

Plasma Assisted Ignition Below Self-Ignition Threshold in Hydrogen-Air and Hydrocarbon-Air Mixtures

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This paper presents measurements of time evolution of hydroxyl (OH) radicals in premixed HC-air flows in the afterglow of a nanosecond pulsed discharge at atmospheric pressure. The temperature ranged from 300 to 800 K (below the self-ignition point). The fuels were methane, ethane, propane and butane, at an equivalence ratio of 0.1 from 400 to 800 K. The plasma was generated by 20 kV pulses of 10 ns duration and a <1 ns rise time at repetition rate of 10 Hz. The tip electrode shape ensured a uniform streamer discharge in the gap of 8 mm. The reactant flow rate was set at ~ 20 cm/s so that each discharge pulse occurred in a fresh gas mixture. Laser induced fluorescence was used to measure the concentration of OH radicals after the discharge. The energy of the excitation laser was adjusted to insure that the measurements were made under saturation conditions for all experiments. The time evolution of OH radicals was tracked by adjusting the delay time between the high-voltage pulse and the concentration measurement.

Introduction

The mechanism of plasma assisted ignition has been intensively discussed in recent years. Several possible mechanisms have been proposed to enhance the ignition with electrical discharges [1]. Recently some progress has been achieved in understanding the mechanisms of plasma assisted ignition and plasma assisted combustion (PAI/PAC) in hydrogen and hydrocarbon fuels from methane to pentane excited by a high-voltage nanosecond discharge at temperatures above a self-ignition threshold [2-8]. The separation of the discharge and ignition processes in time allowed the development of computer models and the numerical simulation of the effect of plasma on ignition. It was shown that the effect under consideration is primarily associated with faster development of chain reactions due to O and H atoms produced by electron impact dissociation of molecules in the discharge phase. This conclusion was corroborated by a good agreement between calculated ignition delay time and experimental data.

For practical purposes it is also important to investigate plasma assisted ignition for conditions below auto-ignition threshold, because they correspond to the ignition regime in automobile engines, gas turbines and heaters. The mechanisms of chemical reactions below self-ignition threshold are widely discussed, but till now there is no validated model of the process with the only possible exception of hydrogen. To simulate PAI/PAC in hydrocarbon-containing mixtures, information is also required regarding the electron impact production rates of active particles in the plasma. These rates are generally calculated based on a numerical simulation of the Boltzmann equation for electrons and using the sets of electron collision cross sections for the main components of the mixtures [9]. Such cross-section sets are available only for the simplest hydrocarbons (CH_4 and C_2H_6) [9] whereas data for more complicated hydrocarbon molecules and radicals are meager and much less reliable (see, for instance, [10-12]).

In current investigation, a study of streamer action on preheated hydrocarbon-air mixture was performed via laser induced fluorescence (LIF) to enhance our knowledge of ignition and flame stabilization kinetics by active species formation in non-equilibrium plasma for low temperature conditions below self-ignition threshold. It was shown that a considerable amount of hydroxyl radicals are produced and sustained in the channel of a streamer propagating through a combustible mixture. OH concentration dynamics over the time in the discharge have been obtained with a temporal resolution down to 100 ns.

Experimental Setup

The experimental installation is shown in Figure 1. It consists of a reaction chamber, a discharge system, a diagnostic system, and a signal generator which synchronizes the plasma and laser. The reaction chamber included a ceramic burner, the electrode system and the gas (fuel and air) supply system, as shown in the dot square in Fig. 1. Gas flows were preheated in thermo-insulated region from 300 K up to 800 K. The mixing chamber and plasma nozzle were made of alumina ceramics for additional thermal and electrical insulation. The discharge gap was set right above the nozzle along the axis of the premixed flow. The diameter of anode (high-voltage electrode) and cathode (grounded electrode) were 200 μm and 500 μm , respectively. The inter-electrode distance was 8 mm. The plasma was generated by ~ 20 kV positive pulses of about 10 ns duration and a less than 1 ns rise time at repetition rate of 10 Hz. The reactant flow rate was set at ~ 20 cm/s so that each discharge pulse occurred in a fresh gas mixture. The optical diagnostic system

consisted of an Nd-YAG-OPO laser system, a photo-electron multiplier (PEM), an optical emission spectroscopy (OES) (not shown here), and a pico-second gated ICCD camera from Stanford Computer Optics 4Picos.

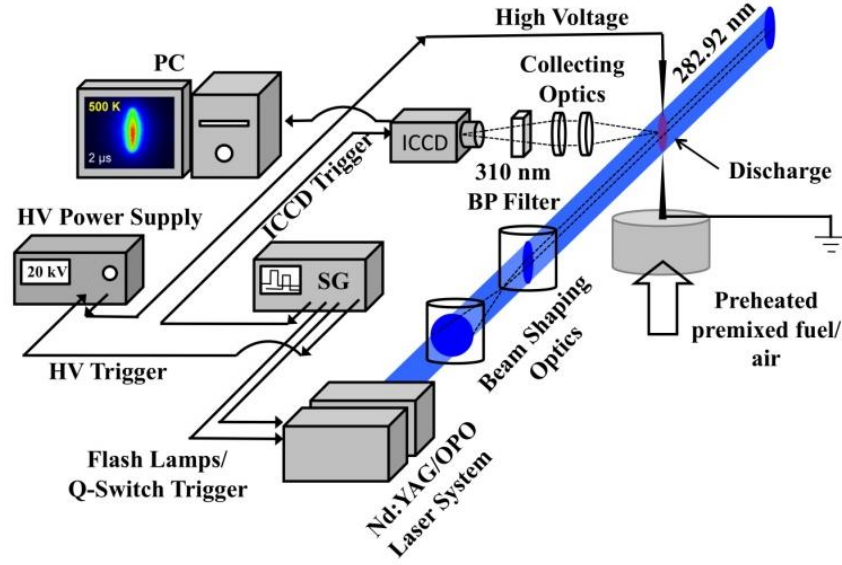


Fig. 1. Experimental facility for time resolved planar laser induced fluorescence diagnostics of plasma-assisted ignition analysis below self-ignition temperature. HV: High Voltage; SG: Signal Generator; ICCD: Intensified Charge Couple Device; BP: Bandpass.

Saturated LIF method was used to measure the concentration of OH radicals after the discharge. BBO-based frequency doubling system generated ultraviolet radiation at 282.92 nm needed for OH Q1(6) transition excitation. Quartz spherical lenses formed high power density in the focal point out of the initial TEM₀₀ mode of laser beam. Fluorescence signals were obtained using a quartz lens and PEM. The energy of the excitation laser was adjusted to 12 mJ/pulse to insure that the measurements were made under saturation conditions for all experiments. The time evolution of OH radicals was tracked by adjusting the delay time between the high-voltage pulse and the concentration measurement using the signal generator (upper left in Fig. 1).

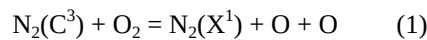
Temperature measurements were performed via OES together with a thermocouple. OES recorded rotational temperature in the discharge zone by capturing emission of second positive system of N₂ molecule at 337.1 nm. The change of the gas temperature was stable within ± 10 K in the discharge gap. Thus, all temperatures shown here were measured by the thermocouple as the initial gas temperatures.

Besides, to enhance our knowledge of the discharge, the ICCD camera was utilized to record the plasma evolution. Through synchronization, this pico-second gated camera enabled to trace the whole streamer development. Moreover, with the help of back-current shunt, incident and reflected voltage pulses were observed by Tektronix DPO4104 oscilloscope.

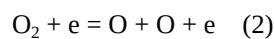
Results and discussion

Figure 2 shows the voltage waveform generated from the nanosecond power supply. It is clearly seen that the voltage pulse on the high-voltage electrode reaches its maximum in $\tau < 1$ ns. This ultra-short rise time leads to stable and repeatable plasma channel formation.

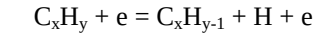
The plasma development can be observed from figure 3. The discharge starts at high voltage electrode and after about 4 ns the streamer channel bridges the discharge gap. Return stroke leads to the potential redistribution along the gap. After this the reduced electric field in the plasma channel becomes lower than the breakdown field (~ 120 Td for room-temperature air) and a slow plasma recombination starts. Typical time of the plasma degradation in this field is several microseconds and this degradation does not affect the discharge current, gas excitation and dissociation during the pulse (~ 10 ns). When voltage decreases the fast quenching of a main emitting state begins.



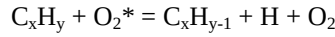
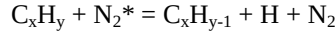
The plasma channel becomes invisible (Figure 3). During the discharge between two needle electrodes, the streamer channel stays uniform, which is beneficial to our experiments. Production of atomic oxygen in the process (1) and by direct electronic impact leads to the formation of the channel with very high initial concentration of radicals [6].



Important additional processes are the processes of fuel dissociation due to collisions with electrons and quenching of electronically-excited states of N_2 and O_2 [6]:



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Radical formation in the near-afterglow of the plasma channel initiates the chain reaction. The rate of chain propagation and chain branching reactions increases with the temperature increase. At low temperature conditions reactions of chain termination and recombination prevail.

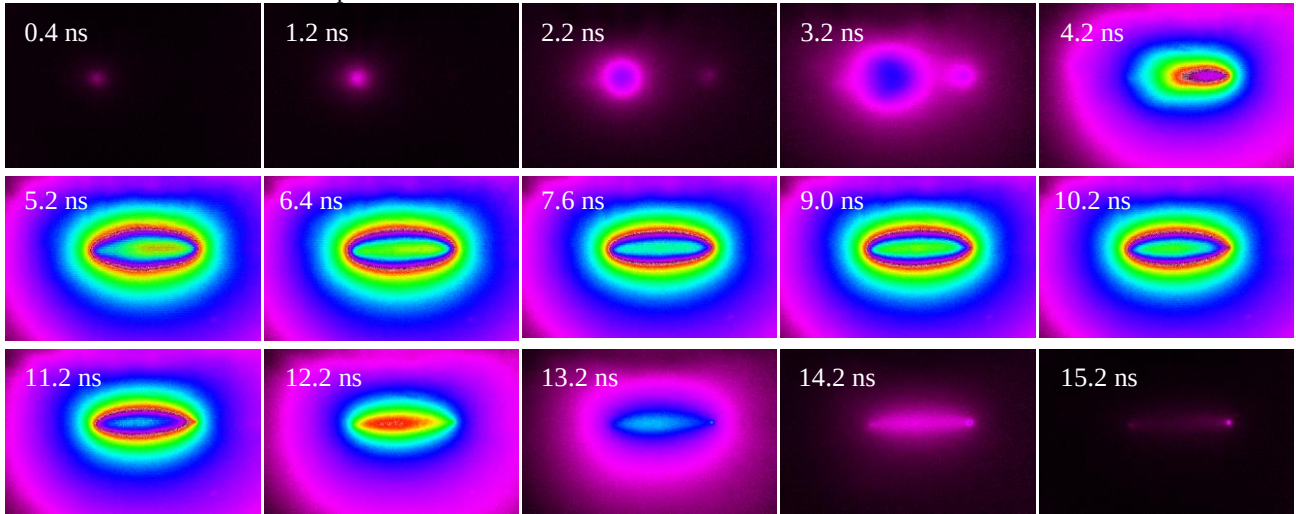


Figure 3. Sequenced ICCD images of plasma discharge development between two electrodes, camera gate is 200 ps. Air, $P = 1 \text{ atm.}$, $U = 20 \text{ kV.}$

The results of time evolution of OH radicals are shown in Figure 4, where the abscissa axis is in logarithm scale. At 300 K, three different equivalence ratios were used ($\phi = 0.1, 1$ and 3.0). The results can be well-interpreted. During first microsecond the electronically-excited species and ions are converted into radicals [6]. The rest of the process is mostly recombination of the initial radicals. In comparison of the [OH] degradation time among all curves, methane curves (for all ϕ) are the longest while butane appears shortest. This behavior is obviously related to the increasing reaction rate constants of $C_xH_y + OH = C_xH_{y-1} + H_2O$ for higher hydrocarbons. Moreover, by adding the portion of fuels from lean to rich conditions, the [OH] degradation rate increases proportionally ($\tau_{0.1}/\tau_{3.0} \sim 8$).

The graph changes significantly when temperature increases even to 400 K. The methane curve shows the time for [OH] to reach its maximum elongates to $\sim 10 \mu\text{s}$. It should be noticed that this value significantly exceeds the time of plasma recombination at atmospheric pressure conditions [6]. Thus some chain propagation/branching reactions may occur even at 400 K. The [OH] degradation order among four fuels is still the same as in 300 K.

A dramatic change happens when the temperature rises to 500 K. The time of maximal [OH] stays in the range of 30-70 μs for all hydrocarbons under investigation. This major increase clearly demonstrates the chain development processes and OH generation continuation after the plasma channel recombination. [OH] is depleted at approximately 1ms, which is probably due to the rate increase of OH consumption reactions with accumulated intermediate products. Another noticeable change is the [OH] degradation order, which is now reversed comparing to previous figures. At 600 K, the picture stays the same. [OH] maximum becomes more pronounced in the time range of 30-80 μs .

The graph starts to change again when temperature reaches 700 K. A third stage of [OH] increase is observed at $\tau > 1 \text{ ms}$. This third stage becomes clear at 800 K, where three maxima of [OH] concentration appear in a single curve. The first peak may be related with initial OH formation in the discharge, the second is probably because of chain reactions below self-ignition threshold limited by accumulation of intermediate species, and the third may correspond to the cool flame kinetics because it was only observed in butane and propane mixtures only.

Figure 5 demonstrates the OH dynamics for two different hydrocarbons: methane and butane at different temperatures. It is clearly seen that at low temperatures OH consumption is very fast due to reactions between OH and

fuels. At elevated temperatures chain branching and chain propagation reactions become faster in butane-air mixture and provide a significant fuel conversion even below a self-ignition threshold.

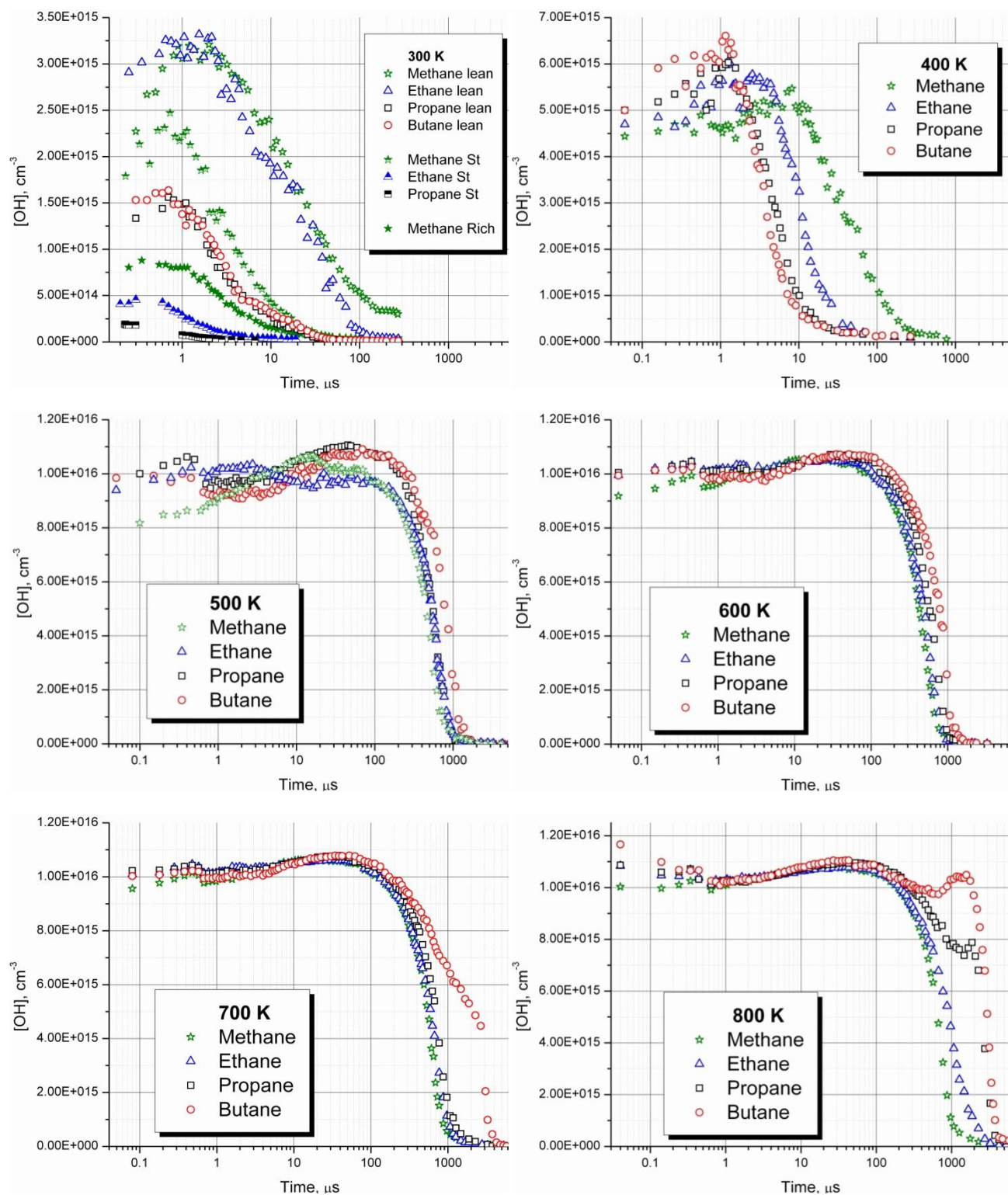


Figure 4. OH evolution over time at six temperature points, from 300 K to 800 K. $P = 1 \text{ atm}$. $\phi = 0.1$

A planar laser induced fluorescence (PLIF) method was used to visualize the OH distribution along the discharge channel (Figure 6). 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 OH $Q_1(6)$ 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 a better 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.

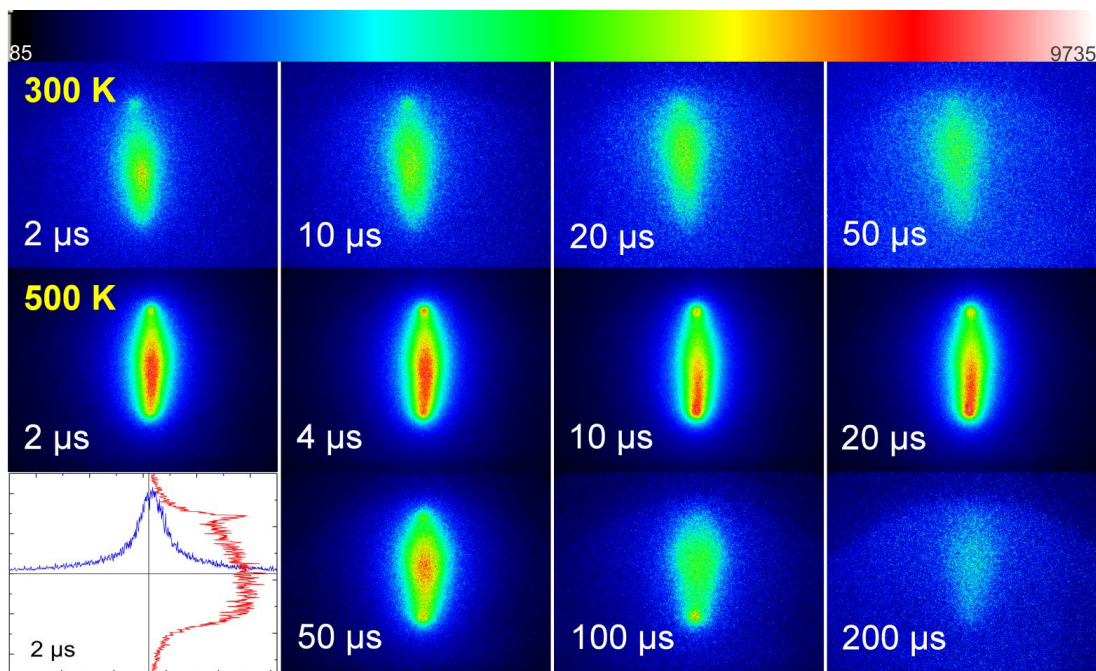


Fig. 7. False-color sequenced PLIF images (PI-MAX ICCD camera) of OH dynamics in the afterglow of nanosecond pulsed discharge. The images in first row were taken at 300 K, and the others were at 500 K. The lower left is an intensity curve at 2 μ s delay after the discharge. The number on each image stands for the delay between the discharge and the ICCD camera.

Figure 7 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 (Figure 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 [14, 15], the dissociative quenching of molecular oxygen through $N_2(C)$ and $N_2(B)$ is an important mechanism of production of atomic oxygen in nitrogen containing mixtures: $N_2(X) + e \rightarrow N_2(B, C) + e$, $N_2(B, C) + O_2 \rightarrow N_2(X) + O + O$.

In the afterglow of the plasma channel, the radical formation like 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. The long life time of OH at 500 K remains an open question since the low temperature kinetics is still under investigation. Figure 3 demonstrates the spatial distribution of the second positive system of nitrogen emission in the discharge. Similarity of the OH and $N_2(C^3)$ distributions demonstrates the importance of quenching channel in atomic oxygen production.

The Cavity Ringdown Spectroscopy (CRDS) method was used to make absolute OH concentration measurements. 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 μ m pinhole was implemented to mode match the laser beam with ringdown cavity. The Nd:YAG/OPO laser system was scanned over the $A^2\Sigma (\nu = 0) \leftarrow X^2\Pi (\nu = 0) (\nu = 0)$ Q1(1) absorption line near 307.9 nm for each delay point. 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.

The results from the CRDS were then compared with our previous saturated LIF results (Figure 8). The relative profile dynamics in LIF has an accuracy of $\sim 5\%$, and the relative accuracy of [OH] from CRD measurement has a much better accuracy $\sim 1\%$. The data from these two techniques are in very good agreement in predicting the dynamics of OH, confirming the validity of 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.

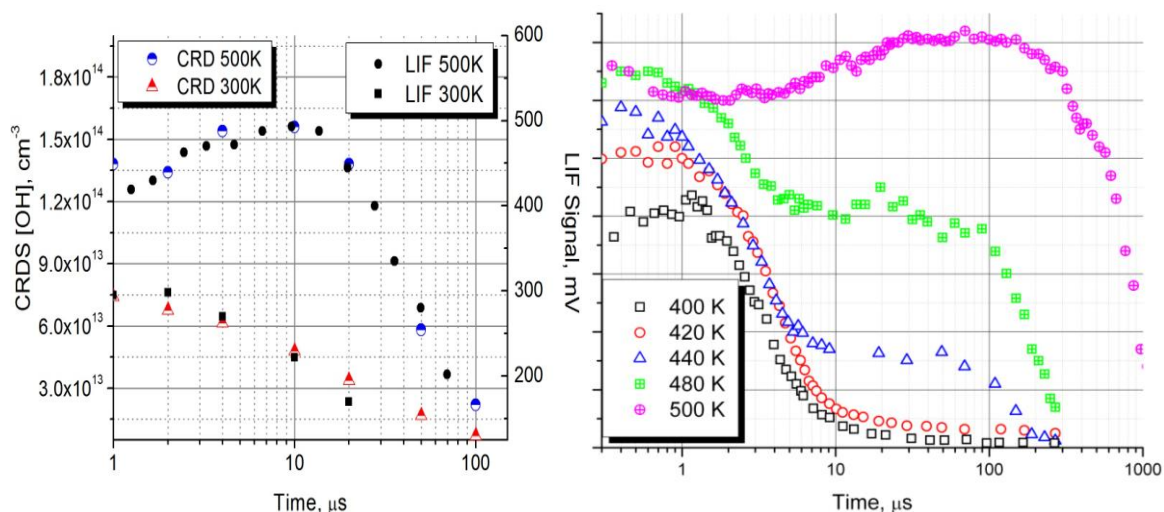


Figure 8. A) The comparison between experimental results from CRD spectroscopy and LIF at both 300 K and 500 K. The abscissa axis of time is in logarithmic scale. B) OH decay dynamics between in lean butane-air mixture at $T = 400\text{--}500\text{ K}$. $\phi = 0.1$.

Conclusions

Experimental setup for plasma-assisted ignition kinetic analysis below a self-ignition threshold has been developed. Preheated gas mixture flow rate is in the range of 20–30 cm/s and guarantees full mixture replacement between high-voltage pulses. Gas excitation is provided with a help of pulsed nanosecond discharge in point-to-point geometry with slightly under-critical electric field. Absolute OH concentration formed in the afterglow of positive nanosecond discharge in preheated hydrocarbon-air flow has been measured. OH initial concentration was in the range of typical flame conditions, and enables to analyze the primary and secondary reaction kinetics. Evidence has been obtained for substantial oxidation chain length existence with discharge chain initiation by radical production from combustible mixtures at temperatures as low as 400–800 K. A new, validated mechanism for low temperature hydrocarbon combustion is required for qualitative description of plasma assisted combustion below self-ignition threshold. This problem is still unsolved at require a lot of new efforts.

Acknowledgments

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