ADVANCES IN AMMONIA COMBUSTION CHEMISTRY AND NH₃ SENSING USING LASER DIAGNOSTICS

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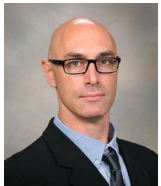
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ABSTRACT

Ammonia (NH₃) is a promising alternative carbon-free fuel. For this reason and others, significant research is directed towards studying NH₃ especially pertaining to its chemical kinetics. A brief review of the literature on ammonia combustion chemistry is provided in this paper, with emphasis on the studies related to fundamental reaction kinetics at elevated temperatures. Until recently, NH₃ was never measured using laser absorption spectroscopy to study its chemical kinetics. This recent NH₃ measurement was conducted by the authors' group using a newly developed laser absorption diagnostic that probes the v_2 fundamental band of NH₃ in the mid-infrared near 10.4 µm. The present study utilized this recently developed NH₃ diagnostic to highlight its capabilities and potential future use for studying ammonia combustion chemistry and also as an ammonia sensor for practical applications. The laser was operated using two methods: a scanned-wavelength method to measure the absorption spectra of NH₃-containing mixtures, and a fixed-wavelength method to measure NH₃ time histories behind reflected shock waves. The scanned-wavelength method was used to determine the NH₃ mole fraction in multi-component gas mixtures; such a method presents future promise when the accurate determination of NH₃ in a sampled gas is needed. The fixed-wavelength method, coupled with a shock tube, was used to follow NH₃ time histories during the oxidation of NH₃/O₂ in Ar; such a method shows promise for studying the chemical kinetics of ammonia.

INTRODUCTION

Securing the energy demand in the next few decades is one of the most challenging tasks facing society. This challenge is exacerbated due to the ever-growing demand for energy (projections indicate nearly 50% increase in world energy consumption by 2050 [1]) and the urgent need to find energy sources with a lower carbon footprint to reduce the levels of CO₂ emissions in the atmosphere. Although renewable energy is expected to cover the majority of the energy demand in the future, the intermittent nature of renewable energy sources necessitates viable energy storage solutions. These energy storage solutions must satisfy two important requirements: (i) the energy storage method must have the capacity to store energy at grid-scale levels, and (ii) the energy storage method must have the ability to store the energy for long periods of time.

Energy storage solutions range from batteries and supercapacitors to pumped hydro, compressed air, and chemical energy storage. Although significant advancements were achieved in the past few decades in the development of batteries and supercapacitors, these methods have relatively low energy densities and appear to have a limitation on their ability to store energy for long periods of time [2]. Furthermore, the limited nature of the raw materials needed to build batteries presents a bottleneck on the large-scale adoption of battery energy storage solutions [3]. Other energy storage methods such as pumped hydro and compressed air storage have the capacity to store grid-scale energy levels. However, these two methods have geological constraints as large dams are needed to implement a pumped hydro station, while suitable underground cavities are typically needed to store the pressurized air. Out of the available energy storage methods, only chemical energy storage can satisfy both energy storage requirements without geological constraints [4].

Chemical energy storage can be in the form of hydrogen (H₂) which can be produced from fossil fuels, biofuel resources, or from the excess energy produced from renewable sources via water electrolysis [5]. However, significant challenges still exist to economically transport and store hydrogen, along with the inherent safety concerns due to its extremely flammable nature [6]. Hydrogen can also be converted to ammonia (NH₃), which is a hydrogen-carrier and carbon-free fuel, via several methods including the mature industrial Haber-Bosch process [7]. Unlike hydrogen, ammonia has well-established infrastructures of production, transportation, and storage thanks to the centuries of use by the fertilizer industry. Ammonia can be converted back to hydrogen via catalytic cracking [8] or can be used itself for energy extraction via fuel cells or direct combustion [4].

The use of ammonia in combustion applications has drawn significant research interest in recent years [9]. However, the use of ammonia as a fuel is challenging due to its unfavorable combustion characteristics such as low flame speed and narrow flammability limits [10]. Ammonia utilization in compression-ignition engines is challenging due to the high resistance to ignition caused by its large minimum ignition energy [11]. The direct use of ammonia in gas turbines is also challenging due to its low flame propagation speed [12]. To overcome these combustion challenges, ammonia blending with other fuels, such as H₂, is considered to improve its combustion characteristics. An additional challenge of ammonia combustion is the higher NOx emissions in the exhaust products. However, NOx reduction after-treatment solutions such as selective catalytic reduction can be implemented to overcome this challenge [13].

The interest in using ammonia for combustion applications has drawn research interest in improving the fundamental understanding of ammonia combustion chemistry. In recent years, considerable experimental research has been conducted on NH₃ and NH₃/H₂ blends to measure ignition delay time [14-19] and laminar burning velocity [20-27]. However, only a limited number of NH₃ experimental studies were conducted to measure speciation data [28-31]. Arguably, most of the recent ammonia combustion research has focused on developing and validating accurate chemical kinetics models as evident by the large number of studies over the past decade [14, 24, 28-30, 32-44]. The majority of these modeling studies utilized global combustion parameters such as ignition delay time and laminar flame speed as validation targets.

Ammonia is a promising sustainable, carbon-free fuel for future combustion applications. For this reason, among others, a significant

body of work exists on ammonia combustion (see below). However, no shock-tube speciation experiments had been performed, and there is still much work to be done in understanding ammonia kinetics. Furthermore, there are no studies of NH_3 speciation using laser absorption methods. This paper details the development and characterization of a novel laser absorption diagnostic for NH_3. This laser diagnostic can then be applied to study NH_3 chemical kinetics behind reflected shock waves as well as in other scenarios in the laboratory or in practical applications.

This paper starts by providing a literature review of the research pertaining to ammonia combustion. Furthermore, details on the selection and characterization of the new laser absorption diagnostic used for NH_3 detection are presented, along with some initial results from an ammonia combustion experiment.

BACKGROUND

The overall purpose of the current effort at Texas A&M University (TAMU) is to perform experiments to measure unique speciation data which can be used to improve the understanding of ammonia combustion chemistry. These speciation data will be obtained using a novel laser absorption diagnostic and will be used as targets to improve the NH_3 kinetics models. Previous (and relatively recent) research on ammonia combustion is extensive. This section of the present paper provides a literature review of the works that are closely related to the present study. First, a brief overview of the previous studies on the use of NH_3 as a fuel to power several types of combustion devices is presented. Second, the previous experimental high-temperature chemical kinetics works, including both NH_3 pyrolysis and oxidation, are reviewed. Note that multiple types of experimental studies were reviewed, but the emphasis was given to shock-tube and speciation studies. Third, a literature review of the major NH_3 modeling works is presented. Finally, a literature review covering the prior studies related to NH_3 spectroscopy, including the available spectral information of NH_3, is summarized; this review included information needed to develop the new laser absorption diagnostic.

Review of Ammonia for Combustion Applications
Even though significant challenges are associated with the use of ammonia as a fuel, several attempts were performed to power combustion devices with NH_3. One of the first attempts was in 1943 during World War II where shortages of diesel initiated the search for an alternative fuel to power the public transportation buses in Belgium. This shortage led to the first use of NH_3 to successfully run the internal combustion engines of 8 buses for more than one year [45]. In the 1960s, NASA and the Air Force conducted hypersonic tests on the X-15 aircraft with its rocket engine powered by ammonia and liquid oxygen. During these tests, the X-15 achieved a world record for the fastest manned aircraft with speeds reaching Mach 6.7 [46]. Also in the 1960s, the US Army carried out a campaign of research to develop a gas turbine powered by NH_3, but these efforts were unsuccessful and later abandoned [47].

In the past decade, significant efforts were dedicated to investigate the use of NH_3 as a fuel for combustion devices such as gas turbines, reciprocating engines, and industrial furnaces. For example, laboratory studies were conducted to investigate the use of NH_3 as a fuel for swirl combustor used in gas turbine [48]. Moreover, in 2016, the first successful operation of a micro gas turbine power by a pure NH_3 fuel was achieved in Japan [12]. In the past few years, significant efforts to advance the use of NH_3 for small-scale gas turbines are ongoing by various research groups, with major contributions particularly from the Institution of Fluid Science at Tohoko University [12] and the Gas Turbine Research Centre at Cardiff University [49].

Review of Ammonia Experimental Kinetics Work
Work on NH_3 chemistry spans many fields such as catalysts, Inorganic chemistry, and high-temperature kinetics. Focus in this section is on reviewing work related to the latter field. NH_3 pyrolysis kinetics work is presented first in a separate subsection, followed by another subsection dedicated to works on NH_3 oxidation kinetics.

NH_3 Pyrolysis
Perhaps one of the earliest investigations of NH_3 gas-phase kinetics was the work of Hinshelwood and Burk in 1925 [50]. In their work, they studied the thermal decomposition of NH_3 with several catalytic surfaces and investigated whether the decomposition of the homogeneous gas-phase reaction can be observed. Although NH_3 decomposition proceeded along the catalytic surfaces, Hinshelwood and Burk noted that no homogenous thermal decomposition of NH_3 was observed up to temperatures of 1050 K. In the early 1960s, Jacobs [51, 52] used a shock tube to generate higher temperatures between 2000 and 3000 K to study the gas-phase kinetics of NH_3. He studied the decomposition of 1-8% NH_3 in Ar utilizing infrared detectors to observe the NH_3 emissions from v_1 and v_3 fundamental bands in the spectral region between 2.7 to 3.2 μm. Jacobs assumed that the natural step of NH_3 decomposition was via:

$$NH_3 + M \rightarrow NH_2 + H + M \qquad\qquad R1$$

By observing the early decay in the emission signal, he inferred one of the earliest reaction rate coefficients of R1 (i.e., k_1).

In between 1960 and 1980, extensive research work was conducted on the kinetics of N/H/O systems that led to measurements of several rate constants of elementary NH_3 reactions. These efforts were summarized in the survey reported by Hanson and Salimian [53]. In this

period, the main NH_3 decomposition reaction (R1) was studied extensively using shock-tube facilities coupled with several diagnostic techniques including NH_3 UV absorption [54], $NH_3/NH_2/NH$ emission [55], atomic resonance absorption of H-atoms (H-ARAS) [56], and mass spectrometric analysis to measure NH_3, NH_2, NH, and N_2 [57]. However, the reported k_1 varied significantly both in terms of the determined pre-exponential A-factor coefficients and the activation energies. Hanson and Salimian concluded that the overall kinetics mechanism of ammonia decomposition was complex and that the reported NH_3 decomposition rates are strongly influenced by secondary reactions. These complications coupled with the large reported uncertainties in k_1 (typically a factor of 0.6 to 2) led to further ammonia decomposition studies.

In 1990, Davidson et al. [43] used a shock-tube facility to perform the first laser absorption measurements during NH_3 decomposition. They quantitatively measured the time-history profiles of NH_2 and NH species produced from the high-temperature (2000–3200 K) decomposition of 0.1–1% NH_3 in Ar. The measured NH_2 and NH profiles allowed them to determine the rate coefficients of the following "secondary" reactions that influenced the determination of R1 rate constant:

$$NH_2 + H \ \rightarrow NH + H_2 \qquad\qquad\qquad R2$$
$$NH_2 + NH \ \rightarrow N_2H_2 + H \qquad\qquad\qquad R3$$
$$NH_2 + NH_2 \ \rightarrow NH + NH_3 \qquad\qquad\qquad R4$$

Furthermore, they reanalyzed the NH_3 decomposition data from four earlier studies by accounting for the effect of the secondary reactions on R1. This reanalysis allowed for an improved determination of the rate coefficient for R1 with an estimated uncertainty of only ±15%. Davidson et al. also proposed a new kinetics mechanism for NH_3 pyrolysis. The study of Davidson et al. was the latest shock-tube study on NH_3 pyrolysis, and their recommended rate coefficient for R1 is currently the accepted value in literature which is adopted by the majority of the recent NH_3 kinetics mechanisms.

NH_3 Oxidation
The high-temperature oxidation kinetics of NH_3 has received a great deal of research work particularly between 1960 and 1980. Most of these early works were conducted in shock tubes [58-61], flow reactors [62, 63], and constant-volume reactors [64-66] to measure several combustion parameters including ignition delay time, flame speed, and flammability limits. However, these early studies lacked accuracy in the reported parameters and presented larger scatter in the data that hinders the repeatability of the experiments. In the 1980s, several shock-tube works to study NH_3 oxidation were reported [67-70]. However, the majority of these works focused on reporting rate coefficients for important NH_3 reactions. For example, Michael et al. [69] used a shock tube to measure the rate coefficient for NH_3+H $\rightleftarrows NH_2+H_2$ using atomic resonance absorption spectroscopy of hydrogen. Furthermore, Salimian et al. [70] performed shock-tube experiments to monitor OH (via laser absorption) and NH_3 (via emission) which allowed the determination of the rate coefficients of $NH_3+O \rightleftarrows NH_2+OH$ and $NH_3+OH \rightleftarrows NH_2+H_2O$.

One of the major reasons for the low accuracy of the early ammonia studies is the fact that NH_3 has a strong tendency to adsorb to the surfaces of the experimental apparatus. This adsorption effect leads to large variations in the NH_3 mixtures that were not accounted for by earlier studies. Recently, Mathieu and Petersen [14] were the first to address the experimental difficulties associated with NH_3 adsorption. In their study, a shock tube was used to measure ignition delay times of NH_3/O_2 in Ar at pressures up to 30 atm. In particular, Mathieu and Petersen employed a passivation method to the surfaces of the apparatus to reduce the influence of ammonia adsorption and improve the accuracy of the tested mixtures. This passivation method was then employed by subsequent shock-tube studies which seems to improve the accuracy and repeatability of the reported ignition delay times.

In the past 10 years, NH_3 fundamental combustion has received a great deal of experimental research work. The majority of these works were focused on measurements of the laminar flame speed of NH_3 [21, 24, 27, 71, 72], NH_3/H_2 [22, 25, 26, 40, 71], NH_3/CH_4 [36, 73, 74], NH_3/syngas [26, 71, 75], and NH_3/alcohols [76] mixtures. These flame speed measurements were conducted mostly in constant-volume reactors or using the heat flux method and mostly covered a pressure range up to 5 atm, with only 3 studies reporting flame speed measurements up to 10 atm. Furthermore, ignition delay time data were reported using shock tubes and rapid compression machines for pressures up to 70 atm. These ignition delay time data were mainly obtained for pure NH_3 [14, 17], NH_3/H_2 [15, 16, 18, 19], and NH_3/CH_4 [77, 78] mixtures. On the other hand, only 5 studies were conducted to measure speciation data, and none of them employed either a shock tube or a laser absorption method (i.e. the proposed research methods). All of these speciation studies were conducted in flow reactors (e.g. tubular flow reactor, jet-stirred, and micro-flow reactor) to measure NH_3, O_2, N_2, H_2, NO, and N_2 [28, 31, 79-81]. These speciation measurements were obtained by sampling the flow and analyzing the gas via mass spectrometer or gas chromatograph; such analysis methods are typically less accurate than the laser absorption method employed by the present study. Furthermore, shock tubes present near-ideal kinetics reactor that eliminate typical flow reactor kinetics concerns such as surface reactions. To summarize the recent research, Fig. 1 graphically illustrates the experimental work on fundamental ammonia combustion in the past 10 years.
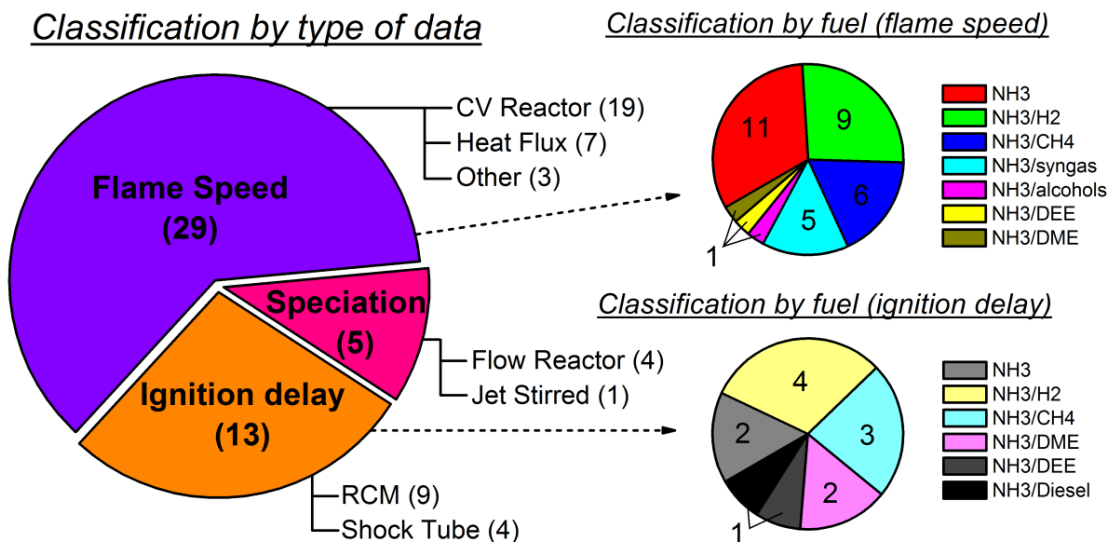
Figure 1: Summary of the fundamental experimental studies of ammonia combustion since 2010. Left graph presents the number of studies (in parentheses) classified by the type of measured data. Right graphs present the number of studies classified by the type of fuel.

Review of Ammonia Modeling Work
Studies on the chemical kinetic modeling of ammonia are extensive. To review these studies, this sub-section provides a summary of selected important studies in chronological order.

One of the earliest kinetic modeling work on NH_3 oxidation is that reported by Miller et al. [82] in 1983. Miller and co-workers compiled a kinetics mechanism consisting of 98 reactions to model the N/H/O system and validated their model against experimental data from burner-stabilized and freely propagating flames of NH_3/O_2 and $NH_3/H_2/O_2$ mixtures. Their model showed an acceptable prediction of the fuel-lean experiments but failed in reproducing the fuel-rich data. A few years later, Miller and Bowman [83] published another kinetic modeling study of NH_3 oxidation. In this study, the focus was on modeling the NO_2 and N_2O formation and removal processes, and the thermal and prompt NO formation to better understand the thermal De-NO_x process. They compiled a mechanism consisting of 307 reactions that contains C1-C2 hydrocarbon oxidation and N/H/O reactions for ammonia oxidation. This model was validated against data of NH_3, NH_2, H, OH, O_2, N_2, and H_2O from ammonia oxidation flames. In general, the model was only able to produce a good agreement with part of the experiment data.

In 1994, Glarborg et al. [84] performed flow reactor experiments to study the thermal De-NO_x process and assembled a new kinetics mechanism to improve earlier models' prediction of their experiments. Moreover, in 2000, Dean and Bozzelli [85] compiled a list of reactions of nitrogen-containing species that are important for high-temperature chemistry. They examine the available rate coefficients of these reactions and provided their recommendation for the best available rates. Their recommendations and list of reactions have been used extensively by subsequent modeling works of NH_3 and other nitrogen-containing species systems. For example, Dagaut et al. [32] studies the oxidation chemistry of hydrogen cyanide (HCN) and assembled a detailed kinetic model that used many of the rate coefficients recommended by Dean and Bozzelli. Similarly, Konnov and De Ruyck [86] studied the decomposition of Hydrazine (N_2H_4) in flames and build a detailed kinetics model that utilized the recommendations of Dean and Bozzelli.

In the past decade, the number of published kinetics mechanisms specifically assembled for NH_3 oxidation has increased significantly. In 2015, Mathieu and Petersen [14] assembled a detailed kinetic model to specifically reproduce their NH_3/O_2 high-pressure, ignition experiments. They also validated their model against other experiments such as NH_3/N_2O, H_2/N_2O, and H_2/NO_2 ignition. The study of Mathieu and Petersen provided a base NH_3 model and a new set of high-pressure ignition delay times that were utilized heavily by subsequent modeling works. In 2016, Song et al. [87] modeled NH_3 oxidation at high pressures and intermediate temperatures using flow reactor experiments, while in 2017 Nakamura et al. [28] modeled NH_3 chemistry under weak flames conditions created in a micro-flow reactor. In 2018, Glarborg et al. [37] compiled a larger detailed kinetics model for nitrogen combustion chemistry that included a sub-mechanism of NH_3 oxidation. Finally, in the past 2-4 years, a large number of modeling works have been produced and validated against global combustion parameters such as ignition delay time and flame speed experiments [24, 29, 35, 36, 39-42, 71].

Review of Ammonia Spectroscopy

Spectroscopic parameters of ammonia are utilized in many fields such as physics, chemistry, and astronomy. For example, NH_3 has a strong influence on the infrared spectrum of Jovian planets [88] where the spectroscopic parameters are needed to determine the abundance of this species on these planets [89]. Spectroscopic parameters are also used to trace NH_3 gas present in the earth's atmosphere [90], which is mostly generated from animal waste and agriculture activities [91]. NH_3 spectroscopic parameters are used in a variety of detection applications ranging from environmental gas analysis [92] and human breath analysis [93] to combustion exhaust monitoring [94] and rocket propellants [95].

Although no spectroscopic measurements of NH_3 have been reported in high-temperature combustion environments, there is significant spectroscopic data at room temperature available in various databases. The HITRAN databases [44] includes information for more than 90,000 NH_3 transitions ranging from pure rotational lines (0-2410 cm^{-1}) to rotational-vibrational transitions up to ~10,000 cm^{-1}. The infrared region (1-15 μm) is an ideal region for NH_3 detection due to its relatively high line strengths. Figure 2 shows a simulation of the line strength in this region using the HITRAN database where several bands are present; the physical meanings of these bands are summarized in Table 1. This infrared region has been well studied by spectroscopists using theoretical and experimental approaches. Experimental studies of this region were based on absorption spectroscopy using a variety of instruments including Fourier-transform spectroscopy, tunable diode lasers, and quantum cascade lasers to characterize spectroscopic parameters such as line positions, line strengths, line shifts, and broadening coefficients [96-99].
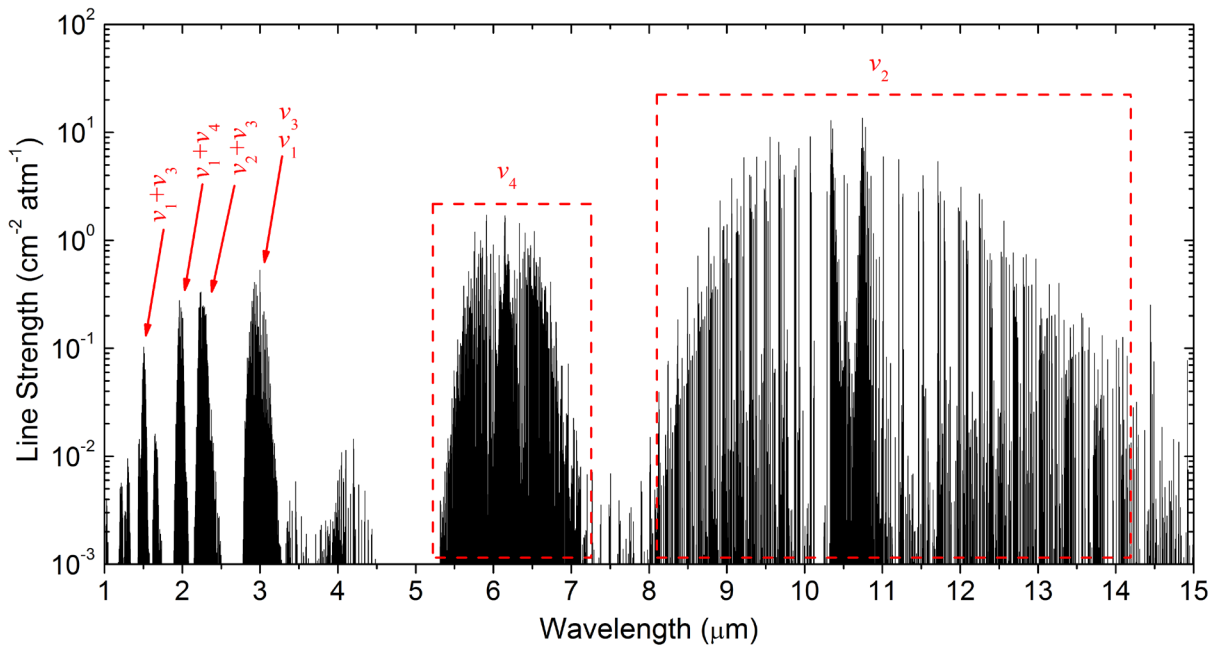

Figure 2: HITRAN prediction of the line strength of NH_3 transitions at 296 K in the Infrared.

Table 1: Summary of the fundamental vibrational bands of NH_3.

Band	Physical meaning	Location (cm^{-1})
v_1	Symmetric stretch	~3336
v_2	Symmetric bend	~932
v_3	Asymmetric stretch	~3443
v_4	Asymmetric bend	~1626

In the infrared, the v_2 fundamental band of NH_3, between 8 and 12 μm, has the highest line strength compared with the other, near-infrared bands. Previous spectroscopic studies of NH_3 in this region are extensive. Kleiner et al. [100] reported NH_3 line parameters that are used in the HITRAN database [44], while Chen et al. [101] provided NH_3 transition frequencies for the v_2 fundamental band. In the v_2 fundamental band, several experimental studies, using Fourier-transform spectroscopy, were conducted to measure line strengths and N_2-, O_2-, H_2-, and self-broadening coefficients [97, 99, 102-107]. Using quantum cascade lasers, line strengths and broadening

coefficients due to collisions of several perturbing species were measured by Owen et al. [98] for six sR(6,K) transitions near 1103.46 cm^{-1}, and by Sur et al. [108] for nine sQ(J,K) transitions in the range of 961.5–967.5 cm^{-1}.

There is a lack of studies focused on characterizing the temperature dependency of the broadening coefficients in the v_2 fundamental band. There are only three studies that investigated the temperature dependency of the broadening coefficients in this band; that of Nemtchinov et al. [105], Guinet et al. [99], and Sur et al. [108] which covered a temperature range of 200–296, 235–296, and 296–600 K, respectively. To the knowledge of the author, in the v_2 fundamental band, there are no reports of NH$_3$ high-temperature broadening coefficient with any molecule for combustion-like temperatures (> 600 K).

NH$_3$ LASER DIAGNOSTIC

Two types of experiments were performed to demonstrate the capabilities of the NH$_3$ laser absorption diagnostic used in the present study. First, static cell experiments were conducted to determine the NH$_3$ mole fraction present in a multi-component mixture. Second, shock-tube experiments were performed to follow NH$_3$ time histories at high-temperature during ammonia oxidation.

NH$_3$ measurements in both types of experiments were obtained using a quantum cascade laser (QCL). The QCL produced light corresponding to the v_2 fundamental band of NH$_3$ near 10.4 µm. The generated light has a narrow linewidth (~ 1.5 MHz) and was tunable over the frequency range of 957.5–963.0 cm^{-1}. This range allowed access to 12 NH$_3$ transitions that were spectroscopically characterized at room and high temperature in our previous study [109]. The laser was operated using a dual current and temperature controller (Arroyo 6310-QCL), and the wavelength of the laser light was monitored via an interferometer wavemeter (Bristol Instruments). The generated QCL light was split into two beams using a 50/50 beamsplitter, and the intensities from the two beams were monitored via two cryogenically cooled, HgCdTe photovoltaic detectors (InfraRed Associates). The static cell and shock-tube experiments utilized the same laser absorption diagnostic but employed different absorption techniques. Therefore, different experimental setups of the laser beams propagation were implemented for the static cell and shock-tube experiments which are illustrated in the schematics presented in Fig. 3a and Fig. 3b, respectively.
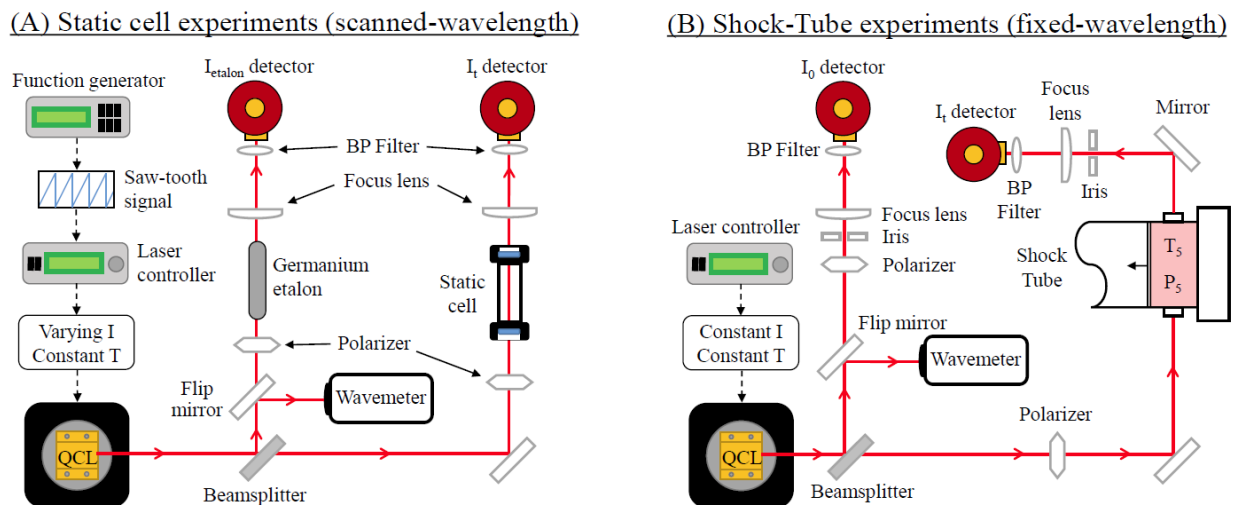

Figure 3: Schematic of the experimental setups employed in the present study for (a) Static cell experiments using the scanned-wavelength method, and (b) Shock-tube experiments using the fixed-wavelength method.

The static cell experiments utilized the scanned-wavelength laser absorption method. In this method, the laser frequency was rapidly scanned to capture the area under the absorption curve (to determine A) so that the NH$_3$ mole fraction (i.e. X_{abs}) can be determined directly via Eq. (2). This frequency scan was implemented by modulating the injection current of the laser using a 500-Hz sawtooth signal from a function generator. The experimental setup for this method was as follows: first, the generated QCL light is split into two beams using a 50/50 beamsplitter. The first beam passed through the static cell then terminated on one of the detectors. The reference intensity (I_0) for a baseline scan was recorded when the static cell was under vacuum, while the transmitted intensity (I_t) to capture the absorption curve was recorded when the NH$_3$-containing mixture was introduced to the cell. The second beam passed through a 5.08-cm solid germanium etalon and then terminated on the second detector. The fringes in the signal from this second beam (I_{etalon}) allowed determination of the relative frequency of the laser light during the scan. A sample raw experiment trace for the scanned-wavelength absorption method is presented in Fig. 4. Further details of this scanned-wavelength laser absorption method can be found in Alturaifi and Petersen [109].
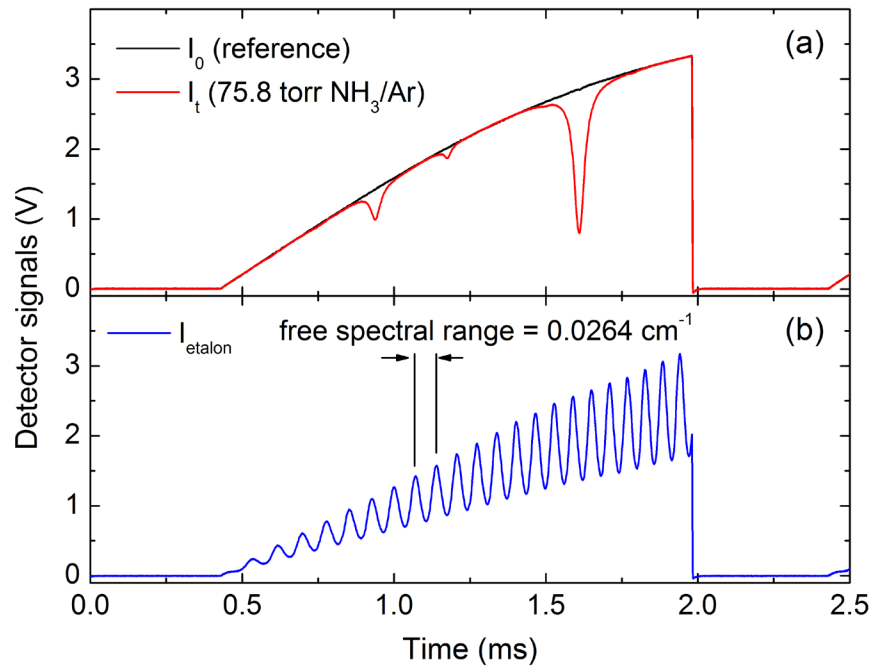
Figure 4: Sample scanned-wavelength experiment showing signals from (a) I_0 and I_t for a 75.8-torr mixture of NH_3/Ar and (b) I_{etalon} used for frequency calibration. The scan covered ~ 0.5 cm^{-1} and captured spectra from three NH_3 transitions near 958.0 cm^{-1}.

The shock-tube experiments employed the fixed-wavelength laser absorption method. In this method, the laser wavelength was fixed at the peak of the sQ(12,12) NH_3 transition at 957.839 cm^{-1} where S and ϕ are accurately known to determine the NH_3 time history (i.e. X_{abs}) using the Beer-Lambert Law. The experimental setup for this method was to split the laser beam into two halves. The first beam was directed towards a reference detector to measure I_0, while the second beam passed through the shock tube then directed into an incident detector to measure I_t. The signals from I_0 and I_t were collected using a differential preamplifier to reject common-mode signals. The laser transmission signal (i.e. I_t/I_0) is then used to infer the NH_3 time histories using Eq. (1). A representative shock-tube experiment showing the laser transmission signal using the fixed-wavelength absorption method is presented in Fig. 5. Detailed data reduction procedures to obtain the NH_3 time histories can be found elsewhere [110].
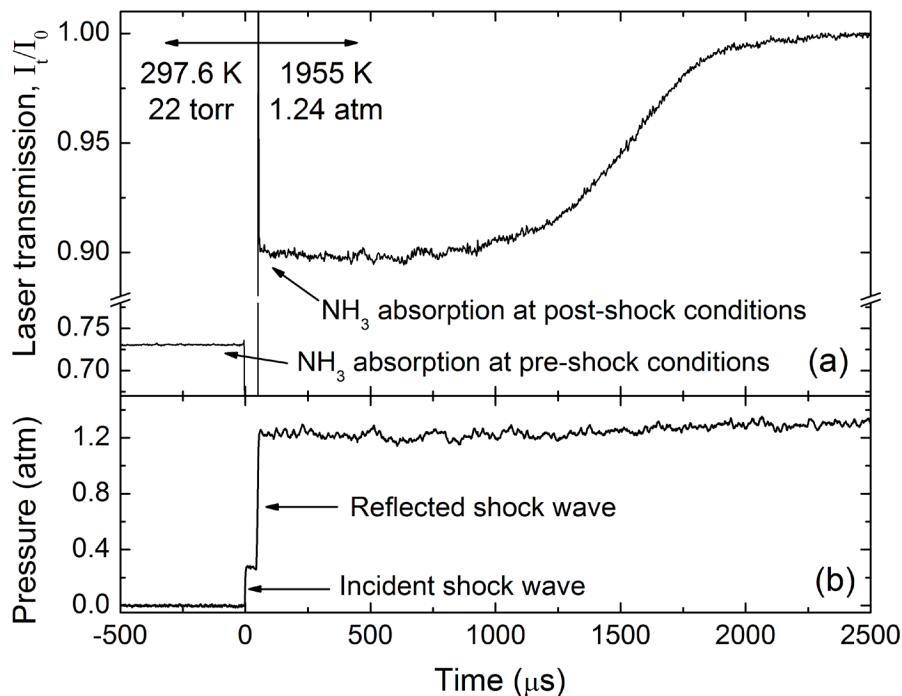

Figure 5: Sample shock-tube experiment using the fixed-wavelength method showing (a) Laser transmission signal and (b) pressure trace.

The shock-tube facility utilized herein was previously described [111]. In brief, the stainless-steel shock tube consists of a driven section with an inner diameter of 16.2 cm and a length of 6.78 m, and a driver section with an inner diameter of 7.62 cm and a length of 3.0 m. Piezoelectric pressure transducers were used to measure the incident shock wave velocity (v_s) as it propagates through the driven section. Using the 1D normal shock wave relations, the extrapolated v_s at the endwall location was used to calculate the reflected-shock pressure (P_5) and temperature (T_5) conditions with an uncertainty of ±1% [112]. The $NH_3/O_2/Ar$ mixtures were prepared via the partial pressure methods in a separate stainless-steel tank. All gases were supplied by Praxair with purity levels above 99.995%.

RESULTS

This section starts by presenting pure NH_3 spectra measurements using the new laser absorption diagnostics and comparing them with the predictions from HITRAN, followed by a presentation of the results from the static cell and shock-tube experiments utilizing the scanned-wavelength and fixed-wavelength methods, respectively. The goal of the static cell experiments was to measure the NH_3 mole fraction present in a multi-component mixture. This capability has a promise to be employed for the accurate determination of the NH_3 concentration present in a sample gas. The goal of the shock-tube experiments was to follow the NH_3 time history at high temperature during ammonia oxidation. This capability presents an excellent opportunity to study the chemical kinetics of ammonia.

Validation Experiments
Scanned-wavelength experiments were performed to validate the laser absorption diagnostics employed herein against the predictions from the HITRAN database. These experiments were conducted in a short cell (18.85 mm long) to capture the absorption curves of pure NH_3 at room temperature and low pressure (~ 15 torr). The absorption curves can be modeled using only the line strengths and self-broadening coefficients of the pertaining transitions; such parameters are available in HITRAN with relatively low uncertainties. The results from these experiments are presented in Fig. 6 where the top panel shows the experimentally captured absorption features from several NH_3 transitions between 957.5 and 962.5 cm^{-1}, while the bottom panel shows the HITRAN predictions. Overall, the experiments showed good agreement with the HITRAN prediction both in terms of the line positions and peak absorption.
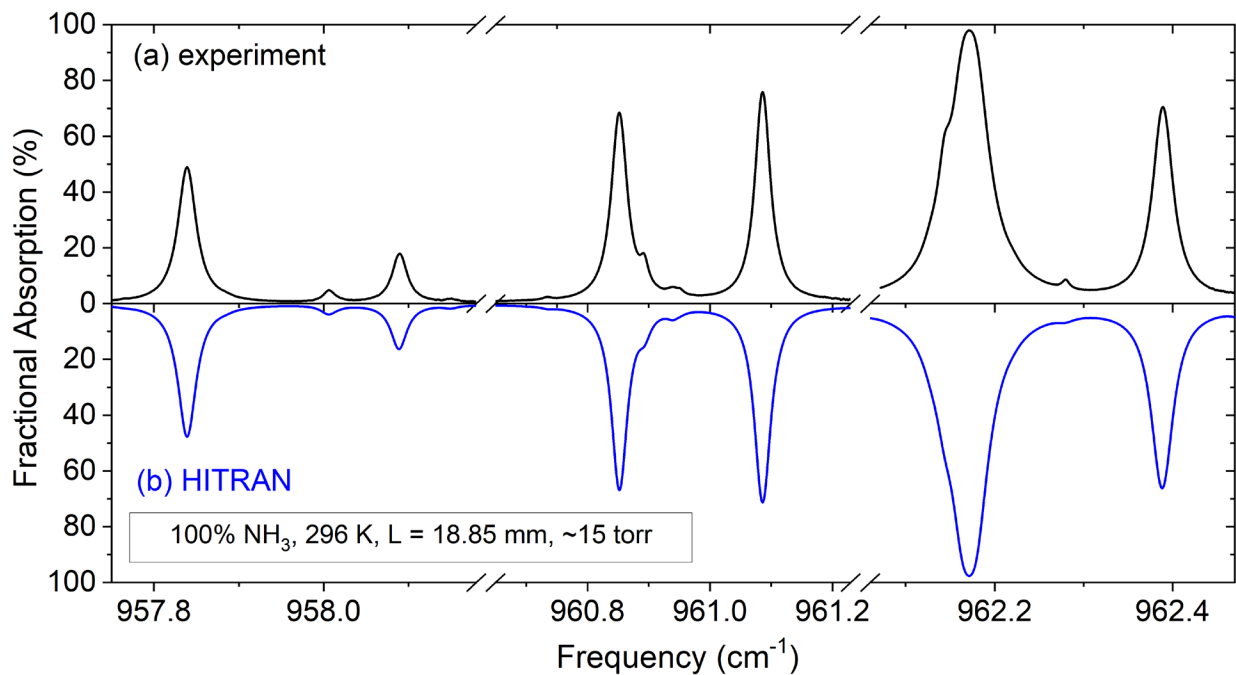

Figure 6: Room-temperature NH_3 spectra for selected transitions near 10.4 μm. (a) Experimental measurements and (b) HITRAN predictions.

Static Cell Measurements
Representative results from the static cell experiments using the scanned-wavelength method are presented in Fig. 7. In these experiments, 3–5% NH_3 was diluted in different bath gases of Ar, O_2, N_2, or He, and the absorption feature from scanning the laser across the sQ(12,12) transition was captured. The absorption features displayed drastically different line shapes due to the differences in the broadening coefficients of the bath gases; these coefficients were reported in our previous work [109]. Regardless of the broadening coefficient, NH_3 concentration in the gas mixture can be determined from the area under the absorption curve, in conjunction with the line strength of the transition. Careful experiment design, by manipulating the pressure P and pathlength L, permits the future use of this diagnostic to measure higher or lower NH_3 concentration in sampled gases regardless of the mixture composition.
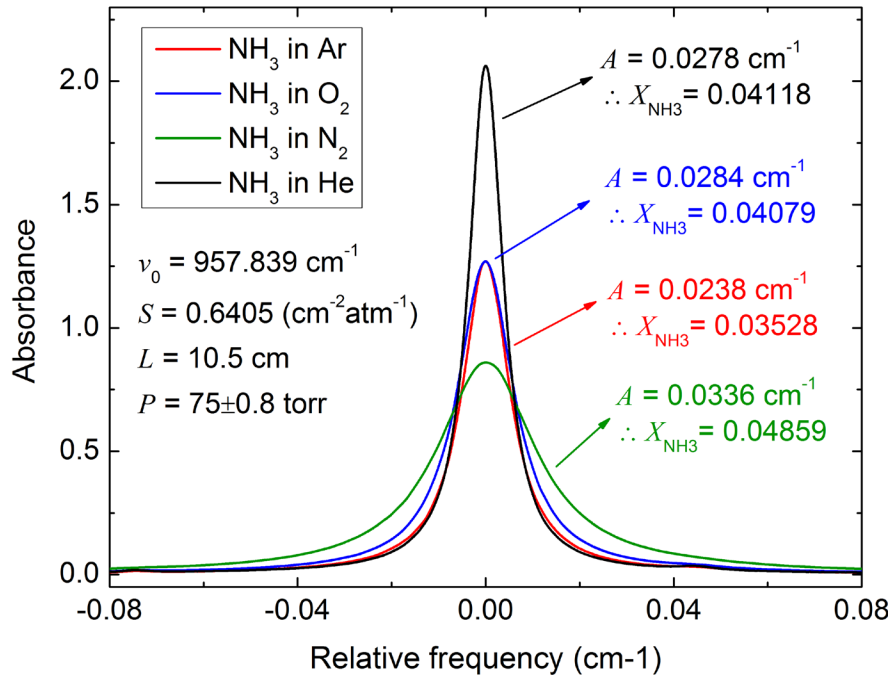
Figure 7: Absorption curves from NH$_3$ diluted in different bath gases of Ar (red), O$_2$ (blue), N$_2$ (green), or He (black). The area under the curve yielded NH$_3$ mole fraction.

Shock-Tube Measurements
A representative result of a shock-tube experiment using the fixed-wavelength method is shown in Fig. 8. This result was obtained from analyzing the transmission signal presented in Fig. 5. The experiment was conducted to follow NH$_3$ time history during the oxidation of a near-stoichiometric mixture of NH$_3$/O$_2$ in 99% Ar at 1955 K and 1.24 atm. Figure 8 also shows the simulation results from recent ammonia kinetics models [14,28,34,36,38]. The experiment result allows for assessment of the accuracy of available ammonia kinetics models. Such assessment is currently ongoing, but one can see that these recent models showed drastically different predictions, indicating the need for similar data to improve the knowledge on ammonia chemical kinetics. In particular, similar NH$_3$ time-history experiments to probe the high-temperature chemistry of nitrogen-based propellants will enhance the knowledge of its relevant chemical kinetics.
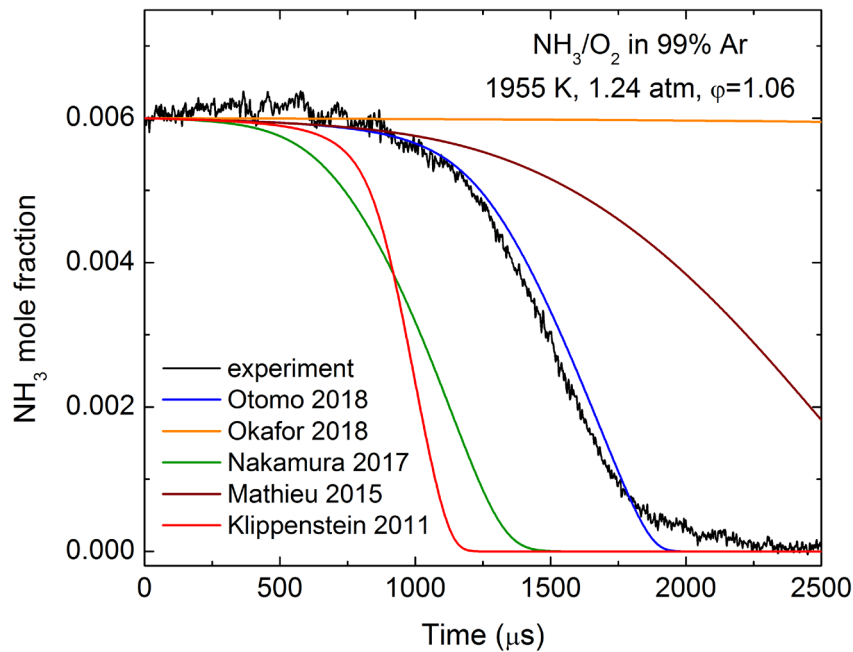

Figure 8: NH$_3$ time-history measurement during the oxidation of a near-stoichiometric mixture of NH$_3$/O$_2$ in 99% Ar at 1955 K and 1.24 atm. Experiments are compared with simulations from recent ammonia chemical kinetic mechanisms [14,28,34,36,38].

CONCLUSIONS

A newly developed NH$_3$ laser absorption diagnostic was utilized to perform experiments and highlight its promise in potential future usage, particularly for chemical kinetics studies. The NH$_3$ laser absorption diagnostic can access several NH$_3$ transitions near 10.4 μm in the ν$_2$ fundamental band. First, experiments to measure NH$_3$ absorption spectra using this new laser diagnostic were conducted and showed good agreement with the predictions from the HITRAN database. Second, the scanned-wavelength method was employed to measure NH$_3$ concentration in a cell containing multi-component gases. By scanning the laser over the sQ(12,12) transition, the area under the absorption curve allowed accurate determination of the NH$_3$ mole fraction in the gas mixture. Furthermore, the fixed-wavelength method was employed to follow an NH$_3$ time history behind a reflected shock wave. This NH$_3$ time history was obtained during the high-temperature oxidation of a near-stoichiometric NH$_3$/O$_2$/Ar mixture. The NH$_3$ time history was compared with the prediction of recent ammonia kinetics models to highlight the need for such data in future model validation.

The presented laser absorption diagnostic will be used in future works to measure NH$_3$ time histories behind reflected shock waves in a variety of mixtures, including mixtures pertaining to fuel-air combustion at engine conditions. These measurements will enable the investigation of NH$_3$ chemical kinetics, with applications to the use of ammonia as a modern fuel.

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