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## 2<sup>nd</sup> Symposium on Ammonia Energy

### Detailed study of NH<sub>2</sub>\* chemiluminescence in ammonia combustion

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#### Introduction

Ammonia combustion is of great interest as it is a zero-carbon fuel, easy to store and transport, and has a high-octane rating which is desirable in spark-ignition engines; making it an attractive fuel. Burning ammonia also comes with some disadvantages like narrow flammability limit, difficulty to ignite, and emission of NO<sub>x</sub> in case of partial combustion. To overcome these difficulties, the flame properties must be studied. The formation of excited molecules as a result of collisions or due to chemical reactions and the subsequent emission of light as these excited molecules return to the ground state is called chemiluminescence. Chemiluminescence is a cheap and non-intrusive diagnostic tool that is often used to obtain various information on flame stabilisation, prediction of NO<sub>x</sub> emissions [1,2], to assess the equivalence ratio [3,4], flame topology before the blowout [5] etc. On assessing the emission spectra of ammonia-air flames, it was seen that the band of NH<sub>2</sub>\* peaks that lied in the orange part of the visible spectrum dominated the spectra. It was these emissions that imparted the orange hue to the ammonia-air flames. From literature [6], it was seen that both NH<sub>2</sub>\* and NH\* are good indicators of the position of the maximum heat release rate. Since the emission intensity of NH<sub>2</sub>\* is higher than NH\*, it is good enough to focus on NH<sub>2</sub>\* as a first step. The aim of this work is to perform NH<sub>2</sub>\* chemiluminescence experiments in both a shock tube configuration and in a Bunsen burner configuration, to understand the chemical kinetics of NH<sub>2</sub>\*, and finally to propose and validate an NH<sub>2</sub>\* sub-mechanism using the obtained experimental data.

#### Materials and Methods

##### Shock tube

The experiments performed at Texas A&M University (TAMU) were conducted in a single-diaphragm, stainless-steel shock tube with a 3-m-long driver section (7.62 cm in diameter) and a 6.78-m-long driven section (16.2 cm in diameter). Helium was used as the driver gas, giving a test time of around 3 ms under the conditions investigated. Five piezoelectric pressure transducers (PCB 113B22) positioned near the end wall of the shock tube, with a well-known spacing between them, were used to measure the velocity of the incident shock wave so T<sub>5</sub> and P<sub>5</sub> could be calculated using 1-D shock relations. Initial composition was X<sub>NH<sub>3</sub></sub> = 0.00605, X<sub>O<sub>2</sub></sub> = 0.00395, X<sub>Ar</sub> = 0.99000. To reduce the effect of NH<sub>3</sub> adsorption in the shock tube, a passivation technique was carried out prior to each experiment in the shock tube, following the procedure described in [7]. To estimate the composition of the initial mixture with accuracy post passivation, the H<sub>2</sub>O time histories were measured during experiments with the use of a laser absorption diagnostic described in Mathieu et al. [8]. Experimental conditions were such that a plateau in the water formation was observed for each experiment. The water concentration at this plateau was then used to back calculate the composition of the original mixture (the amount of O<sub>2</sub> and Ar being unchanged) by fitting the profiles with existing base mechanisms. The equivalence ratio was consistently 0.32 for all runs with an error of ±0.01, indicating high repeatability in the method and a high level of wall adsorption for these very dilute mixtures, despite the passivation method.

Since the conditions behind the reflected shock waves are calculated using the mixture's composition and since the mixture composition and experimental conditions need to be implemented in the model to determine the equivalence ratio (and the temperature profile to vary the absorption coefficient as a function of the computed temperature), an iterative procedure was necessary until converging to the final values.  $\text{NH}_2^*$  measurements were taken using narrowband filters centred at 633 nm, as reported in Pugh et al. [1].

### Bunsen burner

The chemiluminescence from ammonia flames was also studied by performing experiments on a Bunsen burner at atmospheric pressure for premixed ammonia-air mixtures with an equivalence ratio ranging between 0.9 and 1.4. Since ammonia flames are weak in nature, a co-flow of stoichiometric methane-air flame is used to stabilise the main flame. The effect of the pilot flame on the main flame has been studied by changing the power emitted by the pilot flame and it was observed that there was no direct influence of this pilot flame on the parameters measured in the main flame. The mean velocity of the fresh gases at the exit of the burner ranged from 0.18 to 0.2  $\text{m s}^{-1}$ . The exposure time of the camera was set to 200 ms. An instantaneous shot is used for the study as it was seen that an average flame perturbation of over 200 images is small i.e. the induced error % in thickness is 13% for an exposure time of 200 ms. The conversion factor is  $1.75 \times 10^{-2} \text{ mm pix}^{-1}$ . The chemiluminescence set-up consists of a low-speed camera with high resolution (Back-illuminated sCMOS Kuro with a frame size of  $2048 \times 2048 \text{ pix}^2$ ). A visible range objective lens is used for  $\text{NH}_2^*$  as it is found in the visible range of the emission spectra. A filter of interest is mounted upon the lens to record the emissions. For  $\text{NH}_2^*$ , a filter which is centred at 632 nm with a bandwidth of 10 nm and a diameter of 50 mm is used.

### Results and Discussions

Seven different temperatures varying between 2420 K and 1899 K were studied in the TAMU shock tube. The relative  $\text{NH}_2^*$  intensity decreases with the temperature. It was observed that there are two different behaviours exhibited by the cases of high temperature and low temperature. The high temperatures are associated with steeper slopes and sharper peaks, and the lower temperatures have slopes with lower gradients and blunt peaks. For the flames, it was seen that the width of the species increased as the equivalence ratio increased. The experimental data was fitted with Gaussian curves. The peak increased up to an equivalence ratio of 1.2-1.3 and then begins to decrease.

To develop a sub-mechanism for  $\text{NH}_2^*$ , a base mechanism is required. A literature survey on the existing kinetic schemes for ammonia combustion was done and the KAUST (2021) [9] model was chosen as it predicted the evolution of species within the error bars of the experimental data obtained in a JSR, ignition delay times in a shock tube, and laminar flame speeds and provides acceptable predictions for the two sets of data presented herein. This kinetic scheme was tested and modified to fit the decomposition results of Alturaifi et al. [10] and Davidson et al. [11]. For the collision partners, the rate constants were determined by using the collision theory. Thermodynamic properties, normalised by the gas constant, are found through three polynomial fits (see Kopp et al. [12]) using seven coefficients defined for two temperature ranges, 300 K-1000 K and 1000 K-5000 K. For the flames, simulations were done for an equivalence ratio ranging between 0.9 and 1.4 and, unlike the case of the shock tube, it was seen that using the only collisional reactions was not sufficient to reproduce the experimental  $\text{NH}_2^*$  profiles' behaviour and so other chemical reactions are required.

### Conclusions

From the seven different temperatures that were tested in the shock tube, experimental profiles were obtained and it was seen that higher emission intensities were associated with higher temperatures whereas from the Bunsen burner configuration, experiments were performed for equivalence ratio ranging between 0.9 and 1.4 at atmospheric conditions. It was seen that the thicker flames (i.e. higher concentrations of  $\text{NH}_2^*$ ) were associated with richer flames. To model the species, collision reactions were written with rate constants determined by using the collision theory. Other reaction pathways need to be identified to predict the profiles obtained from the Bunsen burner configuration. The present model is capable of predicting the width in case of the flames. For the profiles in the shock tube configuration, the model over predicts. On further probing, it was seen that a lot of work in understanding  $\text{NH}_2$  and  $\text{NO}_x$  chemistry is required to have a good prediction of  $\text{NH}_2^*$ .

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