a sampling-based diagnostic in a conventional shock tube configuration (as opposed to the single-pulse configurations conventionally used in conjunction with GC sampling experiments).

Next, the combined LAS-GC sampling diagnostic was used to study the formation of intermediate hydrocarbon species in low-temperature n-heptane oxidation experiments ($\phi = 0.53$, 760 K, 4.9 atm). Similar to the first phase of experiments, a single sample was extracted at the end of each experiment. However, in this second phase of experiments, the shock tube driver section was modified to allow for variable-test-time experiments. By running a species-yield, sample-extraction
experiment at the same thermodynamic condition multiple times, but changing the effective reaction time (i.e., experiment test time) each time, quasi-time-resolved measurements of intermediate species (C\textsubscript{2}H\textsubscript{4}, CO, H\textsubscript{2}, and C\textsubscript{3}H\textsubscript{6}) were conducted. Discrepancies between laser-measured and model-predicted ignition delay times indicated the overestimation of three primary RO\textsubscript{2} isomerization reaction rates in the model. The three reaction rates were modified to improve agreement of the modeled ignition delay times with the measurements. Final results produced using the modified mechanism were compared to the experimental results; the comparison shows close agreement between the two experimental measurement techniques (laser and GC), and measured species yields confirmed the low-temperature reaction pathways that govern n-heptane decomposition and C\textsubscript{2}H\textsubscript{4}, CO, H\textsubscript{2}, and C\textsubscript{3}H\textsubscript{6} production.

Finally, the combined LAS-GC sampling system was updated to allow for truly time-resolved, GC fast-sampling measurements of reacting-gas composition in conjunction with \textit{in situ} laser absorption measurements. Three distinct gas samples were extracted in 10-ms intervals, before the arrival of the expansion fan, in extended-test-time (>30 ms) shock tube experiments. Two pyrolysis systems were chosen for validation of the LAS-GC-fast-sampling diagnostic: 1.4\% cyclohexene/argon (980-1150 K, 7.3 atm) and 1\% ethane/argon (1060-1153 K, 6.9 atm). Results show close agreement between laser measurements, model predictions, and GC measurements conducted within the first 10 ms of an experiment. Later-time GC measurements show increasing disagreement with laser and model results. Additional experiments and modeling of the late-time sampling events suggest that the discrepancy is most likely due to increased influence of the endwall thermal boundary layer at late times. Suggestions are put forth for how best to circumvent the endwall boundary layer problem and increase the time resolution and accuracy of the time-resolved GC fast-sampling system.

The second low-temperature experimental technique developed in this dissertation involves the measurement of laminar flame speeds in a shock tube. A high-power Nd:YAG laser was used to spark-ignite shock-heated gas mixtures and initiate laminar flame propagation. High-speed, OH*-emission endwall imaging was used to record the propagation of the spherically expanding flames in time, and a non-linear stretch correlation was applied and used to determine the unburned, unstretched laminar flame speed. "Low-temperature" (<600 K) flame speed results were obtained
for stoichiometric methane/air and propane/air mixtures at initial unburned gas conditions of 489-573 K and 391-556 K, respectively, and 1 atm. The low-temperature measurements show close agreement with available literature data and kinetic modeling results, thereby validating the shock-tube laminar flame speed measurement approach. "High-temperature" (>750 K) flame speed results were obtained for a propane/21% O₂-47% N₂-32% He mixture (φ = 0.8) at initial unburned gas conditions of 764-832 K, 1 atm. The high-temperature measurements fall between kinetic model predictions, but the kinetic model results show significant disagreement, highlighting the need for high-temperature flame speed validation data of this kind. These results represent the first laminar flame speed measurements conducted in a shock tube, and the high-temperature results are the highest-temperature, 1-atm laminar flame speed measurements available in the literature.

As an extension of the initial shock-tube flame speed work, single line-of-sight laser absorption diagnostics were added to the imaging setup to allow for the simultaneous measurement of laminar flame speed, temperature, pressure, and species (CO₂ and H₂O) in spherically expanding ethane/air flames. The stoichiometric ethane/air mixtures were initially shock-heated to unburned gas conditions of 449-537 K, 1 atm. The flame speed, temperature, and species measurements showed excellent agreement with modeled results and the pressure measurements agreed closely with simultaneous mechanical pressure measurements.
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Chapter 1

Introduction

Global pandemics notwithstanding, one of the greatest challenges facing scientists today is the race to address global climate change by curbing the emission of greenhouse gases. The past three decades have witnessed a slow but decidedly steady decoupling of our energy resources from fossil fuel supplies; the growing use of renewable energy resources, including solar, wind, geothermal, etc., particularly for electricity generation, is both encouraging and necessary to combat increasing global temperature trends [1]. Even so, many energy sectors still rely heavily on liquid fuels and combustion processes; U.S. natural gas consumption, for example, reached a record high of 32.1 quadrillion Btu in 2019 [2]. The evolution of combustion systems is therefore also necessary to further stem climate change due to emissions.

The development of efficient, next-generation energy and propulsion systems requires improved understanding of chemical kinetics and flame propagation dynamics. Low-temperature (e.g., less than 1200 K) combustion is of particular interest, as non-ideal combustion phenomena at low temperature (e.g., pre-spark heat release, engine knock, etc.) inhibit efficiency optimization of modern-day combustors [3]. The work presented herein describes the development of two measurement techniques designed to provide new fundamental combustion data in low-temperature reacting systems, and in doing so, improve our understanding of fundamental chemical kinetics and flame propagation at previously unexplored temperatures.
1.1 Fundamental combustion research today

Today, much fundamental combustion research involves the development of models to describe observable combustion properties and phenomena, often with the end goal of using these models in a predictive manner to estimate the behavior of next-generation fuels and combustors without the need to extensively test them experimentally. Chemical kinetic models, in particular, are developed to simulate the fundamental chemical reactions governing the pyrolysis (thermal decomposition) or oxidation of a fuel or fuel mixture.

Kinetic model development is an iterative process. Input parameters, such as molecular thermochemical properties, reaction rates and their temperature and pressure dependencies, and transport properties are used to simulate observable combustion parameters such as ignition delay time, species time-histories, or flame speed. These simulated results are then compared to experimental results across a wide range of temperatures, pressures, and stoichiometries. When discrepancies arise between the experimental and simulation results, sensitivity analyses are carried out to determine how sensitive the observable parameters are to the inputs. Reactions with high reaction-rate uncertainties exhibiting high sensitivity to the input parameters are studied further; additional experiments are conducted to obtain more accurate reaction rate measurements. A primary objective of the experimental techniques developed in this work is to provide new, previously unmeasured datasets for chemical kinetic model development and validation.

1.2 Shock tubes in combustion research

Numerous experimental apparatuses are used to obtain data for the development and validation of chemical kinetic models. Reactors commonly used for these fundamental, gas-phase kinetics experiments include, among others, flat-flame burners, jet-stirred reactors, flow reactors, rapid compression machines, and shock tubes. These reactors are designed to access different temperature and pressure regimes, operate at different timescales, and are often optimized for particular diagnostic techniques; their experimental results provide the complementary datasets necessary to develop robust chemical kinetic models.
All of the experiments described in this dissertation were performed in a shock tube. Conceptually, a shock tube is an impulse heater, designed to shock-heat a gas mixture to temperatures of 500-5,000 K (and above) and pressures ranging from sub-atmospheric to 500 atm (and above) for a short period of time (typically ranging from 100s of microseconds to about 100 milliseconds) [4, 5]. Practically speaking, a shock tube is a long tube, sealed at both ends, that is separated into two parts by a plastic or metal diaphragm. One side of the shock tube is filled to low pressure with a test gas mixture of interest (e.g., fuel/oxidizer mixture), while the other side is filled with high-pressure gas, typically nitrogen and/or helium. The high-pressure side is filled with gas until the diaphragm bursts, causing a shock wave to form and travel through the low-pressure gas until it reaches the end of the shock tube and reflects back, further compressing and heating the test gas mixture. Shock tubes, in particular, are considered near-ideal reactors for studying high-temperature gas-phase reactions, as they provide near-instantaneous heating, spatially uniform gas mixtures, and generate a region of stagnant, high-temperature/high-pressure gas behind the reflected shock.

Different shock tube configurations are used for different kinds of experiments. A conventional shock tube operates as described above – after diaphragm rupture, a shock wave propagates in one direction while an expansion fan propagates in the opposite direction, and an experiment ends when the expansion wave reflects back down the length of the shock tube and reaches the test section containing the high-temperature, high-pressure test gas; the expansion wave quenches the reacting gas. The reflecting expansion fans and shock waves within the tube are significantly attenuated with each reflection and eventually die out. Conventional shock tubes are commonly used with in situ diagnostics, such as lasers, that monitor reaction progress in the reacting gas before the arrival of the expansion fan.

Another shock tube configuration relevant to this work is a single-pulse shock tube [6]. A single-pulse shock tube operates, in principle, similarly to a conventional shock tube, but an experiment ends when a strong, manufactured expansion wave, generated by a dump tank located just downstream of the diaphragm, is timed to coincide with an expansion fan caused by the reflected shock reflecting off the driver/driven gas interface. The net result is a high quenching rate at the test-section end of the shock tube and the elimination of subsequent reflected shocks (hence the "single-pulse" moniker). Single-pulse shock tubes are commonly used with sampling-based,
species-yield diagnostics, where samples of gas are extracted from the shock tube after the quenching process has occurred. The composition of the extracted samples is then quantified, often using gas chromatography (GC) or mass spectrometry (MS).

1.3 Summary of motivation

Over the past few decades, kinetics shock tubes have primarily been used for three different kinds of experiments: ignition delay time measurements, species and temperature measurements, and elementary reaction rate constant measurements. Laser absorption diagnostics are commonly used to measure all three parameters [4], but particularly excel at providing *in situ* species mole fraction measurements with high time-resolution. However, it can often be difficult to compare experimental speciation results obtained in a conventional shock tube (using time-resolved laser diagnostics) with those obtained in a single-pulse shock tube (using single-sample analysis techniques). Additionally, while laser diagnostics excel at measuring time-histories of stable and radical species with high time-resolution, there is a limit to the number of species that can be measured simultaneously using optical diagnostics, and not all species relevant to combustion can be easily measured using laser absorption. Similarly, while sampling-based, species-yield techniques excel at characterizing a broad number of stable species simultaneously, they suffer from poor time resolution and cannot be used to measure radical species.

There is therefore a need to combine these two experimental techniques in a single experimental setup in order to directly compare the results and leverage the strengths of both. The first part of this dissertation strives to do just that – combine laser absorption and sampling-based diagnostics in a single, conventional shock tube experiment and develop a GC fast-sampling diagnostic that can be used to extract gas samples from the shock tube before the arrival of the expansion wave.

A combustion parameter that had not previously been measured in a shock tube is laminar flame speed, or the speed at which a planar flame front propagates through a quiescent mixture of unburned reactants. The vast majority of laminar flame speed measurements available in the literature are recorded at temperatures below 500 K [7]; this is primarily due to temperature limitations
associated with the facilities used to conduct these experiments (e.g., constant-volume bombs, counterflow or stagnation flames, planar flames, etc.). Coincidentally, one particular strength of a shock tube facility is its ability to near-instantaneously shock-heat gas mixtures to tunable temperature and pressure conditions. The high-temperature, high-pressure, stagnant gas behind a reflected shock is therefore an ideal environment for the generation of spherically expanding flames at temperatures above 500 K. The latter half of this work therefore represents the addition of a fourth kind of experiment to the arsenal of shock tube capabilities: high-temperature laminar flame speed measurements in a shock tube.

1.4 Scope and organization

This dissertation is divided into two parts: Part I focuses on the development of a GC fast-sampling species diagnostic for use in low-temperature (<1200 K) shock tube experiments, while Part II focuses on the development of a new shock tube technique for measuring constant-pressure laminar flame speeds at previously unexplored temperatures (>500 K).

In Part I, Chapter 2 includes an overview of shock tube operation and theory, and introduces the two complementary techniques used in the GC fast-sampling experiments: laser absorption spectroscopy (LAS) and gas chromatography (GC). Chapters 3 -5 describe the development of the GC fast-sampling diagnostic in three parts: first (Chapter 3), the GC sampling diagnostic is validated through measurement of species yield values in ethylene pyrolysis experiments and comparison with simultaneous laser results; next (Chapter 4), a variable-test-time shock tube setup is used to perform quasi-time-resolved, species-yield, GC-sampling measurements in low-temperature n-heptane oxidation experiments, with simultaneous laser measurements; and finally (Chapter 5), the GC sampling system is modified to allow for the fast-sampling of three gas samples from the shock tube before the arrival of the expansion fan.

In Part II, the development of the shock-tube laminar flame speed measurement method is first described and validated (Chapter 6), then used in conjunction with laser absorption diagnostics to characterize the composition, temperature, and pressure of the burned gas inside the flames (Chapter 7).
Finally (Chapter 8), a summary of all the chapter contents is presented, followed by a discussion of future work.
Part I

GC Fast-Sampling in a Shock Tube
Chapter 2

Overview of experimental techniques

2.1 Introduction

In the GC fast-sampling experiments detailed in this part of the dissertation (Part I), two measurement techniques are simultaneously employed to conduct species measurements in shock tube experiments: laser absorption spectroscopy (LAS) and gas chromatography (GC) analysis. The next three sections of this chapter aim to introduce the reader to the three relevant experimental techniques: shock tube operation and theory (Section 2.2), LAS (Section 2.3), and GC analysis (Section 2.4).

2.2 Shock tube operation and theory

All of the experiments presented herein were conducted in a shock tube, specifically the Aerosol Shock Tube (AST) facility in Stanford’s High Temperature Gasdynamics Laboratory (HTGL). A broad overview of shock tube fundamentals and theory will be presented first (Sections 2.2.1 - 2.2.2), followed by an overview of facility-specific dimensions and uncertainty considerations (Sections 2.2.3 -2.2.5).
2.2. SHOCK TUBE OPERATION AND THEORY

2.2.1 Shock tube fundamentals

As introduced in Section 1.2, a conventional shock tube is a long tube, divided into two parts (a driven and a driver section), most typically by a plastic or metal diaphragm (see Figure 2.1a). To ensure repeatable plastic diaphragm rupture, a four-blade cutter is often located just downstream of the diaphragm.

In preparation for each experiment, the driven section is initially filled to low pressure with a test gas mixture of interest, typically fuel mixed with a diluent or oxidizer mixture; this region of low-pressure gas is denoted Region 1 (see Figure 2.1b). A shock experiment is initiated when high-pressure gas (typically helium or nitrogen, or a mix of both) is rapidly added to the driver section; as the driver section fills, the high-pressure gas pushes the diaphragm into contact with the four-blade cutter, thereby rupturing the diaphragm. The state of the high-pressure gas immediately preceding diaphragm rupture is denoted Region 4 (see Figure 2.1b).

Once the diaphragm ruptures, an incident shock wave forms and propagates through the test gas in the driven section; this once-shocked test gas is referred to as Region 2. An expansion fan simultaneously propagates in the opposite direction, through the driver gas (see Figure 2.1c). When the incident shock reaches the driven section endwall, it reflects back through the test section, further compressing and heating the gas, and leaving in its wake a region of stagnant gas at elevated temperature and pressure: Region 5 (see Figure 2.1d). It is in this region of quiescent, high-temperature, high-pressure gas that reflected-shock experiment measurements are conducted. Diagnostics are typically installed within a few centimeters of the shock tube endwall to facilitate detailed study of the reacting test gas mixtures. An experiment typically ends when the reflected expansion fan (Figure 2.1d) reaches the driven test section, causing a rapid drop in both temperature and pressure, thereby freezing the composition of the test gas. In a typical shock tube experiment, test times range from 100s of microseconds to a few milliseconds.
Figure 2.1: Shock tube operation schematic: (a) conventional shock tube configuration with labeled parts; (b) pre-diaphragm rupture configuration, with regions 4 and 1 indicated; (c) configuration immediately after diaphragm rupture – incident shock propagates through driven section (region 2, post-incident shock gas indicated), expansion fan propagates through driver section; (d) configuration after incident shock reflects off the endwall (region 5, reflected shock, and reflected expansion fan indicated).
2.2. SHOCK TUBE OPERATION AND THEORY

2.2.2 Shock-jump equations

The thermodynamic conditions of regions 2 and 5 described in Section 2.2.1 can be calculated for an idealized shock tube experiment using normal-shock relations. The theory governing normal-shock properties, as they relate to a shock tube experiment, will be summarized here; for a more thorough treatment of the presented content, the reader is referred to a compressible flow reference book, such as that written by John D. Anderson [8].

In the limit of idealized shock tube behavior, and for constant-gamma gas, the Region 4 and Region 1 pressures, $P_4$ and $P_1$, respectively, can be related to the strength of the incident shock as follows:

$$
\frac{P_4}{P_1} = \frac{2\gamma_1 M_1^2 - (\gamma_1 - 1)}{\gamma_1 + 1} \left\{ 1 - \frac{\gamma_4 - 1}{\gamma_4 + 1} \frac{a_1}{a_4} \left( M_1 - \frac{1}{M_1} \right) \right\} - \left( \frac{2\gamma_4}{\gamma_4 - 1} \right) \frac{M_1}{M_1 - 1} \left( \frac{2\gamma_4}{\gamma_4 - 1} \right) - \left( \frac{2\gamma_4}{\gamma_4 - 1} \right)
$$

(2.1)

Here, $M_1$ denotes the Mach number of the incident shock, $\gamma_1$ and $\gamma_4$ are the ratios of constant-pressure and constant-volume specific heats ($c_p/c_v$) for the Region 1 and Region 4 gases, respectively, and $a_1$ and $a_4$ are the speeds of sound of the Region 1 and Region 4 gases, respectively, calculated according to $a = \sqrt{\gamma RT}$, where $T$ is the gas temperature and $R$ is the specific gas constant (the universal ideal gas constant, $R_u$, divided by the molecular weight of the gas).

As can be seen from Equation 2.1, the strength of the generated shock wave ($M_1$) is directly correlated with the magnitude of the pressure differential across the diaphragm, or the ratio $P_4/P_1$; the greater the pressure differential directly before diaphragm rupture (or, the thicker the diaphragm), the stronger the resulting shock will be. Additionally, for a given $P_4/P_1$, as the ratio $a_1/a_4$ is made smaller, the incident shock strength increases. Therefore, for a given pressure ratio across the diaphragm (diaphragm thickness), to maximize the strength of the incident shock, the driver gas should ideally be a low-molecular weight gas at high temperature (large $a_4$), and the driven gas should be a high-molecular weight gas at lower temperature (small $a_1$). Practically speaking, it is difficult and costly to heat the driver section of a shock tube, so in practice, the driver gas is typically maintained at room temperature. To optimize shock strength, many shock tubes therefore use He (molar mass = 4.00 g/mol, $\gamma = 1.67$) or H$_2$ (molar mass = 2.02 g/mol, $\gamma = 1.41$) as the driver gas, and use Ar (molar mass = 39.95 g/mol, $\gamma = 1.67$) as a primary diluent species in driven gas mixtures.
In practice, it is easy to measure $P_1$ – this is simply the steady-state pressure of the driven gas loaded into the shock tube at the start of each experiment. By contrast, it is exceedingly difficult to accurately measure $P_4$, the driver gas pressure immediately preceding diaphragm rupture, as filling the driver section with high-pressure gas until the diaphragm ruptures is, by nature, a transient process. So in practice, the velocity of the incident shock (and its attenuation) is measured directly, using quick-response piezoelectric pressure transducers spaced along the axis of the shock tube (more on this in Section 2.2.4). With the temperature and composition of the Region 1 gas known \textit{a priori}, the speed of sound, $a_1$, can be calculated, and the measured incident shock velocity can be used to calculate $M_1$.

With $M_1$ in hand, the thermodynamic properties of a calorically perfect gas immediately downstream of the incident shock (Region 2) can be readily computed:

$$
\frac{P_2}{P_1} = \left(\frac{2\gamma_1 M_1^2 - (\gamma_1 - 1)}{\gamma_1 + 1}\right)
$$

(2.2)

$$
\frac{T_2}{T_1} = \left(\frac{\gamma_1 M_1^2 - \frac{\gamma_1 - 1}{2} \left(\frac{\gamma_1 - 1}{2} M_1^2 + 1\right)}{\left(\frac{\gamma_1 + 1}{2}\right)^2 M_1^2}\right)
$$

(2.3)

As can be seen in Equations 2.2 and 2.3, the ratios of pressure and temperature across the incident shock are solely dependent on the speed of the incident shock ($M_1$) and the initial condition/composition of the Region 1 gas.

The thermodynamic conditions of the post-reflected-shock, Region 5, gas (once again assuming constant gamma) can similarly be computed:

$$
\frac{P_5}{P_1} = \left\{ \frac{2\gamma_1 M_1^2 - (\gamma_1 - 1)}{\gamma_1 + 1} \right\} \left\{ \frac{(3\gamma_1 - 1)M_1^2 - 2(\gamma_1 - 1)}{(\gamma_1 - 1)M_1^2 + 2} \right\}
$$

(2.4)

$$
\frac{T_5}{T_1} = \frac{2(\gamma_1 - 1)M_1^2 + (3 - \gamma_1)}{(\gamma_1 + 1)^2 M_1^2}
$$

(2.5)

Once again, calculation of the Region 5 gas properties only requires knowledge of the incident shock speed and Region 1 gas conditions.
While equations 2.1 - 2.5 offer a simplistic view of how to calculate the relevant thermodynamic properties associated with an idealized shock tube experiment, in reality, viscosity and heat transfer play a role, and there are a number of non-ideal phenomena that cause properties behind incident and reflected shocks to deviate from their ideal values. For example, in a typical shock tube experiment, the incident shock speed is attenuated, often at a rate of 1-4%/m, as the incident shock wave propagates down the shock tube [9]. This attenuation is largely caused by the formation of a boundary layer along the walls of the shock tube [10–13] and non-ideal rupturing of the diaphragm separating the driver and driven sections [9, 14].

2.2.3 Aerosol Shock Tube (AST) facility

At the time of writing, the AST is one of five shock tubes used for kinetics experiments in the Hanson group. While each shock tube is typically optimized to access certain thermodynamic conditions (low vs. high pressure), measure different classes of fuels (low vs. high vapor pressure), or accommodate particular diagnostic capabilities, the AST is widely considered a multi-purpose tube, used to pioneer new experimental approaches and techniques, largely due to its modular construction and the ease with which new test sections can be interfaced with the existing driver-driven infrastructure. In the past 12 years alone, the AST has been outfitted with an aerosol generation tank to facilitate experiments involving low-vapor pressure fuels [15, 16], a gate valve to facilitate constrained reaction volume (CRV) experiments [17], a "u-bend" driver configuration to enable long-test-time experiments [5], a transparent endwall to facilitate imaging along the axis of the shock tube [18], and most recently, a new endwall configuration for extracting multiple gas samples from a single shock tube experiment [19, 20]. The "aerosol" shock tube moniker, or AST, has persisted, even though the shock tube facility has not been used in conjunction with the aerosol generation tank (from which it gets its name) for a few years now.

One of the AST’s particular strengths lies in its streamlined data collection process, in which data from 10+ analog input channels can be recorded simultaneously (including all piezoelectric PCB transducer time-histories) and fed directly into a graphical user interface-based (GUI-based)
FROSH (FROzen SHock) [21–23] script in MATLAB to enable near-real-time calculation of thermodynamic conditions for each shock experiment (see Section 2.2.4). The recording of time-resolved PCB signals – which are typically not recorded on other facilities, where trigger counter timers are used instead – also allows for detailed troubleshooting of pressure-related phenomena at various locations along the axis of the shock tube. Using the multi-function input/output module (National Instruments PXI-6115) in conjunction with four BNC breakout adapters (BNC-2110), analog data from 10+ channels can be recorded at up to 10 MHz.

The AST facility consists of a 9.73-m long driven section with a round, internal diameter of 11.53 cm, and a 3.63-m long driver section with a round internal diameter of 17.8 cm. In all of the experiments described in this work, driver inserts are used to reduce the inner diameter of the driver section to match that of the driven section (11.53 cm). To enable long-test-time experiments, the driver section can be extended through the addition of a u-bend and discrete driver segments (see Figure 2.2). In this way, the driver length can be extended to 7.74 m, 9.57 m, or 13.42 m (see Appendix A.1 for tabulated shock tube dimensions).

The CRV gate valve, described at length by Campbell et al. [17], is located 39.5 cm from the driven section endwall. The gate valve can be used to constrain a reactive test gas mixture to a volume adjacent to the endwall, thereby physically separating it from a non-reactive buffer gas mixture present in the remaining volume of the driven section. Immediately before the diaphragm
is burst, the gate valve is opened at a speed of 4-11 cm/s (actuation time of 1-4 s), thereby slowly bringing the reactive test gas mixture into contact with the non-reactive buffer gas mixture. By limiting the volume of reactive gas to a small fraction of the overall driven section volume, near-constant-pressure test conditions can be achieved in ignition experiments that would otherwise see a significant increase in test gas pressure and temperature.

Although a permanent feature of the AST infrastructure, the CRV gate valve was not used in any of the shock experiments described in this work. It was, however, used to create a constant-volume chamber for a series of validation experiments; with the gate valve closed, the test section can be separated from the rest of the driven section, thereby creating a cylindrical chamber (11.53-cm diameter, 39.5-cm long), ideal for GC calibration validation (e.g., Appendix E.1.1) and room-temperature absorption cross-section measurements (e.g., Appendix D.1).

Before every shock experiment, the AST driven section is turbo-mechanically pumped (Varian Vacuum Technologies) down to below $2 \times 10^{-5}$ Torr to minimize impurities. The driven section is filled with test gas to the designated $P_1$ pressure, which is measured using a low-pressure Baratron (MKS 628B).

Incident shock speeds are determined by extrapolating shock arrival times, measured by sidewall piezo-electric pressure transducers (PCB 113A26), to the endwall. The AST is equipped with 10 PCBs located at different intervals from the shock tube endwall, with the closest being 2 cm from the endwall, and the farthest being 2.78 m from the endwall (see Appendix A.2). Different subsets of the 10 PCBs are used for different experiments, depending on the availability of analog input channels and sidewall ports. In a typical experiment, 4-6 PCBs are used for incident shock velocity determination.

In each experiment, the system pressure is recorded 2 cm from the shock tube endwall (the same axial location as most laser diagnostic measurements) using a piezoelectric pressure transducer (Kistler, Type 603B1).

### 2.2.4 Calculation of initial thermodynamic conditions ($T_5, P_5$)

The accurate calculation of post-reflected-shock temperature and pressure conditions is of the utmost importance in a shock tube experiment. With initial Region 1 temperature ($T_1$), pressure
(\(P_1\)), and measured incident shock velocity in-hand, the in-house, Rankine-Hugoniot relations-based FROSH algorithm can be used to calculate subsequent post-shock conditions in the shock tube. A brief summary of the FROSH calculation routine will be presented here; for a more in-depth overview the reader is directed to [21–23].

The FROSH algorithm solves the three conservation equations (mass, momentum, energy) across the incident and reflected shock waves. In the current work, chemistry is assumed to be frozen across the shock waves and the ideal gas equation of state is utilized. Across the incident shock, the conservation equations are as follows:

\[
\rho_1 u_1 = \rho_2 u_2 \quad (2.6)
\]

\[
P_1 + \rho_1 u_1^2 = P_2 + \rho_2 u_2^2 \quad (2.7)
\]

\[
H_1 + \frac{1}{2}u_1^2 = H_2 + \frac{1}{2}u_2^2 \quad (2.8)
\]

where the subscripts 1 and 2 denote pre- (Region 1) and post- (Region 2) incident shock gas properties. In accordance with standard convention, \(\rho\) and \(u\) are the gas density and gas velocity (in the Lagrangian, shock reference frame), \(P\) is the gas pressure, and \(H\) is the gas enthalpy (mass basis). Additionally, the ideal gas equation of state can be written:

\[
P = \rho RT = RT/\nu \quad (2.9)
\]

where \(R\) is the specific gas constant, defined as \(R = R_u/MW\), where \(R_u\) is the universal ideal gas constant and \(MW\) is the molecular weight (molar mass) of the gas, \(T\) is gas temperature, and \(\nu\) is specific volume of the gas, defined as \(1/\rho\). The standard Newton-Raphson method is used to iteratively solve the conservation equations, using ideal shock relations (Equations 2.2 and 2.3) to calculate initial guess values.

Similarly, across the reflected shock, the following conservation equations apply:

\[
\rho_2 u_2' = \rho_5 u_5 \quad (2.10)
\]
\[ P_2 + \rho_2 u_2^2 = P_5 + \rho_5 u_5^2 \]  \hspace{1cm} (2.11)

\[ H_2 + \frac{1}{2}u_2^2 = H_5 + \frac{1}{2}u_5^2 \]  \hspace{1cm} (2.12)

Here, the prime superscript (e.g., \( u_2' \)) describes the oncoming gas velocity seen by the reflected shock (in the shock reference frame) as it moves through the Region 2 gas.

The gas velocities in the various reference frames are related as follows, where a capital \( U \) denotes velocity in the lab (Eulerian) reference frame, and subscripts \( IS \) and \( RS \) denote incident and reflected shock, respectively:

\[ u_1 = U_{IS} \]  \hspace{1cm} (2.13)

\[ u_2 = U_{IS} - U_2 \]  \hspace{1cm} (2.14)

\[ u_2' = U_{RS} + U_2 \]  \hspace{1cm} (2.15)

\[ u_5 = U_{RS} - U_5 = U_{RS} \]  \hspace{1cm} (2.16)

The Region 5 initial temperature and pressure conditions are calculated iteratively using the standard Newton-Raphson method, and the ideal shock relations (Equations 2.4 and 2.5) are once again used to provide initial guess values.

2.2.5 Uncertainty in thermodynamic conditions \((T_5, P_5)\)

The uncertainty associated with the calculated Region 5 initial temperature and pressure values can be estimated by taking into account the uncertainty associated with the parameters used to calculate the \( T_5 \) and \( P_5 \) values. Because the \( T_5 \) and \( P_5 \) values are dependent on the \( T_2 \) and \( P_2 \) values, which are in turn dependent on incident shock velocity (and \( T_1 \) and \( P_1 \) values), the uncertainties associated with incident shock velocity and \( T_2 \) and \( P_2 \) will be discussed first.

2.2.5.1 Uncertainty in incident shock velocity

As described in Section 2.2.3, the incident shock velocity, \( U_{IS} \) or \( u_1 \), is calculated using PCB traces to determine shock arrival times at different axial locations within the shock tube and extrapolating the resulting trend to the shock tube endwall. Uncertainty in incident shock velocity is due
to four main parameters: uncertainty in the location of the PCB transducers used to monitor shock distance, uncertainty in endwall location relative to the PCB transducers, uncertainty in the response time of each PCB transducer, and uncertainty due to the linear fit applied to the calculated velocity vs. distance data.

In this work, a Monte Carlo approach is used to calculate the uncertainty associated with the incident shock velocity calculated in each experiment. (For a reference text describing use of the Monte Carlo method in uncertainty propagation, see, for example, [25].) The PCB-related factors (location and response time) both have uncertainty limits associated with them: PCB locations are known $\pm 0.25$ mm (measurement uncertainty) and the PCB response times are known $\pm 0.7$ $\mu$s (provided by manufacturer). The Monte Carlo method was used to determine the impact the propagation of random uncertainty in PCB location and response time has on the incident shock velocity.

For instance, in a shock experiment utilizing 5 PCBs, a single calculation iteration consists of randomly perturbing the location of each PCB (relative to the endwall) independently within its $\pm 0.25$-mm uncertainty range, assuming rectangular randomization (i.e., all values within the $\pm 0.25$-mm range are equally probable), and calculating the resulting incident shock velocity. The randomization was carried out 1800 times, and the resulting incident shock velocity was calculated for each iteration. The results of this exercise are shown for a given pyrolysis experiment (1.3% cyclohexene/Ar, 1121 K, 7.4 atm) in Figure 2.3.

After each iteration, the standard deviation of the calculated incident shock velocities is calculated. A plot of the standard deviation as a function of iteration number is shown in Figure 2.4. As expected, after a certain number of iterations, the standard deviation of the incident shock velocities converges. This final, converged value is taken to be the incident shock velocity standard deviation due to PCB location, $\sigma_{PCB \ loc}$; in the case of the data shown in Figure 2.4, this value would be 1.18 m/s, or 0.17% of the nominal incident shock velocity (703.9 m/s).

In this way, the Monte Carlo method is also used to calculate the incident shock velocity standard deviation due to PCB response time ($\sigma_{PCB \ response}$) and endwall location ($\sigma_{EW}$); the resulting standard deviations calculated for the same experiment shown in Figures 2.3 and 2.4 are tabulated in Table 2.1. The results show that the uncertainty in PCB response time has the largest impact on the subsequent incident shock velocity.
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Figure 2.3: Incident shock velocities calculated with PCB locations randomized within ±0.25 mm, for a given cyclohexene pyrolysis experiment (1.3% cyclohexene/Ar, 1121 K, 7.4 atm)

Figure 2.4: Incident shock velocity standard deviation vs. iteration number, for incident shock velocities calculated with PCB locations randomized within ±0.25 mm, for a given cyclohexene pyrolysis experiment (1.3% cyclohexene/Ar, 1121 K, 7.4 atm). Solid line indicates standard deviation as a function of iteration number, dashed line indicates convergence value.
Next, the uncertainty in incident shock velocity due to the fit used to extrapolate the shock velocity to the endwall must be quantified. Figure 2.5 shows the average shock velocity measurements (difference in PCB locations divided by difference in shock arrival times) plotted at distances halfway between PCB locations. The solid red line denotes the linear fit to the velocity-distance points; the dashed red lines indicate the 1-\( \sigma \) (68%) confidence interval of the fit, and the dotted red lines indicate the standard deviation of the difference between the fit and the four data points.

![Shock velocity vs. distance plot, derived from PCB shock arrival times, for a given cyclohexene pyrolysis experiment (1.3% cyclohexene/Ar, 1121 K, 7.4 atm)](image)

Figure 2.5: Shock velocity vs. distance plot, derived from PCB shock arrival times, for a given cyclohexene pyrolysis experiment (1.3% cyclohexene/Ar, 1121 K, 7.4 atm)

In the experiment shown in Figure 2.5, the 1-\( \sigma \) confidence interval of the fit is 3.41 m/s (also listed in Table 2.1), or 0.48% of the nominal incident shock velocity.

Table 2.1: Incident shock velocity standard deviations, calculated for a representative cyclohexene pyrolysis experiment (1.3% cyclohexene/Ar, 1121 K, 7.4 atm)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>( U_{IS} ) standard deviation (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \sigma_{PCB \ loc} )</td>
<td>1.18</td>
</tr>
<tr>
<td>( \sigma_{PCB \ response} )</td>
<td>2.38</td>
</tr>
<tr>
<td>( \sigma_{EW} )</td>
<td>0.001</td>
</tr>
<tr>
<td>( \sigma_{fit} )</td>
<td>3.41</td>
</tr>
</tbody>
</table>

The overall uncertainty associated with an incident shock velocity calculation is determined by taking the root sum square (RSS) of the \( U_{IS} \) standard deviations associated with PCB location, PCB
response time, endwall location, and extrapolation fit, or:

$$\sigma_{U_{IS}} = \sqrt{\sigma_{PCB \ loc}^2 + \sigma_{PCB \ response}^2 + \sigma_{EW}^2 + \sigma_{fit}^2}$$  \hspace{1cm} (2.17)$$

For the cyclohexene experiment shown in Figures 2.3-2.5, the overall uncertainty in incident shock velocity is 4.32 m/s, or 0.6% of the nominal incident shock velocity. In the shock tube experiments reported in this work, the uncertainty in incident shock velocity typically ranged from 0.4 to 0.8%.

### 2.2.5.2 Uncertainty in $T_2$, $P_2$

As shown in Section 2.2.4, calculation of $T_2$ and $P_2$ requires knowledge of $T_1$ and $P_1$ (the initial test gas temperature and pressure), as well as the velocity of the incident shock, $u_1$, and the composition of the test gas.

$T_1$ and $P_1$ are measured directly, and their associated uncertainties are due to expected measurement error. A K-type thermocouple is used to measure $T_1$; the maximum uncertainty associated with the temperature measurement is assumed to be ±1 K. $P_1$ is measured using a low-pressure capacitance barometer (MKS 627B Baratron) with an uncertainty of ±0.12% of the measurement reading.

The incident shock velocity and its associated uncertainty are calculated as described in the previous section.

Finally, the composition of the test gas, or fuel loading, as well as its associated uncertainty, must be calculated. Test gas composition is typically determined in one of two ways: manometrically (by partial pressures), using a Baratron pressure gauge (MKS Baratron 690A), or optically, using a laser diagnostic, as will be discussed in Section 2.3.1.1. The uncertainty associated with the manometric technique depends on the uncertainty in the pressure measurement (±0.05% of reading), as well as the number of pressure measurements needed to determine the total composition (i.e., number of components added to the mixture); the uncertainty is compounded as more components are added. In a two-component mixture, the uncertainty associated with an optical composition measurement is usually dominated by uncertainty in the fuel’s absorption cross-section measurement (more on
this in Section 2.3.1.1).

The total uncertainties associated with $T_2$ and $P_2$ ($\sigma_{T_2}$, $\sigma_{P_2}$) are calculated by perturbing each influential factor ($T_1$, $P_1$, $u_1$, and fuel loading) by its respective uncertainty, $\sigma$, and calculating the resulting changes in $T_2$ and $P_2$, as follows:

$$
\sigma^2_{T_2} = \left(\frac{dT_2}{dT_1}\right)^2 \sigma^2_{T_1} + \left(\frac{dT_2}{dP_1}\right)^2 \sigma^2_{P_1} + \left(\frac{dT_2}{du_1}\right)^2 \sigma^2_{u_1} + \sum_{i=1}^{N\text{components}} \left(\frac{dT_2}{dX_i}\right)^2 \sigma^2_{X_i} \quad (2.18)
$$

$$
\sigma^2_{P_2} = \left(\frac{dP_2}{dT_1}\right)^2 \sigma^2_{T_1} + \left(\frac{dP_2}{dP_1}\right)^2 \sigma^2_{P_1} + \left(\frac{dP_2}{du_1}\right)^2 \sigma^2_{u_1} + \sum_{i=1}^{N\text{components}} \left(\frac{dP_2}{dX_i}\right)^2 \sigma^2_{X_i} \quad (2.19)
$$

The final summation in both equations represents the impact the uncertainty each test gas mixture component mole fraction, $X_i$, has on the $T_2$ or $P_2$ results, where $i$ is the component number, and $i$ spans from 1 to the number of components, $N_{\text{components}}$.

Figure 2.6: Uncertainty analysis results for $T_2$ and $P_2$ for a given cyclohexene pyrolysis experiment (1.3% cyclohexene/Ar, 1121 K, 7.4 atm)

Figure 2.6 shows the relative contribution of each parameter to the overall uncertainty associated with $T_2$ and $P_2$ for the cyclohexene pyrolysis experiment used to calculate the incident shock velocity uncertainty (1.3% cyclohexene/Ar, 1121 K, 7.4 atm).

Overall, uncertainty in the incident shock velocity is the largest contributor to the uncertainty in
both \(T_2\) and \(P_2\). For the selected cyclohexene pyrolysis experiment, the overall, 1-\(\sigma\) uncertainty in \(T_2\) was \(\pm 5.1\) K, or 0.76%; the uncertainty in \(P_2\) was \(\pm 2.8\) kPa, or 1.3%. Across all the experiments reported in this work, the uncertainty in \(T_2\) typically ranged from 0.5 to 1.0% and the uncertainty in \(P_2\) ranged from 0.9 to 1.6%.

### 2.2.5.3 Uncertainty in \(T_5\), \(P_5\)

The uncertainties associated with \(T_5\) and \(P_5\) are calculated much in the same way as those for \(T_2\) and \(P_2\), by perturbing each influential factor (\(T_1\), \(P_1\), \(u_1\), and fuel loading) by its respective uncertainty, \(\sigma\), and calculating the resulting changes in \(T_5\) and \(P_5\):

\[
\sigma_{T_5}^2 = \left( \frac{dT_5}{dT_1} \right)^2 \sigma_{T_1}^2 + \left( \frac{dT_5}{dP_1} \right)^2 \sigma_{P_1}^2 + \left( \frac{dT_5}{du_1} \right)^2 \sigma_{u_1}^2 + \sum_{i=1}^{N_{\text{components}}} \left( \frac{dT_5}{dX_i} \right)^2 \sigma_{X_i}^2 \tag{2.20}
\]

\[
\sigma_{P_5}^2 = \left( \frac{dP_5}{dT_1} \right)^2 \sigma_{T_1}^2 + \left( \frac{dP_5}{dP_1} \right)^2 \sigma_{P_1}^2 + \left( \frac{dP_5}{du_1} \right)^2 \sigma_{u_1}^2 + \sum_{i=1}^{N_{\text{components}}} \left( \frac{dP_5}{dX_i} \right)^2 \sigma_{X_i}^2 \tag{2.21}
\]

Figure 2.7 shows the relative contribution of each parameter to the overall uncertainty associated with \(T_5\) and \(P_5\) for the cyclohexene pyrolysis experiment shown in Figure 2.6.
As in the $T_2$ and $P_2$ results, the largest contributor to the uncertainty in $T_5$ and $P_5$ is uncertainty in the incident shock velocity. For the selected cyclohexene pyrolysis experiment, the overall, 1-$\sigma$ uncertainty in $T_5$ was ±11.2 K, or 1.0%; the uncertainty in $P_5$ was ±14.5 kPa, or 1.9%. Across all the experiments reported in this work, the uncertainty in $T_5$ typically ranged from 0.6 to 1.2% and the uncertainty in $P_5$ ranged from 1.3 to 3.3%.

### 2.3 Laser absorption spectroscopy (LAS)

Laser absorption spectroscopy, or LAS, is the first of two experimental speciation techniques used in the work presented in this dissertation. When a molecule or atom absorbs a photon and transitions from a lower-energy quantum state to a higher-energy quantum state, absorption is said to have occurred. This concept forms the basis of LAS, a time-resolved technique used, in situ, to quantify the presence of gas-phase species using lasers. In this work, two types of laser absorption measurements are conducted: fixed-wavelength direct absorption (DA) and scanned-wavelength direct absorption (SDA) measurements. Both measurement types will be summarized here, including an overview of how they can each be used to determine mole fraction and/or temperature values, and the uncertainties associated with each.

#### 2.3.1 Fixed-wavelength laser absorption

The governing equation relating laser light absorbance to physical gas properties is known as the Beer-Lambert relation, presented below:

\[
\alpha_\nu = -\ln \left( \frac{I}{I_o} \right)_\nu = n_{abs}\sigma_\nu L
\]  

(2.22)

where $\alpha_\nu$ is absorbance of light at frequency $\nu$ by the absorbing species, $I$ is the light intensity transmitted through the shock tube, $I_o$ is the incident light intensity, $n_{abs}$ is the concentration (mol/m$^3$) of the absorbing species, $\sigma_\lambda$ is the absorption cross-section (m$^2$/mol) of the absorbing species at frequency $\nu$, and $L$ is the absorption path length (m). Frequency is related to wavelength, $\lambda$, by the speed of light ($c = 3 \times 10^8$ m/s), where $\lambda = c/\nu$. In a fixed-wavelength laser absorption experiment,
2.3. LASER ABSORPTION SPECTROSCOPY (LAS)

the laser emission is fixed at the target frequency, or wavelength, for the duration of the experiment.

In shock tube experiments, the light intensities $I$ and $I_o$ are typically measured using photovoltaic detectors with InSb (Hamamatsu Photonics) or HgCdTe (Vigo Systems) semiconductor chips. Each detector is set up on the "catch" side of the shock tube, meaning the laser passes through the shock tube before reaching the detector chip. $I_o$ is measured by evacuating the shock tube and recording the detector response to the incident beam. $I$ is the measured detector response to the laser beam transmitted through the shock tube, recorded for the duration of each experiment. Background light intensity is subtracted from both measurements.

The temperature- and pressure-dependent absorption cross-section of the absorbing species at frequency $\nu$, $\sigma_\nu$, is determined experimentally. The path length, $L$, is typically known for a given facility; in a shock tube, it is the inner diameter, or bore, of the shock tube (11.53 cm for the AST).

2.3.1.1 Fixed-wavelength mole fraction measurement

In most fixed-DA experiments, the Beer-Lambert relation is used to measure species mole fraction. Mole fraction can be calculated from the concentration term in Equation 2.22, where:

$$n_{abs} = \frac{X_{abs}P}{R_uT}$$

(2.23)

Here, $X_{abs}$ is the mole fraction of the absorbing species, $P$ is the system pressure, $R_u$ is the universal ideal gas constant, and $T$ is the gas temperature. In a given shock tube experiment, $P$ is typically measured using a sidewall pressure transducer (as described in Section 2.2.3), and $T$ is either measured (as will be described in Section 2.3.2.1) or modeled using a chemical kinetic simulation (as will be described in Section 3.4.2).

The uncertainty associated with fixed-DA mole fraction measurements can be estimated using error propagation. The laser mole fraction measurement is impacted by uncertainty in incident and transmitted light intensity (typically around $\pm 0.16\%$, but depends on the particular detector), path length ($\pm 0.2$ mm), absorption cross-section measurement, pressure, and temperature. The overall species mole fraction uncertainty can be calculated by perturbing each input parameter by
its maximum uncertainty, $\sigma$, and computing the change in mole fraction value, such that:

$$
\sigma_{X_{abs}}^2 = \left( \frac{dX_{abs}}{dI} \right)^2 \sigma_I^2 + \left( \frac{dX_{abs}}{d\sigma}\right)^2 \sigma_{\sigma}^2 + \left( \frac{dX_{abs}}{dT} \right)^2 \sigma_{T}^2 + \left( \frac{dX_{abs}}{dP} \right)^2 \sigma_{P}^2
$$

Equation 2.24 is used to calculate the uncertainty associated with all of the fixed-DA laser mole fraction measurements presented in this work. The uncertainty in absorption cross-section, temperature, and pressure are the largest contributors to overall uncertainty in laser mole fraction measurements.

2.3.2 Scanned-wavelength laser absorption

A second laser measurement technique used in this work is scanned-direct absorption (SDA). Instead of looking at absorbance at a single frequency or wavelength, as is done in fixed-DA, SDA uses a tunable diode laser to scan across one or more absorbance features in frequency-space. An integrated absorbance value, $A_i$, can be calculated for each feature, $i$, as follows:

$$
A_i = \int_{-\infty}^{\infty} \alpha_{\nu} d\nu = S_i(T) PX_{abs} L
$$

where $S_i(T)$ is the linestrength of transition $i$. The temperature dependence of the transition linestrength can be calculated according to:

$$
S_i(T) = S_i(T_o) \frac{Q(T_o)}{Q(T)} T_o \frac{T}{T_o} \exp \left[ -\frac{hcE''}{k} \left( \frac{1}{T} - \frac{1}{T_o} \right) \right] \left[ 1 - \exp \left( -\frac{hc\nu_o}{kT} \right) \right] \times \left[ 1 - \exp \left( -\frac{hc\nu_o}{kT} \right) \right]^{-1}
$$

where $T_o$ is the reference temperature (296 K), $Q$ is the partition function of the absorbing molecule, $h$ is Planck’s constant, $c$ is the speed of light, $E''$ is the transition’s lower-state energy, $k$ is the Boltzmann constant, and $\nu_o$ is the frequency of the transition linecenter. The partition functions can be calculated from statistical mechanics, while $E''$ and $\nu_o$ can be obtained from a spectral database such as HITRAN [26] or HITEMP [27].
2.3.2.1 Scanned-wavelength temperature measurement

SDA measurements across two separate absorbance transitions can be used to calculate temperature. For a given absorbing species, the ratio, \( R \), of the integrated absorbances of the two transitions ultimately reduces to a ratio of the two linestrengths:

\[
R = \frac{A_1}{A_2} = \frac{S_1(T)PX_{abs}L}{S_2(T)PX_{abs}L} = \frac{S_1(T)}{S_2(T)}
\]  

By applying Equation 2.26 and re-arranging, the temperature of the absorbing gas can be calculated:

\[
T = \frac{\frac{\hbar c}{k} (E''_2 - E''_1)}{\ln R + \ln \left( \frac{S_2(T_0)}{S_1(T_0)} \right) + \frac{\hbar c}{kT_0} (E''_2 - E''_1)}
\]

where \( E''_1 \) and \( E''_2 \) are the lower-state energies of the two transitions.

As can be deduced from Equation 2.28, the primary factors impacting the uncertainty in a temperature measurement obtained in this way are the uncertainties in the reference-temperature linestrengths and the ratio of integrated absorbances. Typical database-provided linestrength values have an estimated uncertainty that can range from 2-20% [26], depending on the species; the uncertainty in the ratio of integrated absorbances largely depends on the goodness-of-fit associated with the analytical lineshape function used for integration (typically a Voigt lineshape profile).

The overall uncertainty associated with an SDA temperature measurement can be estimated much in the same way as shown in Equation 2.24: each variable is perturbed by its maximum uncertainty and the resulting change in temperature is recorded; the root-sum-square of the differential temperature changes yields the overall temperature uncertainty.

2.3.2.2 Scanned-wavelength mole fraction measurement

With the system temperature measurement in-hand, the mole fraction of the absorbing species in the system can also be determined. Rearranging Equation 2.25, the mole fraction of the absorbing species is:

\[
X_{abs} = \frac{A_i}{S_i(T)PL}
\]
where $S_i(T)$ can be the linestrength of either of the two absorption transitions used to calculate temperature (typically, the strongest of the two is chosen). Once again, the uncertainty associated with a mole fraction value measured using SDA is calculated by taking the root-sum-square of the differential mole fraction changes induced in the mole fraction result when each independent variable is perturbed by its maximum uncertainty.

2.4 Gas chromatography (GC)

Gas chromatography, or GC, is the second experimental speciation technique used in this dissertation. GC is a separation method in which the components or molecules being separated are distributed between two phases: a stationary phase (typically a porous media or gel) and a gaseous mobile phase, which moves continuously in one direction. GC is one of the most broadly used analytical techniques in the world; as of 2019, the worldwide market for GC instruments is between $2 and $3 billion, which equates to more than 40,000 instruments sold annually [28].

An interesting historical aside: the term "chromatography" was first coined by the Russian botanist Mikhail Tswett in a pair of papers published in 1906 [29, 30]. In the papers, Tswett discusses his use of powdered calcium carbonate to separate plant pigments. The powdered adsorbant was packed into a small, narrow tube (column) and a solution of plant pigment was poured on top. Soon after, green and yellow rings started to form in the column of adsorbant. By adding more solvent to the column, the rings separated, widened, and moved further down the tube; on occasion, a single ring separated into additional rings, indicating that additional compounds were present. When separation was complete, Tswett pushed the packed column of adsorbant out of its tube and cut the individual bands off with a scalpel. The compounds responsible for the color change could then be desorbed from the packed adsorbant material through use of a solvent. In the second of his two papers, Tswett famously wrote: "Like light rays in the spectrum, the different components of a pigment mixture, obeying a law, are resolved on the calcium carbonate column and then can be qualitatively and quantitatively determined. I call such a preparation a chromatogram and the corresponding method the chromatographic method" [30, 31]. In Greek, the root "chroma" means
2.4. GAS CHROMATOGRAPHY (GC)

"color" and the root "graphein" means "to write"; the literal translation of the term "chromatography" is therefore "color writing." Interestingly enough, Tswett’s last name in Russian (Tsvet) is also the word for color, meaning "chromatography" can also loosely be translated to "Tswett’s writing."

Although derived from the analytical process pioneered by Tswett in the early 1900s, modern-day gas chromatography is distinctly different in its approach and implementation. The subsequent parts of this section provide an overview of the analytical separation process, the specifications of the gas chromatograph used in this work, the process used for analytical method optimization, chromatogram interpretation, and finally, calculations of uncertainty associated with GC measurements. It should be noted that, in keeping with convention, the acronym GC is often used interchangeably to mean either "gas chromatography" (the subject) or "gas chromatograph" (the instrument).

2.4.1 Analytical process and column separation

All gas chromatographs have the same six basic components: a carrier gas supply, flow regulator, sample injector, column (contained in an oven for temperature control), detector, and data acquisition system. These six basic components are depicted in the simplified process diagram shown in Figure 2.8. An inert carrier gas (typically helium, argon, nitrogen, or hydrogen) flows continuously through the inlet, column, and past the detector. The flow regulator controls the flow rate of the carrier gas. The sample of gas to be analyzed is injected into the inlet, where it is mixed with the continuous flow of carrier gas. The carrier gas carries the sample through the GC column. As the sample traverses the column, the constituent components are separated. At the end of the column, the sample components pass a detector, which registers an electrical response proportional to the amount of each component. The resulting detector response data, plotted versus time, is known as a chromatogram.

The column separation process is the most important part of GC analysis. Most columns today are capillary columns, or unfilled columns with a thin coating inside the tube making up the stationary phase. A typical, fused-silica column might be 15-60 m long, have an inner diameter of 0.25 mm, and a stationary-phase film thickness of 0.25 µm. These columns are often called "open tubular," or OT columns. Capillary column stationary phases are usually liquids or very viscous polymers; the most commonly used liquid phases are siloxane polymers or polyethylene glycol. A
column is selected for its ability to interact with and separate out the gas species of interest, typically due to their different molecular weights, boiling points, polarity, etc.

Gas separation occurs as shown in Figure 2.9. In this example, a three-component gas sample is injected into the carrier gas flow. As the gas traverses the column, each component in the gas adsorbs to and desorbs from the stationary phase at a different rate; in this case, the blue triangle "molecules" adsorb/desorb the fastest, while the red circle and green square "molecules" have a slower adsorption/desorption rate with the stationary phase. With the correct temperature, pressure, and flow rate conditions, the column separation process can be optimized to fully separate each of the gas components before the end of the capillary column.

When the separated gas components exit the column, or elute, they pass the detector, one at a time. While the most commonly used detectors are flame ionization detectors, or FIDs, the GC used in this work is equipped with thermal conductivity detectors, or TCDs. A TCD works by comparing the thermal conductivity of the analyte in the carrier gas to the thermal conductivity of the pure carrier gas. When a gas species passes the detector, a difference in thermal conductivity, relative to the pure carrier gas, occurs, resulting in a change in recorded voltage. When the gas component is fully eluted (exits the detector cavity), the output voltage returns to its baseline value, as the thermal
2.4. GAS CHROMATOGRAPHY (GC)

Figure 2.9: Diagram of the GC column separation process
conductivity is once again that of the carrier gas.

When the voltage output is recorded in time, the result is a series of peaks, with each peak corresponding to the presence of an individual gas molecule, and the timing of each peak corresponding to the elution time of the molecule (see Figure 2.9, for example). This series of peaks, presented as voltage vs. time data, is the resulting chromatogram.

2.4.2 Agilent 490 MicroGC specifications

In this work, the instrument used for analysis is a four-column Agilent 490 MicroGC. The GC instrument is modular, in that each column is effectively a separate GC, with its own pneumatics, injector, column, and detector. The GC is designed to handle small injection volumes, spanning a range of 1-10 µL.

The GC is equipped with four columns: a molecular sieve 5 Å (MS 5 Å) column, a PoraPlot Q (PPQ) column, a PoraPlot U (PPU) column, and a CP-Sil 5CB column. Each column targets a specific kind of species or subset of hydrocarbons. Table 2.2 summarizes the relevant properties of the four columns and the species they target for separation.

2.4.3 Method optimization

The collection of column temperatures, pressures, flow rates, and injection volumes used in a GC analysis is known as the analytical "method." Method optimization is an important process that must be carried out before using the instrument for species quantification. By optimizing the temperature, pressure, flow rate, and injection volume for a given column, one can ensure that the column is tuned to successfully and cleanly separate the molecular components of interest. Method optimization is often done in a brute-force manner, in which a gas sample containing species of interest is injected into the GC, and the temperature and pressure conditions of each column are varied parametrically to determine the appropriate conditions for separating the species.

Figure 2.10 shows the effect of changing the temperature of the PPQ column on the spacing of four species peaks (15 ppm each of, from left to right, propene, propane, propyne, and n-butane); column inlet pressure is maintained at 21 psi, while the column temperature is set to 130, 150, or
### Table 2.2: Agilent 490 MicroGC column specifications

<table>
<thead>
<tr>
<th>GC Column</th>
<th>MS 5A column</th>
<th>PoraPlot Q (PPQ) column</th>
<th>PoraPlot U (PPU) column</th>
<th>CP-Sil 5CB column</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length (m)</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>6</td>
</tr>
<tr>
<td>Stationary phase</td>
<td>Molecular sieve</td>
<td>Divinylbenzene</td>
<td>Divinylbenzene, ethylene glycol/dimethylacrylate</td>
<td>dimethyldisiloxane</td>
</tr>
<tr>
<td>Target species</td>
<td>H₂, CO, CH₄, N₂, O₂, noble gases</td>
<td>C$_1$-C$_6$ hydrocarbons, H$_2$S, CO$_2$, SO$_2$, separation of C$_3$H$_6$ and C$_3$H$_8$</td>
<td>C$_1$-C$_6$ hydrocarbons, H$_2$S, CO$_2$, SO$_2$, separation of C$_2$H$_6$, C$_2$H$_4$, and C$_2$H$_2$</td>
<td>C$<em>3$-C$</em>{10}$ hydrocarbons, aromatics</td>
</tr>
</tbody>
</table>
170 °C. As can be seen in this analysis, as temperature is increased, the retention time associated with each species decreases. However, the baseline linearity gets poorer and the three closely packed C$_3$ hydrocarbon peaks cannot be resolved down to the baseline. For this gas mixture, the optimal PPQ column temperature was found to be 120 °C.

Figure 2.10: Effect of column temperature on species peaks (calibration gas mixture includes 15ppm each of propene, propane, propyne, and n-butane)

Figure 2.11 shows the effect of changing the inlet pressure of the PPQ column on the four species peaks shown in the temperature-effect study; the column temperature is maintained at 150 °C, while the pressure is set to 18 or 24 psi. The most significant result of increasing the column pressure is to shift the retention times of all the peaks earlier in time, and to compress the distance between the peaks (note that the x-axis of Figure 2.11a spans 0.6 min, while the x-axis of Figure 2.11b spans 0.4 min). For this gas mixture, the optimal PPQ column pressure was found to be 25 psi.

The nominal method properties used in this work are shown in Table 2.3. Because many of the same species were quantified in the various experiments presented in this dissertation, the method used in each experiment was similar to that presented in Table 2.3. However, when larger hydrocarbon species were quantified (e.g., n-heptane or cyclohexene), the total run time was extended to accommodate their longer retention times.

2.4.4 Chromatogram interpretation

When using a chromatogram to determine the amount of a species present, there are typically two ways to quantify peak size: peak height or integrated peak area. Integrated peak area is the
2.4. GAS CHROMATOGRAPHY (GC)

Figure 2.11: Effect of column pressure on species peaks (calibration gas mixture includes 15ppm each of propene, propane, propyne, and n-butane)

Table 2.3: Nominal GC method specifications

<table>
<thead>
<tr>
<th></th>
<th>MS 5A</th>
<th>PoraPlot Q (PPQ)</th>
<th>PoraPlot U (PPU)</th>
<th>CP-Sil 5CB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Injector Temperature (°C)</td>
<td>110</td>
<td>110</td>
<td>110</td>
<td>110</td>
</tr>
<tr>
<td>Injection time (ms)</td>
<td>40</td>
<td>40</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Column Temperature (°C)</td>
<td>90</td>
<td>120</td>
<td>80</td>
<td>50</td>
</tr>
<tr>
<td>Column Initial Pressure (psi)</td>
<td>16</td>
<td>25</td>
<td>24</td>
<td>21</td>
</tr>
<tr>
<td>Sampling Frequency (Hz)</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Run Time (s)</td>
<td>160</td>
<td>160</td>
<td>160</td>
<td>160</td>
</tr>
<tr>
<td>Carrier Gas</td>
<td>Ar</td>
<td>He</td>
<td>He</td>
<td>He</td>
</tr>
</tbody>
</table>
most common way to characterize peak size, and is the approach used here. In this work, peak integration is carried out using the proprietary Agilent OpenLAB EZChrom software. As shown in Figure 2.12, the software detects the peaks and constructs a linear baseline beneath each peak. The resulting peak area can then be calculated, and the retention time determined.

![Figure 2.12: Screenshot of the Agilent OpenLAB EZChrom software, showing representative peak integration on the PPQ column](image)

Although in-software peak integration is a relatively automated process, the baseline fit is checked for each species in each experiment to ensure proper integration.

### 2.4.5 GC calibration

To quantify the presence of hydrocarbon species in a gas sample of unknown composition, the GC must first be calibrated. This is done by injecting a sample of known composition into the GC and finding the peak areas and retention times corresponding to each species. A calibration curve is generated by analyzing multiple samples of different, known compositions, and plotting the composition values vs. peak area, as shown in Figure 2.13. In this example, two acetylene samples of different composition (1% C\(_2\)H\(_2\)/Ar and 2% C\(_2\)H\(_2\)/Ar) are analyzed and the resulting calibration curve is shown.
2.4. GAS CHROMATOGRAPHY (GC)

The slope of the calibration curve is known as the response factor, $RF$, defined as:

$$RF = \frac{X_{\text{species}}}{A_{\text{peak}}}$$  \hspace{2cm} (2.30)

where $X_{\text{species}}$ is the mole fraction of the species of interest and $A_{\text{peak}}$ is the peak area. When the intercept of the calibration curve is 0, or a single data point is used for calibration, the response factor can be directly used to convert a species peak area to mole fraction.

When shock tube experiments are run at a wide range of temperature conditions, the range of measured species mole fractions is also expected to be large. To accommodate this wide mole fraction range, and account for non-linearity in the detector response, calibration curves of three or more points were typically generated for each species of interest in this work. Instead of fitting a single line to the entire calibration dataset, piecewise linear fits were calculated between consecutive points. The calibration curve is then applied to the peak area measurement corresponding to an unknown quantity, and the resulting mole fraction value can be determined more accurately.
To ensure robustness of calibration, each calibration point used in this work is not derived from a single measurement, but the mean of 3-5 peak area measurements.

2.4.6 Uncertainty in GC mole fraction measurements

Mole fraction measurements obtained by GC analysis are impacted by a number of sources of uncertainty, including calibration gas uncertainty, uncertainty in calibration curve fit, measurement scatter, and repeatability. Each of these effects will be discussed and quantified here.

Calibration gas compositional uncertainty can vary, depending on the source of the gas mixture. In most cases, a pre-prepared calibration gas, acquired from Praxair, Inc., is used for calibration. The quoted, compositional uncertainty associated with these mixtures is nominally ±2%. Calibration gas mixtures prepared manometrically in-house were also used for calibration. The compositional uncertainty associated with mixtures prepared in this way is on the order of 1% – much lower than that of a commercially available gas bottle, due to the high accuracy of the pressure gauges used for mixture preparation.

Calculating the measurement uncertainty associated with the use of a calibration curve is slightly more involved. All of the GC calibration curves (and curve segments) used in this work are generated using linear regressions of the form:

\[ y(x) = mx + c \]

where in this case, the \( y \) variable is mole fraction (\( X_{\text{species}} \)), \( m \) is the slope, \( x \) is peak area (\( A_{\text{peak}} \)), and \( c \) is the intercept. The goal is to calculate the uncertainty associated with a mole fraction value determined using the linear regressions that make up a single-species calibration curve. (A useful resource for calculating experimental uncertainty and linear regression uncertainty is [25]).

The standard error of regression, applied to this scenario, is defined as:

\[ s_y = \left[ \frac{\sum_{i=1}^{N} (y_i - \hat{y}_i)^2}{N - 2} \right]^{1/2} \]

(2.32)

where the numerator is the sum of residuals (\( \hat{y}_i \) is the mole fraction value of each individual point,
and $\hat{y}_i$ is the mole fraction value, obtained from the linear fit, expected to correspond to a given peak area), and $N$ is the number of points used for the fit. The term $s_y$ is calculated for each linear fit, and used to describe the random standard uncertainty associated with a mole fraction value derived from a calibration curve.

Measurement scatter, or the ability of the GC instrument to produce the same result for a single sample, was also quantified. A 5% C$_2$H$_4$/Ar gas mixture (Praxair, Inc.) was introduced to the GC sample line and seven consecutive GC measurements were recorded. The sample line was then vacuumed out and purged. This process was repeated four times, generating four data sets, each with seven data points, as shown in Figure 2.14; the statistics associated with the four datasets are listed in Table 2.4.

![Figure 2.14: Repeatability experiments: 4 sets of 5% C$_2$H$_4$ sample analyses](image-url)
Table 2.4: GC measurement repeatability statistics

<table>
<thead>
<tr>
<th></th>
<th>Set 1</th>
<th>Set 2</th>
<th>Set 3</th>
<th>Set 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avg Mol Frac (%)</td>
<td>4.9911</td>
<td>4.9945</td>
<td>4.9908</td>
<td>4.9949</td>
</tr>
<tr>
<td>Std Dev ($\sigma$)</td>
<td>0.0052</td>
<td>0.0073</td>
<td>0.0036</td>
<td>0.0049</td>
</tr>
<tr>
<td>Rel $\sigma$ (%)</td>
<td>0.1039</td>
<td>0.1462</td>
<td>0.0731</td>
<td>0.0988</td>
</tr>
</tbody>
</table>

Of the four datasets recorded, the maximum standard deviation seen within a single, seven-point dataset was 0.0073% (mole fraction), or a relative standard deviation of 0.15%. These results indicate that there is very little scatter in consecutive GC measurements of the same sample.

The four, seven-point datasets also allow for the quantification of measurement repeatability. Figure 2.15 shows all four datasets plotted alongside each other. Taking into account all 28 points, the average measured mole fraction is 4.99%. When comparing the average of each dataset, the standard deviation is 0.002% (mole fraction), or a relative standard deviation of 0.04%. Overall, these results indicate that ethylene mole fraction measurements in this concentration range are very repeatable.

Figure 2.15: Compilation of all four, seven-point C$_2$H$_4$ measurement sets; red dashed line denotes overall average mole fraction value

This same analysis can be done for multiple species at multiple concentration levels, allowing for the calculation of column- and species-dependent scatter and repeatability values.
2.5. SUMMARY

The overall uncertainty associated with a particular species mole fraction value obtained via GC analysis can be calculated by taking the root sum square of the relative uncertainty associated with all of the relevant parameters described above (calibration gas composition, calibration curve fit, scatter, and repeatability). Across the board, the GC-measured mole fraction uncertainties for gaseous species were approximately 5% or less.

2.5 Summary

In this chapter, three experimental methods have been introduced. A shock tube is the primary device used in this work to rapidly heat test gas mixtures to temperature and pressure conditions of interest. Laser absorption spectroscopy (used at a fixed wavelength or by scanning over a wavelength range) is an in situ diagnostic technique that is used to collect time-resolved mole fraction and temperature measurements in shock tube experiments. Gas chromatography is an additional experimental technique used to quantify the presence of gas molecules in a fixed-volume sample.

In the subsequent chapters of this dissertation, all three experimental methods are used extensively. With the exception of a few validation experiments, all of the experiments presented in this dissertation are conducted in a shock tube. Chapters 3-5 describe the multi-stage development of a combined LAS-GC fast-sampling diagnostic for use in shock tube experiments, and Chapters 6 and 7 describe the development of a new technique for measuring laminar flame speeds in a shock tube; LAS is once again deployed in these experiments to study the compositional and thermal time-history within the flames.
Chapter 3

Species-yield GC measurements with \textit{in situ} LAS

\textit{The contents of this chapter have been published in the journal \textit{Combustion and Flame} [19].}

3.1 Introduction

The purpose of this chapter is twofold: 1) to present the first iteration of a speciation diagnostic that combines GC sampling with a time-resolved, laser-based ethylene measurement in a single conventional shock tube experiment; and 2), to outline a methodology for accurately simulating GC speciation measurements with a detailed kinetic model, as well as a methodology for accurately comparing GC speciation measurements to laser measurements in non-highly dilute experiments. The subsequent sections of this chapter will provide a brief literature review, then describe the specific shock tube configuration used for this work, the combined speciation methods, the methodologies developed to compare GC measurements to kinetic model and laser results, and finally, results obtained using the combined GC sampling/laser absorption diagnostic to study ethylene pyrolysis species yields.


3.2 Background and literature review

Modern chemical kinetic studies in shock tubes employ a variety of diagnostics to probe species concentrations in the high-temperature region behind reflected shock waves. Shock tube speciation techniques can broadly be divided into two categories: post-shock sampled and time-resolved in situ species measurements.

Common post-shock sample analysis methods include gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS) [6, 32, 33]. In both techniques, a gas sample is extracted from the shock tube core after arrival of the expansion wave that quenches the reacting gases. GC analysis, which is of particular interest in the current work, allows for quantification of many different species relevant to combustion, including O\(_2\), N\(_2\), H\(_2\), alkanes, alkenes, and aromatics like benzene and toluene, among others. Single-pulse, magic-hole style shock tubes, of the kind described by Hidaka et al. [32] and Lifshitz et al. [6], are typically preferred for sample-based diagnostics; the use of a dump tank weakens subsequent reflected shock and expansion wave events after the end of the test time, and can lead to higher quenching rates accompanying the arrival of the expansion wave.

Conventional shock tube configurations are often used in conjunction with time-resolved sampling methods or optical diagnostics to obtain species time-histories between the arrival of the reflected shock wave and the arrival of the expansion fan. Time-of-flight mass spectrometry (TOF-MS) is a particularly attractive speciation diagnostic, as it allows for time-dependent quantification of almost any stable species [34]. However, shock tube/TOF-MS test conditions are limited to near-atmospheric pressures due to the low-pressure requirement of the mass spectrometer ion source, and the measurements can suffer from limited temporal resolution and sensitivity. Optical diagnostics can offer a non-intrusive, calibration-free alternative to sample-based species measurements. Laser absorption diagnostics, in particular, can be used to measure multiple hydrocarbon species at the same time, with superior time resolution, at a wide range of pressure and temperature conditions [4]. Absorption diagnostics are also particularly valuable because they can be used to measure time-histories of transient, radical species such as OH, CH, and CH\(_3\), not just stable species. However, there is a limit to the number of species that can be measured simultaneously using optical
diagnostics, and not all species relevant to combustion can be measured easily (e.g. H$_2$).

Due to the complementary nature of the data provided by the post-shock sampling and laser diagnostic speciation techniques, kineticists often use data obtained from multiple shock tubes with different diagnostic capabilities to gain greater insight into the pyrolysis or oxidation of a particular hydrocarbon fuel \[35\]. Less common are experiments that combine both techniques. The first and perhaps only instance of a combined laser absorption/GC speciation experiment in a shock tube was conducted in 1985 by Hidaka et al. \[32\]. Even so, the experiments conducted by Hidaka et al. were distinctly different from those outlined here; the experiments were performed in a modified single-pulse shock tube with a piston, GC sample extraction was very delayed after the arrival of the expansion wave (20 s), and laser absorption measurements conducted at 3.39 µm only provided useful data for the first 300 µs of test time and were susceptible to interference absorbance. Modern laser diagnostics, such as the ethylene diagnostic described in this chapter, are intentionally developed to isolate a single species and allow for its measurement, free from interference.

A challenge of particular interest to the shock tube community is how to best use experimental speciation data to guide development of, and validate results generated by, chemical kinetic models. Shock tube speciation measurements are typically compared to modeled results by supplying a mechanism solver with an initial temperature and pressure, specifying a constant-internal energy/constant-volume or constant-enthalpy/constant-pressure constraint, allowing the solver to step forward in time (iterating on solutions to energy conservation, mass conservation, and gas-phase chemical rate expressions), and finally extracting a species mole fraction value at a specified time. Comparison of laser-based, time-resolved diagnostics and kinetic model results is relatively straightforward. Typical laser measurements begin at "time zero" (arrival of reflected shock) and conclude at the end of Region 5 (the near-constant pressure region between time zero and the arrival of the expansion fan); this interval is commonly referred to as the "test time," $t_{\text{test}}$, of an experiment (see Figure 3.1). The species time-histories obtained during the test time using laser diagnostics can be directly compared to the time-histories output by the model over the same time period. Sampling-based measurements, however, present a greater challenge.

Experiments utilizing GC sampling typically involve analysis of a sample that has been extracted from the shock tube after the test gas has been chemically frozen by the rapid cooling induced by the
expansion fan. Experimentalists have long noted that this cooling occurs over a finite period of time, leading to the concern that reactions continue to take place during this quenching period \cite{6, 32, 37}. Additionally, these reactions occur under time-varying temperature conditions, complicating efforts to accurately model sampling-based data. It is thought that for reactions with sufficiently high activation energies (primarily reactions involving stable species), and experiments with sufficiently high quenching rates, the quenching period will have a negligible effect on the resulting stable species measurements obtained using the GC sampling technique \cite{6, 38}. To account for reactions that do continue to occur during the expansion fan, it is necessary to consider an effective reaction time, $t_{\text{react}}$, (and a temperature time-history) that extends beyond the experiment test time, into the expansion fan.

A common metric, originally proposed by Hidaka et al. \cite{36}, defines $t_{\text{react}}$ as the time between the arrival of the reflected shock front and the point at which pressure has dropped to 80\% of the reflected shock pressure, $P_b$ (see Figure 3.1), during which time the reaction temperature is usually assumed constant. Colket \cite{39} was among the first to directly include chemistry during cooling
by assuming an isentropic relationship between temperature and pressure and obtaining a temperature time-history from a recorded pressure trace. Tang and Brezinsky [38] employed a different approach, which requires use of a chemical thermometer to obtain an average temperature over the effective reaction time (as defined by Hidaka et al. [36]), and allows for the back-calculation of an initial $T_5$ temperature, $T_{5,\text{init}}$, and a time-resolved temperature time-history. A major constraint associated with using a chemical thermometer to back-calculate $T_{5,\text{init}}$ is the need for a highly dilute test gas mixture to ensure relatively isothermal conditions for the duration of the test time. Additionally, if an average temperature is used to describe the effective reaction time, the quenching rate must be sufficiently high to ensure that the temperature time-history is dominated by the intended test conditions, not those during the quenching period. For highly dilute, single-pulse shock tube experiments, it has been found that satisfactory modeling of post-shock GC measurements can be achieved by assuming constant-temperature, constant-pressure conditions and extending the plateau values out to the time at which the pressure would have otherwise dropped to 80% of its maximum plateau value [38, 40]. Even so, this is obviously only an approximation of the reacting system.

An inherent requirement of *in situ* laser diagnostic measurements is the need for sufficient fuel concentration to allow for detectable changes in light intensity due to absorbance. As a result, the typical method used for modeling isothermal, isobaric, highly dilute shock tube experiments cannot be used, and a different methodology must be applied to model the experimental results obtained using the combined diagnostic.

Presented here (Section 3.4) is an accurate method for accounting for the quenching period in chemical kinetic simulations, one that utilizes a measured pressure trace to obtain a model-derived temperature time-history to more accurately simulate the time-evolving thermodynamic conditions experienced by the test gas. Additionally, despite widespread usage of the "80% of $P_5$" effective reaction time metric, it will be shown that a universal, pressure-based metric for determination of effective reaction time is not appropriate for all chemical kinetic studies, particularly those involving test gas mixtures that are not highly dilute and those performed in conventional, non-single-pulse shock tubes.

Despite the wealth of literature containing comparisons of GC speciation measurements to chemical kinetic model results and the associated methods for doing so, there is a relative dearth of
literature on how best to compare GC speciation measurements to time-resolved speciation results obtained using diagnostics typically employed before the arrival of the expansion fan. The methodologies presented herein aim to address this need and reconcile the comparison of results obtained using an inherently time-resolved experimental technique (laser abosorption) with results obtained using an inherently steady-state technique (GC sampling).

3.3 Experimental setup and approach

3.3.1 Shock tube facility

The combined laser and GC steady-state, speciation experiments were performed in the AST facility, described at length in Section 2.2.3. The shock tube was used with its standard, short driver length (3.63 m). The driver gas used in these experiments is pure helium, and the driver section is separated from the driven section by a 0.02-inch thick polycarbonate diaphragm. Driver inserts were employed to obtain near-constant pressure conditions in the test region [41]. Each experiment ends when the reflected expansion fan reaches the driven test section, causing a rapid drop in both temperature and pressure, thereby freezing the composition of the test gas. This shock tube configuration yielded effective test times (time from reflected shock arrival to initial arrival of the rarefaction wave 2 cm from the endwall, see Figure 3.1) of 1.9-3.2 ms at the test conditions of interest.

Incident shock speeds were determined by extrapolating shock arrival times, measured by six sidewall piezo-electric pressure transducers (PCB 113A26), to the endwall (see Section 2.2 for more details). Time-resolved measurements of \( P_5 \) were obtained using a piezoelectric pressure transducer (Kistler 603B1) mounted in the sidewall, 2 cm from the shock tube endwall.

The test gas mixture used in this work (1.0% ethylene/argon) was prepared manometrically (MKS Baratron) with a compositional uncertainty of ±2%. Research-grade, high-purity (> 99.999%) helium, argon, and ethylene gases, supplied by Praxair, Inc., were used.
3.3.2 Ethylene laser absorption diagnostic

Ethylene species time-histories were measured using fixed-wavelength, narrow-linewidth, direct absorption at 10.532 µm. A water-cooled, grating-tuned, CO₂ gas laser (Access Laser Company, model Lasy-4G) was operated at the P14 line. The ethylene diagnostic at 10.532 µm has previously been discussed in great detail [42, 43].

The beam was passed through shock tube sidewall ports located 2 cm from the shock tube end-wall. After passing through the shock tube, the beam was focused using a 10-cm focal length concave mirror into a 2.54-cm diameter, gold-coated integrating sphere (Labsphere, Inc.). A 10.6-µm, narrow bandpass IR filter (fullwidth at half maximum 300 nm) was placed in front of the integrating sphere to filter emission and prevent unwanted light from reaching the detector. A thermoelectric-cooled, photovoltaic IR detector (PVM-2TE, Vigo Systems) was used to measure the transmitted laser beam intensity at a sampling rate of 10 MHz. See Figure 3.2 for a schematic of the laser diagnostic setup.

The measured ethylene concentration was determined using the Beer-Lambert relation, as described in Section 2.3.1. Temperature- and pressure-dependent absorption cross-section values were obtained from the work of Ren et al. [43], and will be summarized here.

High-temperature ethylene absorption cross-sections (Region 5) were calculated as the product of two independent functions of temperature and pressure:

\[
\sigma(T, P) = \sigma(T) \times \chi(P)
\]

(3.1)

where:

\[
\sigma(T) = a_0 + a_1 \times \exp(-T/b_1) + a_2 \times \exp(-T/b_2), P = 1.8 - 5.5 \text{ atm}
\]

(3.2)

and

\[
\chi(P) = 0.68 + 0.47 \times P - 0.16 \times P^2, P = 0.3 - 1.2 \text{ atm}
\]

\[
= 0.82 + 0.2 \times P^{-0.1}, P = 1.2 - 18.6 \text{ atm}
\]

(3.3)

In Equation (3.2), \( a_0 = 4.8, a_1 = 383.7, a_2 = 103.5 \text{ (m}^2/\text{mol}), \) and \( b_1 = 183.0 \) and \( b_2 = 378.8 \text{ (K)}. \) The correlation in Equation (3.3) is valid over the temperature range 643-1959 K.
3.3. EXPERIMENTAL SETUP AND APPROACH

![Figure 3.2: Shock tube schematic with GC endwall sampling system and laser diagnostic](image)

Error propagation analysis was carried out to determine the uncertainty associated with the laser mole fraction measurements (see also Section 2.3.1.1). The laser measurement uncertainty is impacted by uncertainty in incident and transmitted light intensity (assumed to be ±0.16%), path length (±0.2 mm), absorption cross-section correlation (root-mean-square deviation of 1.4%), $T_{5,\text{init}}$ (2-$\sigma$ of 1.8%), and $P_{5,\text{init}}$ (2-$\sigma$ of 2.9%). The error associated with $T_{5,\text{init}}$ and $P_{5,\text{init}}$ is dominated by uncertainty in the incident shock velocity, and initial temperature and pressure ($T_1$, $P_1$). The overall species mole fraction uncertainty analysis was conducted by perturbing each input parameter by its maximum uncertainty and computing the change in mole fraction value (in effect, calculating the partial derivative with respect to each input). The root-sum-square (RSS) of each partial derivative, multiplied by the respective input uncertainty, was then determined. Overall, the 2-$\sigma$ uncertainty associated with a mole fraction measurement obtained using the laser diagnostic was found to be ±6.3%.

3.3.3 GC sampling system (species-yield measurements)

The GC used in this work is a four-column Agilent 490 MicroGC (see Section 2.4.2). Two columns, each equipped with a thermal conductivity detector (TCD), were used for these experiments: a molecular sieve 5Å (MS 5Å) column (hydrogen, H$_2$, and methane, CH$_4$, measurement), and a PoraPlot U (PPU) column (ethylene, C$_2$H$_4$, and acetylene, C$_2$H$_2$, measurement). A multipoint calibration curve was generated for each of the species of interest prior to each set of shock
experiments. The calibration gases used for this work were either prepared manometrically or obtained from Praxair, Inc., with a quoted compositional uncertainty of ±2%.

A fast-acting solenoid valve (Festo MHE3) is mounted on the shock tube endwall via a custom-made, low-volume endwall plug. The plug is designed to minimize dead volume between the shock tube core and the sampling valve. This is achieved by running a stainless steel, 1/4-inch outer diameter, 1/8-inch inner diameter tube down the length of the plug – one end of the tube interfaces with an internal seat within the valve, and the other end is flush with the shock tube endwall, thereby eliminating large pockets of unreacted gas. The resulting dead volume residing within the endwall plug is ∼1.05 mL. A short, 1/8-inch outer diameter tube is inserted into the end of the plug to allow each sample to be extracted from the shock tube core, offset 5 mm from the shock tube endwall. The plug is radially offset from the central axis of the shock tube by 1 inch.

An 1/8-inch outer diameter, 44-inch long, stainless steel tube is attached to the Festo sampling valve and serves as the primary containment vessel for the extracted gas sample. This volume is connected to a 4.8-inch long, 1/4-inch outer diameter, segment of tube with a 1/4-turn ball valve at each end. This segment is used to isolate the first 2.2-mL of sample from the bulk of the sampled gas (see Figure 3.2). The total extracted sample volume (including the 1/8-inch and 1/4-inch sections) is 8.4 mL.

The GC is located on a platform 10 inches above the shock tube. A 6-port, multi-position sampling valve (Valco Instruments Co., Inc. EMT4) resides between the GC inlet and the sample volume to protect the GC from over-pressurization. An annotated photo of the multi-position sampling valve is provided in Figure 3.3. An in-line, 5-µm filter is also used to keep particulate debris out of the GC. When the sample is ready for analysis, the valve aligns the GC inlet port with the sample volume port. The GC extracts a sample from the sample line volume via a 1/16-inch outer diameter, 7.5-inch long, Sulfonert-treated, stainless steel tube. All of the tubing that makes up the sampling system is insulated and maintained at 60 °C during experiments (see Appendix B.1 for a discussion of the experimentally determined optimal sample line temperature). A top-view schematic of the full sampling system is shown in Figure 3.2.

Before running an experiment, the fast-acting valve is closed and the sample line is evacuated. When a shock experiment is conducted, the 1/4-turn valve leading to vacuum is first closed, thereby
3.3. EXPERIMENTAL SETUP AND APPROACH

Figure 3.3: 6-port, multi-position sampling valve, labeled to show the six ports, sample inlet, line to GC, and GC inlet

isolating the evacuated sample line. The sampling event is initiated when the fast-acting valve is triggered by the arrival of the reflected shock wave 2 cm from the endwall; the valve opens 10 ms after the reflected shock arrival (i.e., after the test gas has been fully quenched by the arrival of the expansion fan) and remains open for 0.8 s.

Within 2 s of the completion of the sampling event, the second 1/4-turn valve (upstream of the vacuum valve and pressure transducer) is closed, thereby trapping the first 2.2 mL of gas to enter the sample line. This volume is primarily made up of unreacted test gas that resides in the dead volume present in the plug used to mount the sampling valve to the shock tube, as well as test gas from the endwall boundary layer. The isolated gas volume (2.2 mL) is much greater than the volume of unreacted test gas observed in the endwall sampling experiments (∼1.05 mL). Therefore, by isolating the first 2.2 mL from the rest of the 8.4-mL sample, the remaining 6.2 mL can be analyzed with minimal dilution from unreacted gas or boundary layer gas.

Two samples are extracted from the sample line and analyzed by the GC for each shock experiment. The analysis of the second sample is taken to be the final GC measurement, as the first sample is susceptible to dilution by residual argon in the GC (used to flush out the GC between each
experiment) and trace amounts of unreacted test gas.

The uncertainty associated with the GC measurements is estimated to be ±4.7%; this estimate is the 2-σ uncertainty, obtained by calculating the RSS of the standard deviations due to uncertainty in calibration gas composition (±2%), calibration curve fit uncertainty (±0.5%), and calculated, representative scatter (±0.3%) and reproducibility (±0.8%) trends.

Several experiments and modeling exercises were conducted to assess the experimental design, establish operating protocols, and then validate the results obtained using the GC sampling system: driver gas dilution experiments, non-reactive/cold shock experiments, sampling location (endwall vs. sidewall) experiments, depth-of-sample experiments, and reflected-reflected shock condition calculations. The results of these validation experiments are presented in Appendix B.2.

3.4 Methodology for comparing GC, kinetic model, and laser results

Outlined in the subsequent sections is a methodology for comparing post-expansion fan GC measurements with kinetic mechanism predictions, and a methodology for comparing post-expansion fan GC measurements with time-resolved laser diagnostic measurements.

3.4.1 Comparison of GC measurements and kinetic model results

As mentioned previously, post-expansion fan samples extracted for GC analysis undergo a quenching process of finite duration upon arrival of the expansion wave at the shock tube test section. A true simulation of post-expansion fan sample results must account for both the temperature and pressure change experienced by the test gas during the test time, and the temperature and pressure change due to the quenching process. A methodology for accurately comparing post-expansion fan GC measurements with kinetic model predictions is presented here.

Chemical kinetic solvers require a user-defined, initial gas composition and thermodynamic state in order to proceed. In shock tube kinetic simulations, this initial state is usually defined using singular temperature and pressure values calculated at the beginning of Region 5. The system is then typically modeled as an adiabatic, closed, homogeneous 0-D reactor with an constant-internal energy/constant-volume (UV) or constant-enthalpy/constant-pressure (HP) constraint imposed.
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Figure 3.4: Modeled temperature and species results obtained using the specified-pressure method. 1% ethylene/argon test gas, initial reflected shock conditions: 5.1 atm, 1695 K.

In addition to accepting a single-value pressure input, the kinetic solver CHEMKIN-PRO [44], used in this work, also allows the user to specify time-resolved pressure for the duration of the simulation; at each time step of the simulation, the system pressure is constrained to the provided pressure. Although the supplied pressure trace contains pressure data points at discrete time intervals, the solver uses an adaptive time-step to ensure convergence; linear interpolation is used to determine system pressure at times between the discrete data points. To calculate the constrained-pressure species results presented in this work, the solver is supplied with an initial temperature ($T_{b,\text{init}}$, as calculated using normal-shock relations), species mole fractions, and the pressure trace. The ideal gas equation is used to determine initial system volume and species concentrations. The solver then takes one step forward in time and solves the system of reaction rate equations; the new composition of the reacting system is thereby set, and the change in enthalpy associated with this time step is calculated, as is the resulting change in system temperature and pressure. The calculated pressure is compared to the constraint pressure (i.e., the measured pressure at that given time), and the system enthalpy is iterated upon until the true system temperature is reached and the calculated and constraint pressure values converge. In the experiments described in this work, measured pressure time-histories are obtained 2 cm from the shock tube endwall and used as a basis for this specified-pressure approach. To avoid convergence errors and reduce simulation times, a
least-squares cubic spline approximation of the raw pressure trace is calculated, with knots every 1 ms (see Figure 3.4a). This knot spacing was found to be optimal for capturing large, overall pressure trends, but filtering out small fluctuations due to signal noise (see Appendix B.3 for a discussion of pressure trace impact on model results).

Typical results obtained using the specified pressure method in conjunction with the USC Mech II [45] kinetic model are presented in Figure 3.4 for a 1% ethylene/argon test gas, shock-heated to an initial temperature and pressure of 1695 K and 5.1 atm. Figure 3.4a shows the experimentally measured pressure trace, the corresponding least-squares cubic spline used for modeling, and the resulting temperature trace generated by the model. As can be seen in Figure 3.4b, the modeled time-histories of the four primary species (C$_2$H$_4$, H$_2$, C$_2$H$_2$, and CH$_4$) reflect the quenching process; after the arrival of the expansion fan around 3 ms, the species mole fraction values begin to plateau and ultimately reach a steady state, indicating complete quenching of the chemical reactions. GC samples are extracted starting 10 ms after the arrival of the reflected shock wave 2 cm from the shock tube endwall. Therefore, the most appropriate species mole fraction value for comparison with the GC measurements is the final, ultimate value of each modeled species. In the case of the 1695 K, 5.1 atm shock experiment shown in Figure 3.4b the frozen, modeled H$_2$, C$_2$H$_2$, C$_2$H$_4$, and CH$_4$ mole fractions to be compared to the GC measurements would be: 0.793%, 0.665%, 0.228%, and 81.7 ppm, respectively.

When using the specified-pressure method in conjunction with a kinetic model, the time at which each species freezes becomes readily apparent. Looking closely at Figure 3.4b, C$_2$H$_2$ reaches its steady-state value first, followed closely by H$_2$ and C$_2$H$_4$, and finally CH$_4$. This distribution of freezing times indicates that it is not always appropriate to assign a single quenching time to all of the species in this reacting system, as would typically be done when using the "80% of P$_5$" effective reaction time metric (see Section 3.2).

For comparison with the specified-pressure approach, the experiments were also modeled using the "80% of P$_5$" average pressure approach. For the duration of each simulation, the system pressure was constrained to the average Region 5 pressure ($P_{5,avg}$), a constant-enthalpy constraint was imposed to allow the model to quantify the change in system temperature due to pyrolysis, and a
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final species mole fraction value was extracted from the model data at the time at which the system pressure would otherwise have dropped to 80% of $P_{5, \text{avg}}$. Figure 3.5a shows a time-resolved comparison of the two modeling techniques, and Figure 3.5b shows a comparison of the ultimate $C_2H_4$ mole fraction values obtained using each technique. Both sets of modeling calculations were conducted using USC Mech II [45].

In Figure 3.5a, $P_{5, \text{avg}}$ is the average pressure used in the "80% of $P_5$" approach, while $P(t)$ is the time-resolved pressure used in the specified-pressure approach. HP ($P_{5, \text{avg}}$) is the $C_2H_4$ mole fraction calculated using constant pressure, while HP ($P(t)$) is the $C_2H_4$ mole fraction calculated using specified pressure. $t_{\text{react}}$ denotes effective reaction time, or the time to which the constant-pressure calculations are carried out to determine ultimate species mole fraction values. From the comparison in Figure 3.5a it is clear that the average pressure modeling approach does not satisfactorily capture the quenched species mole fraction value; the approach over-predicts the extent of ethylene decomposition and provides a modeled value at $t_{\text{react}}$ that is approximately 10% lower than that predicted using the specified-pressure approach.
A comparison of the two modeling approaches across the full temperature range (Figure 3.5b) shows similar results – the average pressure approach consistently under-predicts the final ethylene mole fraction values. While it may be tempting to conclude that the average pressure approach provides model predictions that more closely match the experimental GC results, this closer agreement is primarily due to the time at which the final mole fraction value is extracted from the modeled data set. If the final value had been extracted at an earlier time, say 4 ms in the experiment depicted in Figure 3.5a, the average pressure approach would have yielded a final mole fraction value closer to the specified-pressure ultimate mole fraction value; if the final value had been extracted at a later time, say 6.5 ms in Figure 3.5a the final mole fraction value would have been closer to the GC measurement. The disagreement between the model and experimental results is more a comment on the ability (or inability) of the model to accurately predict ethylene pyrolysis across the temperature range of interest.

Although the "80% of $P_0$" modeling approach has been shown to be effective for modeling single-pulse shock tube experimental sampling results in the past, the approach is clearly not sufficient for modeling the experiments presented in this chapter. The inability of this constant, average-pressure approach to capture the same results predicted using a true pressure time-history is thought to be primarily due to two factors.

First and foremost, the constant-pressure approach is typically applied to highly dilute systems, which allows the experiments to be modeled as constant-temperature, constant-pressure processes. Due to the relatively higher fuel concentration used in the current experiments to accommodate the laser measurements (1% ethylene), there is an appreciable drop in temperature that occurs in the constant-pressure region as the fuel pyrolyzes.

Second, due to the use of a conventional shock tube configuration, the rate of quenching experienced by the test gas upon arrival of the expansion fan in the current experiments is lower than quenching rates seen in single-pulse shock tube experiments. For example, in their single-pulse shock tube pyrolysis work, Tang and Brezinsky found the quenching rate in their experiments, defined as the temperature change over the time between the arrival of the expansion fan and the point at which pressure has fallen to 80% of its maximum value, to be $3.64 \times 10^5$ K/s for a 25-bar shock [38]. Other single-pulse shock tube facilities report similar quenching rates, on the order
3.4. METHODOL. FOR COMPARING GC, KINETIC MODEL, AND LASER RESULTS

of $5 \times 10^5$ K/s [36, 46]. In the current work, the quenching rate, calculated in the same way as described by Tang and Brezinsky, was found to be approximately $7 \times 10^4$ K/s – 5-8 times lower than the single-pulse shock tube quenching rates. This slower quenching rate suggests that reactions with lower activation energies likely proceed further into the expansion fan in the current experiments than those conducted in single-pulse shock tubes. This indicates that greater attention must be given to accurately modeling the reactions in the expansion fan in conventional shock tube experiments, as these reactions are expected to significantly impact the ultimate species mole fraction measurements.

3.4.2 Comparison of GC measurements and laser results

The primary challenge that arises when directly comparing laser and GC measurements is one of disparate timescales: laser measurements are recorded during the constant-pressure, nearly constant-temperature region known in shock tube experiments as Region 5, and typically conclude at the end of the test time upon arrival of the reflected expansion fan (1-3 ms); sample extraction and GC analysis measurements occur on a much longer timescale. Much like when comparing model results to GC results, a single laser-measured mole fraction value cannot simply be extracted at the end of the test time and used for comparison with GC results. The laser measurement must be extended into the expansion fan region until the measured mole fraction value is seen to plateau, thereby indicating that the reactions dominating the formation or removal of the relevant species have been quenched.

The absorption cross-section and species concentration terms used to convert measured laser absorbance to species mole fraction are temperature- and pressure-dependent (see Equation (3.1)). To extend a laser measurement into the quenching region, temperature and pressure in the region must be known. Time-resolved, laser-based temperature diagnostics are possible, but are difficult to implement over large temperature ranges. Instead, time-resolved temperature data calculated using chemical kinetic models can be used with relative accuracy.

As with the method described in Section 3.4.1, in order for model-based quantities such as temperature to accurately describe the thermodynamic conditions of the quenching process, an experimentally measured, specified-pressure approach should be used. The time-resolved pressure profile
and corresponding, model-generated temperature profile (see Figure 3.4a) can then be plugged into Equations 3.2 and 3.3 and used to obtain time-resolved absorption cross-section values that reflect the approximate temperature and pressure fluctuations seen in Region 5 and the subsequent quenching region.

Figure 3.6: Laser-measured ethylene mole fraction (calculated using the specified-pressure approach) and measured pressure. Initial reflected shock conditions: 1695 K, 5.1 atm.

Figure 3.6 shows a typical plot of laser-measured ethylene mole fraction, calculated using experimentally measured pressure and modeled temperature, for the same 1695 K, 5.1 atm shock experiment described previously (Section 3.4.1). The laser-measured mole fraction initially decreases rapidly from 1%, then begins to plateau and ultimately reaches a minimum value of 0.18% at approximately 4.8 ms. In each laser experiment, it is this minimum, ultimate plateau value that is taken for comparison with post-shock GC measurements.

Using modeled temperature to extend the laser measurement into the expansion fan increases the uncertainty associated with the measurement, as the final laser measurement is now dependent on the kinetic model used to obtain the temperature. To quantify the impact that choice of model has on the ultimate laser measurement, laser measurements were conducted in 1% ethylene/argon shock experiments ranging 1200-1750 K, at ∼5 atm. The laser measurements were obtained using the specified pressure, modeled temperature approach using temperatures obtained from four different
Figure 3.7: Comparison of ultimate, laser-measured C$_2$H$_4$ mole fractions using four different kinetic models to calculate temperature: USC, LLNL, CRECK, and UCSD.

(a) Ultimate, laser-measured ethylene mole fraction, calculated with four different kinetic models, using the specified-pressure, modeled-temperature approach. $P_s \sim 5$ atm.

In Figure 3.7a, it can be seen that the ultimate laser measurements show close agreement across the entire temperature range. When the data are visualized as a percent deviation from the average mole fraction at each temperature point, as in Figure 3.7b, it can be seen that the greatest differences occur in the 1400-1750 K temperature range – the range in which the final ethylene mole fraction is most sensitive to temperature. At $\sim 1600$ K, a maximum difference of 4.5% is observed between an ethylene mole fraction measurement obtained using temperature from the USC model and a measurement obtained using temperature from the LLNL model. Over the entire temperature range, the average maximum difference is 2.7%. This uncertainty due to choice of kinetic model has been incorporated into the overall uncertainty associated with each laser mole fraction measurement by using the RSS method to combine the average difference due to model choice (2.7%) and the overall uncertainty calculated in Section 3.3.2 (6.3%); the final laser measurement uncertainty, including the influence of kinetic model temperature, was found to be $\pm 8.2\%$. It should be noted that the magnitude of the kinetic model temperature variations could be reduced simply by using lower reactant concentrations (higher dilution).
In summary, specified-pressure and modeled-temperature data can be used to extend laser mole fraction measurements into the expansion fan to allow for direct comparison with GC measurements. Although laser measurements obtained in this way exhibit some dependence on the model chosen to calculate temperature, the dependence is minimal and can be accounted for in the overall uncertainty associated with the measurement.

3.5 Combined LAS and GC species yield results: ethylene pyrolysis

In situ optical and sampled-gas GC results were recorded for the pyrolysis of a 1.0% ethylene/argon fuel mixture over a range of temperatures (1200-2000 K) at ∼5 atm, with an experimental test time of 1.5-3.2 ms. The GC was used to measure the ultimate mole fraction value of four species (ethylene, acetylene, hydrogen, and methane) at each shock condition (see Figure 3.8). The ethylene, acetylene, and hydrogen results were obtained in a single set of experiments using the endwall sampling technique, while the methane results were obtained in a second set of experiments using the sidewall sampling technique (see Appendix B.2.1). Once again, the uncertainty associated with these species mole fraction measurements is estimated to be ±4.7%. The uncertainty associated with $T_{5,\text{init}}$ (the initial reflected shock temperature) for each experiment is estimated to be ±1.8%, as discussed in Section 3.3.2.

As expected, as reaction temperature ($T_{5,\text{init}}$) increases, ethylene yield at the end of the effective reaction time decreases, as it reacts more quickly to form acetylene, hydrogen, and methane. At temperatures above ∼1750 K, acetylene yield decreases as acetylene begins to thermally decompose, most likely forming diacetylene, C$_4$H$_2$. It should be noted that diacetylene cannot be purchased off-the-shelf, thereby making GC quantification of diacetylene a non-trivial matter. (See Appendix B.4 for carbon and hydrogen recovery results for these experiments).

At temperatures below 1700 K, more than 95% of the initial carbon and hydrogen put into the system is recovered through measurement of the four species of interest (see Appendix B.4). As acetylene begins to decompose above 1700 K, measurement of only four species is no longer sufficient to fully capture the carbon and hydrogen in the system. Kinetic modeling of the experiments suggests that if diacetylene had been included in the species of interest, the carbon and hydrogen
3.5. COMBINED LAS AND GC SPECIES YIELD RESULTS: ETHYLENE PYROLYSIS

Figure 3.8: Ultimate GC-measured ethylene, acetylene, hydrogen, and methane (x10) mole fraction results plotted against $T_{b,init}$. 1% ethylene/argon test gas mixture, $P_b \sim 5 \text{ atm}$.

recoveries would have remained above 96% over the entire temperature range.

Figure 3.9 shows a comparison of the experimentally measured (GC and laser) ultimate C$_2$H$_4$, H$_2$, and C$_2$H$_2$ mole fraction values and those predicted by the USC, LLNL, CRECK, and UCSD kinetic models using the specified-pressure approach.

Time-resolved ethylene laser measurements were used to determine an ultimate ethylene mole fraction value for each shock condition. A comparison of the laser- and GC-based ultimate ethylene mole fraction values can be seen in Figure 3.9a. For high-temperature (> 1800 K) shock conditions, this ultimate value was reached well within the experimental test time (< 3.2 ms). For lower-temperature shock conditions (< 1800 K), this ultimate value was reached after the arrival of the expansion wave.

Of the 13 laser and GC ethylene measurements conducted between 1200 K and 1800 K, 9 exhibit a relative difference of less than 7.8% between the two experimental techniques. The average relative difference between the two techniques was found to be 9.5% over the same temperature range. In most cases, this discrepancy can be accounted for by the measurement uncertainty associated with the GC ethylene measurements (±4.7%) and the estimated uncertainty associated with
CHAPTER 3. SPECIES-YIELD GC MEASUREMENTS WITH IN SITU LAS

Figure 3.9: Ultimate GC-measured, laser-measured, and modeled (USC, LLNL, CRECK, and UCSD) C$_2$H$_4$, H$_2$, and C$_2$H$_2$ mole fraction results. Laser C$_2$H$_4$ measurements obtained using temperature modeled using USC Mech v2. 1% ethylene/argon test gas mixture, $P_5 \sim 5$ atm.
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the laser-based mole fraction values (±8.2%). It should be noted that at temperatures above 1800 K, the GC and optical measurements are less reliable, as the ultimate ethylene mole fraction values are approaching the lower detection limits of both techniques.

Each line in Figures 3.9a-c represents a cubic spline of the modeled data points, calculated for each experiment using the specified-pressure approach. (To allow the results presented here to be used for kinetic model evaluation using the specified-pressure approach, time-resolved pressure traces and initial reflected shock conditions for shock experiments across the entire temperature range have been included in the Supplementary Material of the relevant journal paper, [19]). For all three of the primary species of interest, large disagreement is seen between the various model results. This disagreement is particularly apparent when the time-resolved model results are compared to the time-resolved laser ethylene measurements, as seen in Figure 3.10. USC Mech under-predicts the rate of ethylene pyrolysis for the duration of the experiment, while the LLNL, CRECK, and UCSD models over-predict the rate of pyrolysis to varying degrees. These trends are mirrored in the modeled final species mole fraction values plotted in Figure 3.9; USC Mech, in particular, consistently under-predicts the extent of ethylene pyrolysis at all temperature conditions, while LLNL consistently over-predicts the extent of ethylene pyrolysis at all temperature conditions.

A sensitivity analysis reveals a lack of consensus amongst the four kinetic models regarding which reactions dominate ethylene pyrolysis. This suggests that additional work is needed in the development of kinetic models used to describe ethylene pyrolysis, and additional experimental work, beyond the scope of what is presented here, is necessary to guide this development. Nevertheless, the GC and laser results obtained using the combined speciation diagnostic fall within the bounds established by the model predictions throughout the entire temperature range of interest, and likely fall within the uncertainty ranges associated with each of the model predictions.

3.6 Conclusions

A combined laser absorption/species-yield GC sampling diagnostic was developed and implemented on a conventional shock tube. A method was presented for using experimental pressure data to accurately model sampling-based speciation results obtained in shock tube experiments.
CHAPTER 3. SPECIES-YIELD GC MEASUREMENTS WITH IN SITU LAS

Figure 3.10: Comparison of time-resolved laser ethylene measurement and modeled ethylene decomposition (USC, LLNL, CRECK, and UCSD kinetic models). Initial reflected shock conditions: 1695 K, 5.1 atm.

Instead of assuming a constant, average temperature and pressure for the duration of an experiment and pulling out a single species-yield value at a given test time, it is recommended that a measured, time-resolved pressure trace be used to constrain all model simulations; by additionally imposing a constant-enthalpy constraint, the true temperature time-history of the reacting system (including that extending into the expansion fan) can be taken into account. In simulating the GC sampling measurements presented here, this specified-pressure approach shows clear improvement over the commonly used constant-temperature/constant-pressure simulation method. It is therefore strongly recommended that modelers using species-yield, GC sampling results to validate kinetic model performance simulate these results using the specified-pressure approach described herein, instead of simulating the reacting system at averaged temperature/pressure conditions for an estimated reaction-time duration. In order to facilitate this more accurate modeling approach, it is additionally recommended that experimentalists report their time-resolved pressure measurements (in addition to initial, post-shock $T_5$ and $P_5$ conditions and approximate test times) for each experiment when reporting their species-yield results.

A method for accurately comparing time-resolved laser measurements to GC measurements has
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also been described; by using experimental pressure and model-calculated temperature to extend laser measurements into the expansion fan, an appropriate ultimate mole fraction data point can be extracted for comparison with the GC measurements. Extension of the laser measurements into the expansion fan is inherently dependent on a model to determine time-resolved temperature, but for the experiments presented in this work, the sensitivity of the laser measurements to choice of model is found to be insignificant.

Finally, ethylene pyrolysis experiments conducted using the ethylene laser absorption/GC sampling diagnostic show close agreement between the two measurement techniques. Over the temperature range 1200-1800 K, the laser- and GC-based measurements show a mean relative difference of 9.5%. These promising results indicate that the combined laser diagnostic/GC sampling system is a powerful tool that can be used to quantify the presence of absorbing and non-absorbing species in pyrolysis and oxidation studies of hydrocarbon fuels. When modeled correctly, sampled and time-resolved species measurements acquired in tandem have the potential to provide more complete datasets to characterize high-temperature combustion reactions and aid in kinetic model development.
Chapter 4

Quasi-time-resolved GC measurements with in situ LAS

The contents of this chapter have been published in the journal Combustion and Flame [20].

4.1 Introduction

In this work, the combined laser absorption/GC sampling diagnostic presented in Chapter 3 is applied in a variable-test-time shock tube facility and used to quantify the presence of intermediate species in the low-temperature oxidation of 1% \( n \)-heptane (\( n \)-C\(_7\)H\(_{16}\)) in 20.8% O\(_2\)/Ar and 20.8% O\(_2\)/0.21% CO\(_2\)/Ar (equivalence ratio 0.53) at 760 K, 4.9 atm, at different times between first- and second-stage ignition. This approach employs four different laser diagnostics to simultaneously measure initial fuel and time-resolved temperature, CO\(_2\), H\(_2\)O, and C\(_2\)H\(_4\). A variable-length driver is used to control the arrival time of the expansion fan at the shock tube test section, and GC analysis of post-expansion fan, sampled gases is used to obtain quasi-time-resolved \( n \)-C\(_7\)H\(_{16}\), C\(_2\)H\(_4\), CO, H\(_2\), C\(_3\)H\(_6\), and CO\(_2\) measurements. This low-temperature \( n \)-heptane study is the first to provide combined, time-resolved laser and GC intermediate species measurements in a single experiment. Measurements obtained using both techniques are compared to each other, and to initial results predicted by a detailed kinetic model using the experimentally measured pressure trace to constrain the model.
Discrepancies between measured and predicted ignition delay times indicate the overestimation of three primary RO2 isomerization reaction rates. The three reaction rates were modified to improve agreement of modeled ignition delay times with the measurements. Final results produced using the modified mechanism are compared to the experimental results; the comparison shows close agreement between the two experimental measurement techniques, and measured species yields confirm the low-temperature reaction pathways that govern n-heptane decomposition and C2H4, CO, H2, and C3H6 production.

The subsequent sections of this chapter provide background on speciation studies of low-temperature n-heptane oxidation, an overview of the variable-test-time driver modifications used in this work, descriptions of the laser and GC diagnostic systems, and a description of the kinetic model modifications needed in order to bring ignition delay time estimates into alignment with experimental results; finally, laser, GC and modified-model results are compared.

4.2 Background and literature review

n-Heptane is an important surrogate fuel component used to approximate the combustion behavior of complex, real fuels. n-Heptane's strong negative temperature coefficient (NTC) behavior also makes it a valuable reference hydrocarbon for the modeling of longer straight-chain alkanes. As such, n-heptane oxidation has been studied extensively in a variety of experimental facilities. The vast majority of n-heptane studies have focused on ignition delay time measurements; a smaller number have focused on high-temperature, final species measurements; fewer still have reported concentrations of low-temperature, intermediate species, or those produced between first- and second-stage n-heptane ignition.

A succinct review of low-temperature n-heptane experiments targeting intermediate speciation is presented in the work of Karwat et al. [50]; these experiments include gas chromatography and/or mass spectrometry measurements conducted in jet-stirred reactors [51, 52], rapid compression machines (RCMs) [53], pre-mixed laminar flames [54, 55], and flow reactors [56]. In the same publication, Karwat et al. presented one of the first time-resolved, sample-based, intermediate species studies of low-temperature n-heptane oxidation in an RCM; 18 hydrocarbon species were quantified
by GC analysis at eleven different time points between first- and second-stage ignition. Recent low-temperature, \textit{n}-heptane oxidation shock tube studies utilized infrared (IR) laser absorption to obtain time-resolved measurements of \textit{n}-heptane, OH, aldehydes, CO$_2$, and H$_2$O [57], and CO [58].

While laser absorption diagnostics can provide time-resolved species measurements with superior time resolution over a wide range of temperature and pressure conditions, typical shock tube experiments can accommodate only a few species measurements at a time. GC/MS analysis, on the other hand, allows for quantification of dozens of stable species, but with much lower time resolution, and some potential for uncertain variations in gas composition between the undisturbed, post-shock reactive volume and the sample analyzed by the GC. Given the array of low-temperature \textit{n}-heptane oxidation studies utilizing one technique or the other, there is strong need for a comparative study of the results produced by each in order to validate the conclusions drawn – hence the application of the combined laser absorption/GC sampling diagnostic to the study of this kinetic system.

4.3 Experimental setup and approach

4.3.1 Tunable-test-time shock tube facility

The combined laser and GC speciation experiments were performed in an unheated, stainless-steel shock tube with a variable-length driver section (see Section 2.2.3). Typical shock tube configurations yield post-reflected-shock test times on the order of 1-3 ms. However, by lengthening the driver section and tailoring the composition of the driver gas mixture, test times up to 100 ms can be achieved [5].

The length of the driver was varied through use of a solid driver insert. The insert could be secured at various axial locations and was used to obtain driver lengths of 5.8 m and 9.6 m, with a constant inner diameter of 11.5 cm. (See Figure 4.1 for a graphical depiction of the shock tube setup, with the solid driver insert used to achieve a driver length of 5.8 m.) These two driver configurations were used to obtain test times of approximately 5.5 ms and 8 ms. Additional axial driver inserts were also used to obtain near-constant, post-reflected-shock test conditions.

The shock tube driven section is 9.73 m long and has an inner diameter of 11.53 cm. The desired
**4.3. EXPERIMENTAL SETUP AND APPROACH**

![Schematic of the variable-length-driver shock tube setup](image)

**Figure 4.1:** Schematic of the variable-length-driver shock tube setup, with solid driver insert depicted for achieving a driver length of $\sim 5.8$ m.

Test conditions were achieved by using two back-to-back, polycarbonate diaphragms to separate the driven section from the driver section. Before each experiment, the driven section was turbopumped down to $\leq 2 \times 10^{-5}$ Torr.

Incident shock speed was determined by extrapolating shock arrival time, measured by five side-wall piezoelectric pressure transducers (PCB 113A26), to the endwall. The reflected shock speed and post-incident and reflected shock temperature and pressure conditions were calculated using standard normal-shock relations. The $2-\sigma$ uncertainties in the calculated reflected shock temperature ($T_{5,\text{init}}$) and pressure ($P_{5,\text{init}}$) were found to be $\pm 0.8\%$ and $\pm 1.8\%$, respectively, due primarily to uncertainty in the extrapolated incident shock velocity ($\pm 0.3\%$); typical shock attenuation was $1.4\%/m$. Time-resolved pressure was recorded using a piezoelectric pressure transducer (Kistler 603B1) located in the sidewall, 2 cm from the shock tube endwall.

The test gas mixture used in this work was nominally $1.0\%$ $n$-heptane in $20.8\%$ /Ar ($\phi=0.53$). For half the presented experiments, $0.21\%$ of the Ar was replaced with CO$_2$ to allow for laser temperature measurements. The driver gas used in all experiments was 100% helium. Mixtures were prepared manometrically in a stainless-steel mixing tank. The $n$-heptane was obtained from Sigma Aldrich ($\geq 99\%$) and was degassed using the freeze-pump-thaw method. High-purity O$_2$ (99.999%), CO$_2$ (99.99%), helium (99.999%), and argon (99.999%) were obtained from Praxair, Inc.
4.3.2 Laser absorption diagnostics

Four laser diagnostics were used to obtain time-resolved fuel absorbance, H$_2$O mole fraction, and C$_2$H$_4$ mole fraction measurements in all experiments, and CO$_2$ mole fraction and temperature measurements in experiments including 0.21% CO$_2$ in the test gas mixture. Each laser measurement was conducted 2 cm from the shock tube endwall. Each of these diagnostic techniques has been discussed at great length in a previous publication [59–62]. As a result, only a brief overview of the established diagnostics will be provided here.

4.3.2.1 Fuel measurement (3.41 µm)

*In situ* measurements of fuel absorbance were conducted using a wavelength-tunable, distributed feedback (DFB) interband cascade laser (ICL) at 3.41 µm (Nanoplus). An indium antimonide (InSb) detector (InfraRed Associates, IS-2.0) was used to record transmitted light intensity at a sampling rate of 5 MHz. Like other direct laser absorption techniques, this recently developed diagnostic makes use of the Beer-Lambert relation to obtain mole fraction values from measured absorbance at a fixed wavelength [59].

Due to the prevalence of interfering species and the high absorbance of *n*-heptane at the temperatures and pressures relevant to this work, the fuel diagnostic was primarily used to measure initial fuel loading for each experiment. (See Appendix C.1 for a discussion of the importance of using a fuel diagnostic to determine initial fuel loading amount for liquid/low-vapor pressure fuels.) Room-temperature absorption cross-sections for *n*-heptane at 3.41 µm were obtained from Klingbeil et al. [63]. The uncertainty of the initial *n*-heptane mole fraction measurements is estimated to be ±2.0% (2-σ); this uncertainty is dominated by the uncertainty in the room-temperature absorption cross-section measurements.

4.3.2.2 Temperature/CO$_2$ measurement (4.2 µm)

A two-color, scanned-wavelength, direct-absorption technique was used to obtain time-resolved temperature measurements in half of the experiments presented in this work. Two DFB-ICLs (Nanoplus) were scanned over two CO$_2$ rovibrational transitions centered at 2385.77 cm$^{-1}$ (R(62))
4.3. EXPERIMENTAL SETUP AND APPROACH

and 2390.52 cm\(^{-1}\) (R(76)). Due to the low concentration of CO\(_2\) produced between first- and second-stage \(n\)-heptane ignition, approximately 0.2% CO\(_2\) was seeded into the test gas mixture to provide sufficient CO\(_2\) concentration for the transitions of interest to be detected. Each scan was conducted at a rate of 10 kHz using an injection-current tuned, modified sawtooth profile; the optical frequency range of each scan was approximately 1 cm\(^{-1}\). The transmitted light intensity was recorded at a frequency of 5 MHz using two IR detectors (Vigo Systems, PVI-4TE-5 and PVI-2TE-6).

Typical two-color temperature diagnostics (e.g., [60]) relate the ratio of integrated transition absorbance areas to temperature-dependent linestrengths. However, due to significant broadening of the two absorption features of interest, a ratio of peak absorbances was used instead.

The most significant sources of error contributing to the uncertainty in the temperature measurement are the experimentally measured broadening coefficients and the linestrength obtained from the HITRAN database [64]. By perturbing each of the variables by their maximum uncertainty and computing the change in temperature value, the impact of each variable’s uncertainty on the final temperature measurement was calculated. Taking the root-sum-square (RSS) of each differential temperature change yielded typical temperature uncertainties of ±29 K. The uncertainty associated with the CO\(_2\) mole fraction measurements was found to be ±8%.

4.3.2.3 H\(_2\)O measurement (2.48 \(\mu\)m)

A scanned-wavelength, direct-absorption technique was used to obtain time-resolved water mole fraction measurements. A DFB-ICL (Nanoplus) was used to scan across a high-temperature water absorption feature at 4029.524 cm\(^{-1}\). The laser was injection-current tuned at 20 kHz with a modified sawtooth profile, which spanned an optical frequency range of 0.35 cm\(^{-1}\), centered at the absorbance feature of interest. The transmitted light was recorded at 5 MHz using an IR detector (Vigo Systems, PVI-3TE-6).

Frequency-dependent absorbance was calculated across each scan and a least-squares curve-fitting routine was applied to fit a Voigt lineshape to the measured absorbance profile with typical maximum residuals of less than 5%. Temperature-dependent linestrength values were obtained from Goldenstein et al. [61]. The remaining unknown variable necessary for calculating water mole fraction is temperature; measured temperature, obtained using the CO\(_2\) laser diagnostic (when
employed), and modeled temperature, obtained using the LLNL \( n \)-heptane mechanism [65], were both used to compute water mole fractions.

The uncertainty associated with the water mole fraction measurements was obtained by calculating the RSS of the uncertainties associated with the least-squares absorbance fit for each scan, the temperature-dependent linestrength correlation (±2.3%), and the temperature. When a measured temperature profile is used, uncertainty in the water mole fraction measurement within the experiment test time and early in the expansion fan is approximately ±7.2%; when a modeled temperature profile is used, a nominal, estimated temperature uncertainty of ±20 K is imposed, and the overall mole fraction uncertainty is approximately ±5.1%.

4.3.2.4 \( \text{C}_2\text{H}_4 \) measurement (10.532 \( \mu \text{m} \) & 10.675 \( \mu \text{m} \))

Ethylene species time-histories were measured using a two-color, direct absorption technique, which allows for the separation of absorbance due to weakly interfering species from the ethylene measurements. This two-color diagnostic has been outlined in previous work [62].

Two water-cooled, grating-tuned, \( \text{CO}_2 \) gas lasers (Access Laser Company, Lasy-4G and Lasy-4GS) were used to simultaneously record absorbance at two wavelengths for each experiment; one was operated at the P14 \( \text{CO}_2 \) emission line (10.532 \( \mu \text{m} \)), and the other was operated at the P28 line (10.675 \( \mu \text{m} \)). Time-varying light intensity was recorded at each wavelength using a pair of thermoelectric-cooled, photovoltaic IR detectors (Vigo Systems, PVM-2TE-10.6) at a sampling rate of 5 MHz. The ethylene absorption cross-sections at 10.532 \( \mu \text{m} \) and 10.675 \( \mu \text{m} \) were obtained from previous work conducted by MacDonald et al. [62] and Ren et al. [43].

When using a model-derived temperature to calculate ethylene mole fraction, the uncertainty associated with the ethylene measurement is estimated to be ±8.9%. When using a measured temperature to calculate ethylene mole fraction, the uncertainty is estimated to be ±12.4%.

4.3.3 GC sampling system (quasi-time-resolved measurements)

The Agilent 490 MicroGC, described in Section 2.4.2, was used to quantify the presence of five primary species in the post-shock gas samples: \( n \)-\( \text{C}_7\text{H}_{16} \), \( \text{C}_2\text{H}_4 \), \( \text{CO} \), \( \text{H}_2 \), and \( \text{C}_3\text{H}_6 \); \( \text{CO}_2 \) was also
quantified in the experiments containing CO$_2$ in the test gas mixture. Additional 1-alkenes were also quantified using GC analysis, but are not reported here; these results are included in Appendix C.2. Four columns were used in this work: a molecular sieve 5 Å (MS 5Å) column (CO, H$_2$), a PoraPlot Q (PPQ) column (CO$_2$, C$_3$H$_6$), a PoraPlot U (PPU) column (CO$_2$ and C$_2$H$_4$), and a CP-Sil 5CB column (n-C$_7$H$_{16}$). Each column is equipped with a thermal conductivity detector (TCD). A multi-point calibration curve was generated for each of the measured species prior to each set of shock experiments. The calibration gases used for this work were either prepared manometrically or obtained from Praxair, Inc., with a quoted compositional uncertainty of ±2%.

Post-shock samples are extracted through the endwall, as described in Section 3.3.3. A probe protrudes 5 mm off of the endwall surface to allow for sampling outside the thermal boundary layer. The extracted gas sample volume was 8.4 mL. Before GC analysis, water is removed from the sample by a membrane filter (A+ Corporation, Genie 170). All of the sample line tubing is insulated and maintained at 70 °C for the experiments.

For the shorter test time (~5.5 ms) experiments, the sampling event is initiated approximately 10 ms after the passing of the reflected shock wave 2 cm from the endwall, and ends 55 ms later. For the longer test time (8 ms) experiments, the sampling event is initiated 12 ms after the passing of the reflected shock 2 cm from the endwall, and ends 42 ms later. The sample timings were optimized to be as short as possible, while still allowing for sufficient sample line pressure.

For each shock experiment, a single post-shock sample is extracted and analyzed. The GC-measured mole fraction values are obtained on a dry basis, but use of the water laser diagnostic allows for the quantification of the water present in the wet sample. All of the GC results are presented on a wet basis, after scaling to account for the presence of water. The uncertainty associated with each GC species measurement is estimated to be ±4.7%. This is the 2-σ uncertainty, obtained by calculating the RSS of the standard deviations due to measured water present in the sample, uncertainty in calibration gas composition, calibration curve fit uncertainty, and calculated, representative scatter and reproducibility trends (see Section 2.4.6).
CHAPTER 4. QUASI-TIME-RESOLVED GC MEASUREMENTS WITH IN SITU LAS

4.4 Results and discussion

4.4.1 Comparison of laser measurements and model results

Twelve shock experiments were conducted at approximately 760 K and 4.9 atm to obtain sampled GC species measurements at multiple times between first- and second-stage \( n \)-heptane ignition, and simultaneous, time-resolved laser species measurements. The test gas mixture was nominally 1\% \( n \)-heptane in 20.8\% \( \text{O}_2 \)/78.2\% Ar or 20.8\% \( \text{O}_2 \)/0.21\% \( \text{CO}_2 \)/Ar (\( \phi = 0.53 \)). A table summarizing the initial, calculated post-shock temperature and pressure conditions (\( T_{5, \text{init}}, P_{5, \text{init}} \)), test gas mixture composition, and experiment dwell times (\( \Delta \tau_{ \text{dwell} } \), defined as the time between the onset of first-stage ignition, \( \tau_{ \text{IDT} } \), and the arrival of the expansion fan, \( \tau_{ \text{test} } \)) for each individual shock experiment is included in Appendix C.3, Table C.1. \( \tau_{ \text{IDT} } \) is determined by extrapolating the maximum negative slope of the fuel laser absorbance measurement back to the initial baseline. For the experiments presented in this work, \( \Delta \tau_{ \text{dwell} } \) ranged from 2.06-6.13 ms.

A representative plot of measured laser absorbance and pressure, obtained in the longest test time shock experiment, is shown in Figure 4.2. A sudden drop in fuel absorbance around 2 ms is accompanied by a characteristic pressure rise, indicating first-stage ignition (\( \tau_{ \text{IDT} } \)). A simultaneous increase in ethylene and water absorbance confirms the partial oxidation of \( n \)-heptane. The steady decrease in fuel absorbance and the steady increase in ethylene and water absorbance between \( \tau_{ \text{IDT} } \) and \( \tau_{ \text{test} } \) (around 8 ms) indicate slow, steady partial oxidation as the dwell time increases. After 8 ms, the absorbance traces reflect the sudden drop in pressure and temperature accompanying the arrival of the expansion fan; reactions are quenched and the chemistry is frozen before second-stage ignition occurs.

A comparison of the measured temperature (\( T_{ \text{meas} } \)) and mole fraction values, obtained from the absorbance traces shown in Figure 4.2, and the modeled temperature (\( T_{ \text{model} } \)) and mole fraction values from the LLNL \( n \)-heptane kinetic model, is plotted in Figure 4.3. The modeled values were obtained using a specified-pressure approach (an option in the CHEMKIN-PRO [44] simulation software, used in this work), in which the closed, homogeneous reactor pressure is constrained in time by the measured pressure. The initial temperature used in the simulations was the calculated, post-shock temperature (\( T_{5, \text{init}} \)).
4.4. RESULTS AND DISCUSSION

Figure 4.2: Measured laser absorbances and pressure

Figure 4.3: Measured temperature and H₂O, CO₂, and C₂H₄ mole fractions (based on T_{meas}), alongside modeled temperature and mole fractions (LLNL n-heptane detailed mechanism, v3.1 [65]). Model predictions are denoted by dashed lines.
In Figure 4.3, the temperature measurements obtained using the two-color CO\textsubscript{2} diagnostic are denoted by red filled diamonds. Prior to first-stage ignition, $T_{\text{meas}}$ and $T_{\text{model}}$ agree within the uncertainty associated with the measurement ($\pm 29$ K). After first-stage ignition, and before the arrival of the expansion fan, the model predicts a steadily increasing temperature that matches well with the measured temperature. After the arrival of the expansion fan at approximately 8 ms, $T_{\text{meas}}$ and $T_{\text{model}}$ begin to drop off at approximately the same rate, but diverge after $\sim 13$ ms; the measured temperature continues to drop, while the modeled temperature begins to plateau. The $\Delta T$ rise associated with the measured first-stage ignition event in Figure 4.3 is 106 K, while the modeled $\Delta T$ is 122 K. Although the two values are within 16 K, the larger temperature change seen in the model results would indicate an over-prediction of the extent of reaction in first-stage ignition; this over-prediction is apparent in the modeled mole fraction results.

Also plotted in Figure 4.3 are the measured H\textsubscript{2}O, CO\textsubscript{2}, and C\textsubscript{2}H\textsubscript{4} mole fractions, determined using $T_{\text{meas}}$. After $\tau_{\text{IDT}}$, the H\textsubscript{2}O and C\textsubscript{2}H\textsubscript{4} mole fraction measurements steadily increase and reach a plateau value between 10 and 12 ms (approximately 2-4 ms into the expansion fan). After 12 ms, the H\textsubscript{2}O increases, while the CO\textsubscript{2} and C\textsubscript{2}H\textsubscript{4} mole fractions decrease. This trend would seemingly suggest that additional oxidation occurs late in the expansion fan. However, the H\textsubscript{2}O trace in Figure 4.2 shows no significant increase in absorbance beyond 12 ms. The increase in H\textsubscript{2}O mole fraction (and corresponding decrease in CO\textsubscript{2} and C\textsubscript{2}H\textsubscript{4} mole fraction) is instead an artifact of the temperature measurement used to calculate the mole fractions; an inflection point present in the temperature measurement around 18 ms is clearly mirrored in both the H\textsubscript{2}O and C\textsubscript{2}H\textsubscript{4} mole fraction measurements. This would suggest that $T_{\text{meas}}$ becomes less reliable more than 4 ms into the expansion fan. The increase in the measurement error late in the expansion fan is primarily due to the application of the temperature diagnostic outside of its design temperature range. Below 700 K, the absorbance of the R76 line approaches the lower optical limit of 0.1 absorbance (see Figure 4.2), thereby leading to increased measurement uncertainty and significant deviation from the modeled temperature.

When directly comparing the measured and modeled, time-resolved mole fraction values, it can be seen that the kinetic model does not capture the same first-stage ignition delay time present in the measurements. This discrepancy is particularly apparent when comparing the two C\textsubscript{2}H\textsubscript{4} mole
fraction traces – the model predicts a steep rise in \( \text{C}_2\text{H}_4 \) mole fraction almost 0.5 ms before the rise recorded in the measurements. Across all 12 experiments, an average relative difference of 34% (0.8 ms) was observed between modeled and experimental IDT (determined by extrapolating the fuel mole fraction (model) or absorbance (experiment) steepest slope back to the baseline). A comparison of the modeled and measured IDT values for each shock experiment is included in Appendix C.4. This premature, first-stage IDT prediction leads to modeled species results that are not comparable to the measurements. If the modeled IDT is too early, the measured, time-resolved pressure profile used to constrain the model calculations will impose a false pressure increase at the time of measured first-stage ignition, and the dwell time between modeled IDT and the expansion fan arrival will be longer than what occurred in the experiment. Indeed, the modeled plateau \( \text{H}_2\text{O} \) mole fraction value seen in Figure 4.3 is almost 20% higher than the measured plateau mole fraction value, and the modeled plateau \( \text{C}_2\text{H}_4 \) value is almost double the measured value.

A brute-force, IDT sensitivity analysis was conducted and the results are presented in Figure 4.4; here, IDT is calculated by extrapolating the steepest-slope pressure back to the pre-pressure rise baseline. The sensitivity analysis reveals that the first-stage ignition timing is most sensitive to the rate constants of the isomerization (internal H-atom abstraction) reactions of three \( \text{RO}_2 \) species formed by the addition of heptyl radicals to \( \text{O}_2 \). The reactions, along with their reaction rate parameters (pre-exponential A-factor, temperature coefficient, \( n \), and activation energy, \( E_A \)), are listed in Table 4.1.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( A ) (s(^{-1}))</th>
<th>( n )</th>
<th>( E_A ) (cal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 2\text{-C}<em>7\text{H}</em>{15}\text{O}_2 \leftrightarrow \text{C}<em>7\text{H}</em>{14}\text{OOH}(2-4) ) (R1)</td>
<td>( 2.5 \times 10^{10} )</td>
<td>0.0</td>
<td>( 2.045 \times 10^4 )</td>
</tr>
<tr>
<td>( 3\text{-C}<em>7\text{H}</em>{15}\text{O}_2 \leftrightarrow \text{C}<em>7\text{H}</em>{14}\text{OOH}(3-5) ) (R2)</td>
<td>( 2.5 \times 10^{10} )</td>
<td>0.0</td>
<td>( 2.045 \times 10^4 )</td>
</tr>
<tr>
<td>( 4\text{-C}<em>7\text{H}</em>{15}\text{O}_2 \leftrightarrow \text{C}<em>7\text{H}</em>{14}\text{OOH}(4-2) ) (R3)</td>
<td>( 5.0 \times 10^{10} )</td>
<td>0.0</td>
<td>( 2.045 \times 10^4 )</td>
</tr>
</tbody>
</table>

R1, for example, describes the isomerization of 2-heptylperoxy into 2-hydroperoxy-4-heptyl. These reaction rate parameters are derived from an early transition state study conducted by Curran et al. [66]. In the case of the 2-heptylperoxy radical, a six-membered transition state structure
forms, undergoes rapid stabilization, and transfers a secondary H atom to form 2-hydroperoxy-4-heptyl. The calculated rate constants depend on three things: the ring strain energy barrier, the location and type of abstracted H atom, and the degeneracy of H atoms located at that site. In a subsequent study by Curran et al. [67], the original reaction rate parameters presented in [66] were revised; due to changes in thermodynamic parameters, pre-exponential A-factors were reduced by approximately an order of magnitude, and to account for the resulting lower reactivity, activation energy values were reduced as well to match experimental fuel reactivity profiles. Following literature recommendations by Zhu et al. [68], the isomerization reaction rates were reduced once more (E_A values were reduced by 400 cal/mol) to achieve the final values presented in Table 4.1 and [69]. At the time of writing, these RO_2 isomerization reaction rate parameters have been widely adopted and appear in a number of prominent, detailed chemical kinetic mechanisms (e.g., [69, 70]).

To correct the premature, model-predicted IDT, and obtain modeled species data comparable to the measurements, the R1-R3 reaction rate A-factors were scaled by the same factor until the time corresponding to the modeled C_2H_4 steepest-slope point for each experiment aligned with the time
corresponding to the measured $\text{C}_2\text{H}_4$ absorbance steepest-slope point. Figure 4.5 shows the results of this scaling exercise for the same long-time shock experiment shown in Figure 4.3.

![Figure 4.5: Measured temperature and $\text{H}_2\text{O}$, $\text{CO}_2$, and $\text{C}_2\text{H}_4$ mole fractions (based on $T_{\text{meas}}$ and $T_{\text{model}}$), alongside modified-model temperature and mole fraction predictions. Model predictions are denoted by dashed lines.]

The model results obtained using the shock-specific modified isomerization reaction rates show significant improvement over the unmodified-model results; the time-resolved $\text{H}_2\text{O}$ and $\text{C}_2\text{H}_4$ model predictions more closely match the species measurements, and the modeled temperature now reflects a temperature rise closer to that seen in the measurements (103 K). (For clarity, the $\text{CO}_2$ measurements, which showed close model agreement in Figure 4.3, are not re-plotted). Additionally, when the new modeled temperature is used to obtain the measured $\text{H}_2\text{O}$ and $\text{C}_2\text{H}_4$ mole fractions, the measurements asymptote to a final, steady-state value as expected, confirming the suspected inaccuracy of the temperature measurement late in the expansion fan; subsequent reported laser measurements are calculated using modified-model temperatures.

The average A-factor scaling factor across all twelve shock experiments was found to be 0.6 with a standard deviation of 0.1; this average scaling factor was used to modify all three reaction rates and a new, modified chemistry set was created. After modification, the model and experimental IDTs show an average relative difference of 16% (0.4 ms) – a significant improvement over the
4.4.2 Comparison of laser measurements, GC measurements, and model results

Comparisons of GC sample analysis results with time-resolved laser measurements are inhibited by the different timescales associated with each sensing strategy; laser measurements are typically conducted only before the arrival of the expansion fan, while GC analysis is typically applied to determine the composition of a gas sample extracted after the arrival of the expansion fan. However, by extending the laser measurements into the expansion fan using a modified-model temperature, as seen in Section 4.4.1, a final, steady-state plateau value can be extracted from each laser measurement for comparison with the single GC species measurement acquired for each experiment. Additionally, by using the measured pressure to constrain the model reactor pressure time-history, the modeled species results capture the chemistry that occurs during the quenching process induced by the expansion fan, thereby allowing for direct comparison with the GC measurements and the extended laser results.

Figure 4.6 shows a comparison of a time-resolved C\textsubscript{2}H\textsubscript{4} laser measurement with the corresponding model prediction (using a specified-pressure approach with both the original and modified model) for a representative shock experiment; a traditional constant-internal energy/constant-volume (UV) simulation is included for comparison, in large part to show the necessity of using an experimental pressure trace to constrain the model results for these experiments. A large "X" is used to denote the model and simulation mole fraction values taken to be the final steady-state plateau values.

Figure 4.7a-f shows the final \textit{n-}C\textsubscript{7}H\textsubscript{16}, C\textsubscript{2}H\textsubscript{4}, H\textsubscript{2}O, CO, H\textsubscript{2}, and C\textsubscript{3}H\textsubscript{6} mole fraction measurements obtained using the two experimental techniques of interest (laser absorption and GC analysis) and the simulated results obtained using the unmodified and modified LLNL model with a specified-pressure approach for the twelve variable-test-time shock experiments. As described in Section 4.3.3, the GC measurements were recorded on a dry basis (water removed from the sample), but are reported here on a wet basis, using the laser-based water mole fraction measurements to perform the conversion. All of the experimentally measured mole fraction values plotted here
4.4. RESULTS AND DISCUSSION

Figure 4.6: Comparison of laser measurement and model (unmodified and modified) C\textsubscript{2}H\textsubscript{4} results are available in tabulated format in the Supplementary Material accompanying the related publication [20].

As can be seen in Figure 4.7a, modifying the LLNL model yields closer agreement between the GC and model results for n-C\textsubscript{7}H\textsubscript{16} – an average relative difference of 8.3% is observed, versus 32.5% with the unmodified model.

The C\textsubscript{2}H\textsubscript{4} results seen in Figure 4.7b trend as expected: as \( \Delta \tau_{dwell} \) increases, all result sets show an increase in C\textsubscript{2}H\textsubscript{4} mole fraction. The laser and modified-model ethylene results show close agreement at all dwell times; the average relative difference between the laser and modified-model results is 6.3% – less than the \( \pm 8.9\% \) uncertainty associated with the measurement, and significantly less than the average relative difference between the laser and the unmodified-model results (51.8%). This close agreement is best exhibited in the time-resolved results shown in Figure 4.6 – the modified-model rise time and final mole fraction values are consistent with the time-resolved laser measurement. The GC measurements shown in Figure 4.7b are on average 330 ppm lower than the laser measurements. It is hypothesized that this discrepancy may be due to subsequent decomposition after the arrival of the expansion fan (e.g., due to subsequent reflected shocks), which would
Figure 4.7: Comparison of GC, laser, and model results of final $n$-C$_7$H$_{16}$, C$_2$H$_4$, H$_2$O, CO, H$_2$, and C$_3$H$_6$ mole fractions as a function of dwell time.
explain why the additional decomposition is not observed in the laser or model results. However, this hypothesis is unlikely, given the temperature conditions of interest for these experiments.

The steady-state H$_2$O mole fraction results for all experiments are shown in Figure 4.7c. Modifying the LLNL model to more closely match IDT using an average A-factor scalar typically worsens the agreement between measured and modeled H$_2$O. An average relative difference of 9.9% is observed between the measurements and unmodified-model results, while an average relative difference of 36.0% is seen between the measurements and modified-model results. This consistent discrepancy indicates that reducing the reaction rates associated with R1-R3 slows the formation of the resulting hydroperoxyalkyl (QOOH) radicals, which in turn impedes the formation of OH necessary to form H$_2$O. An H$_2$O sensitivity analysis (results provided in Figure 4.8) confirms that the same three isomerization reaction rates modified to improve IDT agreement (R1-R3) dominate the formation of H$_2$O between first- and second-stage ignition.

![Figure 4.8: H$_2$O sensitivity analysis results (LLNL n-heptane detailed mechanism, v3.1 [65])](image)

The remaining GC measurement results in Figure 4.7d-f all show closer agreement with the modified-model results than the unmodified-model results, indicating that the modified chemistry
set more accurately captures the formation of CO, H₂, and C₃H₆ than the original chemistry set. Although the relative disagreement between data points is consistently outside the uncertainty bounds associated with the GC measurements, the model results are mostly encompassed by the scatter seen across all 12 shock experiments.

The CO₂ laser and GC results, obtained for the experiments with CO₂ in the test gas mixture, are not plotted here, but can be found in Appendix C.5. The results show that the amount of CO₂ included in the test gas mixture (0.21%) is maintained throughout each experiment (no significant CO₂ formation is expected before second-stage ignition). The model results fall between the laser and GC measurements, and the laser and GC measurements show an average relative difference of 7.6% – less than the measurement uncertainty bounds. While not kinetically relevant, the CO₂ mole fraction results confirm that there are no losses inherent in the sampling process.

Overall, the fact that modifying the three RO₂ isomerization reaction rates worsens agreement between modeled and measured H₂O mole fraction results, yet improves agreement for a variety of other species, indicates that these three reaction rates are not the only ones that need to be changed to improve overall model performance at low temperatures. As such, the reaction rate scaling factor presented here (Section 4.4.1) should be viewed more as a guide for further model development, not as a definitive, proposed change to the RO₂ isomerization reaction rates.

4.5 Conclusions

A dual laser absorption/GC sampling diagnostic was utilized in a variable-test-time shock tube facility to obtain time-resolved, multi-species measurements in the n-heptane oxidation NTC region (760 K, 4.9 atm). Laser diagnostics were used to obtain time-resolved, in situ temperature and CO₂, H₂O, and C₂H₄ mole fraction measurements. The length of the shock tube driver section was varied to control the timing of the expansion fan arrival at the shock tube endwall, thereby allowing for quenched, post-shock samples to be extracted for GC analysis (n-C₇H₁₆, C₂H₄, CO, H₂, C₃H₆, and CO₂) at different times following first-stage ignition (and before second-stage ignition).

The quasi-time-resolved GC measurements and the truly time-resolved laser measurements were compared to each other and results predicted by the LLNL n-heptane kinetic model [65].
Discrepancies between the modeled and measured first-stage ignition delay times indicate the overestimation of the reaction rates associated with three RO$_2$ (heptylperoxy) isomerization reactions. In order to allow for accurate comparison of the combined diagnostic species results with those predicted by the model, the reaction rates were modified to improve IDT agreement, and the modified-model results were compared to the temperature and species experimental results.

The results obtained using the combined diagnostic provide valuable insight into low-temperature $n$-heptane oxidation kinetics. Reducing the heptylperoxy isomerization reaction rates by the appropriate amount yields $n$-C$_7$H$_{16}$, C$_2$H$_4$, CO, H$_2$, and C$_3$H$_6$ predictions that agree with the measurements, indicating accurate modeling of the $n$-C$_7$H$_{16}$ decomposition and C$_2$H$_4$, CO, H$_2$, and C$_3$H$_6$ production pathways. The lingering disagreement between the modeled and measured H$_2$O mole fractions indicates additional experimental data and analysis are necessary to better understand the coupling between low-temperature IDT and H$_2$O production. The GC and laser measurements show satisfactory agreement, bolstering confidence in the ability of both experimental techniques to provide reproducible speciation data in shock tube experiments.

The results presented above highlight the benefit, if not the necessity, of tackling kinetic model design and validation using a combined laser/GC approach; while the GC measurements validate the final species predictions of a kinetic model, time-resolved laser measurements are necessary to diagnose why discrepancies exist between the measured and modeled results and provide greater insight into transient ignition processes.

The experiments presented next aim to take the work presented here a step further – a truly time-resolved, fast-sampling GC measurement system that allows for direct comparison between time-resolved laser measurements and GC analysis results obtained before the arrival of the expansion fan.
Chapter 5

Time-resolved GC measurements with *in situ* LAS

5.1 Introduction and background

The development of accurate chemical kinetic models for the prediction of next-generation fuel behavior hinges on the highly accurate experimental measurement of global combustion properties (e.g., ignition delay time, flame speed) and fundamental combustion parameters (e.g., reaction rates, species time-histories), particularly at conditions relevant to modern-day combustion systems. Time-resolved measurements of the evolution of chemical species in high-temperature, pyrolysis and oxidation experiments are commonly conducted in shock tubes using optical diagnostics or time-of-flight mass spectrometry (TOF-MS) techniques. Laser absorption diagnostics, in particular, excel at measuring a handful of stable and radical hydrocarbon species simultaneously, with high time-resolution, over a wide range of reflected-shock temperature and pressure conditions [4]. However, laser diagnostics are limited by the number of species that can be measured simultaneously, and not all combustion-relevant species are easily optically accessible (e.g., H₂). TOF-MS, a sampling-based alternative to optical measurements, allows for the time-dependent, simultaneous quantification of all species in a shock tube experiment [34]. However, the technique is generally limited to use in near-atmospheric pressure experiments, due to the low-pressure requirements of
5.1. INTRODUCTION AND BACKGROUND

the ion source. There is therefore an unmet need for a robust speciation technique that can provide broad, time-resolved species measurements in a shock tube at pressures relevant to practical combustion systems.

Presented here is the first implementation of a fast-sampling, finite-volume, GC speciation system for the measurement of combustion-relevant species in the post-reflected-shock reacting gas of a shock tube experiment. Finite-volume, post-shock sample analysis by GC or GC-MS is not, in and of itself, a new technique, but the vast majority of studies presented in the literature report analyses of gas samples that have been extracted from the shock tube after the test gas has been chemically frozen by the arrival of an expansion fan (e.g., [36, 71]); these experiments produce a single yield measurement, per species, per experiment (similar to the results presented in Chapters 3 and 4). Quasi-time-resolved, sampled-gas species measurements were recently reported by Ferris et al. [20] (and presented in Chapter 4), in which the timing of the expansion fan arrival was varied for the same experimental condition, thereby freezing the chemistry and allowing for gas sampling at different extents of reaction; while this approach provides a snapshot of the evolving chemistry, the analyzed gas samples were still extracted after expansion fan-induced quenching.

In this work, finite-volume gas samples are extracted from the reacting test gas before the arrival of the expansion fan and analyzed by GC; use of a long-test-time shock tube facility allows for the extraction of multiple samples in a single experiment. Simultaneous, in situ laser absorption measurements are conducted and serve as a basis of comparison for the sampled-gas results. This chapter represents the culmination of the GC sampling work presented in this dissertation, and the partial realization of a primary goal: to develop a truly time-resolved GC sampling technique to be used in conjunction with time-resolved laser absorption measurements. While fast-sampling experiments of this kind have been previously conducted in a rapid compression machine [72, 73], these are believed to be the first such experiments carried out in a conventional shock tube setup; these are also the first experiments to provide simultaneous fast-sampled GC and laser absorption species measurements.

The subsequent sections of this chapter describe the extended-test-time shock tube facility used in this work, the GC fast-sampling system and complementary laser diagnostics, the two kinetic systems chosen to showcase and validate the time-resolved sampling diagnostic (cyclohexene and
ethane pyrolysis), and the development of a method for directly comparing the GC sampling results to time-resolved laser and model results. The results of the earliest-extracted sample measurements ($t < 10.5 \text{ ms}$) are presented and discussed first, followed by a discussion of the late-time sample measurements ($t > 10.5 \text{ ms}$). Because the late-time GC and LAS measurements show noticeable discrepancies, significant effort has been put into understanding and diagnosing these discrepancies; the chapter concludes with an evaluation of the various phenomena impacting the late-time sampling results and guidance for how these discrepancies can be mitigated in future experimental endeavors.

### 5.2 Overview of kinetic systems

To validate the functionality of the fast-sampling system, two simple kinetic systems were chosen for investigation: the cyclohexene and ethane pyrolysis reaction pathways. An overview of the two kinetic systems is presented here.

#### 5.2.1 Cyclohexene pyrolysis

The thermal dissociation of cyclohexene has been studied extensively (e.g., [74–77]), and it is known that its primary decomposition pathway between 700 and 1200 K is as follows:

$$\text{cyclohexene} \rightarrow \text{ethylene} + 1,3\text{-butadiene} \quad \text{(R5.1)}$$

This reaction is a known reverse of the Diels-Alder cycloaddition pathway. Due to its predictable decomposition behavior, cyclohexene is commonly used as a chemical thermometer in single-pulse shock tube experiments [33, 34, 40, 78].

Because of its popularity, the rate of Reaction R5.1 is also relatively well-known. Stranic et al. measured the reaction rate using an ethylene laser absorption diagnostic and found the following Arrhenius rate constant expression:

$$k = A \exp\left(-\frac{E_A}{RT}\right) = 4.84 \times 10^{14} \exp\left(-31900/T\right) \text{s}^{-1} \quad \text{(5.1)}$$

The maximum uncertainty associated with the reaction rate constant is estimated to be ±21% at
5.2. OVERVIEW OF KINETIC SYSTEMS

5.2.1 Cyclohexene pyrolysis

The test gas composition used in this work was nominally 1.4% cyclohexene/Ar. Test gas mixtures were prepared manometrically (MKS Baratron) and a 3.41-μm laser absorption diagnostic was used to measure and confirm fuel loading in each experiment (see Section 5.3.3). The cyclohexene was obtained from Fisher Scientific (99%) in liquid form and was degassed prior to mixture preparation using the freeze-pump-thaw method. High-purity argon (99.999%) was obtained from Praxair, Inc.

5.2.2 Ethane pyrolysis

The ethane pyrolysis system was additionally chosen for study due to the simplicity of the parent fuel molecule and the fact that its pyrolysis mechanism is relatively well known. Recent work by Shao et al. [79, 80], in particular, has provided more accurate reaction rate measurements for two reactions that play an important role in small-hydrocarbon pyrolysis:

\[
\text{CH}_3 + \text{C}_2\text{H}_6 \rightarrow \text{CH}_4 + \text{C}_2\text{H}_5 \quad (\text{R5.2})
\]

\[
\text{C}_2\text{H}_4 + \text{H} \rightarrow \text{C}_2\text{H}_3 + \text{H}_2 \quad (\text{R5.3})
\]

Figure 5.1 shows the results from a constant-UV simulation of 1% ethane in argon, at the conditions of interest in this work (1100 K, 7 atm), using an updated Foundational Fuel Chemistry v. 1 (FFCM-1) model [81] (modified to include the most recent reaction rate data from Shao et al.). As shown in the plot, the primary species formed in ethane pyrolysis include H\textsubscript{2} and C\textsubscript{2}H\textsubscript{4} (major species), as well as trace amounts of CH\textsubscript{4} and C\textsubscript{2}H\textsubscript{2} (minor species); note that at these conditions, H\textsubscript{2} and C\textsubscript{2}H\textsubscript{4} form at approximately a one-to-one ratio (the plotted lines are coincident). The three primary species (C\textsubscript{2}H\textsubscript{6}, H\textsubscript{2}, and C\textsubscript{2}H\textsubscript{4}) were quantified in the GC sampling experiments.

The test gas composition used in this work was nominally 1% ethane/Ar. Test gas mixtures were prepared manometrically (MKS Baratron). High-purity argon (99.999%) and ethane (99.998%) were obtained from Praxair, Inc.
5.3 Experimental setup and approach

5.3.1 Extended-test-time shock tube facility

The laser and GC sampling experiments were conducted in the AST facility described in Section 2.2.3, outfitted with a driver extension to accommodate long test times. The shock tube driver section is 7.74 m long; the driven section is 9.73 m long, with an inner diameter of 11.53 cm.

Two diaphragm approaches were used to achieve the desired reflected-shock, initial temperature and pressure conditions. A double-diaphragm approach, in which two diaphragms are scored and separated by a finite gas volume, was used in the cyclohexene pyrolysis experiments; diaphragm rupture occurs when the volume between the two diaphragms is rapidly evacuated through use of a dump tank. The polycarbonate diaphragms used in the cyclohexene experiments were 0.04-in thick and scored to a depth of 0.012 in. Un-scored, back-to-back diaphragms (one 0.010-in thick, the other 0.030-in thick) were used in conjunction with a diaphragm cutter in the ethane pyrolysis experiments.

The double-diaphragm approach can be used in place of the more conventional, single-interface
diaphragm-and-cutter approach to more precisely control ultimate driver pressure \( (P_4) \) and therefore initial post-reflected-shock temperature and pressure conditions \( (T_{5,\text{init}}, P_{5,\text{init}}) \). However, in the cyclohexene pyrolysis experiments in particular, non-ideal pressure fluctuations were observed (see, for example, Figure 5.4) and found to be caused by the thick, 0.04-in, scored polycarbonate diaphragms needed to achieve the high-pressure test conditions. The same pressure fluctuations were not observed when unscored, back-to-back, 0.030-in and 0.010-in polycarbonate diaphragms were used with a cutter to achieve the same post-reflected-shock conditions. (See Appendix E.3.2 for a more thorough exploration of this pressure fluctuation phenomenon.) As a result, the double-diaphragm approach was not used in the ethane pyrolysis experiments.

Driver inserts were employed in both sets of experiments to maintain near-constant, post-reflected-shock pressure conditions [41]. To prevent reflection of the reflected shock off the contact surface between driver and driven gas, tailored, binary driver gas mixtures of approximately 65% helium and 35% \( N_2 \) were used. To further prolong the experiment test times, the driver was backfilled with pure \( N_2 \), yielding a final driver gas composition of approximately 48% pure \( N_2 \), 52% binary mixture. High-purity helium (99.998%) and \( N_2 \) (99.998%) were obtained from Praxair, Inc. Using the above strategies, test times of approximately 35 ms were achieved.

Incident shock arrival times were recorded using five sidewall, piezo-electric pressure transducers (PCB 113A26) and used to infer incident shock velocity at the shock tube endwall. Normal-shock relations were used to determine initial post-reflected-shock temperature and pressure conditions \( (T_{5,\text{init}}, P_{5,\text{init}}) \) with an average uncertainty of \( \pm 1.1\% \) and 2.2%, respectively. In each experiment, a time-resolved, sidewall pressure measurement was recorded 2 cm from the endwall using a piezoelectric pressure transducer (Kistler 603B1). Over the duration of each experiment, the post-reflected shock pressure was maintained within 9.5% of its initial value.

5.3.2 GC fast-sampling system (time-resolved measurements)

In each experiment, three distinct gas samples are extracted from the reacting gas, through the endwall, before the arrival of the expansion fan. Three fast-acting solenoid valves (Festo MHE3) are mounted on the shock tube endwall via custom-made, low-volume endwall plugs – the same as those described in Section 3.3.3 and [19]. The effective dead volume in each plug is estimated to
be 1.05 mL. The three endwall plugs are arranged in an equilateral triangle formation, with plug axial centerlines located 3.96 cm apart; each plug is 2.29 cm from the axial centerline of the shock tube (see Figure 5.2). A short, 1/8-inch outer-diameter tube is inserted into each plug to allow the extraction point of each sample to be offset from the shock tube endwall by 3.5 mm.

As described in previous work (Section 3.3.3), an 1/8-inch outer-diameter, stainless steel tube is attached to each endwall sampling valve and serves as the primary containment vessel for the extracted gas sample (see Fig. 5.3). The end of each containment volume is connected to an "isolation" solenoid valve (ASCO 411), which is in turn connected to a 1/4-inch outer-diameter stainless steel tube segment that terminates with a 1/4-turn ball valve. This segment of 1/4-inch tubing, in conjunction with the isolation valve, is used to isolate the first 2.5 mL of collected sample from the bulk of the sampled gas (see Fig. 5.3). A low-speed pressure transducer (Omega PX309) is attached to each isolation volume segment to monitor the final sample pressure. The total volume extracted from the shock tube by each sample line is approximately 8 mL (8.7 mL sample line 1, 8.0 mL sample line 2, 7.9 mL sample line 3). The first sample line is slightly more voluminous than the other two, due primarily to a fitting used to accommodate an in-line PCB pressure transducer.
5.3. EXPERIMENTAL SETUP AND APPROACH

(not pictured in Fig. 5.3). The three sample lines are connected to a 6-port, multi-position sampling valve (Valco Instruments, EMT4, see Figure 3.3) via segments of 1/16-inch outer-diameter, Sulf-nert-treated, stainless steel tube. The sample lines are insulated and maintained above 60 °C during experiments.

![Figure 5.3: 3-D rendering of the GC fast-sampling system](image)

Before each shock experiment, the fast-acting endwall valves are closed and the sample lines are evacuated through the open 1/4-turn valves. Just prior to the start of each experiment, the 1/4-turn valves are closed, thereby isolating the evacuated sample lines. A delay generator (Berkeley Nucleonics Corp., 555 series) is used to trigger each sampling event; the delay generator is triggered by the arrival of the incident shock, 1.05 m from the shock tube endwall. After a 0.3-ms delay, the first fast-acting valve is activated with a 10-ms trigger pulse; the second and third fast-acting valves are triggered 10 ms and 20 ms, respectively, after the first, each with a 10-ms trigger pulse. Figure 5.4 shows the PCB measurement, fast-acting valve trigger signal, and in-line sample pressure measurement for a given experiment; the valve open and close times are also indicated, as deduced from the in-line pressure.

The fast-acting valves are reported to have stock open and close times of less than 2.3 ms and 2.8 ms, respectively. Indeed, in-line pressure measurements indicate that the effective sampling time for
a 10-ms trigger pulse is not, in fact, 10 ms, but closer to 9.3 ms (see Fig. 5.4). As will be discussed in Section 5.5.1, the open time of the fast-acting valve is determined using the first derivative of the in-line pressure signal, and the close time is taken to be the time corresponding to the maximum pressure; the in-line pressure drops rapidly after the valve is closed, indicating no further high-pressure gas is entering the sampling system and the gas in the sample line is equilibrating.

After a delay of 0.9 s following the incident shock arrival, all three isolation solenoid valves are latched closed, thereby separating the initial 2.5 mL of sample (thought to contain endwall boundary-layer gas and unreacted, dead volume gas) from the remaining 5.4-6.2 mL of sample – the composition of which is ultimately quantified via GC analysis. For shock experiments conducted at approximately 7 atm (Region 5 pressure), the equilibrated pressure of the collected samples was approximately 23 psia.

The 6-port, multi-position sampling valve is used to introduce the contents of each sample line to the GC. To minimize cross-contamination between samples, pure argon (99.999%) was hooked up to one of the 6 ports and used to flush or purge the GC between the analysis of each sample; the argon pressure was maintained at the same pressure as the samples (~23 psia).
In each experiment, sample analysis proceeds in five steps: 1) the GC pulls a sample of test gas from Sample Line 1 and analyzes it; 2) the multi-position sampling valve rotates to the pure-argon port, then the GC pulls in a sample of argon and analyzes it; 3) the sampling valve rotates to the port connected to Sample Line 2, then the GC pulls in a sample of test gas and analyzes it; 4) the sampling valve rotates back to the pure-argon port, then the GC pulls in a sample of argon and analyzes it; 5) the sampling valve rotates to the port connected to Sample Line 3, then the GC pulls in a sample of test gas and analyzes it. After each experiment is completed, all three sample lines are evacuated and flushed with argon; an argon sample from each sample line is then analyzed to ensure traces of previous sampled-gas species have been removed.

The Agilent 490 MicroGC (Section 2.4.2) is used to quantify the presence of various hydrocarbons: cyclohexene \((C_6H_{10})\), ethylene \((C_2H_4)\), and 1,3-butadiene \((C_4H_6)\) in the cyclohexene pyrolysis experiments, and ethane \((C_2H_6)\), ethylene \((C_2H_4)\), hydrogen \((H_2)\), and acetylene \((C_2H_2)\) in the ethane pyrolysis experiments. Four columns are used for these experiments: the CP-Sil 5CB column (cyclohexene), the PoraPlot U (PPU) column \((C_2H_4, C_2H_2)\), the PoraPlot Q (PPQ) column \((C_4H_6, C_2H_6)\) and the MS 5Å column \((H_2)\). Each of the columns is equipped with a thermal conductivity detector (TCD). A multi-point calibration curve was generated for each species, and the calibration gas mixtures were prepared manometrically with gases obtained from Sigma Aldrich (≥ 99%) and Praxair, Inc. (99.999%). The estimated uncertainty associated with the GC species measurements was found to be ±6% (cyclohexene) and approximately ±4.7% (ethylene, 1,3-butadiene, ethane, acetylene, hydrogen).

### 5.3.3 Laser absorption diagnostics

Two laser absorption diagnostics were used in the cyclohexene and ethane pyrolysis work to measure fuel loading and ethylene time-history. Initial cyclohexene absorbance was measured using a wavelength-tunable, distributed feedback (DFB) interband cascade laser (ICL) at 3.41 \(\mu m\) (Nanoplus). The room-temperature cyclohexene absorption cross-section at 3.41 \(\mu m\) was measured to be nominally 37.62 m\(^2\)/mol (see Appendix D.1 for full cross-section measurement results). Transmitted light intensity was recorded at 5 MHz with an indium antimonide (InSb) detector (InfraRed
The uncertainty associated with the initial cyclohexene mole fraction measurements is estimated to be ±2.3%, due primarily to uncertainty in the room-temperature absorption cross-section measurement.

Ethylene mole fraction was determined using a water-cooled, grating-tuned, CO$_2$ gas laser (Access Laser Company, model Lasy-4G) operated at the P14 line (10.532 $\mu$m) in conjunction with a photovoltaic IR detector (Vigo Systems, PVM-2TE-10.6). This diagnostic has been discussed at length in previous work [43], and in Section 3.3.2. In the ethane pyrolysis experiments, ethylene measurement is straightforward, as none of the major species present are expected to interfere with absorbance by the dominant ethylene presence.

Ethylene measurement in the cyclohexene experiments, however, is a bit more complex. At the conditions of interest to this study, ethylene, cyclohexene, and 1,3-butadiene all absorb at 10.532 $\mu$m. However, previous studies indicate that Reaction R5.1 is the dominant decomposition reaction at these conditions, which suggests that cyclohexene is reduced, and ethylene and 1,3-butadiene are produced, in a one-to-one ratio. The following relation between ethylene mole fraction, $X_{C_2H_4}$, and cyclohexene mole fraction, $X_{C_6H_{10}}$, can therefore be written:

$$X_{C_2H_4} = X_{C_6H_{10,initial}} - X_{C_6H_{10}}$$  \hspace{1cm} (5.2)

The total absorbance, $\alpha_{10.532\mu m}$, can subsequently be related to ethylene mole fraction as follows:

$$\frac{\alpha_{10.532\mu m}}{nL} = (\sigma_{C_2H_4} + \sigma_{C_4H_6} - \sigma_{C_6H_{10}})X_{C_2H_4} + \sigma_{C_6H_{10}}X_{C_6H_{10,initial}}$$  \hspace{1cm} (5.3)

Ethylene absorption cross-section measurements were obtained from Ren et al. [43], 1,3-butadiene absorption cross-sections were obtained from Stranic et al. [77], and cyclohexene absorption cross-sections were measured in this study (0.44 m$^2$/mol, with minimal temperature dependence below 1120 K– see Appendix D.2 for full results). The total absorbance could thus be broken into the contributions attributed to each absorbing molecule (see Figure 5.5).

As noted previously by Stranic et al. [77], the cyclohexene absorption cross-section is more than an order of magnitude less than the cross-sections of ethylene and 1,3-butadiene, indicating that the change in absorbance due to cyclohexene decomposition and mole fraction uncertainty has
5.4. EARLY-TIME GC RESULTS

Figure 5.5: Pressure and 10.532-µm laser absorbance measurements. Nominal test gas mixture: 1.4% cyclohexene/argon; post-shock initial conditions: 1121 K, 7.4 atm.

minimal impact on the ethylene mole fraction measurement. The overall uncertainty associated with the laser-based ethylene mole fraction measurements is estimated to be ±5.0%, due primarily to uncertainty in temperature.

5.4 Early-time GC results

Time-resolved GC sampling and laser absorption measurements were simultaneously conducted in 1.4% cyclohexene/Ar pyrolysis experiments over a temperature range of 980-1150 K at approximately 7.3 atm, and 1.0% ethane/Ar pyrolysis experiments, over a temperature range of 1060-1153 K at approximately 6.9 atm. As described in Section 5.3.2, three samples were sequentially extracted in 10-ms intervals in each experiment and subsequently analyzed by GC. The results of the first-extracted (t < 10.5 ms) gas sample analyses are presented first, along with a comparison of the early-time GC, laser, and modeled ethylene mole fraction results; finally, late-time (t > 10.5 ms) GC, laser absorption, and model results are presented.

The GC analysis results for the first sample extracted in each experiment are shown in Figure 5.6. The mean, sample-acquisition start time across all experiments was 1.06 ms after the arrival of the reflected shock; the mean acquisition end time was 10.34 ms after the arrival of the reflected shock.
Each mole fraction result represents an effective average over the sample duration.

![Graphs showing mole fraction results for cyclohexene, ethylene, and 1,3-butadiene and ethane, ethylene, and hydrogen in cyclohexene and ethane pyrolysis experiments.](image)

Figure 5.6: GC-measured (a) cyclohexene, ethylene, and 1,3-butadiene mole fraction results and (b) ethane, ethylene, and hydrogen mole fraction results for first-extracted samples (1.06-10.34 ms).

The results in Figure 5.6 trend as expected. In Figure 5.6a, as initial post-reflected-shock temperature increases, the extent of cyclohexene decomposition in the first ~10 ms increases, leading to an increase in ethylene and 1,3-butadiene production. Also, the ethylene and 1,3-butadiene results agree within their estimated uncertainty bounds (±4.7%). And finally, the ethylene and cyclohexene mole fraction results sum to the initial cyclohexene mole fraction (≈1.4%), as expected. Similarly, in Figure 5.6b, the extent of ethane decomposition increases as initial post-reflected-shock temperature increases, and this increase in decomposition is reflected in the increased production of ethylene and hydrogen. The mole fractions of the newly formed products (C\textsubscript{2}H\textsubscript{4} and H\textsubscript{2}) agree within their expected uncertainty bounds (±4.7%), and the ethylene/hydrogen and ethane mole fraction results sum to the initial ethane mole fraction (≈1.0%).

### 5.5 Methodology for comparing time-resolved GC measurements with laser and model results

A persistent challenge in combined GC sampling/laser absorption experiments is how to effectively compare a sampled GC species measurement – a single value – to an *in situ* laser species...
5.5. METHODOLOGY FOR COMPARISON

measurement – inherently time-dependent mole fraction values. In experiments such as these, in which the GC sample is extracted over \( \sim 9.3 \text{ ms} \) from a core of rapidly reacting gas, the comparison is further complicated by the fact that not only is the composition of the target gas changing over the course of the sampling time, but the sampled gas is also not collected uniformly in time. Presented here is a methodology for extracting a single, weighted-average laser and model result, from their respective time-resolved data sets, for comparison with GC results.

5.5.1 Calculation of weighted-average laser and model results

Figure 5.7 shows a representative pressure trace and ethylene-mole-fraction laser measurement from each set of pyrolysis experiments (cyclohexene pyrolysis at 1121 K, 7.4 atm in Figure 5.7a, ethane pyrolysis at 1152 K, 6.7 atm in Figure 5.7b). In both experiments, the post-reflected-shock pressure was maintained over the first 11 ms of the experiment (\( \pm 9.5\% \) in the cyclohexene experiment, \( \pm 5\% \) in the ethane experiment). Kinetic model predictions over the first 11 ms of each experiment are also included; the ethylene mole fraction results were modeled using the CHEMKIN-PRO kinetics solver [44] and a specified-pressure approach, in which the closed, homogeneous reactor pressure is constrained in time by a spline of the measured pressure (red solid line). In the cyclohexene pyrolysis results (Figure 5.7a), a comprehensive cyclohexane mechanism [82], modified to include the secondary reactions relevant to cyclohexene pyrolysis [77], made up the chemistry set. In the ethane pyrolysis results (Figure 5.7b), the FFCM-1 kinetic model [81], modified to include the updated reaction rates measured by Shao et al. [79, 80], was used as the chemistry set. In both cases, the laser-measured ethylene mole fraction increases steadily and shows very close agreement with the model result, well within the uncertainty bounds of the measurement (\( \pm 5\% \)).

Also indicated in Figure 5.7 is the approximate timeframe over which the GC results, plotted in Figure 5.6, were extracted. This sample duration can be deduced for each experiment through the use of a high-speed, PCB pressure transducer at the beginning of the sample line. The time-resolved, normalized sample-line pressure, measured at the inlet of the sample line for an experiment at 1056 K, 7.0 atm, is plotted in Figure 5.8; plotted alongside is the corresponding valve trigger signal and the first derivative of the in-line pressure signal. (These data correspond to the same experiment presented in Figure 5.4).
Figure 5.7: Representative time-resolved pressure and ethylene measurements, with (a) cyclohexene model [77] comparison and (b) modified FFCM-1 model [79–81] comparison (0-11 ms post-reflected shock). Black line indicates raw pressure measurement; red solid line indicates pressure spline used for modeling.

Figure 5.8: In-line normalized sample pressure, with first derivative and 10-ms trigger pulse vs. time after reflected shock arrival. 5.1% CO$_2$/argon test gas, initial post-shock conditions: 1056 K, 7.0 atm.
The valve opening time is approximated using the first derivative of the pressure signal: a line is fit to the steepest slope portion of the first derivative and extrapolated back to the first-derivative baseline signal. The intersection of the two is taken to be the time at which the first bit of gas sample passes the in-line pressure transducer. As can be seen in Figure 5.8, the pressure in the sample line begins to rise approximately 2.4 ms after the beginning of the trigger signal, then rises steeply for ~6.3 ms before plateauing and ultimately reaching its peak 1.7 ms after the end of the trigger signal. The end of the sampling event is taken to be the time corresponding to the pressure maximum. The pressure drops off precipitously after this point, indicating that the valve has fully closed and the gas in the sample line is simply being redistributed/equilibrated.

Of particular interest is the fact that 90% of the total sample pressure is reached in the first 5.5 ms of the 9.3-ms sample. This suggests that inference of a single, laser-based mole fraction value, to be compared with the corresponding GC data, cannot be accomplished through a simple averaging of data points over the time period of the valve being open; the average must be more heavily weighted towards the beginning of the sampling event, commensurate with the time-dependent sampling rate.

The appropriate weighted averaging of the time-resolved laser trace can be achieved by taking the first derivative of the normalized sample-line pressure trace, \( \frac{d(P(t)/P_{max})}{dt} \), and multiplying it by the time-resolved mole fraction measurement, \( X_{C_2H_4}(t) \), such that:

\[
X_{C_2H_4,avg} = \sum_{t=0}^{t_{valve close}} X_{C_2H_4}(t) \frac{d\left(\frac{P(t)}{P_{max}}\right)}{dt} \Delta t
\]  

(5.4)

Here, \( \Delta t \) represents the time between acquired data points. The resulting weighted-average laser measurement, in this case \( X_{C_2H_4,avg} \), can now be directly compared with a sampled-gas GC measurement. It should be noted that one major assumption inherent in the use of this methodology to interpret time-resolved results is the assumption that the gas extracted in each experiment, and subsequently analyzed by GC, has had sufficient time to mix and is not significantly stratified.

While the methodology developed here has been presented in the context of comparing singular GC measurements with time-resolved laser measurements, it should be noted that the same approach must be taken for comparing GC measurements with time-resolved model results – a
weighted-average value must also be obtained from the time-resolved model data. This methodology is employed in subsequent sections to compare the time-resolved GC measurements to time-resolved laser and model results.

5.5.2 Uncertainty in weighted-average laser and model results

The effectiveness of the weighted-average method described above hinges on the ability to accurately identify the start and end times of each sampling event; doing so allows the weighted average of the time-resolved laser and model results to be calculated over the correct time period. Logically, the weighted-average results are more sensitive to the time window used for averaging when the corresponding time-resolved results being averaged are changing rapidly in time, as is often the case at the beginning of pyrolysis experiments (e.g., Figure 5.7).

As described in Section 5.5.1, an in-line pressure trace can be used to identify when sampled gas first passes the pressure transducer and the time period over which sample continues to fill the line. However, these times do not strictly correlate to the true open and close times of the sampling valves, relative to the passage of the reflected shock (time zero); the PCB is located approximately 30 mm downstream of the sampling valve, so there is inherently some delay between when reacting gas begins to exit the shock tube and when it causes a rise in the PCB signal. Therefore, if the valve open and close times derived from the first derivative of the PCB trace were used to calculate the weighted-average laser and model results (as described in Equation 5.4), the averaging would be occurring over a time period that does not directly coincide with the GC sampling event – the averaging time window would be too late. To accurately identify the time window over which the laser and model results should be averaged (noting that they are both measured/calculated relative to the passing of the reflected shock), an offset must be applied to the valve open and close times determined using the in-line PCB trace, shifting the weighted-average data subset range earlier and closer to the true time of sample extraction, relative to time zero.

Experiments were conducted to approximate the time delay between when sampling actually starts and when the PCB first sees sample. A second PCB transducer was placed in the sample line at the next available port, 87.5 cm from the first PCB. Argon shock experiments were conducted at 1149 K, 7.1 atm and 1178 K, 7.4 atm with both PCBs in place (see Figure 5.9). In "Shock 1"
5.5. METHODOLOGY FOR COMPARISON

(Figure 5.9a), there is a 4.6-ms delay between when the first PCB signal begins to rise (just before 6 ms on the x-axis) and when the second PCB signal begins to rise (just before 11 ms on the x-axis). In "Shock 2" (Figure 5.9b), there is a 4.8-ms delay between when the first PCB signal begins to rise (∼6 ms on the x-axis) and when the second PCB signal begins to rise (∼9 ms on the x-axis).

Figure 5.9: In-line pressure traces from two shock experiments, with valve trigger timing. PCB 1 located 30 mm from sampling valve, PCB 2 located 87.5 cm from PCB 1.

From this experimental data, it can be deduced that it takes approximately 4.7 ms for the first wave of sample to travel a distance of 87.5 cm in the sample line. If this velocity is applied to determine the amount of time it would take the sample to traverse the 30 mm between the sampling valve and the first PCB, one finds a travel time of 0.16 ms.

This 0.16-ms value is an estimate of the time delay between when sampling actually starts (when the valve begins to open relative to time zero) and when the sampling event manifests itself in the in-line PCB trace. This value is an approximation, as external factors such as experimental temperature and pressure, valve performance repeatability, etc., can cause the time delay to be higher or lower in an individual experiment. Additionally, the value’s calculation is predicated on the assumption that the amount of time it takes the sample to travel 87.5 cm can, in fact, be correlated with the amount of time it takes the sample to travel the first 30 mm of the sample line.

Nevertheless, the time delay value calculated above helps assign an approximate magnitude (100s of microseconds) to the lower limit of the expected time delay associated with a valve-opening time calculated using an in-line PCB trace. At the other end of the spectrum, one could assume that
the valve opens (and sampling begins) immediately upon the valve trigger signal being sent to the sampling valve (seen to occur approximately 2.6 ms before the pressure signal rise in Figures 5.4 and 5.9). It is therefore known that the sampling valve in each experiment must open, relative to time zero, in the range of 100s of microseconds to 2.6 ms before the in-line PCB initially sees a pressure rise. While any time delay within this range (∼0.16-2.6 ms) is technically possible, the true delay is more likely to fall at the 100s of microseconds end of the spectrum, as even the valve manufacturer (Festo) indicates a valve response time of less than 2.3 ms.

To further investigate the effect that an incorrectly deduced start-of-sampling time may have on the weighted-average laser and model results (and therefore calculate the uncertainty associated with such results), 5 of the C₂H₆/Ar pyrolysis shock experiments (with initial temperatures ranging 1068-1152 K) were analyzed further. Using the first-sample GC measurements as a guide, the time window used for averaging the laser and model results was moved forward in time, 10 microseconds at a time, until the weighted-average laser and model results were brought into agreement with the GC results (within the 5% uncertainty associated with the laser measurements). Across the five experiments, the offset needed to bring the laser measurements into accordance with the GC measurements ranged from 0.24 ms to 0.95 ms, with an average of 0.62 ms (standard deviation 0.31 ms). This average offset time of 0.62 ms was applied to all weighted-average laser and model result calculations presented in the subsequent sections of this chapter, in order to ensure the weighted averages were calculated over the appropriate time frames.

The standard deviation of the time offset results (0.31 ms) was used to calculate the change in weighted average observed when the offset time was shifted by ±0.31 ms. Across all of the ethane pyrolysis experiments, perturbing the 0.62-ms offset by 0.31 ms led to an average difference of 6.2% in weighted-average laser measurements. For all of the early-time, weighted-average laser and model measurements, the uncertainty due to averaging is therefore estimated to be ±6.2%. It should be noted that this uncertainty estimate does not necessarily hold for the weighted-average values calculated later in each experiment (i.e., corresponding to the second and third GC samples extracted in each experiment), as those time-resolved results show a slower rate of change in time. The uncertainty in the late-time weighted-average results, due to the time frame chosen for averaging, will be discussed in Section 5.7.
The overall uncertainty associated with the weighted-average laser measurements is also impacted by the uncertainty in the time-resolved laser measurement itself. The overall uncertainty associated with the early-time, weighted-average laser measurements was calculated by taking the root sum square of the laser measurement uncertainty (±5.0%) and the weighted-average uncertainty (±6.2%), and found to be ±8.0%.

5.6 Comparison of early-time GC and weighted-average laser and model results

To directly compare the early-time GC measurements with the time-resolved laser and model results, the methodology described in Section 5.5 (including the 0.62-ms offset described in Section 5.5.2) is used to calculate a single, weighted-average laser measurement and a single, weighted-average model result over the same time period corresponding to the early-time GC sample results. Figure 5.10 shows the GC-measured ethylene mole fraction results for the first sample extracted in each experiment, plotted alongside the corresponding, weighted-average laser and model results; the cyclohexene pyrolysis results are presented in Figure 5.10a and the ethane pyrolysis results are presented in Figure 5.10b.

In the cyclohexene pyrolysis experiments, the weighted-average model and laser results show close agreement across all temperature conditions, with an average relative difference of 7.5%; this is consistent with the close agreement seen in the time-resolved laser and model results (e.g., Fig. 5.7). The weighted-average laser measurements also show satisfactory agreement with the GC results; across the entire temperature range, the GC and laser results show an average relative difference of 10.6%. Above 1120 K, the absolute difference between the two measurement techniques increases, largely due to the increased time rate-of-change of ethylene mole fraction in the initial ~11 ms of the higher-temperature experiments. Across the entire temperature range, the GC and model results show an average relative difference of 7.6%.

In the ethane pyrolysis experiments, the weighted-average model and laser results show an average relative difference of 13.0%, and the model and GC results show an average relative difference of 13.1%. Meanwhile, the GC and laser results show an average relative difference of 14.4%. The
Figure 5.10: GC, laser, and model ethylene mole fraction results for the first-extracted sample in each experiment ($t < 11$ ms). The cyclohexene model results are calculated using a modified cyclohexane model [77] and the ethane model results are calculated using a modified FFCM-1 model [79–81].

Ethylene mole fraction results for cyclohexene pyrolysis experiments were conducted at higher temperatures, on average, than the cyclohexene experiments, which explains the higher relative difference seen in the ethane experiments. Once again, these results indicate that this fast-sampling diagnostic is best suited for use in low-temperature applications, specifically to study kinetic systems with relatively low species-mole-fraction rates of change. As such, another potential application for this fast-sampling diagnostic could be in flow reactor experiments, where operating temperatures typically range between 500 and 1300 K [83].

The early-time experimental results indicate that not only is it possible to use a finite-volume, sampling-based diagnostic to quantify the composition of a chemically reacting gas in a shock tube experiment prior to the arrival of the expansion fan, but these measurements show close agreement with time-averaged, in situ laser diagnostic measurements.

### 5.7 Late-time GC, laser, and model results

Two additional late-time gas samples were extracted from the reacting core of each pyrolysis experiment, with the final two samples spanning approximately 10.4-19.5 ms and 20.4-29.5 ms, respectively, relative to the passage of the reflected shock. Unlike the early-time extracted gas
measurements, the late-time results show more significant deviation from the corresponding laser and model results. Figure 5.11 shows the same representative pyrolysis experiments seen in Fig. 5.7, this time with time-resolved pressure, laser ethylene measurements, and model results extended out to 32.5 ms. The GC-sample ethylene results are plotted for comparison, with the timing of each GC result aligned with the time corresponding to the weighted-average laser value. The gray rectangles denote the approximate time period over which each sample is extracted from the shock tube; note that the GC measurement values are not centered horizontally within these rectangles, as the GC values are plotted at the weighted-average time associated with each sampling event, and therefore reflect the fact that more of the sample is extracted earlier in the sampling event than later.

In the cyclohexene pyrolysis experiment (Figure 5.11a), the Sample 1 data point shows close agreement with the laser trace as expected, given the results presented in Section 5.6. The second and third data points, however, show significant disagreement between the GC and laser (and model) results. Particularly concerning is the fact that even at the time corresponding to the start of the second and third sampling events (denoted by the left-most edge of the gray rectangles), the GC value is well below the laser measurement, indicating that at no time in that sampling event does the ethylene mole fraction measured by laser at the core of the shock tube resemble the mole fraction obtained using GC sampling. This phenomenon is especially apparent in the Sample 3 measurement, through inspection of its magnitude relative to the time-resolved laser trace recorded over the same time window. From the data presented in Figure 5.11a, it is clear that the disagreement between GC and laser results is worse at later times, and the absolute difference between laser and GC results increases between Sample 2 and Sample 3.

The ethane pyrolysis experiment (Figure 5.11b) shows the same trend: the Sample 1 data point shows close agreement with the laser and model results, but the Sample 2 and Sample 3 data points show increasing disagreement with the corresponding time-resolved laser and model measurements. Once again, at no time over the course of the later sampling events does the laser-measured ethylene mole fraction reflect the ethylene mole fractions obtained using GC sampling.

To better quantify the difference between the late-time GC, laser, and model results, weighted-average laser and model mole fraction values were calculated (as described in Section 5.5) for comparison with the second and third GC sample results in each experiment. The second-
Figure 5.11: Time-resolved pressure and ethylene measurements, with model and GC comparison (0-32.5 ms post-reflected shock). The cyclohexene model results are calculated using a modified cyclohexane model [77] and the ethane model results are calculated using a modified FFCM-1 model [79–81].
third-sampled results for the cyclohexene pyrolysis experiments are plotted in Figure 5.12, while the second- and third-sampled results for the ethane pyrolysis experiments are plotted in Figure 5.13.

![Figure 5.12: GC, laser, and model ethylene mole fraction results for the (a) second- and (b) third-extracted samples in the cyclohexene pyrolysis experiments. The model results are calculated using a modified cyclohexane model [77]. The second samples were extracted over 10.4-19.5 ms and the third samples were extracted over 20.4-29.5 ms.](image)

In the cyclohexene pyrolysis experiments, the Sample 2 GC results are on average 15.4% lower than the corresponding weighted-average laser results, and 23.5% lower than the corresponding weighted-average model results (see Figure 5.12a). The Sample 3 GC results (Figure 5.12b) are low by an average of 17.7% when compared with the weighted-average laser results, and low by an average of 28.9% when compared with the weighted-average model results. In almost all experiments, these relative differences exceed the uncertainty bounds associated with the results. The uncertainty in the GC results is approximately ±4.7%. The uncertainty associated with the weighted-average laser and model results, due to the time period over which averaging occurs, is lower than what was observed for the Sample 1 results (Figure 5.10), due to the slower rate of change in ethylene mole fraction at late times. In the Sample 2 weighted-average results, for example, moving the start of the averaging window 0.31 ms earlier (or, the standard deviation of the valve opening-time delay estimate (Section 5.5.2)) changes the weighted-average laser results by 1.2% and the weighted-average model results by 1.4%, on average. Similarly, moving the start of the averaging window earlier for the Sample 3 measurements changes the weighted-average laser and model results by 0.3% and
0.4%, respectively. Therefore, the uncertainty in the weighted-average laser results is dominated by the experimental uncertainty associated with the laser measurement (±5.0%).

It’s also notable that the laser and model results show greater disagreement at later times: in the Sample 2 results, the averaged laser and model results show a mean relative difference of 9.5%, and in the Sample 3 results, the averaged laser and model results show a mean relative difference of 11.3%. Independent of the averaging, the instantaneous, time-resolved laser and model results at 30 ms show an average relative difference of 10.5% across all of the cyclohexene experiments.

In the ethane pyrolysis experiments, the Sample 2 GC results are on average 30.9% lower than both the corresponding weighted-average laser and model results (see Figure 5.13a); once again, model results are determined using the modified FFCM-1 model [79–81]. The Sample 3 GC results (Figure 5.13b) are 30.2% lower than the corresponding weighted-average laser results, and 36.1% lower than the corresponding weighted-average model results. Once again, these relative differences far exceed the uncertainty bounds associated with the experimental results. Moving the start of the averaging window 0.31 ms earlier for the Sample 2 results changes the weighted-average laser measurements by 1.0% and the weighted-average model results by 1.2%, on average; moving
the start of the averaging window earlier for the Sample 3 measurements changes the weighted-average laser and model results by 0.6%. As in the cyclohexene experiments, the uncertainty in the weighted-average laser results is dominated by the uncertainty in the laser measurement (±5.0%).

Unlike in the cyclohexene experiments, the laser and model results in the ethane pyrolysis experiments agree quite well at later times: in the Sample 2 results, the averaged laser and model results show a mean relative difference of 6.3%, and in the Sample 3 results, the averaged laser and model results show a mean relative difference of 6.2%. The instantaneous, time-resolved laser and model results at 30 ms show an average relative difference of 6.7% across all of the ethane pyrolysis experiments.

Overall, although the early-time (Sample 1) GC measurements seem to agree well with laser and model results, the late-time GC sampling results (Sample 2 and Sample 3) show significant disagreement when compared with laser and model results in both the cyclohexene and ethane pyrolysis experiments. In both sets of experiments, the laser measurements show satisfactory agreement with model results, thereby bringing into question the efficacy of the GC fast-sampling system and its ability to generate accurate, reliable results, particularly at late times. Understanding this discrepancy between late-time GC and laser/model results is critical, as without understanding its source, the discrepancy cannot be corrected and the utility of the fast-sampling system will be limited. To this end, an extensive number of troubleshooting experiments have been carried out, the results of which will be described in Section 5.8.
5.8 Troubleshooting late-time GC sampling results

A number of troubleshooting experiments have been carried out to get to the bottom of the discrepancy observed between late-time, fast-sampled GC results and corresponding laser/model results in long-test-time shock tube experiments. The vast majority of the concerns addressed in the troubleshooting experiments were found to have little impact on the discrepancy between late-time GC and laser/model results. For the sake of brevity, experiments yielding results that showed minimal impact on the late-time discrepancy are presented in Appendix E. A smaller subset of troubleshooting experiments and calculations was found to be useful in probing the discrepancy between late-time GC and laser/model results. These more useful troubleshooting endeavors fall under three main categories: GC analysis error, mass dilution effects, and thermal effects. The specific lines of inquiry are outlined here, and each will be addressed in detail in the subsequent sections.

Troubleshooting efforts addressing GC analysis error include investigation of:

- Carbon/hydrogen accounting

Troubleshooting efforts addressing mass dilution effects include investigation of:

- Isolation volume effectiveness (impact of dead volume on results)

Troubleshooting efforts addressing thermal effects include investigation of:

- Laser and model result sensitivity to initial temperature
- Core gas temperature vs. sample effective temperature time-history
- Endwall thermal boundary layer growth
- Impact of probe length on sampled results
- Impact of thermal boundary layer on sampled mole fraction results

In an effort to conserve resources, the troubleshooting experiments were typically carried out in cyclohexene or ethane pyrolysis systems, not both; if one particular phenomenon was found to
be the cause of the late-time measurement discrepancies in one pyrolysis system, it is assumed that it would be the cause of the late-time measurement discrepancies in the other pyrolysis system as well. Regardless of the pyrolysis system considered in the troubleshooting experiment, the common goal was to figure out which factors led to a sizeable reduction in the disagreement seen between late-time GC and laser/model results.

### 5.8.1 Carbon/hydrogen accounting

A valuable check for determining the reliability of GC analysis results is to calculate the carbon and hydrogen recovery in a given experiment. A set amount of carbon and hydrogen enters the system by way of the parent fuel molecule(s), and by conservation of mass, the same amount of carbon and hydrogen must be present throughout the duration of a shock tube experiment. To ensure that the GC analysis results from the cyclohexene pyrolysis experiments are not artificially low, a carbon recovery check was performed. It is known that at the temperature/pressure conditions of interest, cyclohexene is expected to break down into equal parts C$_2$H$_4$ and 1,3-butadiene (C$_4$H$_6$). As a result, the summation of cyclohexene (C$_6$H$_{10}$) mole fraction remaining and C$_2$H$_4$ (or C$_4$H$_6$) formed should always equal the initial fuel mole fraction (approximately 1.4%, in this case).

A subset of the carbon/hydrogen recovery results from the cyclohexene pyrolysis experiments is presented in Figure 5.14. There are five bars associated with each of the three sample line measurements. The leftmost bar (black) indicates the C$_4$H$_6$ GC measurement, the second bar (red) indicates the C$_2$H$_4$ GC measurement, and the third bar (blue) indicates the C$_6$H$_{10}$ GC measurement. The fourth bar (magenta) represents the sum of the C$_6$H$_{10}$ and C$_2$H$_4$ GC measurements; in an experiment with perfect carbon/hydrogen recovery, this sum is expected to equal the initial C$_6$H$_{10}$ fuel loading amount (∼1.4%). The fifth bar (green) indicates the initial C$_6$H$_{10}$ fuel loading amount for that particular experiment, as measured using the laser fuel diagnostic described in Section 5.3.3.

The four sets of carbon recovery results depicted in Figure 5.14 show the range of results seen in the cyclohexene pyrolysis experiments. The plot in the top left corner shows the results of the experiment having the worst carbon/hydrogen recovery, or the largest disagreement between the summation of C$_2$H$_4$ + C$_6$H$_{10}$ GC results and the initial fuel loading measurement. The plot in the top right corner shows the results of the experiment having the best carbon/hydrogen recovery, or
Figure 5.14: Carbon/hydrogen recovery results for a subset of cyclohexene pyrolysis experiments. GC results from all three sampling events are shown. Ideally, magenta and green bar heights are expected to be equal.
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the smallest disagreement between the summation of $C_2H_4 + C_6H_{10}$ GC results and the initial fuel loading measurement. The bottom row shows two additional experiments, representative of the rest of the data sets, that fall between the "worst-case" and "best-case" scenarios. (The bottom left plot depicts the same experiment shown in Figures 5.7a and 5.11a).

Overall, the carbon recovery results show satisfactory agreement between the summation of GC results and the initial fuel loading measurements. In all experiments except the worst-case experiment (top left plot in Figure 5.14), the summed $C_2H_4 + C_6H_{10}$ GC results agree with the initial fuel loading laser measurements within the uncertainty bounds associated with the measurements. Poor carbon/hydrogen recovery is therefore not a factor in what’s causing the discrepancy between late-time GC and laser/model results.

These carbon/hydrogen recovery results do, however, provide an important clue as to what’s happening in the system. The too-low, late-time $C_2H_4$ results (as compared to the late-time laser/model results) are not caused by simple sample dilution due to an unrelated gas such as air, for example – this would uniformly lower all of the GC measurements ($C_6H_{10}$ included), causing a noticeable difference between the summation of $C_2H_4 + C_6H_{10}$ GC results and the initial fuel loading measurements shown in Figure 5.14. This carbon accounting exercise reveals that if the GC-measured, late-time $C_2H_4$ results truly are low, relative to what they should be (laser/model results), then the corresponding $C_6H_{10}$ measurements are necessarily too high as well. This finding helps narrow the focus of the troubleshooting experiments, as it indicates the discrepancy is likely due to one of two things: mass dilution by initial fuel/argon mixture (i.e., a gas that would enrich the cyclohexene/ethane composition while diluting the presence of the product species) or thermal effects causing retarded pyrolysis chemistry. Mass dilution and thermal effects will be investigated in the following sections.

5.8.2 Isolation volume effectiveness

A 2.5-ml isolation volume is built into the far end of each sample line and used to separate the first 2.5 mL of sample to enter the line from the rest of the sample, which is ultimately analyzed by GC (see Figure 5.3 on Page 93 for reference). This segment of first-sampled gas is thought to
be primarily composed of: 1) unreacted test gas pulled from the dead volume within each sampling plug (a constant volume in a given experiment, equal across all three sample lines), and 2) gas with a cooler temperature time-history residing in the endwall boundary layer (a volume that changes in time, in a given experiment). The dead volume in each sampling plug is estimated to be 1.05 mL, based on plug dimensions. The boundary layer thickness determines the volume of unreacted, cooler gas added to this dead volume (more on the endwall thermal boundary layer in Sections 5.8.5 and 5.8.7). In order for unreacted gas to dilute the gas samples enough to cause a \( \sim 20\% \) (cyclohexene pyrolysis experiments, Section 5.7) or \( \sim 30\% \) (ethane pyrolysis experiments, also Section 5.7) discrepancy between the late-time GC and laser/model results, the amount of unreacted gas entering the sample lines would have to be 20-30\% of the total sample line volume, or approximately 1.6-2.4 mL of the 8-mL volume. If this volume of unreacted gas was entering the late-time sample lines (Sample 2 and 3) and mixing with the entire gas sample, it would imply that the isolation volume was not effectively separating the unreacted gas from the rest of the sample. Experiments were therefore carried out to test the effectiveness of the isolation volume/valve setup.

In each fast-sampling shock experiment, the normally-open valve separating the isolation volume from the rest of the sample line is triggered to close 900 ms after the passing of the incident shock 1.05 m from the shock tube endwall. (By comparison, the three sampling events are triggered to begin 0.3 ms, 10.3 ms, and 20.3 ms after the passing of the incident shock). To test the effectiveness of physically separating the first-sampled, unreacted gas from the rest of the extracted gas sample, an additional experiment was conducted in which the time delay of the isolation valve trigger was set to 20 ms after the passing of the incident shock; the GC and laser results were compared to those from a 900-ms delay experiment at the same conditions. It should be noted that the isolation valves of all three sample lines are triggered to close at the same time (not staggered), due to equipment limitations. Also, additional experimentation showed that the closing response time of the isolation valve (ASCO 411) was approximately 4.4 ms with sample pressures at 1, 2, and 3 atm; the closing time is not strongly correlated with sample line pressure.

In the two experiments, the isolation valve trigger delay time (relative to the passing of the incident shock) was set to either 20 ms or 900 ms. In the case of the 20-ms trigger delay, the isolation valve in the first sample line (Sample Line 1) is expected to close well after the first 10-ms
sample (Sample 1) is fully extracted from the shock tube, which occurs from ~0.4-9.2 ms after the passing of the reflected shock. This is confirmed by the fact that the pressure in the closed-off isolation volume reached the full expected sample pressure (~22 psi).

With a 20-ms trigger delay, the isolation valve in Sample Line 2 is also expected to close after the second 10-ms sample (Sample 2) is fully extracted from the shock tube (from ~10.4-19.2 ms). In this case, the pressure in the closed-off isolation volume reached a maximum value of ~15 psia. This reduced pressure in the isolation volume indicates that the isolation valve closed before pressure in the sample line had fully equilibrated (even though all of the sample had entered the sample line). This reduced pressure is also confirmation that the first bit of sample to enter the sample line is being successfully separated from the remainder of the collected sample.

Unlike in the first two sample lines, the 20-ms trigger delay causes the isolation valve in Sample Line 3 to close midway through collection of Sample 3, which occurs from ~20.4-29.2 ms (recall that the isolation valve has a closing response time of about 4.4 ms). As a result, the isolation valve is expected to isolate a smaller fraction of sample from the rest of the sampled gas, as compared to Sample Line 1 or 2. Sure enough, the recorded pressure in the isolation volume after valve closure was ~4 psia – more than 10 psia lower than the pressure in the Sample Line 2 isolation volume. This lower pressure simply indicates that less of the first-sampled gas is being separated from the rest of the gas sample.

If mass dilution by unreacted gas was truly the cause of the discrepancy between late-time GC and laser/model results, then changing the isolation valve trigger delay time should have a large impact on the late-time GC sampling results. The early-time, Sample 1 results are likely to remain the same; in both experiments (900-ms vs. 20-ms trigger delay), the Sample Line 1 isolation valves are closed >14 ms after sample extraction has occurred, and both sample lines reach the same ultimate pressure, implying that in both cases, the sampled gas pressure has fully equilibrated within the respective sample lines. However, because the extent of mass diffusion in the line is expected to increase in time, if there was a discernible difference between the two results, the Sample 1 results from the 900-ms trigger delay experiment would be expected to be more dilute than the Sample 1 results from the 20-ms trigger delay experiment, as there was more time for the unreacted gas at the far end of the sample line to diffuse into the bulk of the sample. The Sample 2 and Sample
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3 results are expected to show a more pronounced difference between the two experiments; if the 900-ms trigger delay is ineffective at isolating the unreacted gas from the rest of the sample (the valve trigger is too late), then the result of reducing the trigger delay to 20 ms in both sample lines is to more quickly isolate the unreacted gas, thereby preventing it from mixing with the rest of the sample via diffusion. In short, if unreacted gas, trapped in the dead volume of each sampling plug, was having a large impact on the GC sampling results, we would expect the extent of sample dilution (discrepancy between late-time GC and laser/model results) to decrease with the shorter trigger delay time.

The results from these two experiments (one with a consistent 900-ms delay on each sample line’s isolation valve trigger, the other with a 20-ms delay on each sample line’s isolation valve trigger) are presented in Figure 5.15; both ethane pyrolysis experiments were conducted at 1120 K, 6.7 atm. The close agreement in laser results between the two experiments indicates that the speciation results are expected to be highly repeatable at the same temperature/pressure conditions. This implies that any differences seen between the sampling results are expected to be a direct result of the change in isolation valve trigger timing. As can be seen from the Sample 1-3 results in both experiments, changing the isolation valve trigger timing has very little impact on the GC sampling results, across the board. The two sets of GC sampling results agree with each other, within the uncertainty bounds associated with the measurements (±~5%).

To confirm this phenomenon, two additional experiments were conducted, this time with 25- and 30-ms isolation valve trigger delays, at ~1135 K, 6.8 atm. The results are shown in Figure 5.16. Once again, the GC sampling results agree with each other, within the expected uncertainty bounds, and Sample 2 and 3 results show persistent disagreement with the late-time laser results.

Clearly, isolating more or less unreacted gas from the rest of the sample in each GC fast-sampling experiment does not make up for the large discrepancy seen between late-time GC and laser/model results. This indicates that the discrepancy is most likely caused by something that impacts the entire extracted sample, not just the first few milliliters of it.
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Figure 5.15: Impact of isolation valve trigger timing on GC sampling results: 900-ms and 20-ms isolation valve trigger delay. Nominal test gas mixture and conditions: 1% C2H4/Ar, 1120 K, 6.7 atm.

Figure 5.16: Impact of isolation valve trigger timing on GC sampling results: 25-ms and 30-ms isolation valve trigger delay. Nominal test gas mixture and conditions: 1% C2H4/Ar, 1135 K, 6.8 atm.
5.8.3 Laser and model sensitivity to initial temperature

An important parameter necessary for calculating laser-based mole fraction measurements is gas temperature. As described in Section 2.3.1.1, when time-resolved temperature is not measured directly, it can be inferred from simulations, preferably using a specified-pressure approach, in which the closed, homogeneous reactor pressure is constrained in time by a spline of the measured pressure. In the cyclohexene and ethane pyrolysis experiments described here, model results are obtained using the specified-pressure approach, and the resulting temperature time-histories are used to calculate the laser-based mole fraction measurements. All kinetic simulations require user-provided initial parameters, including initial temperature ($T_{5,\text{init}}$), pressure ($P_{5,\text{init}}$), and mole fraction values. In a shock tube experiment, initial mole fraction values are measured, and initial temperatures and pressures are calculated by solving conservation equations (see Section 2.2.4). In the cyclohexene and ethane pyrolysis experiments presented here, the mean, 1-$\sigma$ uncertainty in initial temperature was found to be $\pm 1.1\%$. Depending on the chemical kinetic system, mole fraction results can be highly sensitive to small changes in initial system temperature. To quantify the sensitivity of the laser and model results to initial temperature (and determine if this sensitivity could be the cause of the discrepancy between the late-time GC and laser/model results), the initial temperature of a representative experiment was perturbed by $\pm 1\%$ and the laser and model results were re-calculated. Figure 5.17 shows the ensuing results.

In Figure 5.17, all of the model results are plotted as dashed lines, while all of the laser results are plotted as solid lines. The original, unperturbed model and laser results are plotted in red and blue, respectively. Model and laser results obtained by perturbing $T_{5,\text{init}}$ by $+1\%$ are plotted in purple, while model and laser results obtained by perturbing $T_{5,\text{init}}$ by $-1\%$ are plotted in gray. Perturbing the initial temperature by $\pm 1\%$ has a noticeable effect on the modeled $C_2H_4$ mole fraction. Increasing $T_{5,\text{init}}$ by 1$\%$ (11.2 K) leads to a relative increase in final $C_2H_4$ mole fraction of 5.8$\%$; decreasing $T_{5,\text{init}}$ by 1$\%$ leads to a relative decrease in final $C_2H_4$ mole fraction of 6.9$\%$. Meanwhile, changing the initial temperature (and thereby changing the time-resolved, modeled temperature) has little impact on the time-resolved laser results; the temperature change of $\pm 1\%$ leads to a $\pm 2\%$ relative change in final, laser-measured $C_2H_4$ mole fraction.
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While decreasing the initial temperature used for the simulations by the uncertainty associated with $T_{5,init}$ serves to bring the model results closer to the laser results at late times, it does not bring the model and GC results into agreement. Likewise, changing the initial temperature by ±1% has little impact on the laser results, and certainly cannot make up the almost 20% difference seen between the late-time laser and GC results. It can therefore be concluded that the discrepancy seen between late-time GC and laser/model results is likely not caused by uncertainty in initial experiment temperature.

5.8.4 Core gas temperature vs. sample effective temperature time-history

After concluding that the late-time discrepancy between GC and laser/model results cannot be explained by error in initial experiment temperature ($T_{5,init}$), a logical next question is: what magnitude of temperature change would be necessary to account for the difference between the late-time GC and laser/model mole fraction results? Put another way, if the gas extracted in the GC samples truly is seeing a different temperature time-history than the gas at the core of the shock
Due to its simple, one-step pyrolysis behavior \((C_6H_{10} \rightarrow C_2H_4 + C_4H_6, \text{see Reaction R5.1, page 88})\), cyclohexene is commonly used as a chemical thermometer to quantify the temperature of reacting systems. As mentioned previously, Stranic et al. [77] measured the rate constant of unimolecular cyclohexene decomposition to be:

\[
 k = A \exp\left(-\frac{E_A}{RT}\right) = 4.84 \times 10^{14} \exp\left(-\frac{31900}{T}\right) \text{[1/s]} \tag{5.1}
\]

The corresponding rate equation for cyclohexene decomposition is:

\[
 \frac{d[C_6H_{10}]}{dt} = -k[C_6H_{10}] \tag{5.5}
\]

By combining and rearranging Equations 5.1 and 5.5, an equation can be written for the average or effective temperature, \(T_{\text{eff},C_6H_{10}}\), between two consecutive GC mole fraction measurements of \(C_6H_{10}\), extracted \(\Delta t\) seconds apart:

\[
 T_{\text{eff},C_6H_{10}} = \frac{-E_A}{R \ln \left[ \frac{-\ln \left( \frac{[C_6H_{10}]_2}{[C_6H_{10}]_1} \right)}{\Delta t} \right]} \tag{5.6}
\]

Knowing that \(X_{C_6H_{10}} = X_{C_6H_{10, initial}} - X_{C_2H_4}\) (Equation 5.2), and similarly, \(X_{C_6H_{10}} = X_{C_6H_{10, initial}} - X_{C_4H_6}\), effective temperatures based on consecutive \(C_2H_4\) and \(C_4H_6\) measurements, \(T_{\text{eff},C_2H_4}\) and \(T_{\text{eff},C_4H_6}\), respectively, can also be calculated. These effective temperatures, based solely on GC measurement results, can be compared to time-resolved model (or measured) temperature results to quantify the difference in temperature time-history experienced by the extracted GC samples vs. the core gas in the shock tube.

Interpretation of the time-resolved laser \(C_2H_4\) measurements allowed for the calculation of three distinct, weighted-average, laser-based \(C_2H_4\) values, for direct comparison with GC measurements in each experiment (see Section 5.5.1). These three weighted-average, \(C_2H_4\) laser results allow for the calculation of an effective laser-based temperature, \(T_{\text{eff,laser}}\), calculated in the same manner as
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described above.

Figure 5.18: Effective temperatures from two shock experiments, calculated using GC and laser measurements, compared with model temperature results (time-resolved and averaged).

Figure 5.18 shows the effective temperature results for two experiments, superimposed on the time-resolved model temperature for the corresponding experiment. Four sets of effective temperature values are shown: effective temperatures derived from each of the three GC-measured species (C\textsubscript{6}H\textsubscript{10}, C\textsubscript{2}H\textsubscript{4}, and C\textsubscript{4}H\textsubscript{6}), and effective temperatures derived from the weighted-average laser results. Additionally, average model temperatures ($T_{\text{model,avg}}$) are plotted to facilitate comparison between the calculated effective temperatures and the simulated model temperature. The effective temperature results are plotted at times corresponding to halfway between the times associated with each sampling event.

There are a number of trends worth noting in Figures 5.18a and b. In both experiments, the system temperature decreases in time; this is expected, as cyclohexene pyrolysis is an endothermic process. Also, because the model results are obtained using a specified-pressure approach, the time-resolved model temperature shows somewhat oscillatory behavior, mirroring the oscillatory pressure measured in the system (see, for example, the pressure in Figure 5.17). (An examination of the impact pressure oscillations have on the model and laser results is included in Appendix E.3.2.) By comparing the average model temperature ($T_{\text{model,avg}}$, or blue open diamonds in plots) to the calculated, effective temperatures, it becomes clear that the effective temperatures derived from GC measurements are consistently lower than the average model temperature, and the difference
increases at later times. Meanwhile, the effective temperatures derived from the weighted-average laser measurements ($T_{\text{eff,laser}}$, or green downward triangles) consistently show close agreement with the average model temperatures at later times. (Keep in mind that the first weighted-average laser measurement is highly sensitive to the timeframe of averaging, as discussed in Section 5.5.2, and as shown previously, the late-time weighted-average laser measurements are relatively insensitive to the timeframe of averaging). In these experiments, the average model temperatures and the effective temperatures derived from laser measurements are thought to represent the temperature time-history at the core of the shock tube. The fact that the modeled and laser-derived temperatures agree for the duration of the experiments confirms that the temperature at the core of the shock tube is not susceptible to late-time heat transfer effects. The disagreement seen between the modeled/laser-effective temperatures and the GC-derived effective temperatures, particularly at later times, reinforces the theory that the gas extracted using the fast-sampling system is seeing a different temperature time-history than the bulk gas in the shock tube.

To more accurately quantify the difference between effective temperatures calculated using GC sampling results and average core gas (model) temperatures, effective temperatures using the three GC-measured species were calculated for all of the cyclohexene pyrolysis experiments. The results can be more easily interpreted by calculating a temperature difference, or $T_{\text{model,avg}} - T_{\text{eff}}$, for each effective temperature at each point in the experiment.

Figure 5.19 shows the difference between average model temperatures and effective temperatures calculated using GC sampling results ($C_6H_{10}$, $C_2H_4$, and $C_4H_6$). Individual experiment results are plotted as open symbols (square for $C_6H_{10}$, circle for $C_2H_4$, triangle for $C_4H_6$), while overall average temperature difference results (calculated for each species) are plotted as closed symbols with connecting lines. The results show that on average, the difference between average model temperatures and GC-derived effective temperatures increases with time in each experiment. Additionally, when averaged across all experiments, the temperature difference results are consistent, regardless of which GC-measured species is used to calculate $T_{\text{eff}}$. On average, the Sample 1 GC results reflect a temperature time-history that is 9.7 K cooler than the expected core gas temperature ($T_{\text{model,avg}}$); the Sample 2 GC results reflect a temperature time-history that is 11.1 K cooler than the core gas temperature; and the Sample 3 GC results reflect a temperature time-history that is 19.8 K
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Figure 5.19: Difference between average, model temperature and effective temperatures calculated using GC-measured C\textsubscript{6}H\textsubscript{10}, C\textsubscript{2}H\textsubscript{4}, and C\textsubscript{4}H\textsubscript{6} mole fraction values. Open symbols represent individual experiments, while closed symbols indicate temperature differences averaged across all experiments. Nominal test gas mixture and initial conditions: 1.4% cyclohexene/Ar, 980-1150 K, 7.3 atm.

cooler than the core gas temperature.

Are these temperature differences statistically significant, or can they be accounted for by considering experimental uncertainty? The four primary sources of uncertainty affecting the \(T_{\text{model,avg}} - T_{\text{eff}}\) results include uncertainty in: initial fuel loading ([C\textsubscript{6}H\textsubscript{10}]\_\text{initial} \pm 2.3\%), GC mole fraction measurement (\(X_{\text{C}_6\text{H}_{10}}, X_{\text{C}_2\text{H}_4}, X_{\text{C}_4\text{H}_6} \pm 5\%\)), reaction rate (A-factor \(\pm 21\%\) [77]), and initial \(T_5\) (\(\pm 1.1\%\)). The impact of perturbing these parameters by their respective uncertainties on the resulting difference between average-model and effective temperature results (specifically those calculated using the GC-measured C\textsubscript{2}H\textsubscript{4} mole fractions) is shown in Figure 5.20. This uncertainty analysis has also been carried out considering the \(T_{\text{eff}}\) values calculated using GC-measured C\textsubscript{6}H\textsubscript{10} and C\textsubscript{4}H\textsubscript{6} mole fractions and the resulting plots are provided in Appendix E.4.1; the results show the same trends seen in Figure 5.20.

Figure 5.20a shows how the various parameter uncertainties impact the first \(T_{\text{model,avg}} - T_{\text{eff}}\) point (as seen in Figure 5.19), Figure 5.20b shows how the various parameter uncertainties impact the second point, and Figure 5.20c shows how the various parameter uncertainties impact the third
Figure 5.20: Impact of various parameters on $T_{\text{model,avg}} - T_{\text{eff}}$, for each of the three samples. For simplicity, only the results obtained using C$_2$H$_4$ GC measurements are presented. Red bars are the nominal $T_{\text{model,avg}} - T_{\text{eff}}$ values. Blue bars are the values obtained when parameters are decreased by their respective uncertainties; yellow bars are the values obtained when parameters are increased by their respective uncertainties. Results averaged over 12 cyclohexene pyrolysis experiments. Nominal test gas mixture and initial conditions: 1.4% cyclohexene/Ar, 980-1150 K, 7.3 atm.
point. The red bars represent the nominal $T_{model,avg} - T_{eff}$ values, calculated by averaging $T_{model,avg} - T_{eff}$ across all of the cyclohexene pyrolysis experiments (i.e., the points denoted by solid, blue markers in Figure 5.19). The blue bars represent the $T_{model,avg} - T_{eff}$ values obtained when each parameter is decreased by its respective uncertainty. Likewise, the yellow bars represent the $T_{model,avg} - T_{eff}$ values obtained when each parameter is increased by its respective uncertainty. In effect, the difference in magnitude between the blue and red bars, and the yellow and red bars, indicates how strongly the difference $T_{model,avg} - T_{eff}$ is impacted by the uncertainty of a given parameter.

Across all three points, the difference $T_{model,avg} - T_{eff}$ is most sensitive to initial $T_5$ value. Perturbing $T_{5,init}$ does not directly impact the calculation of $T_{eff}$, but the calculation of $T_{model,avg}$ (see, for example, Section 5.8.3). The uncertainty in reaction rate A-factor has the second largest impact on the $T_{model,avg} - T_{eff}$ difference, followed by uncertainty in GC mole fraction measurement and initial $C_6H_{10}$ fuel loading. Individually, these sources of uncertainty cannot fully account for the difference seen between average model temperatures and GC-derived effective temperatures (when parameters are perturbed by their uncertainty values, $T_{model,avg} - T_{eff}$ never reaches zero). However, the root-sum-square of these individual uncertainties provides more realistic overall uncertainty bounds for the $T_{model,avg} - T_{eff}$ average results.

Figure 5.21: Mean difference between average, model temperature and effective temperatures calculated using GC-measured $C_2H_4$ mole fraction values, averaged across all experiments. Nominal test gas mixture and initial conditions: 1.4% cyclohexene/Ar, 980-1150 K, 7.3 atm.
Figure 5.21 shows the temperature differences, $T_{\text{model,avg}} - T_{\text{eff,C}_2\text{H}_4}$, calculated using the three $\text{C}_2\text{H}_4$ GC measurements conducted in each experiment, averaged across all experiments (the same as presented in Figure 5.19), this time including associated overall uncertainty bars. It is apparent that the early-time $T_{\text{model,avg}} - T_{\text{eff,C}_2\text{H}_4}$ difference (the first point) can almost entirely be accounted for by taking into account the sources of uncertainty impacting $T_{\text{model,avg}}$ and $T_{\text{eff}}$. The late-time $T_{\text{model,avg}} - T_{\text{eff,C}_2\text{H}_4}$ differences, however, far exceed the uncertainty bounds associated with those differences; these late-time differences in temperature are real, not an artifact of experimental uncertainty.

Overall, the temperature history experienced by gas extracted using the fast-sampling system and the temperature history of gas at the core of the shock tube are similar at early times, but differ by up to 20 K at late times. This indicates that whatever is causing the difference in temperature time-history impacts the GC samples more significantly at late times than at early times. Additionally, the temperature difference causing the discrepancy in late-time GC and laser/model mole fraction results is actually quite small – on the order of 2% of the initial experiment temperature. (For perspective, if an isentropic expansion process was assumed to occur at these conditions ($\sim 1000$ K, 7 atm, $\gamma = \sim 1.5$), this 20 K drop would correspond to a pressure drop of 5.8%, or $\sim 0.4$ atm.)

The next step in the troubleshooting process is to identify factors that could be responsible for minimal temperature deviation at early times, but a $\sim 20$ K temperature difference at late times. One such factor is the endwall thermal boundary layer, which will be discussed in the following section.

### 5.8.5 Endwall thermal boundary layer calculation

Thermal boundary layer growth in shock tubes, particularly along the sidewall, is an area of research that has garnered a lot of attention, as sidewall thermal boundary layer growth can lead to non-ideal shock bifurcation and hot spots in what would otherwise be considered a near-homogeneous experiment [9, 13, 84–90]. Thermal boundary layer growth from the shock tube endwall has been most commonly explored in the context of TOF-MS continuous sampling experiments in single-pulse shock tubes [34, 91–99]. In this work, the endwall thermal boundary layer is of particular interest, as its effect on the gas adjacent to the shock tube endwall could adversely affect the fast-sampled GC results. To quantify the potential impact of endwall thermal boundary
layer growth on the GC sampling results, particularly at late times, the thermal boundary layer thickness was calculated in time, and the temperature within the thermal boundary layer was calculated as a function of time and distance from the endwall. The analytical expressions and final results for each are presented here. More formal derivations of both the penetration depth and temperature distribution calculations are presented in Appendix F.

The endwall thermal boundary layer problem can be considered a one-dimensional (i.e., temperature varies in one spatial dimension), semi-infinite (i.e., the gas is bounded at one end, but extends to infinity at the other), transient conduction problem. Energy is transferred from the hot gas at $T_5(t)$ in the shock tube to the cold endwall adjacent to the gas. The gas temperature $T(x,t)$, where $x$ is distance from the shock tube endwall and $t$ is time, can be calculated according to:

$$T(x,t) = T_{EW} + (T_5(t) - T_{EW}) \text{erf} \left( \frac{x}{2\sqrt{\alpha(t)t}} \right)$$  \hspace{1cm} (5.7)

Here, $T_{EW}$ is the temperature at the endwall, assumed to be constant at 298 K temperature (conduction through the endwall material is neglected for simplicity), $T_5(t)$ is the post-reflected-shock gas temperature, which, in the case of the pyrolysis experiments being modeled here, changes in time as fuel pyrolysis progresses, and $\alpha(t)$ is the thermal diffusivity of the gas, defined as:

$$\alpha(t) = \frac{k(t)}{\rho(t)c(t)}$$  \hspace{1cm} (5.8)

where $k(t)$ is the thermal conductivity of the gas, $\rho(t)$ is the gas density, and $c(t)$ is the specific heat capacity of the gas; all three parameters are assumed to change in time, consistent with the changing composition and temperature of the test gas.

Equation 5.7 can be used to visualize the penetration depth of the endwall thermal boundary layer in time. Figure 5.22 shows the expected thermal boundary layer growth into a 1% ethane/argon mixture, initially at 1100 K, 7 atm, at four distinct times after time zero (10, 20, 30, and 40 ms). Here, the thermal boundary layer growth does take into account the changing temperature and composition of the reacting gas at the core of the shock tube. The properties of the test gas in the shock
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tube are simulated in time using a modified FFCM-1 kinetic model [81] (see Section 5.2.2), assuming constant-pressure/enthalpy. The thermal boundary layer calculation does not take into account the slight change in temperature time-history seen at different axial locations along the shock tube; over the distances relevant to the thermal boundary layer, this effect is assumed to be negligible.

Figure 5.22: Endwall thermal boundary layer visualization at 10, 20, 30, and 40 ms after time zero. Nominal test gas mixture and initial conditions: 1% C\textsubscript{2}H\textsubscript{6}/Ar, 1100 K, 7 atm.

Figure 5.22 shows that the endwall thermal boundary layer growth can be thought of almost as a thermal wave moving through the high-temperature gas in the shock tube; as time progresses, the penetration depth of this thermal wave into the high-temperature gas increases. By the time 40 ms has elapsed, the thermal wave has reached a distance of almost 4 mm off the shock tube endwall.

The thickness of the thermal boundary layer can be calculated at a given point in time as the distance at which $T(x, t) = 0.99 \times T_5(t)$. Using this metric, the thermal boundary layer thickness as a function of time can be determined, as seen in Figure 5.23.

The results shown in Figure 5.23 indicate that for the duration of each GC fast-sampling shock tube experiment (0-∼30 ms), the maximum thermal boundary layer thickness is expected to be less than 3.5 mm. The following sections will discuss the impact that sampling from different distances off the endwall has on the GC sampling results, as well as a discussion of the thermal cooling experienced by gas samples pulled through the endwall boundary layer.
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Figure 5.23: Endwall thermal boundary layer (TBL) thickness as a function of time. Nominal test gas mixture and initial conditions: 1% C\textsubscript{2}H\textsubscript{6}/Ar, 1100 K, 7 atm. Gray region indicates the range of TBL thicknesses for initial temperatures 1100 K\textpm5% (the range of temperatures explored in the 1% C\textsubscript{2}H\textsubscript{6}/Ar pyrolysis experiments).

5.8.6 Impact of probe length on sampled results

Experiments were conducted to determine if the length of the probe protruding out of the endwall has an impact on the fast-sampled GC results; if a sample could be extracted from entirely outside of the endwall thermal boundary layer, would the discrepancy between late-time GC and laser/model results go away? In the previous section, it was shown that the endwall thermal boundary layer thickness is expected to grow to approximately 3.5 mm within the experimental test time. Additionally, as described in Section 5.3.2, segments of 1/8-inch outer-diameter tube are used to offset the location of sample extraction from the shock tube endwall by 3.5 mm. While these sampling probes should extend sufficiently far off the endwall to allow for sample collection from outside the thermal boundary layer, additional probes were made to enable sample extraction from distances of 7, 12.5, and 18 mm off the shock tube endwall. By collecting samples from locations further into the shock tube than 3.5 mm, it could be confirmed that each sample was being collected from completely outside the endwall thermal boundary layer. Cylohexene pyrolysis experiments were repeated at approximately the same conditions (1110 K, 7.3 atm), with different probe lengths used.
each time. The time-resolved laser and GC sampling results are shown in Figure 5.24.

![Figure 5.24: Impact of probe length on GC sampling results. Laser and GC sampling measurements recorded in corresponding experiments are plotted in the same color. Nominal test gas mixture and initial conditions: 1.5% cyclohexene/Ar, 1110 K, 7.3 atm.](image)

As can be seen in Figure 5.24, the laser measurements are nearly identical, confirming the repeatability of the experiments, and the GC measurements largely agree within their uncertainty bounds ($\pm \sim 5\%$); the late-time discrepancy between GC and laser results persists, regardless of the probe length used to extract the GC samples. This is an interesting observation, as it implies that the discrepancy in late-time measurements cannot be resolved by sampling from deeper in the shock tube. However, the 1/8-inch probes protruding into the reacting flow could, themselves, be generating secondary boundary layers in their immediate vicinity.

To determine whether or not the protrusions are negatively impacting the GC sampling results, either through secondary boundary layer formation or other flow disruption means, additional experiments were carried out, comparing GC samples extracted with a 5-mm protrusion off the surface of the endwall, and GC samples extracted using no protrusion. Ethane pyrolysis experiments were repeated at approximately the same conditions (1120-1139 K, 6.8 atm), and the protrusion/no protrusion effect was investigated; the results are presented in Figure 5.25.
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Figure 5.25: 5-mm probe vs. no probe impact on GC sampling results. Laser and GC sampling measurements recorded in corresponding experiments are plotted in the same color. Laser measurements are solid lines, GC measurements are plotted as symbols with connecting lines. Nominal test gas mixture and initial conditions: 1% ethane/Ar, 1120-1139 K, 6.8 atm.

Two pyrolysis experiments were conducted with 5-mm protrusions, and three pyrolysis experiments were conducted with no protrusions. Once again, the time-resolved laser measurements provide an indication of the expected trends in GC measurement results: based on temperature/pressure conditions, the 5-mm probe C₂H₄ mole fraction results (black lines/symbols) are expected to fall in the middle of the no-probe C₂H₄ mole fraction results (colored lines/symbols). As can be seen in Figure 5.25, the first and second GC sampling results trend as expected: the 5-mm probe C₂H₄ results fall in the middle of the no-probe results, mirroring the laser measurements. The third GC sampling results, however, deviate from the expected trend. The two late-time, 5-mm probe C₂H₄ measurements (circled on the plot) are expected to fall between the no-probe measurements, but both are more than 5% lower than where they are expected to be, given the trend seen in the 0-mm probe GC results (error bars indicate ~5% uncertainty). This deviation does not appear to be a statistical anomaly – both experiments with 5-mm probes show third-sample results that fall below where they are expected to be, when compared to the other GC measurements and the corresponding laser results.

So, even though changing the length of the probe protruding into the shock tube does not seem
to have an impact on late-time GC sampling results (Figure 5.24), removing probes altogether and sampling directly from the endwall does appear to improve (increase) the GC mole fraction measurements and reduce the discrepancy seen between late-time GC and laser results. This is likely due to the fact that removing the probes also removes any probe-related flow disturbances (secondary boundary layers, etc.). Nevertheless, the GC sampling experiments conducted without probes still show significant, even if reduced, disagreement between laser and GC results. Removing the probes from the experiments helps to simplify the troubleshooting process and conceptualize the problem, as it is now known that the discrepancy persists even in the absence of probes protruding into the reacting flow. With this simplification in mind, the final two installments of this troubleshooting saga address the impact that the endwall thermal boundary layer has on reacting gas being sampled from the endwall in the absence of a protrusion.

5.8.7 Impact of thermal boundary layer on sampled mole fraction results

A simple model was developed to simulate the impact of thermal boundary layer growth on the composition of time-integrated samples collected from a 1% C$_2$H$_6$/Ar pyrolysis experiment at 1100 K, 7 atm. The simple model consists of the superposition of three concepts: (1) the endwall thermal boundary layer grows in time, (2) the composition and temperature of the reacting bulk gas change in time (consistent with a constant-pressure, constant-enthalpy kinetic simulation), and (3) the volume of gas sampled from the shock tube grows as a hemisphere with radius $r(t)$ for the duration of each sampling event. The assumptions made in this analysis will be discussed first, followed by a discussion of the simulated results.

First, the endwall thermal boundary layer is modeled as a 1-D, transient conduction process, wherein the gas within the shock tube is treated as semi-infinite. Chemistry is accounted for, as described in Section 5.8.5. This analysis assumes velocity of the gas within the thermal boundary layer is negligible (mass diffusion is neglected).

Next, the sampled volume in time, $V(t)$, is assumed to be proportional to the pressure rise in the sample line, $P(t)$, i.e., $V(t)/V_{total} = P(t)/P_{max}$. Here, $V_{total}$ is the total extracted volume from within the shock tube at 1100 K, 7 atm, estimated from the known sample line volume ($\sim$8 mL) at 60°C and 24 psia, assuming constant composition and conservation of mass. (For example, for
an 8.7-mL sample residing in Sample Line 1 at 60°C, 24 psia, the equivalent volume inside the shock tube at 1100 K, 7 atm would be 6.7 mL). The in-line sample pressure, measured using a piezoelectric transducer as described in Section 5.5.1 and shown in Figure 5.8 (pg. 100), can be used to calculate the total sample volume extracted from within the shock tube as a function of time. The time-resolved, normalized sample volume corresponding to the same experiment seen in Figure 5.8 is shown in Figure 5.26. The $V(t)/V_{total}$ behavior seen in Figure 5.26 mirrors the behavior seen in the in-line pressure traces: 90% of the sample is collected in the first 6 ms, with only a slight increase in sample collection volume occurring over the last $\sim$3 ms.

The volume extracted from the shock tube is modeled as a hemisphere with growing radius $r(t)$, where $V(t) = \frac{2}{3} \pi r(t)^3$. A depiction of the hemisphere size at three different times – 1, 5, and 9 ms into a given sampling event – can be found in Figure 5.27. In this model, the sampling location is approximated as a point at (0,0), on the endwall along the centerline of the shock tube.

Finally, in this simple model, it is assumed that the thermal boundary layer growth and the sample extraction flow are independent of each other, i.e., the two processes can be superimposed on one another.

The radii of the sampled-gas hemispheres (samples 1-3) are plotted vs. time in Figure 5.28, alongside the expected thermal boundary layer thickness, for a 1% C$_2$H$_6$/Ar experiment at 1100 K,
Figure 5.27: Sampled-gas hemisphere growth in time, at 1, 5, and 9 ms after sample initiation.

Figure 5.28: Endwall thermal boundary layer thickness and sampled-gas hemisphere radius as a function of time. Nominal test gas mixture and initial conditions: 1% ethane/Ar, 1100 K, 7 atm.
7 atm. From this figure, it is clear that, as expected, the thermal boundary layer will have the largest impact on the third-extracted sample, as it represents a larger fraction of the sampling hemisphere radius.

The question is now: how do these three phenomena (boundary layer growth, reacting gas chemistry, and expanding sample volume) come together to impact the overall sampling results? To answer this question, it is necessary to first understand how the growing thermal boundary layer impacts the composition (not just temperature!) of the reacting gas as a function of distance from the endwall. It is useful to first visualize the growing boundary layer by tracking the temperature in time along a fixed axial location. See, for example, Figure 5.29, where the temperature time-histories at 14 distinct axial locations (relative to the shock tube endwall) are tracked in time.

![Figure 5.29: Temperature time-histories at different axial distances from the shock tube endwall. Nominal test gas mixture and initial conditions: 1% ethane/Ar, 1100 K, 7 atm.](image)

At distances farthest out from the endwall (e.g., 3.5 mm), the temperature history follows that of the bulk gas (HP simulation) – the temperature decreases slightly due to endothermic pyrolysis and is minimally impacted by the growing thermal boundary layer. At distances very close to the endwall (e.g., 0.25 mm), however, the thermal boundary layer very quickly causes the temperature of the gas at those axial locations to drop.
Because the post-reflected-shock (Region 5) gas in the shock tube is nominally stagnant (un-moving), it is possible to use the temperature time-history known at each axial location to numerically solve for the gas composition time-history at that same axial location. This is achieved using a brute-force approach, wherein a distinct kinetic simulation is run for each axial position; instead of running a constant-enthalpy/pressure (constant-HP) simulation (as is used to describe the bulk gas chemistry), the simulation at each axial position is constrained using the pre-determined temperature time-history calculated at that position (i.e., the traces depicted in Figure 5.29) and constant pressure.

![Figure 5.30](image)

**Figure 5.30:** \( \text{C}_2\text{H}_4 \) mole fraction time-histories at different axial distances from the shock tube endwall. Nominal test gas mixture and initial conditions: 1% ethane/Ar, 1100 K, 7 atm.

Figure 5.30 shows the simulated \( \text{C}_2\text{H}_4 \) mole fraction results at the same 14 axial positions depicted in Figure 5.29 (0.25-3.5 mm from the shock tube endwall). As expected, at distances far from the endwall (e.g., 3.5 mm), the \( \text{C}_2\text{H}_4 \) formation resembles that seen in the bulk gas (HP simulation); closer to the endwall, very little \( \text{C}_2\text{H}_4 \) is formed, as the early temperature drop caused by the thermal boundary layer does not allow for appreciable \( \text{C}_2\text{H}_6 \) decomposition.

It is useful to visualize the position- and time-dependent \( \text{C}_2\text{H}_4 \) mole fraction distribution within the shock tube at different times using 2-D contour plots, as seen in Figure 5.31. As the experiment
progresses, the presence of C$_2$H$_4$ in the bulk gas increases, due to pyrolysis of C$_2$H$_6$. Simultaneously, the growing thermal boundary layer (the thickness of which is denoted by a dashed black line, and where $T(x,t) = 0.99 * T_5(t)$) causes a growing C$_2$H$_4$ mole fraction gradient in the region closest to the endwall; as the experiment progresses, the thickness of this cooler-gas region grows.

Figure 5.31: Contour plots of C$_2$H$_4$ mole fraction in the shock tube 10, 20, and 30 ms after time zero. Black dashed line shows the corresponding thermal boundary layer thickness. Nominal test gas mixture and initial conditions: 1% C$_2$H$_6$/Ar, 1100 K, 7 atm.

The impact the growing boundary layer has on the composition of the total extracted volume can be quantified numerically by treating each sampling event as a summation of differential volume increases. For example, in the first time step, the differential volume, $dV(t_1)$, extracted from the shock tube resembles a hemisphere of radius $r(t_1)$; $t_i$ ranges from $t_i=0$ (sample initiation) to $t_i=n$ (sample completion). In each subsequent timestep ($t_{i=2...n}$), the differential volume extracted from the shock tube ($dV(t_i)$) resembles a hemisphere shell of thickness $r_{t_i} - r_{t_{i-1}}$ (see the graphical depiction in Figure 5.32).

Over the course of a 10-ms sample, the composition of the gas in each differential volume changes quite a bit, and not just because the core gas composition is changing due to pyrolysis; as the thermal boundary layer grows, the fraction of each differential volume that is made up of cooler, boundary layer gas increases as well. For example, Figure 5.33 shows how the composition of the differential hemisphere shells can change over the course of Sample 3 in an experiment.

To calculate the total C$_2$H$_4$ mole fraction in each differential volume, a Riemann sum approach
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Figure 5.32: 2-D representation of differential hemisphere shells

Figure 5.33: Contour plots of $C_2H_4$ mole fraction with hemisphere shells superimposed to show the composition of differential volumes at three times during the third sampling event: 21 ms, 23.5 ms, and 26 ms after time zero. Black dashed line shows the corresponding thermal boundary layer thickness. Shell thicknesses are exaggerated for the sake of visualization. Nominal test gas mixture and initial conditions: 1% $C_2H_6$/Ar, 1100 K, 7 atm.
is used, in which each hemisphere shell is broken into discrete discs (rings) of thickness \( dx \), where \( x \) ranges from 0 to \( r(t) \) and \( dx \) is 0.005 mm. The inner radius of each hemisphere shell is defined as \( r_{t-1}^2 - x^2 \), and the outer radius is defined as \( r_t^2 - x^2 \), where \( x \) is the distance from the shock tube endwall. A visual representation of this geometry is shown in Figure 5.34.

![Figure 5.34: Breakdown of differential hemisphere shells into rings of thickness \( dx \)](image)

The total volume of each differential hemisphere shell can be found by summing the volume contained in all of its constituent rings. Furthermore, the \( \text{C}_2\text{H}_4 \) mole fraction in each ring can be calculated through knowledge of \( \text{C}_2\text{H}_4 \) mole fraction as a function of axial location in the shock tube (as demonstrated in Figure 5.30); the differential thickness \( dx \) is assumed to be small enough that the \( \text{C}_2\text{H}_4 \) mole fraction in each ring is constant. With the \( \text{C}_2\text{H}_4 \) mole fraction of each individual ring known, the overall \( \text{C}_2\text{H}_4 \) mole fraction composition of a given, differential hemisphere shell volume, \( dV(t_i) \), can also be calculated.

Figure 5.35 shows the simulated \( \text{C}_2\text{H}_4 \) mole fraction composition of differential (hemisphere shell) sample volumes, plotted alongside simulated core gas \( \text{C}_2\text{H}_4 \) composition; the blue curve represents the constant-HP simulation \( \text{C}_2\text{H}_4 \) results, used to model the reacting core gas in the shock tube, and each red curve represents the instantaneous \( \text{C}_2\text{H}_4 \) mole fraction of each differential hemisphere shell volume for the three sampling events. This figure is particularly striking. Over the course of the simulated Sample 1 extraction, the \( \text{C}_2\text{H}_4 \) mole fraction in each differential hemisphere
Figure 5.35: Simulated C\textsubscript{2}H\textsubscript{4} mole fraction composition of differential sample volumes, plotted alongside simulated core gas C\textsubscript{2}H\textsubscript{4} composition. Nominal test gas mixture and initial conditions: 1\% C\textsubscript{2}H\textsubscript{6}/Ar, 1100 K, 7 atm.

shell closely mirrors the composition of the core shock tube gas. Over the first 5 ms, the results show very close agreement, reaching a maximum relative difference of 8.8\% at 5 ms; between 5 and 10 ms, the composition of the differential volumes and that of the core gas begin to diverge, reaching a relative difference of 10.8\% at 10 ms.

In both Sample 2 and Sample 3, the composition of the initial differential volumes pulled from the shock tube contain very little C\textsubscript{2}H\textsubscript{4}, as sample is initially pulled exclusively from within the thermal boundary layer. Once the sampled-gas hemisphere breaks through the boundary layer, however, the composition of the differential sample volumes begins to more closely match the composition of the core gas. Even so, the composition of the differential sample volumes never reaches the true core gas value, as cooler, boundary layer gas continues to be pulled in as well. In Sample 2, the maximum relative difference between differential-volume C\textsubscript{2}H\textsubscript{4} mole fraction and core-gas C\textsubscript{2}H\textsubscript{4} mole fraction is 14.9\% (at 20 ms). In Sample 3, the maximum relative difference between differential-volume C\textsubscript{2}H\textsubscript{4} mole fraction and core-gas C\textsubscript{2}H\textsubscript{4} mole fraction is 17.2\% (at 30 ms).
Figure 5.36: Simulated, average C\textsubscript{2}H\textsubscript{4} mole fraction composition of extracted gas samples, plotted alongside simulated core gas C\textsubscript{2}H\textsubscript{4} composition. Nominal test gas mixture and initial conditions: 1\% C\textsubscript{2}H\textsubscript{6}/Ar, 1100 K, 7 atm.

The time-resolved differential-volume compositions shown in Figure 5.35 can be used to simulate a single, average C\textsubscript{2}H\textsubscript{4} mole fraction value for each sampling event, similar to what is recorded experimentally in each fast-sampling shock experiment. The overall, average C\textsubscript{2}H\textsubscript{4} mole fraction results are plotted in Figure 5.36, alongside the constant-HP simulation of 1\% C\textsubscript{2}H\textsubscript{6}/Ar pyrolysis at 1100 K, 7 atm; the three simulated-average sampling results are plotted at the halfway point of each simulated sampling event. The simulated results show a close resemblance to the trends seen in the experimental sampling results (e.g., Figure 5.11), particularly at late times. By accounting for the impact the composition of the cold, boundary layer gas has on the overall composition of each sample, the late-time discrepancy between sampled GC results and model results can be replicated.

These findings indicate that the discrepancy between late-time GC and laser/model results is likely predominantly due to the growing thermal boundary layer and the cooler gas residing next to the endwall being pulled into the sample line. This observation would suggest that the GC fast-sampling system, in its current iteration, is not well suited to accurately measure species concentrations at late times in shock tube experiments, when the thermal boundary layer is thickest. At the same time, the simulated results show that the fast-sampling diagnostic can be used effectively
at early times when the endwall boundary layer is thin enough to not significantly dilute the sampled gas.

5.8.8 Summary of troubleshooting results

A number of troubleshooting experiments and simulations were carried out to determine what causes the discrepancy in late-time GC sampling results and laser/model results, seen in the cyclohexene and ethane pyrolysis experiments presented in Section 5.7. Carbon/hydrogen accounting showed that the GC sampling results were self-consistent – the discrepancy is not due to sample dilution by an outside gas (e.g., air). The effectiveness of the isolation volume built into each sample line was also explored. Changing the isolation valve timing did not appear to significantly change the GC sampling results, suggesting that dilution by unreacted, dead-volume gas is not causing the discrepancy between GC and laser/model results. Next, the sensitivity of the laser and model results to initial temperature was investigated. Perturbing the initial temperature of the experiments by the associated uncertainty was seen to change the model and laser results slightly, but the change was not large enough to account for the discrepancy with GC results. Next, cyclohexene pyrolysis experiments were revisited, using cyclohexene as a chemical thermometer to determine the effective average temperature of the GC sampling results. This analysis showed that a temperature change of \( \sim 20 \) K could account for the difference between late-time GC and laser/model results.

To better understand the temperature history at different locations within the shock tube, the endwall thermal boundary layer growth was modeled as a 1-D, transient process. In the ethane pyrolysis experiments, the endwall thermal boundary layer is expected to reach a maximum thickness of approximately 3.5 mm in the relevant test time. Multiple probes were used to extract GC samples from the shock tube at three different depths known to be outside of the thermal boundary layer. Changing the probe lengths had minimal effect on the resulting GC measurements. However, it was noticed that removing the probes altogether and sampling directly from the endwall seemed to improve the agreement between late-time GC and laser/model results.

Finally, a simple model was developed to simulate the growing thermal boundary layer’s impact on the composition of each GC sample. By modeling each sampling event as a hemisphere growing in time, and analyzing the composition of each differential volume change, it was found that the
same relative magnitude difference seen between late-time GC and laser/model results could be simulated. It was therefore concluded that the difference between late-time GC and laser/model results is predominantly caused by the endwall thermal boundary layer having an outsize impact on sample results at late times, when the boundary layer is thickest.

If the late-time discrepancy between GC and laser/model results is predominantly caused by the thickness of the endwall thermal boundary layer, then it is worth noting that there are a number of experimental changes that could be made to slow the thermal boundary layer growth, thereby mitigating the impact the thermal boundary layer has on GC sampling results. As shown in Equation F.10, the thickness of the thermal boundary layer is proportional to the square root of \( \alpha \), the thermal diffusivity of the gas mixture; \( \alpha \), in turn, is directly proportional to thermal conductivity, \( k \), and inversely proportional to pressure and specific heat capacity, \( c \) (Equation 5.8). Therefore, to minimize the thermal boundary layer thickness, experiments should be conducted at high pressures, in a bath gas with low thermal conductivity and high specific heat (i.e., the ratio of thermal conductivity-to-specific heat should be minimized). The sampling experiments described in this work were conducted in a bath gas of argon \((k/c(298 \text{ K}, 1 \text{ atm}) = 0.00085 \text{ mol/m-s})\). However, a lower-conductivity (higher-specific-heat) bath gas such as krypton or xenon \((k/c(298 \text{ K}, 1 \text{ atm}) = 0.00045 \text{ mol/m-s} \text{ and } 0.00026 \text{ mol/m-s}, \text{ respectively})\) could be used in place of argon to retard thermal boundary layer growth. While replacing the argon bath gas with krypton or xenon is theoretically possible, it is not necessarily practical, considering the volume of gas required and the associated cost. However, operating at higher pressures is a realistic option, and one that will be discussed as an avenue of potential future work (Section 8.2.1).

5.9 Conclusions

A GC fast-sampling system was developed for broad speciation in extended test-time shock tube experiments. Combined with a 10.532-\( \mu \text{m} \) laser absorption diagnostic, the sampling system was used to measure ethylene production in two pyrolysis systems: 1.4% cyclohexene in argon, from 980-1150 K, at approximately 7.3 atm, and the pyrolysis of 1.0% ethane in argon, from 1060-1153 K, at approximately 6.9 atm. Experiment and kinetic simulation results were presented, and a
method for calculating weighted-average laser measurements for comparison to GC measurements was described. Ethylene mole fraction values measured over the first \( \sim 11 \) ms of each experiment show close agreement between the GC, laser, and model results; mole fractions measured after the first 11 ms show a larger discrepancy. A number of troubleshooting experiments and calculations were carried out to determine the source of the discrepancy. Simulated results show that the difference in late-time GC and laser/model results is primarily due to the growing endwall thermal boundary layer.

These fast-sampling shock tube experiments are the first of their kind, and the results highlight the value of a speciation system that combines complementary time-resolved sampling and laser absorption diagnostics: together, these time-resolved species diagnostics have the potential to provide more complete datasets to characterize reacting systems and aid in kinetic model development. These experiments brought to light a particular shortcoming of the current approach: samples extracted at late times are prone to significant dilution by cold, endwall boundary layer gas. However, the results also show that this approach is feasible and can be successfully used to collect broad speciation data in shock tube experiments at times <5 ms.
Part II

Laminar Flame Speed Measurements in a Shock Tube
Chapter 6

High-temperature laminar flame speed measurements in a shock tube

*The contents of this chapter have been published in the journal *Combustion and Flame* [100].*

6.1 Introduction and background

Laminar flame speed has long been regarded as an important, fundamental property of a fuel/oxidizer mixture due to its use in kinetic model development and its correlation with flame-stability behavior (e.g., flashback, blowoff, and extinction). As such, an extensive collection of premixed flame speed measurements can be found in the literature for a wide variety of fuels at various equivalence ratio, temperature, and pressure conditions, using a number of different experimental apparatuses [7].

Modern, state-of-the-art premixed flame speed experiments typically involve one of four experimental approaches: constant-volume/constant-pressure spherically expanding flames [101, 102], counterflow or stagnation flames [103, 104], burner-stabilized flames (heat flux method) [105], or planar flames obtained using the diverging channel method [106]. Laminar flame speeds measured using these methods are consistently reported with measurement uncertainties of less than 5%
6.1. INTRODUCTION AND BACKGROUND

The advantages and disadvantages of each approach are discussed at length by Egolfopoulos et al. [107], and further examined by Konnov et al. [7]. However, the strengths and intended measurement regimes associated with each method will be briefly reiterated here.

Spherically expanding flame experiments are well suited for a broad range of pressure conditions: \(~0.2 \text{ atm} \rightarrow \sim 10 \text{ atm}\). In fact, spherically expanding flames have proven to be the only reliable flame configuration for high-pressure flame speed measurements, primarily because these experiments are conducted in static reactors and are therefore immune to the high-pressure flow turbulence inherent in flow-based flame speed experiments. Development of a dual-chamber apparatus by Tse et al. [108], in particular, has allowed for the measurement of flame speeds derived from spherically expanding flames at initial pressures in excess of 60 atm.

Stagnation flames, burner-stabilized flames, and flames formed using the diverging channel method are commonly used to obtain flame speed measurements between 0.2 atm and \(~10 \text{ atm}\). While it is difficult to stabilize stagnation flames and diverging-channel flames at pressures below 0.2 atm, burner-stabilized flames are reliably stable and used to measure laminar flame speeds at these low-pressure conditions.

Despite the broad pressure range covered by flame speed results currently available in the literature, certain high-temperature experimental regimes remain difficult to access through use of traditional flame speed measurement methods. For example, it has been noted that very little experimental flame speed data exists above 500 K [7]. Nevertheless, a number of different approaches are currently used to obtain flame speed data at temperatures in excess of 500 K. Metghalchi et al. [109] were the first to record the pressure rise in a constant-volume chamber and apply an isentropic assumption to the pressure and temperature increase experienced by the unburned gas. By starting at initial unburned gas conditions of 500 K and 7.6 atm, conditions up to 40 atm and 700 K could be reached. However, this approach, which is still in use today [110], is limited by the fact that the high-temperature conditions are only accessible at high pressures, due to the isentropic coupling of temperature and pressure; temperature and pressure cannot be varied independently.

A second approach, commonly used in diverging channel experiments to obtain high-temperature flame speed results, is to use a porous burner, external to the channel, to preheat the fuel/oxidizer mixture. Using this strategy, flame speed measurements could be conducted
at unburned gas temperatures up to 650 K [106, 111, 112]. It should be noted that Zhao et al. also obtained flame speed measurements at unburned gas temperatures of 650 K using the wall stagnation method with the addition of inline heaters and heating tapes [113].

A final technique commonly used to obtain high-temperature flame speed estimates is to use a temperature exponent, derived from flame speed measurements conducted at lower temperatures, to extrapolate to higher temperatures. This technique is based on the correlation between initial temperature and flame speed (initially reported by Dugger [114]), described by

\[ S_u = S_{u,ref}(T_u/T_{u,ref})^\alpha, \]

where \( S_{u,ref} \) is the flame speed at the reference temperature, \( T_{u,ref} \), and \( \alpha \) is the empirically derived temperature exponent. In contrast to the other two high-temperature approaches outlined here, this method does not involve direct measurement of the laminar flame speed.

While high-temperature flame speed experiments are of practical importance for the development of reliable kinetic models and the design of next-generation internal combustion and jet engines, so too are flame speed experiments aimed at characterizing large molecular weight fuels. Flame experiments intended to study heavy fuels are often complicated by the fact that to maintain the fuel in a gaseous state, the partial pressure of the fuel must remain well below the fuel’s vapor pressure. This is usually achieved by increasing the unburned gas temperature of the fuel/oxidizer mixture. However, for some fuels, the required unburned gas temperature can often exceed the temperature at which the fuel, given sufficient time to react, begins to pyrolize or auto-ignite. Due to the long timescales associated with the heating of the fuel/oxidizer mixture in conventional experiments (potentially seconds, in flow-based experiments, minutes in static-reactor experiments [110, 115]), flame speed measurements of practical fuels at engine-relevant temperatures and pressures are nearly impossible to conduct using the established methods.

Introduced here is a new experimental technique for the measurement of flame speeds at elevated temperatures and pressures using laser-induced ignition in a shock tube. Shock tubes are near-ideal, 0-D reactors, typically used for measuring high-temperature combustion parameters complementary to flame speeds: ignition delay times, species time-histories, and reaction rates. (For a thorough introduction to shock tube theory and operation, the reader is referred to the seminal work of Gaydon
and Hurle [116]). Shock tubes have never previously been used for laminar flame speed measurements. And yet, shock tubes are ideally suited for addressing the shortcomings associated with conventional laminar flame speed experiments. Readily accessible reflected shock temperatures range from 500 to 3000 K and higher, and reflected shock pressures range from sub-atmospheric to 100s of atmospheres [117]. Additionally, because the heating of the gas is achieved by the passing of a shock wave, the test gas mixture reaches its intended temperature and pressure in a number of microseconds – a timescale much shorter than the characteristic decomposition or autoignition times of practical fuels at combustion-relevant conditions. If the flame’s spark initiation event is delayed long enough following heating, experiments can also be tailored to measure laminar burning rates in mixtures that have undergone various extents of reaction or thermal decomposition. While not of importance for the current work, where the characteristic thermal decomposition/auto-ignition times of the relevant fuels are much longer than the experiment times, this ability to closely control the timing of laminar flame initiation relative to shock-heating could provide new, valuable insight into the high-temperature flame speed behavior of hydrocarbon fuels, particularly those that exhibit negative temperature coefficient (NTC) behavior.

Due to the high-velocity gas flow in each shock tube experiment, use of protruding electrodes, favored in static reactors (e.g., [108, 110, 118]), is not feasible. Instead, laser-induced ignition is used in the current work to ignite the fuel/oxidizer mixtures of interest. While not a newly discovered phenomenon, laser-induced spark ignition has grown in popularity in recent years, due to its promise as a spark source that can operate at high compression ratios, high compression rates, and perform reliably in lean air-to-fuel ratio conditions [119].

In this work, a high-speed camera is used to image flame propagation behind reflected shock waves in a shock tube facility. The flames are initiated by laser-induced spark ignition and the acquired images capture emission from excited hydroxyl radicals (OH*) through a transparent shock tube endwall. The subsequent sections of this chapter include a description of the experimental facility, the image processing and flame speed extrapolation methodologies employed, as well as the unique, high-temperature laminar flame speed results obtained using this new experimental approach. Stoichiometric methane/air and propane/air flame speed results are presented at relatively
lower temperatures to validate the shock tube approach against accepted literature and model results, and finally, new propane flame speed results are presented at previously unattained temperatures (>750 K).

6.2 Experimental setup

6.2.1 Shock tube facility

The flame speed measurements were performed in an unheated, stainless-steel shock tube with a 9.73-m long driven section and a 3.63-m long driver section. The inner diameter of the driven and driver sections was nominally 11.53 cm.

In each shock tube experiment, the shock tube driver section is filled with high-pressure gas until the diaphragm separating the driver and driven sections ruptures, causing an incident shock wave to form and propagate through the test gas in the driven section, thereby compressing and heating the gas; an expansion fan forms simultaneously and propagates through the driver gas. The incident shock reflects off the shock tube endwall, further compressing and heating the test gas, and leaving behind stagnant gas at elevated temperature and pressure ($T_5$, $P_5$).

Five sidewall piezo-electric pressure transducers (PCB 113A26) were used to extrapolate the incident shock velocity to the endwall. Normal-shock relations were then used to calculate $T_{5,init}$ and $P_{5,init}$ values with an estimated 1-$\sigma$ uncertainty of $\pm0.5\%$ and $\pm1.0\%$, respectively.

To reach the variable temperature and pressure conditions of interest, scored and unscored polycarbonate diaphragms of thickness 0.005-0.015 in were used to separate the shock tube driver and driven sections. In the experiments with unscored diaphragms, a four-blade cutter, located just downstream of the diaphragm, was used to ensure repeatable diaphragm rupture. Non-ideal rupturing of the diaphragm has been found to cause small diaphragm particles to travel down the length of the driven section and disturb measurements [120]. To minimize the occurrence of measurement disturbance in the experiments presented here, the shock tube was cleaned after every other shock experiment. On the occasion that a diaphragm piece made it to the test section within the test time of a single flame speed experiment (see, for example, Appendix G.1), the diaphragm piece’s impact on the expanding flame front was readily apparent in the OH* emission images and the experimental
results were discarded; remote ignition events initiated by particles were not observed in any of the experiments presented here.

The driver gas used in these experiments was a mixture of nitrogen and helium. The amount of helium in each mixture varied from 0-80%; the helium fraction was dictated by the desired experimental conditions (more/less helium to attain higher/lower temperature conditions, respectively). Axial driver inserts were employed and optimized for each condition in order to maintain near-constant pressure and temperature conditions in the shock tube test section for the duration of each experiment. Using this configuration, constant-pressure test times between 3.5 ms and 10 ms were achieved.

In each experiment, time-resolved pressure was recorded using pressure transducers (Kistler 603B1) at two axial locations: 2 cm and 10 cm from the shock tube endwall. A representative, time-resolved pressure trace recorded 10 cm from the shock tube endwall (the same axial distance as the initiator spark) can be seen in Figure 6.1. Each experiment ends when a weak shock, reflected off the contact surface between driver and driven gas, reaches the test section, causing the pressure to rise and deviate from its initial, near-constant value.

![Figure 6.1: Representative time-resolved pressure trace, measured 10 cm from the shock tube endwall, with indicated spark timing](image)

The OH* emission images were captured through a UV-transparent, fused quartz endwall. The
Figure 6.2: Shock tube end section schematic with optical-access endwall, laser ignition, and high-speed imaging systems
fused quartz window has a diameter of 13.97 cm and is 2.54 cm thick. The window is held in place by a hollow, cylindrical end cap, which compresses the window onto an o-ring, thereby sealing the shock tube on the face of the window. Additional information about the optical-access endwall can be found in an earlier publication [18]. A schematic of the shock tube end section can be seen in Figure 6.2.

6.2.2 High-speed imaging

A Vision Research Phantom v710 CMOS camera is used to record the OH* emission images. The camera is coupled to a LaVision HS-IRO ultraviolet (UV) intensifier with a gen-II S20 photocathode. The images are recorded at 10,000-50,000 frames per second (10-50 kHz). Higher frame rates were used to capture the faster flame speeds seen at higher temperatures (600 K and above). At 10 kHz, the pixel resolution was $752 \times 752$ pixels, while at 50 kHz, the pixel resolution was $304 \times 304$ pixels. A variable focal length Sodern UV lens is used at the input of the intensifier to focus the camera 10 cm from the shock tube endwall – the location of flame initiation. An Asahi Spectra high-transmission bandpass filter, centered at 313 nm with a 10 nm full-width at half-maximum (FWHM), is used to filter out ambient light and other emission wavelengths.

The image acquisition process is triggered using a delay generator (Berkeley Nucleonics Corporation, 555 Series). A sidewall pressure transducer, located 10 cm from the shock tube endwall, triggers the delay generator when the PCB’s output signal exceeds the delay generator’s 0.2-V trigger threshold. The delay generator then outputs a TTL signal for a duration of 20 $\mu$s after its designated delay time of 50 $\mu$s, thereby initiating the image acquisition process. See Figure 6.3 for a graphical representation of the triggering events.

6.2.3 Laser-induced spark ignition

A Q-switched (pulsed) Gemini 200 Neodymium-doped Yttrium Aluminum Garnet (Nd:YAG) laser is used to ignite the propane/air mixtures via laser-induced spark ignition, 10 cm from the shock tube endwall. The Nd:YAG is frequency-doubled and emits light at 532 nm. The delay
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Figure 6.3: Timeline of shock experiment trigger events (pressure, camera trigger, laser trigger, and laser pulse)

generator, triggered off of a sidewall pressure transducer (described in Section 6.2.2), sends a 300-\(\mu s\) TTL pulse to the laser flashlamp after a delay of 550 \(\mu s\). After a built-in delay of approximately 180 \(\mu s\), the Q-switch fires and the laser emits a single pulse, 5 ns in duration. The laser pulse energy was characterized across the entire output energy range, and although not measured directly for each experiment, the pulse energy used in each experiment was the minimum necessary to reliably produce a spark, and is estimated to be less than 25 mJ. A 150-mm focal length calcium fluoride lens is used to focus the beam down to a waist of approximately 9 \(\mu m\), 10 cm from the shock tube endwall.

Additional experiments were conducted to validate and characterize the laser-induced spark ignition method used in this work. Specifically, the incident laser pulse energy was quantified and the impact of the focusing-lens focal length on flame morphology was explored. The results of these studies are presented in the next three sub-sections.

6.2.3.1 Laser pulse energy measurements

The Gemini 200 Nd:YAG laser used in this work to ignite the shock-heated fuel/air mixtures allows for variable output pulse energy. In each shock experiment, the pulse energy was set to the lowest setting necessary to ignite the mixture. Although not directly quantified in each experiment
6.2. EXPERIMENTAL SETUP

presented in the accompanying publication, the output pulse energy of the laser was quantified in a separate series of experiments using an energy meter (Ophir Starlite with 3A-QUAD sensor).

The ultimate pulse energy was measured across the range of pulse energy settings by positioning the energy meter 16 inches from the laser shutter, with no intermediate optics, and pulsing the laser. As can be seen in Figure 6.4, the ultimate pulse energy ranges from 10 mJ to 45 mJ. To quantify the shot-to-shot repeatability of the pulse energy at each setting, five pulse energy measurements were conducted in succession at each potentiometer setting, in each of the three "trials"; the average standard deviation in pulse energy for the five-pulse data sets was 2.2%. In an effort to quantify the reproducibility of the potentiometer positions used to specify the output energy, the potentiometer settings were incremented in ascending order for Trial 1, descending order for Trial 2, and randomized for Trial 3. The average relative standard deviation in pulse energy across all three trials at a single potentiometer setting was 3.2%. As can be seen in Figure 6.4, the repeatability and reproducibility of the laser pulse energy become less reliable at the higher energy settings.

![Figure 6.4: Measured ultimate laser pulse energy](image)

It should be noted that the ultimate pulse energy measured in the experiments outlined above is a measure of the maximum pulse energy, not the energy deposited into the fuel/air mixture or the spark. Measurements indicate approximately 60% energy loss between the laser and the exit of the shock tube when no spark occurs, indicating significant losses as the beam traverses the optical
setup.

### 6.2.3.2 Spark energy measurements

Experiments were also conducted in an attempt to quantify the spark energy. The laser pulse energy was set to a level at which it would inconsistently generate a spark in air at room temperature (ultimate pulse energy of approximately 13 mJ). The energy meter sensor was placed in the optical path downstream of the shock tube, where it could collect the beam exiting the shock tube test section. The laser was pulsed every 5 seconds, and with each pulse, the energy of the pulse was recorded and the presence (or lack thereof) of a spark was noted. The results are plotted in Figure 6.5.

![Figure 6.5: Measured pulse energy with and without spark event](image)

For the pulses that generated a spark, the average energy collected was 2.32 mJ. For the pulses that did not generate a spark, the average energy collected was 2.67 mJ. The difference in energy indicates the energy used in the formation of the spark plasma: 0.35 mJ.

### 6.2.3.3 Lens focal length study

Previous studies have found that use of the laser-induced spark ignition technique in laminar flame speed experiments often leads to non-ideal (non-spherical) flame shapes [121–124]. These
non-ideal flames typically exhibit a lobe that is offset from the center of the primary flame front in the direction of the incident laser beam. This phenomenon is primarily due to the high amount of laser energy that is focused in the vicinity of the lens focal point. Ignition does not occur at a single point, but rather over an elongated volume in which the incident laser power is sufficiently high to induce photo-ionization of the gas. However, if this high-energy volume is minimized, the location of the ignition event approaches the limit of a point source.

In theory, the geometry of the high-energy volume is dictated by the focal length of the lens used to focus the incident laser beam. If a long-focal length lens is used, the rate of change of the beam diameter as it approaches the lens focal length will be low; the beam waist (and therefore the high-energy volume) will be elongated along the axis of the incoming beam. If a short-focal length lens is used, the rate of change of the beam diameter as it approaches the lens focal length will be high; the beam waist will be less elongated and the high-energy volume will be localized to a shorter length along the axis of the incoming beam (see Figure 6.6).

Figure 6.6: Comparison of short- and long-focal length lens impact on beam waist

Three lenses with three unique focal lengths (f = 320 mm, 200 mm, 150 mm) were tested to determine how lens focal length impacts the formation of multi-lobed flames. These experiments were conducted at room temperature and pressure (296 K, 1 atm), in stoichiometric mixtures of
methane/air (21% O₂, 79% N₂). The laser pulse energy was set to an excessively high level (∼40 mJ) to ensure the formation of multiple lobes in all of the lens experiments. Images from each experiment, taken 3 ms, 4.5 ms, and 7 ms after ignition, can be seen in Figure 6.7. The ignition laser beam is oriented horizontally, and enters from the right.

![Figure 6.7: Comparison of flame morphology caused by three different focal length lenses (f = 150mm, 200mm, 320mm) at three different times after ignition: 3 ms, 4.5 ms, 7 ms. Ignition laser beam enters from the right.](image)

The flame formed using the longest focal length lens (f = 320 mm) shows the most pronounced side lobe; the lobe extends prominently in the direction of the incident laser beam (coming in from the right), and its width is on the order of the diameter of the primary flame front. A less prominent side lobe can be seen in the flame formed using the 200-mm focal length lens; the lobe is significantly smaller than that seen in the f = 320 mm flame, and at late times, its width is approximately half the width of the primary flame. Finally, by using a short-focal length lens (f = 150 mm), a minimally invasive side lobe is formed.

The formation of multi-lobe flames can therefore largely be avoided by minimizing the focal
length of the lens used to focus the incident laser beam and induce ignition. For this reason, the 150-mm lens was used for all of the experiments described in the accompanying publication. The formation of multi-lobe flames could be avoided altogether by additionally lowering the laser pulse energy below the 40-mJ setting used in the focal length experiments.

It should be noted that even without the formation of a side lobe, flames produced by laser-induced spark ignition often resemble an ellipsoid or toroid at early times. This phenomenon has been studied extensively (e.g., [119, 122, 123, 125, 126]), and is largely thought to be due to the extreme high temperatures and pressures caused by the near-instantaneous deposition of laser energy. A spark plasma is generated by a multiphoton ionization process and subsequent electron cascade [119], leading to local temperatures and pressures approaching $10^5$ K and $10^3$ atm. These extreme conditions, local to the spark plasma, lead to rapid expansion and energy dissipation. Within a few microseconds, a shock wave emanates from the high-temperature discharge [126]. The shock wave travels at high velocity away from the spark, leading to overexpansion of the ignition kernel and inward flow along the vertical axis of the spark. At the center of the ignition kernel, the opposing gas flows from the top and bottom halves of the spark collide and deviate outward from the center, creating a pair of symmetric vortices. These vortices lead to the development of a torus or donut shape as the flame begins to grow. This phenomenon has been observed in a wide variety of laser-ignition flame experiments, regardless of mixture composition, further indicating that the plasma-induced vortices are the predominant cause of this toroidal morphology, not chemical heat release or flame propagation [126]. As the flame continues to grow, flame front propagation becomes dominated by competing thermal and mass diffusion processes, which ultimately cause the flame to assume its final, spherical shape.

6.2.4 Test gas mixtures and experimental conditions

Laminar flame speed measurements for two fuels, methane (CH$_4$) and propane (C$_3$H$_8$), are presented in this work. The results encompass two temperature ranges – a "low-temperature" regime ($\sim$400-580 K) and a "high-temperature" regime ($\sim$760-830 K). Low-temperature flame speed measurements were conducted at 1 atm for methane/air and propane/air mixtures with unity equivalence ratios ($\phi = 1.0$). High-temperature flame speed measurements were conducted at 1 atm
for propane-O$_2$-N$_2$-He mixtures ($\phi = 0.8$). In these high-temperature experiments, approximately 32% of the nitrogen otherwise present in the air oxidizer was replaced with helium. This mixture modification was necessary to promote flame stability at the higher temperatures; the addition of helium suppresses thermal-diffusive instabilities by increasing the effective Lewis number ($Le_{\text{eff}}$) of the mixture, and suppresses hydrodynamic instabilities by increasing the relative thickness of the flame front. The effectiveness of helium as a stability enhancer has long been known [127], and its use as an inert diluent is a common strategy employed in high-pressure flame speed experiments [108, 110, 128].

The fuel mixture composition and experimental conditions relevant to each set of experiments can be found in Table 6.1.

High-temperature laminar flame speed experiments are often complicated by the fact that the timescale of fuel thermal decomposition/auto-ignition can be on the order of, or shorter than, the timescale of flame propagation. This can lead to elevated burning rates, due to changing composition of the unburned gas and higher unburned mixture temperatures [129]. In the experiments presented in this work, the ignition delay time of the most reactive mixture (propane in modified air, at 832 K, 1 atm) is approximately 3.1 seconds (simulated as a constant-pressure, 0-D reactor, using AramcoMech 3.0 [130]) – almost three orders of magnitude greater than the time allowed for flame propagation at this condition ($<3$ ms). As a result, the influence of fuel reactivity on the unburned gas mixture composition and temperature (and therefore flame speed) is negligible.

Computational and experimental work conducted by others has brought to light the potential for remote ignition in the cold-wall thermal boundary layer, particularly for fuels such as propane that exhibit NTC ignition behavior [131–133]. The initial thermodynamic conditions presented in this work fall outside the NTC region for propane, and while unburned gas in the cold-wall boundary layer may exist at colder, NTC conditions, the expected ignition delay times are still significantly longer than the timescale of flame propagation (15.6-81.1 s for ignition, $\sim5$ ms for flame propagation); cold-wall boundary layer effects have therefore been neglected.

The methane, propane, oxygen, nitrogen, and helium gases used in these experiments were provided by Praxair, Inc.; their quoted purities were, respectively, 99.0%, 99.5%, 99.993%, 99.999%,
### Table 6.1: Fuel mixture composition and experimental conditions

<table>
<thead>
<tr>
<th>Experiment Type</th>
<th>Test gas composition</th>
<th>Equivalence ratio, $\phi$</th>
<th>Unburned gas temperature, $T_u$ (K)</th>
<th>Pressure (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane Low-temperature</td>
<td>CH$_4$, air (21.0% O$_2$, 79.0% N$_2$)</td>
<td>1.0</td>
<td>489-573 K</td>
<td>1.0 ±0.05</td>
</tr>
<tr>
<td>Propane Low-temperature</td>
<td>C$_3$H$_8$, air (21.0% O$_2$, 79.0% N$_2$)</td>
<td>1.0</td>
<td>391-556 K</td>
<td>1.0 ±0.05</td>
</tr>
<tr>
<td>Propane High-temperature</td>
<td>C$_3$H$_8$, modified air (21.0% O$_2$, 47.4% N$_2$, 31.6% He)</td>
<td>0.8</td>
<td>764-832 K</td>
<td>1.0 ±0.05</td>
</tr>
</tbody>
</table>
and 99.998%. All mixtures were prepared manometrically (MKS Baratron 690A) with a compositional uncertainty of ±2.0%.

6.3 Methodology: image processing and laminar flame speed extrapolation

6.3.1 Image processing

A sequence of raw, UV-intensified, OH* emission images acquired at four different times in a single methane/air flame speed shock tube experiment is presented in Figure 6.8. (The time-resolved pressure trace for the same experiment can be seen in Figure 6.1). Once again, the incoming ignition laser beam is oriented horizontally and enters from the right. Each image can be interpreted as a 2-D projection of the 3-D spherical flame. At early times, the flame resembles an ellipsoid, due to the initial shape of the laser-induced spark plasma [122]. As the surface area of the flame increases in time, the relatively higher curvature (stretch) at the top and bottom of the flames is suppressed and the flame ultimately becomes spherical. The higher intensity ring at the outer edge of the flame indicates the location of the reaction front (region of highest OH* concentration). The smooth, continuous outer edge indicates a stable flame for the duration of the experiment (t ≤ 4 ms). The uniform intensity region seen in the center of the flame indicates a quiescent burned gas region.

![Figure 6.8: OH* emission images acquired in a methane/air (φ = 1.0) laminar flame speed shock tube experiment.](image)

Figure 6.8: OH* emission images acquired in a methane/air (φ = 1.0) laminar flame speed shock tube experiment. The width of each frame is approximately 5 cm. Initial unburned gas conditions: methane/air (φ = 1.0) at 558 K, 1.0 atm.
Asymmetric flame propagation, often observed in other laser-induced spark ignition flame experiments due to the asymmetric deposition of laser energy along the laser line of sight, was mitigated through use of a short focal length lens and minimization of incident laser pulse power (as described in Section 6.2.3.3).

The OH* emission images acquired for each experiment are passed through a processing routine to extract flame radius data as a function of time. A demonstration of the image processing progression can be found in Figure 6.9.

![Image Processing Progression](image)

**Figure 6.9:** Image processing progression: (a) raw image; (b) binarized image; (c) binarized image with centroid and edge points indicated. (Initial unburned gas conditions: methane/air ($\phi = 1.0$) at 558 K, 1.0 atm; image captured 4 ms after ignition.)

First, all images are smoothed using a rotationally symmetric Gaussian low-pass filter. Pre-spark background images are averaged and the average background signal is subtracted from each flame image to minimize the impact of systematic spatial non-uniformities on flame edge detection. The Otsu method [134] is used to calculate two threshold pixel-intensity levels, thereby dividing the image into three intensity bins; the lower threshold value is used to binarize the image. Holes within large, contiguous regions of pixels are filled, and the largest region of contiguous pixels is extracted and used for centroid and edge detection. A Canny edge detection algorithm [135] is used to locate the edges of the flame in each binarized image.

With the flame centroid and edge locations known, the local radius, in pixels, is interpolated
around the circumference of the flame in one-degree increments, measured counter-clockwise from
the positive x-axis. A moving average filter is used to smooth the flame radius data in both the radial
domain (i.e., average neighboring edge point locations) and the temporal domain (i.e., average edge
points along a single angular trajectory in time) prior to subsequent analysis.

To convert the measured radii from the pixel domain to an appropriate length scale, an image
of a ruler, positioned in the shock tube at the camera focal plane, is obtained prior to each set of
experiments. For the experiments presented in this work, the conversion factor ranged from 75-112
pixel/cm.

Figure 6.10 shows representative radius vs. time data, tracked at 60-degree intervals around the
circumference of the flame, for the methane/air flame shown in Figure 6.8. As seen in the presented
data, the flame radii along different radial trajectories closely agree with each other for the duration
of the experiment, indicating that the flame is relatively spherical in shape.

Figure 6.10: Radius vs. time: representative methane/air flame speed experiment with edges tracked
at 60-degree intervals around the circumference of the flame (only a subset of all tracked edges is
shown here for clarity). Time is relative to spark timing. Unburned gas conditions: methane/air
($\phi = 1.0$) at 558 K, 1.0 atm.
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6.3.2 Laminar flame speed extrapolation

With the local flame radius relative to the flame centroid tracked in time, the instantaneous, local stretch rate and flame velocity relative to the burned gas can be quantified. If a flame is not perfectly spherical, as can be seen at early times (Figure 6.8), then the local stretch rate and burned flame speed will vary around the circumference of the flame. To account for this variance, the local stretch rate and burned flame speed are quantified at regular angular intervals around the flame.

To account for any slight aspherical behavior in the flame shape, a general definition of flame stretch rate, $\kappa$ (1/s), is applied,

$$\kappa = \frac{1}{A} \frac{dA}{dt} \tag{6.1}$$

where $A$ is the local flame surface area. Previous studies indicate that the flame shapes generated by laser-induced spark plasmas are symmetric about the axis defined by the incoming laser source [123, 126]. Here, $A$ is the area of the flame calculated by revolving an arc of the flame, defined in regular intervals around the flame circumference ($\theta \pm \delta$), about the axis of symmetry (x-axis) of the flame (see Figure 6.11a).

![Schematics of aspherical flame geometry](image)

Figure 6.11: Schematics of aspherical flame geometry
Burned flame speed, $S_b$, is defined as the time rate of change of the radius position vector normal to the expanding flame front, relative to the stagnant, burned gas. For a perfectly spherical flame with radius $R_f$, the expression for $S_b$ is simply $S_b = \frac{dR_f}{dt}$. For flames that are not perfectly spherical, a divergence angle, $\alpha$, is necessary to calculate the component of the flame radius vector normal to the expanding flame front (see Figure 6.11b). The resulting expression for local burned flame speed is:

$$S_b = \frac{dR_f}{dt} \cos(\alpha)$$ (6.2)

Using Equations (6.1) and (6.2), local stretch rate and burned flame speed can be calculated as a function of time along select radial trajectories of the flame front. In most experiments, the burned flame speed vs. $\kappa$ results were calculated at regular, 30-degree intervals around the circumference of the flame.

Figure 6.12: Burned flame speed vs. stretch rate: representative methane/air flame speed experiment with edges tracked at 60-degree intervals around the circumference of the flame (only a subset of all tracked edges is shown here for clarity). Unburned gas conditions: methane/air ($\phi = 1.0$) at 558 K, 1.0 atm.

Three distinct regions of flame behavior can be seen in the $S_b$ vs. $\kappa$ data presented in Figure 6.12. (Note that the images presented in Figure 6.8 are from the same experiment shown in Figure 6.12). At early times, spherically expanding flames are known to exhibit high burned
6.3. METHODOLOGY

flame speeds and high stretch rates due to thermal conduction from the ignition kernel to the flame front [136, 137]. In Figure 6.8, the two earliest flame images at 1 and 2 ms both exhibit high stretch rates and fall in the "ignition effects" region indicated in Figure 6.12. At late times, it has been shown that as outwardly propagating flames expand past a certain critical radius, the flames experience flow field disturbances caused by confinement-induced, non-zero burned-gas velocities [138, 139], as well as hydrodynamic instabilities caused by the thermal expansion of the gas [140, 141]. Purely confinement-related effects result in a decrease in flame propagation velocity [138, 139, 142], while hydrodynamic instabilities lead to an increase in the average propagation velocity, relative to a smooth, stable flame [140]. As evidenced by the uptick in burned flame speed seen in the methane/air data presented in Figure 6.12, under these particular conditions, flame instabilities exert a stronger influence on the late-time flame propagation than confinement effects.

For all experiments presented in this work, the maximum flame radius used for analysis was kept below 30% of the shock tube inner radius (a metric suggested by Burke et al. [139] to mitigate confinement effects) or below the radius at which flame instabilities in the OH* images were observed – whichever came first. The ability to accurately detect the onset of flame instability is of crucial importance, as it is desirable to use as many flame images as possible for flame speed extrapolation, while not compromising the fidelity of the data set by including images of flames that have developed these instabilities. In flame propagation experiments utilizing Schlieren imaging, the onset of instabilities can be detected visually by the appearance of dark creases across the surface of the flame (see, for example, [143] or [144]). In OH* emission images, the onset of unstable behavior is more subtle, and its detection therefore warrants additional discussion.

In this work, the primary indicator of flame instability is the sudden increase in flame speed observed at late times/low stretch rates. However, this trend in the $S_b$ vs. $\kappa$ data also corresponds with a visible change in the morphology of the flames captured in the OH* emission images. Figure 6.13 shows a sequence of flame images demonstrating the onset of late-time instabilities in a propane/air flame at 532 K, 1 atm. Figure 6.13a shows a smooth, quasi-steady flame with no instabilities; in Figure 6.13b, the high-intensity region indicating the flame-front reaction zone appears to thicken at the top of the flame, indicating flame-front wrinkling; 0.25 ms later (Figure 6.13c), the unstable region at the top of the flame has grown thicker and flame-front wrinkling can now be observed
in two additional locations around the circumference of the flame; in Figure 6.13d, non-uniform emission intensity at various locations within the flame image indicates additional wrinkling of the flame front on the front or back side of the flame.

![Images of OH* emission images showing the onset of flame instabilities](image)

Figure 6.13: Progression of OH* emission images showing the onset of flame instabilities, acquired in a propane/air laminar flame speed shock tube experiment: (a) stable flame; (b)-(d) red arrows mark the first indication of instability. Initial unburned gas conditions: propane/air ($\phi = 1.0$) at 532 K, 1.0 atm.

After ignition effects have died out, and before deceleration due to confinement or acceleration due to flame instabilities, the laminar flame front propagates in a quasi-steady manner (see Figure 6.12, and the images at 3 and 4 ms in Figure 6.8). It is this subset of data, free from the effects of incipient ignition, volume confinement, and instabilities, that is used to infer unstretched, burned gas velocity, $S_b^0$, and Markstein length, $L_b$ [127].

The Markstein length parameter characterizes the variation in local flame speed due to stretch, and can be related to both through the following canonical expression, originally derived for a one-dimensional, planar, steady flame experiencing flame front distortion [127]:

$$ S_b = S_b^0 + L_b \kappa $$

(6.3)

Mathematically, $L_b$ is the slope of a plot of stretched flame speed vs. stretch rate, $\kappa$ (e.g., Figure 6.12); the larger the Markstein length, the stronger the flame stretch. Conceptually, $L_b$ is a characteristic length, proportional to the thermal length of the flame zone [145]. Equation 6.3 is commonly used to analyze experimental flame speed results; however, it is not the only model used to characterize stretch in outwardly propagating, spherical flames.
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In this work, unstretched, burned flame speed \( S_o^b \) and Markstein length \( L_b \) were extrapolated from the appropriate subset of time-resolved stretch rate and burned flame speed data using the following non-linear relation between \( S_b \) and \( \kappa \):

\[
S_b^2 - S_o^b S_b = -S_o^b L_b \kappa \quad (6.4)
\]

Equation 6.4 is a variation on the more conventional extrapolation expression observed by Frankel and Sivashinsky [146] (originally derived by Markstein [127]), in which \( S_b \) is seen to vary linearly with flame curvature, \( 1/R_f \):

\[
S_b = S_o^b - 2S_o^b L_b/R_f \quad (6.5)
\]

Here, Frankel and Sivashinsky assume perfectly spherical flames, wherein the more generalized expression for stretch rate, \( \kappa \), is simplified and written in terms of flame radius, \( R_f \):

\[
\kappa = \frac{1}{A} \frac{dA}{dt} = \frac{2}{R_f} \frac{dR_f}{dt} = \frac{2}{R_f} S_b \quad (6.6)
\]

Equation 6.4 is obtained by rewriting Equation 6.5 in terms of \( \kappa \) (i.e., substituting Equation 6.6 into Equation 6.5).

The extrapolation expression defined in Equation 6.4 is thought to be most appropriate for the data sets presented here, as it has been shown to be most accurate for mixtures with Lewis number greater than unity, at the limit of large flame radius [147, 148]. (Lewis number values calculated for the mixtures of interest in this work can be found in Appendix G.2.) By applying Equation (6.4) to local \( S_b \) vs \( \kappa \) data acquired at regular angular intervals around the flame (e.g., \( 30 \pm 10 \) deg, \( 60 \pm 10 \) deg, etc.), the resulting fit and calculated parameters are effectively based on an average data subset (see Figure 6.14). This approach was found to improve the repeatability and accuracy of the flame speed and Markstein length results, especially for flames that were not perfectly spherical.

Finally, the unburned, unstretched laminar flame speed, \( S_o^u \) (defined as the velocity at which an adiabatic, planar, deflagration front propagates into an unburned mixture of fuel and oxidizer), was calculated according to \( S_o^u = S_o^b (\rho_b/\rho_u) \), where \( \rho_b \) and \( \rho_u \) are the burned and unburned gas...
Figure 6.14: Burned flame speed vs. stretch rate: data subset used for fitting, non-linear fit, and extrapolated unstretched, burned flame speed, $S_o^\circ$. Unburned gas conditions: methane/air ($\phi = 1.0$) at 558 K, 1.0 atm.

densities, respectively, calculated at equilibrium.

6.4 Results

6.4.1 Low-temperature (<600 K) methane flame speed results

Laminar flame speed measurements were conducted in methane/air (21% O$_2$, 79% N$_2$) mixtures ($\phi = 1.0$) at initial unburned gas conditions of 489-573 K, 1 atm. The flame speed results, calculated using the image processing and extrapolation methods outlined in the preceding Methodology section, are plotted in Figure 6.15a; the corresponding Markstein length ($L_b$) measurements are plotted in Figure 6.15b. There exists an abundance of methane laminar flame speed data in the literature, and yet of the "high-temperature" experiments that account for stretch effects, the vast majority are limited to unburned gas temperatures below 445 K (e.g., [115, 149–153]). There exists one data set at the pressure and temperature range of interest to this work – that published by Akram et al. [154], obtained using the diverging channel method. The results from Akram et al. have been plotted alongside the experimental results obtained in this work for comparison.
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Figure 6.15: Stoichiometric methane/air (a) laminar flame speed and (b) Markstein length vs. unburned gas temperature. Figure 6.15a includes a comparison of this work with literature (Akram et al. [154]) and model (AramcoMech 3.0 [130], LLNL [69], USC Mech II [45], FFCM-1 [81]) results. Unburned gas conditions: methane/air ($\phi = 1.0$) at 489-573 K, 1.0 atm.

The flame speeds were simulated as freely propagating, planar flames using the PREMIX code [155] in CHEMKIN-PRO [44]. The computational domain was 20 cm, an adaptive grid size was employed, and mixture-averaged transport properties were used. The following kinetic models were used for comparison with the experimental results (see Figure 6.15a): AramcoMech 3.0 [130], LLNL $n$-alkane mechanism (intended for 2-methyl alkanes and $n$-alkanes up to C8) [69], USC Mech II [45], and the Foundational Fuel Chemistry Model (FFCM-1) [81].

Alongside the measured and modeled flame speed results presented in Figure 6.15a is a line indicating the predicted flame speeds calculated using a temperature-exponent correlation of the form $S_u = S_{u,\text{ref}} (T_u/T_{u,\text{ref}})^\alpha$, where $S_{u,\text{ref}}$ is the flame speed at the reference temperature, $T_{u,\text{ref}}$, and $\alpha$ is the empirically derived temperature exponent. An $\alpha$ value of 1.66 (obtained from [7]) was used to predict the methane/air flame speeds, referenced to the methane/air unburned flame speed at 300 K, as predicted by AramcoMech 3.0 [130].

The temperature-dependent trend seen in the methane/air flame speed measurements in Figure 6.15a is consistent with that seen in the model results, although the measured results are systematically high relative to the models. The experimental results show a maximum relative difference
of 14.7% at 540.3 K when compared with the Aramco model results, and an average relative difference of 6.9% across the entire temperature range of interest. When comparing the flame speed measurements from this work to those obtained by Akram et al., it can be seen that the model results often split the difference between the two experimental data sets. Both sets of experimental results show close agreement with the model results at low temperatures (<500 K). However, the results obtained by Akram et al. show significant divergence from the model results at high temperatures (>550 K), while the results presented in this work show close agreement.

As will be discussed in Section 6.4.5, the y-axis error bars associated with each flame speed point represent the 1-σ uncertainty, taking into account multiple sources of measurement uncertainty and the repeatability of the shock experiments (average of ±3.9%); the x-axis error bars represent the uncertainty in the post-reflected-shock temperature, ±0.5%.

As can be seen in Figure 6.15a, the temperature scaling methodology underpredicts the flame speed results, especially as the unburned gas temperature is increased above 550 K. While the temperature-exponent scaling shows negligible deviation from model results below 500 K, significant deviation is seen as the temperature is increased above 500 K, indicating that temperature exponents derived at lower temperatures are insufficient at predicting flame speed behavior at temperatures much higher than the temperature ranges from which they were derived.

The Markstein length ($L_b$) values shown in Figure 6.15b show a slight upwards trend with temperature and indicate an average value of approximately 0.07 cm at 530 K. It should be noted that there is significant uncertainty associated with these data points, due to the goodness-of-fit associated with the non-linear fit to the $S_b$ vs. $\kappa$ data, as well as uncertainty associated with the extrapolation method used to obtain the unstretched flame speed, $S_b^0$ [147, 156, 157]. The y-axis error bars associated with the $L_b$ measurements represent uncertainty due to the goodness-of-fit only.

Overall, the methane/air flame speed measurements show satisfactory agreement with model and literature results, indicating that flame speed experiments conducted in a shock tube produce reliable results that are consistent with other experimental methods.
6.4. RESULTS

6.4.2 Low-temperature (<600 K) propane flame speed results

Laminar flame speed measurements were also conducted in propane/air (21% O\textsubscript{2}, 79% N\textsubscript{2}) mixtures ($\phi = 1.0$) at initial unburned gas conditions of 391-556 K, 1 atm. The flame speed results are plotted in Figure 6.16a alongside experimental results obtained by Zhao et al. [113], Tang et al. [158], Veloo et al. [159], and Gong et al. [160]; the corresponding Markstein length measurements are plotted in Figure 6.16b alongside experimental results obtained by Tang et al. [158]. All of the literature results account for flame stretch and were obtained using various experimental methods: stagnation flame with linear $0$-stretch extrapolation (Zhao et al.), spherically expanding flame with linear $0$-stretch extrapolation (Tang et al. and Gong et al.), and stagnation flame with non-linear $0$-stretch extrapolation (Veloo et al.). Flame speed simulation results were obtained using AramcoMech 3.0, the LLNL $n$-alkane mechanism, and USC Mech II (FFCM-1 is not intended for predicting the oxidation behavior of alkanes larger than methane); the simulation results are also presented in Figure 6.4.2.

![Figure 6.16: Stoichiometric propane/air (a) laminar flame speed and (b) Markstein length vs. unburned gas temperature. Figure 6.16a includes a comparison of this work with literature (Zhao et al. [113], Tang et al. [158], Veloo et al. [159], and Gong et al. [160]) and model (AramcoMech 3.0 [130], LLNL [69], USC Mech II [45]) results; Figure 6.16b includes a comparison with the Markstein length values of Tang et al. [158]. Unburned gas conditions: propane/air ($\phi = 1.0$) at 391-556 K, 1.0 atm.](image-url)

Across the temperature range of interest, all of the model results are encompassed by the scatter...
in the experimental propane flame speed results, and the majority of the measured results agree with the model predictions within the measurement uncertainty associated with each point (average of ±8.4%). Between 400 K and 500 K, the measurements also show close agreement with the literature results. Once again, these low-temperature propane results serve to validate the shock-tube flame speed measurement approach; the measurements are consistent with model results and results found in the literature.

Temperature-exponent correlation results are also plotted alongside the measured and modeled propane/air flame speed results in Figure 6.16a. An $\alpha$ value of 1.6 (obtained from [7]) was used to predict the propane/air flame speeds, referenced to the propane/air unburned flame speed at 300 K, as predicted by AramcoMech 3.0 [130]. Similar to the methane/air results, the propane/air temperature-correlation results deviate from the model and experimental results at temperatures above 500 K, and this deviation increases with increasing temperature. The inability of the temperature-exponent scaling methodology to predict high-temperature flame speeds once again motivates the need for experimental flame speed measurements above 500 K.

The Markstein length values shown in Figure 6.16b increase as unburned gas temperature increases and range from approximately 0.03 cm at 400 K to approximately 0.08 cm at 550 K. The values reported in this work also appear consistent with $L_b$ values published by Tang et al. [158]. It should again be noted that the error bars shown in Figure 6.16b indicate uncertainty due to the efficacy of the non-linear fit to the $S_b$ vs. $\kappa$ data, and uncertainty due to choice of extrapolation expression has not been included.

### 6.4.3 High-temperature (>750 K) propane flame speed results

High-temperature flame speed results were obtained for propane-O$_2$-N$_2$-He mixtures ($\phi = 0.8$) at 764-832 K, 1 atm (see Figure 6.17); the accompanying Markstein length values can be found in Appendix G.5. These are the first high-temperature flame speed data of this kind. No other experimental data are available in the literature for comparison at these high-temperature conditions. The data are plotted alongside model predictions obtained using AramcoMech 3.0 and the LLNL n-alkane mechanism. Of the four models used for comparison with the lower temperature flame speed results (AramcoMech 3.0, LLNL, USC Mech II, FFCM-1), AramcoMech 3.0 and LLNL are
the only two that include helium in their species lists.

Figure 6.17: Propane/modified-air (21.0% O₂, 47.4% N₂, 31.6% He) laminar flame speed vs. unburned gas temperature. Comparison of this work with model results (AramcoMech 3.0 [130], LLNL [69]). Unburned gas conditions: propane/modified-air (φ = 0.8) at 764-832 K, 1.0 atm.

The high-temperature, propane/modified-air flame speed measurements shown in Figure 6.17 are bounded by the Aramco and LLNL model data sets. The measurement uncertainty associated with the high-temperature flame speed results is slightly higher than that seen for the lower-temperature flame speeds, due to a number of factors. Incorporation of helium gas in the test gas mixture leads to a thicker thermal boundary layer in the shock tube, thereby leading to greater shock attenuation (∼1.3%/m for the high-temperature experiments vs. ∼0.6%/m for the low-temperature experiments). Greater shock attenuation leads to greater uncertainty in the initial post-shock conditions (temperature and pressure), and leads to greater uncertainty in the post-shock conditions over the course of the experiment.

A second factor that is likely causing the higher scatter seen in the high-temperature experiments is related to the range of stretch-rate data points used for unstretched flame speed extrapolation. Due to the relatively small diameter of the shock tube (11.53 cm), flames used for extrapolation tend to have smaller radii (and therefore higher stretch rates) than those used for extrapolation in larger, conventional apparatuses. The higher-temperature, helium-containing datasets used for
extrapolation also exhibit higher stretch rates than those used for the methane/air and propane/air flames (2000-3000 s\(^{-1}\) vs. 400-700 s\(^{-1}\)). At the higher temperatures, flame instabilities set in earlier (at smaller critical radii) than at the lower temperatures, thereby necessitating the use of flame image data points that exhibit a higher degree of stretch. As a result, the data used for extrapolation to zero-stretch at the higher temperatures are much further from the zero-stretch point than those used at the lower temperatures. Therefore, any slight change in the fit yields a much greater change in extrapolated, unstretched flame speed; similarly, any uncertainty in the fit yields a much greater uncertainty in the extrapolated, unstretched flame speed.

Also of note in Figure 6.17 is the large discrepancy between the model predictions; over the 700-900 K temperature range, the average relative difference between the Aramco and LLNL results is 10.4%. (In comparison, the maximum relative discrepancy seen between the low-temperature model results presented in Figure 6.15a (low-temperature methane) and Figure 6.16a (low-temperature propane) is 6.1% and 7.1%, respectively.) This discrepancy at the higher temperatures is likely due to the fact that the model flame speed results have not been validated at these conditions due to the lack of available experimental data; no other experimental data exists for model validation at these temperatures. The disagreement between the two models further highlights the need for experimental flame speed data at temperatures higher than 500 K.

6.4.4 Ignition delay time considerations: bulk gas and cold-wall boundary layer

Pre-flame reactions in the bulk gas can cause unburned gas density to change over the course of a high-temperature flame speed experiment, through evolution of bulk gas composition and temperature. This phenomenon is known to significantly impact the burning rate of the fuel/oxidizer mixture [129]. However, in the experiments presented in this work, the ignition delay times of the fuels of interest (methane and propane), at the conditions of interest, are much greater than the time period related to flame propagation (approximately 5 ms). Table 6.2 includes the simulated ignition delay times (\(\tau_{IDT}\)) for the most reactive conditions for each fuel/oxidizer mixture. The theoretical ignition delay time values were simulated using CHEMKIN-PRO [44], assuming a constant-pressure, 0-D reactor, using AramcoMech 3.0 [130]. Due to the large disparity in relevant timescales (milliseconds for flame propagation, seconds for auto-ignition), and the subsequent lack of thermal
6.4. RESULTS

Table 6.2: Ignition delay times for most reactive conditions for each fuel/oxidizer mixture

<table>
<thead>
<tr>
<th>Mixture Composition</th>
<th>$T_{u, max}$ (K)</th>
<th>P (atm)</th>
<th>$\tau_{IDT}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$, air (21.0% O$_2$, 79.0% N$_2$)</td>
<td>573</td>
<td>1.0</td>
<td>48.3 hrs</td>
</tr>
<tr>
<td>C$_3$H$_8$, air (21.0% O$_2$, 79.0% N$_2$)</td>
<td>556</td>
<td>1.0</td>
<td>280 s</td>
</tr>
<tr>
<td>C$_3$H$_8$, modified air (21.0% O$_2$, 47.4% N$_2$, 31.6% He)</td>
<td>832</td>
<td>1.0</td>
<td>3.1 s</td>
</tr>
</tbody>
</table>

decomposition/oxidation occurring in the experimental test time, the impact of fuel reactivity on flame speed has been deemed irrelevant. However, pre-flame reactions will certainly be more of a concern as experimental conditions deviate from those presented in the current work (e.g., larger hydrocarbon fuels, higher pressures, higher temperatures, etc.), and the resulting burning rates will need to be reported accordingly.

Near-wall gases in the shock tube thermal boundary layer experience a different, cooler temperature-time history than the bulk gas, and may therefore be susceptible to first-stage ignition before the high-temperature bulk gas. This phenomenon has been observed and reported on by numerous researchers, and was most recently discussed by Jayachandran et al. [132, 133]. Nevertheless, due to the magnitude of the ignition delay times associated with the particular experiments presented in this work, cold-wall effects do not play a significant role. See, for example, the IDT Arrhenius plot in Figure 6.18, which maps the NTC behavior relevant to the high-temperature propane experiments presented in this work.

Even if the gas in the boundary layer exists in the NTC domain, the ignition delay time is much greater than the experiment time, and cold wall ignition is therefore not expected.

6.4.5 Uncertainty analysis

The uncertainty associated with the flame speed measurements reported in this work is impacted by a number of factors: initial mixture composition, impurities in the test gas, unburned gas temperature and pressure, pixel-to-cm conversion factor, the fidelity of the second-order $S_b$ vs. $\kappa$ fit, and the burned-to-unburned gas density ratio. To determine the overall uncertainty associated with the flame speed measurements, the above factors were assumed to be uncorrelated; the impact the uncertainty associated with each factor has on the overall flame speed uncertainty was quantified.
Figure 6.18: Constant-pressure ignition delay times for propane/modified-air (21.0% O₂, 47.4% N₂, 31.6% He) mixture (φ = 0.8) at 1 atm

according to the following root-of-sum-of-squares method:

\[
a_{S_u}^2 = \sum_{i=1}^{N} \left( \frac{dS_{u_0}^0}{dQ_i} \right)^2 a_i^2
\]  

(6.7)

Here, \(a_{S_u}^0\) is the overall uncertainty in the laminar flame speed, \(S_{u_0}^0\), \(a_i\) is the uncertainty in each parameter, \(Q_i\), and \(N\) is the number of parameters. A brief summary of each of the factors impacting the overall measurement uncertainty is presented here.

Uncertainty in the initial fuel and oxidizer composition can impact the laminar flame speed through equivalence ratio, while uncertainty in the inert, diluent gas concentration can impact the adiabatic flame temperature. For the low-temperature methane and propane experiments, the fuels were combined manometrically with a pre-made air mixture (21% O₂, 79% N₂) provided by Praxair, Inc.; for the high-temperature propane experiments, each component was added to the mixture independently. Similar to the procedure outlined by Xiouris et al. [110], the absolute partial pressure measurements of each component were treated as independent, uncorrelated variables. The uncertainties in the fuel and oxygen loading pressures (±0.12% of the absolute pressure recorded using a pressure gauge (MKS Baratron 690A)) were used to quantify the uncertainty in equivalence
6.4. RESULTS

ratio (±0.5%). AramcoMech 3.0 [130] was used to perturb the equivalence ratio by its uncertainty and quantify its effect on laminar flame speed. For the high-temperature flame speed experiments, the mole fractions of the inert diluents were perturbed by their respective uncertainties, and AramcoMech 3.0 was used to determine the resulting impact on flame speed.

Impurities in hydrocarbon test gas mixtures can often have a non-negligible impact on combustion parameters. Gas chromatography-mass spectrometry (GC-MS) analysis of the propane gas provided by Praxair, Inc. showed the presence of iso-butane (≈2000 ppm) and ethane (≈500 ppm). The propane flame speeds were re-simulated with the impurities added, using AramcoMech 3.0. At the median temperature for the low-temperature propane experiments (500 K), the relative change in simulated flame speed due to the added impurities was -0.003%. Due to the negligible impact of impurities on the flame speed results, the impact of impurities was neglected for the experiments presented here.

The initial unburned gas temperature and pressure ($T_{5,init}$ and $P_{5,init}$) are calculated as described in Section 2.2.4 using an in-house, Rankine-Hugoniot equation-based algorithm [23]. For all experiments, the target unburned gas pressure was nominally 1 atm (average of 1.00 atm, standard deviation of 0.05 atm). While the proximity of each experiment’s pressure to the nominal pressure impacts each experiment individually (particularly when comparing experimental results to model data calculated at precisely 1 atm), there is also systematic uncertainty associated with each calculated pressure (and temperature) value, due primarily to uncertainty in the incident shock velocity and the initial experimental conditions (loading pressure, composition, etc.). The 1-σ uncertainty associated with the calculated unburned gas temperature was found to be ±0.5% for the low-temperature experiments (±1.1% for the high-temperature experiments), and the uncertainty associated with the calculated unburned gas pressure was found to be ±1.0% for the low-temperature experiments (±2.9% for the high-temperature experiments). AramcoMech 3.0 [130] was again used to independently perturb the initial temperature and pressure values by their associated uncertainties and quantify the impact the uncertainty each initial condition has on the overall flame speed result.

To convert the OH* emission images from a pixel scale to a length scale, a ruler is placed in the shock tube at the camera focal plane. Uncertainty in the pixel-to-centimeter conversion factor leads to non-trivial systematic uncertainty in the final flame speed measurement. Uncertainty in
identifying the ruler mark location was estimated to be \( \pm 1 \) pixel.

There is inherent uncertainty associated with fitting Equation (6.4) to the \( S_b \) vs. \( \kappa \) data and using it to extrapolate an unstretched, burned flame speed, \( S_{ob} \). The 1-sigma uncertainty associated with the non-linear least squares parameter estimate for \( S_{ob} \) was quantified for each data set, and the resulting uncertainty associated with \( S_{ob} \) was calculated. The average 1-\( \sigma \) uncertainties associated with \( S_{ob} \) due to the fit uncertainty for the low-temperature methane, low-temperature propane, and high-temperature propane experiments were \( \pm 0.5\% \), 1.1\%, and 2.5\%, respectively. Other than measurement scatter, uncertainty in the non-linear fit is the largest source of uncertainty in the flame speed measurements.

Although not explicitly accounted for in the uncertainty calculations, it should also be noted that there is uncertainty associated with use of an extrapolation expression to determine unstretched, burned flame speed. Recent work by Jayachandran et al. [156], Wu et al. [157], and Chen [147], has compared extrapolation results to direct numerical simulations and quantified the divergence from the expected unstretched flame speed. For the conditions relevant to this work, using the extrapolation method outlined in Section 6.3.2, the uncertainty associated with extrapolating unstretched flame speed is thought to be 5\% or less. The raw \( S_b \) vs. \( \kappa \) data for each experiment presented here has been included in the Supplemental Material of the related journal paper [100] to preclude data bias due to extrapolation method.

As mentioned in Section 6.3.2, the final laminar flame speed value, \( S_{uo} \), is calculated by multiplying the unstretched, burned flame speed, \( S_{ob} \), by the ratio of burned gas density to unburned gas density, \( \rho_{b}/\rho_{u} \). The unburned and burned gas densities at equilibrium can be easily calculated using standard thermodynamic properties. Three kinetic models (AramcoMech 3.0 [130], the LLNL \( n \)-alkane mechanism [69], and USC Mech Version II [45]) were used to simulate the low-temperature propane flame speed experiments and calculate the resulting density ratios. The average relative standard deviation seen in the modeled density ratio results was found to be 0.07\%, indicating that the species-specific thermodynamic properties used in each model have a negligible impact on the overall flame speed results. More importantly, however, uncertainty in unburned gas mixture composition propagates through to the equilibrium density values. Estimates of the uncertainty in the fuel mixture composition were used to estimate the corresponding density uncertainties, and the
average change in density ratio due to composition uncertainty was found to be ±0.3%. Overall, uncertainty in the density ratio calculation is relatively insignificant compared to the other sources of uncertainty.

The average 1-σ measurement uncertainties associated with the low-temperature methane, low-temperature propane, and high-temperature propane laminar flame speed measurements (due to the sources of uncertainty outlined above) were found to be ±1.3%, 1.8%, and 3.7%, respectively.

By repeating shock experiments at similar post-shock temperature conditions (e.g., the propane flame speed measurements at ~443 K in Figure 6.16a), the repeatability of the shock experiment results could also be characterized. The five points clustered at 443 K, for example, show a maximum difference of 10.7 cm/s, or 12.6%; the standard deviation in the five measurements is 3.7 cm/s, or 4.4%. Scatter over the entire temperature range of each flame speed dataset was quantified by calculating the standard deviation of residuals of least-squares fits (either linear, or of the form $S_{u,\text{ref}}\left(T_u/T_{u,\text{ref}}\right)^\alpha$) to the data. Taking into account repeatability and the sources of measurement uncertainty described above, the average, overall uncertainties associated with the low-temperature methane, low-temperature propane, and high-temperature propane laminar flame speed measurements were 3.9%, 8.4%, and 5.2%, respectively.

6.5 Non-ideal flame phenomenon: multiple flame fronts?

While conducting the multitude of low- and high-temperature flame speed experiments outlined above, an interesting flame phenomenon was observed in a subset of the experimental results: in some experiments, a flame haloing effect was observed, as depicted in Figure 6.19. The 2-D projections of the flame captured by the high-speed camera appear to show multiple flame fronts – a bright, outer emission circle indicating a first flame front, and a bright, inner emission circle indicating a second flame front. In all such experiments, the two flame fronts appear to expand at the same rate, maintaining an approximately constant distance between the “inner” and “outer” flames.

Additional experimentation has shown that the haloing effect is temperature-dependent. Figure 6.20 shows four stoichiometric methane/air flames at four different temperatures (1 atm). Below approximately 570 K, the methane/air flames behave as expected: a single, spherical, laminar flame
CHAPTER 6. HIGH-TEMPERATURE LFS MEASUREMENTS IN A SHOCK TUBE

Figure 6.19: Flame haloing effect observed in a methane/air ($\phi = 1.0$) flame at 592 K, 1.0 atm; times are relative to spark timing.

front expanding in time (Figure 6.20a). Above approximately 570 K, the double-flame morphology begins to appear (Figure 6.20b). Additionally, as temperature increases, the distance between the outer and inner flame edges increases (Figure 6.20b-d). Above approximately 610 K, the flames are fully unstable for the duration of the flame propagation event (Figure 6.20e).

The flame morphology temperature dependence has been shown here for methane/air flames, but the same dual-flame front behavior was observed in stoichiometric ethane/air and propane/air flames as well. In ethane/air flames ($\phi = 1.0$, 1.0 atm), the multi-front behavior occurred at temperatures above approximately 545 K. In propane/air flames ($\phi = 1.0$, 1.0 atm), the multi-front behavior occurred at temperatures above approximately 540 K; at 2 atm, stoichiometric propane/air flames began to show the multi-front behavior at temperatures above approximately 550 K.

Multiple theories have been entertained to explain what causes this haloing effect, including:

- spark shape/energy
- an artifact of capturing OH* emission
- multi-stage ignition (low/high-temperature chemistry)
- flame distortion

Experimental evidence that supports or refutes the theories listed above will be briefly presented here.

The impact of spark energy on the multi-flame front morphology was explored. Two methane/air flame speed experiments were conducted at $\sim$592 K – one with the laser pulse energy set to approximately 18 mJ, the other with the laser pulse energy set to approximately 32 mJ. As can be seen
6.5. NON-IDEAL FLAME PHENOMENON: MULTIPLE FLAME FRONTS?

Figure 6.20: Flame haloing phenomenon as a function of temperature. CH\textsubscript{4}/air flames (\(\phi = 1.0\)), 1.0 atm.
in Figure 6.21, changing the laser pulse energy (and therefore spark energy) has no impact on the appearance of the multi-flame front structure, indicating that the haloing is likely not due to spark shape/energy.

![Figure 6.21: Flame haloing phenomenon with different spark energies. CH₄/air flames (φ = 1.0), 1.0 atm.](image)

To test whether or not the haloing is an artifact of capturing OH* emission, a multi-front flame experiment was repeated with a CH* optical filter, allowing for emission collection at approximately 430 nm instead of 306 nm. A still frame of the CH* emission results from a stoichiometric methane/air flame speed experiment at 625 K, 1.0 atm are shown in Figure 6.22. As can be seen from the CH* image (which is comparable to the OH* image shown in Figure 6.20e), the multi-flame front structure persists, and can still be detected using a CH* emission filter.

Another theory to explain the dual-flame front structure is that the phenomenon is chemistry-related. This theory would imply that the two flames are concentric, and that the outer flame is a weak, "cool" flame, responsible for partially oxidizing the fuel and generating intermediate species, while the inner flame is a "hot" flame, responsible for the consumption of those intermediates and the formation of stable product species. It is this author's belief that this theory is flawed for a number of reasons. First, the multi-flame front behavior is present in methane/air flames. Methane does not exhibit NTC behavior, thus it is not expected to exhibit dual-stage ignition/flame front behavior. Second, if there truly was a cool flame preceding the expansion of a hot flame, emission from the
6.5. NON-IDEAL FLAME PHENOMENON: MULTIPLE FLAME FRONTS?

Figure 6.22: Flame image using CH* spectral filter. Multiple flame fronts still observed in the methane/air ($\phi = 1.0$) flame at 625 K, 1.0 atm.

cool flame would not be of the same intensity as that from the hot flame; as seen in Figures 6.19-6.22, the emission from the "inner" and "outer" flames is clearly of a similar magnitude. Finally, in order for the haloing phenomenon to be explained by low-temperature chemistry, the outer "cool" and inner "hot" flames would need to propagate at approximately equal velocities for the duration of each experiment; this prerequisite alone makes the cool/hot flame theory highly improbable.

The final and most likely theory as to what's causing the flame haloing effect has to do with flame distortion. Experiments were conducted to see if the multi-flame front morphology could be changed by moving the spark location. In all of the experiments presented previously, the spark ignition point is at the center of the shock tube; in these experiments, the spark was offset from the centerline of the tube, closer to the sidewalls, by 0.5 cm in both directions. The results are shown in Figure 6.23.

Interestingly enough, when the spark is offset from the centerline of the shock tube, the two flame front circles no longer remain perfectly concentric. While the inner circle remains roughly centered around the center of the shock tube, the outer circle remains centered around the spark location. This evidence would seemingly confirm that the haloing effect is not related to low-temperature chemistry – if it was, both flames would be expected to remain centered around the spark location. Instead, the evidence (specifically the fact that one of the flames hugs the centerline of the shock tube) suggests that the dual-flame front behavior is most likely related to the cylindrical geometry of the confinement imposed by the shock tube. Additionally, instead of the dual-flame
CHAPTER 6. HIGH-TEMPERATURE LFS MEASUREMENTS IN A SHOCK TUBE

Figure 6.23: Impact of spark location on dual-flame front morphology; X denotes spark location, dashed line marks shock tube centerline. CH$_4$/air flames ($\phi = 1.0$), 1.0 atm, at (a) 584 K, (b) 592 K, (c) 590 K.

Front behavior being caused by concentric flames, it is more likely that the images are capturing the 2-D projection of two flame fronts growing, one in front of the other.

Additional work is needed to determine the exact cause of the dual-flame front behavior seen in the high-temperature, shock-tube flame speed measurements (see Section 8.2.2). However, this phenomenon does not impact any of the flame speed results presented in this chapter, or Chapter 7, as all of the experiments were purposefully conducted in temperature regimes in which the flames were strictly laminar and exhibited no dual-flame behavior.

6.6 Conclusions

Presented here is the first demonstration of high-temperature laminar flame speed measurements conducted in a shock tube. Methane/air, propane/air, and propane/modified-air test gas mixtures were shock-heated to elevated temperatures, the high-temperature gas was ignited via laser-induced spark ignition, and a high-speed, UV-intensified camera captured OH* emission images, which were subsequently used to track flame front growth in time. Stretch effects were accounted for using a published non-linear extrapolation method.

Stoichiometric methane/air and propane/air laminar flame speeds were measured at 1 atm and
temperatures for which some comparative data could be found in the literature (489-573 K and 391-556 K, respectively); these measurements showed satisfactory agreement with the literature results and close agreement with results generated by kinetic models (AramcoMech 3.0, LLNL, USC Mech II, and FFCM-1). These relatively lower-temperature flame speed results serve to validate the shock-tube flame speed measurement approach, although slightly higher scatter can be seen in the shock-tube flame speed measurements when compared to conventional static-reactor flame speed results. Comparisons with flame speed results obtained using temperature-exponent scaling correlations highlight the inability of the temperature-exponent scaling methodology to predict high-temperature flame speeds, particularly those significantly outside the range of temperatures over which the correlation has been derived.

High-temperature propane flame speed measurements were also conducted at previously unreported temperatures (764-832 K) and 1 atm. The high-temperature experiments were conducted at $\phi = 0.8$ in modified air, with approximately 32% of the N$_2$ replaced with helium to suppress thermal-diffusive and hydrodynamic flame front instabilities. The high-temperature flame speed measurements were found to fall between the results predicted by the Aramco and LLNL models.

The results presented here indicate that shock-tube flame speed experiments can successfully duplicate flame speed measurements conducted at lower temperatures (<600 K) in conventional experimental apparatuses, and also provide the opportunity to measure flame speeds at extremely high temperatures (>750 K). While the results obtained in the present shock-tube flame speed experiments may exhibit higher scatter than those obtained in static-reactor flame speed experiments, shock tube experiments allow access to temperature regimes that are inaccessible by static reactor methods. The trade-off of slightly lower precision for higher temperature flame speed data is certainly justifiable. By using a shock tube, flame speed temperature regimes previously inaccessible by conventional means, particularly those relevant to modern-day jet engines and on-road vehicles, can now be explored.
Chapter 7

Laser absorption measurements in high-temperature flames

7.1 Introduction

Laminar flame speed and species profile measurements have long been regarded as important targets for chemical kinetic model development. Modern premixed laminar flame speed experiments allow for flame speed measurements at a wide range of pressure and temperature conditions. Burner-stabilized flat flames are ideal for low-pressure (<0.1 bar) flame speed and species measurements, while the spherically expanding flame is the only flame morphology suitable for high-pressure (>10 bar) flame speed measurements [107]. Conventional laminar flame apparatuses (e.g., constant-volume/constant-pressure bombs, counterflow or stagnation flames, burner-stabilized flames, etc.) can be used to measure flame speeds at initial unburned gas temperatures of up to approximately 700 K, while recent shock tube burning velocity experiments have been conducted at initial temperatures in excess of 800 K [100, 161].

Speciation measurements in premixed laminar flames are commonly carried out in low-pressure flat flame burners, where the flame is thick enough to spatially resolve the reaction zone within the flame. Sampling-based molecular-beam mass spectrometry (MBMS) is a common, effective technique used to conduct broad analysis of stable and radical species present in such flames [162].
However, one of the drawbacks of MBMS is the fact that the pressure of the flame must be kept low enough (<100 Torr) to accommodate the ion source. To obtain species measurements at higher pressures and in other laminar, premixed flame configurations, laser diagnostics, including laser-induced fluorescence (LIF), coherent anti-Stokes Raman scattering (CARS), Rayleigh scattering, and many others have been widely employed [163].

Laser absorption diagnostics have been used previously to measure temperature and pressure within spherically expanding, n-butane/air flames, e.g., the work of Wang et al. [164]. All of the experiments performed by Wang et al., however, were conducted at 298 K, 1 atm.

In this work, single line-of-sight, wavelength-scanned direct absorption diagnostics are used to measure temperature, carbon dioxide (CO$_2$), water (H$_2$O), and pressure in the quiescent burned gas of spherically expanding ethane/air flames initiated behind reflected shock waves in a shock tube; simultaneous, high-speed images of emission from excited hydroxyl radical species (OH*) are used to calculate laminar flame speed. By coupling the high-temperature, laminar flame speed shock tube approach with laser absorption diagnostics, species measurements can be carried out in the interior of spherically expanding flames at previously unexplored temperature conditions.

This work was also motivated by a recent, exhaustive survey of laminar flame speed data available in the literature, conducted by Konnov et al. [7]. The study found that although there exists a relative abundance of "high-temperature" (350-500 K) laminar flame speed data for methane and propane, there are currently no high-temperature data available for ethane. This work aims to fill that gap, while simultaneously providing information about the temperature of, and CO$_2$ and H$_2$O concentrations in, the burned gas region of spherically expanding ethane flames.

### 7.2 Methods and experimental setup

#### 7.2.1 Shock tube facility

The experiments were conducted in a stainless-steel shock tube with a nominal inner diameter of 11.53 cm (see Section 2.2.3 for additional details). The 9.73-m long driven section was separated from the 3.63-m long driver section by a 0.005-inch thick, polycarbonate diaphragm. Driver inserts were employed to maintain near-constant pressure in the shock tube test section for the duration of
CHAPTER 7. LASER MEASUREMENTS IN HIGH-TEMPERATURE FLAMES

Each experiment. Nitrogen-based driver gas mixtures were used to achieve the desired experimental conditions (449-537 K, 1 atm). A variable amount of helium (3.4-13.5%) was added to the nitrogen driver gas to attain the higher temperature conditions (496-537 K), while a variable amount of CO₂ (4.8-52.7%) was added to the nitrogen driver gas to attain the lower temperature conditions (449-488 K). Using this approach, experimental test times of 8.6-14.3 ms were achieved.

Five piezoelectric, sidewall pressure transducers (PCB 113A25) were used to extrapolate incident shock velocity to the endwall, and normal-shock relations were used to calculate initial, reflected-shock temperature and pressure conditions \(T_{5,\text{init}}\) and \(P_{5,\text{init}}\). The estimated 1-σ uncertainty associated with the calculated \(T_{5,\text{init}}\) and \(P_{5,\text{init}}\) values was found to be ±0.4% and ±0.8%, respectively.

The test gas mixture composition used in this work was stoichiometric ethane \((\text{C}_2\text{H}_6)\) in air \((21\% \text{ O}_2, 79\% \text{ N}_2)\), or nominally 5.7% \(\text{C}_2\text{H}_6\), 19.8% \(\text{O}_2\), and 74.5% \(\text{N}_2\). The test gas mixtures were prepared manometrically. The neat ethane, oxygen, and nitrogen components were provided by Praxair, Inc., with the following quoted purities, respectively: 99.0%, 99.993%, and 99.998%.

7.2.2 Laminar flame speed measurements

\(\text{OH}^*\) emission was recorded at 40,000 frames per second (40 kHz) using a Vision Research Phantom v710 CMOS camera, coupled to a LaVision HS-IRO ultraviolet (UV) intensifier, as described in Section 6.2.2. A variable focal length lens (Sodern UV) was used to focus the camera at the location of flame initiation, 10 cm from the shock tube endwall. The resulting image was approximately 5.17 × 5.17 cm, with pixel resolution of 384 × 384 pixels. A spectral bandpass filter (Asahi Spectra), centered at 313 nm with a 10-nm full-width at half-maximum, was used to isolate the \(\text{OH}^*\) emission from ambient light and other emission wavelengths. Image acquisition was triggered by the pressure rise caused by the passing of the incident shock wave, measured using a sidewall pressure transducer located 18 cm from the shock tube endwall.

Laser-induced spark ignition was initiated using a pulsed, Gemini 200 Neodymium-doped Yttrium Aluminum Garnet (Nd:YAG) laser, as described in Section 6.2.3. The laser is frequency-doubled and emits a single, 5-ns pulse at 532 nm in each experiment. Similar to the image acquisition system, the laser pulse was triggered approximately 900 µs after the arrival of the incident
shock wave 18 cm from the shock tube endwall. The beam was focused down to a waist of approximately 9 µm at the center of the shock tube, 10 cm from the shock tube endwall, using a 150-mm focal length, calcium fluoride lens. Although not measured directly for each experiment, the energy per laser pulse is estimated to be approximately 18 mJ. See Figure 7.1 for a schematic of the laser and imaging setups.

A detailed explanation of the methodology used to interpret the OH* images can be found in Section 6.3.1; however a brief overview of the process will be provided here. A multi-level Otsu method is used to binarize each image, and a Canny filter is used to detect the edges of each binarized flame image. The centroid of the flame is tracked in time, the relative radius is interpolated around the circumference of the flame in one-degree increments, and the resulting flame radius data is smoothed using a moving average filter. To obtain a pixel-to-cm scalar, an image was taken of a ruler placed in the shock tube at the 10-cm measurement plane.

The local stretch rate was calculated in regular intervals around the circumference of each flame image. The local burned flame speed was determined at the same intervals by calculating the component of the flame radius vector normal to the expanding flame front in time. Unstretched, burned flame speed was extrapolated from the burned flame speed vs. stretch rate data using a non-linear fit [142]; care was taken to fit the data over a range free of initial spark energy effects and before the onset of confinement effects or flame instabilities. Finally, the unburned, unstretched laminar flame speed was determined by multiplying the burned gas flame speed by the density ratio of burned-to-unburned gas, calculated at equilibrium.

The average uncertainty associated with the ethane laminar flame speed measurements presented in this work was ±4.6%, calculated by taking into account uncertainty in mixture composition, equivalence ratio, initial unburned gas temperature and pressure, the fidelity of the non-linear burned flame speed vs. stretch rate fit, and the repeatability of the measurement results at a given temperature.
Figure 7.1: Shock tube schematic with high-speed imaging and laser absorption diagnostics. (a) Top, cross-sectional view of the shock tube test section (note: the CO\textsubscript{2} and H\textsubscript{2}O diagnostics pass under the tube and up through optical ports 10 cm from the endwall); (b) View of the 10-cm measurement plane.
7.2. METHODS AND EXPERIMENTAL SETUP

7.2.3 Temperature, CO₂, and H₂O laser measurements

7.2.3.1 Theory and line selection

Scanned direct absorption (SDA) was used to spectroscopically measure temperature, CO₂ and H₂O mole fraction. In the SDA approach, laser light is wavelength-tuned across a spectral feature including one or more transitions so that absorbance can be integrated with respect to frequency:

\[
\int_{-\infty}^{\infty} \alpha_{\nu} d\nu = S_i(T)P X_{abs}L = A_i
\]

Here, \(\alpha_{\nu}\) is the spectral absorbance at frequency \(\nu\), \(S_i(T)\) is the linestrength of transition \(i\), \(T\) and \(P\) are the system temperature and pressure, \(X_{abs}\) is the mole fraction of the absorbing species, \(L\) is the time-varying path length, and \(A_i\) is the integrated absorbance. In this study, spectral absorbance data were fit according to the Voigt lineshape model. If two spectral transitions of the same species are sampled simultaneously, temperature can be measured by taking the ratio of the integrated absorbances, calculated using Equation 7.1. Having measured the temperature, and with the system pressure and path length known, the mole fraction of any measured species can be determined.

In these experiments, two CO₂ transitions, centered within close spectral proximity of one another near 4.19 \(\mu\)m, and a single H₂O transition, centered near 2.48 \(\mu\)m, provided the spectral basis from which temperature, CO₂, and H₂O mole fraction were measured. The CO₂ transitions, notated by \(R(v_3"=0,v_2"=0,J"=58)\) and \(R(v_3"=0,v_2"=1,J"=105,106)\), are members of the fundamental \(\nu_3\) band. These transitions have been used previously to determine temperature and CO₂ concentration in combustion applications at relatively low pressures (<1 atm) and high temperatures (>1500 K) [165, 166]. In the current work, the relatively high linestrength of the CO₂ transitions facilitated sensitive measurements with flame diameters as small as 1 cm. The H₂O transition, part of the \(\nu_3\) fundamental vibrational band with a linecenter frequency 4029.524 cm\(^{-1}\), has been previously targeted for sensitive measurements of water at moderate temperatures and pressures [20, 61]. With a high lower-state energy, this transition has the advantage of avoiding ambient water absorption.
7.2.3.2 Measurement scheme

The SDA approach was paired with a time-multiplexed collection scheme, by which one detector collects light from both lasers to simultaneously measure temperature, CO$_2$, and H$_2$O mole fraction. Distributed feedback interband cascade lasers (Nanoplus) were used for both diagnostics, and their transmitted intensities were recorded by a Vigo IR detector (model PVI-3TE-6).

All spectroscopic measurements were made along the same line of sight (LOS); both beams passed vertically through the shock tube, 10 cm from the endwall (see Figure 7.1b). To co-align the two beams, a thin, uncoated glass beamsplitter was oriented to transmit the H$_2$O beam while reflecting the CO$_2$ beam onto the pre-aligned H$_2$O laser path. The two lasers were wavelength-tuned with a 50% duty-cycle and offset from each other so that only one beam was measured by the detector at any given moment. Each laser was tuned below its respective lasing-threshold for the first 20% of the active cycle to provide a dark measurement for characterization of background signal fluctuations. The remaining 80% of the active cycle was dedicated to the spectral scan, which traversed roughly 0.5 cm$^{-1}$ for both lasers, centered about the absorption features of interest. Each diagnostic was cycled at a rate of 10 kHz, yielding 100-μs time resolution.

The interpretation of the raw absorption data required some noteworthy steps. First, the trend of the 20% non-lasing portion of data preceding each active cycle was considered across the entire experiment and fit in order to subtract and correct for any non-ideal signal fluctuations, primarily broadband emission, and to a lesser degree, beam-steering. While fitting each spectral region of interest according to the Voigt lineshape model, only the smallest section of data between non-absorbing scan sections was considered. The non-absorbing regions were confirmed by spectral simulation.

For the CO$_2$ feature, both lines involved in the two-color thermometry strategy, in addition to one auxiliary line (composed of two small transitions, both centered near 2384.1 cm$^{-1}$), were fit, and this produced low-residual fits across the range of conditions observed in each experiment (see Figure 7.2). Only measurements for which the high-temperature (i.e., the weaker) line had a peak absorbance above 0.1 were used, as low signal-to-noise ratio measurements often yielded inaccurate and misrepresentative fits. The H$_2$O feature includes absorption from primarily two
lines, both of which were considered in the fitting routine (see Figure 7.2). Some water data sets demonstrated non-correctable background fluctuations, causing poor lineshape fits, and were thus rejected. Uncertainty in the inferred background adjustment is the largest cause of scatter among the H$_2$O mole fraction measurements from shock to shock.

Figure 7.2: Typical measured CO$_2$ (left) and H$_2$O (right) absorbance for a single spectral scan with Voigt fit overlaid, above; fit residual normalized by maximum absorbance, below. Nominal test conditions: C$_2$H$_6$/air ($\phi = 1.0$), 488 K, 1.0 atm.

In typical shock tube laser absorption experiments, the path length of the absorbing species ($L$ in Equation 7.1) is a well-defined constant – the inner diameter of the shock tube. However, in the present experiments, the length of the absorbing medium is the diameter of the spherically expanding flame. To calculate a species mole fraction, it is therefore necessary to track the width of the flame along the LOS of the absorption diagnostics in time. To locate the beam path in space, a visible beam (650 nm) was co-aligned with the incoming absorption diagnostics; a notecard was placed in the beam path and the resulting scatter off the card was imaged and used to locate the LOS (see Figure 7.3a). A line was fit to the image of the beam path, the intersection points of the linear fit with the flame circumference were tracked in time, and the segment contained within each flame was taken to be the path length at that point in time (see Figure 7.3b-d); the path length corresponding to the time of each laser scan was determined by linear interpolation.
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Figure 7.3: Laser line of sight, superimposed on flame: (a) scattered from visible beam, with linear fit; (b) flame at 2.0 ms, with flame edge (green), LOS (dashed red), and path length (blue) indicated; (c) flame at 3.0 ms; (d) flame at 4.0 ms. Nominal test conditions: C$_2$H$_6$/air ($\phi = 1.0$), 488 K, 1.0 atm.
7.3. RESULTS

After an initial period of transience due to initial spark energy effects, the laser path length bounded by the flame circumference was found to increase linearly in time. To extend the available path length data to late times when flame radii extended beyond the $5.17 \times 5.17$-cm imaging window, a line was fit to the second half of the measured path length data and used to extrapolate late-time path length. It should be noted that this assumption of a constant path length rate-of-change breaks down at late times when flow field disturbances due to confinement effects cause the flame propagation rate to decrease [139]. Across all experiments, the average maximum path length used for the mole fraction measurements was 62% of the shock tube inner diameter.

A number of factors contribute to uncertainty in the measured path length: the ability to precisely line up the 40 kHz images with the 10 kHz laser absorption data ($\pm 1$ image, or $\pm 0.025$ ms), uncertainty in the location of the LOS (slope and lateral movement), and uncertainty associated with converting pixel length to centimeters. Over the subset of data used to determine the steady-state, burned gas temperature and composition for each experiment, the average path length uncertainty was estimated to be $\pm 0.05$ cm, or $\pm 0.7\%$.

The uncertainty associated with the temperature, CO$_2$, and H$_2$O measurements was estimated through error propagation of assumed independent sources. Sources of temperature error included fitting parameter and reference linestrength uncertainty, with a typical 1-$\sigma$ magnitude of $\pm 2\%$. Mole fraction error was influenced by the uncertainties of temperature, reference linestrength, pressure, path length, and the spectral fit. The 1-$\sigma$ magnitude of the CO$_2$ mole fraction measurement uncertainty was typically $\pm 6\%$, while that of H$_2$O was typically $\pm 10\%$, as a result of uncertainty in the background adjustments and relatively low absorbance.

7.3 Results

7.3.1 Ethane laminar flame speed results

Measurements of laminar flame speed, $S_0^o$, were conducted in ethane/air (21% O$_2$, 79% N$_2$) mixtures ($\phi = 1.0$) at initial unburned gas conditions of 449-537 K, 1 atm. The experimental flame speed results are presented in Figure 7.4.

No other high-temperature ethane/air flame speed results could be found in the literature for
comparison. However, the measurements can be compared with results calculated using the PRE-
MIX code in CHEMKIN-PRO [44, 155]. The flames were simulated as freely propagating, planar
flames. The computational domain was 40 cm long; an adaptive grid size and mixture-averaged
transport properties were employed. The following two kinetic models were used to model the
chemically reacting system: AramcoMech 3.0 [130] and USC Mech v2 [45].

As can be seen in Figure 7.4, the ethane laminar flame speed measurements show close agree-
ment with the modeled results, particularly those modeled using USC Mech. When compared with
the USC Mech results across the entire temperature range of interest, the flame speed measurements
show an average relative difference of 3.9%. The modeled AramcoMech results are systematically
low and show an average relative difference of 8.5% when compared to the measured flame speeds.
Overall, the USC Mech model results agree with the flame speed measurements within the uncer-
tainty associated with the measurements (±4.6%); the x-axis error bars represent uncertainty in the
calculated, initial unburned gas temperature (±0.4%).
7.3. RESULTS

7.3.2 Temperature measurement results

The time-resolved temperature measurement for a representative reflected-shock flame speed experiment, obtained using the two-line, SDA approach, can be seen in Figure 7.5a.

![Figure 7.5: Burned-gas temperature measurements: (a) time-resolved temperature measurement, relative to spark timing, for a representative reflected-shock flame speed experiment (initial unburned gas conditions: 488 K, 1.02 atm); (b) equilibrium burned gas temperature vs. unburned gas temperature. Model results are indistinguishable from each other.](image)

Before 2 ms, the temperature measurement is neglected because the peak absorbance of the high-temperature CO$_2$ line is below 0.1. Between 2 ms and 6 ms, the temperature increases and ultimately plateaus. This temperature increase is thought to be due to equilibration of CO$_2$ and H$_2$O in the burned gas and the path-integrated nature of the laser diagnostic – as the flame grows in diameter, the region composed of burned gas at thermal and chemical equilibrium grows as well, and eventually the steady-state temperature is the dominant temperature measured along the LOS. The burned gas temperature plateaus and remains constant 6 ms onwards. This constant temperature is indicative of a steady-state, burned gas region and indicates that heat loss due to radiation does not play an important role over the time frame of interest. The near-constant results also imply no significant temperature non-uniformity along the laser LOS.

For each experiment, the equilibrium burned gas temperature is taken to be the final temperature plateau value, averaged over 3 ms of data. For the experiment shown in Figure 7.5a, for example, the final burned gas temperature was 2293 K. Note that the temperature measurements are obtained
independent of calculated path length.

The equilibrium burned gas temperature for each flame experiment is plotted vs. initial unburned gas temperature in Figure 7.5b. The results are also plotted against simulated burned gas temperatures obtained using AramcoMech 3.0 and USC Mech v2; the modeled temperature results are statistically identical. The burned gas temperature measurements show excellent agreement with the model results – the majority of the temperature measurements agree with the model results within the uncertainty associated with the measurements (±3.2%, taking into account measurement repeatability).

7.3.3 CO\textsubscript{2} and H\textsubscript{2}O results

The time-resolved CO\textsubscript{2} and H\textsubscript{2}O mole fraction measurements for the same representative reflected-shock flame speed experiment shown in Figure 7.5a are presented in Figure 7.6. Similar to the time-resolved burned gas temperature measurements, the CO\textsubscript{2} and H\textsubscript{2}O mole fraction measurements increase between 2 and 6 ms before ultimately reaching a steady-state value. Once again, the equilibrium CO\textsubscript{2} and H\textsubscript{2}O values are taken to be the final plateau values reached in each experiment. Both time-resolved data sets are truncated after 8 ms, as the extrapolated path length behavior is known to deviate from linear beyond this point.

![Figure 7.6: Time-resolved (a) CO\textsubscript{2} and (b) H\textsubscript{2}O mole fraction measurements for a representative reflected-shock flame speed experiment. Initial unburned gas conditions: 488 K, 1.02 atm.](image-url)
The equilibrium, burned gas CO\textsubscript{2} and H\textsubscript{2}O mole fraction measurements for each flame experiment are plotted vs. initial unburned gas temperature in Figure 7.7. The measurements are also plotted alongside modeled CO\textsubscript{2} and H\textsubscript{2}O results (AramcoMech 3.0 and USC Mech v2). Once again, the two modeled burned gas compositions are statistically identical.

The CO\textsubscript{2} mole fraction measurements (Figure 7.7a) show excellent agreement with the simulated results; 63\% of the data points agree with the model results within the uncertainty bounds associated with the measurements (±9.2\%, taking into account repeatability), and the modeled results are largely encompassed by the scatter in the measurements.

The H\textsubscript{2}O mole fraction measurements (Figure 7.7b) also show a trend consistent with the modeled results. However, an average relative difference of 14.3\% is seen between the measurements and simulations. The average uncertainty associated with the H\textsubscript{2}O measurements is estimated to be ±18.0\%; this number takes into account the measurement uncertainty (±10\%) and the repeatability of the measurements at a given temperature. The high degree of scatter seen in the H\textsubscript{2}O measurements is largely due to the background fluctuations described in Section 7.2.3.2.
7.3.4 Pressure measurement results

The collisional width of an absorption transition is proportional to pressure. In scanned-direct absorption measurements such as those used to measure CO$_2$ and H$_2$O in the spherically expanding flames, the full-width half-maximum (FWHM) of a prominent absorption transition, $\Delta \nu_c$, can therefore be used to calculate pressure in the absorbing gas (see Figure 7.8).

![Figure 7.8: CO$_2$ absorption feature, with FWHM $\Delta \nu_c$ indicated (reproduced from Figure 7.2).](image)

The FWHM is typically modeled as the system pressure, $P$, multiplied by the sum of the mole fraction of each perturbing species, $A$, multiplied by collisional broadening coefficients, $2\gamma_{B-A}$, describing the collisional broadening associated with species $A$ colliding with the species whose lineshape is being studied, $B$:

$$\Delta \nu_c = P \sum_A X_A 2\gamma_{A-B}$$  \hspace{1cm} (7.2)

When a CO$_2$ absorption feature is studied, as in the measurements conducted in the ethane/air
flames, the FWHM expression becomes, for example,

$$\Delta \nu_c = P(X_{N_2} \cdot 2\gamma_{N_2-CO_2} + X_{CO_2} \cdot 2\gamma_{CO_2-CO_2} + X_{H_2O} \cdot 2\gamma_{H_2O-CO_2} + ...)$$  \hspace{1cm} (7.3)

where the summation includes all potential CO$_2$ collision partners (N$_2$, CO$_2$, H$_2$O, etc.).

If pressure is known at an initial condition, $P_o$, then system pressure at subsequent times can be related to the initial pressure by recognizing the following:

$$\frac{\Delta \nu_c}{\Delta \nu_{c,o}} \propto \frac{P}{P_o}$$  \hspace{1cm} (7.4)

Here, $\Delta \nu_{c,o}$ is the FWHM value calculated at the initial conditions. After an initial equilibration period, the temperature and species mole fractions within the ethane/air flames reach constant, steady-state values. In effect, after equilibrium is reached, the mole fraction and broadening coefficients in Equation 7.3 are constants. Therefore, at equilibrium, the proportionality stated in Equation 7.4 can be written as an equality; if pressure is known at one point in time, post-equilibration, the time-resolved pressure can be calculated from the time-resolved absorption feature scans.

$$\frac{\Delta \nu_c}{\Delta \nu_{c,o}} = \frac{P}{P_o} \rightarrow P = P_o \frac{\Delta \nu_c}{\Delta \nu_{c,o}}$$  \hspace{1cm} (7.5)

Figure 7.9 shows time-resolved pressure measurements conducted in a single ethane/air flame speed experiment: the pressure derived from the laser CO$_2$ measurements is plotted on top of a sidewall pressure transducer measurement for the same experiment. The optical pressure measurement shows close agreement with the mechanical measurement and largely agrees within the noise associated with the sidewall pressure measurement. Additionally, the laser-based pressure measurement captures the bulk-gas pressure rise at the end of the experiment, seen \(\sim 10\) ms onwards in the sidewall pressure measurement.

It should be noted that the optical and mechanical pressure measurements were conducted at different axial locations in the shock tube – the sidewall pressure transducer was located 2 cm from the endwall, while the laser diagnostic passes through the shock tube 10 cm from the endwall. The result is a slight shift in the time response of the two measurement techniques to pressure events.
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Figure 7.9: Pressure measured via piezoelectric transducer (Kistler) vs. pressure derived from SDA CO$_2$ measurements. Initial unburned gas conditions: 488 K, 1.02 atm.

occurring in the shock tube. For instance, a pressure wave traveling towards the endwall (as seen from 10-14 ms in Figure 7.9) will cause a pressure rise at the 10-cm location before it causes a pressure rise at the 2-cm location. For the experiment shown in Figure 7.9, the Region 5 speed of sound is approximately 434.3 m/s, indicating that it would take approximately 0.18 ms for a pressure wave to travel between the 10-cm location and the 2-cm location. This time offset explains why the laser pressure measurement registers a pressure rise at the end of the flame experiment slightly before the pressure transducer measurement does.

Overall, conducting scanned-direct absorption laser measurements in a burned-gas, equilibrium environment allows for the accurate measurement of pressure within a spherically expanding flame.

7.4 Conclusions

Laminar flame speed, temperature, mole fraction (CO$_2$ and H$_2$O), and pressure measurements were conducted in spherically expanding ethane/air flames at reflected-shock conditions of 449-537 K and 1 atm. High-speed, UV-intensified images of OH* emission were used to deduce flame speed relative to the burned gas, and a non-linear correlation was used to account for stretch effects.
7.4. CONCLUSIONS

The laminar flame speed results agree with the USC Mech v2 model predictions within 4% and are believed to represent the first high-temperature ethane flame speed dataset available in the literature.

Time-multiplexed, scanned direct absorption diagnostics were used to measure temperature, pressure, and CO$_2$ absorbance near 4.19 µm, and H$_2$O absorbance near 2.48 µm. The time-resolved temperature results confirm the presence of a quiescent, burned gas region within the flame, and the ultimate burned gas temperature results largely agree with model results within the uncertainty associated with the measurements. Time-dependent path length values, obtained from the high-speed imaging results, were used to determine CO$_2$ and H$_2$O mole fraction values. The CO$_2$ mole fraction measurements show close agreement with the model results (within uncertainty bounds), while the H$_2$O measurements show an average relative difference of 14.3% and higher scatter. Pressure measurements, obtained using the lineshape properties of the most prominent CO$_2$ absorption feature, also agree with mechanical pressure measurements within the noise associated with the measurements.

The results of the combined laminar flame speed/laser absorption experiments indicate that single line-of-sight laser diagnostics can successfully be applied to the study of spherically expanding flames in shock tubes, thereby allowing for burned gas temperature, pressure, and species measurements at previously unexplored temperature conditions. The effectiveness of using two co-aligned laser diagnostics to measure temperature, pressure, and species mole fractions is also an important observation. In many constant-volume (spherical bomb) flame speed experiments, optical access is limited and flame speeds are derived from sidewall pressure transducer measurements. The results presented here show that by using two optical diagnostics and a single line of sight (two small ports on opposing sides of an enclosure), the amount of information garnered from a single flame speed experiment can be dramatically increased.
Chapter 8

Conclusions

The full body of work presented in this dissertation details the development of two shock tube measurement techniques: a GC fast-sampling technique (in complement to *in situ* laser absorption diagnostics) and a laminar flame speed measurement technique. Although disparate in the information that they provide, both techniques were developed to aid in the development of kinetic models by providing data that could otherwise not be attained using common measurement techniques. As implemented, both techniques were used to probe low-temperature (<1200 K) pyrolysis and oxidation processes. The content of the preceding five chapters will be summarized here, followed by suggestions for future work.

8.1 Summary

8.1.1 Part I: GC fast-sampling in a shock tube

The GC fast-sampling technique was developed in three stages. First (Chapter 3), an endwall sampling system was developed to provide species yield measurements in conventional shock tube experiments. The diagnostic was paired with an *in situ* ethylene laser absorption diagnostic and used to study ethylene pyrolysis, providing measurements of C$_2$H$_4$, H$_2$, and C$_2$H$_2$ yields at conditions ranging from 1200-2000 K at 5 atm. A methodology for accurately comparing species-yield sampling results with laser and model results was also presented. The GC mole fraction results showed
close agreement with laser results, thereby validating the technique. The experimental results were compared with simulation results obtained using four kinetic models; the inconsistent model agreement indicates that further work is needed to understand the kinetics of ethylene pyrolysis.

In the second stage of GC fast-sampling technique development (Chapter 4), the endwall sampling system was applied to the study of low-temperature \( n \)-heptane oxidation. While endwall samples were still extracted after cooling induced by the arrival of the expansion fan (as in the initial diagnostic development work), quasi-time-resolved results were obtained by using a variable-length driver to change the timing of the expansion fan arrival at the shock tube test section. This approach allowed for the quasi-time-resolved quantification of intermediate species (\( \text{C}_2\text{H}_4 \), \( \text{CO} \), \( \text{H}_2 \), and \( \text{C}_3\text{H}_6 \)) present between first- and second-stage \( n \)-heptane ignition. Three laser diagnostics were simultaneously employed to measure temperature, \( \text{CO}_2 \), \( \text{H}_2\text{O} \), and \( \text{C}_2\text{H}_4 \). Laser-measured ignition delay times indicated an overestimation of three primary \( \text{RO}_2 \) isomerization reactions in the kinetic model used for comparison. The three reaction rates were modified to bring the model results into closer agreement with the measured results, and the modified model was used to simulate the quasi-time-resolved GC and \textit{in situ} laser results. Comparisons between modified-model and experimental results showed improved agreement in \( n\text{-C}_7\text{H}_{16} \), \( \text{C}_2\text{H}_4 \), \( \text{CO} \), \( \text{H}_2 \), and \( \text{C}_3\text{H}_6 \) results, indicating that the model modification broadly improves species mole fraction predictions.

In the third stage of technique development (Chapter 5), the endwall sampling system was expanded to include two additional sample lines to accommodate a total of three sampling events in each experiment. Long test-time shock tube experiments were conducted to allow for three consecutive, 10-ms samples to be extracted from the reacting shock tube gas before the arrival of the expansion fan. This time-resolved, fast-sampling technique was applied to the study of two relatively well-known, low-temperature pyrolysis systems: cyclohexene pyrolysis (1.4\% cyclohexene/argon, 980-1150 K, 7.3 atm) and ethane pyrolysis (1\% ethane/argon, 1060-1153 K, 6.9 atm). A time-resolved ethylene laser diagnostic was simultaneously used to provide truly time-resolved, \textit{in situ} results. In both pyrolysis systems, at experiment times <10 ms, GC, laser, and model \( \text{C}_2\text{H}_4 \) results show close agreement; however, at later times (>10 ms), laser and model results show satisfactory agreement, while the GC results are consistently low, by up to 30\%. After carrying out many troubleshooting experiments, it was determined that the late-time discrepancy between GC
and laser/model results is likely due to the increased thermal boundary layer thickness at late times.

The ultimate goal of the GC fast-sampling system is to provide broad speciation data with high
time-resolution in chemically reacting flows. The evolving GC sampling capabilities presented in
this dissertation – evolving from species yield measurements, to quasi-time-resolved measurements,
to time-resolved, pre-expansion fan measurements (with poor time-resolution, no less) – represent
a significant first step towards achieving this ultimate goal. Nevertheless, there is more work to be
done to ensure this technique reaches its full potential; suggestions for future work are outlined in
Section 8.2.1.

8.1.2 Part II: Laminar flame speed measurements in a shock tube

A new shock tube technique was presented for measuring high-temperature (>500 K) laminar
flame speeds (Chapter 6). Shock-heated gas mixtures are ignited via laser-induced spark-ignition
and high-speed, endwall emission imaging is used to capture flame propagation in time. The tech-
nique was used to measure stoichiometric methane/air and propane/air flame speeds at 1 atm and un-
burned gas temperatures below 600 K, and validated through comparison to available literature data
and model results. Stoichiometric, 1-atm, propane/modified-air flame speeds were then recorded at
unburned gas temperatures exceeding 750 K, representing the highest-temperature propane laminar
flame speed data available to date.

Next, single line-of-sight laser absorption diagnostics were deployed in the flame speed exper-
iments, allowing for the simultaneous measurement of laminar flame speed, temperature, species
(CO₂ and H₂O), and pressure in high-temperature, spherically expanding ethane/air flames (449-
537 K, 1 atm). The burned gas, equilibrium temperature and species measurements, as well as the
flame speed measurements, showed close agreement with model results.

As the shock-tube flame speed measurement technique approaches maturity, there are many
emerging opportunities for additional avenues of experimentation; suggestions for future work are
outlined in Section 8.2.2.
8.1.3 Summary of contributions

Significant contributions to the scientific community, stemming from the work conducted in this dissertation, include:

1. A method for accurately modeling post-expansion-fan, sampling-based, GC speciation results obtained in shock tube experiments. This method uses experimentally measured pressure traces to accurately simulate the temperature time-history of the reacting system, thereby improving upon the commonly used approach of assuming an average system temperature and pressure for an estimated reaction-time duration. This method is described in detail in Section 3.4.

2. The first direct comparison of species mole fraction measurements obtained using two different speciation techniques (GC sampling and laser absorption spectroscopy) in a single conventional shock tube experiment (see Chapter 3, specifically Section 3.5).

3. New insights into low-temperature $n$-heptane oxidation chemistry, specifically the fact that the heptylperoxy isomerization (RO$_2$ to QOOH) reaction rates found in common kinetic models are likely too fast, by almost a factor of two. (Chapter 4.4.1).

4. A new experimental technique for measuring laminar flame speeds at previously unexplored, high-temperature conditions (Chapter 6).

5. The highest-temperature laminar flame speed measurements for propane and ethane yet available in the literature (Chapter 6, Section 6.4.3, and Chapter 7, Section 7.3.1).

8.2 Future work

8.2.1 Future GC fast-sampling work

Due to the thermal boundary layer issues observed in the long test-time experiments, it is clear that for fast-sampled results to be accurate, all GC samples must be extracted within the first $\sim$10 ms of a shock tube experiment. Increasing the time-resolution of the GC fast-sampling measurements
is therefore a clear priority. This can only be achieved by reducing the amount of time needed to collect each GC sample; this will simultaneously increase the time-resolution of the GC fast-sampling measurements. There are multiple potential ways to reduce sampling time:

1. Change the geometry of the fast-acting solenoid valves used for sampling. The valve flow orifice is likely the choke point for flow into the sample lines. If the valve geometry was modified to accommodate a higher flow rate, the valves would not need to remain open for 10 ms to collect sufficient sample pressure.

2. Dilute lower-pressure samples to achieve higher sample pressures. If valve modification is not possible, a second option would be to sample for a shorter period of time (e.g., 2 ms), and then dilute each sample with a known amount of inert gas to attain sufficient sample pressure. This approach is not ideal, as it requires accurate knowledge of the dilution ratio and it requires sufficient species presence in the initial sample in order for it to remain detectable post-dilution.

3. Exclusively use this diagnostic in high-pressure experiments (e.g., >10 atm). Increasing the pressure of a shock experiment decreases the amount of time needed to extract a gas sample of equivalent pressure (and simultaneously retards the growth of the endwall thermal boundary layer). While this approach will work, functionally, to both reduce the sampling time and the impact of the thermal boundary layer on the sample composition, it limits the kinds of experiments that this diagnostic can be used to study. Additionally, experiments would need to be conducted to determine if the current Festo MHE3 valves can sustain higher pressures (they are rated to 8 bar, continuous pressure).

Once high time-resolution is achieved, the ultimate goal is to leverage the broad speciation capabilities of the GC fast-sampling system to investigate pressing chemical kinetic mysteries. For example, there is currently no widespread consensus about ethylene pyrolysis chemistry (see Section 3.5). Different kinetic modelers ascribe different levels of importance to the $C_2H_4 + H \leftrightarrow C_2H_3 + H_2$ and $C_2H_4 (+M) \leftrightarrow C_2H_2 + H_2(+M)$ reaction pathways. While the ethyl radical is difficult to measure, it is likely to recombine to form 1,3-butadiene ($C_4H_6$). At certain thermodynamic conditions, chosen specifically to slow down the pyrolysis chemistry, early-time GC
fast-sampling measurements of C\textsubscript{2}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{2}, C\textsubscript{4}H\textsubscript{6}, and H\textsubscript{2} (alongside time-resolved laser measurements of C\textsubscript{2}H\textsubscript{4} and C\textsubscript{2}H\textsubscript{2}) could potentially provide valuable insight into ethylene cracking ratios, based on C\textsubscript{2}H\textsubscript{2} and C\textsubscript{4}H\textsubscript{6} yields.

8.2.2 Future shock-tube laminar flame speed work

The shock-tube laminar flame speed measurement technique is still relatively nascent – the technique was only developed in earnest over the past three years. As such, there are many opportunities for data generation, innovation, and improved understanding of the underlying flame propagation phenomena. Some of these future directions are outlined here.

1. There is still an unanswered question as to the direct cause of the multi-front flames observed in certain temperature regimes (see Section 6.5). To further probe this phenomenon, additional imaging experiments need to be carried out, ideally providing visualization of the flames from the sidewall of the shock tube.

2. To date, all of the laminar flame speed shock-tube experiments have been conducted at or below 2 atm. To make the measurements truly relevant to modern-day combustion systems, the measurement pressures must be much higher (>10 atm). A primary goal of the next phase of experiments should be to conduct measurements at higher pressures.

3. High-temperature flame speed data is valuable to the combustion community. Therefore, time should be invested in generating and publishing a database of high-temperature laminar flame speed measurements at varied temperatures, pressures, stoichiometries, etc., for fundamental hydrocarbon fuels (C\textsubscript{1}-C\textsubscript{4} alkanes and alkenes, for a start).

4. Shock-tube laminar flame speed measurements to date have been limited to CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, C\textsubscript{3}H\textsubscript{8}, n-heptane, and iso-octane. Future experiments should involve the measurement of flame speeds of practical fuels and fuel mixtures, e.g., natural gas, gasolines, diesels, and jet fuels, as well as their additives and bio-derived alternatives.
Appendix A

AST facility specifications

A.1 Facility dimensions (driver/driven)

Table A.1: AST facility dimensions

<table>
<thead>
<tr>
<th>Driven Section</th>
<th>Length</th>
<th>Inner diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>9.73 m</td>
<td>11.53 cm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Driver Section</th>
<th>Length (short)</th>
<th>Length (+1 extension)</th>
<th>Length (+2 extensions)</th>
<th>Length (+3 extensions)</th>
<th>Inner diameter (no negative inserts)</th>
<th>Inner diameter (with negative inserts)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3.63 m</td>
<td>7.74 m</td>
<td>9.57 m</td>
<td>13.42 m</td>
<td>17.8 cm</td>
<td>11.5 cm</td>
</tr>
</tbody>
</table>

A.2 PCB locations
## Table A.2: AST PCB locations

<table>
<thead>
<tr>
<th>PCB #</th>
<th>Distance from endwall (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>278.32</td>
</tr>
<tr>
<td>2</td>
<td>197.06</td>
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<tr>
<td>3</td>
<td>166.61</td>
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<tr>
<td>4</td>
<td>136.14</td>
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<td>5</td>
<td>105.68</td>
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<td>6</td>
<td>64.82</td>
</tr>
<tr>
<td>7</td>
<td>26.76</td>
</tr>
<tr>
<td>8</td>
<td>18.51</td>
</tr>
<tr>
<td>9</td>
<td>10.25</td>
</tr>
<tr>
<td>10</td>
<td>2.00</td>
</tr>
</tbody>
</table>
Appendix B

Species-yield GC measurements with *in situ* LAS: Supplemental material

**B.1 Optimal sample line temperature determination**

To determine the optimal heated temperature for the sample lines, a study involving benzene was conducted. Benzene is a notoriously "sticky" molecule; it adsorbs to surfaces easily, which can lead to significant losses. In this study, a 2000-ppm sample of benzene was introduced to a sample volume. First, the sample composition was analyzed at room temperature (\(\sim 25^\circ C\)). Next, the sample line was heated, roughly in increments of 5 °C, and a new sample was extracted and analyzed at each temperature set point to determine the impact of heating on measured benzene content. Between each increase in temperature, the sample line was given 30 minutes to thermally equilibrate before a new sample was extracted and analyzed. The results of the study are shown in Figure B.1.

As can be seen in the figure above, heating the sample line has a significant impact on the resulting benzene measurement. (Note: benzene content is presented as peak area, which is proportional to mole fraction.) Just by increasing the temperature of the line from 25 °C to 32 °C, the measured amount of benzene present increases by a factor of 1.7. By increasing the temperature from 25 °C to 46.5 °C, the amount of benzene nearly doubles. Above 36 °C, the change in benzene composition...
B.2. Validation experiments

Experiments were conducted to validate the steady-state, species yield results obtained using the first iteration of the GC sampling system: driver gas dilution experiments, non-reactive/cold shock experiments, sampling location (endwall vs. sidewall) experiments, and depth-of-sample experiments. Unless otherwise specified, these validation experiments were primarily conducted using a sidewall sampling system, as sampling from the sidewall represents a worst-case scenario for almost all of the phenomena being explored: driver gas dilution would reach a sidewall sampling location (2 cm from the endwall) before it would reach the endwall, and sidewall depth-of-sample is less pronounced as temperature is further increased; between 40.5 °C and 46.5 °C, for example, the benzene composition only increases by 6.1%. The asymptotic nature of the benzene vs. temperature curve indicates that when the sample line is heated above a certain temperature (e.g., 50 °C), benzene adsorption (moreover, adsorption by any "sticky" molecule) can largely be avoided. In all of the GC sampling experiments presented in this dissertation, the sample lines are heated and maintained above 60 °C, specifically to minimize species adsorption.
experiments are expected to show the greatest differences due to the sidewall boundary layer being thicker than the endwall boundary layer; whether the sample is extracted from the sidewall or endwall is not expected to change how the sampling event itself impacts the measurement outcome (non-reactive/cold shock experiments). A description of the sidewall sampling system, and how it differs from the endwall sampling system, will be presented first, followed by the results of the validation experiments.

B.2.1 Sidewall sampling system overview

For sidewall sampling experiments, a fast-acting solenoid valve (Festo MHE3) – the same valve used in the endwall sampling experiments – is mounted on top of the shock tube, 2 cm from the shock tube endwall via a custom-made sidewall plug. The volume residing within the plug is estimated to be 0.63 mL (just over half of the 1.05 mL of dead volume in the endwall sampling plugs). A 1/4-inch diameter, 33-inch long, stainless steel tube is attached to the Festo sampling valve and serves as the containment vessel for the extracted gas sample (total volume of 14.6 mL – slightly larger than the 8.4 mL extracted in the endwall sampling experiments). The last 4.8 inches of the sample line resides between two 1/4-turn ball valves, which, similar to the endwall experiments, allows the first 2.2 mL of sample to be isolated from the bulk of the extracted gas sample. The sidewall sampling system is diagrammed in Figure B.2.

Figure B.2: Shock tube schematic with GC sidewall sampling system
B.2.2 Dilution experiment results

As described previously (Section 3.3.3), the duration of the post-shock sample extraction from the shock tube was 0.8 seconds. To confirm that no dilution of the post-shock sample by helium driver gas occurs over this extended time period, and to evaluate the arrival time of the driver/driven gas contact surface at the shock tube endwall, seven helium driver gas/argon driven gas shock experiments were conducted at nominal test conditions of 1920 K and 4.7 atm. The sidewall sampling configuration described in Section B.2.1 was used for these experiments. The sampling duration was held constant at 1 second for each experiment (0.2 seconds longer than the typical experimental sampling time), but the sample delay time (sample initiation time after the arrival of the reflected shock wave at the sampling location, 2 cm from the end wall) was varied from 0 to 2.25 seconds. The GC molecular sieve (MS 5Å) column was calibrated to detect trace amounts of helium (< 300 ppm). The results can be seen in Figure B.3.

![Figure B.3: Helium present in post-shock sample as a function of sample delay time (sample duration held constant at 1 sec)](image)

In post-shock samples collected less than 1.5 seconds after the arrival of the reflected shock (i.e., delay time of 0.5 sec + 1 sec sample time), no helium is detected; in samples collected between 1.5 and 2.75 seconds, up to 50 ppm helium are detected; in samples collected after 2.75 seconds,
the amount of helium present increases dramatically. These results indicate that if the end of the sample time is less than 1.5 seconds after the arrival of the reflected shock, no significant sample dilution will occur under these shock conditions. It should be noted that the scatter in the helium measurement at long sample delay times is thought to be due to the non-uniformity of the contact surface interface.

The results illustrated in Figure B.3 represent a worst-case scenario for post-shock sample dilution. At lower test temperatures (obtained by increasing initial test gas fill pressures), the contact surface arrival at the sampling location is further delayed, due to slower diffusion through the test gas. It can therefore be concluded that for the samples extracted over 0.8 seconds at the conditions of interest in the species-yield experiments (1200-1900 K, ∼5 atm), dilution of the post-shock samples by helium driver gas is not a concern.

It is also worth noting that in all GC sampling experiments presented in this dissertation, driver gas dilution can always be detected through use of the molecular sieve, MS 5Å column of the GC. So, although these validation experiments indicate that it takes greater than 1.5 seconds for driver gas helium to make it to the sidewall sampling location, this dilution effect can be checked in real time for each experiment, without the need to conduct a separate set of validation experiments with each new sampling system iteration. Similarly, the same GC column can be used to detect major constituents of air (e.g., N₂ and O₂), providing a valuable, real-time check on whether or not the sample lines or sampling valves are leaking to the outside air. In the case that a leak is detected, the results are discarded, time is taken to diagnose and fix the problem, and the experiment is rerun.

**B.2.3 Non-reactive shock experiment results**

A series of experiments was conducted to confirm that the sampling event itself does not change the composition of the extracted sample. A 0.2% ethylene/balance argon fuel mixture was shock-heated to ∼6 atm and ∼1000 K – a temperature low enough that no thermal decomposition would occur. Once again, the sidewall sampling configuration was used, and the sampling valve was opened for 0.8 sec, starting 10 msec after the arrival of the reflected shock wave at the sampling location.

As seen in Table B.1, GC analysis of post-shock gas samples from five “cold” shock experiments
shows 99.8% recovery of the initial ethylene at these conditions. This indicates a 5 ppm loss of ethylene, on average, between the source gas mixture and the recovered sample analyzed by the GC. These results suggest that at these conditions, negligible dilution occurs and the composition of the sample extracted from the shock tube is statistically identical to the composition of the gas at the core of the shock tube.

Table B.1: Cold shock results: GC-measured ethylene mole fractions ($T_5 \sim 1000K$, $P_5 = 6.0\text{-}6.3$ atm). Nominal, initial ethylene mole fraction is 0.2%.

<table>
<thead>
<tr>
<th>Shock Number</th>
<th>$T_5$ (K)</th>
<th>GC-Measured C\textsubscript{2}H\textsubscript{4} Mole Fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1050</td>
<td>0.1998</td>
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<tr>
<td>2</td>
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<td>3</td>
<td>990</td>
<td>0.1995</td>
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<td>4</td>
<td>1055</td>
<td>0.1993</td>
</tr>
<tr>
<td>5</td>
<td>1060</td>
<td>0.1996</td>
</tr>
</tbody>
</table>

### B.2.4 Impact of sampling location: sidewall vs. endwall sampling

Sidewall boundary layer growth in shock tubes has been studied extensively, and various models have been developed to describe them [13, 89, 167]. Due to the temperature gradient between the shock tube wall and core, the gas that resides in the boundary layer experiences a different, colder temperature time-history than the gas at the core of the shock tube. As the thickness of the boundary layer through which a sample is being extracted increases, the fraction of "colder" gas in the sample increases. Experiments conducted using optical techniques [168] have shown that the thermal boundary layer that forms along the sidewall is thicker than the thermal boundary layer at the endwall.

Nevertheless, it’s worth noting that the samples extracted in these species-yield experiments are not being directly extracted through boundary layers resembling those described by conventional models. These sample extraction events are starting 10 ms after the arrival of the expansion fan and ending 800 ms later. At these timescales, thermal and mass diffusion have occurred, thereby lessening the impact of the boundary layer on the composition of the sampled gas.

To determine the extent to which sampling through the thicker sidewall boundary layer impacts the composition of the sampled gas, shock experiments at various conditions were performed –
first using the sidewall sampling system, then using the endwall sampling system. A 1.0% ethylene/argon fuel mixture was shock-heated to 5 atm and a range of low and high temperatures. By conducting experiments at temperature extrema, the impact of the sampling process on the fuel measurement could be isolated from its impact on product species formed during the pyrolysis process: low-temperature conditions highlight the impact on species formed during the ethylene pyrolysis process, and high-temperature conditions highlight the impact on the fuel, as their respective sampled mole fractions are lowest at those temperatures. It should be noted that both sampling systems (sidewall and endwall) were designed to isolate the first 2.2 mL extracted from the shock tube from the rest of the sampled gas (Section 3.3.3). As such, the results obtained in these experiments are more a comment on the effectiveness of the isolation method when sampling is conducted through a thick boundary layer than a true measurement of the amount of boundary layer gas contained in the extracted sample overall.

GC analysis of the gas samples extracted in this set of experiments focused on three species: ethylene (C\textsubscript{2}H\textsubscript{4}), hydrogen (H\textsubscript{2}), and acetylene (C\textsubscript{2}H\textsubscript{2}). As can be seen in Figure B.4a, the low-temperature sidewall C\textsubscript{2}H\textsubscript{4} measurements are statistically identical to the endwall measurements. This is to be expected, as below 1400 K, less than 10% of the C\textsubscript{2}H\textsubscript{4} has decomposed by the end of the test time; the high mole fraction value minimizes the impact of any slight dilution due to sampling through a thicker boundary layer. Above 1800 K, however, there is a clear difference in C\textsubscript{2}H\textsubscript{4} mole fraction between samples extracted through the sidewall and samples extracted through the endwall. The sidewall C\textsubscript{2}H\textsubscript{4} measurements exhibit significantly more scatter than the endwall measurements (most likely due to the non-uniformity of the sidewall boundary layer at long times), and are at times more than 100% greater than the endwall measurements. The artificial C\textsubscript{2}H\textsubscript{4} enrichment observed in the sidewall samples indicates that the colder gas residing in the sidewall boundary layer is diluting the final sidewall sample.

The results presented in Figure B.4b and Figure B.4c provide additional insight into the composition of the colder sidewall boundary layer gas. Unlike the C\textsubscript{2}H\textsubscript{4} measurements, the H\textsubscript{2} and C\textsubscript{2}H\textsubscript{2} sidewall and endwall measurements are statistically identical at both the low- and high-temperature extrema. This agreement indicates that although there may be sample dilution occurring in the sidewall experiments, the diluent contains very little H\textsubscript{2} or C\textsubscript{2}H\textsubscript{2}. The enrichment seen in the
B.2. VALIDATION EXPERIMENTS

Figure B.4: Comparison of GC mole fraction measurements of three species (C\textsubscript{2}H\textsubscript{4}, H\textsubscript{2}, C\textsubscript{2}H\textsubscript{2}) obtained from sidewall and endwall samples.
high-temperature C$_2$H$_4$ measurements confirms that the diluent is primarily made up of the initial C$_2$H$_4$/argon fuel mixture and has not reacted to the same extent as the core gas.

From the direct comparison of the sidewall and endwall sampling techniques, it can be concluded that when using an appropriate method for isolating the bulk of the boundary layer gas contained in the sample, sidewall and endwall measurements of species not present in the initial test gas are in agreement. However, when a sidewall sampling technique is used to measure the concentration of species found in high concentration in the initial test gas mixture, these measurements can be artificially enriched by the unreacted gas present in the sidewall boundary layer; this effect is particularly apparent when only trace amounts of the initial fuel component are contained in the core gas.

**B.2.5 Impact of sampling depth**

Experiments were conducted to determine if sampling boundary layer gas could be avoided altogether through use of a protrusion to extract a sample from outside the sidewall boundary layer and/or its diffusion zone. Two different 1/8-inch outer diameter, stainless steel tubes were used to allow for post-shock sampling from three different depths within the shock tube: 22 mm from the sidewall (3.5 cm from the shock tube center), 5 mm from the sidewall, and at the sidewall (no probe). Shock experiments using all three protrusion lengths were conducted with a 1% ethylene/argon test gas mixture at approximately 5 atm and 1600 K. The test times for these experiments were nominally 3 msec. Due to the relative insensitivity of H$_2$ and C$_2$H$_2$ mole fraction measurements to sampling through the boundary layer (see Section B.2.4), only C$_2$H$_4$ results will be presented here.

At 1600 K, ethylene decomposition is highly sensitive to temperature. As can be seen in Figure B.5, even a 1% change in temperature can lead to an almost 10% relative change in species mole fraction yield. In an effort to decouple the effects of this temperature sensitivity from differences caused by sample extraction location, a linear fit of species mole fraction measured from the sidewall (i.e., no probe) vs. $T_5$ data has been superimposed on the plot. This line indicates how the ethylene measurements are expected to trend with temperature.

A slight variation in measured ethylene mole fraction can be observed in samples taken from
B.2. VALIDATION EXPERIMENTS

Figure B.5: Comparison of GC-measured ethylene mole fractions from samples extracted at different distances from the shock tube sidewall. Nominal reflected-shock test conditions: 5 atm, ∼1600 K, 3 msec test time.

different depths within the shock tube at the same temperature. The no-probe (sidewall) measurements are consistently higher at all of the temperature points, and the 22-mm and 5-mm long probe measurements are lower and relatively indistinguishable from each other. These results indicate that using a protrusion to sample from outside the boundary layer is an effective tool for mitigating the artificial sample enrichment seen in sidewall measurements taken without a protrusion. Additionally, due to the close agreement of the 5-mm and 22-mm datasets, it would appear that increasing the length of the protrusion beyond 5 mm yields no added benefit. In fact, protruding too far into the flow could change the test conditions by causing non-ideal shock interactions.

The use of a protrusion was also studied at higher temperatures. This time, the sidewall measurements were compared to endwall measurements, with and without a 5-mm protrusion. The shock experiments were conducted using the same 1% ethylene/argon test gas mixture; nominal Region 5 test conditions were 1850-1900 K at 4.7 atm, with a test time of approximately 1.5 msec. Above ∼1850 K, the ethylene yield measurements are not expected to be highly temperature-dependent.

The most striking thing about Figure B.6 is the significant scatter seen in the sidewall measurements taken without using a probe: at approximately the same reaction conditions (1865 K,
Figure B.6: Comparison of GC C₂H₄ mole fraction measurements obtained from sidewall (SW) and endwall (EW) samples, with and without a 5-mm protrusion. Nominal test conditions: 1% C₂H₄/argon test gas, 4.7 atm, ~1850-1900 K, 1.5 msec test time.

4.7 atm), a difference of almost 100% can be observed between two different sidewall measurements. In contrast, sidewall measurements taken with the 5-mm probe agree within 30 ppm of each other, and largely agree with the measurements taken using the endwall sampling system. The protrusion also appears to have a small effect on the endwall measurements – without a protrusion, the measurements are on average 45 ppm higher than those taken with the protrusion.

Use of a protrusion to extract a sample from outside the sidewall thermal boundary layer clearly shows a significant improvement over sampling through the boundary layer – the results are more repeatable and agree more closely with measurements taken through the endwall, which experience minimal boundary layer influence. Measurements taken through the endwall also appear to benefit from use of a small protrusion. It has therefore been concluded that the optimal GC sampling system configuration (for species-yield, post-expansion fan measurements) is one that extracts a sample through the endwall, using a minimally invasive protrusion. This design has ultimately been incorporated into the endwall sampling system described in subsequent chapters of the dissertation.
B.2.6 Summary of validation results

Experiments were conducted to validate the results obtained using the GC sampling system. It was shown that samples extracted over 0.8 seconds would not experience driver gas dilution at the conditions of interest. Non-reactive shock results show that the sampling event itself does not change the composition of the sampled gas, as 99.8% of the pre-shock ethylene concentration was retained. A comparison of sidewall and endwall sampling experiment results shows that post-shock samples extracted from the shock tube sidewall are more susceptible to dilution from boundary layer gas than endwall samples. This dilution has the largest impact on the measurement of species contained in the initial test gas mixture. Experiments conducted with probes protruding beyond the boundary layer indicate that by extracting a post-shock sample from just outside the boundary layer, dilution in both sidewall and endwall samples can be reduced.

B.3 Pressure trace impact on model results

When model results are generated using a specified-pressure approach, it is important to understand how the pressure trace provided to the model can impact the simulated species results. In a shock tube experiment, pressure is typically recorded at a rate of 1-10 MHz. If a pressure trace of that time resolution is fed into a model (total experiment time of, say, 8 ms), the amount of time it takes to complete the simulation will be significant, and the model may experience convergence errors, as the measurement includes rapid pressure fluctuations due to bit noise. A more common approach is to smooth the data before supplying it to the model, either by taking a moving average or calculating a series of cubic splines. In short test-time experiments with particularly well-behaved pressure traces, the Region 5 pressure is also sometimes assumed to be constant – an average over the entire region. Figure B.7 shows the impact of pressure trace smoothing/simplification on modeled mole fraction results, particularly those extended into the expansion fan. The impact of four different pressure traces is modeled: a raw pressure trace (solid red line) and its corresponding modeled \( \text{C}_2\text{H}_4 \) result (dashed red line); a constant, average \( P_5 \) with an appended spline of the expansion fan pressure (solid blue line) and its corresponding \( \text{C}_2\text{H}_4 \) mole fraction result (dashed blue line); a full spline of the Region 5 pressure and ensuing expansion wave, with spline knots spaced every
Figure B.7: Impact of pressure trace smoothing on kinetic model results: raw pressure trace, constant average $P_5$ with splined expansion wave trace, full Region 5 spline with more vs. fewer knots. Nominal test conditions: 1% $C_2H_4$/argon test gas, 1602 K, 5.1 atm.

0.1 msec (solid green line), and its corresponding model result (dashed green line); and finally, a full spline of the Region 5 pressure and ensuing expansion wave, with spline knots spaced every 0.4 msec (solid black line), and its corresponding $C_2H_4$ model result (dashed black line).

From the results in Figure B.7, it’s interesting to see that how a pressure trace is smoothed or simplified really does have a significant impact on the subsequent model results. Using the raw pressure trace, with bit noise fluctuations, leads to a much higher $C_2H_4$ mole fraction result. Also, simply assuming a constant, average $P_5$ value leads to a much lower subsequent model result. (These two approaches show an average relative difference of 11.0%). It should be noted, however, that the efficacy of the constant, average $P_5$ approach will depend on precisely how flat the pressure trace it’s trying to emulate really is; for example, in the experiment shown in Figure B.7, there is a slight, overall drop in pressure over the first 0.5 msec of the experiment – a sign that a constant, average $P_5$ value is perhaps not the best option for approximating pressure in this particular experiment. Finally, it is interesting to note that the two spline results actually show close agreement; the ultimate $C_2H_4$ values obtained using both fits agree within 1.4%.

Overall, this analysis indicates that when modeling a kinetic system using the specified-pressure approach (providing a kinetic simulator like CHEMKIN-PRO with a time-resolved pressure trace
to constrain system pressure), it is important that the data be smoothed to remove rapid signal fluctuations caused by measurement bit-noise. It is suggested that the raw data be smoothed, using a moving average or spline approach. While the precise spacing of splines/averaging window does not drastically impact the final, simulated species results, implementing this approach may add uncertainty on the order of 1-2% to the final species results. Analysis of the impact of pressure trace simplification on model results should be carried out for each kinetic system of interest.

**B.4 Carbon/hydrogen recovery results**

An important indicator of whether or not a GC analysis has captured all relevant species is the amount of carbon and hydrogen recovered in the measurement. With a known amount of fuel (carbon and hydrogen) going into the system, a thorough GC analysis will yield carbon and hydrogen recoveries of 95% and above. Figure B.8 shows the carbon and hydrogen recovery results for the 1% C\textsubscript{2}H\textsubscript{4}/Ar temperature sweep, species-yield results (four analyzed species: C\textsubscript{2}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{2}, H\textsubscript{2}, CH\textsubscript{4}) presented in Chapter 3, Section 3.5.

As can be seen in the carbon recovery results in Figure B.8a, at temperatures below 1700 K, upwards of 95% of the carbon in the system is recovered. However, above 1700 K, the carbon recovery drops, ultimately reaching a minimum of 75% recovery. This drop is mirrored in the decline
in C₂H₂ mole fraction. These trends indicate that the three carbon-containing-species analysis presented in the C₂H₄ pyrolysis results is likely missing at least one species that only begins to form at temperatures above 1700 K, and is likely a product of C₂H₂ pyrolysis. The hydrogen recovery plot (Figure B.8b) offers additional insight into what this species may be.

In the hydrogen recovery plot, >90% of the hydrogen is recovered over the entire temperature range. However, the hydrogen recovery, like the carbon recovery, does begin to drop slightly above 1700 K; this downward trend is much less pronounced than the change seen in the carbon recovery plot. The fact that the hydrogen recovery plot does not decrease as much as the carbon recovery plot indicates that the missing species likely contain(s) more carbon than hydrogen. Carbon and hydrogen recovery results, calculated from kinetic model simulations incorporating one additional species – diacetylene, or C₄H₂ – confirm this hypothesis.

![Figure B.9: Simulated carbon and hydrogen recovery results for ethylene pyrolysis species-yield measurements. 1% ethylene/argon test gas, 5 atm. Simulated using USC Mech II [45].](image)

The simulated carbon and hydrogen recovery plots shown in Figure B.9 show that >95% of the system carbon and hydrogen can be recovered across the entire temperature range, simply by accounting for one additional species. Unfortunately, diacetylene cannot be purchased off-the-shelf, thereby making GC quantification of diacetylene a non-trivial matter.
B.5 Impact of subsequent reflected shocks on GC sampling results

In a conventional shock tube configuration, no dump tank is used to dampen subsequent shocks after the conclusion of the experiment test time. As a result, the post-shock samples extracted from the shock tube (the extraction of which ends 0.81s after the reflected shock arrival) undergo additional compression and expansion processes due to reflected shocks and expansion fans before GC analysis. The first reflected-reflected shock to reach the test section will be the strongest, therefore its impact on the test gas must be quantified.

Figure B.10: Pressure-contour x-t diagram for 1% C$_2$H$_4$/argon test gas, 1602 K, 5.1 atm ethylene pyrolysis experiment

To determine whether the reflected-reflected shock impacts the sampled ethylene pyrolysis results (i.e., promotes additional decomposition), a representative shock tube experiment was modeled using the Wisconsin Shock Tube Laboratory (WiSTL) 2nd order, Muscl-Hancock-Method finite volume code [169] and an x-t diagram was generated. The pressure-contour x-t diagram for a mid-temperature 1% ethylene/argon experiment (1602 K, 5.1 atm) is shown in Figure B.10.

It can be seen in the x-t contour diagram that after the incident shock has been reflected (∼12 ms), the test gas has been shocked to 5.1 atm, as expected. The maximum pressure attained by the test gas after the reflected shock makes it back to the test section about 32 ms later is calculated to be
Figure B.11: Long-time pressure trace recorded for 1% C\textsubscript{2}H\textsubscript{4}/argon test gas, 1602 K, 5.1 atm ethylene pyrolysis experiment

approximately 2.8 atm. The corresponding temperature in this region is less than 1300 K, indicating no additional pyrolysis of the sampled gas species is expected to occur.

For this same experiment, pressure data was collected long after the arrival of the initial expansion fan. As can be seen in Figure B.11, the pressure data captures the arrival of the reflected-reflected shock just after 30 ms. The pressure of the test gas after this reflected-reflected shock is approximately 2.7 atm – very close to the post-reflected-reflected-shock pressure estimated using the WiSTL code.

It can therefore be concluded that although the post-shock sampled gas will experience additional shocks before extraction, the shocks are too weak to promote additional pyrolysis and thus have little effect on the experimental results presented in the accompanying manuscript. However, it should be noted that reflected-reflected shocks could alter the composition of samples containing larger hydrocarbon fuels, or fuels that begin to pyrolyze at temperatures below 1300 K.
Appendix C

Quasi-time-resolved GC measurements with in situ LAS: Supplemental material

C.1 Mixture enrichment of liquid fuels

In shock tube experiments involving liquid or low-vapor pressure fuels (e.g., n-heptane), the fuel is introduced to a diluent or oxidizer mixture using the method of partial pressures (manometrically). After the liquid fuel is purified using the freeze-pump-thaw method, the bulb containing the fuel is heated and opened to the evacuated mixing manifold/mixing tank, thereby allowing fuel vapor to form, travel through the manifold, and enter the mixing tank. The vapor from the bulb is allowed to fill the mixing tank until the desired fuel partial pressure is reached; the bulb is then closed off from the manifold and the additional mixture components are added to the mixing tank until the mixture is complete. The mixture is then actively mixed, using a series of fan blades internal to the mixing tank, for at least an hour.

Over the course of completing the low-temperature \(n\)-C\(_7\)H\(_{16}\) oxidation experiments, it was observed that even when a manometric target of 1% \(n\)-C\(_7\)H\(_{16}\) was consistently maintained in mixture preparation, the initial fuel mole fraction recorded in the shock tube using a 3.41-\(\mu\)m absorption diagnostic did not reflect the same composition. Each mixture was used to run three experiments; the initial \(n\)-C\(_7\)H\(_{16}\) fuel loading mole fraction measurements for 16 experiments (conducted using 6
mixtures – all manometrically mixed to have a nominal composition of 1% $n$-C$_7$H$_{16}$) are plotted in Figure C.1.

As can be seen in Figure C.1, over the course of three consecutive shock experiments, conducted using a single mixture, clear mixture enrichment occurs: between experiment 1 and experiment 2, the $n$-C$_7$H$_{16}$ fuel mole fraction increases, and between experiment 2 and experiment 3, the $n$-C$_7$H$_{16}$ fuel mole fraction increases further. Using a single mixture, the initial fuel mole fraction observed in the shock tube can vary by up 5%.

This mixture enrichment phenomenon is likely caused by adsorption and desorption of the low-vapor pressure $n$-C$_7$H$_{16}$ in the mixing tank. When the $n$-C$_7$H$_{16}$ is first introduced to the mixing tank, a portion of it likely adsorbs to the walls of the mixing tank. As experiments are conducted and the pressure in the mixing tank drops, $n$-C$_7$H$_{16}$ gradually desorbs from the mixing tank walls, thereby leading to mixture enrichment over time. One way to prevent this from happening would be to heat the walls of the mixing tank. However, this leads to additional experimental complications when running experiments in an unheated shock tube. In a typical unheated experiment, the initial gas temperature, $T_1$ is typically ambient temperature; however, if a heated mixture is introduced to an unheated shock tube, what then, is $T_1$? It is some unknown value between room temperature and
the temperature of the heated gas residing in the mixing tank.

To summarize, mixture enrichment over time is to be expected when running experiments with low-vapor pressure fuels. If enrichment cannot be prevented through use of a heated mixing tank and shock tube, the initial fuel mole fraction must be carefully measured in situ to ensure accurate accounting of fuel loading in the shock tube.
C.2 Additional GC measurements: 1-alkenes

Figure C.2: Comparison of GC and model results of final 1-C₃H₆, 1-C₅H₁₀, 1-C₇H₁₄ mole fractions as a function of dwell time
C.3 Summary of experimental conditions and dwell times
### Table C.1: Initial, calculated post-shock temperature and pressure conditions ($T_{5,\text{init}}$, $P_{5,\text{init}}$), test gas mixture composition, and experiment dwell times ($\Delta \tau_{\text{dwell}}$, defined as the time between the onset of first-stage ignition, $\tau_{\text{IDT}}$, and the arrival of the expansion fan, $\tau_{\text{test}}$) for each individual, $n$-$C_7H_{16}$ oxidation shock experiment

<table>
<thead>
<tr>
<th>Shock #</th>
<th>$T_{5,\text{init}}$ (K)</th>
<th>$P_{5,\text{init}}$ (atm)</th>
<th>Initial $n$-$C_7H_{16}$ MF</th>
<th>Initial $O_2$ MF</th>
<th>Initial CO$_2$ MF</th>
<th>Initial Ar MF</th>
<th>$\Phi$</th>
<th>$\Delta \tau_{\text{dwell}}$ (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>764</td>
<td>4.8</td>
<td>0.0099</td>
<td>0.2083</td>
<td>0.0021</td>
<td>0.7797</td>
<td>0.53</td>
<td>2.52</td>
</tr>
<tr>
<td>2</td>
<td>760</td>
<td>5.1</td>
<td>0.0098</td>
<td>0.2078</td>
<td>0.0020</td>
<td>0.7803</td>
<td>0.53</td>
<td>3.07</td>
</tr>
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<td>3</td>
<td>763</td>
<td>5.2</td>
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<td>0.2078</td>
<td>0.0020</td>
<td>0.7803</td>
<td>0.53</td>
<td>3.16</td>
</tr>
<tr>
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<td>0.0102</td>
<td>0.2082</td>
<td>0.0021</td>
<td>0.7795</td>
<td>0.54</td>
<td>3.68</td>
</tr>
<tr>
<td>5</td>
<td>759</td>
<td>4.9</td>
<td>0.0097</td>
<td>0.2083</td>
<td>0.0021</td>
<td>0.7799</td>
<td>0.52</td>
<td>6.03</td>
</tr>
<tr>
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<td>760</td>
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<td>0.0107</td>
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<td>0.0021</td>
<td>0.7992</td>
<td>0.57</td>
<td>0.52</td>
</tr>
<tr>
<td>7</td>
<td>754</td>
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<td>0.0107</td>
<td>0.2082</td>
<td>0.0021</td>
<td>0.7992</td>
<td>0.52</td>
<td>3.16</td>
</tr>
<tr>
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<td>757</td>
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<td>0.0097</td>
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<td>0.0020</td>
<td>0.7995</td>
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<td>3.68</td>
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<td>0.0101</td>
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<td>3.16</td>
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<td>0.0020</td>
<td>0.7992</td>
<td>0.51</td>
<td>3.68</td>
</tr>
</tbody>
</table>
C.3. SUMMARY OF EXPERIMENTAL CONDITIONS AND DWELL TIMES

Table C.2: Mean and standard deviation of the initial, calculated post-shock temperature and pressure conditions \((T_{5,\text{init}}, P_{5,\text{init}})\), test gas mixture composition, and experiment dwell times \((\Delta \tau_{\text{dwell}}, \tau_{\text{test}} - \tau_{\text{IDT}})\) for the \(n\)-C\(_7\)H\(_{16}\) oxidation shock experiments

<table>
<thead>
<tr>
<th></th>
<th>Mean:</th>
<th>Std Dev:</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T_{5,\text{init}}) (K):</td>
<td>759</td>
<td>3</td>
</tr>
<tr>
<td>(P_{5,\text{init}}) (atm):</td>
<td>4.9</td>
<td>0.1</td>
</tr>
<tr>
<td>Initial (n)-C(<em>7)H(</em>{16}) MF:</td>
<td>0.0100</td>
<td>0.0003</td>
</tr>
<tr>
<td>Initial O(_2) MF:</td>
<td>0.2081</td>
<td>0.0003</td>
</tr>
<tr>
<td>Initial CO(_2) MF:</td>
<td>0.00207</td>
<td>4E-05</td>
</tr>
<tr>
<td>Initial Ar MF:</td>
<td>0.7798/0.7819</td>
<td>0.0004/0.0005</td>
</tr>
<tr>
<td>Phi ((\phi)):</td>
<td>0.53</td>
<td>0.01</td>
</tr>
<tr>
<td>(\tau_{\text{test}} - \tau_{\text{IDT}}) (ms):</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>
C.4 Comparison of modeled and measured IDT values
Table C.3: Summary of ignition delay time (IDT) results (measured and modeled) for \textit{n}-heptane oxidation shock experiments

<table>
<thead>
<tr>
<th>Shock #</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>IDT\textsubscript{meas} (laser absorbance, ms):</td>
<td>3.00</td>
<td>2.22</td>
<td>2.41</td>
<td>1.83</td>
<td>2.96</td>
<td>1.90</td>
<td>2.40</td>
<td>2.11</td>
<td>2.41</td>
<td>3.19</td>
<td>3.02</td>
<td>3.18</td>
</tr>
<tr>
<td>IDT\textsubscript{model} (UV, LLNL, ms):</td>
<td>1.77</td>
<td>1.80</td>
<td>1.75</td>
<td>1.87</td>
<td>1.83</td>
<td>1.82</td>
<td>1.86</td>
<td>1.97</td>
<td>1.89</td>
<td>1.79</td>
<td>1.83</td>
<td>1.88</td>
</tr>
<tr>
<td>IDT\textsubscript{model} (SpecP, LLNL, ms):</td>
<td>1.72</td>
<td>1.75</td>
<td>1.74</td>
<td>1.79</td>
<td>1.79</td>
<td>1.77</td>
<td>1.81</td>
<td>1.76</td>
<td>1.78</td>
<td>1.71</td>
<td>1.77</td>
<td>1.79</td>
</tr>
</tbody>
</table>

A-factor scalar to match IDT\textsubscript{meas}: 0.505 0.667 0.600 0.820 0.477 0.800 0.607 0.728 0.615 0.443 0.468 0.438

IDT\textsubscript{model} (SpecP, mod. LLNL, ms): 2.52 2.41 2.43 2.49 2.51 2.44 2.49 2.47 2.45 2.49 2.49 2.49
C.5 CO₂ laser, GC, and model results

Figure C.3: Comparison of GC, laser, and model results of final CO₂ mole fractions as a function of dwell time
C.6 Carbon/hydrogen recovery results

Figure C.4: Carbon and hydrogen recovery results for quasi-time-resolved, $n$-heptane oxidation species-yield measurements. 1% $n$-C$_{7}$H$_{16}$/20.8% O$_{2}$ ($\phi = 0.53$), 757 K, 4.9 atm.
D.1 Room-temperature cyclohexene absorption cross-section measurements (3.41 µm)

Room-temperature, cyclohexene absorption cross-section measurements were conducted at 3.41 µm. Measurements were taken in two sets of experiments, conducted three months apart, spanning a pressure range of 0.5-7.5 Torr. The CRV section of the shock tube (see 2.2.3) was used to create a closed, pressure-controlled environment for the pure (100%) cyclohexene measurements. Figure D.1a shows absorbance vs. pressure, while Figure D.1b shows absorption cross-section vs. pressure (23.3°C).

Data are also tabulated below (Table D.1).
Figure D.1: Cyclohexene (a) absorbance and (b) absorption cross-section measurements at 23.3°C, 3.41 µm
Table D.1: Cyclohexene absorbance and absorption cross-section measurements at 23.3°C, 3.41 µm

<table>
<thead>
<tr>
<th>Pressure (Torr)</th>
<th>α  (-)</th>
<th>σ (m²/mol)</th>
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<tbody>
<tr>
<td>0.491</td>
<td>0.1023</td>
<td>33.4061</td>
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<td>0.496</td>
<td>0.10054</td>
<td>32.49911</td>
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<td>0.919</td>
<td>0.19528</td>
<td>34.06991</td>
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<td>0.923</td>
<td>0.19527</td>
<td>33.9212</td>
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<td>1.514</td>
<td>0.32134</td>
<td>34.03037</td>
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<td>1.517</td>
<td>0.32322</td>
<td>34.16141</td>
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<td>1.572</td>
<td>0.34401</td>
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<td>1.805</td>
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<td>4.298</td>
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<td>4.615</td>
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<td>7.548</td>
<td>1.75159</td>
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</table>
D.2 High-temperature cyclohexene absorption cross-section measurements

High-temperature cyclohexene absorption cross-sections were measured at 10.532 µm; the measurements were obtained by taking the average absorbance recorded in the first 0.1 ms of each shock experiment (1.4% cyclohexene/Ar, 7.3 atm). Absorbance and the resulting absorption cross-section measurements are plotted in Figure D.2a and b.

Data are also tabulated below (Table D.2).

Figure D.2: High-temperature cyclohexene (a) absorbance and (b) absorption cross-section measurements at 7.3 atm, 10.532 µm (1.4% cyclohexene/Ar)
Table D.2: Cyclohexene absorbance and absorption cross-section measurements at high temperatures, 7.3 atm, 10.532 µm

<table>
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<tr>
<th>Temperature (K)</th>
<th>α (-)</th>
<th>σ (m²/mol)</th>
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<td>982.2043</td>
<td>0.06296</td>
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<td>1147.414</td>
<td>0.09285</td>
<td>0.70947</td>
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Appendix E

Additional GC fast-sampling troubleshooting experiments

Additional troubleshooting experiments, not described in the text of Chapter 5, Section 5.8, were conducted to get to the bottom of the late-time GC and laser/model result discrepancy. The additional experiments are divided into three categories (GC analysis error, sampling mechanics, and non-ideal shock experiment phenomena).

Additional troubleshooting efforts addressing GC analysis error include investigation of:

• Calibration technique impact on GC results (Appendix E.1.1)
• Cross-contamination between subsequent samples (Appendix E.1.2)

Additional troubleshooting efforts addressing sampling mechanics include investigation of:

• Cold shock sampling results (Appendix E.2.1)
• Sampling event impact on subsequent samples (Appendix E.2.2)
• Sample analysis order (Appendix E.2.3)

Additional troubleshooting efforts addressing non-ideal shock experiment phenomena include investigation of:
• Laser and model result sensitivity to initial fuel loading (Appendix E.3.1)

• Non-ideal pressure trace impact on sampling results (Appendix E.3.2)

The results of these additional troubleshooting experiments will be presented in the subsequent sections of this appendix.

### E.1 GC analysis error

#### E.1.1 Calibration technique impact on GC results

Within 36 hours of each set of shock tube fast-sampling experiments, the Agilent 490 MicroGC is calibrated to ensure accurate quantification of the measured species. Multi-point calibration curves are generated for each species using commercial calibration gas mixtures, or mixtures made in-house. The mixtures are connected to a manifold, which is connected to all three of the sample lines; the sample lines are heated to 60°C, as in a typical experiment. All three sample lines are evacuated, filled with calibration gas mixture up to the same sample pressure seen in typical shock experiments (23 psi), and then sealed off as they would be in a typical sampling experiment, using the 1/4-turn valves and isolation valves (see the schematic in Figure 5.3 on Page 93). The calibration gas in the three sample lines is then analyzed, as in a typical experiment: a sample is extracted from each sample line and analyzed, with an argon sample analyzed between each test gas sample to preclude cross-contamination. When calibrations are conducted in this fashion, the response factors (MF %/peak area) calculated using the results from each of the three sample lines agree within 1% of each other.

Because GC analysis is a calibration-based speciation method, it is important that the calibrations are carried out in a way that closely mimics the sample analysis process seen in a true experiment. While the calibration process described above uses the same sample lines, valves, pressures, etc., to perform the calibrations, the calibration process is not exactly the same as the sample analysis process in a shock tube experiment, as the gas being analyzed is not originating in (or being extracted from) the shock tube. To confirm that the GC calibration technique is not the cause of
E.1. GC ANALYSIS ERROR

the difference seen between GC sampling results and laser/model results, an experiment was conducted in which a 0.7% C₂H₄/Ar mixture was introduced to the sample lines in two different ways. First, the gas mixture was taken directly from the mixing tank, via the manifold (as in a typical calibration); the three sample lines were filled to 23 psia and the contents of each sample line were analyzed by GC. Next, the CRV section of the shock tube (see Section 2.2.3) was closed off to the rest of the tube, evacuated, and then filled to 3.1 atm with the test gas; the three sample lines were each triggered for a duration of 26 ms to allow the three sample lines to fill to 23 psia, and the contents of each sample line were analyzed by GC. The results of the two methods are shown in Figure E.1, with ±5% error bars included for reference.

Figure E.1: Impact of GC calibration technique on mole fraction results (sample taken straight from mixing tank vs. CRV section of shock tube). Results from all three sample lines (SL 1, SL 2, SL 3) are indicated.

As can be seen in Figure E.1, the mole fraction results obtained when sampling directly from a mixing tank vs. sampling from the shock tube CRV section are statistically identical – there is no discernible difference in GC analysis results when comparing the two methods. Additionally, it is interesting to note that the results from the three sample lines agree with each other within 1% in a given experiment. Finally, it should be noted that the calibration values used to calculate the
mole fraction values for the two experiments were the same as those used to calculate the C$_2$H$_4$ GC mole fractions reported in the late-time cyclohexene/ethane pyrolysis results reported in Section 5.7, indicating that the GC column’s analytical response to 0.7% C$_2$H$_4$ does not change significantly over time, and the original calibration itself is valid.

Overall, by comparing GC analysis results for samples acquired in two different ways (directly from a mixing tank vs. from the shock tube), it can be concluded that the way in which samples are obtained for GC calibration does not have a significant impact on the resulting GC mole fraction results. The way in which the GC is calibrated is therefore not responsible for the difference in ethylene measurement values seen between late-time GC results and laser/model results in the cyclohexene and ethane pyrolysis experiments described in Section 5.7.

E.1.2 Cross-contamination between subsequent samples

Unlike in the steady-state, post-expansion fan GC sampling experiments detailed in Chapter 3 and Chapter 4 of this dissertation, in which only a single gas sample is extracted from the shock tube in each experiment, the time-resolved GC fast-sampling experiments involve the extraction of multiple gas samples in a single experiment. The gas samples are then analyzed by GC in series, with pure argon samples analyzed in between, as described in Section 5.3.2 of Chapter 5. This new sample analysis process brings up a few important questions, including: could the composition of the gas in Sample Line 1, for example, skew the analysis of the gas in Sample Line 2? Similarly, could the analysis of pure argon in between each sample line analysis be artificially diluting the subsequent samples?

An experiment was conducted to determine the extent of cross-contamination between samples analyzed in series. Sample line 1 was filled to 23 psia with a mixture of 1.0% C$_3$H$_6$/Ar and Sample Line 2 was filled to 23 psia with a mixture of 1.0% C$_2$H$_2$/Ar. First, a sample of gas from Sample Line 2 was extracted and analyzed by the GC. Next, the multi-port sampling valve was rotated to the Sample Line 1 position and a sample of gas was extracted from Sample Line 1 and analyzed by the GC. If there was significant carry-over between samples analyzed in series, one would expect to see a significant amount of Sample Line 2 gas (C$_2$H$_2$) in the Sample Line 1 analysis results. The results from the two analyses are presented in Table E.1. To simplify the analysis and eliminate
compounding errors due to calibration uncertainty, the results are presented as chromatograph peak areas. Note that peak areas are directly proportional to "how much" of a species is present, and can be converted to mole fraction measurements via a calibration response factor (% mole fraction/peak area).

Table E.1: GC sample line cross-contamination results, listed in the order in which they were analyzed. Sample Line 1 nominally contains a mixture of 1.0% C\textsubscript{3}H\textsubscript{6}/Ar and Sample Line 2 nominally contains a mixture of 1.0% C\textsubscript{2}H\textsubscript{2}/Ar.

<table>
<thead>
<tr>
<th>Sample Source</th>
<th>C\textsubscript{2}H\textsubscript{2} Peak Area (A.U., PPU column)</th>
<th>C\textsubscript{3}H\textsubscript{6} Peak Area (A.U., PPQ column)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample Line 2</td>
<td>408,268</td>
<td>4,600</td>
</tr>
<tr>
<td>Sample Line 1</td>
<td>5,920</td>
<td>929,805</td>
</tr>
</tbody>
</table>

Approximately 1.5% of the C\textsubscript{2}H\textsubscript{2} present in the Sample Line 2 sample (or 150 ppm) was carried over to the Sample Line 1 sample that was analyzed immediately afterwards. Therefore, the cross-contamination experiment shows that very little sample is carried over between analyses when two samples are analyzed back-to-back. The large difference seen between late-time GC and laser/model results in the time-resolved cyclohexene/ethane pyrolysis experiments is therefore not likely to be caused by cross-contamination between subsequent GC samples.

E.2 Sampling mechanics

E.2.1 Cold shock sampling results

An experiment was conducted to determine if the sampling process itself negatively impacts the sampling results and/or leads to dilution. A "cold shock" experiment (or, an experiment conducted at a cold enough temperature that no chemical change is expected to occur in the test gas mixture) was conducted to confirm that the composition of the initial test gas mixture is maintained throughout the sampling process. A test gas mixture of 0.7% C\textsubscript{2}H\textsubscript{4} was put into the shock tube, and, assuming the sampling process works as it should, 0.7% C\textsubscript{2}H\textsubscript{4} was expected to come out. Figure E.2 shows the results of this cold shock experiment, alongside GC analysis results of the same initial test gas mixture obtained directly from the mixing tank and from the CRV section of the shock tube (the same data sets shown in Figure E.1).
Figure E.2: Comparison of GC analysis results for samples taken directly from the mixing tank, from the shock tube, and extracted from a non-reacting shock experiment (0.7% C$_2$H$_4$, 1108 K, 7.3 atm). Results from all three sample lines (SL 1, SL 2, SL 3) are indicated.

From the results in Figure E.2, it is clear that the sampling event in a shock experiment does not inherently impact the composition of the extracted sample – the composition of the samples extracted from the cold shock experiment are statistically identical to those collected directly from the mixing tank and from the CRV section of the shock tube. It can therefore be concluded that the late-time sampling events themselves are not directly causing the discrepancy seen between late-time GC and laser/model results.

### E.2.2 Sampling event impact on subsequent samples

To determine whether earlier sampling events are impacting later sampling events (i.e., Sample 1 and/or Sample 2 are causing Sample 3 results to be artificially low), an experiment was conducted in which only the third sample was collected and the other two valves were not triggered. The results are compared to an experiment conducted at similar conditions in which all three samples were collected. Figure E.3 shows a comparison of the two experiments (both conducted in 1.4% cyclohexene/Ar at ∼1100 K, 7.3 atm, with 3.5-mm probes).
E.2. SAMPLING MECHANICS

Figure E.3: Comparison of laser and GC analysis results for two experiments, both conducted in 1.4% cyclohexene/Ar at ∼1100 K, 7.3 atm, with 3.5-mm probes. In the first experiment, only the third sampling event was triggered; in the second experiment, all three sampling events were triggered.

From Figure E.3, it is clear that the first and second sampling events in an experiment do not impact the composition of the third sample; the third-sample C$_2$H$_4$ mole fraction results show close agreement (within experimental uncertainty), regardless of whether the first two sampling valves are triggered or not.

Overall, the late-time discrepancy between GC and laser/model results is not caused by earlier sampling events impacting the composition of later samples.

E.2.3 Sample analysis order

Does the order in which the samples are analyzed by the GC impact the analysis results? Put another way, is there some sort of systematic error in which samples that are analyzed last by the GC (those that sit un-analyzed for the longest period of time) consistently yield lower mole fraction results than those analyzed more promptly? To answer these questions, an experiment was conducted in which the order of sample analysis was reversed – the third-extracted sample was analyzed first, followed by the second-extracted sample, followed by the first-extracted sample. The C$_2$H$_4$ mole fraction results are shown in Figure E.4, alongside results analyzed in the conventional
order.

![Graph](image)

Figure E.4: Comparison of laser and GC analysis results for two experiments, both conducted in 1% C₂H₆/Ar at ~1125 K, 6.8 atm, with 5-mm probes. In the first experiment, the three samples were analyzed in the normal order (1,2,3); in the second experiment, the three samples were analyzed in the opposite order (3,2,1).

As seen in the laser results, the experimental conditions are repeatable enough that the three GC-measured C₂H₄ results are expected to agree quite closely. As can be seen in the plotted results, the Sample 2 and Sample 3 GC results for the two experiments are statistically identical – they agree within the uncertainty associated with the measurements. The order in which samples are analyzed by the GC is therefore not the cause of the late-time GC and laser/model result discrepancy.

### E.3 Non-ideal shock experiment phenomena

#### E.3.1 Laser and model sensitivity to initial fuel loading

To gauge the impact that initial fuel loading has on the laser and model results, calculations were carried out in which the cyclohexene absorption cross-section at 3.41 μm (room temperature) was perturbed by ±10% (this has the same effect as perturbing the fuel mole fraction by 10%). Figure E.5 shows the results. As can be seen from the laser mole fraction measurements presented in Figure E.5, changing the initial cyclohexene mole fraction has a negligible effect on the laser...
Figure E.5: Impact of perturbing the initial cyclohexene fuel loading by ±10% on laser and model results. Model results are presented as dashed lines, laser results are plotted as solid lines. Original, unperturbed model (dashed red line) and laser (solid blue line) results are plotted for comparison. Model and laser results obtained by perturbing the initial fuel loading (C₆H₁₀ absorption cross-section) by +10% are plotted in purple; model and laser results obtained by perturbing the absorption cross-section by -10% are plotted in gray. Nominal test gas mixture and initial conditions: 1.3% cyclohexene/Ar, 1121 K, 7.4 atm.
results (recall that initial C$_6$H$_{10}$ mole fraction factors into the laser measurements via Equation 5.3). However, changing the initial cyclohexene mole fraction by 10% does noticeably impact the model results (as to be expected). Increasing the absorption cross-section by 10% (which corresponds to a decrease in initial fuel mole fraction) brings the model C$_2$H$_4$ mole fraction result closer to the laser result; however, the discrepancy between model and GC-measured C$_2$H$_4$ mole fractions at late times cannot be accounted for. Therefore, the difference seen between late-time GC and laser/model results is not caused by laser/model results being too high due to an error in initial fuel mole fraction.

**E.3.2 Non-ideal pressure trace impact**

The time-resolved pressure traces used to calculate the cyclohexene/ethane-pyrolysis laser and model results often experience non-ideal pressure fluctuations (especially the pressure traces recorded in the cyclohexene pyrolysis experiments). To check whether the severity of pressure fluctuations could be the cause of the discrepancy between late-time GC and laser/model results, laser and model results were revisited for a given experiment and two different pressure trace variants were used to recalculate the results. In all three cases (nominal plus two variants), the raw pressure trace was smoothed using a series of cubic splines; each variant used a different number of knots to characterize the pressure trace (different $\Delta t$ between knot locations). The first pressure trace iteration placed knots every $10^{-5}$ sec, or once every 100 data points; the second iteration placed knots every $10^{-4}$ sec (the normal amount of smoothing typically applied to an experiment); and the third iteration placed knots every $10^{-3}$ sec. Using fewer knots leads to greater smoothing of the pressure trace. The three pressure traces were then used to re-calculate the model simulations and laser measurements; the results are shown in Figure E.6. As can be seen from the laser and model results, changing the degree of pressure-trace smoothing has minimal impact on the resulting laser measurements, while causing a slight change in the resulting model simulations. The experimental pressure trace and the way it is incorporated into the laser and model calculations is clearly not the cause of the late-time discrepancy between GC and laser/model results.

Nevertheless, it is worth noting that the pressure oscillations seen in the cyclohexene pyrolysis experiments could be mitigated altogether by using a different diaphragm approach. As mentioned in Section 5.3.1, the cyclohexene pyrolysis experiments used a double-diaphragm configuration, in
Figure E.6: Impact of pressure-trace smoothing on laser and model results. Model results are presented as dashed lines, laser results are plotted as solid lines. Original, normally-smoothed model (dashed red line) and laser (solid blue line) results are plotted for comparison. Model and laser results obtained by smoothing the pressure with cubic splines spaced $10^{-3}$ sec apart are plotted in purple; model and laser results obtained by smoothing the pressure with cubic splines spaced $10^{-5}$ sec apart are plotted in green. Nominal test gas mixture and initial conditions: 1.3% cyclohexene/Ar, 1121 K, 7.4 atm.
which two scored, polycarbonate diaphragms are separated by a finite volume of gas, and diaphragm rupture is induced when the gas volume between the diaphragms is rapidly evacuated. Figure E.7 shows a comparison of pressure traces recorded during four experiments: one double-diaphragm experiment and three experiments conducted using the conventional diaphragm-cutter approach. Note that in the diaphragm-cutter experiments, two unscored (polycarbonate) diaphragms, placed back-to-back, were needed to achieve $P_4$ pressures (154-182 psi) comparable to that seen in the double-diaphragm experiment (171 psi).

Figure E.7: Comparison of the impact of double-diaphragm (scored) and diaphragm-cutter approaches on long-test-time pressure traces. Top: (left) Double-diaphragm approach (two 0.04-in-thick, scored diaphragms), (right) diaphragm-cutter approach with back-to-back (unscored) 0.03-in and 0.01-in diaphragms. Bottom: diaphragm-cutter approach with back-to-back (unscored) 0.03-in and 0.015-in diaphragms (left), and 0.03-in and 0.02-in diaphragms (right). Nominal test gas mixture of 1% $\text{C}_2\text{H}_4/\text{Ar}$, driver gas compositions as indicated.
As can be seen in Figure E.7, the periodic pressure oscillations are only seen in the double-diaphragm experiment (blue trace, top left); when the diaphragm-cutter method is used in conjunction with stacked, thinner diaphragms, no regular pressure oscillations are observed. Even when thinner diaphragms are stacked to achieve higher P₄ conditions (e.g., the "30+20-mil" experiment), the pressure oscillations do not return. It should be noted that the pressure traces depicted in the bottom two plots of Figure E.7 are far from ideal – as noted in the plots, driver inserts have not been optimized to mitigate the steady increase in pressure over the first \( \sim 20 \) ms, and non-ideal peaks and troughs due to sub-optimal driver gas tailoring and backfill fractions can be observed.

It is hypothesized that the periodic pressure oscillations seen in the double-diaphragm experiments can be attributed to the thickness of the polycarbonate diaphragms used. It is likely that the brittle, 0.04-in diaphragm petals have a strong restorative force, and therefore continually try to close after rupture, while the thinner, less brittle diaphragm petals stay open as high-pressure gas flows from driver to driven section. Overall, this investigation would suggest that 0.04-in diaphragms should not be used in long-test-time, double-diaphragm experiments, as they could cause non-ideal pressure oscillations for the duration of each experiment.

E.4 Thermal effects

E.4.1 Core gas temperature vs. sample effective temperature time-history

As mentioned in Chapter 5, Section 5.8.4, additional \( T_{\text{eff}} \) uncertainty analysis results, calculated considering the \( T_{\text{eff}} \) values obtained using GC-measured C₂H₄ and C₄H₆ mole fractions, are included here. The results calculated using GC-measured C₂H₄ mole fractions are reproduced here (from Figure 5.20) for comparison.
Figure E.8: Impact of various parameters (fuel loading, GC mole fraction measurement, reaction rate A-factor, initial $T_5$, for each of the three samples. For simplicity, only the results obtained using C$_2$H$_4$ GC measurements are presented. Red bars are the nominal $T_{model,avg} - T_{eff}$ values. Blue bars are the $T_{model,avg} - T_{eff}$ values obtained when parameters are decreased by their respective uncertainties; yellow bars are the $T_{model,avg} - T_{eff}$ values obtained when parameters are increased by their respective uncertainties. Results averaged over 12 cyclohexene pyrolysis experiments. Nominal test gas mixture and initial conditions: 1.4% cyclohexene/Ar, 980-1150 K, 7.3 atm.
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E.4.2 Impact of thermal boundary layer on particle temperature time-history

The simple thermal boundary layer/sample extraction model presented in Chapter 5, Section 5.8.7, describes how the bulk composition of differential, sampled volumes changes over time; but it does not capture how the composition of those differential sample volumes changes further as they are pulled through the boundary layer on their way to the sampling port in the shock tube endwall. This section aims to quantify this effect.

In the analysis presented here, it is further assumed that the particles extracted from the core of the shock tube travel along radial streamlines, from the outer radius of the hemispheres bounding their differential volumes, to the origin, as depicted in Figure E.9. In the two-dimensional figure, \( \theta \) corresponds to the angle the streamline makes with the endwall, spanning 0-180 degrees. As the particles are extracted, it is also assumed that they travel at a velocity of \( r(t)/t \).

![Figure E.9: Particle paths during sample extraction, demonstrated along three streamlines at 30, 60, and 90\,\text{deg} angles from the shock tube endwall.](image)

What is the change in particle temperature associated with passing through the thermal boundary layer, and most importantly, could this change significantly contribute to the \( \sim 20 \,\text{K} \) temperature change needed to account for the late-time GC and laser/model discrepancy seen in the fast-sampling experiments? To determine the temperature change imparted on particles traveling
through the endwall thermal boundary layer, the model framework described in Chapter 5, Section 5.8.7 (i.e., knowledge of the gas temperature as a function of distance from the endwall at a given time) was used to calculate the temperature time-histories of particles extracted from the reacting gas in the shock tube at various times within each sampling event.

Figure E.10 shows the calculated temperature time-histories of particles extracted from a 1% C₂H₆/Ar pyrolysis shock tube experiment, over the first 1 ms, 5 ms, and 9 ms of the first sampling event (which occurs over the first 10 ms of an experiment – time zero in these plots corresponds to the passing of the reflected shock). Figure E.10a shows the temperature time-history of particles extracted along the 30-degree streamline (relative to the endwall), while Figure E.10b shows the temperature time-history of particles extracted along the 90-degree streamline. Both plots include the temperature time-history from a constant-enthalpy/constant-pressure (constant-HP) simulation (FFCM-1 [81]), meant to represent the temperature time-history of the gas at the core of the shock tube.

![Figure E.10](image)

Figure E.10: Sample Line 1 particle temperature time-histories, for particles extracted over the first 1 ms, 5 ms, and 9 ms of the first sampling event. Nominal simulation conditions: 1% C₂H₆/Ar, 1100 K, 7 atm.

In both plots, a temperature roll-off is observed as the particles are pulled from the core of the shock tube through the thermal boundary layer. The particles traveling along the 30-degree
streamline are seen to enter the thermal boundary layer earlier than those traveling along the 90-degree streamline; this is to be expected. Additionally, the temperature roll-off experienced by the particles traveling the 30-degree streamline is more gradual than that experienced by the particles traveling the 90-degree streamline; this is also to be expected, as the 30-degree particles spend a longer period of time traversing the boundary layer.

Figures E.11 and E.12 show the temperature time-history results for particles extracted over the first 1 ms, 5 ms, and 9 ms of the second and third sampling events, respectively. Similar trends are observed in these simulated results as well: particles traveling along the 30-degree streamline enter the thermal boundary layer sooner, and spend a longer amount of time traversing the boundary layer.

![Figure E.11: Sample Line 2 particle temperature time-histories, for particles extracted over the first 1 ms, 5 ms, and 9 ms of the second sampling event. Nominal simulation conditions: 1% C$_2$H$_6$/Ar, 1100 K, 7 atm.](image)

To determine the impact the temperature time-histories have on the compositional time-histories of the samples being extracted, constant-pressure (7 atm) simulations were run in which the initial composition was set to 1% C$_2$H$_6$/Ar and the system temperature was constrained to each of the temperature time-histories shown in Figures E.10, E.11, and E.12. The mole fraction results can be thought of as the evolving composition of a differential volume of particles being pulled from the core of the shock tube through the endwall.
APPENDIX E. ADD’L. GC FAST-SAMPLING TROUBLESHOOTING EXPERIMENTS

Figure E.12: Sample Line 3 particle temperature time-histories, for particles extracted over the first 1 ms, 5 ms, and 9 ms of the third sampling event. Nominal simulation conditions: 1% C₂H₆/Ar, 1100 K, 7 atm.

(a) \( \theta = 30 \) degrees

(b) \( \theta = 90 \) degrees

The ethylene mole fraction results from these simulations are presented in Figure E.13, Figure E.14, and Figure E.15. The left-hand figures (a) show the C₂H₄ mole fraction results for the differential volumes extracted along the 30-degree streamline, while the right-hand figures (b) show the C₂H₄ mole fraction results extracted along the 90-degree streamline.

Upon inspection of all three sets of figures, it is clear that the reacting-gas chemistry freezes as the gas travels through the thermal boundary layer. Gas traveling along streamlines defined by smaller theta values (starting closer to the thermal boundary layer) spend more time in the thermal boundary layer. This leads to a greater deviation in mole fraction composition between the expected core gas composition (approximated using a constant-HP simulation) and the composition of the gas that ultimately makes it into the sample line (denoted by asterisks in Figure E.13, Figure E.14, and Figure E.15). Additionally, the samples entering the sampling line latest in time (9 ms) are impact by the thermal boundary layer the most, as the boundary layer thickness grows in time. For example, the 9-ms line in Figure E.15a shows the greatest deviation between expected core gas composition and extracted-gas composition. The composition of the gas that reaches the sample line 9 ms into the third sampling event does not accurately reflect the composition of the reacting gas at the core of the shock tube at 9 ms; due to premature cooling, caused by traversing the boundary layer, a relative
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(a) $\theta = 30$ degrees

(b) $\theta = 90$ degrees

Figure E.13: Sample Line 1 $\text{C}_2\text{H}_4$ mole fraction time-histories, for differential particle volumes extracted from the core of the shock tube, over the first 1 ms, 5 ms, and 9 ms of the first sampling event. Asterisks denote final $\text{C}_2\text{H}_4$ mole fraction composition. Nominal simulation conditions: 1% $\text{C}_2\text{H}_6$/Ar, 1100 K, 7 atm.

(a) $\theta = 30$ degrees

(b) $\theta = 90$ degrees

Figure E.14: Sample Line 2 $\text{C}_2\text{H}_4$ mole fraction time-histories, for differential particle volumes extracted from the core of the shock tube, over the first 1 ms, 5 ms, and 9 ms of the second sampling event. Asterisks denote final $\text{C}_2\text{H}_4$ mole fraction composition. Nominal simulation conditions: 1% $\text{C}_2\text{H}_6$/Ar, 1100 K, 7 atm.
Figure E.15: Sample Line 3 C$_2$H$_4$ mole fraction time-histories, for differential particle volumes extracted from the core of the shock tube, over the first 1 ms, 5 ms, and 9 ms of the third sampling event. Asterisks denote final C$_2$H$_4$ mole fraction composition. Nominal simulation conditions: 1% C$_2$H$_6$/Ar, 1100 K, 7 atm.

difference of 5.9% is observed.

Figure E.15b, by comparison, still shows a difference in composition between the ultimate, differential gas volume collected at 9 ms and the shock tube core gas, but the difference in C$_2$H$_4$ mole fraction is only 2.9%.

Overall, this analysis shows that extracted gas samples, especially the differential hemisphere volumes modeled in Chapter 5, Section 5.8.7, are expected to undergo an additional cooling process as they are extracted through the endwall thermal boundary layer. This additional cooling is especially significant at late times in the third sampling event, when modeled C$_2$H$_4$ mole fractions are expected to be, at most, ~3-6% below the simulated core gas composition. The approach presented here is expected to yield the worst-case impact of the thermal boundary layer on the extracted sample results, as it assumes perfect conduction between the differential volumes being extracted and the surrounding gas (i.e., that the temperature of the extracted particles are not simply cooled by the thermal boundary layer/the cooler gas molecules around them, but experience the exact, spatially resolved temperature in the thermal boundary layer as they travel through it).

While the analysis presented in Chapter 5, Section 5.8.7 represents one method for approximating the effect of the thermal boundary layer on the overall composition of extracted samples,
accounting for the impact of gas traveling through the thermal boundary layer will likely contribute to dropping the late-time simulated $\text{C}_2\text{H}_4$ mole fraction results by an additional few percent.
Appendix F

Thermal boundary layer calculation

The endwall thermal boundary layer problem can be treated as a 1-D, semi-infinite, transient heat conduction problem: thermal energy is conducted from the high-temperature, post-reflected-shock gas at the core of the shock tube to the cold endwall. (Derivations similar to this can be found in advanced heat transfer textbooks, for example [170]). A derivation of the time-dependent, thermal boundary layer penetration depth, $\delta(t)$, will first be presented, followed by a derivation of an expression for the temperature within the thermal boundary layer, $T(x,t)$.

F.1 Thermal boundary layer thickness approximation

If a control volume surface is defined, extending from the surface of the shock tube endwall to the outermost edge of the thermal boundary layer at a given point in time, the following energy conservation equation can be written:

$$\dot{q}_{\text{cond}} = \frac{dU}{dt}$$  \hspace{1cm} (F.1)

where $\dot{q}$ is the rate of conduction out of the control volume, at the endwall surface, and $dU/dt$ is the rate of change of the total thermal energy, $U$, in the boundary layer gas.

The rate of conduction heat transfer, $\dot{q}_{\text{cond}}$, can be approximated as:

$$\dot{q}_{\text{cond}} \approx \frac{kA(T_5 - T_{EW})}{\delta_{TBL}}$$  \hspace{1cm} (F.2)
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where $k$ is the thermal conductivity of the gas, $A$ is the area of the heat transfer surface, $T_5$ is the temperature of the gas in the shock tube outside of the thermal boundary layer, $T_{EW}$ is the endwall temperature, and $\delta_{TBL}$ is the thickness of the thermal boundary layer (control volume).

The total energy stored in the control volume can be approximated as:

$$U \approx \Delta T \bar{\rho} \bar{c} \delta_{TBL} A$$  (F.3)

where $\bar{\rho}$ is the average density of the gas in the thermal boundary layer, $\bar{c}$ is the average specific heat of the gas, and $\Delta T$ is the average temperature change of the gas across the boundary layer, which can be approximated as:

$$\Delta T \approx \frac{(T_5 - T_{EW})}{2}$$  (F.4)

Combining equations F.1, F.2, and F.3 leads to:

$$\frac{k A (T_5 - T_{EW})}{\delta_{TBL}} \approx \frac{d}{dt} \left[ \frac{(T_5 - T_{EW})}{2} \bar{\rho} \bar{c} \delta_{TBL} A \right]$$  (F.5)

If the average thermal conductivity, density, and specific heat are assumed constant in time, the following ordinary differential equation can be written:

$$\frac{k}{\delta_{TBL}} \approx \frac{\rho c}{2} \frac{d \delta_{TBL}}{dt}$$  (F.6)

Using the definition for thermal diffusivity ($\alpha$),

$$\alpha = \frac{k}{\rho c}$$  (F.7)

Equation F.6 can be written as:

$$2\alpha \approx \delta_{TBL} \frac{d \delta_{TBL}}{dt}$$  (F.8)

Separating and integrating Equation F.8 leads to:

$$2\alpha t \approx \frac{\delta_{TBL}^2}{2}$$  (F.9)
Solving for the thermal boundary layer thickness, one finds:

\[ \delta_{TBL} = 2\sqrt{\alpha t} \]  

(F.10)

This result indicates that the endwall thermal boundary layer is expected to grow proportionally to \( \sqrt{\alpha t} \).

### F.2 Thermal boundary layer temperature derivation

An energy balance on a differential control volume within the gas next to the endwall yields the following:

\[ \dot{q}_x = \dot{q}_{x+dx} + \frac{\partial U}{\partial t} \]  

(F.11)

where \( \dot{q}_x \) is the rate of conduction out of the control volume surface at \( x \), \( \dot{q}_{x+dx} \) is the rate of conduction into the volume surface at \( x + dx \), and \( dU/dt \) is the rate of change in internal energy of the gas (see Figure F.1).

A Taylor series expansion can be applied to the \( x + dx \) term, yielding:

\[ \dot{q}_x = \dot{q}_x + \frac{\partial \dot{q}_x}{\partial x} dx + \frac{\partial U}{\partial t} \]  

(F.12)
or more succinctly:

\[ 0 = \frac{\partial \dot{q}_x}{\partial x} dx + \frac{\partial U}{\partial t} \]  

(F.13)

The conduction term, \( \dot{q}_x \), can be substituted for using Fourier’s law:

\[ \dot{q}_x = -kA \frac{\partial T}{\partial x} \]  

(F.14)

where \( k \) is the thermal conductivity of the gas (assumed to be constant), \( A \) is the area of the gas surface conducting the heat, and \( T \) is the temperature of the gas.

The total internal energy contained in the control volume, \( U \), is defined as:

\[ U = \rho c A T \ dx \]  

(F.15)

where \( \rho \) and \( c \) are the density and specific heat capacity of the gas, respectively – also assumed to be constant. The change in internal energy with respect to time can therefore be written:

\[ \frac{\partial U}{\partial t} = \rho c A dx \frac{\partial T}{\partial t} \]  

(F.16)

Plugging Equation F.14 and F.16 into Equation F.13 yields:

\[ 0 = \frac{\partial}{\partial x} \left[ -kA \frac{\partial T}{\partial x} \right] dx + \rho c A dx \frac{\partial T}{\partial t} \]  

(F.17)

which simplifies to:

\[ 0 = -k \frac{\partial^2 T}{\partial x^2} + \rho c \frac{\partial T}{\partial t} \]  

(F.18)

Substituting Equation F.7 (thermal diffusivity definition) into Equation F.18 produces the following second-order, partial differential equation (PDE):

\[ \alpha \frac{\partial^2 T}{\partial x^2} = \frac{\partial T}{\partial t} \]  

(F.19)
The boundary conditions associated with this PDE include:

\[ T_{x=0,t} = T_{EW} \]  \hspace{1cm} (F.20)

\[ T_{x,t=0} = T_5 \]  \hspace{1cm} (F.21)

\[ T_{x=\infty,t} = T_5 \]  \hspace{1cm} (F.22)

In effect, the temperature at the endwall is constant (assumed to be room temperature – conduction through the endwall material is neglected for simplicity), the initial temperature of the gas is the \( T_5 \) temperature, and the \( T_5 \) temperature is maintained far away from the endwall.

As written, the PDE in Equation F.19 is difficult to solve. However, it can be transformed into an ordinary differential equation (ODE) through combination of variables. A non-dimensional length scale parameter, \( \eta \), can be defined, relating distance from the shock tube endwall, \( x \), to the thickness of the thermal boundary layer, \( \delta_{TBL} \):

\[ \eta = \frac{x}{\delta_{TBL}} = \frac{x}{2\sqrt{\alpha t}} \]  \hspace{1cm} (F.23)

Now, the goal is to express temperature differentials in Equation F.19 as a function of \( \eta \), where \( T(\eta(x,t)) \). By the chain rule, the partial derivative of \( T \) with respect to \( x \) is:

\[ \frac{\partial T}{\partial x} = \frac{dT}{d\eta} \frac{\partial \eta}{\partial x} \]  \hspace{1cm} (F.24)

From Equation F.23, it is clear that the second term in Equation F.24 can be written:

\[ \frac{\partial \eta}{\partial x} = \frac{1}{2\sqrt{\alpha t}} \]  \hspace{1cm} (F.25)

yielding the following equation for the partial derivative of \( T \) with respect to \( x \):

\[ \frac{\partial T}{\partial x} = \frac{dT}{d\eta} \frac{1}{2\sqrt{\alpha t}} \]  \hspace{1cm} (F.26)

Next, we want the second derivative of \( T \) with respect to \( x \), in order to plug into Equation F.19.
F.2. THERMAL BOUNDARY LAYER TEMPERATURE DERIVATION

Once again using the chain rule, the second derivative can be written as follows:

$$\frac{\partial^2 T}{\partial x^2} = \frac{d}{d\eta} \left( \frac{\partial T}{\partial x} \right) \frac{\partial \eta}{\partial x}$$  \hspace{1cm} (F.27)

Substituting in Equation F.26 and Equation F.25, Equation F.27 becomes:

$$\frac{\partial^2 T}{\partial x^2} = \frac{\partial^2 T}{\partial \eta^2} \frac{1}{4\alpha t}$$  \hspace{1cm} (F.28)

Now, we want to calculate the partial derivative of $T$ with respect to $t$ (time). Using the chain rule:

$$\frac{\partial T}{\partial t} = \frac{dT}{d\eta} \frac{\partial \eta}{\partial t}$$  \hspace{1cm} (F.29)

The partial derivative of $\eta$ with respect to $t$ is found to be:

$$\frac{\partial \eta}{\partial t} = -\frac{x}{4t\sqrt{\alpha t}}$$  \hspace{1cm} (F.30)

Plugging this into Equation F.29,

$$\frac{\partial T}{\partial t} = -\frac{x}{4t\sqrt{\alpha t}} \frac{dT}{d\eta}$$  \hspace{1cm} (F.31)

Equation F.19 now becomes

$$\alpha \frac{\partial^2 T}{\partial \eta^2} \frac{1}{4\alpha t} = -\frac{x}{4t\sqrt{\alpha t}} \frac{dT}{d\eta}$$  \hspace{1cm} (F.32)

Re-arranging and using Equation F.23 to plug in for $x$, the partial differential equation (Equation F.19) can finally be transformed into the following ordinary differential equation:

$$\frac{\partial^2 T}{\partial \eta^2} = -2\eta \frac{dT}{d\eta}$$  \hspace{1cm} (F.33)

The boundary conditions must likewise be transformed:

$$T_{x=0,t} = T_{EW} \rightarrow T_{\eta=0} = T_{EW}$$  \hspace{1cm} (F.34)
To solve Equation F.33, it is useful to first simplify the equation through substitution of a new variable, for example, $w$, where:

$$w = \frac{dT}{d\eta} \quad (F.37)$$

Equation F.33 now becomes:

$$\frac{dw}{d\eta} = -2\eta w \quad (F.38)$$

Integration of Equation F.38 leads to:

$$\ln w = -\eta^2 + C_1 \quad (F.39)$$

where $C_1$ is a constant of integration. Solving for $w$, we find:

$$w = \exp \left( -\eta^2 + C_1 \right) \quad (F.40)$$

Substituting the definition of $w$ back into Equation F.40 leads to:

$$\frac{dT}{d\eta} = \exp \left( -\eta^2 + C_1 \right) \quad (F.41)$$

or

$$\frac{dT}{d\eta} = C_2 \exp \left( -\eta^2 \right) \quad (F.42)$$

Here, $C_2$ is another constant of integration, equal to $\exp(C_1)$.

Separation and integration of Equation F.42 leads to the following expression:

$$T = C_2 \int_0^\eta \exp \left( -\eta^2 \right) d\eta + C_3 \quad (F.43)$$

Here, $C_3$ is yet another constant of integration. The integral in Equation F.43 cannot be solved.
analytically. However, it has a close resemblance to the Gaussian error function:

\[
erf(\eta) = \frac{2}{\sqrt{\pi}} \int_{0}^{\eta} \exp\left(-\eta^2\right) d\eta
\]

Using the definition of the Gaussian error function, Equation F.43 can now be written:

\[
T = C_2 \frac{\sqrt{\pi}}{2} \text{erf}(\eta) + C_3
\]

The constants of integration can be solved for by plugging in the boundary conditions:

\[
C_2 = 2 \frac{(T_5 - T_{EW})}{\sqrt{\pi}}
\]

\[
C_3 = T_{EW}
\]

Finally, the overall expression for the temperature distribution in the thermal boundary layer, originally presented in Section 5.8.5, can be written:

\[
T(x, t) = T_{EW} + (T_5 - T_{EW}) \text{erf}\left(\frac{x}{2\sqrt{\alpha t}}\right)
\]

This equation is ultimately used to calculate the temperature of the gas in the shock tube at a distance \(x\) from the endwall, at time \(t\).

Equation 5.7 can also be used to numerically calculate the thickness of the thermal boundary layer, where the thickness, \(\delta_{TBL}\), is the distance \(x\) from the endwall, at which:

\[
T(x, t) = 0.99 * T_5(t)
\]
Appendix G

High-temperature LFS measurements: Supplemental Material

G.1 Non-ideal shock tube effects

To reduce the influence of particles on flame propagation in the shock tube, the tube was cleaned (swabbed with cheesecloth coated in acetone) after every other experiment. Nevertheless, every once in a while, an errant shock tube diaphragm piece, made of the polycarbonate plastic diaphragm material, makes its way down to the test section and disturbs the flame speed experiment, rendering it useless.

As shown in Figure G.1, disturbances caused by diaphragm pieces are readily apparent in the OH* emission images; the diaphragm piece can be clearly seen entering the back of the flame, traveling upwards and to the right, and exiting the front of the flame at the top right corner. Image datasets in which diaphragm pieces have been detected are discarded and not used for flame speed measurements.
G.1. NON-IDEAL SHOCK TUBE EFFECTS

Figure G.1: Diaphragm piece trajectory through spherically expanding flame (diaphragm piece circled in red). Initial unburned gas conditions: propane/air ($\phi = 1.0$) at 541 K, 1.9 atm.
### G.2 Lewis number calculations

The Lewis number, $Le$, of a gas mixture is defined as the ratio of thermal diffusivity, $\alpha$, to a representative mass diffusivity, $D$, of the mixture [171]:

$$Le = \frac{\alpha}{D} \quad \text{(G.1)}$$

Here, $\alpha$ is defined as in Equation F.7. The Lewis number can be calculated using the mass diffusivity of a reactant that is in excess or deficient in the mixture (e.g., fuel or oxidizer, respectively, in a fuel-rich mixture). An effective Lewis number, $Le_{eff}$, can be calculated as a weighted average of the Lewis numbers of the two reactants [172]. Under stoichiometric conditions, the effective Lewis number reduces to the mean of the two Lewis numbers calculated using each reactant.

Lewis numbers for representative mixtures (and thermodynamic conditions) for each of the three flame speed datasets presented in Chapter 6 (Section 6.4), are presented in Table G.1.

<table>
<thead>
<tr>
<th>Mixture/conditions</th>
<th>$Le_{O_2}$</th>
<th>$Le_{fuel}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$/air ($\phi = 1.0$, 500 K)</td>
<td>1.11</td>
<td>0.95</td>
</tr>
<tr>
<td>C$_3$H$_8$/air ($\phi = 1.0$, 500 K)</td>
<td>1.03</td>
<td>1.70</td>
</tr>
<tr>
<td>C$_3$H$_8$/modified-air ($\phi = 0.8$, 800 K)</td>
<td>1.61</td>
<td>2.53</td>
</tr>
</tbody>
</table>

The effective Lewis number for each of the three mixtures is greater than 1.
G.3. LOW-TEMPERATURE CH$_4$ RESULTS

G.3 Low-temperature CH$_4$ results

The experimental conditions and associated flame speed and Markstein length results for the low-temperature CH$_4$/air flame speed experiments presented in Chapter 6, Section 6.4.1, are reported in Table G.2.

Table G.2: Summary of low-temperature CH$_4$/air flame speed results

<table>
<thead>
<tr>
<th>$T_{unburned}$</th>
<th>$P_{unburned}$</th>
<th>$\rho_{unburned}$</th>
<th>Phi</th>
<th>$S_L$</th>
<th>$S_L$ Uncert.</th>
<th>$L_b$</th>
<th>$L_b$ Uncert.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T$_5$, K)</td>
<td>(P$_5$, atm)</td>
<td>(g/cm$^3$)</td>
<td></td>
<td>(cm/s)</td>
<td>(cm/s)</td>
<td>(cm)</td>
<td>(cm)</td>
</tr>
<tr>
<td>488.9</td>
<td>1.07</td>
<td>7.36E-04</td>
<td>1.00</td>
<td>89.8</td>
<td>3.6</td>
<td>0.060</td>
<td>0.002</td>
</tr>
<tr>
<td>491.4</td>
<td>1.04</td>
<td>7.14E-04</td>
<td>1.00</td>
<td>92.1</td>
<td>3.6</td>
<td>0.046</td>
<td>0.015</td>
</tr>
<tr>
<td>509.1</td>
<td>1.03</td>
<td>6.84E-04</td>
<td>1.00</td>
<td>99.4</td>
<td>3.9</td>
<td>0.047</td>
<td>0.015</td>
</tr>
<tr>
<td>538.0</td>
<td>1.02</td>
<td>6.37E-04</td>
<td>1.00</td>
<td>107.9</td>
<td>4.2</td>
<td>0.066</td>
<td>0.001</td>
</tr>
<tr>
<td>557.9</td>
<td>1.02</td>
<td>6.15E-04</td>
<td>1.00</td>
<td>111.9</td>
<td>4.3</td>
<td>0.077</td>
<td>0.010</td>
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<td>494.9</td>
<td>1.00</td>
<td>6.84E-04</td>
<td>1.00</td>
<td>93.2</td>
<td>3.7</td>
<td>0.080</td>
<td>0.019</td>
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<td>573.1</td>
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<td>120.0</td>
<td>4.9</td>
<td>0.069</td>
<td>0.006</td>
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<tr>
<td>540.3</td>
<td>1.02</td>
<td>6.35E-04</td>
<td>1.00</td>
<td>119.6</td>
<td>4.7</td>
<td>0.086</td>
<td>0.021</td>
</tr>
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<td>6.64E-04</td>
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<td>4.0</td>
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<td>0.011</td>
</tr>
<tr>
<td>545.8</td>
<td>1.02</td>
<td>6.30E-04</td>
<td>1.00</td>
<td>118.2</td>
<td>4.6</td>
<td>0.076</td>
<td>0.010</td>
</tr>
<tr>
<td>550.8</td>
<td>0.98</td>
<td>6.02E-04</td>
<td>1.00</td>
<td>109.6</td>
<td>4.2</td>
<td>0.036</td>
<td>0.031</td>
</tr>
</tbody>
</table>
APPENDIX G. HIGH-TEMPERATURE LFS MEASUREMENTS: SUPP. MAT.

G.4 Low-temperature $C_3H_8$ results

The experimental conditions and associated flame speed and Markstein length results for the low-temperature $C_3H_8/\text{air}$ flame speed experiments presented in Chapter 6, Section 6.4.2, are reported in Table G.3.

Table G.3: Summary of low-temperature $C_3H_8/\text{air}$ flame speed results

<table>
<thead>
<tr>
<th>$T_{unburned}$ ($T_5$, K)</th>
<th>$P_{unburned}$ ($P_5$, atm)</th>
<th>$\rho_{unburned}$ (g/cm$^3$)</th>
<th>Phil</th>
<th>$S_L$ (cm/s)</th>
<th>$S_L$ Uncert.</th>
<th>$L_b$ (cm)</th>
<th>$L_b$ Uncert.</th>
</tr>
</thead>
<tbody>
<tr>
<td>391.2</td>
<td>0.91</td>
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<td>0.99</td>
<td>58.8</td>
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<td>0.020</td>
<td>0.016</td>
</tr>
<tr>
<td>400.3</td>
<td>1.00</td>
<td>8.95E-04</td>
<td>1.00</td>
<td>56.2</td>
<td>4.7</td>
<td>0.051</td>
<td>0.016</td>
</tr>
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<td>58.5</td>
<td>4.9</td>
<td>0.050</td>
<td>0.016</td>
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<td>56.3</td>
<td>4.8</td>
<td>0.042</td>
<td>0.016</td>
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<td>59.0</td>
<td>5.0</td>
<td>0.039</td>
<td>0.016</td>
</tr>
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<td>62.0</td>
<td>5.2</td>
<td>0.045</td>
<td>0.016</td>
</tr>
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<td>0.016</td>
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<td>7.5</td>
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<td>0.033</td>
<td>0.016</td>
</tr>
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<td>0.018</td>
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<td>7.3</td>
<td>0.051</td>
<td>0.019</td>
</tr>
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<td>489.7</td>
<td>1.01</td>
<td>7.43E-04</td>
<td>1.00</td>
<td>94.3</td>
<td>8.0</td>
<td></td>
<td></td>
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<td>7.1</td>
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<td>0.016</td>
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<td>90.4</td>
<td>7.5</td>
<td>0.050</td>
<td>0.018</td>
</tr>
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<td>0.038</td>
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<td>0.016</td>
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<td>0.009</td>
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</table>
G.5 High-temperature \( \text{C}_3\text{H}_8 \) results

The experimental conditions and associated flame speed and Markstein length results for the high-temperature \( \text{C}_3\text{H}_8/\text{modified-air} \) flame speed experiments presented in Chapter 6, Section 6.4.3, are reported in Table G.4.

<table>
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<tr>
<th>( T_{unburned} ) (( T_5 ), K)</th>
<th>( P_{unburned} ) (( P_5 ), atm)</th>
<th>( \rho_{unburned} ) (g/cm(^3))</th>
<th>Phi</th>
<th>( S_L ) (cm/s)</th>
<th>( S_L ) Uncert.</th>
<th>( L_b ) (cm)</th>
<th>( L_b ) Uncert.</th>
</tr>
</thead>
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<td>273.7</td>
<td>18.0</td>
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<td>0.007</td>
</tr>
<tr>
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<td>3.39E-04</td>
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<td>303.5</td>
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<td>0.80</td>
<td>317.0</td>
<td>22.1</td>
<td>0.033</td>
<td>0.014</td>
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<td>3.46E-04</td>
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<td>294.2</td>
<td>13.0</td>
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<td>0.011</td>
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<td>0.011</td>
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<td>0.80</td>
<td>358.7</td>
<td>14.2</td>
<td>0.035</td>
<td>0.003</td>
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</table>
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