Fundamental Mechanisms, Predictive Modeling, and Novel Aerospace Applications of Plasma Assisted Combustion

Yiguang Ju

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Princeton Team members:
Wenting Sun, Joe Lefkowitz, Mruthunjaya Uddi, Sang Hee Won

Collaborators
AFRL: Campbell Carter, Timothy Ombrello
International: Fei Qi, Huijun Guo (USTC)

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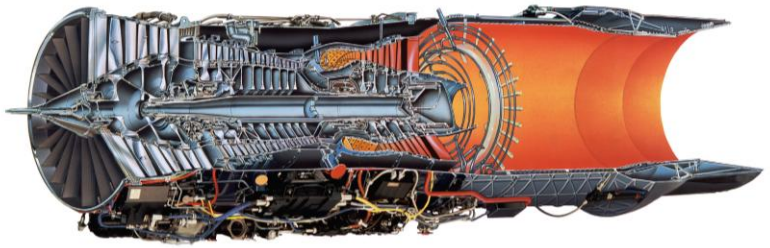
Motivation

Hypersonic propulsion system

F135 engine: (F35, 2011)



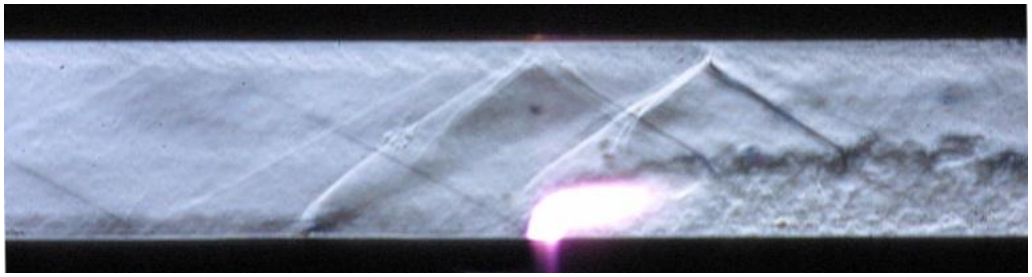
Ignition instability

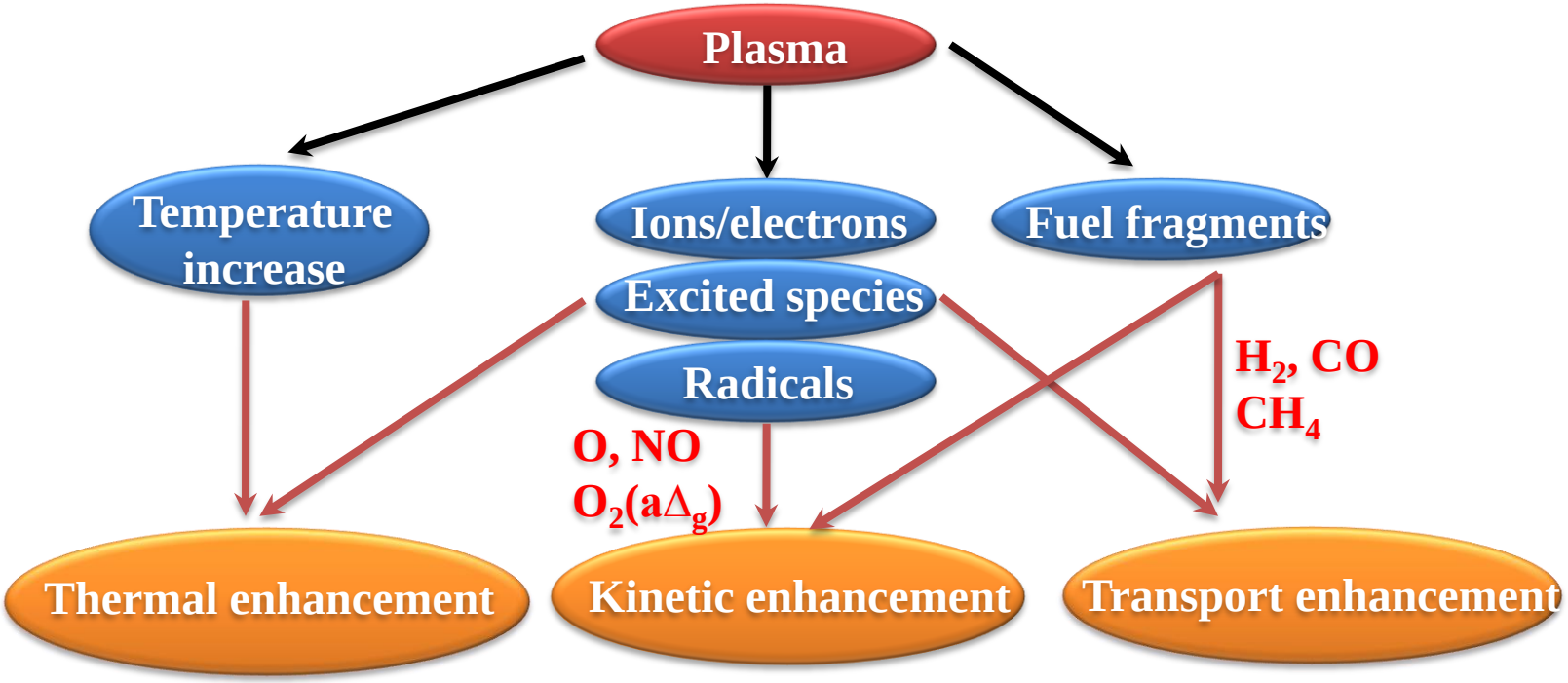
$$Da = \frac{\text{Ignition time (~10ms)}}{\text{Flow residence time (~1ms)}} >> 1$$

Challenges:

- Ignition time, Ignition energy
- Flame stabilization
- Combustion completion

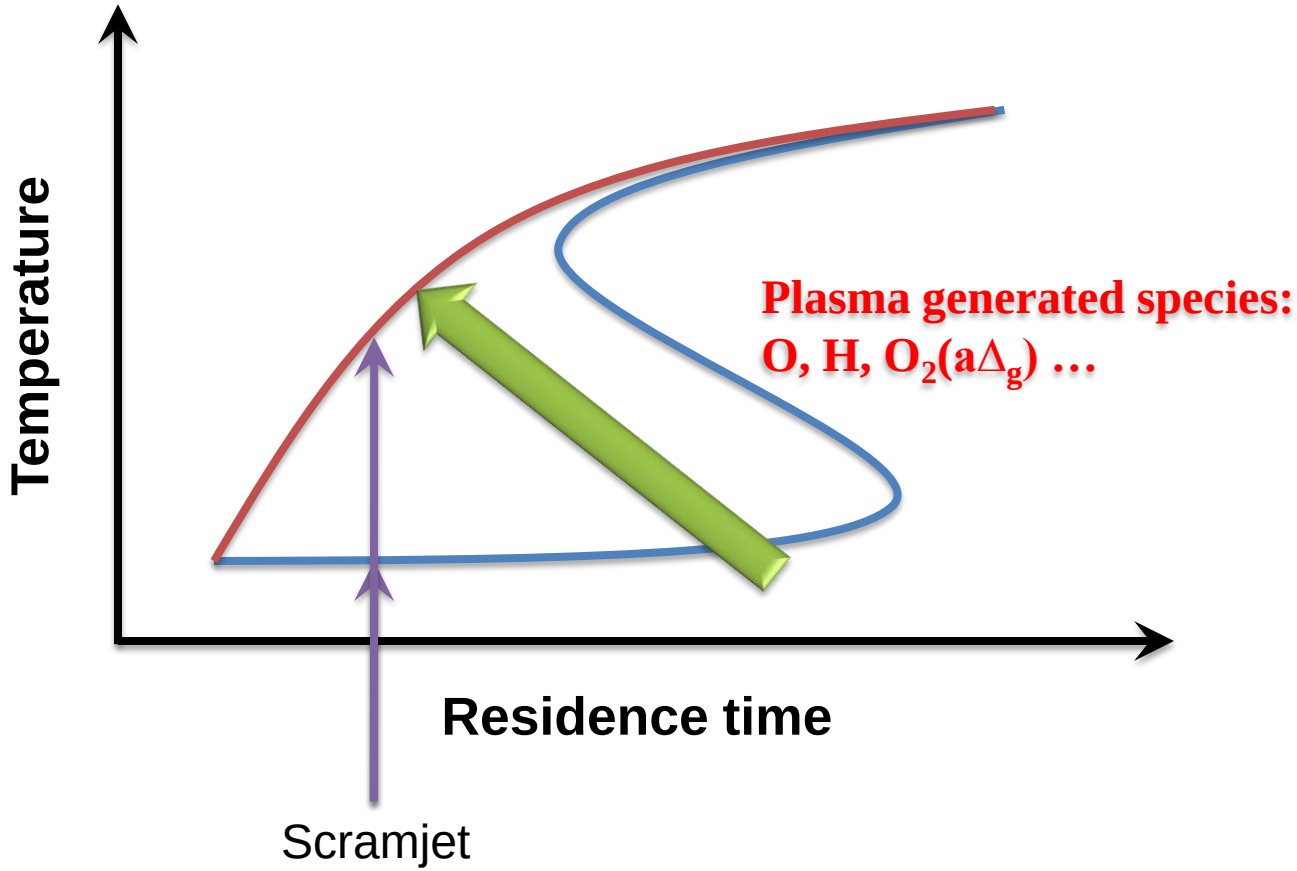
Plasma assisted combustion





Understanding: Good **poor** **marginal**

Change of ignition and extinction diagram: the S-curve transition



Research goals

Understand the fundamental enhancement mechanism of plasma-flame chemistry

Develop new experimental tools to validate plasma flame kinetic mechanism

Develop numerical methods to achieve efficient modeling of detailed plasma flame chemistry

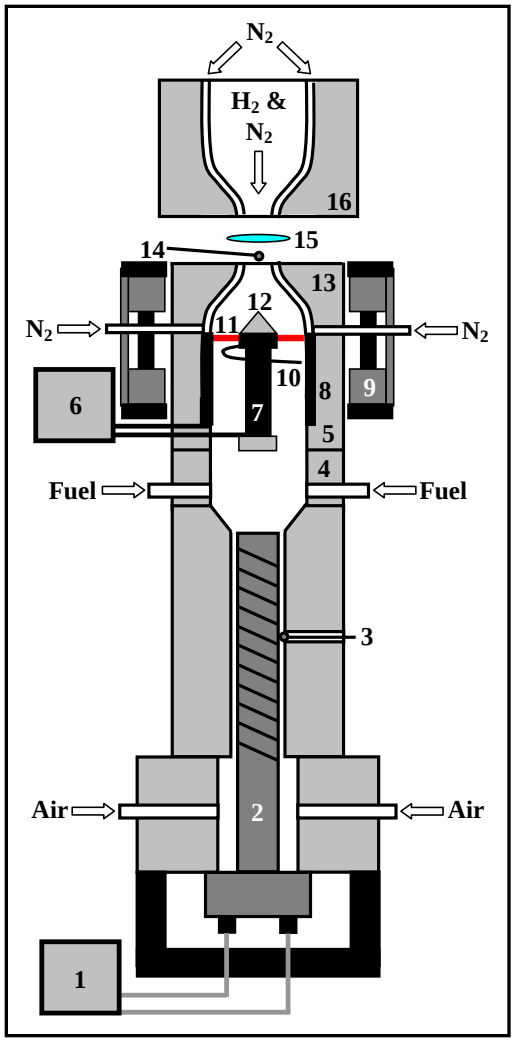
Outline

1. Background

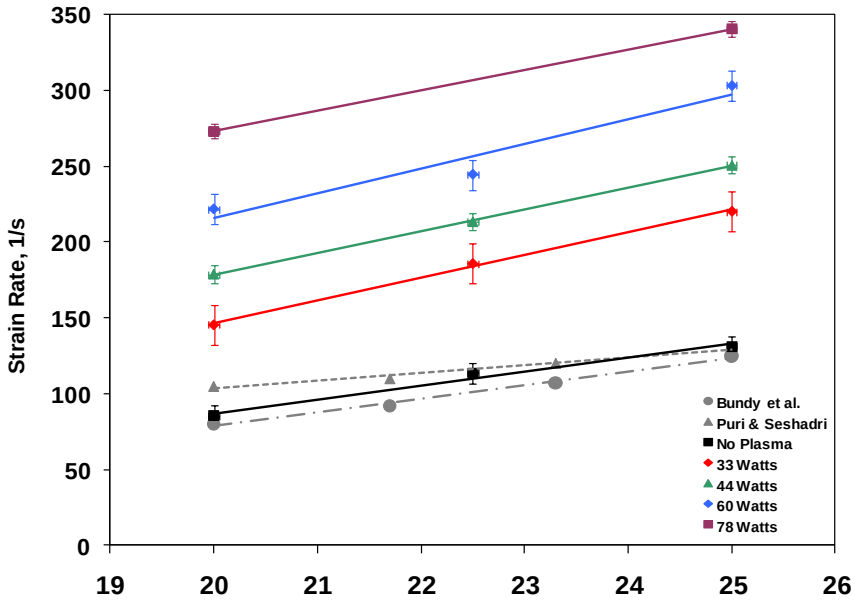
2. Experimental investigations
   - Effects of plasma assisted fuel oxidation on flame extinction
   - Effects of *in situ* plasma discharge on ignition enhancement
   - Molecular beam mass spectrometry study of low temperature chemistry

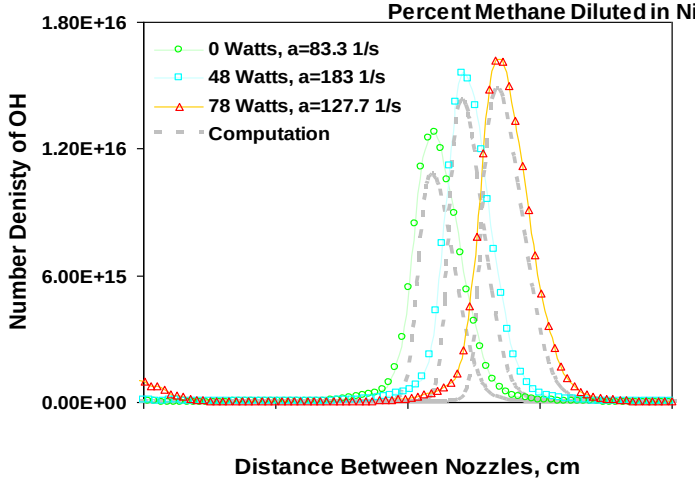
3. Conclusion and future work

Background and previous study: flame extinction



1. Silicon Controlled Rectifier, 2. Silicon carbide heater, 3. R-type thermocouple, 4. Fuel injection spacer 5. MGA plasma power supply, 5. MGA device, 6. MGA power supply, 7. Cathode, 8. Anode, 9. Magnets, 10. Gliding arc initiation wire, 11. MGA, 12. Insulator, 13. Nozzle with N_2 co-flow, 14. K-type thermocouple & FT-IR probe, 15. Diffusion flame, 16. Water-cooled nozzle with N_2 co-flow.



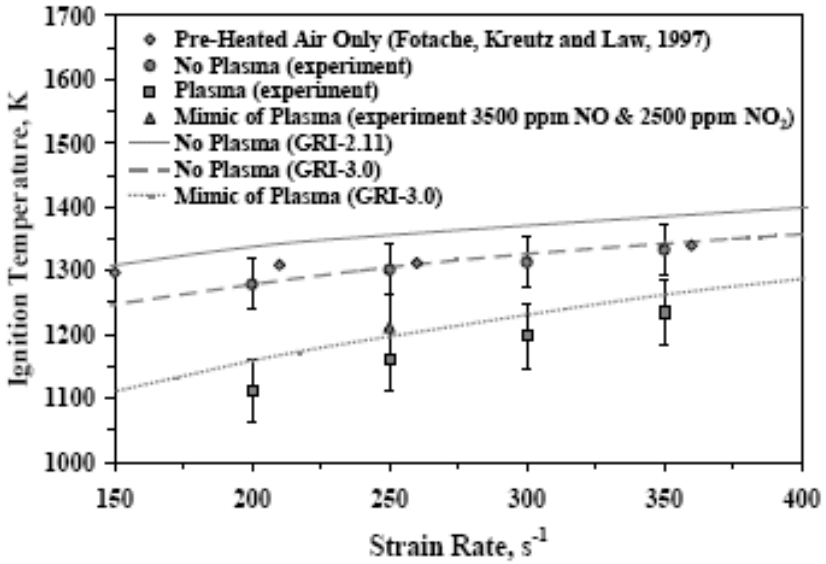


Only thermal effect!

Ombrello, et al, AIAA J, 2006

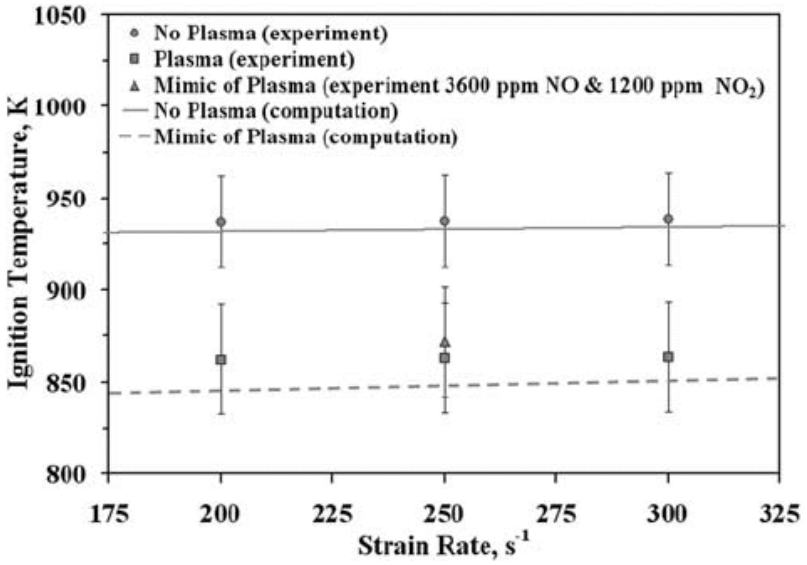
Previous work - Ignition study

CH_4/air counterflow diffusion flame



$$CH_3O_2 + NO \rightarrow CH_3O + NO_2$$
$$CH_3 + NO_2 \rightarrow CH_3O + NO$$

H_2/air counterflow diffusion flame



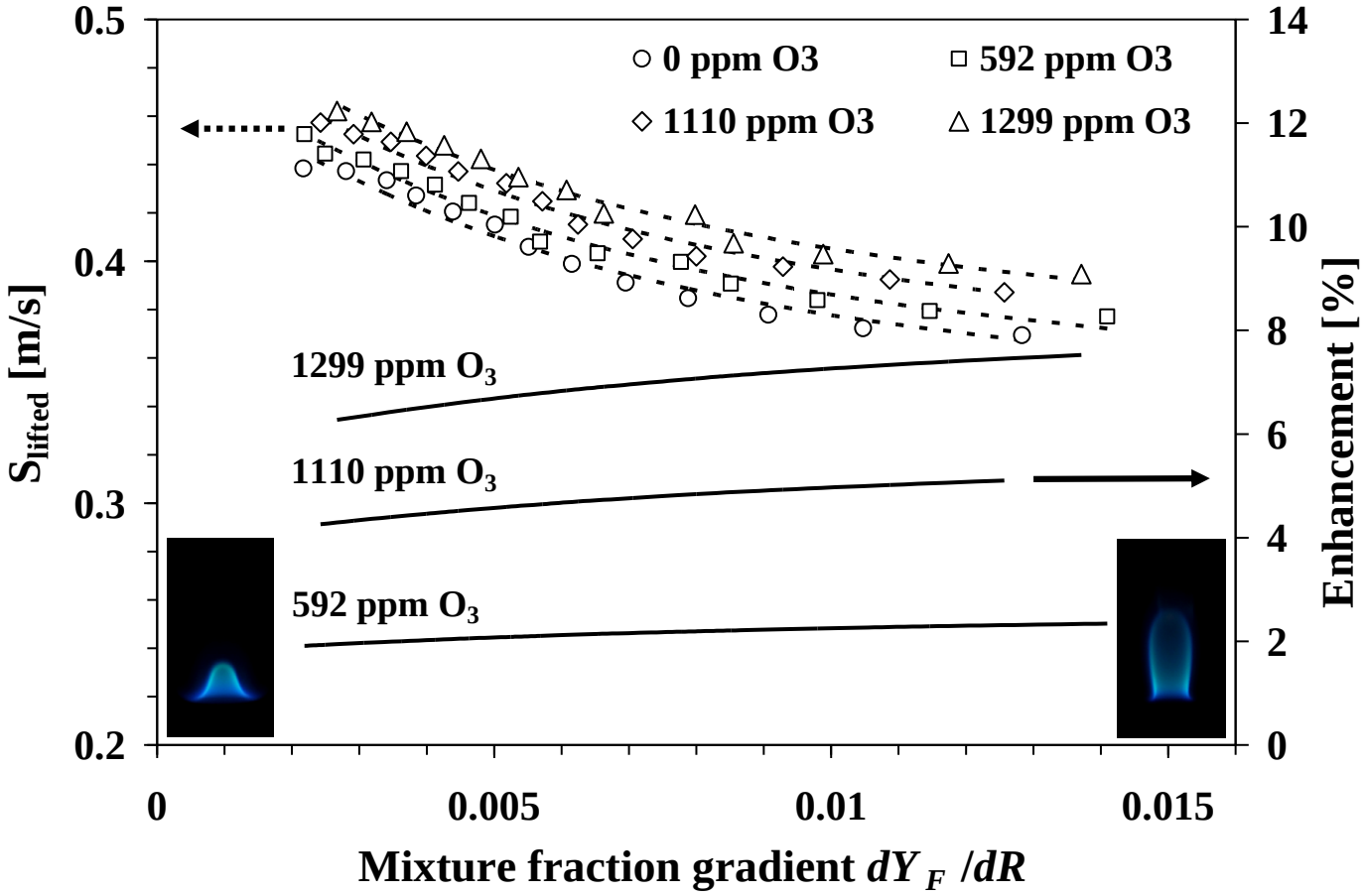
$$HO_2 + NO \rightarrow OH + NO_2$$
$$H + NO_2 \rightarrow OH + NO$$

NO_x catalytic effect

1. **non *in situ* discharge**
2. **Short life times of radicals and excites species**

Ombrello, et al, IEEE Plasma Sci, 2008

Previous researches – O_3



$$S_L \approx S_{lifted} \sqrt{\frac{\rho_b}{\rho_u}}$$

Flame speed extraction

Ombrello, et al, CNF, 2010

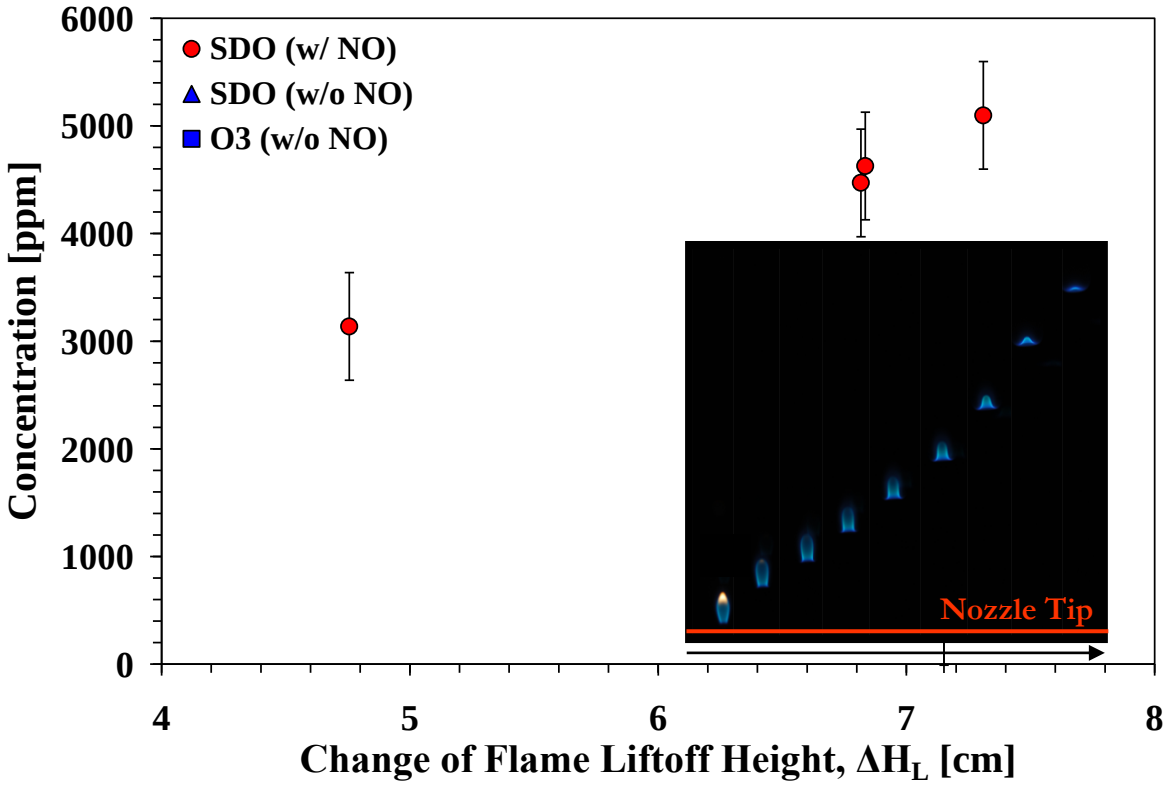
Previous researches – $O_2(a^1\Delta_g)$

$[O_2(a^1\Delta_g)]$, ppm	ΔH_L, mm
3137	4.76
4470	6.82
4627	6.83
5098	7.31

$O_2(a^1\Delta_g) + H = OH + O$ fast

$O_2 + H = OH + O$ slow

→ **≈ 5000 ppm $O_2(a^1\Delta_g)$ → 2-3 % Lifted Flame Speed Enhancement**

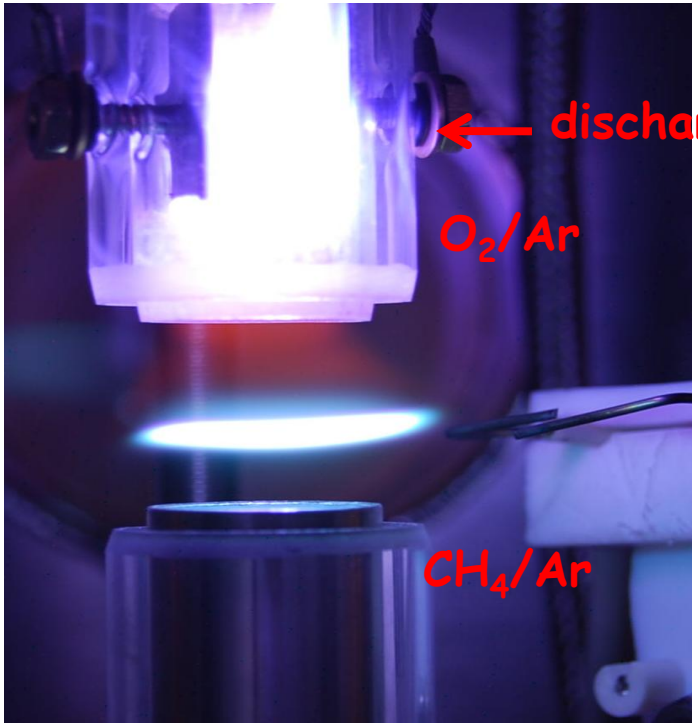


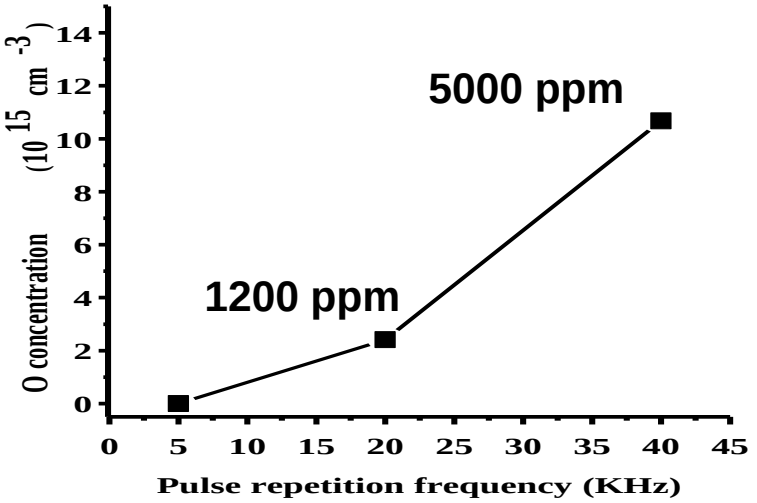
Ombrello, et al, CNF, 2010

Energy Coupling Into Flow

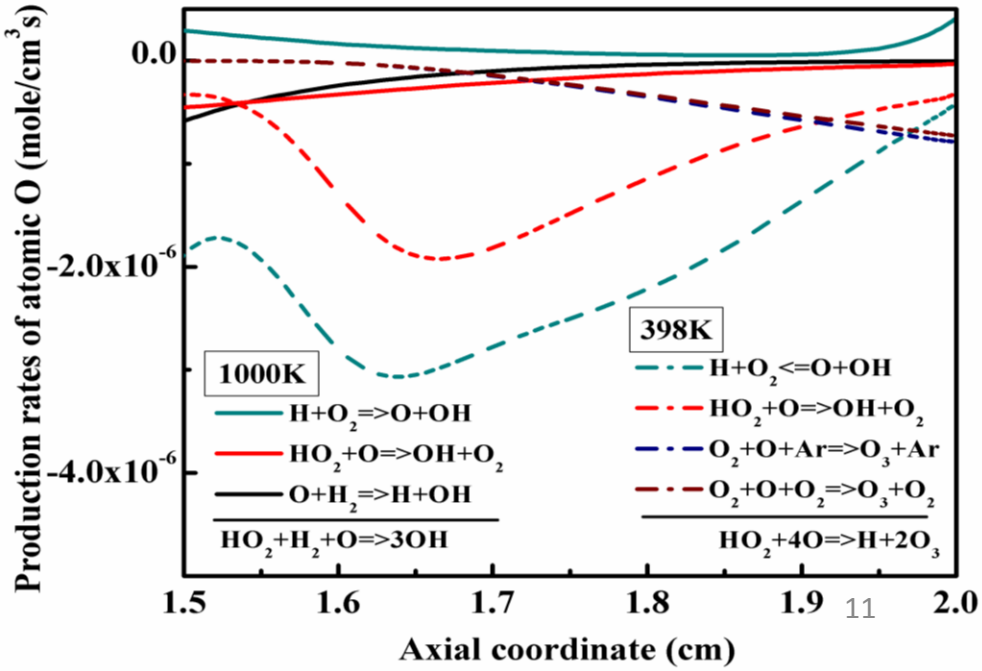
≈ 1 eV to produce $O_2(a^1\Delta_g)$

Previous researches – Atomic oxygen effect





Crossover T: 900 K



O quenched even at 60 Torr:
How to utilize radicals efficiently?

Sun, et al, PCI, 2010

Research focus in the second year

Thrust 1. Kinetic effects of non-equilibrium plasma-assisted fuel oxidation on diffusion flame extinction limits

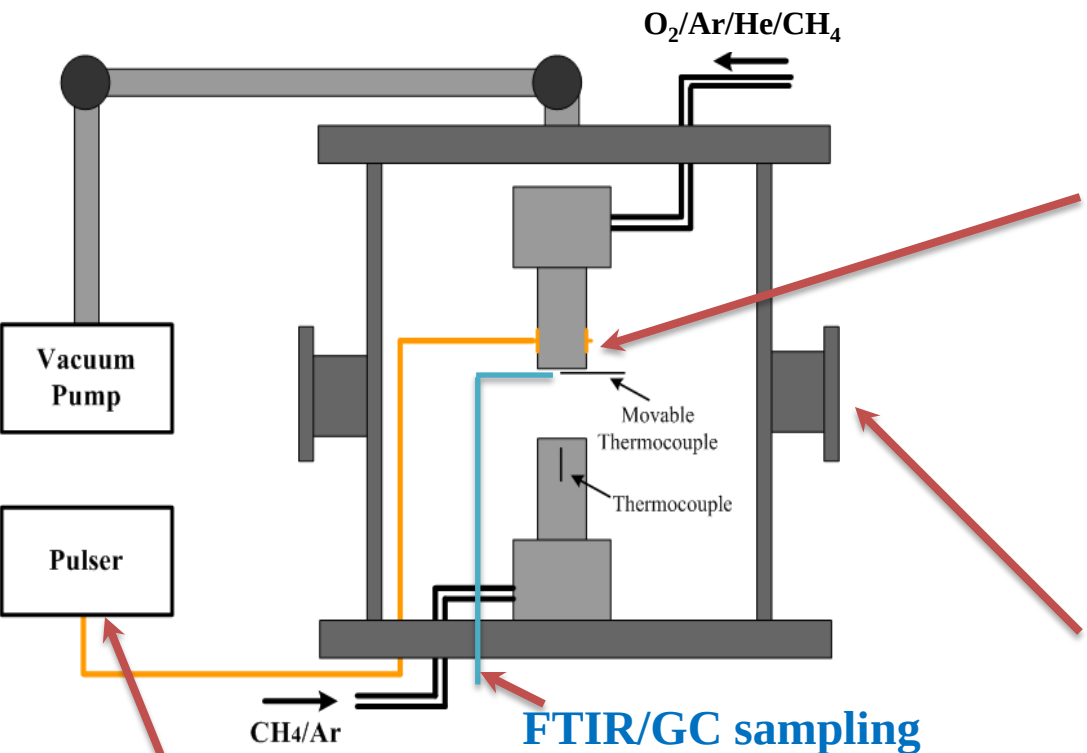
Thrust 2. Direct ignition and the S-curve transition by *in situ* nano-second pulsed discharge

Thrust 3. Plasma flame chemistry study in a flow reactor with Molecular Beam sampling Mass Spectrum (MBMS)

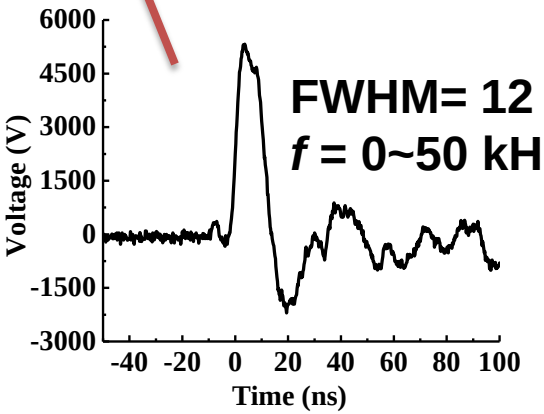
Thrust 4. Development of a plasma assisted jet stirred reactor with molecular beam sampling and a high pressure ignition chamber

Thrust 1. Kinetic effects of non-equilibrium plasma-assisted fuel oxidation on diffusion flame extinction limits

Experimental setup



FTIR/GC sampling (heated)

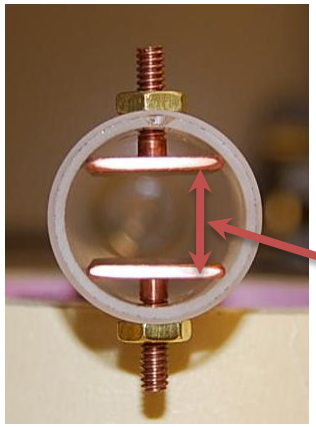


FWHM= 12 ns
***f* = 0~50 kHz**

E/N~10^{-15} Vcm^2

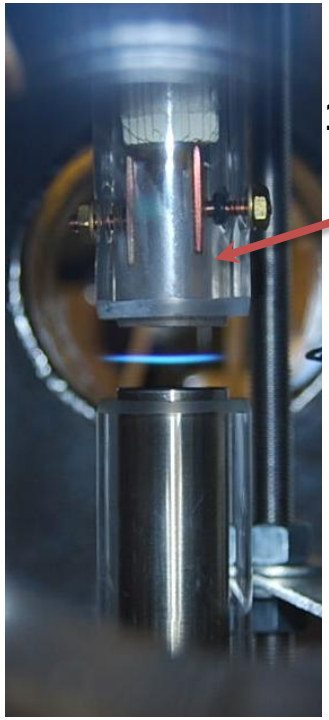
Power~1.3 mJ/Pulse

P= 60 Torr



15 mm × 22 mm

10 mm



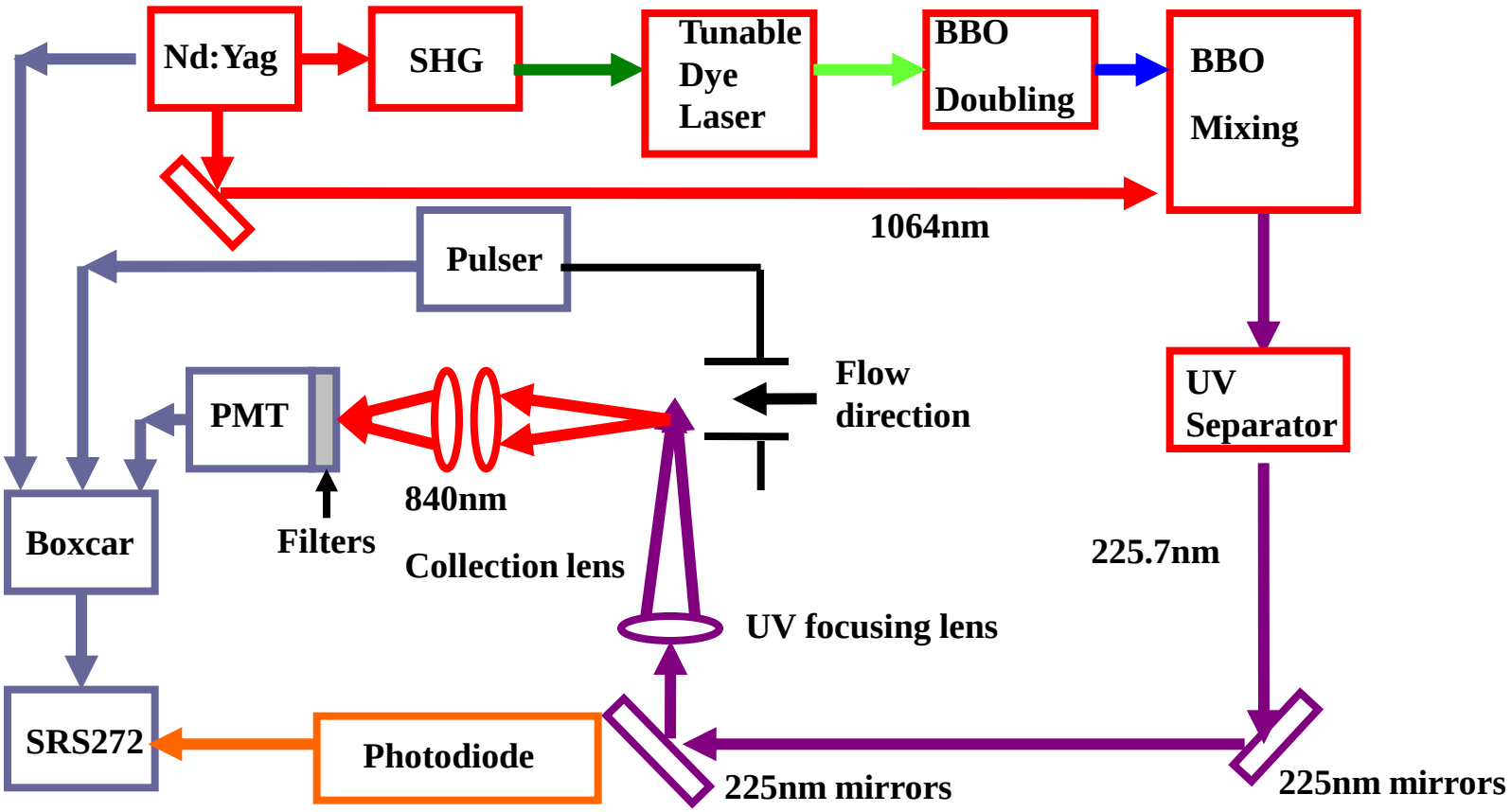
10 mm away from exit

20 & 28 mm ID

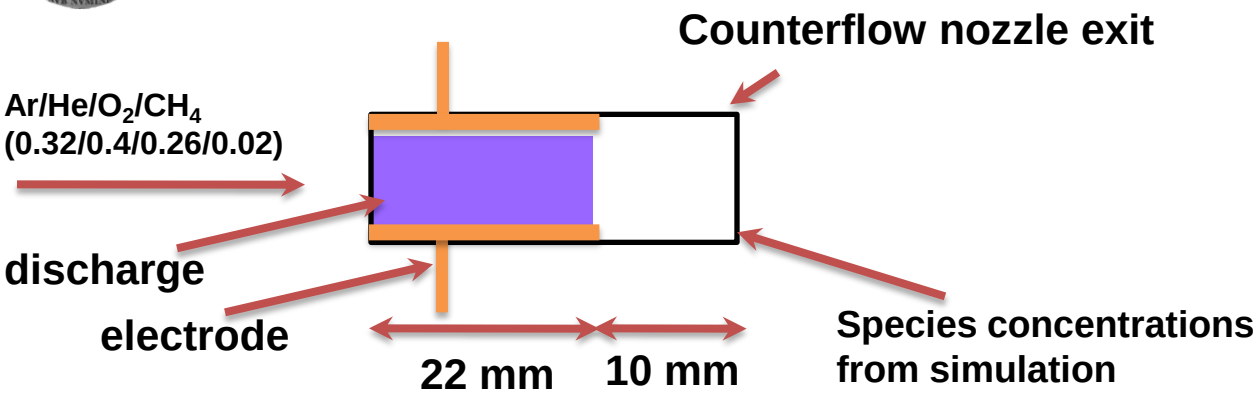
$$a_o = \frac{2U_o}{L}\left(1+\frac{U_f\sqrt{\rho_f}}{U_o\sqrt{\rho_o}}\right)$$

The thermocouple was coated with MgO and covered with grounded Nickel-Chrome sheath to remove EMI

Laser diagnostics schematic



Numerical model



Kinetic model: OSU air plasma model [1,2] with USC mech II in addition of Ar/He/CH_4 related reactions.

Physical model: quasi-one –dimensional flow equation + steady two-term expansion Boltzmann equation [1]

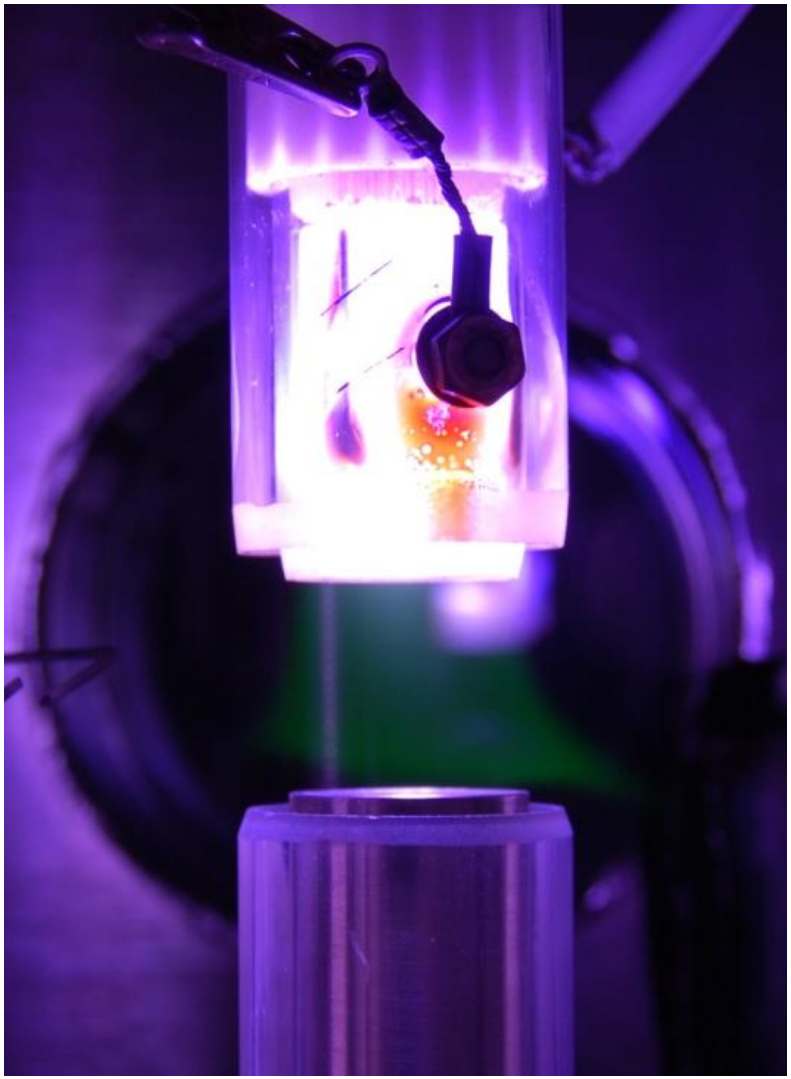
Reactions [1-8]	Rate Const (cm^3s^{-1})
$e + O_2 \rightarrow e + 2O$	$f(E/N)$
$e + O_2 \rightarrow e + O + O(D)$	$f(E/N)$
$e + CH_4 \rightarrow CH_3 + H + e$	$f(E/N)$
$e + Ar \rightarrow Ar^* + e$	$f(E/N)$
$e + Ar \rightarrow Ar(+) + 2e$	$f(E/N)$
$e + He \rightarrow He^* + e$	$f(E/N)$
$e + He \rightarrow He(+) + 2e$	$f(E/N)$
$Ar^* + CH_4 \rightarrow Ar + CH_2 + 2H$	3.3×10^{-10}
$Ar^* + CH_4 \rightarrow Ar + CH + H_2 + H$	5.8×10^{-10}

Reactions	Rate Const (cm^3s^{-1})
$Ar(+) + CH_4 \rightarrow Ar + CH_3(+) + H$	6.5×10^{-10}
$Ar(+) + CH_4 \rightarrow Ar + CH_2(+) + H_2$	1.4×10^{-10}
$Ar^* + CH_4 \rightarrow Ar + CH_3 + H$	5.8×10^{-10}
$Ar^* + CH_4 \rightarrow Ar + CH_2 + H_2$	5.8×10^{-10}
$He(+) + O_2 \rightarrow O(+) + O + He$	$0.6\times10^{-11}T^{0.5}$
$Ar^* + O_2 \rightarrow Ar + 2O$	2×10^{-10}
$He(+) + O_2(a) \rightarrow O(+) + O + He$	$0.6\times10^{-11}T^{0.5}$
$He + 2O \rightarrow He^* + O_2$	1×10^{-33}
$He^* + CH_4 \rightarrow CH + H_2 + H + He$	5.6×10^{-13}

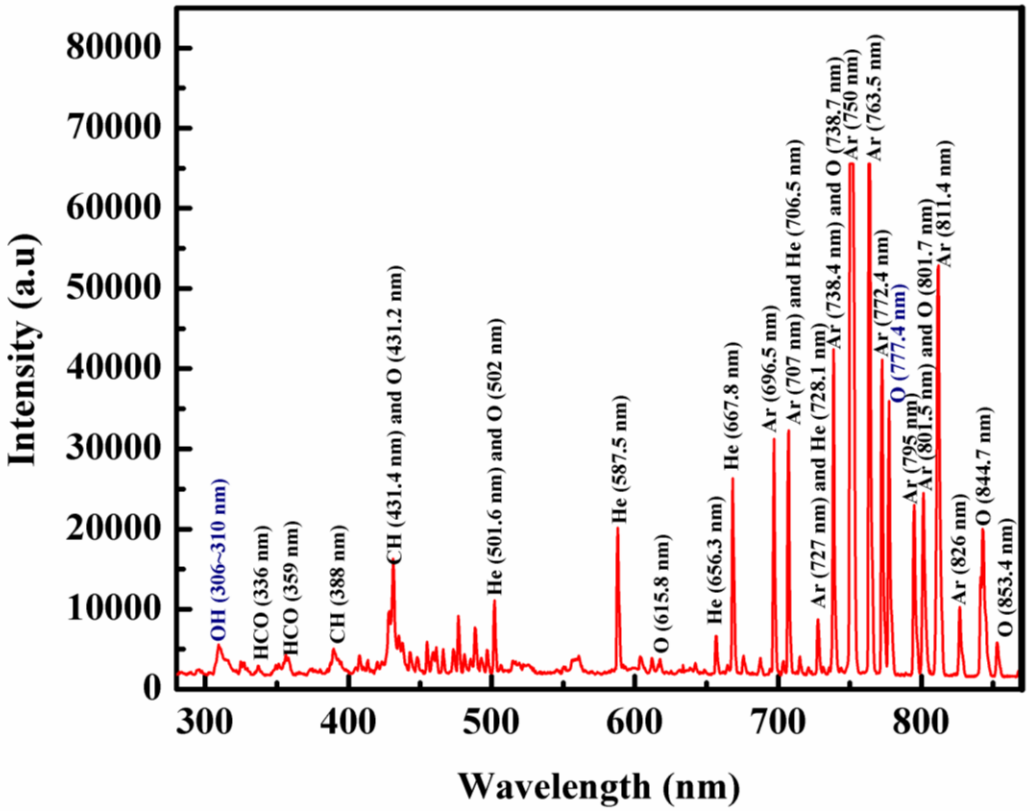
Reference:
[1]. A. Bao, Ph.D thesis (2008) OSU **[2].** M. Uddi et al, PCI 32(2009) 929 **[3].** I.N. Kosarov et al, C&F 156(2009) 221 **[4].** A. Hicks et al, JPD, 38(2005) 3812 **[5].** D.S. Stafford et al, JAP, 96(2004) 2451 **[6].** M. Tsuji et al, JCP, 94(1991) 277 **[7].** A.M. Starik et al, C&F, 157(2010) 313 **[8].** I.N. Kosarev et al, C&F 154(2008) 569

Experimental observations of discharges

O_2(0.26)/Ar(0.32)/He(0.4)/CH_4(0.02)



f=30 kHz

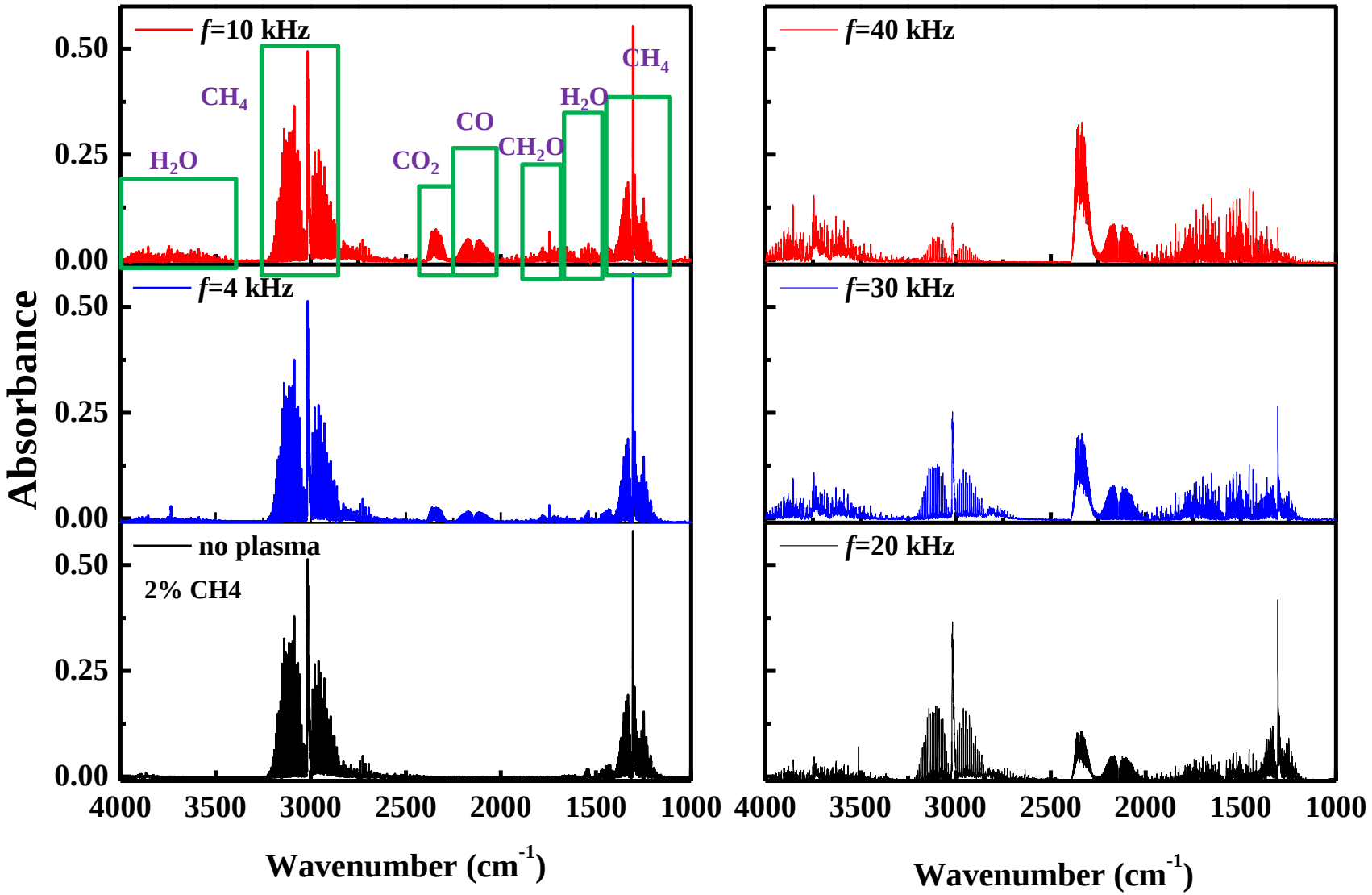


Strongest emission: Ar*, O*

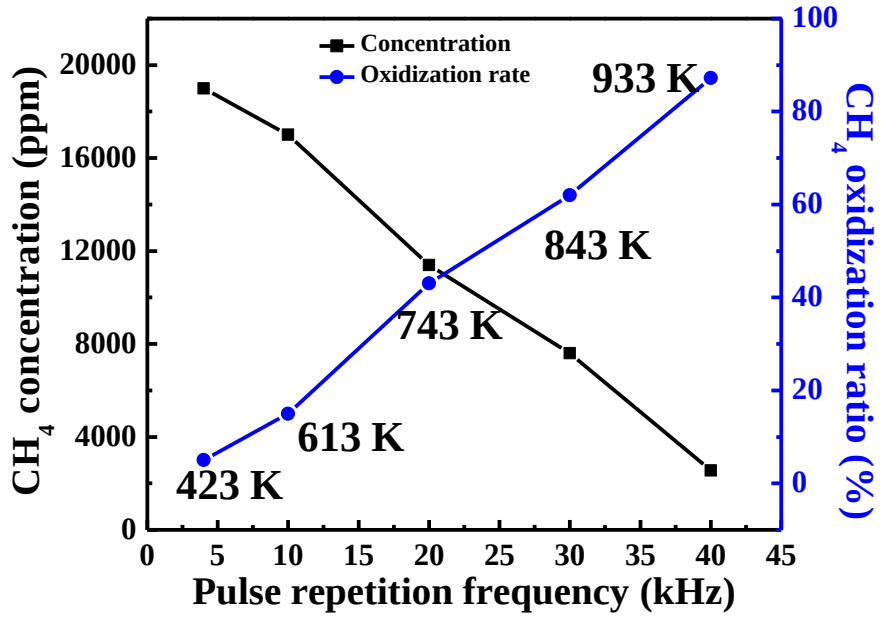
Emissions: He*, OH*, HCO*, and CH*

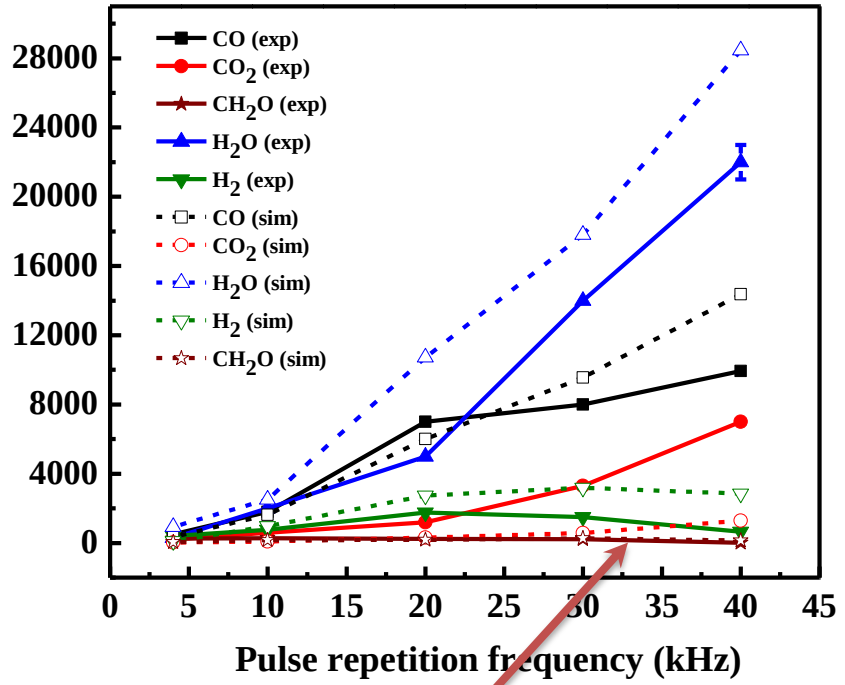
Discharge repetition effect on species concentrations

FTIR spectrum with different pulse frequency

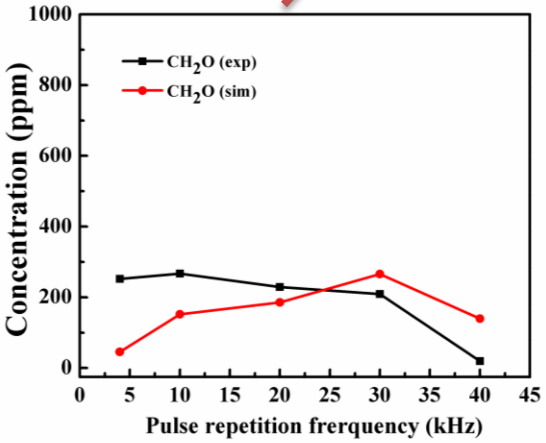


Discharge repetition effect on species concentrations



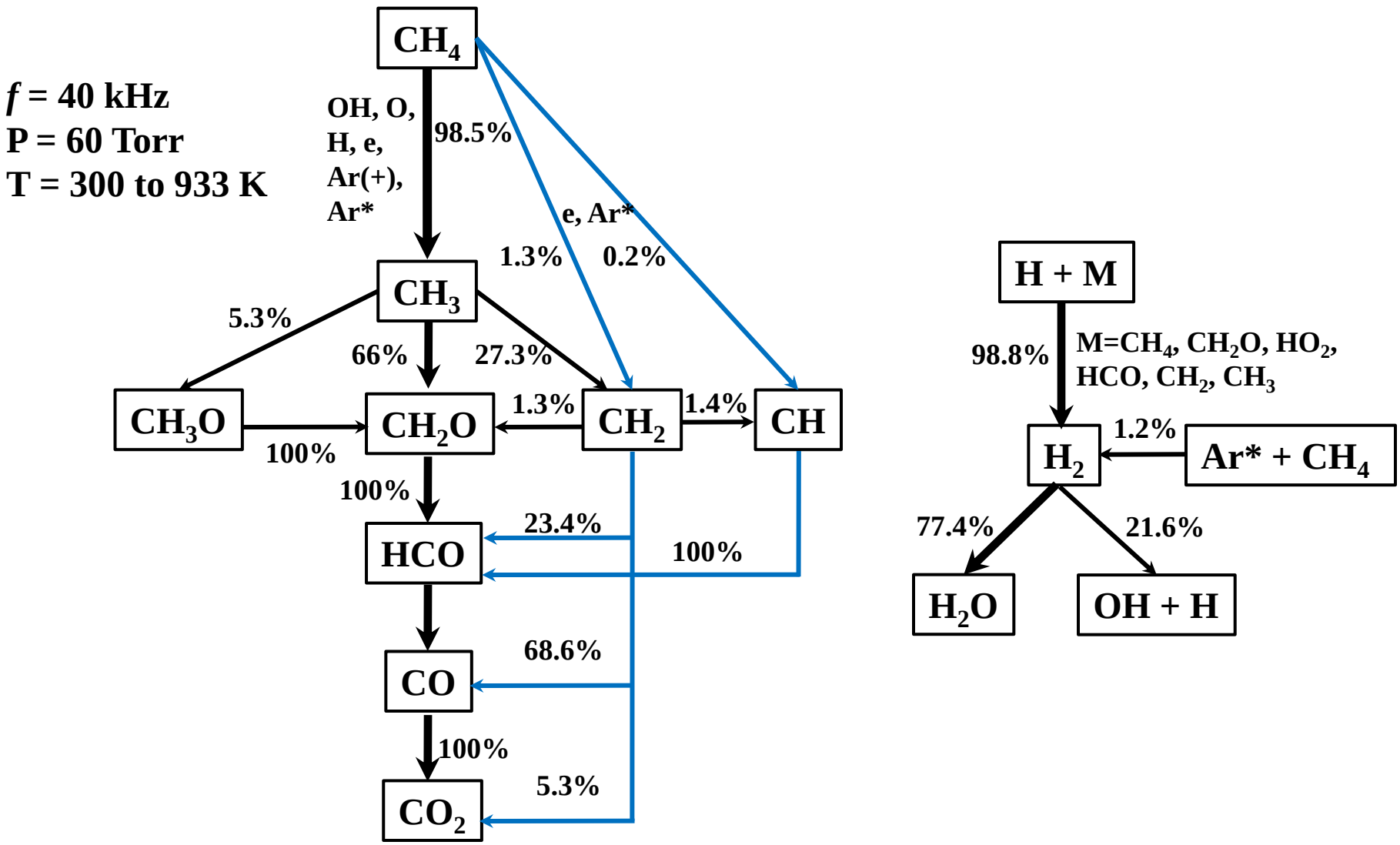


Under prediction: CO_2
Over prediction: CO, H_2, H_2O

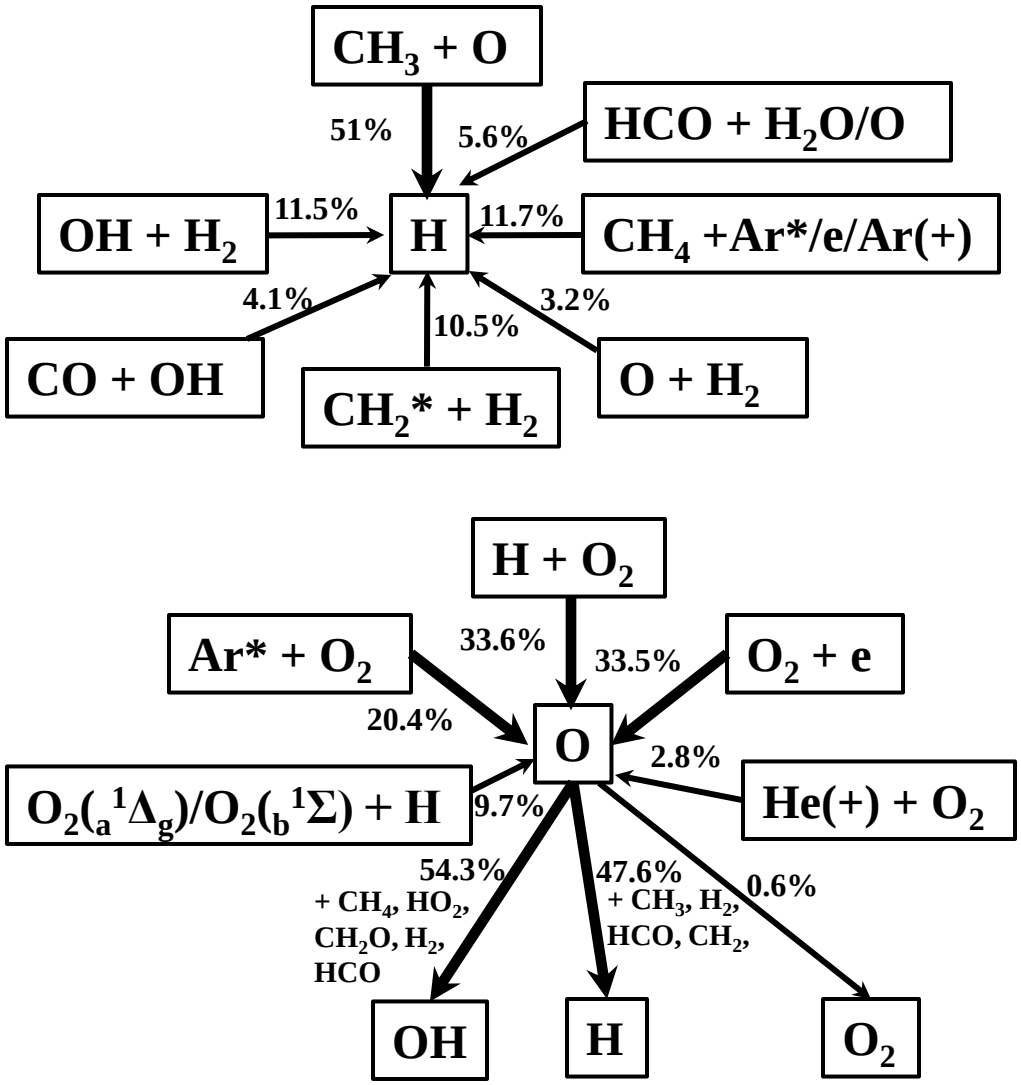


Carbon deficiency: 5%
Relative uncertainties:
<1% for CH_4, CO, CO_2
5% for H_2O and H_2
The uncertainty of CH_2O measurement is 80 ppm

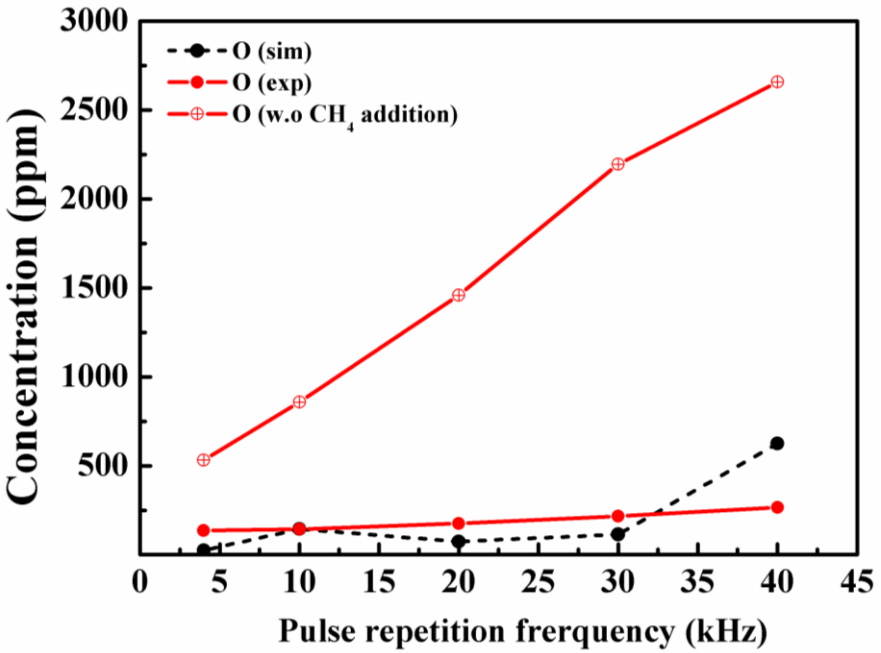
Reaction path analysis-CH_4&H_2



Reaction path analysis-H&O



f = 40 kHz
P = 60 Torr
T = 300 to 933 K

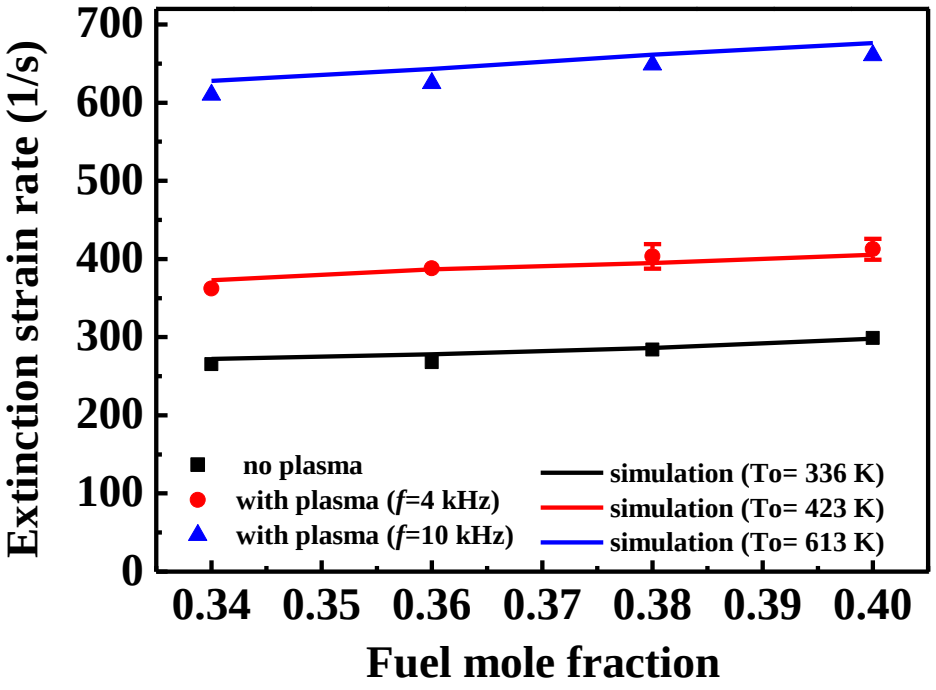


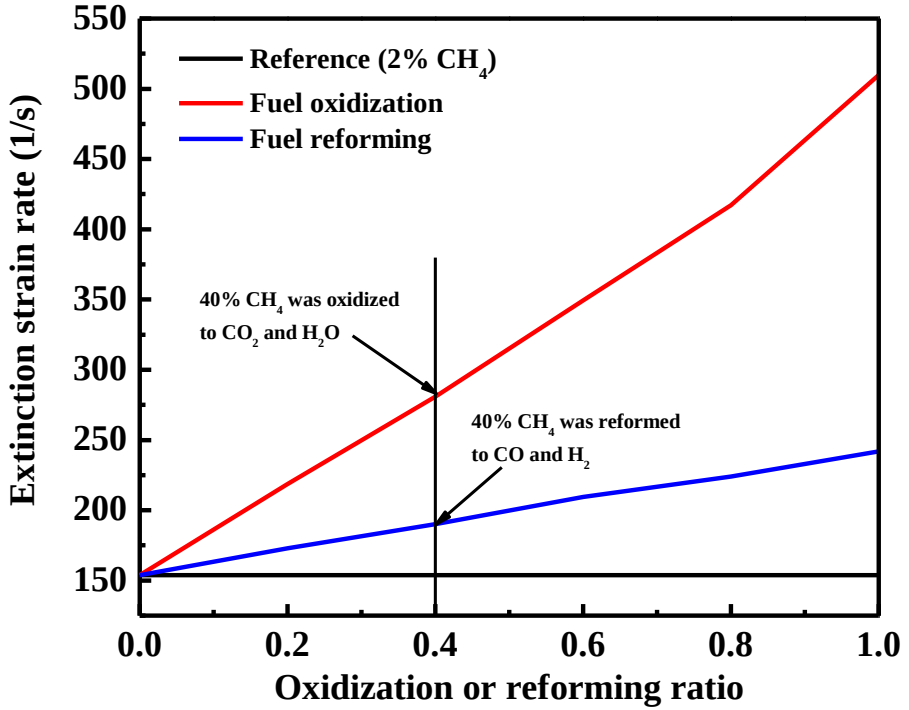
Mechanism was not validated below 700 K
Large uncertainty at low temperature

the reaction rate at 300 K for
$O(^1D) + H_2 = H + OH$ (4.4×10^{10} /cm^{3}s)
is much larger than
$O + H_2 = H + OH$ (2.6×10^{3} /cm^{3}s).

Extinction limit measurement & calculation

Faster fuel oxidization, larger extinction extension





Simulations were performed with experimentally measured boundary conditions.

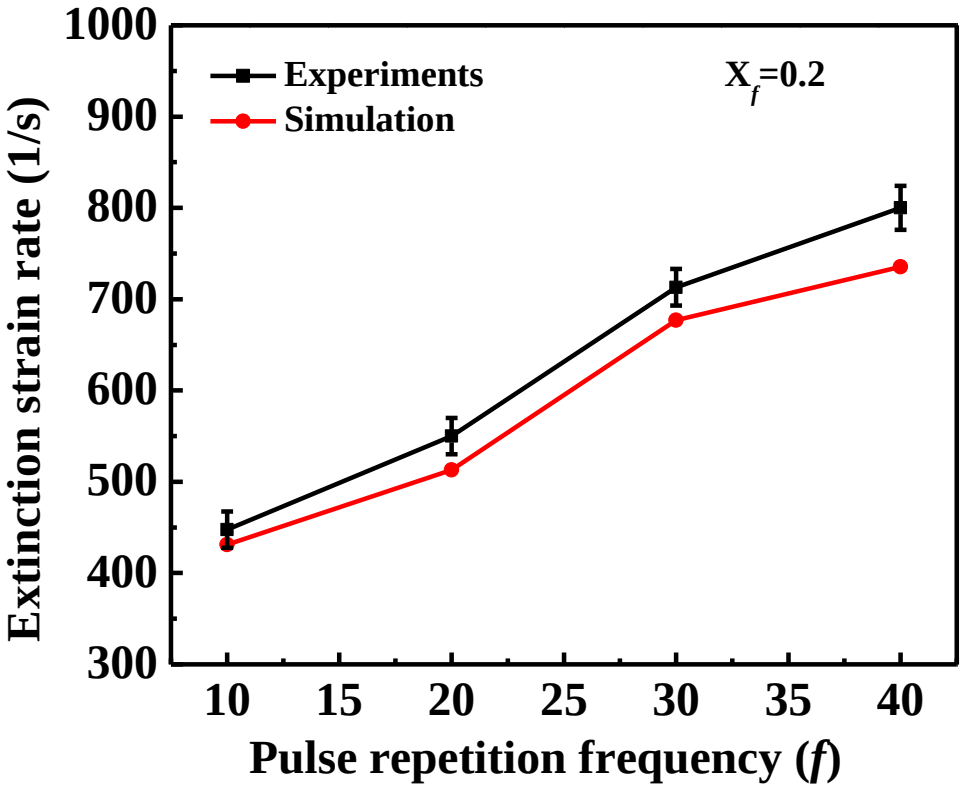
OH, H concentrations were estimated from simulation by matching O concentrations.

Case 1: fuel was oxidized to CO_2 & H_2O
Case 2: fuel was reformed to CO & H_2

Fuel reforming enhancement: fast H_2 chemistry
Fuel oxidization enhancement: extracting chemical enthalpy rapidly

Extinction limit measurement & calculation

CH_4 oxidization ratio (or *f*) increased, extinction limits increased significantly



5.3% enhancement from H_2

The dominant enhancement mechanism is plasma introduced rapid fuel oxidization.

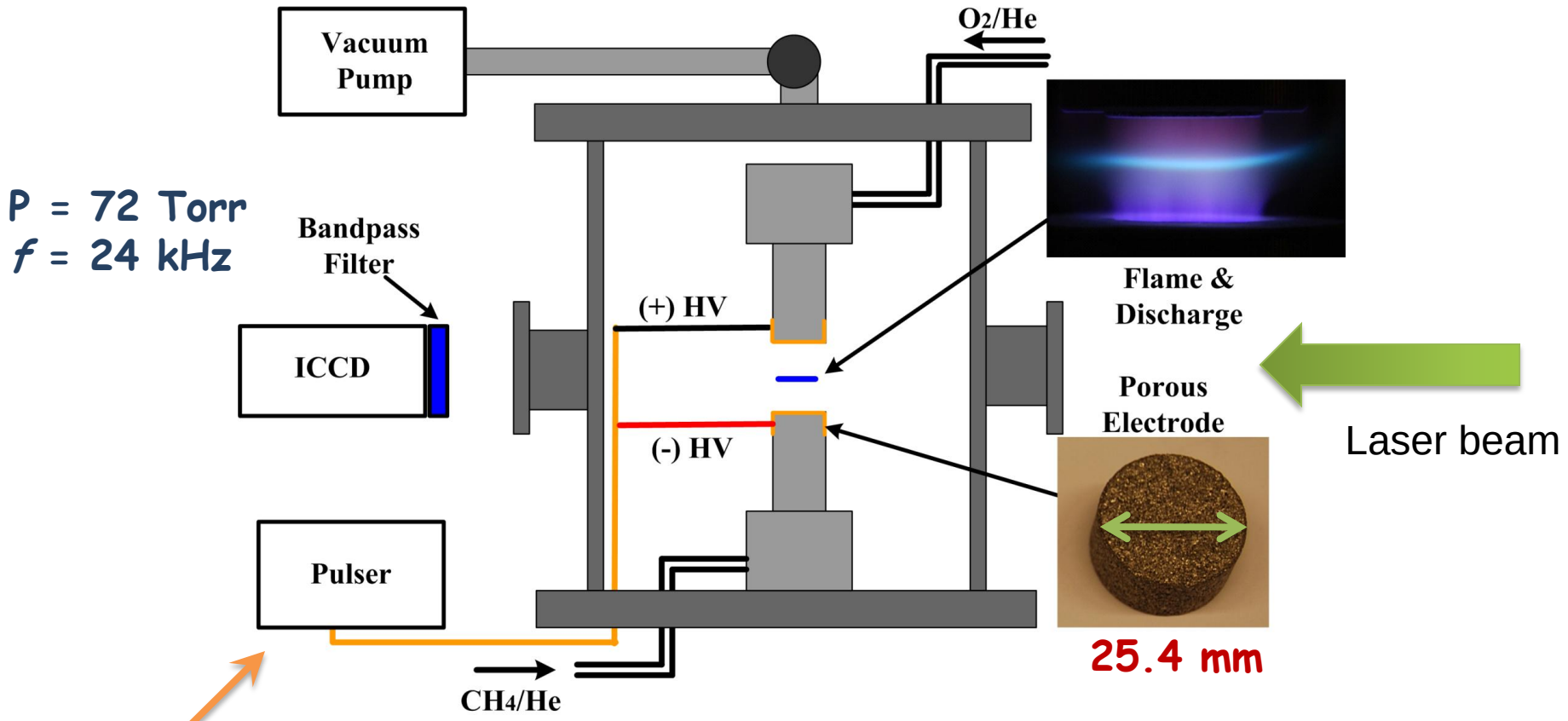
Deviation is due to additional reaction paths, but not significant (10%).

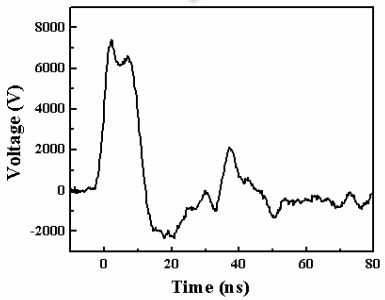
Simulations were performed with experimentally measured boundary conditions.

OH, H concentrations were estimated from simulation by matching O concentrations.

Thrust 2. Direct ignition and the S-curve transition by *in situ* nano-second pulsed discharge

Experimental setup

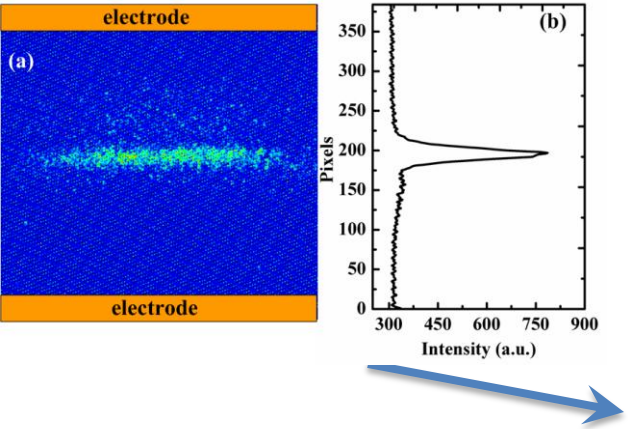


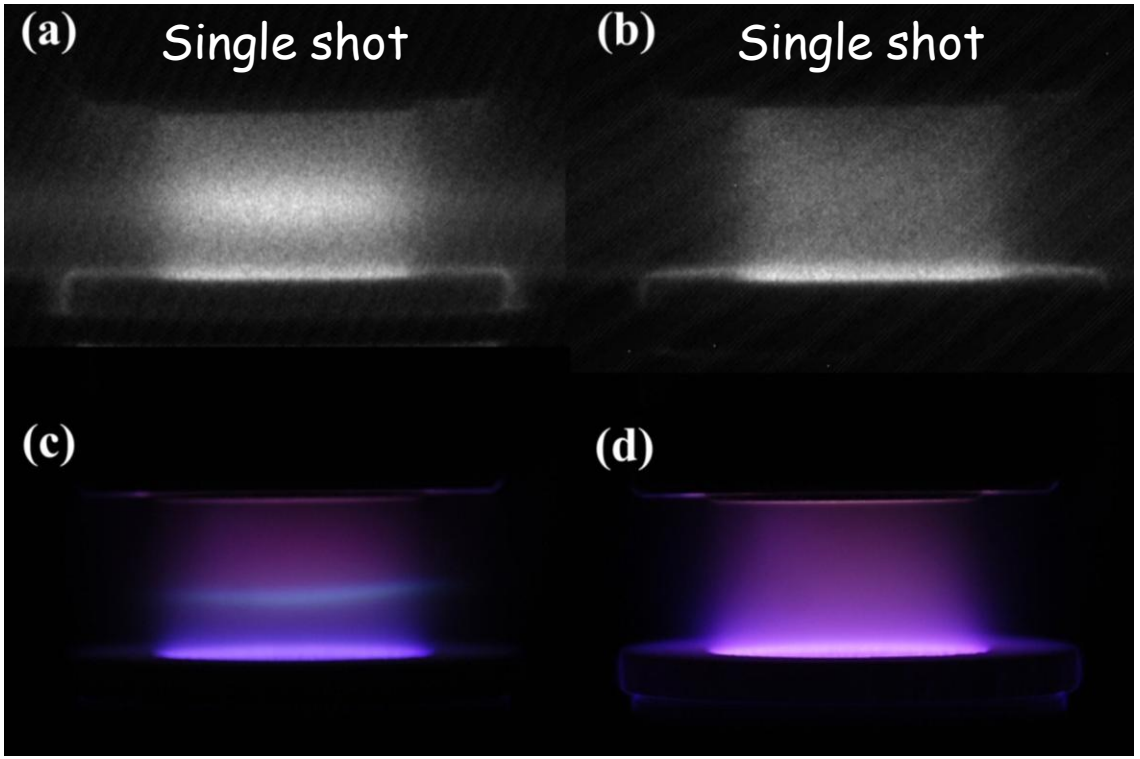


Power ~ 17 W

ICCD images

OH* emission ~310 nm
30 μs gate

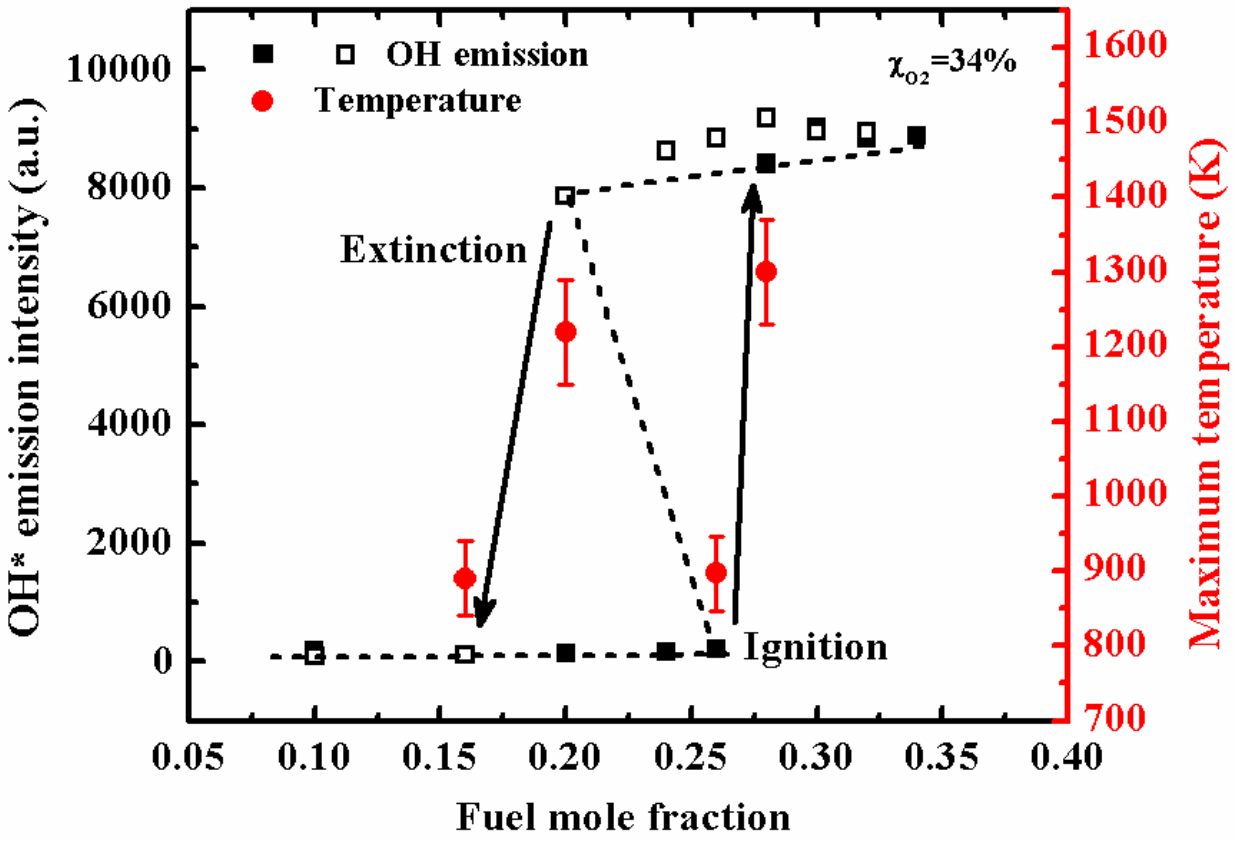




(a) ICCD image, He/O_2 (0.6:0.4) and He/CH_4 (0.75:0.25), 50 ns gate
(b) ICCD image, He/O_2 (0.6:0.4) and He/CH_4 (0.86:0.14), 50 ns gate
(c) direct photo of (a), 50 ms exposure time
(d) direct photo of (b), 50 ms exposure time
P = 72 Torr, *f* = 24 kHz, a = 175 1/s

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

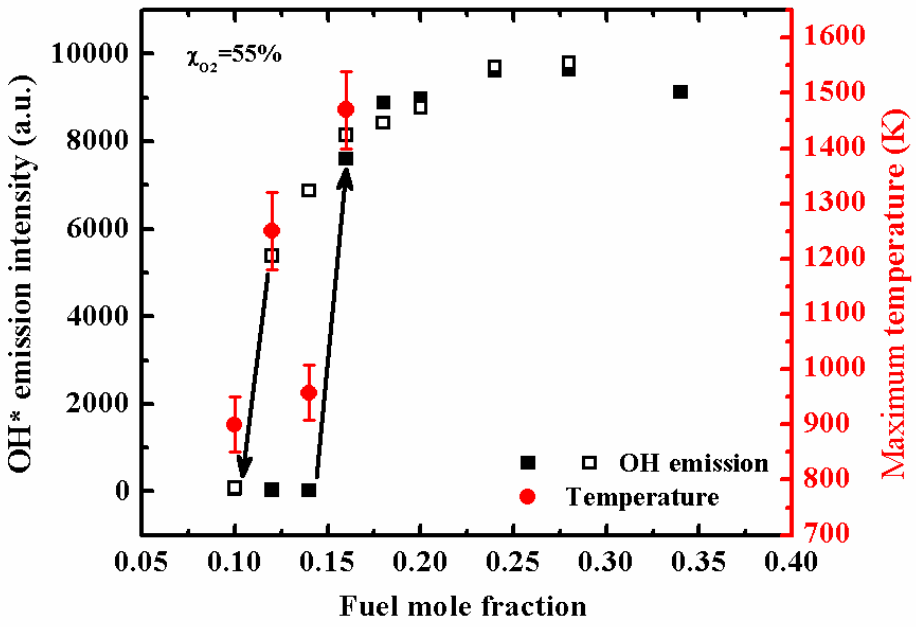
Relationship between OH* emission intensity, local maximum temperature and fuel mole fraction, T_o=650 K, T_f=600 K He/O_2 = 0.66:0.34 , P = 72 Torr, *f* = 24 kHz, a = 400 1/s

[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

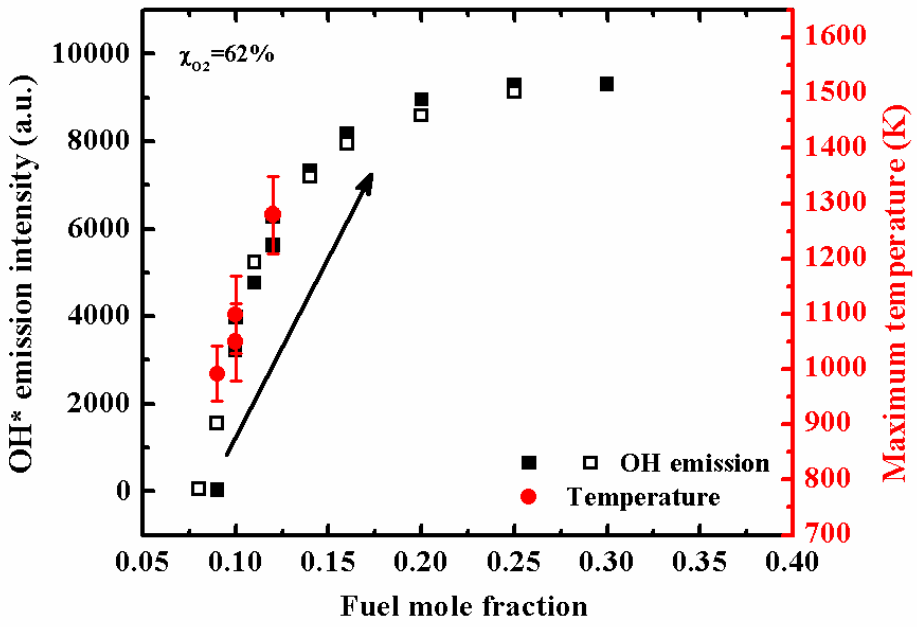
Relationship between OH* emission intensity, local maximum temperature and fuel mole fraction, P = 72 Torr, f = 24 kHz, a = 400 1/s

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)

Numerical modeling

OPPDIF + electron impact
Kinetic mechanism: USC mech II + OSU air plasma model[1]

e + O_2 reactions	Rate (cm^3s^{-1})
e + O_2 → 2O + e	f(E/N)
e + O_2 → O + O(D) + e	f(E/N)
e + O_2 → O_2(+) + 2e	f(E/N)
e + O_2 → O_2(a) + e	f(E/N)

e + CH_4 reactions	Rate (cm^3s^{-1})
e + CH_4 → CH_3 + H + e	f(E/N)
e + CH_4 → CH_2 + H_2 + e	f(E/N)
e + CH_4 → CH_4(+) + 2e	f(E/N)

He related reactions	Rate (cm^3s^{-1})
He + e → He* +e	f(E/N)
He + e → He(+) + 2e	f(E/N)
He* + O_2 → O_2(+) + He + e	$1.5\times10^{-11}T^{0.5}$
He(+) +O_2 → O(+) + O + He	$0.6\times10^{-11}T^{0.5}$
He* + CH_4 → CH + H_2 + H+ He	5.6×10^{-13}

Recombination reactions	Rate (cm^3s^{-1})
e + O_2(+) → 2O	$5.6\times10^{-6}T^{-0.5}$
He(+) + e + M→ He + M	1.4×10^{-8}
e + O_2 + M → O_2(-) + M	$4.2\times10^{-27}T^{-1}$
e + CH_4(+) → CH_3 + H	1.0×10^{-8}

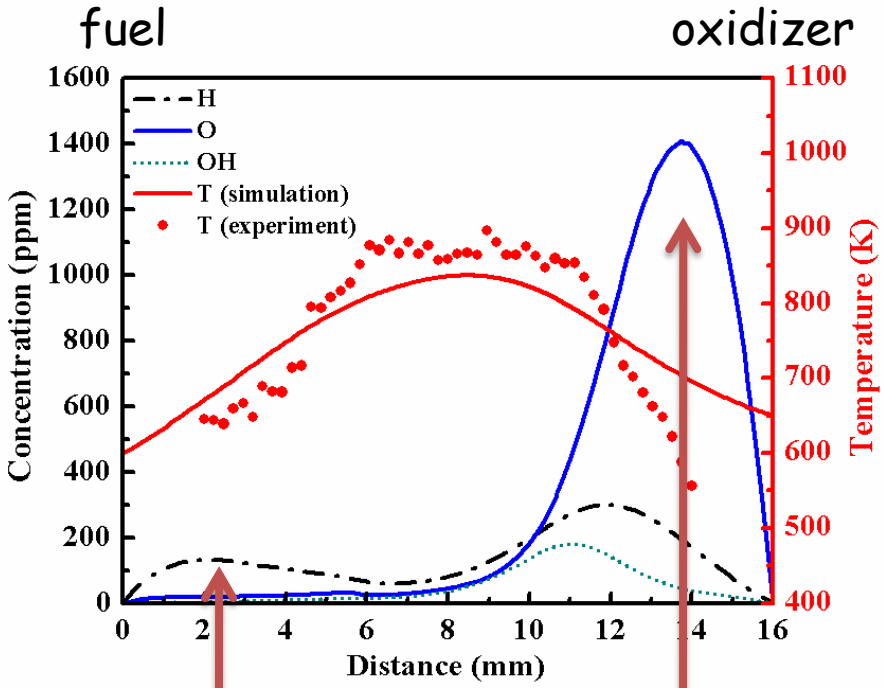
E: electric field, N: particle density

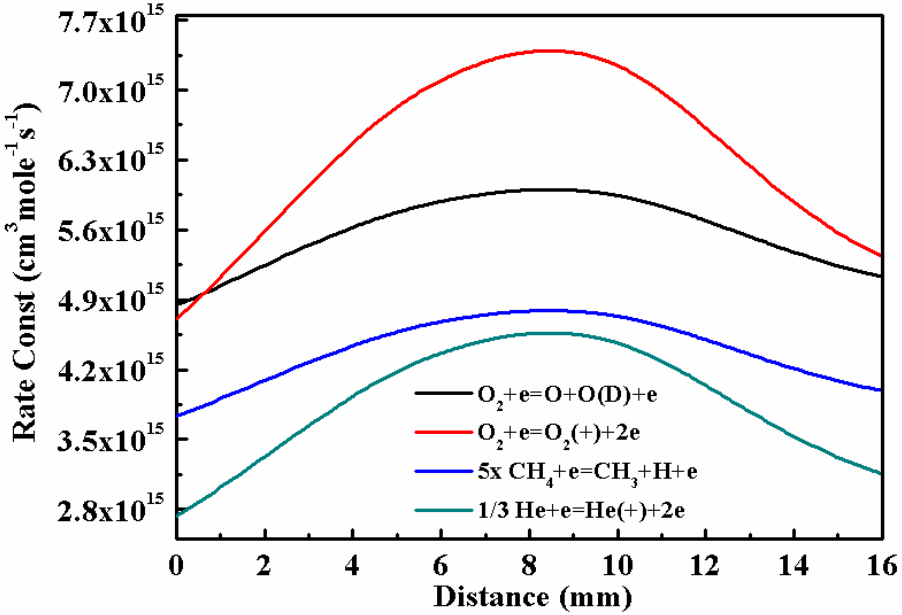
Rate constants: Boltzmann equation solver[1, 2]

[1]. A. Bao, Ph.D thesis (2008) OSU [2]. M. Uddi et al, PCI 32(2009) 929

Simulation results

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



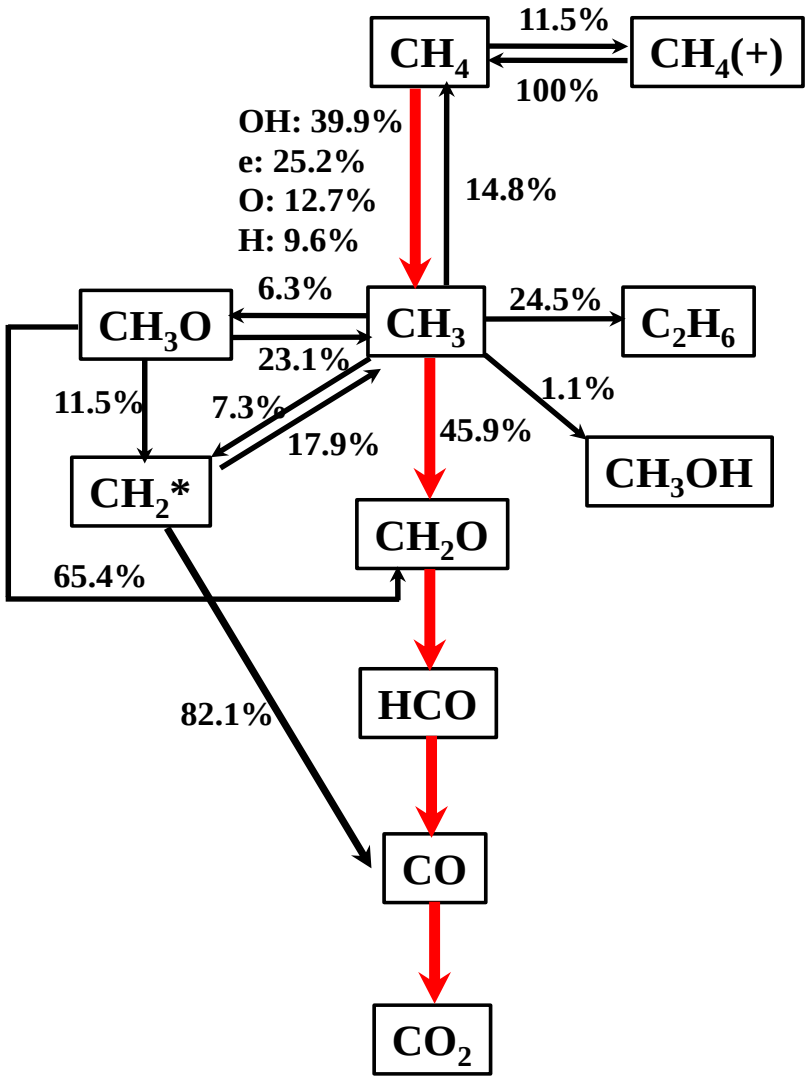


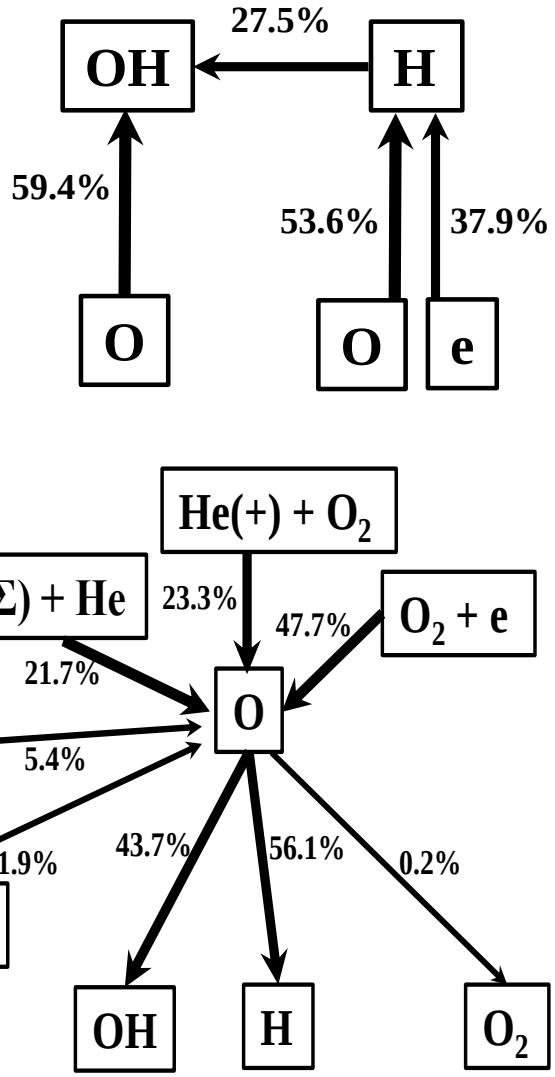
$e + CH_4 \rightarrow CH_3 + H + e$ $e + O_2 \rightarrow O+O(D) + e$

In situ discharge, increased T, increased E/N, increased rate const

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

Path flux analysis

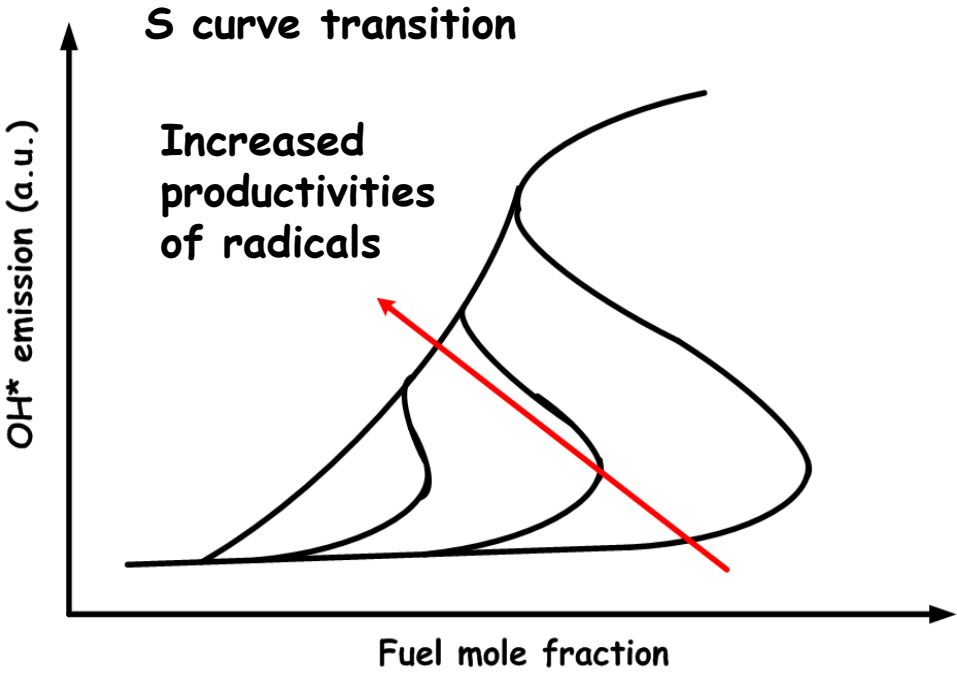




Change of branching ratio

Change of the branching ratio at the reaction zone!

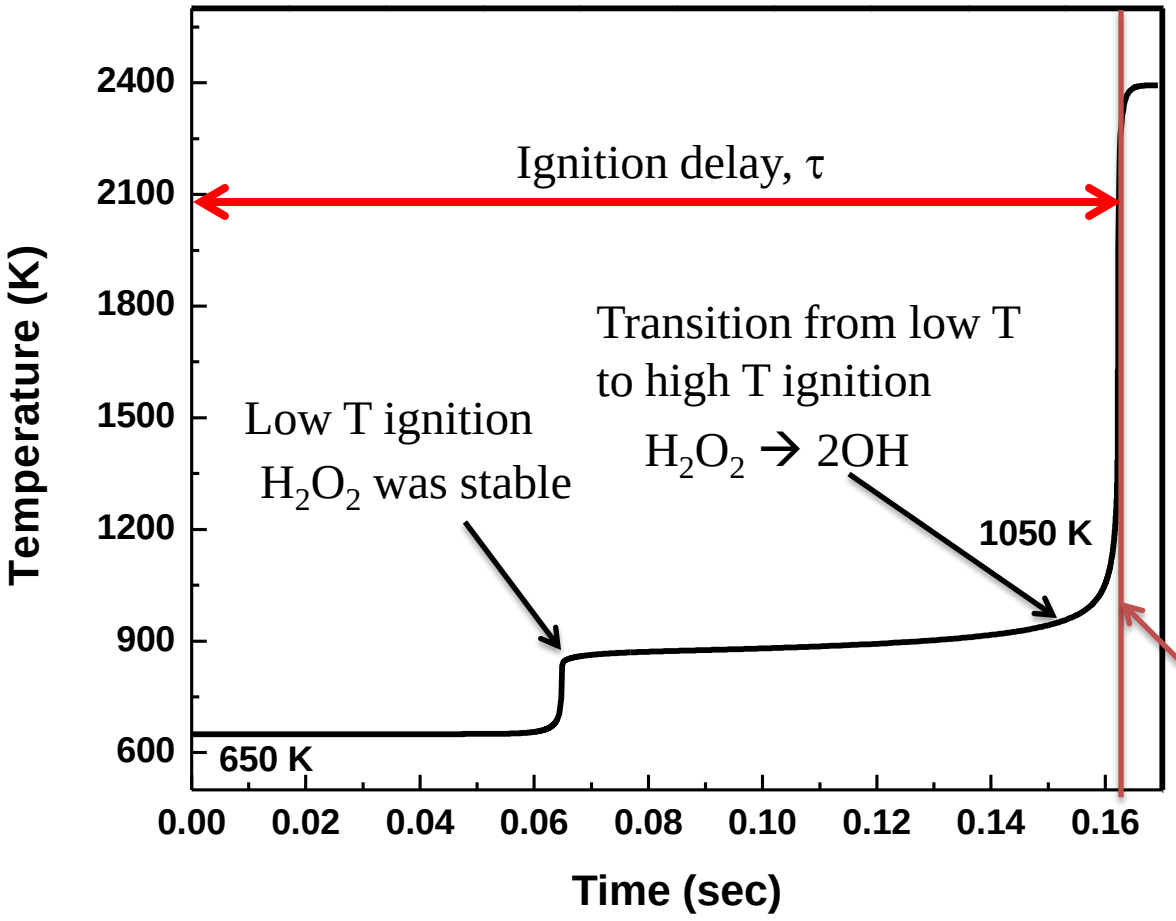
Reactions	Normalized branching ratio	
$H + O_2 = O + OH$	1	
$e + O_2 = O + O(D) + e$	0.48	
$e + O_2 = O + O(+) + e$	0.42	
$e + CH_4 = CH_3 + H + e$	0.22	**1.7**
$He(+) + O_2 = O + O(+) + He$	0.52	
$e + O_2 = 2O + e$	0.06	
$H + O_2 + M = HO_2 + M$	0.2	



76% of O production by e and ions from plasma
Radical generation initiated the reaction zone and controlled the transition!!

Thrust 3. Plasma flame chemistry study in a flow reactor with Molecular Beam sampling Mass Spectrum (MBMS)

Characteristic of low T chemistry

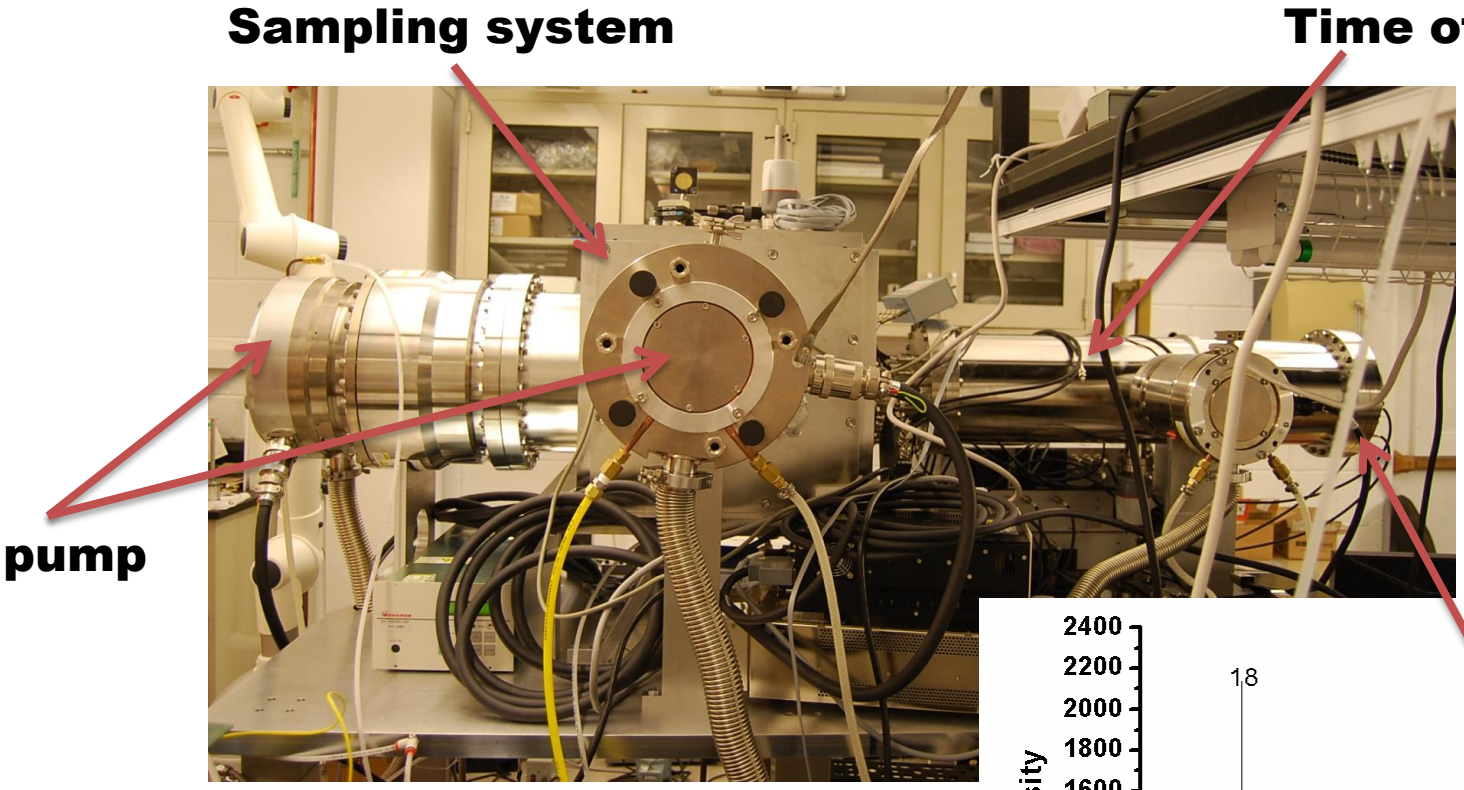


H_2O_2: low T chemistry indicator

Difficulties:
Absorption - overlap with H_2O
GC – decomposition/low reactivity

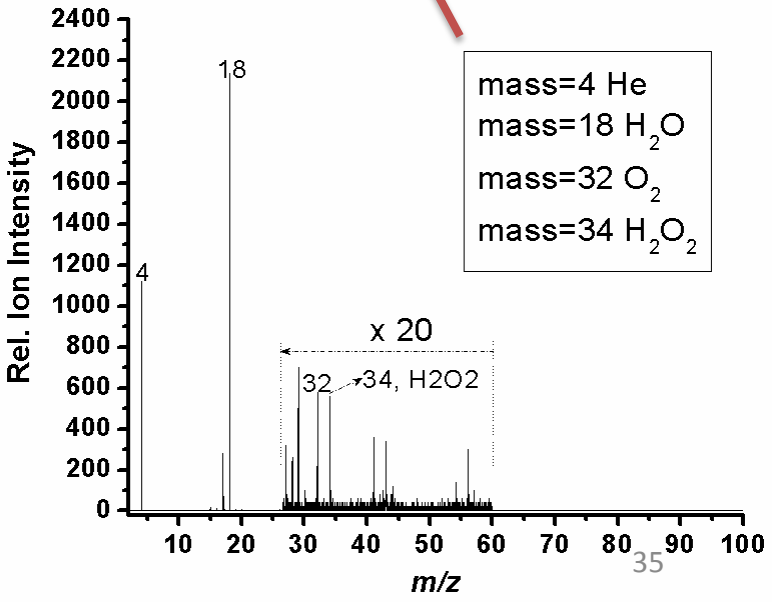
φ=1, n-heptane/air, 1 atm

Molecular Beam Mass Spectrum

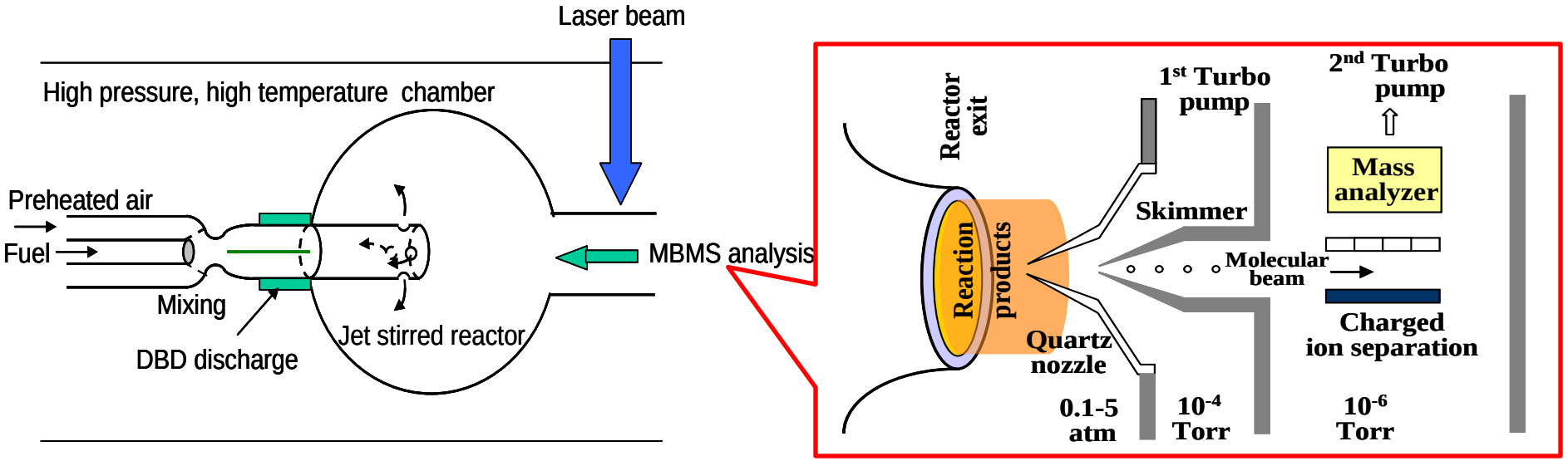


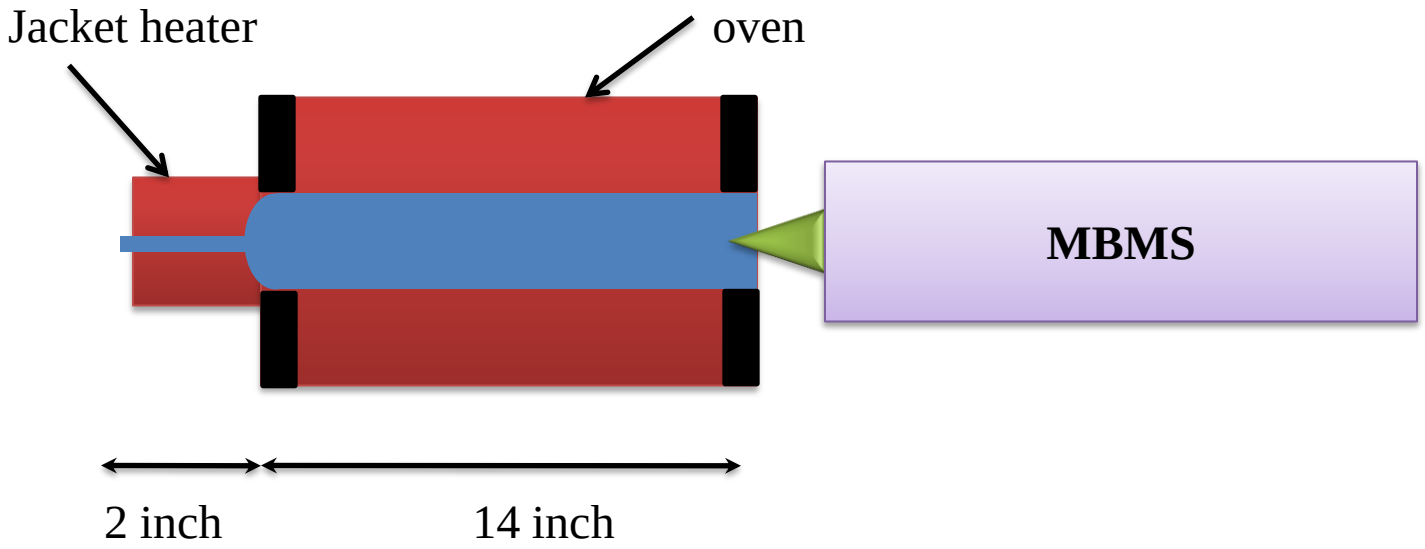
$$\frac{S_1}{S_{He}} = \frac{D_1}{D_{He}} \times \frac{\sigma_1}{\sigma_{He}} \times \frac{\chi_1}{\chi_{He}}$$

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



Schematic of experiments with MBMS

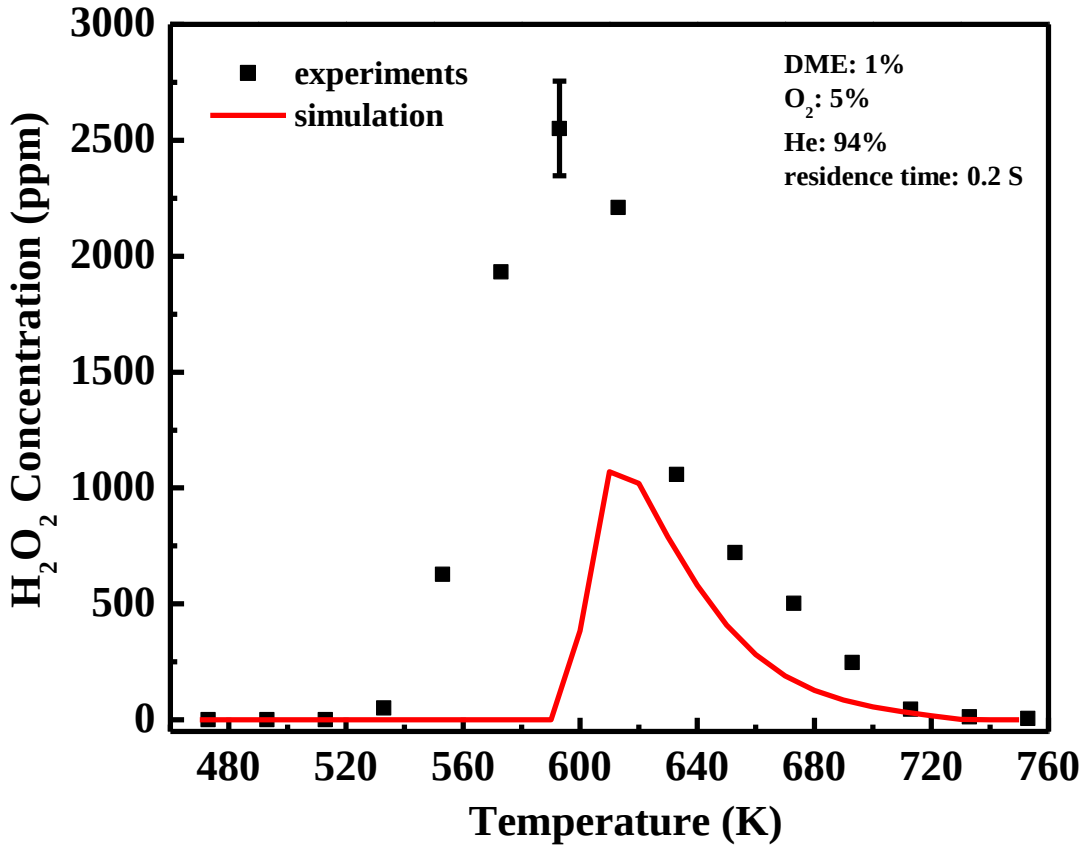




Flow tube experiments

DME: rich low temperature chemistry
Pressure: 1 atm

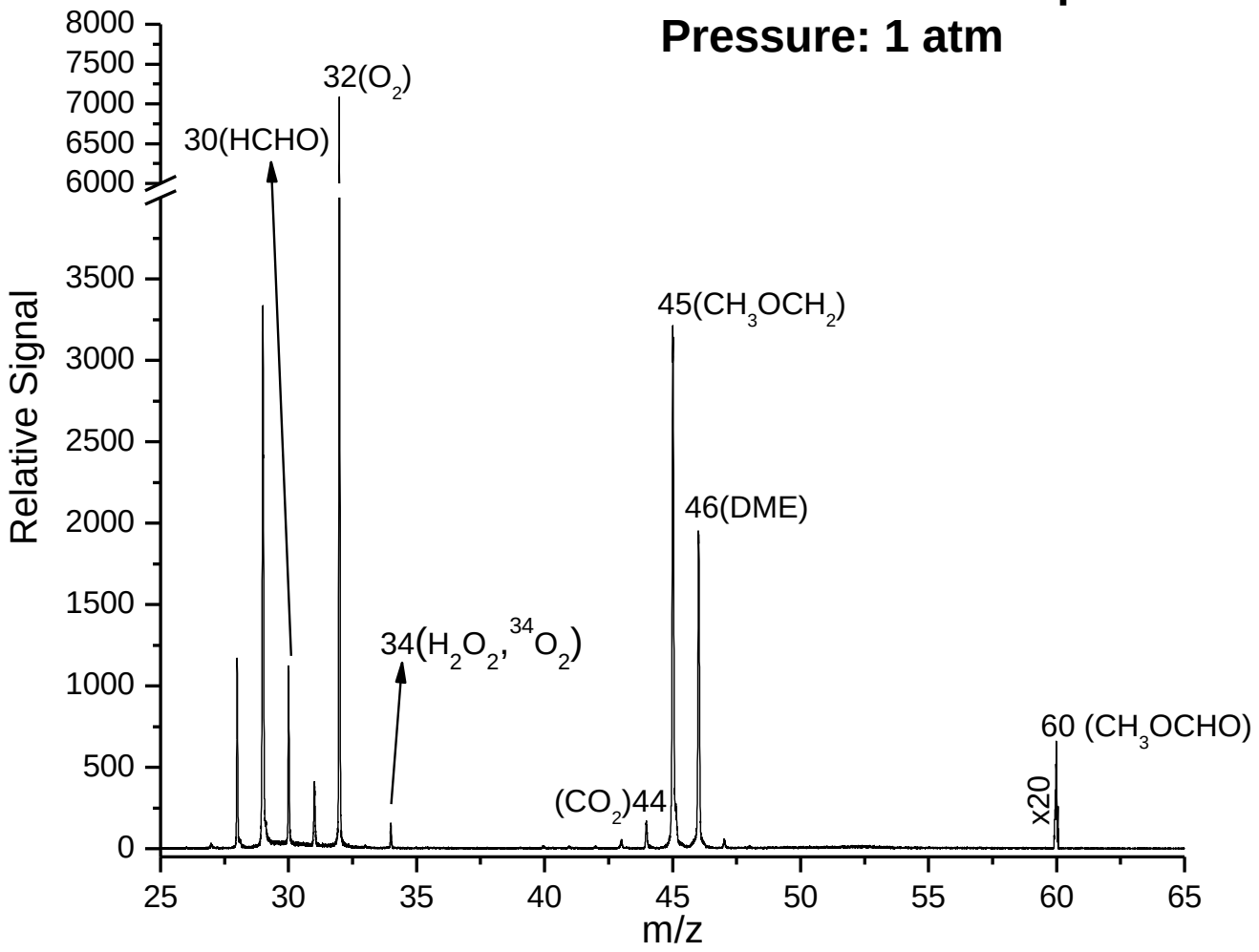
H_2O_2 measurement



DME model: Zhao et al., Int. J. Chem. Kinet., (40) 2008

Flow tube experiments

DME: rich low temperature chemistry
Pressure: 1 atm



Conclusions

1. Plasma can significantly accelerate the fuel oxidization at low temperature to extend the extinction limit dramatically.

2. Major kinetic pathways in plasma assisted combustion were identified .

3. A new counterflow burner with *in situ* discharge was developed. This burner provides a new platform to study kinetic effect of plasma assisted combustion.

4. The *In situ* discharge can maximize E/N at high T flame region, therefore, maximize the electron energy and effect on reaction zone, and enhance ignition and extinction.

5. The *In situ* discharge can dramatically enhance the ignition and modify the classical S-curve to be a monotonic curve.

6. MBMS was developed and H_2O_2 was successfully measured directly for the first time in reacting system, enabling diagnostics of intermediate species in plasma assisted combustion at low T.

Future work

Plasma part:

1. OH PLIF for counter flow diffusion flame with *in situ* discharge and compare with simulations
2. Low temperature plasma assisted combustion for large alkanes
3. Flow reactor experiments on liquid fuel with QCL diagnostics on H_2O, H_2O_2 and HO_2
4. Develop validated plasma flame models

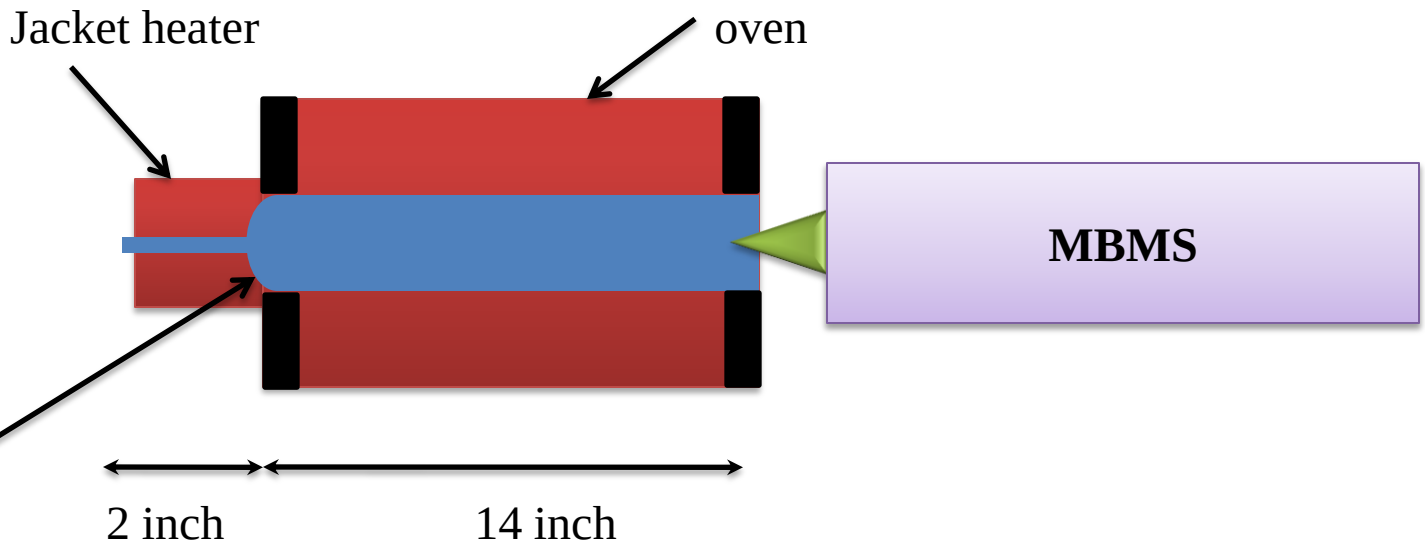
MBMS part:

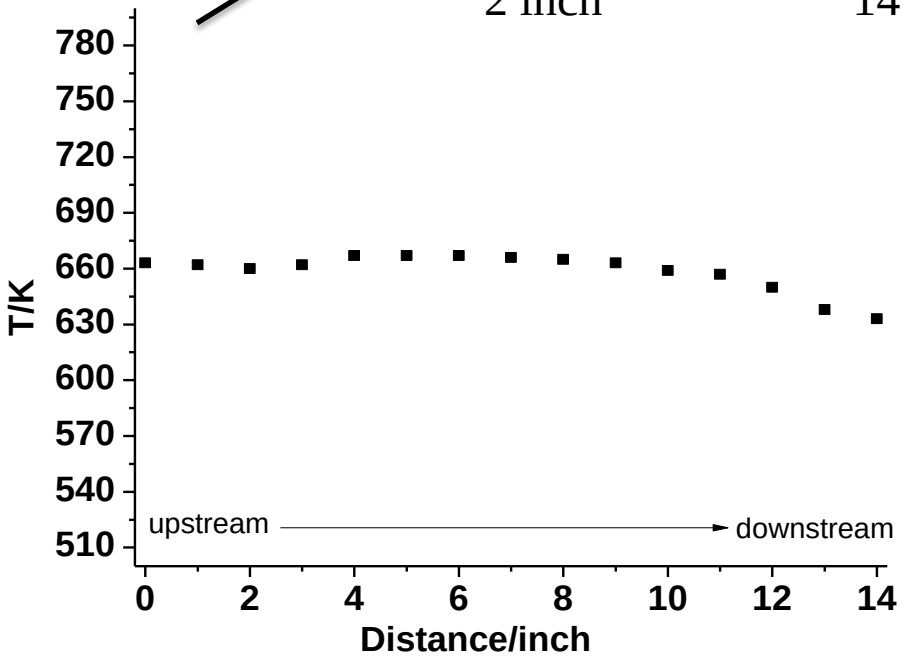
1. Develop a JSR to study the low temperature and high pressure chemistry
2. Integrate JSR with plasma discharge to investigate plasma chemistry
3. Develop advanced light source to ionize the molecular beam

Thanks the support from AFOSR!

Questions?

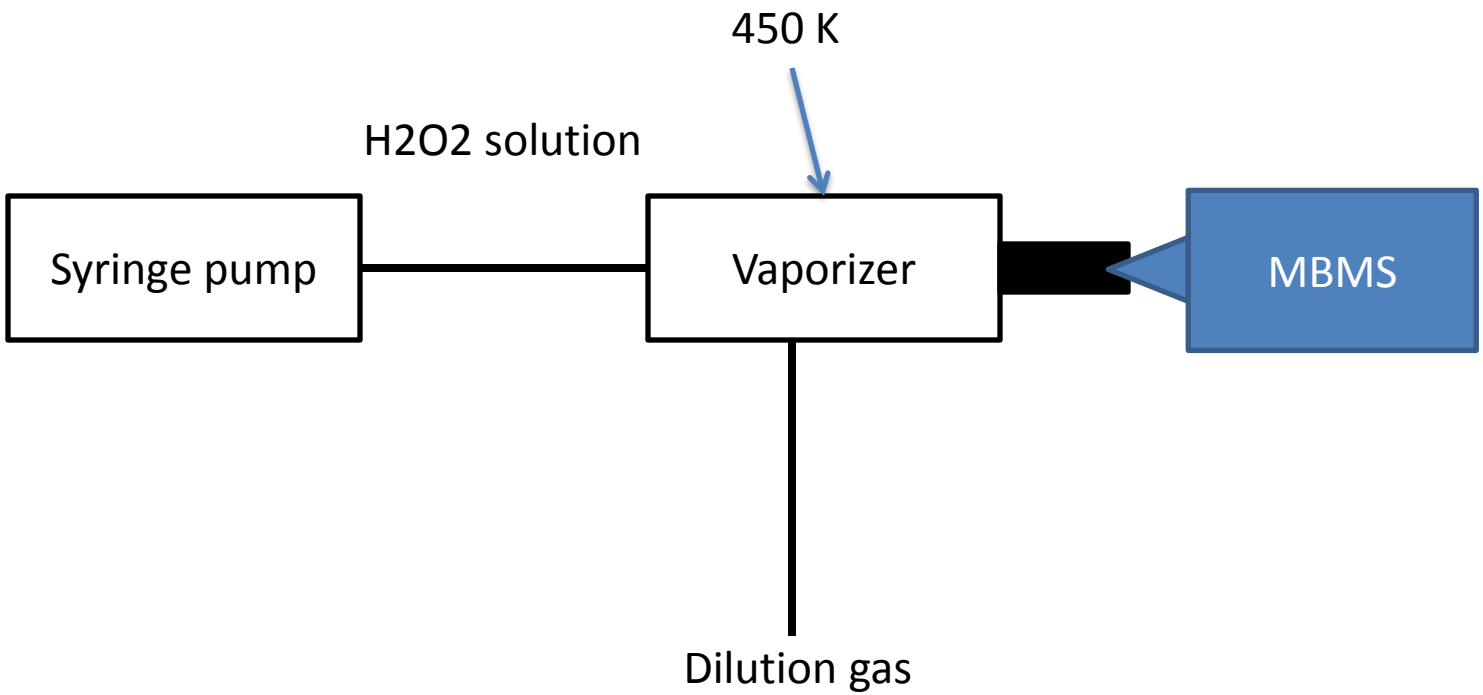
Flow tube experiments

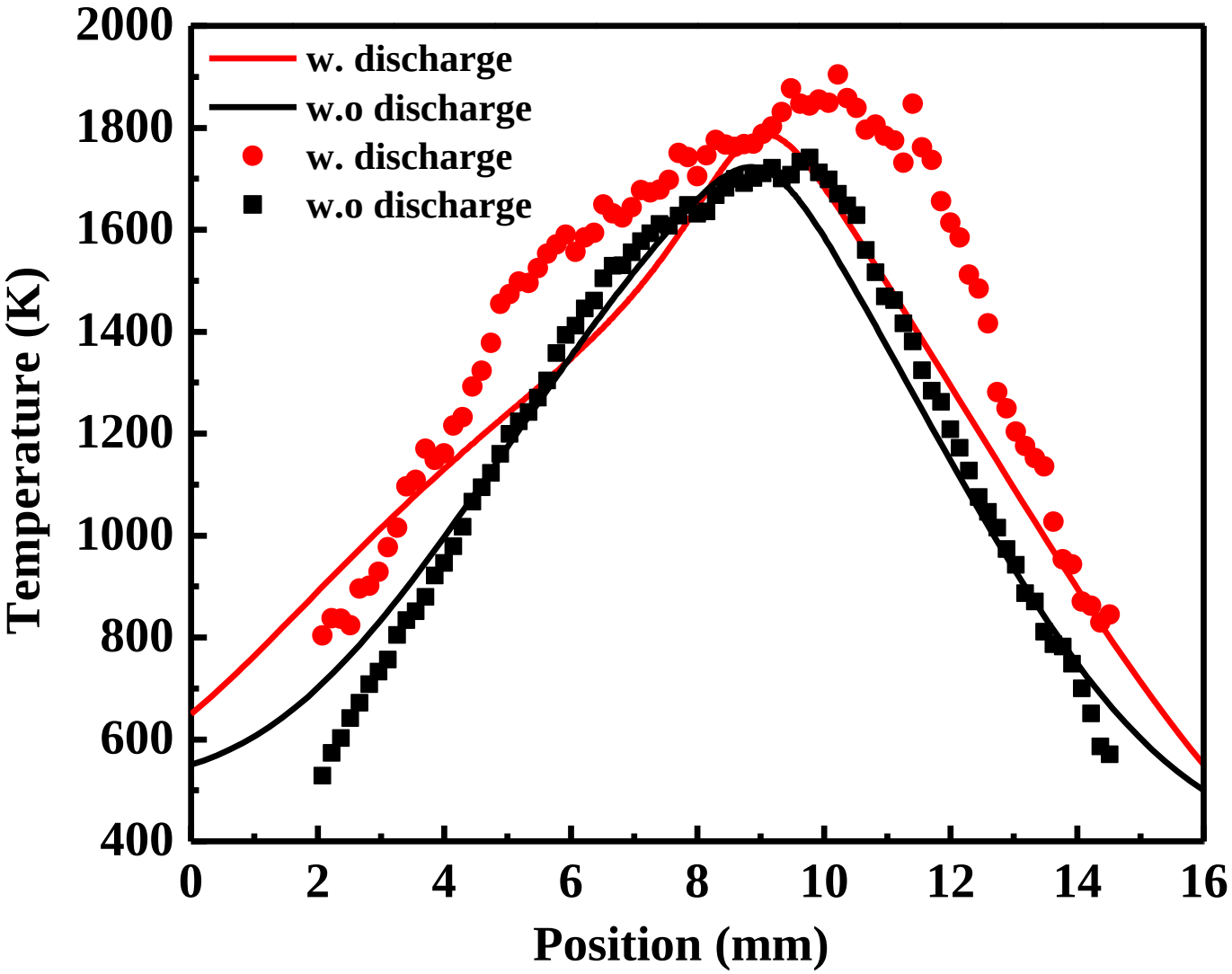




H_2O_2 calibration

Dissociation:
do it quickly
changing H_2O_2 concentrations
monitor O_2 peak





χ_{O2} = 53.5%, χ_{CH4} = 20%, a = 400 1/s