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ABSTRACT


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With global emission regulations becoming stringent, development of new combustion technologies that meet future emission regulations is essential. In this vein, this dissertation presents the application of sensitive diagnostic tools to validate and improve chemical kinetic mechanisms that play a fundamental role in the design of new combustion technologies.

First, a novel high sensitivity laser-based sensor with a wide frequency tuning range (900 – 1000 cm\(^{-1}\)) was developed utilizing pulsed cavity ringdown spectroscopy (CRDS) technique. The novel laser-based sensor was illustrated by measuring trace amounts of multiple combustion intermediates, namely ethylene, propene, allene, and 1-butene in a static cell at ambient conditions. Subsequently, pulsed CRDS technique was utilized to develop an ultra-fast, high sensitivity diagnostic to monitor trace concentrations of ethylene in shock tube pyrolysis experiments. This diagnostic represented the first ever successful application of CRDS technique to transient species measurements in a shock tube. The high sensitivity and fast time response (10 \(\mu\)s) diagnostic may be utilized for measuring other key neutrals and radicals which are crucial in the oxidation chemistry of practical fuels.

Secondly, a quadrupole mass spectrometer (QMS) was employed to measure relative cation mole fractions in atmospheric and low-pressure (30 Torr) flames of methane/oxygen diluted in argon. Lean, stoichiometric and rich flames were
examined to evaluate the dependence of ion chemistry on flame stoichiometry. Spatial distribution of cations was compared with predictions of an existing ion chemistry model. Based on the extensive measurements carried out in this work, modifications were suggested to improve the ion chemistry model to enhance the fidelity of such mechanisms. In-depth understanding of flame ion chemistry is vital to model the interaction of flames with electric fields and thereby pave the way to enable active combustion control for increased efficiency and reduced emissions.

Finally, a compact fast time-response time-of-flight mass spectrometer (TOF-MS) was coupled to the shock tube through a pin-hole end-wall to enable time-resolved species concentration measurements. This diagnostic tool was demonstrated by investigating the decomposition of 1,3,5-trioxane over a wide range of shock conditions. Reaction rate coefficients were extracted by the best fit to the experimentally measured species time-histories. TOF-MS coupled to the shock tube is an ideal diagnostic tool for developing kinetic mechanisms for future fuels due to its ability to simultaneously measure several species during fuel pyrolysis/oxidation processes.
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Chapter 1: Introduction

1.1 Background and Motivation

Despite the growing contribution of alternate sources of energy to the total energy mix, combustion of fossil fuels continues to remain the most dominant mode of energy generation worldwide [1]. As global emission regulations continue to become stringent, it is essential for combustion scientists to develop technologies that can meet the emission standards of the future. Future engine technologies offering better fuel efficiency and lower emissions such as homogeneous compression charge ignition (HCCI), reactivity controlled compression ignition (RCCI) and others operate at low temperature and high pressure conditions. Under these combustion conditions, hydroperoxyl radical (HO$_2$) and hydrogen peroxide (H$_2$O$_2$) are the key intermediate species that control the auto-ignition chemistry for hydrocarbon fuels [2]. Additionally, ethylene, propene, allene, and 1-butene play a crucial role in the oxidation and pyrolysis of large hydrocarbons, either as intermediates [3]–[5] or as precursors to a host of radical intermediates [6]. Therefore, time-history measurements of the aforementioned intermediates in reactive environments will lead to a better understanding of reactions affecting their formation and consumption and will subsequently aid the development and validation of chemical kinetic mechanisms, which are crucial to the development of new combustion-based energy conversion devices. However, it is challenging to accurately quantify intermediates in combustion systems as they exist in small amounts for a short period of time. Therefore, fast, selective and sensitive diagnostics are vital for their accurate identification and quantification.
Furthermore, reduction in soot emission [7] and increase in combustion efficiency [8]–[11] can also be achieved by active control of combustion processes through the use of external electric fields. External electric fields are capable of manipulating flames due to the presence of ions that are produced through chemi-ionization processes (typical mole fractions varying from $10^{-9}$ to $10^{-7}$ [12]). Nevertheless, progress has been hampered by the limited characterization of flame ionization processes, rudimentary ion chemistry models and the lack of experimental data on the distribution of ions in flames. Detailed knowledge of ion chemistry is required to accurately predict the total density of positive and negative charges, which are essential to model the interaction of flames with external electric fields [13]. Consequently, experimental and modeling efforts towards a thorough characterization of flame ion chemistry are needed. Owing to the extremely small concentrations of ions in flames, it is very challenging to implement non-intrusive laser-based diagnostics to measure ion mole fractions. Therefore highly sensitive diagnostic techniques with the capability to differentiate between ions and neutrals are needed.

Lastly, new fuel formulations that reduce emissions are also going to play a leading role in the development of clean combustion technologies. Therefore, a diagnostic tool capable of measuring several species simultaneously during the fuel pyrolysis/oxidation process will be valuable in developing kinetic mechanisms for novel future fuels [14], [15].

This dissertation presents the successful development/characterization of diagnostics needed in the aforementioned applications. Firstly, a novel laser-based sensor that uses a widely tunable external cavity quantum cascade laser (EC-QCL) coupled to a high reflectivity mirror cavity to obtain high sensitivity over a wide
wavelength range from 10 to 11.11 μm (1000 – 900 cm\(^{-1}\)) is developed. The high sensitivity of the sensor over a wide tuning range enables trace measurements of target molecules: ethylene, propene, allene, and 1-butene. The high sensitivity and fast time-response of the novel laser-based sensor is demonstrated by recording ethylene concentration time-histories in shock tube pyrolysis experiments. The novel sensor developed here can be utilized for measuring other crucial combustion intermediates that cannot be detected using traditional single-pass direct absorption techniques.

Secondly, the present effort seeks to provide a comprehensive dataset to aid the development and validation of predictive ion chemistry models for methane oxidation. Quadrupole mass spectrometer (QMS) is selected as the diagnostic of choice for measuring flame ion profiles as it provides high sensitivity and ability to differentiate between ions and neutrals. The goal is accomplished by first characterizing the QMS and then utilizing it to measure relative ion mole fractions in atmospheric and low-pressure methane-oxygen flames diluted in argon. It is expected that the database presented in this work will be used to develop and validate detailed and skeletal ion mechanisms for methane oxidation.

Lastly, a compact fast time-response high repetition rate time-of-flight mass spectrometer (TOF-MS) capable of measuring all species with mass to charge ratios between 1 to \(~300\) is coupled to the shock tube through a pin-hole end wall. The TOF-MS coupled to the shock tube is capable of measuring species concentration time-histories of several species simultaneously during fuel pyrolysis/oxidation experiments. To demonstrate the capability of the TOF-MS, a relatively simple reaction (thermal decomposition of 1,3,5-trioxane) is studied over a wide range of
experimental conditions. Due to the unique capability of this setup in simultaneously providing the concentration time-histories of the reactants, intermediates and products during the reaction process, it is well-suited to conduct targeted fuel pyrolysis/oxidation studies to develop chemical kinetic mechanisms for novel future fuels.

1.2 Overview of the Dissertation

This dissertation describes in detail the development and characterization of two different diagnostic techniques and their application to different combustion systems.

Chapter 2 describes the application of a novel CRDS based laser sensor to measure trace amounts of multiple combustion intermediates (ethylene, propene, allene, and 1-butene) in a static cell. The chapter commences by discussing the numerous applications of laser-based sensors and the reasons for their growing adoption followed by brief overview of the importance of various gases that can be measured using the sensor developed in this work. Then, the theory of pulsed cavity ringdown spectroscopy (CRDS) technique is presented, followed by a discussion of the benefits and challenges associated with using pulsed CRDS technique. The chapter discusses in detail the cavity alignment procedure, challenges of using EC-QCL, sensor optimization and validation. Sensor detection limit is presented using two methodologies and the chapter concludes by demonstrating the application of the novel laser-based sensor to measure species concentrations in the atmosphere as well as in multi-gas mixtures. The author acknowledges the support of Ph.D. student Bidoor Al-Saif during the CRDS measurements.
Chapter 3 describes in detail the application of the novel laser-based sensor to measure species time-histories in a shock tube. The chapter starts by discussing the motivation for developing the diagnostic, followed by the experimental details of the sensor. The shock tube facility based at KAUST is described briefly followed by a detailed discussion of the results describing the measurements of ethylene time-histories in a variety of shock tube conditions. The author acknowledges the help and support of Dr. Ettouhami Essebbar during the setting up of CRDS sensor on the shock tube.

Chapter 4 starts by introducing another sensitive diagnostic technique i.e. mass spectrometry and discussing its advantages and challenges. Then, the chapter discusses in detail the implementation of QMS to measure relative cation mole fractions in atmospheric flames of methane/oxygen diluted in argon. Subsequently, the chapter describes in detail the experimental setup and the experimental methodology used for measuring the cation profiles in flames. The numerical model and the ion mechanism used for predicting the ion profiles are also discussed. Neutral species measurements are then presented and used to validate the setup. This is followed by a description of the cation profile measurements in flames of different equivalence ratios. The chapter concludes by suggesting changes to enhance the ion chemistry mechanism. The author acknowledges the technical expertise provided by Ph.D. student Jie Han and Dr. Memdouh Belhi in carrying out the ion simulations presented in this chapter. The author also acknowledges the support of Dr. May Chahine and Dr. Hatem Selim during the mass spectrometric measurements.

Chapter 5 describes the implementation of QMS to measure relative cation mole fraction profiles in low-pressure flames of methane/oxygen diluted in argon. The
Chapter 5 starts by describing the motivation for the study followed by details of the experimental setup, experimental methodology, numerical methods and ion chemistry model. The validation of the setup is presented followed by relative cation mole fraction profiles in lean, stoichiometric and rich flames. The chapter concludes by proposing changes to improve the ion chemistry model. The author acknowledges Ph.D. student Bingjie Chen and Dr. Hatem Selim for their support during the measurements. The technical expertise provided by Ph.D. student Jie Han and Dr. Memdouh Belhi in carrying out the simulations presented in this chapter is also acknowledged. The author also acknowledges Ph.D. student Yasin Karakaya and Prof. Tina Kasper for sharing their TOF-MS measurement results.

Chapter 6 describes the implementation of compact fast-time response TOF-MS to measure species concentration time-histories in a harsh environment (shock tube). To demonstrate the capability of the technique, a relatively simple reaction (thermal decomposition of 1,3,5-trioxane) is studied. The chapter starts by discussing the motivation for measuring the thermal decomposition rate of 1,3,5-trioxane. Next, the TOF-MS systems is described in detail along with the experimental methodology. The chapter concludes by presenting the reaction rate coefficients extracted by the best fit to the experimentally measured species concentration time-histories and comparing them with the theoretical rates. The author acknowledges the support and help of Dr. Binod Giri during the TOF-MS measurements. The author also acknowledges the technical expertise of Dr. Binod Giri and Dr. John M.H. Lo in calculating the theoretical rates of 1,3,5-trioxane decomposition presented in this chapter.
Chapter 7 summarizes the work presented in this dissertation and proposes future directions in which the current work can be extended.

Appendix describes the challenges faced during the implementation of microwave interferometry technique to measure electron-concentration time-histories in shock tube fuel oxidation experiments. Solutions to the challenges are proposed along with the description of a design change that had to be made to the microwave interferometer for future experiments.
Chapter 2: CRDS Measurements in a Static Cell

This chapter starts by mentioning the applications of laser-based sensors and the reasons for their growing adoption followed by a brief overview of the importance of various gases that can be measured using the sensor developed in this work. Then, the theory of pulsed cavity ringdown spectroscopy (CRDS) technique is presented, followed by a discussion of the benefits and challenges associated with using pulsed CRDS technique. It is followed by a detailed description of the design of the novel sensor developed in the current work. Lastly, sensor validation using CO$_2$ absorption lines is presented followed by a demonstration of the sensor to measure small amounts of multiple gases in a static cell.

2.1 Introduction

The monumental advancements in laser technology over the past few decades have made laser-based sensors ubiquitous in a wide array of applications including noninvasive medical diagnostics[16]–[18], environmental pollution monitoring[19]–[21], industrial process control [22], [23], detection of explosives [24], [25] and several others. Laser sensors have gained attention primarily due to their ability to carry out real-time, non-intrusive measurements of species with high sensitivity and selectivity. Recent improvements in laser technology such as the advent of external cavity quantum cascade lasers (EC-QCL) with wide tuning ranges of the order of 100 cm$^{-1}$ enable spectroscopic measurements of broadband absorbers as well as multiple species with a single laser. The ability of EC-QCL based sensors to measure multiple species owing to their extensive tuning range is an enormous advantage when
compared with competing diode laser-based sensors that can usually measure only a single species because of their narrow operating ranges. Coupling of laser with a mirror cavity comprising high reflectivity mirrors can increase the sensitivity of the laser-based sensor by approximately two orders of magnitude or larger depending on the reflectivity of the mirrors used to form the cavity. Therefore, a widely-tunable laser when coupled with a mirror cavity that retains high reflectivity over a broad wavelength range enables trace detection of multiple species and has applications in environmental pollution monitoring, industrial gas sensing and combustion. In this vein, we have developed and validated a novel laser-based sensor that uses a widely tunable EC-QCL coupled to a high finesse mirror cavity to obtain high sensitivity over a wide wavelength range from 10 to 11.11 µm (1000 – 900 cm⁻¹). We demonstrate the high sensitivity of the sensor over a wide tuning range by measuring trace amounts of ethylene, propene, allene (propadiene), and 1-butene, first individually and later in a multi-gas mixture.

Ethylene, propene, allene, and 1-butene were selected in this work since they play a crucial role in the oxidation and pyrolysis of large hydrocarbons, either as intermediates [3]–[5] or as precursors to a host of radical intermediates [6]. Additionally detection of trace amounts of volatile organic compounds such as ethylene and propene is vital in the study of air quality. Industrial emissions, waste incineration plants and vehicle exhaust fumes are the major sources of ethylene and propene in the atmosphere. Ethylene and propene can rapidly undergo oxidation reactions producing ground-level ozone [26], [27], which has adverse effects on crops and human health [28]–[31]. Moreover, the aforementioned target molecules are widely used as feedstock or intermediates in chemical and petroleum industries and
thereby a single sensor that can measure all four gases in trace amounts will be invaluable in their leak detection.

Ethylene has previously been measured in trace concentrations using a variety of sensitive absorption techniques. Photoacoustic spectroscopy has been extensively used for monitoring trace ethylene in a number of studies. Altuzar et al. [19] developed a CO$_2$ gas laser based photoacoustic spectrometer to measure ethylene concentrations in air samples from different locations in Mexico city. Recently, Weidmann et al. [20] developed an ethylene sensor based on direct absorption in a multi-pass Herriot cell to monitor ethylene from vehicle exhaust and in air samples from a busy urban tunnel. They reported a noise equivalent sensitivity of 30 ppb for ethylene with 80 seconds of total acquisition time. Manne et al. [32], [33] performed a proof-of-concept study to measure ethylene using four strategies, namely pulsed cavity ringdown spectroscopy, cavity-enhanced spectroscopy [32], intrapulse and interpulse spectroscopic techniques with a multi-pass cell [33]. They reported detection limits in the range of 5 ppb to 130 ppb with 5 to 10 seconds of integration time.

Recently, Chrystie et al. [27] developed a laser-based sensor to non-intrusively measure propene mole fractions of the order of 0.1% or larger in a transient chemical reactor (shock tube). In general, there has been little work on the development of laser-based sensors for the detection of propene, allene or 1-butene. Detection of propene, allene, and 1-butene has traditionally been carried out using mass spectrometry [5] or gas chromatography techniques [6], [34], both of which require sampling using physical probes. The narrow tuning range of previously used laser sources generally limited the optical sensors to the detection of a single molecule and
this probably made laser sensors unappealing as compared to the gas sampling techniques that can detect all the target molecules simultaneously. The wide tuning range and high sensitivity of the current sensor, coupled with the traditional advantages of laser-based sensors such as non-intrusiveness, portability, robustness and rapid response, make it better suited for environmental monitoring and industrial gas sensing applications.

2.2 Theory of CRDS

Cavity ringdown spectroscopy (CRDS) with pulsed or continuous lasers is a highly sensitive absorption technique that has been used previously in the development of calibration-free trace gas diagnostics. The theory of CRDS has been detailed previously [35], and is presented briefly to clarify the notation used in this study. In CRDS, light from a laser source enters a stable optical cavity and undergoes multiple passes. In the case of pulsed lasers, when the laser pulse ends, the light inside the cavity decays exponentially. The decay rate depends on the length of the cavity, the reflectivity of the mirrors forming the cavity and absorption losses inside the cavity. The decay time constant, also called the ringdown time, is the time taken for the light intensity to fall to 1/e of its initial value. It is given as:

\[
\tau = \frac{L}{c[(1-R)+\alpha d]}
\]  

(1)

In the absence of any absorbing molecules inside the cavity, the ringdown time is given as:
\[ \tau_0 = \frac{L}{c[1-R]} \]  

(2)

In the above equations, \( L \) is the total length of the cavity, \( c \) is the speed of light, \( R \) is the reflectivity of the mirrors forming the cavity, \( \alpha \) is the absorption coefficient in \( \text{cm}^{-1} \) and \( d \) is the absorption path-length. By measuring the decay time constants in the presence and absence of absorbing species, the absorption coefficient can be calculated from

Equation (1) and (2) as:

\[
\alpha = \frac{L}{ed} \left( \frac{1}{\tau} - \frac{1}{\tau_0} \right)
\]

(3)

The absorption coefficient, \( \alpha \), is related to absorbance through path-length, \( L \), as:

\[ \alpha = \frac{\text{Absorbance}}{L} \]

(4)

From the Beer-Lambert Law, absorbance is given as:

\[
\text{Absorbance} = \ln(I_0 / I) = P \chi S(T) \phi_v(P,T,L) = \sigma(P,T) L (P \chi / (k_B T))
\]

(5)

Here, \( I_0 \) is the incident intensity and \( I \) is the transmitted intensity of the laser. Absorbance is a function of the total pressure of the gas, \( P \), the mole fraction of the absorbing species, \( \chi \), the linestrength, \( S \), the lineshape \( \phi_v \) and the path-length \( L \). Absorbance can also be written as the product of absorption cross-section \( \sigma \), number density of absorbing species \( N \) (\( N = P \chi / (k_B T) \)) and path-length \( L \). Equation (4) in conjunction with Equation (5) enables the determination of the mole fraction of the absorbing species if spectroscopic parameters (\( S \) and \( \phi_v \)) are known. In case of large
molecules with less distinct absorption features, the mole fraction of the absorbing species can be obtained when the absorption cross-section is known.

2.3 Benefits

Many types of cavity-based absorption techniques have been developed over the years, such as multi-pass cells, cavity ringdown spectroscopy (CRDS), cavity enhanced absorption spectroscopy (CEAS), off-axis integrated cavity output spectroscopy (OA-ICOS), intracavity laser absorption spectroscopy (ICLAS), optical feedback (OF) cavity techniques, and noise-immune cavity-enhanced optical heterodyne molecular spectroscopy (NICE-OHMS). Measurements performed using CRDS can achieve better spatial resolution compared to multi-pass cells and other cavity-based techniques such as off-axis CEAS. Moreover, CRDS measurements are immune to laser intensity fluctuations since the ringdown time does not depend on the intensity of the laser. Pulsed CRDS, when implemented with high-repetition-rate lasers, offers significantly better temporal resolution compared to cw-CRDS. These features make pulsed-CRDS well-suited for studying homogeneous transient systems.

Previously, multi-pass cells were used to increase the path-length and, therefore, sensitivity of measurements carried out in a homogenous transient chemical reactor (shock tube) [36], [37]. However, the twelvefold increase in path length obtained in those studies resulted in only a fivefold increase in sensitivity because the laser intensity loss was dominated by the losses caused by shock tube windows present inside the cavity. Recently, Sun et al. [38], [39] utilized OA-ICOS technique to develop sensitive diagnostics for shock tube kinetic studies. They were able to achieve high sensitivity by replacing shock tube windows with cavity mirrors. The cavity used for OA-ICOS experiments by Sun et al. [38], [39] is similar to the cavity
used by CRDS experiments in terms of the optical components; however, the alignment procedure is different. OA-ICOS is an off-axis technique in which the laser beam is transmitted at a small angle with respect to the cavity axis such that the beam undergoes multiple passes while traversing different paths along an oval. On the other hand, CRDS is an on-axis technique wherein the laser beam undergoes multiple passes by going back and forth on the same path. Due to this fundamental difference in the way the laser beam undergoes multiple passes within the cavity, the spatial resolution of CRDS is better than OA-ICOS. The off-axis alignment required for OA-ICOS technique [38], [39] limited the spatial resolution of the measurements to 5 mm which translates to 5µs time resolution for typical shock velocity of 1000 m/s. In shock tube transient experiments, small spatial resolution is desired along the axial (shock-propagation) direction to achieve adequate time resolution and therefore CRDS technique is preferred over off-axis cavity based techniques.

2.4 Challenges

Although CRDS is a very promising diagnostic technique, it has some limitations. CRDS is an absorption based diagnostic and is best suited to study homogeneous systems where density/concentration gradients do not exist along the line-of-sight. High reflectivity mirrors (~ 99.99%) which form an integral part of all cavity based techniques are currently not available beyond 10 µm wavelengths. At certain wavelengths, the only option is to utilize mirrors with modest reflectivity (>99.9%) which reduces the sensitivity of the diagnostic.

2.5 Experimental Details

The experimental setup for the novel sensor is shown in Figure 2-1. We used a pulsed EC-QCL (Daylight Solutions 11100-UT), tunable over 9.53-12.95 µm (775-
1020 cm\(^{-1}\)), with the maximum average power of 15 mW. Laser pulse widths can be varied between 40 to 500 ns and repetition frequencies as high as 100 kHz are possible. Single mode emission at the wavelength of interest was achieved by adjusting the laser head temperature and diffraction grating orientation via the laser controller. Single mode emission was ensured by viewing the laser spectrum using a spectrum analyzer (Bristol 721). The IR beam emitted by EC-QCL was co-aligned with a 10 mW He-Ne laser (632 nm) to facilitate the cavity alignment process. The IR beam emerging from the EC-QCL head was directed into an optical cavity formed by two plano-concave mirrors (II-VI Infrared) with 1 m radius of curvature, 1" diameter, and a manufacturer specified reflectivity of 99.5% at 10.6 \(\mu\)m (943.39 cm\(^{-1}\)). The ringdown mirrors were placed 70 cm apart to form a stable optical cavity configuration. A plano-convex lens (ZnSe, 500 mm focal length) was positioned between the EC-QCL head and the ringdown cavity to improve the mode-matching between the laser beam and the \(\text{TEM}_{00}\) mode of the cavity. A concave mirror (Aluminum, 100 mm focal length) stationed at the exit of the optical cavity was used to focus the IR beam on a thermoelectrically-cooled photovoltaic detector (Vigo PVMI 3TE-10.6), with a bandwidth of 10 MHz. The detector signal was recorded with a digital oscilloscope (Tektronix DPO 3014) having a sampling rate of 2.5 GS/s.
Figure 2-1 Experimental setup used for pulsed CRDS employed for carrying out species measurements in the static cell. BS: Beam Splitter, MMO: Mode matching optic.

2.5.1 Cavity Alignment Procedure

The procedure used for aligning the optical cavity is described in this section. First, it was ensured that the laser beam passed through the center of all the optics that lie on the path of the beam from the laser head to the detector. This task was accomplished with the help of the visible He-Ne laser beam which was co-aligned with the infrared laser beam as mentioned earlier. Next, the mirror mounts along with the optical cell were fixed at the desired location and were adjusted to ensure that the laser beam passes through their centers. A ringdown mirror was then placed in the kinematic mirror mount close to the detector side and the ringdown mirror position was adjusted to ensure that the laser beam retraced its path and went back into the infrared laser head. The second ringdown mirror was then placed in the second mirror mount and was adjusted to ensure that the back reflection went back into the laser head. At this point, a decay curve was observed on the oscilloscope. The alignment of the second ringdown mirror was then fine-tuned to maximize the signal on the oscilloscope to complete the alignment procedure.
2.5.2 Challenges of Using EC-QCL

Although the EC-QCL can emit IR radiation over a wide wavelength range (9.53-12.95 µm), its tuning range is not mode-hop free. Therefore, laser head temperature and grating orientation had to be iteratively tuned to avoid mode-hops. However, the strategy to tune temperature and diffraction grating was not successful for all the desired wavelengths. Despite this limitation, the wide tunability of the EC-QCL proved to be an enormous advantage in our quest to develop a sensor capable of detecting multiple species in trace amounts.

2.5.3 EC-QCL Pulse Width Optimization

To make the best use of the energy available from the pulsed laser, the pulse width was varied to identify its optimum value. Frequency down-chirp of the laser was determined by passing the laser beam through a Fabry-Perot Germanium etalon (free spectral range of 0.016 cm\(^{-1}\)) and detecting the transmitted beam with a high bandwidth (500 MHz) photovoltaic detector. Transmitted laser signals, with and without the etalon, are shown in Figure 2-2 for a 100 ns pulse width. The wavenumber tuning (ω-tuning) or the frequency chirp of the laser increased from 0.032 cm\(^{-1}\) at 80 ns pulse width to 0.08 cm\(^{-1}\) at 120 ns pulse width. This increase in the frequency chirp is an undesired effect because it leads to artificial broadening of the spectral absorption transitions. However, an increase in pulse width also increases the amount of energy entering the optical cavity, thereby increasing the signal-to-noise ratio (SNR) of the transmitted laser signal. Laser pulse width of 100 ns which resulted in a frequency chirp of 0.064 cm\(^{-1}\) was, therefore, used as a compromise to
achieve relatively low frequency chirp and high SNR. The frequency chirp of 0.064 cm\(^{-1}\) leads to negligible artificial broadening because of the relatively broad spectral features of the molecules of interest (full-width at half-maximum of \(~0.15\ cm^{-1}\)). In the experiments reported here, the ringdown time varied between 100 – 400 ns depending on the absorption losses inside the ringdown cavity.

![Figure 2-2 Detector signals for 100 ns laser pulse width. The etalon has an FSR of 0.016 cm\(^{-1}\).](image)

2.5.4 Gas Mixture Preparation

The gas cell, with the two ringdown mirrors at its two ends, was connected to a cylinder of gas to be measured. The cell was also connected to two calibrated pressure transducers (MKS 627D capacitance manometers with 1000 and 10000 Torr full-scale pressure range and accuracy of 0.12%) and a vacuum pump.

High purity propene (99.95%), allene (99.5%), 1-butene (99.95%) gases, dilute mixture of ethylene (1051 ppm ethylene in argon), dilute mixture of carbon dioxide (1.05% carbon dioxide in nitrogen), ultra-pure nitrogen (99.999%) and ultra-pure argon (99.999%) supplied by Abdullah Hashim Industrial Gases & Equipment Co. Ltd. were used for the experiments. The dilute mixtures of individual gases were
prepared manometrically using a gas handling system. The pressure in the gas handling system was monitored by two pressure transducers (MKS 627D capacitance manometers with 100 and 1000 Torr full scale range). In the majority of cases, multiple dilution steps were required to achieve the desired final concentration of target gases.

2.6 Sensor Validation and Optimization

The sensor was validated using carbon dioxide as a test molecule because its spectroscopic parameters (linestrength, lineshape) are very well-known [40]. Carbon dioxide has relatively strong absorption lines in the 930 – 985 cm\(^{-1}\) wavelength region and the ringdown mirrors have their maximum reflectivity near 944 cm\(^{-1}\). However, ethylene has a very strong vibrational band (\(v_7\)) centered near 949.533 cm\(^{-1}\) and even trace amount of ethylene, present as an impurity, can cause appreciable interference. Therefore, simulations were performed using the HITRAN database [40] to identify absorption lines of CO\(_2\) where the interference from ethylene is minimal, see Figure 2-3. Subsequently, two absorption lines of CO\(_2\) centered near 938.69 cm\(^{-1}\) and 974.62 cm\(^{-1}\) having negligible interference from ethylene were selected to demonstrate the wide tuning range of this sensor.
With a view to minimizing the effect of artificial broadening due to the frequency chirp of the laser at 100 ns pulse widths, absorption measurements of CO$_2$ were performed at a relatively high pressure of 1200 Torr. Figure 2-4 shows a comparison between the simulated and measured absorption coefficients for the absorption lines centered near 938.69 cm$^{-1}$ and 974.62 cm$^{-1}$. Each measured data point was obtained by using Equation (3) and determining the ringdown time for pure N$_2$ ($\tau_0$) and for a 1.05% CO$_2$/N$_2$ mixture ($\tau$) both measured at a pressure of 1200 Torr. In Figure 2-4, the green line represents the absorption coefficient obtained by convoluting the simulated absorption coefficient with a top hat profile of 0.064 cm$^{-1}$ width which corresponds to the frequency chirp of a 100 ns laser pulse width. The measured absorption coefficient agrees very well with the convoluted absorption coefficient in both wavelength regions, thereby validating the pulsed-CRDS setup.
Figure 2-4 Comparison of measured absorption coefficients with HITRAN simulations [25]. Mixture: 1.05% CO2/N2; T = 296 K; P = 1200 Torr.

To determine the minimum detection limit and optimum averaging time, Allan Variance of the ringdown times was calculated at each wavelength of interest. The ringdown times were measured at regular intervals of $\sim 10 \text{ cm}^{-1}$ across the entire range of the sensor ($900 – 1000 \text{ cm}^{-1}$). The tuning range of the sensor was limited to $900 – 1000 \text{ cm}^{-1}$ due to the reflectivity of the ringdown mirrors dropping sharply beyond this wavenumber range. The reflectivity of the high finesse mirrors is a function of wavenumber and can be determined by measuring the ringdown time in a static cell under vacuum at the wavenumber of interest. The wide tuning range ($900 – 1000 \text{ cm}^{-1}$) achieved by the sensor enables access to the strong vibrational bands of all the target molecules. The static cell was filled with ultra-pure argon to a pressure of 760 Torr, and the detector signal was recorded at each wavenumber step for a time period of 40 ms which corresponds to 4000 ring-down events. In the current work, Allan Variance was calculated using the new algorithm proposed by Huang and Lehmann [41] as it leads to significant reduction in noise and more accurate location of optimum averaging time when compared with the traditional algorithm. The Allan Variance drops very steeply initially and reaches minima around averaging time of
4 ms for the majority of wavenumbers as presented in Figure 2-5. Therefore, 4 ms which corresponds to 400 ring-down events was selected as the averaging time for all the measurements reported here. For the averaging time of 4 ms, the Allan Variance is lower than $1.9 \times 10^{-7}$ cm$^{-1}$ across the entire range of the sensor. The high repetition rate of the laser (100 kHz) enables to achieve milli-second time resolution even after averaging 400 events and is valuable for carrying out species time-history measurements in transient environments.

![Figure 2-5 Allan Variance as a function of averaging time for different wavenumbers. The gray vertical line indicates the location of minimum Allan variance.](image)

The high sensitivity of the sensor over a wide tuning range of 100 cm$^{-1}$ makes it an ideal diagnostic to measure trace concentrations of multiple gases. To demonstrate the capability of the sensor for multi-species detection, four hydrocarbon molecules (ethylene, propene, allene and 1-butene) with strong absorption bands in the operating range of the sensor were selected as discussed earlier. Figure 2-6 shows the absorption coefficient for trace amounts of the four molecules at a nominal temperature of 296 K and pressure 760 Torr. At the given experimental conditions, the peak absorption
coefficients for the ppm-level concentration of all gases are larger than $3.7 \times 10^{-5}$ cm$^{-1}$, which is about two orders of magnitude higher than the sensor detection limit of $1.9 \times 10^{-7}$ cm$^{-1}$, thereby enabling the sensor to measure trace amounts of these hydrocarbon gases. The absorption peaks for all molecules are very well separated except the peaks of propene and 1-butene which lie within 0.9 cm$^{-1}$ of each other. Ethylene has strong absorption band ($v_7$) centered near 949.533 cm$^{-1}$ that can be attributed to CH$_2$ wagging, while propene has strong absorption band ($v_{19}$) centered near 912.62 cm$^{-1}$ due to CH$_2$ twisting and wagging [42]. Strong peaks of 1-Butene are observed near 911.71 cm$^{-1}$ which are attributed to the CH$_2$ out of plane bending mode [43]. Allene absorption near 901.8 cm$^{-1}$ is assigned to one of the weaker lines of $v_4$ vibrational band centered at 865 cm$^{-1}$ which is attributed to CH$_2$ twisting [44]. Absorption measurements for all the species were carried out near the peaks of their absorption coefficients.

![Absorption coefficients of selected target gases over the operating wavelength range of the sensor.](image)

*Figure 2-6* Absorption coefficients of selected target gases over the operating wavelength range of the sensor.
2.7 Results and Discussion

This section presents the comparison of experimentally measured absorption coefficients with the absorption coefficients reported in Pacific Northwest National Laboratory (PNNL) database [45] for trace amounts of various gases. Then, results from the linearity test and the detection limit of the sensor are presented. Lastly, the sensor is used to measure trace amounts of gases in a multi-gas mixture. The PNNL database uses nitrogen as the bath gas for the measurement of absorbance. However, the effect of bath gas on the absorption spectra is negligible for ethylene and other large molecules at room temperature [46].

2.7.1 Trace Gas Mixtures

The capability of the sensor to measure trace concentrations was initially demonstrated by measuring small amounts of ethylene, propene, allene and 1-butene individually. All measurements reported here were performed at a nominal temperature of 296 K and pressure of 760 Torr. The absorption coefficients for varying mole fractions of each gas were measured, and representative data are shown in Figure 2-7. The measurements reported in PNNL database have a maximum uncertainty of 3%. In the current work, the distance between the ringdown mirrors is same as the absorption length. Therefore, the absorption coefficients measured using CRDS technique depend only on the ringdown times and the noise in the ringdown times is the primary source of uncertainty. The uncertainty at each wavelength is determined by calculating the absorption coefficient when the ringdown time (τ) is perturbed by one standard deviation (around 7 ns) and is shown in Figure 2-7 for two representative wavelengths of ethylene mixture (uncertainty bars in red color). The uncertainty depends on the absorbance and is greater at lower ringdown times (large
absorbance). The measured absorption coefficients for all four hydrocarbons agreed very well with the PNNL database within the experimental uncertainty which confirms the sensor accuracy and sensitivity to trace amounts of target species.

Figure 2-7 Comparison of measured absorption coefficients with the PNNL Database [30].

T = 296 K; P = 760 Torr.

2.7.2 Linearity Test

To ascertain the linearity of the sensor, absorption coefficients of varying concentrations of ethylene, propene, allene and 1-butene were measured while keeping the laser at a fixed wavelength for each molecule (Figure 2-8). The mole fractions were varied over 0.52 to 11 ppm for ethylene, 2.1 to 34 ppm for propene, 10.3 to 197 ppm for allene and 5.7 to 101 ppm for 1-butene. Figure 2-8 shows the
measured absorption coefficients for all molecules plotted against the corresponding absorption coefficient obtained using the PNNL database. The data points are lying on or near the reference line (purple color), thereby confirming the linear response of the sensor for different concentrations of target gases.

![Graph showing measured absorption coefficients plotted against absorption coefficients obtained using the PNNL database](image)

**Figure 2-8** Measured absorption coefficients plotted against absorption coefficients obtained from PNNL database [30]. $T = 296 \text{ K; } P = 760 \text{ Torr.}$

### 2.7.3 Detection Limit

Detection limits for individual gases were obtained by successively diluting gas mixtures in argon bath gas and measuring the absorption coefficient at each dilution step till the measured absorption coefficient reached an asymptotic value. This procedure for determining the detection limit is being referred to as the mixture dilution method in this work. The absorption coefficients measured during the mixture dilution method are shown for propene in Figure 2-9 and detection limits are reported for all gases in Table 2-1. The detection limits for all gases follow the same trend as observed in Allan Variance analysis (Figure 2-5) with allene measured near 902.4 cm$^{-1}$ having the worst value of the detection limit and ethylene measured near 950.08 cm$^{-1}$ having the best detection limit. However, the detection limits calculated using Allan
Variance analysis are almost an order of magnitude smaller than the values obtained using mixture dilution method. Mixture dilution method leads to larger values for detection limits because it is affected by the uncertainties in the ringdown times for both the absorber gas and the bath gas (argon), whereas the Allan Variance analysis only considers the uncertainties in the ringdown times of the bath gas. Therefore, the mixture dilution method provides more realistic values of detection limits and has been subsequently used to report the minimum detection limit for each molecule in terms of ppb calculated at a nominal temperature of 296 K and pressure of 760 Torr (Table 2-1). The detection limits in terms of ppb were calculated at the peak absorption coefficient for each molecule within the operating wavelength range of the sensor. The detection limits presented here provide a very good estimate of the uncertainty (one standard deviation) in the absorption measurements reported in this study.

Figure 2-9 Absorption coefficients measured as a function of mixture dilution. $T = 296 \text{ K}; P = 760 \text{ Torr}.$
Table 2-1 Detection limits determined using the mixture dilution method.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Molecule</th>
<th>Wavenumber [cm⁻¹]</th>
<th>Detection Limit [cm⁻¹]</th>
<th>Detection Limit [ppb]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ethylene</td>
<td>950.08</td>
<td>7.6 x 10⁻⁷</td>
<td>17</td>
</tr>
<tr>
<td>2</td>
<td>Propene</td>
<td>912.11</td>
<td>2.6 x 10⁻⁶</td>
<td>134</td>
</tr>
<tr>
<td>3</td>
<td>Allene</td>
<td>902.4</td>
<td>6 x 10⁻⁶</td>
<td>754</td>
</tr>
<tr>
<td>4</td>
<td>1-Butene</td>
<td>912.71</td>
<td>2.8 x 10⁻⁶</td>
<td>378</td>
</tr>
</tbody>
</table>

2.7.4 Multi-gas Mixtures

The ability of the sensor to detect multiple species was demonstrated by applying the sensor to a multi-gas mixture containing trace amounts of target gases. The multi-gas mixture composition was selected to contain gases at 1% of their 8-hour Time-weighted-Average (TWA) exposure limits. The TWA exposure limits for ethylene, propene, allene and 1-butene are 200 ppm [47], 500 ppm [47], 1000 ppm [48] and 250 ppm [47] respectively. Therefore, a mixture containing 2 ppm, 5 ppm, 10 ppm and 2.5 ppm of ethylene, propene, allene and 1-butene respectively diluted in argon would be needed. Before preparing the multi-gas mixture, it was decided to check for potential interference between propene and 1-butene by plotting the absorption coefficients as a function of wavenumber using PNNL database (Figure 2-10). From Figure 2-10, it can be concluded that it will be challenging to back out
the concentration of 1-Butene in the gas mixture of aforementioned composition, and therefore it was decided to exclude 1-butene for the multi-gas mixture. The multi-gas mixture was prepared manometrically to contain trace amounts of ethylene, propene and allene diluted in argon gas. Accurate determination of the mole fractions of individual gases in the three-gas-mixture will be sufficient proof to demonstrate the capability of the current sensor. The final mixture composition as measured manometrically was 2.2 ppm ethylene, 5.2 ppm propene, and 10 ppm allene.

![Graph](image.png)

**Figure 2-10** Absorption coefficients for multi-gas mixture calculated using PNNL Database [30]. \( T = 296 \, K; \, P = 760 \, \text{Torr}. \)

Figure 2-11 shows the absorption coefficients for individual gases as calculated using PNNL database as well as the measured absorption coefficients of the mixture. The total absorption coefficient of the mixture calculated using PNNL database is shown in purple triangles, while the measured total absorption coefficient is in red circles. The calculated value of total absorption coefficients had to be shown in terms of symbols at specific wavelengths because the frequencies at which the absorption
coefficients of ethylene, propene and allene were reported in PNNL database differed slightly from each other. The total absorption coefficient was measured at 4 specific wavenumbers, - three near the peaks of the three species and one near an off-line ethylene frequency. The concentration of ethylene may be calculated using differential absorption strategy since the contribution of allene and propene to the total absorbance at the on-peak and off-peak frequencies of ethylene remained same and can thus be subtracted. After subtracting the off-peak absorbance from the on-peak absorbance of ethylene, the ethylene concentration was calculated to be 2.3 ppm, which is 4.5% higher than the expected value of 2.2 ppm as prepared manometrically. Since the total absorbance was measured at a particular wavenumber for propene and allene each, we were left with a system of two linear equations containing two unknowns; i.e. the mole fraction of propene \( x_P \) and the mole fraction of allene, \( x_A \). The two linear equations after excluding the contribution of ethylene in the total absorbance can be written as follows:

\[
1.04 x_P + 0.116 x_A = 6.552 \\
1.45x_P + 2.8x_A = 38.12
\]

On solving the above set of linear equations, we obtained \( x_P \) to be 5.1 ppm and \( x_A \) to be 11 ppm. The mole fraction of propene is within 2% of the expected value of 5.2 ppm, whereas the mole fraction of allene is 10% higher than the expected value of 10 ppm. The overestimation of allene absorbance is possibly due to the relatively larger contribution of impurities to the total measured absorbance near 901.55 \( \text{cm}^{-1} \). Repeated attempts were made to carry out absorption measurement closer to the allene peak (901.85 \( \text{cm}^{-1} \)), but consistent mode-hopping of the laser near the allene peak made all such attempts futile. Despite these minor challenges, the novel laser-
based sensor has shown its capability to accurately measure trace amounts of individual gases in a multi-gas mixture.

![Absorption coefficients for multi-gas mixture.](image)

**Figure 2-11 Absorption coefficients for multi-gas mixture.** $T = 296 \text{ K}; P = 760 \text{ Torr}$.

To demonstrate the potential of the sensor to measure trace species in the atmosphere, ethylene concentrations were measured in air collected from our laboratory and in air samples collected from a car park. Due to the potential interference from carbon dioxide at $949.47 \text{ cm}^{-1}$, these ethylene concentration measurements were carried out at a nearby frequency of $949.835 \text{ cm}^{-1}$ (Figure 2-12). In the laboratory air, the concentration of ethylene was found to be 55 ppb. The sample collected from the car park had an ethylene concentration of 415 ppb. The elevated levels of ethylene can be attributed to the unburnt hydrocarbon exhaust from automobiles and to the greenhouse located in the vicinity of the car park. The higher concentration of ethylene observed in the car park is within the previously reported values of ethylene.
(17 to 800 ppb) in urban areas [49]. From the various measurements reported here, it can be concluded that the novel sensor developed in this work has immense potential to be employed for environmental pollution monitoring and gas sensing in chemical and petroleum industries.

Figure 2-12 Absorption coefficients for atmospheric air. T = 296 K; P = 760 Torr.
Chapter 3: CRDS Measurements in Shock Tube

This chapter discusses in detail the implementation of novel laser-based sensor to carry out ultra-fast and sensitive measurements of species time-histories in a challenging environment (shock tube). In what follows, we first present the motivation for developing the ultra-fast and sensitive diagnostic for transient combustion systems. We then, present a detailed description of the design and optimization of our sensitive and fast time-response diagnostic. Lastly, we demonstrate its capability to carry out fast time-response and sensitive species concentration measurements by recording ethylene concentration time-histories in shock tube pyrolysis experiments.

3.1 Introduction

Fast-time response diagnostics capable of performing sensitive measurements are invaluable in the study of transient combustion systems such as shock tubes, internal combustion engines, and gas turbines. High-sensitivity diagnostics can be employed to detect trace species, such as HO$_2$ and H$_2$O$_2$, important for low-temperature chemistry [2], [50]–[52]. These species and other combustion radicals have been difficult to measure using currently available measurement techniques [2], [53], [54]. Ability to measure very small concentrations at very fast rates can be quite
useful in the measurement of reaction rate coefficients. In this work, we have developed a highly sensitive ultra-fast diagnostic based on pulsed cavity ringdown spectroscopy (CRDS) and deployed it for making in situ species time-history measurements in shock tube chemical kinetic experiments.

A shock tube is a transient homogeneous reactor which almost instantaneously creates a test environment of high-temperature and high-pressure gases. Due to these unique characteristics, it has been widely used in chemical kinetic studies for the past few decades. Since the test environment in a shock tube exists only for a few milliseconds, it is imperative to use diagnostic tools with fast time-response. Therefore, continuous-wave (cw) laser absorption spectroscopy based diagnostics with microsecond time resolution [7] have extensively been used for measuring species concentrations in shock tube experiments. Since absorption-based diagnostics are most commonly used for measuring species concentrations in shock tube experiments, a closer look at Beer-Lambert law provides us the possible routes to increase the sensitivity of these diagnostics:

\[
\text{Absorbance} = \ln\left( \frac{I_0}{I} \right) = P \chi S(T) \phi_v(P,T)L
\]  

Here, \(I_0\) is the incident intensity and \(I\) is the transmitted intensity of the laser. Absorbance is a function of the total pressure of the gas, \(P\), the mole fraction of the absorbing species, \(\chi\), the linestrength, \(S\), the lineshape \(\phi_v\) and the path-length \(L\). For a specific experimental condition (fixed \(T, P\) and \(\chi\)), linestrength and path-length play a decisive role in deciding the measurement sensitivity for a given molecule. Linestrength depends on the molecular transition being probed and stronger vibrational bands can be chosen to increase the diagnostic sensitivity within the limits
of laser availability and interference from other species. The only other parameter that can be varied is the absorption path-length. However, shock tubes and other transient combustion systems usually have small physical dimensions that result in single-pass absorption path-lengths of the order of 1 – 20 cm. Therefore, the only possible solution to increase path-length and consequently the measurement sensitivity is to employ cavity-based techniques which make the laser light undergo multiple passes through the absorbing medium. Among the numerous cavity based techniques available, pulsed CRDS offers the best combination of simplicity and spatial resolution as discussed earlier in Section 2.3.

In this work, we have used the high-repetition-rate (100 kHz) external cavity quantum cascade laser (EC-QCL) and relatively low reflectivity (99.8%) mirrors to develop an ultra-fast high-sensitivity diagnostic based on pulsed-CRDS. Numerous previous pulsed-CRDS studies [55]–[59] utilized optical cavities with high reflectivity mirrors (>-99.99%) to obtain substantial increases in sensitivity. However, the time resolution of such cavities is much lower than that required to carry out measurements in homogeneous transient chemical reactors like shock tubes. Here, we harness the low reflectivity (99.8%) of the optical cavity mirrors to obtain measurement times of less than 1 µs. In what follows, we present a detailed description of the sensitive and fast time-response diagnostic. We then demonstrate its capability to make fast time-response and sensitive species concentration measurements by recording ethylene concentration time-histories in shock tube pyrolysis experiments. To our knowledge, this is the first successful application of the CRDS technique to shock tube kinetic experiments.
3.2 Experimental Details

3.2.1 Pulsed CRDS Sensor

The experimental setup used in this work (Figure 3-1) is similar to the one used for static cell measurements (Figure 2-1) and utilized the same pulsed EC-QCL (Daylight Solutions). The cavity on the shock tube was formed by two plano-concave mirrors with 20 cm radius of curvature, 12.5 mm diameter and reflectivity of 99.8% at 10.6 µm (II-VI Infrared). Small diameter mirrors had to be used because of the limited optical access available on the shock tube. Mirrors were glued to custom designed plugs which were then mounted on the shock tube ports located at a distance of 2 cm from the shock tube end-wall. The mirrors were flush to the inside wall of the shock tube. Alignment of the ringdown cavity was achieved by using three fine adjustment screws (Thorlabs FAS100) which allowed three-axis rotation of the custom designed plugs. The significantly larger laser linewidth (0.064 cm\(^{-1}\)) compared to the cavity mode width (~ 0.00002 cm\(^{-1}\)) eliminated the need to lock the laser to the ringdown cavity. Here, the infrared laser beam leaking out of the optical cavity was focused on to a thermoelectrically-cooled, optically-immersed photovoltaic detector (Vigo PVI 4TE-10.6-1x1-TO8-BaF2). The photo-detector was custom-designed to have a high bandwidth of 500 MHz to adequately resolve relatively short ringdown times (~ 40 - 180 ns). The detector signal was recorded with a digital oscilloscope (Tektronix DPO 3014) having a sampling rate of 2.5 GS/s.
Figure 3-1. Experimental setup used for pulsed CRDS employed for a carrying out species measurements in shock tube. BS: Beam splitter, MMO: Mode matching optics, BPF: Band pass filter.

3.2.2 Shock Tube Facility

All measurements reported in this work were performed in a 14.2 cm diameter stainless steel shock tube. The shock tube facility consisted of a 9-meter long driven section and a variable length driver section with a maximum length of 9 meters. The incident shock velocity was measured using five PCB 113B26 piezoelectric pressure transducers (PZTs) that were located axially along the last 1.3 m of the driven section. The incident shock speed at the end-wall was determined by linear extrapolation of the velocity profile. One-dimensional shock-jump equations were used to calculate the conditions (temperature, pressure) behind the reflected shock wave. Ethylene mixtures were prepared manometrically in a stainless steel mixing tank equipped with a magnetic stirrer.

3.3 Results and Discussion

The diagnostic is applied to measure ethylene time-histories behind reflected shock waves in ethylene pyrolysis experiments. The pulsed CRDS measurements were carried out near the peak of the ethylene Q-branch at a fixed frequency of
949.472 cm$^{-1}$. The laser frequency was carefully selected after carrying out spectral simulations using HITRAN database [40] to consider potential interference from species produced during ethylene pyrolysis. Earlier, Pilla et al. [60] had selected a nearby frequency of 949.487 cm$^{-1}$ for measuring ethylene concentrations in ethylene pyrolysis experiments. Their detailed analysis showed that absorption interference is negligible at their probe frequency. The absorption coefficient measured using pulsed CRDS technique was converted to ethylene concentrations by utilizing the absorption cross-sections reported for ethylene at nearby frequency of 949.487 cm$^{-1}$ [61]. The ethylene absorption cross-sections have an uncertainty of less than 1.4% over a wide temperature and pressure range (643 – 1959 K and 0.3 – 18.4 bar). For all measurements reported here, laser pulse width of 100 ns was used which resulted in a frequency chirp of 0.064 cm$^{-1}$.

A stable optical cavity is necessary for pulsed CRDS to function properly and the cavity locking can potentially be disturbed by the arrival of the shock wave and other related disturbances at the measurement location. Shock waves are accompanied by mechanical vibrations as well as significant changes in temperature, pressure and refractive indices of the shock-heated gases. Mechanical vibrations perturb the mirror alignment while changes in the density and refractive index of shock-heated gas cause beam steering. These combined effects can potentially disturb cavity locking and make the application of CRDS technique to shock tubes quite complicated. Therefore, these effects were considered very carefully during the development of the diagnostic reported here. The cavity locking was then investigated by measuring the ringdown times before and after the arrival of the incident and reflected shock waves for non-reactive (argon) experiments. The pressure trace and the ringdown times for a
representative non-reactive shock are presented in Figure 3-2. The arrival of both the incident and the reflected shock waves, identified by the sudden jumps in the pressure trace, did not cause any significant reduction in the value of the ringdown time, indicating that the cavity locking was maintained throughout the experiment. The mean value of the ringdown time reduced from 178 ns in pre-shock conditions to 167 ns behind the reflected shock due to the absorbance by trace impurities present in argon gas.

![Figure 3-2 Measured pressure (blue trace) and ringdown times (black dots) for a non-reactive (pure argon) shock. Reflected shock conditions are 1976 K (T_s) and 1.99 bar (P_s).](image)

The standard deviation in the measured ringdown times for the non-reactive shock, shown in Figure 3-2, is 8.6 ns. The minimum detectable absorption coefficient can then be calculated as:

\[
\alpha_{\text{min}} = \frac{1}{c} \left( \frac{\sigma}{(\tau_0 - \sigma)\tau_0} \right)
\]

where \(\sigma\) is the standard deviation in the ringdown time, \(c\) is the speed of light and \(\tau_0\) is the measured ringdown time. The minimum detectable absorption coefficient
comes out to be $1.08 \times 10^{-5}$ cm$^{-1}$ which is a significant increase as compared to $2.95 \times 10^{-4}$ cm$^{-1}$ [61] achieved using single-pass direct absorption based diagnostic for the Q-branch of ethylene.

The increased sensitivity of pulsed-CRDS technique enables detection of trace concentrations of the species of interest and the use of dilute mixtures. When using highly dilute reactive mixtures in shock tube kinetic experiments, the temperature and pressure remain almost constant throughout the reactive experiment. Since the knowledge of temperature and pressure is required to convert the measured absorption coefficient to concentration time-histories, having a constant temperature and pressure reduces the uncertainty in measured species concentration time-histories. Additionally, the use of dilute mixtures enables the operation of the shock tube close to ideal conditions of constant volume and energy (constant UV). Finally, when measuring reaction rate coefficients, dilute mixtures provide sensitivity to the target reaction and minimize the interference from secondary reactions.

With the knowledge that the cavity locking was not being disturbed due to the arrival of shock waves as well as the perturbations that accompany it, the diagnostic was applied to reactive experiments of ethylene pyrolysis. The diagnostic was first used to measure ethylene concentration time-history at reflected shock temperatures where ethylene is not expected to decompose. Figure 3-3 shows the measured ethylene concentration time-history for 316 ppm C$_2$H$_4$/Ar mixture at reflected shock conditions of 1306 K and 2.43 bar. As expected, ethylene concentration remained constant throughout the experiment. We can also observe excellent agreement between CRDS measurement and prediction of Marinov et al. [62] chemical kinetic model. The constant ethylene concentration measured over 1.5 ms was further proof that the
cavity locking was not disturbed by arrival of the shock waves and the accompanying mechanical vibrations. The measured ethylene concentration has a standard deviation of 34 ppm for the conditions of Figure 3-3.

The CRDS diagnostic was then utilized to measure ethylene pyrolysis at higher reflected shock temperatures. Figure 3-4 shows the ethylene concentration time-history measured at reflected shock conditions of 1845 K and 1.96 bar. The uncertainty in ethylene concentration measurements depends mainly on the uncertainties in the measured ringdown times and has been calculated as explained previously in Section 2.7.1. The standard deviation depends on the ringdown time being measured and has been estimated for low absorbance case from the measurement of ringdown times in non-reactive argon shock experiments (ringdown times of ~170 ns) and for high absorbance case from the experiments where ethylene concentration remained constant (ringdown times of ~40 ns). Standard deviations of 9.6 ns and 3.3 ns were determined for the low absorbance and high absorbance cases.
respectively and led to maximum uncertainty of 25 ppm in the measurement of ethylene concentration. Time zero has been set to coincide with the start of the test time, i.e., when the reflected shock wave arrives at the measurement location. Sensitivity analysis was carried out for the aforementioned reflected shock conditions to identify the reactions which significantly affect ethylene time-history. The most dominant reaction at high temperatures is the decomposition of ethylene to form acetylene and hydrogen:

\[ \text{C}_2\text{H}_4 + \text{Ar} \xrightarrow{k_1} \text{C}_2\text{H}_2 + \text{H}_2 + \text{Ar} \]

The rate coefficient \(k_1\) for ethylene decomposition reaction was extracted from the experimentally measured ethylene concentration profile at 1845 K and is listed in Table 1. The measured rate constant compares well with the measurement of Ren et al. [61] and the prediction of Marinov et al. [62].

Table 3-1. Measured rate constant for ethylene decomposition \(\text{C}_2\text{H}_4 + \text{Ar} \xrightarrow{k_1} \text{C}_2\text{H}_2 + \text{H}_2 + \text{Ar}\) at 1845 K and 1.96 bar

<table>
<thead>
<tr>
<th></th>
<th>(k_1) (cm(^3)mol(^{-1})s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>(2.2 \times 10^8)</td>
</tr>
<tr>
<td>Ren et al. [61]</td>
<td>(2.4 \times 10^8)</td>
</tr>
<tr>
<td>Marinov et al. [62]</td>
<td>(3.08 \times 10^8)</td>
</tr>
</tbody>
</table>

For relatively slow transient situations, noise in species concentration can be further reduced by averaging the decay time over two successive pulses, as shown in Figure 3-5. Averaging two successive ringdown times leads to a small reduction in the standard deviation and subsequently in the uncertainty of the measurements. Standard deviations of 8 ns and 2.7 ns were obtained for low absorbance and high absorbance cases respectively and were used to estimate the uncertainty in ethylene concentration.
measurements. Averaging the decay times over two successive pulses reduced the maximum uncertainty in ethylene concentration measurements to 21 ppm. Due to dilute ethylene mixture used here, Marinov et al. model [62] predicts a temperature drop of less than 5 K and a pressure drop of less than 5 mbar during the measurement time of 1.5 ms. Previous experimental studies which reported ethylene concentration time-histories in ethylene pyrolysis experiments [60], [61] relied on chemical kinetic models to provide temperature during the reaction and the model temperature was then used to convert absorbance profiles to ethylene mole fractions. In the current work, the use of dilute ethylene mixture led to negligible temperature change (~ 5 K) during pyrolysis which removed the dependence on kinetic model for the calculation of ethylene mole fractions. Additionally, as mentioned earlier, the use of dilute mixture increases the sensitivity of the measurement to the unimolecular decomposition rate of ethylene. We believe the results of this study can be used to obtain improved value of the rate coefficient of ethylene unimolecular decomposition.

Figure 3-4 Ethylene time-history profile for 316 ppm C₂H₄/Ar. Reflected shock conditions are 1845 K (Tₛ) and 1.96 bar (Pₛ). Uncertainty bars are shown in green color.
Figure 3-5 Ethylene time-history profile for 316 ppm C\textsubscript{2}H\textsubscript{4}/Ar. In this case, two successive laser pulses are averaged to increase SNR. Reflected shock conditions are 1845 K (T\textsubscript{5}) and 1.96 bar (P\textsubscript{5}). Uncertainty bars are shown in green color.

Figure 3-6 shows the sensitivity gain that can be achieved by using higher reflectivity mirrors. Ethylene detection limit is plotted at two conditions, i.e., room temperature and pressure (black line) and at a temperature and pressure representative of typical fuel pyrolysis conditions (red line). The detection limit for ethylene was calculated by assuming that the value of σ/τ\textsubscript{0} obtained for current work remains same for other mirror reflectivities. The increase in absorption sensitivity possible by using high reflectivity mirrors comes at the cost of measurement time resolution (defined as 5τ\textsubscript{0}) which increases to tens of microseconds for high reflectivity mirrors. Moreover, the use of high reflectivity mirrors necessitates using high power lasers. Despite these challenges, the tremendous gain in sensitivity offered by pulsed cavity ringdown spectroscopy makes it a very promising tool for studying species time-histories in shock tubes and other homogeneous systems. Future ethylene diagnostics which target a specific detection limit or time resolution can potentially be designed using Figure 3-6. As an example, for a target time resolution of 5 μs, Figure 3-6 shows that
the ethylene detection limit will be 52 ppb at room temperature and pressure (297 K and 1 bar) and 2.45 ppm at 1800 K and 2 bar. It is to be noted that the value of $\sigma/\tau_0$ depends on the specific experimental setup and, among other factors, varies with mirror reflectivity. Figure 3-6 attempts to give the reader a general idea about the benefits and challenges of using higher reflectivity mirrors.

![Figure 3-6 Estimated ethylene detection limit and time resolution as a function of mirror reflectivity for pulsed CRDS.](image)

Compared to the widely used single-pass direct absorption based diagnostics, the pulsed CRDS diagnostic developed in this study is able to achieve significant increase in sensitivity, as illustrated by the trace ethylene concentrations measured in shock tube experiments. The minimum detectable absorption coefficient was calculated after almost every reactive experiment by measuring ringdown times in a non-reactive argon shock and it remained constant throughout the experimental campaign spanning several days. Due to the maximum pulse repetition rate of 100 kHz, the time gap between successive data points was 10 $\mu$s. However, each ringdown event lasted for less than 1 $\mu$s for all experiments. Lasers with higher repetition rates can be utilized to further improve the sensitivity or time-resolution of the current diagnostic. To our
knowledge, this work presents the first successful demonstration of the implementation of the cavity ringdown technique with high-repetition-rate lasers to measure species time-histories in a shock tube.
Chapter 4: Atmospheric Flame Ion Measurements using QMS

This chapter describes the application of QMS to investigate ion chemistry in atmospheric flames. The chapter starts with an introduction to mass spectrometry (MS) and is followed by two sections discussing the benefits and challenges of using MS for species measurements. Then, the motivation for the current work is presented followed by a detailed description of the QMS experimental setup, including the characterization of the mass discrimination factor. We then present the measured ion mole fraction profiles in lean and stoichiometric flames along with thermocouple measurements of flame temperature. Lastly, we compare our ion measurements with numerical simulations carried out using an established ion chemistry model [63], [64] and suggest selected modifications that improve the qualitative agreement between experimental and numerical data.

4.1 Introduction

Combustion chemistry is a complex process involving a large number of radical species, ions, reactive intermediates, and products. Qualitative and quantitative concentrations of reactants, products, and reactive intermediates may be obtained by various combustion diagnostic methods. Mass spectrometry (MS) is a powerful tool to analyze reacting gas species. It has been extensively employed to study complex reactive environments such as flames and plasmas [65], [66]. In MS, reacting gases from a flame/chemical reactor are sampled through a miniscule (sub-mm) opening in the sampling probe and expanded rapidly through the sampling cone and skimmer orifices via multiple stages of differential pumping leading to the formation of a
molecular beam. The species in the molecular beam are subsequently separated using mass spectrometry. When measuring neutral species and radicals, electron-impact ionization is generally used to ionize the molecules before guiding them through the mass spectrometer. Naturally occurring flame ions are transferred through charged skimmer cones and ion optics and directed through the mass spectrometer. The mass spectrometer filters the species on the basis of their mass-to-charge ratio before directing them through to the detector.

Two types of mass spectrometers are routinely used to separate the species on the basis of their mass to charge ratio: quadrupole mass spectrometer (QMS) and time-of-flight mass spectrometer (TOF-MS). QMS consists of four parallel metal rods with opposing rods connected together electrically. Radio frequency voltage is then applied successively to each rod pair which ensures that ions with only a certain mass-to-charge ratio will pass through the quadrupole and reach the detector, all other ions have unstable trajectories and collide with the rods.

TOF-MS filters species on the basis of their time of flight from the source to the detector. Due to the fundamental difference in the way the TOF-MS filters species, it can record all the species (within the upper mass limit) simultaneously as compared to detecting one species at a time. Moreover, single cycle mass scan in TOF-MS can be completed rapidly thereby enabling time resolution of the order of a few micro-seconds which makes it suitable for measuring species time-histories in transient systems. However, TOF-MS systems with micro-second time resolution usually suffer from low mass-resolution because in such systems, the time-of-flight is reduced to improve the time resolution. Conversely, QMS filters masses at a much
slower pace and is more suited to study species concentrations in steady systems such as laminar flames.

### 4.2 Benefits

Mass spectrometry is one of the most extensively used diagnostic tools in the combustion community because of its excellent sensitivity and ability to detect all species with mass-to-charge ratios below a certain upper limit. The upper mass limit depends on the type of mass filter being used with QMS having a upper mass limit of \( \sim 4000 \), while TOF-MS have no upper limits [66]. This unique ability of excellent sensitivity combined with the ability to detect several species simultaneously gives it an unprecedented advantage over all other diagnostic techniques that are capable of detecting only a few species at best. Furthermore, mass spectrometers can differentiate between flame ions and neutrals because neutrals can be observed on the detector only when the gas sample is ionized, while flame ions do not require any ionization. The aforementioned capabilities make mass spectrometers ideal for studying reaction kinetics as well as ion chemistry in flames and other combustion systems.

### 4.3 Challenges

The decision to select mass spectrometer as the diagnostic tool of choice requires the knowledge of its limitations. Mass spectrometer is an intrusive diagnostic tool because it utilizes a probe to extract the gas sample. The sampling probe can cause variations in temperature and concentration profiles [67], [68], while optical diagnostic techniques such as laser-based sensors do not suffer from this limitation. At high electron-impact ionization energies, fragments of molecules are formed during the ionization process, which can make the process of assigning a unique
molecular formula to ions challenging. Additionally, water clusters can be formed during the sampling process which require careful data analysis to avoid distortion of data [69].

4.4 Motivation

Flame chemi-ionization produces ions in trace quantities, with typical mole fractions varying from $10^{-9}$ to $10^{-7}$ [12]. Ion current sensors have been used to control spark advance timing [70], knock [71] and in-cylinder pressure [72]. In addition to these applications, there has been an increasing interest in understanding ion chemistry to enable effective application of external electric fields for active control of combustion processes. Electric fields have been shown to reduce emissions [7], extend the operability of combustion devices and improve combustion efficiency [8], [10]. Nevertheless, progress has been hampered by the limited characterization of flame ionization processes, rudimentary ion chemistry models and the lack of experimental data on the distribution of ions in flames. Detailed knowledge of ion chemistry is required to accurately predict the total density of positive and negative charges, which are essential to model the interaction of flames with external electric fields [13]. Consequently, experimental and modeling efforts towards a thorough characterization of flame ion chemistry are needed.

Owing to the extremely small concentrations of ions in flames, it is very challenging to implement non-intrusive laser-based diagnostics to measure ion mole fractions. Compared to other diagnostic techniques, mass spectrometry (MS) provides high sensitivity and the ability to differentiate between ions and neutrals and consequently has been used for measuring ions in flames for the past six decades.
Deckers and Van Tiggelen [80] succeeded for the first time in detecting flame ions in $10^{-5}$ Torr vacuum. Their seminal work was followed by that of Knewstubb and Sugden [73], who developed a sensitive MS to measure ions in atmospheric hydrogen-oxygen-nitrogen flames. Calcote and Reuter [74] demonstrated the use of MS to measure ions in low pressure ethylene-oxygen flames. Goodings et al. [78], [81] conducted a detailed study of positive and negative ion chemistry by measuring relative ion concentrations in methane-oxygen Bunsen flames using a QMS. Rodrigues et al. [79] measured cations and anions in two regions of a stoichiometric propane-oxygen atmospheric flame using a QMS.

There have been few detailed experimental studies on the distribution of ionized species in premixed methane-oxygen flames [78], [81]–[83]. Goodings et al. [78], [81] performed a detailed study of methane ion chemistry by sampling ions from lean and rich premixed atmospheric Bunsen-type flames. The flames were sampled through a 0.1 mm diameter pinhole in a platinum-iridium disk [78]. However, Goodings et al. [78], [81] did not report flame temperatures. The lack of temperature information and the inherent two-dimensional conical flame structure make it difficult to compare simulations and measured ion concentration profiles [63], [64] directly. Furthermore, since ion concentration data for methane-oxygen flames are available from a single research group, there is the need for additional studies to evaluate sampling and facility effects on the experimental data.

The present work aims at studying ion chemistry by measuring cation mole fraction profiles in methane-oxygen flames using a QMS. This study is expected to improve the understanding of flame ion chemistry and the data collected herein will serve as benchmark for the testing of numerical models for ion chemistry.
4.5 Experimental Details

Here, a water-cooled stainless-steel McKenna burner of 6 cm diameter (Holthuis & Associates) is used to establish premixed methane-oxygen flat flames with argon as the diluent gas. The flow rates and equivalence ratios used in this study are given in Table 4-1. The mass flow controllers (MKS, 1179B) have an uncertainty of ±5% of the full range (5 standard liters per minute (SLPM) with standard conditions being 273.15 K and 1 atm). The temperature of the cooling water entering the burner was kept constant at 15 °C. The premixed flames were surrounded by a co-flow of argon to avoid reactions/diffusion with the surrounding air. In the absence of the Argon shield, a strong signal for NO⁺ ions was observed in the burnt gas region of the flame, indicating reaction with air. The flow rate of the Argon shield gas was increased until the NO⁺ ion signal disappeared from the recorded mass spectra. The McKenna burner was mounted on a vertical translation stage with a minimum step size of 10 µm. The flame was oriented vertically in order to avoid changes in flame shape due to buoyancy. In this work, a modified Hiden HPR-60 system equipped with a triple filter QMS (EQP, 300 m/z range) is used to measure ion profiles as a function of height above the burner surface. A 5 mm long alumina cone of 90° angle and 0.1 mm aperture was used for sampling the flame gases. The gases were sampled along the centerline of the flat flame and transferred via a molecular beam to the mass spectrometer using three stages of differential pumping (Figure 4-1). The first and second stage skimmer cones had orifice sizes of 0.6 mm and 2 mm, respectively. The separation between the tips of the sampling cone and first stage skimmer cone was 8 mm. The axial distance between the tips of first and second stage skimmer cones was 18.35 mm. A turbomolecular pump (Edwards STP-iXR2206) with a pumping speed of 2200 l/s was used to maintain pressure near 10⁻³ Torr in the first stage. Pressure in
the second and third stages was maintained near $10^{-6}$ and $10^{-7}$ Torr respectively, by using a turbomolecular pump (Edwards nEXT240D 160W) with pumping speed of 240 l/s in each stage. In order to detect naturally occurring ions in flames, electrical potentials of -40 V and -20 V were applied to the first stage and second stage skimmer cones, respectively. The voltages applied to the skimmer cones help in funneling the ions into the sampling system. The transmission of molecules through the two skimmer cones is primarily due to physical gas expansion and differential pumping via molecular beam sampling. During supersonic gas expansion there is an enrichment of the heavier species caused by several factors, including diffusive separation, shock wave effects, background gas invasion, molecular collisions, and preferential transverse migration of the lighter molecules [84]. We assume that these physical processes are similar for the detection of ions and neutrals. Therefore, mass discrimination factor determined for neutrals can be applied to charged species measurements. The QMS system used in the current study is a combined mass spectrometer and an energy filter. Therefore, in the third stage, ions are transmitted through an energy filter where the ions are filtered on the basis of relative kinetic energy before passing through the quadrupole and reaching the detector. The flame temperature was measured using an SiO$_2$ coated platinum-30% rhodium / platinum-6% rhodium (Type-B, Omega) thermocouple with a bead size of 0.38 mm. Thermocouple readings were corrected for radiation effects [85], [86]. Radiation heat transfer from the thermocouple bead to the burner and water-cooled sampling flange was considered via appropriate view factors [87]. Radiation corrections for thermocouple readings ranged from 30 to 203 K for flame temperatures between 1083 and 1867 K, respectively.
Table 4-1 Flame parameters. The reactant mixture enters the burner at 23 °C for all flames. Pressure is 1 atm. Standard conditions are 273.15 K and 1 atm.

<table>
<thead>
<tr>
<th>Flame</th>
<th>Equivalence ratio</th>
<th>CH(_4) flow rate, SLPM</th>
<th>O(_2) flow rate, SLPM</th>
<th>Ar flow rate, SLPM</th>
<th>Total flow rate (CH(_4) + O(_2) + Ar), SLPM</th>
<th>Ar shield flow rate, SLPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.54</td>
<td>1.28</td>
<td>4.72</td>
<td>2</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>2</td>
<td>1.01</td>
<td>1.99</td>
<td>3.95</td>
<td>2.06</td>
<td>8</td>
<td>8</td>
</tr>
</tbody>
</table>

Figure 4-1 Schematic diagram of the experimental setup consisting of a flat flame McKenna burner and quadrupole mass spectrometer (QMS).
4.6 Numerical Model

The source code PREMIX [88] is used to simulate the premixed flames in the current study. The experimental flame is modeled as a 1D burner stabilized premixed flat flame. The solution domain is 10 mm and possible effects due to the position of the sampling cone with respect to the burner have been neglected. The number of points is more than 100 and the minimum mesh size is approximately 1µm.

Unlike neutrals, charged species are affected by the electric field generated by other charged particles, and they are coupled through the Poisson equation for the voltage. As a result, two modifications are implemented in the PREMIX code. First, the Poisson equation is added to the system of equations solved by the solver TWOPNT within PREMIX:

\[ \frac{d^2V}{dx^2} = -\frac{e}{\epsilon_0} \sum q_i n_i, \]

where \( e = 1.6 \times 10^{19} \) C is the elementary charge, \( \epsilon_0 = 8.85 \times 10^{-12} \) F/m is the vacuum permittivity, \( q_i \) and \( n_i \) are the charge and number density of the species \( i \), respectively. The electric field strength \( E \) is determined from the electric potential as:

\[ E = -\frac{dV}{dx}. \]

Second, the mass flux for charged species \( J_i \) is modified to include the drift diffusion flux [89]:

\[ J_i = -\rho D_i \frac{dY_i}{dx} + \frac{q_i}{|q_i|} \mu_i \rho Y_i, \]
where \( \rho \) is the mixture density and \( Y_i \) is the mass fraction of the species \( i \). \( D_i \) and \( \mu_i \) are the mixture-averaged diffusivity and mobility of the charged species \( i \), respectively. The transport coefficients of ions are calculated from Blanc’s law [90], which applies in the thermal limit. To compute the binary transport coefficients of ions, the Lennard-Jones potential is not suitable, as it does not take into account the effect of the ion electric charge. As suggested in [91], the (n,6,4) and Coulomb interaction potentials are used to describe the ion-neutral and ion-ion interactions, respectively. For electrons, a constant value of 0.4 m\(^2\)/V-s, recommended in the work of [92], is used for the electron mobility, and its diffusivity is computed from the Einstein relation [90]:

\[
D_i = \mu_i k_B T / q_i,
\]

where \( k_B \) is the Boltzmann constant and \( T \) is the gas temperature.

PREMIX conserves the flux balance for species on the upstream boundary and uses zero gradient for all variables on the downstream boundary as explained in [93]. The same boundary conditions are also applied to charged species but the drift flux of charged species on the upstream boundary is set to zero and only the diffusion flux is retained as follows [94]:

\[
\dot{m}' \epsilon_i = \dot{m}'' Y_i - D_i \rho Y_i \frac{dX_i}{dx},
\]

where \( \dot{m}'' \) is the mass flow rate, \( \epsilon_i \) is the known incoming mass flux fraction. \( X_i \) and \( Y_i \) are the mole and mass fractions, respectively.

4.7 Chemical Mechanism

In the current work, an improved ARAMCO 1.3 mechanism [95], [96] is used for modeling neutral species. This mechanism is chosen because it is constructed in a hierarchical fashion and describes the combustion of C1-C2 fuels. Furthermore the
prediction of the concentration of the CH radical, which plays a key role in chemi-
ionization process, is found to be satisfactory as discussed in [96].

Ion chemistry mechanisms in flames are much less developed compared to the
mechanisms for neutral species. This paper adopts the ion mechanism assembled by
Prager [63], [64] which was evaluated by comparing against the experimental data of
Goodings et al. [78], [81] and analyzed in a recent uncertainty quantification study by
Kim et al. [97]. The mechanism consists of 11 charged species (i.e. H_3O^+, C_2H_5O^+,
CH_5O^+ and HCO^+, O_2^-, OH^-, O^-, CHO_2^-, CHO_3^-, CO_3^- and E^-) and 67 elementary
reactions. This mechanism, unfortunately, does not include C_3H_3^+, which appears in
negligible amounts in stoichiometric flames, but is dominant in rich flames [78]. The
inclusion of rich ion chemistry reactions is the subject of ongoing efforts and will be
reported at a later date. In the current work, the rate constants of most reactions that
were specified in Prager’s ion mechanism [63], [64] are updated according to the
UMIST database [98]. The experimentally determined [99]–[102] rates of chemi-
ionization and recombination are adopted as recommended in [63], [64].

The predictions of ion chemistry model may involve a high degree of
uncertainty (up to a factor of 2) because of the large uncertainties in the kinetic and
thermodynamic data for ions [97]. The transport properties have limited effect on the
ion distributions reported in the current work, as discussed in [91].

4.8 Results and Discussion

4.8.1 Neutral Species

Validation of the experimental setup was first carried out by measuring neutral
species in the same lean and stoichiometric premixed flames (Table 4-1). Flame
neutrals were ionized by electron-impact ionization at 20 eV and guided through to the detector. Figure 4-2 compares the measured mole fraction profiles of major neutral species with model predictions obtained using two different temperature profiles for each of the two flames studied here. The “unperturbed flame temperature” corresponds to the flame temperature measured using the thermocouple in the absence of the sampling cone. The “stretched flame temperature” profiles for all cases discussed in this work were obtained by shifting the axial position of the peak temperature to the position where H₂O mole fraction peaks [103]. However, the temperature at the burner surface was kept the same as the unperturbed case. In the region between the burner surface and the axial position corresponding to peak H₂O mole fraction, the temperature profile providing the best agreement of simulations with the measurements of major neutrals species (Figure 4-2) was selected. It is pertinent to point out that the ST profile is not expected to accurately represent the flame temperature in the presence of the sampling probe, but is being used here in order to qualitatively understand the influence of probe perturbation on the conclusions of the current ion study. Further details on the need to define “stretched temperature profile” are discussed later.
Figure 4-2 Measured neutral species (symbols) and simulations (lines). Simulations obtained using unperturbed temperature profile (UT) and stretched temperature profile (ST).

When the UT profile (Figure 4-2) was used to constrain the simulations, the simulated ion profiles were shifted by 0.8 mm and 1.53 mm for lean and stoichiometric premixed flames, respectively, to match the position of the H$_3$O$^+$ peak in each flame (shown later). A relatively large cone angle (90°) was used in the experiments to minimize the loss of ions to the walls of the sampling cone, but this resulted in greater probe perturbation of the flame front especially in the stoichiometric flame. Consequently, a relatively larger than usual axial shifting of simulation results was required. However, no axial shifting was implemented for simulations utilizing the ST profile. Overall, the simulated mole fractions obtained using both temperature profiles reproduced the experimental data satisfactorily in the burnt gas regions of both flames.

4.8.2 Cation Measurements

Mass scans were carried out over mass-to-charge ratios (m/z) between 1 and 300. Different regions of the flame were scanned to identify dominant ions under lean and stoichiometric conditions. Figure 4-3 shows mass spectra of the dominant positive ions detected in the reaction zone of the lean flame (Flame 1 in Table 4-1),
corresponding to a height of 1.5 mm above the burner. The ordinate in Figure 4-3 has been scaled with respect to the most abundant ion in the reaction zone. In the reaction zone, the major ions are C\textsubscript{2}H\textsubscript{3}O\textsuperscript{+}, hydrates (water adducts) of C\textsubscript{2}H\textsubscript{3}O\textsuperscript{+}, hydrates of CH\textsubscript{2}O\textsuperscript{+}, H\textsubscript{3}O\textsuperscript{+} ion and its hydrates. It is important to note that hydrates do not exist in the flame and are an artifact of the sampling process. The hydrates are formed in the boundary layer region near the tip of the sampling cone and/or during the supersonic expansion through the sampling cone [69]. Therefore, the relative mole fractions of hydrates are lumped together with the primary ion.

![Figure 4-3 Mass spectra of ions extracted from the reaction zone of a lean (\(\phi = 0.54\)) premixed flame.](image)

Since the QMS system used in the current study is a combined mass spectrometer and energy analyzer, the mass scan obtained at a given relative kinetic energy level does not give enough information to obtain relative ion mole fractions. Ion mole fractions may be compared once the integrated area of the ion energy distribution curve is measured and the mass discrimination of the system is determined. In order to obtain the desired relative mole fractions, the following procedure was adopted. First, a mass scan was carried out at an optimum relative kinetic energy to identify all ions present in the flame, as shown in Figure 4-3. From the mass scan, the dominant
ions were selected and an energy scan was carried out for the ions of interest. Figure 4-4 shows the ion energy distribution curve for mass 43 (C$_2$H$_3$O$^+$) in the reaction zone at 1.5 mm above the burner. The area under the ion energy distribution curve is a good representation of the ion mole fraction and this area is found to be repeatable within 10% of the reported values. Therefore, all the relative ion mole fractions reported in this work have a maximum uncertainty of ±10%.

![Figure 4-4 Ion energy distribution curve for C$_2$H$_3$O$^+$ ion in a lean ($\phi = 0.54$) premixed flame.](image)

With the integrated energies calculated, mole fraction profiles for ions of similar masses may be plotted and compared. However, the measurement of relative mole fractions requires the mass discrimination factor (MDF) of the system to be characterized [104]. The MDF of the present QMS system depends on two parameters, namely, the transmission efficiency and the enrichment factor [104]. The transmission efficiency represents the percentage of ions of a given mass that pass through the quadrupole mass filter while oscillating in an unstable trajectory on their way to the detector. Some of the ions are lost because of the inappropriate RF and DC potentials that they are subjected to [105], [106] or due to the fringing field [107].
Typically, ions with higher mass have a higher tendency to drift off the mass filter due to the aforementioned effects. The enrichment factor represents the tendency of ions to diffuse out of the molecular beam causing a concentration enrichment of less diffusive ions. Unlike the transmission efficiency, the enrichment factor is higher for heavier molecules, which have smaller thermal velocity and less transverse drift behind the nozzle of the sampling and skimmer cones [108]. Therefore, the enrichment of heavier gas species at the centerline of the molecular beam caused by the supersonic expansion and beam skimming must be taken into account by incorporating the enrichment factor, when converting the detector signals to relative mole fractions.

The two effects discussed above compensate each other since the enrichment factor favors heavier ions, while the transmission efficiency of the quadrupole favors lighter ions. We measured the MDF of the current system as the product of the two factors by flowing various gas mixtures of known concentrations through the QMS using the same sampling system. The mixtures contained gases with a suitable distribution of molecular weights: H₂ (2 amu), CH₄ (16 amu), C₂H₂ (26 amu), C₂H₄ (28 amu), C₃H₆ (42 amu), C₇H₈ (92 amu) and three Xe isotopes (129, 132, and 136 amu). Mass scans were carried out at several electron ionization energies to generate a large dataset from which the MDF was calculated as shown in Figure 4-5. Electron impact cross-sections (EICS) were taken from literature [109]–[113] for all the molecules present in the calibration mixture. The relation between the ion signal Sᵢ and the MDF, for a specific ion, i, at a given height above the burner is given by:

\[ Sᵢ (y) = Xᵢ * FKT(y) * MDFᵢ * EICSᵢ \]  

(7)
where $X_i$ is the species mole fraction, $EICS_i$ is its electron impact cross-section and $FKT(y)$ is the instrument sampling function. Therefore, the integrated ion signal from the detector is divided by the MDF to correct for the mass discrimination occurring in our QMS system.

For the purpose of fitting, the MDF had to be split in two regions with mass 42 being the cut-off point. In the low mass region (m/z below 42), MDF increases with increasing m/z ratio which indicates that enrichment factor is dominant. In the high mass region (m/z above 42), MDF reduces with increasing mass implying that the effect of transmission efficiency is larger compared to the enrichment factor.

![Mass discrimination factor (MDF) measured for a few molecules.](image)

The instrument sampling function $FKT$ depends on the bulk properties of the flame sample and remains same for all the species being measured [114]. It is calculated as:

$$FKT(y) / FKT(y_0) = S_i(y) / S_i(y_0) * X_i(y) / X_i(y_0)$$
Where \( y_0 \) is the reference location. Since Ar mole fraction remained constant across the flame, the above equation reduced to the ratio of Ar signal at different heights above the burner. Since the Ar signal was also almost constant across the height of the flame for both flames studied here, the FKT was almost unity and the ion signal was scaled with MDF to yield relative ion mole fractions across the flame. The FKT and MDF corrected ion signals are presented as relative ion signal profiles for lean and stoichiometric premixed flames and are plotted in Figure 4-6 and Figure 4-7, respectively.

Figure 4-6 shows relative ion signal profiles, “unperturbed flame temperature” and “stretched flame temperature” as a function of height above the burner for the lean premixed flame. The highest temperature reached in the unperturbed lean premixed flame is 1440 K as obtained from thermocouple measurements corrected for radiative losses. The most abundant flame ions are \( \text{C}_2\text{H}_3\text{O}^+ \), \( \text{CH}_5\text{O}^+ \) and \( \text{H}_3\text{O}^+ \) in agreement with previous findings [78], [83]. Among these three ions, \( \text{H}_3\text{O}^+ \) is dominant and decays to 50% of its peak value at an axial distance of 3.1 mm from the location of its peak. The rise of \( \text{H}_3\text{O}^+ \) from 50% of its peak value to its peak is much faster and occurs in 0.85 mm. The other ions, namely, \( \text{C}_2\text{H}_3\text{O}^+ \) and \( \text{CH}_5\text{O}^+ \), are formed and consumed in the thermal layer of the flame. All ions obtained in this region are formed by proton transfer to neutrals/intermediates. The \( \text{C}_2\text{H}_3\text{O}^+ \) ion is formed by the protonation of ketene (\( \text{CH}_2\text{CO} \)), \( \text{CH}_5\text{O}^+ \) formed by the protonation of methanol, and \( \text{H}_3\text{O}^+ \) is formed by the protonation of water. There are other pathways to form ions but protonation of neutrals/intermediates is thought to be the dominant mechanism [78].
Figure 4-6 Relative ion signal profiles, measured unperturbed flame temperature and stretched temperature profile for a lean (\(\phi = 0.54\)) premixed flame. Relative ion signals have a maximum uncertainty of \(\pm 10\%\).

Figure 4-7 shows relative ion signal profiles, “unperturbed flame temperature” and “stretched flame temperature” as a function of height above the burner for the stoichiometric premixed flame. The highest temperature reached in the unperturbed flame is 1867 K. As expected, the peak temperature in the stoichiometric flame is higher than that in the lean premixed flame. For the stoichiometric flame, the most abundant ions are \(\text{C}_2\text{H}_3\text{O}^+\) and \(\text{H}_3\text{O}^+\). All other ions, such as \(\text{CH}_2\text{O}^+\), \(\text{C}_3\text{H}_3^+\) and \(\text{C}_2\text{HO}^+\) have almost an order of magnitude lower signals than \(\text{C}_2\text{H}_3\text{O}^+\) and \(\text{H}_3\text{O}^+\). \(\text{H}_3\text{O}^+\) is the most dominant ion and persists over a wide region. All ions other than \(\text{H}_3\text{O}^+\) are formed and consumed in a narrow region inside the preheat zone of the flame. Compared to the lean premixed flame, \(\text{H}_3\text{O}^+\) is produced and consumed rather quickly and its ion signal increases from 50% of its peak value to the peak value in 0.2 mm and reduces to 50% of its peak value within 0.7 mm from the location of its peak.
Figure 4-7 Relative ion signal profiles, measured unperturbed flame temperature and stretched temperature profile for a stoichiometric ($\phi = 1.01$) premixed flame. Relative ion signals have a maximum uncertainty of ±10%.

Additionally, the peak signal of $\text{H}_3\text{O}^+$ in stoichiometric flames is almost a factor of two higher than its peak signal in lean flames. The increase in peak $\text{H}_3\text{O}^+$ signal can be attributed to the fact that stoichiometric flames contain higher densities of CH radical, which play a critical role in the formation of $\text{H}_3\text{O}^+$ [97]. The faster decay of $\text{H}_3\text{O}^+$ in stoichiometric flames is due to the recombination being faster for higher $\text{H}_3\text{O}^+$ signal values/relative mole fractions [97]. The significantly faster production of $\text{H}_3\text{O}^+$ in stoichiometric flames is due to higher flame temperatures obtained in stoichiometric flames, which increase all the reaction rates. Additionally, $\text{C}_3\text{H}_3^+$ and $\text{C}_2\text{HO}^+$ are also observed in the stoichiometric flame, however, their signals are lower as compared to the signals of $\text{C}_2\text{H}_3\text{O}^+$ and $\text{H}_3\text{O}^+$. The formation of $\text{C}_3\text{H}_3^+$ and $\text{C}_2\text{HO}^+$ ions has been explained [82] as a two-step process involving $\text{C}_2\text{H}_3\text{O}^+$:

$$\text{C}_2\text{H}_3\text{O}^+ + \text{O} \rightarrow \text{C}_2\text{HO}^+ + \text{H}_2\text{O}$$

$$\text{C}_2\text{HO}^+ + \text{C}_2\text{H}_2 \rightarrow \text{C}_3\text{H}_3^+ + \text{CO}$$
For both lean and stoichiometric flames, the most abundant flame ions are C\(_2\)H\(_3\)O\(^+\) and H\(_3\)O\(^+\). Goodings et al. [78] also observed these ions in lean premixed Bunsen flames, however, their relative amounts were different compared to our observations. In the current study, the peak signal of H\(_3\)O\(^+\) was 1.6 times the peak signal of C\(_2\)H\(_3\)O\(^+\) in the lean flame, while in the lean conical flame of Goodings et al.[78], peak H\(_3\)O\(^+\) signal was about 7 times the peak C\(_2\)H\(_3\)O\(^+\) signal. Furthermore, in the current study, both H\(_3\)O\(^+\) and C\(_2\)H\(_3\)O\(^+\) form at around the same axial distance from the burner while in the lean flame of Goodings et al. [78], H\(_3\)O\(^+\) forms at an axial location where C\(_2\)H\(_3\)O\(^+\) signal is nearing its peak value. There are two other possible reasons for the differences between this work and Goodings et al. [78]. Firstly, this work is using a flat flame McKenna burner, whereas Goodings et al. [78] used a conical flame. The reaction zone in an atmospheric flat flame is of the order of 0.1 mm [66], while the height of the luminous reaction zone in the Bunsen flame used by Goodings et al. [78] was 6.5 mm for the lean flame, which makes the flames structure of the conical flame easier to resolve spatially. The significantly thicker reaction zone of the Bunsen flame explains the different axial locations at which H\(_3\)O\(^+\) and C\(_2\)H\(_3\)O\(^+\) start to form in the Bunsen flame as compared to the flat flame. Secondly, different equivalence ratios were used in both studies (\(\phi = 0.216\) in Goodings et al. and \(\phi = 0.54\) in the current study). Moreover, Goodings et al. [78] measured ions with m/z up to 55, thereby possibly neglecting the contribution from hydrates of ions whose m/z can be greater than 55. Figure 4-8 shows ion signals for C\(_2\)H\(_3\)O\(^+\) and its hydrates for the stoichiometric premixed flame of the current study. The hydrates of C\(_2\)H\(_3\)O\(^+\) contribute significantly to the total ion signal, particularly, in the region near the burner. The sum of signals from C\(_2\)H\(_3\)O\(^+\) and all its hydrates leads to a peak signal which is about 80% higher than the signal of C\(_2\)H\(_3\)O\(^+\) alone. Conversely, hydrates of
H$_3$O$^+$ with m/z > 55 do not contribute significantly to the total H$_3$O$^+$ signal in the stoichiometric flame (Figure 4-9). The sum of the ion signals from H$_3$O$^+$ and all its hydrates leads to a peak signal which is about 1.2% higher than the signal of H$_3$O$^+$ hydrates with m/z <= 55 only. In case of stoichiometric flames, the peak signal of H$_3$O$^+$ is 1.8 times the peak signal of C$_2$H$_3$O$^+$ if all the larger hydrates are included. However, if ions with m/z > 55 are excluded, peak H$_3$O$^+$ signal becomes 3 times peak C$_2$H$_3$O$^+$ signal.

**Figure 4-8** Contribution of different hydrates of C$_2$H$_3$O$^+$ in the stoichiometric (ϕ = 1.01) premixed flame. Ion signals have a maximum uncertainty of ± 10%.
Figure 4-9 Contribution of different hydrates of $\text{H}_3\text{O}^+$ in the stoichiometric ($\phi = 1.01$) premixed flame. Ion signals have a maximum uncertainty of ± 10%.

4.8.3 Modeling Results

Figure 4-10 shows a qualitative comparison of the experimentally measured relative ion mole fractions with the simulation results obtained using Prager’s mechanism with the “unperturbed temperature profile” (UT) (Figure 4-10 (a)) and “stretched temperature profile” (ST) (Figure 4-10 (b)) for the stoichiometric premixed flame. For all comparisons shown here, the experimentally measured ion profiles have been scaled to match the peak simulated mole fraction of $\text{H}_3\text{O}^+$. As mentioned earlier, when the UT profile (Figure 4-10 (a)) was used to constrain the simulations, the simulated ion profiles were shifted by 1.53 mm for stoichiometric premixed flames to match the position of the $\text{H}_3\text{O}^+$ peak. Simulations results were not shifted when ST profile was used (Figure 4-10 (b)). The measured profiles of both $\text{H}_3\text{O}^+$ and $\text{C}_2\text{H}_3\text{O}^+$ are in good agreement with the Prager’s mechanism with both temperature profiles, in terms of the decay rate while the relative peak value for $\text{C}_2\text{H}_3\text{O}^+$ is overestimated for the ST profile case. The axial distance between the peaks of $\text{H}_3\text{O}^+$ and $\text{C}_2\text{H}_3\text{O}^+$ is also captured well by the simulations with both temperature profiles, however, the $\text{H}_3\text{O}^+$
peak appears earlier for the simulation utilizing ST profile. For both cases, the measured relative mole fraction of \( \text{CH}_5\text{O}^+ \) is lower than the simulated value.

Figure 4-10 Comparison of experimental data with simulated ion mole fraction profiles obtained using Prager’s ion mechanism while utilizing (a) unperturbed temperature profile (UT) and (b) stretched temperature profile (ST) for the stoichiometric premixed flame \((\phi = 1.01)\). Relative ion signals have a maximum uncertainty of \( \pm 10\% \).

Figure 4-11 shows simulated ion mole fraction profiles for \( \text{H}_3\text{O}^+ \), \( \text{C}_2\text{H}_3\text{O}^+ \) and \( \text{CH}_5\text{O}^+ \) ions in the lean premixed flame for both temperature profiles. It is apparent in both cases that the mole fraction of \( \text{H}_3\text{O}^+ \) increases steadily in the burnt gas region. As cations and anions are coupled through the electric field, the mole fraction of \( \text{CO}_3^- \) (not presented here) is unrealistically high in the post flame zone also. In order to understand the reason for the observed behavior of \( \text{H}_3\text{O}^+ \) mole fraction, production and consumption pathways of \( \text{H}_3\text{O}^+ \) and \( \text{CO}_3^- \) ions were examined thoroughly.

Prager [64] described a similar issue and speculated that this erroneous behavior occurs when the temperature in the burnt gases is rather low, such as in a lean flame. This issue can be attributed to the high uncertainty in the thermodynamic data of \( \text{CO}_3^- \). As per Prager’s ion mechanism [64], the following three reactions are responsible for the production and consumption of \( \text{CO}_3^- \):
Our detailed analysis indicated that the backward rate of the $\text{CO}_3^-$ generation channel ($\text{O}^- + \text{CO}_2 + \text{O}_2 \leftrightarrow \text{CO}_3^- + \text{O}_2$) slows down significantly at low temperatures. Even though there are two consumption channels for $\text{CO}_3^-$, their rates are not high enough to consume $\text{CO}_3^-$. As a result, the production of $\text{CO}_3^-$ is larger than its consumption, and this causes its accumulation in the post flame region. The same problem was observed for $\text{CHO}_3^-$. To resolve these issues, we added two detachment reactions described by Goodings et al. [81]:

- $\text{CO}_3^- + \text{OH} \rightarrow \text{CO}_2 + \text{HO}_2 + E^- \quad (A, n, E_a: 3.55 \times 10^{15}, -0.25, 0)$
- $\text{CHO}_3^- + \text{OH} \rightarrow \text{CO}_3^- + \text{H}_2\text{O} \quad (A, n, E_a: 3.50 \times 10^{15}, -0.25, 0)$

The Arrhenius parameters of these two reactions were calculated using the ADO (Average Dipole Orientation) theory [115].
Figure 4-11 Simulated ion mole fraction profiles for the lean premixed flame (φ = 0.54) obtained using Prager’s mechanism with unperturbed temperature profile (UT) and stretched temperature profile (ST) [64].

Figure 4-12 shows a qualitative comparison of experimentally measured ion mole fraction profiles with simulation results obtained using Prager’s mechanism when the two electron detachment reactions above are included. Here, the simulated ion profiles have been shifted by 0.8 mm to match the position of the H$_3$O$^+$ peak when UT profile was used to constrain the simulations. Prager’s mechanism containing the above two detachment reactions addresses the issue of increasing H$_3$O$^+$ mole fractions in the burnt gas region for both temperature profiles (Figure 4-12 (a) and (b)). However, the simulated mole fraction of H$_3$O$^+$ is notably lower than that of C$_2$H$_3$O$^+$ for both temperature profiles, contrary to our observations for lean premixed flames as well as previous experimental data in literature [78]. Further investigation showed that this behavior is caused by an unanticipated formation channel of O$^-$ from the backward direction of the reaction:

\[ \text{O}^- + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{O}_2 + \text{E}^- \]

This reaction was written as irreversible in previous literature [116], while it was included as a reversible reaction in the present ion mechanism [63], [64]. Therefore, the reaction was made irreversible to reduce the inconsistency between the peak values of H$_3$O$^+$ and C$_2$H$_3$O$^+$. Herein, Prager’s ion mechanism which reflects the following changes will be referred to as the “modified mechanism”:

1. Addition of detachment reaction for CO$_3$ and CHO$_3$.
2. Making the reaction \( \text{O}^- + \text{H}_2\text{O} \Rightarrow \text{H}_2\text{O}_2 + \text{E}^- \) irreversible.

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Figure 4-12 Comparison of experimental data with simulated ion mole fraction profiles obtained by adding two electron detachment reactions to Prager’s mechanism while utilizing (a) unperturbed temperature profile (UT) and (b) stretched temperature profile (ST) for the lean premixed flame ($\phi = 0.54$). Relative ion signals have a maximum uncertainty of ± 10%.

Figure 4-13 shows a qualitative comparison of experimentally measured ion mole fraction profiles with simulation results obtained using the modified mechanism for the lean premixed flame. For both temperature profiles, the peak value of $\text{C}_2\text{H}_3\text{O}^+$ is now much closer to $\text{H}_3\text{O}^+$, however, it is still slightly larger than $\text{H}_3\text{O}^+$. The simulated $\text{H}_3\text{O}^+$ profiles agree relatively well with the measured relative $\text{H}_3\text{O}^+$ mole fraction for both temperature profiles, while the measured $\text{CH}_5\text{O}^+$ relative mole fractions are higher than the simulated values. The simulated value of $\text{C}_2\text{H}_3\text{O}^+$ is about a factor of 2 greater than the measured relative mole fraction of $\text{C}_2\text{H}_3\text{O}^+$. Further improvements in the ion chemistry mechanism are needed to reconcile these differences and are beyond the scope of this paper.
Figure 4-13 Comparison of experimental data with simulated ion mole fraction profiles obtained using the modified mechanism while utilizing (a) unperturbed temperature profile (UT) and (b) stretched temperature profile (ST) for the lean premixed flame ($\phi = 0.54$). Relative ion signals have a maximum uncertainty of ± 10%.

Figure 4-14 shows ion mole fractions of $\text{H}_3\text{O}^+$, $\text{C}_2\text{H}_3\text{O}^+$ and $\text{CH}_3\text{O}^+$ for the stoichiometric premixed flame simulated using the original Prager’s mechanism [63], [64] and the modified mechanism for both temperature profiles. As expected, the ion mole fraction profiles differ when different temperature profiles are used, however, the modifications implemented to Prager’s mechanism in this study have negligible effect on the mole fraction profiles of all the three ions in the stoichiometric premixed flame because of the higher temperatures encountered in these flames. As mentioned earlier, the problems experienced in the simulation of lean premixed flame using Prager’s mechanism were mainly due to the low reaction rates of consumption channels of $\text{CO}_3^-$ and $\text{CHO}_3^-$ and this problem does not occur at higher temperatures.

From the simulation results reported above, it can be observed that the changes recommended to improve Prager’s mechanism do not depend on the choice of the temperature profile used to constrain the simulations.
From the measurements and comparisons reported here, it can be concluded that the flame equivalence ratio dictates the shape of flame ion mole fraction profiles and the production and consumption rates are smaller in lean flames as compared to stoichiometric flames. The difference in ion production rate can be attributed to the stoichiometric flames being hotter compared to lean flames. Different ion consumption rates are caused by the difference in recombination rates which are strongly dependent on ion mole fractions. Since stoichiometric flames have higher ion mole fractions, recombination is faster in such flames as compared to lean flames. For all the flames measured in this study, H$_3$O$^+$ was the most dominant ion across various regions of the flame. Therefore, any non-intrusive study attempting to measure ion mole fraction profiles in flames should certainly have H$_3$O$^+$ among its list of target ions.

The identity of the dominant ions from the current work confirms the early observation of Goodings et al.[78] for similar mixtures. However, the quantity of
these ions relative to each other were different in our study. While in the present work the peak $\text{H}_3\text{O}^+$ mole fraction was 1.6 times the peak mole fraction of $\text{C}_2\text{H}_3\text{O}^+$, in the Bunsen flame of Goodings et al. [78], peak $\text{H}_3\text{O}^+$ mole fraction was about 7 times the peak $\text{C}_2\text{H}_3\text{O}^+$ mole fraction. Additionally, in the current study, both $\text{H}_3\text{O}^+$ and $\text{C}_2\text{H}_3\text{O}^+$ emerge at around the same axial distance from the burner while in the lean flame of Goodings et al. [78], $\text{H}_3\text{O}^+$ forms at an axial location which is near the peak of $\text{C}_2\text{H}_3\text{O}^+$ profile. These differences can be attributed to the use of different burners and different equivalence ratios for lean flames.
Chapter 5: Low-Pressure Flame Ion Measurements using QMS

This chapter expands on the theme of Chapter 4 by presenting experimentally measured ion mole fractions in low-pressure methane-oxygen flames. Firstly, we discuss the motivation to extend the flame-ion work to low-pressure flames followed by a brief description of the QMS experimental setup and the numerical framework used to carry out simulations. We then present the detailed cation measurements for methane-oxygen flames and compare against numerical simulations carried out using an established ion chemistry model [64]. Lastly, we present a sensitivity analysis to highlight critical ion-molecule reactions and suggest possible areas of improvement to the ion chemistry mechanism.

5.1 Introduction

In-depth understanding of ion chemistry in flames is vital to developing high-fidelity predictive models that accurately describe the effect of external electric fields on combustion plasma. However, current ion chemistry models are rudimentary because of lack of detailed experimental studies on the distribution of ionized species in flames. Consequently, significant efforts need to be directed towards providing a comprehensive dataset of flame ion measurements at different operating conditions to aid the development and validation of ion chemistry models.

There have been a handful of studies on the detailed distribution of ions in methane flames. Goodings et al. [78], [81] performed a detailed study of methane ion chemistry by measuring relative cation and anion signals in lean and rich premixed atmospheric Bunsen-type flames, although temperature profiles were not reported.
Recently, Alquaity et al. [117], [118] used a QMS to measure relative mole fractions of positive ions and flame temperature in atmospheric premixed methane-oxygen flat flames as presented in Chapter 4. However, the flame structure was not fully resolved due to the relatively small flame thickness (~ 1 mm) at 1 atm.

The predicted ion concentration profiles in previous modeling studies [64], [119] were significantly narrower compared to the existing experimental data for atmospheric flames. Modeling studies attributed the disagreement to the lack of temperature information and insufficient spatial resolution due to the thin flame front at 1 atm. Therefore, additional experiments at low-pressure, which circumvent the aforementioned limitations are critical to address these remaining issues.

The present effort seeks to extend the atmospheric flame ion work presented in Chapter 4 by carrying out relative ion mole fraction measurements in low-pressure methane-oxygen flames. Burner-stabilized laminar premixed low-pressure flat flames are selected to achieve high spatial resolution for cation measurements carried out using a QMS. Additionally, a high mass resolution TOF-MS is utilized to identify and distinguish ions with the same nominal mass.

5.2 Experimental Setup and Method

A stainless-steel water-cooled 6 cm diameter McKenna burner (Holthuis & Associates) was used to establish burner-stabilized premixed methane-oxygen-argon flat flames at 30 Torr (Figure 5-1). The flow rates and equivalence ratios used in this study are reported in Table 5-1. The flow rates were controlled via mass flow controllers (MKS, 1179B), which have an uncertainty of ±1% of the full range (5 SLPM). The McKenna burner was mounted on a motorized translation stage (SMC, LEY-25RC-350G-S5) with a positioning repeatability of ± 0.02 mm. Measurements
carried out on different days showed that the spatial location of ion profiles was repeatable within ± 0.5 mm. The modified Hiden HPR-60 QMS system described in detail in Section 4.5 was used to measure ion profiles as a function of height from the burner surface. A 24 mm long nickel cone of 57° angle and 0.4 mm aperture was used for sampling the gases along the centerline of the flat flame. Three stages of differential pumping were used, where the first and second stage skimmer cones had orifice sizes of 0.3 mm and 2 mm, respectively. In order to detect naturally occurring ions in flames, electrical potentials of -33 V and -51 V were applied to the first stage and second stage skimmer cones, respectively. The flame temperature was measured in the absence of the sampling cone using an SiO₂ coated Type-B (Omega) thermocouple with a bead of 0.38 mm diameter. Thermocouple readings were corrected for radiation effects [85] with corrections ranging from 83 to 195 K for flame temperatures between 1521 and 2091 K. The burner surface temperature was measured using a laser thermometer gun (Traceable, Model # 4483) and found to be between 328.15 and 331.15 K depending on the stoichiometry of the flame.

Table 5-1 Flame conditions. The reactant mixture entered the burner at 23 °C for all flames. The cooling water temperature was 25 °C. Chamber pressure was 30 Torr. Flow rates are given in SLPM.

<table>
<thead>
<tr>
<th>Flame</th>
<th>Equivalence ratio</th>
<th>CH₄ flow rate</th>
<th>O₂ flow rate</th>
<th>Ar flow rate</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>0.75</td>
<td>3</td>
<td>1.25</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1.25</td>
<td>2.5</td>
<td>1.25</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>1.5</td>
<td>1.61</td>
<td>2.14</td>
<td>1.25</td>
<td>5</td>
</tr>
</tbody>
</table>
The procedure used for obtaining relative ion profiles has been detailed previously (Section 4.8.2), so only a brief description is given here. Firstly, mass scans were performed at various heights above the burner to identify dominant ions. Next, energy scans were performed for each ion to obtain its total signal. The area under the energy distribution curve is a good representation of the ion density and was found to be repeatable within 10%. Therefore, all the relative ion mole fractions reported in this work have a maximum uncertainty of 10%. The integrated ion signal for each ion was then scaled with the mass discrimination factor (MDF) of the QMS system. The MDF was measured by flowing various gas mixtures of known mole fractions through the QMS while ensuring that the pressure in the first pressure reduction stage remained the same as in flame measurements. The MDF corrected signal was scaled with the instrument sampling function (FKT) [114] to yield relative ion mole fractions across the flame. Hydrates of flame ions formed during the sampling process were lumped together with the parent ion, as is the norm in experimental ion studies [83].
Additionally, a high mass resolution ($m/\Delta m \approx 4000$ at $m/z = 28$ & $m/z$ range: 15-2000) time-of-flight mass spectrometer (TOF-MS, Kaesdorf) at the University of Duisburg-Essen [120] was used to facilitate the identification of ions with the same nominal mass-to-charge ratios, which cannot be separated using the QMS. A schematic of the TOF-MS is shown in Figure 5-2. A Hastelloy cone of $\sim 54^\circ$ angle and 0.55 mm aperture was used for sampling the gases from the centerline of the flat flame.

![TOF-MS schematic diagram](image)

**Figure 5-2 Schematic diagram of the TOF-MS at University of Duisburg-Essen**

1. Translation stage
2. Low Pressure Chamber
3. Ion Funnel
4. Octapole Ion Guide
5. Quadrupole Ion Guide
6. Reflectron

5.3 **Numerical Methods and Model**

Low-pressure flames were modeled as one-dimensional burner-stabilized premixed flat flames using the PREMIX [88] code. Two modifications were implemented in the code to account for the transport of charged species as detailed in Section 4.6 and described briefly here. Firstly, the electric potential was added as an additional variable and the Poisson equation for the potential was solved. Secondly, the drift diffusion flux was included in the mass flux for charged species [91]. Ion
transport was modeled according to a mixture-averaged approach with suitable potentials [91] and the electron mobility was set to 0.4 m²/V·s [92]. In the present work also, a modified AramcoMech 1.3 C₀ – C₂ mechanism [95] was used for neutral species. The modification was carried out to improve the prediction of CH radical, which is responsible for the generation of electrons and ions via chemi-ionization [97].

The ion mechanism assembled by Prager et al. [64] was added to the base ARAMCO 1.3 mechanism to predict cation profiles in this work also. The ion chemistry mechanism contains 4 cations (H₃O⁺, C₂H₃O⁺, CH₅O⁺ and CHO⁺), 6 anions (O₂⁻, O⁻, OH⁻, CHO₂⁻, CHO₃⁻ and CO₃⁻), electron e⁻, and 67 elementary reactions. Rate parameters for most reactions in the ion chemistry mechanism [64] were updated according to the most recent data available in the UMIST 2012 database [98]. Although alternative rate parameters for chemi-ionization and recombination reactions are available from the UMIST database, we retained the parameters given in [64] as they were determined experimentally and found to be most appropriate [91], [97].

5.4 Results and Discussion

5.4.1 Neutral Species

Validation of the experimental setup was first carried out by measuring neutral species in the same flames (Figure 5-3) used for ion measurements. Flame neutrals were ionized by an electron gun operating at ~ 20 eV. Figure 5-3 compares the measured mole fraction profiles of major neutral species (CH₄, O₂, CO, CO₂ and Ar) with model predictions as a function of the height above the burner (HAB) for the three flames studied here. As commonly done in probe-based flame measurements
the experimental data have been shifted towards the burner by 1, 2 and 4 mm for lean, stoichiometric and rich premixed flames, respectively, to match with the predicted species profiles. A relatively large cone angle (57°) was used here to get adequate cation signals. The larger than usual cone angle resulted in perturbation of the flame front, and, consequently, relatively large axial shifting of experimental data. The rates of species formation and decay were markedly slower in the rich flame as compared to other flames. Overall, simulated mole fractions reproduced the experimental data adequately across all flames. Disagreement in methane and oxygen mole fractions near the reaction zone of rich flame may be attributed to probe effects, as discussed previously. Reasonable agreement between the measured and simulated neutral species validates the experimental setup and methodology.

![Figure 5-3 Measured neutral species (symbols) and simulations (lines). Measurements are shifted towards the burner surface by 1, 2 and 4 mm for lean, stoichiometric and rich flames, respectively.]

**5.4.2 Cation Measurements**

Figures 5-4, 5-5, and 5-6 report cation profiles as a function of the height above the burner for the three flames together with model predictions. Although, the simulation results presented here were obtained by using the ion mechanism described in Section 5.3, utilizing modified Prager mechanism (Section 4.8.3) also yields the same results. The experimental ion profiles have been scaled to match the peak mole
fraction of H$_3$O$^+$ from simulations. Furthermore, the experimental data have been shifted towards the burner by 1 to 4 mm, as mentioned previously for neutral species.

In the lean flame (Figure 5-4), the most abundant flame ions, in the order of high to low ion signals, are H$_3$O$^+$ (m/z = 19 + 37 + 55 + 73), ions at m/z of 47 (+ 65), CH$_5$O$^+$ (m/z = 33 + 51 + 69), and C$_2$H$_3$O$^+$ (m/z = 43 + 61 + 79). The m/z values in parentheses indicate the mass of the parent ion and its hydrates. Although other pathways to form ions have been proposed, protonation of neutrals/intermediates is considered to be the dominant mechanism [78]. Hydronium (H$_3$O$^+$) is formed by the protonation of water, CH$_5$O$^+$ is formed by the protonation of methanol, and C$_2$H$_3$O$^+$ is formed by the protonation of ketene (CH$_2$CO).

High-resolution measurements via TOF-MS in a similar lean ($\phi = 0.8$) methane/oxygen flame carried out at the University of Duisburg-Essen indicate that the large signal at m/z = 47 (+ 65) reflects contributions from CH$_3$O$_2^+$ and C$_2$H$_5$O$^+$. Protonation of formic acid can form CH$_3$O$_2^+$ [83], while C$_2$H$_5$O$^+$ may be formed by the protonation of structural isomers, ethanol and dimethyl ether [83]. Numerical simulations of neutral species in the lean flame showed negligible amounts of ethanol compared to formic acid and dimethyl ether, which suggests that the signal at m/z = 47 (+ 65) is primarily due to the protonation of formic acid and dimethyl ether.

Positive ions found in smaller amounts include C$_3$H$_3^+$ (m/z = 39 + 57 + 75) and ions with m/z = 45 (+ 63) reflecting contributions from C$_2$H$_5$O$^+$ and CHO$_2^+$, m/z = 31 (+ 49) from CH$_3$O$^+$ and C$_2$H$_7^+$, and m/z = 59 (+ 77) due to C$_2$HO$^+\cdot$H$_2$O, C$_3$H$_5^+\cdot$H$_2$O and C$_3$H$_7$O$^+$. We remark that, in the lean flame, the maximum signal for C$_3$H$_3^+$ is at m/z = 75, which could be identified as a hydrate of C$_3$H$_3^+$ or a hydrate of C$_3$H$_5$O$^+$ (protonated methyl ketene). Cataloging of flame cations using high mass resolution
TOF-MS allowed for the correct identification of targets having very similar m/z values. However, this device cannot differentiate between isomers and ions having equal number of C/H/O, for example, C$_3$H$_5$O$^+$·H$_2$O and C$_3$H$_5^+$·(H$_2$O)$_2$.

Figure 5-4 Ion mole fractions from experiments (symbols with dashed lines) and simulations (solid lines in corresponding color) for the lean premixed flame (\( \phi = 0.5 \)). Measured flame temperature (red symbols with red line) also shown. Experimental relative ion profiles have been scaled to match the peak mole fraction of simulated H$_3$O$^+$. Simulation data include results for C$_2$H$_3$O$^+$, CH$_3$O$^+$ and H$_3$O$^+$. Relative ion signals have a maximum uncertainty of \( \pm 10\% \).

Hydronium (H$_3$O$^+$) is the most dominant ion and reaches its peak downstream of the peak of other ions. Its rate of increase is quite rapid as it rises from 75% its peak value to the peak over an axial distance of about 0.95 mm. The rapid rise can be attributed to the fact that chemi-ionization occurs only in the thin reaction zone and protonation of H$_2$O accelerates when H$_2$O mole fraction rises sharply. Hydronium decays rather slowly, going from peak to 75% of the peak in about 7.5 mm, because of the relatively slow recombination reaction rates.

For the stoichiometric flame (Figure 5-5), the most abundant ions, in the order of high to low signals, are H$_3$O$^+$, C$_2$H$_3$O$^+$, CH$_3$O$_2$$^+$ + C$_2$H$_7$O$^+$ and CH$_5$O$^+$. As observed in the lean flame, H$_3$O$^+$ is the most dominant ion and persists over a broad region of
the flame. Compared to the lean flame, additional ions at m/z = 53 (+ 71) with contribution from C$_3$HO$^+$ and C$_4$H$_5^+$ have been observed. These ions were not reported in previous studies [78], [82], [83]. Two distinct peaks are observed for m/z = 39 + 57 + 75, where the first peak is dominated by m/z = 75 and the second peak by m/z = 39. These two peaks most likely indicate that the signal at m/z = 75 is due to the C$_3$H$_5$O$^+$ hydrate with some contribution from C$_3$H$_3^+$, while the second peak corresponds solely to the C$_3$H$_3^+$ ion.

The hydronium signal increases from 75\% of its peak value to the peak in about 0.8 mm and decays to 75\% of its peak over an axial distance of about 5.7 mm. The decay in the stoichiometric flame is faster than in the lean flame. Additionally, the experimental peak H$_3$O$^+$ signal is almost a factor of two higher than in the lean flame. Increased H$_3$O$^+$ mole fraction is ascribed to higher CH densities in the stoichiometric flame, which play a key role in the formation of H$_3$O$^+$ [97]. Faster H$_3$O$^+$ decay in stoichiometric flames is due to the recombination being faster for larger H$_3$O$^+$ concentrations [97].
Figure 5-5 Ion mole fractions from experiments (symbols with dashed lines) and simulations (solid lines in corresponding color) for the stoichiometric premixed flame ($\phi = 1$). Experimental relative ion profiles have been scaled to match the peak mole fraction of simulated H$_3$O$^+$. Simulation data include results for C$_2$H$_3$O$^+$, CH$_5$O$^+$ and H$_3$O$^+$. Relative ion signals have a maximum uncertainty of ± 10%.

Figure 5-6 shows measured ion profiles, flame temperature and comparison with simulations for the rich flame (Flame 3 in Table 5-1). Compared to the stoichiometric flame, no additional ions were observed. However, the relative abundance of the ions was different. Major flame ions, in the order of high to low signals, are H$_3$O$^+$, C$_3$H$_3^+$, C$_2$H$_5$O$^+$ and CH$_3$O$_2^+$ + C$_2$H$_7$O$^+$. The relative cumulative signal from C$_3$HO$^+$ and C$_4$H$_5^+$ is higher than the corresponding signal for the stoichiometric flame. Once more, C$_3$H$_3^+$ (m/z = 39 + 57 + 75) has two distinct peaks with first peak dominated by m/z = 75 and second peak by m/z = 39, leading to the same conclusions as in stoichiometric flame.

It is interesting to note that the formation and consumption rates of all major ions in the rich flame are slower than their corresponding rates in the lean and stoichiometric flames. This trend is similar to the slow decay and formation rates of neutrals in the rich flame. Hydronium is produced and consumed rather slowly in the rich flame. Its signal increases from 75% of its peak value to the peak in about 4.5
mm and decays to 75% of its peak over a very large axial distance of ~ 14 mm. Experimental measurements show that despite decaying slowly, hydronium signal in rich flame is about 2 times smaller than in the stoichiometric flame. Presence of considerable amounts of C$_3$H$_3^+$ near the H$_3$O$^+$ peak hints at the possible existence of an indirect reaction pathway between the two ions. Eraslan et al. [121] had proposed the formation of C$_3$H$_3^+$ by an ion-molecule reaction between C$_2$H$_2$ and CH$_3^+$. An earlier numerical work [119] had proposed the formation of CH$_3^+$ through proton transfer from either H$_3$O$^+$ or CHO$^+$ to CH$_2$. Moreover, simulated profiles of neutral species in rich flame (Figure 5-7) show CH$_2$ and C$_2$H$_2$ reaching a maximum where C$_3$H$_3^+$ peaks. The most probably pathway linking H$_3$O$^+$ to C$_3$H$_3^+$ is: H$_3$O$^+$ + CH$_2$ $\leftrightarrow$ CH$_3^+$ + H$_2$O followed by CH$_3^+$ + C$_2$H$_2$ $\leftrightarrow$ C$_3$H$_3^+$ + H$_2$. Our analysis suggests that ion chemistry mechanisms should include both CH$_3^+$ and C$_3$H$_3^+$ in order to simulate rich flames adequately.

![Figure 5-6](image.png)

Figure 5-6 Ion mole fractions from experiments (symbols with dashed lines) and simulations (solid lines in corresponding color) for the rich premixed flame ($\phi = 1.5$). Experimental relative ion profiles have been scaled to match the peak mole fraction of simulated H$_3$O$^+$. Simulation data include results for C$_3$H$_2$O$^+$, CH$_3$O$^+$ and H$_2$O$^+$. Relative ion signals have a maximum uncertainty of ± 10%.
5.4.3 Modeling Results

Figures 5-4, 5-5 and 5-6 report the data from simulations and a comparison with measured cation profiles. It should be noted that the ion chemistry model does not include CH$_3$O$_2^+$ and C$_2$H$_7$O$^+$ which are abundant across all flames. Additionally, the model does not contain pathways for C$_3$H$_3^+$ which is quite large in the rich flame. Since only relative ion densities are available from the experimental data, the mole fractions of all ions are scaled with respect to the predicted peak mole fraction of H$_3$O$^+$.

The peak of C$_2$H$_3$O$^+$ relative to H$_3$O$^+$ is under-estimated in lean and stoichiometric flames and over-estimated in the rich flame. However, the location of the C$_2$H$_3$O$^+$ peak relative to that of H$_3$O$^+$ is captured correctly by the model. The predicted CH$_3$O$^+$ peak value relative to H$_3$O$^+$ is within 12% of the experimental data for the lean flame, while the CH$_3$O$^+$ peak value is over-estimated in the stoichiometric flame and under-estimated in the rich flame. The predicted CH$_3$O$^+$ peaks too early relative to the peak of C$_2$H$_3$O$^+$ for all three flames. Furthermore, for all flames, the sum of all simulated...
ions excluding \( \text{H}_3\text{O}^+ \) is under-estimated which suggests that that the \( \text{H}_3\text{O}^+ \) mole fraction may be over-estimated in the ion mechanism. This is seen clearly in Figure 5-8 for the stoichiometric flame. Based on the disagreements observed, it may be argued that there are missing cation species and reaction pathways that must be added to the ion chemistry model to reconcile the differences between experimental data and simulations.

![Figure 5-8 Ion mole fractions from experiments (symbols) and simulations (lines) for the stoichiometric flame (\( \phi = 1 \)).](image)

Relative ion signals have a maximum uncertainty of \( \pm 10\% \).

For all the flames studied here, the simulated decay rate of \( \text{H}_3\text{O}^+ \) is more rapid than measured experimentally. This observation is consistent with results from previous modeling studies [64], [119], wherein simulated decay rates were faster than those in experiments [78]. The discrepancy in decay rate was attributed to the limitations in spatial resolution and lack of temperature information in the experimental data. In the present work, the flame temperature profile has been measured carefully and used to constrain the simulations. Additionally, a sensitivity analysis was performed to study the effect of uncertainty (maximum 65 K) in
thermocouple-based temperature measurements on the H$_3$O$^+$ profile, and it was found to be negligible. Furthermore, reasonable agreement in the prediction of neutral species (Figure 5-3) implies that the current experimental data do not suffer from spatial resolution issues.

Figure 5-9 shows the sensitivity of H$_3$O$^+$ to the rate constants of key reactions. Positive sensitivity coefficient indicates reactions leading to the formation of H$_3$O$^+$, while reactions with a negative coefficient are responsible for its consumption. Sensitivity analysis was carried out at the peak of H$_3$O$^+$ and at 75% and 50% of the peak during the decay. It is interesting to note that the sensitivity coefficients of all reactions are almost independent of flame stoichiometry. At or near the peak, H$_3$O$^+$ is most sensitive to the chemi-ionization reaction CH + O $\leftrightarrow$ CHO$^+$ + E$^-$ across all three flames. However, during the decay (at 50% of the peak), H$_3$O$^+$ is sensitive to its recombination with electrons. The hydronium recombination rate depends significantly on its peak mole fraction and an over-estimation of the peak value can lead to significantly faster decay [97]. We conclude that, in view of the important discrepancies in the predicted H$_3$O$^+$ decay rate, the rate constant of chemi-ionization reaction merits further scrutiny.
Figure 5-9 Sensitivity analysis of H$_3$O$^+$ at the peak and during the decay in lean, stoichiometric and rich flames.
Chapter 6: TOF-MS Measurements in Shock Tube

This chapter continues on the theme of the previous two chapters by utilizing a similar diagnostic (MS) to measure reaction rate coefficients in a harsh environment (shock tube). The capability of the compact time-of-flight mass spectrometer (TOF-MS) to measure species concentration time-histories in transient systems is demonstrated in this work by measuring the unimolecular decomposition rate of 1,3,5-trioxane over a wide range of experimental conditions. Firstly, the motivation for investigating the unimolecular decomposition of 1,3,5-trioxane is discussed followed by a detailed description of the TOF-MS experimental setup. Then, we give a detailed account of the experimental methodology and calibration procedure. Lastly, the decomposition rates extracted by the best fit to the experimentally measured species concentration time-histories are presented and compared with the theoretical rates.

6.1 Introduction

Formaldehyde (CH\textsubscript{2}O) is an important intermediate in the combustion of hydrocarbon fuels. It is formed during the oxidation of alkanes, natural gas, alcohols, aldehydes, ethers and others \[122\]–\[124\]. Its importance in combustion led to a number of high temperature kinetic studies for its pyrolytic dissociation \[125\]–\[127\] and bimolecular reactions \[122\], \[128\]–\[131\]. A substantial number of earlier studies\[126\], \[128\], \[130\], \[132\]–\[137\] consisted of utilizing 1,3,5-trioxane (C\textsubscript{3}H\textsubscript{6}O\textsubscript{3}) as a clean thermolytic source of formaldehyde to avoid the problem of formaldehyde polymerization. These studies assumed the reaction
\[ \text{C}_3\text{H}_6\text{O}_3 \rightarrow 3 \text{CH}_2\text{O} \]  

(Reaction 1)

to be an instantaneous process at high temperatures (above 1300 K \( \tau < 0.5 \mu\text{s} \)) [126] to yield three formaldehyde molecules via a simple unimolecular and probably a concerted mechanism [133], [138]. This mechanism for 1,3,5-trioxane decomposition was confirmed in a laser schlieren study by Irdam and Kiefer [135] and later by Aldridge et al. [133] and Hochgreb and Dryer [134].

Hogg et al. [132] and Burnett and Bell [136] measured the rate coefficients for the thermal dissociation of trioxane in a static reactor at \( T = 545 \) to 620 K and \( p \leq 100 \) Torr. The values of the rate coefficients reported by Hogg et al. [132] are about 40% higher than those reported by Burnett and Bell [136] at a specific temperature. Hogg et al. [132] consistently observed that the final pressure of their reactor was three times the initial pressure and concluded that the pressure rise was caused due to the dissociation of trioxane to form three formaldehyde molecules. This conclusion was later supported by the shock tube study of Irdam and Kiefer [135] who observed the dissociation of trioxane over 950 to 1270 K and 138 to 362 Torr using laser schlieren technique. Their computed density gradient profiles, in accordance with reaction (1), were found to agree very well with the experimentally measured profiles suggesting that formaldehyde is the sole product of 1,3,5-trioxane dissociation. They also reported RRKM rates and falloff based on the selected molecular parameters that were most consistent with the experimental data [132], [135], [136]. Almost a year later, Aldridge et al. [133] studied reaction (1) in a static reactor over the temperature range of 523 – 603 K and pressures of 25 - 800 Torr. In addition to the experimental work, they performed RRKM calculations using the data from BAC-MP4 quantum chemical method. Their theoretical approach adequately predicted their experimental
values of the rate coefficients. However, their experimental and theoretical values were found to be significantly lower than earlier studies [132], [136]. In another similar study, Hochgreb and Dryer [134] measured the rate coefficients for 1,3,5-trioxane dissociation over the temperature range of 700 – 800 K in an atmospheric pressure flow reactor. Their reported values closely matched with the high pressure limiting rate coefficients predicted by RRKM calculations of Irdam and Kiefer [135] and extrapolated values of Hogg et al. [132] and Burnett and Bell [136]. However, the measured rate coefficients of Hochgreb and Dryer [134] were found to be at least a factor of two higher than the extrapolated values of Aldridge et al [133]. Based on the analysis of the reaction products, both studies [133], [134] confirmed formaldehyde to be the exclusive dissociation product of 1,3,5-trioxane. In a recent study, Wang et al. [137] developed a laser absorption technique to quantitatively measure formaldehyde (CH$_2$O) and acetaldehyde (CH$_3$CHO) concentrations. The CH$_2$O laser diagnostic was then utilized to investigate unimolecular dissociation of 1,3,5-trioxane behind reflected shock waves over 869 to 1037 K and $p \approx 1596$ Torr. Their measured rate coefficients at high temperatures were found to overlap nicely with Irdam and Kiefer [135] data at 350 Torr which suggest that their data at these pressures are already at or close to the high pressure limit. However, their low temperature data near 900 K were lower by a factor of two than the extrapolated value of Hochgreb and Dryer [134]. Due to the existing discrepancies in literature, an additional study rendering a detailed kinetic analysis is warranted to fully ascertain the rate coefficients of the thermal dissociation of 1,3,5-trioxane.

In this work, shock tube experiments were performed to investigate the thermal unimolecular dissociation of 1,3,5-trioxane over a wide range of experimental
conditions using a high-repetition rate time-of-flight mass spectrometer. This work provides new experimental data to ascertain the rate coefficients of unimolecular decomposition of 1,3,5-trioxane.

6.2 Experimental Details

6.2.1 Shock Tube (ST) Facility

Thermal dissociation of 1,3,5-trioxane was investigated behind reflected shock waves in a stainless steel shock tube at temperatures ranging from 775 to 1082 K and pressures near 900 Torr. The shock tube facility has been described previously (Section 3.2.2), therefore, only a brief description is provided here. Both the driver and driven sections of the shock tube are 9 m long with an inner diameter of 14.2 cm. The length of the driver section can be varied depending on the required test time. For the experiments reported herein, a shorter (~ 3 m) driver section was used that enabled us to achieve 1.5 ms of uniform pressure (and temperature) behind reflected shock waves. (See Figure 6-1.) The incident shock velocity was measured using five PCB 113B26 piezoelectric pressure transducers (PZTs) that were located axially along the last 1.3 m of the driven section. The incident shock speed at the end-wall was determined by linear extrapolation of the velocity profile. One-dimensional shock-jump equations were used to calculate the conditions (temperature and pressure) behind the reflected shock wave. The uncertainty in the measured velocity was found to be ± 0.2% which translates into < 1% uncertainty in the calculated reflected shock temperature and pressure.
Figure 6-1 Representative pressure trace showing the incident and reflected shock time windows. The experimental conditions are $p_s = 1065$ Torr, $T_s = 910$ K, mixture composition of 2.69% Ar/1.2% C$_3$H$_6$O$_3$/96.11% Ne.

Mixtures containing varying concentrations of 1,3,5-trioxane, argon and neon were prepared manometrically in a 24-liter stainless steel mixing tank equipped with a magnetic stirrer. Before preparing the mixtures, the stainless steel tank was evacuated to a pressure below $10^{-5}$ Torr. In the current set of experiments, argon was used as an internal standard and neon was used as a bath gas due to the comparatively high electron-impact ionization cross-sections of argon. Homogenous mixtures were prepared by mixing gases in the magnetically-stirred mixing tank. The purity of chemicals and gases used were: 1,3,5 trioxane (Sigma Aldrich, ≥99%, degassed several times before use), argon (99.9999%, AHG) and neon (99.999%, AHG).
6.2.2 Time-of-Flight Mass Spectrometer (TOF-MS)

The coupling of shock tube (ST) with time-of-flight mass spectrometer (TOF-MS) for high temperature kinetic studies is a challenging task. These challenges and successful operation of ST/TOF-MS have been amicably discussed in early studies by Moulton [139], [140], Bradley and Kistiakowsky [141], Krizancic et al. [142], Voldner and Trass [143] and recently by Tranter et al. [144] and Dürrstein et al. [145]. Our coupling and configuration for the ST/TOF-MS is similar to the existing facilities in Karlsurhe [146], [147] and Duisberg-Essen [145], [148]. For kinetics studies, the samples behind the reflected shock waves are drawn continually through a conical nozzle (inner opening angle of 120°) of precise pin hole size of 75 μm (±10%, Frey GmbH, Germany) centered in the end-wall of the driven section of the shock tube. The choice for the size of the nozzle is dictated by the need of keeping the ion source pressure of TOF-MS as low as possible (≤ 10⁻⁵ Torr) to avoid any damage to the ion source while operating the shock tube at pressures between 500 and 2250 Torr. The tip of the conical nozzle protrudes about 1 mm into the shock tube that ensures molecular beam sampling from the core shock-heated zone. This avoids the contamination of the sample by the cold thermal boundary layer that grows to the shock heated zone following the reflection of the shock wave. A detailed discussion on the growth of the thermal boundary layer and its effect pertinent to the kinetic studies using ST/TOF-MS can be found elsewhere [139], [143], [144]. For our operating conditions, the molecular beam exiting the nozzle undergoes rapid quenching in less than 1 μs and only a small portion of the beam reaches the ion source of the TOF-MS (Stefan Kaesdorf Inc., Munich). In these studies, direct sampling from the nozzle is employed without using a skimmer. We did not employ nozzle-skimmer sampling system for three reasons: (i) the nozzle-skimmer sampling
system skims off most of the molecular beam that consequently diminishes the signal intensity significantly; (ii) this arrangement requires differentially pumped molecular beam sampling interface. In our current setup, both the ion source and flight tube of TOF-MS can be pumped down to \(10^{-7}\) Torr, and a pressure below \(10^{-3}\) Torr cannot be achieved in the skimmer section of the interface due to its compactness. The inability to create a high vacuum in the skimmer section will result in inadequate quenching of the molecular beam. A rapid quenching of the representative sample from the shock heated zone via a supersonic jet expansion is very crucial in these kinds of experiments. (iii) Precise alignment of the skimmer with respect to the nozzle is critical. This alignment is challenging to achieve. A little misalignment by few degrees may lead to the ionization of the molecular beam that has originated from the vicinity of the shock tube wall and hence may have been affected by the cold thermal boundary layer.

For a successful operation of ST/TOF-MS system, the separation distance between the sampling orifice and ionization location plays a crucial role. In the original design, this separation was 42.75 mm. To increase the sensitivity, we modified our coupling to reduce this separation to 35.75 mm. As the molecular beam reaches the ionization zone of the ion source, it is bombarded with electrons to produce ions. Our TOF-MS employs a two-stage ion extraction for space-focusing that compensates the ions starting from different locations of the ionization zone. The experiments reported here used optimum ionization energy of 34 eV that greatly suppressed the ionization of the bath gas (neon). It entails an important aspect of the experiment to avoid saturation of the micro-channel plate (MCP, Photonics Inc., USA, type E25-10-D-SET) detector. The TOF-MS can be operated up to a maximum
repetition rate of 150 kHz (6.7 μs), however, in this study, a repetition rate of 100 kHz (10 μs) was employed. The reduced repetition rate helps to avoid saturation of the MCP detector and any intermingling of the ions from successive ionization events. The MCP signal is amplified using a pre-amplifier that enables us to use the lowest possible voltage supply to the MCP, thus avoiding saturation of the detector. This is crucial when TOF-MS is operated at the high repetition rates ≥ 100 kHz. To avoid any possible arcing of the ion source due to sudden rise in pressure, the TOF-MS is automatically shut down after 1 second using an interlock system. The analog signal from MCP detector was recorded using an 8-bit digitizer (Agilent U1071A) at a sampling rate of 1 GHz for a total recording time of 2.5 ms. For each shock wave experiment, the recorded data contains about 500 μs of pre-shock data and the remaining 2 ms of post-shock data. The recorded data, representing mass spectra for a total of 2500 ionization events, was de-convoluted into sub-packets (containing mass spectra for each ionization event) using an in-house Matlab code. The time-histories for the species of interest were obtained by integrating the peaks from successive ionization events.

6.3 Results and Discussion

Figure 6-2 shows a sample profile for the raw data obtained from our ST/TOF-MS experiment. Here, the downward spikes are the signal intensities of various species and the upward spikes are the timing signal. A single 10 μs time segment taken from the post-shock condition (1.4 ms after the arrival of reflected shock; \( T_5 = 1082 \) K and \( p_5 = 1.2 \) bar) is displayed in Figure 6-3 where all peaks are identified. In Figure 6-3, the rising part of the timing signal is the start of ionization, whereas the falling part indicates the injection of ion packets for that particular ionization event.
The time window between the falling and the rising parts of the timing signal corresponds to the duration of ionization. In these experiments, the ionization duration was set to 1 µs. In our measurements, the reaction progress was monitored simultaneously for the reactant, 1,3,5-trioxane (C₃H₆O₃), and the product, formaldehyde (H₂CO). As can be seen, the reactant observed at m/z 31 for H₃CO⁺ (a strong fragment of trioxane as the parent ion is not observed) has reacted away completely at this relatively late reaction time (1.4 ms). Clearly, an ionization interval of 10 µs is long enough to accommodate all ions that appear in a given ionization event without intermingling of ions from successive events. The m/z ratio for each peak appearing in the mass spectrum is determined using the relationship, \( m/z = a(t_f)^2 + b(t_f) + c \); where \( t_f \) is the time-of-flight of the ions, \( a, b \) and \( c \) are constants determined via calibration. Apart from Ar (m/z 40) and Ne (m/z 20), the remaining peaks (m/z 30, 29 and 28) correspond to formaldehyde (m/z 30) and its fragments CHO⁺ (m/z 29) and CO⁺ (m/z 28). This clearly indicates that formaldehyde is the sole product of 1,3,5-trioxane dissociation. The experiments carried out in the current work thus provide further evidence that formaldehyde is the only product of 1,3,5-trioxane dissociation.
Figure 6-2 Raw ST/TOF-MS data obtained at a repetition rate of 100 kHz. The experimental conditions are $p_5 = 825$ Torr, $T_5 = 990$ K, mixture composition of 5.06% Ar/1.25% C$_3$H$_6$O$_3$/93.69% Ne.

Figure 6-3 A 10 $\mu$s time segment, after 1.4 ms of reaction time, showing the reaction products of 1,3,5-trioxane dissociation. The mass spectrum shows the fragments of formaldehyde. Ions are identified by their $m/z$ values in the parentheses. Experimental conditions: $p_5 = 900$ Torr, $T_5 = 1082$ K, mixture composition of 3.49% Ar/1.58% C$_3$H$_6$O$_3$/94.93% Ne. The inset figure shows an excellent separation of masses differing by $m/z$ 1.

The peaks of interest from each ionization event were integrated using an in-house Matlab code to generate peak area versus time profiles. The area of each peak is scaled by the peak area of the internal standard. Here, we used argon (Ar) as internal standard to correct any variations in the sensitivity of TOF-MS. Absolute concentration-time profiles for trioxane and formaldehyde were obtained from calibration experiments using the relationship $I_x/I_{Ar} = m P_x P_{Ar}$, where $m$ is the calibration factor; $I$ and $p$ are the ion intensity and partial pressure of the species ($x$), respectively. The calibration curves are shown in Figure 6-4. The calibration experiments were performed near 900 Torr and about 600 K for trioxane and about 1200 K for formadehyde. Near 600 K, trioxane does not dissociate within the time scale of our experiments. Similarly at about 1200 K of our ST/TOF-MS experiments, a constant
concentration-time profile for formaldehyde was achieved via instantaneous dissociation of trioxane. For the calibration experiments, the partial pressure of trioxane was varied by keeping argon (internal standard) concentration constant. A typical plot for the concentration-time profiles of 1,3,5-trioxane and formaldehyde is shown in Figure 6-5.

![Figure 6-4 Calibration curves for 1,3,5 trioxane (A) and formaldehyde (O) from ST/TOF-MS measurements.]

These experiments were carried out around $T_5 = 600 \text{ K} \text{ (trioxane)}$ or $1200 \text{ K} \text{ (formaldehyde)}$ and $p5 = 900 \text{ Torr}$. 

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Figure 6-5 Concentration-time profiles for 1,3,5-trioxane (C$_3$H$_6$O$_3$) and formaldehyde (HCHO). Experimental conditions are $p = 818$ Torr, $T = 990$ K, mixture composition of $[Ar] = 6.70 \times 10^{-7}$ mol/cm$^3$, $[C_3H_6O_3] = 1.66 \times 10^{-7}$ mol/cm$^3$, $[Ne] = 1.24 \times 10^{-5}$ mol/cm$^3$. Solid lines are the best fit of kinetic simulation.

The details of the quantum chemical calculations are beyond the scope of this dissertation and are discussed at length in [149]. For the kinetic simulation, the rate constant reported by Irdam and Kiefer [135] was used as an initial estimate and was varied iteratively to obtain the best fit with the measured concentration-time profiles. An example of such kinetic simulations is shown in Figure 6-5 (solid lines). The extracted rate coefficients from all our experiments are listed in Table 6-1 and plotted with the literature data in Figure 6-6. As can be seen, the data obtained in the current work fills up the void spaces in the mid-temperature range and encompass both the Irdam and Kiefer [135] and Wang et al. [137] data at high temperatures. Our values of the rate coefficients ($\pm 30\%$) measured near 900 Torr compare very well with that reported by Irdam and Kiefer [135] and Wang et al. [137] ($\pm 20\%$) at pressures of 350 and 1596 Torr, respectively. This indicates that the measured rates over 350 – 1596
Torr are quite close to the high-pressure limit. As we expect to see little or no pressure dependence for reaction (1) at low temperatures, our rate coefficients at the lower temperature end show an excellent agreement with the data from Hochgreb et al. [134] and also with the extrapolated value of the low pressure and low temperature data from Hogg et al. [132] and Burnett and Bell [136].

The experimental data was further rationalized in terms of RRKM calculations using the data from ab-initio calculations [149]. Based on the parameters compiled in Table 6-2, we computed pressure- and temperature- dependent rate coefficients for reaction (1) using Kiefer et al.[150], [151] RRKM program script. As can be seen in Figure 6-6, our calculated RRKM rates match very well with the available experimental data at all temperatures and pressures with an average absolute deviation of 16.5%. The low temperature data of Aldridge et al. [133] appear to be too slow and are not captured by our calculations. Excluding the data from Aldridge et al. [133], the calculated rate coefficients ($k(T, p)$) were found to be most consistent with the available data for a barrier height ($E_0$) of 46.5 kcal/mol. Furthermore, we note that the RRKM results reported here are for neon as bath gas while Irdam and Kiefer [135] used krypton and Wang et al. [137] used argon as bath gas in their experiments. However, the bath gas is expected to cause negligible change in the calculated values of the rate coefficient. The parameters for the calculated values of the pressure-dependent rate coefficient are compiled in Table 6-3 over the temperature range of 500 to 1400 K.
Figure 6-6 Comparison of the calculated rate coefficients with the experimental data. (*) this work at ≈ 900 Torr, (o) 290-362 Torr [135]; (Δ) 138 -178 Torr [135]; (Δ) 20 – 80 Torr [132]; (θ) ≤ 100 Torr [136]; (---) 760 Torr [134]; (□) 800 Torr [133]; (△) 1596 Torr [137]; lines represent our RRKM calculations at pressures ($p = \infty$ (black), 1596 (purple), 900 (blue), 326 (red), 158 (green) Torr (1596 Torr, 326 and 158 Torr were chosen for calculations as these are the mean pressures for the Wang et al. [137] and Irdam and Kiefer [135] experiments, respectively). The inset figure highlights the match between the theory and experiments at higher temperatures.

Table 6-1 Experimental Values of the Rate Coefficients Extracted via Kinetic Simulation of the Measured Concentration-Time Profiles of Trioxane and Formaldehyde.

<table>
<thead>
<tr>
<th>$T_s$ (K)</th>
<th>$P_s$ (Torr)</th>
<th>[Ar] (mol/cm$^3$)</th>
<th>[C$_3$H$_6$O$_3$] (mol/cm$^3$)</th>
<th>[Ne] (mol/cm$^3$)</th>
<th>$k$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>775 ± 6</td>
<td>908</td>
<td>4.65 x 10$^{-7}$</td>
<td>2.16 x 10$^{-7}$</td>
<td>1.81 x 10$^{-3}$</td>
</tr>
<tr>
<td>Species</td>
<td>A, B, C (cm⁻¹)</td>
<td>(v_i) (cm⁻¹)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------------</td>
<td>----------------</td>
<td>-----------------------------------------------------------------------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,3,5-Trioxane</td>
<td>0.173748</td>
<td>293, 293, 462, 501, 501, 714, 913, 913, 928, 940, 1031, 1031, 1137, 1137, 1187, 1194, 1272, 1272, 1333, 1368, 1368, 1436, 1436, 1457, 2877, 2877, 2887, 3082, 3082, 3085</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.173748</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.096858</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TS</td>
<td>0.141732</td>
<td>515i, 201, 202, 274, 274, 344, 434, 434, 434, 1272, 1272, 1333, 1368, 1368, 1436, 1436, 1457, 2877, 2877, 2887, 3082, 3082, 3085</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 6-2 Rotational Constants (A, B, and C) and Harmonic Frequencies (\(v_i\)) of the Stationary Points Calculated at the MP2/aug-cc-pVDZ Level of Theory. Frequencies are scaled by 0.9615.
<table>
<thead>
<tr>
<th>CH(_2)O</th>
<th>9.333951</th>
<th>1142, 1204, 1468, 1661, 2863, 2944</th>
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<tr>
<td></td>
<td>1.261052</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.110958</td>
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</table>

<table>
<thead>
<tr>
<th>Collision Parameters:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_3)H(_6)O(_3)</td>
<td>(\sigma = 6.042 \ \text{Å}; \ \varepsilon/k = 533 \ \text{K})</td>
</tr>
<tr>
<td>Ne</td>
<td>(\sigma = 2.82 \ \text{Å}; \ \varepsilon/k = 32 \ \text{K})</td>
</tr>
<tr>
<td>(&lt;\Delta E&gt;_{\text{down}})</td>
<td>500 cm(^{-1})</td>
</tr>
</tbody>
</table>

**Table 6-3** The parameters Obtained from the Fit\(^a\) of the Calculated Values for the Pressure-Dependent Rate Coefficient over the Temperature Range of 500 to 1400 K.

\(^a\)\(k(T) = A \ T^n \exp(-E_a/RT)\) in the units of cm\(^3\), mol, s, cal and K.

<table>
<thead>
<tr>
<th>(P) (Torr)</th>
<th>(A)</th>
<th>(n)</th>
<th>(E_a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>(8.49 \times 10^{81})</td>
<td>-19.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>60528</td>
</tr>
<tr>
<td></td>
<td></td>
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<tr>
<td>---</td>
<td>---</td>
<td>----------</td>
<td>--------</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>7.76 x 10^77</td>
<td>-19.65</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>3.45 x 10^71</td>
<td>-17.40</td>
</tr>
<tr>
<td>4</td>
<td>158</td>
<td>2.85 x 10^69</td>
<td>-16.72</td>
</tr>
<tr>
<td>5</td>
<td>326</td>
<td>4.23 x 10^65</td>
<td>-15.48</td>
</tr>
<tr>
<td>6</td>
<td>760</td>
<td>2.70 x 10^60</td>
<td>-13.82</td>
</tr>
<tr>
<td>7</td>
<td>900</td>
<td>2.08 x 10^59</td>
<td>-13.47</td>
</tr>
<tr>
<td>8</td>
<td>1596</td>
<td>2.51 x 10^55</td>
<td>-12.24</td>
</tr>
<tr>
<td>9</td>
<td>7600</td>
<td>1.56 x 10^44</td>
<td>-8.74</td>
</tr>
<tr>
<td>10</td>
<td>76000</td>
<td>2.15 x 10^29</td>
<td>-4.16</td>
</tr>
<tr>
<td>11</td>
<td>∞</td>
<td>6.85 x 10^15</td>
<td>0</td>
</tr>
</tbody>
</table>
Chapter 7 Summary and Future Work

7.1 Summary of Results

7.1.1 CRDS Measurements in Static Cell

A novel widely-tunable laser-based sensor based on pulsed cavity ringdown spectroscopy has been successfully developed and used for performing sensitive absorption measurements of ethylene, propene, allene and 1-butene in the mid-IR. The high sensitivity of the laser-based sensor enables sub-ppm detection limits of 17 ppb, 134 ppb, 754 ppb and 378 ppb for ethylene, propene, allene and 1-butene respectively at a nominal temperature of 296 K and pressure of 760 Torr in 70 cm static cell. Trace amounts of ethylene, propene, allene and 1-butene were measured individually as well as simultaneously in a multi-gas mixture containing gases at 1% of their TWA exposure limits, except 1-butene. Simultaneous measurements of all four target molecules can be carried out within four minutes with the bulk of the time spent on tuning the laser to the wavelength of interest. The sensor is suitable for measuring trace amounts of aforementioned gases in the atmosphere as was demonstrated by measuring ethylene in a sample of laboratory air and an air sample collected from a car parking facility. To the best of our knowledge, this is one of the first successful implementations of the pulsed CRDS technique to measure trace amounts of multiple gases in 900 – 1000 cm\(^{-1}\) region. Furthermore, this is the first laser-based sensor capable of measuring trace amounts of propene, allene, and 1-butene.
7.1.2 CRDS Measurements in Shock Tube

A novel highly-sensitive ultra-fast diagnostic based on pulsed cavity ringdown spectroscopy has been successfully developed and used for performing sensitive absorption measurements of ethylene in a shock tube experiment. The fast time-response diagnostic achieved a noise-equivalent detection limit of $1.08 \times 10^{-5}$ cm$^{-1}$ at 100 kHz which is a tremendous gain over the sensitivity of commonly used single-pass direct absorption techniques. High sensitivity of this diagnostic tool enables measurement of ethylene concentrations as low as 15 ppm at shock conditions of 1845 K and 1.96 bar. At room temperature and pressure (296 K and 1.01 bar), comparatively large absorption cross-sections of ethylene near 949.472 cm$^{-1}$ bring the ethylene detection limit down to 294 ppb for a path length of 14.2 cm. The high sensitivity and fast time response diagnostic can be utilized for measuring other neutral molecules and radicals which cannot be detected using single-pass direct absorption techniques. We believe this is the first time that pulsed CRDS technique was successfully used to measure species time-histories in a shock tube.

7.1.3 Atmospheric Flame Ion Measurements Using QMS

A molecular beam mass spectrometer was used to measure ion signals across lean and stoichiometric premixed atmospheric flat flames of methane and oxygen in argon diluent. Ion profiles of all major ions were measured and relative ion signal profiles were obtained. The flame temperature was measured using a SiO$_2$ coated thermocouple and appropriate radiation corrections were applied to the thermocouple readings. The flame ion signal profiles measured at different equivalence ratios showed that the shape of the ion signal profile depends significantly on the flame equivalence ratio due to recombination rates being proportional to the peak
signal/relative mole fraction of ions. Thus, the higher the peak ion signal, the steeper
the decrease of the ion signal in the burnt gases. In both lean and stoichiometric
flames, C₂H₅O⁺ and H₃O⁺ ions were the most dominant. Subsequently, the measured
ion signal profiles were compared with simulations carried out using an established
ion chemistry mechanism [63], [64]. Based on the experimental results, three
modifications were suggested to the ion mechanism to improve the agreement
between simulation results and experiments. In lean premixed flames using the
modified mechanism, the simulated H₃O⁺ profile agreed well with the measured
relative H₃O⁺ mole fraction, while the measured CH₃O⁺ mole fractions were higher
than the simulated values. The simulated value of C₂H₅O⁺ was about a factor of 2
greater than the measured relative mole fraction. In the stoichiometric premixed
flame, the measured profiles of both H₃O⁺ and C₂H₅O⁺ were in good agreement with
the modified mechanism. Contrary to the observations in lean premixed flames, the
peak measured mole fraction of CH₃O⁺ was significantly lower than the simulated
value. Since accurate prediction of total ion density distribution is necessary to model
the interaction of electric field with flames, it is essential to improve Prager’s ion
chemistry mechanism to reduce the discrepancy between the predicted distribution of
individual ions and the corresponding experimental data. The use of 1-D flat flame
produced by the McKenna burner along with the measurement of flame temperature
should simplify the task of comparing the experimental data with one-dimensional
models, thereby improving our understanding of weak flame plasmas.

7.1.4 Low-Pressure Flame Ion Measurements Using QMS

Detailed relative cation mole fraction measurements were carried out in premixed
30 Torr flat flames of methane. Relative ion mole fraction profiles show strong
dependence of the identity of dominant ions and their spatial distribution on the flame equivalence ratio. In lean and stoichiometric flames, the five most dominant ions are \( \text{H}_3\text{O}^+ \), \( \text{CH}_3\text{O}_2^+ \), \( \text{C}_2\text{H}_5\text{O}^+ \), \( \text{C}_2\text{H}_3\text{O}^+ \) and \( \text{CH}_5\text{O}^+ \). In rich flame, \( \text{H}_3\text{O}^+ \), \( \text{C}_3\text{H}_3^+ \) and \( \text{C}_2\text{H}_3\text{O}^+ \) appear in large quantities. For all flames, \( \text{H}_3\text{O}^+ \) is the most dominant ion. Simulated \( \text{H}_3\text{O}^+ \) decay rate is found to be much faster than observed experimentally, most-likely due to the over-estimation of the peak value of \( \text{H}_3\text{O}^+ \). Sensitivity analysis showed that near the peak location, \( \text{H}_3\text{O}^+ \) is most sensitive to the chemi-ionization reaction \( \text{CH} + \text{O} \leftrightarrow \text{CHO}^+ + \text{e}^- \), and its rate constant may need to be revisited.

In summary, our data provide the following new insights into the methane oxygen ion chemistry:

1. The current study showed that the prediction of notably faster \( \text{H}_3\text{O}^+ \) decay was due to inadequacies in the ion chemistry model and not due to experimental issues as previously postulated [64], [119].

2. Cataloging of ions facilitated using a high mass resolution TOF-MS allowed the conclusive identification of selected ions with very similar \( m/z \) values.

3. \( \text{CH}_3\text{O}_2^+ \) and \( \text{C}_2\text{H}_7\text{O}^+ \) were found to be among the major ions in lean flame and need to be included in future ion chemistry models.

4. We highlighted the possibility of an indirect reaction pathway between \( \text{C}_3\text{H}_3^+ \) and \( \text{H}_3\text{O}^+ \) in rich flames, proceeding through \( \text{CH}_3^+ \). This new route suggests that both \( \text{CH}_3^+ \) and \( \text{C}_3\text{H}_3^+ \) and related reactions should be included in ion chemistry models to simulate rich flame conditions.

5. For the first time, ions at \( m/z = 53 \) (± 71) reflecting contributions from \( \text{C}_3\text{HO}^+ \) and \( \text{C}_4\text{H}_8^+ \) were observed in stoichiometric and rich flames.
To the best of our knowledge, the present effort represents the first detailed measurements of cations in canonical low-pressure methane-oxygen-argon flames. It is expected that the database presented in this work will be used to develop and validate detailed and skeletal ion mechanisms for methane oxidation. Since the ion distribution profiles significantly impact the overall flame chemistry in presence of an electric field, better ion mechanisms are essential to design new combustion systems that utilize external electric fields for active control of combustion processes.

7.1.5 TOF-MS Measurements in Shock Tube

The capability of compact fast time-response TOF-MS to measure species concentration time-histories in transient systems was demonstrated by investigating the thermal unimolecular dissociation of 1,3,5-trioxane behind reflected shock waves over 775 K – 1082 K and pressures near 900 Torr. Reaction progress was monitored using a time of flight mass spectrometer as a diagnostic tool. It was found that formaldehyde is the sole product of 1,3,5 trioxane dissociation. Reaction rate coefficients were extracted by the best fit to the experimentally measured concentration–time histories. The new experimental data serves as a validation and extension of kinetic data published earlier by other groups. Calculated values for the pressure limiting rate coefficient can be expressed as $\log_{10} k_\infty (s^{-1}) = [15.84 - (49.54 \text{ (kcal/mol)/2.3RT})] (500–1400 \text{ K})$

7.2 Recommendation for Future Work

7.2.1 CRDS Measurements in Shock Tubes/Transient Systems

Under low-temperature and high-pressure combustion conditions, hydroperoxyl radical (HO$_2$) and hydrogen peroxide (H$_2$O$_2$) are key intermediate
species in the oxidation of hydrocarbon fuels [2]. Therefore, measurements of HO$_2$ and H$_2$O$_2$ time-histories in reactive environments are crucial to the development and validation of chemical kinetic models that describe low temperature and high pressure oxidation of fuels and will aid in the design of next-generation combustion systems.

Hydroperoxyl radical (HO$_2$) and hydrogen peroxide (H$_2$O$_2$) despite being key combustion intermediates have hitherto not been measured in shock tube experiments because they cannot be detected using the traditionally used single-pass direct absorption techniques. Since shock tube is a transient chemical reactor, detecting these species requires an in-situ technique which combines the characteristics of high sensitivity with high time resolution. Among the various cavity based techniques explored, pulsed CRDS offers the best combination of sensitivity and time resolution. Since this dissertation has presented the first successful demonstration of pulsed CRDS technique to measure species time-histories in shock tube experiments, future experiments need to be designed that target the aforementioned key combustion intermediates and other trace species of interest. Although, pulsed CRDS technique has been implemented only in shock tube in the current dissertation, it can be successfully utilized to measure species concentrations in other homogenous combustion systems such as rapid compression machine, laminar flames etc.

7.2.2 Non-Intrusive Flame Ion Measurements Using Cavity Enhanced Techniques

The ion chemistry work presented in this dissertation has shown H$_3$O$^+$ to be the most dominant ion in methane flames, in agreement with the observations of previous studies. Since QMS is an intrusive diagnostic tool, measurements carried out using a non-intrusive diagnostic technique capable of measuring the concentration of
H$_3$O$^+$ ion will be a very valuable addition to the existing database of QMS measurements. Detecting hydronium ion (H$_3$O$^+$) is an extremely challenging task due to its trace concentrations in flames and requires a highly sensitive diagnostic technique such as CRDS. Hydronium ion has four fundamental vibrational modes [152] among which $v_2$ (inversion mode) and $v_3$ (O–H asymmetric stretching mode) are the strongest. Transitions for $v^\pm_3 \leftrightarrow 0^\pm$ band have been observed in 3207 to 3692 cm$^{-1}$ [153] while previously measured line positions of $v_2$ (1$^-$ $\leftrightarrow$ 0$^+$) band of H$_3$O$^+$ are from 756 to 1201 cm$^{-1}$ [154]. Due to trace concentrations of hydronium ion and strong interference from H$_2$O and CO$_2$, there are only a handful of absorption lines of hydronium ion that have relatively low interference from these neutral species. However, with large uncertainties in hydronium absorption cross-section database, there is a strong possibility that the seemingly interference free absorption lines also suffer from interference. Therefore, the diagnostic required for measuring hydronium ion should also be able to differentiate between ions and neutrals. An optical technique known as velocity modulation spectroscopy (VMS) is the most promising diagnostic tool to detect hydronium ion as it suppresses the absorption features of neutrals so the interference from these exceedingly dominant neutral species is avoided [155]. Therefore, one potential future direction is to combine the CRDS technique presented in this dissertation with VMS to non-intrusively measure hydronium ion concentrations in low-pressure flames.

7.2.3 Unravelling the Secret of Flame Ionization Detector

This dissertation presented the investigation of methane-oxygen ion chemistry in atmospheric and low-pressure flames using QMS. The experimental setup (low-pressure burner coupled to QMS) can be used to study the ion chemistry of other
hydrocarbons (ethylene, acetylene and others) to investigate the influence of C/H ratio on the ion chemistry and obtain more validation targets that will aid in the development of a robust ion chemistry mechanism. Further, a detailed experimental plan can be developed to systematically study numerous hydrocarbon fuels to understand their ion chemistry and thereby attempt to satisfactorily explain the working of flame ionization detector (FID), which currently is not well understood.

Appendix: Non-Intrusive Electron Concentration Measurements Using Microwave Interferometry in the Shock Tube

Introduction

Microwave interferometry is a diagnostic tool capable of non-intrusively measuring the electron concentrations in a flame plasma. Due to its fast-time response, it can be utilized to measure electron concentration time-histories in shock tube oxidation experiments. The electron concentration measurements can be used as a validation target for developing ion chemistry mechanisms. This section describes in detail the challenges faced in utilizing the interferometer to carry out electron concentration measurements in the KAUST shock tube. The principle of operation of the microwave interferometer (MWI) and its experimental design is detailed in [156], [157] and will not be repeated here for the sake of brevity.

The MWI utilized in this work was custom-designed by Millitech Inc. The MWI emits electro-magnetic waves at 94 GHz (3.2 mm wavelength) and is capable of measuring electron densities in the range \(10^{10} - 10^{16}\) electrons/cm\(^3\). MWI is able to
measure electron density since electrons alter the phase and the amplitude of the electromagnetic waves passing through them. The presence of electrons also changes the refractive index of the test sample and as such a material with known refractive index is traditionally used for validating new MWI setups. For weak plasmas such as flames, the total phase shift varies with the electron number density. Since the measured phase shift is directly proportional to the wavelength, microwaves are 2-5 orders more sensitive than IR and visible light. To understand the material discussed in the next section, the reader is strongly advised to review Chapter 4 in [157].

**Challenges**

MWI was utilized to measure the electron time-histories in shock tube oxidation experiments of four hydrocarbon fuels: methane, ethylene, propane and acetylene. The four fuels were selected to obtain electron density measurements for different C/H ratios. Lean, stoichiometric and rich mixtures of methane diluted in argon were used for the oxidation experiments. For all other fuels, only their stoichiometric mixtures were used to carry out the electron concentration time-history measurements. Significant amount of post-processing of the raw data was required to back out the electron concentration time-histories and some of the experimental issues discussed below were observed only after recording and comparing considerable amount of data from the experimental dataset. The problems faced in this initial campaign are mentioned below:

1. Significantly poor signal to noise ratio (SNR) was observed when ignition delay time was less than 1ms for all the oxidation experiments. Moreover, the background noise was inconsistent and non-repeatable.
2. Some of the fuel oxidation shocks were repeated at the same shock conditions to check for repeatability. However, it was observed that the electron concentration time-histories varied for the same experimental conditions in few cases. The reason for this lack of repeatability is currently not well understood.

3. For the first campaign, thermal ionization of argon gas was selected to validate the experimental setup. However, the experimentally measured electron concentration time-histories did not agree well with previous experiments reported in literature [158], [159]. The disagreement was attributed to the high sensitivity of argon ionization rates to the impurities present in the shock tube as reported in earlier works.

**Possible Solutions**

Anyone interested in utilizing the MWI to measure electron concentration time-histories should consider going through the following steps (in no particular order) to overcome some of the challenges faced during the first shock tube campaign:

1. The first step is to validate the MWI using a material with a well-known refractive index. A plastic sheet made of Rexolite is an ideal candidate to validate the MWI since its refractive index is known. These validation measurements will help in quantifying the noise in the amplitude and phase of the MWI and also aid in verifying the repeatability of MWI experiments which are essential steps towards characterizing the MWI.

2. Secondly all possible source of noise should be investigated with the aim of mitigating them as much as possible. Noise in MWI signal can be caused by a variety of reasons such as movement of plugs containing the MWI horns, vibration of MWI at the time of arrival of shock waves and others.
3. Thirdly, the spatial resolution in the entire region between the horn and antenna needs to be characterized. Initial tests indicated that the MWI beam is diverging and MWI starts to respond even when a plastic plate/dielectric material is 17 mm away from the axis of the horn/antenna. A close inspection of the shock tube ports in which the horn and antenna were placed indicated a height difference of 7 mm between the ports holding the horn and the antenna. Since the outer diameter of the horn is 14 mm, horn and antenna were significantly misaligned and it is entirely plausible that this led to multiple reflections of microwave beam between the highly polished inner surfaces of the shock tube. The misalignment of the horn and the antenna can explain some of the non-repeatable background noise observed during shock tube experiments. To overcome this issue, new shock tube plugs were machined which allow the horn and the antenna to be perfectly aligned.

4. Finally, the next set of experiments should be carried out at low temperatures to ensure long ignition delay times as the SNR was poor for ignition delay times less than 1 ms.

Another problem with the initial experiments was that the current design of the MWI does not contain a variable phase shifter, which led to difficulties in backing out phase shifts from the MWI output. The variable phase shifter is used to draw the Smith diagram (calibration ellipse) by varying the phase setting in the phase shifter at different attenuation levels [160]. The attenuation levels are varied using an attenuator. In a flame plasma, the test beam undergoes both attenuation and phase change, therefore, utilizing the Smith diagram, the phase change of the test beam with respect to the reference beam can be easily backed out. In the absence of the variable
phase shifter, the MWI output obtained in the case of thermal ionization of argon has to be used as the calibration ellipse to back out the phase shifts, however this procedure is non-ideal. Therefore, two variable phase shifters each with a maximum allowable phase shift of 180° were recently purchased from Millitech Inc. Lastly, a peculiarity of MWI operation is that its outputs tend to drift significantly for 1-2 hours after initial start-up. Therefore, all measurements should be carried out once it is ensured that the drift is negligible over the period of time of the measurement. The information contained in this section combined with Chapter 4 of [157] are expected to assist the reader in successfully utilizing the MWI to measure electron concentration time-histories in shock tube oxidation experiments.
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