New combustion regimes and kinetic studies of plasma assisted combustion

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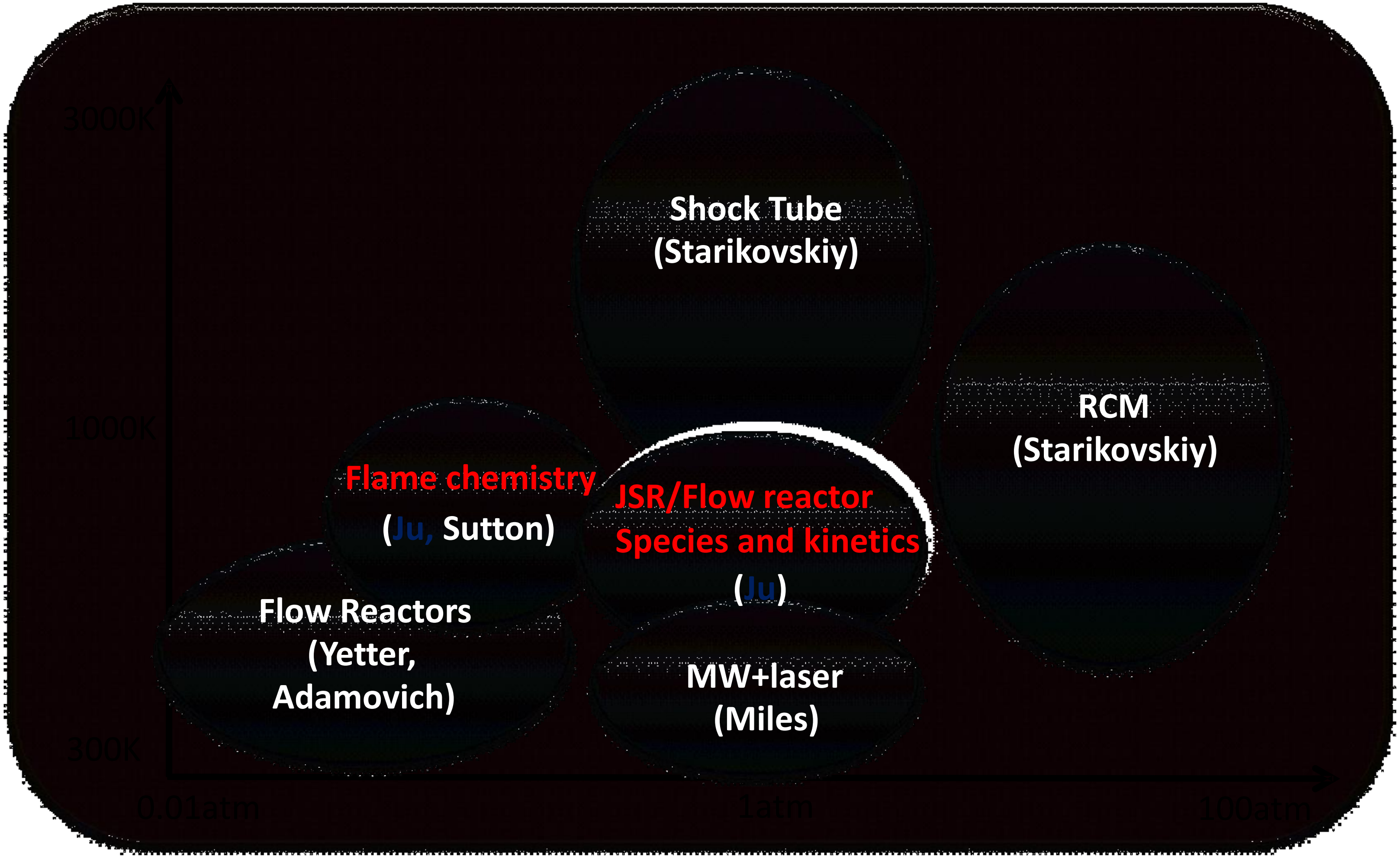
MURI Facility Summary and collaborative team structure



Shock Tube
(Starikovskiy)

RCM
(Starikovskiy)

Flame chemistry
(Ju, Sutton)

JSR/Flow reactor
Species and kinetics
(Ju)

Flow Reactors
(Yetter,
Adamovich)

MW+laser
(Miles)

(*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)

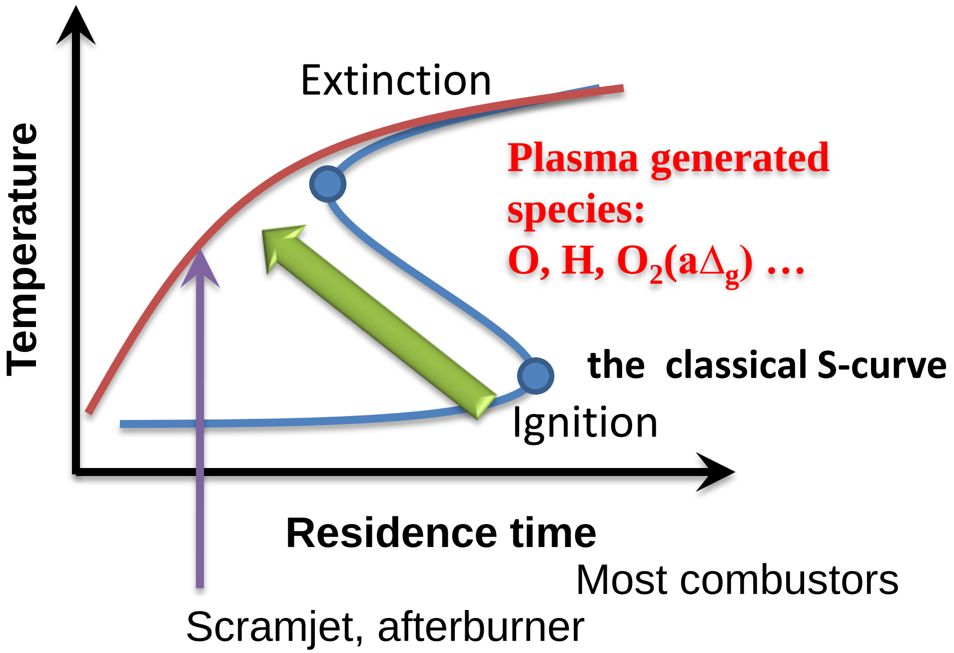
3. Ignition enhancement and minimum ignition energy by plasma discharge (Task 6: Ignition, Flame Initiation and the Minimum Ignition Energy)

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

Technical questions:

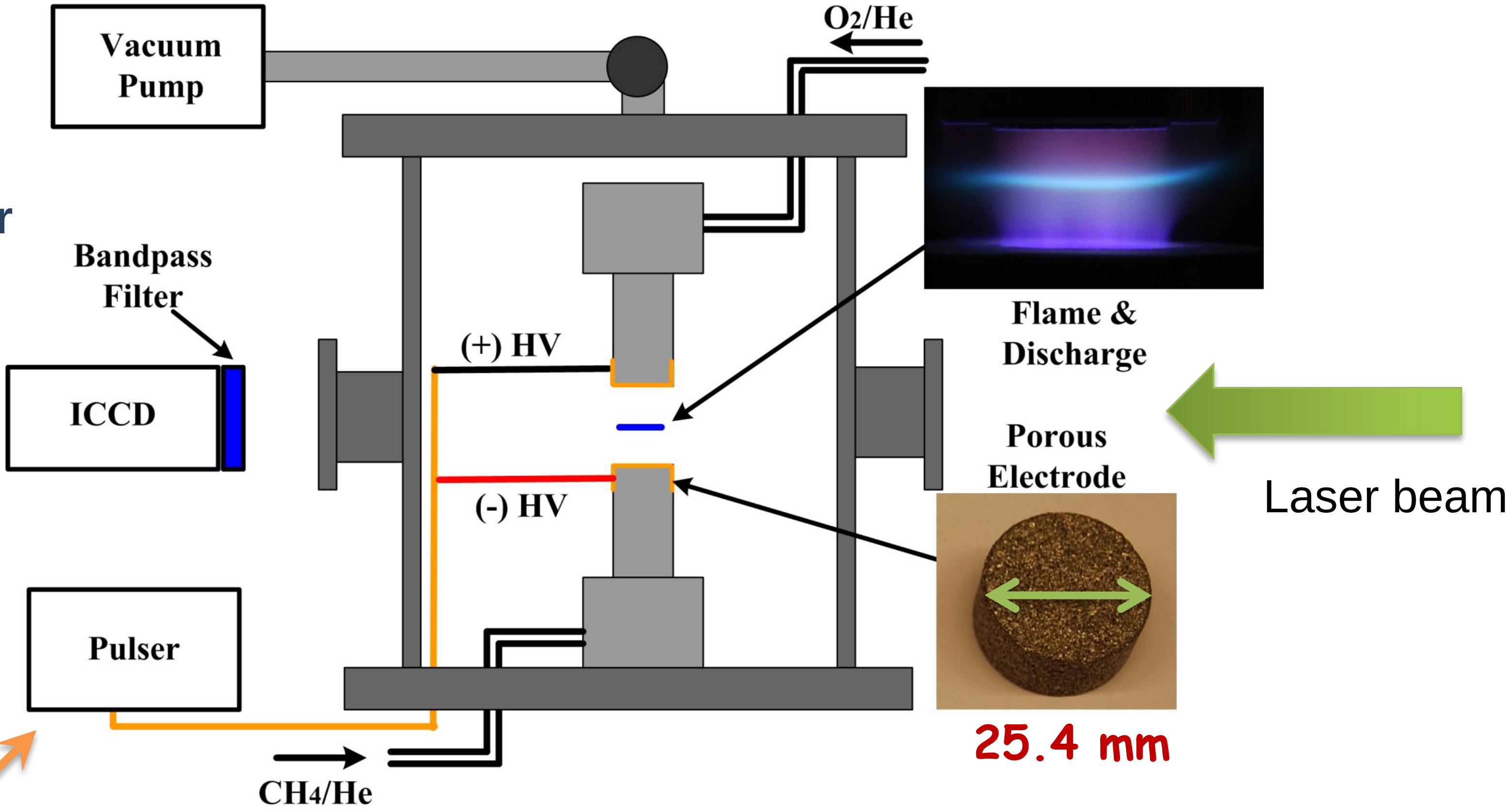
- Can plasma assisted combustion enhances sublimit combustion so that the ignition and extinction limit disappear on the classical S-curve?
- What happens when JP-8 has low temperature ignition chemistry?
  How does PAC interact with low temperature chemistry ? relevant or not?

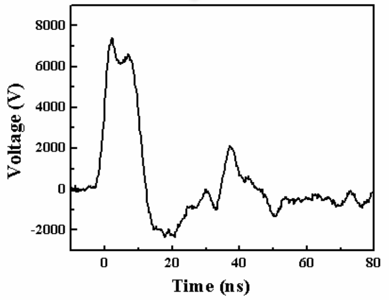
Disappear of the "S-curve" ⇨ **The new monotonic ignition curve**



Experimental method (in-situ plasma discharge)

P = 72 Torr
f = 24 kHz





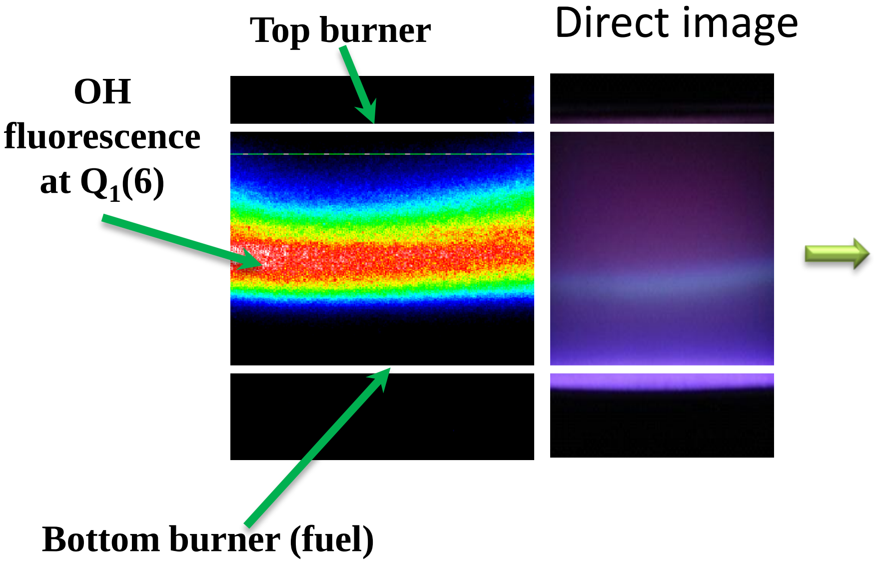
Peak Voltage = 7.8 KV

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

Power ~ 17 W (repetitive pulses)

OH PLIF measurement (CH_4/O_2 sublimit flames)

a= 400 1/s, X_o = 55%, X_f = 20%, *f* = 24 kHz, P=72 Torr, UV power = 2 mj/pulse

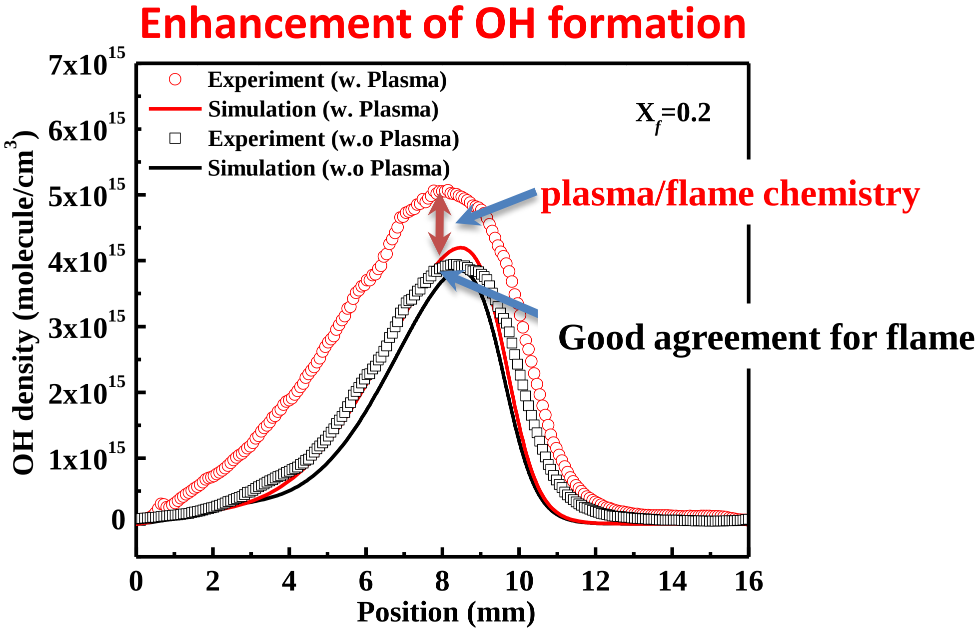


Top burner

Direct image

OH fluorescence at $Q_1(6)$

Bottom burner (fuel)

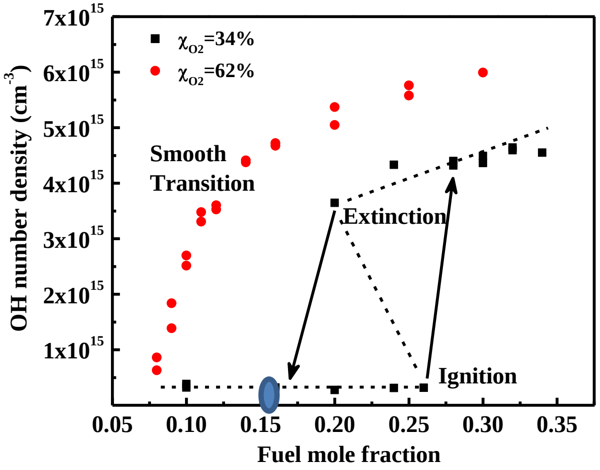


Enhancement of OH formation

plasma/flame chemistry

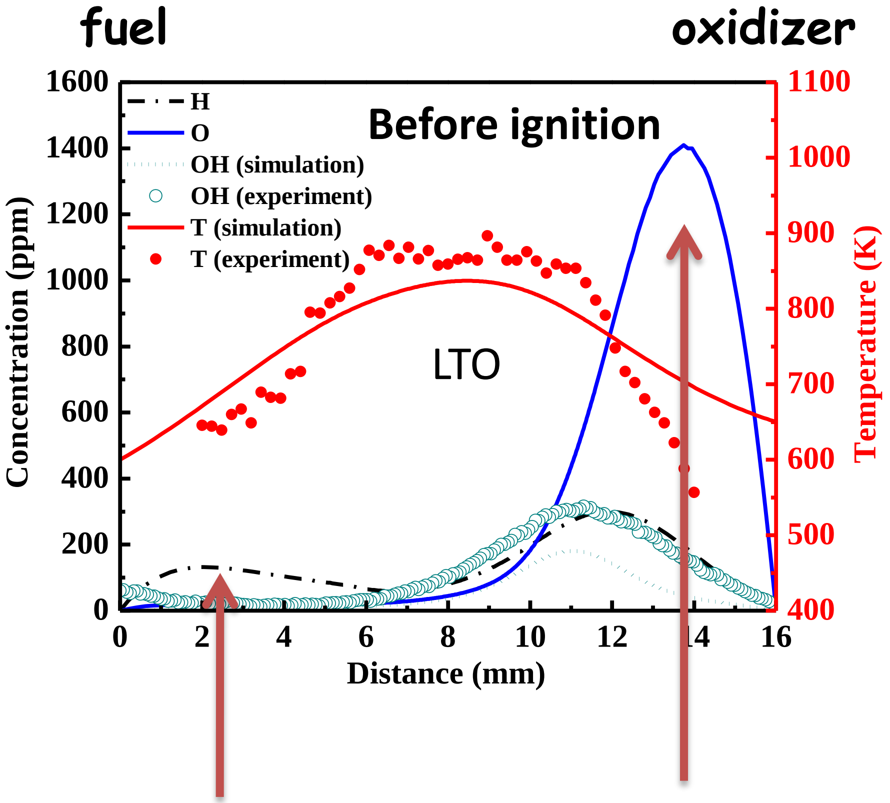
Good agreement for flame

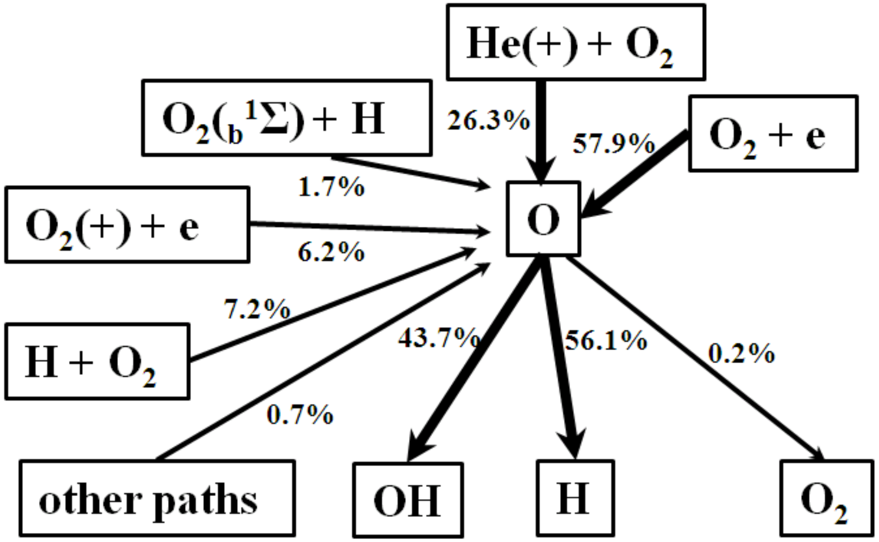
S-shaped ignition/extinction curve measurement: OH PLIF



Numerical modeling of PAC and path flux analysis

$X_{O2} = 0.34$, $X_{CH4} = 0.16$, P = 72 Torr, f = 24 kHz, a = 400 1/s





$e + CH_4 \rightarrow CH_3 + H + e$ $e + O_2 \rightarrow O + O(D) + e$

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

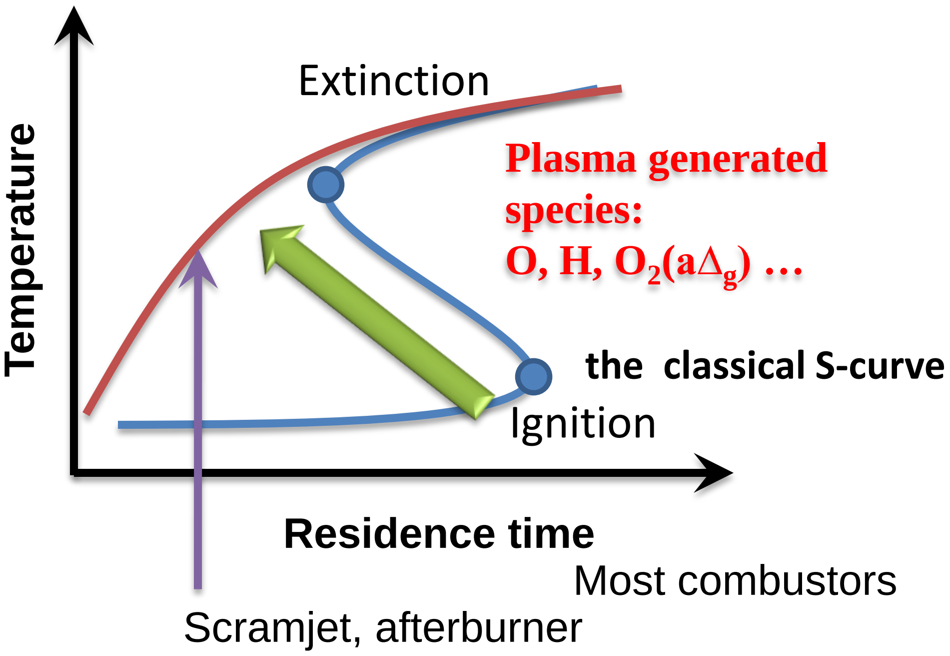
Electron and ion impact dissociation are the key in PAC .

New ignition transition curve with plasma assisted combustion

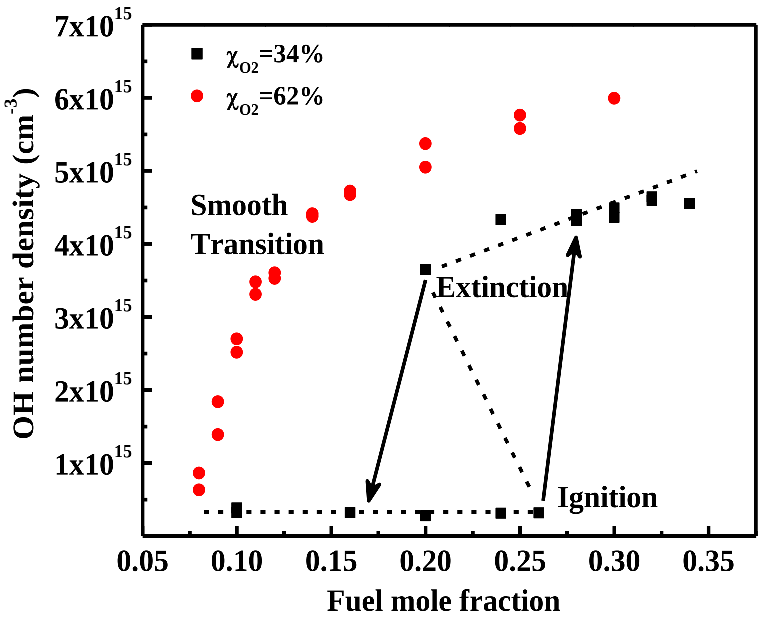
Hypothesis

Experimental observation
A new combustion regime

Disappear of the “S-curve”



The S-curve transition

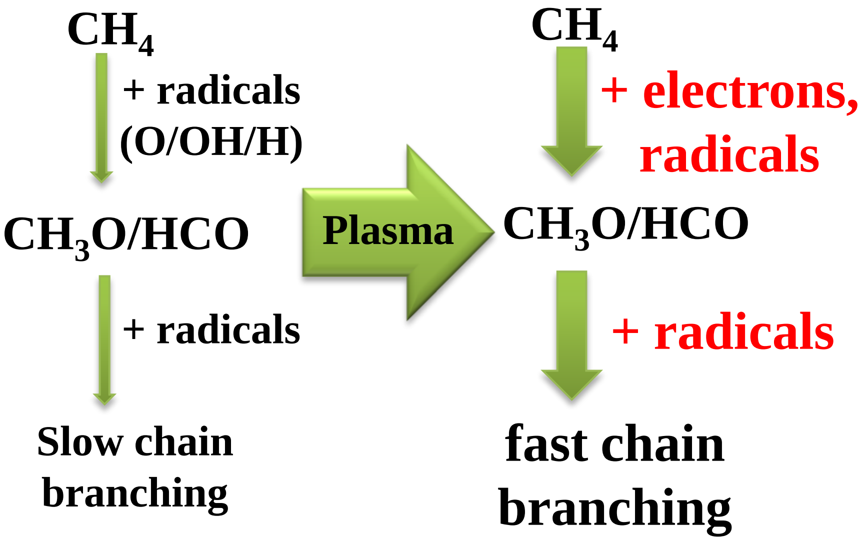


- Extended flammable regine
- No extinction limit

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 (LTI and gas phase) as example



CH_4

+ radicals (O/OH/H)

CH_3O/HCO

+ radicals

Slow chain branching

Plasma

CH_4

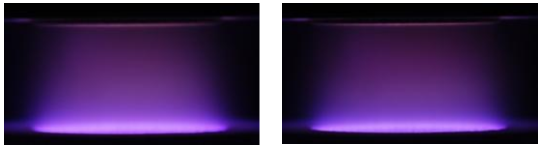
+ electrons, radicals

CH_3O/HCO

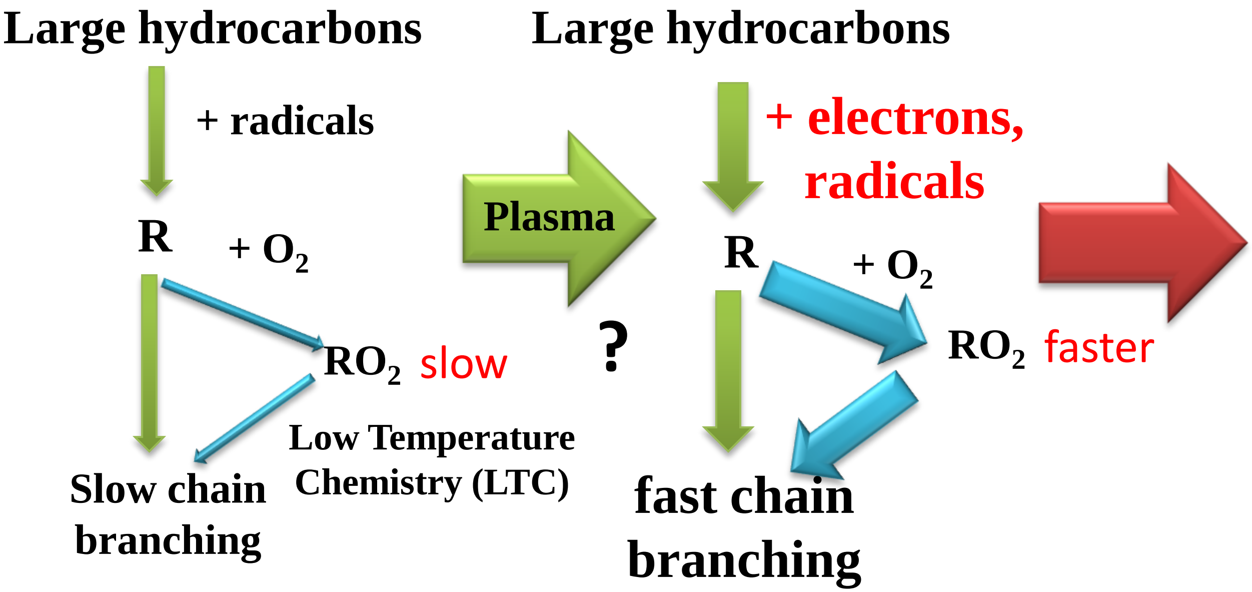
+ radicals

fast chain branching

Same chemiluminescence before CH_4 plasma assisted ignition



High temperature chemistry only



Large hydrocarbons

+ radicals

R

+ O_2

RO_2 slow

Low Temperature Chemistry (LTC)

Slow chain branching

Plasma

?

Large hydrocarbons

+ electrons, radicals

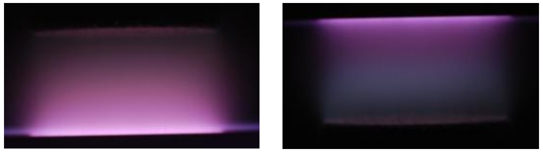
R

+ O_2

RO_2 faster

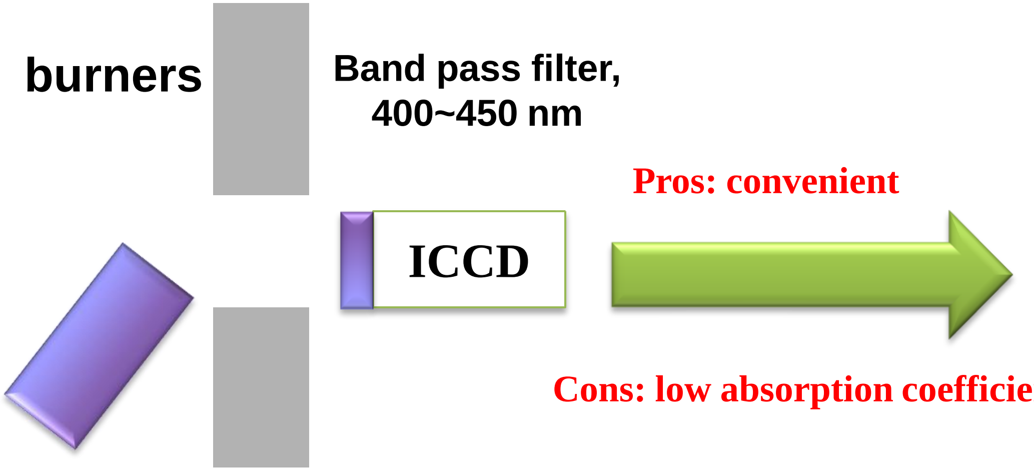
fast chain branching

Different chemiluminescence before DME ignition



How does LTC affect ignition and extinction?

CH_2O PLIF at 355 nm from Nd:YAG laser



burners

Band pass filter,
400~450 nm

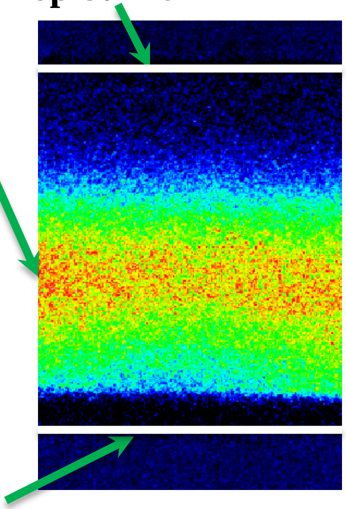
ICCD

Pros: convenient

Cons: low absorption coefficient

Nd:YAG laser
355 nm

Before ignition with plasma



CH_2O PLIF

$A^1A_2 \rightarrow X^1A_1$
band

Strong

?

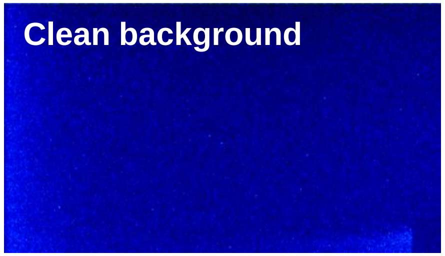
Further identification of CH_2O LIF

no LIF from cold flow

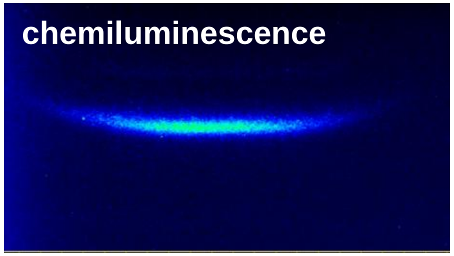
LIF close to fuel side

switch fuel/oxidizer side
CH_2O LIF on the fuel side

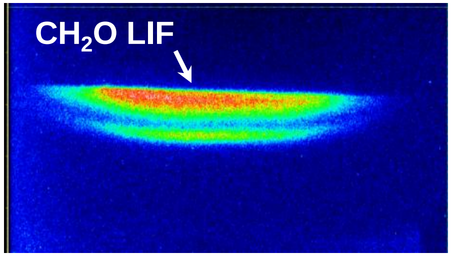
cold flow w. laser



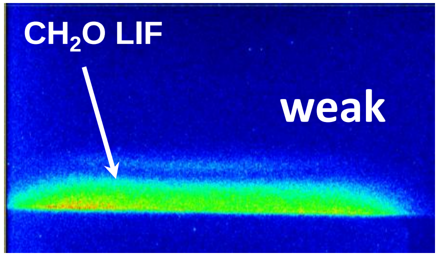
flame w.o laser



flame w. laser



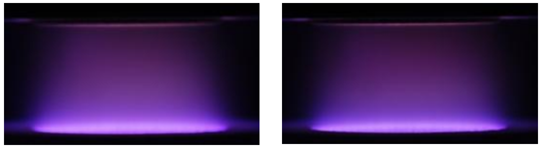
flame w. laser



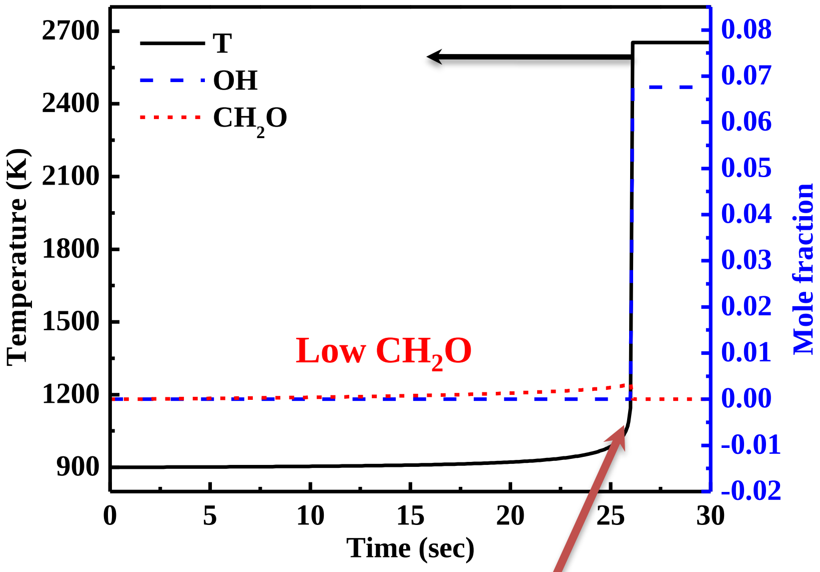
without discharge

CH_2O formation in CH_4 and DME ignition …

Same chemiluminescence before CH_4 plasma assisted ignition

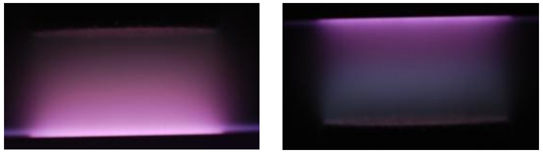


$CH_4/O_2/He$ (0.15/0.55/0.3)
P = 72 Torr, T_0 = 900 K

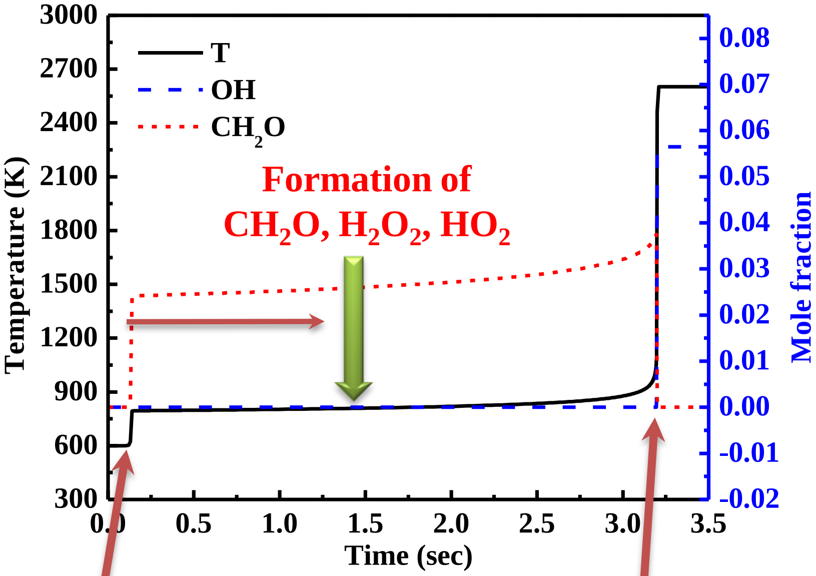


High T ignition
Marked by OH

Different chemiluminescence before DME ignition



$DME/O_2/He$ (0.1/0.55/0.35)
P = 72 Torr, T_0 = 600 K

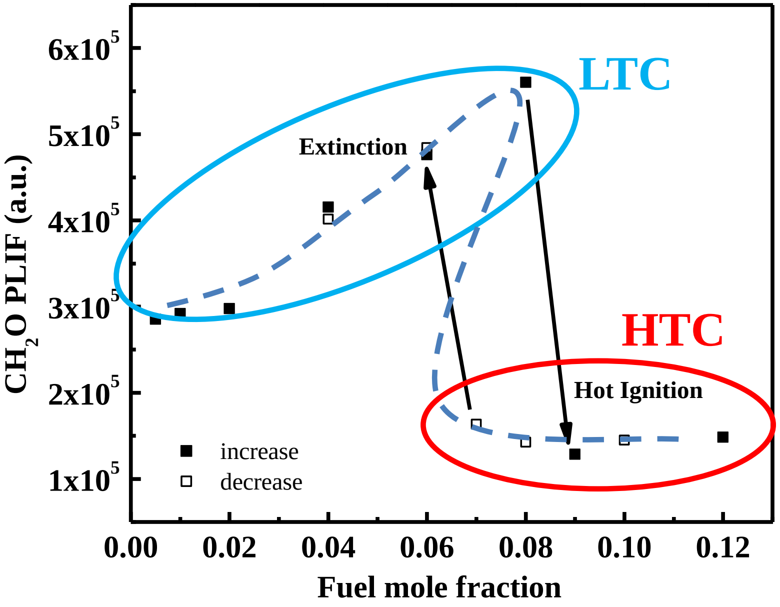


Low T ignition
CH_2O can be used as a marker

High T ignition
$H_2O_2 \rightarrow 2OH$

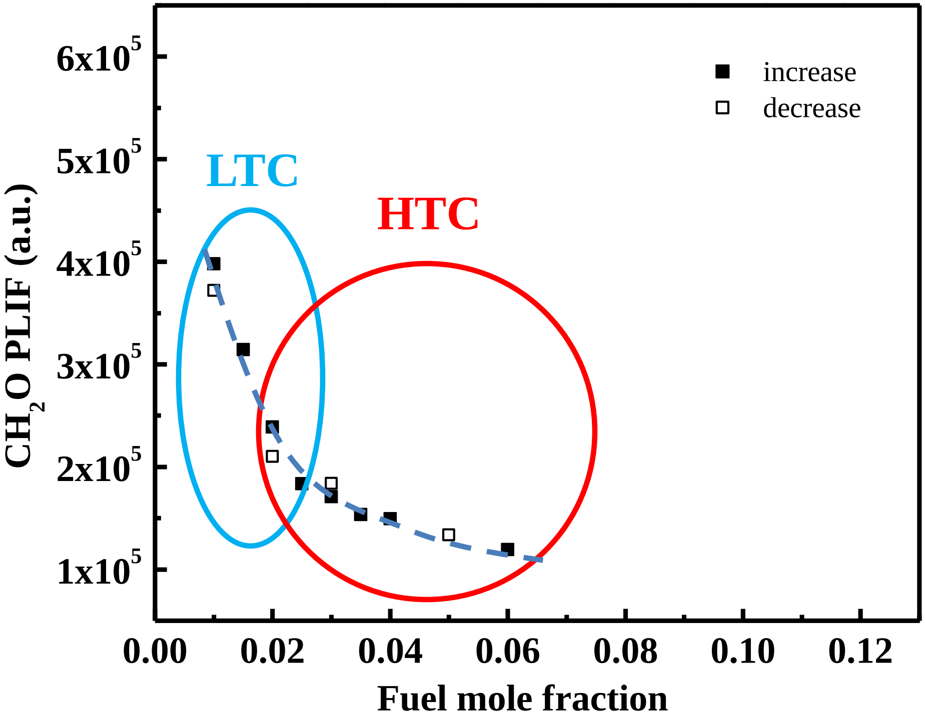
CH_2O measurements: ignition and extinction

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



S-Curve

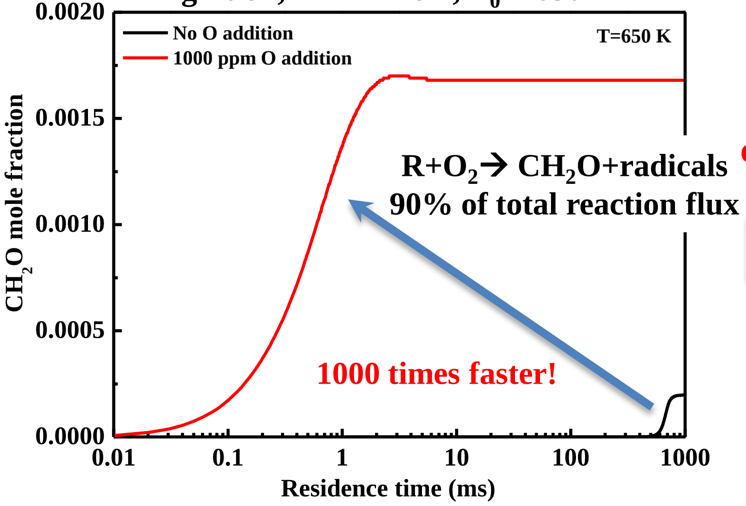
P = 72 Torr, a= 250 1/s, *f* = 34 kHz,
X_{O_2}=60%, varying X_f



New ignition/extinction curve without extinction limit

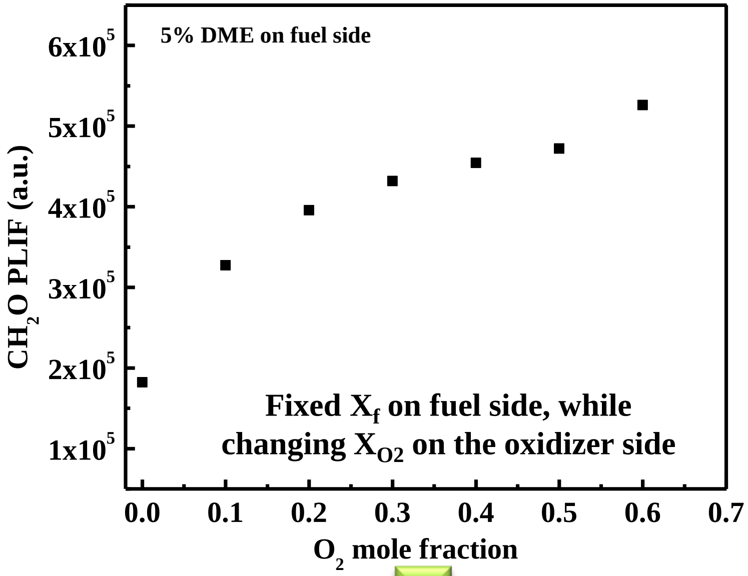
Competition between { **low T RO_2 kinetics**
high T chain branching reactions

Kinetics of plasma assisted low temperature combustion



0-D modeling of DME/O_2/He (0.03/0.1/0.896) ignition, P = 72 Torr, T_0 = 650 K

Sensitive to O_2 concentration?



Implication

Plasma assisted combustion dramatically changed the low temperature chemistry

Plasma

Faster LTC ← **Slow LTC**

Turbulent transport

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

Prompt radical production from plasma

↓

Fast H abstraction (formation of R)

↓

Fast LTC (RO_2 reactions)

↓

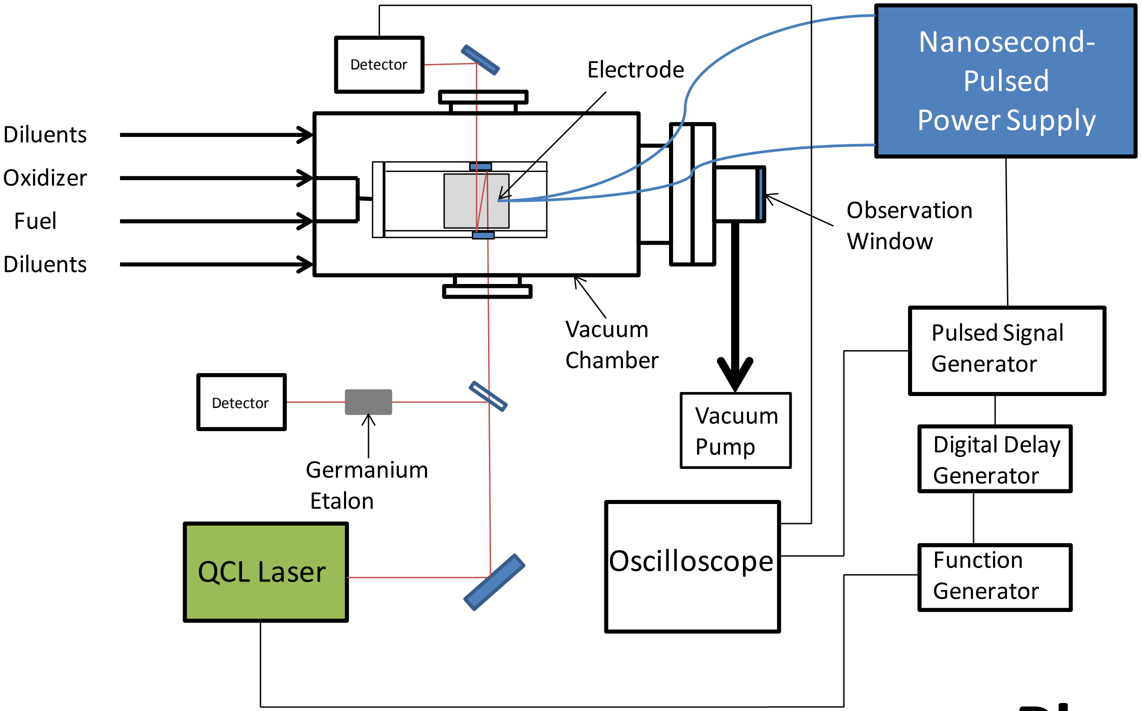
Results can be extended to other large fuels

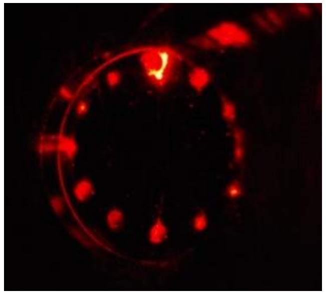
2. Multispecies diagnostics in a flow reactor
(Task 3: Multispecies measurements)

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 mm^3
- Fuel: C_2H_4
- 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)

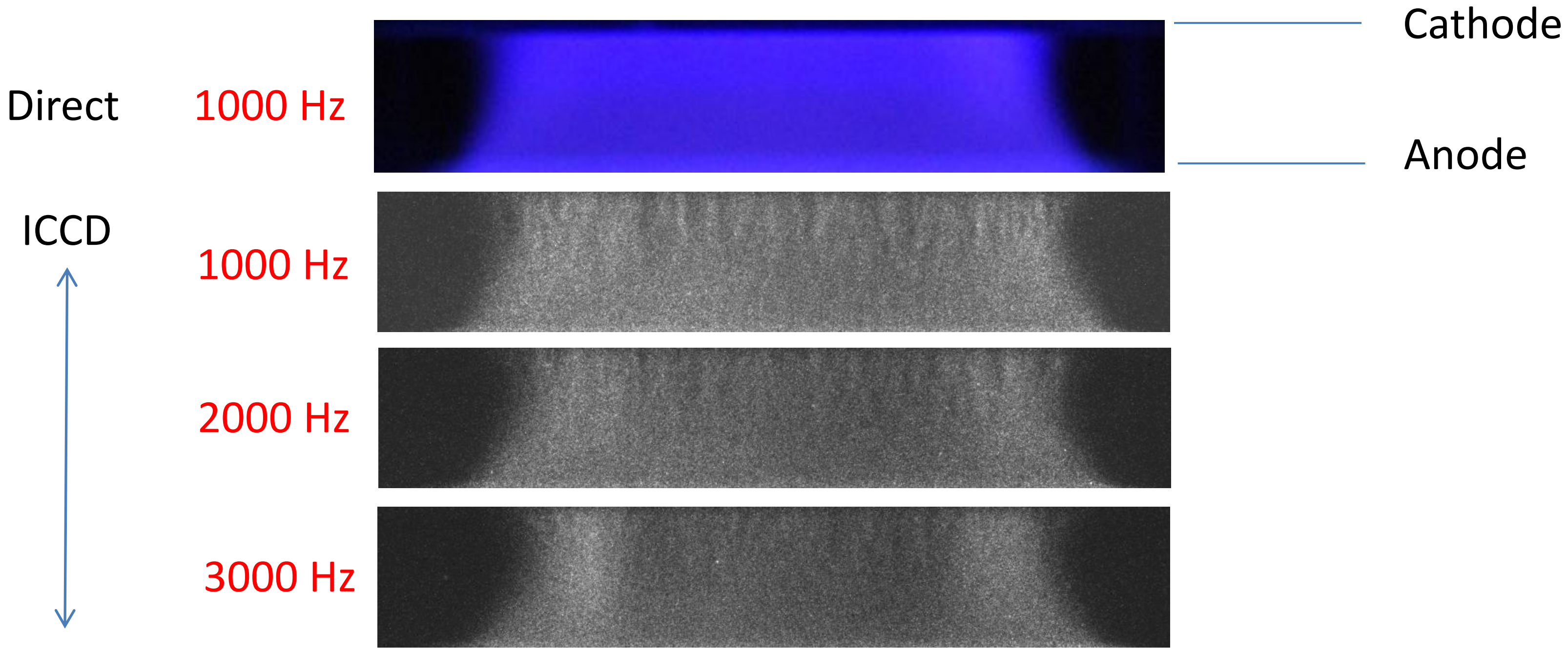
Plasma Properties

- Electrode (40 x 45 mm^2)
- 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: C_2H_4/O_2 with 75% AR, 60 Torr, V_{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

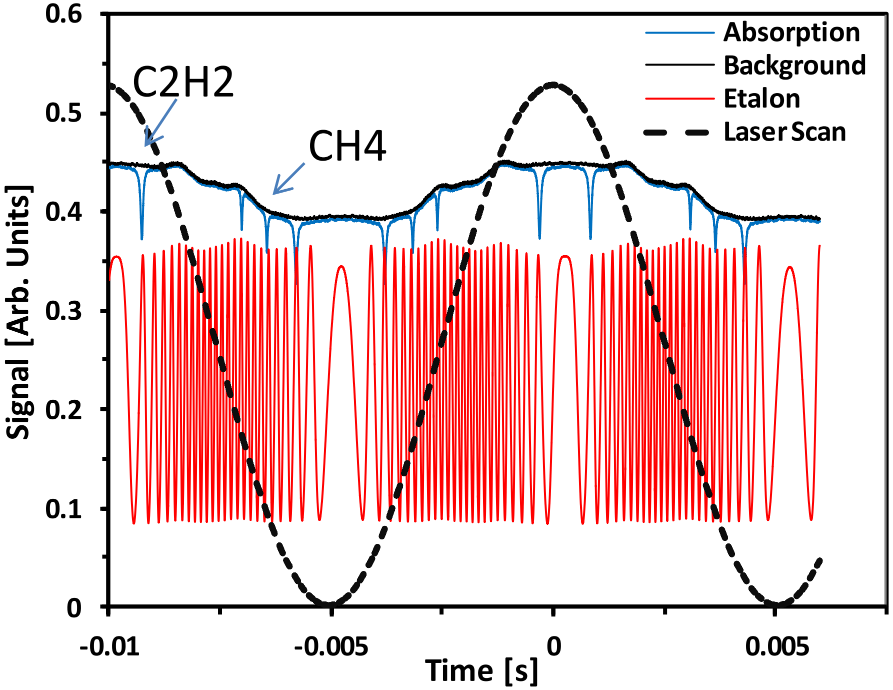
$$\frac{I_\nu}{I_{0\nu}} = \exp\left(-\alpha(\nu, P, T)NL\right) = \exp\left(-\sum_i S_i(T)g_V(\nu_i - \nu)NL\right)$$

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

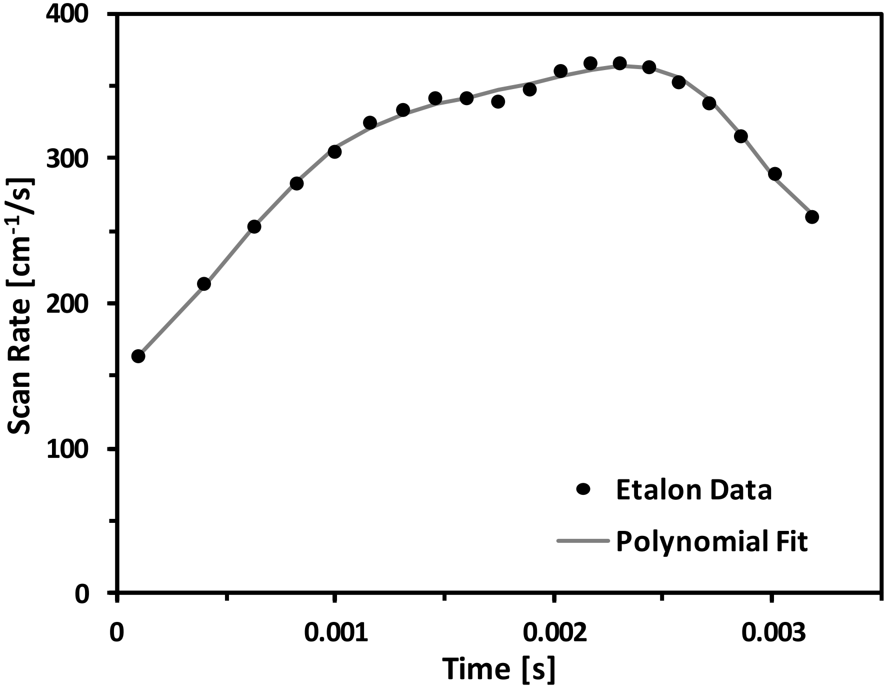
- **Multispecies diagnostics**: Line strengths from HITRAN database for **H_2O, C_2H_2, CH_4**, C_2H_4, C_2H_6, CO_2, CO, O_3, OH, HO_2, H_2O_2, CH_2O, NO, N_2O, NO_2
- **Temperature measurements**: Line strength on $S_i(T)$ for temperature measurements
- **Species sensitivity**: Multipass and Wavelength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

Absorption spectrum and wavelength scan

Signal vs. laser scan time and etalon fringes

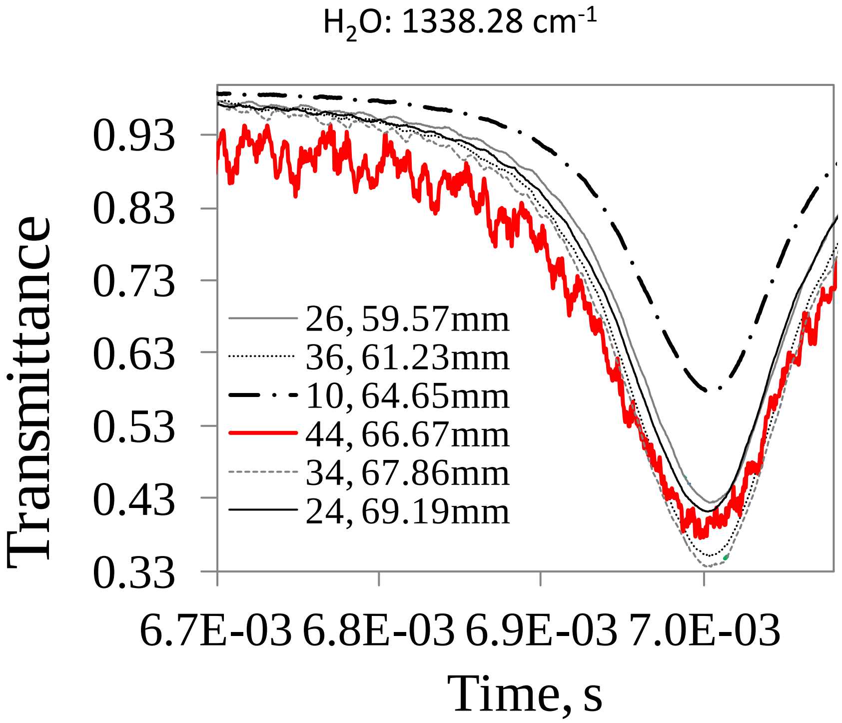


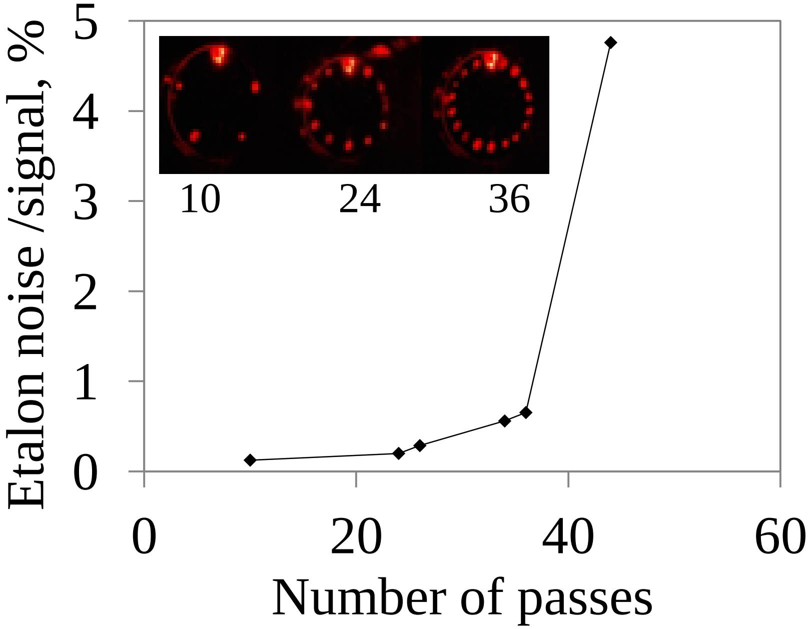
Calibrated wavelength vs. time



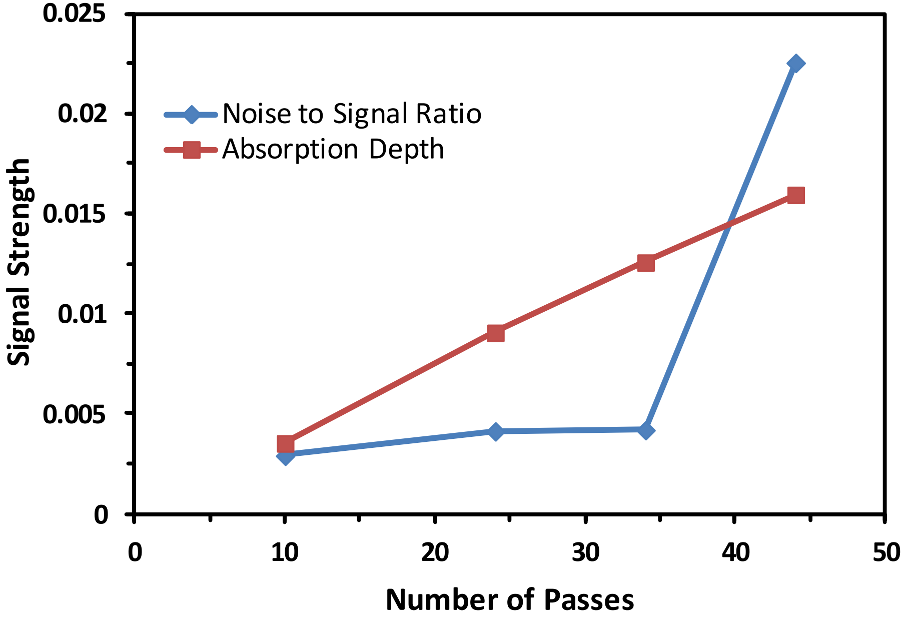
Multipass Mini Herriott Cell Signal and Noise Properties

12.7 mm in cell diameter





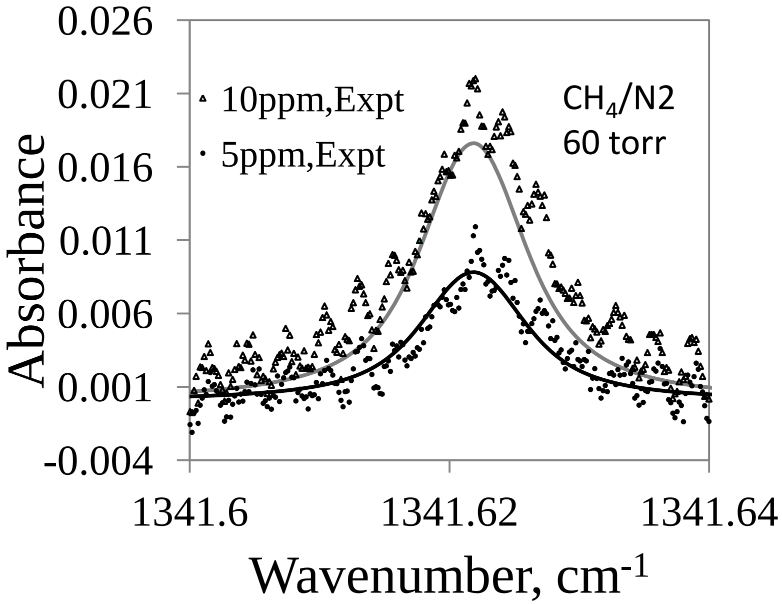
- **Increase of pass number increase the sensitivity but a very high pass number causes large etalon noise**

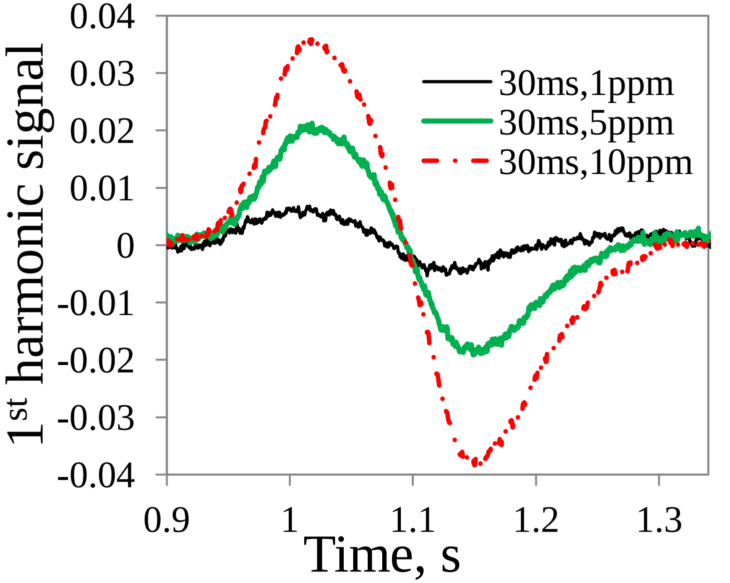


Measurement of CH_4: Direct Absorption vs. Wavelength Modulation

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

f=50 kHz – 1 MHz



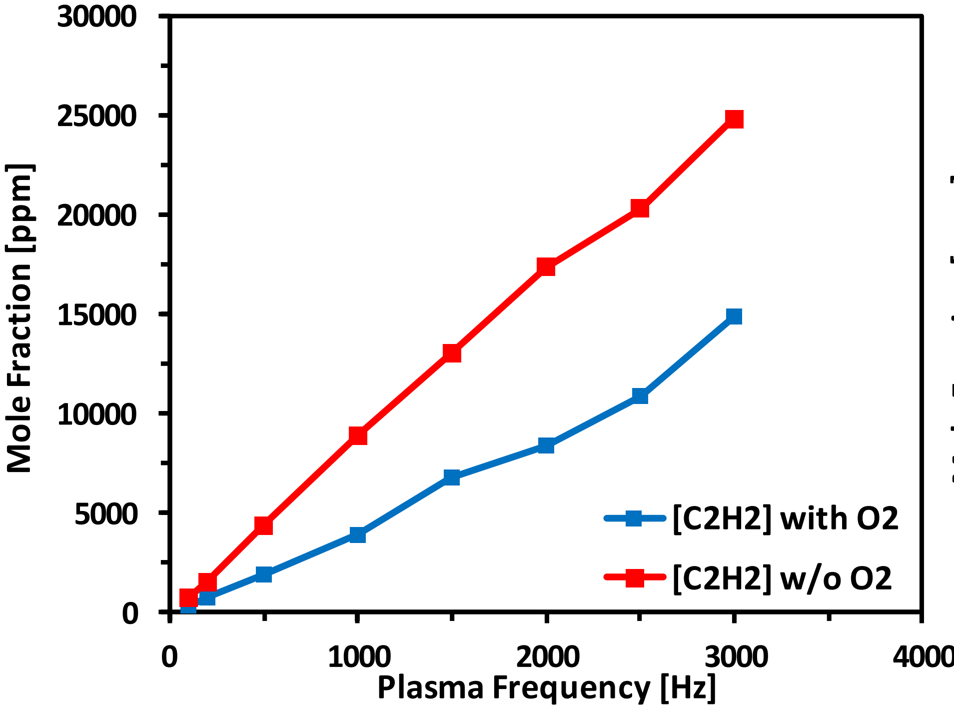


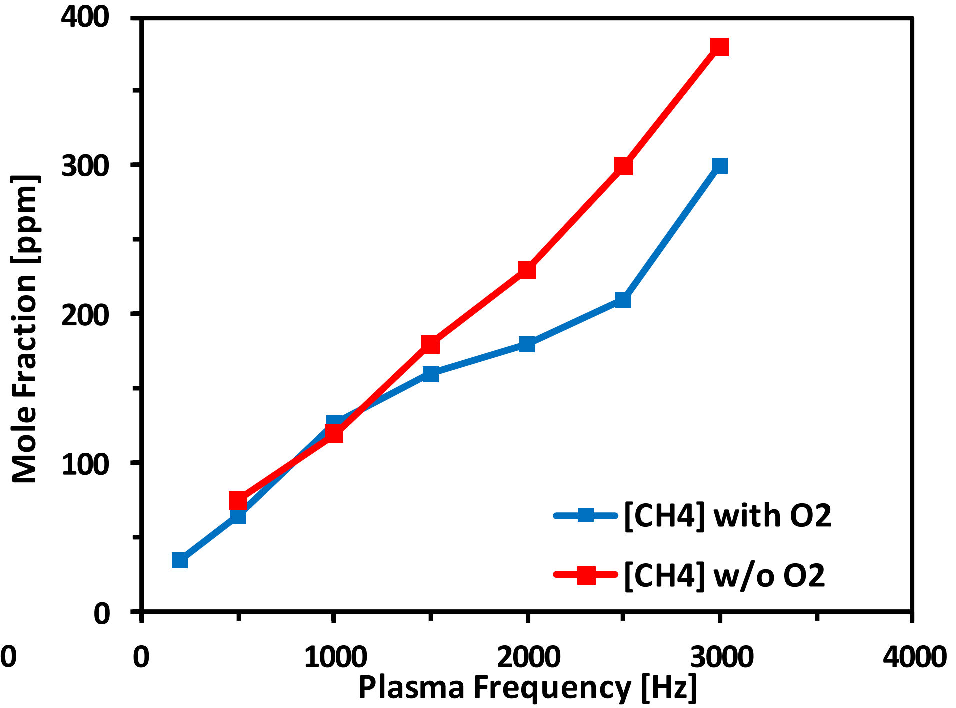
Direct absorption measurement of CH_4

Wavelength modulated absorption measurement of CH_4

CH_4/C_2H_2 production by plasma: pyrolysis vs. oxidation

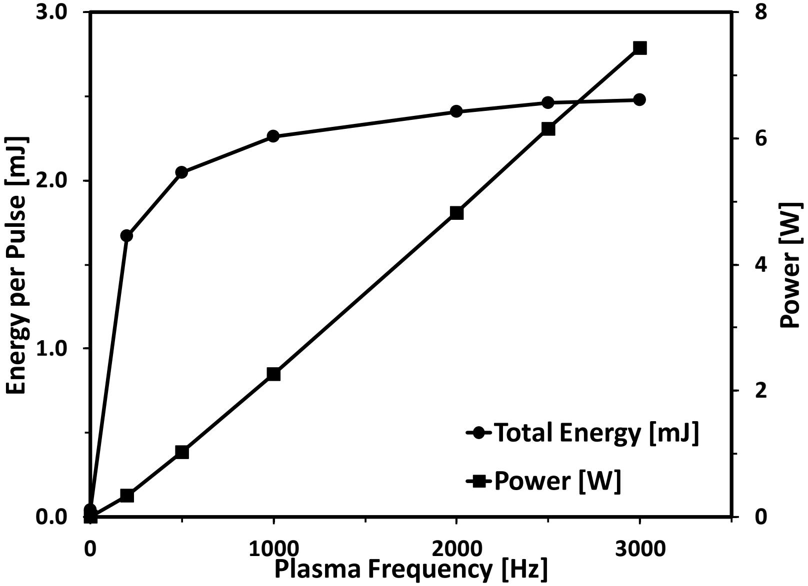
- Ar/C_2H_4, fuel mole fraction of 0.0625, 60 torr
- $Ar/O_2/C_2H_4$ mixtures, 25% reactants and ϕ=1. Same fuel concentration

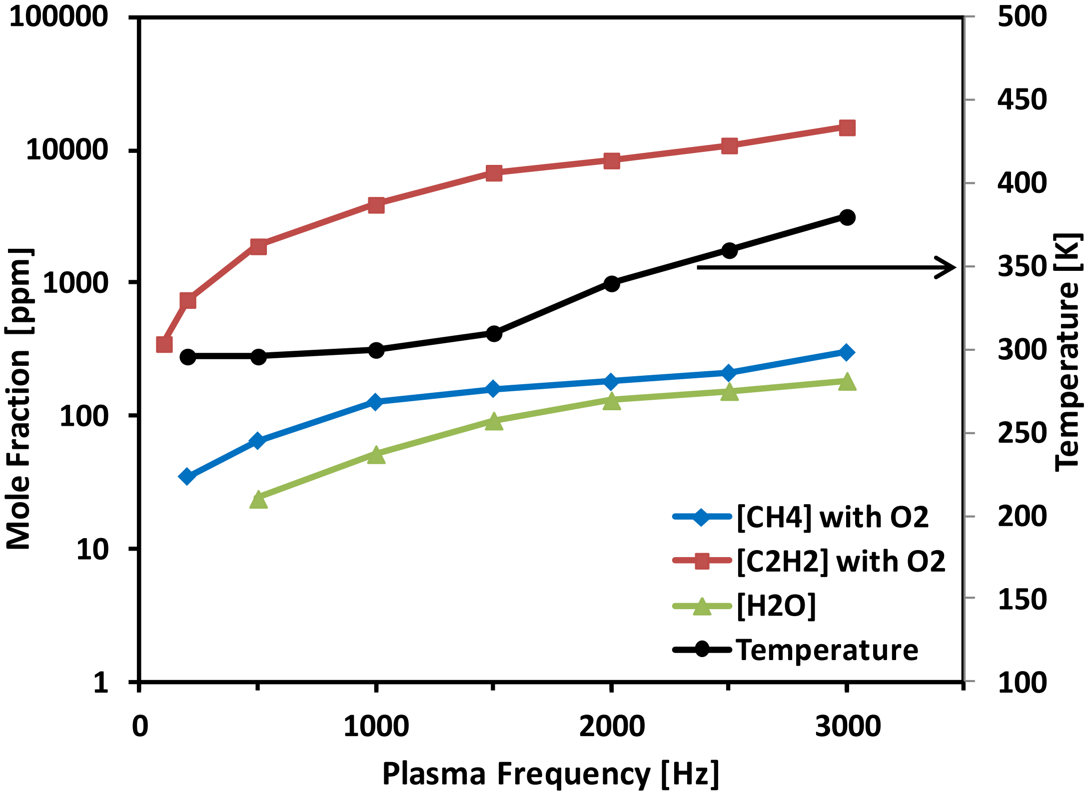




Effects of plasma frequency on temperature and species

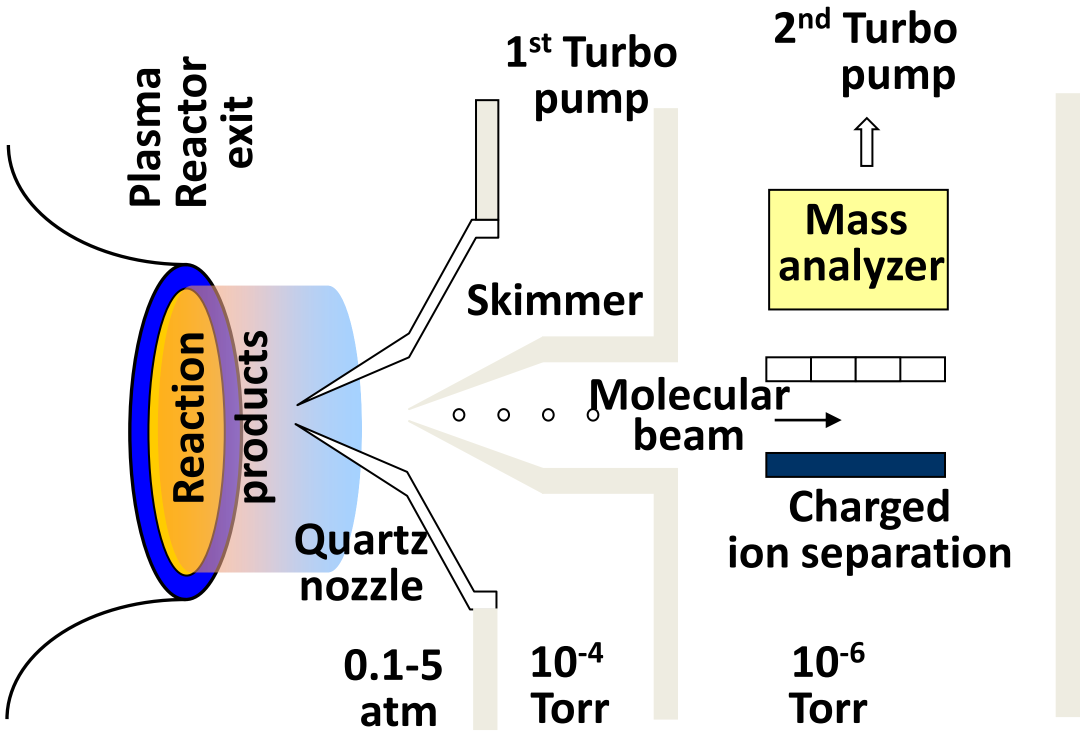
Ar/O_2/C_2H_4 mixtures with 25% reactants and ϕ=1, 60 torr



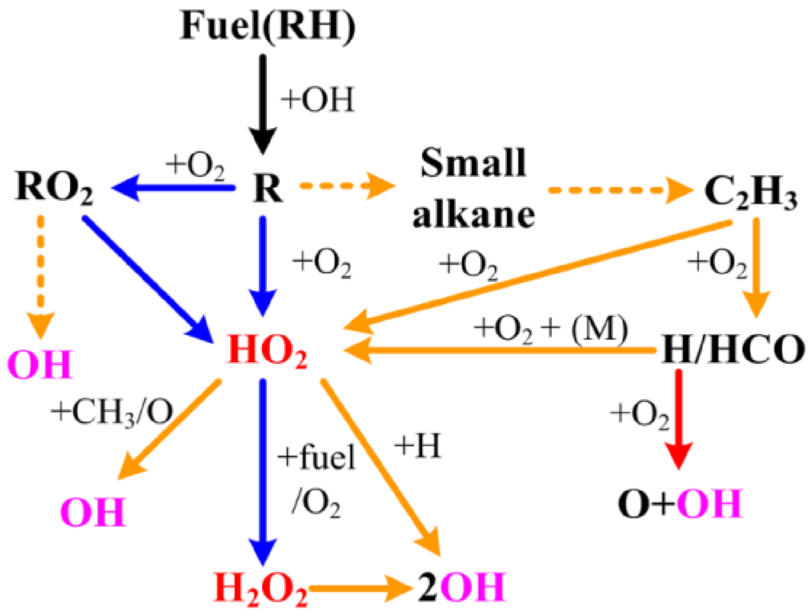


2b. Measurements of H_2O_2 and Intermediate Species in Low Temperature Dimethyl Ether (DME) Oxidation

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



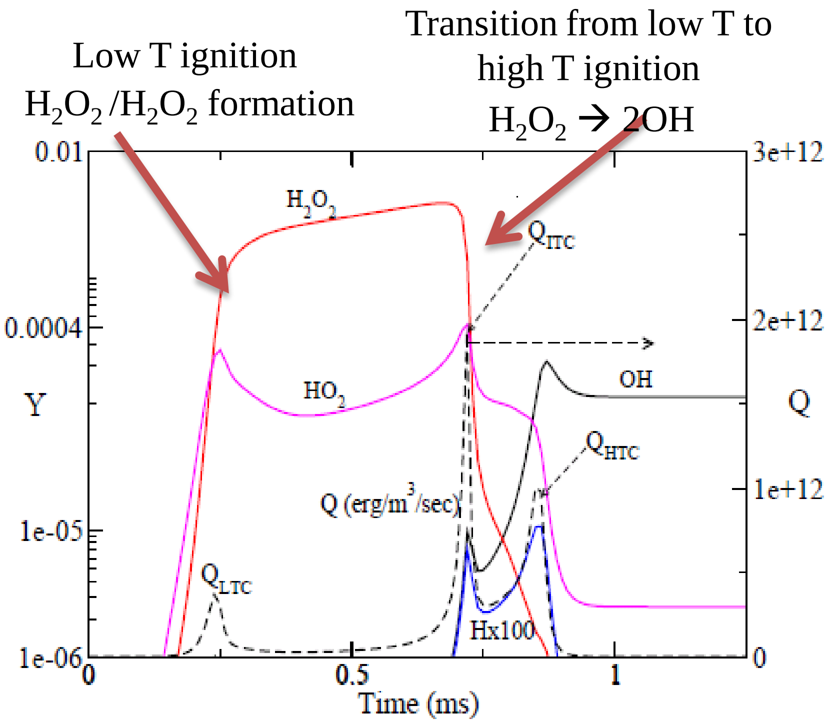
The role of intermediate species, HO_2, H_2O_2 in low/high temperature kinetics



🟦 **Low temperature**

🟨 **Intermediate temperature**

🟥 **High temperature**


Low T ignition

H_2O_2 /H_2O_2 formation

Transition from low T to high T ignition

$H_2O_2 \rightarrow 2OH$

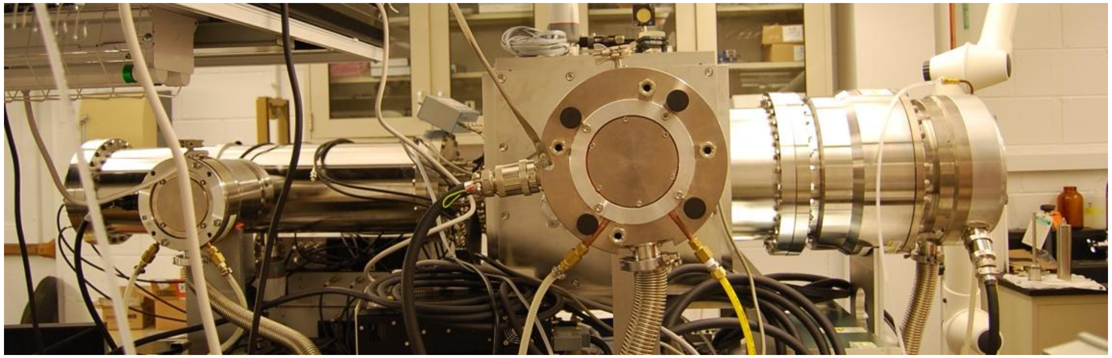
Schematic of low temperature ignition process

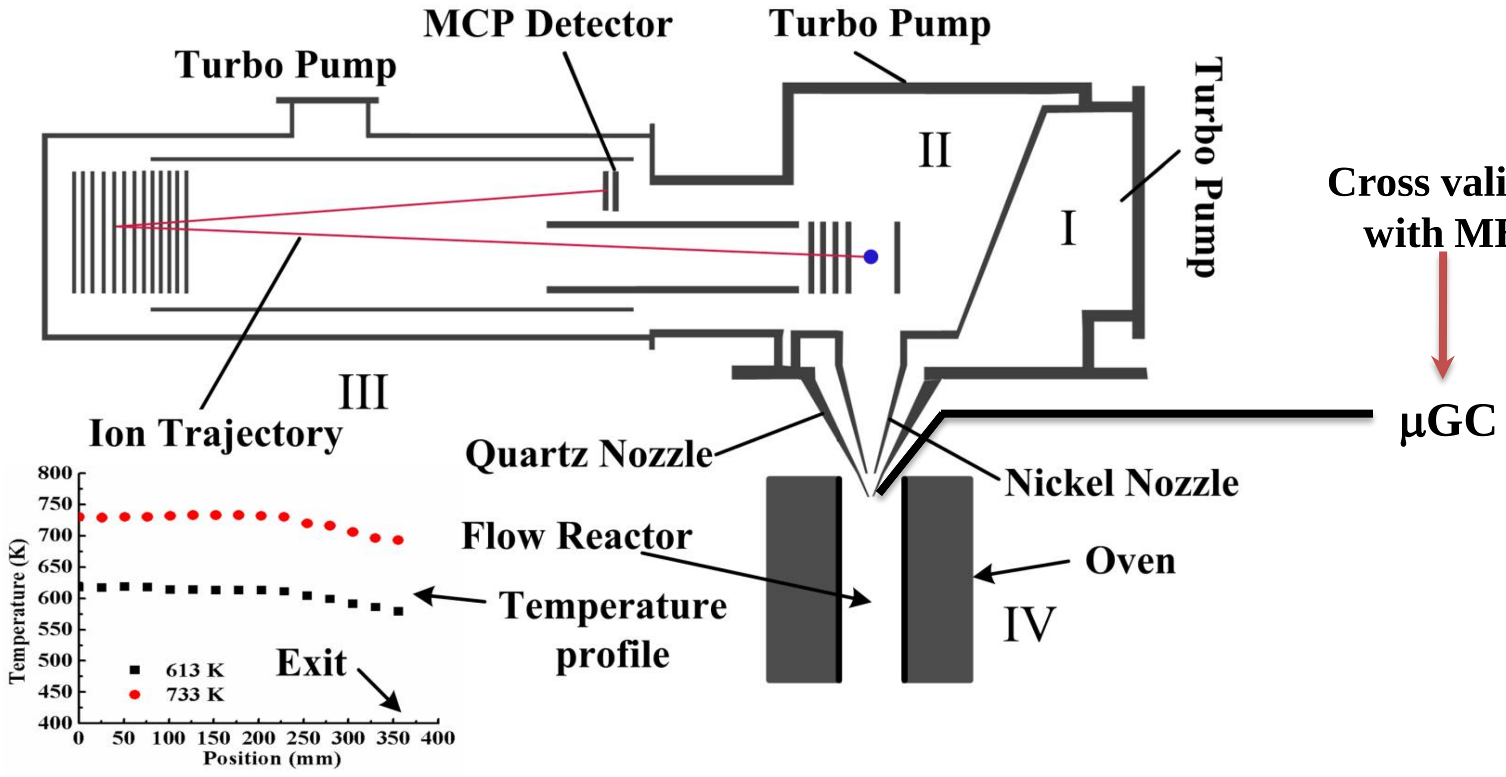
However, measurements of H_2O_2 and HO_2 is difficult…

- **Indirect measurement of H_2O_2:** Sensitive H_2O absorption at 2.5 um (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



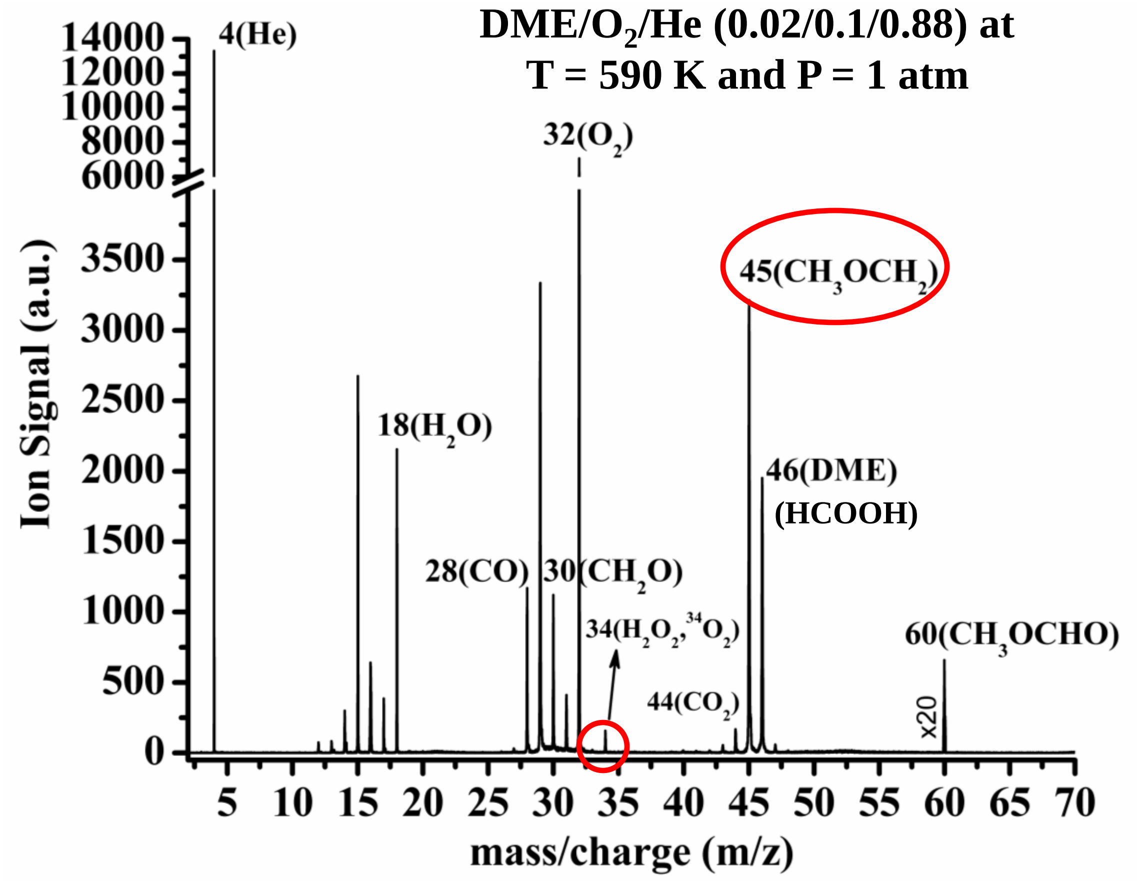


Cross validation with MBMS

μGC

P = 1 atm, τ = 1.7 s

Mass spectrum and calibration



DME/O_2/He (0.02/0.1/0.88) at T = 590 K and P = 1 atm

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

S : signal intensity

D : mass discrimination factor

σ : cross sections

χ : mole fractions

Calibration:

H_2O_2:

H_2O_2/H_2O (30.8% wt) + He

Corrected H_2O_2 concentration via $2H_2O_2 \rightarrow 2H_2O + O_2$ and subtraction of $^{34}O_2$ signal

CH_2O, CH_3OCHO:

Measured *D*, σ from Ref.[1]

Fragmentation:

Constant ratio, can be removed from post processing

Mass overlap:

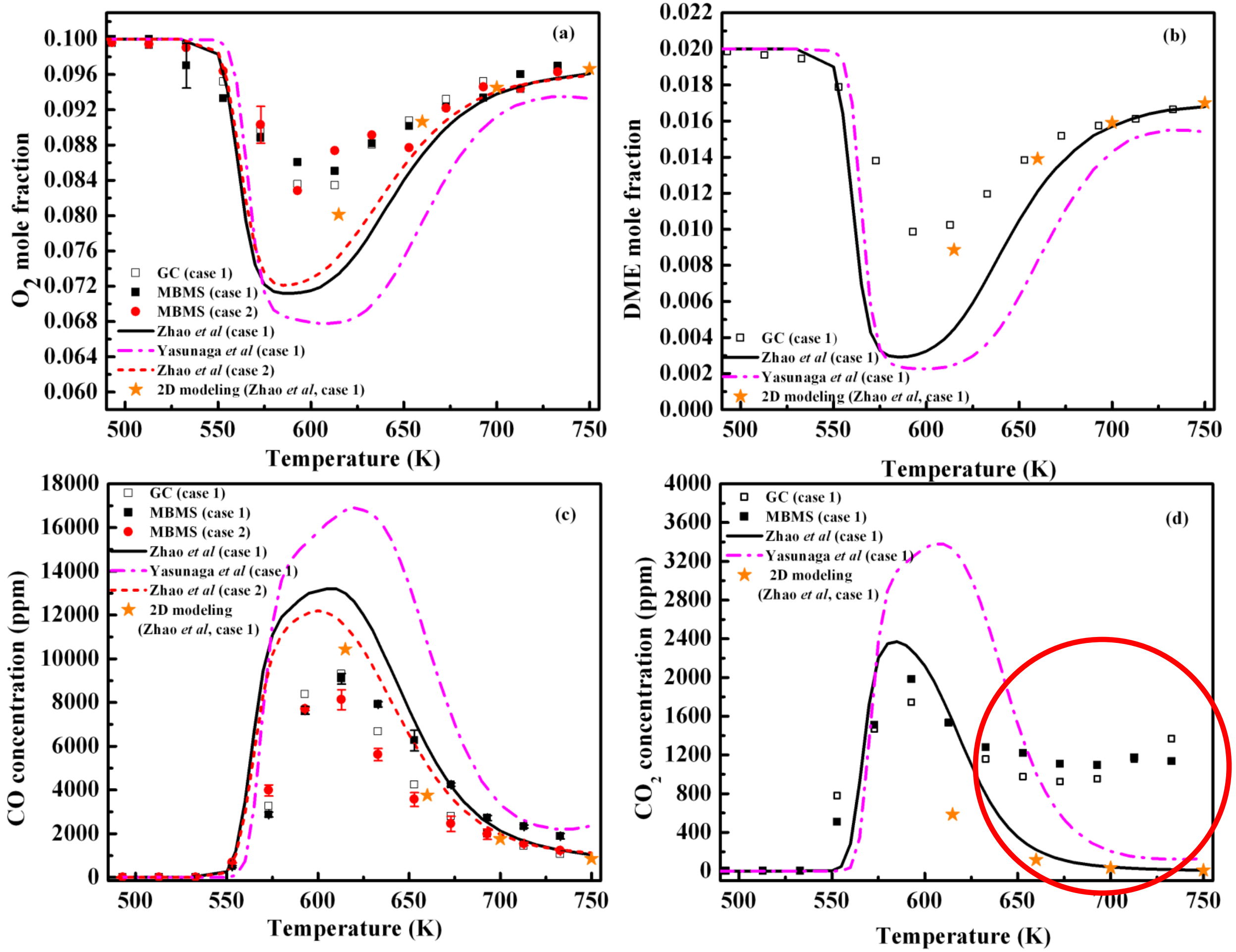
DME & HCOOH, N_2 & CO

1. http://physics.nist.gov/ionxsec

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

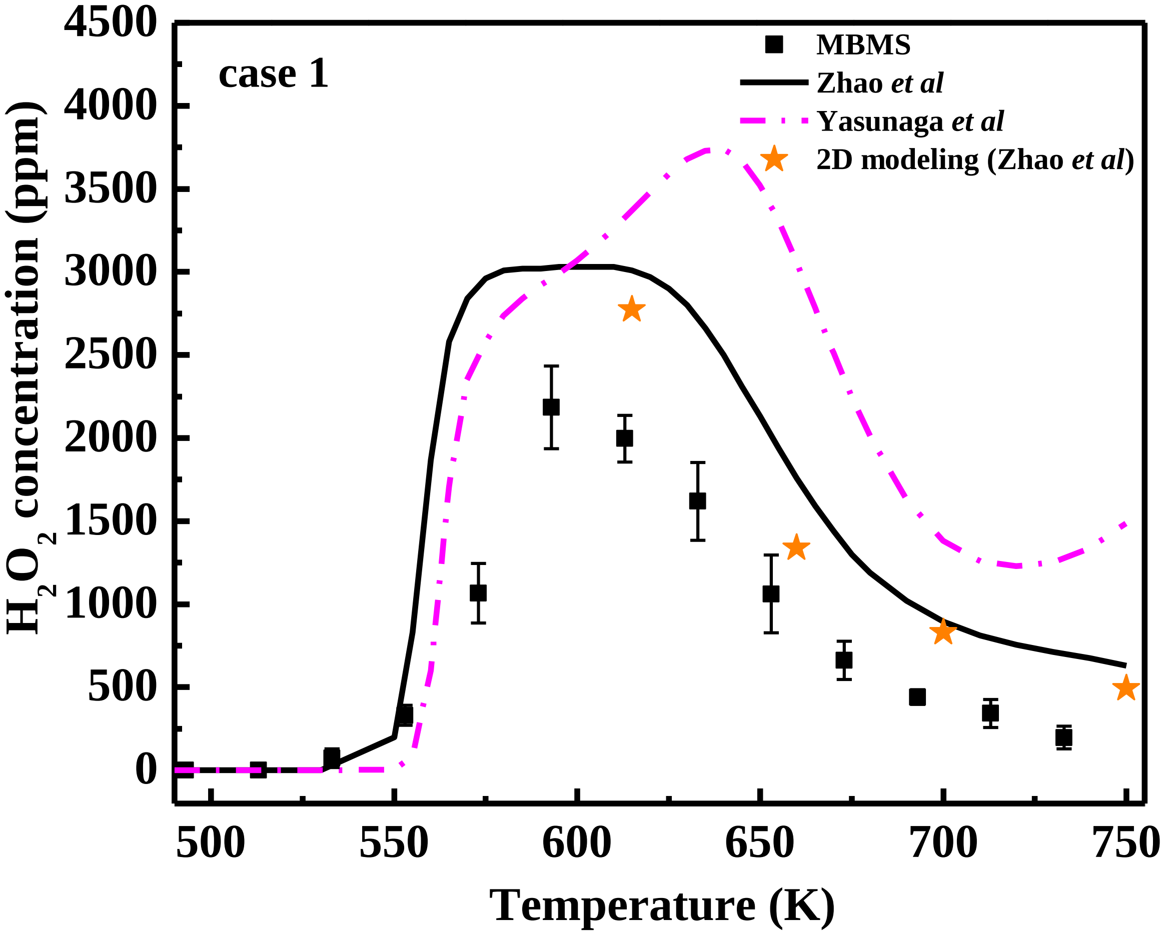


High CO_2 production

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

H_2O_2 measurement

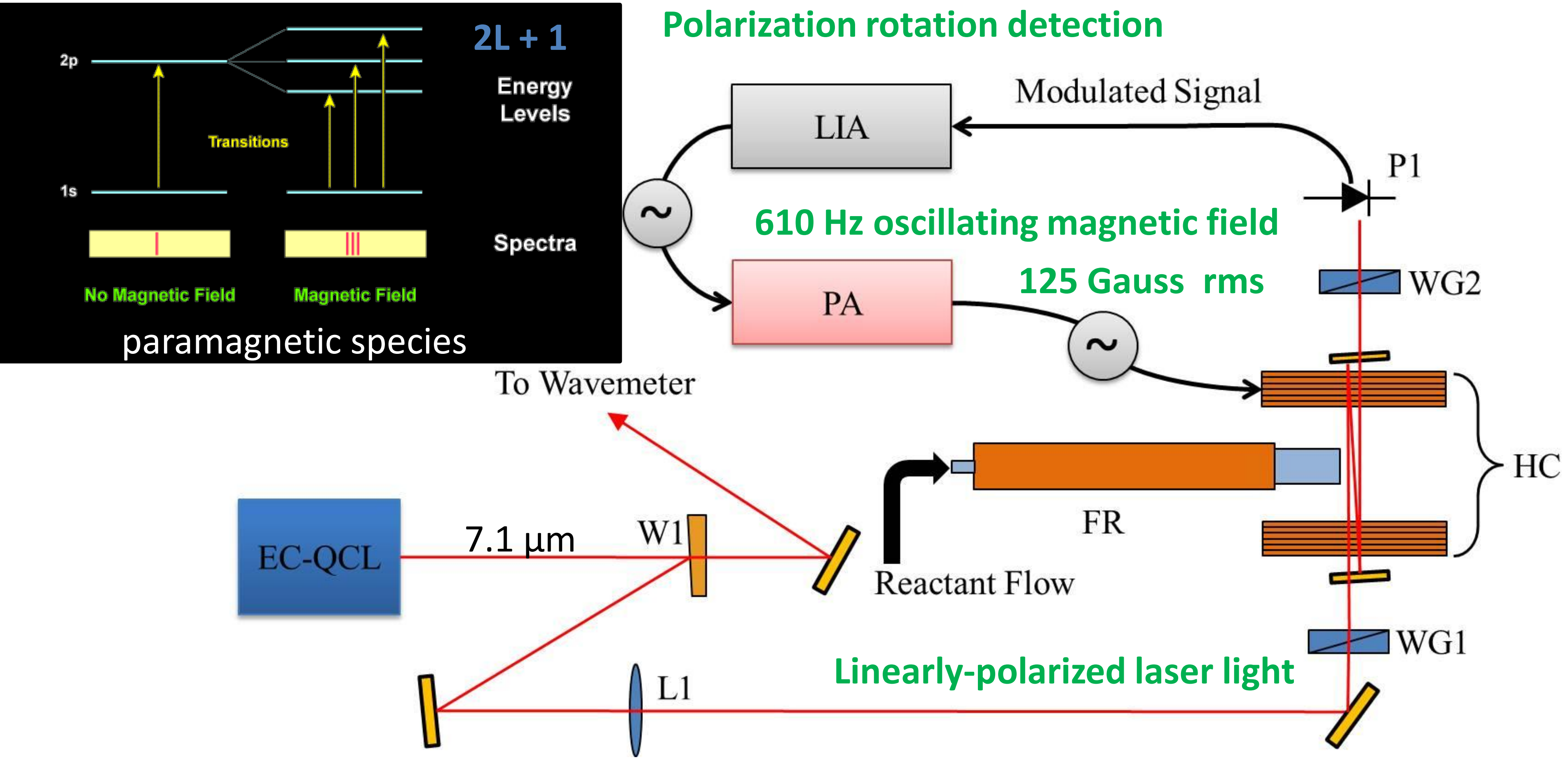


Good agreement for H_2O_2 formation
Different predictions from different models

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

Quantitative HO_2 Measurement (very challenging!):

Mid infra-red Faraday Rotation Spectroscopy (FRS), 1396 cm^{-1}



2L + 1

paramagnetic species

Polarization rotation detection

610 Hz oscillating magnetic field

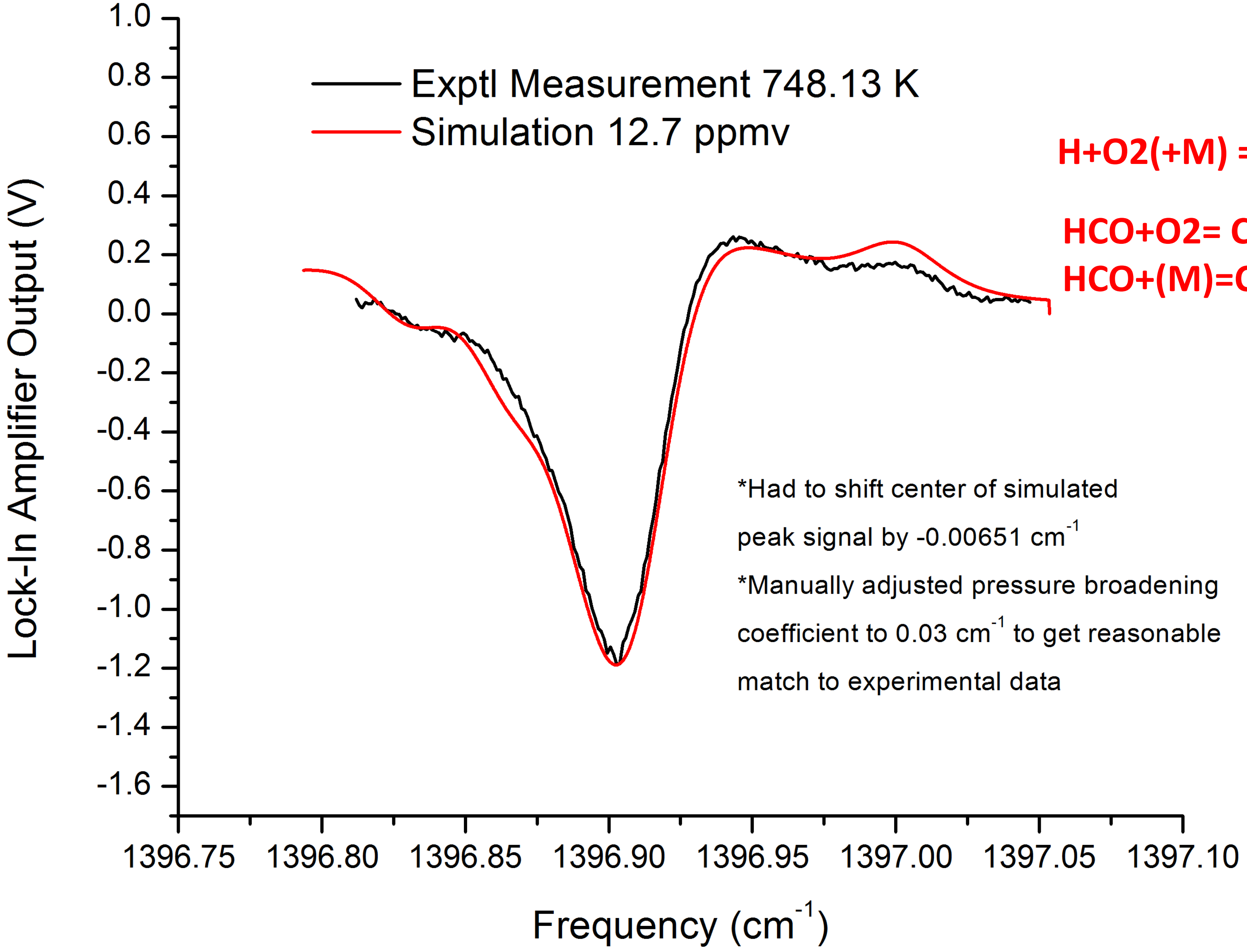
125 Gauss rms

7.1 µm

Linearly-polarized laser light

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

Sub-ppm level HO_2 measurement in DME/air flow reactor (1atm, 748K)



*Had to shift center of simulated peak signal by -0.00651 cm^{-1}

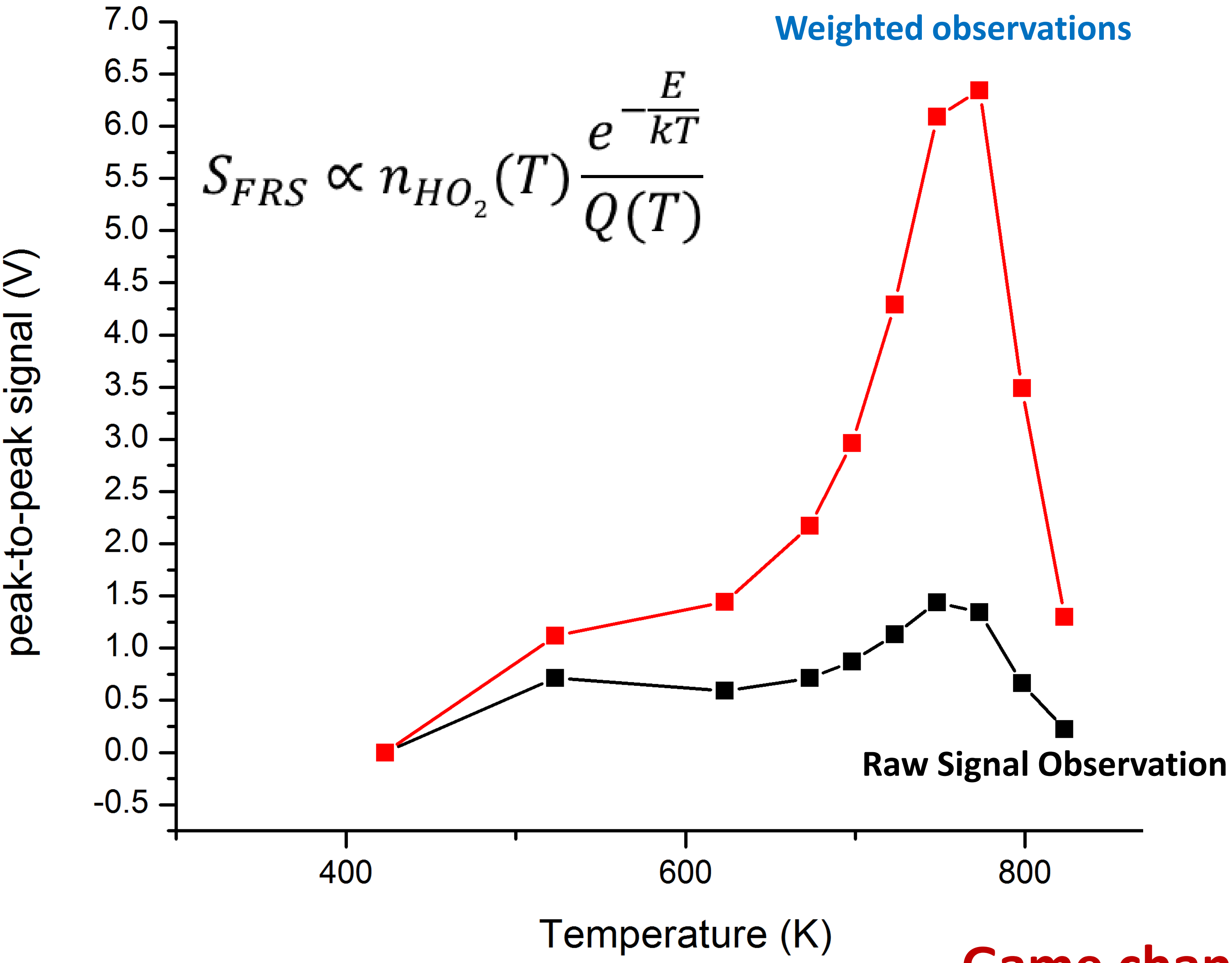
*Manually adjusted pressure broadening coefficient to 0.03 cm^{-1} to get reasonable match to experimental data

H+O2(+M) = HO2(+M),

HCO+O2= CO+HO2

HCO+(M)=CO+H

Temperature Dependence of HO2 Signal in a flame reactor



$$S_{FRS} \propto n_{HO_2}(T)\frac{e^{-\frac{E}{kT}}}{Q(T)}$$

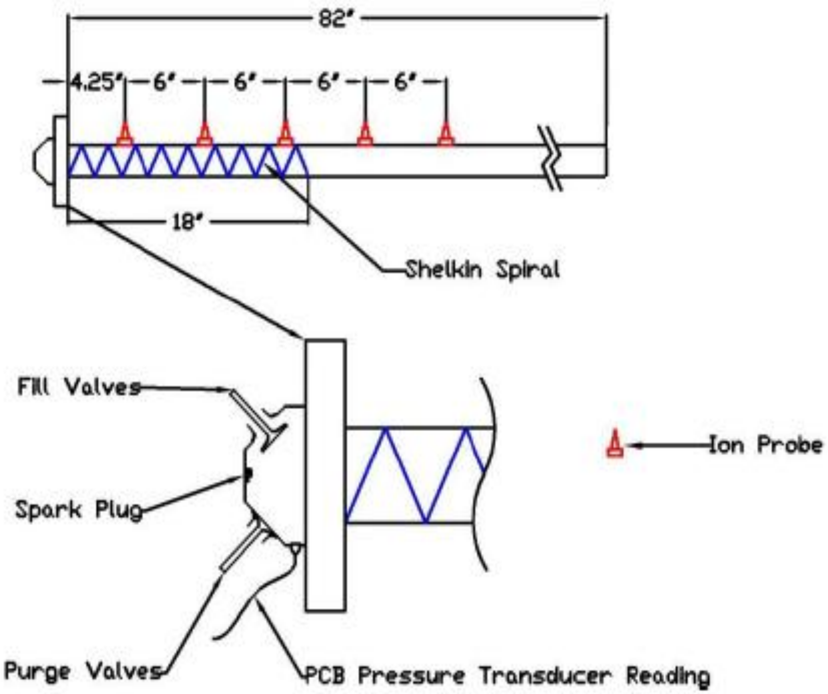
Game changer?!

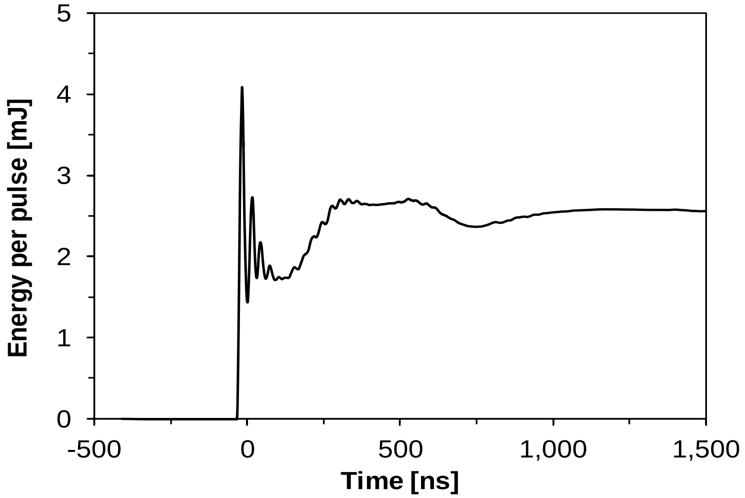
3. Ignition Enhancement and the critical ignition energy by Pulsed Nanosecond Discharge - Pulse Detonation Combustor/Engine

(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 discharges[1]
  - 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





Sample Voltage Trace

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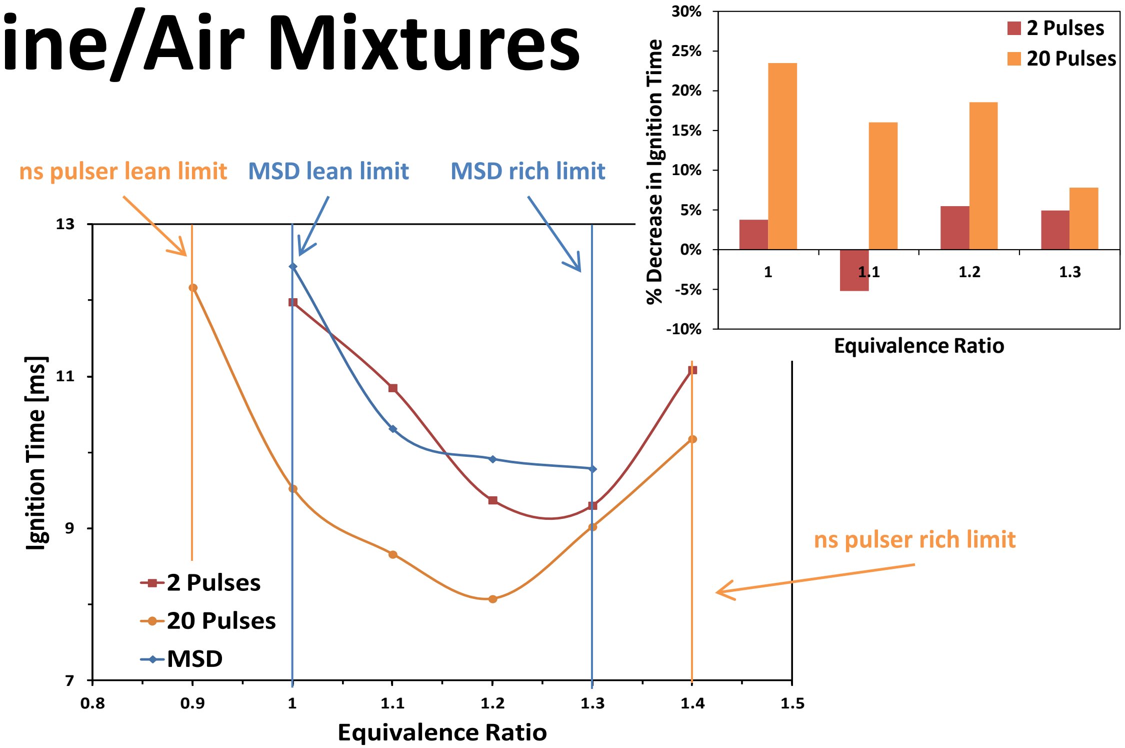
[1] S. V. Pancheshnyi, D. A. Lacoste, A. Bourdon, C. O. Laux, *IEEE Trans. On Plasma Science*, vol. 34 (2006).

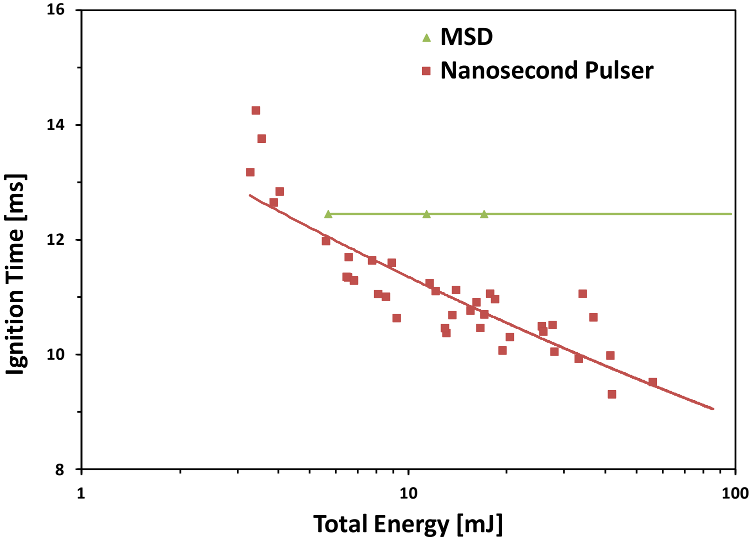
Aviation gasoline/Air Mixtures

- **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

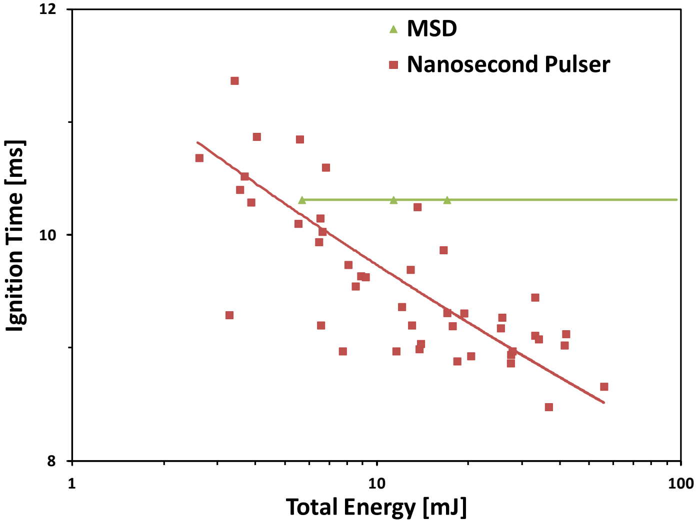


- **Pulse energy and plasma frequency are varied at fixed equivalence ratio**
- Total energy = energy/pulse x number of pulses
- Ignition time decreases with total energy for ns-pulser case

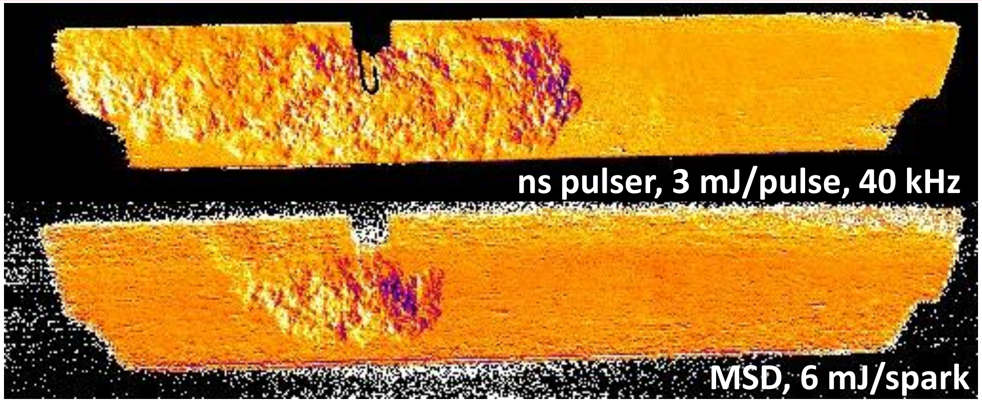
Eq. Ratio=1.0



Eq. Ratio=1.1



Schlieren Imaging



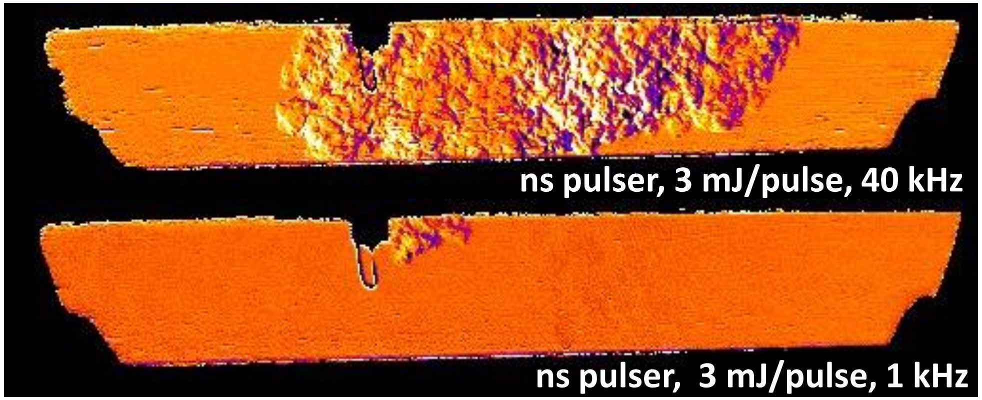
Comparison with conventional ignition

Φ=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



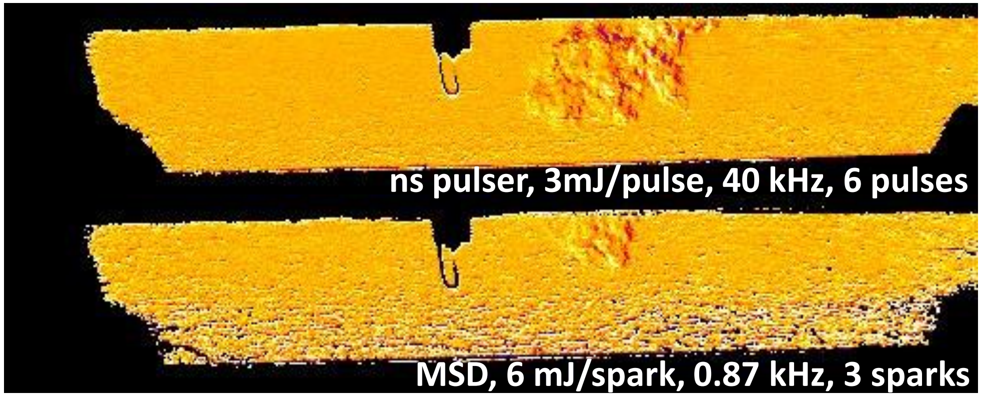
Effect of high frequency

Φ=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

Φ=0.8 Methane/Air

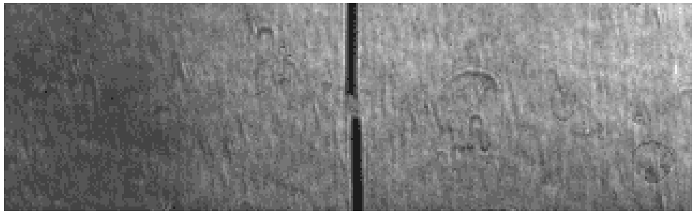
Top: ns pulser, 6 pulses at 40 kHz

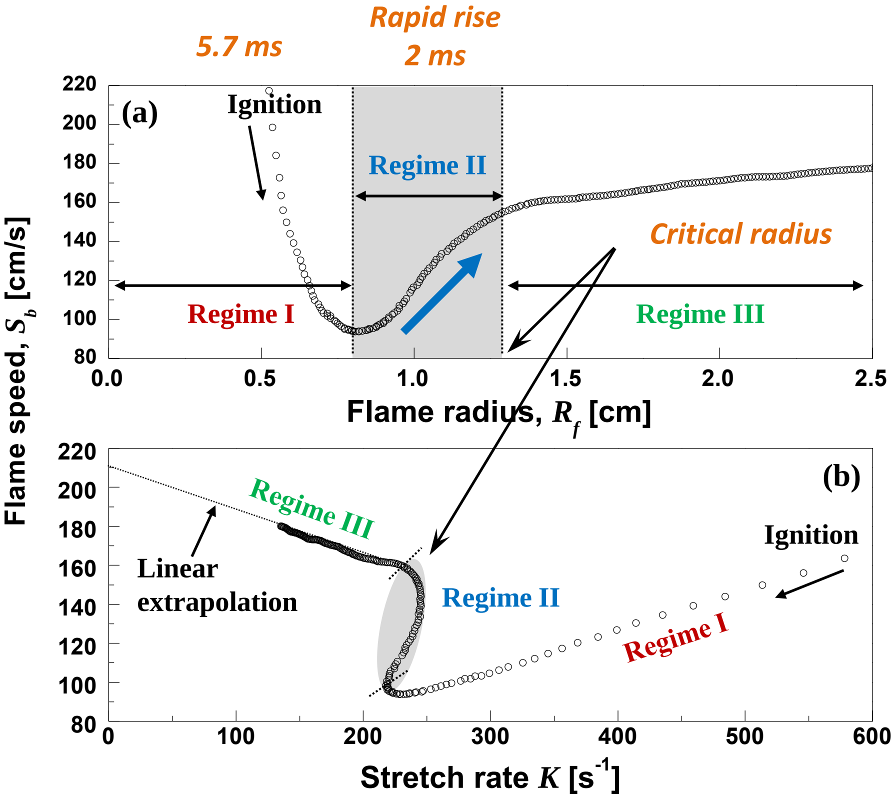
Bottom: MSD, 3 sparks at 0.87 kHz

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 study^2
- Ignition failure vs. Critical radius

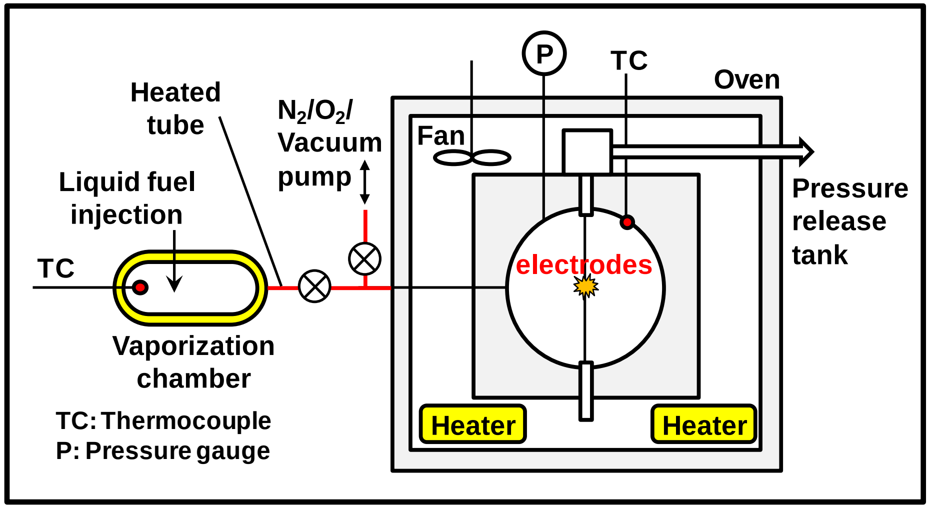


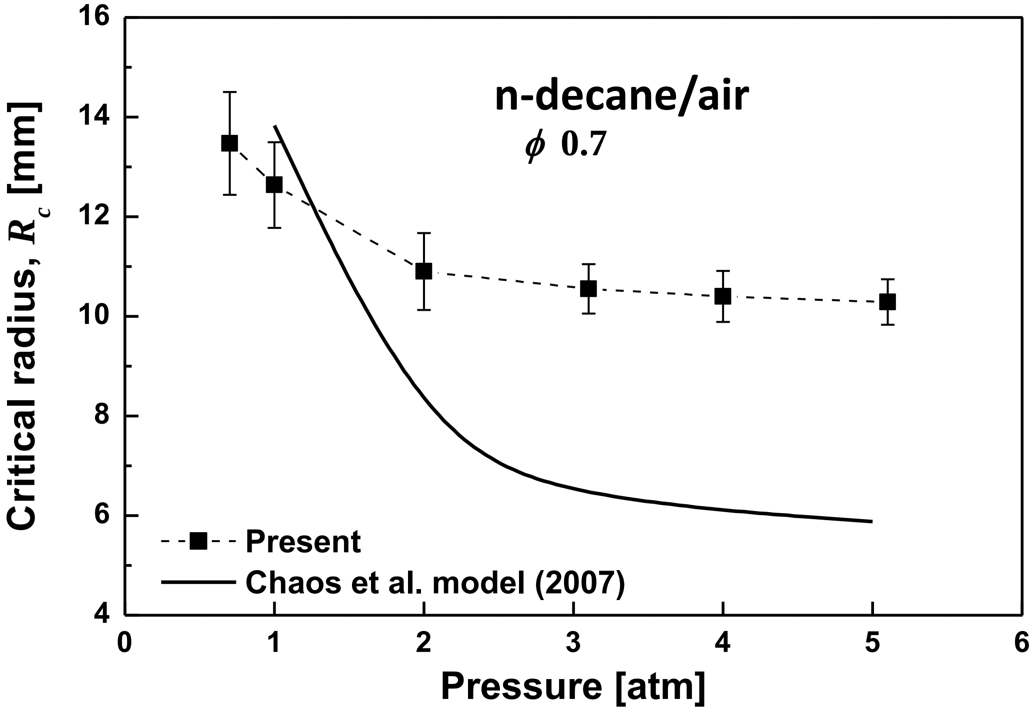


< *n*-Decane/Air at ϕ 0.7, 1 atm, 400 K >

Kim et al., Proc. Combust. Institute, Vol. 34, 2012

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 increases 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-infra red absorption spectroscopy and MBMS system are developed and successfully measured H2O2 and other intermediate species.

6. A mid-infrared Faraday rotation spectroscopy method is developed and successfully measured HO2 in a flow reactor.

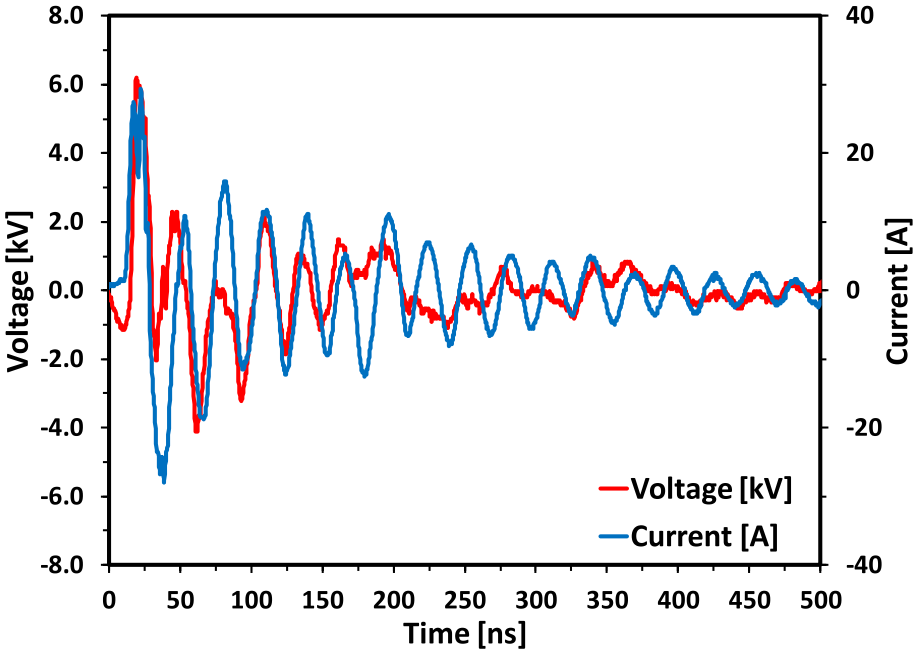
Acknowledgement

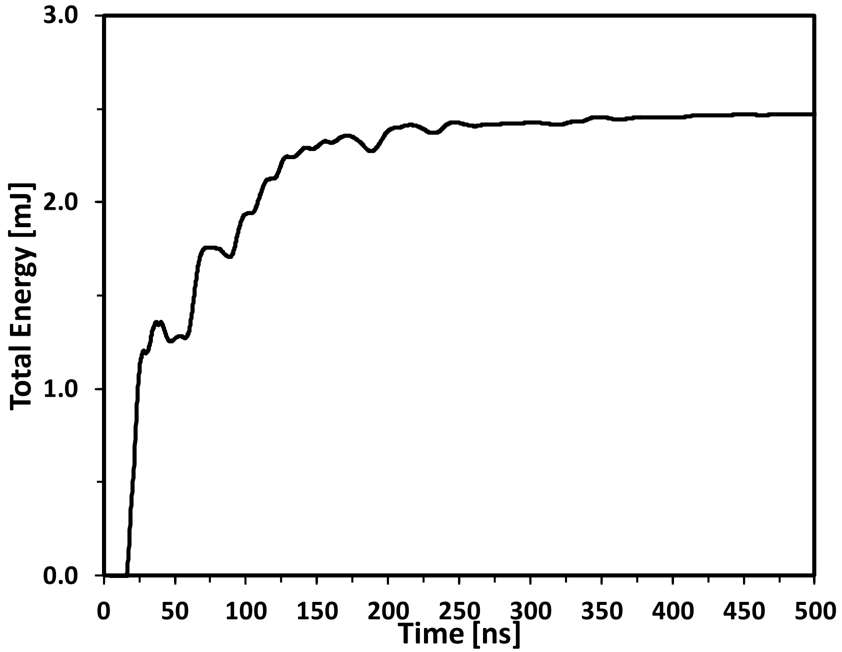
This work was supported by the plasma **MURI** research grant from the Air Force Office of Scientific Research (Drs. Chiping Li, Julian Tishkoff).

Thank you!

QUESTIONS & COMMENTS?

Measurement Technique



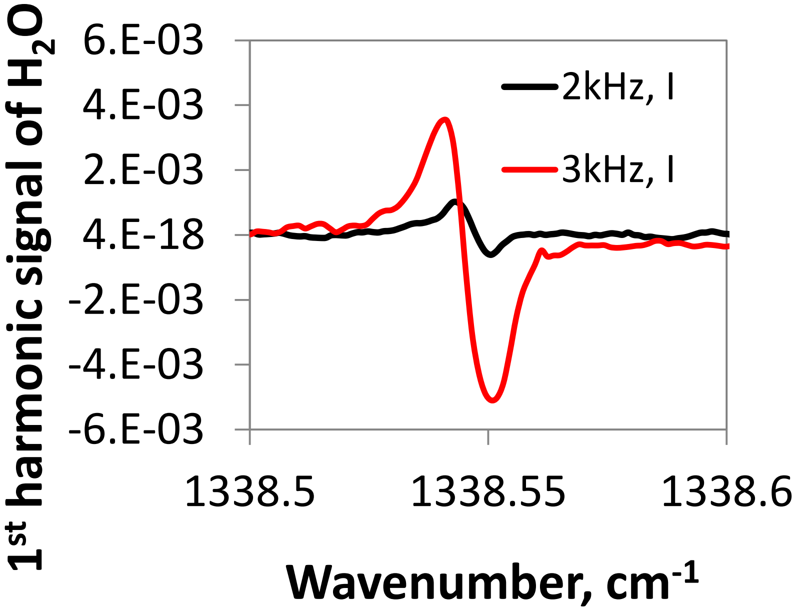


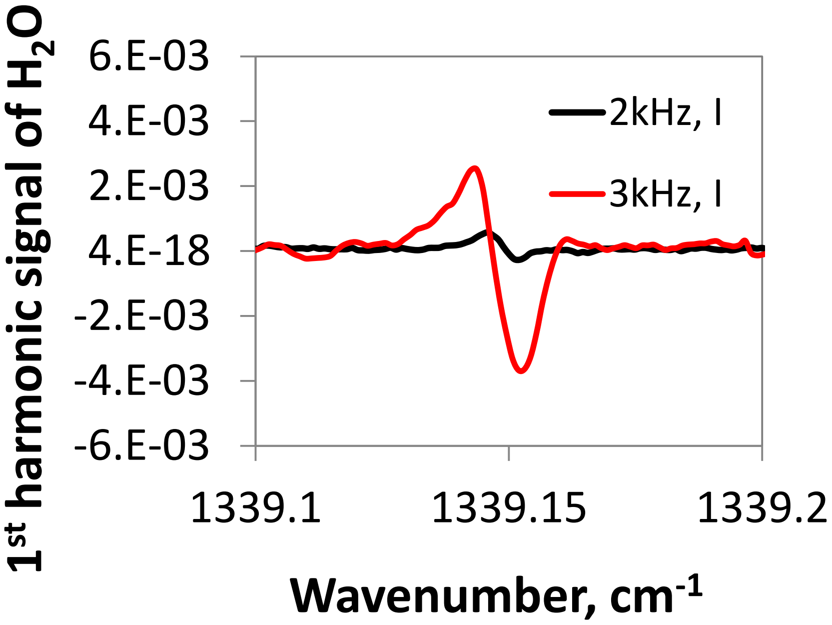
- Current and voltage are measured for each condition
  - Voltage probe: LeCroy high voltage probe (PPE20KV)
  - Current probe: Pearson Coil (Model 6585)
- Peak voltage for all experiments ≈ 6 kV
- The total energy is computed by integrating the power over a long enough time scale for all reflections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

H_2O and temperature measurements with plasma discharge

H_2O 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



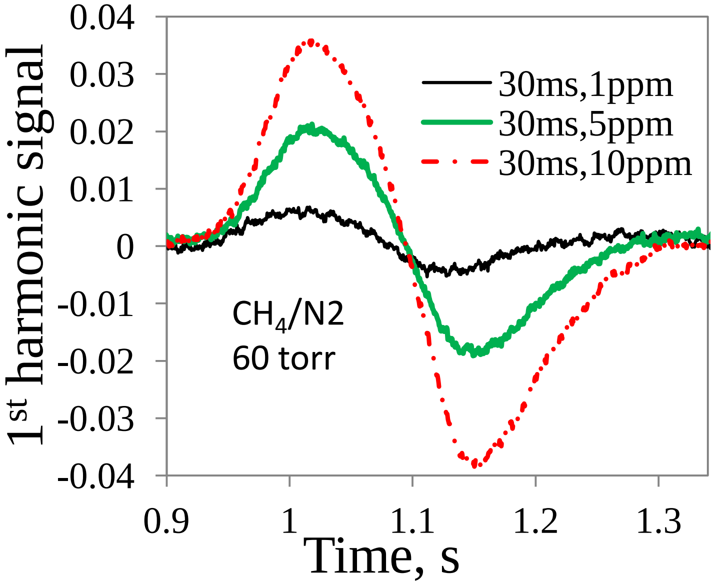


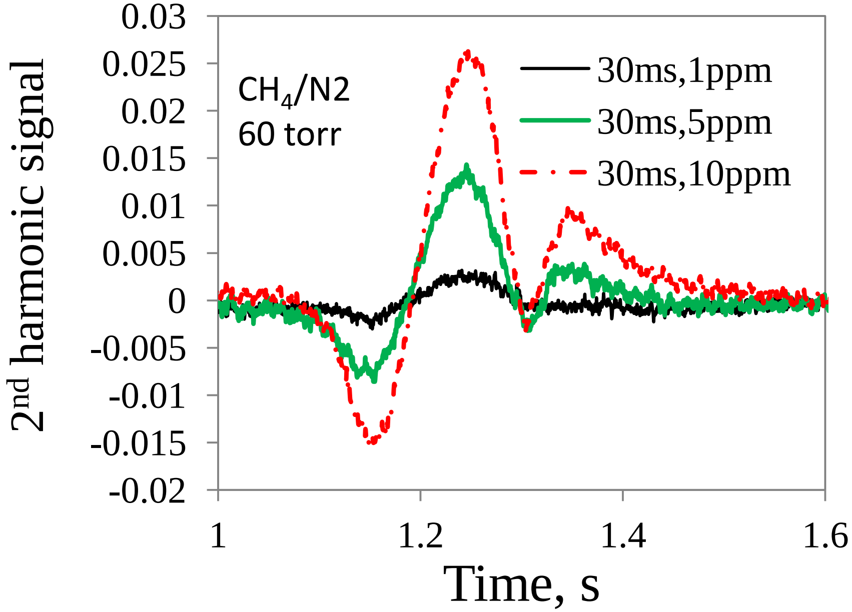
HITRAN: J. Quant. Spectrosc. Radiat. Transfer, 111, 2139–2150 (2010).

Wavelength modulated absorption measurement of CH_4

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

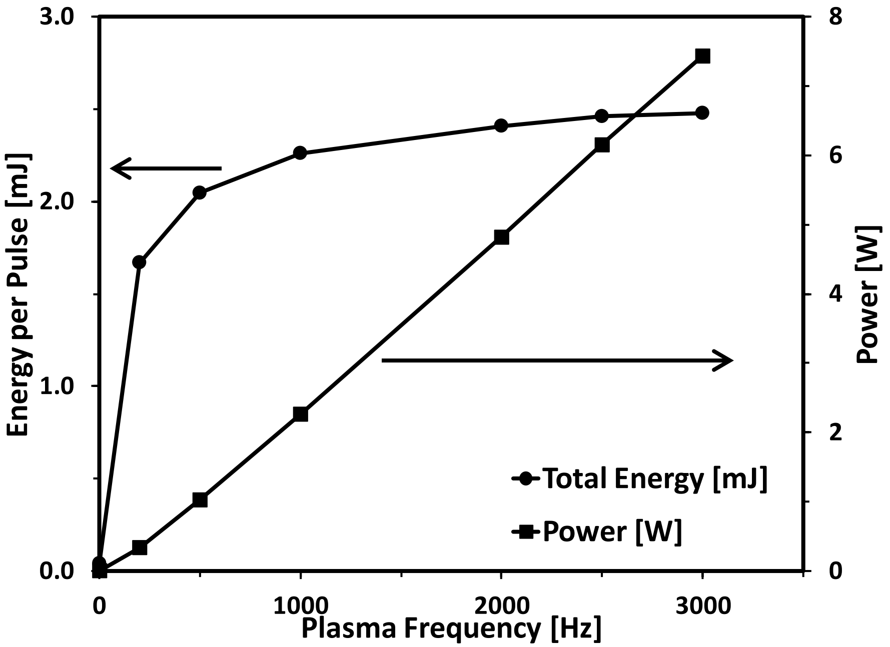
f=50 kHz – 1 MHz

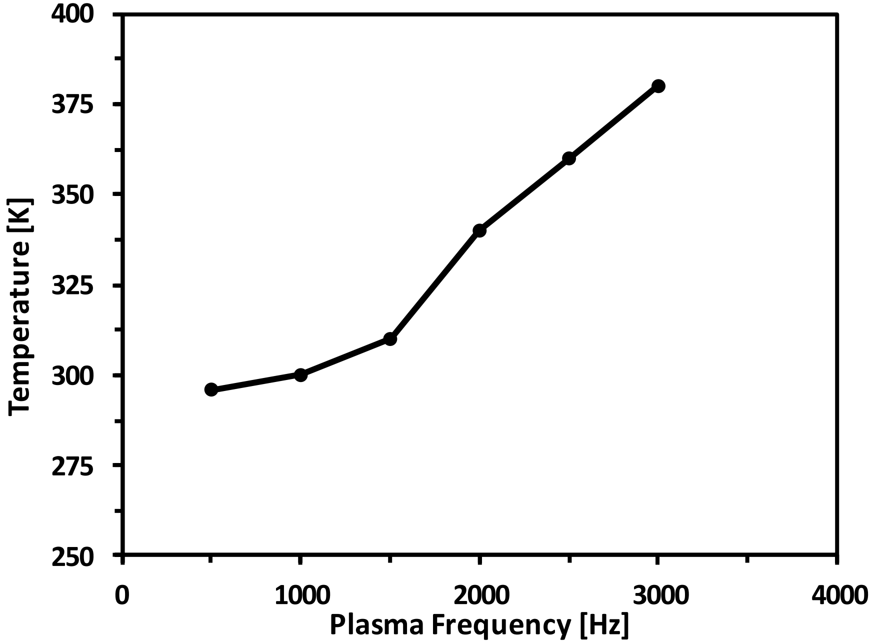




Laser was scanned at 0.1Hz and modulation at along with using lock in amplifier

Results for Continuous Plasma

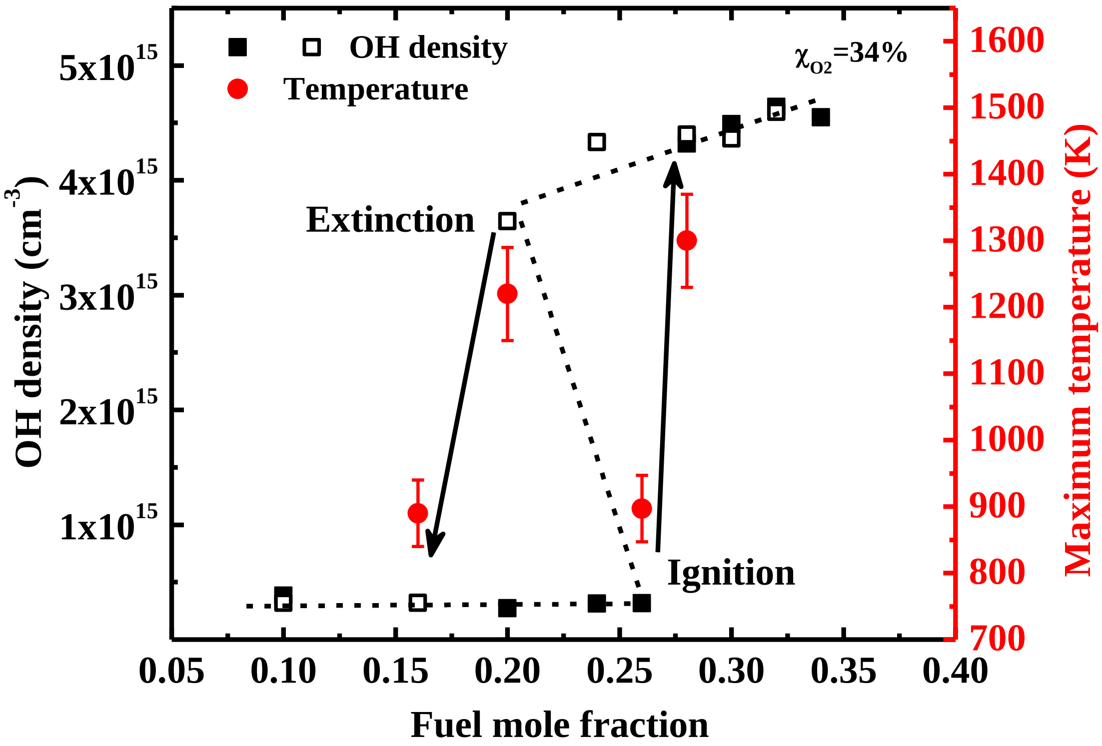




- Results are for $Ar/O_2/C_2H_4$ mixtures with 25% reactants and $\phi=1$
- The flow speed is 40 cm/s and the pressure is 60 Torr
- Per pulse energy is dependent on plasma repetition frequency
  - Seed electrons and ions left over from previous pulse provide for easier breakdown
  - This effect levels off after about 1000 Hz
- At high pulse repetition frequency, temperature scales linearly with plasma power

Classical S-curve

hysteresis between ignition and extinction: S curve



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

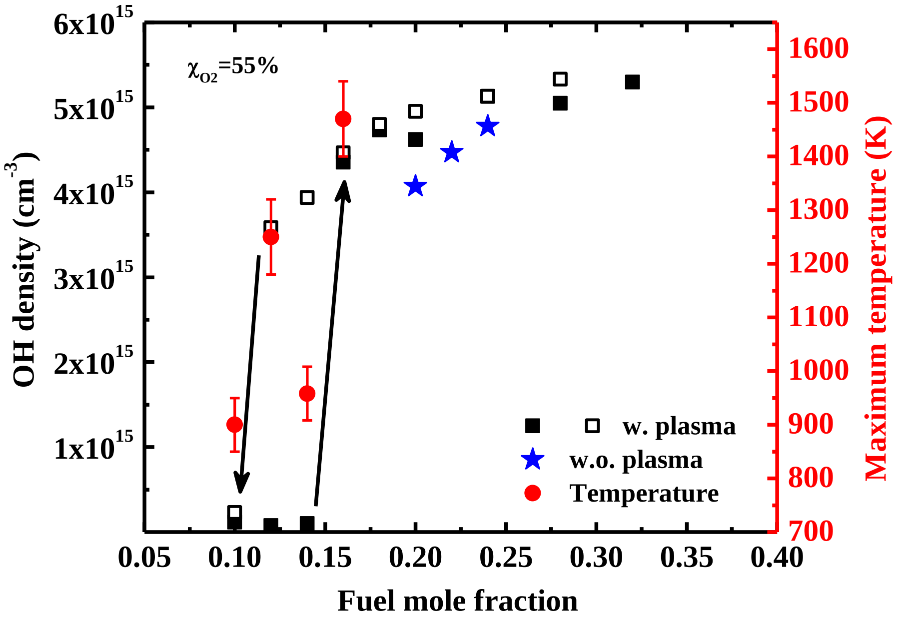
Relationship between OH density, local maximum temperature and fuel mole fraction, T_o=650 K, T_f=600 K He/O_2 = 0.66:0.34 , P = 72 Torr, *f* = 24 kHz, a = 400 1/s

[1] R.B. Miles, W.R. Lempert, J.N. Forkey, Meas. Sci. Technol. 2001 [2]J.A. Sutton, J.F. Driscoll, *Exp Fluids* 2006

S-curve transition

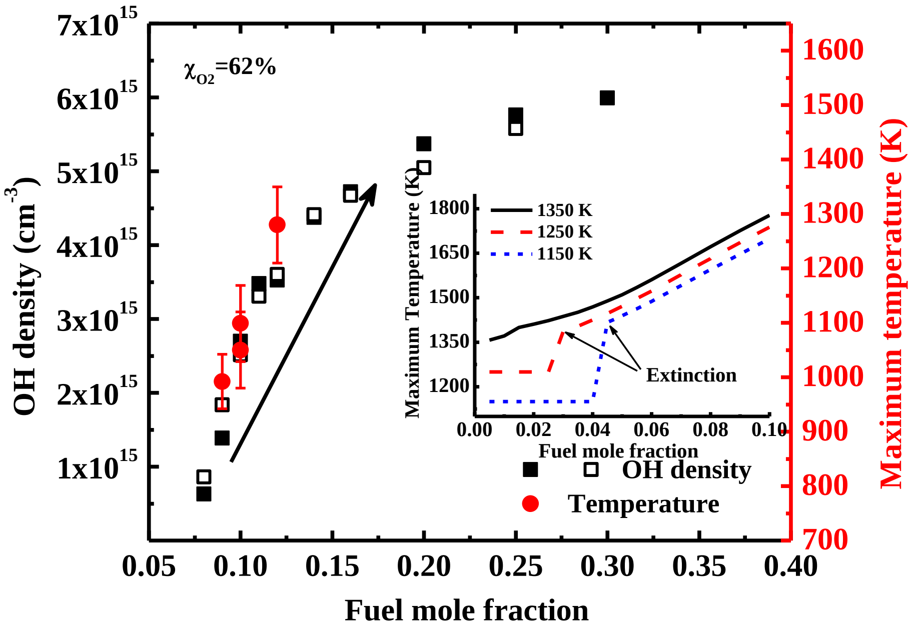
Relationship between OH density, local maximum temperature and fuel mole fraction, P = 72 Torr, *f* = 24 kHz, a = 400 1/s

He/O_2 = 0.45:0.55



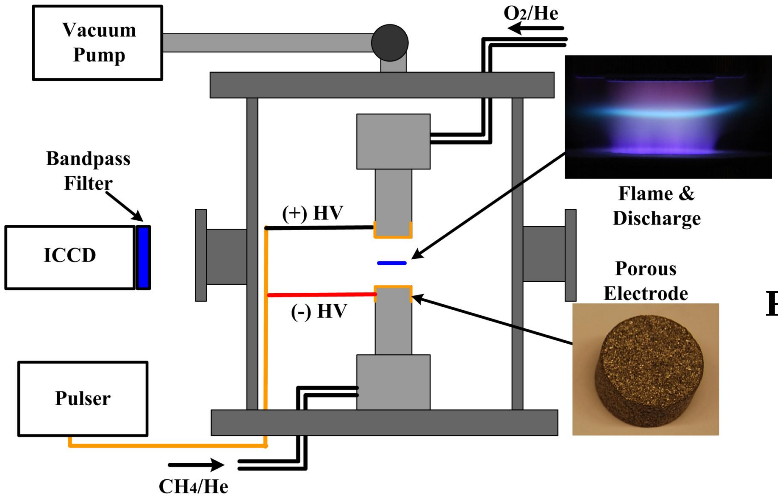
ignition and extinction points were pushed to lower fuel concentrations

He/O_2 = 0.38:0.62



monotonic ignition and extinction curve (monotonic *S*-curve)

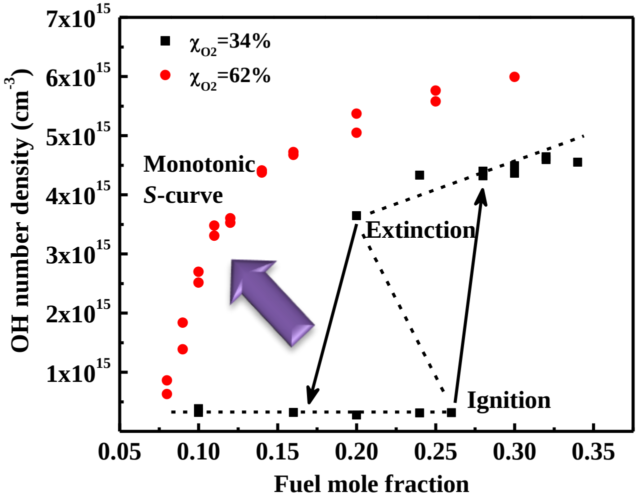
1. New flame and ignition regimes with *in situ* nano-second pulsed discharge



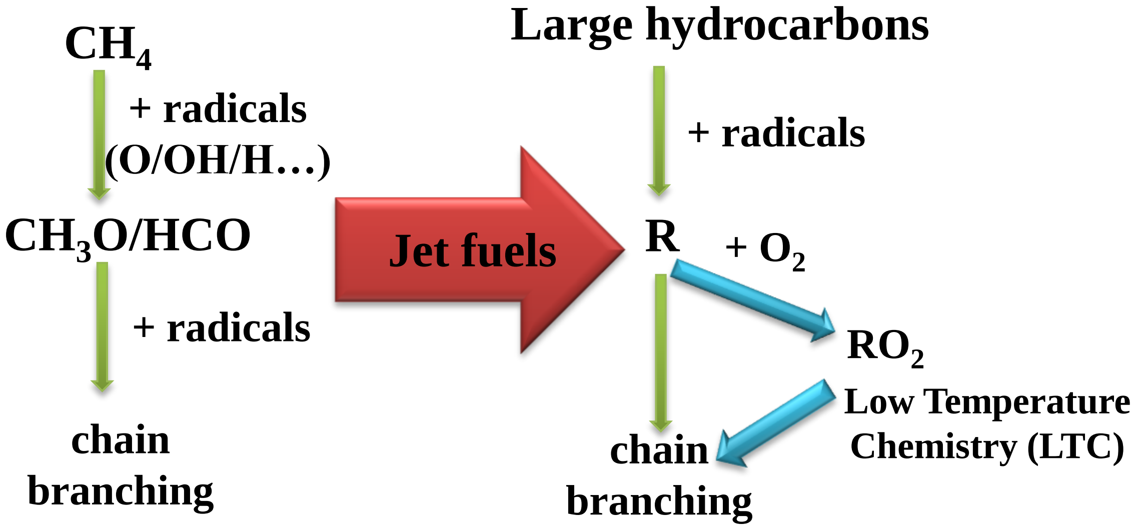
Coupling effect

Radical generation

a= 400 1/s, X_o = 55%, X_f = 20%, *f* = 24 kHz, P=72 Torr, UV power = 2 mj/pulse



Radicals produced by *in situ* discharge :
Dramatically increased the reactivity of CH_4 (no extinction limit)



CH_4

+ radicals (O/OH/H…)

CH_3O/HCO

+ radicals

chain branching

Jet fuels

Large hydrocarbons

+ radicals

R

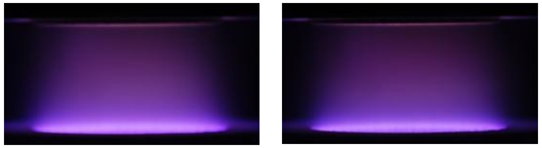
+ O_2

RO_2

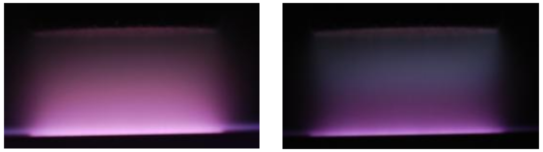
Low Temperature Chemistry (LTC)

chain branching

Same chemiluminescence before CH_4 ignition



Different chemiluminescence before DME ignition



CH_2O

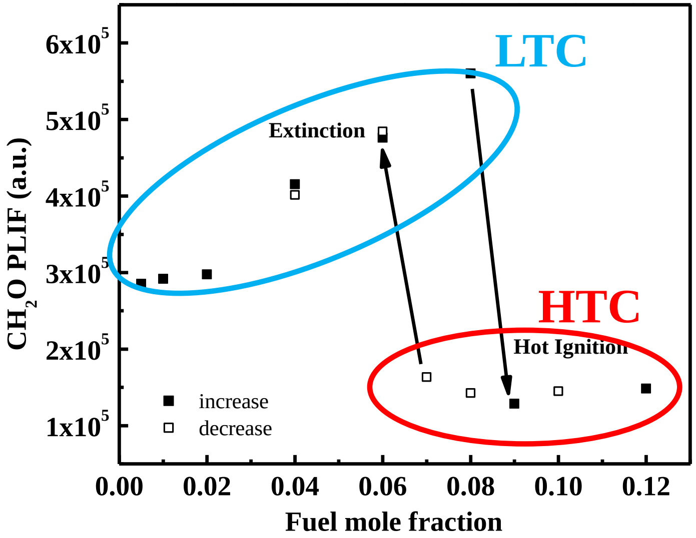
Ignition

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

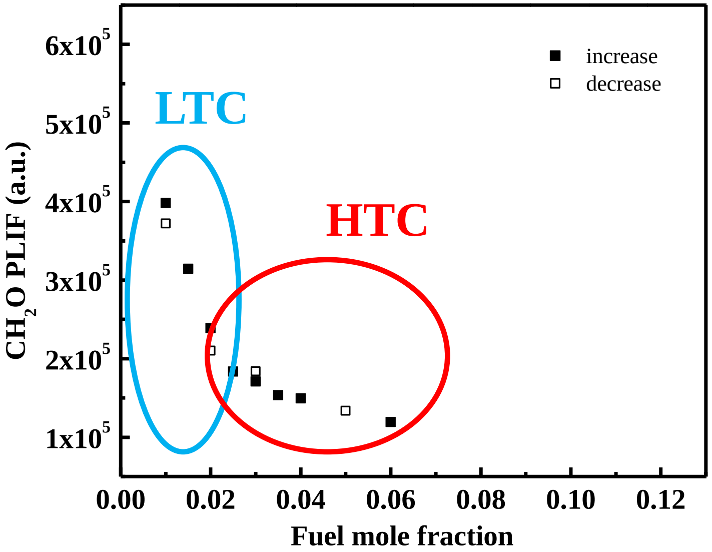
P = 72 Torr, a= 250 1/s, *f* = 24 kHz, X_{O_2}=40%, varying X_f



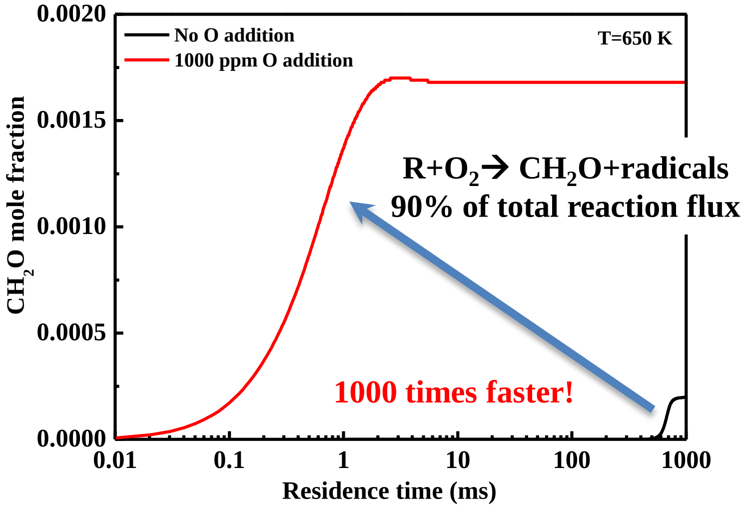
Smooth transition between LTC to HTC

Increased radical production

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



Plasma assisted low temperature chemistry



$R+O_2 \rightarrow CH_2O$+radicals
90% of total reaction flux

1000 times faster!

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

Slow LTC

Important for

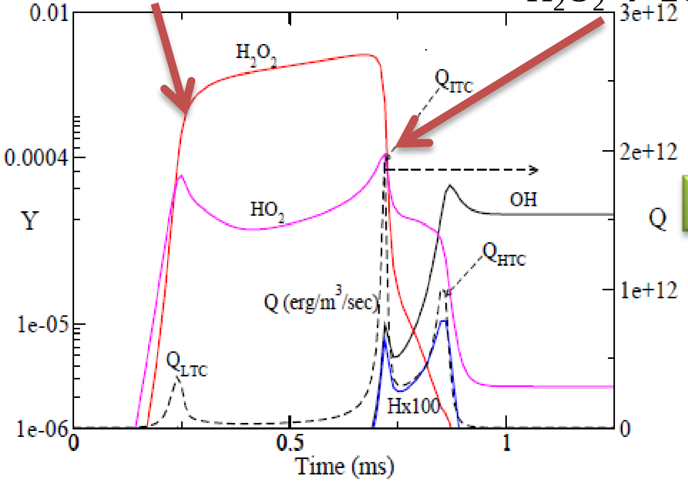
- **PAC**
- **Turbulent combustion at small time scales**

Kinetic studies

Importance of LTC and the critical role of H_2O_2

Low T ignition
H_2O_2 is stable

Transition from low T to high T ignition
$H_2O_2 \rightarrow 2OH$



H_2O_2: low T chemistry indicator

How to detect?

Indirect measurement:
Sensitive H_2O absorption at 2.5 um (Hong et al, 2009)

Direct measurement:
Laser absorption at 7.8 um at low pressure non-reactive flow (Aul, et al, PCI, 2011)

$H_2O_2/H_2O/Ar$ mixture in shock tube

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 °C)[1]

Challenging for combustible mixtures

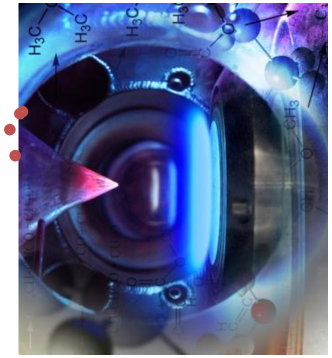
H_2O_2

LTC

DME

MBMS

Low Pressure MBMS for flame



Different masses

Mass spectrometry

1. Ludwig, et al, JPC. A 2006