SHOCK TUBE STUDIES OF THERMAL DECOMPOSITION REACTIONS USING ULTRAVIOLET ABSORPTION SPECTROSCOPY

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Abstract

Several elementary thermal decomposition reactions of importance in combustion systems have been investigated using ultraviolet laser absorption spectroscopy and high-temperature shock tube methods. These studies are broken into three categories: 1) the decomposition of alkanes, 2) the incubation and decomposition of CO$_2$, and 3) the decomposition of the benzyl radical and toluene.

Mixtures of four alkanes dilute in argon were shock heated to determine rate coefficients for five C-C bond fission reactions:

\[
\begin{align*}
    C_2H_6 & \rightarrow CH_3 + CH_3 \\
    C_3H_8 & \rightarrow CH_3 + C_2H_5 \\
    i-C_4H_{10} & \rightarrow CH_3 + i-C_3H_7 \\
    n-C_4H_{10} & \rightarrow CH_3 + n-C_3H_7 \\
    n-C_4H_{10} & \rightarrow C_2H_5 + C_2H_5
\end{align*}
\]

The progress of reaction was monitored by measuring methyl radical (CH$_3$) concentration using narrow-linewidth laser absorption at 216.62 nm. Experiments were performed over the temperature range of 1297 to 2034 K and pressure range of 0.13 to 8.8 atm. The rate coefficient determinations were fit using Rice-Ramsperger-Kassel-Marcus (RRKM) and master equation calculations using a restricted (hindered) Gorin model for the transition states. These fits provide analytic expressions for the low- and high-pressure-limit rate coefficients and falloff parameters in the Troe pressure broadening formulation.

The thermal decomposition of CO$_2$

\[
    CO_2 + M \rightarrow CO + O(^3P) + M
\]

was investigated behind shock waves at temperatures of 3200 to 4600 K and pressures of 0.44 to 0.98 atm. Ultraviolet laser absorption at 216.5 and 244 nm was used to monitor the CO$_2$ concentration with microsecond time resolution, allowing the observation of a pronounced incubation period prior to steady CO$_2$ dissociation for the first time, confirming the expected bottleneck in collisional activation of this triatomic molecule.
Master-equation calculations, with a simple model for collisional energy transfer, were carried out to describe the measured incubation times and decomposition rate coefficient. The master equation calculations suggest that the energy transferred per collision must have a greater than linear dependence on energy.

The decomposition of benzyl and toluene

\[
\begin{align*}
\text{C}_6\text{H}_5\text{CH}_2 & \rightarrow \text{C}_7\text{H}_6 + \text{H} \quad (7) \\
\text{C}_6\text{H}_5\text{CH}_3 & \rightarrow \text{C}_8\text{H}_5\text{CH}_2 + \text{H} \quad (8) \\
\text{C}_6\text{H}_5\text{CH}_3 & \rightarrow \text{C}_8\text{H}_5 + \text{CH}_3 \quad (9)
\end{align*}
\]

was investigated behind shock waves at temperatures of 1398 to 1782 K and pressures around 1.5 atm. Benzyl radicals were detected using laser absorption at 266 nm to monitor the progress of reaction. The fast decomposition of benzyl iodide (C₆H₅CH₂I) dilute in argon behind shock waves provided an instantaneous benzyl (C₆H₅CH₂) source enabling the measurement of the rate coefficient for reaction (7) by monitoring the pseudo-first-order decay in benzyl absorption at 266 nm. Rate coefficients for reactions (8) and (9) were determined by monitoring benzyl absorption at 266 nm during the shock heating of toluene dilute in argon. RRKM/master equation calculations were carried out for the two-channel toluene decomposition using a restricted (hindered) Gorin model for the two transition states providing extrapolation of the measured rate coefficients to the high-pressure-limit.
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Chapter 1: Introduction

1.1 Motivation

The design and optimization of combustion systems relies heavily on accurate predictive modeling. Models for combustion systems typically involve mathematical solution of a set of partial and ordinary differential equations describing heat transport, fluid dynamics, and chemistry. Solution of these equations provides information regarding performance such as efficiency and pollutant emissions. The importance of chemistry in modeling combustion systems varies significantly depending on the type of combustion system. For instance, in a highly turbulent combusting flow the fluid dynamics may play a more important role than the chemistry and a kinetic model might be able to predict important observables with a reduced chemistry scheme or even a one-step global reaction rate. However, in many combustion systems the rates of individual elementary chemical reactions are significant in governing overall performance. For instance, the ignition timing, and therefore stability, of a homogenous charge compression ignition (HCCI) engine is governed by chemical kinetics, not transport phenomena. Optimization of advanced combustion systems, such as HCCI, can only be realized when the chemical reactions that govern their performance are well understood.

One class of reactions important in describing the overall ignition characteristics of a fuel/oxidizer mixture are thermal decomposition reactions (also called dissociation reactions). These reactions are often responsible for the initial fragmentation of a fuel undergoing oxidation and therefore the overall rate of ignition, or ignition delay time, of a given fuel/oxidizer mixture is often sensitive to the rates of decomposition reactions. In addition, thermal decomposition reaction rate coefficients have the interesting characteristic of exhibiting pressure-dependence, providing another complication in the modeling and measurement of their rates.

The subject of the studies presented here is the measurement of reaction rate coefficients for several important thermal decomposition reactions. These studies are
broken up into three main topics: 1) the decomposition of alkanes, 2) the decomposition and incubation of CO$_2$, and 3) the decomposition of benzyl radicals and toluene. In all of these studies shock-heating was used to initiate thermal decomposition and ultraviolet laser absorption diagnostics were used to monitor either product or reactant species.

1.2 Background

1.2.1 Alkane decomposition

The thermal decomposition of alkanes plays an important role in alkane oxidation, particularly at high-temperatures (>1000 K) where C-C fission reactions often are the dominant initiation steps. In addition the reverse reactions, alkyl radical recombination, play an important role as termination steps. The importance of these reactions is quantified by the large sensitivity that global combustion phenomena, such as ignition delay and flame speed, show for the reaction rate coefficients of these decomposition/recombination reactions [1-2]. The following alkane decomposition reactions are the focus of this study:

\[
\begin{align*}
  & C_2H_6 \rightarrow CH_3 + CH_3 \\
  & C_3H_8 \rightarrow CH_3 + C_2H_5 \\
  & i-C_4H_{10} \rightarrow CH_3 + i-C_3H_7 \\
  & n-C_4H_{10} \rightarrow CH_3 + n-C_3H_7 \\
  & n-C_4H_{10} \rightarrow C_2H_5 + C_2H_5
\end{align*}
\]

(1) (2) (3) (4) (5)

As an example, the sensitivity of propane ignition delay time on various reactions is shown in Figure 1.1, where the ignition delay time is defined as the time to the peak rate of change in the OH radical concentration. At 1500 K and 1.0 atm the ignition delay shows the greatest sensitivity to propane decomposition, reaction (2). The ignition delays of other alkanes show similar sensitivity to decomposition reactions motivating this study [1-2].

Reaction (1) has been extensively studied in both the dissociation and recombination directions across a broad range of temperatures. Previous high-temperature shock tube measurements have utilized different techniques: gas chromatography in a single-pulse shock tube [3], H-atom atomic resonance absorption
spectroscopy (ARAS) [4-5], infrared absorption of ethane at 3.39 \( \mu \text{m} \) [6], xenon lamp absorption of \( \text{CH}_3 \) [7], laser-schlieren [8-9], and laser absorption of \( \text{CH}_3 \) [10-13]. Reaction (1) has also been the subject of many theoretical studies of varying levels of complexity [14-22,92]. At low-temperature (<1000 K) the theoretical studies agree with one another and with the experimental data quite well, due in a large part to the excellent low-scatter recombination data of Slagle et al. [23] (296-906 K), but at higher temperatures the theoretical high-pressure rate coefficients show some disagreement with one another and experimental data. High-temperature data with very low scatter are thus needed, in order to resolve these disagreements. A comparison of the results of the previous experimental studies at high-temperatures for the rate coefficient of reaction (1), \( k_1 \), is shown in Figure 1.2.

Reaction (2) has been studied previously to a lesser degree than reaction (1), with previous high-temperature studies including single-pulse shock tube studies [24-25] and several studies utilizing time-resolved techniques: H-atom ARAS [26], laser-schlieren [27], and 3.39 \( \mu \text{m} \) absorption of propane [28-30]; additionally, a recent recombination study of reaction (2) has been performed by Knyazev and Slagle [31] over the temperature range 301 to 800 K. Reaction (2) has also been examined using various levels of unimolecular theory [14,17,31-33]. The results of the previous experimental studies on propane decomposition are compared in Figure 1.3.

Reaction (3) has been studied previously at high-temperature using single-pulse shock tube techniques [34], 3.39 \( \mu \text{m} \) absorption of iso-butane [35], and UV lamp absorption of \( \text{CH}_3 \) [36]. The results of these previous experimental studies for \( k_3 \) are shown in Figure 1.4. Reactions (4) and (5) have not been studied in great detail at high-temperatures, although there is one shock tube study of note in which UV lamp absorption of \( \text{CH}_3 \) was employed to determine \( k_4 \) [37]. The reaction (5) rate coefficient has not been previously determined at high-temperatures but, there have been several low-temperature studies performed primarily in flow tubes [38-40].

### 1.2.2 \( \text{CO}_2 \) decomposition and incubation

The spin forbidden thermal decomposition of carbon dioxide

\[
\text{CO}_2 + \text{M} \rightarrow \text{CO} + \text{O}^{(3}\text{P}) + \text{M}
\]  

(6)
behind shock waves has been the subject of many experimental studies [41-56], dating back to the 1960’s, due to interest in modeling hypersonic flows and very high-temperature combustion phenomena such as detonation waves. While several of the experimental studies agree on the rate coefficient for CO$_2$ decomposition, none have observed an incubation period prior to decomposition. Despite the lack of experimental findings for CO$_2$ incubation, two analytical master equation calculations have predicted such a phenomenon [57-58].

When a molecule is rapidly heated by the passing of a shock wave, energy in the translational and rotational modes equilibrates quite rapidly (µs), but the vibrational modes equilibrate at a somewhat slower rate that can often be observed [59-74]. At temperatures high enough for the molecule to dissociate, this finite rate of energy transfer leads to the observation of a delay in the onset of steady dissociation, and this delay is defined as the incubation time [59]. Although observed for several diatomic species (e.g., O$_2$ [60-62], N$_2$ [63], CO [64]), incubation times have only been observed for a few polyatomic species. The common characteristic required to observe incubation in a polyatomic molecule has been a relatively high lowest vibrational frequency, which causes a bottleneck in collisional activation. The first observation of incubation in a polyatomic was reported by Dove et al. [65] in N$_2$O decomposition behind shock waves. These experimental findings were later analyzed using master equation techniques by Forst and Penner [57], Yau and Pritchard [58], and Dove and Troe [66]. Kiefer and co-workers also have observed incubation times in several hydrocarbons using the laser-schlieren technique [67-70]. Barker and co-workers analyzed the Kiefer results for cyclohexene and norbornene using numerical master equation techniques [71-72]. Recently Hippler and co-workers have observed incubation times in CH$_3$ [73] and toluene decomposition [74] and performed numerical master equation analysis for these reactions.

### 1.2.3 Benzyl radical and toluene decomposition

Aromatic fuels have received considerable attention in the past few years due to interest in developing detailed mechanisms to describe their oxidation [75-79]. Although detailed mechanisms are in development, there is a lack of high-quality experimental rate
coefficient data for the reactions of importance in describing aromatic oxidation. One class of reactions that is poorly understood and is of importance in these mechanisms is the thermal decomposition of aromatics.

For instance, the decomposition of benzyl radicals

$$C_6H_5CH_2 \rightarrow C_7H_6 + H$$ (7)

plays a major role in the oxidation of aromatic hydrocarbons, particularly toluene, as a source of H-atoms. As is the case of most reactions involving aromatics, benzyl decomposition is not well understood and previous rate coefficient measurements show large scatter and disagreement. Previous high-temperature measurements have been made behind shock waves using ultraviolet absorption [80-85] and H-atom ARAS [86-87]. A comparison of the findings of these previous studies is given in Figure 1.5.

The decomposition of toluene is one of the most important initiation steps in the oxidation of toluene at moderate- to high-temperatures (>1200 K). Despite its importance the decomposition of toluene is not well understood due to complications in its measurement. The primary complication is that toluene decomposition takes place via two channels

$$C_6H_5CH_3 \rightarrow C_6H_5CH_2 + H$$ (8)
$$C_6H_5CH_3 \rightarrow C_6H_5 + CH_3$$ (9)

making isolated measurement of the two rate coefficients, $k_8$ and $k_9$, difficult. Additionally, fast secondary and recombination reactions occur in parallel with the decomposition, further complicating kinetic isolation of reactions (8) and (9). Previous measurements of toluene decomposition have been made at high-temperatures behind shock waves using time-of-flight mass spectrometry [89], laser-schlieren [89], ultraviolet absorption [81,83,84,85,91], and H-atom ARAS [74,88,90]. Additionally, laser-excitation techniques used to measure energy specific rate coefficients for toluene decomposition have been performed [93-94]. A comparison of the results of these studies for the overall decomposition rate, $k_8 + k_9$, is shown in Figure 1.6 and the branching ratio, $k_8/(k_8 + k_9)$, in Figure 1.7.
1.3 Scope and organization of thesis

The objectives of this work were to make low-uncertainty measurements of the rate coefficients for reactions (1)-(9). To achieve this goal ultraviolet laser absorption diagnostics were developed and spectroscopic measurements carried out for the detection of methyl radicals (CH₃), carbon dioxide (CO₂), and benzyl radicals (C₆H₅CH₂). These laser diagnostics allowed measurement of rate coefficients for reactions (1)-(9) at high-temperatures behind shock waves. The resulting rate coefficient data (and in the case of CO₂, incubation times) were fit using computational techniques based on Rice-Ramsperger-Kassel-Marcus (RRKM) theory and the master equation for internal energy. In addition to the chemical kinetic studies outlined above, a thermometry technique was developed, using ultraviolet CO₂ absorption, to characterize the temperature time-history of shock-heated mixtures.

In Chapter 2 a description of the shock tube and laser diagnostics used in these studies is given. Additionally, Chapter 2 contains a description of the spectroscopic measurements made to enable determination of the reaction rate coefficients. Chapter 3 describes the basis for the RRKM/master equation computational techniques used to fit the experimentally determined rate coefficients. Chapters 4-6 contain the major findings of these studies, the determination of rate coefficients for reactions (1)-(9). Chapter 4 contains the findings for alkane decomposition, Chapter 5 the findings for CO₂ decomposition and incubation, and Chapter 6 the findings for benzyl radical and toluene decomposition. Conclusions and recommendations for future work are made in Chapter 7.

Appendix A contains tabulation of all of the rate coefficient and incubation time determinations presented in Chapters 4-6. Appendix B contains the uncertainty analysis for the rate coefficient determinations for reactions (1)-(9). A thermometry technique using ultraviolet CO₂ absorption and its application to non-reacting and reacting shock-heated mixtures is described in Appendix C. Instructions for the synthesis of azomethane are given in Appendix D. The reaction mechanism used for the modeling of the benzyl and toluene decomposition experiments is given in Appendix E. Finally, Appendix F provides x-t diagrams and a discussion of the wave dynamics and test time for the shock tube used in the studies presented in this thesis.
Figure 1.1: Sensitivity ($S_{\text{ign},i} = \frac{d\tau_{\text{ign}}}{dk_i}[k_i/\tau_{\text{ign}}]$) of propane ignition delay time to various reactions, based on GRI Mech 3.0 [95]. Conditions: stoichiometric propane in air, 1500 K, and 1.0 atm.

Figure 1.2: Previous experimental data for the ethane decomposition rate coefficient, $k_1$, normalized to 1 atm; taken from Davidson et al. (1995) [11].
Figure 1.3: Previous experimental data for the propane decomposition rate coefficient, $k_2$.

Figure 1.4: Previous experimental data for the iso-butane decomposition rate coefficient, $k_3$. 
Figure 1.5: Previous experimental data for the benzyl radical decomposition rate coefficient, $k_7$.

Figure 1.6: Previous experimental data for the toluene overall decomposition rate coefficient $k_8 + k_9$. Luther et al. [94] performed a laser excitation study to determine the rate coefficient at infinite pressure.
Figure 1.7: Previous experimental data for the toluene decomposition branching ratio \( \frac{k_8}{k_8 + k_9} \). Luther et al. [94] performed a laser excitation study to determine the branching ratio at infinite pressure.
Chapter 2: Experimental methods

This chapter describes the shock tube facility and the laser diagnostics used for the measurement of reaction rate coefficients, $k_1$-$k_9$. The three sections on laser diagnostics also describe the measurement of absorption cross-sections for the three species of interest (CH$_3$, CO$_2$, and benzyl).

2.1 Shock tube facility

The experiments reported in this thesis were performed behind both incident and reflected shock waves in a helium pressure-driven stainless-steel shock tube. The driven section is 8.54 m long and the driver section 3.35 m long; both sections have an inner diameter of 14.13 cm. The shock tube driven and driver sections are separated by a polycarbonate diaphragm 0.005 to 0.08” in thickness. The diaphragm is ruptured as the driver section is filled with helium by a set of cutter blades configured in a cross geometry. The bursting pressure of the diaphragm is controlled by the thickness of the diaphragm and the position of the cutter blades.

Prior to each experiment the driven section was evacuated with a vacuum system consisting of a zeolite-trapped mechanical pump and a Varian V-250 turbomolecular pump, providing ultimate pressures of $10^{-7}$ torr with a typical leak rate of $10^{-6}$ torr per minute (when evacuated overnight). Shock velocities were measured with five piezoelectric pressure transducers (PCB 113A26 transducer, PCB 483B08 amplifier) spaced axially over the last 1.5 m of the tube. The signals from the five transducers were sent to four Philips PM6666 counter timers with resolution of 0.1 µs to determine the shock passage time interval. The shock velocities measured from the shock passage time intervals were extrapolated to the endwall using a linear attenuation profile with typical attenuation rates of 0.8 to 1.5% per meter. In addition to the five pressure transducers used for shock velocity an additional Kistler transducer (603B1 transducer and 5010B amplifier) was used to measure the pressure time-history during shock-heating. The pre-
shock initial mixture pressure was measured using one of two high-accuracy MKS Baratron 690A capacitance manometers (100 and 10,000 Torr models) with output given by two MKS 270D signal conditioners. The incident and reflected shock conditions were calculated using the normal shock equations; uncertainty in the experimental pressure and temperature are ~1% and ~0.7%, respectively, with the primary contribution being the uncertainty in the measured shock velocity; for details on the uncertainty analysis for pressure and temperature see J.T. Herbon’s Ph.D. thesis [96]. For most of the experiments presented here, vibrational equilibrium can be assumed immediately behind the incident and reflected shock; the one exception, is the experiments involving CO₂. In these experiments the finite rate of V-T transfer plays an important role and is discussed later in this chapter and in Chapter 5.

Mixtures were made in a turbo-pumped stainless-steel mixing tank (12-liter) with an internal stirring system and were allowed to mix for at least four hours prior to experiments. Research grade argon (99.999%) was used as the driven carrier gas. The gas mixtures were introduced into the mixing tank through a high-purity gas mixing manifold. The manifold allowed for introduction of both gases from high-pressure cylinders and liquid chemicals with vapor pressure into the mixing tank. The gas pressures were monitored with two high-accuracy MKS Baratron 690A capacitance manometers (100 and 10,000 Torr models). The mixing tank pressure was monitored with a Setra 280E capacitance pressure transducer (250 psia). The mixing tank and mixing manifold were evacuated with a mechanical pump and Varian V-80 turbomolecular pump, providing pressures of 10⁻⁶ Torr and leak rates of 10⁻⁶ Torr/min when evacuated overnight.

Optical measurements were made at a location 2 cm from the endwall in the case of reflected shock experiments and a location of 29 cm from the endwall for incident shock experiments. The shock-heated gases were accessed through 0.75” diameter flat windows made of either UV fused silica or CaF₂ flush mounted to the inner radius of the shock tube.
2.2 CH₃ ultraviolet laser absorption diagnostic

Prior to the studies performed for the determination of rate coefficients for reactions (1)-(5) a suitable diagnostic was needed for the quantitative detection of methyl radicals (CH₃), a product species of reactions (1)-(4). Methyl radicals are known to absorb near 216 nm in the B²A₁' ← X²A₂'' electronic system [97]. The distinctive features of the spectra are the P+Q band peak and the R band peak located at 216.62 nm and 215.9 nm respectively at high-temperature [98]; see Figure 2.1 for the CH₃ absorption spectrum. The absorption at the P+Q band peak shows less variation with temperature than the R band peak. Therefore, 216.62 nm (the P+Q peak) was chosen as the wavelength of choice for detecting methyl at high temperatures.

2.2.1 Optical setup

The optical setup used to generate 216.62 nm laser radiation is shown in Figure 2.2. Laser light at 433.24 nm (200-400 mW) was created by pumping a Coherent 699-05 ring dye laser, operating on stilbene 420 dye (50 psi dye jet pressure), with 7 W (all-lines UV) from a Coherent Innova 25/7 Ar⁺ laser. The output of the dye laser was then frequency-doubled in a Spectra-Physics Wavetrain external doubling cavity using an angle-tuned beta barium borate (β-BaB₂O₄, BBO) crystal to create 216.62 nm laser radiation with a linewidth of 40 MHz. The wavelength was monitored by passing a portion of the dye laser output (undoubled) into a Burleigh WA-1000 Wavemeter (uncertainty ±0.017 cm⁻¹); mode quality was monitored by passing a portion through a scanning interferometer. The doubled ultraviolet beam (2-3 mW at 216.62 nm) was passed to the shock tube where it was split into two components: one passing through the shock tube roughly 1-2 mm in diameter to be absorbed by CH₃ (I), the other was detected prior to absorption as a reference (I₀). These two beams were detected using UV enhanced S1722-02 Hamamatsu silicon photodiodes (risetime < 0.5 µs, 4.1 mm diameter) installed in Thor Labs PDA55 detectors and recorded on a digital oscilloscope. The intensity noise characteristics of the Ar⁺ pump output (all-lines UV), dye laser output (433.24 nm), and frequency doubled output (216.62 nm) are given in Figure 2.3 and Table 2.1.
Figure 2.3 demonstrates that the intensity noise in the Ar\textsuperscript{+} pump and dye laser are comparable but the intensity noise in the 216.62 nm doubled output is substantially greater than that of the 433.24 nm dye laser output. The noise amplification in the harmonic output is due to frequency instability in the dye laser fundamental. The actively stabilized Wavetrain doubling cavity can only track frequency changes that occur at less than 10 GHz per second; instabilities that result in frequency changes that occur at faster rate result in intensity noise in the harmonic output (216.62 nm).

The Coherent 699-05 ring dye laser was passively stabilized with two etalons contained in the intra-cavity assembly (ICA): a 10 GHz thick etalon and a 225 GHz thin etalon. These etalons caused an attenuation of about 40% of the broadband power but ensured a single frequency within an effective 40 MHz linewidth (±20 MHz). The instantaneous linewidth of the laser is a fraction of a hertz when operating in a single mode but dye jet fluctuations broaden the linewidth resulting in this effective linewidth of 40 MHz. However, the rate of jitter of the instantaneous linewidth within the effective 40 MHz linewidth is not controllable and the frequency jitter induced intensity noise results in the doubling cavity. A two-beam common-mode rejection scheme can be used to reject the noise in the 216.62 nm laser beam providing acceptable signal-to-noise for shock tube experiments in the resulting absorbance (minimum detection ~0.1% absorbance), see Figure 2.4 and Table 2.1.

The detection of 216.62 nm laser radiation (and the other wavelengths discussed later in this chapter) was carried out using modified Thorlabs PDA55 detectors. The detectors are modified by replacing the stock 1 mm diameter Thorlabs silicon photodiode with a UV-enhanced Hamamatsu S1722-02 4.1 mm in diameter. The UV-enhanced photodiode allows for greater UV sensitivity down to 200 nm without sacrificing time response. The PDA55 detectors are easily modified by unsoldering the stock photodiodes and soldering in the Hamamatsu photodiodes.

Unfortunately deep UV light damages silicon [199]. Therefore, we were careful in the manner in which we detected UV laser radiation (216, 244, and 266 nm). After exposure to focused laser radiation the photodiodes exhibit reduced sensitivity to UV light at the location where the laser beam was focused. In fact a sensitivity hole in the detector at the location of the focused laser beam occurs, as shown in Figure 2.5 for 266
nm light. The reduced sensitivity at the beam location can manifest itself as beam steering noise in shock wave experiments. To avoid burning sensitivity holes in the detectors and to avoid beam steering fluctuations it was determined the best solution for detection is to expand the beam onto the detector using a lens so that it covers the majority of the 4.1 mm diameter photodiode surface. Additionally, one must be very careful to never leave the UV beam incident on the detector unless aligning or performing an experiment.

2.2.2 CH₃ absorption coefficient measurements and results

For determination of the methyl absorption coefficient at 216.62 nm, methyl radicals were generated immediately behind shock waves by the dissociation of a precursor. Three different precursors were used for various temperature ranges: azomethane (CH₃N₂CH₃) for the lowest temperatures (1219-1687 K), methyl iodide (CH₃I) for intermediate temperatures (1733-2146 K), and ethane (C₂H₆) for the highest temperatures (1938-2501 K). Low concentrations of these precursors (200 or 400 ppm) were mixed with argon prior to experiments. Azomethane is not sold commercially and was synthesized using the method of Jahn [99] which has previously been found to be cleaner and easier than the method of Renaud and Leitch [100]; see Appendix D for synthesis instructions. The CH₃ precursors were chosen for a given experiment such that they would dissociate quickly behind the shock wave. In the case of experiments performed behind reflected shock waves, care was taken not to dissociate the precursor behind the incident shock wave, as this would lead to the formation of ethane, via reaction (10) below, which would then slowly dissociate behind the reflected shock wave. This problem necessitated the use of incident shock heating for some experiments.

In a given experiment, regardless of the precursor, the CH₃ profiles had the same temporal characteristics. At time zero the shock wave (incident or reflected depending on the experiment) passed the laser beam causing a schlieren (density deflection) spike in the signal. Following shock heating the CH₃ absorbance (-ln(I₀/I)) rises immediately to a peak due to the decomposition of the precursor and then decays primarily due to methyl-methyl reactions:

\[
CH₃ + CH₃ \rightarrow C₂H₆
\]  (10)
\[
\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_5 + \text{H}
\] (11)

The absorbance traces allow the extraction of the absorption coefficient at 216.62 nm by back-extrapolating the early time decay in absorbance to time-zero and using Beer’s law

\[
\frac{I}{I_0} = \exp(-k_{\lambda, \text{CH}_3} P X_{\text{CH}_3} L)
\]

where \(I\) is the transmitted laser intensity, \(I_0\) is the reference beam intensity, \(k_{\lambda, \text{CH}_3}\) [atm\(^{-1}\)cm\(^{-1}\)] is the temperature-dependent \text{CH}_3 absorption coefficient at 216.62 nm, \(P\) [atm] is the total pressure, \(X_{\text{CH}_3}\) is the \text{CH}_3 mole fraction, and \(L\) is the absorption path length (diameter of the shock tube 14.13 cm). Additionally, the total rate coefficient for \text{CH}_3 + \text{CH}_3, k_{10} + k_{11}, can be fit to the decay in absorbance. See Figure 2.6 for an example experiment and Figure 2.7 for the absorption coefficient results with comparison to previous studies. The uncertainty in the absorption coefficient obtained by these experiments, estimated to be ±5%, is the result of uncertainties in experimental temperature and pressure, uncertainties in the initial concentration of methyl precursors, and uncertainties associated with the fitting of experimental traces. A least-squares expression for the absorption coefficient is given by

\[
k_{\lambda, \text{CH}_3} = 1.475 \times 10^4 T^{-1.004} \exp(2109K/T) \text{ [atm}\(^{-1}\)\text{cm}\(^{-1}\)]
\]

Additionally, no pressure-dependence in the \text{CH}_3 absorption coefficient was detectable in experiments up to 8 atm.

The current absorption coefficient results are in good agreement with the previous laser absorption results from our laboratory, Davidson et al. [101], but the scatter in the data is only ±5%, at least a factor of two smaller than the scatter in the data of Davidson et al. The broadband lamp measurements of Glänzer et al. [102] and Möller et al. [103] are in good agreement with the current determination, while the broadband lamp determination of Tsuboi [104] lies lower than the current determination. The narrow line-width measurements of Hwang et al. [105] (213.9 nm) and Du et al. [106] (215.94 nm) differ from the current findings due to the different wavelengths used in these studies.

### 2.3 CO\(_2\) ultraviolet laser absorption diagnostic

Ultraviolet absorption due to vibrationally hot CO\(_2\) was used to investigate the incubation and decomposition of CO\(_2\). In addition the ultraviolet absorption of hot CO\(_2\) provides opportunity for thermometry measurements in high-temperature gases.
Appendix C describes thermometry measurements behind shock waves in reacting and non-reacting mixtures similar to the measurements Jeffries et al. [107] and Mattison et al. [108] have made in pulse detonation engines and reciprocating internal combustion engines. Measurement of absorption cross-sections were made at four available laser wavelengths: 216.5, 244, 266, and 306 nm.

2.3.1 Optical setup

Continuous-wave laser radiation was generated at four different wavelengths: 216.5 nm (2-3 mW) was generated by doubling the output of an Ar\textsuperscript{+} pumped dye-laser, operating at 433 nm, in a BBO external frequency-doubling cavity, described above in section 2.2.1; 306 nm (2-3 mW) was generated by intra-cavity frequency doubling in a Nd:YVO\textsubscript{4}-pumped (532 nm) dye laser operating at 612 nm, as described in previous OH radical studies by Herbon and co-workers [96]; and 244 and 266 nm (1.5 mW each) were produced by the single pass of a focused laser beam at 488 nm (Ar\textsuperscript{+} line at 7 W) and 532 nm (Nd:YVO\textsubscript{4} at 5 W) through angle-tuned BBO. The harmonics (244 and 266 nm) were separated from the fundamental beams (488 and 532 nm) with a set of Pellin-Broca prisms. See Figure 2.8 for a schematic of the optical setup used to generate 244 and 266 nm laser radiation. The intensity noise characteristics of the 244 and 266 nm output are shown in Figure 2.9 and Table 2.1. Again a two beam common-mode rejection scheme was used to reject the noise in the 244 nm signal providing acceptable signal-to-noise for shock tube experiments in the resulting absorbance (minimum detection \textasciitilde0.1% absorbance).

The UV laser beams were split into two components: one, \textasciitilde1 mm in diameter, passing through the shock tube to be absorbed by CO\textsubscript{2} (I), and one detected prior to absorption as a reference (I\textsubscript{0}). These two beams were detected using silicon photodiodes (Thor Labs PDA55 detector and Hamamatsu S1722-02 diode) and recorded on a digital oscilloscope. The absorption cross-sections were determined using Beer’s law

\[
\frac{I}{I_0} = \exp(-\sigma_{CO_2}(\lambda,T) n_{CO_2} L)
\]

where I is the transmitted laser intensity, I\textsubscript{0} is the reference beam intensity, \(\sigma_{CO_2}(\lambda,T)\) [cm\textsuperscript{2}molecule\textsuperscript{-1}] is the wavelength- and temperature-dependent CO\textsubscript{2} absorption cross-section, \(n_{CO_2}\) [molecules cm\textsuperscript{-3}] is the CO\textsubscript{2} number density, and L is the absorption path.
length (diameter of the shock tube 14.13 cm). For these experiments absorption cross-sections were not derived for experiments in which the absorbance was less than 0.7%.

2.3.2 CO₂ ultraviolet absorption cross-section measurements

The absorbance (\(\text{ln}(I_0 / I)\)) traces for several experiments are shown in Figure 2.10. The passage of the incident and reflected shock waves cause two schlieren spikes in the signal, due to steering of the beam off the detector. After the passage of the reflected shock (marked by a strong schlieren induced signal), there is a very short risetime in the absorption signal (~1-5 µs depending on the temperature and pressure) prior to the steady absorption due to hot CO₂. The absorption cross-section is determined during this plateau. This short induction time is caused by the CO₂/Ar V-T relaxation process [109-110] which brings the vibrationally cold CO₂ to an excited vibrational condition where absorption is possible. The observation of this induction time provides evidence that the high-temperature UV absorption of CO₂ comes from a vibrationally-excited CO₂ ground state \((^1\Sigma_g^+)\). It has been shown by Spielfiedel et al. [111] that molecules with excited bending modes could account for the hot CO₂ absorption at wavelengths longer than 200 nm because of the significantly greater Franck-Condon overlap these states have with the bent CO₂\(^1\Sigma_g^+)\) electronically excited upper state. The data shown in Figure 2.10 are at temperatures below 3000 K and do not show significant thermal decomposition in the first 200 µs. Note, also that the incident shock conditions also reach the vibrationally equilibrated conditions within the incident shock-heating time period for all experiments presented here.

At higher temperatures (>3000 K) the CO₂ undergoes thermal decomposition and the absorption traces show temporal decay at long times behind the reflected shock; an example experiment is shown in Figure 2.11. This example shows a significant induction prior to constant absorption following the incident shock due to vibrational relaxation; the vibrational equilibrated conditions behind the incident shock are 1812 K and 0.161 atm. Although, the vibrational relaxation is resolved after the incident shock, it is not resolved after the reflected shock because the higher temperature and pressure behind the reflected wave have a much faster vibrational energy transfer rate. Following the passage of the reflected shock wave an incubation period is observed in the absorption prior to the
thermal decomposition. The reflected shock conditions are 3838 K and 0.820 atm for the experiment in Figure 2.11. To our knowledge this is the first observation of incubation proceeding decomposition in CO₂, incubation is discussed in detail in Chapter 5. The absorption cross-section was determined for these decomposition experiments in the incubation plateau prior to dissociation, and therefore, the cross-section determination does not depend on knowledge of the subsequent chemistry. Additionally, the experimental temperature during the plateau is not in question for these high-temperature experiments because the CO₂ vibrational temperature equilibrates to the translational temperature within ~1 µs (the vibrational relaxation time in these high-temperature decomposition experiments).

2.3.3 CO₂ ultraviolet absorption cross-section results

The measured absorption cross-sections at the four wavelengths are plotted versus temperature in Figure 2.12 and compared with the data from the earlier study from our laboratory [112]. The agreement between the two studies is excellent for temperatures between 1800 to 2800 K; at higher temperatures, the extrapolation from the earlier lower temperature data would predict too large a cross section.

Due to the spectrally smooth nature of the UV CO₂ absorption feature [112] the current absorption cross-section results can be fit to a semi-empirical form

\[ \ln \sigma_{\text{CO}_2}(\lambda, T) = a + b\lambda \]

where \( a = c_1 + c_2T + c_3/T \) and \( b = d_1 + d_2T + d_3/T \). The cross-section, \( \sigma_{\text{CO}_2}(\lambda, T) \), is in units of \( 10^{-19} \text{ cm}^2\text{molecule}^{-1} \), the wavelength, \( \lambda \), is in units of 100 nm, and the temperature, \( T \), is given in units of 1000 K. The following parameters provide a best fit to the data: \( c_1 = 0.05449, c_2 = 0.13766, c_3 = 23.529, d_1 = 1.991, d_2 = -0.17125, \) and \( d_3 = -14.694 \). As is shown in Figure 2.12 the scatter of the data about the fit is quite small with a 1-\( \sigma \) standard deviation of ±1.8\%. It should be noted that this semi-empirical expression for the absorption cross-section should not be extrapolated outside the temperature and wavelength range of the data, but based on experience from the Schulz et al. [112] study interpolation is justified.

The uncertainty in the CO₂ cross-sections obtained in these experiments is the result of uncertainties in the experimental temperature and pressure, uncertainties in the
initial CO$_2$ concentration, and uncertainties associated with the signal-to-noise of a given experiment. The experiments in which the smallest absorption was monitored (low $T$ and long $\lambda$) provide cross-sections with the highest uncertainty. The majority of the cross-section results have uncertainties less than 5%; only a few of the smallest absorption cross-sections measured at 244 and 266 nm have larger uncertainties, with the largest uncertainty of 14%.

A comparison of the new cross-section determinations with those of Schulz et al. [112] (Figures 2.11 and 2.12) shows that the agreement is quite good in the middle of the temperature range, with deviations of 30% and 40% respectively at the highest and lowest temperatures of the Schulz et al. study which is within the reported uncertainty for the Schulz et al. data at the low- and high-temperature extremes. At low-temperatures the difference in the current findings and Schulz et al. is likely due to limited signal-to-noise in the Schulz et al. experiment; as the noise in the spectra (Figure 2.13) shows, the Schulz et al. results at low-temperatures and long wavelengths are significantly more uncertain than the current results due to poorer signal-to-noise. At high temperatures the current absorption cross-sections are lower than those of Schulz et al. due to their use of data impacted by CO$_2$ thermal decomposition. The current experiments indicate that the mechanism used in the Schulz et al. study (GRI Mech 3.0 [95]) to account for decomposition by CO$_2$ has a rate coefficient for CO$_2$ → CO + O that is too fast. Schulz et al. calculated the average mole fraction of CO$_2$ during their averaging time period using the GRI mechanism, thus giving a low CO$_2$ mole fraction. Thus they inferred an absorption cross-section that is too large. The current cross-section results do not rely on a chemical model to account for decomposition at high-temperature due to the microsecond time resolution provided by laser absorption.

2.3.4 CO$_2$ ultraviolet absorption ground state energy levels

The hot CO$_2$ pre-dissociative absorption is a continuum spectral feature caused by the intersection of many electronic-vibrational-rotational lines, with a dense energy spectrum typical of a triatomic. If one uses a quasi-diatomic approximation to describe these optical transitions [113], it can be shown that the absorbance at a given wavelength, $\lambda$, is described by
\[ \sigma_{CO2}(\lambda, T)n = \sigma_{CO2, eff}(\lambda)n_1 = [\sigma_{CO2, eff}(\lambda)n / Q_{vib}] \exp(-\varepsilon_1(\lambda) / kT) \]

where the average absorption takes place from a population with density \( n_1 \) at a lower state vibrational energy \( \varepsilon_1(\lambda) \) above the zero-energy ground state and where \( \sigma_{CO2, eff}(\lambda) \) is an effective cross-section for absorption. The vibrational partition function, \( Q_{vib} \), is given by

\[ Q_{vib} = [1 - \exp(-\theta_1/T)]^{-1}[1 - \exp(-\theta_2/T)]^2[1 - \exp(-\theta_3/T)]^{-1} \]

where \( \theta_1 = 1999 \) K, \( \theta_2 = 960 \) K, and \( \theta_3 = 3383 \) K. This description of the temperature-dependent absorption cross-section allows estimation of the effective vibrational energy of the absorbing lower state, \( \varepsilon_1(\lambda) \). The top graph in Figure 2.14 shows a plot of the product of the measured cross-section, \( \sigma_{CO2}(\lambda, T) \), with the vibrational partition function, \( Q_{vib} \) versus inverse temperature. This plot shows the product, \( \sigma_{CO2}(\lambda, T)Q_{vib} \), is linear with a slope that provides an estimate of the absorbing lower state energy, \( \varepsilon_1 \). The cross-section measurements provide lower state energies of 1.09 eV (8790 cm\(^{-1}\)), 1.48 eV (11940 cm\(^{-1}\)), 1.79 eV (14440 cm\(^{-1}\)), and 2.34 eV (18870 cm\(^{-1}\)) for absorption of photons at 216.5, 244, 266, and 306 nm respectively; these results can be expressed with

\[ \varepsilon_1(\lambda) = -1.94 + 0.014 \lambda \] [eV]

where the wavelength, \( \lambda \), is in nm. The lower state energy results are compared to previous determinations made by Eremin et al. [114] (193 nm) and Zabelinskii et al. [115] (238 and 300 nm) in the bottom graph of Figure 2.14 with good agreement. Unfortunately, this simplified photophysical model does not allow for an assignment of the absorption at a given wavelength to a specific vibrational level(s) because of the complex nature of the triatomic energy spectrum. Also, note that the linearity of \( \sigma_{CO2}(\lambda, T)Q_{vib} \) deviates slightly at the highest temperatures (top graph Figure 2.14). This deviation might be caused by enhanced absorption due to transitions to electronic states other than \( ^1B_2 \) such as \( ^1A_2, ^3A_2, \) and \( ^3B_2 \) that occurs at the highest temperatures where there is more highly excited population.
2.4 Benzyl radical ultraviolet laser absorption diagnostic

Benzyl radicals have strong broadband absorption in the ultraviolet from 245 to 275 nm [82,116] (see Figure 2.15) allowing detection of benzyl at 266 nm using the technique described in section 2.3.1 for generation of 266 nm laser radiation. Shock wave experiments were performed using the fast decomposition of benzyl iodide as a benzyl source. The experiments allowed determinations of the absorption cross-section of benzyl at 266 nm and the rate coefficient for benzyl decomposition, reaction (7). Here the absorption cross-section results are discussed and in Chapter 6 the decomposition rate coefficient is discussed.

2.4.1 Benzyl radical absorption cross-section measurements and results

Benzyl radicals (C₆H₅CH₂) were generated immediately behind shock waves via the dissociation of benzyl iodide

\[ \text{C}_6\text{H}_5\text{CH}_2\text{I} \rightarrow \text{C}_6\text{H}_5\text{CH}_2 + \text{I} \]  

(12)

Benzyl iodide, supplied by the Narchem Corporation (Chicago, IL) at 99% purity, was mixed with argon in the mixing tank at concentrations of 50 and 100 ppm prior to experiments. Benzyl iodide has a fusion temperature of 24.5º C at 1 atm. Therefore, for the successful introduction of benzyl iodide into the mixing tank the room temperature was raised to 26º C to increase the benzyl iodide vapor pressure and the tank was heated to 35º C and 45º C using a resistance heating tape to avoid wall condensation. The two sets of experiments (mixing tank at 35º C and 45º C) resulted in identical absorption cross-section results providing confidence that the benzyl iodide concentration in the mixtures was accurate as determined manometrically. Additionally, the benzyl iodide was cycled through several freeze-pump-thaw cycles prior to introduction into the mixing tank to avoid impurities from high volatility species. Mixtures were allowed to mix overnight prior to shock wave experiments to allow for complete mixing.
The absorbance at 266 nm for an example experiment is shown in Figure 2.16. Prior to the incident shock wave, no 266 nm absorption by benzyl iodide was detected at the low initial pressure, $P_1$. The passing of the incident shock wave causes a schlieren spike in the signal and the test gas is compressed and heated causing the benzyl iodide to absorb (1% absorbance at $t \approx 60$ µs in Figure 2.16). Behind the incident shock wave the benzyl iodide ($C_6H_5CH_2-I$ bond strength 51 kcal/mol) slowly dissociates into the more strongly absorbing benzyl radical and an I-atom. While the incident shock temperature is not sufficient to induce benzyl radical decomposition, the benzyl can combine to give stable dibenzyl

$$C_6H_5CH_2 + C_6H_5CH_2 \rightarrow C_6H_5CH_2CH_2C_6H_5 \quad (13)$$

The passage of the reflected shock wave causes complete dissociation of the benzyl iodide and the small amount of dibenzyl (Bz-Bz bond strength 65.2 kcal/mol) that was formed in the incident test time yielding one benzyl per benzyl iodide in the test mixture. The absorbance at time-zero after the reflected shock wave passing gives the 266 nm absorption cross-section of the benzyl radical. The absorbance at time-zero was found by back-extrapolating the steady decay in the absorbance signal to time-zero, defined as the center of the schlieren spike.

The decay in the absorbance signal after the passing of the reflected shock wave is primarily due to the decomposition of benzyl yielding a more weakly absorbing $C_7H_6$ molecule of unknown structure and an H-atom [117]

$$C_6H_5CH_2 \rightarrow C_7H_6 + H \quad (7)$$

To determine the rate coefficient for benzyl decomposition, reaction (7), the decay in absorbance was fit by using a detailed kinetic mechanism and accounting for the interfering absorption due to benzyl fragments and toluene. Toluene is formed by the secondary reaction

$$C_6H_5CH_2 + H \rightarrow C_6H_5CH_3 \quad (14)$$

and decays by reactions (8) and (9). Chapter 6 contains discussion of the fit of the benzyl decay for determination of $k_7$ and the study of toluene decomposition, reactions (8) and (9).

The absorbance at long times (Figure 2.16) decays to approximately a constant value. Assuming a complete one-to-one conversion of benzyl to benzyl fragments at long
times, the absorption cross-section of the benzyl fragments was determined. The absorption cross-section of the benzyl fragments is needed for the rate coefficient studies presented in Chapter 6 where benzyl fragment interfering absorption must be accounted for.

The results for the absorption cross-section of benzyl radicals and benzyl fragments are given in Figures 2.16 and 2.17 with comparison to previous experimental studies. The benzyl radical and benzyl fragment absorption cross-sections showed no temperature-dependence from 1428 to 1730 K with values of $\sigma_{C_6H_5CH_2} = 1.9 \pm 0.19 \times 10^{-17}$ cm$^2$molecule$^{-1}$ and $\sigma_{C_7H_6} = 3.4 \pm 0.51 \times 10^{-18}$ cm$^2$molecule$^{-1}$ respectively. The results for the benzyl radical absorption cross-section are in good agreement with the flash photolysis measurement of Ikeda et al. [116] but are about 50% lower than the shock tube results of Müller-Markgraf and Troe [82], see Figure 2.17. Müller-Markgraf and Troe examined the absorption spectra of benzyl behind shock waves at 1600 K using a Xe high-pressure discharge lamp dispersed with a monochromator. In comparison to the laser absorption measurements presented here, the Müller-Markgraf and Troe lamp measurements have noise at least a factor of ten larger due to the limited spectral brightness and optical collection efficiency of their lamp absorption measurements. Therefore, the resulting absorption cross-section measured by Müller-Markgraf and Troe is significantly less certain than the current measurement. However, the results of the current benzyl fragment absorption cross-section measurements are in excellent agreement with the measurements of Müller-Markgraf and Troe (Figure 2.18).
Table 2.1: Laser RMS intensity noise for 1 ms measurement.

<table>
<thead>
<tr>
<th>Optical component</th>
<th>RMS Intensity noise over 1 ms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detector dark noise (Thor Labs PDA55 detector with UV enhanced S1722-02 Hamamatsu silicon photodiodes)</td>
<td>0.56 mV</td>
</tr>
<tr>
<td><strong>216.62 nm</strong></td>
<td></td>
</tr>
<tr>
<td>Ar$^+$ pump (all-lines UV)</td>
<td>±0.098%</td>
</tr>
<tr>
<td>699-05 dye laser (433.24 nm)</td>
<td>±0.15%</td>
</tr>
<tr>
<td>Doubling cavity output (216.62 nm)</td>
<td>±0.78%</td>
</tr>
<tr>
<td>216.62 nm absorbance after common-mode rejection</td>
<td>±0.09%</td>
</tr>
<tr>
<td><strong>244 nm</strong></td>
<td></td>
</tr>
<tr>
<td>244 nm doubled Ar$^+$ line</td>
<td>±0.13%</td>
</tr>
<tr>
<td>244 nm absorbance after common-mode rejection</td>
<td>±0.09%</td>
</tr>
<tr>
<td><strong>266 nm</strong></td>
<td></td>
</tr>
<tr>
<td>266 nm doubled Nd:YVO$_4$</td>
<td>±0.06%</td>
</tr>
<tr>
<td>266 nm absorbance after common-mode rejection</td>
<td>±0.06% (common-mode rejection does not improve noise for 1 ms duration but does cancel very slow intensity fluctuations)</td>
</tr>
</tbody>
</table>
Figure 2.1: Absorption spectra of CH$_3$ B$^2$A$_1$ $\leftrightarrow$ X$^2$A$^\prime$ electronic system at 1565 K, Oehlschlaeger et al. [118].

Figure 2.2: Schematic of 216.62 nm experimental setup: M, mirror; BS, beam splitter; L, lens; D, detector; PT, piezoelectric pressure transducer; and Kistler, shielded Kistler piezoelectric pressure transducer.
Figure 2.3: Laser intensity noise measured with Thor Labs PDA55 detector and Hamamatsu S1722-02 silicon photodiode. Top graph, Ar$^+$ pump output (all-lines UV), RMS noise is ±0.098%; middle graph, dye laser output (433.24 nm), RMS noise is ±0.15%; bottom graph, doubling cavity output (216.62 nm), RMS noise is ±0.78%.
Figure 2.4: Absorbance signal at 216.62 nm using two-beam common-mode rejection with Thor Labs PDA55 detectors and Hamamatsu S1722-02 silicon photodiodes, RMS noise is ±0.09%.

Figure 2.5: Modified Thorlabs PDA55 (Hamamatsu S1722-02 silicon photodiode) detector spatial sensitivity at 266 nm after a focused 1 mW 266 nm beam was incident on the photodiode surface.
Figure 2.6: Example azomethane decomposition data and modeling. Reflected shock conditions: 1561 K, 1.622 atm, 200 ppm azomethane/Ar; laser wavelength = 216.62 nm, $k_{\lambda,CH_3} = 34.3 \text{ cm}^{-1}\text{atm}^{-1}$.

Figure 2.7: Temperature dependent CH$_3$ absorption coefficient at 216.62 nm. Solid squares, azomethane data; solid circles, methyl iodide data; solid triangles, ethane data; solid line, fit from this study; x, Davidson et al. [101]; open circles, Tsuboi [104]; dashed line, Möller et al. [103]; dotted line, Glänzer et al. [102]; dash-dot line Du et al. [106] (215.94 nm); dash-dot-dot line, Hwang et al. [105] (213.9 nm).
Figure 2.8: Schematic of 244 and 266 nm experimental setup: L, lens; BBO, beta barium borate frequency doubling crystal; PB, Pellin-Broca prism; M, mirror; BS, beam splitter; D, detector; PT, piezoelectric pressure transducer; and Kistler, shielded Kister piezoelectric pressure transducer.
Figure 2.9: Laser intensity noise measured with Thor Labs PDA55 detector and Hamamatsu S1722-02 silicon photodiode. Top graph, 244 nm output (doubled 488 nm Ar\(^+\) line), RMS noise is ±0.13%; bottom graph, 266 nm output (doubled 532 nm Nd:YVO\(_4\)), RMS noise is ±0.06%.
Figure 2.10: Example CO$_2$ absorbance for experiments at 216.5, 244, 266, and 306 nm.

Figure 2.11: Example CO$_2$ absorbance at 216.5 nm for experiment with thermal decomposition. Initial mixture: 2% CO$_2$ / Ar. Vibrationally equilibrated incident shock conditions: 1812 K and 0.161 atm. Initial (prior to decomposition) vibrationally equilibrated reflected shock conditions: 3838 K, 0.820 atm. Note the vibrational relaxation after incident shock-heating and the incubation period prior to decomposition after reflected shock-heating.
Figure 2.12: Temperature-dependence of the UV CO$_2$ absorption cross-section. Solid symbols, experimental results: squares, 216.5 nm; circles, 244 nm; triangles, 266 nm; diamonds, 306 nm. Solid lines, semi-empirical fit to current data; dashed lines, Schulz et al. [112].

Figure 2.13: Wavelength-dependence of the UV CO$_2$ absorption cross-section. Solid symbols and line, current data: squares, 3050 K; circles, 2610 K, diamonds, 2010 K; stars, 1630 K. Dashed lines, Schulz et al. [112].
Figure 2.14: Product of cross-section and vibrational partition function ($\sigma_{\text{CO}_2}Q_{\text{vib}}$) versus inverse temperature (top graph) and ground state energy versus wavelength (bottom graph). Top graph: solid squares, 216.5 nm data; solid circles, 244 nm data; solid triangles, 266 nm data; solid diamonds, 306 nm data; solid lines, least-squares fit of form $\sigma_{\text{CO}_2}(\lambda,T)Q_{\text{vib}} = \sigma_{\text{CO}_2,\text{eff}}(\lambda)\exp(-\varepsilon_1/T)$. Bottom graph: squares, current results; line, linear fit to current results; open circles, Eremin et al. [114]; ×, Zabelinskii et al. [115].
Figure 2.15: Benzyl radical spectrum at 1600 K, Müller-Markgraf and Troe [82].

Figure 2.16: Example 266 nm absorbance during benzyl iodide decomposition. Reflected shock conditions: 1615 K, 1.556 atm, 50 ppm benzyl iodide/Ar.
Figure 2.17: Benzyl radical absorption cross-section at 266 nm. Solid squares, this study; open circle, Ikeda et al. [116]; open triangle, Müller-Markgraf and Troe [82].

Figure 2.18: Benzyl fragment absorption cross-section at 266 nm. Solid squares, this study; open triangle, Müller-Markgraf and Troe [82].
Chapter 3: Theory and computational techniques

3.1 Unimolecular theory

Many reactions, such as dissociation, association, and isomerization reactions, experimentally exhibit pressure-dependence as well as temperature-dependence. Lindemann first proposed a mechanism in 1922 to explain this phenomenon [119]. He proposed that these reactions take place in two steps:

\[ A + M \rightleftharpoons A^* + M \quad \text{ (e, de)} \]

\[ A^* \rightarrow P \quad \text{ (uni)} \]

The molecule \( A \) is energized by collision with collider \( M \) in reaction (e). Molecule \( A \) then can be deactivated by collision, reaction (de), or can proceed to products by reaction (uni). Applying a steady-state approximation for the population of \( A^* \) the rate of reaction can be written

\[
\frac{d[P]}{dt} = \frac{k_e [A][M]}{1 + k_{de}[M]/k_{uni}}
\]

and the rate coefficient in the high-pressure-limit ([M] → \( \infty \)) and low-pressure-limit ([M] → 0) can be defined respectively as

\[
k_\infty = \frac{k_{uni}k_e}{k_{de}}
\]

\[
k_0 = k_e[M]
\]

At intermediate pressures, the so-called falloff regime, the Lindemann apparent first order rate coefficient \( k^1 \) can be defined as

\[
\frac{k^1}{k_\infty} = \frac{k_0}{1 + k_0/k_\infty} = F_L
\]
The Lindemann mechanism demonstrates that the apparent first-order rate coefficient is limited by collisional excitation at low-pressure and the unimolecular conversion at high-pressure. However, experimental findings have shown that typically the falloff is much “broader” than that given by the Lindemann model. In other words the value \([M]_{1/2} = k_0/k_\infty\) defined as the concentration when \(k^{1/2}_1/k_\infty = 1/2\) is found experimentally to be smaller than that predicted by the Lindemann model. To better describe the experimentally observed falloff the energy-dependence of the activation and unimolecular steps must be considered.

The modern technique commonly used to calculate the energy dependence of unimolecular reaction rate coefficients is described by Rice-Ramsperger-Kassel-Marcus (RRKM) theory [120]. According to RRKM theory the energy-specific unimolecular rate coefficient \(k(E)\) is given by

\[
k(E) = l^\dagger \frac{W^\dagger(E - E_0)}{h\rho(E)}
\]

where \(l^\dagger\) is the reaction path degeneracy, \(W^\dagger(E - E_0)\) the sum of states of the transition state, \(\rho(E)\) the density of states of the reactant molecule, and \(h\) Planck’s constant. The energy \(E\) is measured relative to the zero-point energy of the reactant molecule and the threshold energy \(E_0\) is the difference between the zero-point energies of the reactant and transition state.

The competition between excitation and unimolecular conversion results in different population distributions at low- and high-pressure. At high-pressure the unimolecular conversion is rate-limiting and an equilibrium Boltzmann distribution is maintained through collisions. However, at low-pressure unimolecular conversion occurs faster than collisional activation and the population is depleted above the reaction threshold. See Figure 3.1 for a schematic representation of the population distribution in these two regimes. Because the population maintains a Boltzmann distribution at infinite pressure the high-pressure rate coefficient can be calculated by averaging the RRKM result for \(k(E)\) over the Boltzmann population \(f(E)\):
where

\[ f(E) = \frac{P(E)e^{-E/kT}}{Q} \]

and \( Q \) is the total partition function.

With a simple expression for the high-pressure-limit rate coefficient the challenge of modern unimolecular theory has been to describe the falloff to the low-pressure-limit. In the falloff regime, collisional activation plays a role in determining the magnitude of the rate coefficient; therefore, a method is needed to describe collisional energy transfer. Several methods have been developed; in this work the master equation for internal energy is solved numerically to describe energy transfer following the work of Barker and others [123-124].

The master equation can be written by considering the time evolution of the population, \( \rho_i \), of the reactant molecule at a given energy level \( i \) simultaneously undergoing unimolecular reaction and collisional activation and deactivation

\[
\frac{\partial \rho_i}{\partial t} = \omega \sum_j \left( P_{ij} \rho_j - P_{ji} \rho_i \right) - k_i \rho_i
\]

where \( \omega \) is the inelastic collision frequency, \( k_i \) the energy-specific rate coefficient from RRKM theory, \( P_{ij} \) the probability that a molecule in energy level \( j \) will undergo collisional transition into level \( i \), and \( P_{ji} \) the probability that a molecule in energy level \( i \) will undergo collisional transition into level \( j \). The first term in the master-equation represents the rate of population growth in level \( i \) due to collisional transfer into the level, the second term represents the rate of population decay in level \( i \) due to collisional transfer out of level \( i \), and the last term represents the rate of population leaving level \( i \) due to unimolecular reaction (dissociation in this thesis). It should be noted that the one-dimensional master equation formulation, given above, neglects the population dependence on angular momentum by assuming that all rotational degrees of freedom are in thermal equilibrium (i.e., rotational energy transfer is much faster than vibrational energy transfer). The master equation has been solved analytically for some special cases.
[57-58, 121-122], usually involving small molecules, but for practical systems the master equation must be solved numerically by discretizing the energy domain of interest.

### 3.2 Master equation / RRKM computational techniques

In the studies presented here master equation simulations have been performed using the MultiWell code developed by Barker [123-124]. MultiWell performs stochastic numerical solution to the energy grained master equation. Additionally, MultiWell allows for master equation solution to reaction systems involving multiple channels, for example in this thesis n-butane decomposition, reactions (4)-(5), and toluene decomposition, reactions (8)-(9). In MultiWell the energy-specific rate coefficient can be calculated using one of two methods: 1) RRKM theory, described above or 2) the inverse Laplace transform method.

For calculations in which RRKM theory is used to calculate \( k(E) \) the density of states of the reactant molecule and sum of states of the transition state must be calculated. This can be done using DenSum, an auxiliary code to MultiWell. DenSum uses the Stein-Rabinovitch [127] version of the Beyer-Swinehart algorithm [128] for exact counts of states of the molecule and allows the degrees of freedom of the molecule to be input as harmonic oscillators, Morse oscillators, or free rotors. RRKM theory requires a model for the transition state in order to calculate its sum of states. Many techniques for modeling the transition state of dissociation reactions have been developed but in this work the simple restricted Gorin model will be used [120,129-130]. The transition state was located at the maximum of an effective potential, using the Lennard-Jones form of the potential: \( r^* = (6D_0/RT)^{1/6} \). The restricted Gorin transition state is similar to its product fragments. The transition state frequencies of vibration are assumed to be those of the product fragments and internal rotations are represented by the moments of inertia of the product fragments with hindrance, \( \eta \), chosen to reproduce experimental data. Additionally, in this work the externally active k-rotor was included in the density and sum of states calculations.

An alternative to RRKM theory for calculation of the energy-specific rate coefficient \( k(E) \) is the inverse Laplace transform method given by Forst [125-126]
\[ k(E) = A_∞ \frac{\rho(E - E_∞)}{\rho(E)} \]

where \( A_∞ \) and \( E_∞ \) are the Arrhenius parameters for the high-pressure-limit rate coefficient and \( \rho \) is the density of states for the parent dissociating molecule; in this formulation the reaction path degeneracy has been included in \( A_∞ \). The inverse Laplace transform method is useful when the pressure of interest is nearly in the low-pressure-limit where the rate coefficient is rate-limited by collisional activation and therefore, accurate calculation of \( k(E) \) is not necessary. In this thesis the inverse Laplace transform method is used in simulations of \( \text{CO}_2 \) incubation and decomposition because at the conditions of the experiments reported here the decomposition is nearly in the low-pressure-limit [44].

The last major input to MultiWell to be discussed here is the collisional energy transfer probability density function, \( P_{ij} \). MultiWell has ten choices for the functional form of the collisional energy transfer probability density function; the large number of choices is due to the substantial research and debate on this subject. For the work presented in this thesis, the exponential-down model is used for alkane decomposition and \( \text{CO}_2 \) incubation and decomposition

\[ P_{ij} = \frac{1}{N_j} \exp \left( -\frac{E_j - E_i}{\alpha_j} \right) \text{ for } E_j > E_i \]

where \( N_j \) is a normalization factor and \( \alpha_j \) is equal to the average energy transferred in deactivating collisions, \(<\Delta E>_{\text{down}}\), when the exponential-down model is employed [120]. The collisional energy transfer parameter, \( \alpha_j \), is fit to the experimental data in the falloff and can have energy- and/or temperature-dependence. In the case of toluene decomposition accurate measurements of \( P_{ij} \) have been made by Luther and co-workers [131-132]. They have chosen to represent their results in the following form which was also adopted for the toluene master equation calculations performed in this work:

\[ P_{ij} = \frac{1}{N_j} \exp \left( -\left[ \frac{E_j - E_i}{\alpha_j} \right] \gamma \right) \text{ for } E_j > E_i \]

The additional term \( \gamma \) allows for enhanced or decreased probabilities in the wings of the distribution.
In general there are two adjustable parameters for every calculation: 1) the hindrance parameter applied to the Gorin transition state internal rotations, \( \eta \), and 2) the energy transfer parameter \( \alpha \). The hindrance parameter, \( \eta \), affects \( k(E) \) and therefore the high-pressure-limit. The value of the energy transfer parameter, \( \alpha \), controls the rate of the falloff to the low-pressure-limit. The specifics of each master equation calculation are left to the results sections: Chapters 4-6.

### 3.3 Troe formulation for falloff

As stated above, rate coefficients determined experimentally exhibit falloff behavior which is “broader” than that predicted by the Lindemann mechanism. Troe and co-workers have empirically developed an analytic expression to describe unimolecular rate coefficients in the falloff regime [200]. In the Troe formulation the first-order rate coefficient, \( k^1 \), is given by

\[
k^1 = F_L F k_\infty
\]

where \( F_L \) defines the Lindemann falloff relation, \( k^1/k_\infty \) given above, and \( F \) is an empirical pressure broadening factor fit to experimental data or in some cases a theoretical calculation. The pressure broadening factor, \( F \), is given by Troe and co-workers as

\[
\log F = \frac{\log F_{\text{cent}}}{1 + \left[ \frac{\log P_r + C}{N - 0.14(\log P_r + C)} \right]^2}
\]

with \( N = 0.75 - 1.27\log F_{\text{cent}} \), \( C = -0.4 - 0.67\log F_{\text{cent}} \) and \( P_r = k_e[M]/k_\infty \). The pressure broadening factor, \( F \), is defined in terms of a temperature-dependent variable \( F_{\text{cent}} \)

\[
F_{\text{cent}} = (1 - a) \exp(-T / b) + a \exp(-T / c) + \exp(-d / T)
\]

\( F_{\text{cent}} \) is a factor (determined from fit to experimental data) by which the rate coefficient of a unimolecular reaction at temperature \( T \) and reduced pressure of \( P_r = k_e[M]/k_\infty = 1.0 \) is less than the value \( k_\infty /2 \) which it would have if it behaved according to the Lindemann formulation. CHEMKIN [135] allows the user to input the parameters \( a, b, c, \) and \( d \) for a given reaction to prescribe \( F_{\text{cent}} \) and the pressure broadening factor, \( F \), is calculated via the above Troe formulation.
Figure 3.1: Reactant population energy distribution under high-pressure-limit conditions (solid) and under falloff conditions (dashed). Under falloff conditions the unimolecular dissociation step occurs at a rate fast enough such that the equilibrium Boltzmann distribution cannot be maintained by collisions and the population is depleted above the reaction threshold.
Chapter 4: Alkane decomposition

This chapter describes the measurement of rate coefficients for the decomposition of ethane, propane, iso-butane, and n-butane, reactions (1)-(5). These measurements were made in the shock tube facility using the CH$_3$ laser absorption diagnostic at 216.62 nm described in Chapter 2.

4.1 Determination of rate coefficients

Experiments were performed behind incident and reflected shock waves at temperatures of 1297 to 2034 K and pressures of 0.13 to 8.8 atm for the measurement of $k_1$-$k_5$ with mixture concentrations ranging from 100 to 400 ppm of the four alkanes of interest (ethane, propane, iso-butane, and n-butane) dilute in argon. Narrow-linewidth laser absorption was used for ~ppm sensitive CH$_3$ detection. The low concentrations provided isolated sensitivity to the decomposition rate coefficients of interest. Additionally, rate coefficients were only fit to the early time behavior of the CH$_3$ profiles to maintain kinetic isolation of the decomposition reactions and to avoid interfering absorption from other product species that are formed at longer times.

In order to determine rate coefficients for reactions (1)-(5), the measured CH$_3$ mole fractions were fit using detailed kinetic models. Fortunately, the low initial concentrations used in these experiments allowed fits that are fairly insensitive to the choice of rate coefficients for reactions other than reactions (1)-(5). In the case of ethane and propane the GRI Mech 3.0 [95] mechanism was used, for iso-butane the mechanism of Wang et al. [133] was used, and for n-butane the mechanism of Marinov et al. [134] was used. The only rate coefficients changed in these mechanisms, for the purpose of fitting the experimental data, are those of reactions (1)-(5). Computations were done using CHEMKIN 2.0 and SENKIN [135-136].

In the case of ethane and propane the kinetic modeling is quite simple, the initial rise of CH$_3$ provides a direct fit to reaction (1) or (2), as there is only one decomposition
path for these molecules at the conditions of these experiments. Additionally, during the early rise, interfering absorption due to C\textsubscript{2}H\textsubscript{4} and C\textsubscript{2}H\textsubscript{2} is negligible; the absorption coefficients for these two species have been measured by several groups [37,98,137] and were verified with good agreement prior to the current experiments [118]. An example data trace and sensitivity plot for ethane decomposition is shown in Figure 4.1. Notice that interfering reactions have essentially no influence on the fit of reaction (1). An example propane decomposition experiment and sensitivity is shown in Figure 4.2. Here the primary interfering reaction is C\textsubscript{3}H\textsubscript{8} + H and, because of the low initial propane concentration, it has little effect on the fit of reaction (2).

For the iso-butane decomposition experiments the initial rise of CH\textsubscript{3} provides a direct fit to reaction (3). The rate coefficient was fit only to the early time behavior of the CH\textsubscript{3} traces because at longer times a complication arises from interfering absorption. Example data and sensitivity are given in Figure 4.3; notice that the model fits the first 75 μs of the trace well but then diverges slightly from the experiment at longer times due to interfering absorption. Experiments were performed to identify possible interfering absorbing species (C\textsubscript{3}H\textsubscript{6}, C\textsubscript{2}H\textsubscript{4}, and C\textsubscript{2}H\textsubscript{2}) in iso-butane decomposition [118]. The absorption coefficients of these species at 216.62 nm were measured by monitoring 216.62 nm laser absorption during shock heating. It was found that although none of these species had absorption coefficients large enough to be of concern at the early times where the iso-butane decomposition rate coefficient was determined, the decomposition products of C\textsubscript{3}H\textsubscript{6} showed moderately strong absorption. These C\textsubscript{3} decomposition products are likely responsible for the interference in the iso-butane decomposition experiments; similar interference was reported by Koike and Morinaga [36].

Analysis of the CH\textsubscript{3} profiles obtained from the n-butane experiments is complicated by the fact that there are two parallel channels for n-butane decomposition, reactions (4) and (5), and thus the CH\textsubscript{3} profiles must be fit in terms of the overall decomposition rate coefficient, \(k_{4}+k_{5}\), and the branching ratio, \(k_{4}/(k_{4}+k_{5})\). The overall rate of decomposition, \(k_{4}+k_{5}\), is determined by fitting to the early-time behavior of the CH\textsubscript{3} concentration profile. At longer times the CH\textsubscript{3} concentration rolls off to a peak before methyl-methyl recombination brings about a decay in the CH\textsubscript{3} concentration. The peak in the methyl concentration is controlled by the branching ratio, \(k_{4}/(k_{4}+k_{5})\), and thus the
branching ratio can be inferred by fitting to the peak in CH$_3$ concentration. See Figure 4.4 for an example data trace and sensitivity plot. Interfering chemistry at longer times provides a bit more uncertainty in the fits (sensitivity in Figure 4.4), but fortunately the primary interfering reaction is methyl recombination which has been measured here in reverse and is relatively well-known (±20%). Interfering absorption is negligible in the n-butane decomposition case because the subsequent C$_3$ product fragments are in lower concentration than in the iso-butane case.

The present rate coefficient determinations for reactions (1)-(5) are tabulated in Appendix A and shown in Figures 4.5-4.9 on Arrhenius plots along with least-squares fits; the experimental scatter about the least-squares fits is small (±10% in $k_1$, ±7% in $k_2$, ±7% in $k_3$, ±12% in $k_4$, and ±21% in $k_5$). The primary contributions to uncertainties in the rate coefficients are: temperature, CH$_3$ absorption coefficient, fitting the data to computed profiles, and uncertainties resulting from interfering chemistry. These uncertainties give overall uncertainties in $k_1$-$k_5$ of ±19%, ±26%, ±25%, ±31%, and ±31%, respectively. See Appendix B for details of the uncertainty analysis.

### 4.2 RRKM / master equation calculations

Single-channel (ethane, propane, and iso-butane) and multi-channel (n-butane) RRKM calculations with numerical solution to the 1-D (internal energy) master equation were carried out using a restricted (hindered) Gorin model for the transition state for the decomposition of the four alkanes of interest. These calculations provided falloff curves that were fit to the current alkane decomposition rate coefficient determinations and in the case of ethane and propane the calculations were also fit to two previous recombination studies. The methyl/methyl recombination data of Slagle et al. [23] (296-906 K) and the methyl/ethyl recombination data of Knyazev and Slagle [31] (301-800 K) were fit respectively with RRKM / master equation calculations to extend the findings for ethane and propane decomposition to lower temperatures.

Two parameters were adjusted in the calculations to provide a best fit to the experimental rate coefficient determinations: the hindrance, $\eta$, on the restricted internal rotations in the transition state and the energy transfer parameter, $\alpha$, in the exponential down energy transfer model. Previous studies [16,138-139] have reported that the
hindrance parameter follows the functional form, \( \eta = a + bT^{-1/6} \). This functional form was found to hold for both iso-butane and n-butane decomposition over the temperature range of the experiments performed in these studies (1310-1551 K for iso-butane and 1297-1601 K for n-butane). However, the large temperature-range of data fit for ethane (296-1924 K) and propane (301-1653 K) decomposition could not be fit using the above simple functional form of the hindrance parameter. For the broad temperature range examined for ethane and propane the hindrance parameter was found to asymptote from high-temperature to a nearly constant value at lower temperatures; see Figure 4.5. Lennard-Jones parameters for the various species were taken from [140]; the molecular frequencies [141-143], moments of inertia [16,33,143-145], heats of formation [146-147], and barrier heights [144,147-150] were taken from various references for the RRKM / master equation calculations and are listed in Table 1.

The exponential-down collisional energy transfer model was used with a temperature-dependent collisional energy transfer parameter, \( \alpha \), which was fit to the current experiments and low-temperature recombination data. The resulting best-fit expressions for the energy collisional transfer parameter for argon collisions with the four alkanes are also given in Table 1. The falloff behavior of the current experiments could not be accurately fit without a temperature-dependent \( \alpha \); similar results have been given by Klippenstein and Harding [22], Knyazev and Slagle [31,151] and Knyazev and Tsang [152].

### 4.3 Analytic Arrhenius / Troe expressions for rate coefficients

The RRKM/master equation calculations provided rate coefficients in both the high-pressure and low-pressure limits for reactions (1)-(5) which were fit using two- and three-parameter analytic Arrhenius expressions and the Troe formulation for the pressure broadening falloff factor, \( F_{\text{cent}} \). Accurate three parameter analytic expressions \( AT^n \exp(-E/T) \) for \( k_\infty \) and \( k_0 \) over large temperature ranges are difficult to develop due in part to the simplicity of the pre-exponential temperature dependence term, which is a function of the change in specific heat from reactant to transition state \( \langle \Delta C_p^1 \rangle \). One coefficient to
represent the heat capacity term over a large range of temperatures is simply not enough (most polynomial expressions for heat capacitance contain five terms). Therefore, in the case of ethane and propane analytic expressions for reactions (1) and (2), in the Troe formulation, are given over a smaller temperature range than that for which the RRKM calculations were carried out and the resulting pre-exponential temperature dependences are large. The reaction (1) rate expressions for 700 to 1924 K are:

\[ k_{\infty,1}(T) = 1.88 \times 10^{50} T^{-9.72} \exp(-54020 \text{ K}/T) \text{ [s}^{-1}] \]

\[ k_{0,1}(T) = 3.72 \times 10^{65} T^{-13.14} \exp(-51120 \text{ K}/T) \text{ [cm}^3\text{mol}^{-1}\text{s}^{-1}] \]

\[ F_{\text{cent},1}(T) = 0.61 \exp(-T/100 \text{ K}) + 0.39 \exp(-T/1900 \text{ K}) + \exp(-6000 \text{ K}/T) \]

The reaction (2) rate expressions for 600 to 1653 K are:

\[ k_{\infty,2}(T) = 1.29 \times 10^{37} T^{-5.84} \exp(-49010 \text{ K}/T) \text{ [s}^{-1}] \]

\[ k_{0,2}(T) = 5.64 \times 10^{74} T^{-15.74} \exp(-49680 \text{ K}/T) \text{ [cm}^3\text{mol}^{-1}\text{s}^{-1}] \]

\[ F_{\text{cent},2}(T) = 0.69 \exp(-T/50 \text{ K}) + 0.31 \exp(-T/3000 \text{ K}) + \exp(-9000 \text{ K}/T) \]

Analytic expressions for the decomposition of iso-butane and n-butane, reactions (3)-(5), are given over the smaller temperature range of the current experimental findings and therefore, are given in the two-parameter Arrhenius form. The reaction (3) rate expressions for 1320 to 1560 K are:

\[ k_{\infty,3}(T) = 4.83 \times 10^{16} \exp(-40210 \text{ K}/T) \text{ [s}^{-1}] \]

\[ k_{0,3}(T) = 2.41 \times 10^{19} \exp(-26460 \text{ K}/T) \text{ [cm}^3\text{mol}^{-1}\text{s}^{-1}] \]

\[ F_{\text{cent},3}(T) = 0.75 \exp(-T/750 \text{ K}) \]

The reaction (4) rate expressions for 1320 to 1600 K are:

\[ k_{\infty,4}(T) = 4.28 \times 10^{14} \exp(-35180 \text{ K}/T) \text{ [s}^{-1}] \]

\[ k_{0,4}(T) = 5.34 \times 10^{17} \exp(-21620 \text{ K}/T) \text{ [cm}^3\text{mol}^{-1}\text{s}^{-1}] \]

\[ F_{\text{cent},4}(T) = 0.28 \exp(-T/1500 \text{ K}) \]

And the reaction (5) rate expressions for 1320 to 1600 K are:

\[ k_{\infty,5}(T) = 2.72 \times 10^{15} \exp(-38050 \text{ K}/T) \text{ [s}^{-1}] \]

\[ k_{0,5}(T) = 4.72 \times 10^{18} \exp(-24950 \text{ K}/T) \text{ [cm}^3\text{mol}^{-1}\text{s}^{-1}] \]

\[ F_{\text{cent},5}(T) = 0.28 \exp(-T/1500 \text{ K}) \]

It should be noted that these analytic expressions, fit to the RRKM / master equation calculations, differ from those calculations by no more than ±10%. Figures 4.11-4.15 show the current data, RRKM calculations, and selected previous experimental studies on
falloff plots; Figures 4.16-4.20 show the current high-pressure-limit rate coefficients with comparison to selected theoretical studies.

4.4 Discussion

4.4.1 Comparison with previous experimental studies

The current findings for reactions (1)-(4) are compared with previous experimental studies in Figures 4.11-14; there are no previous high-temperature experimental results for comparison to the reaction (5) results shown in Figure 4.15. The current findings for reaction (1) are in good agreement with the dissociation data of Davidson et al. [11], although the current experimental scatter is much improved. The low pressure (~1 atm) recombination data of Du et al. [13] and the high pressure (~50-100 atm) recombination data of Hwang et al. [12] show fair agreement with the current study, although their results are both slightly lower than the current data and RRKM fits.

The current findings for reaction (2) are in good agreement with the work of Al-Alami and Kiefer [27]. At low-temperatures the current findings are in good agreement with the work of Simmie et al. [29] but at higher temperatures their results are significantly lower and their scatter increased. Both the measurements of Hidaka et al. [30] and Chiang and Skinner [26] are significantly lower than the current findings. Of concern are the high activation energies reported by Hidaka et al. and Chiang and Skinner for their 2 atm (falloff) experiments. Their data cannot be reconciled with the present findings or other theoretical results.

The current findings for reaction (3) are in fairly good agreement with the iso-butane 3.39 µm laser absorption measurements of Hidaka et al. [35], particularly at lower temperatures. A comparison of the current $k_3$ and $k_4$ results with both studies by Koike and Morinaga [36-37] shows poor agreement. Koike and Morinaga measured CH$_3$ using lamp absorption at 216 nm during the shock heating of mixtures of 1-2.8% iso-butane or n-butane dilute in argon. The large initial concentrations of reactant used in their experiments provide results that are highly sensitive to the choice of the other rate coefficients in their reaction mechanism. Their low findings for $k_3$ and $k_4$, in comparison to the current findings, is likely due to their choice of a slow rate for methyl
recombination, which is of significant sensitivity in their experiments. Koike and Morinaga [36-37] employ a rate for methyl recombination that is a factor of two slower at 1450 K than the currently accepted rate, which has an uncertainty of ±20%.

4.4.2 Comparison with previous theoretical calculations

As stated above, the current data for reactions (1)-(5) was fit with RRKM/master equation calculations by adjusting two parameters: the collisional energy transfer parameter, $\alpha$ (which influences falloff), and the hindrance parameter for the internal rotors, $\eta$, in the transition state (which influences $k_\infty$). The current data and RRKM analysis suggests an increase in $\alpha$ with temperature and a stronger falloff in $k_\infty$ (increased hindrance) at higher temperatures than the previous theoretical studies predict for both reactions (1) and (2), see Figures 4.16-4.17. The previous theoretical models do a good job of predicting the low-scatter data of Slagle et al. [23] and Knyazev and Slagle [31], but previous high-temperature experimental data had excessive scatter which made accurate theoretical fitting difficult; in fact, many theoretical studies predict high-temperature rates that were simply extrapolated from the low-temperature results.

A comparison of the current high-pressure-limit rate coefficients for reactions (3)-(5) can be found in Figures 4.18-4.20. The current findings for $k_{\infty,3}$ are about a factor of 2 to 3 greater than the theoretical RRKM prediction of Tsang [17] and the review recommendation of Warnatz [153] but show essentially the same activation energy. The RRKM expression given by Tsang [17] was guided by the only high-temperature data available at the time that of Koike and Morinaga [36], thus Tsang’s high-pressure-limit recommendation is lower than the current finding.

The current findings for $k_{\infty,4}$ are in good agreement with the QRRK predictions of Dean [14] and the review recommendations of Warnatz [153] although the activation energy of the current study is somewhat lower. The lower activation energy for n-butane at high-temperatures is consistent with the results for ethane and propane decomposition where the temperature-range of data is more complete. At high-temperatures the increased hindrance on the transition state internal rotations causes a reduction in the high-pressure-limit rate coefficient and the high-pressure-limit rate coefficient falls off
more at high-temperature than a simple extrapolation from low-temperature would predict.

The current findings for $k_{\infty,5}$ are about a factor of three smaller than the QRRK predictions of Dean [14] but in good agreement with the review recommendations of Warnatz [153]. The results of the current study for reactions (4) and (5) give a branching ratio, $k_4/(k_4+k_5)$, that is approximately 0.5 (1320-1600 K), in agreement with the recommendation of Warnatz [153].

In addition the results of the current study for ethane and propane decomposition, $k_1$ and $k_2$, are compared with the most recent International Union of Pure and Applied Chemistry (IUPAC) recommendations (Baulch et al. [201]) in Figures 4.11, 4.12, 4.16, and 4.17. The IUPAC recommendation for ethane decomposition is in relatively good agreement with the current study. However, the IUPAC recommendation for propane decomposition is in large disagreement in the falloff regime, Figure 4.12. The IUPAC recommendation suggests a much more dramatic falloff for propane, with rate coefficients that are significantly lower than the current data in the falloff regime.

### 4.4.3 Geometric mean rule

Additionally, the measurements of $k_1$, $k_2$, and $k_5$ allow a test of the validity of the geometric mean rule [31,154-155]. The geometric mean rule is often used to predict rate coefficients for decomposition or radical cross reactions, when data are not available and is written

$$k_{AB} = 2(k_{AA}k_{BB})^{1/2}$$

where $k_{AB}$ is the rate coefficient of $A + B$, $k_{AA}$ is the rate coefficient of $A + A$, and $k_{BB}$ is the rate coefficient of $B + B$. This equation can easily be arranged for the rate coefficient for $n$-$\text{C}_4\text{H}_{10} \rightarrow \text{C}_2\text{H}_5 + \text{C}_2\text{H}_5$ in terms of the rate coefficients for $\text{C}_2\text{H}_6 \rightarrow \text{CH}_3 + \text{CH}_3$ and $\text{C}_3\text{H}_8 \rightarrow \text{CH}_3 + \text{C}_2\text{H}_5$ and the appropriate equilibrium constants. The resulting rate coefficient for reaction (5) predicted by the geometric mean rule is in good agreement with the current measurements, see Figure 4.20. This test, although limited, suggests that the geometric mean rule is a good estimator for high-temperature alkane decomposition rates.
Table 4.1: Parameters used in RRKM / master equation calculations for alkane decomposition.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Heat of Formation (0K)</th>
<th>Moments of Inertia (amu Å²)</th>
<th>Frequencies (cm⁻¹)</th>
<th>Active 1-D external rotor (amu Å²)</th>
<th>Active 2-D internal rotor (amu Å²)</th>
<th>Barrier at 0 K</th>
<th>Energy transfer parameter</th>
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<tr>
<td>C₂H₆</td>
<td>-16.34 kcal/mol</td>
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<td>α = 0.8 x (T [K]) cm⁻¹</td>
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<td>C₃H₈</td>
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<td>i-C₅H₁₀</td>
<td>-25.43 kcal/mol</td>
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<td>CH₃CH₂H₇</td>
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\[ \text{C}_2\text{H}_6 \]

Heat of Formation (0K) [146]: -16.34 kcal/mol
Moments of Inertia (amu Å²) [16]: 25.3 (inactive); 25.3 (inactive); 6.3 (active), \( \sigma = 3 \)
Frequencies (cm⁻¹) [141]: 2977(4), 2954, 2896, 1469(4), 1382(2), 1190(2), 995, 822(2), 260

\[ \text{CH}_3 \cdots \text{CH}_3 \]

Frequencies (cm⁻¹) [141]: 3184(4), 3002(2), 1384(2), 580(2)
Active 1-D external rotor (amu Å²) [16]: 6.3, \( \sigma = 3 \)
Active 2-D internal rotor (amu Å²) [145]: 1.76, \( \sigma = 2; \eta \) (see Fig. 5)
Active 2-D internal rotor (amu Å²) [145]: 1.76, \( \sigma = 2; \eta \) (see Fig. 5)
Barrier at 0 K [146]: 87.6 kcal/mol
Energy transfer parameter: \( \alpha = 0.8 \times (T \text{[K]}) \text{cm}^{-1} \)

\[ \text{C}_3\text{H}_8 \]

Heat of Formation (0K) [148]: -19.69 kcal/mol
Moments of Inertia (amu Å²) [144]: 67.75 (inactive); 59.84 (inactive); 17.3 (active), \( \sigma = 1 \)
Frequencies (cm⁻¹) [143]: 2977, 2973, 2968(2), 2967, 2962, 2887(2), 1476, 1472, 1464, 1462, 1392, 1378, 1338, 1278, 1192, 1158, 1054, 940, 936, 369, 268, 216

\[ \text{CH}_3 \cdots \text{C}_2\text{H}_6 \]

Frequencies (cm⁻¹) [141-142]: 3184(2), 3002, 1384(2), 580, 3112, 3033, 2987(2), 2942, 1440(3), 1366, 1175(2), 1138, 528(3)
Active 1-D external rotor (amu Å²) [144]: 17.3, \( \sigma = 1 \)
Active 1-D internal torsion (amu Å²) [143,145]: 3.1, \( \sigma = 3 \)
Active 2-D internal rotor (amu Å²) [145]: 1.76, \( \sigma = 2; \eta \) (see Fig. 5)
Active 1-D internal rotor (amu Å²) [33]: 4.87, \( \sigma = 1; \eta \) (see Fig. 5)
Active 1-D internal rotor (amu Å²) [143]: 22.3, \( \sigma = 1; \eta \) (see Fig. 5)
Barrier at 0 K [146-147]: 87.9 kcal/mol
Energy transfer parameter: \( \alpha = 1.2 \times (T \text{[K]}) \text{cm}^{-1} \)

\[ \text{i-C}_5\text{H}_{10} \]

Heat of Formation (0K)[147]: -25.43 kcal/mol
Moments of Inertia (amu Å²)[144]: 114.1 (inactive); 67.0 (inactive); 64.9 (active), \( \sigma = 1 \)
Frequencies (cm⁻¹)[143]²:
Active 1-D external rotor (amu Å²)[144]: 64.9, \( \sigma = 1 \)
Active 1-D internal torsion (amu Å²)[143,145]²:
Active 2-D internal rotor (amu Å²)[145]: 3.38, \( \sigma = 3 \)
Active 2-D internal rotor (amu Å²)[145]: 1.76, \( \sigma = 2; \eta = 265.4 - 616.9 T^{-1/6} \)
Active 1-D internal rotor (amu Å²)[143]²:
Active 1-D internal rotor (amu Å²)[143]²:
Barrier at 0 K[144]: 86.8 kcal/mol
Energy transfer parameter: \( \alpha = 0.8 \times (T \text{[K]}) \text{cm}^{-1} \)
### n-C$_4$H$_{10}$

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**CH$_3$...n-C$_3$H$_7$**

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<td>Active 1-D internal torsion (amu Å$^2$)</td>
<td>3.37, $\sigma = 3$</td>
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<td>Active 2-D internal rotor (amu Å$^2$)</td>
<td>1.76, $\sigma = 2$; $\eta = 439.5 - 1186.5 \ T^{1/6}$</td>
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<td>15.40, $\sigma = 1$; $\eta = 439.5 - 1186.5 \ T^{1/6}$</td>
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<td>Active 1-D internal rotor (amu Å$^2$)</td>
<td>56.76, $\sigma = 1$; $\eta = 439.5 - 1186.5 \ T^{1/6}$</td>
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<tr>
<td>Barrier at 0 K</td>
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**C$_2$H$_5$...C$_3$H$_5$**

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<td>Active 1-D external rotor (amu Å$^2$)</td>
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<td>Active 1-D internal torsion (amu Å$^2$)</td>
<td>12.05, $\sigma = 2$</td>
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<td>Active 1-D internal rotor (amu Å$^2$)</td>
<td>4.87, $\sigma = 1$; $\eta = 282.6 - 672.8 \ T^{1/6}$</td>
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<td>22.3, $\sigma = 1$; $\eta = 282.6 - 672.8 \ T^{1/6}$</td>
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<td>4.87, $\sigma = 1$; $\eta = 282.6 - 672.8 \ T^{1/6}$</td>
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<td>Barrier at 0 K</td>
<td>87.3 kcal/mol</td>
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<tr>
<td>Energy transfer parameter:</td>
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* Frequencies for i-C$_4$H$_{10}$, i-C$_3$H$_7$, and n-C$_3$H$_7$ are from ab initio calculations at the DFT B3LYP/6-31G** level scaled by 0.962.

* Moments for n-C$_4$H$_{10}$, i-C$_3$H$_7$, and n-C$_3$H$_7$ are from ab initio calculations at the DFT B3LYP/6-31G** level.
Figure 4.1: Example ethane data, modeling, and sensitivity. Reflected shock conditions: 1589 K, 1.664 atm, 202 ppm C₂H₆. Top graph: solid line, fit to data using GRI Mech 3.0 [95] and adjusting $k_1$; dashed lines, variation of $k_1 \pm 50\%$. The spike at 0 µs is caused by deflection of the diagnostic beam by the reflected shock wave. $S = \frac{dX_{CH_3}}{dk_i} \left( \frac{k_i}{X_{CH_3,local}} \right)$, where $k_i$ is the rate constant for reaction i and $X_{CH_3,local}$ is the local CH₃ mole fraction.

Figure 4.2: Example propane data, modeling, and sensitivity. Reflected shock conditions: 1433 K, 4.535 atm, 201 ppm C₃H₈. Top graph: solid line, fit to data using GRI Mech 3.0 [95] and adjusting $k_2$; dashed lines, variation of $k_2 \pm 50\%$; dotted lines, variation of rate coefficient for $H + C_3H_8 \rightarrow C_3H_7 + H_2$ by ±50%. $S = \frac{dX_{CH_3}}{dk_i} \left( \frac{k_i}{X_{CH_3,local}} \right)$, where $k_i$ is the rate constant for reaction i and $X_{CH_3,local}$ is the local CH₃ mole fraction.
Local CH₃ Sensitivity, S

Time \[\mu \text{s}\]

\[S = \frac{\text{d}X_{\text{CH}_3}}{\text{d}k_i} \left(\frac{k_i}{X_{\text{CH}_3,\text{local}}}\right), \text{where } k_i \text{ is the rate constant for reaction } i \text{ and } X_{\text{CH}_3,\text{local}} \text{ is the local CH}_3 \text{ mole fraction.}\]
Figure 4.5: Experimental data and least-squares fits for $\text{C}_2\text{H}_6 \rightarrow \text{CH}_3 + \text{CH}_3$. Filled squares, 1.6 atm data, $k_1 = 1.08\times10^{12} \exp(-31200K/T)$; filled triangles, 4.2 atm data, $k_1 = 4.01\times10^{12} \exp(-32400K/T)$; filled stars, 7.5 atm data, $k_1 = 1.55\times10^{13} \exp(-34200K/T)$; open squares, 0.13-0.22 atm data.

Figure 4.6: Experimental data and least-squares fits for $\text{C}_3\text{H}_8 \rightarrow \text{CH}_3 + \text{C}_2\text{H}_5$. Filled squares, 1.7 atm data, $k_2 = 1.97\times10^{13} \exp(-32400K/T)$; filled triangles, 4.3 atm data, $k_2 = 5.10\times10^{13} \exp(-33400K/T)$; filled stars, 7.9 atm data, $k_2 = 4.97\times10^{13} \exp(-33100K/T)$; open squares, 0.19-0.23 atm data.
Figure 4.7: Experimental data and least-squares fits for i-C$_4$H$_{10}$ → CH$_3$ + i-C$_3$H$_7$. Filled squares, 1.7 atm data, $k_3 = 4.98 \times 10^{14}$ exp(-34800K/T) s$^{-1}$; filled triangles, 4.4 atm data, $k_3 = 1.71 \times 10^{15}$ exp(-36300K/T) s$^{-1}$; filled stars, 8.4 atm data, $k_3 = 3.59 \times 10^{15}$ exp(-37000K/T) s$^{-1}$; open squares, 0.21-0.25 atm data.

Figure 4.8: Experimental data and least-squares fits for n-C$_4$H$_{10}$ → CH$_3$ + C$_3$H$_7$. Filled squares, 1.7 atm data, $k_4 = 4.15 \times 10^{13}$ exp(-32800K/T) s$^{-1}$; filled triangles, 4.2 atm data, $k_4 = 4.59 \times 10^{14}$ exp(-35700K/T) s$^{-1}$; filled stars, 8.3 atm data, $k_4 = 3.33 \times 10^{14}$ exp(-35300K/T) s$^{-1}$; open squares, 0.20-0.25 atm data.
Figure 4.9: Experimental data and least-squares fits for \( \text{n-C}_4\text{H}_{10} \rightarrow \text{C}_2\text{H}_5 + \text{C}_2\text{H}_5 \). Filled squares, 1.7 atm data, \( k_5 = 3.82 \times 10^{14} \exp(\text{-}36200\text{K}/T) \text{s}^{-1} \); filled triangles, 4.2 atm data, \( k_5 = 9.30 \times 10^{15} \exp(\text{-}40200\text{K}/T) \text{s}^{-1} \); filled stars, 8.3 atm data, \( k_5 = 5.21 \times 10^{15} \exp(\text{-}39400\text{K}/T) \text{s}^{-1} \); open squares, 0.20-0.25 atm data.

Figure 4.10: Hindrance parameter temperature dependence. Filled squares, RRKM fit to \( k_1 \) data of current study; filled circles, RRKM fit to \( k_2 \) data of current study; open squares, RRKM fit to \( k_1 \) data of Slagle et al. [23]; open circles, RRKM fit to \( k_2 \) data of Knyazev and Slagle [31].
Figure 4.11: Falloff plot for C$_2$H$_6$ → CH$_3$ + CH$_3$. Solid symbols, current study; open symbols, Davidson et al. [11]; open symbols with x, Du et al. [13]; half filled symbols, Hwang et al. [12]; solid lines, RRKM/master equation results with $\alpha = 0.8 \times (T \text{[K]}) \text{cm}^{-1}$; dashed lines, Baulch et al. [201] IUPAC recommendation.

Figure 4.12: Falloff plot for C$_3$H$_8$ → CH$_3$ + C$_2$H$_5$. Solid symbols, current study; open symbols, Al-Alami and Kiefer [27]; half filled symbols, Simmie et al. [29]; open symbols with line, Hidaka et al. [30]; open symbols with x, Chiang and Skinner [26]; solid lines, RRKM/master equation results with $\alpha = 1.2 \times (T \text{[K]}) \text{cm}^{-1}$; dashed lines, Baulch et al. [201] IUPAC recommendation.
Figure 4.13: Falloff plot for i-C$_4$H$_{10}$ → CH$_3$ + i-C$_3$H$_7$. Solid symbols, current study; open symbols, Hidaka et al. [35]; half filled symbols, Koike and Morinaga [36]; solid lines, RRKM/master equation results with $\alpha = 0.8 \times (T \text{[K]}) \text{ cm}^{-1}$.

Figure 4.14: Falloff plot for n-C$_4$H$_{10}$ → CH$_3$ + n-C$_3$H$_7$. Solid symbols, current study; open symbols, Koike and Morinaga [37]; solid lines, RRKM/master equation results with $\alpha = 1.2 \times (T \text{[K]}) \text{ cm}^{-1}$. 
Figure 4.15: Falloff plot for n-C₄H₁₀ → C₂H₅ + C₂H₅. Solid symbols, current study; solid lines, RRKM/master equation results with α = 1.2 x (T [K]) cm⁻¹.

Figure 4.16: High pressure rate coefficient for C₂H₆ → CH₃ + CH₃ (700-1924K). Symbols, current RRKM results (listed on figure); solid line, fit to current RRKM results; dashed line, Klippenstein and Harding [22]; dotted line, Hessler and Ogren [20]; dot-dashed line, Wagner and Wardlaw [15]; gray line, Baulch et al. [201] IUPAC recommendation.
Figure 4.17: High pressure rate coefficient for \( \text{C}_3\text{H}_8 \rightarrow \text{CH}_3 + \text{C}_2\text{H}_5 \) (600-1653 K). Symbols, current RRKM results (listed on figure); solid line, fit to current RRKM results; dashed line, Mousavipour and Homayoon [33]; dotted line, Knyazev and Slagle [31]; dot-dashed line, Tsang [17]; dot-dot-dashed, Dean [14]; gray line, Baulch et al. [201] IUPAC recommendation.

Figure 4.18: High-pressure rate coefficient for \( \text{i-C}_4\text{H}_{10} \rightarrow \text{CH}_3 + \text{i-C}_3\text{H}_7 \). Symbols, current RRKM results (listed on figure); solid line, fit to current RRKM results; dashed line, Tsang [17]; dotted line, Warnatz [153].
Figure 4.19: High-pressure rate coefficient for $n$-C$_4$H$_{10} \rightarrow$ CH$_3$ + n-C$_3$H$_7$. Filled squares, current RRKM results (listed on figure); solid line, fit to current RRKM results; dashed line, Dean [14]; dotted line, Warnatz [153].

Figure 4.20: High-pressure rate coefficient for $n$-C$_4$H$_{10} \rightarrow$ C$_2$H$_5$ + C$_2$H$_5$. Filled circles, current RRKM results (listed on figure); solid line, fit to current RRKM results; dashed-dot line, Dean [14]; dashed-dot-dot line, Warnatz [153]; dashed line, result using the geometric mean rule.
Chapter 5: CO$_2$ incubation and decomposition

This chapter discusses the measurement of incubation times and the rate coefficient for CO$_2$ decomposition, reaction (6). These measurements were made in the shock tube facility using CO$_2$ laser absorption at 216.5 and 244 nm described in Chapter 2.

5.1 Determination of incubation times and decomposition rate coefficients

Mixtures of 1% and 2% CO$_2$ dilute in argon were heated behind reflected shock waves in the shock tube facility described in Chapter 2. The incident shock conditions ranged from 1547 to 2123 K and 0.08 to 0.2 atm and the reflected shock conditions ranged from 3209 to 4601 K and 0.44 to 0.98 atm. The reflected shock pressure and temperature were taken to be the vibrationally equilibrated conditions and have uncertainties of ~1% and ~0.7% respectively. Despite the observation of incubation times, vibrational relaxation in the lower energy levels occurs rapidly behind the incident and reflected shock waves [109-110]. The vibrational relaxation times behind the incident and reflective waves for the conditions of these experiments are 9 to 11 $\mu$s and 0.7 to 0.9 $\mu$s respectively, based on the vibrational relaxation measurements of Simpson et al. [109].

The progress of reaction was monitored by observing laser absorption by CO$_2$ at 216.5 and 244 nm using the previously measured absorption cross-sections for CO$_2$ at these two wavelengths [156] as described in Chapter 2. The absorbance for an example experiment at 216.5 nm is shown in Figure 5.1. The passage of the incident shock wave causes a schlieren spike in the signal, due to steering of the beam off the detector, after
which the CO$_2$/Ar mixture vibrationally relaxes to the vibrationally equilibrated temperature. The vibrational relaxation causes an induction in the CO$_2$ absorption. However, the vibrational relaxation after the passage of the incident shock wave was always sufficiently fast ($\tau_{\text{rel}} = 9-11$ $\mu$s) for the use of the vibrationally equilibrated incident shock temperature in the calculation of the reflected shock conditions. Additionally, the observed induction times in the absorbance after the incident shock waves are in good agreement (~10%) with previous measurements of vibrational relaxation times by Simpson et al. [109] and Kamimoto and Matsui [110]. After the passage of the reflected shock wave the absorbance quickly rises due to the increase in temperature and pressure and the vibrational relaxation is not resolved. Based on the previous measurement by Simpson et al. [109], the vibrational relaxation time behind the reflected shock wave in this example (Figure 5.1) is 0.7 $\mu$s. While the experimental time resolution is not sufficient to observe the vibrational relaxation behind the reflected shock wave a pronounced incubation period is observed prior to the onset of steady dissociation.

The bond energy of CO$_2$ is quite large (125.7 kcal/mol, 43970 cm$^{-1}$) in comparison to the average energy, therefore only a small fraction of the energy distribution plays a role in the dissociation. Dissociation can only proceed when vibrational levels are populated near the threshold, and a steady dissociation rate is not established until the shock-heated CO$_2$ is near a steady-state vibrational distribution. Establishing population in the highest levels of the vibrational distribution near the threshold takes considerably more time than is required for vibrational relaxation in the low-lying levels probed in vibrational relaxation experiments; therefore, the incubation time is significantly longer than the vibrational relaxation time.

The incubation times were determined from the experimental traces by extrapolating back the decay in absorbance, due to dissociation, to the steady absorbance level achieved after the passage of the reflected shock wave (Figure 5.1). With the end of the incubation period defined as time zero for chemical reaction, the decay in absorbance was fit by adjusting the CO$_2$ decomposition rate, reaction (6), in the mechanism given in Table 5.1. Because of the high CO$_2$ concentrations (1-2%) the endothermic decomposition caused a non-negligible decrease in temperature as the reaction
proceeded. The temperature-dependence of the rate coefficient and the absorption cross-section was taken into account by modeling the decomposition with a constant volume constraint. The temperature-dependence of the absorption cross-section is known from previous measurements (Chapter 2 and [156]). However, to treat the temperature-dependence (activation energy) of the rate coefficient, the activation energy was initially assumed and the A-factor was adjusted, in an Arrhenius expression, for a best fit to each experimental absorbance trace. The resulting rate coefficient determinations were fit with a new Arrhenius expression and the A-factor was again adjusted to provide a best fit to each experimental trace. This procedure was performed iteratively until the rate coefficient converged (three iterations). To avoid significant influence on the rate coefficient determinations by the temperature time-history and the fitting procedure, the absorption traces were fit over the earliest possible time periods. In fact, if the temperature history is ignored and the reflected shock conditions are assumed constant throughout the experiment, the resulting rate coefficients differ only by <15% from those obtained by accounting for this effect. The rate coefficient results for reaction (6) from 3200 to 4600 K and around 0.5 to 1 atm can be expressed using a two-parameter Arrhenius representation

\[
k_6(T) = 3.14 \times 10^{14} \exp(-51300 \text{ K} / T) \text{ [cm}^3\text{mol}^{-1}\text{s}^{-1}]
\]

with 1-σ standard deviation of ±8% in the scatter of the data about the fit. The estimated uncertainty in the rate coefficient determinations is ±21%, see Appendix B. This uncertainty is primarily based on uncertainty in the temperature history, as the absorption cross-section has very small uncertainty (<5%), the experimental signal-to-noise is large, and the two secondary reactions in Table 5.1 have an almost negligible impact on the fits. The experimental findings for both the second order rate coefficient and incubation times are shown in Figures 5.2 and 5.3 and a summary of the experimental results is given in Table A.5.

5.2 Master equation calculations

One-dimensional energy-grained master equation calculations, as described in Chapter 3, were carried out to determine a suitable energy transfer model for description of both the measured decomposition rate coefficient and the incubation times. The master
equation calculations were performed assuming that the translational and rotational CO$_2$
temperatures relax immediately following the passage of the reflected shock wave and
the vibrational temperature is initially at the incident shock value. The vibrational
distribution then evolves due to CO$_2$-Ar collisional energy transfer and the vibrational
states reach a steady distribution before steady dissociation. The computed incubation
times and decomposition rate coefficients were derived in the same manner as they were
from the experiments, by tracking the time-dependent fractional population of CO$_2$.

Due to the sparse density of states of CO$_2$ the master equation calculations were
carried out for a fairly large dimension of 2000 levels over the energy range of 80000
cm$^{-1}$. A double array was implemented with a grain size of 25 cm$^{-1}$ for the first 1000
levels and the remaining 1000 levels equidistantly spaced over the entire energy domain
(0-80000 cm$^{-1}$). Reducing the dimension of the grained master equation significantly
reduced computational time but dramatically influenced the temporal evolution of the
population. However, increasing the level dimension above 2000 resulted in no change to
the computed results.

5.2.1 Energy-specific rate coefficient $k(E)$

The decomposition of CO$_2$ at the conditions of these experiments is nearly in the
low-pressure-limit [45]. Therefore, the decomposition rate coefficient calculated via the
master equation is significantly more sensitive to the collisional energy probability
density function, $P_{ij}$, than the energy specific rate constant, $k(E)$. Due of the lack of
sensitivity of the rate coefficient and the lack of an accurate potential energy surface the
inverse Laplace transform method was used, described in Chapter 3, to calculate $k(E)$.
The Arrhenius parameters calculated by Yau and Pritchard [157] were used, $A_\infty = 1.80 \times$
10$^{12}$ s$^{-1}$ and $E_\infty = 127.3$ kcal/mol, for calculation of $k(E)$ via the inverse Laplace transform
method. Reasonable perturbation of these parameters did not substantially affect the
master equation results for the decomposition rate coefficient and incubation times. The
density of states, $\rho(E)$, was calculated using the DenSum code of Barker [123] with the
graining technique described above and the known CO$_2$ frequencies. Additionally, the
CO$_2$ two-dimensional external rotor was considered active in the density of states
calculations because of the Coriolis interaction between it and the two degenerate bending modes [57].

5.2.2 Energy transfer

The observed incubation times and rate coefficients are most sensitive to the form of energy transfer probability density function, $P_{ij}$, chosen for solution of the master equation. The exponential model with an energy dependent step size down (Chapter 3) was chosen:

$$P_{ij} = \frac{1}{N_j} \exp\left(-\frac{E_j - E_i}{\alpha(E_j)}\right)$$

The parameter $\alpha(E_j)$ was fit to the experimental incubation times and decomposition rate coefficients with guidance from previous energy transfer studies on triatomics. Although there is a wealth of literature on CO$_2$ V-T state-to-state transfer at low energies, there have been no direct studies for CO$_2$ energy transfer at the high energies encountered in shock tube experiments and important during dissociation. However, there have been several studies on energy transfer at high energies for other triatomics in rare gases: NO$_2$ [158-159], SO$_2$ [160-161], and CS$_2$ [160,162-163]. All three of these molecules are of interest because they have enhanced energy transfer at high energies due to the mixing of excited electronic states with the electronic ground state causing rapid intramolecular vibrational energy redistribution (IVR) at energies near that of the excited electronic states. However, enhanced IVR due to mixing of electronic states has not been reported for CO$_2$. These studies [158-163] also report a dependence on energy that is greater than linear for the energy transferred per collision, $<\Delta E>$, at energies below that where enhancement due to electronic state mixing occurs. Several of these studies suggest a quadratic dependence on energy for the energy transferred per collision ($<\Delta E> \sim <E>^2$) in the lower energy range [160-163]. It is likely that CO$_2$ behaves similarly to these other triatomics without the enhancement due to electronic state mixing. Therefore, the form

$$\alpha(E_j) = C_0 + C_1 E_j^2$$

was chosen for the energy transfer parameter, $\alpha$, with $C_0$ and $C_1$ as adjustable parameters. The experimental incubation times and decomposition rate coefficients were best fit by $C_0 = 30$ cm$^{-1}$ and $C_1 = 3.0 \times 10^{-7}$ (cm$^{-1}$)$^{-1}$. Fits were attempted with other models such as
Luther and coworker’s empirical generalized exponential model with linear dependence of $\alpha$ on energy [164]. The observed incubation times were always longer than the predictions using this model, leading to the same conclusion that Dove and Troe [66] made in their master-equation study of N$_2$O incubation behind shock waves: the energy transfer parameter, $\alpha$, must increase with a greater than linear dependence on energy. Although the suggested model provides a satisfactory fit of the current experimental results, the data covers a limited range and is not sufficiently isolated to energy transfer effects to conclude that this model is complete or unique. For instance, it can not be determined if the energy transfer parameter, $\alpha$, varies with temperature. Also, it may be possible to fit the experimental data with other functional forms of the energy transfer probability density function, $P_{ij}$, such as the complete biexponential function. The master equation results for the incubation times are included in Figure 5.3, an example master equation calculation of the fractional CO$_2$ concentration is shown in Figure 5.4, and a summary of the parameters used in the master equation calculations are given in Table 5.2.

5.3 Discussion

5.3.1 CO$_2$ decomposition rate coefficient

A comparison between the current findings for the CO$_2$ second-order decomposition rate coefficient and several previous experimental studies is shown in Figure 5.2. The current findings agree very well with the studies of Burmeister and Roth [41], Ebrahim and Sandeman [43], and Hardy et al. [44]. Although the rate coefficient result differs in magnitude with Kiefer [46], it does agree on activation energy; however, the current findings disagree with the activation energies reported by Fujii et al. [42] and Dean [47]. There has been discussion of the influence of impurities on reported activation energies for this rate coefficient [44], perhaps this is the reason for the differences in activation energies of the Fujii et al. [42] and Dean [47] studies. Regardless, the spread in the rate coefficient at any temperature for all of the previous experiments, in Figure 5.2, is only a factor of three. If the Kiefer [46] and Dean [47] results are excluded, the spread is reduced to a factor of less than 1.5. The estimated uncertainties of the current
experimental study are small (±21%) and the excellent agreement with references [41], [43] and [44] gives confidence in the current rate determination.

5.3.2 CO₂ incubation

Incubation is a collisional phenomenon, therefore, incubation times are plotted in terms of total Lennard-Jones collisions, \( Z_{L-J}[M] \Delta t_{inc} \), in Figure 5.3, where \( Z_{L-J}[M] \) is the Lennard-Jones collision rate for CO₂-argon collisions (1/s). The number of incubation collisions was experimentally found to increase with decreasing temperature and can be expressed as \( Z_{L-J}[M] \Delta t_{inc} \sim T^{-5.1} \); the temperature-dependence is also satisfactorily reproduced by the master equation simulations, see Figure 5.3. This temperature-dependence is very similar to the findings of Hippler and co-workers for methyl radical incubation [73]; Dove et al. [65] also found strong temperature-dependence in N₂O incubation times.

Analytic master equation solutions for incubation in CO₂ dissociation have been reported by Forst and Penner [57] and Yau and Pritchard [58]. In both of these calculations the exponential energy transfer probability density function, \( P_{ij} \), was used with a constant energy transfer parameter, \( \alpha \). These studies both predict approximately 2500 incubation collisions at 3500 K for CO₂ in a rare gas, an order of magnitude fewer collisions than was experimentally measured and predicted in the master equation simulations using the quadratic energy dependence in \( \alpha \). The difference in these master equation results demonstrates the importance of modeling the energy dependence of \( \alpha \) to predict energy transfer during the activation period. While the present model adequately explains the observed incubation times and decomposition rate coefficients, experiments are needed that isolate the energy transferred per collision, \( <\Delta E> \), at specific energy and temperature, for improved modeling of chemical reaction systems where energy transfer plays a dominant role.
Table 5.1: Reaction mechanism for CO₂ decomposition system.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate coefficient [cm³ mol⁻¹ s⁻¹] and third body efficiencies</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(6) CO₂ + M → CO + O + M</td>
<td>3.14 x 10⁻¹⁴ exp(-51300 K / T) Ar/ 1/ CO₂/ 7/ CO/ 3</td>
<td>rate coefficient this study; 3rd body efficiencies from [153]</td>
</tr>
<tr>
<td>O₂ + CO ↔ O + CO₂</td>
<td>2.50 x 10⁻¹² exp(-24056 K / T)</td>
<td>[153]</td>
</tr>
<tr>
<td>2O + M ↔ O₂ + M</td>
<td>1.20 x 10⁻¹⁷ T⁻¹.⁰ Ar/ 0.83/ CO₂/ 3.6/ CO/ 1.75</td>
<td>[153]</td>
</tr>
</tbody>
</table>

Table 5.2: Parameters used in master equation calculations for CO₂ thermal decomposition.

| CO₂ heat of formation at 0 K                        | -93.96 kcal/mol                                                   |
| 2-D moment of inertia (coriolis active)            | 43.20 amu Å²                                                       |
| CO₂ vibrational frequencies (cm⁻¹)                 | 1333, 2349, 667(2)                                                |
| Lennard Jones parameters CO₂                        | σ = 3.47 Å, ε/k = 114 K                                           |
| Lennard Jones parameters Ar                         | σ = 3.94 Å, ε/k = 201 K                                           |
| High pressure limit Arrhenius parameters for       | $A_\infty = 1.80 \times 10^{12}$ s⁻¹, $E_\infty = 127.3$ kcal/mol |
| inverse Laplace transform calculation of $k(E)$    |                                                               |
| Energy transfer parameter                           | $\alpha(E) = 30 + 3.0 \times 10^7 E^2$ [cm⁻¹]                   |

Figure 5.1: Example experiment and fit (dark line): CO₂ absorbance ($\ln(I_0/I)$) at 216.5 nm. Initial mixture 2% CO₂/Ar. Vibrationally equilibrated shock conditions: 1812 K and 0.161 atm. Initial (prior to decomposition) vibrationally equilibrated reflected shock conditions: 3838 K, 0.820 atm.
Figure 5.2: Second order rate coefficient for CO$_2$ + Ar $\rightarrow$ CO + O + Ar: filled squares with error bars, current experimental results; heavy solid line, fit to current data; dashed line, Burmeister and Roth [41]; solid line, Fujii et al. [42]; dash-dot line, Ebrahim and Sandeman [43]; short dash line, Hardy et al. [44]; dash-dot-dot line, Kiefer [46]; smaller dotted line, Dean [47].

Figure 5.3: Number of Lennard-Jones collisions in CO$_2$-Ar incubation period ($Z_{L-J}[M]\Delta t_{inc}$): experiment, open circles with error bars; master equation, filled squares.
Figure 5.4: Example master equation result for experiment denoted with an asterisk (*) in Table A.5. Initial conditions: $T_{\text{trans}} = T_{\text{rot}} = 4171$ K, $T_{\text{vib}} = 1943$ K, and $P = 0.735$ atm. Open circles, master equation calculation; solid line, fit to calculation for determination of incubation time and rate coefficient.
Chapter 6: Benzyl and toluene decomposition

This chapter discusses the measurement of thermal decomposition rate coefficients for benzyl decomposition, reaction (7), and toluene decomposition, reactions (8) and (9). These measurements were made in the shock tube facility using laser absorption at 266 nm as described in Chapter 2.

6.1 Benzyl decomposition

6.1.1 Determination of benzyl decomposition rate coefficient

Fröchtenicht et al. [117] have shown that the benzyl radical decomposes to yield an H-atom and a C_7H_6 fragment of unknown structure

\[ \text{C}_6\text{H}_5\text{CH}_2 \rightarrow \text{C}_7\text{H}_6 + \text{H} \]  

(7)

The Fröchtenicht et al. [117] experiment utilized photon-induced decomposition of benzyl in a molecular beam with mass spectrometry detection to identify the C_7H_6 product. H-atom ARAS measurements [74,87] also indicate that one H-atom is produced per benzyl undergoing decomposition. Other benzyl decomposition pathways have been suggested including pathways leading to C_5H_5 + C_2H_2 products and C_4H_4 + C_3H_3 products [202]. However, the most recent direct high-temperature experimental studies have concluded that the C_7H_6 + H pathway is the dominant pathway [74,87,117] and quantum chemical calculations have confirmed this pathway [80]. In the current study the decomposition of benzyl, reaction (7), was studied behind reflected shock waves at temperatures of 1461 to 1730 K and pressures of 1.467 to 1.666 atm using ultraviolet laser absorption for detection of benzyl at 266 nm. Benzyl was generated by the fast decomposition of benzyl iodide

\[ \text{C}_6\text{H}_5\text{CH}_2\text{I} \rightarrow \text{C}_6\text{H}_5\text{CH}_2 + \text{I} \]  

(12)
Experiments were performed with mixtures of 50 and 100 ppm benzyl iodide dilute in argon. The low concentrations provided isolated sensitivity to the decomposition of benzyl, reaction (7). The progress of reaction was monitored using benzyl absorption at 266 nm. However, interfering absorption due to benzyl fragments and toluene must be accounted for.

To determine the rate coefficient for reaction (7) the measured 266 nm absorbance was fit using a detailed reaction mechanism given in Appendix E and the measured absorption cross-sections for benzyl radicals and the interfering absorbers (benzyl fragments and toluene). The reaction mechanism was largely developed by Hippler, Troe, and co-workers [74,81-82,91]. Fortunately, the current low concentration benzyl decomposition experiments show little sensitivity to secondary chemistry. Therefore, excellent agreement between fit and experiment was obtained by adjusting only the rate coefficient for reaction (7). The absorption cross-sections for benzyl and benzyl fragments were determined in the same experiments used here for the determination of the benzyl decomposition rate (see section 2.4). The absorption cross-section for toluene was determined in the toluene decomposition experiments, discussed later in this chapter. Computations were done using CHEMKIN 2.0 and SENKIN [135-136].

The measured absorbance during an example benzyl decomposition experiment is shown in Figure 6.1. As described in section 2.4 after the passage of the reflected shock wave the fast dissociation of benzyl iodide provides an immediate yield of benzyl radicals and thus the absorption cross-section can be determined. The decay in the absorbance signal then can be fit by adjusting \( k_7 \) in the reaction mechanism and appropriately accounting for absorption due to benzyl fragments, formed via reaction (7), and toluene formed by benzyl/H-atom recombination

\[
C_6H_5CH_2 + H \rightarrow C_6H_5CH_3
\]  

(14)

The example in Figure 6.1 illustrates the best fit achieved by adjusting \( k_7 \) and the contributions to the 266 nm absorbance from the three absorbing species: benzyl, benzyl fragments, and toluene. As noted in section 2.4, the absorption cross-section of benzyl fragments was determined from the constant absorption observed at long times and assuming complete one-to-one conversion of benzyl into benzyl fragments. The sensitivity for benzyl concentration for the experiment shown in Figure 6.1 is given in
Figure 6.2. Notice that the benzyl concentration shows isolated sensitivity to reaction (7) at early times allowing a direct fit without interference from secondary reactions. The isolated sensitivity to reaction (7), due to the low concentration of benzyl iodide precursor, provides a pseudo-first-order fit only complicated by the interfering absorption. Therefore, uncertainties in the initial concentration of benzyl iodide and the benzyl absorption cross-section do not affect the uncertainty in the rate coefficient determination.

The present rate coefficient determinations for reaction (7) are tabulated in Appendix A and shown in Figure 6.3 on Arrhenius plot along with a least-squares fit. The rate coefficient at 1.5 atm given by the least-squares fit can be expressed as

$$k_7(T) = 8.20 \times 10^{14} \exp(-40600 \, K/T) \, [s^{-1}]$$

where the RMS experimental scatter about the fit is ±11%. The overall uncertainty of the rate coefficient is estimated at ±25%. The primary contributions to the uncertainty in the rate coefficient are uncertainties in: temperature, fitting the data to computed profiles, and interfering absorption. See Appendix B for details pertaining to the uncertainty analysis.

### 6.1.2 Comparison with previous studies

Comparison of the results of the current study with the results of four previous shock tube studies is also shown in Figure 6.3. The current data agree very well with the UV absorption study of Hippler et al. [81] (~0.5 atm) and the H-atom ARAS study of Braun-Unkhoff et al. [87] (~2 atm); although, the scatter of the current data is significantly reduced from that of these previous studies. In addition, the current data for $k_7$ is in agreement with the IUPAC review recommendation, Baulch et al. [201]. (The IUPAC review recommends the rate coefficient previously determined by Braun-Unkhoff et al. [87].) The rate coefficient results of the UV absorption study of Jones et al. [80] (~10-12 atm) and the H-atom ARAS study of Rao and Skinner [86] (~0.6 atm) are approximately an order-of-magnitude lower than the results of the current study. The experimental rate coefficient results of Jones et al. [80] and Rao and Skinner [86] have scatter of approximately an order-of-magnitude and therefore probably have uncertainties of at least an order-of-magnitude if not greater. The current rate coefficient determinations have significantly less uncertainty due to the low concentrations used and
high sensitivity of the laser absorption technique. Based on the findings for toluene decomposition (section 6.2), it is expected that \( k_7 \) is somewhat in the falloff at the highest temperatures of this study. However, because the \( \text{C}_7\text{H}_6 \) decomposition product is of unknown structure (i.e., the transition state is of unknown structure) a RRKM/master equation calculation cannot be performed to extrapolate the rate coefficient experimental determinations to the high-pressure-limit.

### 6.2 Toluene decomposition

#### 6.2.1 Determination of toluene decomposition rate coefficients

Mixtures of 200 and 400 ppm of toluene dilute in argon were shock-heated behind reflected shock waves while absorption at 266 nm, primarily due to benzyl radicals, was monitored. Reflected shock conditions ranged from 1398 to 1782 K and 1.44 to 1.58 atm. Toluene is known to decompose via two parallel channels [74,91]

\[
\begin{align*}
\text{C}_6\text{H}_5\text{CH}_3 & \rightarrow \text{C}_6\text{H}_5\text{CH}_2 + \text{H} \quad (8) \\
\text{C}_6\text{H}_5\text{CH}_3 & \rightarrow \text{C}_6\text{H}_5 + \text{CH}_3 \quad (9)
\end{align*}
\]

Therefore, the benzyl absorbance profiles must be fit in terms of the overall decomposition rate coefficient, \( k_8 + k_9 \), and the branching ratio, \( k_8 / (k_8 + k_9) \). The time dependence of the benzyl sensitivity to the overall decomposition rate coefficient and the branching ratio allows for the separation of these two parameters. The overall rate of decomposition, \( k_8 + k_9 \), can be determined by fitting the early-time behavior of the benzyl absorbance profile. At longer times the benzyl absorbance rolls off and the benzyl sensitivity shifts towards the branching ratio allowing a fit of this parameter.

The measured 266 nm absorbance, see Figure 6.4 for an example, was fit by adjusting the overall decomposition rate and the branching ratio in the detailed mechanism given in Appendix E and developed primarily by Hippler, Troe, and co-workers [74,81-82,91]. As in the case of benzyl decomposition the absorption cross-sections of benzyl, benzyl fragments, and toluene must be accounted for. The contribution each of these three absorption components has toward the total signal is shown in Figure 6.5. The toluene absorption cross-section at 266 nm as determined from the time-zero absorption during these experiments was found to be \( \sigma_{\text{C}_6\text{H}_5\text{CH}_3} = 5.9 \pm 0.5 \)
x $10^{-19}$ cm$^2$molecule$^{-1}$ with no temperature-dependence for the range of 1398 to 1782 K. The benzyl and benzyl fragment absorption cross-sections were used as determined in Chapter 2. A benzyl sensitivity calculation for the conditions of Figure 6.4 is shown in Figure 6.6. The calculation shows strong sensitivity to the overall decomposition rate, $k_8+k_9$, and the branching ratio, $k_8/(k_8+k_9)$. However the sensitivity calculation also shows unavoidable interference from fast secondary reactions:

$$\text{C}_6\text{H}_5\text{CH}_2 \rightarrow \text{C}_7\text{H}_6 + \text{H} \quad (7)$$
$$\text{C}_7\text{H}_6 + \text{H} \rightarrow \text{C}_6\text{H}_5\text{CH}_2 \quad (15)$$
$$\text{C}_6\text{H}_5\text{CH}_3 + \text{H} \rightarrow \text{C}_6\text{H}_5\text{CH}_2 + \text{H}_2 \quad (16)$$

The rate coefficients for reactions (7) and (16) are well known with uncertainties of ±25% and ±30%, respectively. Reaction (7) is part of the current study and reaction (16) has been previously measured by Hippler and co-workers [81]. Per the recommendation of Eng et al. [74], the benzyl fragment $\text{C}_7\text{H}_6$ is assumed to be able to recombine with H to yield benzyl, reaction (15). The value of $k_{15}$ was taken from Eng et al. [74] and has large uncertainty contributing to uncertainty in the determinations for $k_8$ and $k_9$.

The rate coefficient results for toluene decomposition at 1.5 atm are given in Figures 6.7 and 6.8 with least-squares fits. Expressions for the rate coefficients for reactions (8) and (9) at 1.5 atm given by the least-squares fits are

$$k_8(T) = 2.09 \times 10^{15} \exp(-44040 \text{ K}/T) \text{[s}^{-1}]$$
$$k_9(T) = 2.66 \times 10^{16} \exp(-49260 \text{ K}/T) \text{[s}^{-1}]$$

where the RMS experimental scatter about the fits is ±13% and ±17% for $k_8$ and $k_9$ respectively. The rate coefficient determinations for reactions (8) and (9) are tabulated in Appendix A. The primary contributions to uncertainties in the rate coefficients are uncertainties in: temperature, absorption cross-sections, fitting the data to computed profiles, and interfering chemistry. These uncertainties give overall uncertainties in $k_8$ and $k_9$ of ±39%, and ±39% respectively. See Appendix B for details of the uncertainty analysis.

### 6.2.2 RRKM / master equation calculations

Multi-channel RRKM calculations with numerical solution to the 1-D (internal energy) master equation were carried for the decomposition of toluene. The two
transition states were modeled using a restricted Gorin model. The calculations provided extrapolation of the experimental determinations at 1.5 atm to the high-pressure-limit. The calculation allowed for a fit of the data with one adjustable parameter: the hindrance, $\eta$, on the restricted internal rotations of the two transition states. The probability function for collisional energy transfer for deactivating collisions has been accurately measured by Luther and co-workers [131-132] and their result was used in these calculations. Luther and co-workers [131-132] give the probability density function using a modified exponential-down formulation

$$P_j = \frac{1}{N_j} \exp\left(-\left[\frac{E_j - E_i}{\alpha_0 + \alpha_1 E_j}\right]^\gamma\right) \text{ for } E_j > E_i$$

where for toluene-argon collisions $\alpha_0 = 43.5 \text{ cm}^{-1}$, $\alpha_1 = 4.2 \times 10^{-3}$, and $\gamma = 0.70$. Lennard-Jones parameters for toluene and argon [140], the molecular frequencies [91,141,165-167], moments of inertia [91,93,145,166], heats of formation [146,168-171], and barrier heights [146,168-171] were taken from various references and are listed in Table 6.1.

The RRKM/master equation calculations provided calculation of rate coefficients in the high-pressure-limit for reactions (8) and (9), for 1398 to 1782 K, which can be expressed with two-parameter Arrhenius expressions

$$k_{x,8}(T) = 8.32 \times 10^{15} \exp(-45890 \text{ K}/T) [\text{s}^{-1}]$$
$$k_{x,9}(T) = 1.48 \times 10^{17} \exp(-51350 \text{ K}/T) [\text{s}^{-1}]$$

These expressions along with the RRKM/master equation results for 1.5 atm are shown in Figures 6.7 and 6.8. Comparison between the least squares fit to the experimental data and the RRKM/master equation result for 1.5 atm shows excellent agreement.

### 6.2.3 Comparison with previous studies

The results of the current toluene decomposition study, in terms of the overall decomposition rate coefficient and the branching ratio, are compared to previous studies in Figures 6.9 and 6.10. The current findings for the overall decomposition rate coefficient agree, with deviation of less than a factor of two, with previous results of Eng et al. [74], Braun-Unkhoff et al. [88], and Luther et al. [94]. However the results for the overall decomposition rate coefficient of Pammidimukkala et al. [89] and Rao and
Skinner [90] are significantly lower than the current findings (Figure 6.9). The results of the current study for the branching ratio are in good agreement with the previous findings of Eng et al. [74] and Luther et al. [94]. However, the results of the current study are in disagreement with the results of Pammidimukkala et al. [89], Rao and Skinner [90], and Braun-Unkhoff et al. [87]. The current data set and the H-atom ARAS experiments of Eng et al. [74] clearly show that the toluene decomposition channel leading to benzyl is more dominant than the channel leading to phenyl. On these grounds, the low branching ratios given by the earlier Pammidimukkala et al. [89] (1987) and Rao and Skinner [90] (1989) are probably erroneous. Additionally, the relatively low uncertainties of the current results and the good agreement with the low concentration (high kinetic isolation) H-atom ARAS results of Eng et al. [74] lends confidence to the results presented here.

A comparison of the toluene decomposition results with the most recent IUPAC recommendations (Baulch et al. [201]) is also made in Figures 6.7-6.10. The IUPAC recommendation for the toluene → benzyl + H channel, $k_8$, shows good agreement. However, the recommendation for the toluene → phenyl + CH$_3$ channel, $k_9$, shows large disagreement. The IUPAC recommendation has far too low an activation energy and A-factor in comparison to the current study and precious studies. This disagreement results in disagreement in the magnitude of the branching ratio and the temperature-dependence, Figure 6.10.
Table 6.1: Parameters used in RRKM / master equation calculations for toluene decomposition.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat of Formation (0K) [168]</td>
<td>$17.50 \text{ kcal/mol}$</td>
</tr>
<tr>
<td>Moments of Inertia (amu $\text{Å}^2$) [93]</td>
<td>$290.7$ (inactive); $200.7$ (inactive); $89.2$ (active), $\sigma = 2$</td>
</tr>
<tr>
<td>Frequencies (cm$^{-1}$) [165]:</td>
<td>$3085, 3070, 3058, 3037, 3028, 2979, 2950, 2920, 1604, 1584, 1493, 1455(3), 1378, 1331, 1313, 1208, 1176, 1153, 1080, 1040(2), 1028, 1002, 983, 973, 893, 841, 784, 734, 690, 620, 524, 467, 406, 347, 217$</td>
</tr>
<tr>
<td>Internal rotation (amu $\text{Å}^2$) [167]:</td>
<td>$3.139$</td>
</tr>
<tr>
<td>Frequencies (cm$^{-1}$) [91]:</td>
<td>$3060(2), 3050, 3040, 3030, 2930, 2860, 1600, 1550, 1480, 1440(2), 1350, 1330, 1300, 1270, 1160(2), 1070, 1010, 980(2), 950, 890, 820, 810, 750, 640, 610, 600, 520, 420, 360(2), 290, 170$</td>
</tr>
<tr>
<td>Active 1-D external rotor (amu $\text{Å}^2$) [93]:</td>
<td>$89.2$, $\sigma = 2$</td>
</tr>
<tr>
<td>Active 2-D internal rotor (amu $\text{Å}^2$) [91]:</td>
<td>$186.07$, $\sigma = 1$; $\eta = 99.84%$</td>
</tr>
<tr>
<td>Active 2-D internal rotor (amu $\text{Å}^2$) [91]:</td>
<td>$275.00$, $\sigma = 1$; $\eta = 99.84%$</td>
</tr>
<tr>
<td>Barrier at 0 K [168-169,171,204]:</td>
<td>$88.86 \text{ kcal/mol}$</td>
</tr>
<tr>
<td>Frequencies (cm$^{-1}$) [141,166]:</td>
<td>$3085, 3071, 3052, 3073, 3060, 1593, 1499, 1441, 1433, 1344, 1226, 1086, 1080, 1067, 1027, 1011, 976, 971, 966, 878, 813, 708, 629, 605, 586, 416, 400, 3184(2), 3002, 1383(2), 580$</td>
</tr>
<tr>
<td>Active 1-D external rotor (amu $\text{Å}^2$) [93]:</td>
<td>$89.2$, $\sigma = 2$</td>
</tr>
<tr>
<td>Active 1-D internal torsion (amu $\text{Å}^2$) [145,166]:</td>
<td>$3.421$, $\sigma = 3$</td>
</tr>
<tr>
<td>Active 2-D internal rotor (amu $\text{Å}^2$) [145]:</td>
<td>$1.760$, $\sigma = 2$; $\eta = 82%$</td>
</tr>
<tr>
<td>Active 2-D internal rotor (amu $\text{Å}^2$) [145]:</td>
<td>$1.760$, $\sigma = 2$; $\eta = 82%$</td>
</tr>
<tr>
<td>Active 2-D internal rotor (amu $\text{Å}^2$) [166]:</td>
<td>$80.66$, $\sigma = 1$; $\eta = 82%$</td>
</tr>
<tr>
<td>Active 2-D internal rotor (amu $\text{Å}^2$) [166]:</td>
<td>$172.02$, $\sigma = 1$; $\eta = 82%$</td>
</tr>
<tr>
<td>Barrier at 0 K [146,168,170]:</td>
<td>$102.58 \text{ kcal/mol}$</td>
</tr>
</tbody>
</table>
Figure 6.1: Example 266 nm absorbance during benzyl iodide decomposition. Reflected shock conditions: 1615 K, 1.556 atm, 50 ppm benzyl iodide/Ar. Solid line, best fit to absorbance by adjusting $k_7$; dashed line, contribution to absorbance from benzyl; dotted line, contribution to absorbance from benzyl fragments; dot-dashed line, contribution to absorbance from toluene.

Figure 6.2: Local sensitivity for benzyl concentration for conditions of experiment given in Figure 6.1. $S = (dX_{\text{benzyl}} / dk_i) (k_i / X_{\text{benzyl,local}})$, where $k_i$ is the rate constant for reaction i and $X_{\text{benzyl,local}}$ is the local benzyl ($C_6H_5CH_2$) mole fraction.
Figure 6.3: Rate coefficient for benzyl decomposition, reaction (7): filled squares with error bars, current experimental results (~1.5 atm); heavy solid line, fit to current data; dash-dot-dot line, Hippler et al. [81] (~0.5 atm); dashed line, Braun-Unkhoff et al. [87] (~2 atm) and Baulch et al. [201]; dotted line, Jones et al. [80] (~10-12 atm); dash-dot line, Rao and Skinner [86] (~0.6 atm).

Figure 6.4: Example 266 nm absorbance during toluene decomposition. Reflected shock conditions: 1593 K, 1.461 atm, 200 ppm toluene/Ar. Solid line, fit to data by adjusting overall decomposition rate, $k_8 + k_9$, and branching ratio, $k_8/(k_8 + k_9)$; dotted lines, variation of $k_8 + k_9 \pm 50\%$; dashed lines, variation of $k_8/(k_8 + k_9) \pm 30\%$. 
Figure 6.5: Contribution to 266 nm absorbance from benzyl (dashed line), benzyl fragment (dashed-dotted line), and toluene (dotted line) for example experiment given in Figure 6.4.

Figure 6.6: Local sensitivity for benzyl concentration for conditions of experiment given in Figure 6.4. $S = \frac{dX_{benzyl}}{dk_i} (k_i / X_{benzyl,local})$, where $k_i$ is the rate constant for reaction $i$ and $X_{benzyl,local}$ is the local benzyl ($C_6H_5CH_2$) mole fraction.
Figure 6.7: Rate coefficient for $C_6H_5CH_3 \rightarrow C_6H_5CH_2 + H$, reaction (8): filled squares with error bars, current experimental results (~1.5 atm); solid gray line, fit to current data; solid black line, RRKM / master equation result for $k_{8,\infty}$; dashed line, RRKM / master equation result for $k_8(1.5$ atm); dotted line, Baulch et al. [201] IUPAC recommendation for $k_{8,\infty}$.

Figure 6.8: Rate coefficient for $C_6H_5CH_3 \rightarrow C_6H_5 + CH_3$, reaction (9): filled circles with error bars, current experimental results (~1.5 atm); solid gray line, fit to current data; solid black line, RRKM / master equation result for $k_{9,\infty}$; dashed line, RRKM / master equation result for $k_9(1.5$ atm); dotted line, Baulch et al. [201] IUPAC recommendation for $k_{9,\infty}$.
Figure 6.9: Comparison with previous data for the toluene overall decomposition rate coefficient $k_8 + k_9$. Luther et al. [94] performed laser excitation study to determine rate coefficient at infinite pressure.

Figure 6.10: Comparison with previous data for the toluene decomposition branching ratio $k_8 / (k_8 + k_9)$. Luther et al. [94] performed laser excitation study to branching ratio at infinite pressure.
Chapter 7: Conclusions

7.1 Summary of results

The objective of the research presented in this thesis was to make accurate measurements of rate coefficients for several decomposition reactions of importance in combustion systems. The topics are broken into three categories: 1) the decomposition of alkanes, 2) the incubation and decomposition of CO₂, and 3) the decomposition of benzyl and toluene. Sensitive ultraviolet laser absorption for detection of product or reactant species was used to monitor the progress of reaction in shock-wave initiated thermal decomposition experiments. The rate coefficient and incubation results were fit using computational techniques based on RRKM theory and the one-dimensional master equation.

7.1.1 Alkane decomposition

Laser absorption of methyl radicals at 216.62 nm provided a sensitive, high-accuracy method to determine the decomposition rates for ethane, propane, iso-butane, and n-butane:

\[
\begin{align*}
C_2H_6 & \rightarrow CH_3 + CH_3 \\
C_3H_8 & \rightarrow CH_3 + C_2H_5 \\
i-C_4H_{10} & \rightarrow CH_3 + i-C_3H_7 \\
n-C_4H_{10} & \rightarrow CH_3 + n-C_3H_7 \\
n-C_4H_{10} & \rightarrow C_2H_5 + C_2H_5
\end{align*}
\]

Using this technique measurements of \(k_1-k_5\) were made in the falloff regime with experimental conditions ranging from 1297 to 2034 K and 0.13 to 8.8 atm [172-173]. Expressions for the high- and low-pressure-limit rate coefficients and Troe-formulated falloff parameters for reactions (1)-(5) were determined from RRKM/master equation calculations fit to the experimental data. The reaction (1) rate expressions for 700 to 1924 K are:
\[ k_{∞,1}(T) = 1.88 \times 10^{50} T^{-9.72} \exp(-54020 \text{ K}/T) \text{ [s}^{-1}] \]
\[ k_{0,1}(T) = 3.72 \times 10^{65} T^{-13.14} \exp(-51120 \text{ K}/T) \text{ [cm}^3\text{mol}^{-1}\text{s}^{-1}] \]
\[ F_{\text{cent},1}(T) = 0.61 \exp(-T/100 \text{ K}) + 0.39 \exp(-T/1900 \text{ K}) + \exp(-6000 \text{ K}/T) \]

The reaction (2) rate expressions for 600 to 1653 K are:
\[ k_{∞,2}(T) = 1.29 \times 10^{37} T^{-5.84} \exp(-49010 \text{ K}/T) \text{ [s}^{-1}] \]
\[ k_{0,2}(T) = 5.64 \times 10^{74} T^{-15.74} \exp(-49680 \text{ K}/T) \text{ [cm}^3\text{mol}^{-1}\text{s}^{-1}] \]
\[ F_{\text{cent},2}(T) = 0.69 \exp(-T/50 \text{ K}) + 0.31 \exp(-T/3000 \text{ K}) + \exp(-9000 \text{ K}/T) \]

The reaction (3) rate expressions for 1320 to 1560 K are:
\[ k_{∞,3}(T) = 4.83 \times 10^{16} \exp(-40210 \text{ K}/T) \text{ [s}^{-1}] \]
\[ k_{0,3}(T) = 2.41 \times 10^{19} \exp(-26460 \text{ K}/T) \text{ [cm}^3\text{mol}^{-1}\text{s}^{-1}] \]
\[ F_{\text{cent},3}(T) = 0.75 \exp(-T/750 \text{ K}) \]

The reaction (4) rate expressions for 1320 to 1600 K are:
\[ k_{∞,4}(T) = 4.28 \times 10^{14} \exp(-35180 \text{ K}/T) \text{ [s}^{-1}] \]
\[ k_{0,4}(T) = 5.34 \times 10^{17} \exp(-21620 \text{ K}/T) \text{ [cm}^3\text{mol}^{-1}\text{s}^{-1}] \]
\[ F_{\text{cent},4}(T) = 0.28 \exp(-T/1500 \text{ K}) \]

And the reaction (5) rate expressions for 1320 to 1600 K are:
\[ k_{∞,5}(T) = 2.72 \times 10^{15} \exp(-38050 \text{ K}/T) \text{ [s}^{-1}] \]
\[ k_{0,5}(T) = 4.72 \times 10^{18} \exp(-24950 \text{ K}/T) \text{ [cm}^3\text{mol}^{-1}\text{s}^{-1}] \]
\[ F_{\text{cent},5}(T) = 0.28 \exp(-T/1500 \text{ K}) \]

The estimated uncertainties in \( k_1-k_5 \) are ±19%, ±26%, ±25%, ±31%, and ±31% respectively. This is the first study in which several of these reactions have been studied using adequately dilute mixtures in order to sufficiently isolate the decomposition reactions and the results for \( k_5 \) represent the first high-temperature measurement of this rate coefficient. Additionally, these rate determinations provide a test of validity for the geometric mean rule used for rate coefficient estimation. The current data set does in fact suggest that the geometric mean rule is a good estimator of decomposition or association rate coefficients.

### 7.1.2 CO\(_2\) incubation and decomposition

Incubation prior to the thermal decomposition of CO\(_2\)

\[ \text{CO}_2 + \text{M} \rightarrow \text{CO} + \text{O}(^3\text{P}) + \text{M} \quad (6) \]
was observed for the first time in reflected shock wave experiments, confirming the expected bottleneck in collisional activation of CO$_2$ [174]. The thermal decomposition of carbon dioxide was investigated behind reflected shock waves at temperatures of 3200 to 4600 K and pressures of 0.44 to 0.98 atm. Ultraviolet laser absorption at 216.5 and 244 nm was used to monitor the CO$_2$ concentration with microsecond time resolution. The second order rate coefficient for CO$_2$ dissociation was measured with good agreement with several previous shock tube studies. The second-order rate coefficient for CO$_2$ decomposition, reaction (6), over the temperature range of 3200 to 4600 K and around 0.5 to 1 atm is given by

$$k_6(T) = 3.14 \times 10^{14} \exp(-51300 \text{ K}/T) \text{[cm}^3\text{mol}^{-1}\text{s}^{-1}]$$

with estimated uncertainty of ±21%. The number of incubation collisions was found to range from $7 \times 10^3$ at 4600 K to $3.5 \times 10^4$ at 3200 K. Master equation simulations, with a simple model for collisional energy transfer, were carried out to describe the measured incubation times and unimolecular rate coefficient. It was found that the experimental incubation times could not be simulated without a collisional energy transfer parameter, $\alpha$, that increased with a greater than linear dependence on energy. An exponential model for the energy transfer probability density function, $P(E,E')$, with a quadratic energy dependence for $\alpha$ was found to adequately represent the experimental incubation times.

### 7.1.3 Benzyl and toluene decomposition

The decomposition of benzyl radicals and toluene

\[
\begin{align*}
\text{C}_6\text{H}_5\text{CH}_2 & \rightarrow \text{C}_7\text{H}_6 + \text{H} \quad (7) \\
\text{C}_6\text{H}_5\text{CH}_3 & \rightarrow \text{C}_6\text{H}_5\text{CH}_2 + \text{H} \quad (8) \\
\text{C}_6\text{H}_5\text{CH}_3 & \rightarrow \text{C}_6\text{H}_5 + \text{CH}_3 \quad (9)
\end{align*}
\]

was studied at high-temperatures behind shock waves using laser absorption of benzyl radicals at 266 nm to monitor the progress of reaction. The rate coefficient for benzyl decomposition, reaction (7), determined at 1.5 atm and 1461 to 1730 K is given by

$$k_7(T) = 8.20 \times 10^{14} \exp(-40600 \text{ K}/T) \text{[s}^{-1}]$$

and the rate coefficients for the two-channel toluene decomposition, determined at 1.5 atm and 1398 to 1782 K are given by

$$k_8(T) = 2.09 \times 10^{15} \exp(-44040 \text{ K}/T) \text{[s}^{-1}]$$
\[ k_9(T) = 2.66 \times 10^{16} \exp(-49260 \frac{K}{T}) \text{[s}^{-1}] \]

Additionally, the toluene decomposition rate coefficient results were extrapolated to the high-pressure-limit with RRKM/master equation calculations, the resulting rate expressions for 1398 to 1782 are given by

\[ k_{x,8}(T) = 8.32 \times 10^{15} \exp(-45890 \frac{K}{T}) \text{[s}^{-1}] \]

\[ k_{x,9}(T) = 1.48 \times 10^{17} \exp(-51350 \frac{K}{T}) \text{[s}^{-1}] \]

The results for \( k_7\)-\( k_9 \) are in agreement with several previous experimental studies while in disagreement with others. The low concentrations used and the high levels of signal-to-noise provided by the laser absorption technique allowed for the determination of \( k_7\)-\( k_9 \) with small uncertainties relative to previous studies, ±25%, ±39%, and ±39% in \( k_7\)-\( k_9 \) respectively. These results put firm boundaries on the values these rate coefficients of significant importance in describing toluene combustion.

### 7.2 Recommendations for future work

#### 7.2.1 High-pressure ethane and propane decomposition measurements

The current measurements for ethane and propane decomposition are a bit far from the high-pressure-limit to adequately judge theoretical calculations of the high-pressure rate coefficient. The ethane measurements are a factor of ten from the high-pressure limit at 1500 K and the measurements for propane decomposition are a factor of four from the high-pressure limit at 1500 K. Measurements around 100 atm, possible in the Stanford High Pressure Shock Tube facility, would be much closer to the high-pressure-limit than the current data set and would provide insight into the amount of high-temperature roll-off in the high-pressure rate coefficient. However, performing these experiments would not be trivial because of inherent difficulties of laser absorption at high-pressure, see Ph.D. thesis by E.L Petersen [175].

#### 7.2.2 Oxidation of toluene

Due to its importance as a representative aromatic fuel, toluene has begun to receive attention in the combustion modeling community; consequently there are several
comprehensive oxidation mechanisms under development [75-79]. In addition, many of
the reaction rate coefficients of importance are poorly known. One of these reactions is
the benzyl + O₂ reaction. At high-temperatures the decomposition of toluene initiates
toluene oxidation. Therefore, the benzyl + O₂ reaction is an important reaction in the
early stages of toluene oxidation. Measurement of the benzyl + O₂ rate coefficient could
be made by monitoring benzyl, at 266 nm, in shock-heated mixtures of small
concentrations of benzyl iodide in an excess of oxygen dilute in argon. The benzyl iodide
would immediately decompose behind the reflected shock wave leaving benzyl which
would react in a pseudo first-order manner with the excess oxygen. Of course this
reaction would compete with the benzyl decomposition reaction measured as part of the
work of this thesis.

7.2.2 HO₂ and H₂O₂ reactions

It is known that during hydrogen and hydrocarbon oxidation at lower
temperatures (~700-1200 K) the chain branching mechanism changes from the familiar
high-temperature mechanism, rate limited by H + O₂ → OH + O, to one in which
reactions involving hydrogen peroxide (H₂O₂) and the hydroperoxy radical (HO₂) control
chain branching. However, at these temperatures the rate coefficients of many important
reactions involving HO₂ and H₂O₂ have large uncertainties. New measurements of these
rate coefficients with smaller uncertainties are needed for the accurate modeling of these
systems. Additionally, an understanding of low-temperature hydroperoxy chemistry is
needed before one can attack the larger problem of peroxy (RO₂) chemistry important in
low-temperature large hydrocarbon oxidation.

Fortunately, the HO₂ radical has strong absorption from 200 to 230 nm and can be
detected using the 216 nm laser setup developed as part of this thesis for methyl radical
measurements. Additionally, the hydroxyl radical (OH) is an important species in the
reactions of interest and can be detected using laser absorption at 306 nm. The following
reactions show strong sensitivity in low- to moderate-temperature combustion and are
candidates to be studied using HO₂ and OH laser absorption:

\[ H + H₂O₂ → HO₂ + H₂ \] (17)
\[ HO₂ + HO₂ → O₂ + H₂O₂ \] (18)
\[ \text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2 + \text{H}_2\text{O} \quad (19) \]
\[ \text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 \quad (20) \]

Accurate measurements of rate coefficients for reactions (17)-(20) would be a significant contribution to the combustion community.
## Appendix A: Rate coefficient data

Table A.1: Summary of experimental results for C2H6 decomposition.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Temperature [K]</th>
<th>Pressure [atm]</th>
<th>$k_1$ [1/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>398 ppm C2H6 / Ar</td>
<td>1503</td>
<td>0.219</td>
<td>4.2 x 10**2 *</td>
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<tr>
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<td>0.207</td>
<td>8.2 x 10**2 *</td>
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<td>0.196</td>
<td>1.6 x 10**3 *</td>
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<td>0.181</td>
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<td>0.167</td>
<td>7.5 x 10**3 *</td>
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<td>0.148</td>
<td>1.8 x 10**3 *</td>
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<td>0.126</td>
<td>2.7 x 10**3 *</td>
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<td>202 ppm C2H6 / Ar</td>
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<td>5.2 x 10**4</td>
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<td>1.576</td>
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<td>5.7 x 10**4</td>
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<td>8.059</td>
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* indicates incident shock experiments
Table A.2: Summary of experimental results for C₃H₈ decomposition.

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<th>Mixture</th>
<th>Temperature [K]</th>
<th>Pressure [atm]</th>
<th>$k_2$ [1/s]</th>
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<td>0.206</td>
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</table>

* indicates incident shock experiments

Table A.3: Summary of experimental results for i-C₄H₁₀ decomposition.

<table>
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<tr>
<th>Mixture</th>
<th>Temperature [K]</th>
<th>Pressure [atm]</th>
<th>$k_2$ [1/s]</th>
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<td>1352</td>
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</table>

* indicates incident shock experiments
Table A.4: Summary of experimental results for n-C₄H₁₀ decomposition.

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<th>Mixture</th>
<th>Temperature [K]</th>
<th>Pressure [atm]</th>
<th>( k_4 ) [1/s]</th>
<th>( k_5 ) [1/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>399 ppm n-C₄H₁₀ / Ar</td>
<td>1337</td>
<td>0.250</td>
<td>7.0 \times 10^2</td>
<td>6.0 \times 10^7 *</td>
</tr>
<tr>
<td>399 ppm n-C₄H₁₀ / Ar</td>
<td>1432</td>
<td>0.226</td>
<td>3.5 \times 10^3</td>
<td>2.0 \times 10^7 *</td>
</tr>
<tr>
<td>399 ppm n-C₄H₁₀ / Ar</td>
<td>1500</td>
<td>0.213</td>
<td>8.5 \times 10^3</td>
<td>6.8 \times 10^3 *</td>
</tr>
<tr>
<td>399 ppm n-C₄H₁₀ / Ar</td>
<td>1560</td>
<td>0.203</td>
<td>1.5 \times 10^4</td>
<td>1.2 \times 10^3 *</td>
</tr>
<tr>
<td>399 ppm n-C₄H₁₀ / Ar</td>
<td>1381</td>
<td>0.235</td>
<td>1.5 \times 10^3</td>
<td>1.2 \times 10^4 *</td>
</tr>
<tr>
<td>200 ppm n-C₄H₁₀ / Ar</td>
<td>1479</td>
<td>1.673</td>
<td>1.3 \times 10^4</td>
<td>1.3 \times 10^4</td>
</tr>
<tr>
<td>200 ppm n-C₄H₁₀ / Ar</td>
<td>1601</td>
<td>1.677</td>
<td>4.5 \times 10^4</td>
<td>4.5 \times 10^4</td>
</tr>
<tr>
<td>200 ppm n-C₄H₁₀ / Ar</td>
<td>1436</td>
<td>1.752</td>
<td>5.5 \times 10^3</td>
<td>4.8 \times 10^3</td>
</tr>
<tr>
<td>200 ppm n-C₄H₁₀ / Ar</td>
<td>1344</td>
<td>1.869</td>
<td>9.0 \times 10^2</td>
<td>6.0 \times 10^2</td>
</tr>
<tr>
<td>200 ppm n-C₄H₁₀ / Ar</td>
<td>1541</td>
<td>1.659</td>
<td>2.3 \times 10^4</td>
<td>2.2 \times 10^4</td>
</tr>
<tr>
<td>200 ppm n-C₄H₁₀ / Ar</td>
<td>1360</td>
<td>1.786</td>
<td>1.4 \times 10^3</td>
<td>1.0 \times 10^3</td>
</tr>
<tr>
<td>198 ppm n-C₄H₁₀ / Ar</td>
<td>1376</td>
<td>4.282</td>
<td>2.5 \times 10^3</td>
<td>2.0 \times 10^3</td>
</tr>
<tr>
<td>198 ppm n-C₄H₁₀ / Ar</td>
<td>1447</td>
<td>4.303</td>
<td>8.0 \times 10^3</td>
<td>8.0 \times 10^3</td>
</tr>
<tr>
<td>198 ppm n-C₄H₁₀ / Ar</td>
<td>1404</td>
<td>3.778</td>
<td>4.3 \times 10^3</td>
<td>3.0 \times 10^3</td>
</tr>
<tr>
<td>198 ppm n-C₄H₁₀ / Ar</td>
<td>1520</td>
<td>4.208</td>
<td>3.0 \times 10^4</td>
<td>3.0 \times 10^4</td>
</tr>
<tr>
<td>200 ppm n-C₄H₁₀ / Ar</td>
<td>1414</td>
<td>8.183</td>
<td>5.0 \times 10^3</td>
<td>5.0 \times 10^3</td>
</tr>
<tr>
<td>200 ppm n-C₄H₁₀ / Ar</td>
<td>1344</td>
<td>8.340</td>
<td>1.3 \times 10^3</td>
<td>1.0 \times 10^3</td>
</tr>
<tr>
<td>200 ppm n-C₄H₁₀ / Ar</td>
<td>1297</td>
<td>8.411</td>
<td>5.0 \times 10^2</td>
<td>3.0 \times 10^2</td>
</tr>
<tr>
<td>200 ppm n-C₄H₁₀ / Ar</td>
<td>1479</td>
<td>8.064</td>
<td>1.4 \times 10^4</td>
<td>1.2 \times 10^4</td>
</tr>
</tbody>
</table>

* indicates incident shock experiments

Table A.5: Summary of experimental results for CO₂ decomposition and incubation.

<table>
<thead>
<tr>
<th>( P_5 ) [atm]</th>
<th>( T_5 ) [K]</th>
<th>( P_5 ) [atm]</th>
<th>( T_5 ) [K]</th>
<th>( k_6 ) [cm³ mol⁻¹ s⁻¹]</th>
<th>( \Delta t_{sed} ) [µs]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2% CO₂ / Ar</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.198</td>
<td>1547</td>
<td>0.975</td>
<td>3209</td>
<td>3.4 \times 10^7</td>
<td>24</td>
</tr>
<tr>
<td>0.186</td>
<td>1624</td>
<td>0.927</td>
<td>3393</td>
<td>9.0 \times 10^7</td>
<td>25</td>
</tr>
<tr>
<td>0.189</td>
<td>1627</td>
<td>0.944</td>
<td>3399</td>
<td>1.0 \times 10^8</td>
<td>25</td>
</tr>
<tr>
<td>0.171</td>
<td>1722</td>
<td>0.866</td>
<td>3624</td>
<td>2.1 \times 10^8</td>
<td>26</td>
</tr>
<tr>
<td>0.170</td>
<td>1761</td>
<td>0.862</td>
<td>3717</td>
<td>3.4 \times 10^8</td>
<td>23</td>
</tr>
<tr>
<td>0.157</td>
<td>1802</td>
<td>0.800</td>
<td>3814</td>
<td>4.0 \times 10^8</td>
<td>23</td>
</tr>
<tr>
<td>0.161</td>
<td>1812</td>
<td>0.820</td>
<td>3838</td>
<td>4.9 \times 10^8</td>
<td>22</td>
</tr>
<tr>
<td>0.146</td>
<td>1889</td>
<td>0.753</td>
<td>4021</td>
<td>9.4 \times 10^8</td>
<td>10</td>
</tr>
<tr>
<td>0.131</td>
<td>1999</td>
<td>0.684</td>
<td>4281</td>
<td>2.1 \times 10^9</td>
<td>9</td>
</tr>
<tr>
<td>0.084</td>
<td>2088</td>
<td>0.443</td>
<td>4494</td>
<td>3.6 \times 10^9</td>
<td>23</td>
</tr>
<tr>
<td>1% CO₂ / Ar</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.193</td>
<td>1607</td>
<td>0.950</td>
<td>3369</td>
<td>9.0 \times 10^7</td>
<td>28</td>
</tr>
<tr>
<td>0.187</td>
<td>1629</td>
<td>0.924</td>
<td>3420</td>
<td>9.5 \times 10^7</td>
<td>31</td>
</tr>
<tr>
<td>0.179</td>
<td>1686</td>
<td>0.890</td>
<td>3558</td>
<td>1.8 \times 10^8</td>
<td>20</td>
</tr>
<tr>
<td>0.175</td>
<td>1723</td>
<td>0.876</td>
<td>3645</td>
<td>2.1 \times 10^8</td>
<td>25</td>
</tr>
<tr>
<td>0.170</td>
<td>1725</td>
<td>0.847</td>
<td>3650</td>
<td>2.6 \times 10^8</td>
<td>20</td>
</tr>
<tr>
<td>0.167</td>
<td>1767</td>
<td>0.837</td>
<td>3751</td>
<td>3.2 \times 10^8</td>
<td>15</td>
</tr>
<tr>
<td>0.156</td>
<td>1837</td>
<td>0.788</td>
<td>3918</td>
<td>6.6 \times 10^8</td>
<td>12</td>
</tr>
<tr>
<td>0.144</td>
<td>1867</td>
<td>0.732</td>
<td>3989</td>
<td>7.6 \times 10^8</td>
<td>14</td>
</tr>
<tr>
<td>0.144</td>
<td>1943</td>
<td>0.735</td>
<td>4171</td>
<td>1.6 \times 10^9</td>
<td>13*</td>
</tr>
<tr>
<td>0.139</td>
<td>1955</td>
<td>0.713</td>
<td>4200</td>
<td>1.5 \times 10^9</td>
<td>14</td>
</tr>
<tr>
<td>0.136</td>
<td>2022</td>
<td>0.701</td>
<td>4358</td>
<td>2.3 \times 10^9</td>
<td>12</td>
</tr>
<tr>
<td>0.131</td>
<td>2037</td>
<td>0.676</td>
<td>4394</td>
<td>2.7 \times 10^9</td>
<td>10</td>
</tr>
<tr>
<td>0.128</td>
<td>2074</td>
<td>0.664</td>
<td>4484</td>
<td>3.6 \times 10^9</td>
<td>12</td>
</tr>
<tr>
<td>0.123</td>
<td>2123</td>
<td>0.637</td>
<td>4601</td>
<td>4.8 \times 10^9</td>
<td>11</td>
</tr>
</tbody>
</table>

2 - incident shock conditions
5 - reflected shock conditions
* - see Figure 5.4 for master equation calculation
Table A.6: Summary of experimental results for benzyl radical decomposition.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Temperature [K]</th>
<th>Pressure [atm]</th>
<th>$k_7$ [1/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 ppm benzyl iodide / Ar</td>
<td>1715</td>
<td>1.484</td>
<td>3.9 x 10^4</td>
</tr>
<tr>
<td>100 ppm benzyl iodide / Ar</td>
<td>1669</td>
<td>1.471</td>
<td>2.3 x 10^4</td>
</tr>
<tr>
<td>100 ppm benzyl iodide / Ar</td>
<td>1669</td>
<td>1.458</td>
<td>2.5 x 10^4</td>
</tr>
<tr>
<td>100 ppm benzyl iodide / Ar</td>
<td>1704</td>
<td>1.502</td>
<td>3.9 x 10^4</td>
</tr>
<tr>
<td>100 ppm benzyl iodide / Ar</td>
<td>1680</td>
<td>1.460</td>
<td>2.7 x 10^4</td>
</tr>
<tr>
<td>100 ppm benzyl iodide / Ar</td>
<td>1551</td>
<td>1.581</td>
<td>4.1 x 10^4</td>
</tr>
<tr>
<td>100 ppm benzyl iodide / Ar</td>
<td>1601</td>
<td>1.532</td>
<td>9.0 x 10^4</td>
</tr>
<tr>
<td>100 ppm benzyl iodide / Ar</td>
<td>1499</td>
<td>1.591</td>
<td>1.6 x 10^4</td>
</tr>
<tr>
<td>100 ppm benzyl iodide / Ar</td>
<td>1461</td>
<td>1.666</td>
<td>6.5 x 10^2</td>
</tr>
<tr>
<td>50 ppm benzyl iodide / Ar</td>
<td>1615</td>
<td>1.556</td>
<td>9.8 x 10^3</td>
</tr>
<tr>
<td>50 ppm benzyl iodide / Ar</td>
<td>1700</td>
<td>1.467</td>
<td>2.9 x 10^4</td>
</tr>
<tr>
<td>50 ppm benzyl iodide / Ar</td>
<td>1522</td>
<td>1.597</td>
<td>2.5 x 10^4</td>
</tr>
<tr>
<td>50 ppm benzyl iodide / Ar</td>
<td>1428</td>
<td>1.649</td>
<td>3.0 x 10^2</td>
</tr>
<tr>
<td>50 ppm benzyl iodide / Ar</td>
<td>1566</td>
<td>1.485</td>
<td>5.0 x 10^3</td>
</tr>
<tr>
<td>50 ppm benzyl iodide / Ar</td>
<td>1610</td>
<td>1.545</td>
<td>9.2 x 10^3</td>
</tr>
<tr>
<td>50 ppm benzyl iodide / Ar</td>
<td>1730</td>
<td>1.490</td>
<td>5.1 x 10^4</td>
</tr>
</tbody>
</table>

Table A.7: Summary of experimental results for toluene decomposition.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Temperature [K]</th>
<th>Pressure [atm]</th>
<th>$k_8$ [1/s]</th>
<th>$k_9$ [1/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 ppm toluene / Ar</td>
<td>1643</td>
<td>1.516</td>
<td>6.0 x 10^4</td>
<td>3.1 x 10^4</td>
</tr>
<tr>
<td>100 ppm toluene / Ar</td>
<td>1587</td>
<td>1.560</td>
<td>2.1 x 10^3</td>
<td>1.1 x 10^3</td>
</tr>
<tr>
<td>100 ppm toluene / Ar</td>
<td>1555</td>
<td>1.562</td>
<td>1.3 x 10^3</td>
<td>5.0 x 10^2</td>
</tr>
<tr>
<td>200 ppm toluene / Ar</td>
<td>1580</td>
<td>1.508</td>
<td>1.7 x 10^3</td>
<td>7.0 x 10^2</td>
</tr>
<tr>
<td>200 ppm toluene / Ar</td>
<td>1593</td>
<td>1.461</td>
<td>1.9 x 10^3</td>
<td>1.0 x 10^3</td>
</tr>
<tr>
<td>200 ppm toluene / Ar</td>
<td>1782</td>
<td>1.438</td>
<td>3.6 x 10^4</td>
<td>2.0 x 10^4</td>
</tr>
<tr>
<td>200 ppm toluene / Ar</td>
<td>1497</td>
<td>1.580</td>
<td>3.4 x 10^2</td>
<td>1.2 x 10^2</td>
</tr>
<tr>
<td>400 ppm toluene / Ar</td>
<td>1562</td>
<td>1.527</td>
<td>1.2 x 10^3</td>
<td>7.0 x 10^2</td>
</tr>
<tr>
<td>400 ppm toluene / Ar</td>
<td>1429</td>
<td>1.518</td>
<td>8.0 x 10^3</td>
<td>2.5 x 10^3</td>
</tr>
<tr>
<td>400 ppm toluene / Ar</td>
<td>1647</td>
<td>1.431</td>
<td>4.5 x 10^3</td>
<td>3.0 x 10^3</td>
</tr>
<tr>
<td>400 ppm toluene / Ar</td>
<td>1398</td>
<td>1.504</td>
<td>4.0 x 10^4</td>
<td>1.2 x 10^4</td>
</tr>
<tr>
<td>400 ppm toluene / Ar</td>
<td>1745</td>
<td>1.484</td>
<td>2.0 x 10^4</td>
<td>1.3 x 10^4</td>
</tr>
</tbody>
</table>
Appendix B: Uncertainty analysis

The uncertainty estimates for the rate coefficient determinations for reactions (1)-(9), given in Chapters 4-6, were determined by considering the combination of several possible sources of error. Assessment of the uncertainty in rate coefficient determinations was performed for individual experiments representing the extreme temperature limits for each data set. The limits of the temperature range for each data set usually represent the maximum uncertainty conditions for that data set with the lowest temperature experiments typically exhibiting the greatest uncertainty for decomposition experiments. The error sources considered for each rate coefficient are given in Tables B.2-B.10 for reactions (1)-(9) for the experimental condition which represents the condition of maximum uncertainty for each data set. The primary contributions to uncertainties in the rate coefficients considered are uncertainties in: temperature, absorption cross-sections, fitting the data to computed profiles, and uncertainties resulting from secondary chemistry. The individual contributions of each error source were determined by perturbing each error source to the estimated positive and negative bounds of its 2-σ uncertainty and re-fitting the experimental traces by adjusting the rate coefficient of interest. The resulting uncertainty in the rate coefficient for each individual error source were combined using the root-sum-squares (RSS) method, which assumes that the uncertainty contributions are uncorrelated and are estimated to similar probabilities (e.g., 2-σ probability that the true value falls within the ± error limit). Table B.1 gives the estimated uncertainties for the rate coefficients for reactions (1)-(9), respectively. In the case of two-channel reactions, n-butane and toluene, the uncertainty in the overall rate of decomposition and branching ratio are combined using the RSS method to determine the uncertainty in the two different branches.
Table B.1: Uncertainties in $k_1$-$k_9$.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$2\sigma$ estimated uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) $C_2H_6 \rightarrow CH_3 + CH_3$</td>
<td>±19%</td>
</tr>
<tr>
<td>(2) $C_3H_8 \rightarrow CH_3 + C_2H_6$</td>
<td>±20%</td>
</tr>
<tr>
<td>(3) $iC_4H_{10} \rightarrow CH_3 + iC_3H_7$</td>
<td>±25%</td>
</tr>
<tr>
<td>(4) $nC_3H_{10} \rightarrow CH_3 + nC_3H_8$</td>
<td>±31%</td>
</tr>
<tr>
<td>(5) $nC_3H_{10} \rightarrow C_2H_5 + C_2H_3$</td>
<td>±31%</td>
</tr>
<tr>
<td>(6) $CO_2 + Ar \rightarrow CO + O + Ar$</td>
<td>±21%</td>
</tr>
<tr>
<td>(7) $C_6H_5CH_2 \rightarrow C_7H_6 + H$</td>
<td>±25%</td>
</tr>
<tr>
<td>(8) $C_6H_5CH_3 \rightarrow C_6H_5CH_2 + H$</td>
<td>±39%</td>
</tr>
<tr>
<td>(9) $C_6H_5CH_3 \rightarrow C_6H_5 + CH_3$</td>
<td>±39%</td>
</tr>
</tbody>
</table>

Table B.2: Uncertainty analysis for ethane decomposition rate coefficient, $k_1$; initial reflected shock conditions: 1421 K, 1.859 atm, and 402 ppm $C_2H_6/Ar$.

<table>
<thead>
<tr>
<th>Error source</th>
<th>$2\sigma$ uncertainty in error source</th>
<th>Uncertainty in $k_1$ from positive perturbation</th>
<th>Uncertainty in $k_1$ from negative perturbation</th>
<th>$2\sigma$ average uncertainty contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental uncertainties</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature and pressure</td>
<td>± 0.7%, ± 1%</td>
<td>-16%</td>
<td>19%</td>
<td>17.5%</td>
</tr>
<tr>
<td>Fitting (signal/noise)</td>
<td>± 5%</td>
<td>5%</td>
<td>-5%</td>
<td>5%</td>
</tr>
<tr>
<td>CH$_3$ absorption coefficient</td>
<td>± 5%</td>
<td>-5%</td>
<td>5%</td>
<td>5%</td>
</tr>
<tr>
<td>Mixture concentration</td>
<td>± 0.43 ppm $C_2H_6$</td>
<td>&gt;0.5%</td>
<td>&gt;0.5%</td>
<td>&gt;0.5%</td>
</tr>
<tr>
<td>Secondary chemistry uncertainties</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>No sensitive interfering reactions</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total $2\sigma$ R.S.S. uncertainty:</td>
<td></td>
<td></td>
<td></td>
<td>±19%</td>
</tr>
</tbody>
</table>

Table B.3: Uncertainty analysis for propane decomposition rate coefficient, $k_2$; initial incident shock conditions: 1365 K, 0.244 atm, and 399 ppm $C_3H_8/Ar$.

<table>
<thead>
<tr>
<th>Error source</th>
<th>$2\sigma$ uncertainty in error source</th>
<th>Uncertainty in $k_2$ from positive perturbation</th>
<th>Uncertainty in $k_2$ from negative perturbation</th>
<th>$2\sigma$ average uncertainty contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental uncertainties</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature and pressure</td>
<td>± 0.7%, ± 1%</td>
<td>-17%</td>
<td>20%</td>
<td>18.5%</td>
</tr>
<tr>
<td>Fitting (signal/noise)</td>
<td>± 5%</td>
<td>5%</td>
<td>-5%</td>
<td>5%</td>
</tr>
<tr>
<td>CH$_3$ absorption coefficient</td>
<td>± 5%</td>
<td>-5%</td>
<td>5%</td>
<td>5%</td>
</tr>
<tr>
<td>Mixture concentration</td>
<td>± 0.43 ppm $C_3H_8$</td>
<td>&gt;0.5%</td>
<td>&gt;0.5%</td>
<td>&gt;0.5%</td>
</tr>
<tr>
<td>Secondary chemistry uncertainties</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H+$C_3H_8 \rightarrow C_3H_2 + H_2$</td>
<td>x2, ±2</td>
<td>-14%</td>
<td>20%</td>
<td>17%</td>
</tr>
<tr>
<td>Total $2\sigma$ R.S.S. uncertainty:</td>
<td></td>
<td></td>
<td></td>
<td>±26%</td>
</tr>
</tbody>
</table>
Table B.4: Uncertainty analysis for iso-butane decomposition rate coefficient, \( k_3 \); initial reflected shock conditions: 1310 K, 1.815 atm, and 201 ppm i-C\(_4\)H\(_{10}\)/Ar.

<table>
<thead>
<tr>
<th>Error source</th>
<th>2-(\sigma) uncertainty in error source</th>
<th>Uncertainty in ( k_3 ) from positive perturbation</th>
<th>Uncertainty in ( k_3 ) from negative perturbation</th>
<th>2-(\sigma) average uncertainty contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experimental uncertainties</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature and pressure</td>
<td>± 0.7%, ± 1%</td>
<td>-19%</td>
<td>22%</td>
<td>20.5%</td>
</tr>
<tr>
<td>Fitting (signal/noise)</td>
<td>± 5%</td>
<td>5%</td>
<td>-5%</td>
<td>5%</td>
</tr>
<tr>
<td>CH(_3) absorption coefficient</td>
<td>± 5%</td>
<td>-5%</td>
<td>5%</td>
<td>5%</td>
</tr>
<tr>
<td>Mixture concentration</td>
<td>± 0.86 ppm i(_2)C(<em>4)H(</em>{10})</td>
<td>&gt;0.5%</td>
<td>&gt;0.5%</td>
<td>&gt;0.5%</td>
</tr>
<tr>
<td>Interfering absorption</td>
<td>± 10% in resulting X(_{CH3})</td>
<td>-10%</td>
<td>10%</td>
<td>10%</td>
</tr>
<tr>
<td><strong>Secondary chemistry uncertainties</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H+i-C(<em>4)H(</em>{10}) → i-C(_4)H(_9) + H(_2)</td>
<td>x2, (\pm 2)</td>
<td>-7%</td>
<td>10%</td>
<td>8.5%</td>
</tr>
<tr>
<td><strong>Total 2-(\sigma) R.S.S. uncertainty:</strong></td>
<td></td>
<td></td>
<td></td>
<td>±25%</td>
</tr>
</tbody>
</table>

Table B.5: Uncertainty analysis for overall n-butane decomposition rate coefficient, \( k_4 + k_5 \); initial incident shock conditions: 1337 K, 0.250 atm, and 399 ppm n-C\(_4\)H\(_{10}\)/Ar.

<table>
<thead>
<tr>
<th>Error source</th>
<th>2-(\sigma) uncertainty in error source</th>
<th>Uncertainty in ( k_4 + k_5 ) from positive perturbation</th>
<th>Uncertainty in ( k_4 + k_5 ) from negative perturbation</th>
<th>2-(\sigma) average uncertainty contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experimental uncertainties</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature and pressure</td>
<td>± 0.7%, ± 1%</td>
<td>-19%</td>
<td>22%</td>
<td>20.5%</td>
</tr>
<tr>
<td>Fitting (signal/noise)</td>
<td>± 10%</td>
<td>10%</td>
<td>-10%</td>
<td>10%</td>
</tr>
<tr>
<td>CH(_3) absorption coefficient</td>
<td>± 5%</td>
<td>-5%</td>
<td>5%</td>
<td>5%</td>
</tr>
<tr>
<td>Mixture concentration</td>
<td>± 0.43 ppm n(_2)C(<em>4)H(</em>{10})</td>
<td>&gt;0.5%</td>
<td>&gt;0.5%</td>
<td>&gt;0.5%</td>
</tr>
<tr>
<td><strong>Secondary chemistry uncertainties</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-C(<em>4)H(</em>{10}) + H → H(_2) + sC(_4)H(_9)</td>
<td>x2, (\pm 2)</td>
<td>-5%</td>
<td>7%</td>
<td>6%</td>
</tr>
<tr>
<td>CH(_3) + CH(_3) → C(_2)H(_6)</td>
<td>±19%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td><strong>Total 2-(\sigma) R.S.S. uncertainty:</strong></td>
<td></td>
<td></td>
<td></td>
<td>±24%</td>
</tr>
</tbody>
</table>

Table B.6: Uncertainty analysis for n-butane decomposition branching ratio, \( k_4/(k_4 + k_5) \); initial incident shock conditions: 1337 K, 0.250 atm, and 399 ppm n-C\(_4\)H\(_{10}\)/Ar.

<table>
<thead>
<tr>
<th>Error source</th>
<th>2-(\sigma) uncertainty in error source</th>
<th>Uncertainty in ( k_4/(k_4 + k_5) ) from positive perturbation</th>
<th>Uncertainty in ( k_4/(k_4 + k_5) ) from negative perturbation</th>
<th>2-(\sigma) average uncertainty contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experimental uncertainties</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature and pressure</td>
<td>± 0.7%, ± 1%</td>
<td>-3%</td>
<td>4%</td>
<td>3.5%</td>
</tr>
<tr>
<td>Fitting (signal/noise)</td>
<td>± 10%</td>
<td>10%</td>
<td>-10%</td>
<td>10%</td>
</tr>
<tr>
<td>CH(_3) absorption coefficient</td>
<td>± 5%</td>
<td>-5%</td>
<td>5%</td>
<td>5%</td>
</tr>
<tr>
<td>Mixture concentration</td>
<td>± 0.43 ppm n(_2)C(<em>4)H(</em>{10})</td>
<td>&gt;0.5%</td>
<td>&gt;0.5%</td>
<td>&gt;0.5%</td>
</tr>
<tr>
<td><strong>Secondary chemistry uncertainties</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-C(<em>4)H(</em>{10}) + H → H(_2) + sC(_4)H(_9)</td>
<td>x2, (\pm 2)</td>
<td>-3%</td>
<td>4%</td>
<td>3.5%</td>
</tr>
<tr>
<td>CH(_3) + CH(_3) → C(_2)H(_6)</td>
<td>±19%</td>
<td>17%</td>
<td>-15%</td>
<td>16%</td>
</tr>
<tr>
<td><strong>Total 2-(\sigma) R.S.S. uncertainty:</strong></td>
<td></td>
<td></td>
<td></td>
<td>±20%</td>
</tr>
</tbody>
</table>
Table B.7: Uncertainty analysis for CO₂ decomposition rate coefficient, \( k_6 \); initial reflected shock conditions: 3209 K, 0.975 atm, and 2% CO₂/Ar.

<table>
<thead>
<tr>
<th>Error source</th>
<th>2-( \sigma ) uncertainty in error source</th>
<th>Uncertainty in ( k_6 ) from positive perturbation</th>
<th>Uncertainty in ( k_6 ) from negative perturbation</th>
<th>2-( \sigma ) average uncertainty contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental uncertainties</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial temperature and pressure</td>
<td>( \pm 0.7% ), ( \pm 1% )</td>
<td>-12%</td>
<td>13%</td>
<td>12.5%</td>
</tr>
<tr>
<td>Temperature and pressure change due to decomposition</td>
<td>( \pm 15% )</td>
<td>15%</td>
<td>-15%</td>
<td>15%</td>
</tr>
<tr>
<td>Fitting (signal/noise)</td>
<td>( \pm 5% )</td>
<td>5%</td>
<td>-5%</td>
<td>5%</td>
</tr>
<tr>
<td>CO₂ absorption cross-section</td>
<td>( \pm 5% )</td>
<td>-5%</td>
<td>5%</td>
<td>5%</td>
</tr>
<tr>
<td>Mixture concentration</td>
<td>( \pm 0.13% ) in ( X_{CO2} )</td>
<td>&gt;0.2%</td>
<td>&gt;0.2%</td>
<td>&gt;0.2%</td>
</tr>
<tr>
<td>Secondary chemistry uncertainties</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>No sensitive interfering reactions</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Total 2-\( \sigma \) R.S.S. uncertainty: \( \pm 21\% \)

Table B.8: Uncertainty analysis for benzyl decomposition rate coefficient, \( k_7 \); initial reflected shock conditions: 1428 K, 1.649 atm, and 50 ppm benzyl iodide/Ar.

<table>
<thead>
<tr>
<th>Error source</th>
<th>2-( \sigma ) uncertainty in error source</th>
<th>Uncertainty in ( k_7 ) from positive perturbation</th>
<th>Uncertainty in ( k_7 ) from negative perturbation</th>
<th>2-( \sigma ) average uncertainty contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental uncertainties</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature and pressure</td>
<td>( \pm 0.7% ), ( \pm 1% )</td>
<td>-20%</td>
<td>24%</td>
<td>22%</td>
</tr>
<tr>
<td>Fitting (signal/noise)</td>
<td>( \pm 5% )</td>
<td>5%</td>
<td>-5%</td>
<td>5%</td>
</tr>
<tr>
<td>Benzyl absorption cross-section</td>
<td>( \pm 20% )</td>
<td>0% (due to pseudo-1( ^{st} )-order conditions)</td>
<td>0% (due to pseudo-1( ^{st} )-order conditions)</td>
<td>0%</td>
</tr>
<tr>
<td>Interfering species absorption cross-sections</td>
<td>( \pm 20% )</td>
<td>-10%</td>
<td>10%</td>
<td>10%</td>
</tr>
<tr>
<td>Mixture concentration</td>
<td>( \pm 5 ) ppm benzyl iodide</td>
<td>0% (due to pseudo-1( ^{st} )-order conditions)</td>
<td>0% (due to pseudo-1( ^{st} )-order conditions)</td>
<td>0%</td>
</tr>
<tr>
<td>Secondary chemistry uncertainties</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( C_6H_5CH_3 \rightarrow C_6H_5CH_2 + H )</td>
<td>( \pm 30% )</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
</tr>
</tbody>
</table>

Total 2-\( \sigma \) R.S.S. uncertainty: \( \pm 25\% \)
Table B.9: Uncertainty analysis for overall toluene decomposition rate coefficient, \( k_8 + k_9 \); initial reflected shock conditions: 1429 K, 1.518 atm, and 400 ppm toluene/Ar.

<table>
<thead>
<tr>
<th>Error source</th>
<th>2-( \sigma ) uncertainty in error source</th>
<th>Uncertainty in ( k_8 + k_9 ) from positive perturbation</th>
<th>Uncertainty in ( k_8 + k_9 ) from negative perturbation</th>
<th>2-( \sigma ) average uncertainty contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experimental uncertainties</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature and pressure</td>
<td>( \pm 0.7%), ( \pm 1% )</td>
<td>-21%</td>
<td>27%</td>
<td>24%</td>
</tr>
<tr>
<td>Fitting (signal/noise)</td>
<td>( \pm 5% )</td>
<td>5%</td>
<td>-5%</td>
<td>5%</td>
</tr>
<tr>
<td>Benzyl absorption cross-section</td>
<td>( \pm 20% )</td>
<td>-15%</td>
<td>15%</td>
<td>15%</td>
</tr>
<tr>
<td>Interfering species absorption cross-section</td>
<td>( \pm 20% )</td>
<td>-5%</td>
<td>5%</td>
<td>5%</td>
</tr>
<tr>
<td>Mixture concentration</td>
<td>( \pm 20 \text{ ppm toluene} )</td>
<td>-5%</td>
<td>5%</td>
<td>5%</td>
</tr>
<tr>
<td><strong>Secondary chemistry uncertainties</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{C}_6\text{H}_5\text{CH}_3 + H \rightarrow \text{C}_6\text{H}_5\text{CH}_2 + H_2 )</td>
<td>( \pm 50% )</td>
<td>-11%</td>
<td>13%</td>
<td>12%</td>
</tr>
<tr>
<td>( \text{C}_7\text{H}_6 + H \rightarrow \text{C}_6\text{H}_5\text{CH}_2 \times 2, \div 10 )</td>
<td></td>
<td>0</td>
<td>6%</td>
<td>3%</td>
</tr>
<tr>
<td>( \text{C}_6\text{H}_5\text{CH}_2 \rightarrow \text{C}_7\text{H}_6 + H )</td>
<td>( \pm 25% )</td>
<td>3%</td>
<td>-2%</td>
<td>2.5%</td>
</tr>
<tr>
<td>Total 2-( \sigma ) R.S.S. uncertainty:</td>
<td></td>
<td></td>
<td></td>
<td>( \pm 32% )</td>
</tr>
</tbody>
</table>

Table B.10: Uncertainty analysis for overall toluene decomposition branching ratio, \( k_8 / (k_8 + k_9) \); initial reflected shock conditions: 1429 K, 1.518 atm, and 400 ppm toluene/Ar.

<table>
<thead>
<tr>
<th>Error source</th>
<th>2-( \sigma ) uncertainty in error source</th>
<th>Uncertainty in ( k_8 ) from positive perturbation</th>
<th>Uncertainty in ( k_8 ) from negative perturbation</th>
<th>2-( \sigma ) average uncertainty contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experimental uncertainties</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature and pressure</td>
<td>( \pm 0.7%), ( \pm 1% )</td>
<td>-2%</td>
<td>3%</td>
<td>2.5%</td>
</tr>
<tr>
<td>Fitting (signal/noise)</td>
<td>( \pm 5% )</td>
<td>5%</td>
<td>-5%</td>
<td>5%</td>
</tr>
<tr>
<td>Benzyl absorption cross-section</td>
<td>( \pm 20% )</td>
<td>-10%</td>
<td>10%</td>
<td>10%</td>
</tr>
<tr>
<td>Interfering species absorption cross-section</td>
<td>( \pm 20% )</td>
<td>-5%</td>
<td>5%</td>
<td>5%</td>
</tr>
<tr>
<td>Mixture concentration</td>
<td>( \pm 20 \text{ ppm toluene} )</td>
<td>-5%</td>
<td>5%</td>
<td>5%</td>
</tr>
<tr>
<td><strong>Secondary chemistry uncertainties</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{C}_6\text{H}_5\text{CH}_3 + H \rightarrow \text{C}_6\text{H}_5\text{CH}_2 \times 2, \div 2 )</td>
<td></td>
<td>-7%</td>
<td>8%</td>
<td>7.5%</td>
</tr>
<tr>
<td>( \text{C}_7\text{H}_6 + H \rightarrow \text{C}_6\text{H}_5\text{CH}_2 \times 2, \div 10 )</td>
<td></td>
<td>-13%</td>
<td>18%</td>
<td>15.5%</td>
</tr>
<tr>
<td>( \text{C}_6\text{H}_5\text{CH}_2 \rightarrow \text{C}_7\text{H}_6 + H )</td>
<td>( \pm 21% )</td>
<td>9%</td>
<td>-8%</td>
<td>8.5%</td>
</tr>
<tr>
<td>Total 2-( \sigma ) R.S.S. uncertainty:</td>
<td></td>
<td></td>
<td></td>
<td>( \pm 23% )</td>
</tr>
</tbody>
</table>
Appendix C: CO₂ thermometry

C.1 Introduction

The development of optical diagnostic techniques for the characterization of shock-heated flows has long been a topic of interest to the chemical kinetics, hypersonics, and supersonic combustion research communities. Characterization of the temperature time-history behind shock waves with microsecond time-resolution is of particular importance in understanding the effects of non-ideal gasdynamics on measurements made in shock-heated flows. For example, high-temperature reaction rate coefficients are often measured in shock tubes and can be quite sensitive to temporal changes in the temperature behind the shock front. Characterization of the temperature time-history behind the shock wave allows quantification of the uncertainties in rate coefficients determined in shock tube experiments. Additionally, knowledge of the temperature time-history can allow for an extension of the usable test time behind shock waves.

Early temperature measurements made behind shock waves used line reversal and two-line emission techniques, where the concentration of the emitting species need not be known [176]. These techniques typically employ atomic lines rather than molecular lines due to the greater oscillator strengths of atomic species. Thus, an atomic species must be naturally present in the shock-heated mixture or one must be seeded, a situation that may or may not be desirable.

More recently scanned-wavelength laser absorption, pioneered by Hanson and co-workers [177-180], has been used for temperature measurements behind shock waves. These methods involve rapidly scanning a narrow-linewidth continuous wave laser source over two absorption features; the resulting line-intensity ratio provides information about the population distribution of the corresponding molecular state and thereby enables the temperature to be inferred. Like emission techniques, the absorption line-intensity ratio method provides temperature independent of a known concentration. Hanson and co-workers have made temperature measurements in shock-heated flows.
using scanned-wavelength absorption of hydroxyl radicals (OH) at 306 nm [177-178] and nitric oxide (NO) at 225 nm [178-179]. Additionally, Phillippe and Hanson [180] reported temperature measurements made behind shock waves using wavelength-modulation absorption spectroscopy of molecular oxygen (O$_2$) at 760 nm.

Previous temperature measurements made behind shock waves using laser absorption have been limited by the tuning rate of the laser sources to a temporal resolution of 3 to 10 kHz [177-180]. Here a fixed-frequency laser absorption technique is presented that provides 1 MHz temporal resolution. The technique takes advantage of the spectrally smooth absorption due to CO$_2$ in the ultraviolet region (190-310 nm) [112], see Chapters 2 and 5, and therefore is insensitive to collisional broadening that often limits scanned-wavelength diagnostics at elevated pressures. In fact this diagnostic is best suited for high-temperatures and pressures, a regime where many other techniques fail.

At room temperature CO$_2$ is transparent at wavelengths longer than 205 nm [181], but at high-temperature (>1000 K) CO$_2$ has significant absorption in the 190 to 310 nm spectral range due to vibrationally excited molecules [112,156]. Jeffries et al. [107] and Mattison et al. [108] have investigated the feasibility of a thermometry technique using the strongly temperature-dependent CO$_2$ absorption cross-section in this region. Here this technique is demonstrated for the measurement of temperature in both non-reacting and reacting (methane ignition) shock-heated mixtures.

C.2 CO$_2$ temperature diagnostic

The ultraviolet absorption by vibrationally excited CO$_2$ has been previously discussed in Chapter 2. The spectrally smooth nature of the absorption and its strong temperature-dependence enables two-wavelength absorption-based thermometry in high-temperature gases where CO$_2$ is present. Additionally, the absorption cross-section shows no pressure dependence in experiments up to 8 atm and none is expected at higher pressures, due to its smooth pre-dissociative nature, enabling high-pressure temperature measurements.

Absorption of a narrow-linewidth laser source along a uniform path can be described by the Beer-Lambert law

$$\text{absorbance} = \ln(I/ I_0) = -\sigma n L$$
where $I$ is the transmitted laser intensity, $I_0$ is the incident beam intensity, $\sigma$ \([\text{cm}^2\text{molecule}^{-1}]\) is the absorption cross-section, $n$ \([\text{molecules cm}^{-3}]\) is the number density of the absorbing species, and $L$ \([\text{cm}]\) is the absorption path length. The CO$_2$ absorption cross-section $\sigma_{\text{CO}_2}(\lambda, T)$ is independent of pressure, in the wavelength range of interest, and can be described using a semi-empirical form

$$\ln \sigma_{\text{CO}_2}(\lambda, T) = a + b\lambda$$

given in Chapter 2.

Taking the ratio of absorbance at two different laser wavelengths gives

$$\frac{\text{absorbance}(\lambda_1)}{\text{absorbance}(\lambda_2)} = \frac{\sigma_{\text{CO}_2}(\lambda_1, T)n_{\text{CO}_2}L}{\sigma_{\text{CO}_2}(\lambda_2, T)n_{\text{CO}_2}L} = \frac{\sigma_{\text{CO}_2}(\lambda_1, T)}{\sigma_{\text{CO}_2}(\lambda_2, T)} = R(T)$$

allowing the measurement of temperature, independent of knowledge of CO$_2$ concentration or path length. For the measurements presented here laser radiation at 244 and 266 nm was chosen, see Figure 2.8. These two wavelengths can be conveniently generated with available laser sources, avoid most major interference absorption, and have an appropriate wavelength separation for measurement of temperature in the region of interest in shock wave experiments and combustion studies. A polynomial expression for temperature as a function of the absorbance ratio (cross-section ratio) from 1500-4500 K is given by

$$T = (2.857 \times 10^4)R^4 - (3.043 \times 10^4)R^3 + (1.478 \times 10^4)R^2 + (9.57 \times 10^2)R + 1041 \text{[K]}$$

where $R$ is the ratio of 266 to 244 nm absorbance ($R = \text{absorbance}(266 \text{ nm}) / \text{absorbance}(244 \text{ nm})$).

The CO$_2$ absorption cross-section at 244 and 266 nm is plotted versus temperature in Figure 2.12 and the ratio of 266 to 244 nm absorbance is plotted versus temperature, using above equation, in Figure C.1. The uncertainty in temperature measurements made using the absorbance ratio method is limited by the magnitude of the fractional absorption, particularly at the more weakly absorbing wavelength 266 nm. The measured ratio has greater uncertainty at low-temperature due to smaller absorbance (lower signal-to-noise), and therefore the inferred temperature is more uncertain at lower temperatures. An uncertainty in absorbance, due to signal-to-noise limitations, of $\pm0.1\%$ ($\pm0.001$) is generally achievable in shock wave experiments regardless of the magnitude of the absorbance. The uncertainty in measured temperature is mapped as a function of
temperature and the product of partial CO$_2$ pressure and path length ($P_{CO2}L$) in Figure C.2; notice that the uncertainty decreases at higher temperature and pressure. The uncertainties given assume an uncertainty of ±0.1% in absorbance (-ln($I/I_0$) = ±0.001) and the contours represent the percentage uncertainty in the measured temperature. The favorable uncertainty contours in Figure C.2 demonstrate the attractiveness of this diagnostic for high-pressure, high-temperature measurements.

### C.3 Experimental

The experiments described here were performed using the optical setup shown in Figure 2.8 and the shock tube described in Chapter 2. Laser radiation at 244.061 nm (~5 GHz linewidth) and 266.075 nm (<5 MHz linewidth) was produced by the single pass of a focused laser beam at 488 (488.122) nm (Ar$^+$ line) and 532 (532.15) nm (Nd:YVO$_4$) through angle-tuned BBO as described in Chapter 2. The two UV laser beams (1.5 mW each) were split into two components: one component, less than 1 mm in diameter, passing through the shock tube windows (UV fused silica) at a location 2 cm from the endwall, and one detected prior to absorption as a reference. The beams were detected using amplified S1722-02 Hamamatsu silicon photodiodes (risetime < 1.0 µs, 4.1 mm diameter) and recorded on a digital oscilloscope.

Experiments were performed with several different test gas mixtures to demonstrate the diagnostic and to characterize the effect of energy release behind shock waves. Experiments were first performed in test mixtures of 5 and 10% CO$_2$ dilute in argon. Finally, experiments were performed in several stoichiometric mixtures of CH$_4$/O$_2$/CO$_2$/Ar to demonstrate the diagnostic in experiments with varying levels of energy release due to chemical reactions.

### C.4 Results and discussion

An example non-reacting experiment is shown in Figures C.3-C.5 for a 10% CO$_2$/Ar test mixture. Figure C.3 shows the measured absorbance at 244 and 266 nm and the pressure measured with the Kistler piezoelectric pressure transducer. Figure C.4 shows the temperature inferred with the 266/244 absorbance ratio method described
above. The temperature is fairly constant for 2 ms before several abrupt changes due to wave interactions. These changes are due to interaction of the reflected shock wave with the contact surface (helium/test gas interface) and interaction of the reflected shock wave with the rarefaction wave (expansion of helium driver gas). Additionally, a comparison of the measured temperature is made with the temperature calculated from the pressure trace via the assumption of an isentropic relationship between pressure and temperature

\[ T = T_0 \left( \frac{P}{P_0} \right)^{\frac{\gamma-1}{\gamma}} \]

A comparison of the temperature measured with the absorbance ratio method and that resulting from the isentropic assumption shows excellent agreement (Figure C.4), with a difference in the two of no greater that 2% for this experiment (Figure C.5). Note that the specific heat ratio, \( \gamma \), for the 10% CO\textsubscript{2}/Ar mixture (Figure C.4) varies only 0.02% over the temperature range (1800-2200 K) of this experiment. Therefore, the isentropic relationship given above, assuming a constant \( \gamma \) is valid. This agreement serves both to validate the CO\textsubscript{2} temperature sensor and to confirm that for shock wave experiments with no energy release the isentropic assumption holds; other studies have shown similar results [177,186]. Thus in typical reaction rate experiments where there is negligible energy release, changes in post-shock temperature can be inferred directly from the pressure trace, without optical measurements. This result emphasizes the potential utility of precise, quantitative pressure measurements during reaction rate experiments where small uncertainties in temperature can lead to large errors in inferred rates. For example, a 1% uncertainty in temperature at 1500 K (±15 K) can lead to a 30% uncertainty in the measured dissociation rate coefficient for a molecule with an activation energy of 80 kcal/mol.

A comparison between the temperature measured immediately after the passage of the reflected shock and that calculated with the ideal normal shock relations is given for the entire set of experiments in Figure C.6. The scatter in the difference between the measured temperature and the ideal temperature has a 1-\( \sigma \) standard deviation of 0.6% and is no greater than 2.3%. Additionally, the scatter shows no trend over a wide range of fractional absorption, demonstrating the precision of the thermometry measurement technique for a range of conditions. Note, the CO\textsubscript{2} absorbance at 266 and 244 nm ranges
from 0.5 to 13% and 2 to 32%, respectively, illustrating the large dynamic range of conditions investigated. Because the CO$_2$ absorption cross-section was measured behind shock waves in the same experimental facility, the excellent agreement between the measured temperature and calculated temperature is not a complete confirmation of the accuracy of the technique. Rather, the agreement is an indication of the consistency of the laser absorption technique and shock velocity measurement, which gives the ideal shock temperature. However, because the shock wave calculation for temperature has an uncertainty of <1% the agreement between measured temperature and calculated temperature demonstrates that the measurement scatter is within the uncertainties given in Figure C.1.

To demonstrate the CO$_2$ absorption technique for thermometry in combustion systems, and to characterize the effects of energy release on temperature in shock tube studies, a set of ignition experiments in CH$_4$/O$_2$/CO$_2$/Ar mixtures were performed. Three mixtures were used: (1) 1% CH$_4$/ 2% O$_2$/ 10% CO$_2$/ dilute in argon, (2) 2% CH$_4$/ 4% O$_2$/ 10% CO$_2$/ dilute in argon, and (3) 4% CH$_4$/ 8% O$_2$/ 10% CO$_2$/ dilute in argon. Prior to the ignition experiments the absorption cross-sections of O$_2$ and CH$_4$ at the two wavelengths of interest, 244.061 and 266.075 nm, were measured. Absorption by CH$_4$ at these wavelengths was undetectable but absorption by hot O$_2$ was detectable and the measured cross-sections are given in Figure C.7 for ~1 atm. In the shock wave ignition experiments presented here the interference at 266.075 nm is negligible and needs not be accounted for, but the larger interference at 244.061 nm was accounted for. The absorption by O$_2$ at 244.061 nm was estimated (with a chemical model described below) and subtracted from the overall measured 244.061 nm absorbance to obtain the portion of the signal due to CO$_2$ absorption. This correction causes greater uncertainty in the resulting temperature measurements relative to the non-reacting case. These corrections may or may not be needed in practical combustion thermometry depending on the relative CO$_2$ to O$_2$ concentrations. Also, the interference due to O$_2$ can be avoided with a continuous-wave laser source which can be tuned in wavelength to an O$_2$ absorption minimum. Simulations of the O$_2$ spectrum at 2000 K and 1 atm in this wavelength range have been carried out using the LIFSIM calculator developed by Bessler et al. [187]. The results for the O$_2$ spectrum around 244 nm are given in Figure
C.8. The current laser source sits in the wing of an absorption feature, but the interference could be reduced by a factor of seven by tuning between two absorption lines to 243.99 nm.

In Figure C.9 the absorbance at 266 and 244 nm (measured and corrected for O\textsubscript{2} interference) is given for an example experiment; the O\textsubscript{2} contribution to the absorption ranges from 4 to 15\% of the measured total absorption. For the three different test mixtures the resulting temperature time-histories are given in Figure C.10 with comparison to model results calculated using a constant volume constraint and the GRI Mech 3.0 methane combustion mechanism [95]. The correction applied to 244 nm absorbance for the O\textsubscript{2} interference was also determined by using the output of the GRI Mech 3.0 mechanism for the O\textsubscript{2} mole fraction and the measured temperature dependence of the O\textsubscript{2} absorption cross-section.

A comparison between constant volume model calculations and measured temperature (Figure C.10) shows good agreement for the ignition delay and the overall trends in temperature. However, the post-ignition temperature plateau measured with laser absorption is lower, in all three cases, than that predicted with the constant-volume model. This shortcoming of the constant volume model is expected because as energy is released due to ignition and the test gas temperature begins to rise at the test section location (2 cm from endwall) the hot combustion gases will expand down the shock tube resulting in a somewhat lower temperature plateau. (Note that the measured lower temperature in the post-ignition plateau was accounted for when determining the O\textsubscript{2} interference absorption cross-section at 244 nm.) For the examples given in Figure C.10 the measured post-ignition temperature rise is 60 to 75\% of that predicted by the constant volume model. Additionally, in the bottom graph of Figure C.10 the steep rise in temperature at ignition is due to the passage of a blast wave emanating from the shock tube endwall. When shock-heated fuel/oxidizer mixtures are of great enough energy content a blast wave is formed at the endwall and propagates down the shock tube reaching the optical location before the mixture is able to auto-ignite [188]. This is a common problem with ignition time measurements made at sidewall locations in energetic mixtures. Davidson and Hanson [189] have recently reported measurements of the post-ignition pressure plateaus in shock wave ignition experiments for iso-octane and
n-heptane. Consistent with their findings, we found temperature plateaus lower than that predicted with the constant-volume model. The current temperature measurements provide needed targets for improved models for reflected shock waves in reacting gases. A model that includes both the finite-rate chemistry and transport in the shock tube is needed to accurately model experiments with significant energy release, such as these.

C.5 Summary

A thermometry technique with microsecond time-resolution is demonstrated in shock wave experiments. The technique uses the highly temperature-dependent spectrally-smooth ultraviolet absorption feature of CO$_2$. The ratio of absorbance measured at 266 and 244 nm with fixed frequency continuous-wave laser sources is used to infer the temperature. The technique is demonstrated by monitoring temperature in non-reacting CO$_2$/argon mixtures after shock-heating. A comparison between the measured temperature and that resulting from an isentropic assumption between pressure (measured with a piezoelectric transducer) and temperature shows excellent agreement. Temperature measurements were also made in shock wave experiments with energy release due to the ignition of CH$_4$/O$_2$/CO$_2$/argon mixtures. It was found that the measured post-ignition temperature plateau was somewhat lower than that predicted with a constant-volume model due to expansion of the hot combusted gases down the shock tube.
Figure C.1: Ratio of 266 to 244 nm absorption cross-section; also referred to as absorbance ratio, $R$.

Figure C.2: Uncertainty in measured temperature for given temperature and product of partial CO$_2$ pressure and path length ($P_{CO2}L$). The contours represent lines of constant uncertainty in the temperature measurement assuming an uncertainty in measured absorbance of ±0.1% ($-\ln(I/I_0) = ±0.001$).
Figure C.3: Example non-reacting experiment: measured absorbance at 266 and 244 nm and measured pressure. Initial reflected shock conditions from ideal shock relations: 10% CO$_2$/Ar, 2138 K and 1.226 atm.

Figure C.4: Measured temperature (dark line) vs isentropic temperature (light line) for experiment in Figure C.3. Measured temperature determined from absorbance ratio (absorbance traces given in Figure C.3). Isentropic temperature determined from pressure measurement (given in Figure C.3).
Figure C.5: Comparison of measured temperature to isentropic temperature from the results given in Figure C.4.

Figure C.6: Comparison of measured post-shock temperature to temperature calculated with the ideal shock relations. Post-shock vibrational equilibrium was assumed.
Figure C.7: Molecular oxygen absorption cross-section at 244.061 and 266.075 nm (1 atm).

Figure C.8: Molecular oxygen absorption spectrum around 244 nm for 2000K and 1 atm, calculated using LIFSIM calculator [187]. Current doubled Ar\(^+\) line is at 244.061 nm, a source at 243.99 nm would reduce the interference due to O\(_2\) by a factor of seven.
Figure C.9: Example absorbance for energetic ignition experiment. Initial reflected shock conditions: 1% CH$_4$/ 2% O$_2$/ 10% CO$_2$/ Ar, 2085 K and 1.297 atm. 266 nm and 244 nm measured absorbance, dark lines; corrected (O$_2$ interference) 244 nm absorbance, light line.
Figure C.10: Measured temperature (solid thick lines) versus constant volume calculation (solid thin lines). Top graph (initial reflected shock conditions): 1% CH₄/ 2% O₂/ 10% CO₂/ Ar, 2085 K, and 1.297 atm. Middle graph: 2% CH₄/ 4% O₂/ 10% CO₂/ Ar, 1890 K, 1.358 atm. Bottom graph: 4% CH₄/ 8% O₂/ 10% CO₂/ Ar, 1851 K, 1.277 atm. Post-shock vibrational equilibrium was assumed. Error bars represent a 1-σ confidence interval.
Appendix D: Azomethane synthesis

This appendix describes the process used to synthesize azomethane. The method used is that of Jahn [99] and the below instructions were developed by David F. Davidson at Stanford University.

D.1 Chemicals

The following chemicals are needed:

1) Sodium acetate (MW 82.03 Aldrich# 24,124-5)
2) Copper chloride (II) dihydrate (FW 170.48 Aldrich# 22,178-3)
3) 1,2-dimethylhydrazine dihydrochloride (DMHZ, MW 133.02 Aldrich# D16,180-2)
4) Distilled water

D.2 Supplies

The following supplies are needed to make and hold solutions:

1) 1 liter graduated cylinder
2) funnel
3) Kimwipes
4) scale/balance
5) weighing papers
6) bottle to hold sodium acetate solution 1-2 liter with wide mouth cap
7) bottle to hold copper chloride solution 1-2 liter with wide mouth cap
8) plastic bottle to hold waste solution 1 gallon with cap
9) secondary containment basin for chemicals and bottles

The following supplies are needed to make brown mud:

1) 1 liter beaker, open mouth
2) glass stirring rod/ rubber policeman
The following supplies are needed to dry brown mud:

1) long spoon  
2) Buchner funnel, and seal  
3) Florence flask with vacuum connection  
4) filter paper for Buchner funnel  
5) vacuum hose connection and vacuum pump

The following supplies are needed to heat brown mud:

1) flat bottom heating flask with connection to vacuum manifold  
2) oil dish for heating flask  
3) heating plate  
4) thermometer to 150° C

The following supplies are needed to trap azomethane:

1) long neck AirFree flask and valve  
2) LN$_2$ dewar for flask  
3) larger dewar for LN$_2$ supply  
4) glass manifold for flask, pump and heating flask clamps and orings vacuum  
   line adapters for 3 connections  
5) two chemistry stands and clamps

**D.3 Directions for azomethane production**

1) Mix 1 molar NaCH$_3$CO$_2$ solution (MW 82.03) in one liter of distilled water.  
2) Mix 1 molar CuCl$_2$:2H$_2$O solution (FW 170.48) in one liter of distilled water.  
3) Dissolve **fully** 10 grams DMHZ in 300 cc of sodium acetate solution.  
4) Add 300 cc of cupric chloride solution.  
5) Brown mud azomethane:(CuCl)$_2$ complex will precipitate.  
6) Wash through aspirated Buchner funnel/paper filter with 1 liter of water.  
7) Dry at room temperature by aspirating through funnel or free-standing.  
8) Break into two amounts. Store one for later use.  
9) Put in heating flask, break up and press onto bottom of flask to form even layer.  
10) Then heat in oil bath to 125-150 ° C to release azomethane trapping with LN$_2$.  


11) Heating flask cleans easily with water.

**D.4 Azomethane yield**

The 10 grams (0.0752 moles) of DMHZ is fully dissolved in the aqueous sodium acetate solution and then oxidized by the cupric chloride solution resulting in a precipitate, (CuCl)$_2$:($\text{CH}_3$)NN($\text{CH}_3$). The precipitate then is heated causing its thermal decomposition

$$(\text{CuCl})_2$:($\text{CH}_3$)NN($\text{CH}_3$) \rightarrow (\text{CuCl})_2 + (\text{CH}_3$)NN($\text{CH}_3$)$$

Assuming a 70% yield, per Jahn [99], the 0.0752 of DMHZ gives 0.0526 moles of azomethane (3.0 grams) which at STP is 1.2 liters or in a 100 mL flask is 12 atm. This method provides very clean gaseous azomethane for making mixtures because any other impurities (CH$_3$CO$_2$, (CuCl)$_2$:($\text{CH}_3$)NN($\text{CH}_3$), that make their way to the LN$_2$ trap will have very low vapor pressures in comparison to the azomethane and will not vaporize when making mixtures.
Appendix E: Mechanism used for benzyl and toluene decomposition

Table E.1: Reaction mechanism used for modeling toluene and benzyl decomposition experiments, rate coefficients in the form $k = AT^b \exp(-E_a / RT)$.

<table>
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<tr>
<th>Reaction</th>
<th>$A$ [cm, mol, s]</th>
<th>$b$</th>
<th>$E_a$ [cal/mol]</th>
<th>Ref.</th>
</tr>
</thead>
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<tr>
<td>(7) $C_6H_5CH_2 \rightarrow C_7H_6 + H$ (1.5 atm)</td>
<td>$8.20 \times 10^{14}$</td>
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<td>80670</td>
<td>this study</td>
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<td>(8) $C_6H_5CH_3 \rightarrow C_6H_4CH_2 + H$ (1.5 atm)</td>
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<td>(9) $C_6H_5CH_3 \rightarrow C_6H_5 + CH_3$ (1.5 atm)</td>
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</tr>
<tr>
<td>(12) $C_6H_5CHI \rightarrow C_6H_4CH_2 + I$</td>
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<tr>
<td>(14) $C_6H_5CH_2 + H \rightarrow C_6H_4CH_3$</td>
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<td>0</td>
<td>[190]</td>
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<tr>
<td>(15) $C_6H_6 + H \rightarrow C_6H_4CH_2$</td>
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<td>0</td>
<td>[74]</td>
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<tr>
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<td>$C_6H_5 + C_6H_4CH_3 \rightarrow C_6H_6 + C_6H_5CH_2$</td>
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<td>0</td>
<td>11940</td>
<td>[193]</td>
</tr>
<tr>
<td>(13) $C_6H_5CH_2 + C_6H_4CH_2 \rightarrow C_6H_4CH_2CH_2C_6H_5$</td>
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<td>( \text{H} + \text{C}_2\text{H}_4 \leftrightarrow \text{C}_2\text{H}_5 + \text{H}_2 )</td>
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<td>( 6.14 \times 10^{6} )</td>
<td>1.74</td>
<td>10450</td>
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Appendix F: Shock tube gasdynamics

The gasdynamic wave interactions that occur during shock tube experiments can be described using x-t diagrams. Assuming ideal inviscid compressible flow, the shock tube can be modeled using the simple one-dimensional wave propagation equations derived from conservation of mass, momentum, and energy [176,203]. The resulting reflected shock test-time is limited at high-temperatures (strong shocks) by the interaction of the reflected shock wave with the driver-driven gas contact surface. At low-temperatures (weak shocks) the test-time is limited by the interaction of the reflected shock wave with the rarefaction (expansion) head that is generated by the breakage of the diaphragm and the subsequent blow down of the high-pressure driver gas.

F.1 High-temperature test-time

In the high-temperature (strong shock) case, when the test-time is limited by the reflected shock wave interaction with the contact surface, three possible wave interactions can occur. When the speed of sound in region 2 (incident condition) is greater than the speed of sound in region 3 (condition behind the contact surface), \( a_2 > a_3 \), the reflected shock wave decelerates when it passes through the contact surface generating a second shock wave that travels back towards the endwall and reflects off of it causing the pressure at the test-location to incrementally increase. See Figure F.1 for a x-t schematic and the top graph in Figure F.5 for an example pressure trace for this case.

When the speed of sound in region 2 is greater than the speed of sound in region 3, \( a_3 > a_2 \), the reflected shock wave accelerates when it passes through the contact surface generating a rarefaction wave that propagates back to the endwall and reflects off of it. This rarefaction wave then generates another shock wave when it interacts with the contact surface. These wave interactions cause the pressure at the test-location to initially decrease, due to the rarefaction wave generated by the reflected shock interaction with the contact surface. However, at later times the pressure will increase due to the
generation of a shock wave when this newly created rarefaction wave interacts with the contact surface. These types of wave interactions are responsible for the temperature and pressure profiles shown in Figures C.3 and C.4 where the pressure falls and rises after about 2 ms of test-time. See Figure F.2 for a x-t schematic and the middle graph in Figure F.5 for an example pressure trace for this case. Note that the final decrease in pressure at 3 ms (Figure F.5) is due to the rarefaction head propagating through the test-location.

Finally, if the sound speeds in region 2 and 3 are equal, \( a_2 = a_3 \), the reflected shock wave passes through the contact surface without a change in speed and the contact surface is brought to rest allowing significantly longer test times. This limiting case is called shock tailoring; see Figure F.3 for a x-t schematic of this case.

**F.2 Low-temperature test-time**

When the diaphragm breaks and the incident shock wave is generated, a rarefaction head is launched towards the driver endwall. This wave reflects off the driver endwall and proceeds down the shock tube following the incident shock and contact surface. For cases when the incident shock speed is slow, the rarefaction head can pass through the contact surface and directly interact with the reflected shock wave. In this case the pressure at the test-location simply decays when the rarefaction wave reaches it. This happens for cases when the reflected shock temperature is low (weak shock). See Figure F.4 for a x-t schematic and the bottom graph in Figure F.5 for an example pressure trace for this case.

**F.3 Reflected shock test-time and pressure traces**

Experimental pressure traces for three of the cases described above are shown in Figure F.5. The three pressure traces shown in the figure illustrate that the pressure slightly increases during the test-time until reflected shock interactions with either the contact surface or the rarefaction wave disrupt the test-time causing a more drastic discontinuous decrease or increase in the pressure. The slight increase in the pressure during the test-time is due to non-ideal effects behind the reflected shock wave. After the shock wave reflects off the endwall, it travels into a gas with non-uniformities due to
incident shock wave attenuation. These non-uniformities cause small compression waves to propagate back to the test-location and thus cause a slight increase in pressure and temperature during the test-time; see Petersen Ph.D. thesis [175] for details.

The three pressure traces in Figure F.5 show the limitation of the test-time by the three different wave interactions shown in the x-t diagrams given in Figures F.1, F.2, and F.4. The test-time was determined from the experimental pressure traces by estimating the time at which the discontinuous change in pressure occurs. The experimental test-time is plotted versus reflected shock temperature for several experiments in Figure F.6. Note that the test-time peaks around 1800 K and falls off to low- and high-temperature due to reflected shock interaction with the rarefaction head and contact surface respectively.
Figure F.1: Schematic of x-t diagram for high-temperature (strong shock) case where $a_2 > a_3$.

Figure F.2: Schematic of x-t diagram for high-temperature (strong shock) case where $a_3 > a_3$. 
Figure F.3: Schematic x-t diagram for high-temperature (strong shock) case where $a_2 = a_3$, tailored condition.

Figure F.4: Schematic x-t diagram for low-temperature (weak shock) case where reflected shock interaction with rarefaction wave limits test-time.
Figure F.5: Example pressure traces measured with KISTLER piezoelectric transducer. Top graph: example high-temperature (strong shock) case where $a_2 > a_3$ (Figure F.1 x-t diagram). Middle graph: example high-temperature (strong shock) case where $a_3 > a_2$ (Figure F.2 x-t diagram). Bottom graph: example low-temperature case (Figure F.4 x-t diagram).
Figure F.6: Measured test-time as a function of reflected shock temperature for helium driven argon shocks.
References


