

Emission Spectra from Oxygenated Ammonia Spherical Laminar Flames

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1 Introduction

The increase of harmful impacts caused by CO₂ emissions released from hydrocarbon combustion in the power generation sector has led to the exploration of alternative, environment-friendly energy sources. Renewable energy is, of course, the primary candidate. However, renewable energy sources are intermittent, leading to liability in the form of energy storage. Energy storage methods include thermal storage, mechanical storage, chemical storage, and batteries. Hydrogen (H₂) has been a good candidate as a chemical storage element with no CO₂ fingerprint, and it can be utilized as an energy carrier. However, H₂ has some drawbacks such as its extremely flammable nature and the high economical cost related to its storage and transportation [1]. On the other hand, ammonia (NH₃) is a promising chemical storage candidate. However, it has low flammability limits which means that it is also difficult to ignite. Additionally, its storage and transportation costs are significantly cheaper than those for H₂. For example, low-pressure propane tanks can be used when handling NH₃ [1].

As for any fuel, a detailed chemical kinetics mechanism for NH₃ is necessary to understand its combustion chemistry. One primary key for validating a kinetics mechanism is the laminar flame speed. The literature has a great deal of experimental studies of NH₃ laminar flame speed [2-5], but with several inconsistencies in the reported data. One of the main challenges of laminar flame speed measurements of ammonia, especially via outwardly propagating flame setups, is its low flame speed at room temperature (< 10 cm/s). In this case of low flame speed, the buoyancy effect dominates the flame, leading to difficulties in determining the flame speed. To overcome these difficulties, several additives are often added to the NH₃ mixtures to boost the flame speed and to avoid any buoyancy effect [2-5]. Another possibility to overcome these difficulties is to use oxygen-enriched mixtures to increase the flame speed [2, 5]. In the present study, the focus was on studying pure ammonia, so the latter option (oxygen-enriched mixture) was selected.

In addition to the laminar flame speed being one aspect to understand the combustion behavior of NH₃, one other aspect of improving the understanding of the combustion chemistry of NH₃ is to explore the emission spectra of spherically expanding flames under controlled, laboratory conditions. As a result, in the present study the chemiluminescence spectra of an oxygen-enriched mixture of NH₃ + (25% O₂ + 75% N₂) was investigated. All initial conditions such as pressure and temperature were kept constant for all cases except when varying the equivalence ratio to study its effect on the NH₃ emission spectra.

Emission spectra of NH_3 -containing mixtures has grabbed the attention of combustion research groups in recent years. For instance, Zhu et al. [6] looked into the emission spectra of premixed $\text{NH}_3/\text{H}_2/\text{air}$ flames, focusing on the ultraviolet (UV) and visible ranges. They utilized a counterflow burner setup in their investigation coupled with a special chemiluminescence arrangement. In their study, they focused on varying three different parameters and studied their effect on the emission spectra. These parameters included NH_3 fuel fraction (from 0.55 to 0.90), equivalence ratio (from 0.35 to 1.70), and strain rates (from 50 to 300 /s). Moreover, Mashruk et al. [7] investigated the chemiluminescence emission spectra of premixed $\text{NH}_3/\text{CH}_4/\text{air}$ swirling flames. They varied the equivalence to cover a range of 0.6 to 1.3, NH_3 fuel fraction between 0 to 0.70, and Reynolds number ranging from 10,000 to 40,000.

In all of these studies, NH_3 was always coupled with another fuel (i.e. H_2 or CH_4). In addition, to the best of the authors' knowledge, no emission spectra of neat NH_3 was studied using a spherically expanding flame apparatus. Therefore, the goal of this study was to provide new emission spectra from a spherically expanding flame of neat NH_3 in an oxygen-enriched mixture. Furthermore, the laminar flame speed for the same mixture was also measured. This paper starts by presenting the experimental setup including a description of the utilized constant-volume vessels and imaging system, the chemiluminescence setup, and the fuel mixture preparation. Next, the oxy-ammonia emission results are presented, followed by a presentation of the obtained laminar flame speed data.

2 Experimental Setup

All experiments were conducted using one of the constant-volume chambers designed for different flame speed measurements at Texas A&M University (TAMU). Two different optical diagnostics were adopted in this study. First, a modified Z-type schlieren imaging setup coupled with a high-speed camera was used to obtain laminar flame speed results. Second, a fiber-coupled spectrometer equipped with an intensified charge-coupled device (ICCD) camera was used to capture the emission spectra of the investigated mixtures. Experiments utilizing the schlieren imaging setup were conducted first. The main reason behind that was to provide a reference frame for every condition (i.e. $\phi = 0.8, 1.0, \text{ and } 1.2$) where the flame size stays the same. This reference frame was then used to tune the gate delay time on the other optical diagnostic setup (i.e. spectrometer) to ensure that the captured spectra were within the same flame ball for each equivalence ratio, which was about a 9.5-cm flame diameter. A similar experimental setup was utilized by the current research group previously [8]. Detailed descriptions are following.

A high-temperature, high-pressure (HTHP) vessel having a cylindrical shape was used in the current study. It has an internal diameter of 31.8 cm, a length of 28 cm, and a volume of 25.8 L. This vessel was designed for experiments with initial temperatures and pressures up to 600 K and 30 atm, respectively. Detailed description of this vessel can be found in previous works [9-14]. The HTHP vessel has two, opposed, glass windows with a diameter of 12.7 cm allowing for optical diagnostics of a near-constant pressure spherical flame using the schlieren technique. The spherically propagating flame was captured using a modified Z-type schlieren imaging setup along with a high-speed camera at a rate of 3000 fps. Additionally, a mercury lamp was used on this setup as a light source. The collected images were then processed using an in-house Python code that was designed to capture the flame-front edges. Then, with the help of the non-linear equation examined by Chen [15], the laminar flame speeds were determined. Lastly, the burned-to-unburned density ratios for all experiments were quantified using chemical equilibrium calculations, which then were used to compute the unstretched, unburned flame speed.

Emission spectra of the oxy-ammonia mixtures were captured using a fiber-coupled spectrometer (Princeton Instruments, model: IsoPlane 160) equipped with an ICCD camera (Princeton Instruments, model: PIMax4). The width of the vertical entrance slit was set to 150 μm . In the current study, the main goal was to obtain preliminary results of the oxy-ammonia flame spectra for the UV and visible ranges. As a result, a low resolution, with a grating of 300 lines/mm was used to record the data. This grating produces a spectral resolution of 0.204 nm/pixel, approximately. For these lower-resolution tests, the measurable wavelength bandwidth was limited to 200 nm, although the camera/spectrometer setup

sensitive to a broader range (i.e. 200 to 850 nm). Therefore, three single-shot experiments were required for every condition to cover the 200-to-800-nm spectral range. These three experiments were distributed at three different locations on the spectrum range, starting at 300 ± 100 nm, then 500 ± 100 , and finally 700 ± 100 nm. A calibration of the camera/spectrometer system was done utilizing Princeton Instruments Intellical calibration and a Hg lamp. The signal intensity was not calibrated as the calibration only applies in the visible region. However, the peak emission line at 283 nm was scanned across the pixel array by changing the spectrometers central wavelength position. Scanning the emission line across the pixel array confirmed negligible intensity variation across the pixel array. Taking advantage of the 12.7-cm diameter glass windows on the HTHP vessel, a collimating lens was set at the center of one of the two windows to capture the emission at the desired flame size. Figure 1 shows a schematic of the spectrometer optical setup and test vessel.

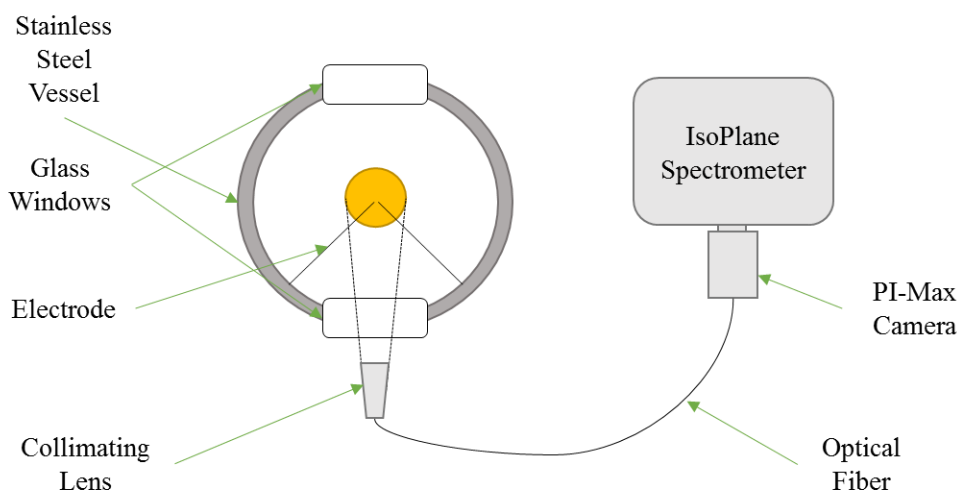


Figure 1: Schematic of the camera/spectrometer system along with the HTHP vessel.

The investigated mixture in this study contained NH_3 (99.995%) as the fuel, whereas the oxygen-enriched mixture was 25% oxygen (O_2) and 75% nitrogen (N_2). The higher percentage of O_2 was to provide a faster flame to overcome the buoyancy effect observed during a typical NH_3/Air experiment. The experimental procedures start with adding the NH_3 to the HTHP vessel to the desired partial pressure corresponding to the targeted equivalence ratio. Following that, O_2 and N_2 are added separately to their desired partial pressures to satisfy the 25% O_2 and 75% N_2 goal. Something to note here is that between every component the entire manifold is flushed twice with the next component to be added. After adding all components, the mixture is then left for 10 minutes before ignition to ensure a homogeneous mixture. Just before ignition, the final total pressure is recorded using the manifold's 0-1000 torr pressure gauge, while the final temperature is recorded using the thermocouple mounted on the vessel. To investigate the effect of fuel/oxidizer mixture on the recorded spectra, three different mixtures were investigated: lean, stoichiometric, and rich with equivalence ratios of 0.8, 1.0, and 1.2, respectively. In addition, laminar flame speeds for the equivalence ratio range of 0.8-1.4 were obtained. For all of these experiments, the initial conditions were fixed at 1 atm and 423 K.

3 Results and Discussion

As mentioned in the previous section, three different mixtures were investigated. These mixtures were prepared as $\text{NH}_3/\text{enriched-air}$ (25% O_2 and 75% N_2) with three different equivalence ratios of 0.8, 1.0, and 1.2. The initial pressure and temperature of the mixtures in the vessels were fixed at 1 atm and 423 K, respectively. In this section, a result of the emission spectra of $\text{NH}_3 + (25\% \text{O}_2 + 75\% \text{N}_2)$ mixture

over the wavelength range of 200 to 800 nm is presented. Following that, the experimental laminar flame speed over an equivalence range of 0.8 to 1.4 is shown, accompanied by laminar flame speed predictions using a previously published chemical kinetics model.

Figure 2 presents the emission spectra of an $\text{NH}_3 + (25\% \text{O}_2 + 75\% \text{N}_2)$ mixture. Three different equivalence ratios were investigated, namely 0.8, 1.0, and 1.2 over a wavelength range from 200 to 800 nm, covering the UV and visible range. In this figure, all intensities were normalized by the maximum intensity, which in this case the intensity around 310 nm. Not surprisingly, the OH^* signal can be seen around 310 nm wavelength for all three equivalence ratios, providing the strongest signal for the stoichiometric case (as expected) compared to the lean and rich ones. Adjacent to the OH^* feature, one can see the peak of what most likely is NH^* , at approximately 339 nm. Moving toward the visible range, a wide, broadband feature can be seen for all mixtures. Within this broadband, NH_2^* was detected at 5 different locations, namely, 543 nm, 572 nm, 605 nm, 634 nm, and 663 nm. In addition, at 735 nm a peak was detected and it could be NH_2^* or HNO . The NH_2^* features captured between 543 and 663 nm were becoming stronger as the mixture got richer. The NH_2^* feature captured at 605 nm, the NH^* feature at 339 nm, and the OH^* feature at 310 nm were also captured in a previous published study [7]. The experimental apparatus used in [7] was a swirl flame setup, while in the current study a spherically propagating flame apparatus was used. This agreement in detecting different radical species utilizing different experimental apparatus will pave the road towards more advanced chemiluminescence investigation of ammonia flame mixtures adopting the spherically propagating flame apparatus.

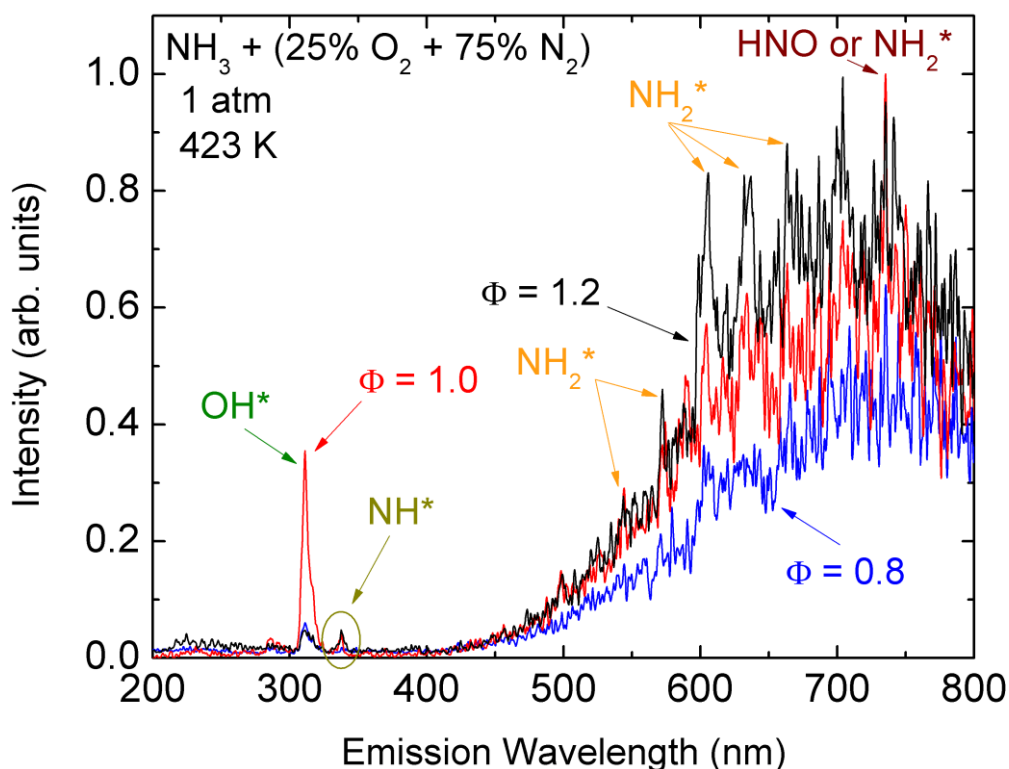


Figure 2: Measured emission spectra of $\text{NH}_3 + (25\% \text{O}_2 / 75\% \text{N}_2)$ at 1 atm, 423 K, and three different equivalence ratios.

Laminar flame speeds for the studied mixture were also obtained for the equivalence ratio range of 0.8 to 1.4 and initial pressure and temperature of 1 atm and 423 K, respectively. Figure 3 shows the laminar flame speed results against equivalence ratio. Along with those, a prediction of laminar flame speed for the same mixture was generated using the chemical kinetics model of Wang et al. [16] using the Chemkin-Pro software package. The flame speed results of $\text{NH}_3 + (25\% \text{O}_2 + 75\% \text{N}_2)$ followed the

expected pattern where the flame speed peaks at an equivalence ratio near 1.1 with a value of 22.7 cm/s. The laminar flame speed predictions obtained by the Wang et al. [16] mechanism show some deviation from the experimental results, especially on the lean side; it appears to be closer on the rich side. Some repeated experiments were done (i.e., 3 repeats for $\phi = 1.2$) to come up with a reasonable experimental laminar flame speed uncertainty. The t-student distribution with a 99% confidence interval was adopted and resulted in an error of 1.2 cm/s (i.e. 5.7%) for the laminar flame speed of the $\text{NH}_3 + (25\% \text{O}_2 + 75\% \text{N}_2)$ mixture.

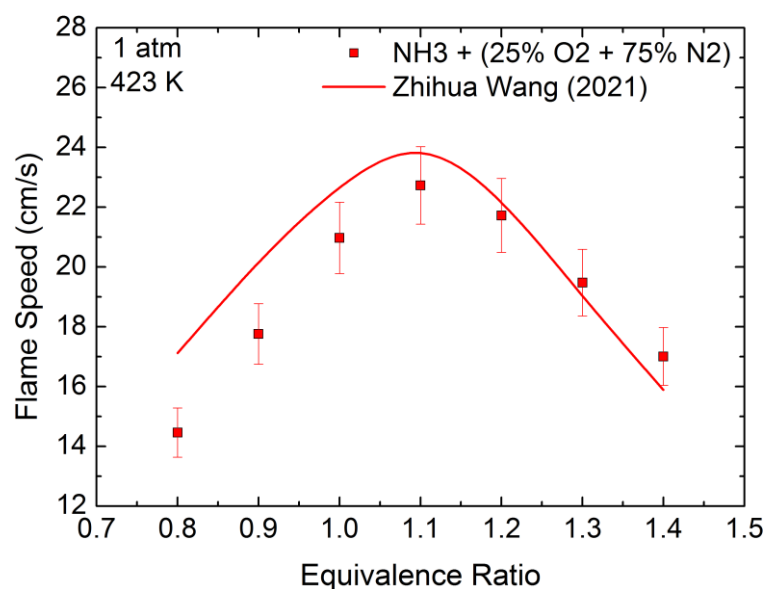


Figure 3: Measured laminar flame speeds of $\text{NH}_3 + (25\% \text{O}_2 / 75\% \text{N}_2)$ at 1 atm and 423 K.

4 Conclusion

An oxy-ammonia mixture was investigated with the focus on the emission spectrum for the range of 200 nm to 800 nm. Some excited species were spotted for different mixtures. For instance, OH^* feature was noticeable at approximately 310 nm for lean, stoichiometric, and rich condition, with the one at stoichiometric being the strongest as expected. Also, there was some evident of a contribution from NH^* at a wavelength of 339 nm for all three mixture condition ($\phi = 0.8, 1.0, \text{ and } 1.2$). Finally, the visible range (~ 400 to 800 nm) experienced a wide broadband feature with an NH_2^* feature at 5 different locations, namely, 543 nm, 572 nm, 605 nm, 634 nm, and 663 nm. In addition, at 735 nm a peak was detected that could be due to NH_2^* or HNO . Moreover, the laminar flame speeds of the aforementioned oxy-ammonia mixture were obtained for the whole of equivalence ratios between 0.8 and 1.4. Along with those, a previously published chemical kinetics model was utilized to predict the laminar flame speed for similar conditions. These predictions showed some deviation (2 to 18 %) from the obtained laminar flame speed data.

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