Emission Spectroscopy of Nanosecond Pulsed Plasma Discharges in Ammonia/Air Flames

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Abstract: Emission spectroscopy of atmospheric pressure nanosecond (ns) pulsed plasma discharges in ammonia/air flames has been conducted. Key characteristics of single ns pulse and ammonia/air flames itself are obtained by identification of peaks in spectra. The time-resolved spectroscopy measurements further reveal discharge dynamics in ammonia/air. Moreover, the spatially resolved H_α line intensity provides insight into the kinetics effect on ammonia combustion enhancement.

Keywords: Spectroscopy, nanosecond pulsed plasma discharges, ammonia/air flames

1. Introduction

Over the past decades, plasma-assisted combustion (PAC) has been recognized as one of the most promising technologies for overcoming critical challenges in combustion processes, such as lean blowout and pollution emission issues [1]. As for ammonia (NH_3) combustion, currently the most popular for its huge potential of decarbonization in energy production, the plasma discharge effects remain open to the combustion community.

Nanosecond (ns) pulsed discharge, a type of non-equilibrium plasma, has been widely applied in the combustion of various hydrocarbon fuels and has shown significant effects on combustion enhancement in previous studies [2]. However, the applications of ns pulsed discharges on ammonia-fuelled flames have been scarcely studied yet. It is thus of primary interest for us to unravel the characteristics of ns plasma discharge in ammonia/air flames. Particularly, for discharges on the ns time scale, it is quite challenging to temporally resolve the discharge dynamics. In addition, for systems where plasma discharge and combustion chemistry processes coexist, little is known about the plasma-chemistry kinetics in ammonia/air flames, which is key to combustion enhancement. Therefore, there is an urgent need to characterize the ns pulsed discharge in ammonia/air flames.

In this work, we specifically chose a standard McKenna burner to produce a quasi-one-dimensional flat ammonia/air flame, and a pin-to-pin discharge configuration to produce ns pulsed discharges. Main efforts are devoted to measuring the emission spectra in the wavelength range from 200 nm to 800 nm. Characteristics of ns pulsed discharge in ammonia/air flames are further discussed.

2. Experimental setup

Fig. 1 shows a schematic of the experimental setup, including a McKenna burner, a nanosecond pulsed discharge, and a spectroscopy measurement system. The stainless-steel McKenna burner consists of two porous plugs for the central main- and co-flow gases. We supplied premixed ammonia/air to the main flow, and air for the co-flow. A built-in water-cooling system guarantees a constant inlet temperature at room temperature of around 298 K. A plate placed above the burner serves as a stabilizer to maintain the lifted flat flame, which can be regarded as quasi-one-dimensional, and thus a standard platform for kinetics study. The bulk flow rates of NH_3 and main air are 3.75 and 13.5 SLM, yielding a flow velocity at the nozzle of 11.1 cm/s. The thermal power is approximately 0.88 kW providing that NH_3 is completely consumed. An equivalence ratio of 1.0 and a small global strain rate of 5.5 s^{-1} ensure a steady stagnation planar flame.

For the nanosecond pulsed discharge configuration, the stabilizing plate provides an anchor point for a pin, which is connected to a high-voltage pulsed power supply (model FPG 200-1NM1). Another pin is placed on the burner nozzle and grounded. With a distance between these two pins of 20 mm in the current study, the pin-to-pin configuration can efficiently generate the pulsed plasma discharges. Here, we focus on the interaction between a single pulse and the flame rather than the synergy between multiple pulses, so the frequency is set to 1 Hz.

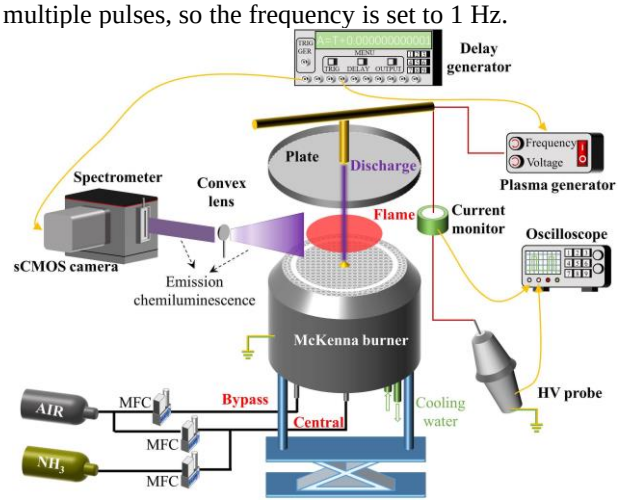

Fig. 1. A schematic of the experimental setup.

The voltage and current waveforms of the ns pulsed discharge at an applied voltage of 30 kV are shown in Fig. 2. The gas breakdown occurs at 8.5 kV, and after that, the voltage decreases to 3.4 kV. Subsequently, it reaches a peak voltage of 26.9 kV and the peak current is 103 A. The full width at half maximum (FWHM) of the discharge is around 6 ns. After the breakdown, the voltage and current drop dramatically, and then oscillate due to the capacitive impedance in the circuit until around 500 ns. The energy deposition in a single pulse discharge is estimated to be 9

μJ/pulse, indicating that the present plasma is quite energy-efficient compared to the thermal power of 0.88 kW.

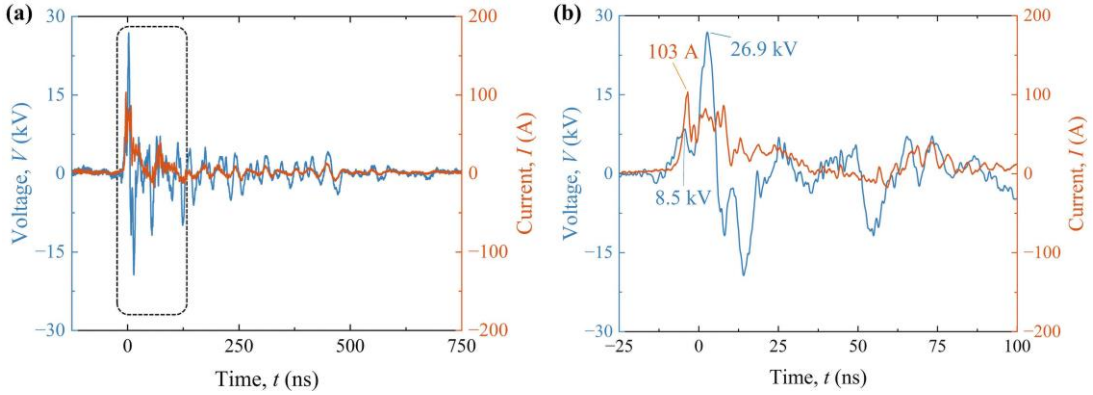

Fig. 2. Voltage and current waveforms of ns pulsed discharge at an applied voltage of 30 kV: (a) within 750 ns (b) a zoom-in view within 100 ns.

The chemiluminescence emission is focused onto the slit of a spectrometer (Princeton Instrument, model IsoPlane 160) through a concave lens (f = 150 nm). The spectra are captured by an sCMOS camera (Andor iStar 18x-63) equipped with the spectrometer. A slit width of 250 μm and a grating of 1200 groove/mm are chosen for a satisfying spectral resolution of 0.02 nm/pixel. The spatial resolution of each frame is 9 μm/pixel. As the chemiluminescence from discharge is much stronger than that from the flame, the camera gate width is set to be 20 ns and 500 μs for the ammonia/air flames with and without discharge, respectively. For the cases with pulsed discharge, a multi-channel delay generator (model DG535) is used to control the time sequence between the discharge and the camera. The efficiency of the spectroscopy system is calibrated using a standard light source (Thorlabs SLS301).

3. Results and discussion

In previous studies on methane/air flames using the ns pulsed discharge, we observed only one emission peak in the time domain after a 1 Hz discharge pulse [3]. Interestingly, however, in ammonia/air combustion, we have observed a primary and secondary emission peak with a time separation of around 70-80 ns within one single pulse period. Although this, here, we focus on the primary emission of discharge in ammonia/air.

We first examined the emission spectra of stoichiometric ammonia /air flames without discharges. Fig. 4 illustrates the spatially resolved spectral contours, where the abscissa and ordinate represent wavelength and axial distance, respectively. Fig. 4 is a plot of integrated chemiluminescence intensity with different wavelengths from 20 snapshots. As seen in Fig. 3(a), the OH band ($A^2\Sigma^+ \rightarrow X^2\Pi^1$) around 310 nm can be observed. And a relatively weak NH band ($A^3\Pi \rightarrow X^2\Sigma^-$) around 337 nm is also recognized. It can be seen that OH and NH are mainly produced adjacent to the flame front, while NH disappears in the post-flame zone. In Fig. 3(b-c), the spectrum from 500 nm to 800 nm shows broad bands from the NO_2 (500-600 nm) [4] and NH_2 α-band (540-550 nm) [5], which is the main contributor to the orange chemiluminescence of the NH_3/air flame. In the region of 550-700 nm, there is a strong continuum band. Possibly due to the low NO concentration and the low quantum efficiency of the sCMOS camera in the ultraviolet region, the NO band in the 220-260 nm range was not observed in the present work.

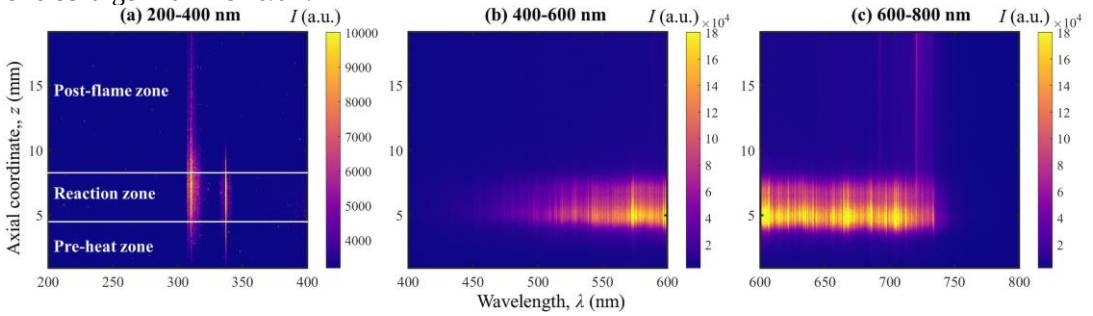

Fig. 3. Spatially resolved emission spectra of the stoichiometric ammonia/air flame. The pre-heat, reaction, and post-flame zones are marked by white lines.

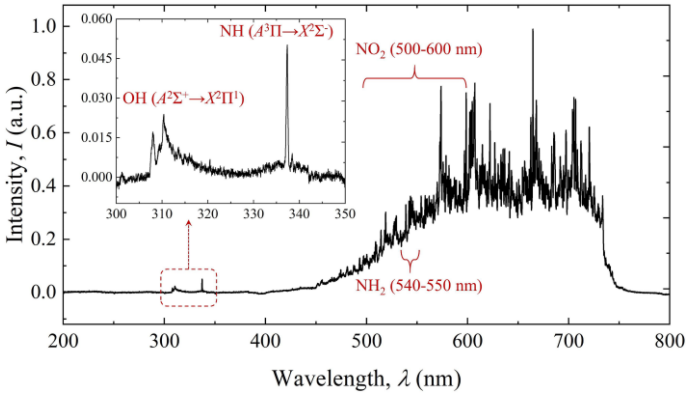

Fig. 4. Spectral intensity of the stoichiometric ammonia/air flame. The inset is a zoom-in view of OH and NH bands.

When applying a 1 Hz ns pulsed discharge on the stoichiometric ammonia/air flame, the spatially resolved contour and integrated intensity curve are illustrated in Fig. 5 and Fig. 6, respectively. Since we used a small gate width of 20 ns here, which can basically remove emission chemiluminescence from the ammonia/air combustion itself, the captured spectral signals mainly come from the plasma-induced species inside the discharge column. It can be easily observed that the bands of nitrogen have the strongest signals in the whole examined wavelength range. Within 300-450 nm, these excited N_2 bands of the second positive system ($C^3\Pi_u \rightarrow B^3\Pi_g$) with Δv = 2, 1, 0, -1, -2, and -3 are observed in Fig. 6.. Among them, the transitions with Δv = 0 are stronger than others. The band of N_2^+(B-X) in the first negative system is also observed.

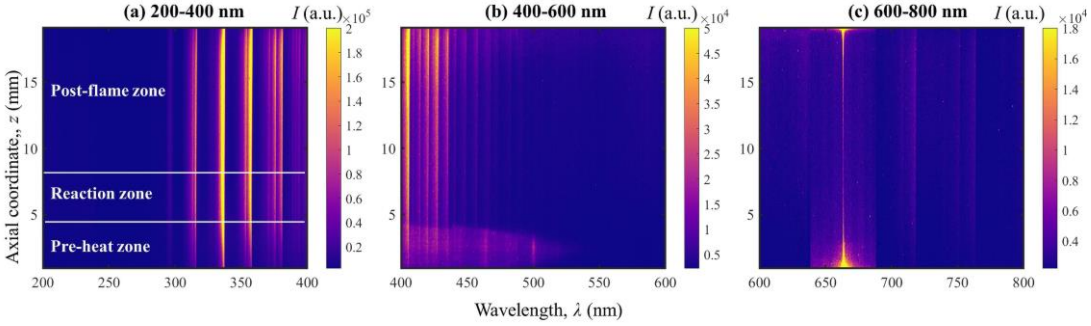

Fig. 5. Spatially resolved emission spectra of the ns pulsed discharge in the stoichiometric ammonia/air flame.

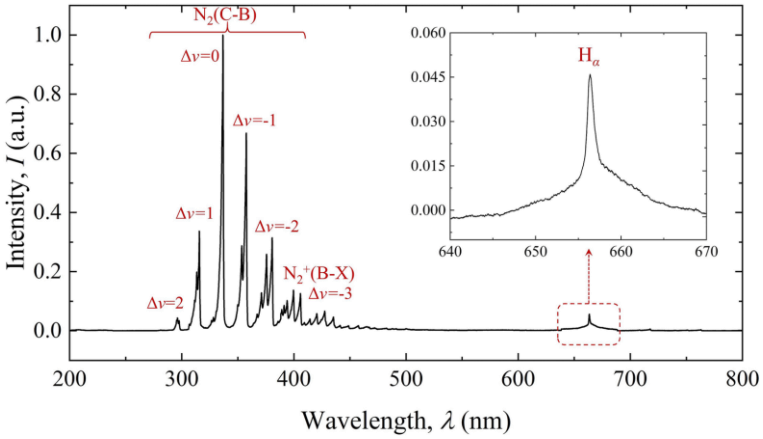

Fig. 6. Spectral intensity of the ns pulsed discharge in ammonia/air flame. The inset is a zoom-in view of H_α line.

Considering the nanosecond time scale, time-resolved measurements for ns pulsed discharge are always challenging. In addition, the difficulties increase dramatically due to the jitter of the plasma discharge device with a magnitude of a few to ten ns. Thus, the time-resolved measurement was carried out as such: the camera gate width is set to be 2.5 ns, close to the lower threshold of the sCMOS camera. And the jitter is corrected by simultaneously monitoring the camera gate and the voltage signal given by the monitor of the pulse generator.

Here, we focus on three N_2(C-B) bands (Δv = 1, 0, and -1) in the primary emission. As seen in Fig. 7, the abscissa and ordinate denote the time delay and the frame-integrated intensity of each band, respectively. From the experimental

data and the corresponding fitting curve, it can be observed that in three N_2 bands and their summation, there exist statistically two Gaussian peaks with FWHMs of 2.5 and 2.0 ns. Fig. 7 also plots the voltage in the right *y*-axis. Obviously, the gaussian shapes of the N_2(C-B) band coincide with those of the voltage curve. According to the reported plasma kinetics, the initial excitation of N_2 by plasma mainly originates from the impact reactions via electrons, e.g., $e + N_2 \rightarrow e + N_2(C)$ [6]. Assuming that the number of N_2 molecules in the ground state changes little within a few ns, it suggests that the number density of excited N_2 mainly depends on the electron number density. In other words, the aforementioned temporal measurement may be used to roughly access the trend of electron number density. To some extent, this time-resolved measurement provides us an insight into the temporal distribution of the electron number density during an electron avalanche.

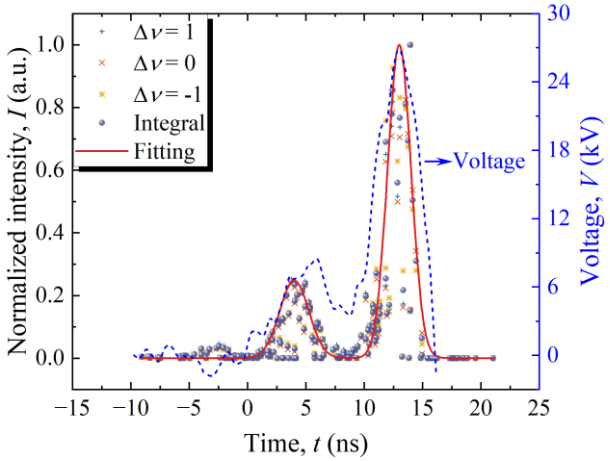

Fig. 7. Normalized time-resolved spectral intensity at three N_2 bands. The symbols represent experimental data and the line is a fitting curve using gaussian profiles.

Moreover, an α-excitation band from H atoms around 656 nm is observed. Thus, except for the combustion chemistry pathway, the plasma discharge provides another channel of H production. According to Faingold et al., H atoms can be extracted from NH_3 molecules by electron collision reactions: $e + NH_3 \rightarrow e + NH_2 + H$ [7]. Atomic hydrogen helps produce more O and OH through collisions with fuel molecules and constitute a radical pool with O and OH, thus playing an important role in the chain-branching reactions. Furthermore, we plot the intensity of H_α band along the axial centerline of flame in Fig. 8. The data is collected around 660±0.5 nm. The axial profile of H_α band intensity appears symmetric, which resembles that of electric strength. And it should be noted that the stagnation flame temperature has a different axial profile from Fig. 8. It thus suggests that the production of plasma-induced atomic hydrogen is dominated by the discharge, while the flame affects little. The quantitative relationship between the electric field and plasma-induced H* needs further investigation when experimental measurements of the electric field are available.

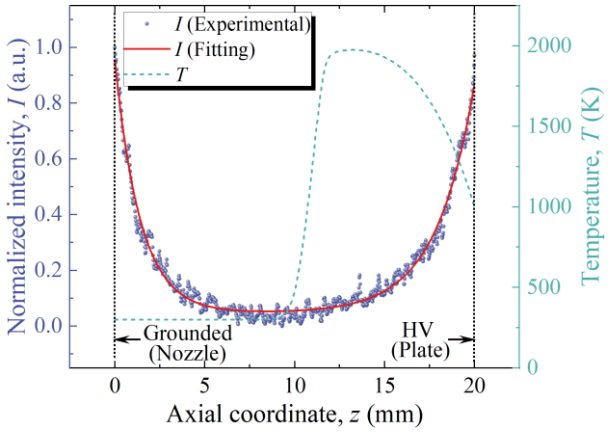

Fig. 8. Spatially resolved intensity of H_α band and numerical temperature profile. The symbols are experimental data and the line is a fitting curve using an Asymmetric Double Sigmoidal model.

4. Conclusions

This work presents emission spectroscopy applications in plasma-assisted NH_3/air combustion. When applying the ns pulsed discharge on an NH_3/air flame, the predominant feature of the plasma emission, i.e., the N_2(C-B) bands with different vibrational levels of the second positive system, are discussed. Furthermore, time-resolved measurements are subsequently performed on several N_2 bands. It is novel that all the temporal profiles show a trend with two gaussian peaks, which may be related to the evolution of electron number density in the first few ns during breakdown. Moreover, the H_α band from plasma-induced atomic hydrogen is observed, which is an indication of the kinetic effects of ns pulsed discharge.

5. Acknowledgments

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6. References

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