Time resolved PLIF and CRD diagnostics of OH radicals in the afterglow of plasma discharge in hydrocarbon mixtures

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Abstract: Two types of diagnostic techniques have been used to investigate the OH radical dynamics in the afterglow of a pulsed nanosecond discharge. The time resolved Planar Laser Induced Fluorescence (PLIF) imaging and Cavity Ring-Down (CRD) techniques provide the information of spatial distribution and absolute concentration of OH, respectively. Experiments were carried out using a lean methane/air mixture (φ=0.1) at atmospheric pressure for temperatures of 300 K and 500 K. The nanosecond pulsed discharge was formed in a pin to pin electrode system. PLIF imaging indicated uniform OH radical dynamics along the discharge channel, and CRD spectroscopy showed a long life time (>200 µs) for [OH] at 500 K. This life time is not predicted by any existing kinetic models. The absolute [OH] from CRD was consistent with our previous [OH] measurements using Laser Induced Fluorescence (LIF). Comparison of OH radical emission dynamics with discharge emission dynamics from excited nitrogen revealed a close similarity in spatial distribution and allowed clarification of the mechanisms of atomic oxygen formation.

Keywords: Non-equilibrium plasma; Plasma-assisted ignition; Laser-induced fluorescence; Nanosecond pulse discharge

1. Introduction

The application of thermal plasma in combustion has a long history which could be dated back at least as far as the early spark ignition engines for automobile applications. In recent decades, particular interest has developed in non-equilibrium discharge assisted ignition and combustion [1-2]. Progress has been made in understanding the mechanism of plasma assisted ignition and plasma assisted combustion in hydrogen and hydrocarbon fuels. In most of these studies hydrocarbons from methane to pentane have been excited by a high-voltage nanosecond pulsed discharge at temperatures above the self-ignition threshold [3-9]. However, as technology moves toward new age combustion systems that require ignition, flame stabilization, and reaction completion with relatively short residence times at initial temperatures below the self-ignition threshold, it has become increasingly important to investigate these mechanisms at these temperatures. The ultimate goal of this work is to expand existing chemical mechanisms to include the effects of plasmas at these lower temperatures.

In our previous research [10], the laser induced fluorescence (LIF) technique has been employed to measure the time resolved hydroxyl (OH) radical in the afterglow of nanosecond pulsed plasma. To further investigate the influence of the nanosecond discharge, two different spectroscopy techniques have been employed in this study. Cavity ring down (CRD) spectroscopy allowed the measurement of the absolute concentration of OH radicals and planar laser induced fluorescence (PLIF) facilitated visualization of the spatial and temporal distribution
of OH along the plasma discharge channel following the plasma pulse.

### 2. Experimental Setup

The experimental installation is shown in Fig. 1. It consists of a reaction chamber, a discharge system, two types of optical diagnostic setups (a, b), and a signal generator that synchronized the plasma and laser. The test gas mixture was blended from methane and air, corresponding to an equivalence ratio of 0.1. The detailed description of the reaction chamber can be found in [10]. The discharge gap was set directly above the nozzle along the axis of the preheated flow. The diameter of the anode (high voltage electrode) and cathode (grounded electrode) were 200 μm and 500 μm, respectively. The interelectrode distance was 8 mm. The plasma was generated by ~ 20 kV positive pulses of 10 ns in duration with less than 1 ns rise time at a repetition rate of 10 Hz. The reactant flow rate was set at about 30 cm/s to allow each discharge pulse to occur in a fresh gas mixture.

Figure 1(a) illustrates the planar laser induced fluorescence method used to visualize the OH distribution along the discharge channel. The Nd:YAG/OPO (Continuum Powerlite 9010 YAG/Sunlite Optical Parametric Oscillator (OPO)) laser system generated the ultraviolet radiation at 282.92 nm needed for $\text{A}_2\Sigma (v=1) \leftarrow \text{X}_2\Pi (v=0) \text{Q1(6)}$ transition excitation. Quartz cylindrical lenses were used to create a laser sheet across the whole discharge channel. Fluorescence images of OH were obtained using a bandpass filter (310 nm, 12 nm FWHM) with an ICCD camera (Princeton Instruments, PI-MAX II). All the images were taken with 20 accumulations in order to obtain good resolution. The time evolution of OH dynamics was tracked by adjusting the delay between the high-voltage pulse and the laser using the signal generator.

The Cavity Ringdown Spectroscopy (CRDS) method used to make absolute OH concentration measurements is illustrated in Figure 1(b). The 50 cm optical cavity was constructed of two highly reflective plano concave mirrors (Los Gatos, R = 99.95%). A 2:1 Keplerian telescope coupled with a 50 μm pinhole was implemented to mode match the laser beam with ringdown cavity. The Nd:YAG/OPO laser system was scanned over the $\text{A}_2\Sigma (v=0) \leftarrow \text{X}_2\Pi (v=0) \text{Q1(1)}$ absorption feature near 307.9 nm for each delay point (Fig. 2). The exponential decay of light exiting the cavity was collected with a PMT (Hamamatsu R562) and averaged over 40 consecutive laser pulses on a 500 MHz digital oscilloscope (LeCroy LT342). The averaged ringdown signal was then sent to a LabView data acquisition program and fit to an exponential function. The ringdown time was extracted from the exponential fit and plotted versus wavelength.

![Figure 1](image.png)

**Figure 1.** Schematic illustration of the time resolved planar laser induced fluorescence (a) and cavity ring down spectroscopy (b) of plasma-assisted ignition analysis below self-ignition temperature. HV: High Voltage; SG: Signal Generator; ICCD: Intensified Charge Couple Device; BP: Bandpass.

### 3. Results and Discussion

Figure 2 shows the false color PLIF images of OH dynamics at two temperatures, 300 K and 500 K. These spatially resolved OH images appear quite uniform along the discharge gap, which has been clearly illustrated by the intensity curve. By comparing this with the discharge emission
dynamics in our previous work [3], we found the spatial similarity between the emission of excited nitrogen and OH radicals. This correspondence indicates that the excitation of nitrogen accounts for the production of atomic oxygen (O) and in turn formation of hydroxyl radical (OH). As demonstrated in [5, 11], the dissociative quenching of molecular oxygen through \( \text{N}_2(C) \) and \( \text{N}_2(B) \) is an important mechanism of production of atomic oxygen in nitrogen containing mixtures:

\[
\text{N}_2(X) + e \rightarrow \text{N}_2(B, C) + e, \\
\text{N}_2(B, C) + \text{O}_2 \rightarrow \text{N}_2(X) + \text{O} + \text{O}.
\]

In the afterglow of the plasma channel, the formation of radicals (particularly OH) initiates the chain reactions. The rates of chain propagation and chain branching reactions increase with increasing temperature, which can be shown through the comparison of results at 300 K and 500 K.

![Figure 2](image_url) False-color sequenced PLIF images (PI-MAX ICCD camera) of OH dynamics in the afterglow of nanosecond pulsed discharge. The images in first row were taken at 300 K, and the others were at 500 K. The lower left is an intensity curve at 2 μs delay after the discharge. The number on each image stands for the delay between the discharge and the ICCD camera.

In the CRDS experiments, absolute concentrations of OH were calculated by relating the measured CRDS ringdown times (\( \tau \)) to the molecule’s (A) absorption coefficient (equation (1)) (Note: See Table 1 for a compilation of all the parameters used to calculate OH concentrations in equation (1)).

\[
\alpha = [A] \sigma = (R_L/c)[1/\tau_R - 1/\tau_o] \quad (1)
\]

\( R_L \) is the ratio of cavity length (L) to absorber length (l), \( \tau_o \) is the off resonance ringdown time, \( \tau_R \) is the ringdown time on resonance, and \( c \) is the speed of light. The absorption cross section (\( \sigma \)) of the Q1(1) transition was calculated from the Einstein B coefficient [12] and was determined to be \( 5.08 \times 10^{-16} \text{ cm}^2 \) at 295 K. The absorption cross section was then temperature corrected for experimental conditions.

<table>
<thead>
<tr>
<th>Plasma Discharge</th>
<th>Temp . (K)</th>
<th>( \sigma ) (cm²)</th>
<th>L (cm)</th>
<th>( \iota ) (cm)</th>
</tr>
</thead>
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<tr>
<td></td>
<td>300</td>
<td>4.84 x 10^{-16}</td>
<td>50</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>1.76 x 10^{-16}</td>
<td>50</td>
<td>0.2</td>
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<table>
<thead>
<tr>
<th>Delay (μs)</th>
<th>( \tau_o ) (sec)</th>
<th>( \tau_R ) (sec)</th>
<th>( \tau_o ) (sec)</th>
<th>( \tau_R ) (sec)</th>
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<tr>
<td>1</td>
<td>3.95 x 10^{-7}</td>
<td>1.47 x 10^{-7}</td>
<td>4.18 x 10^{-7}</td>
<td>1.89 x 10^{-7}</td>
</tr>
<tr>
<td>2</td>
<td>3.83 x 10^{-7}</td>
<td>1.53 x 10^{-7}</td>
<td>4.06 x 10^{-7}</td>
<td>1.89 x 10^{-7}</td>
</tr>
<tr>
<td>4</td>
<td>3.88 x 10^{-7}</td>
<td>1.63 x 10^{-7}</td>
<td>4.05 x 10^{-7}</td>
<td>1.75 x 10^{-7}</td>
</tr>
<tr>
<td>10</td>
<td>3.97 x 10^{-7}</td>
<td>1.89 x 10^{-7}</td>
<td>4.06 x 10^{-7}</td>
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</tr>
<tr>
<td>20</td>
<td>4.07 x 10^{-7}</td>
<td>2.27 x 10^{-7}</td>
<td>4.08 x 10^{-7}</td>
<td>1.87 x 10^{-7}</td>
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<td>4.11 x 10^{-7}</td>
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</tr>
<tr>
<td>200</td>
<td>4.17 x 10^{-7}</td>
<td>3.94 x 10^{-7}</td>
<td>-</td>
<td>-</td>
</tr>
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</table>

The results from the CRDS were then compared with our previous saturated LIF results [10] (Fig. 3). The relative profile dynamics in LIF has an accuracy of ~5%, and the absolute accuracy of [OH] from CRD measurement has a much better accuracy ~1%. The data from these two techniques are in very good agreement in predicting the dynamics of OH, confirming the validity of our previous results using saturated LIF. Moreover, the CRD technique provides an accurate means of measuring absolute concentrations of OH in the afterglow of the discharge, which is essential for developing accurate chemical kinetic models that can predict the enhanced combustion reactivity due to the plasma discharge.
Figure 3. The comparison between experimental results from CRD spectroscopy and LIF at both 300 K and 500 K. The abscissa axis of time is in logarithmic scale.

4. Conclusions

Two types of diagnostic techniques have been set up to facilitate the investigation of the kinetics of plasma assisted ignition below the self-ignition threshold. The results confirmed the high chemical reactivity at low temperature in the afterglow of a nanosecond discharge. Besides, the PLIF diagnostics has shown that the homogeneous distribution of OH formation along the whole channel, and the CRD spectroscopy has provided the absolute number density of OH radical, which can be further used for kinetic model development.

Acknowledgments

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References