SHOCK TUBE MEASUREMENTS OF CH$_3$+O$_2$ KINETICS
AND THE HEAT OF FORMATION OF THE OH RADICAL

By

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Abstract

The reaction of methyl radicals (CH$_3$) with molecular oxygen (O$_2$), a rate-controlling process in the ignition of natural gas under radical-poor conditions, has been investigated in high-temperature shock tube experiments. The overall rate coefficient, $k_1 = k_{1a} + k_{1b}$, and individual rate coefficients for the two high-temperature product channels, (1a) producing CH$_3$O+O and (1b) producing CH$_2$O+OH, were determined using ultra-lean mixtures of CH$_3$I and O$_2$ in Ar/He. Narrow-linewidth UV laser absorption at 306.7 nm was used to measure OH concentrations, for which the normalized rise time is sensitive to the overall rate coefficient $k_1$ but relatively insensitive to the branching ratio of the individual channels and to secondary reactions. Atomic resonance absorption spectroscopy measurements of O-atoms were used for a direct measurement of channel (1a). Through the combination of measurements using the two different diagnostics, rate coefficient expressions for both channels were determined. Over the temperature range 1590 to 2430K, $k_{1a} = 6.08 \times 10^7 T^{1.54} \exp(-14005/T) \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$ and $k_{1b} = 68.6 T^{2.86} \exp(-4916/T) \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}$. The overall rate coefficient is in close agreement with a recent \textit{ab initio} calculation and one other shock tube study, while comparison of $k_{1a}$ and $k_{1b}$ to these and other experimental studies yields mixed results. In contrast to one recent experimental study, reaction (1b) is found to be the dominant channel over the entire experimental temperature range.

The standard heat of formation of the hydroxyl radical (OH) at 298 K, $\Delta_fH^{298}(\text{OH})$, a fundamental thermochemical parameter influencing the equilibrium constants of many combustion and atmospheric chemical reactions, has been determined from shock tube measurements spanning the temperature range 1964 to 2718 K and at pressures of 1 to 2.4 atm. Low-concentration, lean and stoichiometric mixtures of H$_2$ and O$_2$ in Ar produce well-controlled levels of OH in a “partial equilibrium” state, with little or no sensitivity to the reaction kinetics. The partial equilibrium OH concentrations are
dependent only on the thermochemical parameters of the reacting species, with the heat of formation of OH being the most significant and uncertain parameter. Narrow-linewidth UV laser absorption at 306.7nm is used to measure OH concentrations with sufficient accuracy (2-4%) to clearly determine the value of the heat of formation. Over the entire range of experimental conditions, the average determination is $\Delta_{f}H_{298}^\circ(OH) = 8.92 \pm 0.16$ kcal/mol (37.3 ± 0.67 kJ/mol) with a standard deviation of $\sigma = 0.04$ kcal/mol (0.17 kJ/mol). This value is 0.40 to 0.48 kcal/mol (1.7 to 2.0 kJ/mol) below the previously accepted values, and agrees with recent theoretical calculations, experimental studies using the positive-ion cycle, and calculations using thermochemical cycles.
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Chapter 1: Introduction

1.1 Motivation

Modern combustion systems are ideally designed to achieve high thermal efficiency and low pollutant emissions, while the end users of these systems are additionally interested in high reliability and the lowest obtainable cycle cost necessary to produce the desired propulsive force, mechanical motion, electricity, or heat. The development of combustion systems is greatly enhanced by accurate detailed models and computational methods which can predict, with high confidence, how a proposed design will function and how perturbations to the design can lead to an optimization of its performance. Models for combustion systems typically incorporate information about combustion chemistry, fluid dynamics, and heat transfer. Because of the complex physical nature of combusting matter, particularly in turbulent flows, combustion chemical kinetic mechanisms assembled for computational purposes are often simplified or “reduced” to improve computational efficiency while still reproducing the most critical features of the fully detailed model – features such as autoignition time, flame speed, or pollutant formation characteristics. These reduced mechanisms, however, can only be as accurate as the fully detailed mechanisms or experimental data on which they are based, and they are somewhat limited in application to the specific combustion environment or combustion parameters for which they are optimized.

Accurate, predictive detailed combustion chemistry mechanisms require 3 major components: 1) a complete set of reactions, 2) reaction rate coefficients for every reaction (with accurate rate expressions for the most important reactions), and 3) thermodynamic and thermochemical data for each species, along with the complete temperature and pressure dependence for (2) and (3). The mechanisms’ success in recreating real combustion phenomena is largely dependent on careful experimental determinations of rate coefficient and thermochemical parameters of the reactions and
species in the model. In addition, theoretical calculations are increasingly a vital part of this process. As theoretical methods are validated by prudent experimental measurements, confidence is gained in the theory, which can then be pushed farther and faster to explore model parameters which are difficult or impossible to determine experimentally. Until the time that theoretical methods are unwaveringly accurate, however, well-thought-out experimental determination of critical combustion parameters will be an essential means by which to improve the accuracy of combustion chemical kinetic mechanisms.

In this thesis work, a shock tube has been used to perform carefully designed measurements of combustion chemical kinetic and thermochemical parameters. Two specific projects are highlighted here: a measurement of the reaction rate of $\text{CH}_3 + \text{O}_2 \rightarrow $ products, an important reaction in the combustion of natural gas and other hydrocarbon fuels; and a high-temperature determination of the standard heat of formation of the hydroxyl radical (OH) at 298 K, $\Delta f H^{\circ}_{298}(\text{OH})$. Supporting work has also been performed which enhances the reliability of the spectroscopic diagnostics and experimental methods used in this investigation.

1.2 Background

1.2.1 $\text{CH}_3 + \text{O}_2 \rightarrow$ products

The reaction of methyl radicals with molecular oxygen plays a role in the oxidation of many alkanes, and is often the rate-controlling reaction during the methane ($\text{CH}_4$) ignition process under radical-lean combustion conditions. The three well-known product channels are:

\begin{align*}
\text{CH}_3 + \text{O}_2 & \rightarrow \text{CH}_3\text{O} + \text{O} \quad (1a) \\
& \rightarrow \text{CH}_2\text{O} + \text{OH} \quad (1b) \\
& (+\text{M}) \rightarrow \text{CH}_3\text{O}_2 (+\text{M}) \quad (1c)
\end{align*}

Channels (1a) and (1b) are the dominant reaction pathways at combustion temperatures, and channel (1c) is thought to become important below 1500 K as well as at higher pressures [1]. Figure 1.1 shows the sensitivity of CH$_4$ ignition times to these and other reactions.
Due to the importance of the CH$_3$ + O$_2$ reaction in hydrocarbon oxidation, it has been the focus of numerous experimental [2-24] and theoretical [1,11,24-27] investigations. The published rate coefficient values are plotted in Figs. 1.2 and 1.3. Shock tube experimental studies have ranged from CH$_4$ oxidation [4-6,9,12,14,17,18,21,22,24] to ultra-lean experiments using CH$_3$ precursors such as methyl iodide (CH$_3$I) [16,19], azomethane ((CH$_3$)$_2$N$_2$) [7,8,11,13,15,23], and ethane (C$_2$H$_6$) [3,13,19]. The diagnostics utilized include optical absorption of OH [4,5,7,12,19,24], CH$_3$ [12], CO [11,23,24], H$_2$O [23], N$_2$O [4], CH$_4$ [18], and H- [3,15,17,19] and O-atoms [3,15-17,19]; optical emission of OH [4], CO [9,13], and CO$_2$ [9,13]; CO flame band emission [5,6,14]; post-shock density gradients [21]; pressure [4]; and time-of-flight mass spectrometry [8]. Other experimental work includes flow reactor studies [10,20] and Knudsen cell experiments [2] utilizing mass spectrometry. In spite of the effort devoted to studying this reaction, there remains disagreement regarding the overall rate coefficient, $k_1 = k_{1a} + k_{1b}$, and the individual rate coefficients of the two major product channels at combustion temperatures.

As discussed in Hwang et al. [12], early studies suffered from the lack of accurate knowledge of, and sometimes exclusion of, important secondary chemistry. Experiments were performed with the expectation of chemical isolation, when in fact the measured results were influenced by chemistry in addition to reaction (1). Aside from secondary chemistry, Yu et al. [24] point out that the a priori assumption of dominance of either channel (1a) or (1b) influenced the rate coefficients reported for these reactions. Michael et al. [16] note that the yields of some species, such as OH and CO, in CH$_4$ ignition experiments are somewhat insensitive to whether the initial reaction pathway proceeds through channel (1a) or (1b). Consequently, investigations purporting to measure one or the other could not always discern which reaction they were in fact measuring, and most likely they were observing the combined effects of both channels. For these reasons, and due to the complexity of the subsequent secondary chemistry, previous experimental studies have resulted in reaction rate coefficients for channels (1a) and (1b) which span more than a factor of four and over an order of magnitude, respectively.

Even the most recent high-temperature studies, including three experimental studies and one theoretical calculation, have not provided consensus values for the
overall rate and branching ratio, \( \alpha = \frac{k_{1a}}{k_1} \). Figures 1.4 and 1.5 display the effective overall rate and branching ratio from high-temperature studies in only the last 10 years. The study of Yu et al. [24] utilized measurements of OH and CO rise times in lean CH\(_4\) ignition experiments. Starting with a theoretical calculation for \( k_{1b} \) (which was fit, in part, to data from two earlier studies [2,10]), these workers fit their experimental data by fixing \( k_{1b} \) to the calculated value and adjusting \( k_{1a} \). The final experimental expression for \( k_{1a} \) was found to compare favorably to their theoretical calculation of that channel. Michael et al. [16] measured O-atom concentrations in ultra-lean CH_3I / O_2 experiments and reported that, for temperatures between 1600 and 2100K, reaction (1a) is the only significant channel and that the rate of this reaction is substantially lower than that reported by Yu et al. In addition, Michael et al. were unable to fit their O-atom data if channel (1b) was included in the model. Hwang et al. [12] measured OH and CH\(_3\) in lean CH\(_4\) ignition experiments similar to those of Yu et al. They reported a rate coefficient for channel (1a) that is in close agreement with Michael et al., but they found that the rate of channel (1b) could not be reduced to zero. Recent \textit{ab initio} calculations of Zhu et al. [1] agree with the overall rate of Yu et al. to within 10\% in their overlapping temperature range, but the calculated branching ratio \( \alpha \) is approximately 25\% to 45\% lower. Among these most recent studies, \( k_{1a} \) has a spread of a factor of \( \sim 3 \) and \( k_{1b} \) ranges from being dominant to being negligible.

Given the lack of agreement among recent studies, a shock tube study of the reaction \( \text{CH}_3+\text{O}_2 \rightarrow \text{products} \) was undertaken using cw laser absorption spectroscopy of OH and O-atom atomic resonance absorption spectroscopy (ARAS) measurements. This study was designed to overcome many of the obstacles which have previously prevented actual experimental determination of both high-temperature channels within one study, and it provides a self-consistent basis for comparison to measurements from other laboratories.

1.2.2 The heat of formation of OH

Detailed chemical kinetics models for combustion and atmospheric chemistry require not only chemical reactions and their rate coefficients, but also accurate thermochemical and thermodynamic parameters for all species involved. Incorrect
thermochemical data can lead to erroneous kinetic modeling via calculation of reverse rate coefficients through the equilibrium constant. Accurate thermochemical parameters, particularly the heat of formation, are typically difficult to measure or calculate directly, and species for which the uncertainties in thermochemical parameters are small enough to be ignored in combustion modeling are very few [28]. Parameters for radical species, in particular, are difficult to obtain due to their reactivity and small concentrations at convenient experimental conditions. Because of the importance of radicals, such as OH, in the ignition process of all fuels and in atmospheric chemistry, accurate thermochemical parameters must be used to correctly model the chemistry.

Recently, renewed attention has been given to the heat of formation of the OH radical. Ruscic et al. [29,30] have suggested that the generally accepted standard heat of formation of OH at 0 K, \( \Delta_f H^\circ_0(\text{OH}) = 9.35 \text{ kcal/mol} \) [31] or \( \Delta_f H^\circ_0(\text{OH}) = 9.18 \text{ kcal/mol} \) [32], is too high by up to 0.5 kcal/mol, based on both new experimental measurements of the OH positive-ion cycle and ab-initio electronic structure calculations. These authors provide an in-depth analysis of past determinations of the heat of formation of OH and the two successive bond dissociation energies of water, \( D_0(\text{H-OH}) \) and \( D_0(\text{O-H}) \). The previously accepted value for \( \Delta_f H^\circ_0(\text{OH}) \) is based on a value of the dissociation energy of OH, \( D_0(\text{O-H}) \), determined from a short Birge-Sponer extrapolation [33] of the potential energy surface from spectroscopically measured vibrational energy levels [34]. Through their analysis, Ruscic et al. show that the Birge-Sponer extrapolation, while very short (~1.5 vibrational levels), has significant errors leading to an underprediction of \( D_0(\text{O-H}) \) and therefore an overprediction of \( \Delta_f H^\circ_0(\text{OH}) \). In another recent paper, Joens [35] used available experimental data and thermochemical cycles of H\(_2\)O and H\(_2\)O\(_2\) to infer a value for \( \Delta_f H^\circ_0(\text{OH}) \) in essential agreement with Ruscic et al. [29,30]. These recent studies highlight the previous methods that have been used to determine the heat of formation.

The present study of the heat of formation of OH was motivated by these recent results and the impact that such a change in a fundamental thermochemical parameter like \( \Delta_f H^\circ_0(\text{OH}) \) would have on other thermochemical parameters and many combustion and atmospheric chemistry reactions. An additional motivation was that experiments in our own laboratory of shock-initiated combustion of CH\(_4\)/O\(_2\) and C\(_2\)H\(_6\)/O\(_2\) mixtures [36,37] have revealed that kinetic models consistently underpredict the OH concentration.
in the post-ignition plateau region by as much as 10-15%. An example of such an experiment is shown in Fig. 1.6. This amount of discrepancy for an OH laser absorption measurement is alarming, as the diagnostic is highly quantitative and OH measurements are considered to be better than ±3% accurate at these conditions. The discrepancy indicates that either 1) the diagnostic has significant unforeseen errors or 2) the plateau is sensitive to an erroneous thermochemical parameter which controls the plateau concentration of OH.

Hypothesis (1) has been investigated here through a careful evaluation and review of the spectroscopic information used in the calculation of absorption coefficients, as well as further measurements of OH lineshape collision broadening and collision shift parameters. Through these investigations, the methods and parameters for calculation of OH spectral absorption coefficients have been updated and improved. However, these improvements do not go far enough to explain the OH plateau discrepancy.

Hypothesis (2) draws from the fact that the sensitivity of OH plateaus to kinetic rate parameters is very small compared to the sensitivity to thermochemical parameters, particularly the heat of formation of OH. Figure 1.7 is a kinetic sensitivity analysis for the experiment in Fig. 1.6. In the plateau region, the sensitivity to all reaction rates is essentially zero, and the plateau concentrations are wholly controlled by the thermochemical parameters of the species involved in the partial equilibrium plateau. Of these species, the thermochemistry of OH is the most in question. The discrepancy in the plateau OH concentration thus represents an opportunity to perform measurements of the heat of formation of OH. This work details the experimental planning and results of an independent determination of $\Delta_f H^{298}_\text{OH}$ using shock-heated mixtures of H$_2$ and O$_2$.

1.3 Scope and organization of thesis

The objectives of this research were: 1) to design and perform high-precision, low-uncertainty measurements of the overall reaction rate of CH$_3$+O$_2$→products and to determine the rates for the individual product channels, 2) to perform unique high-temperature measurements of the heat of formation of OH, and 3) to enhance the reliability of the diagnostics and shock tube techniques utilized for these and future combustion chemistry measurements.
Chapter 2 describes the experimental apparatus and diagnostic techniques used in this work. Information is presented regarding the shock tube facility, equipment, and design changes implemented to improve the facility and enable sensitive measurements using low concentration mixtures. The OH laser absorption diagnostic is discussed. An apparatus for O-atom measurement using the ARAS technique was built, characterized, and calibrated for use in kinetics experiments and is described here.

Chapters 3 and 4 contain the primary experimental work in this thesis. The investigation of the reaction $\text{CH}_3+\text{O}_2\rightarrow\text{products}$ is presented in Chapter 3. This chapter describes the unique approach developed to experimentally determine the individual product channels. The design of experiments, results, and uncertainty analysis are given. Chapter 4 details the high-temperature measurement of the heat of formation of OH. The results, their comparison to other recent determinations, and a detailed uncertainty analysis are provided. Chapter 5 concludes with suggestions for ongoing work in related topic areas.

An important review of OH spectroscopy and the calculation of spectral absorption coefficients is given in Appendix A. Measurements of OH lineshape collision-shift and collision-broadening parameters are presented in Appendix B. Appendix C details an uncertainty analysis for the calculation of the temperature and pressure behind the reflected shock wave, based on uncertainties in the incident shock velocity and initial conditions. Appendix D gives further details on the ARAS technique. Appendix E is a discussion of the partial equilibrium state in $\text{H}_2/\text{O}_2$ mixtures which is used to determine the heat of formation of OH.
Figure 1.1: Sensitivity of CH$_4$ ignition times to various reactions [37]. Mixture is 9.1% CH$_4$ / 18.2% O$_2$ / Ar. Conditions are 1500 K, 1.8 atm.

Source: GRI-Mech 3.0 (http://www.me.berkeley.edu/gri_mech/)
Zhu et al. (2001)  
Michael et al. (1999)  
Hwang et al. (1999)  
Yu et al. (1995)  
Braun-Unkhoff et al. (1993)  
Klatt et al. (1991)  
Wu et al. (1990)  
Zellner and Ewig (1988)  
Dean and Westmoreland (1987)  
Saito et al. (1986)  
Hsu et al. (1983)  
Bhaskaran et al. (1980)  
Teitelboim et al. (1978)  
Brabbs and Brokaw (1975)  
Baulch et al. (review) (1992)  
GRI-Mech 3.0

Figure 1.2: Previous rate coefficient data for $k_{1a}$.

Zhu et al. (2001)  
Seire et al. (2001)  
Yu et al. (1995)  
Braun-Unkhoff et al. (1993)  
Grela et al. (1992)  
Zellner and Ewig (1988)  
Saito et al. (1986)  
Hsu et al. (1983)  
Bhaskaran et al. (1980)  
Teitelboim et al. (1978)  
Brabbs and Brokaw (1975)  
Baulch et al. (review) (1992)  
GRI-Mech 3.0

Figure 1.3: Previous rate coefficient data for $k_{1b}$. 

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Figure 1.4: Recent data for the effective overall rate coefficient ($k_1 = k_{1a} + k_{1b}$).

Figure 1.5: Recent data for the effective branching ratio ($\alpha = k_{1a} / k_1$).
Figure 1.6: Experimentally measured OH and model calculation [37]. Mixture is 0.1% CH$_4$ / 0.2% O$_2$ / balance Ar.

Figure 1.7: Sensitivity analysis for the experiment in Figure 1.6.
Chapter 2: Experimental apparatus and diagnostics

This chapter discusses the shock tube, gas mixing system, and diagnostics utilized for the experiments performed in this work. Details of the equipment and diagnostics, their operation, and experimental techniques are given.

2.1 Experimental facilities

2.1.1 Shock tube

The shock tube experiments described in this thesis were performed behind reflected shock waves in a new 14.13 cm inner-diameter high-purity, electropolished (to passivate the surface) stainless steel shock tube.\footnote{The shock tube facility was designed and built by Matthew A. Oehlschlaeger, with assistance from the author and other researchers.} This shock tube consists of an 8.54 m driven section and a 3.35 m driver of the same inner diameter, separated by a polycarbonate diaphragm, and is pressure-driven with helium gas. The diaphragm is ruptured by stationary crossed knife blades, and the driven pressure ($P_4$) at the time of diaphragm break is controlled by changing diaphragm thickness and/or the position of the knife blades. Multiple stacked diaphragms have also been used with success to achieve particular break conditions. Aluminum foil diaphragms of 0.0005-0.003” thickness were tried in a few experiments to check for noticeable changes in measured impurity effects.

Between experiments the driven section of the shock tube is evacuated to typically < 1 µtorr using mechanical and turbomolecular pumps; the leak-plus-outgassing rate is typically < 20 µtorr/minute. Overnight pump-down can achieve an ultimate pressure of ~ 0.25 µtorr with a leak-plus-outgassing rate of ~ 0.5 µtorr/minute.
Shock velocity is measured using five axially spaced PCB Piezotronics 113A26 piezoelectric transducers (PZT’s) and a 6-channel amplifier (PCB 483B08) connected to four Philips PM6666 interval timers with a resolution of 0.1 µs. The shock trajectory is fit to the velocity data using a linear attenuation profile and extrapolated to the endwall; the typical incident-shock attenuation rate for Ar bath gas is 1-1.5 %/m. Post-shock conditions are calculated from the extrapolated endwall shock velocity, initial pressure, and initial temperature using standard shock wave relations and assuming chemically frozen and vibrationally equilibrated gases. For some of the work in this dissertation, vibrational equilibration cannot necessarily be assumed without careful consideration of the characteristic vibrational relaxation times of the mixture. Uncertainty in the calculation of the initial reflected-shock temperature and pressure (T_5 and P_5) is typically on the order of 0.7% and 1%, respectively. An uncertainty analysis for T_5 and P_5 is provided in Appendix C.

The post-shock gases are optically accessed through 0.75” diameter windows centered 2 cm from the endwall and mounted flush to the inner radius of the shock tube. For OH laser absorption experiments, the window material was typically sapphire, UV fused silica, or CaF_2 with a nominal thickness of 0.125”. A fifth PZT, Kistler model 603B1 with model 5010B amplifier, is mounted at this same axial location and is used to measure the pressure-time history of the experiment. All PZT’s are recessed ≈ 1 mm from the inner diameter surface and coated with 1 mm of red silicone RTV to protect them from thermal shock and temperature-induced changes in their sensitivity.

The shock tube’s driven section was occasionally cleaned using clean cloth rags and methanol. During the kinetics work discussed in Chapter 3, ultra-high-purity gases and very low reactant concentrations were used in the gas mixtures; therefore cleaning was performed sparingly and usually not until the presence of diaphragm particles in the test section began to disturb the measurements. Following a cleaning the shock tube must be evacuated to high vacuum overnight to remove residual solvent and water vapor from the shock tube walls. Typically the first three to five shocks were run with pure Ar or pure O_2 at very high temperatures to assist in driving the remaining solvent off of the walls and removing it during the pump-down cycle.
2.1.2 Gas mixing facility

Gas mixtures were prepared manometrically in a 12-liter stainless steel and aluminum mixing cylinder and mechanically mixed with a magnetically driven stirrer. Gases were connected to the mixing cylinder, vacuum system, and shock tube via a stainless steel welded-tubing manifold with stainless steel bellows-sealed valves. Gas pressures were measured using high-accuracy MKS Baratron 690A capacitance manometers with MKS 270D signal conditioner/display readouts. Two transducers, with useful ranges of 100 torr and 10,000 torr, are connected to the manifold and permit accurate and precise measurement of the minor constituents as well as the final mixture pressure. The same transducers are also utilized for measurement of the pre-shock pressure in the driven section, $P_1$. A Varian ionization pressure gauge is mounted to the vacuum manifold for measurement of high vacuum during pump-down of the mixing system. A Setra 280E capacitance pressure transducer is mounted directly to the mixing cylinder in order to provide full-time measurement of the tank pressure. During mixture preparation, even with slow filling rates, the gases in the cylinder become slightly heated. Typically the final pressure of the mixture will drop 0.3-0.5% over the first hour or two of mixing as the gases cool down. This sensor enables monitoring of the cool-down process and the final equilibrated mixture pressure, and is a constant measure of the remaining gas mixture pressure during sets of shock tube experiments.

The gas manifold, mixing cylinder, and all gas lines are evacuated using mechanical and turbomolecular pumps connected directly to the manifold and cylinder via 1”-diameter fittings. Previous to the current work, a direct-drive mechanical pump alone was used to evacuate the mixing cylinder, with an ultimate vacuum pressure limit of $> 1$ mtorr. Addition of the turbomolecular pump, along with design changes that shortened the length and increased the diameter of all vacuum lines, both increased effective pumping speed and decreased the ultimate pressure. Shock wave experiments performed before and after the mechanical changes confirmed a significant improvement in residual impurities and, therefore, the ability to make accurate low-concentration gas mixtures. The mixing cylinder can be evacuated to $\sim 2$ µtorr overnight, with leak-plus-outgassing rates of $\sim 100$ µtorr/minute. Less than 1 µtorr can be achieved after 2-3 days, with the lowest recorded pressure of 0.63 µtorr and leak-plus-outgassing rate of 8.6
µtorr/minute after more than one week of pumping. The manifold alone, without the mixing cylinder, is routinely pumped down to < 1 µtorr between experiments.

2.1.3 Mixture preparation

One goal in designing the mixture preparation procedure is to minimize uncertainties stemming from the measurement of gas pressures. The combination of 100-torr and 10,000-torr capacitance manometers was chosen in large part due to the requirements of this work. The ultra-low-concentration mixtures used for the chemical kinetics experiments in Chapter 3 were prepared using a double dilution process, whereas higher-concentration mixtures in Chapter 4 were prepared in a single dilution. Mixture preparation procedures were kept as consistent as possible from mixture to mixture.

The methyl precursor used in these experiments, methyl iodide (CH$_3$I), was 99.5% pure and is commonly available from chemical suppliers. It has a vapor pressure of ~ 400 torr at room temperature. Methyl iodide is a toxic substance, so caution must be observed in its handling.

Samples of CH$_3$I were prepared inside a fume hood by pouring the desired amount of liquid into a glass flask with a sealing valve, such as the Airfree® type made by Chemglass, Inc. The valve is closed, and liquid remaining above the valve is removed by pumping it out with a vacuum line. The flask is then taken from the fume hood and connected to the shock tube mixing manifold. Before making a mixture, the air and any other high-volatility compounds must be removed from the flask through a freeze-pump-thaw cycle. A bath of liquid nitrogen (LN$_2$) is used during this process to cool down the flask and the liquid inside. Once it starts to cool, the flask is opened up to the mixing manifold and the mechanical pump is used to evacuate the gases while further cooling the liquid to the frozen state. Typically some amount of cavitation is visible as air and other gases come out of solution in the liquid, until eventually the liquid is frozen solid. At this point the turbomolecular pump can be activated and the pressure in the system decreases to < 10 µtorr. After reaching a stable vacuum, the LN$_2$ is removed and the liquid is allowed to slowly warm up. The flask valve can be shut once the pressure reaches a few hundred µtorr. As the frozen CH$_3$I becomes liquid, if bubbles are seen escaping the liquid, this is an indication that some high-volatility gases were still trapped in the solid
phase, and the freeze-pump-thaw cycle should be repeated until no such bubbles are seen upon thawing of the solid. Following preparation of the sample, the liquid should be shielded from all light sources to slow down the photolytic decomposition of CH$_3$I. After a few days, if the sample has a yellow tint, this is an indication that some amount of decomposition has occurred. The sample should be disposed of, the flask rinsed out, and a new sample should be prepared.

A new gas mixture is prepared once the mixing manifold and tank have been evacuated to a satisfactory vacuum, usually after a minimum of 12 hours of turbopumping. The steps for making a 5ppm CH$_3$I / 1.5% O$_2$ / 10% He / balance Ar mixture are shown in Table 2.1. During the entire process, the mechanical stirrer is constantly moving to enhance mixing and reduce stratification of the different component gases. The primary source of uncertainty in preparing gas mixtures is the accuracy of the pressure gages. Based on company literature and assuming a room-temperature deviation of $\pm 2^\circ$C, calculated uncertainties in a calibrated Baratron range from 0.13%, 0.16%, 0.43%, and 3.22% of the reading for measurements at full scale (F.S.), 10% F.S., 1% F.S., and 0.1% F.S., respectively. To minimize uncertainties, the goal is to keep the smallest pressure measurement as large as possible within the range of the available gages. To this end, the pressures in steps 1 and 4 are kept fairly close to one another. Otherwise, one of them will be smaller and incur an increased potential for error. As mentioned in the previous section, while the high-pressure mixture cools down the pressure will drop slightly. The tank is closed-off at this point, so the Setra pressure reading before and after mixing should be noted as an indication of the relative change in the final pressure reading from steps 2 and 7.

Initially, a short mixing time, $\sim$1-2 hours, was used in step 8. However, incomplete mixing was suspected due to the initial low OH yields which slowly increased over the first few shocks of the mixture. Experiments run with mixtures containing C$_2$H$_6$ rather than CH$_3$I gave consistent results, lending confidence that loss of CH$_3$I to wall adsorption was not a significant problem. Therefore, the conclusion was that the stratification of the gases during filling and the short mixing time precluded complete mixing of the gases. The procedure in Table 2.1 was therefore adopted for all low-concentration experiments in Chapter 3.
2.2 OH laser absorption diagnostic

Concentration time-histories of OH were measured using cw laser absorption of transitions in the A-X(0,0) system near 306.7nm. The laser absorption technique for OH was initially developed in our laboratory [38] and has been steadily improved upon, including studies of line shape owing to collision broadening [39] and collision shift (see Appendix B). The R₁(5) transition is most commonly used due to its isolated lineshape and high linestrength over a range of temperatures at typical shock tube conditions, although other nearby transitions have also been used in this work as a check of the spectroscopic database and experimental procedures.

2.2.1 Experimental setup

The diagnostic layout is shown in Fig. 2.1. A diode-pumped solid-state laser (Coherent Verdi or Spectra Physics Millenia at 5W of cw 532nm radiation) is used to pump a frequency-doubled Spectra Physics 380 dye laser operating on Rhodamine 6G dye, producing several mW of UV light. Typically 4-6 mW of UV was available, although anywhere from 7 to more than 10 mW has been achieved. The UV power output is highly dependent on the age of the dye, condition/cleanliness of the doubling crystal and other cavity optics, and the configuration, alignment, and focus adjustments of the cavity optics. While the UV power is sufficient, the laser cavities in use in our laboratory are nearing 15 to 25 years in age and they are no long capable of producing the same power levels as when they were new, probably due to aging and obsolete intracavity optics and cavity mirrors. The laser cavity has been modified by previous workers to permit rapid-tuning of the laser frequency [40], a feature used in the collision-shift and -broadening measurements described in Appendix B. Portions of the visible light output from the cavity are used to monitor laser wavelength, mode quality, and power. The fundamental laser wavelength is measured with a Burleigh Instruments WA-1000 Wavemeter®, and the mode quality is visualized using a 2 GHz free spectral range (FSR) Burleigh Instruments confocal scanning interferometer (spectrum analyzer) and RC-46 spectrum analyzer controller.

The detection layout at the shock tube is similar to a setup suggested by Petersen [41] in his high pressure work. Before entering the shock tube, the UV laser output is
split into two beams using a beamsplitter with a coating that gives 27% reflection. Each beam is focused onto a fast-response Silicon photodiode/amplifier package, and the intensities in the two beams are balanced by adjusting the angle of a neutral density filter placed in one beam’s path. The balanced signals provide common-mode noise reduction, typically yielding at least a factor of 10 improvement in RMS baseline noise. Previous laser absorption designs used uncoated UV fused silica beamsplitters to split off ~5% of the laser beam before and after the shock tube. The angle of the beamsplitters (and therefore the collection lens and detector position) were adjusted to balance the detector signals. The new design has the advantage of decreasing the number of polarization-sensitive optics on the exit side of the shock tube (much more important in very high pressure experiments than in the current work), and increasing the laser power on the detectors. In general, higher laser power on the detectors is always beneficial (up to the point of damaging the detectors), as it lifts the signal above the noise floor of the detector/amplifier electronics and permits lower gain/higher bandwidth settings. Balancing is also made much easier by the angle-adjustment of the neutral density filter, enabling fine tuning of its fractional transmission. An iris in each beam path blocks secondary reflections of the laser beam from entering the lens and detector, and Brewster-angled UG-5 Schott glass filters placed in front of the detector faces reduce noise from background light sources and shock tube emission. The detector signals are then digitized and stored for analysis in an 8-channel, 12-bit, 10 MHz sample rate (20 MHz maximum in single-channel mode) Gagescope data acquisition system and computer.

A low-pressure (~25 torr) microwave discharge in a flowing cell of He and water vapor produces low concentrations of OH and is used as a spectrally unshifted reference for the line-center absorption wavelength of the desired OH transition. This cell, shown in detail in Fig. 2.2, was built primarily for use in collision-shift measurements where the laser wavelength was rapidly tuned over the entire absorption lineshape. It was also utilized for some fixed-frequency measurements and to check the Wavemeter calibration, as described below.

The flowing cell is constructed from 0.5” O.D. Pyrex tubing, with O-ring-sealed “T” fittings at either end. The fittings are machined to Brewster’s angle and U.V. fused silica windows are epoxied to the fittings to form the ends of the cell. Helium gas at ~1
atm flows through a glass saturator (a “bubbler”) containing liquid water and then into one end of the cell. A vacuum pump constantly evacuates the cell through the other end, and a needle valve between the saturator and cell controls the pressure in the cell as measured with an MKS Baratron 100-torr capacitance manometer, model 122AA-00100AB, and displayed on an MKS PDR-D-1 readout. A ball-type shut-off valve isolates the cell from the vacuum pump when not in use. The UV beam is sampled before and after this reference cell and the light is detected by matched UV-enhanced Si photodiode/amplifier packages.

The reference cell was used in the following manner. In a fixed-frequency experiment the Wavemeter enables rough tuning of the laser wavelength, while prior to each experiment the laser is finely tuned (within a laser cavity mode spacing of 0.016 cm\(^{-1}\) in the UV) to the peak absorption in the reference cell. This method provides an absolute calibration of the laser wavelength at the time of the shock to the (near) vacuum line-center wavelength of the desired OH transition, \(\nu_0\). The benefit of using the reference cell is that it eliminates any absolute errors in the Wavemeter reading due to slight misalignment or poor resolution. If the absorption transition’s line-center wavelength at shock tube conditions is significantly different than at vacuum, based on knowledge of the collision shift (see Appendix B), the Wavemeter can be used to make relative adjustments in the laser wavelength.

The Wavemeter has an estimated uncertainty of \(\pm 0.017\) cm\(^{-1}\), dominated by the uncertainty in the reference laser’s wavelength of \(\pm 500\) MHz [42]. The precision of the Wavemeter’s readout is 0.01 cm\(^{-1}\). Over several experiments, comparison of the Wavemeter reading to the known vacuum line-center wavelength (as determined by peak absorption in the OH reference cell) was typically quite consistent within the Wavemeter readout precision of \(\pm 0.01\) cm\(^{-1}\); and after some time the Wavemeter was trusted as the primary reference. However, caution must be observed during the alignment of the laser beam into the Wavemeter. Observations confirmed that, for accurate readings, the incoming beam should be aligned with the output HeNe laser beam over a distance of at least 1 m before entering the Wavemeter. Slight misalignment, while still enabling the Wavemeter to produce a reading, can cause errors on the order of 0.01-0.02 cm\(^{-1}\). This translates into errors of 0.02-0.04 cm\(^{-1}\) in the frequency-doubled laser beam, resulting in
potential absorption coefficient errors of up to ~ 6% (at 1800 K, 1.4 atm) if the error is not accounted for.

2.2.2 OH diagnostic improvements

A few improvements to the laser absorption diagnostic have been implemented during this work, including a new pump laser, large area detectors, a careful review of the calculation of spectral absorption coefficients (given in Chapter 3 and Appendix A), and the diagnostic layout described above. The Coherent Verdi solid-state pump laser has considerably lower noise, better power stability and pointing stability, and easier day-to-day operation than the previous Ar+ pump lasers. The improved power stability and pointing stability, in particular, greatly improve dye laser operation because the incoming pump beam is stable over time and between activity cycles on different days. The lower noise spectrum amplitude of the solid-state laser and the absence of the low-frequency intensity noise often seen on the older Ar+ lasers both translate into lower noise on the dye laser output beam. This, in turn, results in quieter absorption signals. Measurements of the two pump laser sources indicated 0.63% RMS noise for the Ar+ laser compared to 0.068% RMS noise for the Coherent Verdi laser. The frequency-doubled dye laser output, when pumped by each of the lasers and carefully balanced to achieve common-mode noise rejection, yielded an improvement of more than a factor of 5 in RMS noise in the pre-shock regime, from 0.38% absorption noise with the Ar+ laser to 0.063% noise with the new solid-state laser. This RMS noise level represents the detection limit for OH at a signal/noise ratio of 1. A large portion of this improvement is due to the higher available laser power from the new solid-state pump laser compared to the aging Ar+ laser.

The change in pump laser sources also affects the performance of the dye. Due to the higher absorption coefficient of Rhodamine 6G dye (R6G or Rhodamine 590) at 532 nm compared to the multiple wavelengths in the Ar+ pump lasers, the standard dye concentration should be decreased in order to maintain the desired 80-90% absorption of the pump beam by the dye jet. This change in dye concentration vs. absorption for the two pump lasers was verified experimentally by measuring the laser power transmitted through the dye jet. Pure ethylene glycol was circulated in the laser, and concentrated
dye solution was added in steps while the transmitted laser power was observed. The optimal dye concentrations for 88% absorption in the dye jet were found to be 0.33 g/L and 0.97 g/L for the 532 nm laser and the multi-line output of the Ar+ laser, respectively.

It should be noted that other dyes and concentrations may be used with success. For example, increasing the dye concentration will typically red-shift the wavelength peak of the fluorescence curve. The benefit of shifting the peak must be weighed against the possibility of decreases in performance and stability as we move away from the optimum concentration for a given dye/solvent/pump power and wavelength combination. The best dye selection for a specific application is one which balances high fluorescence yield at the desired laser wavelength with dye lifetime and cost. While both Rhodamine B (RB or Rhodamine 610) and R6G were considered for this work, R6G was typically used to take advantage of its long lifetime and relatively high fluorescence yield. Because R6G has a peak fluorescence yield near 590 nm, red-shifting the dye or using a combination of R6G and RB may actually give improved dye laser output power. This combination was not attempted here.

The detectors used for the reference and transmitted beams have also been updated to specially built large area detectors. The photodiodes are Hamamatsu S1722-02 UV-enhanced Si with a 4.1-mm-diameter active area, and were mounted in PDA-55 amplifier packages by ThorLabs, Inc. The photodiode’s window surface was not sandblasted to reduce etalon effects in the detector window during scanned-wavelength experiments, as some previous detectors have been. Rather, the detectors were placed at a slight angle to the oncoming beam to destroy any potential etalon effects. The large diode area reduces sensitivity to beam steering caused by the passing shock wave and flow disturbances. The amplifiers include integrated adjustable gain and, simultaneously, frequency bandwidth, permitting rough optimization of the signal-to-noise for a given laser input power and time-response requirement. The detector/amplifier combination yielded a maximum bandwidth of 10 MHz at the lowest gain setting.

2.3 O-atom ARAS diagnostic

Atomic resonance absorption spectroscopy (ARAS) measurements in shock tube chemical kinetics research are well established and have been recently reviewed [43,44].
The discussion in the following sections will pertain only to the present diagnostic setup. Design, optimization, and modeling of the ARAS diagnostic and its comparison to previous ARAS work are given in Appendix D.

2.3.1 Experimental setup

Oxygen atom concentrations were measured using an ARAS setup similar to that used earlier in our laboratory [45-47]. The layout of the diagnostic is shown in Fig. 2.3. The ARAS lamp is constructed of a 0.5” outer-diameter medium-wall Pyrex tube, inserted into the shock tube port with a trapped O-ring creating the vacuum seal on the tube’s outside diameter. A gas mixture of 1% O₂ / He flows into the port through a drilled hole, enters the Pyrex tube near the shock tube window, and flows out away from the shock tube. The gas pressure is measured by a 100-torr MKS Baratron 122AA-00100AB capacitance manometer mounted at the end of the Pyrex tube with an O-ring “T”-fitting, and the lamp is continuously pumped by a CENCO Hyvac 7 mechanical pump through 0.5” diameter gas lines and a molecular sieve foreline trap. A shut-off ball valve between the lamp and the vacuum pump provides isolation when the pump is not running. The lamp was run at a pressure of 6 torr for all experiments in this work, although other lamp pressure/gas mixture combinations were investigated. Lamp pressure is controlled by throttling the flow with a needle valve located between the gas cylinder and the lamp. The high gas flow rate through the lamp is limited only by the pumping speed.

An Opthos Instruments McCarroll-type microwave discharge cavity [48] and model MPG-4-260 microwave power supply are used to create the discharge in the gas at an input power of 70W. The discharge cavity is cooled by a strong flow of compressed air: a regulator pressure of ~ 53 psig (when flowing) connected to ~ 30’ of 1/4” diameter tubing and unrestricted flow into the discharge cavity. A 0.7-meter SPEX 1500SP vacuum UV monochromator is used to isolate the resonant radiation from the atomic oxygen triplet $^3S^0 \rightarrow ^3P$ transitions at 130.22, 130.49, and 130.60 nm, rejecting emitted radiation from minor lamp gas impurities and other O-atom emission lines. The inlet and outlet slits were set to 3 mm (the maximum adjustable width) to maximize light collection, giving a spectral acceptance bandwidth of 3 nm. High-resolution (smaller slit
monochromator scans of the lamp output emission indicate negligible non-resonant emission within this spectral bandwidth. The radiation is detected by a Hamamatsu R1259 solar-blind photomultiplier tube (PMT) mounted in a vacuum-capable housing from Products for Research, Inc. The window of the PMT forms a vacuum seal with an O-ring in the housing. The entire volume including the shock tube outlet port, monochromator, up to the PMT window was evacuated using a Duo Seal 1397 mechanical vacuum pump to ~ 10 mtorr ultimate pressure. Input and output slits with 1.5-mm widths installed next to the shock tube windows limit the measurement time resolution of the system to ~ 3 μs. The inlet port has a 2 mm thick, 0.75”-diameter MgF₂ plane parallel window and the outlet port has a 0.75”-diameter plano-convex MgF₂ lens with a focal length of 11 cm at 130 nm (nominally 15 cm at 248 nm), both mounted so that the flat optical face is flush with the shock tube inner radius.

The PMT was powered with a Stanford Research Systems PS350 low-noise high-voltage power supply, typically set near 440V. The PMT output was connected to a 1000-ohm load resistance, amplified by a gain of 10 and low-pass-filtered to 300 kHz in a Stanford Research Systems SR560 preamplifier, and finally captured by the Gagescope data acquisition system for analysis. Care was taken to limit the anode output current to less than 1/20 of the input current to the dynode chain to ensure linear performance of the PMT.

2.3.2 Calibration

The ARAS diagnostic was calibrated using three different gas mixtures: 3 ppm, 9 ppm, and 31 ppm N₂O / Ar. Rather than only using the O-atom plateau as has been done in previous studies [49], the current work also relies upon the well-studied rate coefficient for the decomposition of N₂O. Model calculations use the rate coefficient from a composite fit performed by Ross et al. [49] of 6 independent ARAS studies of the N₂O decomposition reaction, with a mean deviation of ± 26%. The entire absorption trace is utilized for calibration purposes, and mapped to a calculation of [O] vs. time. This mapping was performed for all 17 calibration experiments, and the entire data set was plotted as absorbance \( ABS = \sigma_{O-atoms} \times [O] \times L \) vs. [O], sometimes referred to as a curve of growth (COG). The slope of this curve is proportional to the O-atom absorption cross-
section, $\sigma_{O\text{-atoms}}$. That the kinetic calibration procedure has reasonable uncertainty was verified by comparing the absorbance of the O-atom plateau (which is insensitive to the kinetic rate) in the 3 ppm experiments with the early part of the rise in the 9 ppm experiments, and a similar comparison of the 9 ppm and 31 ppm N$_2$O experiments. Each of these comparisons agrees within 5%, indicating that the N$_2$O decomposition rate might be in error on the order of 5%. The use of the entire O-atom traces allows averaging over many points to create the curve of growth, while limiting the actual number of experiments. Calibration measurements over the range 1460-2480 K indicated no measurable dependence of the absorption cross section on temperature. Estimated uncertainties for this calibration method are ±10% based on the comparison of the O-atom plateaus and other small uncertainties. The composite COG data are shown in Fig. 2.4, as is a 5th-order, zero-constrained fit to the data. Transforming this into a relationship for the O-atom absorption cross section yields:

$$\sigma_{O\text{-atoms}} = 2.8161 \times 10^{-16} \, AB^4 - 8.2967 \times 10^{-16} \, AB^3 + 4.8263 \times 10^{-16} \, AB^2 - 1.7767 \times 10^{-15} \, AB + 5.5714 \times 10^{-15}$$

(2.1)

A linear fit of $AB < 0.3$ yields an O-atom cross section of $\sigma_{O\text{-atoms}} \sim 5.4 \times 10^{-15}$ cm$^2$, very close to $\sigma_{O\text{-atoms}} = 5.6 \times 10^{-15}$ at $AB = 0$ from Equation (2.1).

2.3.3 Absorption by other species

The absorption cross sections for N$_2$O and O$_2$ were determined and accounted for as part of the data reduction process. For each experiment, the cross section of the secondary species was assumed to be independent of temperature. By measuring the transmitted intensity during the pre-shock ($I_1$) and incident shock ($I_2$) conditions and calculating the absorber concentration in each regime, we can back out the absorption cross section for species X and the baseline intensity ($I_o$) by applying the Beer-Lambert relation twice for $i = 1, 2$: $I_i/I_o = \exp(-\sigma_X[X]_i L)$. The measured signal is then converted into total absorbance: $ABS_{total}(t) = -\ln(I(t)/I_o)$. The absorbance due to O-atoms is found simply by subtracting the absorbance due to the secondary species from the total absorbance: $ABS_{O\text{-atoms}}(t) = ABS_{total}(t) - ABS_X(t)$. Here, $ABS_X(t) = \sigma_X[X]_5(t) L$ where $[X]_5(t)$ represents the concentration of secondary species X as a function of time. If the absorption cross section of species X is correct, then $ABS_{O\text{-atoms}}(t=0)$ should be equal to
zero. This was typically the case, although uncertainties in measuring $I_1$ and $I_2$ lead to some level of scatter in the data. For each experiment, $\sigma_k$ and therefore $I_o$ were adjusted slightly to force $ABSO_{O-\text{atoms}}(t=0) = 0$. Finally, the concentration of O-atoms is calculated using the absorption cross section determined in the calibration experiments: $[O-\text{atoms}] (t) = \frac{ABSO_{O-\text{atoms}}(t)}{(\sigma_{O-\text{atoms}}(ABSO_{O-\text{atoms}}) \times L)}$.

Experiments with O$_2$ yielded an absorption cross section $\sigma_{O_2} \sim 4.0 \times 10^{-19}$ cm$^2$, with a standard deviation of $0.17 \times 10^{-19}$, that was insensitive to temperature. When the $\sigma_{O_2}$ is actually adjusted to force the absorbance to be identical to zero at time zero, the average cross section was $\sigma_{O_2} \sim 4.3 \times 10^{-19}$ cm$^2$ with a standard deviation of $0.21 \times 10^{-19}$. This experimental value of $\sigma_{O_2}$ can be compared to the reported measurement by Bhaskaran et al. [3] of $\sigma_{O_2} = 5 \times 10^{-19}$ cm$^2$. For N$_2$O, the cross section was measured to be $\sigma_{N_2O} \sim 6.8 \times 10^{-17}$ cm$^2$, with a standard deviation of $1.7 \times 10^{-17}$ cm$^2$. This is comparable to the value from Bhaskaran et al. of $\sigma_{N_2O} = 6 \times 10^{-17}$ cm$^2$.

Table 2.1: Low-concentration mixture preparation procedure.

<table>
<thead>
<tr>
<th>Step</th>
<th>Process</th>
<th>Total pressure [torr]</th>
<th>Gage used</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Add minor constituent (CH$_3$I)</td>
<td>11.2</td>
<td>100 torr</td>
</tr>
<tr>
<td>2</td>
<td>Add second constituent (O$_2$)</td>
<td>5000</td>
<td>10,000 torr</td>
</tr>
<tr>
<td>3</td>
<td>Mix for 4 hours</td>
<td>~5000</td>
<td>Setra</td>
</tr>
<tr>
<td>4</td>
<td>Bleed slowly to 760 torr; pump slowly</td>
<td>11.2</td>
<td>100 torr</td>
</tr>
<tr>
<td>5</td>
<td>Refill second constituent (O$_2$)</td>
<td>75</td>
<td>100 torr</td>
</tr>
<tr>
<td>6</td>
<td>Add third constituent (He)</td>
<td>575</td>
<td>10,000 torr</td>
</tr>
<tr>
<td>7</td>
<td>Add bath gas</td>
<td>5000</td>
<td>10,000 torr</td>
</tr>
<tr>
<td>8</td>
<td>Mix overnight</td>
<td>~5000</td>
<td>Setra</td>
</tr>
</tbody>
</table>
Figure 2.1: Layout of the OH laser absorption diagnostic. Labeled optics are: (f), UG-5 Schott glass filter; (l), lens; (i), iris; (NDf), neutral-density filter; (b1), UV fused silica beam splitter; (b2), 27% beamsplitter; (p), thin-film polarizer.

Figure 2.2: OH absorption reference cell.
Figure 2.3: O-atom ARAS diagnostic layout.

Figure 2.4: O-atom ARAS calibration curve. Only a fraction of the complete data traces are shown here as symbols. Solid line is a zero-constrained 5th-order polynomial fit to all data.
Chapter 3: CH$_3$ + O$_2$ → products

This chapter discusses the shock tube experiments designed and performed for the measurement of the rate of the reaction CH$_3$ + O$_2$ → products. A unique combination of experiments is used to distinguish the individual rate expressions for the two high-temperature product channels important in combustion systems.

3.1 Introduction

The reaction of methyl radicals with molecular oxygen has two important product channels at combustion temperatures:

$$
\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{O} + \text{O} \quad (1a)
$$

$$
\rightarrow \text{CH}_2\text{O} + \text{OH} \quad (1b)
$$

Previous attempts to measure the rate coefficients of these channels are discussed in Chapter 1, with the significant result that the published rates vary greatly among different studies. This variance is in large part due to the inherent difficulty of distinguishing the action of one channel from the other in a typical combustion system. Both reactions are potentially controlling at the same point in the combustion process, and, without a priori knowledge of their rate coefficients, it is not possible to determine which might be dominant or whether they might share in the control of the process. The ambiguity in the knowledge of the relative rates of these reactions, as well as the underlying secondary chemistry, has prevented definitive measurement of the individual rate coefficients.

The present work overcomes these limitations by utilizing the similarity and difference in the product reaction pathways of channels (1a) and (1b). At combustion temperatures the methoxy radical (CH$_3$O) in channel (1a) will primarily decompose into formaldehyde (CH$_2$O) and an H-atom. In an environment of excess O$_2$, this H-atom will rapidly react with the O$_2$ to produce OH and O. At this point in the combustion process, both channels (1a) and (1b) have produced one CH$_2$O molecule and one OH radical,
whereas channel (1a) has additionally produced two highly reactive O-atoms. Experiments were designed to take advantage of these different product species.

The utilization of two separate diagnostics with unique kinetic sensitivities allows experimental determination of both $k_{1a}$ and $k_{1b}$. The approach involved two distinct steps. First, the overall rate coefficient, $k_1 = k_{1a} + k_{1b}$, was measured in experiments that were relatively insensitive to the branching ratio, $\alpha = k_{1a}/k_1$, and to secondary chemistry. In these experiments, the normalized OH rise time was measured in shock-heated ultra-lean CH$_3$I / O$_2$ mixtures. Having established a value for $k_1$, $k_{1a}$ was then determined in another set of experiments that was sensitive almost entirely to the rate of channel (1a). In these experiments, measured O-atom profiles were fit by adjusting $k_{1a}$ and holding the overall rate coefficient fixed. Brief iteration between these two sets of data quickly converged to self-consistent values for both $k_1$ and $k_{1a}$, from which an expression for $k_{1b}$ was determined.

3.2 Experimental apparatus

All experiments in this thesis were carried out in the shock tube facility described in Chapter 2. Concentration time-histories of OH were measured using cw laser absorption of the R$_1$(5) transition in the A-X(0,0) system near 306.7 nm as described in Section 2.2. Oxygen atom concentrations were measured using the ARAS setup and calibration described in Section 2.3. For each ARAS experiment, the calculated absorbance of O$_2$ or N$_2$O was subtracted from the total measured absorbance to yield the absorbance due only to the O-atoms.

3.3 Experimental details

3.3.1 OH laser absorption measurements to determine $k_1$

Experiments to determine $k_1$ were carried out in ultra-lean mixtures of CH$_3$I and O$_2$ using measurements of OH concentration time-histories. The four mixture compositions are given in Table 3.1. Other methyl-radical precursor species were also considered for this work. Ethane (C$_2$H$_6$) is a commercially available gas and very convenient to work with, however its usefulness would be limited to temperatures $> 2000$
K due to its slow decomposition rate. Azomethane ((CH₃)₂N₂) decomposes easily at low temperatures, but caution must be used as it may decompose and react behind the incident shock wave at higher temperatures. It is also inconvenient, in that azomethane cannot be purchased and must be synthesized in the laboratory. CH₃I was chosen for the entire set of experiments because it is easy to work with and its decomposition is well characterized at the conditions of interest for this study.

Mixtures were optimized to achieve good signal/noise, short OH rise times (< 100 µs) to minimize effects of boundary layer-induced changes in the reflected shock temperature and pressure, optimum sensitivity to and isolation of the overall reaction rate coefficient, and minimum sensitivity to the branching ratio as well as secondary reactions. Effects of O₂ vibrational relaxation were minimized by the addition of helium. Sensitivity analysis indicates that the initial rate of increase of the OH concentration is sensitive primarily to reactions (1a) and (1b). Specifically, the normalized rise time from 10-50% of the peak OH concentration, Δt(10-50%), yields high sensitivity to the overall rate coefficient k₁ and low sensitivity to the branching ratio α and secondary reactions. Therefore, the overall rate coefficient could be determined independent of an a priori assumption of dominance by either channel. Use of the 10-50% rise time gives almost identical sensitivities as does the half rise time, τ₁/₂, used in other recent investigations [12,24], with the added benefit that it is insensitive to small errors in the determination of time zero. Although several secondary reactions become important at the OH peak, normalizing the rise time by the peak mole fraction deemphasizes this sensitivity and allows reaction (1) to be well isolated.

An example brute-force sensitivity analysis calculated using the GRI-Mech 3.0 mechanism [37], updated with the new values for k₁a and k₁b and the heat of formation of OH given in Chapter 4, is shown in Fig. 3.1. Sensitivity of Δt(10-50%) for each reaction i was calculated by individually perturbing rate coefficients and using the following equation:

\[ S_i = \left( \frac{\Delta t(2k_i) - \Delta t(0.5k_i)}{2k_i - 0.5k_i} \right) \times \frac{k_i}{\Delta t(k_i)} \]  

(3.1)

For the sensitivity to α, kᵢ was replaced by α and the factors 2 and 0.5 were replaced by the multiplicative factors which made α = 1 or 0. As can be seen in Fig. 3.1, sensitivity
of $\Delta t(10\text{-}50\%)$ is dominated by the overall reaction rate $k_1$, and the sensitivity to the branching ratio $\alpha$ is approximately 1/10 the $k_1$ sensitivity. The secondary reaction uncertainties and their effect on the final reduced reaction rate coefficient are taken into account in the uncertainty analysis.

### 3.3.2 O-atom ARAS measurements to determine $k_{1a}$

To determine $k_{1a}$, experiments were performed using the mixture compositions given in Table 3.2. The experimental mixtures and conditions were chosen to optimize the sensitivity to reaction (1a), deemphasize reaction (1b) and other secondary chemistry, achieve good signal/noise (maximize O-atom absorption and minimize $O_2$ absorption), and reduce effects of vibrational relaxation of $O_2$. An example sensitivity calculation performed with the SENKIN program [50] is shown in Fig. 3.2. The O-atom concentration is strongly sensitive to the O-atom product channel, (1a), and only weakly sensitive to the OH product channel (1b) and secondary reactions.

The present O-atom experiments differ slightly from those in Michael et al. [16]. Whereas they used ~ 1.6-2.5 ppm $CH_3I$ / 6-11% $O_2$, the present mixtures use lower $O_2$ and higher $CH_3I$ concentrations. While this mixture choice gives slightly poorer kinetic isolation, there are several reasons for this selection of reaction mixtures. First, the larger diameter of our shock tube increases the absorption path length of all absorbers, including $O_2$. Because molecular oxygen has a very large absorption cross section at 130 nm, even with only 1.5% $O_2$ up to 38% of the lamp emission is absorbed by the $O_2$. Higher $O_2$ concentrations therefore decrease signal levels and thus the signal/noise ratio. Second, high $O_2$ concentrations result in increased vibrational relaxation effects on the temperature and pressure and degrade shock tube performance. The goal was to minimize both the temperature and pressure gradients as the $O_2$ relaxed vibrationally, as well as the relaxation time itself.

In the present study, by keeping $O_2$ concentrations low and adding 10% helium (He), these relaxation issues were minimized, and good confidence was maintained in the calculated temperature and pressure. The addition of helium reduces the vibrational relaxation time of a mixture of 1.5% $O_2$ / Ar at 1800 K, 1.4 atm from 32 $\mu$s to 4 $\mu$s, calculated for the mixture using coefficients from Millikan [51]. The addition of helium
also results in higher confidence in the temperature and pressure calculated from the normal shock equations, in that the post-incident shock gases are fully relaxed by the time the reflected shock returns, and the post-reflected shock gases quickly equilibrate before significant chemistry takes place. In addition, potential effects that vibrational non-equilibrium may have on the chemistry itself are avoided.

Higher CH$_3$I concentrations than in Michael et al. [16] were used due to the lower absorption cross section of our lamp configuration and also to minimize the relative effects of residual impurities in the gas handling system (see the next section).

3.3.3 Impurity issues

Ultra-lean, ultra-low concentration gas mixtures were required in this work in order to achieve high chemical isolation of and sensitivity to the title reactions. This means creating mixtures with ppm-level hydrocarbon concentrations and %-level oxygen concentrations. The obvious concerns with this situation are 1) the ability to make well-controlled accurate mixtures and 2) the potential effects of residual impurities in the gas handling system and shock tube. The mixture-making process was discussed in Section 2.1.3. The amount of residual impurities, their reduction and control, and their effect on the chemical kinetic measurements are discussed here.

Prior to the work on CH$_3$+O$_2$, experiments had been performed in this shock tube using a variety of large hydrocarbon fuels. In addition, hydrocarbon solvents, specifically acetone and methanol, are typically used to clean the shock tube walls. Because of the concern of hydrocarbon impurities, experiments for this work were initially performed with a mixture of 10% O$_2$ / Ar (no added hydrocarbon). In these experiments, a finite level of OH was measured using the OH laser absorption diagnostic. After a few more shocks, this level decreased somewhat as residual cleaning solvents were removed from the shock tube walls by the action of the shock waves and vacuum system; however, the level seemed to bottom out near 10 ppm OH at shock temperatures near 1800 K. In an effort to try to characterize the OH behavior and its source, model calculations with ~ 8 ppm CH$_3$ added to the mixture gave a reasonable match to the measured temporal behavior and plateau OH concentrations. This level of effective
“impurity” was clearly unacceptable for this work, and a plan was developed to find and fix the impurity source.

Impurities can only come from a limited number of sources in a shock tube system: the gas bottles, surfaces and semi-trapped volumes in the gas handling system (valves, piping, mixing tank, and connections of these components), the vacuum system (primarily backstreaming pump oil), and crevices and surfaces in the shock tube itself. To track down the general area of the impurity source, experiments were performed with pure O₂ while different parts of the system were bypassed. First, O₂ was flowed into the shock tube through the mixing manifold but without using the mixing tank. This resulted in a drop of the measured OH from 10.5 to 6.4 ppm. Next, the O₂ was connected directly to a port in the middle of the shock tube (bypassing the manifold), and the level dropped to near 1 ppm at 1700 K. When the oxygen cylinder was moved so that the gas flowed from the endwall back towards the diaphragm, no change was observed. This removed the possibility that the fill gases were sweeping residual impurity vapors from the whole tube length down to the endwall and amplifying their effect. This set of experiments quickly identified the mixing manifold and mixing tank as the most likely major sources of impurities. Supporting this conclusion was the observation that impurities seemed to increase over a few days’ time as a particular mixture remained in the mixing tank.

The gas mixing system was originally evacuated with only a two-stage direct-drive mechanical pump. This pump had an ultimate vacuum no lower than 1 mtorr (1x10⁻³ torr) at the pump and typically much higher vacuum at the farthest reaches of the system. This was now deemed to be unsatisfactory, and a new vacuum system was designed incorporating a turbomolecular pump. The new setup is described in Section 2.1.2. An effort was made to keep all vacuum lines as large in diameter and short in length as possible to improve system pumping speed, and the previous 100”-long ¼”-diameter fill line from the mixing manifold to the shock tube was replaced by a 40”-long 3/8”-diameter line. New vented stem inserts were installed in all of the bellows-sealed valves to reduce the possibility of slow-leakage of trapped gasses within the valve mechanism.

Vacuum performance of the rebuilt gas mixing system was greatly improved, with ultimate vacuum pressures of ~ 1 µtorr. New experiments with a 100% O₂ “mixture” in
the tank produced OH plateaus of ~ 2 ppm near 1750 K. A 10% O₂ / Ar mixture (similar to potential chemical kinetics experiments) yielded 0.8 ppm and 2 ppm OH near 1850 K and 2150 K, respectively. Mixtures with 0.32 ppm CH₃ and 0.8 ppm CH₃ “impurity” were sufficient to model the OH production. These impurity levels were now at or below previous experiments where the mixing system was bypassed – indicating that the major issues in the mixing system had been rectified.

Attempts were made to further reduce the impurity level. All shock tube ports were removed, cleaned, and replaced with the absolute minimum amount of vacuum grease required to maintain vacuum integrity. Both the shock tube and mixing tank were baked at high vacuum in an attempt to drive adsorbed impurity species from the walls and crevices of these vessels. These actions yielded negligible improvement, and in fact the impurity was typically temporarily worse until the baked-off species had been sufficiently eliminated from the system and everything settled back down to levels achieved before baking. Aluminum foil diaphragms 0.001” and 0.003” thickness were tried in place of the polycarbonate diaphragms, as the plastic has been known to shed measurable levels of H-atoms during the diaphragm burst process. This, again, produced little change in the effective impurity. Finally, gases with higher stated purity were used, including 99.9999% purity Ar (in place of the original 99.999%) and 99.999% pure O₂ (in place of the original 99.993%). Neither of these had a significant effect.

While the experimentally measured effects of the “impurities” were not completely negligible, they were significantly smaller and well-characterized with discrete but small levels of CH₃ (or H-atoms at the highest temperatures) added to the mixture. With a realistic assessment of our resources, the decision was made to accept the current performance of the system, characterize the impurity, and include it in the analysis for all future kinetics experiments. The issue would be revisited if it became a limiting uncertainty in this work.

Impurity effects were characterized independently for each gas mixture, using experiments with no added CH₃I. Both in OH and O-atom experiments, measurable radical concentrations were modeled with CH₃ radicals added to the nominal O₂ / Ar mixture. At the highest temperatures of this study (> 2400 K), the impurity behavior was modeled more closely with H-atoms as the surrogate (or real) impurity species. The
impurity effect was characterized as a function of temperature for each O₂ / Ar mixture, and the effect generally increased with temperature, O₂ concentration, and residence time in the mixing tank. For the latter reason, experimental mixtures were only used for 2 days and then discarded.

For each mixture composition, a separate identical mixture was made without CH₃I and experiments were performed to assess impurity effects on the OH or O-atom absorption measurements over the temperature range for that particular mixture. Measured effects in OH experiments could typically be modeled by < 1.5 ppm “impurity” CH₃, and had < 7% influence on the final measured value for k₁. At the highest temperatures of this study, the impurity was modeled by 1-2.5 ppm H-atoms. In O-atom experiments with a 1.5% O₂ / 10% He / Ar mixture (no CH₃I), ~ 0.6 ppm CH₃ was included in the model calculations, and had a small effect, typically 10-20%, on the final rate coefficient k₁₁a. The impurity level became a dominant uncertainty for k₁₁a only in the lowest concentration, lowest temperature measurements. Although the effect of the impurity is accounted for in the data reduction process, it is also included as an uncertainty.

3.3.4 Experiments

To determine k₁, 46 experiments were performed at temperatures and pressures ranging from 1570-2710 K and 1.07-1.88 atm. For k₁₁a, 33 experiments were performed at temperatures and pressures of 1590-2430 K and 1.10-1.45 atm.

Experiments were modeled using the GRI-Mech 3.0 mechanism [37], with the addition of the CH₃I decomposition reaction [52]. For this reaction and all 3-body reactions, M = He and O₂ were given relative rate coefficients (referred to as “enhanced third body efficiencies” in the Chemkin-II report [53]) equal to 1x and 1.4x the rate for M = Ar, respectively.
3.4 Data and results

3.4.1 Experimental data

The pressure trace and raw laser signals from a typical OH absorption experiment are shown in Figs. 3.3 and 3.4. The pressure trace is relatively flat for the first 1 ms, followed by a gradual increase in the pressure. This behavior was typical of experiments in Ar bath gas, and is an indication of some non-ideal gasdynamic perturbations to the shocked gas conditions (e.g. weak compression waves reflecting off of protruding surfaces in the shock tube, such as the diaphragm section, etc.). The laser signals are captured with the detectors set at a -3dB frequency bandwidth of 2.7 MHz, and sampled at 10 MHz with the Gagescope system. The laser signals indicate slow movement in the baseline laser power. This type of common-mode noise is easily compensated for, and the reduced absorbance trace, shown in Fig. 3.5 prior to any smoothing or averaging, is quite flat and well-behaved in the pre-shock regime. The pre-shock RMS noise level, calculated over the 1 ms previous to the incident shock arrival, is equal to 0.085% absorption. An example normalized OH data trace is shown in Fig. 3.6, along with model calculations performed with CHEMKIN-II [53]. The trace has been smoothed using a moving averaging window of width 2 µs, resulting in a pre-shock RMS noise level equal to 0.040% absorption. The overall rate, $k_1$, was adjusted to fit the experimental rise time $\Delta t(10-50\%)$ normalized to the peak mole fraction.

The raw PMT signal and the reduced absorbance for a typical O-atom ARAS measurement are shown in Figs. 3.7 and 3.8. These signals have been filtered with a 300 kHz low-pass filter in the pre-amplifier and sampled at a rate of 10 MHz. The absorption by molecular oxygen in the incident shock and reflected shock conditions is evident, and the absorbance baseline is compensated for absorption by molecular oxygen at the pre-shock initial conditions. At high absorbance, the relative noise increases due to the low signal levels. The absorbance given in Fig. 3.8, after subtraction of the absorbance due to O$_2$ and transformation into O-atom mole fraction through the ARAS calibration curve Equation (2.1), is shown in Fig. 3.9 along with model calculations. No smoothing has been performed on this signal; however it could have been smoothed to some extent without loss of information. The absorption by O$_2$ is evident in the incident and reflected
shock waves, although the negative magnitudes shown in this figure are meaningless. The overall rate coefficient $k_1$ was held fixed at the measured rate coefficient for this temperature (from the fit to all OH data) and the trace was fit by adjusting $k_{1a}$. Although the fit is quite good over the entire range of the measurement and is typical of all of the O-atom experiments, only the initial portion of the trace up to 225 µs was used to determine $k_{1a}$. Figure 3.10 displays the experiment from Fig. 3.9, but extended out to 1 ms of test time. The model compares favorably with the experimental data trace even at these longer test times, capturing the slight curvature shifts in the O-atom mole fraction growth. In the latter portion of the trace, the slight departure of measured $X(O$-atoms$)$ from the model indicates increasing sensitivity to secondary chemistry (see Fig. 3.2). Iteration between model fits of all OH experiments and all O-atom experiments by first holding $k_{1a}$ fixed, then $k_1$ fixed, results in final converged rate coefficients for both $k_1$ and $k_{1a}$.

3.4.2 Rate coefficient expressions and fit to the data

The derived values for $k_1$ from all OH experiments are shown in Fig. 3.11 and Table 3.1. A least-squares fit of the data was produced using the sum of two non-Arrhenius 3-parameter rate coefficient expressions, reflecting that $k_1$ is a sum of two individual rate expressions for $k_{1a}$ and $k_{1b}$. The procedure for fitting these data is described below. Also shown in Fig. 3.11 are the results from three recent experimental investigations [12,16,24] and a theoretical calculation [1]. The present study provides a direct measurement of $k_1$. In the other experimental investigations, $k_1$ was inferred from the final set of rate coefficients that were used to fit their data. The present work most closely matches Yu et al. [24] and Zhu et al. [1]. Inferred values for $k_1$ from Hwang et al. [12] and Michael et al. [16] are approximately 50% and 4 to 8.5 times lower, respectively, than the present study.

The present experimental values for $k_{1a}$ are shown in Fig. 3.12 and Table 3.2. The data were fit using a 3-parameter non-Arrhenius expression, based on the theoretical expression of Zhu et al. [1]. From transition state theory, the parameters in a rate expression of the form $k(T) = A*T^B*exp(-C/T)$ can be related to molecular properties of the reactants and the transition state, i.e. the molecular structure and vibrational
frequencies [54]. The parameters A and B are functions solely of the specific heat and the entropy, and can be calculated readily from molecular properties, whereas C includes the dissociation energy. While there is high confidence in the pre-exponential parameters, the parameter C is the least certain. For the fit of our $k_{1a}$ data, the Zhu et al. expression was used and only the parameter C was adjusted. Over the temperature range 1590K-2430K, the data are described by the expression $k_{1a} = 6.08 \times 10^{7} T^{1.54} \exp(-14005/T)$ cm$^3$ mol$^{-1}$ s$^{-1}$. The standard error of fit is $\pm 11.7\%$ (see Section 3.5.3). The C-parameter for $k_{1a}$ was adjusted only 730 K from the value of Zhu et al., C = 13275.5 K. Also shown in Fig. 3.12 are the measured rate coefficients from three recent experimental investigations and the theoretical calculation of Zhu et al. The present determination is directly in line with the measurement of Hwang et al. [12], and only 32% higher than the value from Michael et al. [16]. The above expression is 42-55% lower than Yu et al. [24], and 26-37% lower than the theoretical value of Zhu et al. in the overlapping temperature ranges.

The rate coefficient for the second channel, $k_{1b}$, can now be inferred from the measurements of $k_1$ and the fitted expression for $k_{1a}$. The entire OH data set for $k_1$ in Fig. 3.11 was fit using the sum of two non-Arrhenius expressions, one for $k_{1a}$ (fixed as determined above) and one for $k_{1b}$. Once again, the expression for channel (1b) from Zhu et al. [1] was used as a starting point, and only the C-parameter was adjusted. The least-squares fit to all 46 data points yields the expression $k_{1b} = 68.6 T^{2.86} \exp(-4916/T)$ cm$^3$ mol$^{-1}$ s$^{-1}$ with a $\pm 12.9\%$ standard error of fit (see Section 3.5.3). The C-parameter for $k_{1b}$ was adjusted only -199 K from the value of Zhu et al., 5115.4 K. This final curve fit for $k_1$ is shown in Fig. 3.11.

3.5 Discussion

3.5.1 Comparison to other studies

This study differs in several ways from earlier work on these reactions. Unlike previous determinations, by measuring $k_1$ in a manner that is mostly independent of $\alpha$, no a priori assumptions are made regarding the contributions of either channel in order to measure $k_1$. In most other investigations, the overall rate, $k_1$, and rates for the individual
product channels often depended, sometimes strongly, on the accuracy of the assumed rate coefficient for one of the channels. In addition, the use of very low CH$_3$I / O$_2$ ratios has enabled sensitive measurement of the overall reaction rate without significant sensitivity to secondary chemistry.

While the present expression for $k_{1a}$ is in agreement with Michael et al. [16] and Hwang et al. [12], the measurement of the overall rate $k_1$ and the inference of $k_{1b}$ represent a significant departure from these two studies. The present experimental rate expression for $k_{1b}$ is 2-3x higher than the rate used by Hwang et al. in the modeling of their data, and the dominance of channel (1b) in our study clearly disagrees with the conclusion of Michael et al. that this channel is unimportant.

A recent literature debate [55-57] centers on boundary layer-induced temperature effects in shock tube experiments, and the correction that has been systematically applied by some investigators [12,16] and not by others [24]. In CH$_4$ ignition experiments identical to Yu et al. [24], Hwang et al. [12] measure comparable characteristic OH induction times yet their published rate for $k_{1a}$ is a factor of 2.5x lower than Yu et al. In that study, the authors make the observation that the average applied temperature correction of 24 K, based on boundary layer interaction with the reflected shock wave, is the primary cause for the difference in their final rate coefficient for $k_{1a}$ compared to Yu et al. They further suggest that if the appropriate correction were applied to the experiments of [24], excellent agreement between the two studies is obtained. In the ensuing literature debate, the justification and reliability of a standard boundary layer-induced temperature correction was both refuted [55] and supported [56,57].

The very nature of the high sensitivity to temperature of the CH$_4$ ignition time studies (+24 K $\rightarrow$ 2.5x uncertainty in $k_{1a}$) calls into question their desirability as sensitive measurement of the title reactions. As pointed out by Michael et al. [56], experiments in ultra-low concentration CH$_3$I mixtures are much less sensitive to slight temperature changes than are CH$_4$ ignition experiments. Therefore, the use or non-use of boundary layer corrections had little effect on their final reduced chemistry. The same argument applies to the present study. In addition, the larger diameter of our shock tube (14.13 cm compared to 8.26 cm [24], 9.74 cm [16], and a rolled-square shock tube with diameter 6.35 cm [12]) results in smaller temperature effects due to the growth of the boundary
layer, as the perturbation is a surface-to-volume ratio effect [58,59]. Finally, all kinetic measurements in the present study were performed at experimental test times well under 200-300 µs, and thus any potential gas dynamic changes in temperature and pressure due to boundary layer growth are only in their early stages of development. For these reasons, systematic temperature corrections were not applied in this study and are believed to be of little consequence to the final rate coefficient expressions.

3.5.2 Constrained vs. unconstrained rate expression fits

The present fits to the experimental data, constrained by the pre-exponential coefficients of Zhu et al. [1], can be compared to similar curve fits without any constraints on the parameters. Performing an unconstrained 3-parameter fit of the \( k_{1a} \) data in Fig. 3.12 results in a standard error of fit similar to that for the constrained fit. An unconstrained 6-parameter fit of the \( k_1 \) data in Fig. 3.11 (fixing the expression for \( k_{1a} \) from the unconstrained fit) results in standard error of fit of 8.2%, compared to 12.9% in the final constrained fit using the Zhu et al. pre-exponential coefficients. The slight deviation of the \( k_1 \) fit from the data at high temperatures in Fig. 3.11 is due to the simultaneous constraint of the \( k_{1a} \) expression determined from the O-atom experiments and the Zhu et al. pre-exponential coefficients for \( k_{1b} \). The differences in the fitting parameters between the unconstrained and constrained fits are small, as evidenced by the almost imperceptible changes in the quality of the fits, and are well within the uncertainty bounds of the present measurements. Therefore, the pre-exponential coefficients from the theoretically-determined expressions of Zhu et al. have been retained, and the data is fit by adjusting only the C-parameter. Basing the fits on the theoretical calculations of Zhu et al. gives higher confidence in extrapolating the present rate expressions outside of the present experimental temperature range. The change in the C-parameter for \( k_{1a} \) represents an adjustment in the heat of formation of \( \text{CH}_3\text{O} \) of \( \approx +6.1 \text{ kJ/mol} \). This modification is on the order of previous uncertainties in the heat of formation [60]. The C-parameter for \( k_{1b} \) changed slightly from the value of Zhu et al., representing an adjustment in the barrier height of \( \approx -1.7 \text{ kJ/mol} \).
3.5.3 Uncertainty analysis

The confidence limits in the new rate expressions are evaluated from the scatter in the experimental measurements and an assessment of systematic uncertainties. The scatter in the data is characterized by the standard error of fit, $S_{yx}$, a measure of the precision with which a function $y(x)$ describes the behavior of the set [61]. Because the rate coefficient data span more than an order of magnitude, the deviation of an individual data point from the curve fit is considered as a percent deviation rather than an absolute number. The standard error of fit is calculated using Equation (3.2):

$$S_{yx} = \sqrt{\frac{\sum_{i=1}^{N} \left( \frac{y_i - y_{ci}}{y_{ci}} \right)^2}{\nu}}$$  \hspace{1cm} (3.2)

In this equation, $N$ is the number of data points; $y_i$ and $y_{ci}$ are the measured and curve fit values (rate coefficients) at a given value of the dependent variable (temperature); and $\nu$ is the degrees of freedom of the fit and is equal to $N - (m+1)$, where $m$ is the order of the polynomial used to fit the data. For our fit we have one free variable, similar to a 0th order polynomial, so $m = 0$. As previously mentioned, the curve fits of the data in Figs. 3.11 and 3.12 yield standard errors of fit of 12.9% and 11.7% for $k_1$ and $k_{1a}$, respectively.

Detailed assessments of the possible systematic errors for $k_1$ and $k_{1a}$ were performed for individual experiments at the high- and low-temperature limits of this study. These points typically represent the expected maximum-uncertainty conditions, as anticipated error sources limited the expansion of the experimental set to a wider range of temperatures. The error sources considered for this analysis are shown in Table 3.3. Potential errors are propagated through to their effect on $k_1$ or $k_{1a}$ through the technique of sequential perturbation [61]. In this technique, each independent variable’s uncertainty limits are individually applied to the data reduction process or chemical kinetic model (or both, in the case of temperature and pressure), and the fit parameter ($k_1$ or $k_{1a}$) is adjusted to refit the experiment in view of the perturbed conditions. The adjustment required in the fit parameter is therefore the uncertainty in $k_1$ or $k_{1a}$ from that perturbation of the independent variable. The absolute uncertainty contributions in the positive and negative direction for each variable are averaged to give the approximate total uncertainty contribution from that variable. Shown in Table 3.3 is an example
analysis for a $k_{1a}$ experiment at 2428 K. The individual contributions are combined using the root-sum-squares method, a calculation which is valid for uncorrelated errors which have all been estimated to similar probabilities (e.g. 95% probability that the true value falls within the ± error limits). For the specific example in Table 3.3, the total estimated uncertainty in $k_{1a}$ is ± 35%.

In Table 3.3, uncertainty limits in important secondary rate coefficients have been assessed based on a recent literature review and evaluation [62], the most current and accepted study of a particular reaction, and/or a comparison of the GRI-Mech 3.0 rate to the currently accepted rate coefficient. The reactions were each considered individually in the analysis.

An alternative method for estimating the uncertainties due to secondary reaction rate coefficients is to update all relevant reaction rate coefficients at once and refit the data using the revised mechanism. The base mechanism used in this work, GRI-Mech 3.0, is a set of reactions, rate coefficient expressions, and thermodynamic data based on a particular starting mechanism and modified through a constrained optimization process to fit a specific set of experimental targets [37]. The most recent optimization round was finished in 1998, and therefore does not consider new reaction rate data, thermochemical data, or experimental targets which have been published during the past six years. The proper method for updating the GRI-Mech mechanism is through another round of optimization, including a newly evaluated starting mechanism and potentially an expanded and updated set of experimental targets. This is a very time-intensive process, however, and beyond the scope of this thesis. Rather, a revised mechanism was created simply by updating rate coefficients for the secondary reactions important to this work.

To this end, an extensive literature review was performed for the most sensitive secondary reactions (based on sensitivity analyses performed in Sections 3.3.1 and 3.3.2), and out of this set 13 reactions were chosen to be revised. Information regarding the updated reactions is given in Table 3.4. For most reactions the recent review and evaluation by Baulch et al. [62] was accepted, except for the pressure-dependent CH$_2$O decomposition reaction rates which were taken from Friedrichs et al. [63]. Also, while the rate for CH$_3$ decomposition from [62] was accepted here, their evaluation did not consider the theoretical work on which the rate in [37] is based and does not include
pressure dependence. Changing this particular pair of rate coefficients appears to have a strong effect, so the new mechanism was applied both with and without a revision in the rate for CH$_3$ decomposition.

Evaluation of 5 experiments using the updated mechanism did not make a significant difference in the resulting rate coefficients, as shown in Table 3.5. While this exercise is one way to estimate about how differently an updated mechanism might behave, it is not a proper assessment of uncertainties for several reasons. First, it assumes that a correlated “uncertainty” is applied when making the unidirectional adjustment in all of the reaction rates to their new values. While new studies of these rates may, in fact, be closely connected to one another, the entire set of revised rates is not necessarily correlated. The new rates come from many different sources, some of which will be more accurate than others and more or less consistent with other experimental work. Second, this assessment does not take into account the true uncertainty limits applicable to each of the updated rate coefficients. Finally, GRI-Mech is a mechanism derived through optimization and is constrained to fit a large set of experimental data targets. Simply updating individual reaction rates to create a new mechanism ignores the desired result that the mechanism should best-fit a global set of data. For these reasons, the treatment of individual reaction uncertainties, as exemplified in Table 3.3, is accepted as the true contribution of secondary chemistry to the total uncertainties in $k_1$ and $k_{1a}$.

For the temperature range 1600 K to 2400 K, a conservative estimate of the uncertainty in $k_1$ is, on average, ± 22%, with little variation in this estimate at the lowest and highest temperatures. Similar analysis for $k_{1a}$ yields ± 33%. Systematic propagation of these uncertainties to $k_{1b}$ gives ± 27% at 1600 K and ± 41% at 2400 K, although this is considered to be somewhat conservative given the scatter in the experimental data. At the lowest temperatures, the uncertainty estimate is dominated by the reactions of formaldehyde with O-atoms and OH+HO$_2$→O$_2$+H$_2$O, impurity effects, and calibration of the ARAS system. At higher temperatures, uncertainty in reflected shock temperature and pressure and the ARAS calibration are dominant.
3.5.4 Secondary chemistry and OH peak sensitivity

The rate measurements of $k_1$ in this work are relatively insensitive to secondary chemistry, as discussed in the previous section. This chemical isolation is due, in part, to the normalization of the traces to the peak OH mole fraction. The normalization process sensitizes the rise time to the reactions of interest and deemphasizes the secondary reactions which control the peak OH mole fraction. However, the OH measurements in this study are, in fact, quantitative, and the comparison of the measured and modeled OH concentration time-histories may be able to reveal something about the most important secondary reactions. Several reactions have high sensitivities at the OH peak, with varying dependence on temperature, and together they control the peak OH mole fraction and the subsequent decay towards equilibrium.

Figure 3.13 depicts the deviation of the measured OH peak from the model calculations, expressed as a percentage of the modeled OH peak. The deviation ranges from -10% to +25%, and a clear non-monotonic temperature dependence is evident over five different reaction mixtures (including a 10 ppm CH$_3$I / 10% O$_2$ mixture not used in the $k_1$ determination). Sensitivity analyses were performed for the various mixtures over their respective ranges of shock tube conditions; the composite analysis in Fig. 3.14 displays the temperature-dependent peak OH sensitivity for the most important secondary reactions. As is evident in Fig. 3.14, multiple reactions have coincident, high sensitivities at the OH concentration peak. Many of these reactions also suffer from large uncertainties at these temperatures.

The information presented in Figs. 3.13 and 3.14 merits a closer examination in order to determine which reactions are most likely causing errors in the OH peak concentration. Some reactions can be immediately deemed unlikely culprits due to the temperature-dependence of their sensitivities, the magnitude or direction of their uncertainties, or both. The reaction $2\text{OH} \rightarrow \text{O} + \text{H}_2\text{O}$ has an estimated uncertainty of $\pm 25\%$ \[^{[62]}\], so although it displays the highest sensitivity in Fig. 3.14, it is unlikely that it is producing the size of errors plotted in Fig. 3.13. In addition, the highest sensitivities for this reaction are found above 1800 K where the OH peak error is decreasing towards zero. The two CH$_2$O decomposition channels also become sensitive only above 1900 K, where the OH peak error is small. Thus their uncertainties, while larger than those for
$2\text{OH} \rightarrow \text{O+H}_2\text{O}$, will not compensate for the highest OH peak errors located between 1650 K and 2050 K. The rate coefficients for the pair of HCO reactions, $\text{HCO+M} \rightarrow \text{H+CO+M}$ and $\text{HCO+O}_2 \rightarrow \text{HO}_2\text{+CO}$, are expected to change from the current GRI-Mech 3.0 expressions, but in equal proportions. The HCO decomposition reaction has been reported to be a factor of 2 slower than the GRI-Mech 3.0 rate [62,64], and the rate coefficient of the reaction $\text{HCO+O}_2 \rightarrow \text{HO}_2\text{+CO}$ was also recommended to be a factor of 2 slower than the value used in GRI-Mech 3.0 [62]. Thus, updating these two reaction rates together will have little net effect.

The reaction $\text{H+O}_2\text{+Ar} \rightarrow \text{HO}_2\text{+Ar}$ has been recently measured by Bates et al. [65], and its new rate expression is 50% of the GRI-Mech 3.0 rate expression. Updating this reaction, therefore, will make the OH peak error somewhat worse. On the other hand, the reaction $\text{OH+CH}_2\text{O} \rightarrow \text{HCO+H}_2\text{O}$ has recently been measured in our laboratory [66], and the new measurements confirm the evaluation by Baulch et al. [62] that the rate should be lowered by 50% from the GRI-Mech 3.0 value. This change will decrease the OH peak deviation.

The three remaining reactions in Fig. 3.14 are the most probable cause of the OH peak deviations shown in Fig. 3.13. This suggestion is due, in part, to their large uncertainties but especially because the temperature-dependence of their sensitivities closely matches the temperature-dependence of the OH peak deviation. The reaction $\text{OH+HO}_2 \rightarrow \text{O}_2\text{+H}_2\text{O}$ has large uncertainties stemming from limited high-temperature measurements and complex temperature dependence. At low temperatures, the reaction rate decreases with temperature, but this appears to change dramatically near 1250K to strong positive temperature dependence. Hippler et al. [67] observed this swing in temperature dependence, and while they do not provide an uncertainty for their measurements, the evaluation of Baulch et al. [62] suggests a factor of 3 uncertainty at these high temperatures. The rate of the reaction $\text{O+CH}_2\text{O} \rightarrow \text{OH+HCO}$ is based on a fit of the relatively well-established low-temperature data with one or more of the sparse high temperature data points – most of which come from flame or shock tube measurements fit using some type of chemical mechanism. There appears to be a lack of direct measurements; nevertheless, Baulch et al. [62] assign an uncertainty to this reaction of only a factor of 2. Finally, the reaction $\text{CH}_2\text{O+O}_2 \rightarrow \text{HO}_2\text{+HCO}$ has very
limited data of questionable reliability at the shock tube conditions of the present study. The existing shock tube measurements [16,68] indicate a higher activation energy than the limited low temperature measurements [69] and theoretical calculations [16,70] support. The evaluation of Baulch et al. [62] estimates the uncertainty to be a factor of 2 at 600K rising to a factor of 3 at 2500K.

These three reactions, along with some smaller potential contributions from the other reactions in Fig. 3.14, are most likely responsible for the OH peak deviation displayed in Fig. 3.13. However, their contributions as a function of temperature (i.e., their sensitivities multiplied by their errors) will not necessarily follow the same temperature dependence shown in Fig. 3.14, and several reactions will need to be adjusted.

Trial fits were performed by adjusting a specific secondary reaction or set of reactions to fit the OH peak, while readjusting k_1 to retain the fit to the normalized OH rise time. In general, these adjustments to fit the peak had less than ±15% effect on the measurement of k_1, but a consistent solution to the peak mismatch problem over a range of temperatures and mixtures could not be simply determined. To resolve the true adjustments required for the correct reactions, improved direct determinations for the rates of these secondary reactions, an optimization scheme, or both, could be undertaken. Potential directions for this work are discussed in Section 5.3.

3.6 Conclusions

The present work provides a direct measurement of the high-temperature channels of the reaction of CH₃ and O₂. Through choice of experimental conditions and use of dilute reactant mixtures and a sensitive OH diagnostic, the experiments are sensitive primarily to the sum of the two channels, (1a) and (1b), and relatively insensitive to the branching ratio. Having established values for k_1 that are independent of the individual channel rate coefficients, measurements of O-atoms provide a determination of k_{1a} and, consequently, k_{1b}.

The results of the current investigation can be compared to recent work in other laboratories. The values for k_1 presented here are within 10% of the k_1 values from Yu et al. [24] and calculations of Zhu et al. [1] over the entire experimental temperature range.
The expression for $k_{1a}$ is within 27% of both Michael et al. [16] and Hwang et al. [12]. However, the combination of our $k_1$ measurement and our $k_{1a}$ measurement is not consistent with the conclusion of Michael et al. that reaction (1b) is unimportant. Rather, our work suggests that over the entire range of temperatures studied, 1570-2700 K, channel (1b) is the dominant product channel. This conclusion is supported by Yu et al., Hwang et al., and Zhu et al., for whom channel (1b) is dominant up to 1870 K, 1800 K, and 2380 K, respectively.
Table 3.1: Experimental data for $k_1 \times 10^{10}$ cm$^3$mol$^{-1}$s$^{-1}$.

<table>
<thead>
<tr>
<th>13ppm CH$_3$I / 7.5% O$_2$</th>
<th>16ppm CH$_3$I / 6.3% O$_2$</th>
<th>20ppm CH$_3$I / 5% O$_2$</th>
<th>30ppm CH$_3$I / 2.5% O$_2$</th>
</tr>
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<tbody>
<tr>
<td>10% He / balance Ar</td>
<td>10% He / balance Ar</td>
<td>10% He / balance Ar</td>
<td>10% He / balance Ar</td>
</tr>
<tr>
<td>$T_5$ [K]</td>
<td>$k_1$</td>
<td>$T_5$ [K]</td>
<td>$k_1$</td>
</tr>
<tr>
<td>---------------------------</td>
<td>---------------------------</td>
<td>---------------------------</td>
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Table 3.2: Experimental data for $k_{1a} \times 10^{10}$ cm$^3$mol$^{-1}$s$^{-1}$.

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49
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<th>Uncertainty in $k_{1a}$ from negative perturbation</th>
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<tr>
<td>O+CH$_3$→Products</td>
<td>×1.25, ×0.75</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O$_2$+CH$_3$O$\rightarrow$HO$_2$+HCO</td>
<td>×2, ÷2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O+H$_2$→H+OH</td>
<td>×1.20, ×0.80</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Experimental uncertainties</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shock tube $T_5$, $P_5$</td>
<td>$T_5 \pm 0.87%$</td>
<td>-19.7%</td>
<td>19.7%</td>
<td>19.7%</td>
</tr>
<tr>
<td></td>
<td>$P_5 \pm 1.15%$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fitting (signal/noise)</td>
<td>$\alpha (= k_{1a}/k_1) \pm 3%$</td>
<td>3.1%</td>
<td>-3.1%</td>
<td>3.1%</td>
</tr>
<tr>
<td>Impurity estimate</td>
<td>+50%, -100%</td>
<td>-4.5%</td>
<td>9.0%</td>
<td>6.8%</td>
</tr>
<tr>
<td>Mixture concentration</td>
<td>± 0.021ppm CH$_3$I</td>
<td>0.0%</td>
<td>0.0%</td>
<td>0.0%</td>
</tr>
<tr>
<td></td>
<td>± 0.004% O$_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ARAS calibration</td>
<td>$\sigma$(O-atoms) ± 10%</td>
<td>-20.0%</td>
<td>20.0%</td>
<td>20.0%</td>
</tr>
<tr>
<td>$k_1 = k_{1a} + k_{1b}$</td>
<td>± 20%</td>
<td>-5.4%</td>
<td>5.9%</td>
<td>5.6%</td>
</tr>
</tbody>
</table>

Total R.S.S. Uncertainty: ±35%

---

<sup>a</sup> Not every experiment was sensitive to all sources listed.

<sup>b</sup> Actual source uncertainties were assessed for each individual experiment in the uncertainty analysis.
Table 3.4: Revised reaction rate coefficients.

<table>
<thead>
<tr>
<th>Reaction in GRI-Mech</th>
<th>New rate expression [cm$^3$mol$^{-1}$s$^{-1}$]</th>
<th>Source</th>
<th>$k_\text{new}/k_{\text{GRI}}$</th>
<th>$k_\text{new}/k_{\text{GRI}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1600K, 1.65atm</td>
<td>2400K, 1.15atm</td>
</tr>
<tr>
<td>O+CH$_3$→H+CH$_2$O</td>
<td>6.7x10$^{13}$</td>
<td>[62] a</td>
<td>1.33</td>
<td>1.33</td>
</tr>
<tr>
<td>O+CH$_3$→H+H$_2$+CO</td>
<td>1.7x10$^{13}$</td>
<td>[62] a</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>O$_2$+CH$_2$O→HO$_2$+HCO</td>
<td>2.44x10$^{2.5T}$exp(-18350/T)</td>
<td>[62]</td>
<td>0.76</td>
<td>1.44</td>
</tr>
<tr>
<td>H+O$_2$+Ar→HO$_2$+Ar</td>
<td>6.9x10$^{18T^{-1.2}}$</td>
<td>[62] b</td>
<td>0.51</td>
<td>0.43</td>
</tr>
<tr>
<td>H+HO$_2$+M→CH$_2$O+M</td>
<td>See reference</td>
<td>[63] c</td>
<td>0.99</td>
<td>0.65</td>
</tr>
<tr>
<td>H$_2$+CO+M→CH$_2$O+M</td>
<td>See reference</td>
<td>[63] c</td>
<td>1.88</td>
<td>1.70</td>
</tr>
<tr>
<td>OH+CH$_3$→CH$_3$(s)+H$_2$O</td>
<td>1.1x10$^{16T^{-0.9}}$exp(-275/T)</td>
<td>[62] d</td>
<td>0.50</td>
<td>0.56</td>
</tr>
<tr>
<td>OH+CH$_3$O→HCO+H$_2$O</td>
<td>1.39x10$^{16}$exp(-304/T)</td>
<td>[62]</td>
<td>0.48</td>
<td>0.33</td>
</tr>
<tr>
<td>HCO+M→H+CO+M</td>
<td>4.0x10$^{13}$exp(-7820/T)</td>
<td>[62]</td>
<td>0.54</td>
<td>0.69</td>
</tr>
<tr>
<td>HCO+O$_2$→HO$_2$+CO</td>
<td>2.7x10$^{10T^{-0.6}}$exp(236/T)</td>
<td>[62]</td>
<td>0.40</td>
<td>0.48</td>
</tr>
<tr>
<td>OH+HO$_2$→O$_2$+H$_2$O</td>
<td>9.27x10$^{5}$exp(-8810/T)</td>
<td>[62]</td>
<td>0.98</td>
<td>1.59</td>
</tr>
<tr>
<td>H+CH$_3$+M→CH$_3$+M</td>
<td>1.0x10$^{16}$exp(-45600/T)</td>
<td>[62] f</td>
<td>~8</td>
<td>~1.4</td>
</tr>
<tr>
<td>CH+H$_2$+M→CH$_3$+M</td>
<td>6.6x10$^{13}$exp(-42800/T)</td>
<td>[62] f</td>
<td>~8</td>
<td>~3.0</td>
</tr>
</tbody>
</table>

a The total rate for both channels is unchanged. The new branching ratio is 0.8/0.2 in [62] compared to 0.6/0.4 in GRI-Mech 3.0.

b Rate is given in $k_\infty$ [cm$^3$mol$^{-2}$s$^{-1}$]. $k_\infty = 6.02x10^{12}[0.321T^{0.56} + 2.9x10^4]$ [cm$^3$mol$^{-1}$s$^{-1}$]. $F_c$ = 0.51 for M=Ar.

c Use the fit to RRKM calculations in [63] for both channels. New rates are for the decomposition direction.
d Rate is given in $k_\infty$. Rate coefficient is pressure dependant. $k_\infty = 3.9x10^{16T^{-5.8}}$exp(485/T) [s$^{-1}$] and $F_c = 0.664$exp(-T/3569) + 0.336exp(-T/108) + exp(-3240/T). $k = [k_\infty / (k_\infty + k_\infty[M])]F_c$ for M=He, where

$$ \log F = \frac{[\log(1 - \log(\frac{k_\infty}{k_\infty} [M]) / k_\infty])^2}{0.75 - 1.27 \log F_c} $$

e GRI-Mech 3.0 has 2 rate expressions, which are added together for all temperatures. Here, only the high temperature (1300-2000K) expression is used from [62].
f New rate is written in the decomposition direction without pressure dependence.

Table 3.5: Effect of revised mechanism on reduced rate coefficients.

<table>
<thead>
<tr>
<th>T$_5$ [K]</th>
<th>P$_5$ [atm]</th>
<th>Mixture</th>
<th>Change in k$_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1604</td>
<td>1.88</td>
<td>13.28ppm CH$_3$I / 7.62% O$_2$ / 10.1% He / Ar</td>
<td>+13%</td>
</tr>
<tr>
<td>2432</td>
<td>1.21</td>
<td>30.1ppm CH$_3$I / 2.51% O$_2$ / 9.82% He / Ar</td>
<td>+3.8% (+11.3%) a</td>
</tr>
<tr>
<td>2709</td>
<td>1.07</td>
<td>30.1ppm CH$_3$I / 2.51% O$_2$ / 9.82% He / Ar</td>
<td>-2.8% (+17.0%)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>T$_5$ [K]</th>
<th>P$_5$ [atm]</th>
<th>Mixture</th>
<th>Change in k$_{1a}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1619</td>
<td>1.45</td>
<td>5.14ppm CH$_3$I / 1.51% O$_2$ / 10.0% He / Ar</td>
<td>+12.5%</td>
</tr>
<tr>
<td>2428</td>
<td>1.12</td>
<td>10.23ppm CH$_3$I / 1.53% O$_2$ / 10.6% He / Ar</td>
<td>-11.3% (+14.1%)</td>
</tr>
</tbody>
</table>

a Value in parentheses is the rate change when the GRI-Mech rate for CH$_3$ decomposition is retained.
Figure 3.1: Brute force sensitivity analysis for OH experiments at $T = 1800$ K, $P = 1.4$ atm using GRI-Mech 3.0 with the new values for $k_{1a}$ and $k_{1b}$. Mixture is 16 ppm CH$_3$I / 6.25% O$_2$ / 10% He / Ar.

Figure 3.2: O-atom sensitivity analysis at $T = 1800$ K, $P = 1.4$ atm using GRI-Mech 3.0 with the new values for $k_{1a}$ and $k_{1b}$. Mixture is 5 ppm CH$_3$I / 1.5% O$_2$ / 10% He / Ar. The six most sensitive reactions are shown.
Figure 3.3: A typical pressure trace from a shock tube measurement. Calculated conditions are $T_5 = 1811 \text{ K}, P_5 = 1.42 \text{ atm}$.

Figure 3.4: Raw data for an OH absorption experiment, showing the reference ($I_o$) and transmitted ($I_{\text{trans}}$) signals. The reference signal has been offset for the purpose of clarity.
Figure 3.5: OH absorbance trace resulting from the raw signals in Fig. 3.4.

Figure 3.6: An example OH experiment at T = 1806 K, P = 1.41 atm, derived from the traces in Figs. 3.4 and 3.5. Mixture is 16.1 ppm CH\textsubscript{3}I / 6.28\% O\textsubscript{2} / 10.2\% He / Ar. Calculated lines: bold solid line, k\textsubscript{1} = 1.05\times10^{10} \text{ cm}^{3}\text{mol}^{-1}\text{s}^{-1} and k\textsubscript{1a} = 2.35\times10^{9} \text{ cm}^{3}\text{mol}^{-1}\text{s}^{-1} (\alpha = 0.225) to fit both the OH rise time and subsequent O-atom measurements; bold dashed lines, k\textsubscript{1} ± 25\%.
Figure 3.7: PMT output signal from an ARAS measurement. The absorption by O₂ is evident immediately behind the incident and reflected shock waves.

Figure 3.8: The raw signal from Fig. 3.7 converted into absorbance. Absorption by O₂ at the initial conditions has been accounted for through adjustment of the baseline.
Figure 3.9: An example O-atom experiment at $T = 1846 \, K$, $P = 1.34 \, atm$, derived from the traces in Figs. 3.7 and 3.8. Mixture is $5.14 \, ppm \, CH_3I / 1.51\% \, O_2 / 10.0\% \, He / Ar$. Calculated lines: bold solid line, $k_1 = 1.35 \times 10^{10} \, cm^3mol^{-1}s^{-1}$ and $k_{1a} = 3.45 \times 10^9 \, cm^3mol^{-1}s^{-1}$ ($\alpha = 0.255$) to fit both the O-atom experiment and earlier OH rise time measurements; bold dashed lines, $k_{1a} \pm 25\%$.

Figure 3.10: The experiment from Fig. 3.9, extended out to 1 ms of test time. The model captures the shifts in the curvature of the O-atom mole fraction growth, even as sensitivity to secondary chemistry causes slight deviations in the traces at long test times.
Figure 3.11: Comparison of the present overall rate coefficient $k_1$, open squares and solid line, to other recent determinations.

Figure 3.12: Comparison of the present rate coefficient $k_{1a}$, open squares and solid line, to other recent determinations.
Figure 3.13: Comparison of measured OH peak concentrations to model calculations.

Figure 3.14: Secondary reaction sensitivities at the OH peak concentration.
Chapter 4: The heat of formation of OH

This chapter details a high-temperature measurement of the standard heat of formation of OH, Δ$_{f}^{298}$H$_{298}$(OH), using a shock tube. The unique experimental approach is presented, and the results are discussed and compared to previous values of the heat of formation.

4.1 Introduction

Various methods have been utilized to determine the heat of formation of OH and are briefly discussed in Chapter 1. In contrast to experimental studies at room temperature, the present work makes use of the partial equilibrium of reactions involving the OH radical behind reflected shock waves in H$_2$/O$_2$/Ar mixtures. In the partial equilibrium state, calculated OH concentrations are sensitive primarily to thermodynamic parameters and not reaction rates. Details on the partial equilibrium model can be found in Appendix E.

Six major species participate in the partial equilibrium state in H$_2$ / O$_2$ mixtures. Table 4.1 shows the heats of formation for these six species and an evaluation of their uncertainties [28]. Of the thermochemical parameters for these six species, Δ$_{f}^{298}$H$_{298}$(OH) has by far the largest uncertainty. The heat of formation of OH may therefore serve as a fitting parameter in comparisons of measured OH profiles to those calculated with either a kinetic mechanism or using the partial equilibrium model, with very little error due to uncertainties in other thermochemical parameters.

4.2 Experimental apparatus

All experiments in this thesis were carried out in the shock tube facility described in Chapter 2. Concentration time-histories of OH were measured using cw laser
absorption of the R₁(5) transition in the A-X(0,0) system near 306.7 nm as described in Section 2.2.

4.3 Review of OH spectral absorption coefficients

In the initial phase of the current work, a review of recent OH spectroscopic and molecular data was undertaken, and the method for calculating absolute absorption coefficients was carefully scrutinized. The absorption of spectrally narrow laser radiation as it passes through a uniform volume containing an absorbing species is related to the concentration of the species through the Beer-Lambert relation:

\[ T_\nu = \frac{I}{I_o} = \exp(-k_\nu P_{tot} X_{OH} L) \]  \hspace{1cm} (4.1)

Here \( T_\nu \) is the fractional transmission at frequency \( \nu \), \( I_o \) is the incident power, \( I \) is the transmitted power, \( k_\nu \) is the spectral absorption coefficient, \( P_{tot} \) the total pressure, \( L \) the path length, and \( X_{OH} \) the mole fraction of OH. The absorption coefficient is the product of the integrated line strength, \( S_{lu} \), and the line shape function \( \phi(\nu) \): \( k_\nu = S_{lu} \phi(\nu) \). The line strength of a given transition is dependent on temperature and molecular properties alone, whereas the line shape function is dependent on temperature, pressure, and collision partner species, with the functional dependencies changing for different transitions [71]. The integrated line strength can be most easily calculated in the form given by Goldman and Gillis [72]:

\[ S_{lu}(T) = \frac{1}{8\pi c \nu^2} \left( \frac{N}{P_{OH}} \right) \frac{\exp(-1.4388 E''/T)}{Q_{tot}} A_{ul}(2J'+1)[1-\exp(-1.4388 \nu/T)] \]  \hspace{1cm} (4.2)

Here \( J' \) is the upper-state rotational quantum number. In this equation, parameters that must come from measured or calculated values found in the literature are the transition frequency, \( \nu \), the lower-state rotational energy term value, \( E'' \), the Einstein A-coefficient, \( A_{ul} \), and the total internal partition function, \( Q_{tot} \). The most precise measurements of transition frequencies in the (0,0) band of the A-X system of OH have been performed by Stark et al. [73], which, at least for the R₁(5) transition, have not changed significantly from the earlier values given in Goldman and Gillis [72]. The values for \( E'' \) and \( A_{ul} \) (up to \( \nu'' = 2 \)) have been recently tabulated [74], the values for \( A_{ul} \) coming from calculations...
of relative transition probabilities [75] which are set on an absolute scale through an earlier radiative lifetime measurement [76] and tabulated in a software program [77]. The values for $E''$ are for the present purposes indistinguishable from those calculated and tabulated earlier in [72] and [73].

The total internal partition function, $Q_{\text{tot}}$, requires careful attention. Various levels of approximation are often invoked when calculating the partition function or its components, particularly if the different components are calculated separately ($Q_{\text{tot}} = Q_{\text{elec}}Q_{\text{rot}}Q_{\text{vib}}$) without proper regard for anharmonicity, vibration-rotation interaction, spin-splitting, and lambda-doubling. In the current work, only full summations over all relevant energy states or accurate polynomial representations of such summations were used in the calculation of the total internal partition function. The vibrational and electronic/rotational energies are calculated separately and added together for the final partition function summation. For the vibrational term values, fitted and tabulated Dunham coefficients [75] are used to calculate the vibrational term values up to $v'' = 13$. For the electronic/rotational component, the energy term values are calculated up to $J'' = 40.5$, using the appropriate formulas for the inverted, spin-split, lambda-doubled $X^2\Pi$ ground state [78] and molecular constants [75,79], including vibration-rotation interaction. The vibrational and electronic/rotational energy term values are added together, and a partition function summation is performed over all energy levels, up to $J'' = 40.5$ and $v'' = 8$, or enough to converge for the given experimental conditions.

A Voigt line shape profile is used for calculating the absorption coefficient at a given wavelength, utilizing the measured collision broadening [39] and collision shift coefficients (see Appendix B) for Ar. The collision width was verified in new experiments using Rea’s rapid-tuning technique [40] and found to lie within the combined error limits (see Appendix B). Uncertainty in the collision width is taken as the limits of the uncertainty bars in [39], $\pm 12\%$. Uncertainty in the collision shift has a negligible effect on the measured OH mole fraction at the conditions of this study.

4.4 Experimental conditions

The experiments were designed to be sensitive primarily to thermochemical parameters, rather than reaction rate coefficients, by taking advantage of the partial...
equilibrium state occurring at the end of the ignition process. Gas mixtures were prepared manometrically in a stainless steel mixing cylinder and mechanically mixed with a magnetically driven stirrer. Component gases were high-purity H₂ (99.999%), O₂ (99.993%), and Ar (99.998%). Reactant mixture composition was chosen on the basis of several factors. For good signal-to-noise and resolution, experiments ideally involved 40-80% peak absorption. To maintain confidence in the post-shock conditions, OH induction times were kept below 200 µs, and typically were much shorter. Mixtures were restricted to low concentrations to reduce effects of energy release. Finally, stoichiometries of Φ=0.5 (4000 ppm H₂ / 4000 ppm O₂ / balance Ar) and Φ=1.0 (8000 ppm H₂ / 4000 ppm O₂ / balance Ar) were used for the above reasons as well as their low sensitivities to reaction rate coefficients. Very rich or very lean mixtures display significantly increased sensitivity of the plateau X_{OH} to various rate coefficients, even at conditions producing a fairly flat “plateau”. The chosen stoichiometries provided a reasonably flat or slowly decaying OH profile over a somewhat broad range of temperatures.

4.5 Data and results

4.5.1 Experiments

In the present work, reflected-shock temperatures ranged from 1964 to 2718 K. Pressures typically ranged from 1 to 1.4 atm; however, one set of experiments was performed at higher pressures up to 2.4 atm to ensure insensitivity of the evaluated \( \Delta_f H^{298}_\text{f(OH)} \) to pressure. One additional experiment was also conducted using the R₁(6) absorption transition to check consistency of the spectroscopic database. Finally, a series of experiments was performed in which the laser frequency was rapidly tuned over the full lineshape. These data allowed us to verify the broadening coefficients, and the peak absorption of the lineshape provided an additional measurement of the OH plateau for comparison to fixed-frequency experiments.

Results of a typical fixed-frequency shock tube experiment are shown in Fig. 4.1. After a brief induction period the OH concentration rapidly increases and achieves a plateau value. At the conditions of Fig. 4.1, only a very slight decay of the OH is visible.
during the test time. The measured OH mole fraction, $X_{\text{OH}}$, is compared to a model calculation at constant T, P conditions. For the purposes of modeling the OH traces, the mechanism used was the H$_2$-O$_2$ subset of GRI-Mech 3.0 [2], along with its thermodynamic database. Other thermodynamics databases also were used in data reduction for comparison purposes. Calculations were performed using the Chemkin-II chemical kinetics simulation package [53].

4.5.2 Fitting the data

Each experiment was individually fit by adjusting the heat of formation of OH in the model thermodynamics until the calculated OH plateau matched the measured OH peak/plateau. In the NASA polynomial representation of $C_p(T)$ [80], a sixth term ($a_6$) is introduced as the integration constant for the calculation of $H(T)$:

$$\frac{H^o}{RT} = a_1 + a_2 \frac{T}{2} + a_3 \frac{T^2}{3} + a_4 \frac{T^3}{4} + a_5 \frac{T^4}{5} + \frac{a_6}{T}$$ (4.3)

This term is independent of temperature and therefore represents a constant offset in the enthalpy $H(T)$ for all temperatures. Fitting the model to the data involved adjustment of $a_6$ in the high temperature polynomial. The overall goodness of the fit is evident in Fig. 4.1. The effective change in $a_6$ (from its original value) was applied to the $a_6$ term in the low temperature polynomial. This adjusted low temperature polynomial was then used to calculate $H(298) = \Delta H^o_{298}(\text{OH})$. For the experiment of Fig. 4.1, $\Delta H^o_{298}(\text{OH})$ changed from the GRI-Mech 3.0 value of 9.403 kcal/mol to 8.887 kcal/mol.

4.5.3 Uncertainty analysis

A thorough uncertainty analysis was carried out for each of four experiments representing the full range of experimental conditions: high temperature, lower temperature, and higher pressure (all at $\Phi = 0.5$), and one experiment for $\Phi = 1$. For a given source of error, the uncertainty is applied to the data reduction and carried through to a change in the $X_{\text{OH}}$(measured) vs. $X_{\text{OH}}$(model). The various sources of error affected either the reduction of the raw absorption data to $X_{\text{OH}}$, the calculation of $X_{\text{OH}}$, or both. The difference in the offset of each of the measured and calculated peak OH mole fractions then represents the uncertainty in fitting the measured OH mole fraction due to
this source of error. The uncertainty in mole fraction from each source was combined with the uncertainty from all other sources of error in the peak mole fraction, assuming uncorrelated uncertainties. Finally, the combined total uncertainty in $X_{\text{OH}}$ is used to define an uncertainty in $\Delta_{f}H_{298}^{o}(\text{OH})$ for the given experiment.

The major sources of uncertainty and their effect on $\Delta_{f}H_{298}^{o}(\text{OH})$ are displayed in Figs. 4.2 and 4.3 for conditions near the experimental high- and low-temperature limits. For the nominal conditions (the conditions of Figs. 4.1 and 4.2) the dominant source of uncertainty is the absolute absorption linestrength ($\pm 2\sigma$ error = $\pm 2\%$). However, at lower temperatures and higher pressures, uncertainty in the collision-broadened linewidth becomes more important and contributes almost half of the total uncertainty. For linestrength, collision broadening, and collision shift, the uncertainty is taken directly from that reported in the literature and Appendix B. Uncertainty in the measured shock velocity was based on the measured variations in pressure transducer response and the quality of the shock trajectory fit, and was propagated through to uncertainties in $T_5$ and $P_5$ and on to an uncertainty in $\Delta_{f}H_{298}^{o}(\text{OH})$ (see Appendix C).

Uncertainty due to (or rather sensitivity to) reaction rate coefficients was determined by adjusting each individual rate coefficient in turn and determining its effect on the OH peak, with error limits taken from Baulch et al. [81] or more recent measurements/literature reviews. These calculations are plotted as a function of temperature in Fig. 4.4. It is clear from Figs. 4.2 and 4.3 that kinetics play no significant role in the determination of the peak mole fraction at these conditions. At the lower-temperature conditions of Fig. 4.3, the OH decays slightly faster and therefore the peak OH shows some increased sensitivity to the kinetics; however, the kinetic sensitivity is still negligible compared to the absorption linestrength and collision-broadening uncertainties. Below 1950K, sensitivity to kinetic rate coefficients rises significantly, thus setting the low-temperature limit for this experimental measurement strategy.

4.5.4 Results

Values of the heat of formation derived using the above methods are shown for all experiments in Fig. 4.5. Representative error bars are given for the two experiments of Figs. 4.2 and 4.3. Also displayed are lines representing the older and most recently used
values for $\Delta_f H_{298}^{\circ}$(OH) found in several databases. The Sandia database [82] incorporates $\Delta_f H_{298}^{\circ}$(OH) = 9.32 kcal/mol taken directly from the NIST-JANAF tables [32]. GRI-Mech 3.0 [37] uses $\Delta_f H_{298}^{\circ}$(OH) = 9.40 kcal/mol, which is the same as in the tables of Gurvich et al. [31]. The database by Burcat [83] uses $\Delta_f H_{298}^{\circ}$(OH) = 8.97 kcal/mol, which is calculated based on $\Delta_f H_0^{\circ}$(OH) = 8.83 kcal/mol [29] but uses a NASA polynomials and coefficients code (PAC) for the enthalpy increments [83,84]. The mean value over all our experiments is $\Delta_f H_{298}^{\circ}$(OH) = 8.92 kcal/mol (37.3 kJ/mol). This number is in close agreement with the value of Ruscic et al. [30], $\Delta_f H_{298}^{\circ}$(OH) = 8.91 ± 0.07 kcal/mol (37.3 ± 0.29 kJ/mol). Over the four experiments where detailed uncertainty analysis has been performed, the uncertainty assigned to our value is, on average, ± 0.16 kcal/mol (± 0.67 kJ/mol). Standard deviation from the mean (taken over all experiments) is 0.04 kcal/mol (0.17 kJ/mol).

To check for sensitivity to thermodynamic parameters other than $\Delta_f H_{298}^{\circ}$(OH), two other chemical kinetics thermodynamics databases were used to reduce all experiments. The change in the reduced $\Delta_f H_{298}^{\circ}$(OH) using these different databases is shown in Fig. 4.6. The average value of $\Delta_f H_{298}^{\circ}$(OH) obtained using the Sandia database [82] was 0.01 kcal/mol higher, where the value inferred using the Burcat database [83] was 0.003 kcal/mol lower. Over the temperature range of the present measurements, the difference among these three databases increases monotonically with temperature so that the difference in the value of $\Delta_f H_{298}^{\circ}$(OH) derived using Sandia vs GRI-Mech 3.0 thermodynamics actually ranges from 0.003 to 0.018 kcal/mol over 1964-2718K. The difference using the Burcat vs. GRI-Mech 3.0 database ranges from -0.002 to -0.007 kcal/mol. This systematic variation in the reduced $\Delta_f H_{298}^{\circ}$(OH) with temperature is suggestive of differences in thermodynamic parameters due to varying levels of approximations used in their calculation. The similarities between the reduced values using the three databases indicate relatively good agreement for the thermodynamics and thermochemistry of the other species involved (H₂, O₂, H, O, and H₂O) as well as the sensible enthalpy and entropy calculations for OH.
4.6 Discussion

4.6.1 Verification of the sensible enthalpy

Because the experiments are fit at high temperatures, care must be taken to ensure the accuracy of the integration of the specific heat, $C_p$, from 298 K to the experimental temperature. An error in the sensible enthalpy, $H(T) - H(298)$, would lead directly to an error in the reduced $ΔfH^o_{298}$(OH). To examine the magnitude of this error, the total internal partition function, calculated previously, was used in the following formula to calculate $H(T)$:

$$H(T) = RT^2 \left( \frac{d \ln(Q_{\text{int}})}{dT} \right) + \frac{5}{2} RT$$

This calculation provided two interesting results. First, as asserted by Ruscic et al. [29,30] and given in tables by Gurvich et al. [31], the present calculation confirmed that the difference between $ΔfH^o_0$ and $ΔfH^o_{298}$ should be 0.06 kcal/mol, rather than the 0.14 kcal/mol in the NIST-JANAF table [32]. The NIST-JANAF table points out this discrepancy in the discussion, indicating that $H(0 \text{ K}) - H(298 \text{ K})$ should be -2.107 kcal/mol (-8.816 kJ/mol), not -2.192 kcal/mol (-9.172 kJ/mol) as given in the actual tables. Second, the current calculation of $H(T) - H(298)$ up to high temperatures (at least 3000K) yields excellent agreement with the careful calculations and tabulations of Gurvich et al. [31] and the polynomial fit expressions in the GRI-Mech 3.0 thermodynamics. At the highest temperature of the present study (2700K), the other three databases [32,82,83], agree with each other but are 0.03 kcal/mol lower than the present calculation. One might expect, therefore, that fitting the experimental OH data using these other databases may result in a maximum deviation of $ΔfH^o_{298}$(OH) on the order of 0.03 kcal/mol.

4.6.2 The OH absorption oscillator strength

The dominant uncertainty at the nominal conditions (see Fig. 4.2) is the absorption oscillator strength. While relative transition probabilities can now be calculated with high accuracy [75], the limitation on the oscillator strength is the measurement of the radiative lifetime of OH. Many measurements of this parameter have
been made; however, the value most often quoted is that by German [76], \( \tau_{\text{rad}} = 688 \pm 14 \) ns, where the uncertainty limits are \( \pm 2\sigma = \pm 2\% \). This uncertainty transfers directly to a \( \pm 2\% \) uncertainty in the absolute oscillator strength. An independent study by Dimpfl and Kinsey [85] has confirmed this lifetime measurement, yielding a published value of 686 \( \pm 14 \) ns. The present work has retained the \( \pm 2\% \) error bounds of German [76] in our own uncertainty analysis for \( \Delta_{f}H^0_{298}(\text{OH}) \).

It can be shown that any source of error which has a constant temperature-independent fractional effect on the measured OH concentration, such as an error in \( S_{\text{lu}} \) or the absorption pathlength, when applied across the whole temperature range of experiments would impact the data reduction of \( \Delta_{f}H^0_{298}(\text{OH}) \) in such a way as to create a temperature-varying value for \( \Delta_{f}H^0_{298}(\text{OH}) \). This is unphysical, and is a primary reason why data were taken over a range of temperatures. As no temperature dependence is evident in Fig. 4.5, the data provide relative assurance that any error in the integrated line strength is small enough to be hidden within the data scatter and other uncertainty sources.

4.6.3 Comparison to previous work

From Fig. 4.5, it is clear that the current work agrees with the most recent value of \( \Delta_{f}H^0(\text{OH}) \) from Ruscic et al. [30]. Their recommendation is \( \Delta_{f}H^0_{\text{a}}(\text{OH}) = 8.85 \pm 0.07 \) kcal/mol (\( 37.0 \pm 0.29 \) kJ/mol), yielding a value at 298K of \( \Delta_{f}H^0_{298}(\text{OH}) = 8.91 \pm 0.07 \) kcal/mol (\( 37.3 \pm 0.29 \) kJ/mol). Another recent study utilizes thermochemical cycle analysis alone to arrive at a similar value of \( \Delta_{f}H^0(\text{OH}) = 8.88 \pm 0.03 \) kcal/mol (\( 37.14 \pm 0.12 \) kJ/mol), yielding a value at 298K of \( \Delta_{f}H^0_{298}(\text{OH}) = 8.94 \pm 0.03 \) kcal/mol (\( 37.4 \pm 0.12 \) kJ/mol) [35]. The present study, using a method quite different from that of either [30] or [35], has found agreement with the new lower value for \( \Delta_{f}H^0_{298}(\text{OH}) \) given by both [30] and [35]. As in both other studies, the uncertainty in the present study is less than half of the difference between the old and new values, clearly differentiating it from the previous high values. Taking the average of all three studies, weighted by their uncertainties, yields a recommended value of \( \Delta_{f}H^0_{298}(\text{OH}) = 8.93 \) kcal/mol, with an uncertainty of \( \sim \pm 0.07 \) kcal/mol.
4.6.4 Implications

The reported change in $\Delta H_F^{\circ}(\text{OH})$ translates to a factor of $\exp\left[-\delta(\Delta H_f^o)/RT\right]$ change in rate parameters deduced from equilibrium constants and, of course, to equilibrium constants themselves. In addition, if the value for OH is used to deduce thermochemical parameters of other species, those parameters will also be affected. Some of these effects have been discussed by others [30,35].

4.7 Conclusions

The standard heat of formation of OH, $\Delta H_F^{\circ\,298}$(OH), has been determined from high temperature shock tube experiments. Measurements over the temperature range 1964 to 2718 K yielded an average determination of $\Delta H_F^{\circ\,298}$(OH) = 8.92 ± 0.16 kcal/mol (37.3 ± 0.67 kJ/mol), with a standard deviation in the measurement of $\sigma = 0.04$ kcal/mol (0.17 kJ/mol). The current study agrees very well with two other recent determinations of $\Delta H_F^{\circ\,0}$(OH) and corroborates the suggestion that the previously accepted values, $\Delta H_F^{\circ\,298}$(OH) = 9.32-9.4 kcal/mol, are in error.
Table 4.1: Heats of formation.

<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta_f H_{298}^{o}$ [kcal/mol]</th>
<th>Uncertainty [kcal/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>52.10</td>
<td>0.001</td>
</tr>
<tr>
<td>O</td>
<td>59.56</td>
<td>0.024</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>-57.80</td>
<td>0.010</td>
</tr>
<tr>
<td>OH</td>
<td>9.18</td>
<td>0.29</td>
</tr>
<tr>
<td>H$_2$</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>O$_2$</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Source: Burcat and Gardiner [28]

Figure 4.1: Experimentally measured and modeled OH mole fraction time-histories. Conditions are $T = 2590$ K, $P = 1.075$ atm, and the mixture is 4002 ppm H$_2$ / 3999 ppm O$_2$ / balance Ar. The OH concentration is modeled using GRI-Mech 3.0 and the GRI-Mech 3.0 thermodynamics database, with 0.5 ppm additional H-atoms to match the induction time. The fit required a change in $\Delta_f H_{298}^{o}(OH)$ from 9.403 to 8.887 kcal/mol.
Figure 4.2: Uncertainty analysis for the experiment in Fig. 4.1. Individual error sources were applied one at a time, and their effect on $X_{OH}(\text{model})$ vs. $X_{OH}(\text{measured})$ was noted. The total combined uncertainty in $X_{OH}$ was then used to determine an uncertainty in $\Delta H^\circ_{298}(\text{OH})$ for this experiment. All other kinetic rate coefficients (not shown here) gave uncertainties in $\Delta H^\circ_{298}(\text{OH})$ of less than $\pm 0.0012$ kcal/mol. The combined uncertainties in $X_{OH,\text{peak}}$ are $+2.40\% / -2.55\%$, which translates into $\Delta H^\circ_{298}(\text{OH}) = 8.89 +0.15 / -0.14$ [kcal/mol].
<table>
<thead>
<tr>
<th>No.</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Oscillator strength (+/- 2%)</td>
</tr>
<tr>
<td>2</td>
<td>Collision broadening (Δν +/- 12%)</td>
</tr>
<tr>
<td>3</td>
<td>Wavemeter reading (+/- 0.01 cm⁻¹ in the uv)</td>
</tr>
<tr>
<td>4</td>
<td>Collision shift (typically negligible)</td>
</tr>
<tr>
<td>5</td>
<td>Shock velocity measurement (T₁ and P₁ correlated)</td>
</tr>
<tr>
<td>6</td>
<td>T₁ measurement</td>
</tr>
<tr>
<td>7</td>
<td>P₁ measurement</td>
</tr>
<tr>
<td>8</td>
<td>Detection noise / data fitting</td>
</tr>
<tr>
<td>9</td>
<td>Mixture composition (sensor error, H₂ and O₂ correlated)</td>
</tr>
<tr>
<td>10</td>
<td>Estimated initial contaminants in tank</td>
</tr>
<tr>
<td>11</td>
<td>Estimated initial contaminants in shock tube</td>
</tr>
<tr>
<td>12</td>
<td>Addition of H-atoms in model to match τᵦ</td>
</tr>
<tr>
<td>13</td>
<td>H+O₂ → OH + O</td>
</tr>
<tr>
<td>14</td>
<td>O+H₂ → OH+H</td>
</tr>
<tr>
<td>15</td>
<td>OH+H₂ → H₂O+H</td>
</tr>
<tr>
<td>16</td>
<td>H+O₂+Ar → HO₂+Ar</td>
</tr>
<tr>
<td>17</td>
<td>2OH → O+H₂O</td>
</tr>
<tr>
<td>18</td>
<td>H+OH+M → H₂O+M</td>
</tr>
<tr>
<td>19</td>
<td>H+HO₂ → OH+OH</td>
</tr>
</tbody>
</table>

Figure 4.3: Uncertainty analysis for a low temperature experiment. Conditions are T₅ = 1999 K, P₅ = 1.272 atm, and the mixture is 4026 ppm H₂ / 4024 ppm O₂ / balance Ar. The combined uncertainties in X_OH,peak are +2.98% / -3.06%, which translates into Δ hdc^H(OH)_{298} = 8.92 +0.14 / -0.13 [kcal/mol].
Figure 4.4: Uncertainty in the measurement of $\Delta_h^f_{298}$(OH) due to kinetic rate coefficient uncertainties. The five most significant reactions are shown. The increase in OH plateau sensitivity to several reactions effectively places a low-temperature limit on the current measurement scheme.
Figure 4.5: Experimentally derived values for $\Delta f^\circ_{298}(\text{OH})$. (▲): Current data; Solid line: Mean of current data, $\Delta f^\circ_{298}(\text{OH})=8.92$ [kcal/mol]. Standard deviation from the mean is $\sigma = 0.04$. Previous values are given for reference.

Figure 4.6: Change in the measured $\Delta f^\circ_{298}(\text{OH})$ values when the data is reduced using two additional thermodynamic databases. Data in Fig. 4.5 was reduced using the GRI-Mech 3.0 thermodynamic database [37]. (■): Chemkin thermodynamics database [82]; (△): Burcat database [83].
Chapter 5: Conclusions

5.1 Summary of results

5.1.1 CH₃ + O₂ → products

The work presented in this thesis represents a unique experimental determination of the rate coefficient for the reaction CH₃+O₂→products and its individual high-temperature product channels:

\[ \text{CH}_3+\text{O}_2 \rightarrow \text{CH}_3\text{O}+\text{O} \quad (1a) \]
\[ \text{CH}_3+\text{O}_2 \rightarrow \text{CH}_2\text{O}+\text{OH} \quad (1b) \]

Through a combination of diagnostics which take advantage of the commonality and difference in the product channels and their subsequent reaction pathways, temperature-dependent reaction rate coefficient expressions for each individual reaction could be determined. This determination was completely experimental, with no \textit{a priori} assumptions required or imposed in order to resolve the product channel contributions.

The overall rate coefficient, \( k_1 \), was first determined in a series of experiments designed to be sensitive to \( k_1 \) but insensitive to the branching ratio, \( \alpha \), and secondary reactions. With \( k_1 \) established, a series of experiments was conducted with almost exclusive sensitivity to \( k_{1a} \). Brief iteration between the two series of experiments resulted in the following rate coefficient expressions for the temperature range 1590 to 2430 K:

\[
\begin{align*}
    k_{1a} & = 6.08 \times 10^7 T^{1.54} \exp(-14005/T) \text{ cm}^3\text{mol}^{-1}\text{s}^{-1} \\
    k_{1b} & = 68.6 T^{2.86} \exp(-4916/T) \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}
\end{align*}
\]

For the measurement of \( k_{1a} \), the average estimated uncertainty over this temperature range is ± 33%, with a standard error of fit of 11.7%. The \( k_1 \) measurements have an average estimated uncertainty of ± 22% with a standard error of fit of 12.9%. Propagation of these uncertainties through to \( k_{1b} \) results in a fairly conservative estimate of ± 27% at low temperatures and ± 41% at high temperatures for that channel.
The present measurements of $k_1$ compare well with one other recent shock tube measurement [24] and an *ab initio* theoretical calculation [1]. In particular, the conclusions of this work lend support to the theoretical calculations with only small changes recommended in the energetics of the potential energy surface. While the rate for $k_{1a}$ agrees with two other recent shock tube studies [12,16], the final rate expressions presented here clearly disagree with the recent conclusions of Michael et al. [16] which suggest that $k_{1b}$ is unimportant. Rather, as has been concluded by most investigations and was presumed by the earliest studies of methane oxidation, channel (1b) is found to be the dominant channel up to high temperatures - in this study at least to 2700 K.

5.1.2 Heat of formation of OH

A unique, high-temperature measurement of the standard heat of formation of the OH radical, $\Delta_f H^\circ_{298}(OH)$, has been performed using a shock tube. Equimolar mixtures of $H_2$ and $O_2$ in an Ar bath gas produced controlled concentrations of OH in the post-ignition partial equilibrium state behind the reflected shock wave. The OH plateau concentrations were sensitive primarily to thermochemical parameters, of which the heat of formation of OH was both the most sensitive and most uncertain parameter. By design, the OH plateau was very insensitive to kinetic rate coefficients.

High-accuracy measurements of OH using laser absorption were performed. The spectroscopy and calculation of OH absorption coefficients were carefully reviewed and updated in an effort to minimize uncertainties. Measurements were compared to and fit by model predictions both from the analytical solution of the partial equilibrium state and from full kinetic models.

A series of experiments over the temperature range 1964 K to 2718 K yielded a temperature-independent average value of the heat of formation of $\Delta_f H^\circ_{298}(OH) = 8.92 \pm 0.16$ kcal/mol, with a standard deviation in the measurement of $\sigma = 0.04$ kcal/mol. The temperature independence of the measured values is a validation of the spectroscopic parameters and experimental methods used in this work. The current study agrees very well with the extensive theoretical and experimental room-temperature study of Ruscic et al. [30] and the thermochemical cycle calculations of Joens [35], and corroborates the
suggestion that the previously accepted values, $\Delta_{f}H^\circ_{298}(\text{OH}) = 9.32$-$9.4$ kcal/mol, are in error.

5.1.3 Publications

The work detailed in this thesis has been published in the following papers:


5.2 Recommendations for future work: Facilities and diagnostics

Future ultra-low concentration, ultra-lean experiments are limited by two primary issues: the presence of low-concentration impurity species in the gas handling system and/or shock tube, and the lower limit of OH detection caused by the presence of beam steering and other shock tube- and flow-related perturbations on the diagnostic laser beam.

5.2.1 Facilities improvement and impurity reduction

The presence and effects of impurities in the measurements of $\text{CH}_3 + \text{O}_2 \rightarrow \text{products}$ was an unfortunate but characterizable problem. The significance of the impurities was
particularly enhanced in these experiments due to the combination of 1) the desired ultra-low concentrations of CH$_3$I, meaning that any detectible level of impurity immediately became a significant fraction of the reactant concentration, and 2) the high mole fractions of O$_2$, which reacted very readily with the minute levels of impurity species. The existence of the impurities had several consequences. The effects could be fairly well-characterized through the measurements of OH and O-atoms in mixtures without CH$_3$I; however, because the exact identity and character of the impurity species was unknown, their presence must necessarily increase the uncertainty in the true mixture composition and therefore the final rate coefficients. Consequently, CH$_3$I concentrations in the reaction mixtures were kept high enough such that the assumed impurity species surrogate, typically CH$_3$, was a small fraction of the known reactant concentrations. As improved isolation of the title reactions could have been achieved with lower CH$_3$I concentrations and lower CH$_3$I/O$_2$ ratios, the relatively high lower-limit of CH$_3$I prevented ideal experimental design.

The impurity effect created extra work in that each new mixture concentration (with different levels of O$_2$) was characterized in a separate sense of experiments, essentially doubling the number of mixtures, experiments, and the amount of data reduction required for each data set.

The impurities also affected the calibration of the O-atom ARAS diagnostic. Most previous investigators have calibrated ARAS diagnostics using the plateau O-atom concentrations produced from completely dissociated N$_2$O in very low concentration (~1-5ppm) experiments. In the current work, low-concentration O-atom measurements were quite obviously affected, as the O-atom concentration never reached the plateau but rather peaked prematurely and decayed as the O-atoms reacted with the impurity. This issue forced a new calibration method, whereby higher concentrations were utilized and the well-studied N$_2$O decomposition rate was used to model the O-atom time-history for comparison to the experiments. While the new calibration method enabled a large range of concentrations to be modeled in relatively few experiments, sensitivity to uncertainty in the kinetic decomposition rate increased the uncertainty in the final O-atom calibration.

Further improvement to the gas handling, mixing, and shock tube facilities is recommended. The most likely remaining source of much of the impurities is the mixing
cylinder itself, based on the observation that impurity effects tend to increase with mixture residence time in the cylinder. The present mixing cylinder is constructed of an electrolyzed stainless steel body with a machined aluminum base, sealed by a large O-ring, and the mixing vanes which appear to be formed of brass. There are many crevices and some rough surfaces in which low-volatility species may be trapped or adsorbed, only to slowly diffuse into the gas mixture as it resides in the cylinder. An improved mixing cylinder might be constructed of a seamless stainless steel cylinder, with or without mixing vanes. Diffusive mixing or creative gas porting to enhance turbulent mixing during the fill might replace the extra surface area and complexity of the mixing vanes. Another option used in many shock tube laboratories is large glass bulbs, typically several in order to have sufficient volume for a set of experiments.

Improvement of the vacuum capabilities of the mixing cylinder and gas handling system should also reduce impurity effects, as evidenced by the significant improvements gained with the redesign and assembly of the existing turbomolecular vacuum pump system (see Section 3.3.3). Vacuum capability will automatically be enhanced with a superior leak-free mixing cylinder, and additional effort may find other sources of leaks in the gas handling system. Calculations should be performed to determine the limiting orifices in the vacuum system, as the valves and connections, not the pump itself, are the limiting factor in the pumping-speed capabilities.

Impurity effects, although smaller, were also observed independent of the gas mixing system in pure O\textsubscript{2} experiments with the source gas connected directly to a shock tube port. These impurities have several potential sources, including crevices between shock tube sections, O-ring seals, and adsorbed species on the shock tube walls. Once again, a lower ultimate vacuum pressure is recommended as a means to help reduce effects of the impurities. Vacuum pressure can be enhanced by further leak detection and removal, addition of another pump or relocation of the pumping system nearer to the endwall and test ports (it is currently located in the center of the driven section), and improvement of effective pumping speeds through redesign of vacuum pathways and larger pumps if dictated. Previous researchers have also attained improvement in impurity levels through the use of non-hydrocarbon cleaning solvents, greaseless or metal seals for ports and shock tube sections, aluminum diaphragms, and bake-out processes.
The latter two were tested in this work with little improvement, although the bake-out was limited to lower temperatures than have been used by other researchers.

5.2.2 Diagnostics improvements

Improved kinetic isolation of reactions of interest can sometimes be obtained by using very low-concentration reactant mixtures. With that benefit, however, comes the challenge of measuring ever-decreasing absorption signals. After the aforementioned impurity issues are resolved, or in cases where they are not important, low reactant-concentration experimental schemes are eventually limited by the signal-to-noise or detection limitations of the diagnostics. Several potential improvements to the OH laser absorption diagnostic are discussed here.

The first, easiest, and most certain variation which would improve OH absorption signals would be to use a stronger absorption transition within the A-X(0-0) band. In the current laser setup, a temperature-tuned AD*A crystal is utilized for the intracavity frequency doubling process. The range of attainable phasematched frequencies is limited by the temperature-tuning range of the crystal, in this case 25 to 100°C. Within this tuning range, the strongest absorption transition at shock tube temperatures is the $Q_{1}(3)$ transition at 308.24 nm. The $Q_{1}(3)$ Einstein A-factor is 2x larger than that for the $R_{1}(5)$ transition, and the line center absorption coefficient is 2x higher at 1500K and 70% higher at 2500K. It is a fairly well-isolated line and thus has only minor influence from adjacent lineshapes (although the $Q_{21}(3)$ lineshape is nearby and a full spectral calculation should always be performed). The collision-broadening and collision-shift coefficients have been characterized for this transition in Appendix B, with relatively high precision and accuracy due to its high intensity and reasonable isolation from adjacent transitions. For reference, the broadening parameter is almost identical to that for $R_{1}(5)$, while the shift parameter is somewhat smaller. Even higher absorption coefficients could be attained with other transitions in the $Q_{1}$ and $Q_{2}$ rotational branches; however this would require a different frequency doubling crystal (potentially angle-tuned rather than temperature-tuned phasematching) and lineshape parameter characterization experiments for these new transitions. The relative benefit of these slightly stronger transitions in the $Q_{1}$ and $Q_{2}$ branches is most likely not worth the
increased difficulty of angle-tuning an intracavity doubling crystal (adjustments to optimize the phasematching angle simultaneously affect the cavity alignment, which does not happen in temperature-tuned crystals).

Another avenue to improved signal-to-noise measurements may be through the use of multiple passes of the laser beam. Multi-passing a laser beam in shock tube experiments has been attempted in the past with success [86], as have multi-pass lamp absorption diagnostics [87,88]. Multiple passes of the laser beam have the obvious benefit of enhancing the absorbance by increasing the path length, but questions remain as to its real potential for improving signal-to-noise. The primary question pertains to the location of origin of the perturbations to the beam intensity and/or direction of propagation which are causing the noise in the first place. For example, if the beam is being deflected in a random manner by gasdynamic effects in the post-shock region, that deflection may cause one or more consequences. The beam may encounter locations of poorer transmission in the shock tube windows or any downstream optic (e.g. dust specks, scratches, etc.). Alternatively, the beam may be moving off of the uniform sensitive area of the photodiode. Another type of beam perturbation can occur in very high pressure shock tube experiments, where photoelastic effects in the shock tube windows have caused polarization scrambling and subsequent attenuation of the beam by downstream optical surfaces [41].

Depending on the origin and character of the perturbation of the beam, a multiple-passing scheme may or may not yield improved detection limits. If each successive pass of the beam through the post-shock gases and/or windows yields an additive intensity perturbation on the beam, no additional beam passes will yield any improvement and may, in fact, prove to be detrimental to the signal. If the additive perturbation is in the propagation direction of the beam, the multi-passing beam alignment must be relatively tolerant of beam steering and adequate collection optics and sufficient optical apertures must be capable of channeling the roving output beam into the detection system.

Initial attempts at multi-pass absorption were performed in the present work, with somewhat limited improvement in signal-to-noise. Here, the beam was passed 3 or 5 times in a vertical zig-zag pattern between two external mirrors. In these trials, signal-to-noise improved by ~2x with either 3 or 5 passes. The limited improvement may have
been an artifact of the increasing beam diameter combined with the limited exit aperture required to achieve the multiple reflections. (It should also be noted that at the time of these trials, the detectors had suffered as-yet-undetected damage from high intensity UV beams, creating a very non-uniform sensitive area.)

Two potential multi-pass schemes may yield drastically improved signal-to-noise, depending, of course, on their specific design and the characteristics and origin of the beam perturbations. One scheme involves a multi-pass cell utilizing curved mirrors either external to the shock tube windows or in place of the shock tube windows themselves. This type of system, developed by Baer et al. [89] for static cell measurements, yields extremely long path lengths and, depending on its tolerance to beam steering, may or may not yield strong improvements in signal-to-noise. Other designs with fewer passes are certainly possible. A potential limitation of this type of cell is the spatial requirements of the beam pattern, which would necessarily limit the time resolution of the system due to the shock transit time across the multiple beams. The beam pattern may be able to be manipulated, however, such that it is not much wider than one beam diameter in the direction of the shock tube axis. This multi-pass detection scheme, called integrated cavity output spectroscopy (ICOS) [89], is currently being investigated in our laboratory.

A second potential scheme is similar to the ICOS design, except that the beam would be propagated perpendicularly through the center of the windows/mirrors in a single overlapping path. If the mirrors were placed external to the shock tube windows (which would most likely be the case), the windows would be given an anti-reflection coating to reduce losses. The benefits to this scheme over the ICOS design is the better time resolution capability due to the spatially-narrow absorption beam path, and perhaps less sensitivity to beam steering due to the non-prescribed beam path. It is unclear at this time whether such a scheme will be more or less tolerable to beam deflections during the multiple passes. The dangers in this scheme are that any potential optical resonance between the perpendicular surfaces in the cavity, particularly the high-reflectivity cavity mirrors, must be destroyed or otherwise overcome, as the window-flexing, vibrations, or other optical path perturbations will potentially create moments of resonant behavior and spurious high optical transmission through the cavity. One method to overcome the
resonance effects may be to install a constantly vibrating cavity optic, like a mirror mounted to a piezoelectric transducer with a white-noise or constant high-frequency driver signal, which would result in a consistent level of on-and off-resonance output that would blur out any spurious resonance effects.

A third technique for drastically improving signal-to-noise in shock tube experiments is UV frequency modulation (FM) absorption spectroscopy. This technique has already proven highly successful in shock tube research for the species $^1\text{CH}_2$ [90], $\text{NH}_2$ [91,92], and $\text{HCO}$ [64], all of which have absorption transitions in the visible wavelengths. These examples of FM spectroscopy have typically resulted in detectivity improvements of factors of 10-20. Frequency modulation spectroscopy has the distinct advantage of canceling out flow- and shock tube-related perturbation effects on the beam, as the system is only sensitive to differential absorption and not common-mode effects on the frequency sidebands. Development of a UV FM technique for OH was initially considered for the work on $\text{CH}_3+\text{O}_2\rightarrow$products, but was set aside in favor of other more pressing projects. In the end, its potential enhanced sensitivity was deemed unnecessary and in fact would have been even less important in light of the impurity limitations on the low-concentration mixtures. Although its sensitivity was not required, advantage could have been gained from lower noise and smoother data traces.

The equipment has been acquired and an initial design and troubleshooting of the setup was accomplished. For this work, a specially made 1GHz phase modulator was built by Quantum Technologies, Inc. using (5) 1x1x18 mm $\beta$-barium-borate (BBO) crystals. In the initial work with this setup some phase modulation was evident, but there was also evidence of non-ideal polarization behavior in the phase modulator resulting in an elliptically-polarized output beam being created from a linearly polarized input beam. This issue must be resolved in order for the system to function properly.

Initial characterization and calibration of the FM system will be aided by the use of the OH reference cell, described in Chapter 2, which can create steady OH concentrations for long periods of time. An additional benefit in our laboratory is the ability to rapidly-scan the UV laser wavelength across the whole transition lineshape and well into the wings, and to do so multiple times in a given shock tube experiment. This capability would enable facile evaluation of the FM lineshape at shock tube conditions,
rather than multiple experiments to map out the lineshape as has been done in previous work [92]. Well-known OH concentrations are easy to produce using the partial equilibrium plateaus in H₂/O₂ mixtures, and detailed lineshape information for previously characterized and isolated lines like the R₁(5) and Q₁(3) transitions will provide further understanding of the system calibration and expected FM absorption coefficient.

5.3 Recommendations for future work: Kinetics

One primary goal of the present work on CH₃+O₂→products was to design and execute experiments which were as insensitive as possible to secondary reaction rates. This goal was achieved in part through the use of ultra-lean, ultra-low-concentration mixtures. For the measurement of k₁, fitting the normalized OH rise time desensitized the k₁ measurement to any uncertainties in the secondary reactions that control the OH peak concentration. In the O-atom measurements, the data fit was limited to the initial portion of the species concentration time-histories where kinetic isolation was maintained.

While only the normalized traces were used for the determination of k₁, these measurements did produce quantitative OH peak concentrations which can be compared to model calculations. In general, the measured and calculated OH peaks did not agree with one another, and the mismatch exhibited smooth and non-monotonic temperature dependence as given in Fig. 3.13. Several reactions display high sensitivities at the OH peak, as given in Fig. 3.14, and the next challenge is to deconvolve which secondary reaction rates are in error, by what magnitude, and the temperature dependence of their error.

Of the sensitive reactions which control the OH peak, some have relatively well-known rate coefficients, while others have very sparse or highly uncertain data at shock tube temperatures and therefore should be studied further. Table 3.3 provides a list of reactions and their estimated uncertainties, some of which also feature strongly in Fig. 3.14. These uncertainties were assessed based on the most recent evaluation of Baulch et al. [62], in comparison with the actual rates used in GRI-Mech 3.0.
Similarly, the long-time O-atom concentrations are sensitive to secondary reactions with relatively high uncertainties. The most important secondary reactions in the O-atom measurements have been included in Table 3.3.

The improvement in secondary reaction rate coefficients can be approached on two fronts. First, dedicated high-sensitivity well-isolated kinetics experiments might be designed to accurately measure some secondary rates and decrease their estimated uncertainties. Reactions with outstanding uncertainties and limited measurements at shock tube temperatures include OH+HO$_2$→H$_2$O+O$_2$, CH$_2$O+O$_2$→HO$_2$+HCO, and O+CH$_2$O→OH+HCO. The state of knowledge on these reactions was discussed in Section 3.5.4.

A second and perhaps less pragmatic approach to investigating the secondary chemistry is to use the quantitative data from the present OH and O-atom measurements in a constrained optimization scheme. This type of mechanism optimization has been discussed in detail by Frenklach et al. [93], and has been used extensively in the optimization of the GRI-Mech series of natural gas combustion mechanisms [37]. Optimization is an ideal procedure for fitting several sets of data with several variable reaction rates. In the present circumstances, the combination of both quantitative OH and O-atom data, with their distinct reaction sensitivities over a range of mixtures and shock conditions, will lend extra information to the optimization, in addition to the normalized OH rise time.

One last recommendation pertains to the development and evolution of optimized mechanisms such as GRI-Mech 3.0. In the present work on CH$_3$+O$_2$→products, the rates for $k_{1a}$ and $k_{1b}$ were adjusted to fit the present set of measurements alone, while ignoring the larger set of target data to which the original mechanism was optimized. This is somewhat antithetical to the true intention of the optimization process, which is to build a mechanism that takes into account a wide variety of data and is optimized to best-fit the whole collection of evaluated experimental targets. While the author believes that the present experiments were well-designed and carefully executed, the resulting rate coefficients, where different from the starting mechanism, will impact the quality of the mechanism’s agreement with the specific GRI-Mech targets which are also sensitive to the adjusted rate coefficients (e.g. CH$_4$ ignition time targets similar to Fig. 1.1). The
proper procedure for improving the whole chemical mechanism would be to perform a full re-optimization after making the following changes. First, the mechanism should include the present OH rise time data, O-atom concentration data, and OH peak concentration data as new targets. The new rates for $k_{1a}$ and $k_{1b}$ should be retained in the starting mechanism. Appropriate uncertainty limits, as determined in Chapter 3, should be enforced as the constraints on $k_{1a}$ and $k_1$ (and therefore $k_{1b}$). Finally, reactions for which new experimental data has been published should be re-evaluated and updated in the new starting mechanism. Some of these reactions are listed in Table 3.4.

A new, full optimization of the GRI-Mech mechanism is a large undertaking and is beyond the scope of this thesis. Such an optimization run, including the new starting rates, targets, and constraints, will most likely result in changes to other reactions sensitive to the new targets and some original targets which share sensitivities with reactions (1a) and (1b). This is the expected and desired outcome. As this is a constrained optimization, provided that the constraints on all reaction rate coefficients are appropriately assigned, the optimization should only result in a superior overall combustion mechanism. Such an improved combustion mechanism, finally, is the true and anticipated goal of the experimental work presented in this thesis.
Appendix A: Calculation of OH spectral absorption coefficients

A.1 Introduction

Chemical kinetics research often involves measurements of species concentration or mole fraction as a function of time. Whether one is interested in sensitive measurements of individual fundamental reaction rate coefficients, or species profiles for use in evaluating a chemical reaction mechanism, accuracy and precision in the species concentration data is typically a requirement. Uncertainties enter into measurements in several forms, including both random and systematic experimental errors and noise, and uncertainties in calculated parameters such as spectroscopic line strengths and line shapes. In the case of absorption, an experiment involves measuring the fractional absorption and is described (for a uniform path length $L$) by the Beer-Lambert law:

$$(\text{Transmission}) = 1 - (\text{Absorption}) = \frac{I_{\text{trans}}}{I_0} = \exp(-k_\nu PXL) \quad (A.1)$$

Data reduction of measured absorption to obtain mole fraction, $X$, is therefore dependent on pressure, pathlength, and the spectral absorption coefficient $k_\nu$ – which is itself a function of temperature, pressure, absorption frequency, and collision partners. Estimation of measurement uncertainties must take into account the individual uncertainties in each of these parameters.

This appendix will discuss calculation of the absorption coefficient, $k_\nu$. Calculation of $k_\nu$ includes two parts: the integrated absorption intensity, $S_{lu}$, and the line shape factor $\phi(\nu)$:

$$k_\nu = S_{lu} \phi(\nu) \quad (A.2)$$

While different forms exist for $S_{lu}$, the following equation described by Goldman and Gillis [72] is most frequently and most easily used for narrow-linewidth laser absorption:
\[
S_{lu}(T) = \frac{1}{8\pi c v^2} \left( \frac{N}{P_{OH}} \right) \frac{\exp\left(-1.4388E''/T\right)}{Q_{tot}} A_{ul}(2J'+1) \left[1-\exp\left(-1.4388v'/T\right)\right]
\]

(A.3)

Calculation of \( S_{lu} \) requires values for the lower-state energy, \( E'' \), the Einstein A-coefficient, \( A_{ul} \) (which is related to the oscillator strength of a transition), the transition frequency, \( v \), and the total partition function, \( Q_{tot} \). Researchers requiring quantitative measurements are interested in the accuracies of each of these parameters in Equations (A.2-A.3), and how they relate either directly or indirectly to an absorption coefficient uncertainty and therefore potential errors in the measured species concentration. Experimental prudence demands that such parameters are calculated or controlled to the highest possible precision and accuracy, so that measurements are dominated only by random or otherwise uncontrollable uncertainties. A survey of recent spectroscopic data is given here, and the calculation of the total partition function is described.

### A.2 Spectroscopic data

Over 40 years have passed since the first extensive publication on the UV bands of OH by Dieke and Crosswhite [94]. In this time period, numerous researchers have undertaken studies of the UV, IR, and microwave absorption and emission spectra of OH. The spectroscopy of OH and a survey of literature on the UV bands of OH up to 1990 have been described previously by Rea [95].

Until 1998, the most complete tabulation of OH line parameters for the A-X(0,0) band was by Goldman and Gillis [72], who listed transition frequencies, A-coefficients, lower-state energy levels, and values or formulas for use in calculating the partition function. Using their methods and data, along with appropriate line shape factors, the absorption coefficient can be easily calculated for lines with \( J'' \) up to 40.5. This is the database on which Rea and other researchers in our laboratory have based OH concentration measurements in the past. However, over the last 10 years, researchers have extended the spectroscopic database to include measurements of more spectral lines in the UV, IR, and microwave regions and, in particular, improved accuracy of spectral line positions for the (0,0) band. These data permit improved fitting of spectroscopic constants, yielding increasingly accurate values for energy levels and providing more precise input parameters for the calculation of rotational transition probabilities.
The most recent measurements of the OH A-X(0,0) transition frequencies have been performed by Stark et al. [73]. Rotational lines up to \( J^\prime = 30.5 \) were measured from Fourier-transform spectra of a hollow-cathode source, with absolute line position accuracies of \( \sim 0.001 \text{ cm}^{-1} \) for the strongest lines. Sets of molecular parameters and rotational term values (lower-state energy values, \( E^\prime \)) were derived from these measured line positions. These measured transition frequencies are still the most precise data available today, and should be used as the vacuum line-center frequencies when calculating and modeling the spectral absorption coefficient.

Luque and Crosley have performed the most recent calculations [75] and tabulation [77] of absolute transition probabilities for the OH A-X system. These supercede earlier calculations by Chidsey and Crosley [96] and others. Improvements and extensions to measured band transition probabilities, as well as new spectral data at high vibrational levels, have together enabled better calculation of the potential curves and a more accurate form for the electronic transition moment. This, in turn, has lead to higher accuracy in the relative, rotational level-dependent transition probabilities. Relative probabilities are put on an absolute scale using the experimentally-determined radiation lifetime [76]. Values of \( A_{\text{ul}} \) in this new work can vary significantly from the older tabulation of Goldman and Gillis, with differences of 0.5-5\% for \( J \leq 25 \) in main transitions and 5-20\% in satellite transitions. For satellite transitions at higher \( J \), differences can be up to a factor of 2 [74].

Finally, Gillis et al. [74] repeated the tabulation of Goldman and Gillis [72], now utilizing the line position measurements of Stark et al. [73] and the updated transition probabilities of Luque and Crosley [77]. They also extended the tabulation beyond the (0,0) band to include the six strongest bands of the OH A-X system. Once again, their tabulation includes the Einstein A-coefficients (which are taken exactly from Luque and Crosley [77]), transition frequencies, and lower-state energy values \( E^\prime \). The frequencies and \( E^\prime \) values were calculated using the molecular constants of Stark et al. [73]. For the strong, low \( J^\prime \), \( R_1 \)-branch lines of the (0,0) band these calculations agree with the measurements of Stark et al. to 0.001 cm\(^{-1} \) for \( \nu \) and better than 2 parts per million for the \( E^\prime \) values. For \( \nu^\prime > 0 \), the \( E^\prime \) of Gillis et al. [74] include a vibrational contribution using the constants of Coxon [97]. It is not clear why they choose to use the constants of
Coxon rather than those of Luque and Crosley [75], which are determined from a fit including higher vibrational levels than that of Coxon. However, for \( v'' = 0,1,2 \) the differences between using these two sets of constants is negligible.

In the attempt to calculate accurate integrated linestrengths, \( S_{iu} \), the most recent parameter values should be used. These would include A-coefficients from Luque and Crosley [77], \( E'' \) values from Gillis et al. [74], and the measured transition frequencies of Stark et al. [73]. Of these parameters, the largest uncertainty arises from the experimental radiative lifetime of German [76]. This value is required to transform the calculated relative transition probabilities, which themselves have quite good accuracy, into absolute values. The reported 3\( \sigma \) uncertainty by German is \( \pm 3\% \) and translates directly into an uncertainty in the integrated line strength.

### A.3 Partition functions

The total internal partition function, \( Q_{\text{tot}} \), describes the number of ways that the thermal energy in a group of molecules is divided up among the allowed quantized energy levels. It enters the calculation of \( S_{iu} \) as a part of the Boltzmann fraction, describing the percentage of all absorbing molecules which exist in a given energy state at thermal equilibrium. Thus, the partition function directly influences the absorption coefficient of a particular transition and should be calculated as accurately as possible.

The true partition function, \( Q(T) \), is found by summing over all possible energy levels of a molecule:

\[
Q(T) = \sum_i g_i \exp(-hcE_i/kT)
\]

where \( E_i \) is the total energy of the molecule in a given level \( i \), and \( g_i \) is the degeneracy of the energy level (i.e., the number of possible states of the molecule which have the same quantum number assignments and thus the same energy). The total partition function, \( Q_{\text{tot}} \), can be factored into an individual partition function for each type of independent energy mode. Except at very low temperatures, it is quite accurate to separate the total energy into electronic energy and a combined vibrational-rotational energy. With somewhat reduced accuracy, this vibrational-rotational energy can be separated into vibration and rotation components. The loss of exactness in this separation is due to the
centrifugal effects of the rotation on the vibrational modes, and the influence of the vibrational motion on the rotational moment of inertia [98]. Higher-order terms can be utilized to compensate both the rotational and vibrational term energy formulas for these intermodal effects. Therefore, it is reasonable to separate the energies and thus factor the partition function – requiring one to simply calculate the partition function contributions: 

\[ Q_{\text{tot}} = Q_{\text{elec}} Q_{\text{vib}} Q_{\text{rot}}. \]

Various simplifying approximations have been invoked in the past for use in calculating the different components of the partition function, most likely for ease of computation and lack of data on high-lying energy states or higher order constants for the term energy equations. While these approximations allow an estimated value for \( Q_{\text{tot}} \) to be quickly calculated, they are often grossly incorrect at one or both ends of the temperature spectrum. However, with computers and simple programs it is easy to calculate the full summations for the partition function, using the improved spectral and energy level information made available over the past 2 decades. It is only sensible to perform this full calculation to obtain the most accurate value for \( Q_{\text{tot}} \).

To understand the improvement in \( Q_{\text{tot}} \) when a full summation is calculated, the approximations others have used in the past can be examined. The simplest model for a diatomic molecule is called the rigid rotor / simple harmonic oscillator (SHO). In this model, valid only at high temperatures or for small rotational constants (\( B_v \)) (i.e., for many closely-spaced rotational energy states), the rotational partition function \( Q_{\text{rot}} \) summation can be approximated by an integral [78], yielding simply:

\[ Q_{\text{rot}} = \frac{kT}{\hbar B_v} \tag{A.5} \]

where \( B_v \) is the rotational constant of the molecule. Here \( B_v = B_0 = 18.536 \), using the rotational constants given by Luque and Crosley [75]. In the rigid rotor approximation, this rotational constant would apply to all vibrational levels of the molecule.

The vibrational partition function of a simple harmonic oscillator is derived by assuming that the energy difference between adjacent vibrational levels is constant. In this case, the full sum in Equation (A.4) can be reduced to the form:

\[ Q_{\text{vib}}(T) = \frac{\exp(-\hbar G(0)/kT)}{[1-\exp(-\hbar \omega_v/kT)]} \tag{A.6} \]
If the energy is referenced to the $v = 0$ state, this form is:

$$Q'_\text{vib}(T) = \frac{1}{[1 - \exp(-\hbar \omega_v / kT)]}$$  \hspace{1cm} (A.7)

The simple harmonic oscillator approximation works fine at low temperatures, where only the first couple of vibrational states have considerable population. However, at higher temperatures the upper vibrational states begin to be populated. As these states are closer together than are the lower states, the large assumed spacing of the harmonic oscillator will give an erroneously low partition sum.

The electronic partition function component can be accounted for in a couple of different ways. An approximate method involves calculating the electronic partition function and rotational partition function separately. In the $X^2\Pi$ state of OH, each set of energy levels with the same quantum number $N$ is actually made up of four spin-split, lambda-doubled energy states. Because it is an intermediate Hund’s case (a) and (b), the spin-splitting starts off quite large at low $N$ values (~100 cm$^{-1}$), but approaches zero at higher $N$. An approximation to a full summation can be made by assuming that these four spin-split, lambda-doubled states represent a simple degeneracy in the electronic partition function. The electronic partition function $Q_{\text{elec}}$ is then typically written as:

$$Q_{\text{elec}} = \sum_n g_e \exp(-\hbar c T_e(n)/kT)$$ \hspace{1cm} (A.8)

The degeneracy, $g_e$, would be 4.0. Due to the first excited state of OH having $T_e = 32,684$ cm$^{-1}$, all the exponential terms except for the ground state ($T_e = 0$) drop out at typical combustion temperatures, leaving $Q_{\text{elec}} = 4.0$. The rotational partition function would then ignore this four-way splitting, either by using the rigid rotor approximation or summing the energy states over all quantum numbers $N$ – assuming one state for each $N$ at the average energy of all states with that same quantum number. At higher temperatures, where many upper rotational states are populated, this approximation of $Q_{\text{elec}} = 4.0$ is fairly accurate. Because the spin-splitting of the upper rotational states is approaching zero, the assumption that all states with quantum number $N$ have the same energy is a decent approximation. However, at low temperatures, the difference in energy between states having the same $N$ is significant. When only relatively few states
are populated, their correct energy values must be used to obtain an accurate partition sum.

As long as correct energy level information is available, the most accurate calculation of the combined electronic/rotation partition function is a full summation over sufficient energy states such that further addition of more terms adds negligibly to the partition function. In this case, each of the four spin-split, lambda-doubled states is an individual term in the summation, and the only degeneracy is the $(2J+1)$ associated with the number of possible directions of the angular momentum vector. This is the procedure adopted by Goldman and Gillis [72] for their table of $Q_R \equiv Q_{elec}Q_{rots}$ and it is the preferred method for obtaining the correct partition function at any temperature. One must always be cautious that the summation is carried out far enough for the given temperature – i.e. the summation should converge and additional terms should add effectively nothing. The table in [72] is based on a summation up to $J'' = 40.5$, and values are given for temperatures up to 6000 K. Researchers in our laboratory have used these data, fit appropriate portions of it to a polynomial, and used this fit as a means to interpolate $Q_R$ to other temperatures not given in the table with errors of less than 0.1%. For example, a fit by Rea of the values from 1000-4000 K yielded the following polynomial fit [95] (note that his thesis contains a sign error, and the last term should be negative):

$Q_R = -5.10988 + 0.14867T + 1.54549 \times 10^{-6}T^2 - 2.2404 \times 10^{-11}T^3$  \hspace{1cm} (A.9)

The most recent tabulations of energy levels [99], based on molecular constants from fits to the spectral measurements of Stark et al., are also listed up to $J'' = 40.5$. The new level tabulations yield $Q_R$ values which agree with Goldman and Gillis to within 0.01% up to 6000 K. As noted earlier, the summation must be carried out far enough that further terms add negligibly to the partition function. This can be checked by adding terms for $J'' = 41.5-50.5$ from a paper by Melen et al. [100]. Adding these terms changes $Q_R$ by only +0.1% at 6000 K; and we can conclude that the tables in Goldman and Gillis are sufficient for temperatures up to 6000 K. However, as the temperature increases beyond 6000 K these additional energy terms must be included in the sum for the sake of accuracy. Comparing $Q_R$ from Equation (A.9) to the full summation from $J'' = 0.5-50.5$, the polynomial equation agrees with the full summation to within 0.01% from 1000-4000
K, and within 0.03% up to 6000 K. Therefore, Equation (A.9) is retained to describe $Q_R$ from 1000-6000 K.

For the vibrational partition function, large improvements can be had over the simple harmonic assumption. Goldman and Gillis [72] suggest that the SHO approximation agrees with a full summation to within 0.2% at 4600 K. This is incorrect as pointed out by Rea [95], and the difference is actually more on the order of 3.8%. However, Rea and others in our laboratory maintained usage of the SHO approximation at typical combustion temperatures. Goldman [101] suggests a one-term anharmonic approximation (AHO) which does a decent job of capturing the major anharmonic effects:

\[
Q_{vib}(T) = \frac{1}{1 - \exp(-1.4388\omega_c / T)} \left\{ 1 + \frac{2.8776\omega_c x_c}{T} \exp(-1.4388\omega_x / T) \left[ 1 - \exp(-1.4388\omega_c / T) \right]^2 \right\} \tag{A.10}
\]

This equation is now only ~0.5% low at 4600 K. Although this is a great improvement, as the temperature increases this error will also increase significantly. Since the goal is the highest available accuracy, it is necessary to calculate $Q_{vib}$ as completely as possible. Therefore, a full summation should be used and implemented into any program designed to calculate absorption strengths as a function of temperature.

The summation for $Q_{vib}$ can be carried out using vibrational data from at least three different published sources, all giving nearly the same result. For the summation, the vibrational term energies must be calculated, and the sum should be carried out to sufficiently high levels that it converges. Molecular constants for use in calculating vibrational term energies can be found in Huber and Herzberg [79], where the constants were derived using vibrational data up to $v = 5$. Similar constants can be found in the recent work by Luque and Crosley [75], where data up to $v = 13$ were utilized in the calculation of potential curves and fitting of spectroscopic constants. Either of these sets of coefficients can be used in the Dunham series expansion for the term values:

\[
G(v) = \omega_x \left( v + \frac{1}{2} \right)^2 - \omega_x x_c \left( v + \frac{1}{2} \right)^2 + \omega_x y_c \left( v + \frac{1}{2} \right)^3 + \ldots \tag{A.11}
\]

These term values are then input into Equation (A.4), along with the degeneracy $g = 1$, to calculate $Q_{vib}$. Summing up to $v = 13$, these two sets of coefficients yield values within
0.02% of one another at 6000 K. In addition, it should be noted that the terms for \( v = 12 \) and \( v = 13 \) contribute 0.06% and 0.04%, respectively, to the vibrational partition sum.

A third set of vibrational data is the tabulated term values of Coxon and Foster [102]. These are given up to \( v = 10 \), and a partition sum using these values yields agreement with the previous calculations to better than 0.1% up to 6000 K.

### A.4 Conclusions

Table A.1 has been constructed to compare these approximate and full summation methods for calculating components of the total internal partition function as a function of temperature. Error in the total partition function, \( Q_{\text{tot}} \), from using simple approximations can be calculated from consideration of the error in the individual components and remembering that \( Q_{\text{tot}} = Q_R Q_{\text{vib}} \). Total errors assumed by using the rigid rotor, simple harmonic oscillator approximations are 3% at 3000K, increasing at both higher temperatures and up to 10.5% at room temperature. These errors are large and unnecessary, and only full summations of the partition functions, or mathematical fits to the full summations, should be used in future calculations of spectral absorption coefficients.
Table A.1: Comparison of calculation methods for the partition functions.

<table>
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<tr>
<th>T [K]</th>
<th>Elec./rot. approx. ( Q_e ) (Rigid Rotor)</th>
<th>( \frac{Q_{rot}}{Q_e} ) Summation up to ( J''=40.5 )</th>
<th>% error in R.R. approx.</th>
<th>SHO approx.</th>
<th>AHO approx.</th>
<th>Full sum to ( v=13 )</th>
<th>% error in SHO approx.</th>
<th>% error in AHO approx.</th>
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<td>69.997</td>
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</tr>
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<td>-0.87</td>
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Appendix B: Measurements of collision shift in the OH A-X(0,0) band

B.1 Introduction

B.1.1 Motivation

Narrow-linewidth lasers have been employed as a diagnostic tool in shock tube chemical kinetics research for over 20 years. The high signal/noise ratio, species selectivity, and improved detectivity compared to broadband optical techniques (such as lamp absorption or emission) make laser absorption and fluorescence attractive for use in complex reacting flows, where many species are present and often the molecule of interest exists in concentrations on the order of parts-per-million. Quantitative absorption measurements using a narrow-linewidth light source require accurate knowledge of the spectral absorption coefficient, which is simply the product of the integrated line intensity and the lineshape function: \( k_\nu = S_{lu} \phi(\nu) \). Calculation of integrated absorption intensities for OH has been reviewed in Appendix A. The lineshape function, \( \phi(\nu) \), for an individual spectral line is a function of temperature, pressure, and the species with which the molecule of interest is interacting. In this appendix, the absorption lineshape of OH will be explored.

An understanding of the lineshape parameters is critical to accurate laser measurements, particularly for more advanced diagnostics. Recently workers in our laboratory and other institutions have developed and applied frequency modulation (FM) absorption techniques in shock tube research, increasing the sensitivity (decreasing the lower detection limit) of certain species by over a factor of 10 [64,90-92]. Such improvements enable significantly lower concentrations to be used in chemical kinetics
experiments, thereby providing better isolation of the chemistry of interest and reducing the influence of secondary reactions. Compared to simple absorption experiments, where the laser wavelength is often tuned to the peak of a strong transition to attain maximum absorption signal, FM absorption is performed by tuning the laser wavelength to a location on the lineshape which has the greatest slope. The frequency modulation process creates frequency sidebands centered about the carrier frequency. Only the differential absorption of the sidebands is detected, and any common-mode signal disturbances such as flow turbulence and beam steering, window effects, vibration, or laser power fluctuations are cancelled out.

The use and calibration of such an FM technique for OH would especially benefit from accurate lineshape information, as the FM absorption coefficient (with the laser tuned to the side of the lineshape) is much more sensitive to the broadening and shift of the line than is the more commonly used peak absorption coefficient [90]. Figure B.1 illustrates the magnitude of shift expected for OH lineshapes. At these conditions (1500 K, 4 atm), absorption at the lineshape peak may be affected by ~ 7% if the shift is unaccounted for. On the other hand, initial calculations suggest that the FM absorption signal could be affected by as much as 25% based on the same magnitude of collision shift. The need to correctly model the OH lineshape to achieve highly accurate measurements, both for conventional absorption techniques and especially for FM techniques, is evident.

B.1.2 Background

The most commonly used lineshape for modeling the absorption transitions of many molecules is a shifted Voigt profile. This symmetric profile is constructed from a convolution of the Gaussian lineshape (an effect due to the molecular velocity distribution), and a Lorentzian lineshape (due to state-perturbing collisions with other molecules). The shift of the line-center frequency is simply described by $\Delta \nu = \Sigma \delta P_i$, where $P_i$ is the partial pressure of the collision partner; and the collision shift coefficient has the form $\delta(T) = \delta(T_{\text{ref}})[T_{\text{ref}}/T]^n$ cm$^{-1}$atm$^{-1}$. Simple kinetic theory of hard-sphere collisions predicts a value of $n = 0.5$ for the temperature exponent, while in practice $n$ typically ranges between 0.5 and 1.
The spectroscopic lineshape parameters of the OH radical have been experimentally researched by several authors. Numerous studies of the collision broadening over a wide range of transitions and conditions have been undertaken in our lab and elsewhere [39,103-107]. The collision shift, on the other hand, has not been as thoroughly examined, and the limited condition space which has been studied is shown in Fig. B.2. The first measurement by Shirinzadeh et al. [104] was performed for a single transition, P₁(2), in the A-X(0,0) band at room temperature for a variety of collision partner species. Their work verified the linear pressure-dependence of the shift and collision width up to one atmosphere. Previous investigators in our laboratory [106] explored the collision shift and width of the A-X(0,0) R-branch bandhead at high pressures and determined coefficients appropriate to a single high-temperature point for this composite absorption spectrum. Finally, Kessler et al. [107] studied broadening and shift of the A-X(1,0) band of OH in a hydrogen-air flame. Their measurements of collision shift were limited to 3 transitions and were necessarily performed in a mixture of collision-partner species in the post-flame gases. These three studies provide a starting point for estimating collision-shift parameters, but are limited in their information regarding the dependences on temperature, rotational state, rotational branch, and collision partner at the high-temperature conditions typical of shock tube kinetics experiments. Because of the interest in quantitative, high sensitivity measurements of OH in our laboratory, more complete information regarding the collision shift of the OH molecule is needed.

The present work includes collision-shift measurements for several transitions in the A-X(0,0) band for the most common shock tube bath gases, Ar and N₂. Particular focus is on the R₁(5) transition, due to its frequent usage in shock tube experiments, and the P₁(1) and P₁(2) transitions for the purpose of comparison with the room-temperature data of Shirinzadeh et al. Trends are observed in the collision shift dependence on temperature, rotational quantum number (J'), and collision-partner species.

B.2 Experimental details

Experiments in this work were performed using the shock tube facility and OH laser diagnostic described in Chapter 2. Partial equilibrium plateau levels of OH (see
Chapter 4 and Appendix E) were produced using equimolar mixtures (0.2% or 0.3% each) of H\textsubscript{2} and O\textsubscript{2} in a bath of either Ar or a 50/50 mixture of Ar and N\textsubscript{2} gas. All mixtures were > 99% bath gas.

Post-reflected-shock temperature and pressure are calculated using the initial conditions and the measured shock velocity. For experiments in Ar, the temperature and pressure behind the reflected shock wave are calculated assuming chemically frozen and vibrationally equilibrated gases in both the incident and reflected shock regimes. However, for experiments in N\textsubscript{2}/Ar the post-shock gases are initially vibrationally frozen, and the relatively slow vibrational relaxation is predicted to cause an exponential decay in the pressure and translational temperature of the gases. To complicate the situation slightly, in the actual experiments with N\textsubscript{2} the pressure at the test section was observed to increase slowly after passage of the shock wave, most likely due to minor gasdynamic non-idealities. Therefore, the actual temperature and pressure at the time of the lineshape measurements were evaluated using the following approximations.

First, the vibrationally frozen and fully vibrationally equilibrated reflected shock conditions were each calculated using the ideal shock equations and assuming vibrationally frozen incident conditions in each case. The characteristic vibrational relaxation time at the reflected shock conditions was calculated for the mixture using the expressions of Millikan and White [51]. This relaxation time was used to estimate the expected temperature and pressure change with time as the gases relax from the frozen to fully equilibrated states. A slight increase in pressure was observed; however this increase is not due to relaxation, but rather other gasdynamic effects are producing a (likely) isentropic increase in pressure which is larger than the pressure decay due to vibrational relaxation. The actual measured relative pressure increase with time is therefore used to determine the pressure increase from the initial vibrationally frozen conditions.

The translational temperature at the test times of interest is approximated in two steps. First, the temperature decay due to vibrational relaxation (in the absence of other gasdynamic effects) is estimated as a function of time. Next, the measured pressure increase (above the calculated ideal pressure) is used to estimate the temperature increase due to the (likely) isentropic gasdynamic effects through the following relationship:
\[ T_s/T_{so} = (P_s/P_{so})^{(\gamma-1)/\gamma}. \] In the end, the pressure at the test time of interest is found to be slightly above the initial shock conditions, whereas the temperature is somewhat lower than the initial conditions due to the combined effects of vibrational relaxation and other gasdynamic effects.

The test conditions ranged from 1550-3080 K and 1.5-7.6 atm, with the standard conditions being 2500 K and 2 atm. Between each experiment, the shock tube driven section was evacuated to less than 25 \( \mu \)torr using mechanical and turbomolecular pumps. The range of transitions that were studied was limited by the population of the lower state in the low temperature reference cell (the population must be high enough to get a meaningful unshifted reference lineshape), the tuning range of our frequency doubling crystal, and the exclusion of significantly overlapping transitions. Separate fixed-wavelength absorption experiments were conducted to ensure that OH concentration levels remained approximately constant during the time interval required for a collision-shift measurement.

The experimental setup is shown again for reference in Fig. B.3. The main component of the optical diagnostic is a rapid-tuning frequency-doubled dye laser previously developed in our laboratory [40,95]. The fast sweep rate (3 kHz) enables at least 2 full scans over the shifted and broadened OH lineshape during the experimental test time, and the wide tuning range (over 4 cm\(^{-1}\)) ensures that the scan extends well into the wings of the lineshape. The laser remains in single-mode operation throughout the entire tuning range. The instantaneous spectral linewidth of this laser is on the order of < 1 MHz and is therefore not a significant source of instrument broadening when compared to the Doppler-broadened OH linewidth in the shock tube of > 8 GHz. Further experimental details are similar to those found in [39,40,95,105].

The UV output of the rapid-tuning dye laser is directed through both the shock tube and the flowing, low-pressure (25 torr) He/H\(_2\)O microwave discharge cell described in detail in Section 2.2.1. The microwave discharge serves as a source of OH which has relatively small spectral collision shift. It is therefore an effective reference for measuring the shift at the higher-pressure shock tube conditions. The UV beam is sampled before and after this reference cell using reflections from two UV fused silica beam splitters, and the light is detected by matched UV-enhanced Si
The front surfaces of the Si photodiodes have been sandblasted to diffuse the light and prevent etaloning effects. The shock tube optical setup is similar to that of the reference cell, except that only one optically coated beam splitter is used. The detectors are placed at an angle to prevent etaloning in the photodiode window surfaces.

With the laser beam blocked, the detector outputs (or inputs to the digital oscilloscope) are set to zero. The beam is then unblocked and the transmitted ($I$) and reference ($I_o$) signals are carefully balanced by adjusting the incidence angle, and therefore the transmissivity, of a neutral density filter placed in one beam path. This balancing is very important to achieving the best possible common-mode noise rejection and, additionally, removing any artifacts from the strongly oscillating laser intensity during a scan cycle. Signals from the reference cell, shock tube, etalon, and pressure transducer were all digitized and sampled at a rate of 10 MHz using a digital oscilloscope.

### B.3 Data Reduction

#### B.3.1 Preparation of the signal traces

The collision shift was determined from independent lineshape fits of the simultaneous absorption in the reference cell and shock tube. For each absorption signal, the stored $I$ and $I_o$ signals were reduced to an absorbance using the Beer-Lambert relationship for the spectral transmission, $T_{\nu} = (I/I_o)_\nu = \exp(-k_{\nu}P_{OH}L)$ where $P_{OH}$ is the partial pressure of OH and $L$ is the path length. Assuming that $P_{OH}$ and the effective path length are unchanging with time, the absorbance, $\text{ABS}_{\nu} = -\ln(I/I_o)_\nu = k_{\nu}P_{OH}L$, is therefore directly proportional to the spectral absorption coefficient, $k_{\nu}$.

The raw signals for an example experiment are given in Fig. B.4. Suitable segments of the shock tube and reference cell absorbance traces were converted from time-basis to frequency-basis spectral absorbance using the etalon transmission peaks [40]. Because the dual-rhomb tuner inside the laser cavity is driven by a sinusoidal voltage and results in a nominally sinusoidal modulation of laser frequency vs. time, Rea et al. [40] used a sine wave function to transfer the data from time-basis to frequency-
basis. An example of this fitting process is shown in Fig. B.5. Close examination of the fitting residuals during the present work has indicated that the tuning function is not a perfect sine wave, and that assumption of a sine wave results in rather structured and systematic fitting residuals (errors in the fit) on the order of ± 0.4 GHz (in this example). This residual could not be rationalized as an artifact of limited electronic system time-response, as such an effect would produce asymmetrical rather than the observed symmetrical residuals (centered about the mid-point of the sinusoidal scan). Therefore, in this work a 7th-order polynomial fit was used for each individual half-cycle of the laser sweep. A higher-order polynomial did not further improve the fit. The polynomial fit consistently gave lower residuals (~ ± 0.04 GHz) with no apparent structure. For this particular example, the two different fits of the etalon trace result in an effective ~ 1% difference in the deduced collision shift parameter.

In the data reduction process, special care must be taken in balancing the $I$ and $I_o$ signals and assigning the unabsorbed baseline, as uncertainty in the baseline can cause erroneous fits particularly in more complex lineshapes [108]. The broad scan range of the laser results in a strong oscillation in the laser intensity as the wavelength is scanned over the optimal phasematching frequency for a specific doubling crystal temperature (see Fig. B.4). If the beams are not carefully balanced to provide a flat zero-absorbance baseline, any residual modulation in the absorbance signal will confuse the fitting routine and will have an impact on the reduced collision shift and broadening parameters. In the absence of absorption or other one-beam-only effects, two types of perturbations can create a situation in which the two signals are not perfectly balanced or a flat baseline is not achieved: 1) a gain difference or 2) a DC offset in the two beams and their electrical detection and amplification systems. Balancing of the $I$ and $I_o$ signals during data reduction was accomplished by examining both the $((I/I_o))$ and $(I - I_o)$ traces in the pre-shock time period. In the case of a differential gain in the reference and transmitted signals (but no DC offset), the $((I/I_o))$ signal will exhibit a constant offset error (i.e. it will be close to, but not identically equal to, 1.00). On the other hand, the difference signal will exhibit a modulation at the same frequency as the driving frequency for the dual-rhomb tuner. This modulation occurs because of the oscillation on the laser intensity during the scan. The baseline error can be simply eliminated by scaling one of the traces
by a constant $C_1$ to achieve a flat absorbance equal to zero in the pre-shock regime: $\text{ABS} = -\ln\left(\frac{I}{C_1}/I_o\right) = 0.00$. For most experiments, $C_1 = 1 \pm 0.01$ (i.e., balancing was better than 1%). In the case of a DC offset between the $I$ and $I_o$ signals (such as might be caused by a constant external background light signal on one detector, a bumped optic, a shift in the electrical ground, etc.), just the opposite occurs. The $(I/I_o)$ trace will exhibit a modulation and the $(I - I_o)$ trace will exhibit a constant offset error (i.e., it will be close but not identically equal to 0). This type of baseline error is eliminated by subtracting a constant voltage, $C_2$, from one signal, until $\text{DIFF} = (I - C_2) - I_o = 0.00$. The two constants are iteratively adjusted until both signals are flat, and $\text{ABS} = -\ln\left([I - C_2]/C_1/I_o\right) = 0.00$ and $\text{DIFF} = [(I - C_2)/C_1] - I_o = 0.00$.

Occasionally a slight polynomial baseline adjustment was permitted if it was obviously needed for a particular experiment. This was used sparingly, however, as a non-flat baseline has implications for the measured collision shift. It was most often used for the reference cell absorption signals, where physical adjustment and optimization of the balancing prior to an experiment was not as convenient as for the shock tube absorption signals. Fitting of the reference cell lineshapes, having much narrower linewidths than the shock tube lineshapes, suffered fewer negative ramifications from a slight baseline adjustment.

Other perturbations on the signals, in addition to those mentioned above, can also have an effect on the quality of the baseline. These perturbations cannot be cancelled out through balancing the transmission and reference signals, and are visible on both the absorbance and difference signals. Of most concern are etalon resonance effects created in plane-parallel transmissive optics. Weak etalon effects on the laser beams produce repetitive intensity modulations on one or both of the laser signals as the laser frequency is scanned – modulations which may or may not be cancelled out through common-mode rejection depending on their location of origin in the optical train. Careful attention was paid to the use of angled optical surfaces, with Schott glass filters and the reference cell windows mounted at Brewster’s angle to minimize reflective losses. The shock tube windows had a 30’ wedge angle. The Si photodiode window surfaces were either sandblasted (to diffuse the light and prevent etaloning) in the case of the reference cell
detectors, or placed at an angle to the oncoming beam (to destroy resonance effects) in the case of the shock tube detectors.

In addition to etalon effects, the laser diagnostic system also exhibited sensitivity to what appeared to be subtle polarization modulation in the UV beam. Even when all possible optical surfaces were removed, a distinct modulation was present on both the \((I/I_o)\) and \((I - I_o)\) traces that could not be removed through the baseline adjustments discussed above. The only remaining optic which could not be physically removed was the beamsplitter itself. The reflectivity of the coated beamsplitter is polarization sensitive; which is to say that a small polarization modulation would manifest itself as a modulation in the transmitted and reflected signal fractions and thus a modulation on the absorbance trace. Placement of a thin-film polarizer in the beam path prior to the beamsplitter was required in order to eliminate the modulation in the absorbance signal, as it transformed any weak polarization modulation in the incoming beam into a weak amplitude modulation which is easily handled through common-mode rejection. The resulting peak-to-peak modulation in the absorbance trace was typically lower than 0.0005 (0.05% of the laser intensity).

B.3.2 Lineshape fits and collision shift measurement

The reference cell and shock tube traces were individually fit to Voigt lineshape profiles. In the shock tube trace, the Doppler width was held to that appropriate for the calculated temperature at the reflected shock conditions. The collision-broadening coefficient was allowed to move freely during the fit. For comparison, fits were also performed with the collision width held to previously measured values [39]. For transitions in rotational branches for which there has been no measurement, the collision width appropriate to a given \(J''\) value for the \(R_1\) branch was used as a starting estimate. In general, it was found that allowing the collision-broadening parameter to adjust freely had a minor effect, less than 1% in most cases, on the derived collision-shift value. The experiments in which the collision-broadening parameter had a larger effect were situations in which 2 or 3 lines were partially overlapping. In these cases, the fitting uncertainty for finding \(\nu_o\) (the line-center frequency) was typically larger than for isolated transitions and added significantly to the uncertainty due to the assumed collision
parameter. The fitted line-center positions of the reference cell lineshapes, being much less influenced by collisions, were not sensitive to the choice of collision-broadening parameter.

Shown in Fig. B.6 are the reduced absorbances, Voigt fits, and fitting residuals for a typical collision shift measurement for the $R_1(5)$ transition. The residual indicates that there is 1-2\% difference at the peak absorbance between the best-fit Voigt lineshape and the measured lineshape in the shock tube. The shape of this residual is characteristic of that found when a Voigt profile is used to fit more complex profiles which include motional narrowing [109]. Because of the clear evidence of asymmetry and narrowing, use of a Voigt profile will slightly underpredict the actual line-center shift which would be found if a more realistic (and complex) profile model were used [95]. This situation is discussed further in Section B.4.5.

The derived collision-shift measurements from two consecutive sweeps of the lineshape (forward and reverse) were averaged to cancel the difference in electronic phase lag between the reference cell and shock tube detector/amplifier packages. This phase lag was consistently on the order of 770 ns (with the older reference cell detectors lagging the newer shock tube detectors) and was dependent on the gain/bandwidth setting of the shock tube detectors. The effect of the phase lag is evident from the difference in the measured shift for two consecutive sweeps, and is similar to effects seen by previous researchers.

### B.3.3 Uncertainty calculations

Uncertainty limits for individual collision shift measurements include estimated uncertainty contributions from the following sources: the 95\% confidence bands for determination of the line center frequency $\nu_o$, uncertainties in shock pressure and temperature, any uncertainty due to the application of a non-flat baseline adjustment, uncertainty due to the assumed collision broadening coefficient (typically only important for overlapping transitions), and the estimated collision shift at the reference cell conditions. The reference cell collision shift was assumed to be zero throughout the data reduction process; however the room temperature shift value from Shirinzadeh et al. [104] (helium collision partner at $T = T_{cell}$, $P = 25$ torr) was used as an upper limit to the
potential reference cell collision shift and was considered as an uncertainty. For experiments in a 50/50 mixture of Ar and N\textsubscript{2}, the collision shift derived for N\textsubscript{2} has an additional uncertainty contribution from the previously measured Ar collision shift parameter, as the shift coefficient in N\textsubscript{2} is simply the total measured shift minus the contribution from Ar. Individual uncertainty sources were combined using the root-sum-squares method for errors in the positive and negative direction. Uncertainties are generally quite higher for transitions which have overlapping lineshapes with other nearby transitions, due to the challenge of accurately determining the line-center frequency $\nu_o$ independently for each transition. Often the weakest of the overlapping transitions has the largest uncertainty. This is true for the following combinations of lines: R\textsubscript{i}(11) (weak) / R\textsubscript{i}(7) (strong); Q\textsubscript{21}(3) (weak) / P\textsubscript{i}(1) (strong) / Q\textsubscript{i}(3) (strongest, but spectrally farther from the other 2 transitions); Q\textsubscript{21}(1) (weak) / Q\textsubscript{i}(1) (strong); and R\textsubscript{i}(1) (weak) / R\textsubscript{21}(1) (strong).

The uncertainty limits in the fitted temperature exponent $n$ are estimated either from the standard error in the parameter fit or from a combination of the positive and negative estimated uncertainties in the individual experiments. In the case of the P\textsubscript{i}(2) transition, for example, the lower limit of [104] is combined with the upper limit of the present high-temperature measurements and the $n$-parameter is refit. As the uncertainties for individual experiments have essentially been estimated at the 95% confidence level, this estimated uncertainty in $n$ is representative of ±2 standard deviations.

### B.4 Results and discussion

#### B.4.1 Temperature dependence of collision shift

Previous to this work, the only existing collision partner-specific measurements of OH collision shift were Shirinzadeh et al. [104] at room temperature and Davidson et al. [106] at 1735 K. Davidson et al. determined a temperature exponent of $n_{Ar} = 0.45$ by fitting their single data point for the (0,0) bandhead at 60 atm, 1735 K with the 1 atm, 298 K data for the P\textsubscript{i}(2) transition of Shirinzadeh et al. This fit is not entirely appropriate, as collision shift is expected to be a function of the lower-state rotational quantum number $J^\prime$. The goal of the present work was to characterize the temperature dependence of the
collision shift for specific individual transitions. The focus is on the R_1(5) and R_21(5) lines, as well as the P_1(1)/P_1(2) lines. Measurements have also been made for additional transitions in the R_1, R_2, Q_1, and Q_21 branches.

A set of 20 collision shift experiments for R_1(5) were performed over the temperature range 1555-3080 K. The nominal pressure was 2 atm. Experiments near 4 atm and 7.5 atm indicate that the collision shift is linear with pressure. The broad scanning range of the ring dye laser permitted the simultaneous measurement of the weaker R_21(5) transition and its collision shift in this set of experiments. These two lines are sufficiently spectrally separated that they have no influence on each other’s lineshape or the reduced shift parameter.

Collision-shift data for R_1(5) and R_21(5) are shown on log-log plots in Figs. B.7 and B.8. Representative error bars, calculated as discussed in Section B.3.3, are shown for a few points and are typically on the order of +2.3%/-1.7% for the R_1(5) transition and +5%/-4.5% for R_21(5). Fitting each data set to a line yields the shift coefficient expressions \( \delta_{\text{Ar}} = -0.0085*(2500/T)^{0.76} \text{ cm}^{-1}\text{atm}^{-1} \) and \( \delta_{\text{Ar}} = -0.0081*(2500/T)^{0.84} \text{ cm}^{-1}\text{atm}^{-1} \) for R_1(5) and R_21(5), respectively. The 2x standard error for the fit of \( n \) is ± 0.047 for R_1(5) and ± 0.11 for R_21(5). The overall standard errors of fit (2x standard deviation) for R_1(5) and R_21(5) are 4% and 9%, respectively. The scatter is somewhat larger than the estimated 2\( \sigma \) uncertainties, indicating that there are some small random errors that are not completely accounted for in the uncertainty analysis. Note that the direction of the shift is negative, towards lower frequencies, as expected. The direction of shift was easily observed by comparing the shift direction to the known relative position of the R_21(5) and R_1(5) transitions.

A set of 4 measurements of collision shift for the P_1(1) transition in Ar were performed over the temperature range 1560-3070 K and pressure range 1.55-2.7 atm. A linear fit to the data yields \( \delta_{\text{Ar}} = -0.0050*(2500/T)^{0.73} \text{ cm}^{-1}\text{atm}^{-1} \). Due to the upper-limit of the temperature tuning range of our crystal, it was not possible to sweep the laser over the P_1(2) transition. However, the P_1(1) transition can be used to estimate the P_1(2) shift value. From the trend of shift vs. \( J'' \) (discussed in the next section), the shift for P_1(2) will be roughly 8% greater than the value measured for P_1(1). The temperature dependence for P_1(2) can be then be determined from the present estimated P_1(2) data.
alone or with the addition of the room temperature point of Shirinzadeh et al. [104]. Both of these fits are shown in Fig. B.9, along with the P$_1$(1) data. The temperature exponent is only slightly different for the two fits, $n = 0.73 \pm 0.08$ for the present data alone compared to $n = 0.81 \pm 0.03$ including the data point of [104] (uncertainty given is 2x the standard error for the fitted $n$ parameter). Uncertainty limits for the $n$-values of the P$_1$(2) shift can also be found by combining the upper error limit of [104] and the lower error limit of the present high temperature points to get the upper limit of $n$, and vice-versa for the lower limit. Using such a fit, the $n_{Ar}$ was found to be $0.81 \pm 0.025 / -0.03$ (essentially the two-standard-deviation uncertainty).

The results of all measurements for these and other transitions in Ar are given in Table B.1. In some cases, only one data point was captured for a given transition. In these situations and for transitions in which the error bars or scatter in the data resulted in a meaningless temperature dependence, a simple value for the shift at 2500 K, 1 atm is provided. Over all transitions in Ar bath gas for which a temperature dependence could be determined, the average temperature coefficient was $n_{Ar} = 0.79 \pm 0.08$ (one standard deviation).

In the study by Davidson et al. [106], a temperature coefficient $n_{Ar} = 0.45\pm0.08$ was derived by fitting the high-J$^\alpha$ bandhead data at 1735 K with the room temperature P$_1$(2) data of Shirinzadeh et al. [104]. This is now shown to be incorrect, as shift is highly dependent on the specific transition. However, a comparison can be made between the derived bandhead collision shift parameter of [106] and the present data for the R$_1$(7) and R$_1$(11) transitions, as these two transitions are prominent in the bandhead spectrum. Using the parameters for R$_1$(7) and R$_1$(11) from Table B.1 and assuming $n \approx 0.92$ for both transitions, the present measurements for R$_1$(7) and R$_1$(11) overlap with [106] just barely within the combined uncertainty bounds. As the measurements of [106] are a convolution of several transitions, more specific comparisons in an attempt to generate new shift parameters are not meaningful.

**B.4.2 Collision-partner dependence of collision shift**

A limited number of experiments were performed in mixtures with a bath gas of 50% N$_2$ / 50% Ar to explore the relative collision shift induced by N$_2$. The temperature
dependence is best estimated by fitting the present high temperature data for the P_{1}(1)
transition (again slightly adjusted to estimate the shift for the P_{1}(2) transition) along with
the room temperature value of [104]. This data and fit are given in Fig. B.10. The fitted
expression is \( \delta_{N_2} = -0.0045*(2500/T)^{0.55} \text{ cm}^{-1}\text{atm}^{-1} \), indicating a somewhat lower \( n \) for N\(_2\)
compared to Ar and an overall lower shift coefficient. The 2\( x \) standard error for fitting \( n \)
is \( \pm 0.10 \), whereas taking the estimated uncertainty limits in the individual measurements
also yields \( n \pm 0.10 \) (2 std. deviations).

The relative collision shift induced by N\(_2\) compared to Ar can be seen from
examination of the data in Table B.2. Comparing the collision shift in N\(_2\) and Ar for each
individual transition (normalized to 2500 K), the N\(_2\)-induced collision shift is consistently
lower than that for Ar. Over all transitions, \( \delta_{N_2}/\delta_{Ar} = 0.77 \) with a standard deviation of
0.09.

B.4.3 Rotational quantum number dependence of collision shift

A distinct relationship between the collision shift and rotational quantum number
was observed for almost every rotational branch of the OH A-X(0,0) band studied here.
In general, the collision shift increases in magnitude with increasing \( J'' \) up to at least \( J'' = 7.5 \). The R\(_1\)(7)/R\(_1\)(11) lines deviate from this trend and were not included, but are
deemed to have somewhat higher uncertainty due to their closely overlapping lineshape
profiles. Figure B.11 gives the comparison of the shift coefficient at 2500 K for all
transitions in Ar, and Fig. B.12 gives the same for N\(_2\). In the case of Ar, exclusive of the
Q\(_1\) branch the average trend is an increase of \( 4.0\times10^{-4} \pm 4\times10^{-5} [\text{cm}^{-1}\text{atm}^{-1}/J''] \). For N\(_2\)
the trends indicate an increase of \( 3\times10^{-4} \pm 1\times10^{-4} [\text{cm}^{-1}\text{atm}^{-1}/J''] \) (excluding the R\(_{21}\)
branch data).

B.4.4 Collision-broadening measurements

Collision-broadening parameters for transitions in the R\(_1\) branch in bath gases of
both Ar and N\(_2\) have been previously studied in shock tube experiments by Rea et al.
[39]. Similar parameters can also be determined from the present experiments with the
same methods, providing a means for comparison and validation of the two studies.
Once again, particular focus is placed on the R_1(5) and P_1(1) transitions for the reasons mentioned in Section B.4.1.

All shock tube experiments were reanalyzed to obtain the collision broadening parameters. As in [39], the Doppler width is held fixed to the calculated shock temperature and the collision width is adjusted to best-fit the lineshape. Unlike for the collision shift measurements in previous sections, the lineshape fit is constrained to match the measured lineshape peak. As is apparent in Fig. B.6, the non-normalized best fit of the OH lineshape does not result in a residual of zero at the lineshape peak. The mismatch is due to the effects of motional narrowing, which are not accounted for in the assumed Voigt profile (see the next section). The reason for the peak-normalization constraint in the collision-width fits is that the derived collision-width parameters eventually will be utilized to calculate spectral absorption coefficients in laser absorption experiments using a Voigt-function approximation to the lineshape. Because quantitative measurements require an accurate line-center absorption coefficient, the best broadening parameters for use with a Voigt profile will reproduce the correct lineshape function at line center. The peak normalization (and adjustment of the collision broadening parameter) has typically < 0.5% effect on the deduced collision shift, except in circumstances where 2 or more transitions have overlapping lineshapes.

Collision-broadening data for the R_1(5) transition are given in Fig. B.13. This figure is analogous to Fig. 6 in Rea et al. [39]. A fit to the present data yields the expression \(2\gamma_{Ar} = 0.026 \times (2500/T)^{0.83} \text{ cm}^{-1}\text{atm}^{-1}\). In contrast to the collision shift, collision broadening has very weak, if any, dependence on \(J''\) for Ar bath gas [39]. Therefore, the comparison of the high-temperature R_1(5) data with room-temperature P_1(2) data is appropriate in an effort to determine the temperature dependence of the broadening coefficient. Inclusion of the room-temperature point of Shirinzadeh et al. [104] yields a very similar expression, \(2\gamma_{Ar} = 0.026 \times (2500/T)^{0.79} \text{ cm}^{-1}\text{atm}^{-1}\), with only a practically imperceptible difference in the temperature exponent. Converting the results of Rea et al. to a reference temperature of 2500K yields an almost identical expression for this transition: \(2\gamma_{Ar} = 0.027 \times (2500/T)^{0.80} \text{ cm}^{-1}\text{atm}^{-1}\) for the fit including Shirinzadeh et al.

Broadening parameters for various transitions for both Ar and N_2 bath gases are given in Tables B.3 and B.4. Where appropriate, the data from [39] is also given for
comparison. In general, quite good agreement is found between the present data and that of Rea et al. The collision-broadening data provide a validation of the experimental techniques and data reduction procedures used here, and add information for a few more transitions outside of the R₁ rotational branch.

B.4.5 Motional narrowing and Galatry lineshapes

In his extensive work on the OH lineshape parameters, Rea investigated more complex lineshape fits which include motional narrowing and collision shift [95]. A detailed discussion of different lineshape models, their applicability to OH, and generalized relationships between various lineshape parameters is given in that work. In addition, lineshape data from an H₂/O₂ flame are reanalyzed using motionally narrowed lineshape functions, and the effect on the derived broadening parameter for H₂O is examined. The OH radical was found to be best described by a generalized Galatry lineshape. This particular lineshape model includes effects of motional narrowing as well as a correlation between velocity-changing (lineshape narrowing) and state-perturbing (lineshape broadening and shifting) collisions [109].

In the work by Rea, a completely accurate generalized Galatry fit was prevented only by the lack of temperature-dependent collision-shift parameters, or, more specifically, knowledge of the vacuum line-center (unshifted) frequency relative to the measured high-temperature lineshape. With the addition of the present measurements of collision shift, generalized Galatry fits of the lineshape data are now possible, and the effects of progressively more complex lineshape models on the deduced broadening and shift coefficients can be explored.

Trial lineshape fits for 2 different well-isolated transitions, R₁(5) and R₂(7), were performed to examine the consequences of the assumption of a Voigt lineshape profile on the “real” lineshape parameters for collision shift and collision broadening. Figure B.14 illustrates a progressive fit of the spectrally well-isolated R₂(7) line using first a shifted Voigt profile (collisionally broadened), followed by a shifted standard Galatry profile (symmetric, collisionally broadened and motionally narrowed), and finally the generalized Galatry profile (asymmetric, collisionally broadened and motionally narrowed). This progressive fit is similar to that suggested by Rea [95] (and analogous to
his Fig. 5.7) and described in detail by Varghese and Hanson [109]. These fits are performed without normalization of the peak. The progressive change in the shape and magnitude of the fitting residuals are exactly as described by [95,109].

Three different experiments near $T = 2500$ K and $P = 1-2$ atm were refit, all yielding quite similar effects. Compared to the Voigt profile fit, the Galatry profile required a larger broadening coefficient due to the counter-acting motional narrowing of the lineshape. On average, the broadening coefficient was 13% higher when motional narrowing was included in either the standard or generalized Galatry fits. Of particular importance, the inclusion of motional narrowing effects improved the line-center fit of the lineshape. When asymmetry was allowed into the lineshape profile through the generalized Galatry model, the collision-shift coefficient became, on average, 13% higher. The final residual (or lack thereof) shown in Fig. B.14 seems to indicate that this isolated lineshape is more accurately described by the generalized Galatry profile than the simpler Voigt profile.

Although the OH lineshape is clearly well-modeled with a motionally narrowed and asymmetrically shifted profile, the Voigt profile is a reasonable approximation for the current range of shock tube conditions. If the broadening and shift parameters from the fit in Fig. B.6 were used, the line-center absorption coefficient would only be in error on the order of 1-2%. However, having measured the broadening coefficients with the lineshapes normalized to the peak, the error in the line-center absorption coefficient will be negligible, as long as the proper shift and collision parameters are utilized. As the shifted Voigt profile is simpler than the Galatry profile (only 2 parameters – shift and width), easier to calculate, and quite commonly used, it will most likely remain the model of choice until conditions are found where the lineshape errors inherent in this approximation are simply unacceptable. The shift and broadening coefficients given in Tables B.1 and B.3 will give quite accurate line center peak absorption coefficients for the conditions of most shock tube chemical kinetics work.

**B.5 Conclusions**

The present work examines the collision-shift and -broadening parameters for several transitions of the A-X(0,0) band of OH in bath gases of Ar and N$_2$. The collision
shift is shown to clearly obey the form $\delta(T) = \delta(T_{\text{ref}}) [T_{\text{ref}}/T]^n$. The shift is a function of the lower-state rotational quantum number, generally increasing with increasing $J''$, and also appears to vary somewhat depending on the specific rotational branch of the transition. The shift is also found to be, on average, 23% lower for $N_2$ bath gas compared to Ar.

Measurements of collision-broadening are in good agreement with the previous measurements of Rea et al. [39]. Collision broadening parameters for additional transitions outside of the $R_1$ rotational branch are presented here and add to the existing database.

As suggested by Rea [95], the lineshape of OH is found to be more accurately described by a generalized Galatry profile, which includes effects of motional narrowing and a certain level of correlation between velocity-changing and state-perturbing collisions. The assumption of a Voigt lineshape profile in the data reduction process underestimates both the actual collision broadening (due to ignorance of motional narrowing effects) and collision shift (due to ignorance of asymmetry in the lineshape) by approximately 13% for each parameter.
Table B.1: Collision-shift parameters for Ar.

<table>
<thead>
<tr>
<th>Transition</th>
<th>No. of expts.</th>
<th>Temperature range [K]</th>
<th>$\delta_\lambda$ (2500K) $[10^{-3} \text{cm}^{-1} \text{atm}^{-1}]$</th>
<th>Avg. estimated unc. $[10^{-3} \text{cm}^{-1} \text{atm}^{-1}]$</th>
<th>$n$</th>
<th>Unc. in $n$ $[2\sigma]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_1 (5)$</td>
<td>20</td>
<td>1555-3080</td>
<td>8.5</td>
<td>+0.2, -0.15</td>
<td>0.76</td>
<td>0.05</td>
</tr>
<tr>
<td>$R_1 (7)$</td>
<td>4</td>
<td>1550-3022</td>
<td>8.3</td>
<td>+0.25, -0.20</td>
<td>0.92</td>
<td>0.1 $^a$</td>
</tr>
<tr>
<td>$R_{21} (5)$</td>
<td>19</td>
<td>1555-3080</td>
<td>8.1</td>
<td>+0.45, -0.40</td>
<td>0.84</td>
<td>0.11</td>
</tr>
<tr>
<td>$R_{21} (7)$</td>
<td>4</td>
<td>1550-3022</td>
<td>8.7</td>
<td>+0.90, -0.90</td>
<td>0.68</td>
<td>0.22</td>
</tr>
<tr>
<td>$Q_1 (3)$</td>
<td>4</td>
<td>1558-3074</td>
<td>6.6</td>
<td>+0.30, -0.20</td>
<td>0.78</td>
<td>0.03</td>
</tr>
<tr>
<td>$P_1 (1)$</td>
<td>4</td>
<td>1558-3074</td>
<td>5.0</td>
<td>+0.25, -0.20</td>
<td>0.73</td>
<td>0.08</td>
</tr>
<tr>
<td>$P_1 (2)$</td>
<td>4</td>
<td>1558-3074</td>
<td>5.4 $^b$</td>
<td>+0.30, -0.25</td>
<td>0.81 $^b$</td>
<td>0.03</td>
</tr>
<tr>
<td>$R_1 (1)$</td>
<td>1</td>
<td>2474</td>
<td>7.2</td>
<td>+0.95, -0.85</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_1 (4)$</td>
<td>1</td>
<td>2444</td>
<td>8.7</td>
<td>+0.45, -0.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_1 (6)$</td>
<td>1</td>
<td>2498</td>
<td>9.1</td>
<td>+0.55, -0.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_1 (11)$</td>
<td>4</td>
<td>1550-3022</td>
<td>7.9</td>
<td>+1.30, -1.30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_{21} (1)$</td>
<td>1</td>
<td>2474</td>
<td>6.5</td>
<td>+1.05, -1.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_{21} (4)$</td>
<td>1</td>
<td>2444</td>
<td>8.1</td>
<td>+0.65, -0.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_3 (1)$</td>
<td>1</td>
<td>2525</td>
<td>6.5</td>
<td>+0.55, -0.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_3 (7)$</td>
<td>1</td>
<td>2529</td>
<td>9.2</td>
<td>+0.70, -0.45</td>
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<td></td>
</tr>
<tr>
<td>$R_3 (8)$</td>
<td>1</td>
<td>2477</td>
<td>9.5</td>
<td>+1.00, -0.90</td>
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<td></td>
</tr>
<tr>
<td>$Q_3 (1)$</td>
<td>1</td>
<td>2508</td>
<td>5.2</td>
<td>+0.50, -0.40</td>
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<td></td>
</tr>
<tr>
<td>$Q_{21} (1)$</td>
<td>1</td>
<td>2508</td>
<td>6.1</td>
<td>+0.60, -0.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Q_{21} (3)$</td>
<td>4</td>
<td>1558-3074</td>
<td>6.6</td>
<td>+0.40, -0.35</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Uncertainty calculated from max/min error bars

$^b$ Values are for the fit including [104]
Table B.2: Collision-shift parameters for N\textsubscript{2}.

<table>
<thead>
<tr>
<th>Transition</th>
<th>No. of expts.</th>
<th>Temperature range [K]</th>
<th>$\delta_v(2500\text{K})$ [$10^{-3}\text{cm}^{-1}\text{atm}^{-1}$]</th>
<th>Avg. estimated unc. [$10^{-3}\text{cm}^{-1}\text{atm}^{-1}$]</th>
<th>$n$</th>
<th>$n$ [2\sigma]</th>
</tr>
</thead>
<tbody>
<tr>
<td>P\textsubscript{1}(2)</td>
<td>2</td>
<td>2288-2816</td>
<td>4.5</td>
<td>+0.50, -0.40</td>
<td>0.55</td>
<td>0.10</td>
</tr>
<tr>
<td>R\textsubscript{1}(5)</td>
<td>3</td>
<td>2293-2808</td>
<td>6.1</td>
<td>+0.30, -0.20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R\textsubscript{21}(5)</td>
<td>3</td>
<td>2293-2808</td>
<td>5.7</td>
<td>+0.65, -0.65</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R\textsubscript{1}(1)</td>
<td>1</td>
<td>2487</td>
<td>5.2</td>
<td>+1.5, -1.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R\textsubscript{1}(7)</td>
<td>1</td>
<td>2499</td>
<td>6.6</td>
<td>+0.30, -0.20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R\textsubscript{1}(11)</td>
<td>1</td>
<td>2499</td>
<td>4.4</td>
<td>+1.4, -1.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R\textsubscript{21}(1)</td>
<td>1</td>
<td>2487</td>
<td>5.9</td>
<td>+1.8, -1.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R\textsubscript{21}(7)</td>
<td>1</td>
<td>2499</td>
<td>6.0</td>
<td>+1.0, -1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Q\textsubscript{1}(1)</td>
<td>1</td>
<td>2414</td>
<td>4.2</td>
<td>+0.80, -0.55</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Q\textsubscript{1}(3)</td>
<td>2</td>
<td>2288-2816</td>
<td>5.0</td>
<td>+0.50, -0.30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Q\textsubscript{21}(1)</td>
<td>1</td>
<td>2414</td>
<td>4.9</td>
<td>+0.90, -0.70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Q\textsubscript{21}(3)</td>
<td>2</td>
<td>2288-2816</td>
<td>5.3</td>
<td>+0.65, -0.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R\textsubscript{2}(1)</td>
<td>1</td>
<td>2474</td>
<td>5.9</td>
<td>+0.80, -0.55</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P\textsubscript{1}(1)</td>
<td>2</td>
<td>2288-2816</td>
<td>4.2</td>
<td>+0.35, -0.30</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table B.3: Collision-broadening parameters for Ar.

<table>
<thead>
<tr>
<th>Transition</th>
<th>No. of expts.</th>
<th>Temperature range [K]</th>
<th>This study only</th>
<th>With Rea et al. [39]</th>
<th>With Rea et al. [39]</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$2\gamma_{\text{Ar}(2500\text{K})}$ [cm$^{-1}$ atm$^{-1}$]</td>
<td>$n$</td>
<td>$n$</td>
</tr>
<tr>
<td>R$_1$(5)</td>
<td>20</td>
<td>1555-3080</td>
<td>0.026</td>
<td>0.83</td>
<td>0.79</td>
</tr>
<tr>
<td>R$_1$(7)</td>
<td>4</td>
<td>1550-3022</td>
<td>0.023</td>
<td>1.01</td>
<td>0.86</td>
</tr>
<tr>
<td>R$_1$(11)</td>
<td>4</td>
<td>1550-3022</td>
<td>0.030</td>
<td>0.83</td>
<td>0.73</td>
</tr>
<tr>
<td>P$_1$(1)</td>
<td>4</td>
<td>1558-3074</td>
<td>0.027</td>
<td>0.90</td>
<td>0.78</td>
</tr>
<tr>
<td>R$_2$(5)</td>
<td>19</td>
<td>1555-3080</td>
<td>0.027</td>
<td>0.88</td>
<td>0.78</td>
</tr>
<tr>
<td>Q$_1$(3)</td>
<td>4</td>
<td>1558-3074</td>
<td>0.026</td>
<td>0.78</td>
<td>0.79</td>
</tr>
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<td>Q$_2$(3)</td>
<td>4</td>
<td>1558-3074</td>
<td>0.025</td>
<td>0.90</td>
<td>0.80</td>
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</table>

Table B.4: Collision-broadening parameters for N$_2$.

<table>
<thead>
<tr>
<th>Transition</th>
<th>No. of expts.</th>
<th>Temperature range [K]</th>
<th>This study only</th>
<th>With Rea et al. [39]</th>
<th>With Rea et al. [39]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$2\gamma_{\text{N}_2(2500\text{K})}$ [cm$^{-1}$ atm$^{-1}$]</td>
<td>$n$</td>
<td>$n$</td>
</tr>
<tr>
<td>R$_1$(5)</td>
<td>4</td>
<td>2051-2808</td>
<td>0.033</td>
<td>0.58</td>
<td>0.88</td>
</tr>
<tr>
<td>R$_1$(7)</td>
<td>1</td>
<td>2499</td>
<td>0.029</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R$_1$(11)</td>
<td>1</td>
<td>2499</td>
<td>0.029</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R$_2$(5)</td>
<td>4</td>
<td>2051-2808</td>
<td>0.033</td>
<td>0.71</td>
<td>0.88</td>
</tr>
<tr>
<td>P$_1$(1)</td>
<td>2</td>
<td>2288-2816</td>
<td>0.035</td>
<td>0.86</td>
<td></td>
</tr>
</tbody>
</table>
Figure B.1: Effects of collision shift on the line-center absorption coefficient.

Figure B.2: Condition space for existing measurements of OH collision shift. Solid line: \( P_1(2) \) line in the (0,0) band, Ar and \( \text{N}_2 \) as well as other collision partners [104]; (●): (0,0) band head [106]; (∇ and dotted line): (1,0) band, \( \text{H}_2\text{O} \) and \( \text{N}_2 \) collision partners [104].
Figure B.3: Experimental setup for collision shift measurements, including the shock tube and scanning laser diagnostic.
Figure B.4: Example experimental data for the R_{1}(5) and R_{21}(5) absorption transitions. Conditions are T_5 = 2525 K, P_5 = 2.07 atm.
Figure B.5: Fit of etalon transmission peaks to transfer measured spectral information from time-basis to frequency-basis. Successive transmission peaks have 2 GHz spacing (4 GHz in the UV). Sinusoidal (previous work) and polynomial (present work) functions have been used to fit the data.
Figure B.6: Example experiment for the R₁(5) transition. Conditions are $T_5 = 2525$ K, $P_5 = 2.07$ atm. Only a fraction of the data points are shown for clarity. The residuals show clear evidence of motional narrowing. In addition, the asymmetric behavior in the wings of the shock tube lineshape residual can be observed.
Figure B.7: Collision shift data for the R_{1}(5) transition of OH. (■): $P_5 = 1.5$-2.7 atm; ($\triangle$): $P_5 = 4$ atm; (○): $P_5 = 7.5$ atm. Linear fit of all data yields $\delta_A = -0.0085 \exp(2500/T)^{0.76}$ cm$^{-1}$ atm$^{-1}$ for this transition.

Figure B.8: Collision shift data for the R_{21}(5) transition of OH. (■): $P_5 = 1.5$-2.7 atm; ($\triangle$): $P_5 = 4$ atm; (○): $P_5 = 7.5$ atm. Linear fit of all data yields $\delta_A = -0.0081 \exp(2500/T)^{0.84}$ cm$^{-1}$ atm$^{-1}$ for this transition.
Figure B.9: Collision shift data for the P1(1) and P1(2) transitions of OH in Ar. (■): P1(1) data of current study; (□): estimated P1(2) data of current study; (▲): room temperature P1(2) data from [104]. Linear fit of all P1(2) data (dashed line) yields $\delta_{Ar} = -0.0054 \times \exp(2500/T)^{0.81}$ cm$^{-1}$ atm$^{-1}$ for this transition.

Figure B.10: Collision shift data for the P1(1) and P1(2) transitions of OH in N2. (■): P1(1) data of current study; (□): estimated P1(2) data of current study; (▲): room temperature P1(2) data from [104]. Linear fit of all P1(2) data yields $\delta_{N2} = -0.0045 \times \exp(2500/T)^{0.55}$ cm$^{-1}$ atm$^{-1}$ for this transition.
Figure B.11: Collision shift coefficients for OH in Ar bath gas, normalized to 2500 K. Symbols for different rotational branches are: (■): R_1; (□): R_{21}; (◇): R_2; (▲): Q_1; (▼): Q_{21}. Excluding the Q_1 branch, the average change in collision shift with increasing $J''$ is $4 \times 10^{-4} \pm 4 \times 10^{-5}$ [cm$^{-1}$atm$^{-1}$/$J''$].

Figure B.12: Collision shift coefficients for OH in N$_2$ bath gas, normalized to 2500 K. Symbols for different rotational branches are: (■): R_1; (□): R_{21}; (▲): Q_1; (▼): Q_{21}. Excluding the R_{21} branch, the average change in collision shift with increasing $J''$ is $3 \times 10^{-4} \pm 1 \times 10^{-4}$ [cm$^{-1}$atm$^{-1}$/$J''$].
Figure B.13: Collision-broadening data for the R_1(5) transition in Ar. (■): P_5 = 1.5-2.7 atm; (△): P_5 = 4 atm; (○): P_5 = 7.5 atm; (▲): room-temperature data from [104]. Solid line is a fit to present data only; dashed line includes data from [104].
Figure B.14: Progressive lineshape fits for the $R_2(7)$ line in Ar at 2530 K, 2.08 atm. In this example, assumption of the Voigt profile underestimates the actual normalized collision shift parameter ($s$) and Voigt broadening parameter ($y$) by 11.6% each.
Appendix C: Shock velocity and $T_5$, $P_5$ uncertainty analysis

This appendix describes an analysis for estimating the uncertainty in the calculated ideal shock conditions immediately behind the reflected shock wave, based on estimated uncertainties in various measured parameters as well as the quality of the shock velocity measurement.

C.1 Motivation

The accurate knowledge of post-shock temperatures and pressures in shock tube chemical kinetics experiments is critical to successful measurements of rate coefficient parameters. This issue was clearly demonstrated in Section 3.5.1, where a difference of 25 K (~1.5%) was found to be the primary cause of a factor of three discrepancy in the reported results for $k_{1a}$ from two previous investigations.

The determination of the correct temperature and pressure is typically separated into two parts. The first concern is the calculation of the ideal shock conditions immediately behind the shock wave at the test location (optical diagnostic ports), based on an accurate determination of the incident shock wave velocity and the initial conditions. Any non-ideal effects must subsequently be taken into account, including temperature and pressure changes with time due to chemical heat release, boundary layer growth behind the incident shock wave, and vibrational relaxation of the shocked gases. For the work in this thesis, chemical heat release was not an issue due to the very low concentration mixtures utilized. However, in other experimental situations the heat release is typically accounted for during the chemical modeling of the experiment by assuming that constant $U,V$ conditions apply. Boundary layer effects were assumed to be negligible in the post-shock regime (due to the large shock tube diameter – see Section 3.5.1). The attenuation of the incident shock wave is accounted for in the shock velocity
linear regression analysis (see below). Finally, vibrational relaxation effects, typically affecting mixtures with large concentrations of diatomic species, can be minimized by decreasing the mole fraction of diatomics and adding helium or other light gases to speed up the relaxation process. When these options are not suitable, published relaxation-time relationships for various relaxing-gas/bath-gas combinations can be used to estimate the relaxation rate from vibrationally frozen to vibrationally equilibrated temperature and pressure conditions [51].

This appendix will focus only on the calculation of the ideal shock conditions immediately behind the reflected shock wave and the estimated uncertainties in that calculation.

C.2 Shock velocity measurement and uncertainty calculation

The conditions immediately behind the reflected shock wave are calculated using the well-known ideal shock relations [110]:

\[
T_2 = T_1 \left[ \frac{2(\gamma - 1)M^2 + (3 - \gamma)}{(\gamma + 1)^2 M^2} \right] \left[ (3\gamma - 1)M^2 - 2(\gamma - 1) \right] \tag{C.1}
\]

\[
P_2 = P_1 \left[ \frac{2\gamma M^2 - (\gamma - 1)}{\gamma + 1} \right] \left[ \frac{(3\gamma - 1)M^2 - 2(\gamma - 1)}{(\gamma - 1)M^2 + 2} \right] \tag{C.2}
\]

where \( M = \) incident shock Mach number \( \equiv V/a_i \), and \( a_i = \) the speed of sound at the initial conditions \( \equiv (\gamma R T_i)^{1/2} \). Input parameters in these equations which must be measured for each experiment include the shock velocity at the endwall, \( V_{endwall} \), the initial temperature, \( T_i \), and the initial pressure, \( P_i \). The ratio of specific heats, \( \gamma \), is determined from the thermodynamic data of the mixture species.

The initial conditions \( T_i \) and \( P_i \) are measured before each experiment, and the instrument uncertainties can be estimated for each of these quantities. The specific heat ratio, \( \gamma \), is assumed to have negligible uncertainty. The shock velocity is the most critical parameter, and an analysis is developed here to understand the uncertainty in its measurement.
The shock velocity is measured using five PCB Piezotronics piezoelectric pressure transducers (PZT’s) connected to four interval timers with 0.1 \( \mu \)s time-resolution. The pressure rise in the incident shock wave at successive PZT’s triggers the start and end for each interval timer. The four velocity measurements are fit to a linear regression and extrapolated to the endwall to determine the velocity at the endwall. The gas volume at the optical test ports, located only 2 cm from the endwall, is assumed to obtain conditions very similar those at the endwall. Uncertain quantities in the determination of \( V_{endwall} \) are therefore the interval distances, \( d_{xi} \), the interval times, \( dt_i \), and the location of the endwall, \( x_{endwall} \). The \( dx_i \) uncertainty was estimated at \( \delta x = \pm 0.25 \) mm, based on a \( \pm 0.12 \) mm tolerance in the location dimensions for each PZT port. The \( dt_i \) uncertainty was assessed by performing experiments in which all five transducers were mounted at the same plane along the shock tube axis. The variation in the time at which each PZT reached the trigger-threshold voltage gives an indication of the potential error due to individual PZT time response. Results of one of these experiments are shown in Fig. C.1. Based on a few shocks at various conditions, the spread between the earliest and latest PZT time response at the trigger threshold appeared to be near \( \delta t = 0.7 \) \( \mu \)s. While a specific PZT may tend to be consistently later or earlier than others, in general it was observed that relative positions of the PZT’s did not necessarily remain constant from shock to shock. Therefore, the maximum spread was retained as the estimated uncertainty in the measured time intervals due to the potential time response difference of two consecutive PZT’s.

A spreadsheet was developed to perform a weighted linear regression analysis of the incident shock velocity measurements and to analyze the uncertainty in the determination of the endwall shock velocity. The equations used here follow the linear regression analysis discussion in Bevington and Robinson [111]. The incident shock wave velocity at each measurement point \( i \) (mid-way between successive PZT’s) is determined quite simply by:

\[
V_i = y_i = \frac{dx_i}{dt_i}
\]  

(C.3)

Estimated uncertainties for each velocity point, \( \sigma_i \), can be calculated based on assumed uncertainties in \( dt_i \) and \( dx_i \):

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\[
\sigma_i = V_i \left[ \left( \frac{\delta x}{dx_i} \right)^2 + \left( \frac{\delta \xi}{dt_i} \right)^2 \right]^{\frac{1}{2}}
\]

(C.4)

Using the estimated uncertainties as weighting factors and assuming initial guesses for the linear fit parameters \(a\) and \(b\), a goodness-of-fit parameter, \(\chi^2\), can be calculated:

\[
\chi^2 = \sum_i \left[ \frac{1}{\sigma_i^2} (y_i - (a - bx_i))^2 \right]
\]

(C.5)

The optimum fit is determined by the parameters \(a\) and \(b\) that minimize the weighted sum of the squares of the deviations, \(\chi^2\) (i.e., a “least-squares” fit). The parameters \(a\) and \(b\) can be found by setting to zero the partial derivatives of \(\chi^2\) with respect to each of the parameters. Rearranging them into a pair of linear simultaneous equations in \(a\) and \(b\), the solution can be found using the method of determinants. The problem is reduced to directly solving the following equations:

\[
a = \frac{1}{\Delta} \left( \sum \frac{x_i^2}{\sigma_i^2} \sum \frac{y_i}{\sigma_i^2} - \sum \frac{x_i y_i}{\sigma_i^2} \right)
\]

(C.6)

\[
b = \frac{1}{\Delta} \left( \sum \frac{1}{\sigma_i^2} \sum \frac{x_i y_i}{\sigma_i^2} - \sum \frac{x_i}{\sigma_i^2} \sum \frac{y_i}{\sigma_i^2} \right)
\]

(C.7)

\[
\Delta = \sum \frac{1}{\sigma_i^2} - \left( \sum \frac{x_i}{\sigma_i^2} \right)^2
\]

(C.8)

The standard deviation for the fit, \(\sigma\), can be calculated based on the scatter in the linear regression:

\[
\sigma^2 = \frac{1}{N - 2} \sum (y_i - a - bx_i)^2
\]

(C.9)

where \(N\) is the number of data points. If the uncertainties used to calculate \(\sigma_i\) have been appropriately estimated, and if \(\sigma_i\) is approximately the same for all points, \(\sigma\) should be approximately equal to \(\sigma_i\). Substituting \(\sigma\) from Equation (C.9) into Equation (C.5) yields \(\chi^2 \approx (N - 2)\). So, if in Equation (C.5) \(\chi^2 < (N - 2)\), the uncertainty in one or more parameters has been overestimated; conversely if \(\chi^2 > (N - 2)\), the scatter in the velocity data indicates the presence of higher random uncertainties than the estimated uncertainty suggests. The error in the time interval measurement \(dt_i\) is the dominant uncertainty.
Because the maximum rise time variation has been measured ($\delta t = 0.7 \mu s$), the estimated uncertainty $\sigma_i$, calculated with this $\delta t$, is retained as a minimum uncertainty. If $\chi^2 > (N - 2)$, the estimate used for $\delta t$ should be increased until $\chi^2 = (N - 2)$. The uncertainty $\sigma_i$ is then used to calculate the uncertainty in the fit parameters $a$ and $b$, by taking partial derivatives of Equation (C.6) and Equation (C.7) and substituting them into the error propagation equation. This equation, for a general function $z = f(u,v, \ldots)$ is (assuming uncorrelated errors):

$$\sigma_z^2 \equiv \sigma_a^2 \left( \frac{\partial z}{\partial u} \right)^2 + \sigma_b^2 \left( \frac{\partial z}{\partial v} \right)^2 + \ldots$$  \hspace{1cm} (C.10)

The uncertainties in $a$ and $b$ can be reduced to:

$$\sigma_a^2 = \frac{1}{\Delta} \sum \frac{x_i^2}{\sigma_i^2} \hspace{1cm} (C.11)$$

$$\sigma_b^2 = \frac{1}{\Delta} \sum \frac{1}{\sigma_i^2} \hspace{1cm} (C.12)$$

Finally, the velocity at the endwall is calculated from the fit parameters $a$ and $b$, and the uncertainty in the endwall velocity determination is calculated from uncertainties in $a$, $b$, and $x_{endwall}$ through the error propagation equation. For the endwall velocity, Equation (C.10) is:

$$\sigma_{V_{endwall}}^2 = \sigma_a^2 + \sigma_b^2 x_{endwall}^2 + (\delta x_{endwall})^2 b^2$$  \hspace{1cm} (C.13)

An example shock velocity measurement and calculated uncertainty are shown in Fig. C.2. In this example $\chi^2 = 1.27$, indicating that the assumed uncertainties in $dt_i$ and $dx_i$ were appropriate and perhaps a little overestimated, given the scatter in the data. Also shown in Fig. C.2 is the uncertainty in the velocity at the endwall, $\sigma_{V_{endwall}}$, determined from Equation (C.13).

**C.3 Calculation of uncertainties in $T_5, P_5$**

Now that the uncertainty in the shock velocity at the endwall has been properly ascertained, it must be propagated, along with the estimated uncertainties in $T_1$ and $P_1$ from instrumental errors, through to uncertainties in $T_5$ and $P_5$. To do this, the error propagation equation (C.10) is once again utilized, requiring partial derivatives of
Equations (C.1) and (C.2) with respect to $V_{\text{endwall}}$, $T_1$, and $P_1$ (remembering that the incident shock Mach number $M$ includes both $V_{\text{endwall}}$ and $T_1$).

The example experiment shown in Fig. C.2 resulted in $T_5$ and $P_5$ uncertainties of $\pm 0.73\%$ and $\pm 1.06\%$, respectively, at 1929 K and 2.18 atm. These numbers assume uncertainties in $T_1$ and $P_1$ of $\pm 0.3$ K and $\pm 0.05$ torr, respectively.

C.4 Discussion

The detailed analysis described above was undertaken for several reasons. Most importantly, it provides a method by which to calculate appropriate, defensible uncertainties for the conditions immediately behind the reflected shock wave. The analysis also provides insight into the limiting aspects of these uncertainties. For example, the analysis shows that the calculation of $P_5$ is quite sensitive to uncertainties in $T_1$ ($\pm 1$ K in $T_1$ results in $\sim \pm 0.5\%$ uncertainty in $P_5$), whereas $T_5$ is quite insensitive to $T_1$ ($\pm 1$ K in $T_1$ results in $\sim \pm 0.023\%$ uncertainty in $T_3$). The goodness-of-fit parameter $\chi^2$ provides an indication of how well-controlled the shock velocity measurement is, as a large $\chi^2$ is a warning that there may be problems with one or more PZT’s or that the assumption of a linearly decaying velocity profile is not valid. Consistent deviation patterns in the shock velocity trace may point to a particular PZT suffering from a poor response time. That PZT, once identified, can be replaced or moved to a less sensitive location (in the port closest to the diaphragm, for example). The uncertainty analysis also points out when “good” is “good enough” – that is, if the standard deviation in the velocity profile is less than the estimated uncertainties, no further corrections or fixes need to be made to the PZT’s. If, on the other hand, the estimated uncertainties are still too high, effort must be made to decrease uncertainties in the PZT rise times, $T_1$, or $P_1$.

In the careful analysis detailed above, uncertainties in $T_5$ are estimated to be less than 1%. Given the other previously mentioned non-ideal effects which occur in shock tube experiments, it is unlikely, at least in this author’s experience, that uncertainties below those calculated in the present example could even be believed. Therefore, it is not recommended to make attempts at further improving the shock velocity measurement beyond maintaining the observed performance presented here. Of larger concern are the non-ideal effects which create perturbations to the initial shock conditions, such as the
gradual increase in the pressure observed after ~ 1 ms of test time in the example of Fig. 3.3.
Figure C.1: A shock tube experiment to determine the variation in PZT rise times at the interval timer trigger-threshold voltage. All five transducers are located in the same plane perpendicular to the axis of the shock tube. The inset shows the pressure rise from initial to incident shock pressures. The trigger threshold is typically set to ~10% of the incident pressure rise.

Figure C.2: An example shock velocity measurement and calculated uncertainties.
Appendix D: ARAS system design, optimization and theory

This appendix includes discussion on a few topics related to atomic resonance absorption spectroscopy (ARAS) and further describes the design and optimization of the ARAS diagnostic utilized for the measurements of the rate coefficient of \( \text{CH}_3+\text{O}_2 \rightarrow \) products. First, the two-layer model for microwave discharge atomic emission lineshapes is described in brief. Some specific design considerations for the present experimental apparatus are discussed. Finally, the results of the calibration experiments are roughly fit to a three-layer model by assuming reasonable lamp parameters.

D.1 Atomic resonance absorption spectroscopy

Atomic resonance absorption spectroscopy (ARAS) diagnostics have been used for several decades as a means to measure the concentrations of various atomic species, including (but not exclusively) O, N, H, and C as well as I, Cl, and Br. The application of ARAS techniques in shock tube research is also well-established and has been recently reviewed [43,44]. The ARAS diagnostic apparatus used in the present work is detailed in Section 2.3. ARAS is different from narrow-linewidth techniques such as cw laser absorption, in that the source of the radiation is the resonant emission from electronically excited atomic species rather than from a laser. The excited atomic species are produced by dissociation of molecular precursor species inside of a flowing microwave discharge “lamp.” The resulting resonant emission lineshape has a spectral profile with a line width on the same order of magnitude as the absorption lineshape of the atomic species at shock tube conditions of interest. The emission lineshape is further complicated in lamp configurations with relatively high atomic concentrations, as the radiation emitted by the excited atoms is simultaneously absorbed by ground-state atoms both inside the discharge and also in the cooler “reversal” region just outside of the discharge.
Relationships which describe the emission and absorption processes in ARAS systems are provided in a number of references. The two-layer model for a resonance line emission source (three layers including the absorbing medium of interest) was first detailed by Braun and Carrington [112]. The three layers include: an optically thick emitter, a reversing layer, and a separate absorbing layer. While the separation into layers is an approximation to the true nature of the concentration gradients within a flowing gas discharge, the model has been widely accepted – and validated – with only some changes to assumptions about temperature conditions within the lamp itself. The three layers represent, in order: the discharge region which contains both emitting and absorbing atoms; the region between the end of the hot discharge and the window of the lamp, in which a lower concentration of ground state absorbing atoms may exist (but no upper-state emitting atoms); and the gas volume being interrogated – for the present work, a shock tube.

Summarizing the arguments of Braun and Carrington, the optical depth at line center for layer \( n \), \( D_n \), is simply described by \( D_n = \sigma_{on} N_n L_n \); where \( \sigma_{on} \) is the absorption cross section at line center for the conditions in layer \( n \), \( N_n \) is the concentration of absorbing species, and \( L_n \) is the optical path length of the layer. Assuming a Doppler-broadened lineshape function (negligible Lorentzian, or pressure, broadening), the line-center absorption cross section is related to the oscillator strength, \( f_{osc} \), by the following expression:

\[
\sigma_{on} = \left( \frac{f_{osc}}{\delta_n} \right) \frac{\pi^{1/2} e^2}{m_e c}
\]  \hspace{1cm} (D.1)

where \( \delta_n \) is the 1/e half-width of the Doppler lineshape at the temperature \( T_n \):

\[
\delta_n = \left( \frac{\nu_o}{c} \left( \frac{2RT_n}{m} \right) \right)^{1/2}
\]  \hspace{1cm} (D.2)

In Equation (D.1), \( e = 4.803 \times 10^{-10} \text{ cm}^{3/2} \text{ g}^{1/2} \text{s}^{-1} \) and \( m_e \) is the mass of an electron, 0.91095x10^{-30} kg. In Equation (D.2), \( m \) is the mass of the atom, \( \nu_o \) is the line-center frequency, \( c \) is the speed of light, and \( R \) is the gas constant. Assuming Doppler-broadened lineshapes for both emission and absorption, the frequency-dependent
intensity emitted from the discharge region (layer 1) is given by an expression derived in Mitchell and Zemansky [113]:

\[ I_1(\nu) \propto \left[ 1 - \exp\left(-D_1 \exp\left(\frac{\nu - \nu_o}{\delta_1}\right)\right) \right] \quad (D.3) \]

Layer 2, the reversal layer, is defined simply as an absorbing layer, with the emanating intensity given by:

\[ I_2(\nu) \propto I_1(\nu) \exp\left(-D_2 \exp\left(\frac{\nu - \nu_o}{\delta_2}\right)\right) \quad (D.4) \]

Finally, the intensity transmitted through layer 3 (the shock tube) is given by:

\[ I_3(\nu) \propto I_2(\nu) \exp\left(-D_3 \exp\left(\frac{\nu - \nu_o}{\delta_3}\right)\right) \quad (D.5) \]

The integrated absorbance in the shock tube, defined in Chapter 3 as \( ABS = \sigma_{D\text{-atoms}*}[O]*L = -\ln(I/I_o) \) is defined by the model as:

\[ ABS = \sigma_{eff} N_3 L_3 = -\ln \frac{\int_{-\infty}^{\infty} I_3(\nu) d\nu}{\int_{-\infty}^{\infty} I_2(\nu) d\nu} \quad (D.6) \]

Here, \( \sigma_{eff} \) is the effective absorption cross section in the shock tube. The calibration curve determined by Equation (2.1) is only an effective cross section and is not related to the line-center absorption cross section defined in Equation (D.1), except perhaps in isolated cases of very low self-absorption and reversal in the lamp combined with very large Doppler absorption line widths in layer 3. In this situation the \( \sigma_{eff} \), typically smaller than \( \sigma_{o3} \), will approach \( \sigma_{o3} \) in the limit of small absorption.

The two-layer model description of resonance lamps has been investigated and experimentally validated by several researchers, including high-resolution emission

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\[ \text{The expression is rigorously true for an emitting layer of vanishingly small cross section (a thin element of finite length in the emission direction), but gives satisfactory description for resonance lamps in which gas pressure is low enough to render secondary and tertiary resonance radiation small compared to primary resonance radiation.} \]
lineshape measurements [114-116] and empirical measurements of the calibration curves [116-120]. Of particular interest is the study of Maki et al. [119], in which the authors endeavored to measure not only the effective cross section, but also the concentration of H-atoms and the temperature profile of the discharge region. The calibration curve could thus be calculated from the theory and measured parameters alone, requiring no adjustable parameters. These authors achieved quite good agreement between the theoretically and empirically determined calibration curves.

D.2 Design and optimization considerations

In the planning and design phase of this work, several observations and decisions were made which affect the final quality and performance of the ARAS diagnostic. Some design choices were made based on a literature review, some for experimental convenience, and some from empirical investigation. This section highlights observations made during this process.

D.2.1 ARAS diagnostics: monochromator vs. atomic filter

In resonance lamps such as the microwave discharge system described in Section 2.3, the presence of non-resonant emission at wavelengths other than the O-atom transitions near 130.5 nm requires a procedure for determining the fraction of the total emission that is, in fact, resonant with the absorption transitions of ground-state O-atoms in the shock tube gases. Figure D.1 shows the output spectrum of the ARAS lamp at the conditions used for the work in Chapter 3, namely a mixture 1% O₂ / He at 6 torr with ~70 W of microwave power. For the measurement in Fig. D.1, the monochromator input and output slit widths were set to 100 µm in order to resolve the individual lines from one another. (Although the monochromator does not have enough resolution to fully resolve the lineshapes, the O-atom triplet lines are spaced far enough to be observed individually.) During an actual shock tube experiment, the monochromator slits were each set to 3 mm to include the whole O-atom triplet and maximize light throughput. The spectrum as measured by the PMT is, of course, a convolution of the spectral output of the lamp with the spectral transmission and response functions of the optics, the monochromator and the PMT. The non-resonant radiation (NR) typically arises from
small impurities present in the lamp gases, on the walls of the lamp system, or from leaks in the system allowing atmospheric air into the flow. In the case of oxygen, there is also a very weak pair of O-atom lines near 135 nm and a moderately strong emission line at 115 nm.

Two experimental procedures for isolating the resonant radiation fraction have been discussed in the literature. The first and most straightforward is the use of a monochromator to spectrally disperse and filter the lamp emission, as described in Section 2.3 and utilized in this work. This is also the method used previously by other researchers in our laboratory. The second method relies upon a separate measurement of the NR fraction, made possible by the complete absorption of the resonant radiation in an atomic filtering section.

An atomic filter for O-atoms, first described by Lee et al. [121], consists of a second fast-flowing microwave discharge with very low pressures of 100% O₂. The products of this discharge pass through the optical path between the ARAS lamp and the shock tube. When the filter is turned on, all resonant lamp emission near 130.5 nm is removed by the strong absorption by ground-state atoms in the filter section, and only the NR fraction of the lamp emission remains. Application of this filter in shock tube kinetics experiments has been described by Sutherland and co-workers [16,49,58,120,122,123].

The apparent benefit of using the O-atom filter over the VUV monochromator relates to the lamp emission intensity (i.e., signal-to-noise ratio) vs. the effective absorption cross section obtainable in these two systems. When using a monochromator, emission intensity at the PMT is greatly reduced due to poor reflectivity of optical surfaces inside the monochromator. This loss of signal necessitates higher emission intensities and therefore higher O-atom concentrations in the lamp (higher pressure, O₂ concentration, lamp power, or a combination of all three), typically resulting in a more self-absorbed and reversed lineshape and a lower effective absorption cross section (see Section D.3). The advantage of the O-atom filter method is that much lower O-atom concentrations can be used in the lamp, yielding emission lineshapes which are closer to the ideal Doppler-broadened profile and thus giving higher effective absorption cross sections. High absorption cross sections enable experimental work using reduced-
concentration reaction mixtures, typically resulting in increased kinetic isolation of the desired reaction rate coefficient. Researchers applying the O-atom filter technique typically use resonance lamp mixtures of <0.1% O₂/He at 2 torr or less of pressure. They also employ a CaF₂ window somewhere in the optical train, as it cuts off all wavelengths below 121 nm. There are additional complications in this method, however, which must be considered.

The use of the atomic filter is based on the desire to know the NR fraction in the reflected shock conditions. Most studies have done this by measuring the NR fraction before each experiment. However, as pointed out by Ross et al. [49], the NR fraction does not always remain constant throughout the vacuum conditions, initial fill conditions, and the incident and reflected shock conditions – specifically when another absorber is present in the mixture. If this secondary absorber has a wavelength-dependent absorption cross section, the relative absorption of the resonant radiation vs. the NR by the secondary absorber will change as the mixture is introduced into the shock tube and then shocked to higher densities. In the case of Ross et al. [49], high N₂O concentrations significantly affected the NR fraction between the vacuum, initial and reflected shock conditions. In one example in their study, the NR fraction changed from 0.69 in the pre-shock conditions to 0.38 in the reflected conditions. In most studies the ARAS system has been calibrated in the absence of large concentrations of secondary absorbers; thus, to have a meaningful absorption measurement of only the O-atom concentration, the NR radiation must be carefully characterized throughout the range of experimental conditions and accounted for in the data reduction process. A detailed description of their method is given by Ross et al. [49].

For the work undertaken in this dissertation, kinetic isolation of the title reactions required significant mole fractions of O₂, a species which has strong wavelength-

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3 It should be noted that while Fig. D.1 indicates ~10% of the total radiation is at wavelengths other than the O-atom triplet, it has been observed in our laboratory that using lower O-atom concentrations in the lamp (lower mole fractions, lower pressure, or lower microwave power) tends to increase the NR fraction. That is, lower concentrations result in less 130 nm radiation but the impurities remain as strong or stronger because more energy is available to excite those species. Thus, the problem of NR radiation and properly accounting for its absorption gets more significant as the lamp concentrations are decreased.
dependent absorption features throughout the spectral bandwidth of the PMT. Thus, to use the atomic filter method, once it was calibrated, would have required at least twice as many kinetics experiments – the second half being run with the atomic filter turned on in order to characterize the NR fraction at reflected shock conditions. Rather, the VUV monochromator method was selected for two primary reasons. First, using the monochromator simplifies the experimental setup due to the absence of the second microwave discharge and its associated hardware. As mentioned, it also significantly reduces the number of experiments required. Second, due to the impurity issues discussed in Section 3.3.3, higher concentrations of CH$_3$I were used in this work than, for example, in the work of Michael et al. [16]. In addition, the path length (i.d.) of our shock tube is greater than in [16]. The increased product of [O]$^*L$ suggested that a slightly desensitized diagnostic was actually preferred so that the absorption was not so quickly saturated at high O-atom mole fractions.

The effective absorption cross sections measured through the present calibration experiments can be compared to the cross sections achieved by other researchers in different lamp configurations. Table D.1 compares the effective cross sections from several researchers in the limit of very low absorption. If temperature dependence was reported, the value corresponding to 2000K is reported in the table. The most direct comparison to the present work is that of Dean [47]. In his thesis, Dean reported a slightly temperature-dependent cross section, but all measurements were considered to be within the Beers-Law limiting behavior (i.e., constant cross sections as a function of [O]). His relation yields $\sigma_{O\text{-atoms}} = 4.3 \times 10^{-15}$ cm$^2$, although this fit seems particularly sensitive to one mixture at the low end of the temperature range. Considering his data and a temperature-independent fit of $ABS$ vs. [O] yields $\sigma_{O\text{-atoms}} = 5.2 \times 10^{-15}$ cm$^2$, in excellent comparison with the results presented in Section 2.3.2.

D.2.2 Optimization of the lamp design and optics

The output characteristics of an ARAS diagnostic, including signal-to-noise ratio and the effective absorption cross section, are highly dependent on the specific operating conditions and dimensions of the lamp. As is demonstrated in the next section, the effective absorption cross section is very sensitive to the species concentrations in the
emitting and reversal layers of the lamp. The absorbing species in these two layers act to reduce the emission intensity at the line-center wavelengths, creating a self-absorbed and reversed emission lineshape. The strongest emission intensity is located in the wings rather than the peak of the absorption lineshape, thus reducing the effective absorption cross section. To achieve high absorption cross sections in the shock tube, the optical densities in these regimes must be kept as low as possible. In the discharge itself, a tradeoff must be made between high intensity / good signal-to-noise (high concentrations) and low self-absorption / high effective absorption cross sections (low concentrations). The presence of the reversal layer is simply an experimental convenience, in that typically there is some distance between the end of the plasma discharge and the window of the lamp. However, Lifshitz and coworkers [115,116,124] have developed lamps with essentially zero reversal length by placing the lamp window within the microwave discharge cavity. This lamp yields higher effective absorption cross sections than the more standard design pioneered by Davis and Braun [125], which these authors also investigated for comparison.

In the present work, the ARAS diagnostic was very similar to that used previously in our laboratory [47], with the exception that a commercially built McCarroll-type microwave discharge cavity was used rather than the homemade 1” diameter cavity. The McCarroll cavity design [48] has extensions connected to the original Evenson-Broida 1/4-wave cavity design [126] and enables improved power coupling into the flowing discharge gases. It is desired to have the discharge located as close as possible to the shock tube (to minimize the reversal length in the lamp), and the Evenson-Broida cavity had problems with discharge stability and power coupling at high microwave power settings. The problems were assumed to be caused by the proximity of the shock tube, which may behave like a large electrical ground and interfere with the electric fields in the plasma. In the final design, the end of the McCarroll cavity was located less than 0.25” from the shock tube port, resulting in a reversal length of approximately 1.5” (mostly inside the port itself, between the discharge and the shock tube window).

The present work retained the lamp operating conditions (mixture and pressure) and the monochromator used by Dean [47], except that higher microwave power was used here (70 W vs. 50 W). As in Dean, a MgF₂ lens was used in place of the exit
window in the shock tube. The lens yielded slight improvement in collection efficiency, mitigated somewhat by the higher thickness (~3.4mm at its center) and the resulting increased absorptive losses. The largest limitation in collection efficiency was the distance from the lens to the monochromator inlet. In the current shock tube layout, unlike that used by Dean, the inertial “dead-mass” (to which the driven section is mounted) prohibited the monochromator and its cart from being placed next to the shock tube ports. The lens approximately matched the f/7 aperture of the monochromator; however the magnification in the optical system caused a large portion of the light to be lost. In this lens system, if the shock tube inlet slit is considered to be the optical “object” at a distance of ~15 cm, the optical “image” is located at a distance of ~41 cm with an associated magnification of ~2.8. All of the light emanating from the object slit area (~0.15 cm x 1 cm) cannot be collected by the monochromator’s inlet aperture of 0.3 cm (slit width) x 1.2 cm (field stop due to PMT sensitive area height) and the extra light is lost. Significant improvement could be obtained if the monochromator inlet slit was located ~15 cm from the lens, and the lens changed to a focal length of 7.5 cm at 130 nm (nominally 10 cm at 248 nm). A magnification of 1 would result, and all light collected by the lens and apertured by the shock tube slits would be imaged onto the monochromator entrance slit. Calculations suggest that an approximate 3x signal improvement could be obtained.

Several other experimental parameters were adjusted to optimize the diagnostic’s performance. The gas flow rate in the lamp was maximized through the use of large diameter (1/2 inch) connections between the lamp and the vacuum pump. As observed by Davis and Braun [125], in lamps where the atomic species is produced through dissociation of a molecular species, slow gas flow rates (and long gas residence times) result in strong emission from the molecular species. In the case of O-atoms, the O₂ emission can dominate O-atom emission if the flow rates are not high enough. This was observed in our laboratory in the initial lamp and gas-handling design, where small-diameter gas lines were used and the flow was throttled between the lamp and the vacuum pump rather than between the gas cylinder and the lamp. Increasing the flow rate such that the discharge is somewhat dull in color results in the best spectral purity [125], and the in the present setup the flow rate was increased as much as possible given
the available vacuum pump and other hardware. In addition, leak-proof connections for the lamp and supply gas were important, as an air leaks into the system will produce strong N-atom emission. The leak rates into the lamp can be easily checked by closing the needle valve at the inlet to the lamp and evacuating the lamp volume.

Given a specific lamp operating condition, a few other details will ensure the highest possible signal-to-noise of the system. The monochromator must be evacuated using a vacuum pump, as even low pressures of air will absorb significant amounts of the light at 130 nm. In this work, monochromator pressures were typically ~ 10 mtorr, although even lower vacuum could have been achieved by using a turbomolecular pump (the unit which had previously been mounted to the monochromator was unavailable at the time). The electrical connections and signal conditioning of the PMT output also play a role in the signal-to-noise ratio, although the primary limitation is the level of radiant intensity arriving at the PMT.

Consistent day-to-day operation of the ARAS diagnostic is vital to high-quality absorption measurements, as the calibration of the diagnostic is sensitive to the lamp operating conditions. After the diagnostic system was built and characterized, operation of the lamp was very simple. Once the cavity was properly tuned for a specific flow condition (pressure, microwave power, and flow rate), as indicated by ~ 0 W power being reflected, it was very stable and typically did not need to be readjusted. Retuning the cavity was necessary, however, whenever any of the flow conditions were changed. Daily operation involved: 1) pumping out the lamp and checking the leak rate, 2) establishing the discharge gas flow rate and pressure and the cooling air flow, and 3) turning up the microwave power. Often the discharge would ignite itself when the input power reaches a certain level, particularly at low operating pressures. Otherwise, a small piezo-electric sparker or a Tesla coil was used to ignite the discharge. Between shock tube experiments the microwave power was turned down to zero and the gas flow was shut off to save gas mixture (the cooling air flow remained on until the cavity had sufficiently cooled).
D.3 Calibration and the two-layer model for the lamp

The empirical calibration curve given in Fig. 2.4 indicates that the absorption cross section, which is proportional to the slope of the curve, decreases as the absorbance and $[O]$ increase. To further understand the cause of the non-linear behavior of the effective absorption cross section, an attempt was made to fit the calibration curve using the simple two-layer lamp model described in Section D.1. This exercise provides insight into the consequences of the chosen lamp parameters, and the model can be perturbed to examine how changes to the lamp may roughly affect the diagnostic’s performance.

The model in Section D.1 can be applied directly to the O-atom ARAS lamp, with the following additions. First, the O-atom transition near 130 nm is actually a triplet transition with values for the total electronic angular momentum of $J = 0, 1,$ and 2 for the transitions at 130.603 nm, 130.486 nm, and 130.217 nm. The degeneracies of these three transitions are given by $g_J = 2J + 1$. The transitions are spectrally separated such that their lineshapes can be considered individually. Thus, Equations D.3-D.5 are evaluated for each of the three transitions, including the degeneracies for each transition. In addition, at the shock tube temperatures the relative populations in the three lower energy states ($\varepsilon_J = 226.977 \text{ cm}^{-1}, 158.265 \text{ cm}^{-1},$ and $0.0 \text{ cm}^{-1}$, respectively) will be determined by the Boltzmann distribution. (The next highest energy level, the $^1D$ state, is at 15868 cm$^{-1}$ and has inconsequential population at shock tube conditions of interest here.) Equations D.3-D.5, for the individual multiplet transitions with different $J$ are therefore:

$$I_{1J}(\nu) \propto \left\{ 1 - \exp\left[ -g_J D_1 \exp\left( \frac{\nu - \nu_o}{\delta_1} \right)^2 \right] \right\} \quad (D.7)$$

$$I_{2J}(\nu) \propto I_{1J}(\nu) \exp\left[ -g_J D_2 \exp\left( \frac{\nu - \nu_o}{\delta_2} \right)^2 \right] \quad (D.8)$$

$$I_{3J}(\nu) \propto I_{2J}(\nu) \exp\left[ -D_3 \left( g_J \exp\left( \frac{1.44 \varepsilon_J}{T_3} \right) \right) \exp\left( \frac{\nu - \nu_o}{\delta_3} \right)^2 \right] \quad (D.9)$$
In Equation D.9, $Q_3$ represents the total internal partition function. The theoretically predicted absorbance, $ABS$, and effective O-atom absorption cross section, $\sigma_{\text{eff}}$, are given by:

$$ABS = \sigma_{\text{eff}} N_3 L_3 = -\ln \left( \frac{\sum_{J=0}^{2} \int J_{3J}(\nu) d\nu}{\sum_{J=0}^{2} \int J_{2J}(\nu) d\nu} \right) \quad (D.10)$$

To generate a theoretical description of the lamp emission, reasonable values must be assumed for several parameters. These parameters include the length of the discharge (layer 1) and reversal (layer 2) regions, $L_1$ and $L_2$; the appropriately averaged temperature of these two layers, $T_1$ and $T_2$; and the O-atom concentrations in these two layers, $N_1$ and $N_2$. All of these parameters are highly dependent on the specific design and operating conditions of the lamp, including microwave power, cooling air flow rate, physical dimensions, lamp gas concentrations, lamp gas pressure, and lamp gas flow rate. Thus, previous investigations of ARAS diagnostics can only serve as a guide and cannot provide values that have any certainty.

For the present calculations, the 6 variables were determined from reasonable estimates as well as a fit of the calculated calibration curve to the empirical curve of Fig. 2.4. Given that the McCarroll cavity extends approximately 5.85” from end-to-end, $L_1$ was estimated to be 5.5”. The reversal length, $L_2$, was estimated to be roughly the distance between the end of the discharge cavity and the shock tube window/slit, approximately 1.5”. The effective temperature of the discharge region, $T_1$, was estimated based on high resolution lineshape measurements of Balmer-$\alpha$ and -$\beta$ transitions of H-atoms and D-atoms from the work of Lifshitz et al. [115]. Based on their measurements of Doppler-widths vs. lamp power, 70 W of input power would yield an effective temperature of 800 K in the discharge. It is important to emphasize that this is extremely uncertain – the discharge temperature is very sensitive to lamp operating conditions such as the cooling air flow rate. However, as an initial estimate 800 K is a reasonable choice. The temperature of the reversal layer, $T_2$, was taken to be 298 K. This is a fairly good estimate based on discharge temperature measurements with a thermocouple by Maki et al. [119]. In that study, the authors found that the actual temperature profile has a peak at
the center of the discharge and decays to near room temperature on either end (Earlier investigations of the two-layer model had assumed, for lack of better information, that \( T_1 = T_2 \)).

Having set the first four parameters, the O-atom concentrations in layers 1 and 2 were adjusted in an attempt to best-fit the calibration curve given in Fig. 2.4. An additional piece of information for this fitting process was the measurement of relative intensities of the three multiplet components in Fig. D.1. Figure D.2 shows a close-up view of the O-atom triplet lines. While the lineshapes cannot be fully resolved by our monochromator, the relative peak intensities of the three transitions shown in Fig. D.2 will be directly proportional to the integrated intensity of the three transitions (since the 100 µm slits provide a 59 cm\(^{-1}\) bandwidth, and each transition has a linewidth of < 1 cm\(^{-1}\)). At these lamp conditions, the three transitions are approximately equal in their integrated intensities, with the \( J = 0 \) transition slightly lower than the other two.

The calibration curve was fit with the two-layer model by assuming shock tube conditions of 2000 K and 1.2 atm (roughly the mean of the calibration experimental conditions, \( \sim 1600-2400 \) K). The O-atom mole fractions giving a reasonable fit to the initial part of the curve were \( X_1 = 0.002 \) and \( X_2 = 0.0001 \), indicating that roughly 10% of the \( \text{O}_2 \) dissociates in the lamp and only 1/20 of the resulting O-atoms diffuse into the reversal layer. Given that much is unknown about the real lamp parameters, these O-atom numbers are acceptable for the moment. The fit is shown in Fig. D.3. Comparing the effective absorption cross sections from the empirical curve and the calculated curve, the values agree within 2.5% up to \( \text{ABS} = 1.0 \), and within 10% up to \( \text{ABS} = 1.25 \). The fitted O-atom concentrations also provide excellent agreement for the modeled relative integrated intensities of the multiplet transitions, in the ratio of 1.04:1.025:1 for \( J = 2,1,0 \). Other assumptions, for example higher values of \( T_2 \), produced relative integrated intensities which did not match the measured spectrum in Fig. D.2.

Given these starting assumptions, it is possible to ask what the model predicts for the temperature-dependence of the cross section over the range of conditions of interest. The calibration curve was calculated again using the conditions 2400 K, 1.1 atm and 1600 K, 1.45 atm, and these curves are shown in Fig. D.3. Clearly, the agreement is poor and the model prediction is even outside of the scatter of the experimental data. The
deviation from the data indicates that the model assumptions are not quite right – which is not surprising, given the number of unknowns. In addition, highly reversed lamp emission lineshapes (as certainly this is) will yield effective absorption cross sections which are particularly sensitive to pressure broadened absorption lineshapes. While pressure broadening has not been specifically investigated for O-atoms, a pressure-sensitive absorption cross section has been measured for N-atoms [45]. The lack of pressure-broadening in the lineshape model may be responsible for the deviation of the 2000 K fit at high $ABS$ in Fig. D.3, but it also may have resulted in incorrect fit parameters yielding incorrect temperature dependence in the model.

One benefit of the model is the capability to visualize the emission and absorption lineshapes, in order to understand the cause of the fall-off of the absorption cross section at high $ABS$. A diagram of the lamp and shock tube is provided in Fig. D.4, along with the calculated relative lineshapes using the two-layer model fit parameters at 2000 K. Specifically, the lineshapes for the $J = 1$ transition are provided, although the other two transitions are very similar with slightly different amounts of reversal. It is evident from Fig. D.4 that the reversal of the emission lineshape has the effect of moving the bulk of the radiant intensity into the wings of the absorption lineshape, where the absorption cross section is smaller. As the emission passes through the shock tube, it is again preferentially absorbed in the center and the intensity peaks are pushed farther and farther into the wings, where the absorption cross section gets smaller and smaller. Thus, the integrated effective absorption cross section decreases as the absorbance in the shock tube increases, producing the calibration curve given in Figs. 2.4 and D.3.
Table D.1: Reported values for $\sigma_{\text{O-atoms}}$ in the low absorbance limit.

<table>
<thead>
<tr>
<th>Absorption cross section [$10^{-15}$ cm$^2$]</th>
<th>Lamp conditions</th>
<th>Atomic filter conditions or monochromator</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.4</td>
<td>6 torr, 1% O$_2$ / He, 70 W</td>
<td>VUV monochromator</td>
<td>This work</td>
</tr>
<tr>
<td>11.0</td>
<td>1.8 torr, 0.1 % O$_2$ / He, 50 W</td>
<td>0.5 torr, 100% O$_2$</td>
<td>[16]</td>
</tr>
<tr>
<td>6.1</td>
<td>10 torr, 0.0862% O$_2$ / He, 100 W</td>
<td>8 torr, 9.54% O$_2$ / He</td>
<td>[49]</td>
</tr>
<tr>
<td>17.0</td>
<td>Purified He w/ O$_2$ impurities</td>
<td>0.5 torr, 100% O$_2$</td>
<td>[120]</td>
</tr>
<tr>
<td>4.6</td>
<td>4 torr, 100 W</td>
<td>Not specified</td>
<td>[15]</td>
</tr>
<tr>
<td>4.3a</td>
<td>6 torr, 1% O$_2$ / He, 50 W</td>
<td>VUV monochromator</td>
<td>[45,47]</td>
</tr>
<tr>
<td>4.0</td>
<td>5 torr, 10% O$_2$ / He</td>
<td>VUV monochromator</td>
<td>[127]</td>
</tr>
<tr>
<td>6.3</td>
<td>6 torr, 1% O$_2$ / He</td>
<td>VUV monochromator</td>
<td>[128]</td>
</tr>
</tbody>
</table>

*Using the data from [47], a temperature-independent fit of $ABS$ vs. [O] yields $\sigma_{\text{O-atoms}} = 5.2 \times 10^{-15}$.
Figure D.1: Emission spectrum of the O-atom ARAS lamp configuration. Operation parameters were: gas mixture, 1% $O_2$ / He; microwave power, $\sim$70 W; pressure, 6 torr. Monochromator slits were set to 100 $\mu$m for this scan.

Figure D.2: Close-up of the O-atom multiplet from Fig. D.1.
Figure D.3: Experimental ARAS calibration curve compared to calculations using the two-layer model. Solid line and symbols: experimental data and polynomial fit; dashed line: model fit at 2000 K; dotted lines: model calculations for 1600 K and 2400 K using the same assumed lamp parameters.

Figure D.4: Effects of lamp self-absorption and line reversal on the emission lineshape.
Appendix E: The partial equilibrium of H₂/O₂ mixtures

E.1 The partial equilibrium hypothesis

The partial equilibrium state achieved by H₂/O₂ mixtures in shock tube experiments was first hypothesized by Schott [129] to explain the observed super-equilibrium OH radical concentrations following the induction period and ignition. The hypothesis is summarized in this appendix.

The overall reaction for hydrogen combustion is given by:

\[ 2 \text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O} \]  \hspace{1cm} (E.1)

There are six major species participating in the combustion process, namely H₂, O₂, H, O, OH, and H₂O. Thermodynamic equilibrium considerations require two atom balance relationships for H and O, and four independent reactions including one with a mole-number change and therefore pressure-dependence. The mechanism associated with the explosion limits and induction-time chemistry is:

\[ \text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O} \]  \hspace{1cm} (E.2)
\[ \text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H} \]  \hspace{1cm} (E.3)
\[ \text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H} \]  \hspace{1cm} (E.4)

As these three reactions are all mole-conserving, they alone cannot complete the stoichiometry of Reaction (E.1), and recombination reactions must eventually take place. At experimental conditions above the explosion limits, however, the OH production through Reactions (E.2-E.4) is much faster than its removal by recombination reactions, and it overshoots its final equilibrium concentration.

During the induction period, Reactions (E.3) and (E.4) are faster than Reaction (E.2), and the O and OH radicals achieve a quasi-steady state while the H-atoms are produced according to the stoichiometry (equal to E.2 + E.3 + 2xE.4):
\[ 3H_2 + O_2 = 2H_2O + 2H \]  
(E.5)

As the initial reactants are depleted and OH, H, O, and H\(_2\)O are formed in the post-induction period, recombination reactions and the reverse of Reactions (E.2-E.4) will become important. However, at high temperatures and low densities the recombination process is often slow, and the dominant change in the reaction process becomes the reversal of Reactions (E.2-E.4). Reactions (E.2-E.4) thus achieve equilibrium and the concentrations of the species involved are related through the equilibrium constants of these three reactions.

Two more equations can be written from Reactions (E.2-E.4) which, in addition to Reaction (E.5), represent the stoichiometric formation of H, O, and OH from H\(_2\) and O\(_2\):

\[ H_2 + O_2 = H_2O + O \]  
(E.6)

\[ H_2 + O_2 = 2 OH \]  
(E.7)

The equilibration of Equations (E.5-E.7) (which achieve equilibrium simultaneously with Reactions (E.2-E.4)) is very rapid, and constantly keeps pace with any changes in concentrations due to slow recombination processes. That is, these three reactions remain in equilibrium even if some recombination occurs. However, if we further assume that this process is so rapid that the bimolecular reactions reach equilibrium before any recombination has occurred, we have reached a state of partial equilibrium of Reactions (E.2-E.4) (or (E.5-E.7)) with no change in the mole number, \( n = \) moles/total mass. Thus, a stoichiometric condition can be written which balances the concentrations of the non-diatomic species with the change in the total mole number:

\[ (n_o - n)\rho = \frac{1}{2} \left( [H_2O] - \left( \frac{\rho}{\rho_o} \right) [H_2O]_o - [H] - [O] \right) = 0 \]  
(E.8)

In this expression \( n_o, \rho_o, \) and \([H_2O]_o\) are the initial mole number, density, and H\(_2\)O concentrations before any reaction occurs. Equations (E.5-E.8), along with the 2 atom balances for H and O, define the partial equilibrium state. According the hypothesis by Schott, this partial equilibrium state is a good approximation to the conditions at the OH peak at high temperatures and low densities.

The benefit of the partial equilibrium hypothesis, if it holds true, is that the OH peak concentrations at such experimental conditions are solely dependent on the
thermochemistry of the species involved in the partial equilibrium and essentially insensitive to any kinetic rate coefficients and their associated uncertainties. Quantitative and high accuracy measurements of partial equilibrium species concentrations thus provide a test of the thermochemical and thermodynamic properties of the species involved, without interference from or sensitivity to kinetic rate coefficients.

E.2 Solution and testing of the partial equilibrium hypothesis

The partial equilibrium hypothesis can be tested by solving for the analytical solution of the partial equilibrium state and comparing to the peak OH mole fractions calculated with a full kinetic mechanism. A comparison of the two calculations will indicate the appropriateness of the hypothesis, within the uncertainty limits of the kinetic rate coefficients in the mechanism.

Solution of the partial equilibrium state involves six equations and six unknowns. The unknowns are the six species concentrations: \([H], [O], [H_2O], [OH], [H_2], \) and \([O_2]\). The six equations include two atom mole balances

\[
2[H_2]_o V_o = ([H] + [OH] + 2[H_2] + 2[H_2O])V
\]  
\[
2[O_2]_o V_o = ([O] + [OH] + 2[O_2] + [H_2O])V
\]

three equilibrium relations

\[
K_5 = \frac{[H]^2[H_2O]^2}{[H_2]^3[O_2]} = \exp\left(\frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}\right)_5
\]  
\[
K_6 = \frac{[H_2O][O]}{[H_2][O_2]} = \exp\left(\frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}\right)_6
\]  
\[
K_7 = \frac{[OH]^2}{[H_2][O_2]} = \exp\left(\frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}\right)_7
\]

and the mole conservation relationship, Equation (E.8). The quantities \(V_o\) and \(V\) are the initial and partial equilibrium specific volumes, respectively.

To test the hypothesis, the partial equilibrium model was solved for the conditions 2500 K, 1 atm and a mixture of 0.4% \(H_2\) / 0.4% \(O_2\) using the thermodynamic data from [82]. Simultaneously, a kinetic calculation was performed with Chemkin II [53] for a
mixture of 0.4% H$_2$ / 0.4% O$_2$ / Ar, using the H$_2$/O$_2$ mechanism developed by Masten [130] and the same thermodynamic data [82]. The Chemkin calculation and a sensitivity calculation using the Senkin program [50] are shown in Figs. E.1 and E.2. As can be seen in Fig. E.1, all species reach a relatively flat plateau following the induction and ignition periods. The resulting partial equilibrium concentrations and concentration peaks for all six species agreed to within 0.4% for the two different calculations. Note that the partial equilibrium concentrations are not equivalent to the full thermodynamic equilibrium concentrations. However, at these conditions the recombination is a slow process and not visible in the graphs. The partial equilibrium model is found to apply even when the slow recombination process is more visible, in which case the peak OH radical concentration overshoot is comparable to the analytical solution. The excellent comparison supports the validity of the partial equilibrium approximation for these conditions.

The analytical solution of the partial equilibrium state provides at least two benefits for the OH enthalpy of formation study in Chapter 4. First, comparison of the partial equilibrium model concentrations to full kinetic calculations at various conditions indicates the conditions under which the partial equilibrium model begins to deviate from the full kinetic calculation. This deviation foretells the rising importance of recombination reactions or other behavior outside of the typical induction time / explosion limit mechanism. (In the actual work discussed in Chapter 4, sensitivity analyses performed using the Senkin program, as in Fig. E.2, were primarily used to detect sensitivity of the OH peak/plateau to kinetic reaction coefficients.) Second, the analytical model provides straightforward insight into the theoretical effect of changes of the heat of formation of OH, or other species, on the calculated partial equilibrium concentrations. In particular, the uncertainties in the thermochemical parameters of partial equilibrium species other than OH can be applied to determine their effect on the experimental determination of the enthalpy of formation of OH.
Figure E.1: Chemkin calculation for comparison to the partial equilibrium model. Conditions are 2500 K, 1 atm with a mixture of 0.4% H₂ / 0.4% O₂ / Ar. Mechanism is from Masten [130] and thermodynamic data from Kee et al. [82].

Figure E.2: Sensitivity calculations for the conditions of Fig. E.1.
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