

New combustion regimes and kinetic studies of plasma assisted combustion



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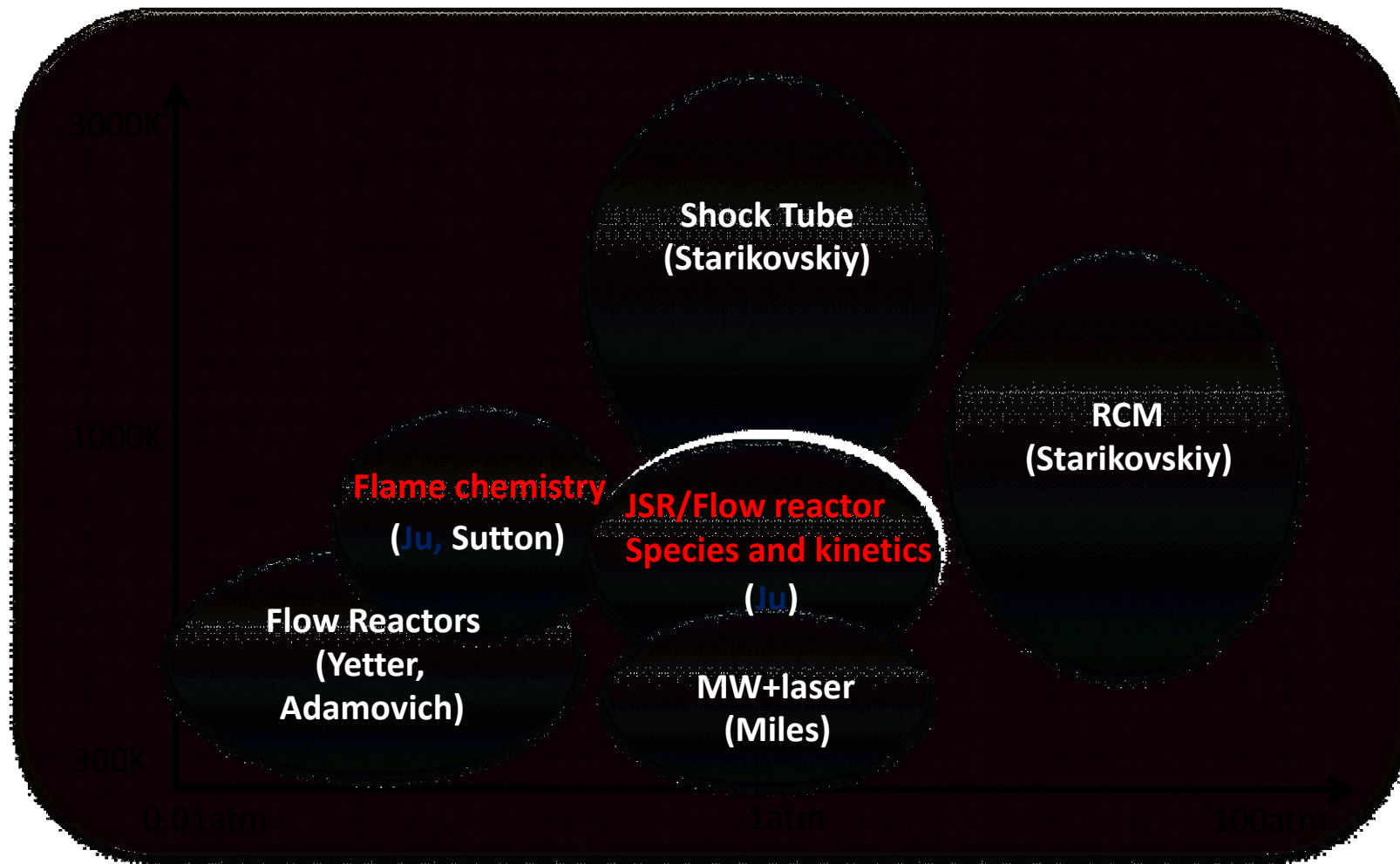
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Nov.6-7, 2012 MURI Plasma 3rd Yr Review Meeting

MURI Topic #11: Chemical Energy Enhancement by Nonequilibrium Plasma Species

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MURI Facility Summary and collaborative team structure



(*All facilities designed and fabricated specifically for this program.)

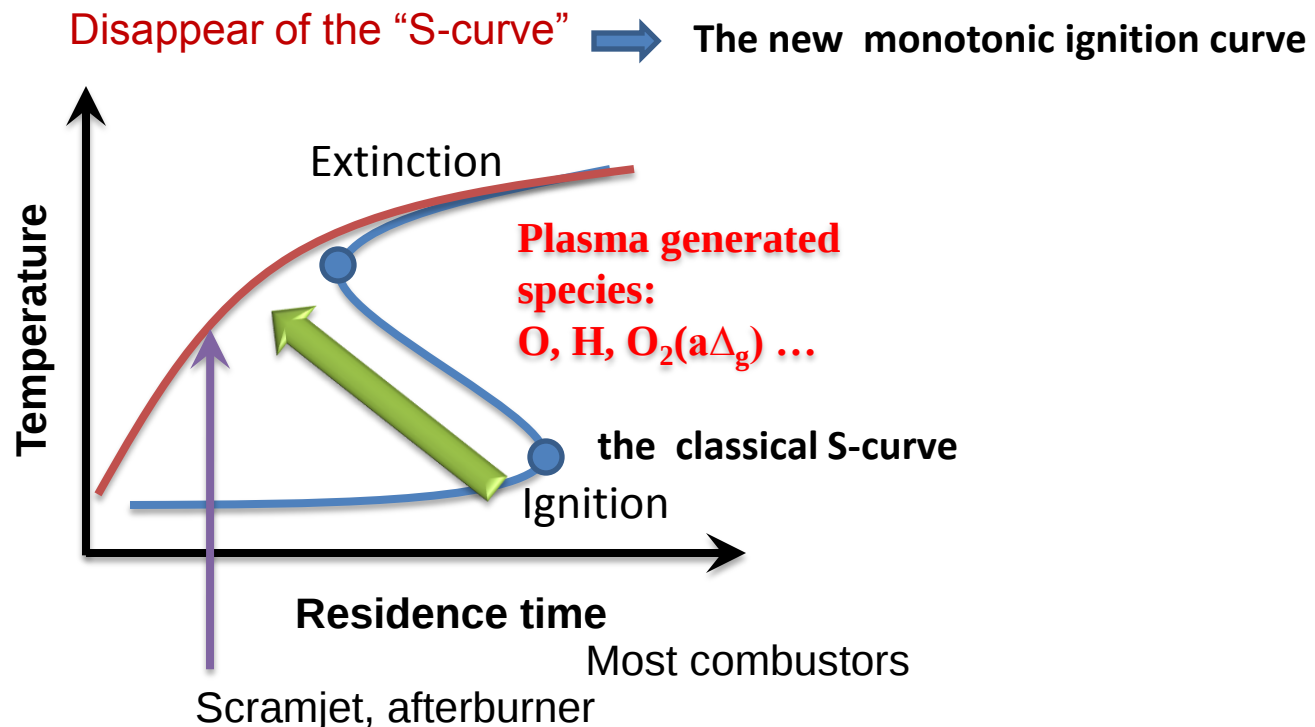
Today's Presentation

- 1. New combustion regimes and kinetic studies of in situ plasma discharge in counterflow flames
(Tasks 8 and 9: Kinetic model validation)**
- 2. Multispecies diagnostics in a flow reactor with Mid-IR and molecular beam mass spectroscopy (MBMS)
(Task 3: Multispecies measurements)**
- 3. Ignition enhancement and minimum ignition energy by plasma discharge
(Task 6: Ignition, Flame Initiation and the Minimum Ignition Energy)**

1. New flame and ignition regimes with *in situ* nano-second pulsed discharge

Technical questions:

- . Can plasma assisted combustion enhances sublimit combustion so that the ignition and extinction limit disappear on the classical S-curve?
- . What happens when JP-8 has low temperature ignition chemistry?
How does PAC interact with low temperature chemistry ? relevant or not?





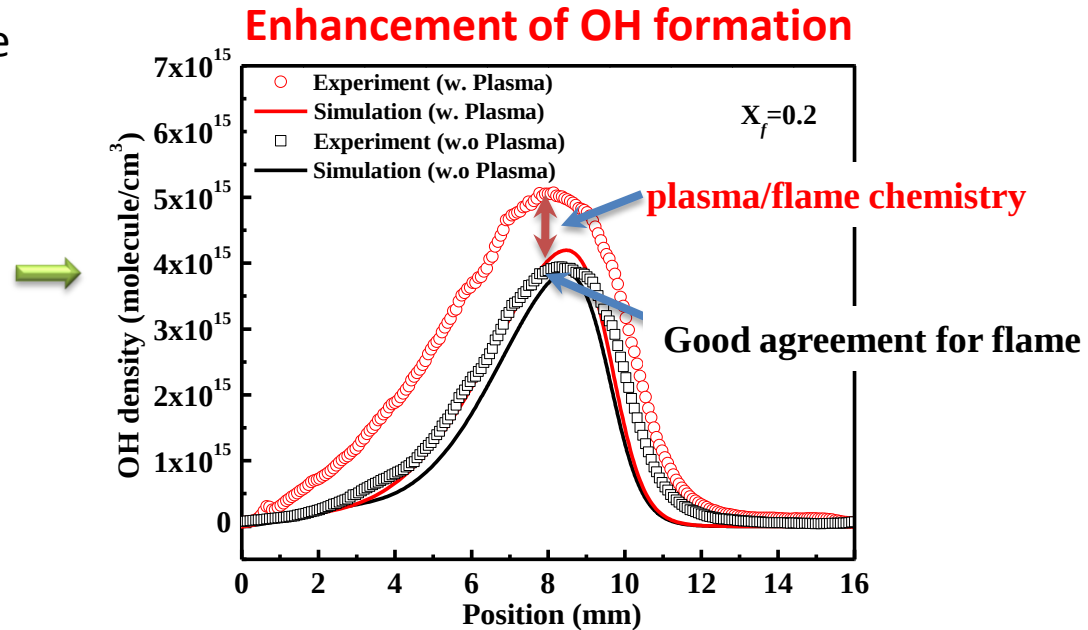
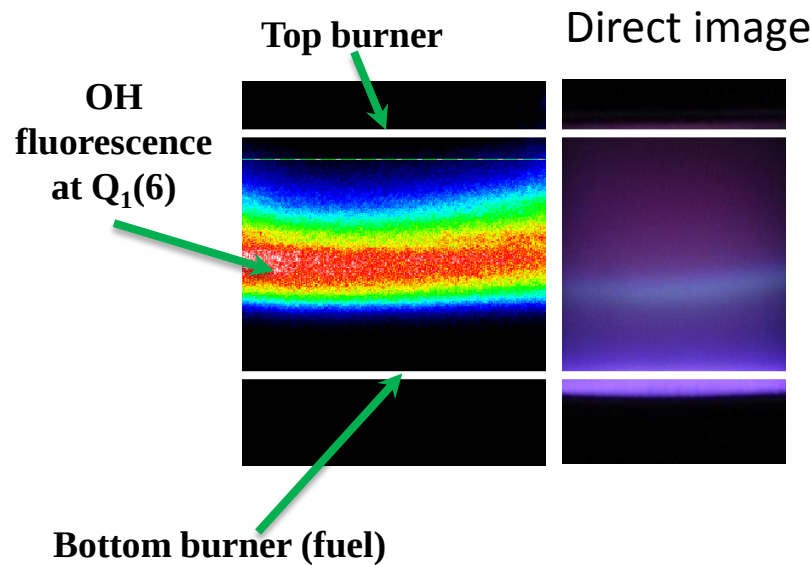
E = 7500 V/cm, E/N ~ 900 Td

Power ~ 17 W (repetitive pulses)

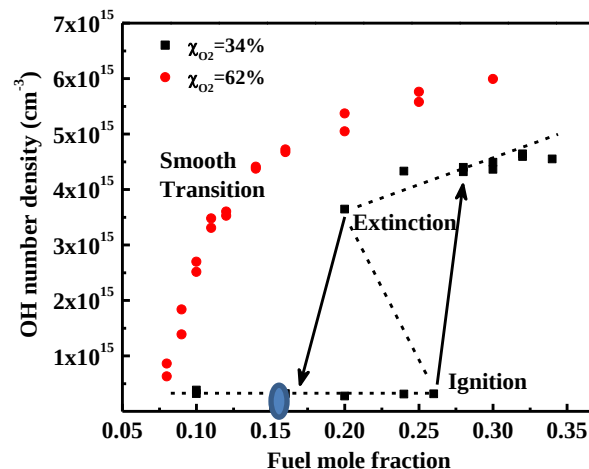
OH PLIF measurement (CH_4/O_2 sublimit flames)



$a = 400 \text{ 1/s}$, $X_o = 55\%$, $X_f = 20\%$, $f = 24 \text{ kHz}$, $P = 72 \text{ Torr}$, UV power = 2 mJ/pulse



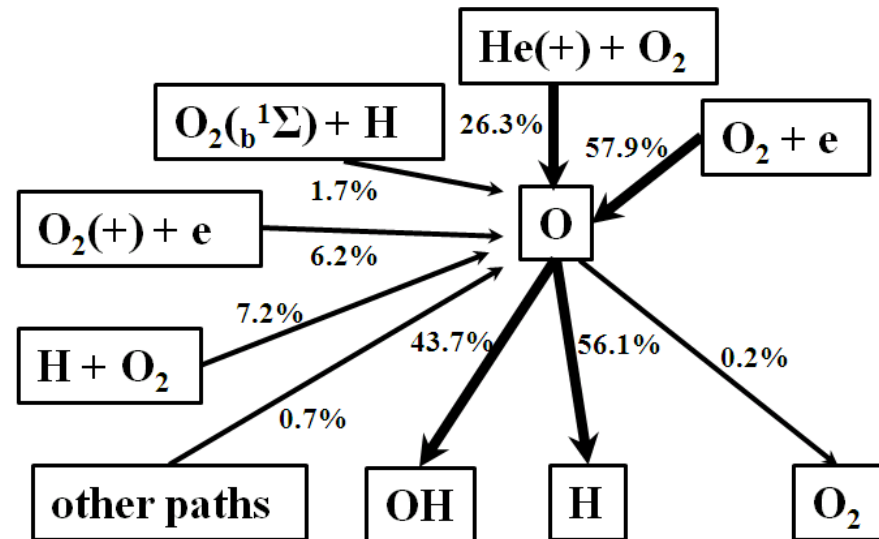
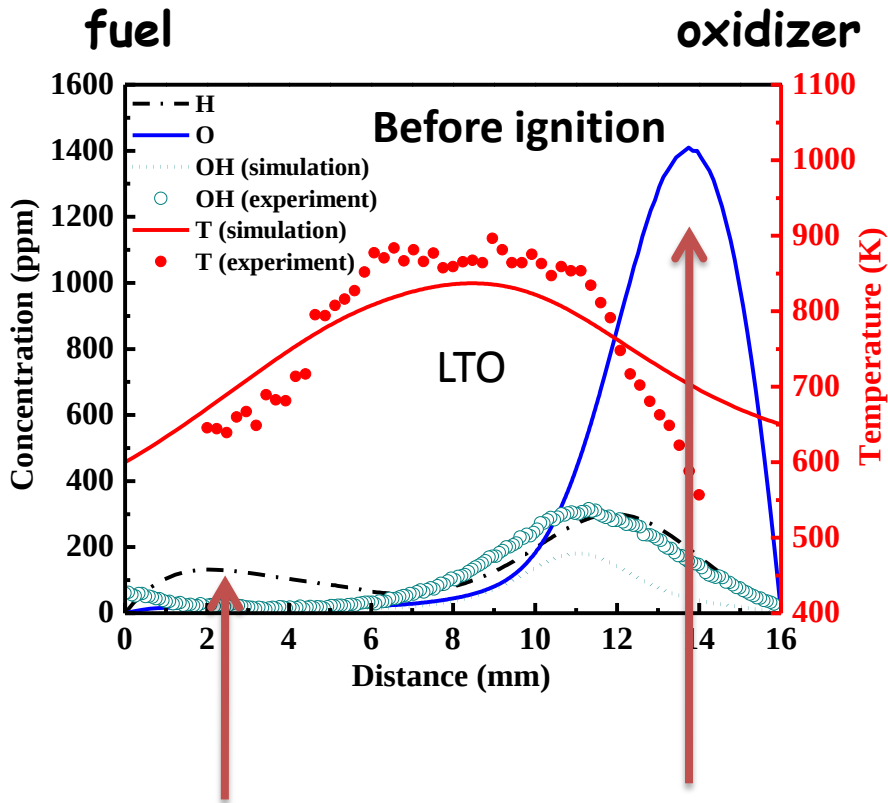
S-shaped ignition/extinction curve measurement: OH PLIF



Numerical modeling of PAC and path flux analysis



$$X_{O_2} = 0.34, X_{CH_4} = 0.16, P = 72 \text{ Torr}, f = 24 \text{ kHz}, a = 400 \text{ 1/s}$$



no flame, but reaction zone was built up by radicals generated from plasma

Electron and ion impact dissociation are the key in PAC .

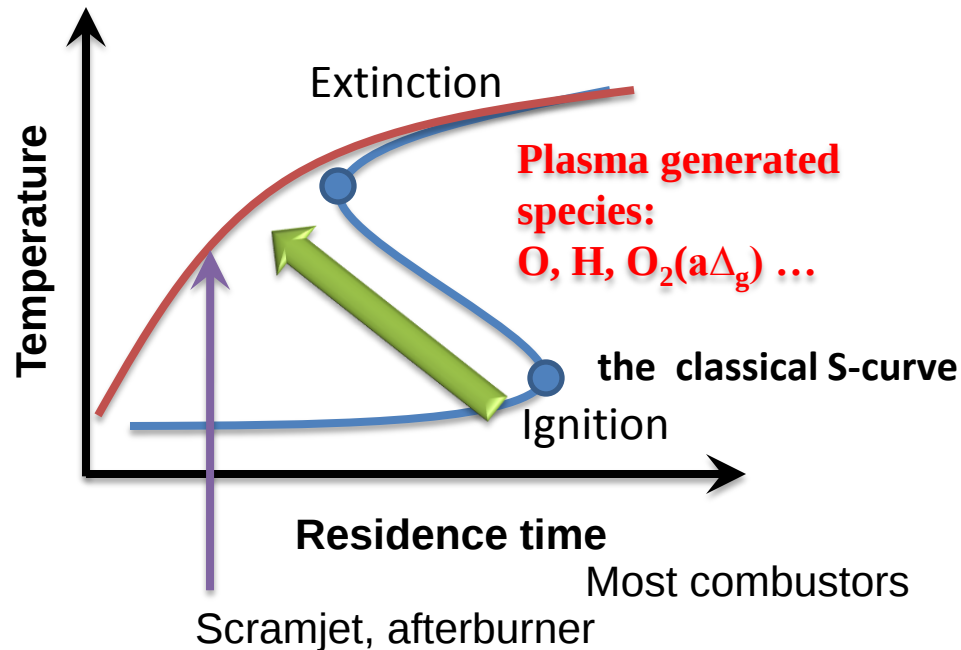
New ignition transition curve with plasma assisted combustion

Hypothesis

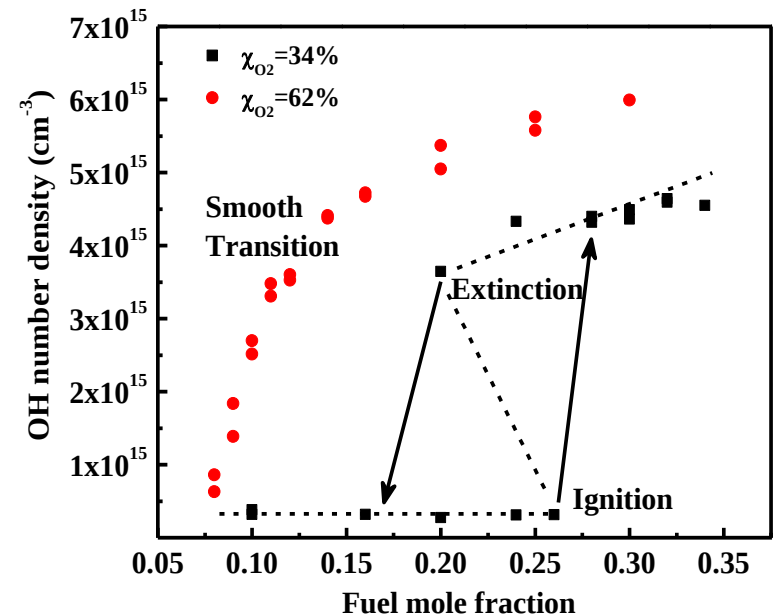


Experimental observation
A new combustion regime

Disappear of the “S-curve”



The S-curve transition

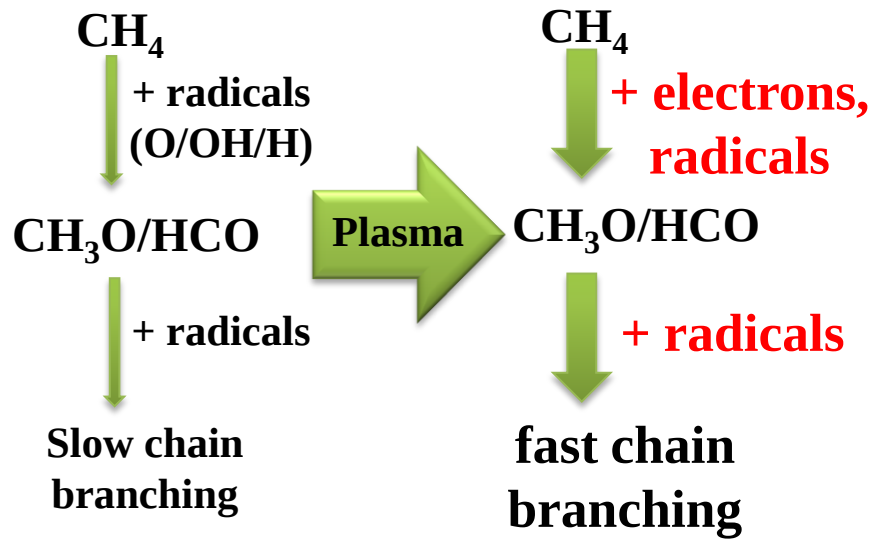


- Extended flammable regime
- No extinction limit

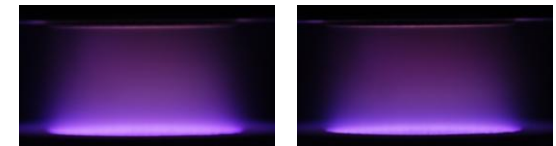
What if a fuel (JP-8) has low temperature chemistry?

How does low temperature chemistry make a difference?

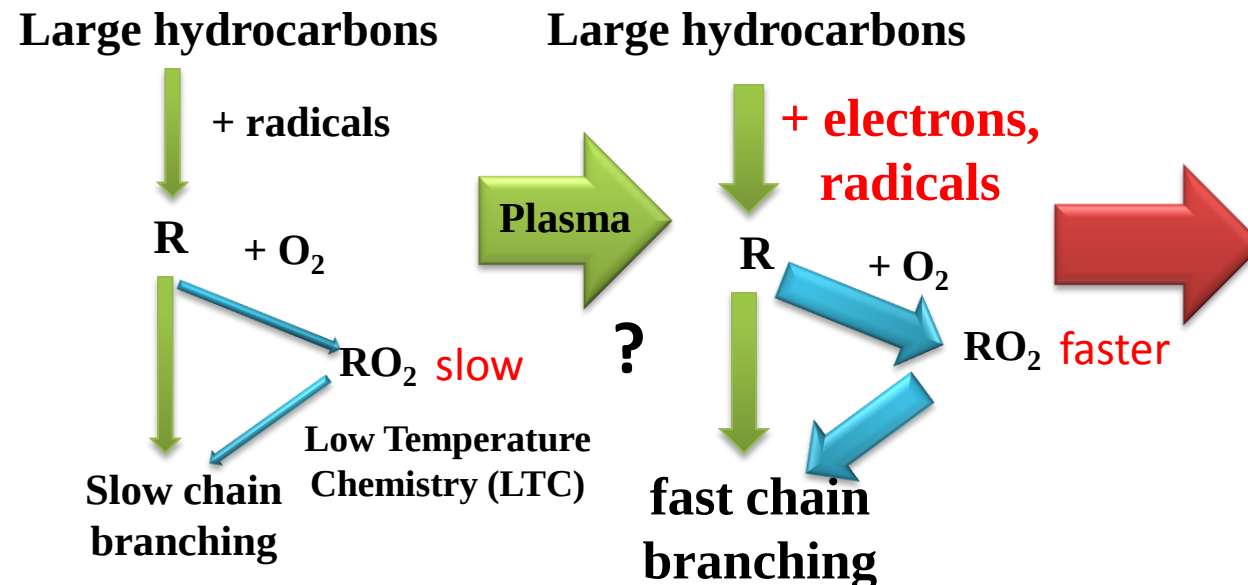
From CH_4 to jet fuel, using DME (LTC and gas phase) as example



Same chemiluminescence before CH_4 plasma assisted ignition



High temperature chemistry only

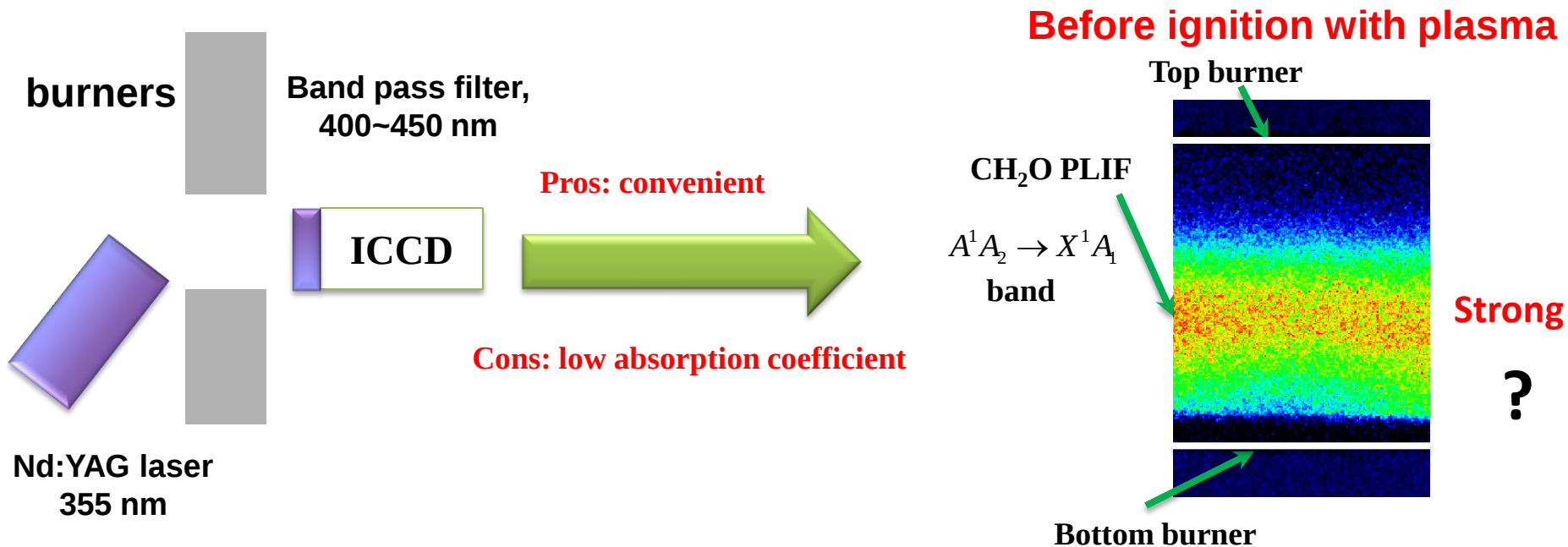


Different chemiluminescence before DME ignition



How does LTC affect ignition and extinction?

CH₂O PLIF at 355 nm from Nd:YAG laser



Further identification of CH₂O LIF

no LIF from cold flow

LIF close to fuel side

switch fuel/oxidizer side
CH₂O LIF on the fuel side

cold flow w. laser

flame w.o laser

flame w. laser

flame w. laser

Clean background

chemiluminescence

CH₂O LIF

CH₂O LIF

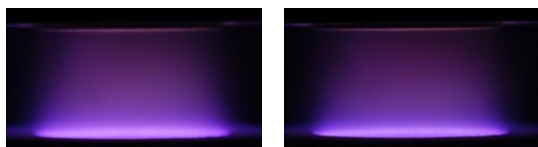
weak

without discharge

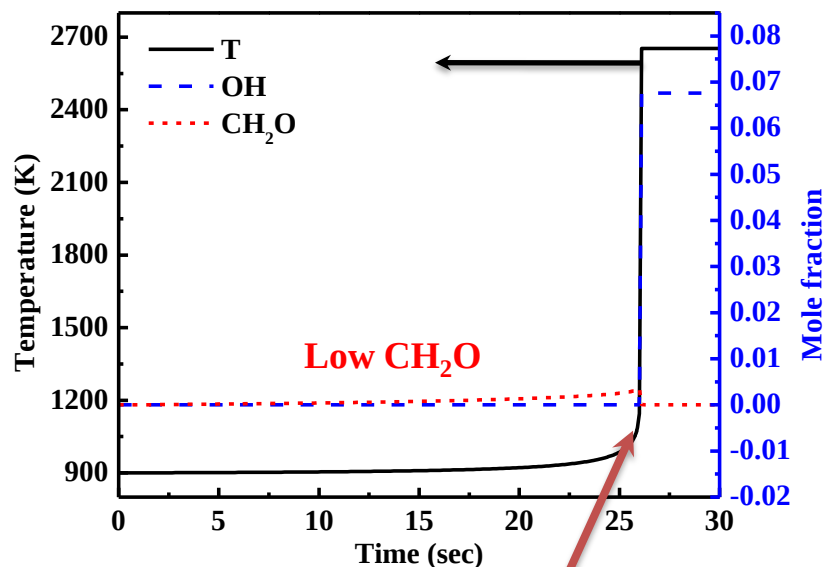
CH₂O formation in CH₄ and DME ignition ...



Same chemiluminescence
before CH₄ plasma assisted ignition



CH₄/O₂/He (0.15/0.55/0.3)
P = 72 Torr, T₀ = 900 K

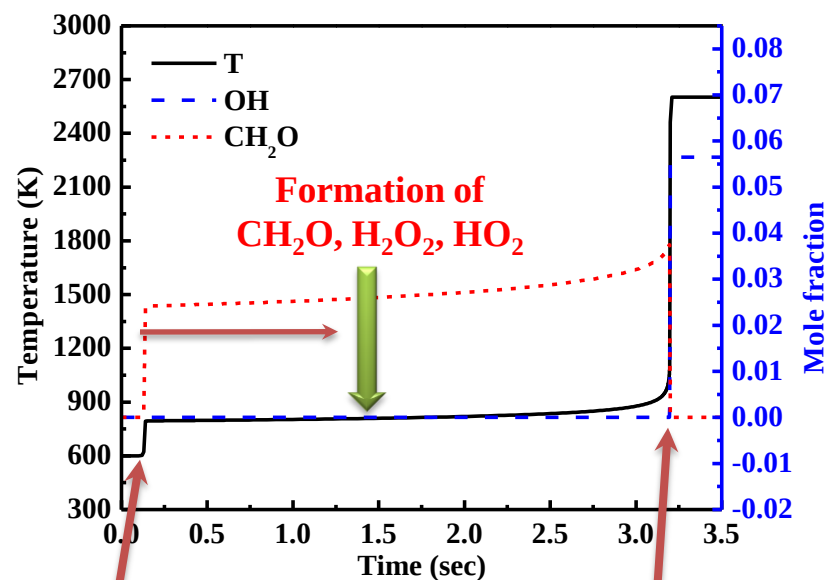


High T ignition
Marked by OH

Different chemiluminescence
before DME ignition



DME/O₂/He (0.1/0.55/0.35)
P = 72 Torr, T₀ = 600 K

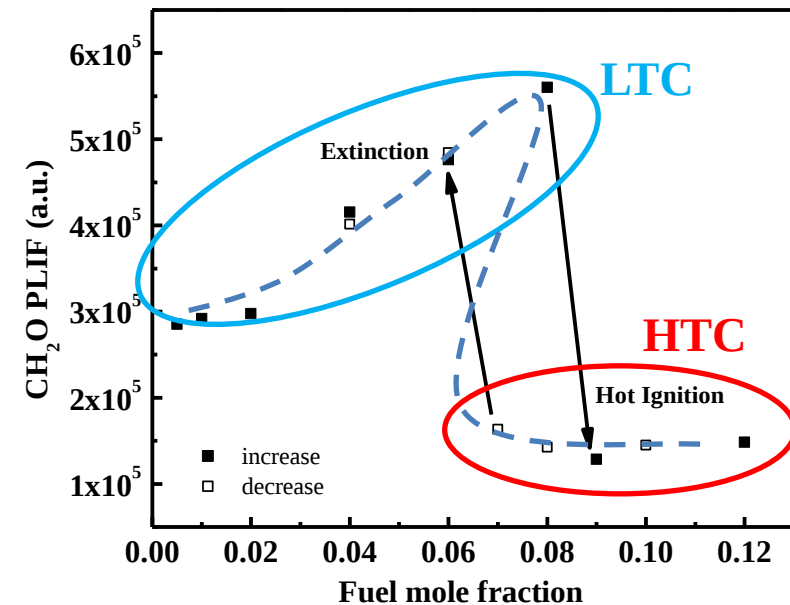


Low T ignition
CH₂O can be used
as a marker

High T ignition
H₂O₂ → 2OH

CH₂O measurements: ignition and extinction

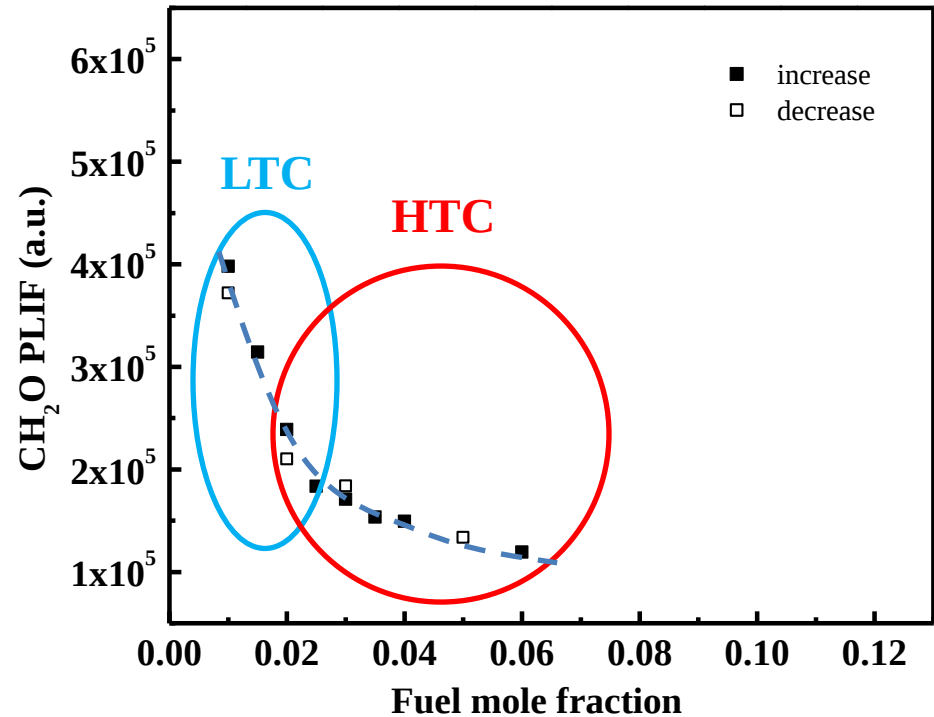
$P = 72 \text{ Torr}$, $a = 250 \text{ 1/s}$, $f = 24 \text{ kHz}$
 $X_{O_2} = 40\%$, varying X_f



S-Curve



$P = 72 \text{ Torr}$, $a = 250 \text{ 1/s}$, $f = 34 \text{ kHz}$,
 $X_{O_2} = 60\%$, varying X_f

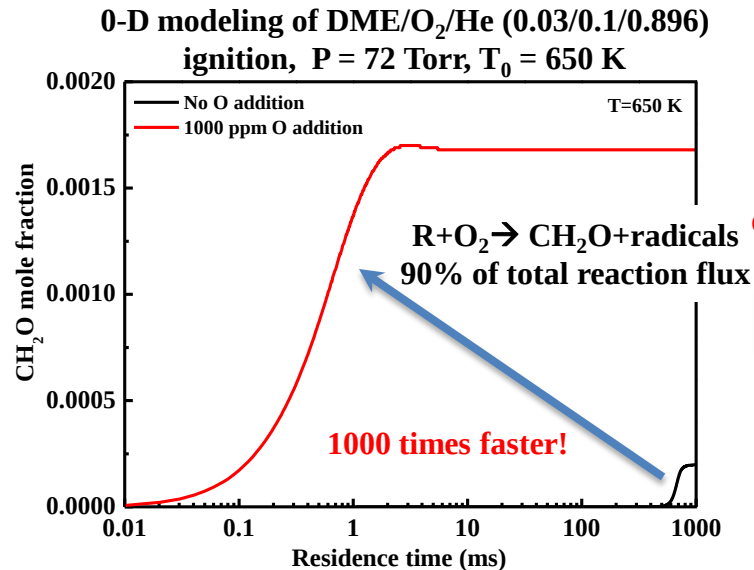


New **ignition/extinction** curve without extinction limit

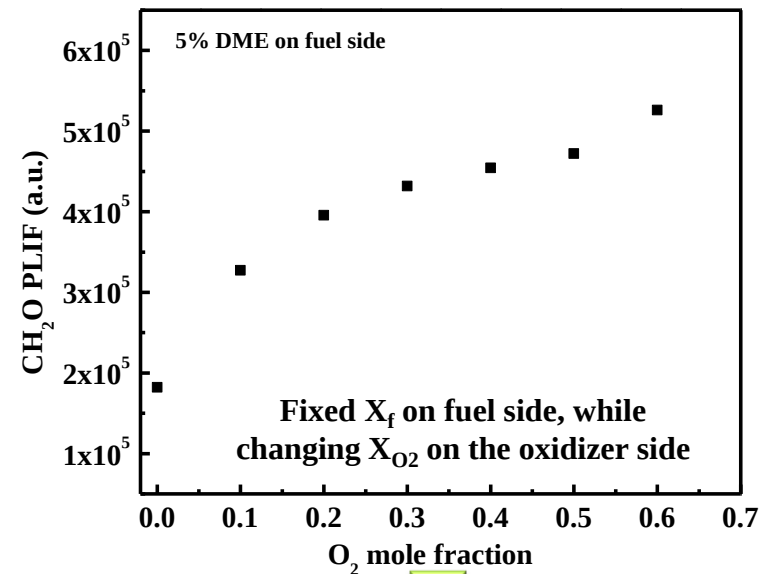
Competition between

low T RO₂ kinetics
 high T chain branching reactions

Kinetics of plasma assisted low temperature combustion



Sensitive to O₂ concentration?



Implication

Plasma assisted combustion dramatically changed the low temperature chemistry

Plasma

Faster LTC

Slow LTC

Turbulent transport

Prompt radical production from plasma

Fast H abstraction (formation of R)

Fast LTC (RO₂ reactions)

Results can be extended to other large fuels

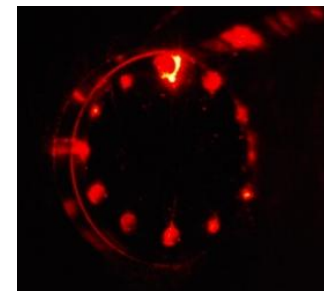
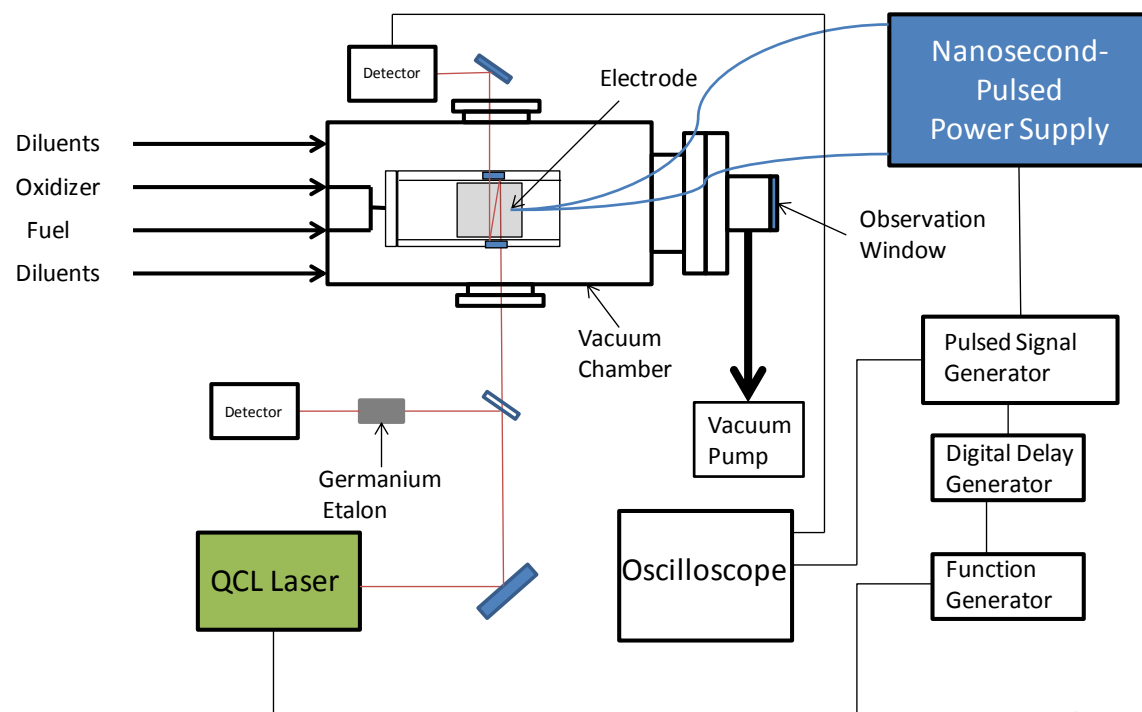
- LTC in Plasma assisted combustion
- LTC in turbulent combustion at engine time scales

2. Multispecies diagnostics in a flow reactor (Task 3: Multispecies measurements)

In situ intermediate species diagnostics beyond radicals

2a Multispecies Diagnostics in Repetitively-pulsed Nanosecond Discharge in a Laminar Flow Reactor

Experimental setup



Mini-Herriott cell showing 24 pass configuration

Reactor/Diagnostics

- Reactor size: 58.2 x 14 x 152 mm³
- Fuel: C₂H₄
- Pressure: 60 Torr
- Flow speed in the reactor: ~40 cm/s
- Mid-IR QCL laser: 1296 cm⁻¹ – 1423 cm⁻¹
- Multi-pass Mini-Herriott cell (12.7 mm OD)

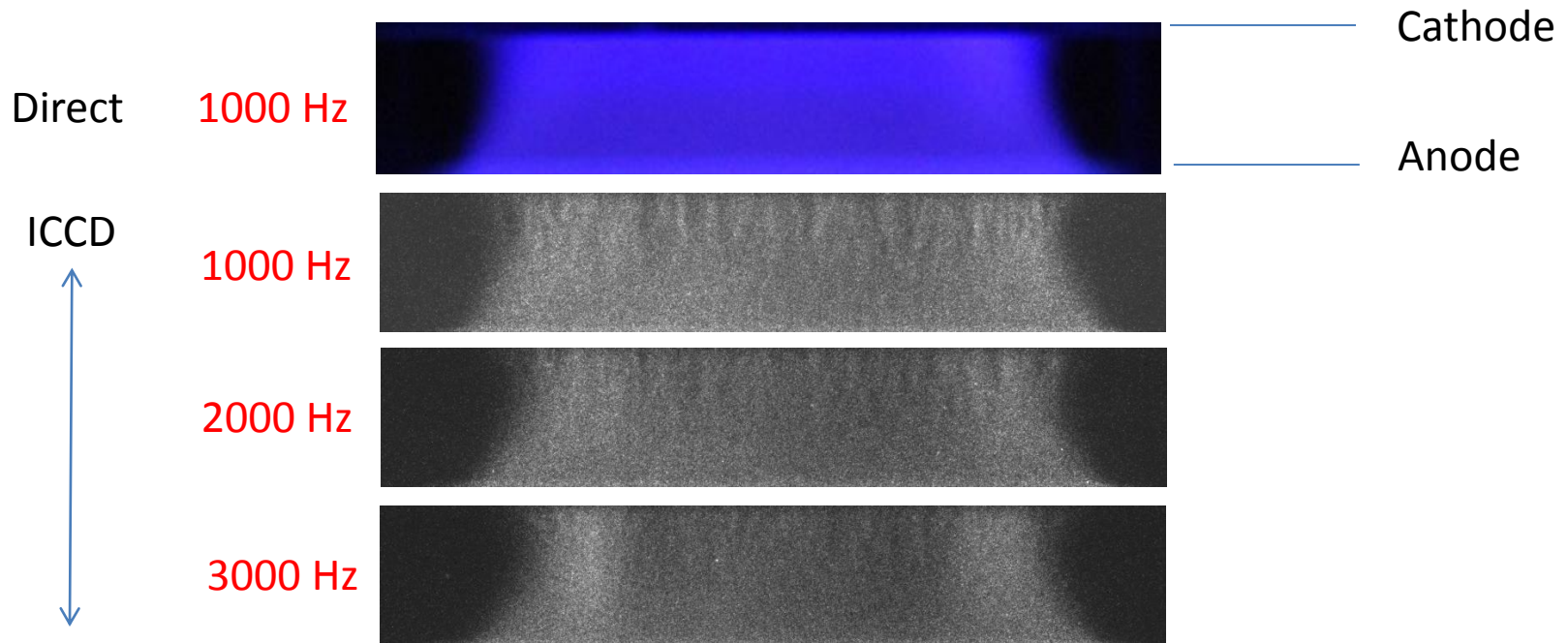
Plasma Properties

- Electrode (40 x 45 mm²)
- Repetitively -pulsed nanosecond DBD discharge
- 0- 40 kHz pulse repetition rate
- 12 nanosecond pulse duration
- 5-20 kV peak voltage

Direct and ICCD Images of Plasma Discharge in a Reactor

Stoichiometric mixtures: $\text{C}_2\text{H}_4/\text{O}_2$ with 75% AR, 60 Torr, $V_{\text{max}} = 6$ kV

- Direct Image: 1 kHz, 3.6 mJ/pulse, 2 s exposure time.
- ICCD images: Gate time = 100 ns, Gain = 250



Absorption Spectroscopy

Beer-Lambert Law

$$\frac{I_{\nu}}{I_{0\nu}} = \exp(-\alpha(\nu, P, T) NL) = \exp\left(-\sum_i S_i(T) g_{\nu}(\nu_i - \nu) NL\right)$$

I_{ν} = Transmitted Signal

$I_{0\nu}$ = Laser Signal

α = Absorption coefficient

i = Denotes absorption line with center frequency ν_i

ν = Light wavelength

S = Line strength of absorption line

T = Temperature

L = Path length of light

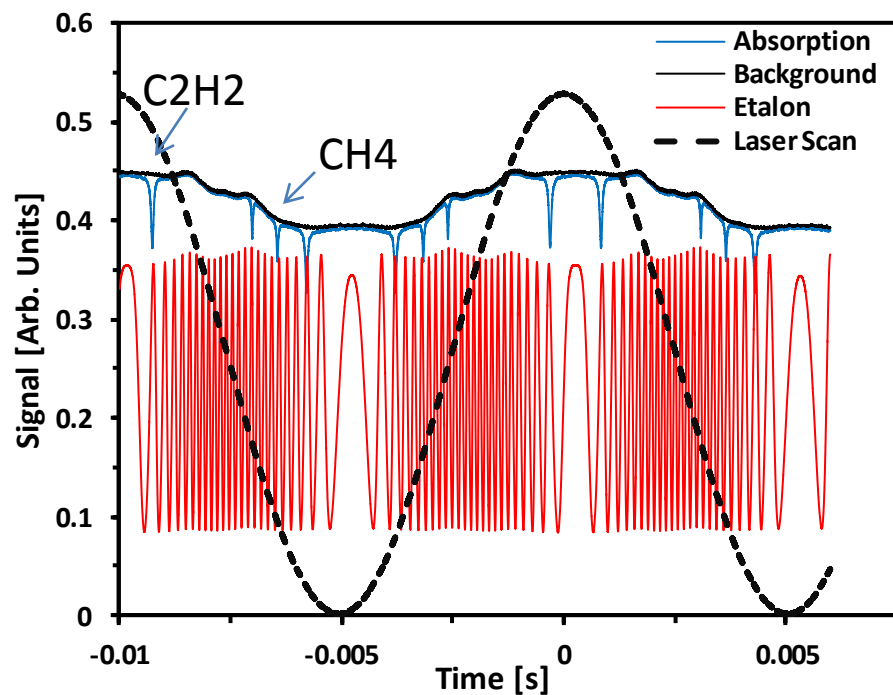
N = Number density of absorbers

g = Voigt profile line broadening function

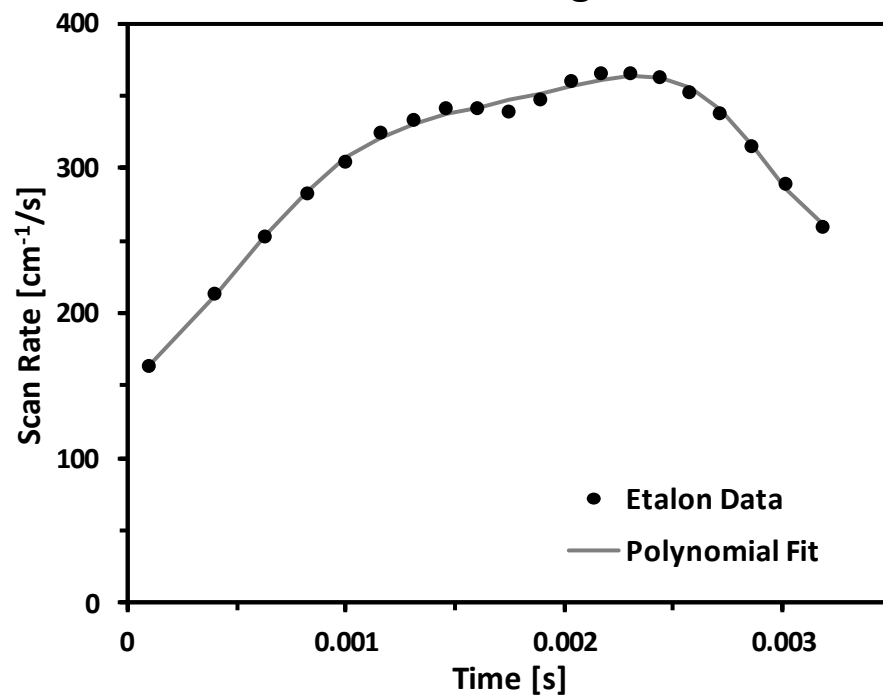
- **Multispecies diagnostics:** Line strengths from HITRAN database for H_2O , C_2H_2 , CH_4 , C_2H_4 , C_2H_6 , CO_2 , CO , O_3 , OH , HO_2 , H_2O_2 , CH_2O , NO , N_2O , NO_2
- **Temperature measurements:** Line strength on $S_i(T)$ for temperature measurements
- **Species sensitivity:** Multipass and Wavelength modulations

Absorption spectrum and wavelength scan

Signal vs. laser scan time and etalon fringes

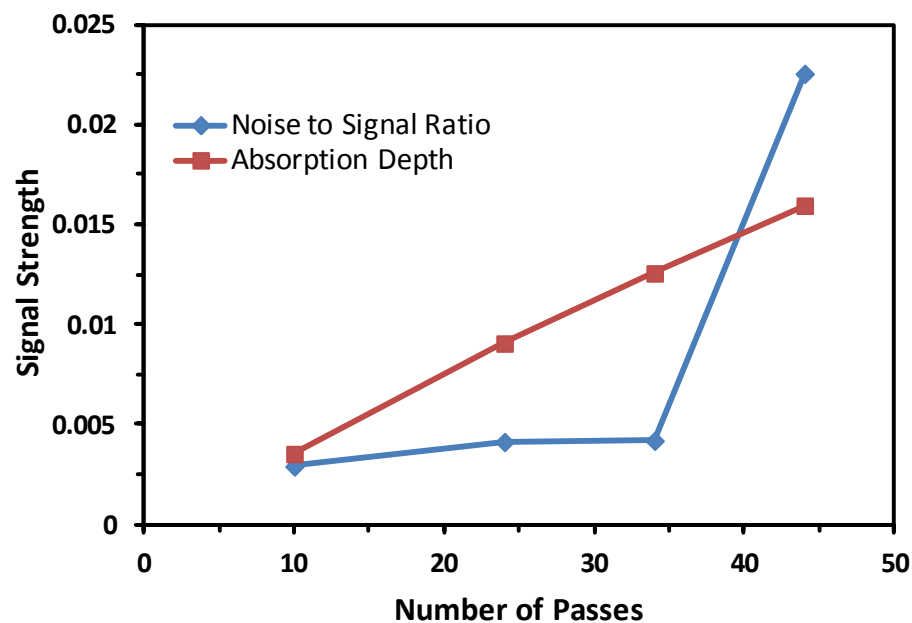
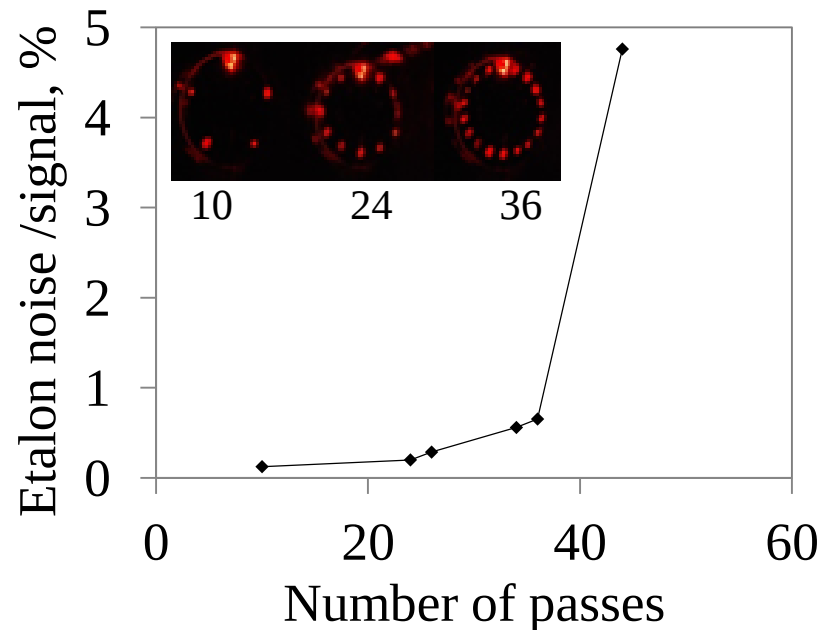
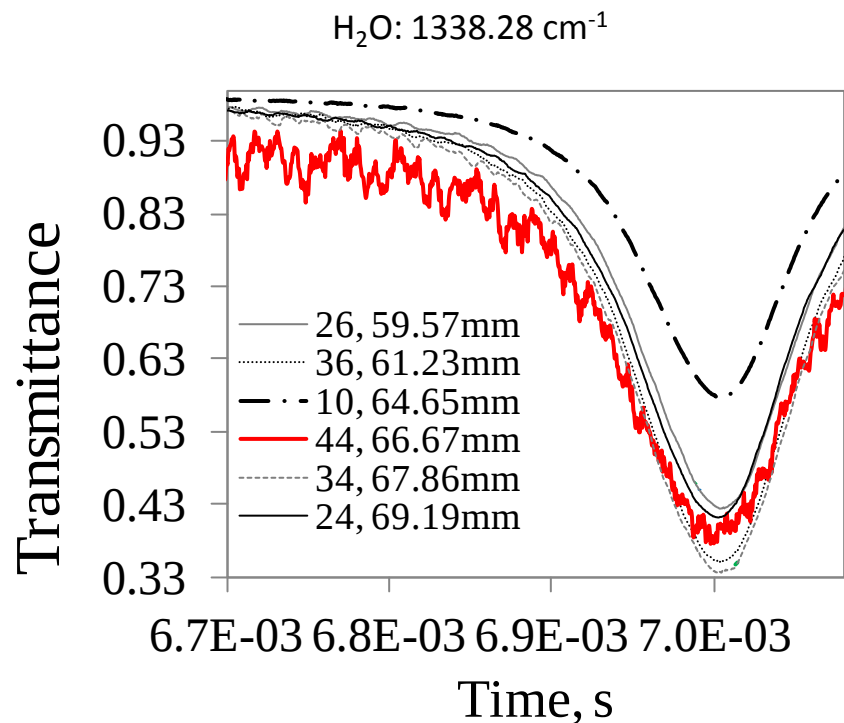


Calibrated wavelength vs. time



Multipass Mini Herriott Cell Signal and Noise Properties

12.7 mm in cell diameter

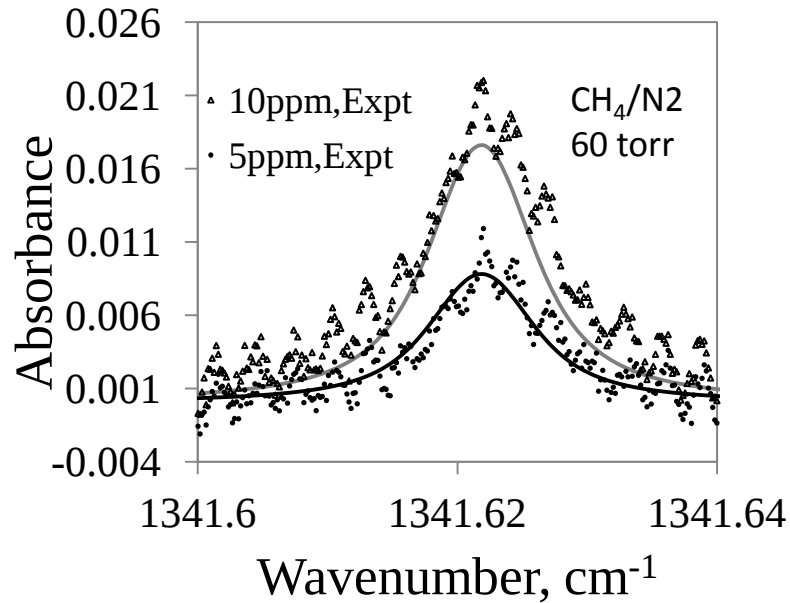


- Increase of pass number increase the sensitivity but a very high pass number causes large etalon noise

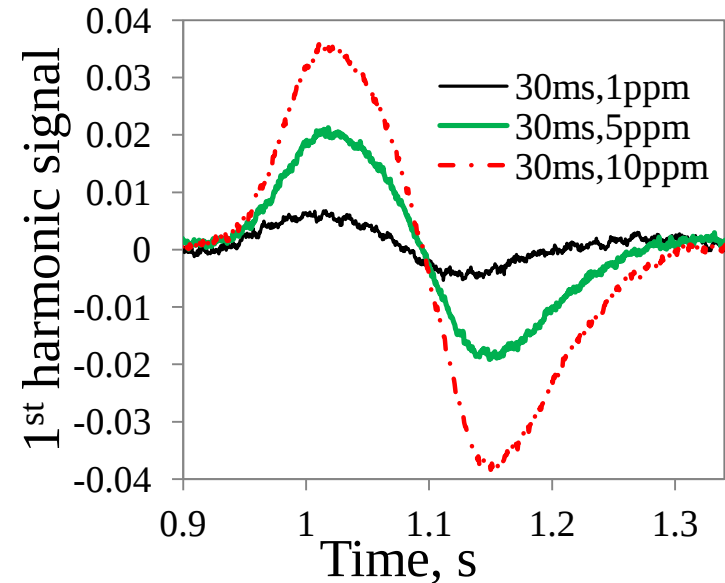
Measurement of CH₄: Direct Absorption vs. Wavelength Modulation

$$\nu(t) = \nu_0 + a \sin(2\pi f t)$$

$$f = 50 \text{ kHz} - 1 \text{ MHz}$$



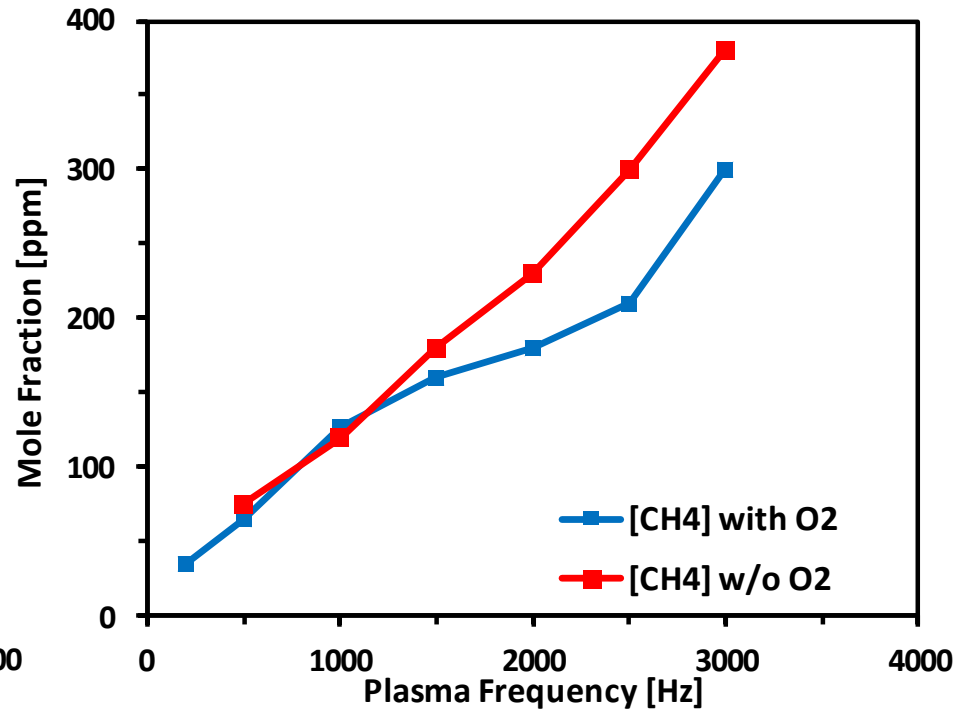
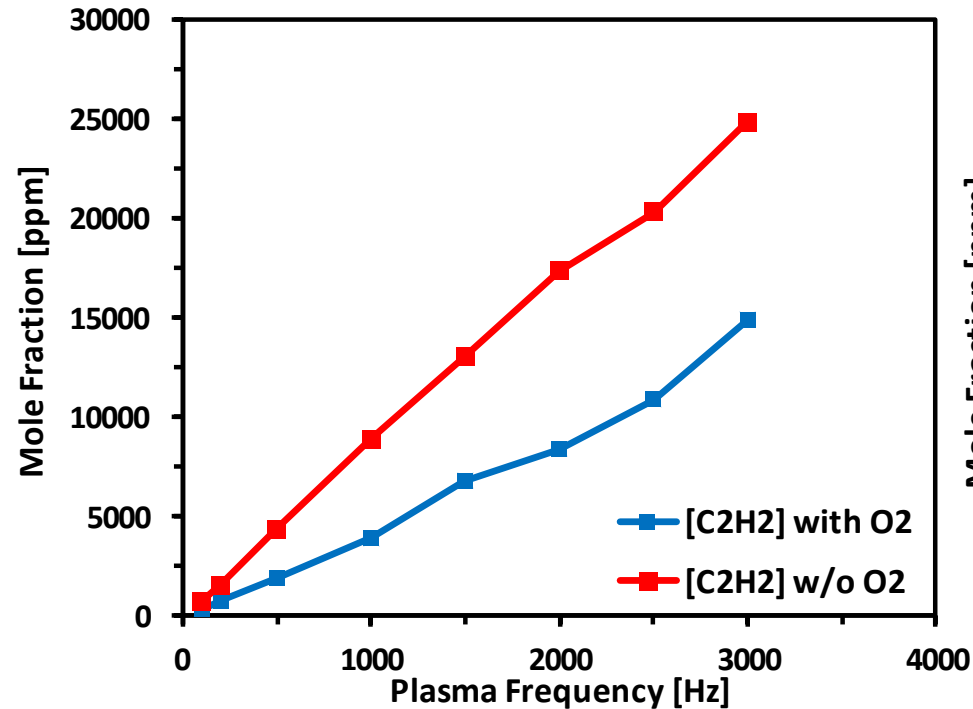
**Direct absorption
measurement of CH₄**



**Wavelength modulated absorption
measurement of CH₄**

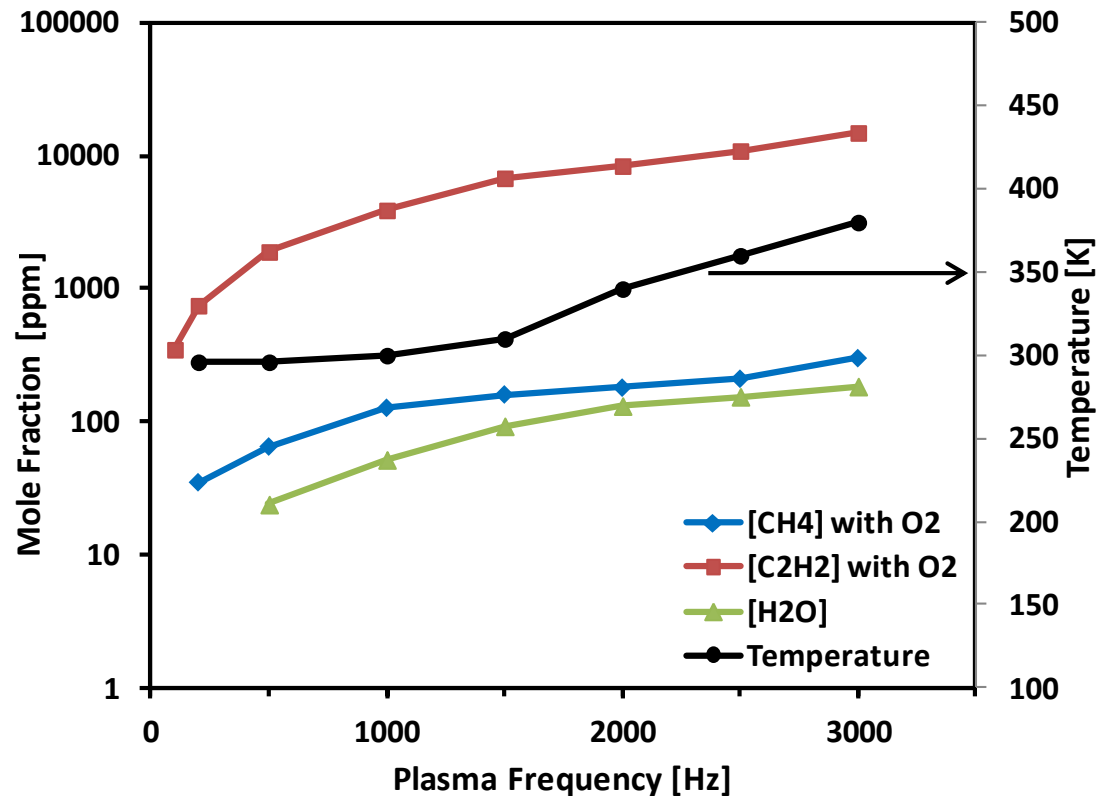
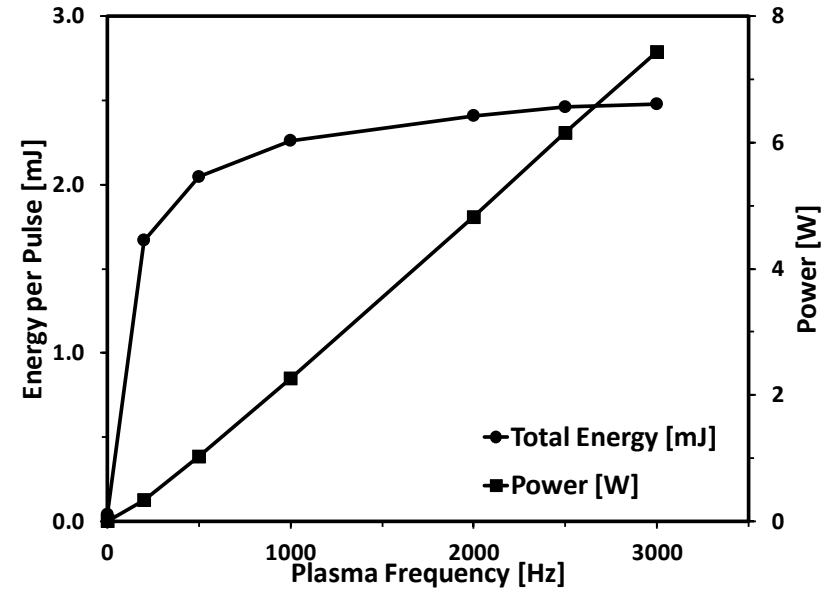
CH₄/C₂H₂ production by plasma: pyrolysis vs. oxidation

- Ar/C₂H₄, fuel mole fraction of 0.0625, 60 torr
- Ar/O₂/C₂H₄ mixtures, 25% reactants and $\phi=1$. Same fuel concentration



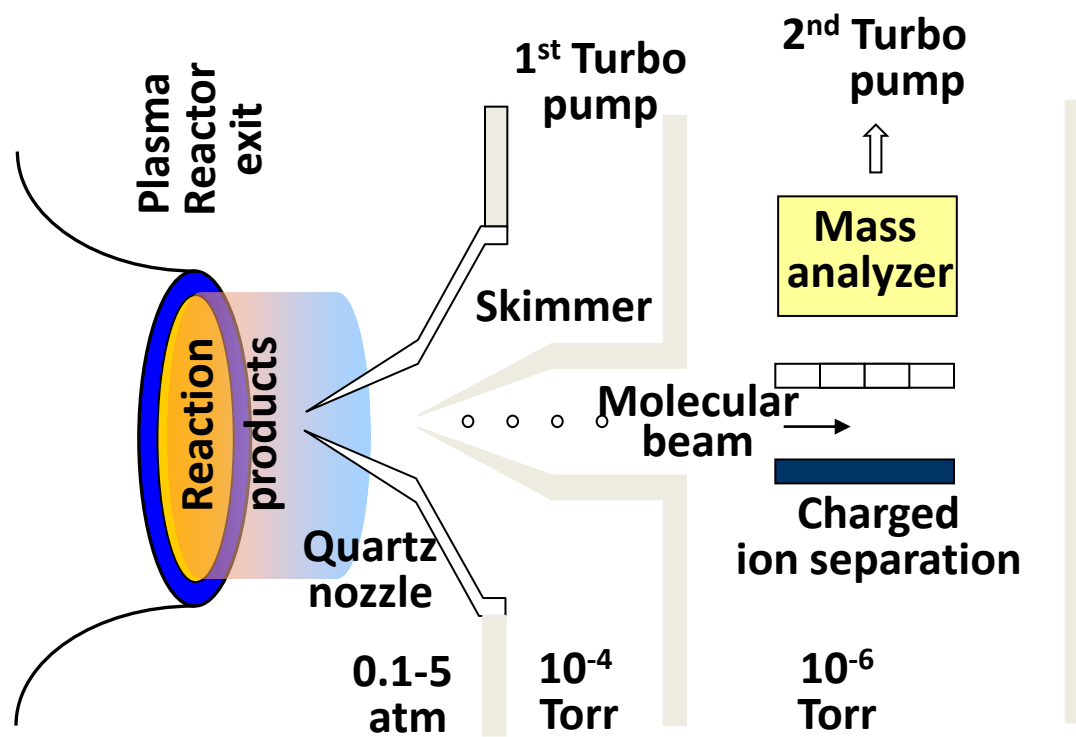
Effects of plasma frequency on temperature and species

Ar/O₂/C₂H₄ mixtures with 25% reactants and $\phi=1$, 60 torr

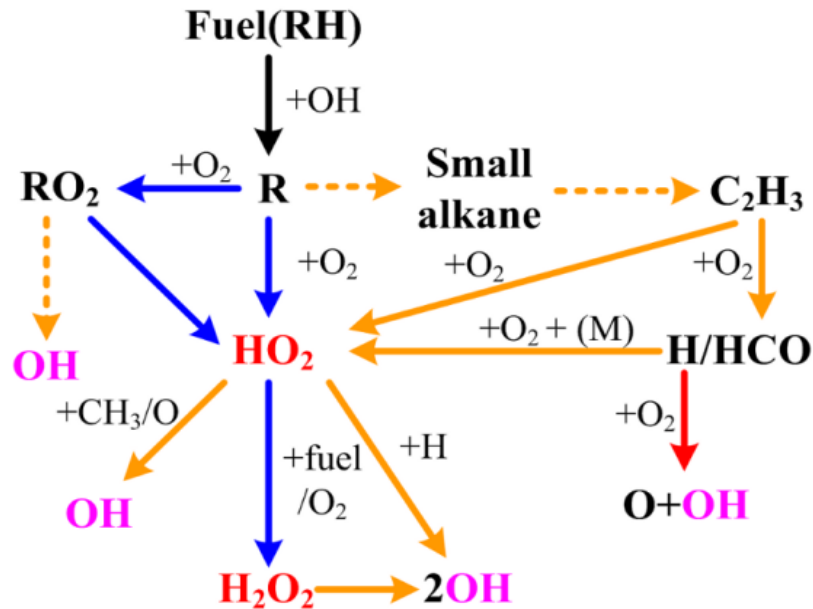


2b. Measurements of H_2O_2 and Intermediate Species in Low Temperature Dimethyl Ether (DME) Oxidation

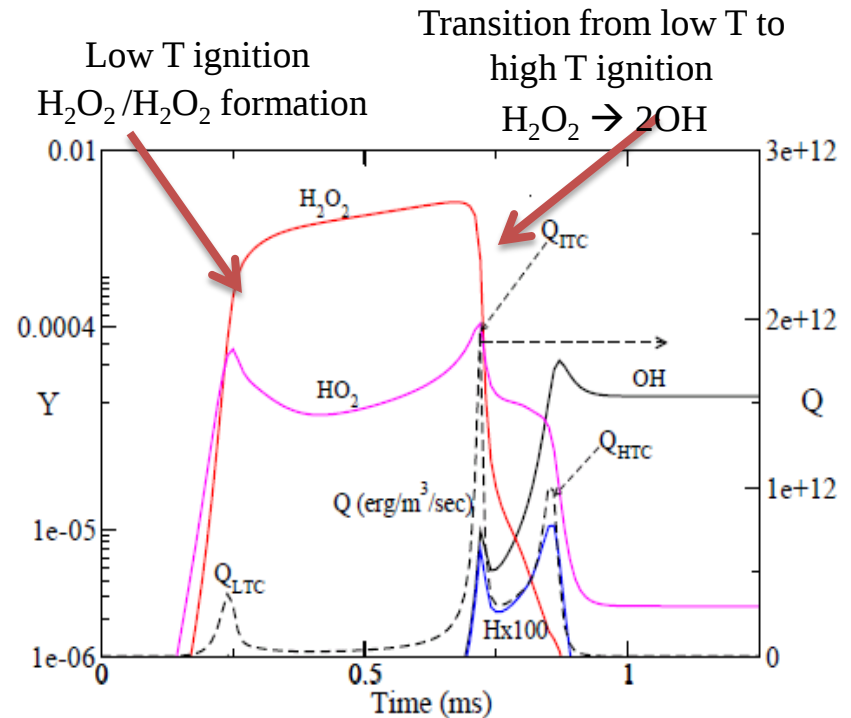
Task 3. *Species Measurements by molecular beam mass spectrometry (MBMS)*



The role of intermediate species, HO_2 , H_2O_2 in low/high temperature kinetics



- Low temperature
- Intermediate temperature
- High temperature



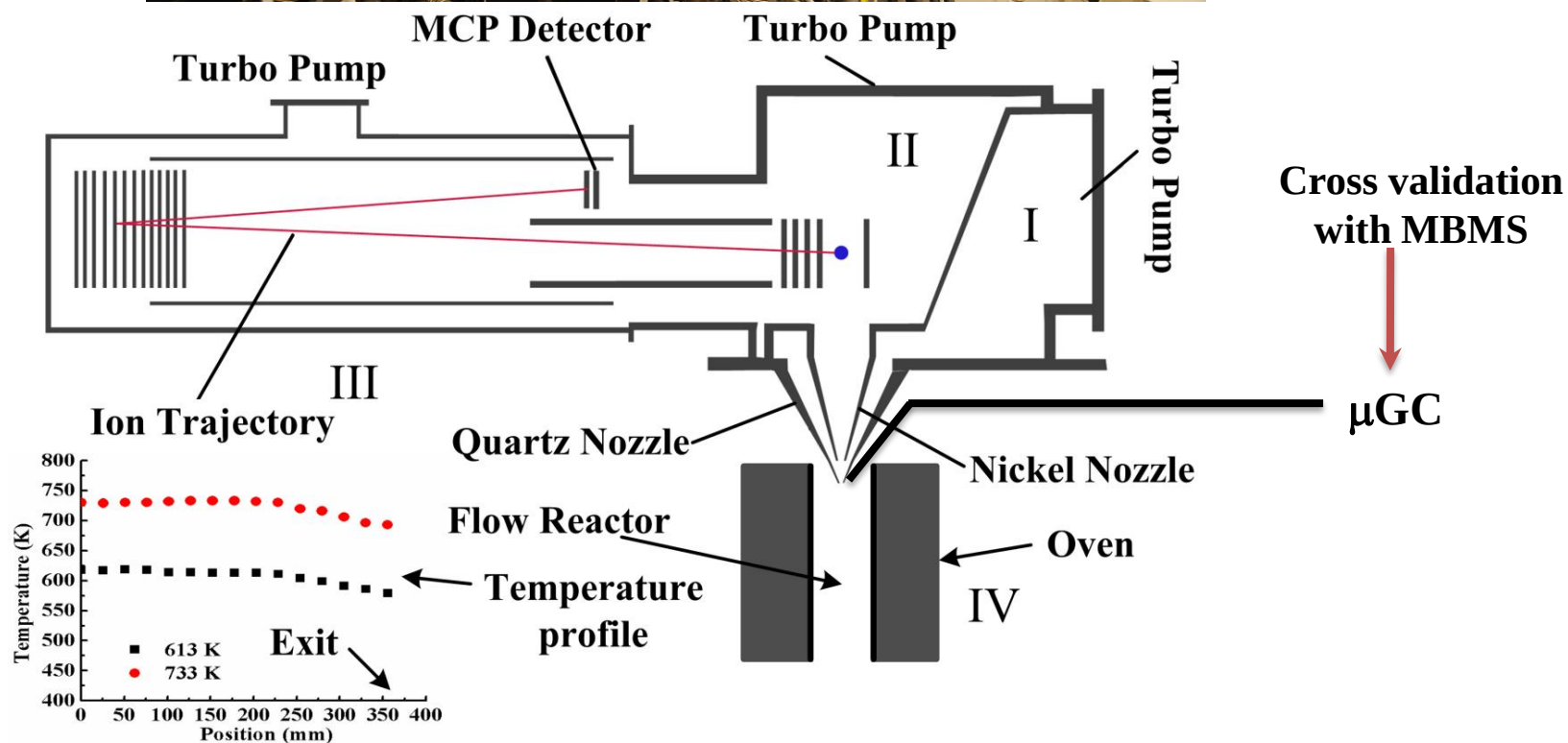
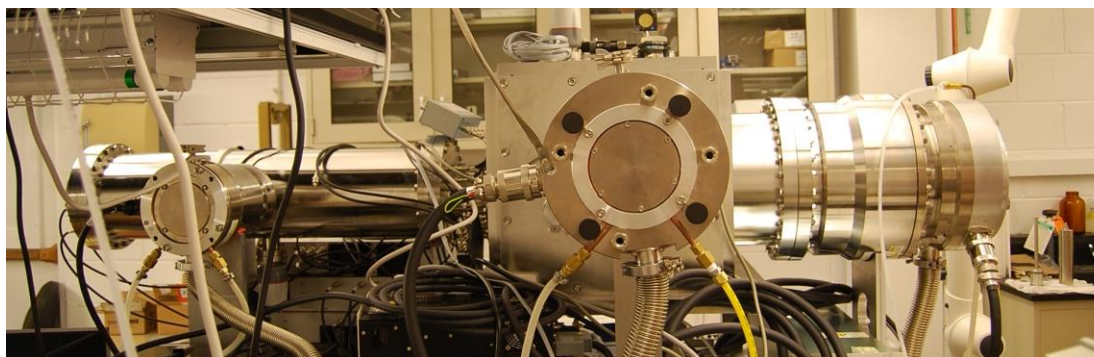
Schematic of low temperature ignition process

However, measurements of H_2O_2 and HO_2 is difficult...

- Indirect measurement of H_2O_2 : Sensitive H_2O absorption at 2.5 μm (Hong et al, 2009).
- Direct measurement: UV Photo fragmentation-OH LIF, (Li, et al, PCI, 2012).

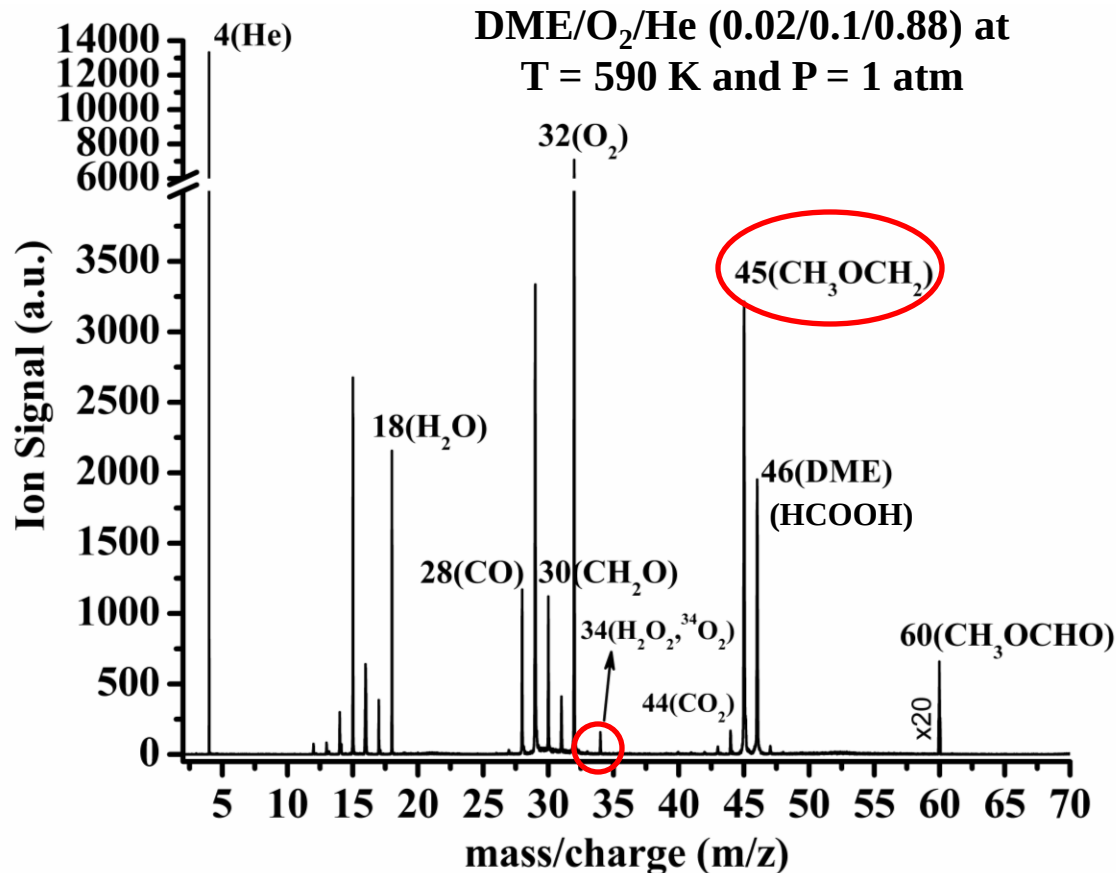
Difficult to separate H_2O_2 from HO_2 , and other large hydrocarbons

Experimental setup



$$P = 1 \text{ atm}, \tau = 1.7 \text{ s}$$

Mass spectrum and calibration



$$\frac{S_i}{S_{He}} = \frac{D_i}{D_{He}} \times \frac{\sigma_i}{\sigma_{He}} \times \frac{\chi_i}{\chi_{He}}$$

S : signal intensity
D : mass discrimination factor
σ : cross sections
χ : mole fractions

Calibration:

H₂O₂:
H₂O₂/H₂O (30.8% wt) + He

Corrected H₂O₂ concentration via
2H₂O₂ → 2H₂O + O₂ and
subtraction of ³⁴O₂ signal

CH₂O, CH₃OCHO:
Measured D, σ from Ref.[1]

Fragmentation:

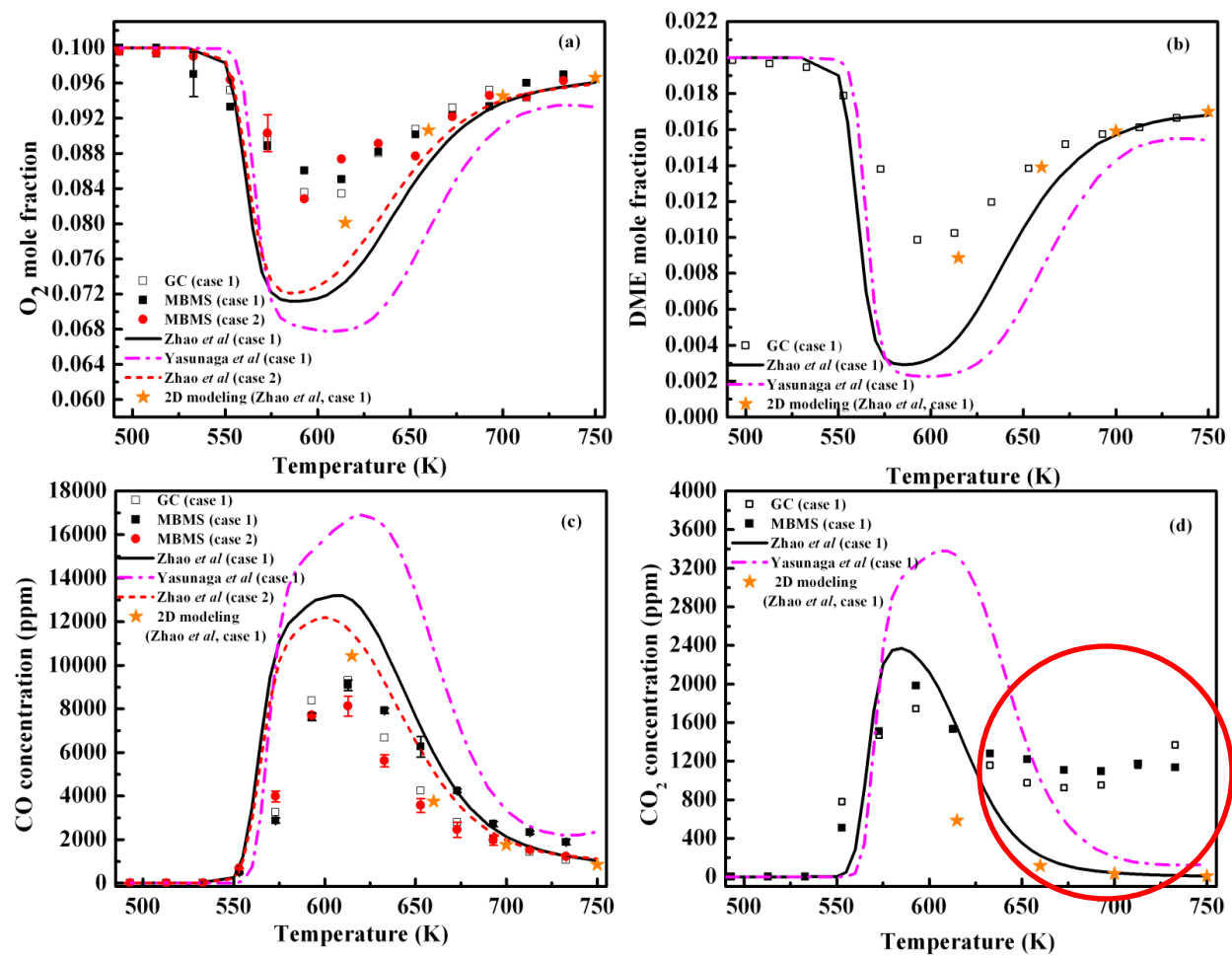
Constant ratio, can be removed
from post processing

Mass overlap:

DME & HCOOH, N₂ & CO

Major species measurements

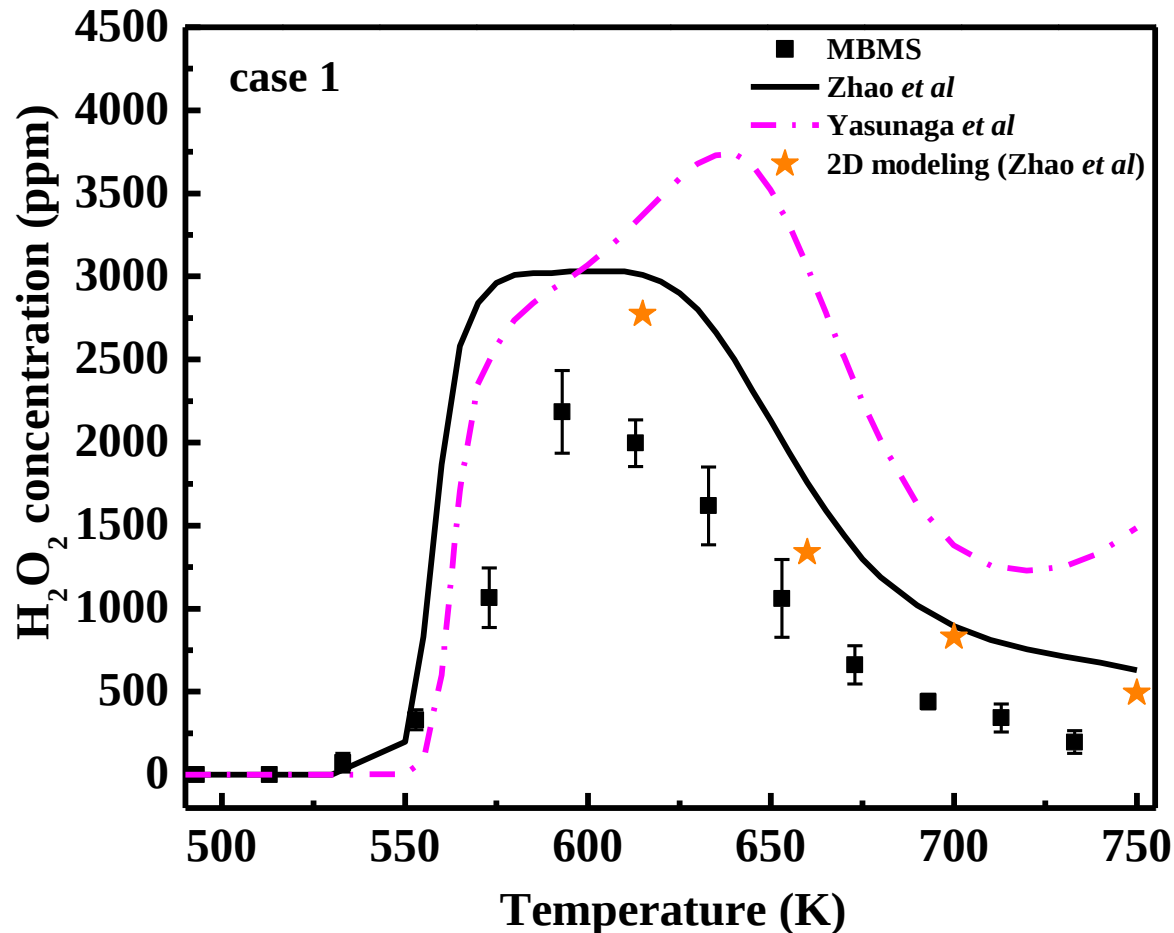
Good agreement between micro-GC and MBMS quantification → validation of MBMS techniques
2-D simulations give good agreement with data; 0-D simulations are semi-quantitative



High CO₂ production

0-D Models show reasonably good agreement for LTC temperature window and peak reactivity
Yasunaga et al model has overall higher reactivity and wider LTC temperature window

H₂O₂ measurement

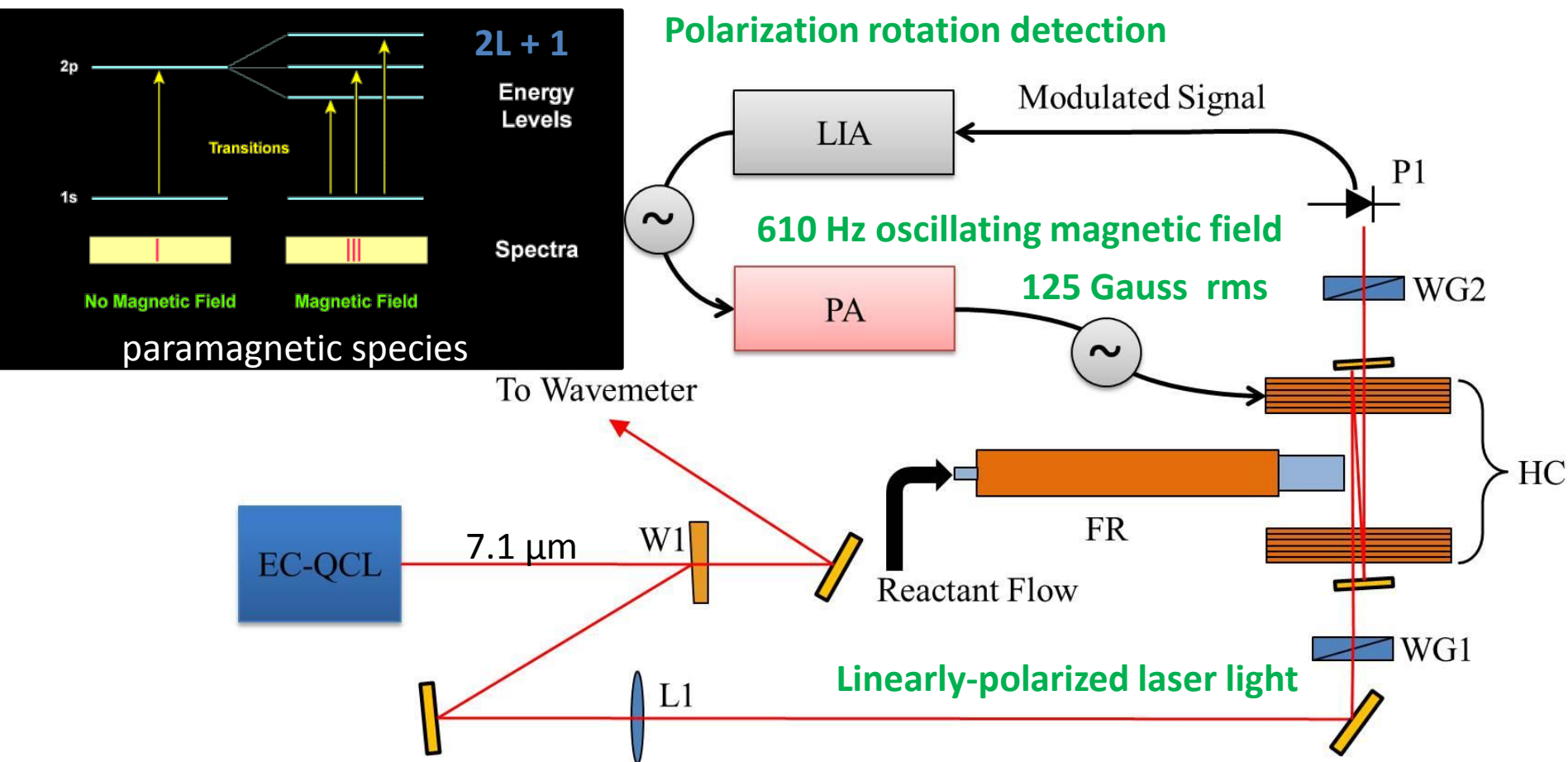


Good agreement for H₂O₂ formation
Different predictions from different models

2c. Development of a Mid-IR Faraday Rotational Spectroscopy Method to quantify HO₂

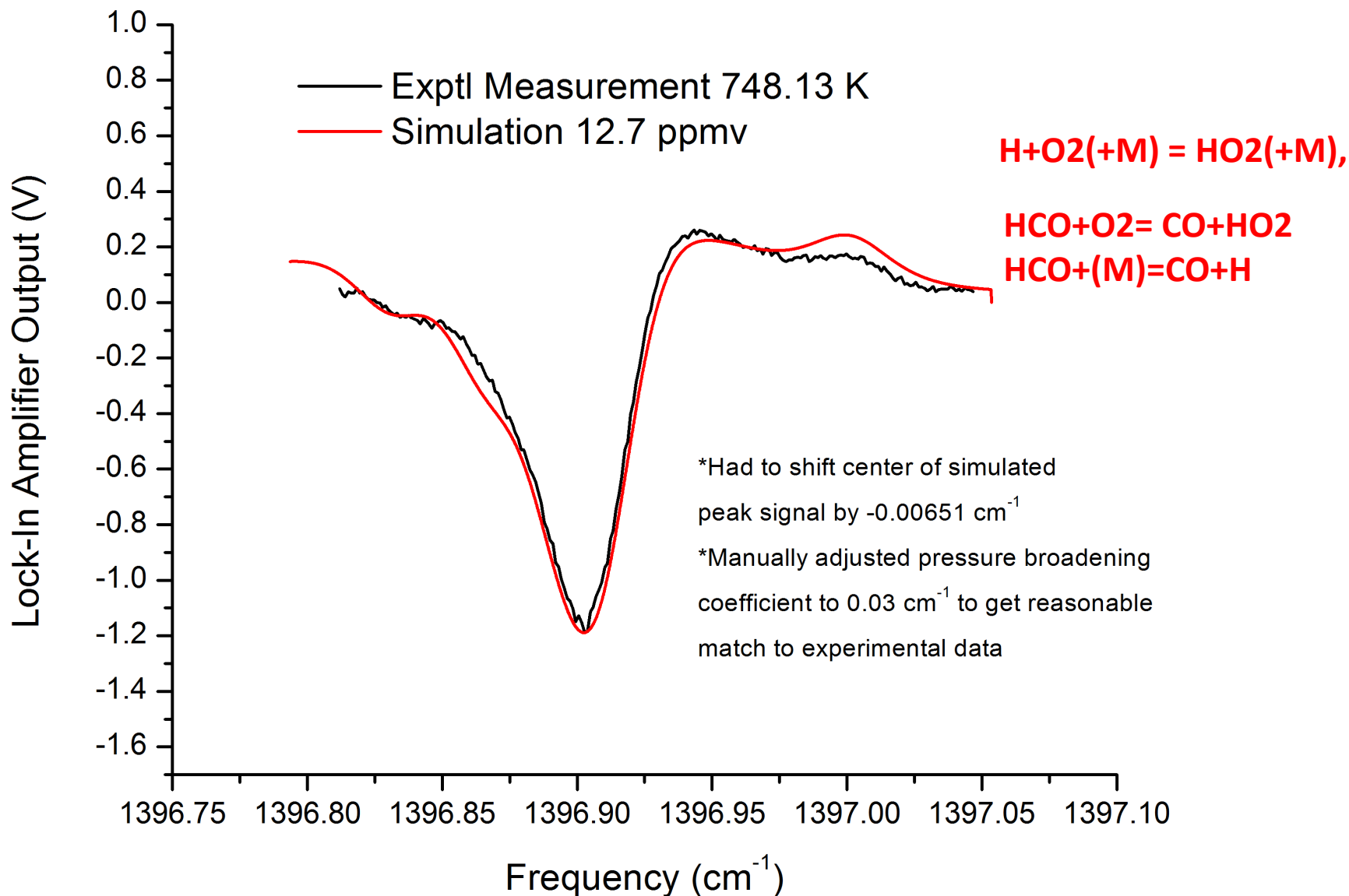
Quantitative HO₂ Measurement (**very challenging!**):

Mid infra-red Faraday Rotation Spectroscopy (FRS), 1396 cm⁻¹

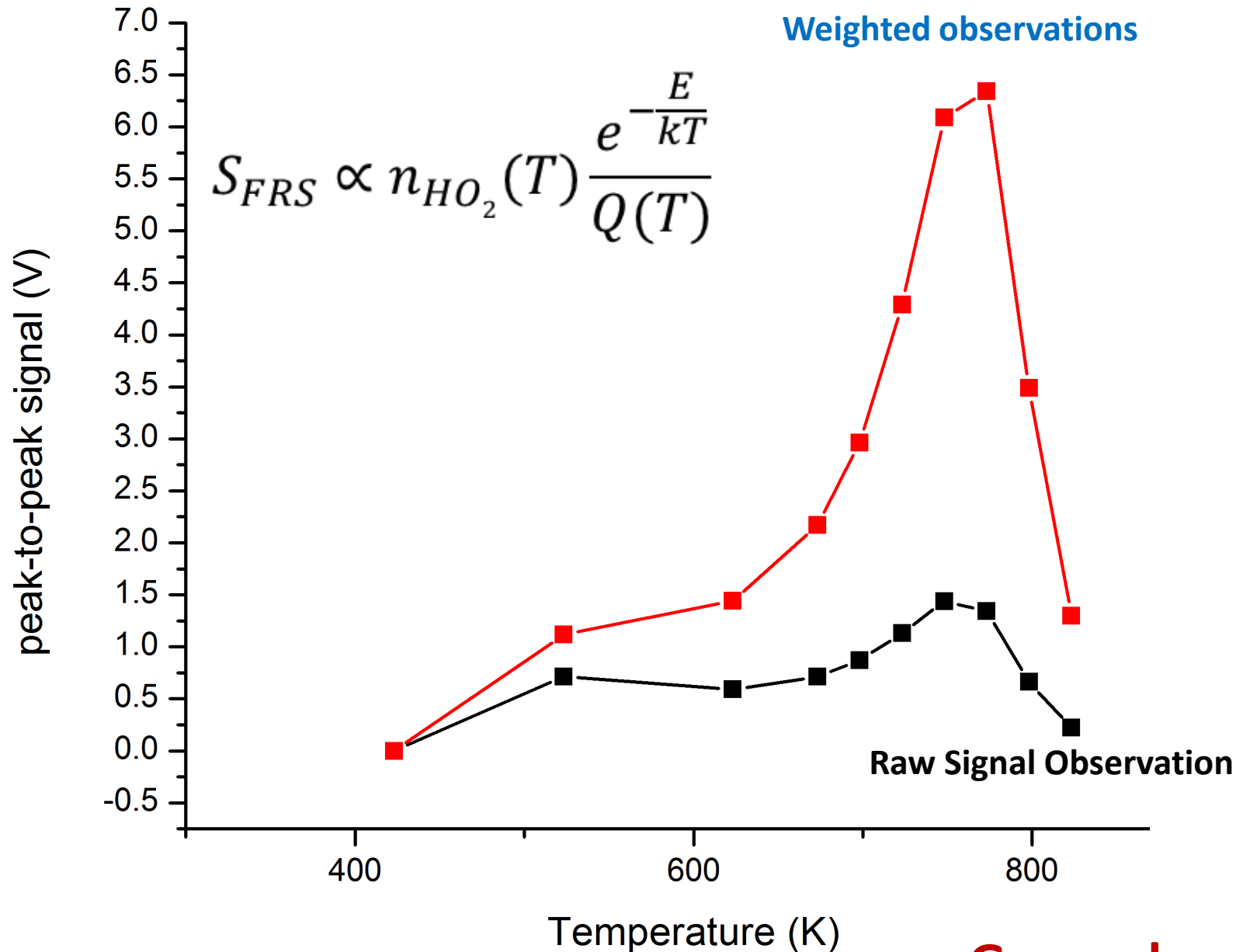


Brian Brumfield, Wenting Sun, Gerard Wysock, and Yinguang Ju, submitted to JACS, 2012

Sub-ppm level HO₂ measurement in DME/air flow reactor (1atm, 748K)



Temperature Dependence of HO₂ Signal in a flame reactor



Game changer?!

3. Ignition Enhancement and the critical ignition energy by Pulsed Nanosecond Discharge - Pulse Detonation Combustor/Engine

(with Timothy Ombrello, Fred Schauer, and John Hoke of the AFRL)

Thrust 1 Task 6. *Ignition Initiation Time and Minimum Ignition Energy*

• **Motivation:**

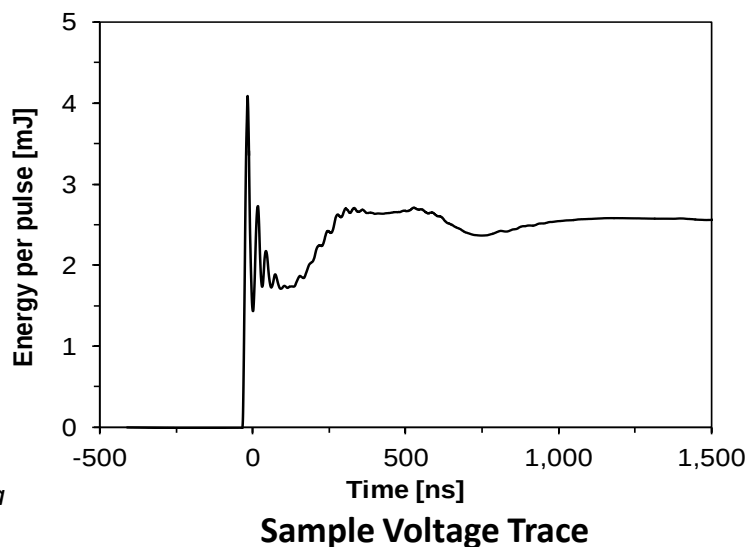
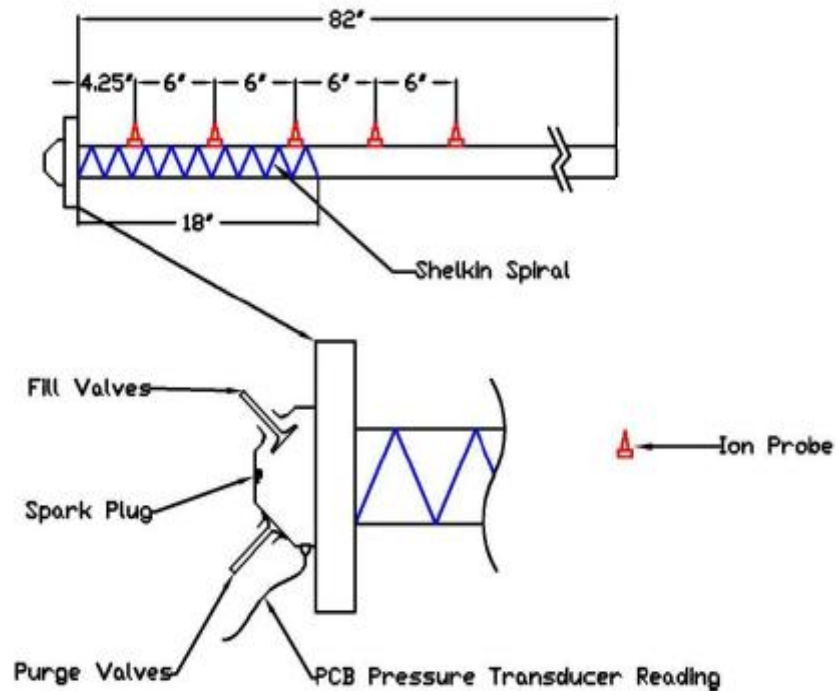
- Demonstrate non-equilibrium plasma enhances ignition in a real PDE vs. a spark plug.
- Proof-of-concept studies have shown **decrease in ignition time for propane/air mixtures** in a quiescent environment and atmospheric pressure using repetitively pulsed nanosecond discharges¹
- Depositing more energy faster has potential benefits **for short residence-time, highly turbulent environments** present in a range of propulsion devices

• **Power Supply:**

- Nanosecond power supply delivers 12-ns pulses up to 40 kV (peak) & 40 kHz
- 1-5 mJ/pulse deposited into gas

• **Experiment:**

- Spark plug machined into point-to-point electrode geometry with a 1.4 mm gap
- Nanosecond discharge compared with lab standard *Multiple Spark Discharge* (MSD)
 - Consumes 115 mJ/pulse but deposits only 4-8 mJ/pulse into gas
 - Gives multiple sparks of the same energy each. Number of sparks cannot be controlled
- Ion probes used to quantify wavespeed
- Ignition is determined when pressure trace reaches a slope of 5 V/s on PCB trace
- Schlieren imaging performed at 100,000 fps



1. S. V. Pancheshnyi, D. A. Lacoste, A. Bourdon, C. O. Laux, *IEEE Trans. On Plasma Science*, vol. 34 (2006).

Aviation gasoline/Air Mixtures

➤ Equivalence ratio is varied along with number of pulses at fixed plasma energy/pulse and plasma frequency

➤ **Nanosecond pulser decreases ignition time up to 25% compared to MSD**

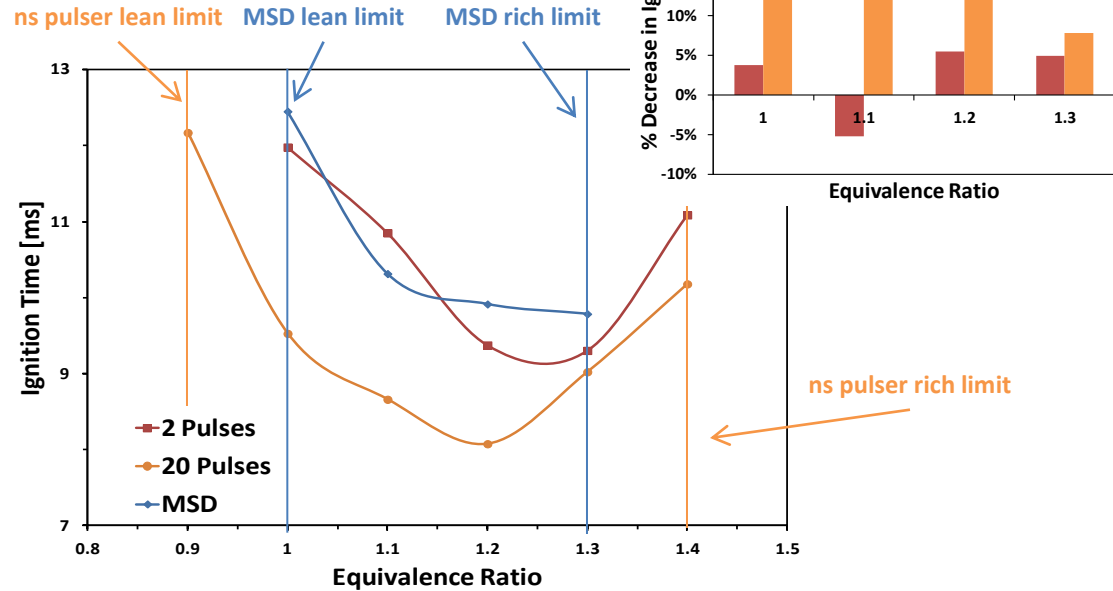
- Pulsed discharge allows more energy to be coupled into gas in a shorter time period than MSD ignition system.
- **Advantageous for the turbulent, small residence-time flows in the PDE**

➤ Plasma properties:

- Plasma energy: 2.8 mJ/pulse on average
- Plasma frequency: 40 kHz

➤ MSD spark system currently in use:

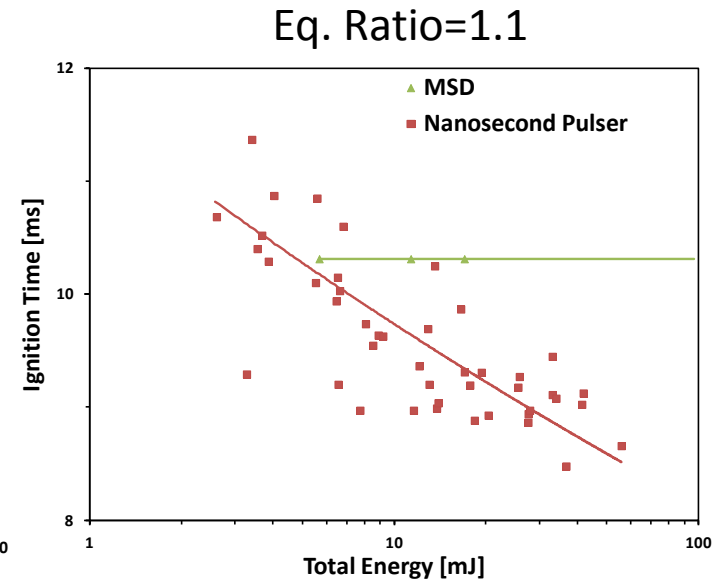
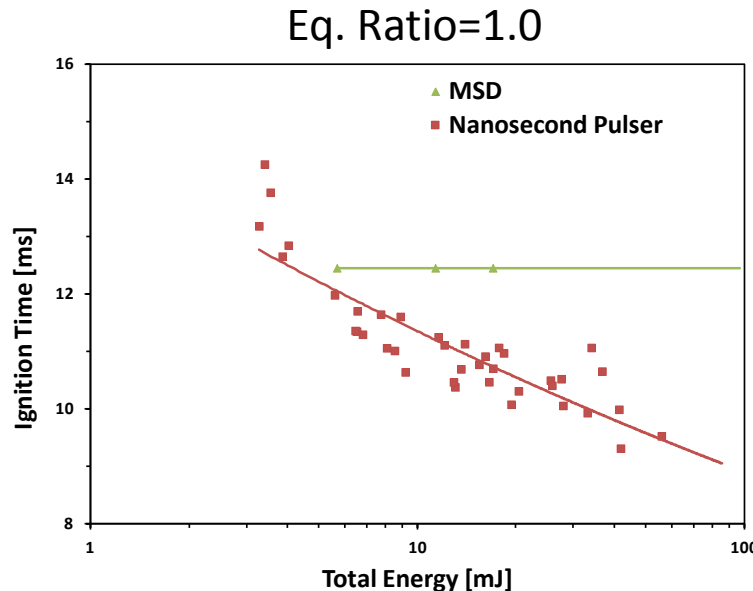
- Spark energy: 5.7 mJ/spark
- Multiple sparks (1-12 possible)
- Spark frequency: 0.87 kHz



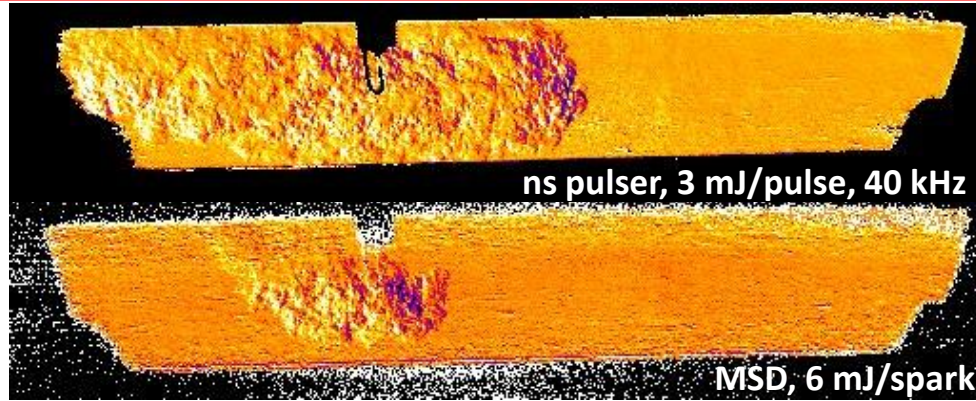
➤ **Pulse energy and plasma frequency are varied at fixed equivalence ratio**

➤ Total energy = energy/pulse x number of pulses

➤ Ignition time decreases with total energy for ns-pulser case



Schlieren Imaging



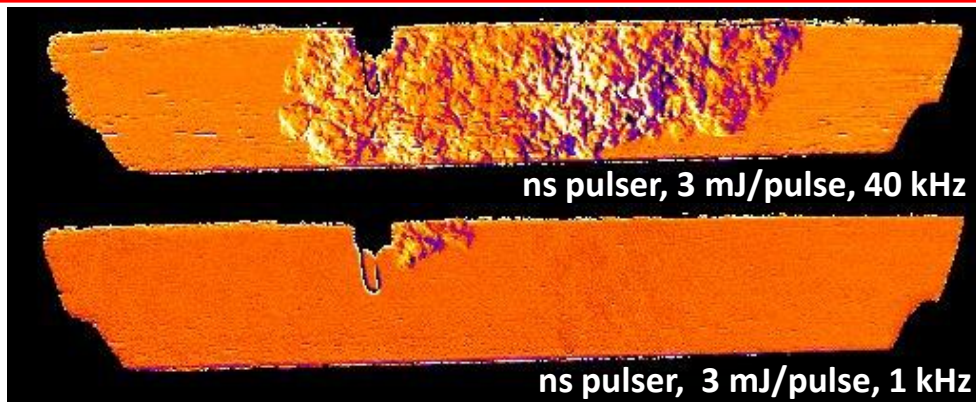
Comparison with conventional ignition

$\Phi=1$ Ethylene/Air

Top: ns pulser, 20 pulses at 40 kHz

Bottom: MSD, 3 sparks at 0.87 kHz

Time shown is 3 ms after first discharge



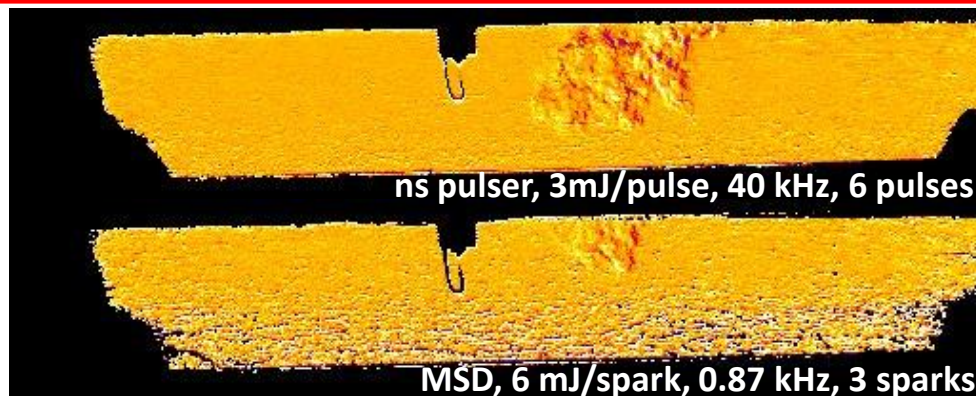
Effect of high frequency

$\Phi=1$ Methane/Air

Top: ns pulser, 5 pulses at 40 kHz

Bottom: ns pulser, 5 pulses at 1 kHz

Time shown is 7 ms after first discharge



Lean equivalence ratio, equal energy

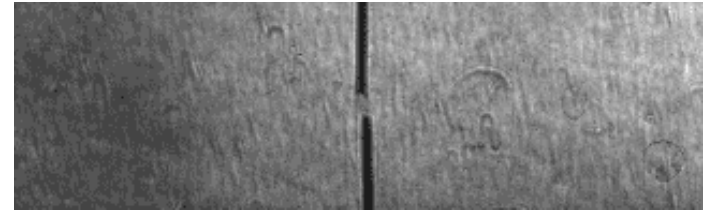
$\Phi=0.8$ Methane/Air

Top: ns pulser, 6 pulses at 40 kHz

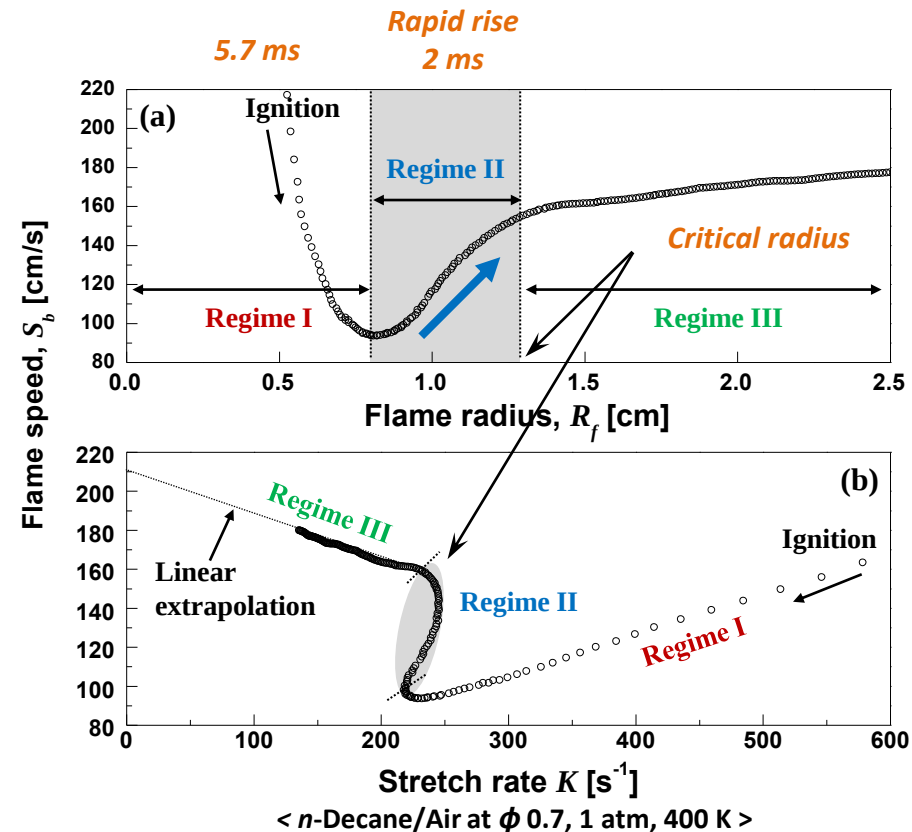
Bottom: MSD, 3 sparks at 0.87 kHz

Time shown is 7 ms after first discharge

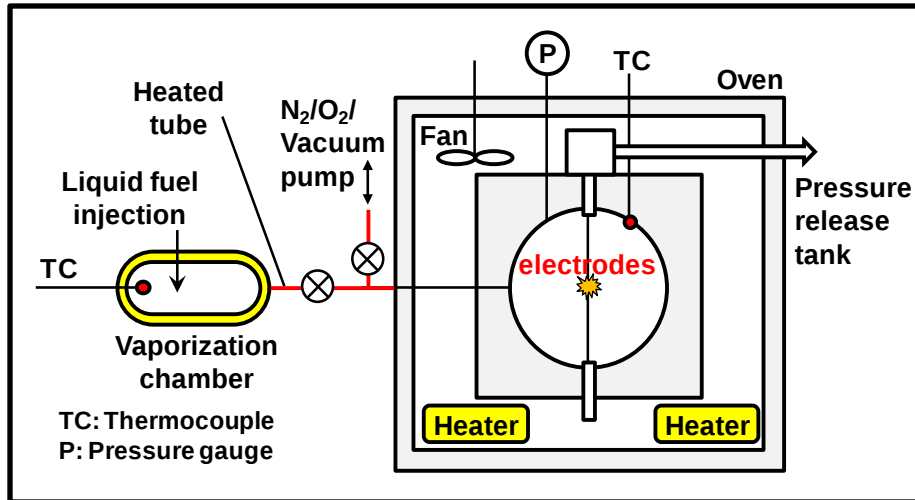
Ignition/ Flame initiation/Critical radius



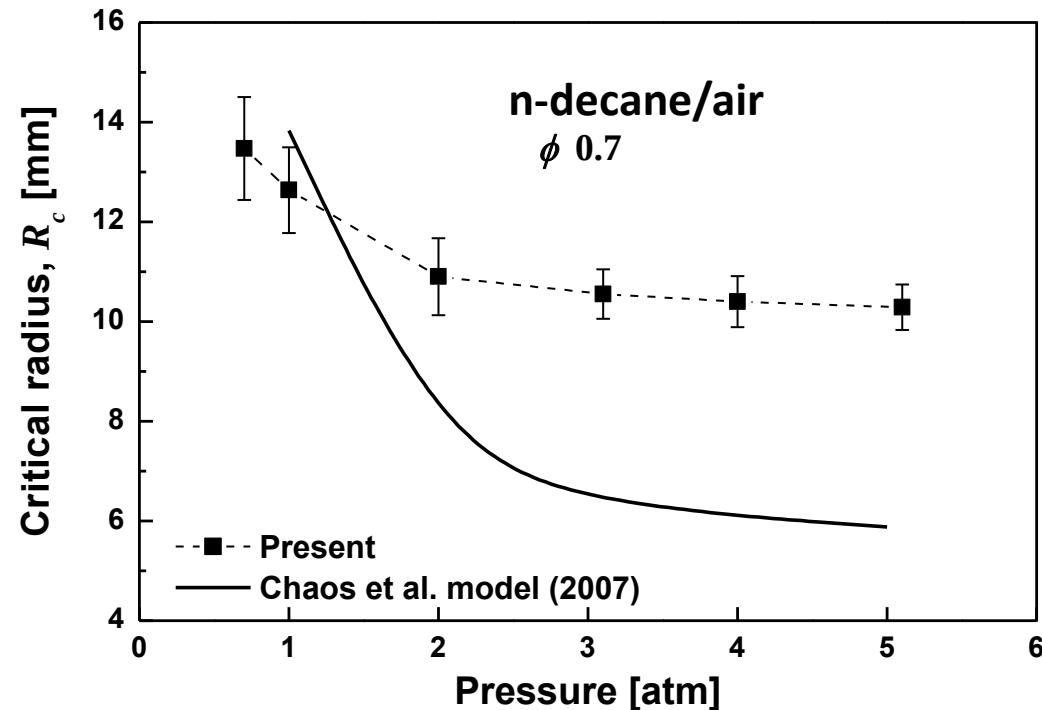
- Three distinct flame regimes
 - **Regime I**
 - Spark assisted ignition kernel
 - **Regime II**
 - Transition from ignition kernel to normal flame
 - **Weak flame regime**
 - **Regime III**
 - Self-sustained stable propagating flame
- Consistent with previous study²
- Ignition failure vs. Critical radius



Measurements of critical flame radius for ignition vs. pressure



- What is the effect of plasma discharge volume?
- What is the effect of turbulence?



Conclusions

1. *In situ* discharge can significantly increase the kinetic effect of plasma and achieve sublimit combustion.
2. A new monotonic ignition transition regime was observed with PAC.
3. PAC enhances low temperature chemistry and may change combustion kinetics in engine conditions with very short residence time.
4. PAC shortens ignition delay time in turbulent PDE combustion environment. Large volume discharge helps to drive the ignition kernel to overcome the critical flame radius at reduced pressure.
5. A reactor coupled mid-infrared absorption spectroscopy and MBMS system are developed and successfully measured H_2O_2 and other intermediate species.
6. A mid-infrared Faraday rotation spectroscopy method is developed and successfully measured HO_2 in a flow reactor.

Acknowledgement

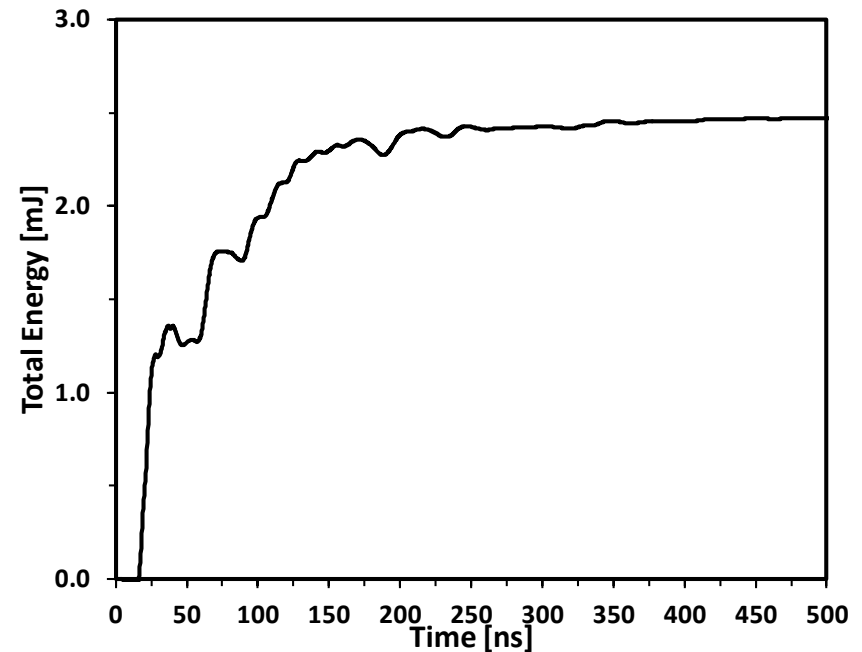
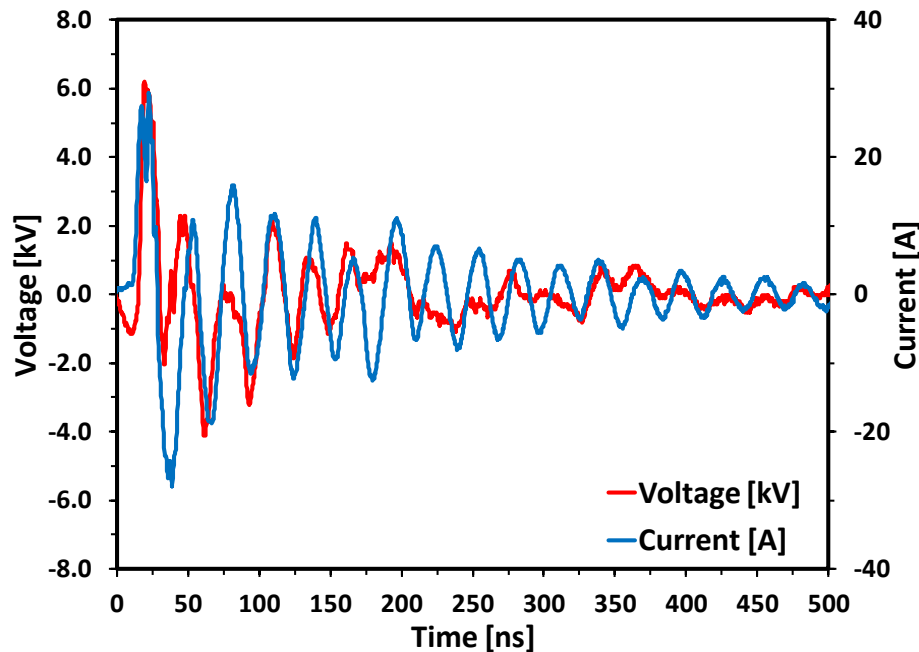


This work was supported by the plasma **MURI** research grant from the Air Force Office of Scientific Research (Drs. Chiping Li, Julian Tishkoff).

Thank you!

QUESTIONS & COMMENTS?

Measurement Technique

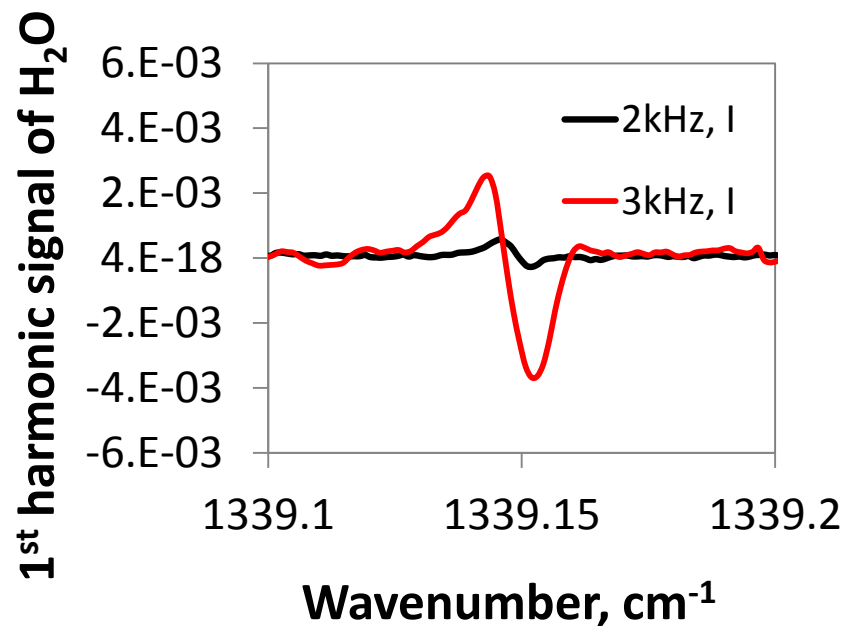
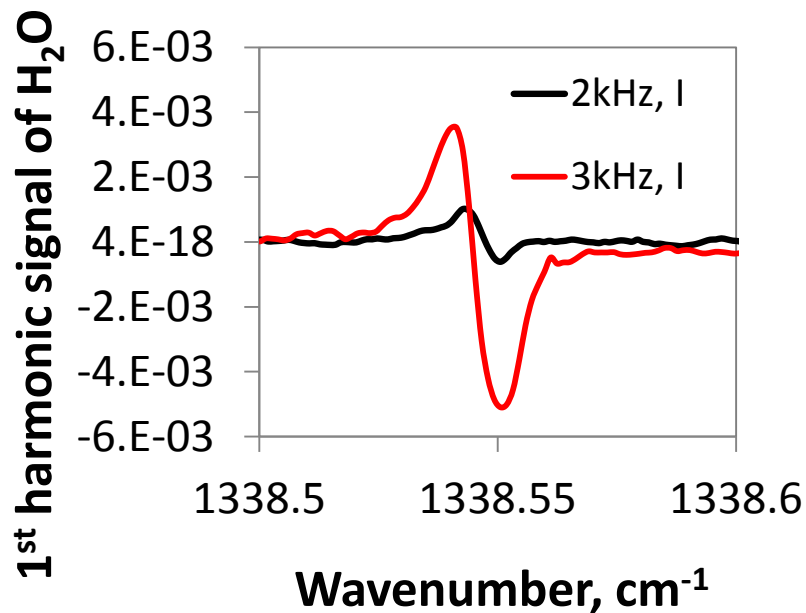


- Current and voltage are measured for each condition
 - Voltage probe: LeCroy high voltage probe (PPE20KV)
 - Current probe: Pearson Coil (Model 6585)
- Peak voltage for all experiments ≈ 6 kV
- The total energy is computed by integrating the power over a long enough time scale for all reflections to be included

H₂O and temperature measurements with plasma discharge

H₂O lines at 1338.5 cm⁻¹ and 1339.15 cm⁻¹

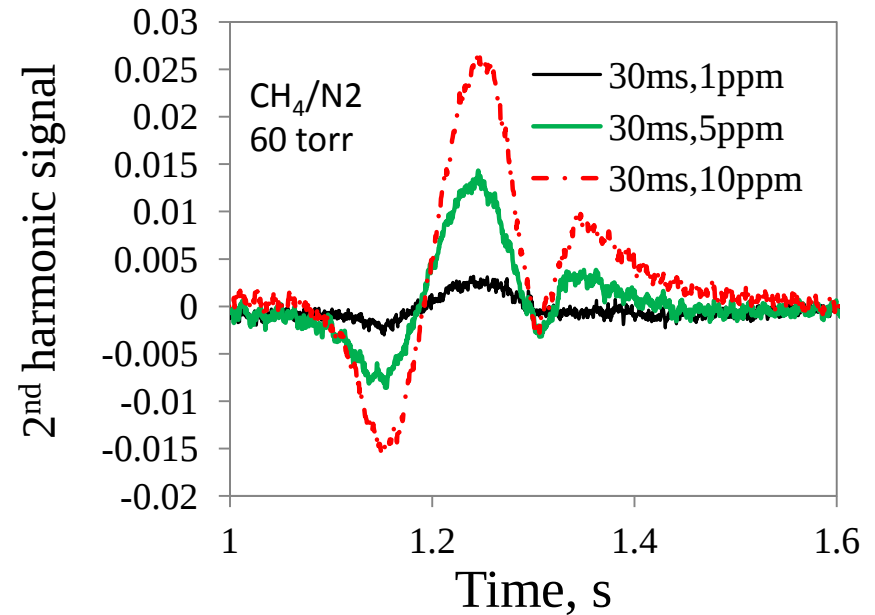
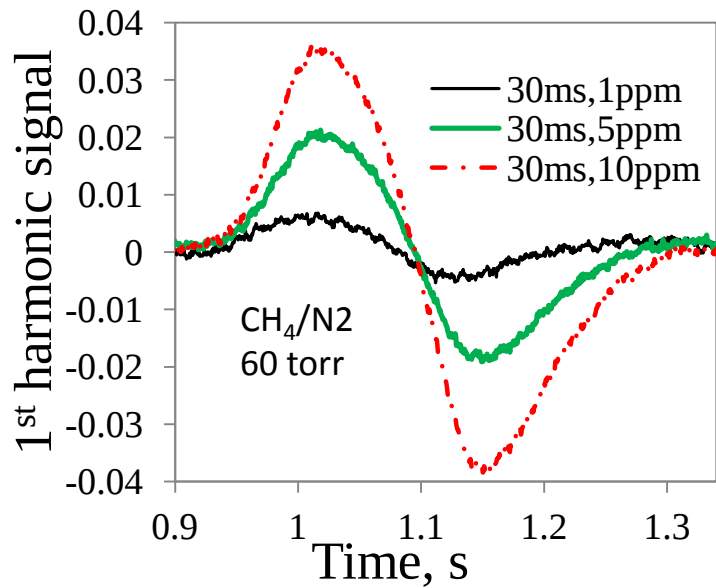
- Laser scan: 100 Hz, f=1 MHz, t_{RC}= 7.5 μs
- Voigt profile fitting HITRAN for number density and temperature



HITRAN: J. Quant. Spectrosc. Radiat. Transfer, 111, 2139–2150 (2010).

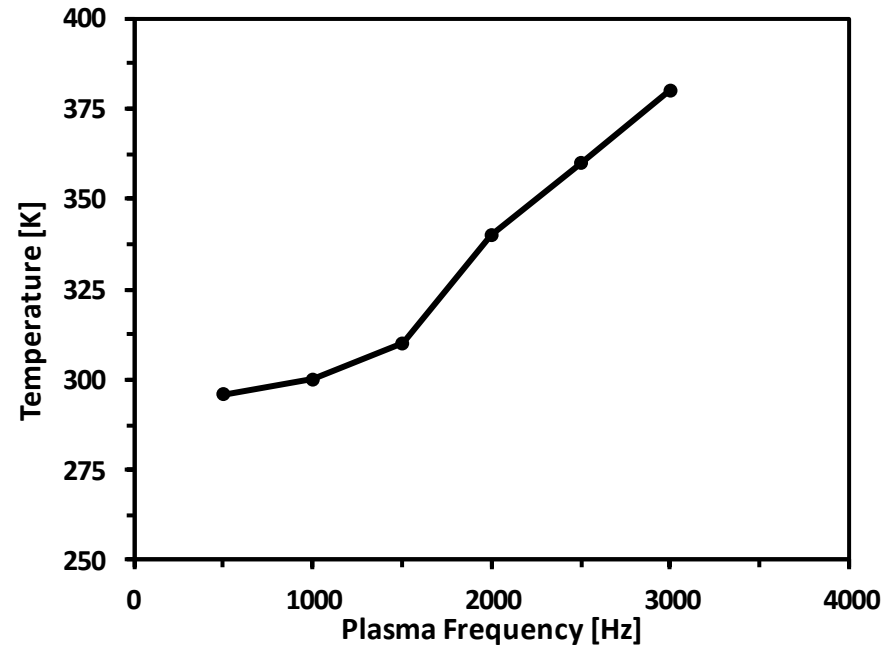
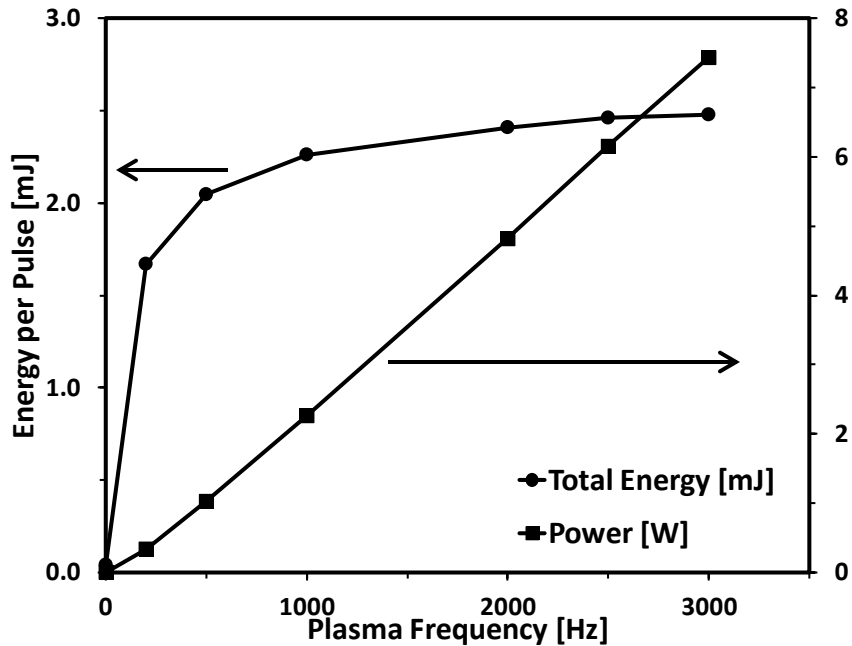
Wavelength modulated absorption measurement of CH₄

$$\nu(t) = \nu_0 + a \sin(2\pi ft) \quad f = 50 \text{ kHz} - 1 \text{ MHz}$$



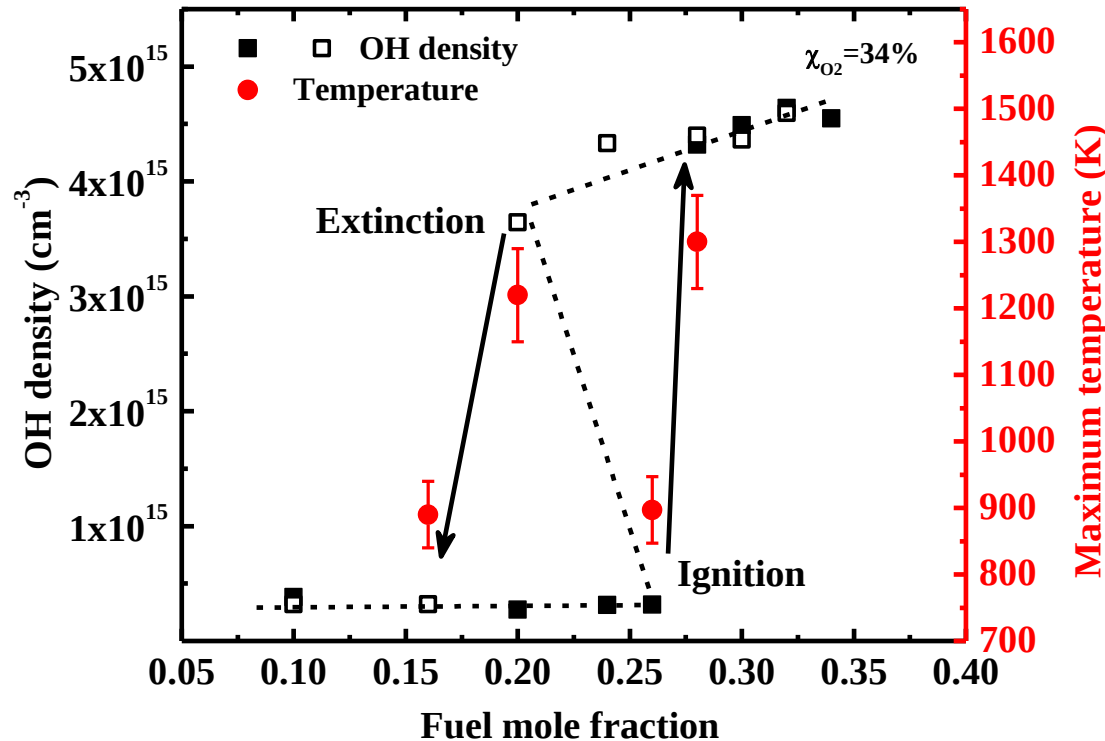
Laser was scanned at 0.1Hz and modulation at
along with using lock in amplifier

Results for Continuous Plasma



- Results are for $\text{Ar}/\text{O}_2/\text{C}_2\text{H}_4$ mixtures with 25% reactants and $\phi=1$
- The flow speed is 40 cm/s and the pressure is 60 Torr
- Per pulse energy is dependent on plasma repetition frequency
 - Seed electrons and ions left over from previous pulse provide for easier breakdown
 - This effect levels off after about 1000 Hz
- At high pulse repetition frequency, temperature scales linearly with plasma power

hysteresis between ignition and extinction: S curve



Rayleigh Scattering^[1,2]
method for T
measurement at 532
nm from Nd:YAG laser

Relationship between OH density, local maximum temperature and fuel mole fraction,
 $T_0 = 650 \text{ K}$, $T_f = 600 \text{ K}$ He/O₂ = 0.66:0.34, $P = 72 \text{ Torr}$, $f = 24 \text{ kHz}$, $a = 400 \text{ 1/s}$

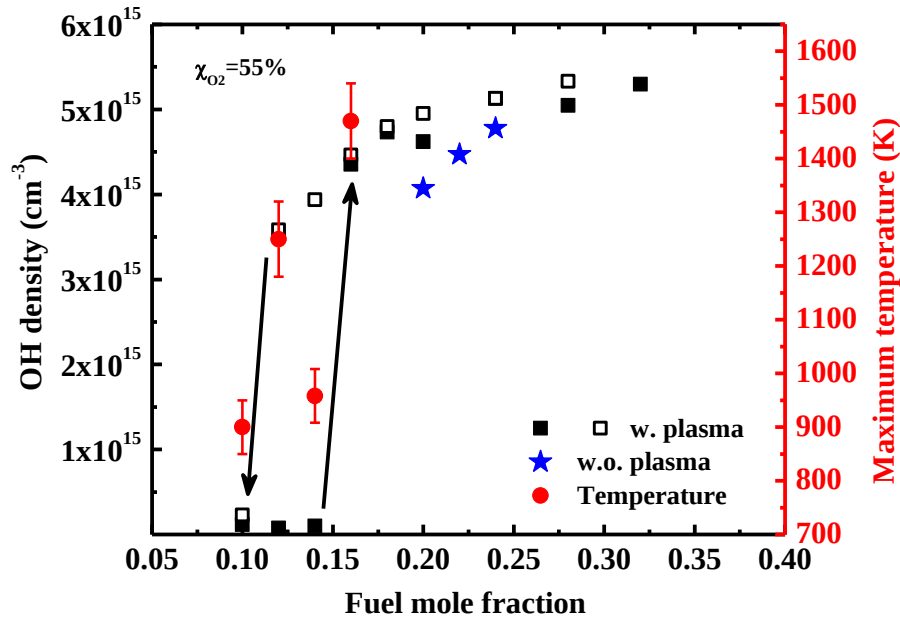
S-curve transition



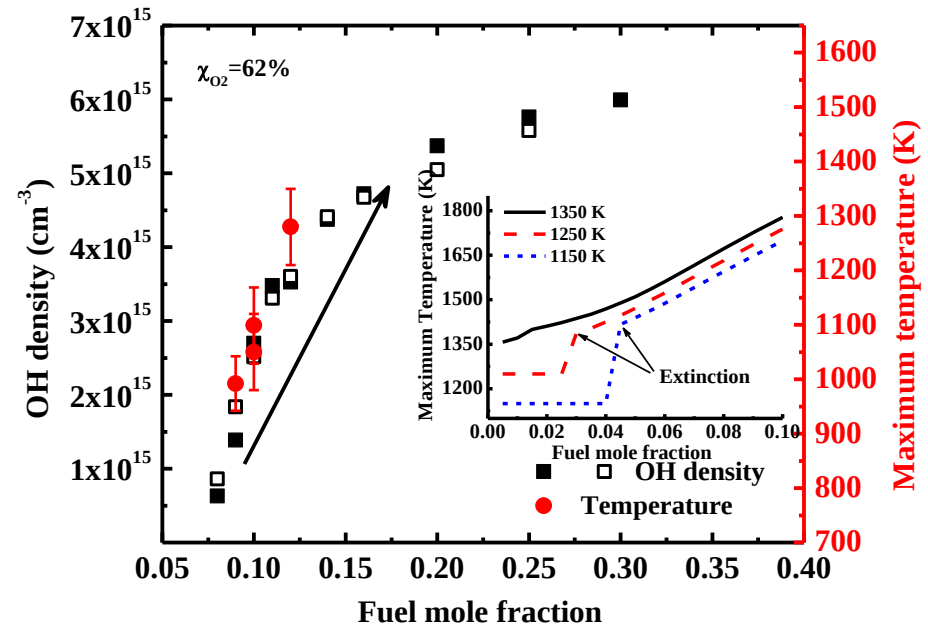
Relationship between OH density, local maximum temperature and fuel mole fraction, $P = 72$ Torr, $f = 24$ kHz, $a = 400$ 1/s

$\text{He}/\text{O}_2 = 0.45:0.55$

$\text{He}/\text{O}_2 = 0.38:0.62$



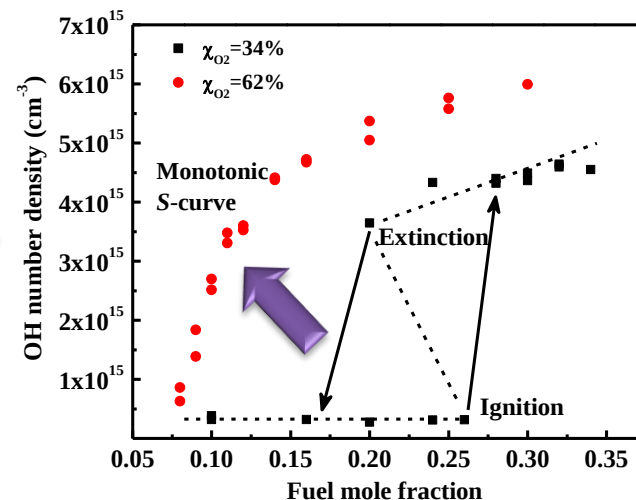
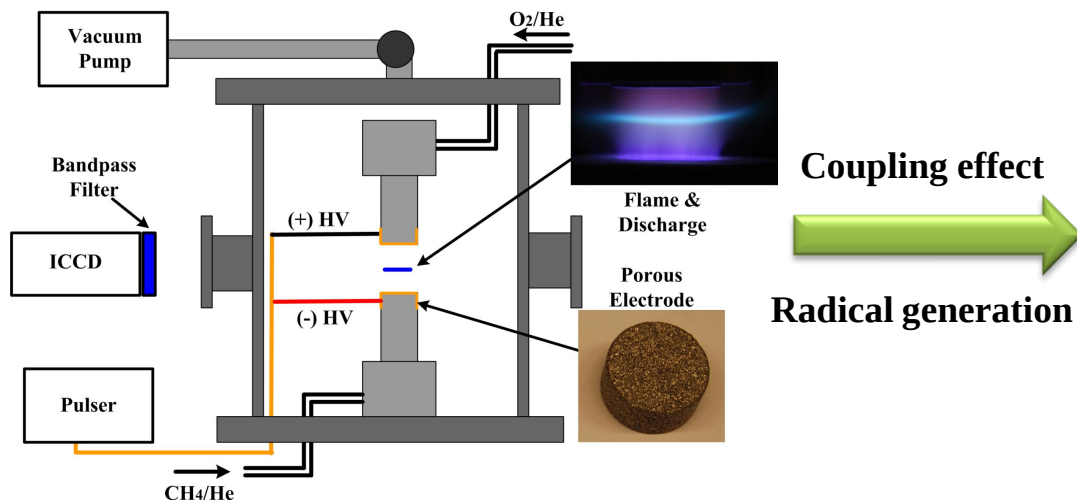
ignition and extinction points were pushed to lower fuel concentrations



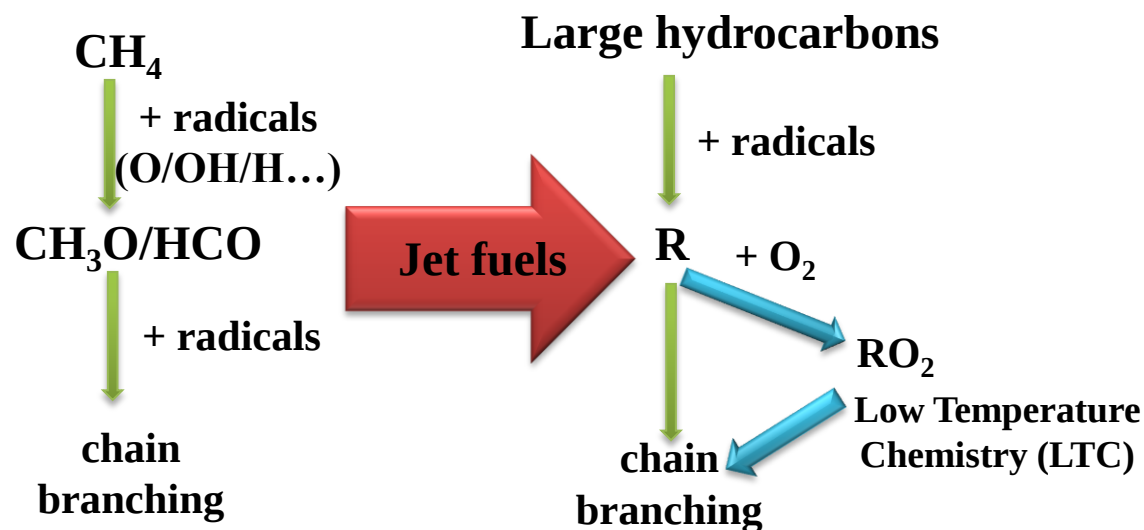
monotonic ignition and extinction curve (monotonic S-curve)

1. New flame and ignition regimes with *in situ* nano-second pulsed discharge

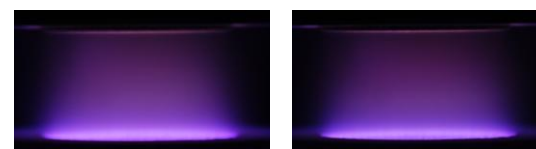
$a = 400 \text{ 1/s}$, $X_0 = 55\%$, $X_f = 20\%$, $f = 24 \text{ kHz}$, $P = 72 \text{ Torr}$,
UV power = 2 mJ/pulse



Radicals produced by *in situ* discharge :
Dramatically increased the reactivity of CH₄ (no extinction limit)



Same chemiluminescence
before CH₄ ignition



Different chemiluminescence
before DME ignition



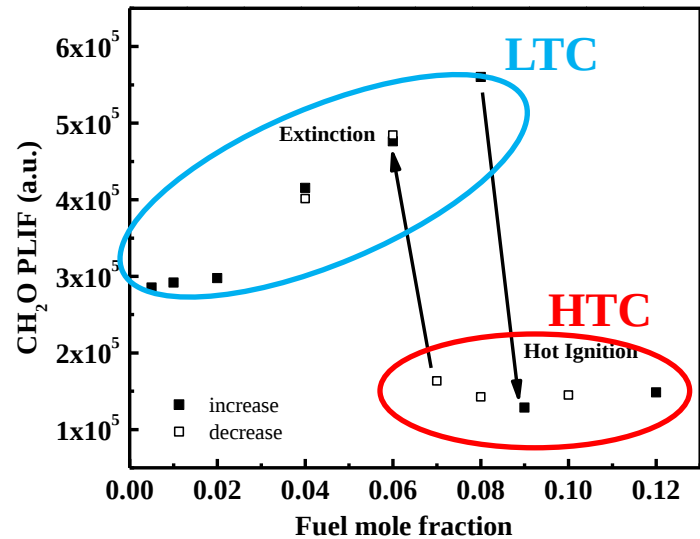
→ Ignition

**How does LTC affect
ignition and extinction?**

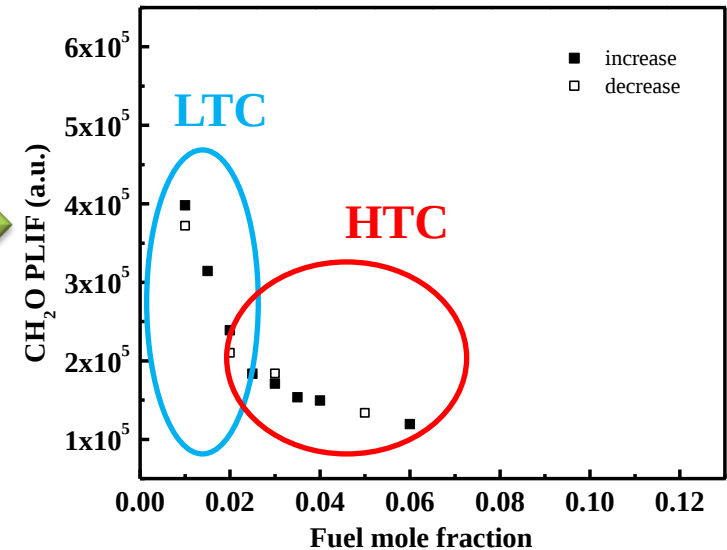
Kinetic effect of plasma assisted low temperature combustion for CH_3OCH_3 ignition

CH_2O PLIF measurements at 355 nm to characterize LTC

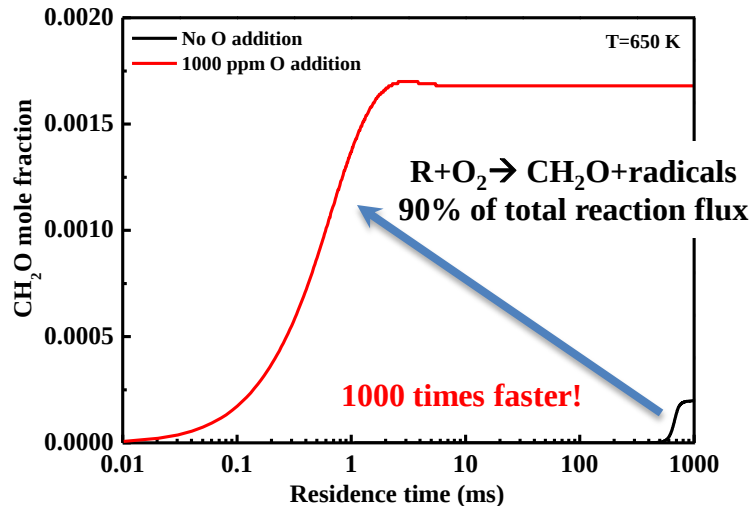
$P = 72 \text{ Torr}$, $a = 250 \text{ 1/s}$, $f = 24 \text{ kHz}$, $X_{\text{O}_2} = 40\%$, varying X_f



$P = 72 \text{ Torr}$, $a = 250 \text{ 1/s}$, $f = 34 \text{ kHz}$, $X_{\text{O}_2} = 60\%$, varying X_f



Plasma assisted low temperature chemistry



Plasma assisted combustion dramatically changed the "**SPEED**" of low temperature chemistry

Slow
LTC



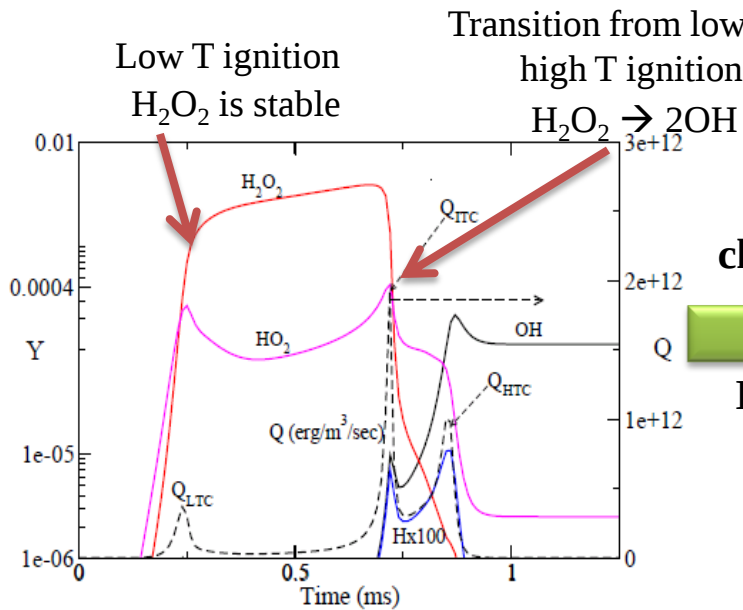
Important for

- PAC
- Turbulent combustion at small time scales



Kinetic studies

Importance of LTC and the critical role of H_2O_2



H_2O_2 : low T chemistry indicator

How to detect?

Indirect measurement:

Sensitive H_2O absorption at 2.5 μm
(Hong et al, 2009)

$\text{H}_2\text{O}_2/\text{H}_2\text{O}/\text{Ar}$ mixture in shock tube

Direct measurement:

Laser absorption at 7.8 μm at low pressure non-reactive flow (Aul, et al, PCI, 2011)

Photofragmentation-LIF

(Li, et al, PCI, 2012)

HCCI

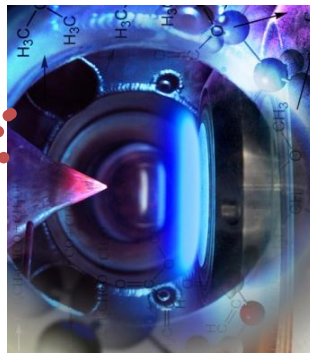
In-situ and high pressure?

Interference with HO_2 and H_2O

Calibration (H_2O_2 decomposes $> 55^\circ\text{C}$)¹

Challenging for combustible mixtures

Low Pressure MBMS for flame



Different masses

Mass spectrometry

H_2O_2

LTC

DME

MBMS