High-Temperature Absorption Coefficient Measurement of NH_2 at 597 nm

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1 Introduction

With the hope of reducing carbon footprints, fuels are being replaced with more climate-friendly options. Methane, a fuel for propulsion and energy production, produces carbon dioxide, a common greenhouse gas. Currently, hydrogen and ammonia have been considered potential replacements for methane due to both molecules missing carbon atoms, resulting in zero carbon dioxide production during combustion [1]. An issue with integrating ammonia into combustion is that ammonia chemical kinetics are undeveloped. Stable molecules such as NH_3, N_2O, and H_2O are well researched, but intermediate radical concentrations, such as NH_2 and NH, are unknown during combustion [1-7], thereby resulting in prediction deviations between multiple, prominent chemical kinetics models. A few previous studies have done this. Notably, Kohse-Höinghaus et al. and Votsmeier et al. have defined absorption coefficients for NH_2 at 597.375 nm, with Davidson et al. providing NH_2 data for ammonia pyrolysis [4, 8, 9]. However, Davidson et al. is the only article with NH_2 traces, therefore there is an absence of NH_2 data for chemical kinetics refinement. As a result, there is some variability in predicted NH_2 concentrations for ammonia pyrolysis. Ammonia pyrolysis at 2400 K and 1 atm is shown in Fig. 1 to depict the NH_2 variability between a few prominent models. The NH_2 concentrations in Fig. 1 were calculated to simulate the conditions behind a reflected shock wave, including 99% dilution with Ar.

To assist in resolving ammonia kinetics, an NH_2 laser diagnostic was developed. The new diagnostic uses a tunable diode laser stationed at 1197.75 nm producing 230 mW of power. The laser is connected to a waveguide mixer that changes the wavelength to 597.375 nm at 8.7 mW, which according to the literature, is an optimal wavelength to measure NH_2. This diagnostic is paired with an established NH_3 diagnostic stationed at 10440.17 nm. Both diagnostics are used with the aerospace shock tube (AST) located at the Texas A&M University (TAMU) turbomachinery laboratory. This study uses the NH_2 and NH_3 diagnostics during ammonia pyrolysis to obtain temporal concentrations during the high-temperature conditions within the shock tube. Using an accurate NH_3 model, such as Alturaifi et al. 2022, the NH_2 laser will be calibrated, resulting in a full absorption coefficient curve for NH_2. Provided in this paper is a summary of the experimental methodology, including descriptions of the shock-tube facility and the two-laser absorption diagnostic setups. Results from the experiments are then presented, with an emphasis on the measurement of NH_2 time histories under NH_3 pyrolysis to obtain a calibration for the spectroscopic absorption coefficient of NH_2.

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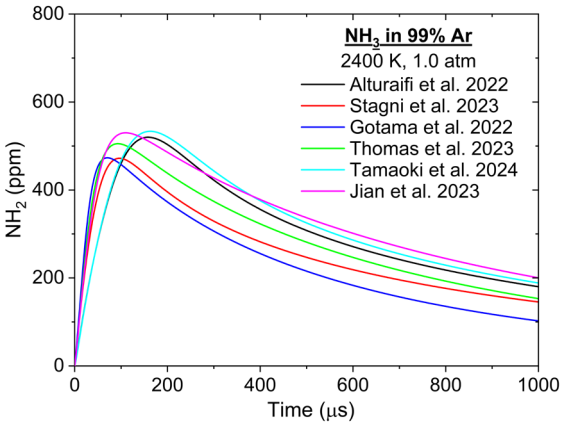

Figure 1: A comparison of ammonia models predicting NH_2 concentrations during ammonia pyrolysis at 2400 K, 1 atm. The models include Alturaifi et al. 2022 [2], Stagni et al. 2023 [10], Gotama et al. 2022 [11], Thomas et al. 2023 [12], Tamaoki et al. 2024 [13], and Jian et al. 2023 [14].

2 Methodology

The aerospace shock tube (AST) at Texas A&M University (TAMU) was chosen for this study. The AST features a driven section with a 16.2-cm diameter, at 7.88 m long, and a driver section at 7.62-cm diameter at 3.25 m long. The AST is a high-purity, pressure-driven shock tube featuring 8 sidewall ports evenly circumferentially spaced, 1.6 cm from the endwall. The current diagnostic setup for the AST is shown in Fig. 2. Seven ports are used for optical access, 6 for laser transmission, and the last port for photomultiplier tube access. Additionally, along the last 1.56 m of the driven section, 5 PCB Piezotronics pressure transducers (model 113A22) are placed, with the last pressure transducer being located 1.6 cm from the endwall. This study only employed the NH_3 and NH_2 diagnostics, but future integration of a CO or N_2O laser diagnostic is possible with the current setup.

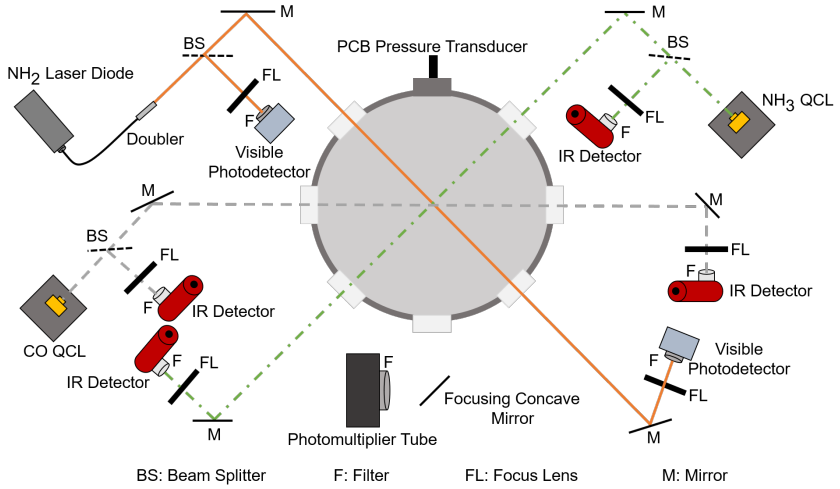

Figure 2: General schematic of the diagnostics located 1.6 cm from the endwall.

The NH_3 laser diagnostic is the same diagnostic found in Alturaifi et al. [2, 3]. The NH_3 diagnostic is comprised of a quantum cascade laser operating at 31.1°C at a wavelength of 10440.17 nm at ~27

mW. Detailed information on the data processing methodology of NH_3 in accordance with the Beer-Lambert law can be found in many works by Alturaifi and coworkers [2, 3]. An issue with operating with NH_3 in a stainless-steel shock tube is that NH_3 absorbs onto stainless-steel [2, 3]. As the mixture is inserted into the shock tube, the NH_3 concentration is going to be less than the initial amount made within the mixing tank. To prevent this loss of NH_3, a method known as passivation is used. Passivation entails using some of the mixture to coat the walls of the stainless steel with ammonia, and removing the excess gas prior to filling the shock tube with the intended amount of mixture [2]. Although this method is very efficient, it is not perfect, so it is possible to still have a differing concentration from the original mixture. For oxidation studies where the equivalence ratio is a key aspect in modeling, this uncertainty would be noticeable, but this study intends to only inspect ammonia pyrolysis. Therefore, it is acceptable to have some ammonia loss as long as the NH_3 diagnostic is able to measure directly the starting concentration.

To measure ammonia concentrations, a few modifications are done to the Beer-Lambert Law. The absorption of ammonia changes drastically between the pre- and post-incident shock condition. Additionally, ammonia does not experience pyrolysis until it reaches temperatures greater than about 1650 K [2, 4]. The pre- (T_1) and post-incident (T_2) shock temperature, on average, are 293 and 1130 K. Additionally, pressure varies between 0.02 atm and 0.23 atm for pre (P_1) and post-incident (P_2) shock conditions. Constant conditions are assumed since the post-incident shock conditions only exist for a short period of time (~50 μs). Using this assumption and modifying the Beer-Lambert relationship under the assumption the mole fraction (X_{Abs}) and test section length (L) are kept constant and the signal between the pre- and post-incident shock conditions are unchanged, the equation below is obtained where the change in signal is directly contributed to the change in pressure and absorption coefficient (k_v).

$$X_{Abs} = \frac{\ln\left(\left({}^{I_t}/_{I_0}\right)_{avg,2} * \left({}^{I_0}/_{I_t}\right)_{avg,1}\right)}{L(P_1 k_{v,1} - P_2 k_{v,2})}$$

The NH_2 laser absorption diagnostic is comprised of a tunable diode laser operating at 1197.75 nm at 230 mW. The laser is connected to a waveguide mixer through a single-mode fiber. The waveguide mixer takes the incoming beam and halves the wavelength (597.375 nm). The power of the beam out of the waveguide mixer is significantly lower than the incoming power (~8.7 mW). Similar to the NH_3 diagnostic, the NH_2 is separated into two beams, with one going straight to a visible photodetector (I_0) and the other traversing the shock tube into a different photodetector (I_t). Preferably, a similar data processing method to the NH_3 diagnostic would be adopted. However, NH_2 spectroscopic data is relatively unknown. Fortunately, a few studies have observed NH_2 absorption in the visible spectrum. Dressler and Ramsay detailed NH_2 absorption line strengths between 513.5 and 630 nm, followed by Green and Miller observing relative NH_2 concentrations across a burner using a 597.375-nm laser [15, 16]. Kohse-Höinghaus et al. applied the same wavelength to measure the absorption coefficient of NH_2 between 1600 and 3200 using an ammonia pyrolysis mechanism and NH_3 photolysis [8]. This study was shortly followed by Davidson et al., which applied the absorption coefficient to measure NH_2 concentrations during ammonia pyrolysis [4]. The results from that study produced the only available NH_2 data for chemical kinetics calibration to date.

Since the initial study by Kohse-Höinghaus et al., there has been a correction for the absorption coefficient of NH_2 by Votsmeier et al. who outlined that the absorption coefficient is off by around 30% between the temperatures of 1600 and 1950 K, which is approximately the uncertainty attached to the absorption coefficient in the original study [8, 9]. There is a possibility for a higher-temperature absorption coefficient deviation to also occur in Kohse-Höinghaus et al. since Votsmeier et al. did not investigate higher-temperatures (2000 to 3200 K) absorption coefficients. In addition to this, Kohse-

Höinghaus et al. created an ammonia pyrolysis mechanism to calibrate the NH_2 laser and obtain the absorption coefficient curve. To reiterate the method from Kohse-Höinghaus et al., a wavelength of 597.375 nm was used to measure NH_2 concentration during NH_3 pyrolysis. However, the chemical kinetics for ammonia has significantly improved within the last decade. Therefore, a modernization of methodology outlined by Kohse-Höinghaus et al. was adopted. Rather than creating a new kinetics mechanism, the model outlined in Alturaifi et al. 2022 is used. Alturaifi et al. 2022 has verified the NH_3 pyrolysis kinetics model, making it ideal for calibration purposes [2]. Note, NH_3 concentrations are accurate within the model, but NH_2 concentrations are relatively unknown, therefore the calibration timeframe should be limited. To apply this constraint, a sensitivity analysis for NH_2 based on each condition is conducted, where the maximum calibration time is determined based on the time it takes for all NH_2 destruction reactions to sum to 0.05.

Figure 3 depicts an example of a sensitivity analysis done for one of the experiments included in this study. As shown, the majority of NH_2 production occurs from $NH_3 + M \leftrightarrow NH_2 + H + M$ and $NH_3 + H \leftrightarrow NH_2 + H_2$. These reactions are dominant in the beginning of ammonia pyrolysis, with no known destruction reactions occurring until around 50 to 100 µs. As previously mentioned in this study, NH_2 kinetics are unknown, therefore it is entirely possible that there are additional reactions not accounted for. To be conservative in the absorption coefficient measurements, this study limited the calibration time to as little amount of time under the maximum allotted time. For reference, Fig. 3 depicts a maximum calibration time (τ_{Max}) of 217 µs, yet only 100 µs were actually used for calibration purposes. Extending this calibration time past 100 µs does not change the absorption coefficient, but any slight changes to the calibration time were used to define an uncertainty. Therefore, the calibration time is limited to only the necessary time without major changes in the absorption coefficient. The calibration time is often around 30-70% less than the maximum available calibration time. Using this method, a full absorption coefficient curve for NH_2 is obtained.

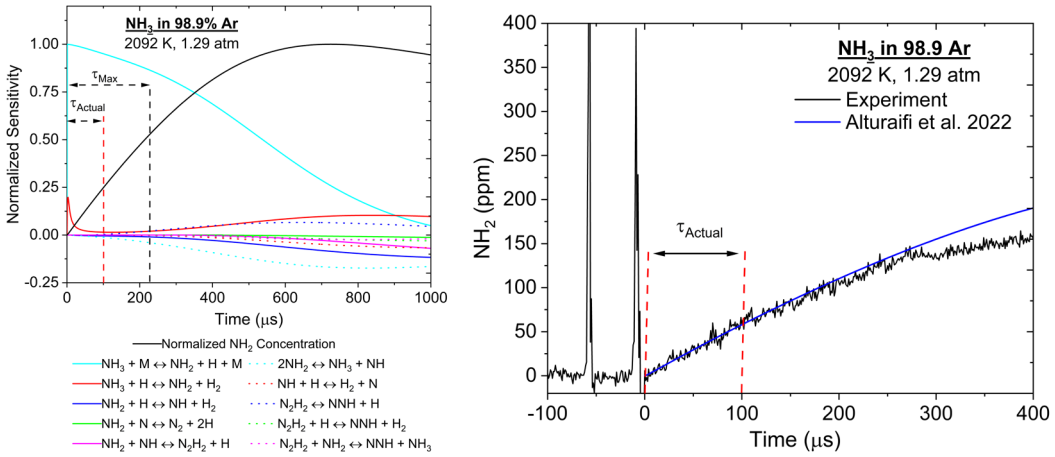

Figure 3: Sample NH_2 profile plotted along with the simulation from Alturaifi et al., 2022 [2]. The calibration window used for this experiment is boxed with dashes. τ_{Max} depicts the maximum amount of time allowable for calibration purposes using the criteria mentioned earlier in this section. τ_{Actual} is the amount of time used for calibration purposes. Left figure shows the sensitivity analysis and the right figure shows the extraction of the absorption coefficient, both at 1.29 atm, 2092 K.

3 Results

Three different mixtures of 0.008/0.20/0.792 NH_3/He/Ar, 0.008/99.2 NH_3/Ar, and 0.003/99.7 NH_3/Ar were used for the calibration experiments. Temperatures of 1993 to 2671 K were targeted.

Temperatures above 2700 K were avoided since the maximum calibration time would only be around 8-10 μs, thus making it difficult to calibrate the laser with a similar amount of accuracy. Temperatures below 1900K were also avoided due to the low NH_2 concentrations, making it difficult to measure. For these temperature ranges, different precursor molecules, like CH_3NH_2 or NH_3/H_2 blends, should be investigated. The original amount of ammonia is calculated using the NH_3 diagnostic. Next, the mixture composition is updated, and the post-reflected shock conditions are recalculated. The pyrolysis model from Alturaifi et al. computes the NH_3 and NH_2 profiles based on the new conditions. The NH_2 model is then compared with the NH_2 experiments to obtain the absorption coefficient per Section 2.3. An example of this process is shown in Fig. 3.

Figure 4 depicts the measured absorption coefficient compared with Kohse-Höinghaus et al., Votsmeier et al., Mertens et al., and Clees et al. The measured absorption coefficient in this study aligns well with the previous literature. The difference from Kohse-Höinghaus et al. is best described by the significant improvements in ammonia kinetics [8]. As for Votsmeier et al., it is more difficult to pinpoint where the deviation between the absorption coefficients occurred. Although it is closer to the current study, Votsmeier et al. did use a model for CH_3NH_2. At the time of the study, monomethylamine had a couple of well-defined reactions, but similar to this study and Kohse-Höinghaus et al., NH_2 kinetics are fairly unknown [9]. Additionally, using a large molecule such as monomethylamine requires more reactions, thereby increasing the uncertainty in NH_2 reactions, and therefore in the measurements. The absorption coefficient curve obtained in this study agrees with the absorption coefficient from Mertens et al. and Clees et al. [17, 18]. For future studies, the absorption coefficient curve from Mertens et al. will be used since the current absorption coefficient curve in this study agrees extremely well with Mertens et al. and Mertens et al. is validated for a larger range of temperatures [18].

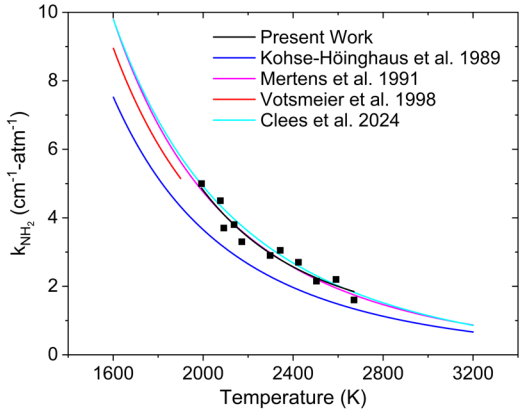

Figure 4: NH_2 absorption coefficient based on temperature. The best fit calculated with the experimental results from this study is $k_{NH_2} = 9.6989 \times 10^{10}/T^3 - 4.7499 \times 10^7/T^2 + 9.1168 \times 10^3/T$. Based on the variation of the absorption coefficient from variables such as calibrating time and human error, the uncertainty is estimated to be ± 15%. The results are plotted with the absorption coefficient best fits from Kohse-Höinghaus et al. [8], Votsmeier et al. [9], Mertens et al. [18], and Clees et al. [17].

4 Conclusion

An NH_2 laser diagnostic has been developed and tested to assist in resolving ammonia kinetics. The NH_2 laser absorption diagnostic was utilized along an NH_3 laser diagnostic for initial ammonia concentration verification during ammonia pyrolysis. Using the Alturaifi et al., 2022 model, the absorption coefficient for NH_2 was obtained and compared with the previous studies from Kohse-Höinghaus et al., Mertens et al., Votsmeier et al., and Clees et al. at a wavelength of 597.375 nm. The

NH2 absorption coefficient curve from Mertens et al. will be used for future NH2 studies due to the significant agreement with this work and larger temperature validation.

Acknowledgments

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