Plasma Assisted Combustion: Flame Regimes and Kinetic Studies

Yiguang Ju, Joseph Lefkowitz, Tomoya Wada, and Sanghee Won

Department of Mechanical and Aerospace Engineering, Princeton University

Princeton, NJ 08544, USA

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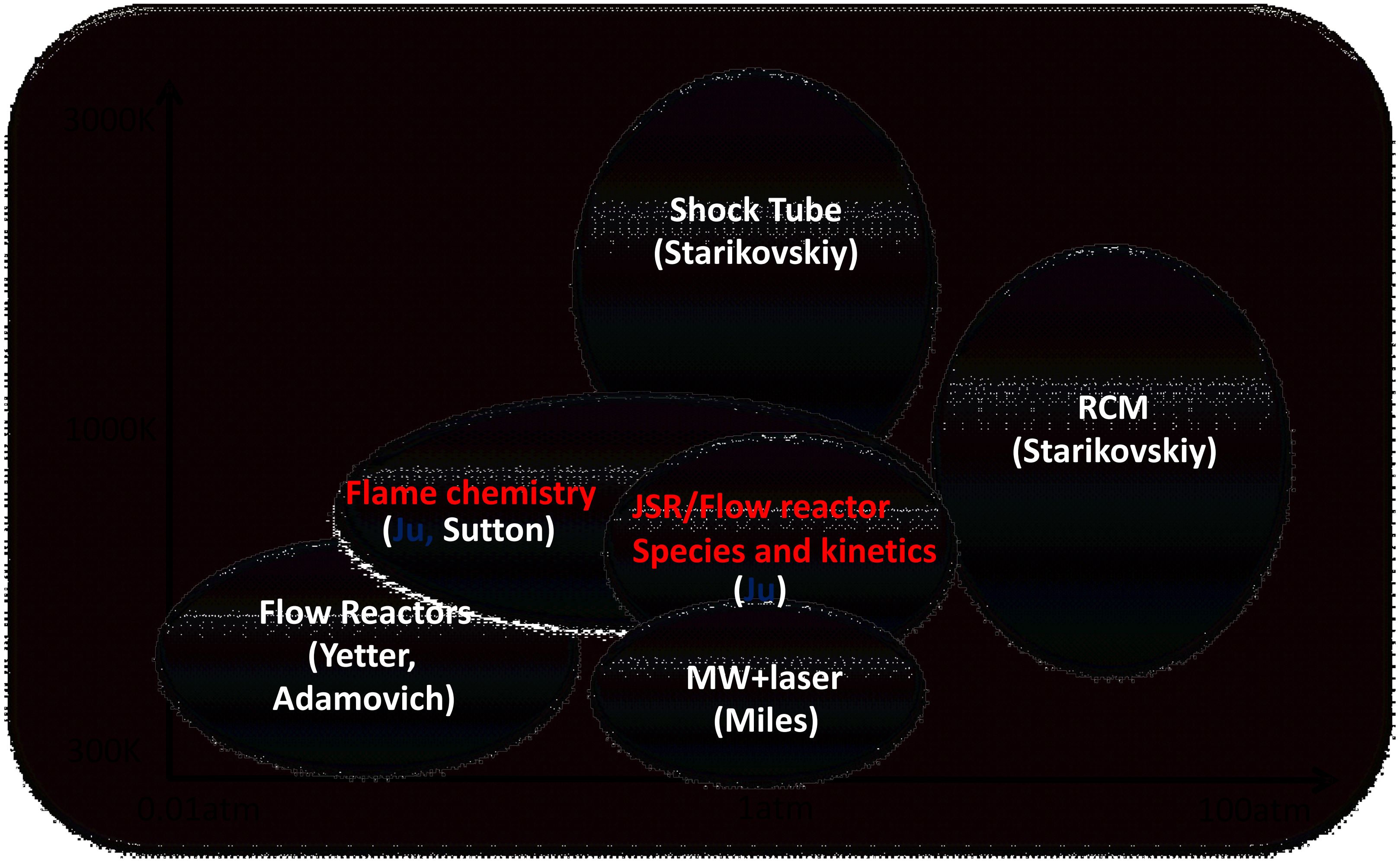
MURI Facility Summary and collaborative team structure



Today's Presentation (2014)

1. Plasma activated low temperature combustion & cool flames (liquid fuels: dimethyl ether, n-heptane)

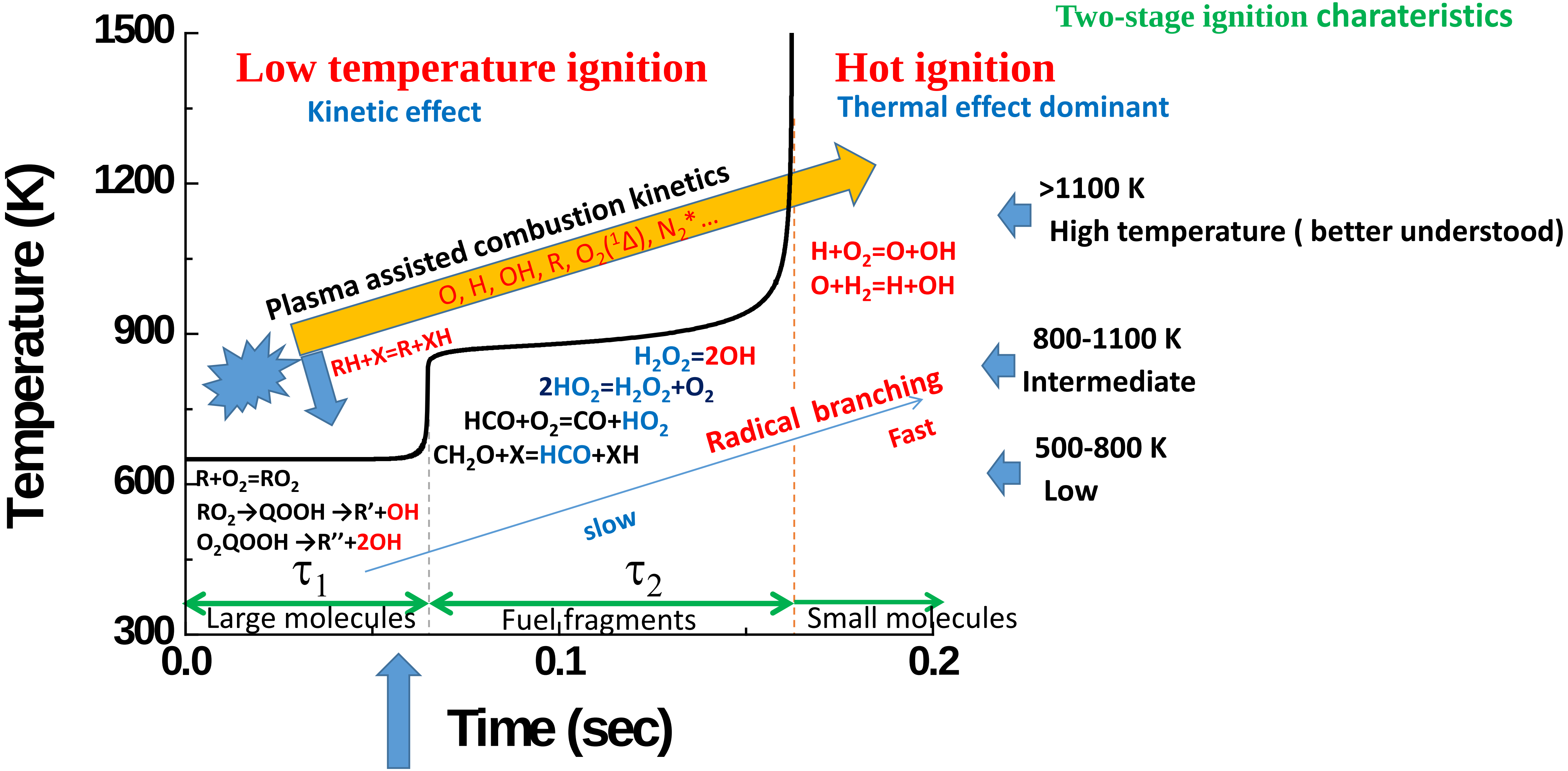
2. Plasma assisted mild combustion (flame regimes)

3. In-situ and time accurate multispecies diagnostics in a plasma flow reactor (kinetics)

4. Development of low temperature and high pressure plasma combustion mechanism (HP-MECH/plasma) (collaboration)

1. Plasma Activated Low Temperature Combustion and cool flames for liquid hydrocarbon fuels

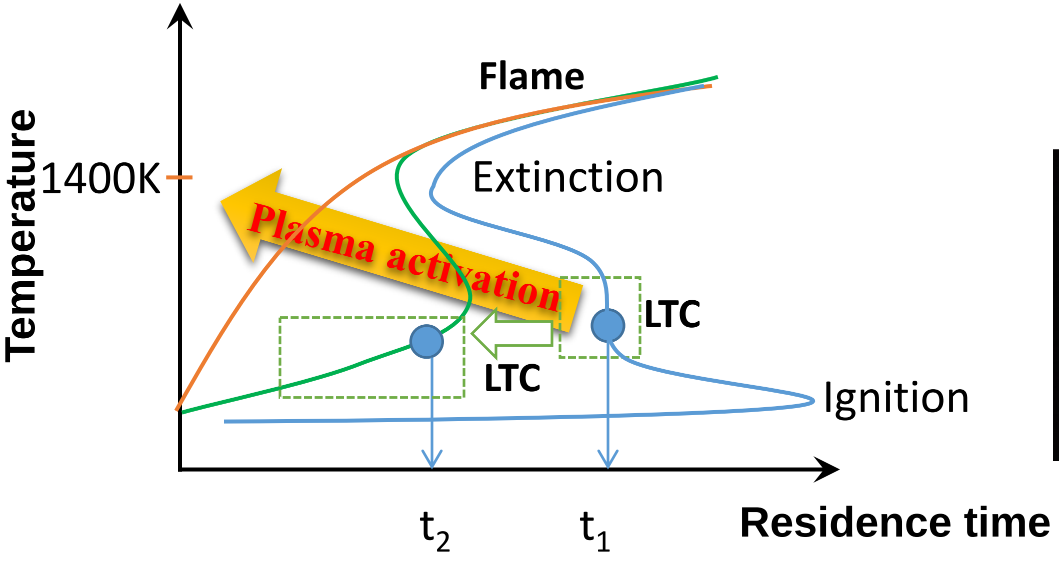
Two-stage ignition charateristics



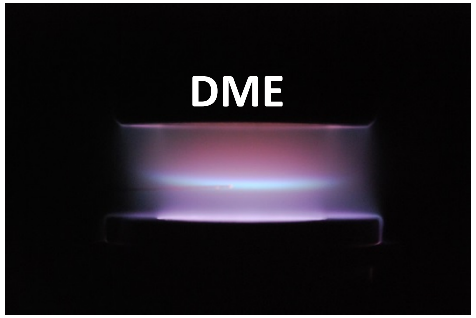
Plasma has more kinetic enhancement effect in lower temperature combustion

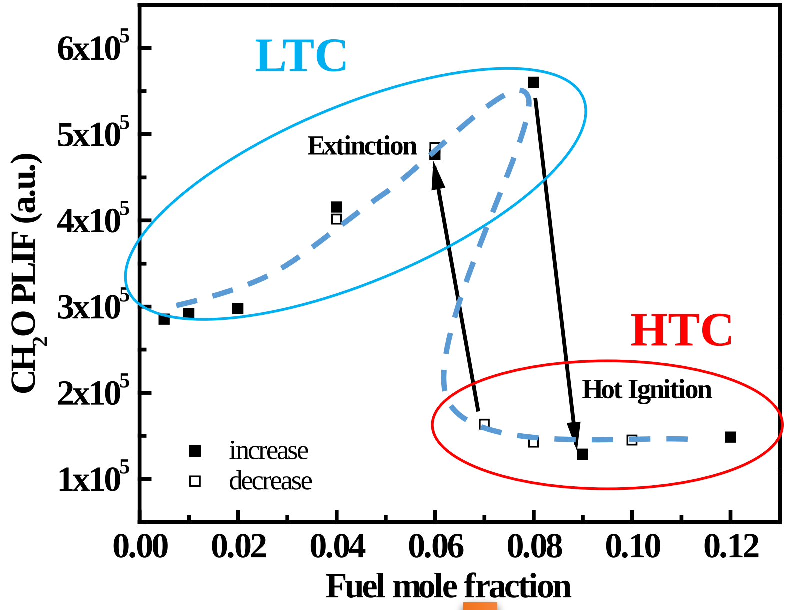
However, poorly studied and understood…

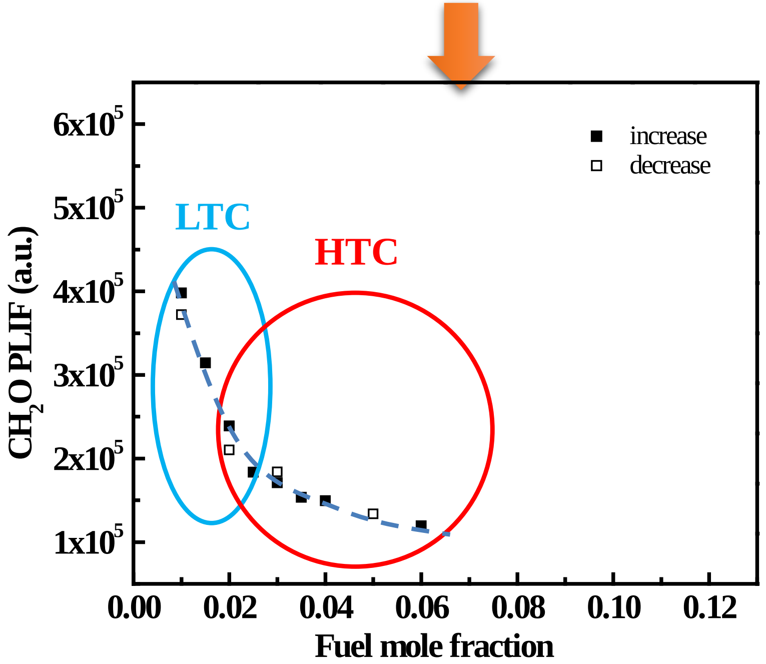
1.1 Plasma activated low temperature combustion of liquid fuels: flame regime changes



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







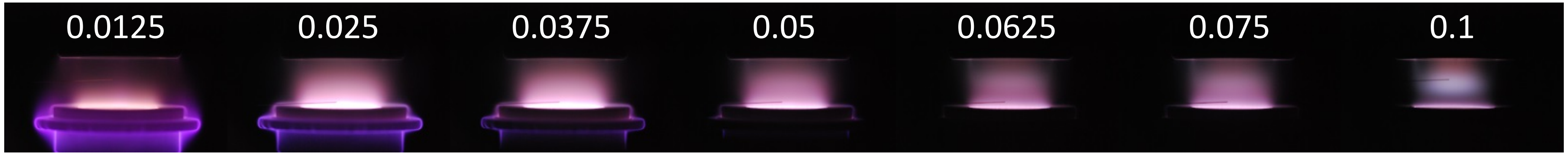
$t_2 << t_1$
So it occurs in ms or even without an extinction limit!

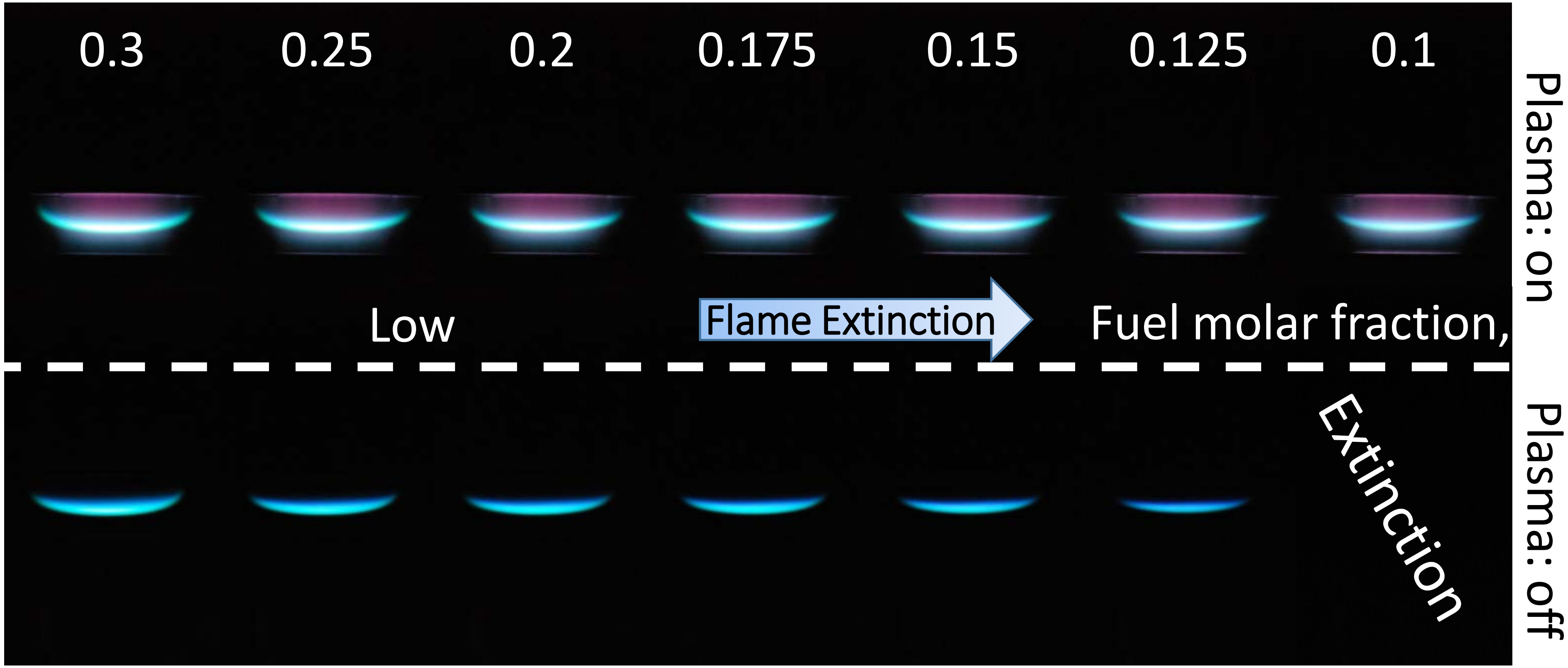
P = 72 Torr, a= 250 1/s,
f = 34 kHz,
X_{O_2}=60%, varying X_f

Sun et al. 2014, Combustion & Flame.

1.1 Plasma activated low temperature combustion: n-heptane

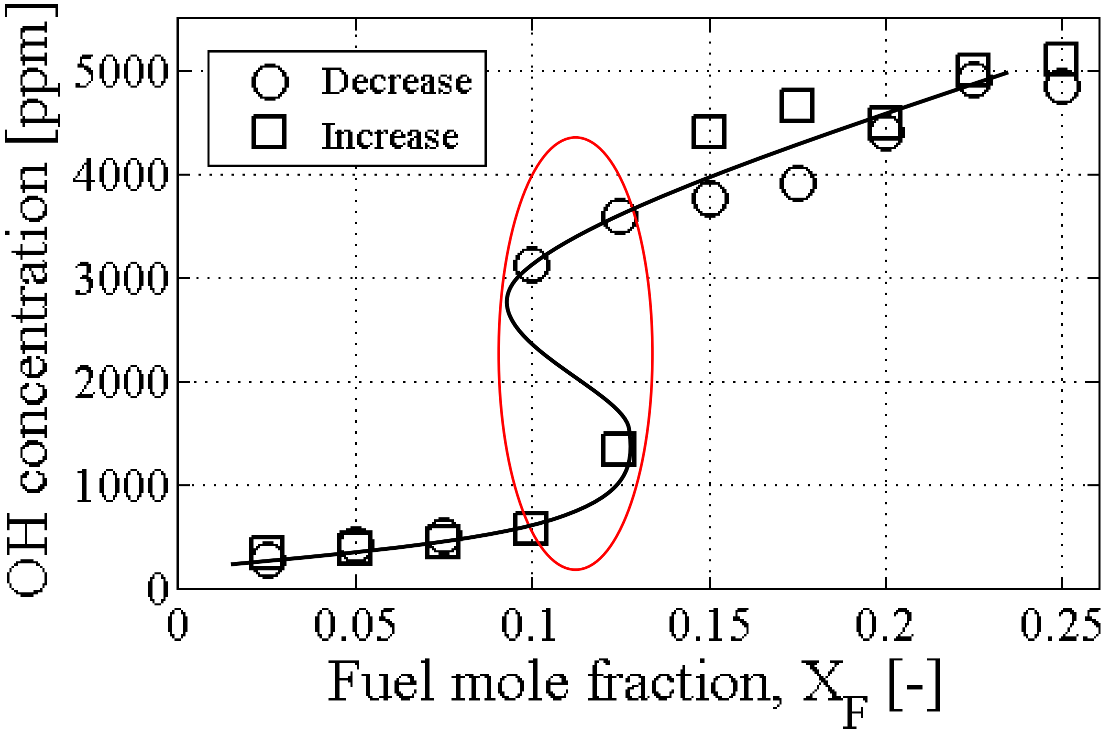
Fuel molar fraction, X_F Ignition High



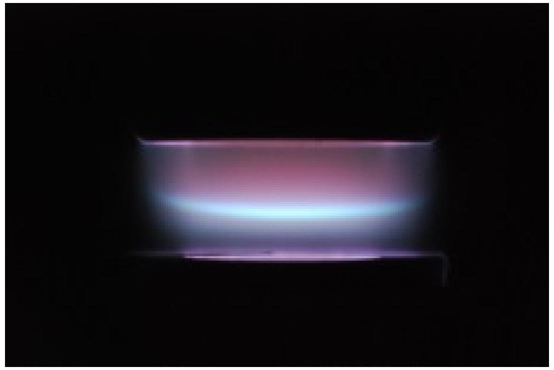


- Fixed O_2 molar fraction (X_{O2} = 0.3) and stretch rate (a = 150 s^{-1})

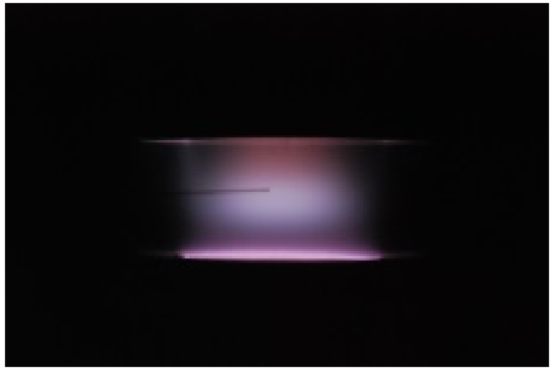
OH-PLIF measurement with varied X_F (n-heptane)



Flame

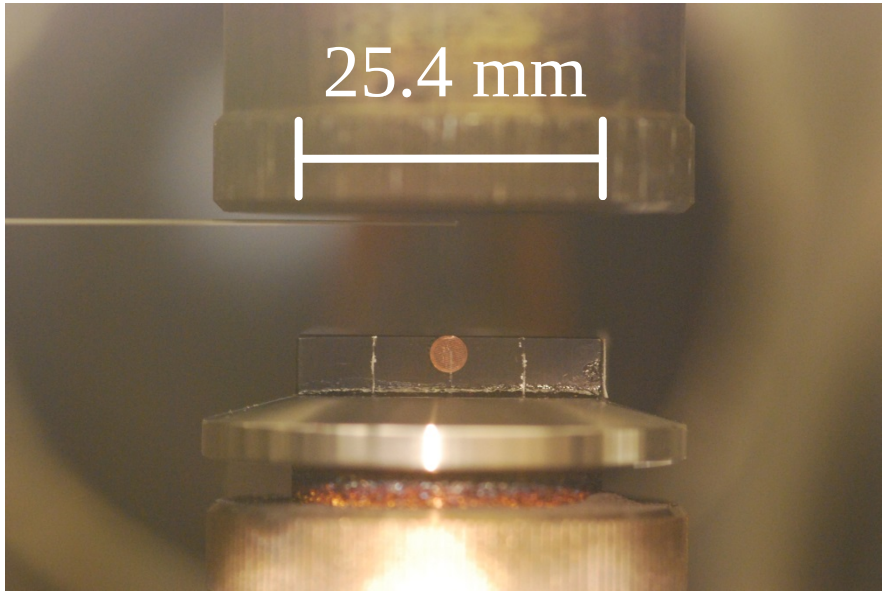


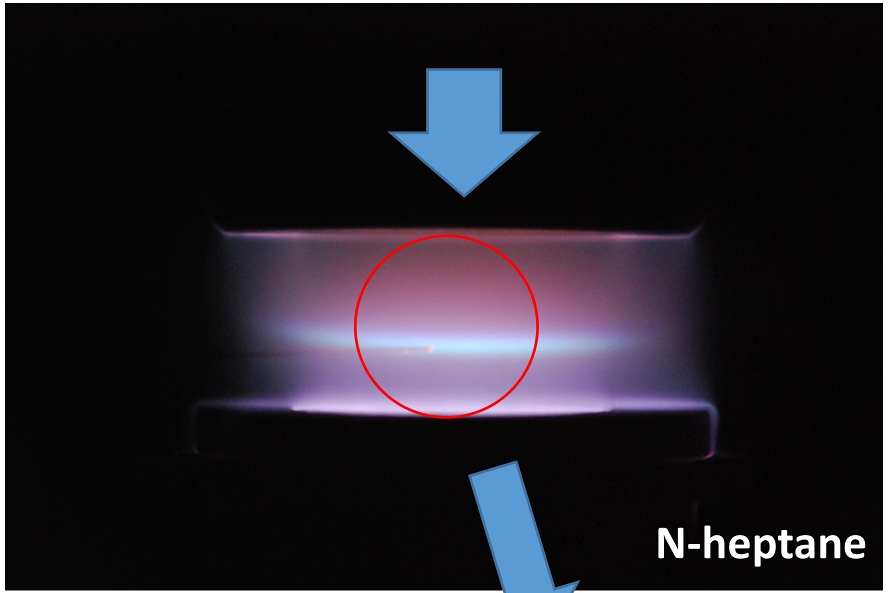
Ignition



- Hysteresis (S-Curve, thin and thick reaction zones)
- Flame: Combustion chemistry dominated regime at high temperature and,
- Ignition: Plasma chemistry dominated regime at low temperature

Species measurements in plasma assisted low temperature combustion



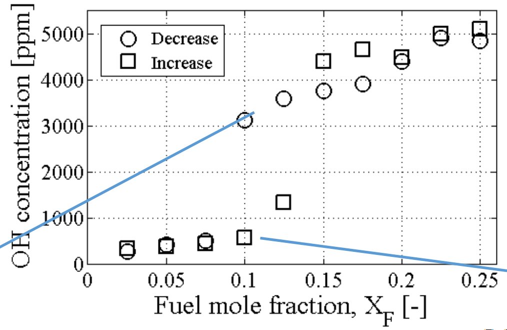


- Probe O.D.: 363 μm
- Adjust position (Vert. & horiz.)
- Negligible influence on the flame

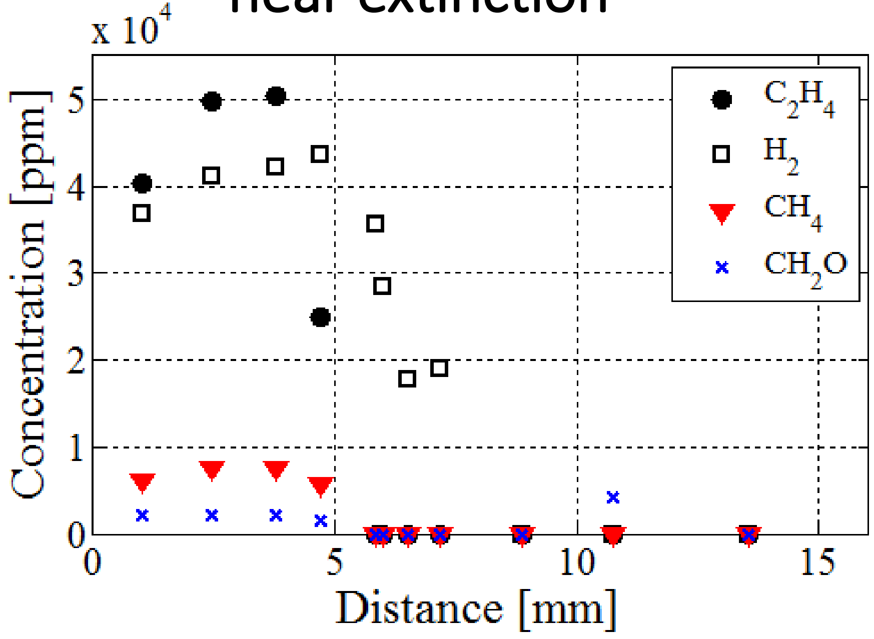
Species **distribution** near ignition and extinction

(X_F = 0.1, X_O = 0.3, and a = 150 s^{-1})

Providing validation targets

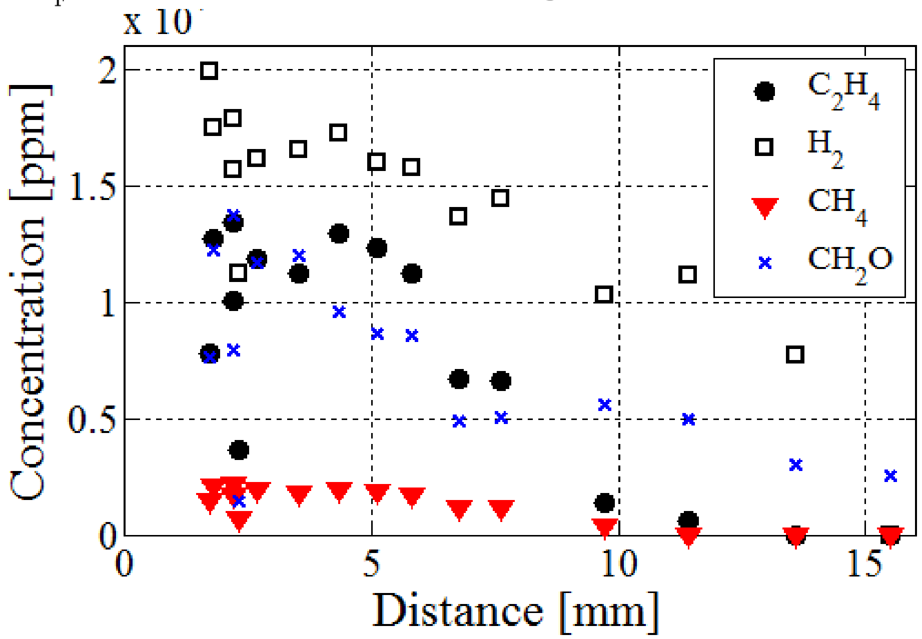


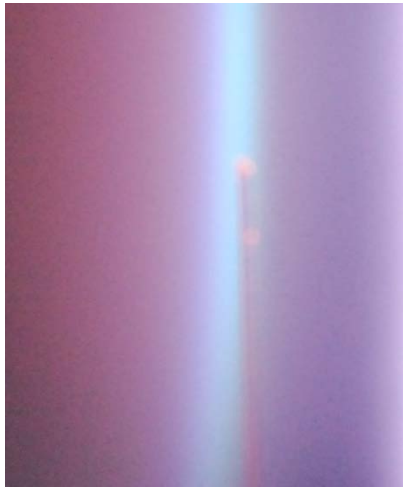
near extinction



High temperature chemistry

near ignition

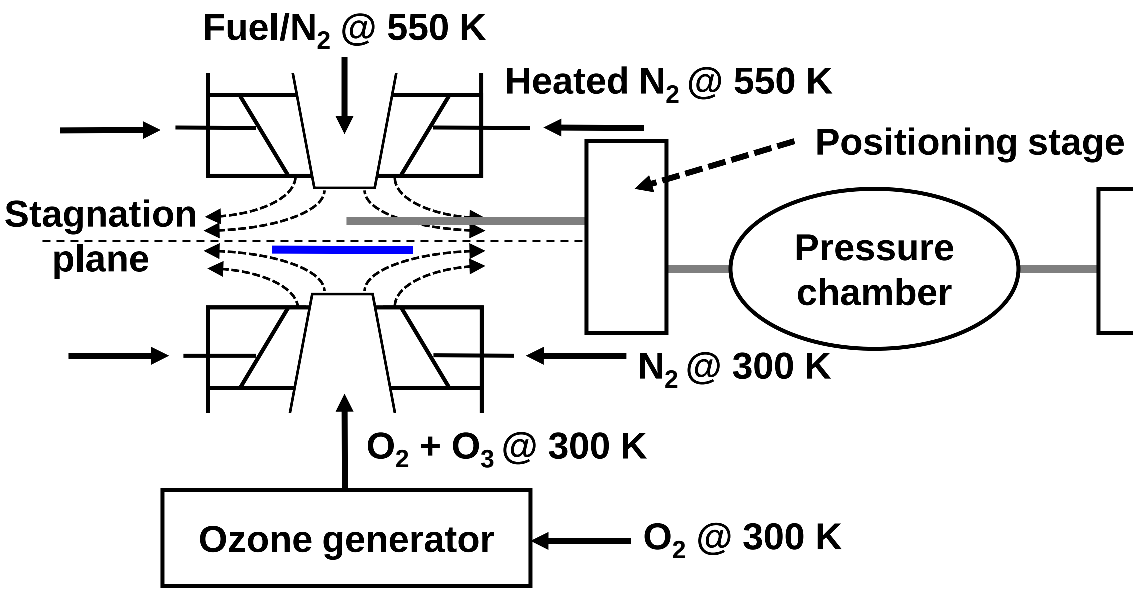


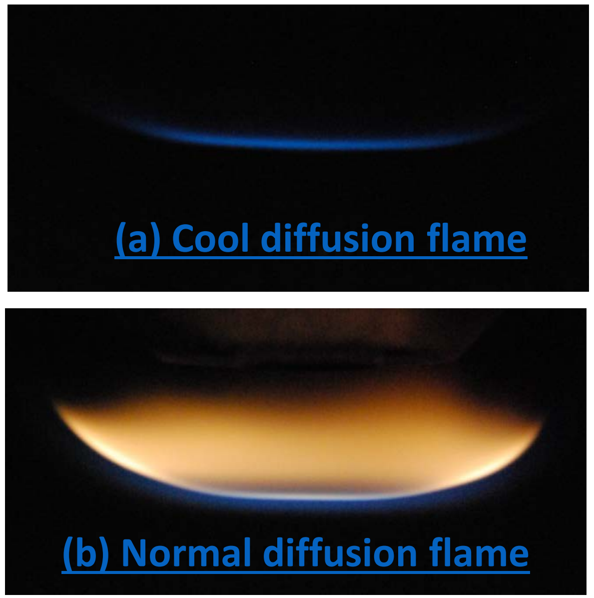


Low temperature chemistry

1.2 Experimental study of plasma assisted diffusional cool flames

- A heated counterflow burner integrated with vaporization system[1]
  - n-heptane/nitrogen vs. oxygen/ozone
- Ozone generator (micro-DBD) produces 2- 5 % of ozone in oxygen stream, depending on oxygen flow rate
- Speciation profiles by using a micro-probe sampling with a micro-GC.[2]



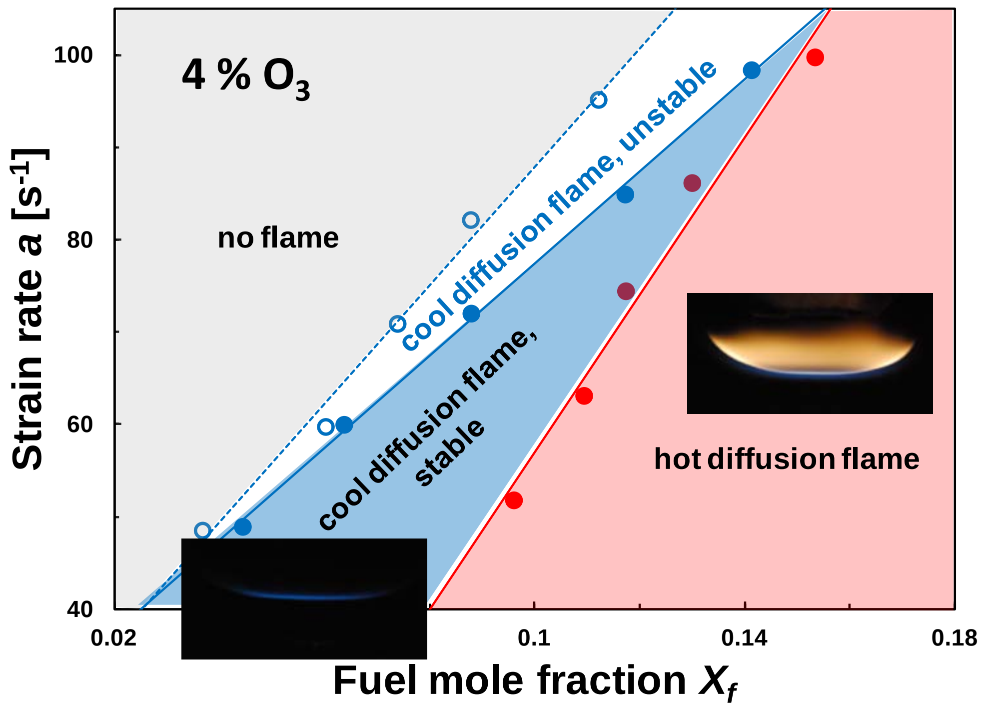


1) S. H. Won, et al., Combust. Flame 157 (2010)
2) J. K. Lefkowitz, S. H. Won, et al., Proc. Combust. Inst. 34 (2013)

Stability diagram of diffusional cool flames

- Lower X_f, higher a; no flame initiated.
- Higher X_f, lower a; ***normal diffusion flames***
- Intermediate X_f and lower a; ***cool diffusion flames***

- Unstable regime extended
  - As increasing both a and X_f
  - Continuous ignition and extinction of cool flames

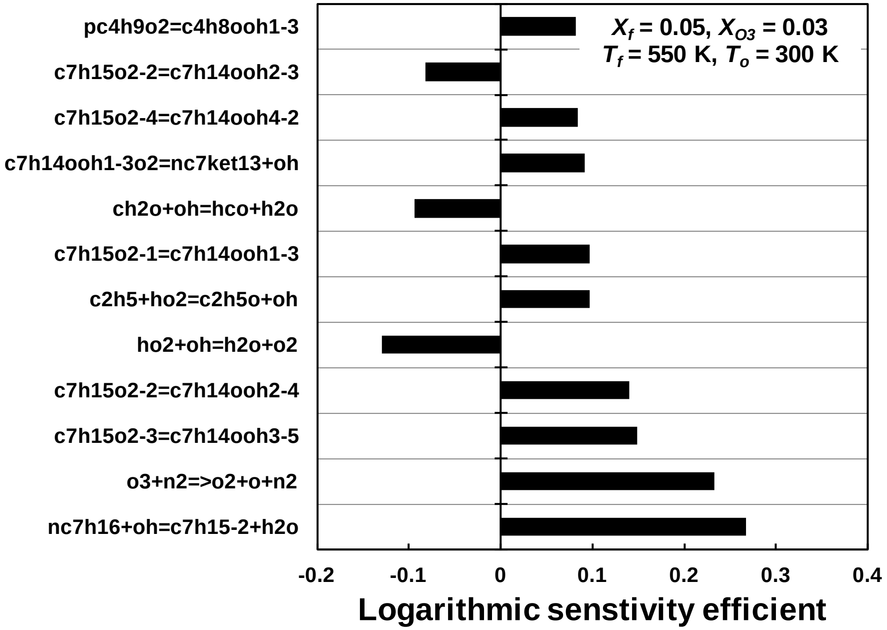


Cool flames extends the auto-ignition limit!

Sensitivity Analysis near Extinction

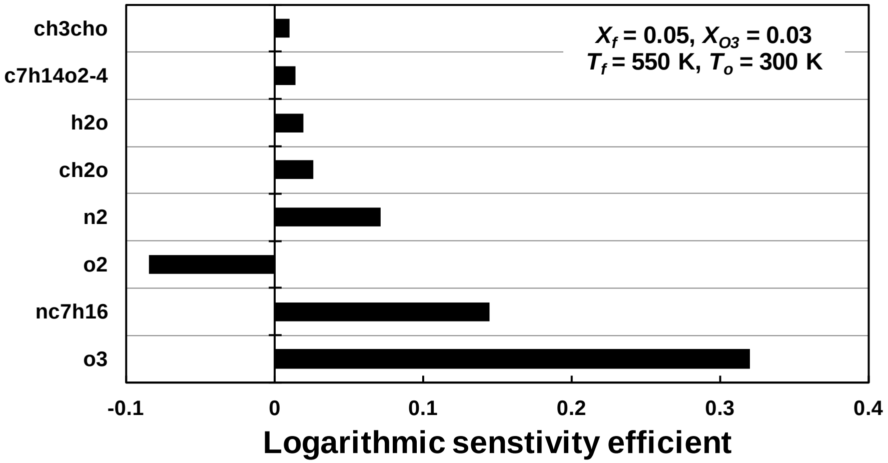
Reactions

- Importance of low temperature chemistries
  - RH + OH (~ 15% heat production)
  - R + O_2 reactions (~40%)
  - QOOH reactions
  - HO_2 reactions



Transport

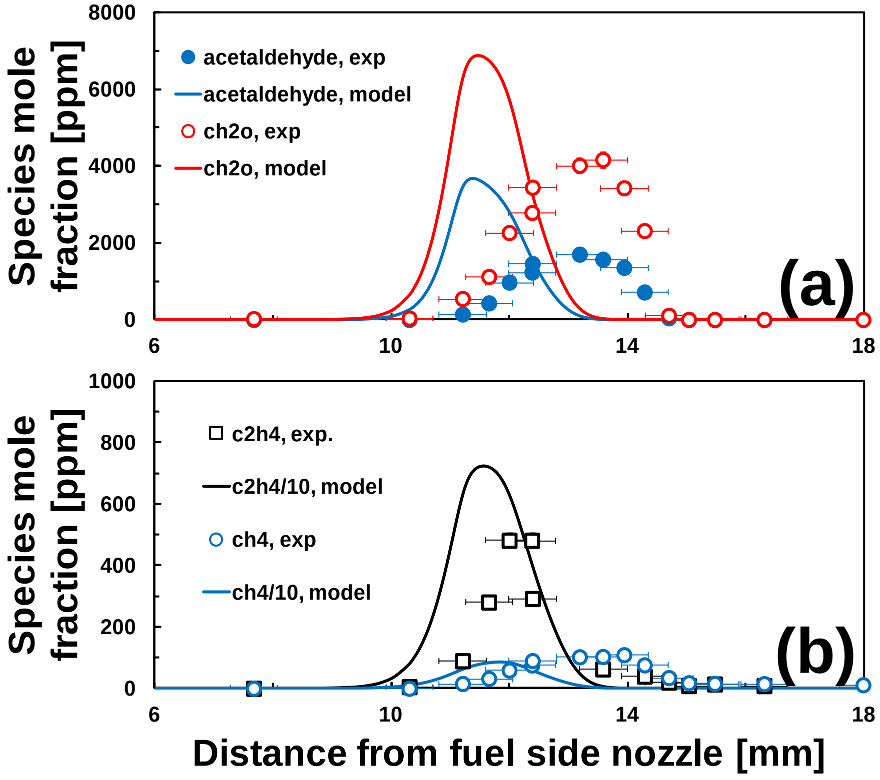
- Very sensitive to ozone diffusion
  - $O_3 + N_2 \rightarrow O_2 + O + N_2$ for initiation of radical pool.
  - Thus, fuel diffusion is important as well.
- Strong sensitivity to CH_2O
  - Indicator of low temperature reactivity[1]

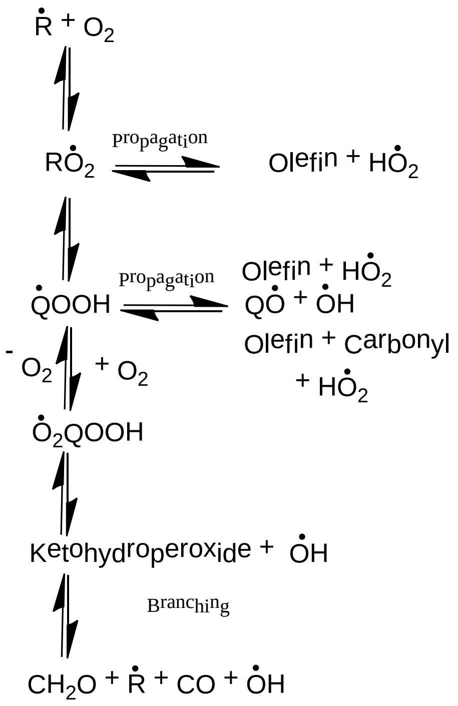


1) S. H. Won et al, Combust. Flame 161 (2014) 475-483

Speciation Profiles and validation of kinetics

- Reasonable prediction of acetaldehyde and CH_2O
- Significant over-estimation of C_2H_4 and CH_4 formation
  - Factor of 10.

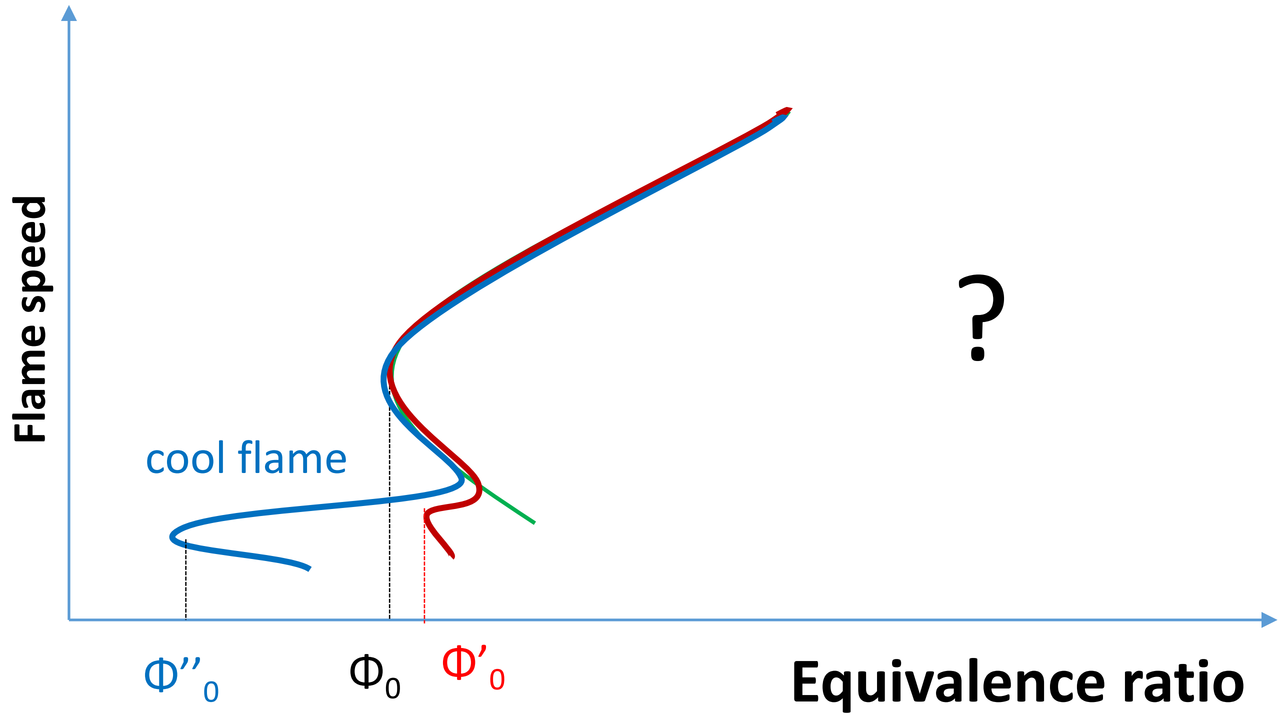




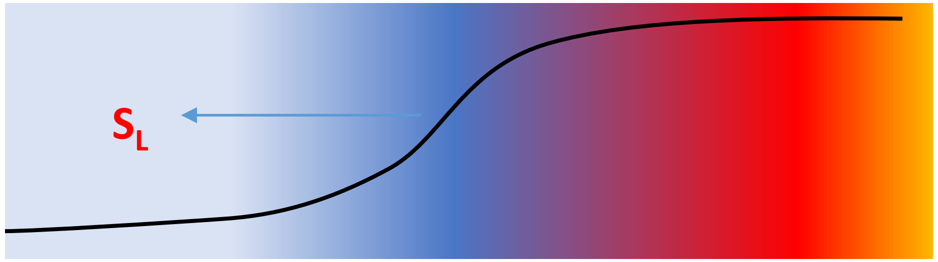
1.3 Plasma assisted premixed cool flames

- Lean Flammability Limit:

Normal flame vs. cool flame



1.3a. Numerical results of Freely propagating 1D planar cool flames



- **Geometry**

  1D freely propagating flames

- **Mixture and Kinetic model**

  Fuel: Dimethyl ether   Oxidizer= $(1\text{-}x)O_2 + xO_3$,   x=0 - 0.1,   p=1 atm

  Ozone chemistry & Dimethyl ether model

  Ombrello, et al., *Combustion and Flame*, Vol. 157, 2010

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

  Liu et al., Combustion and Flame, 160 (2013)

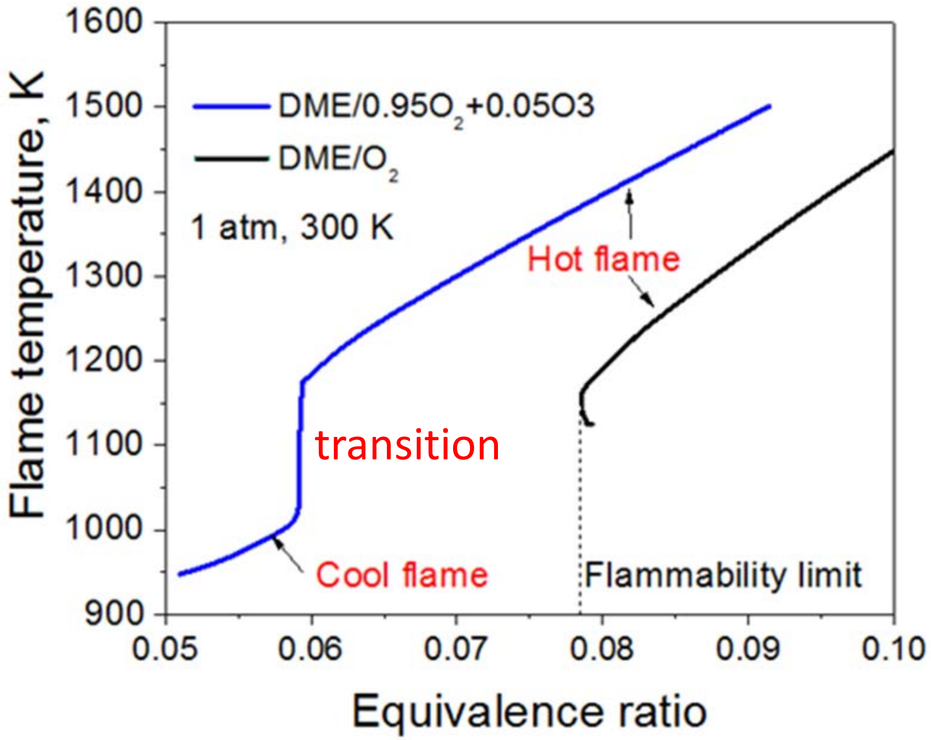
- **Numerical method**

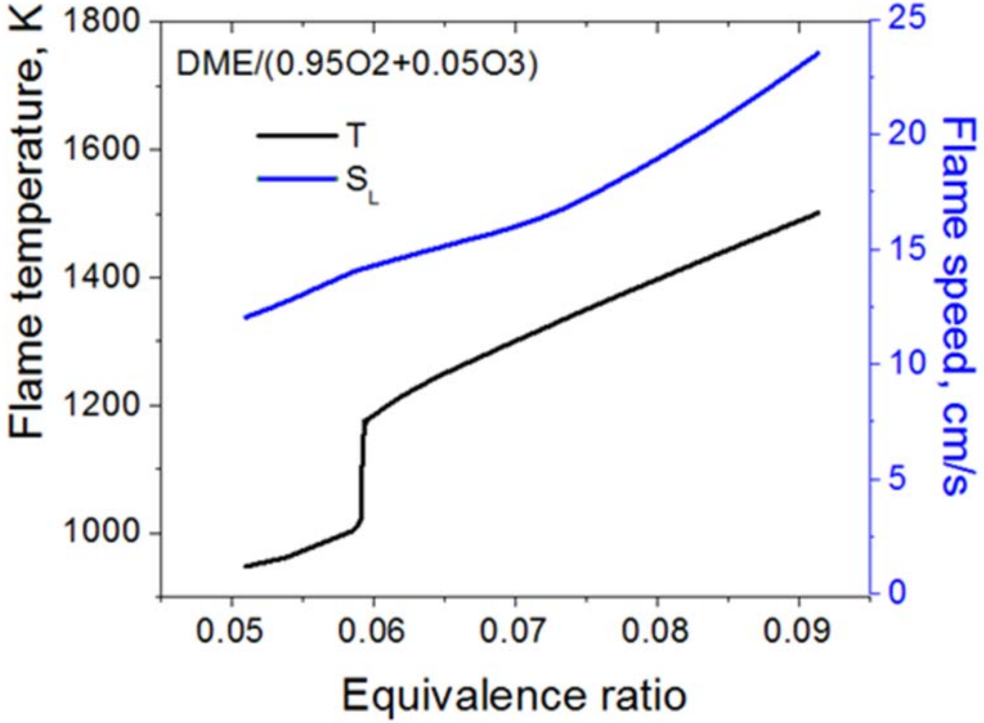
  Modified Chemkin with arc-continuation method

  Radiation (Optically thin model for CO2, H2O, CO, CH4)

  Ju et al. JFM, 1997

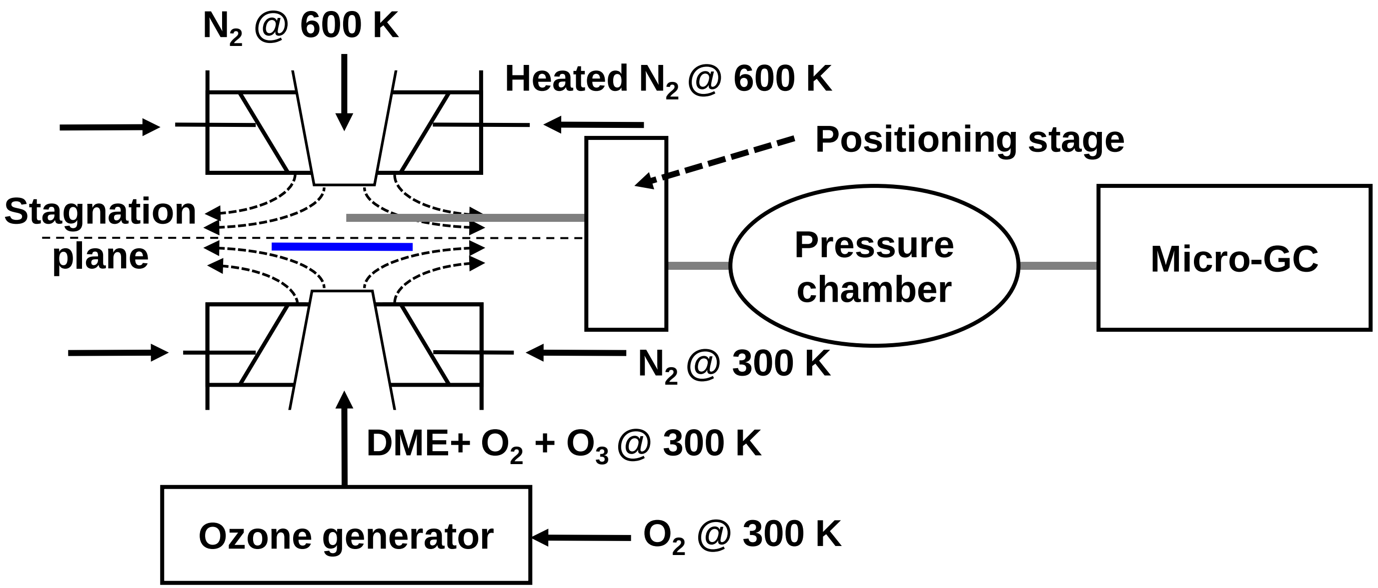
- **Lean Flammability Limit Extension by formation of cool flames**

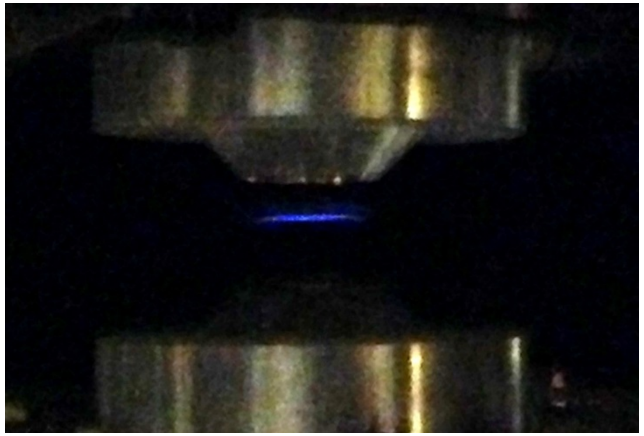




- Lean limit of φ = 0.078 w & WO 5% ozone addition
- Ozone promote cool flames
- Three flame regimes
- Cool flames significantly extends the lean burn limit of normal flames
- Cool flames can have a high flame speed between (~15 cm/s)

Experimental observation of premixed cool flames

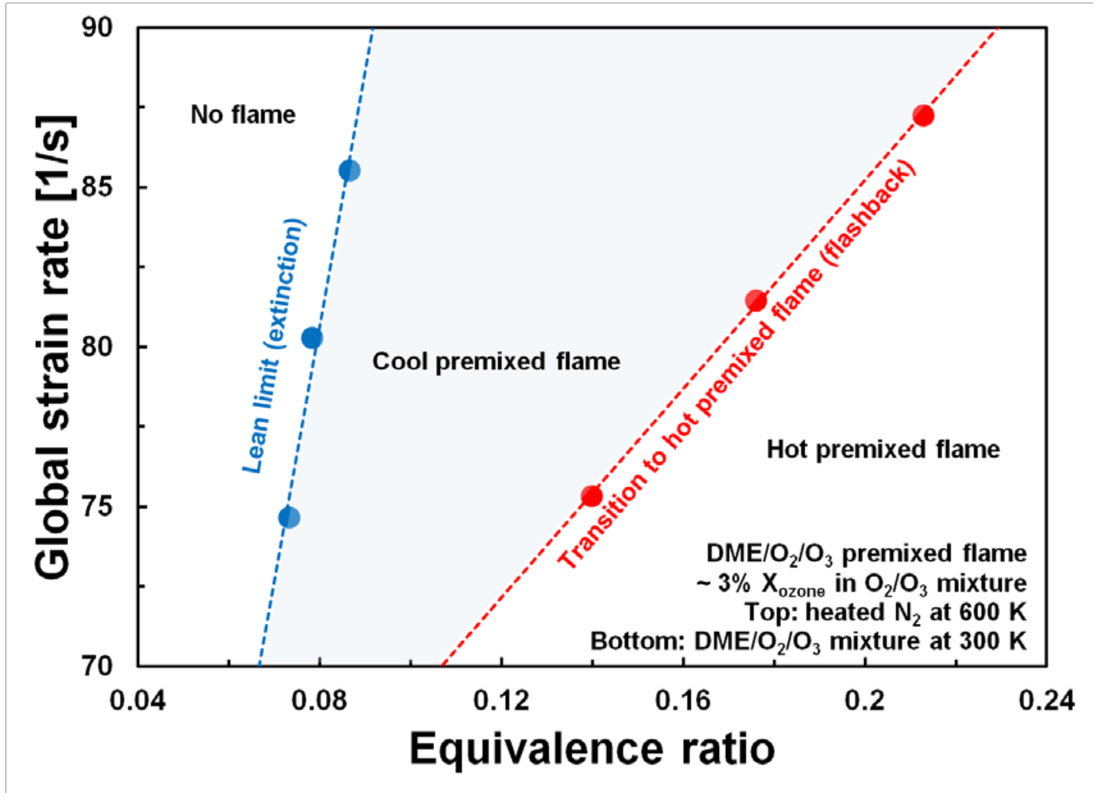




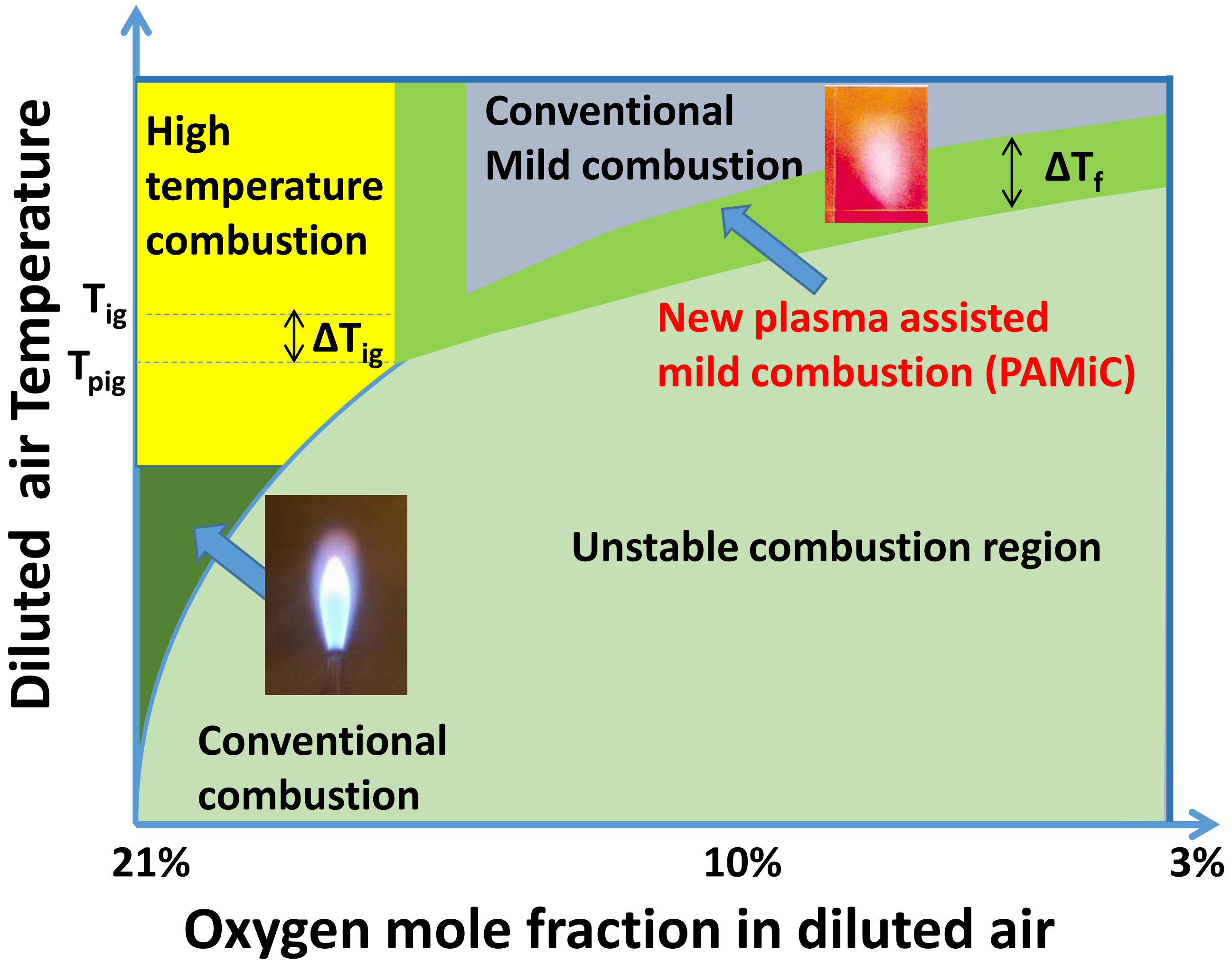
- Temperature of N_2= 600K
- Temperature of DME/O_3/O_2=300 K
- Strain rate=80 s^{-1}
- Ozone concentration: 3%

Premixed Cool Flame stability/regime diagram

- Three flame regimes found:
  - Unburned mixture past lean limit
  - Stable cool flames
  - Transition regime to hot flame
- Lean limit slightly increases with strain
- Width of stable cool flame region doubles from 75 s^{-1} to 85 s^{-1}

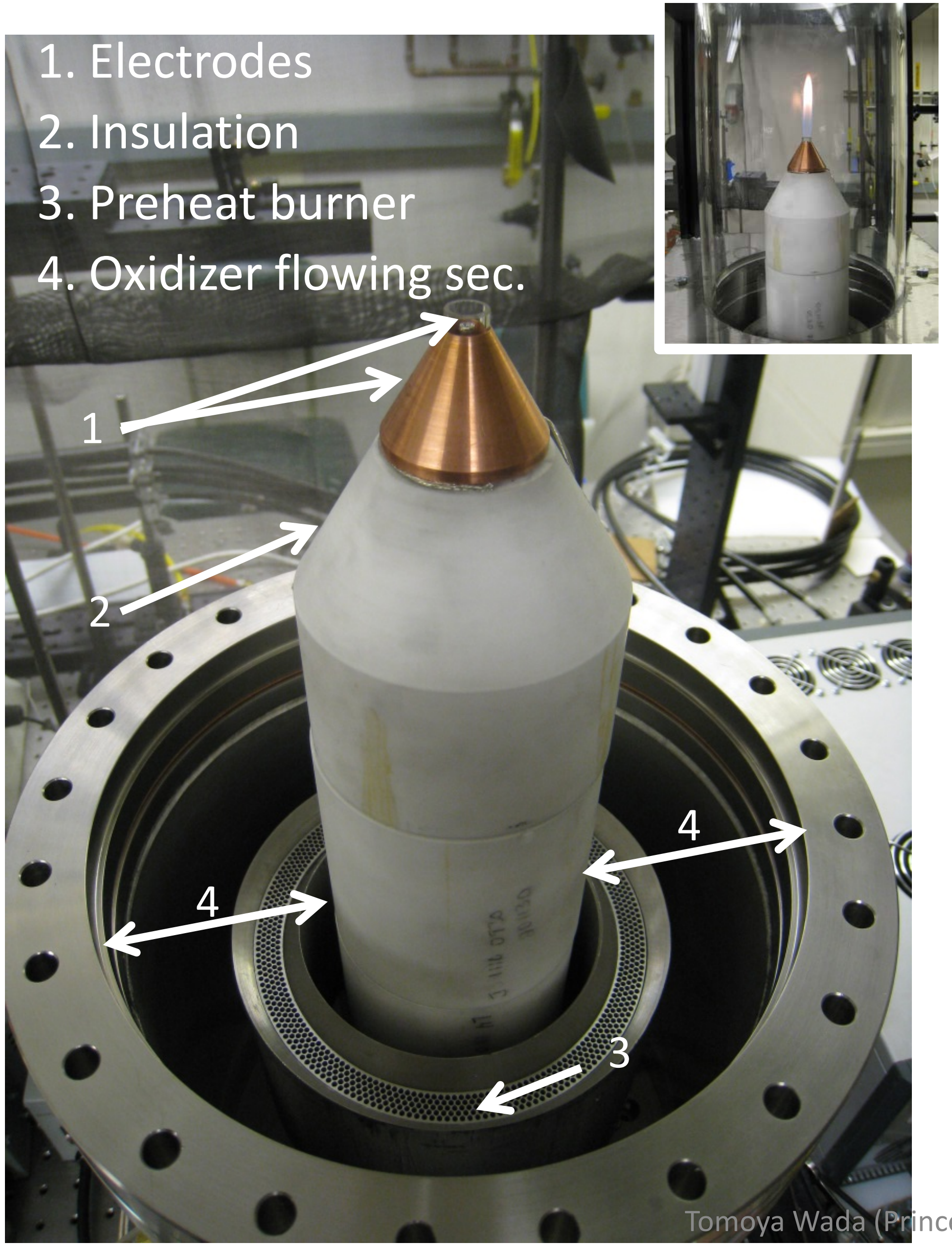


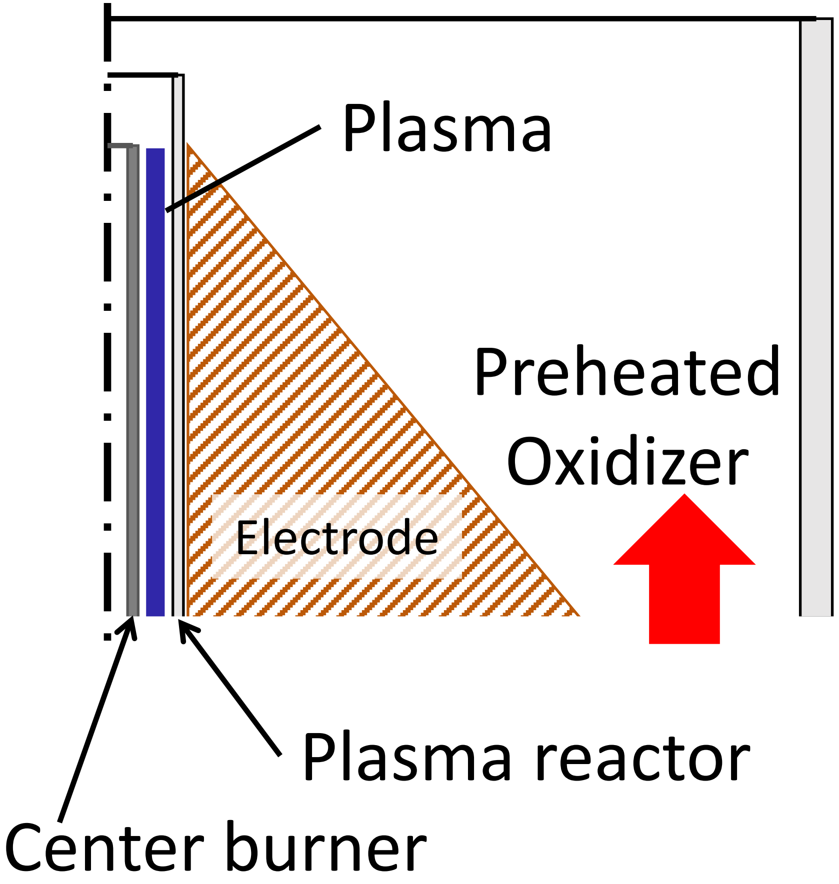
2. Plasma assisted mild combustion



Can plasma extend the boundary of mild combustion to lower temperature?

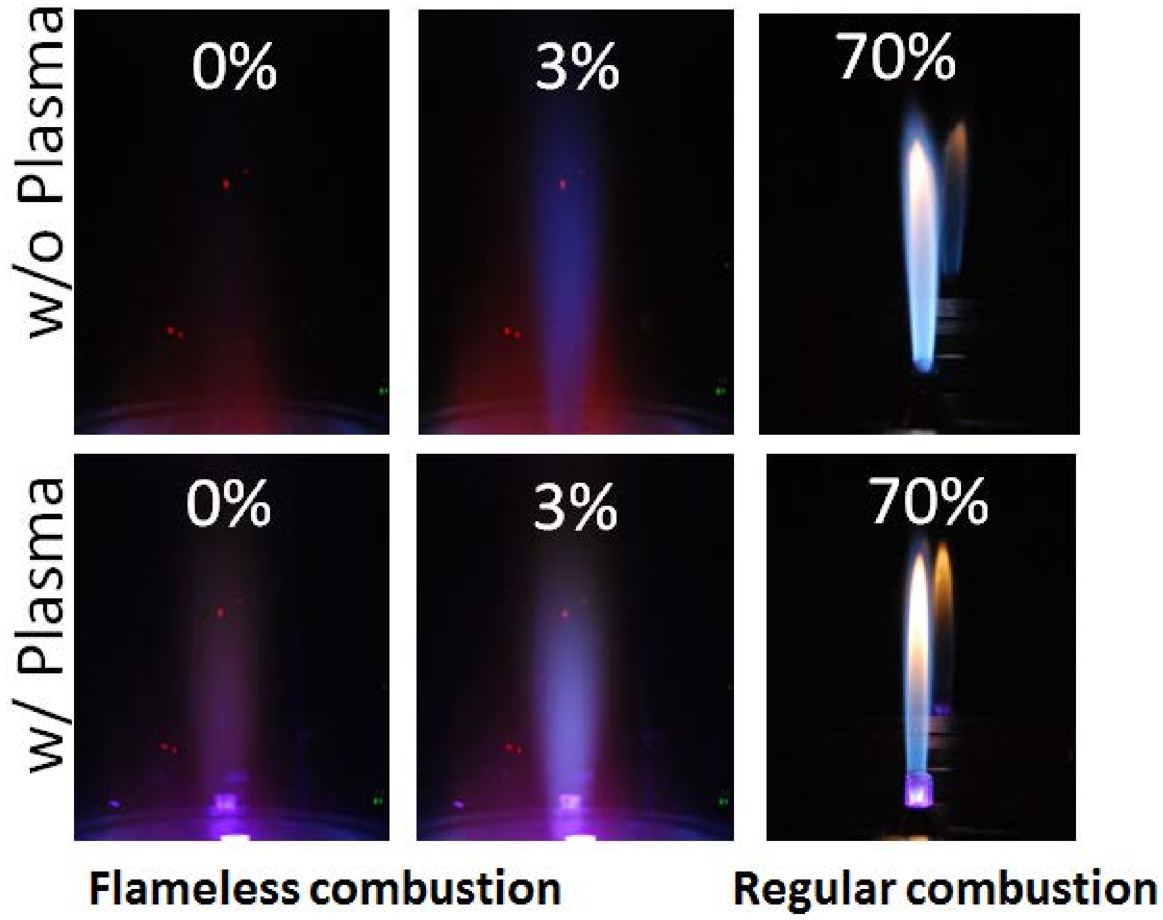
Mild combustion: co-axial burner





Center burner (Fuel/N_2)
Plasma reactor (lean mix.)

MILD combustion w/ and w/o plasma



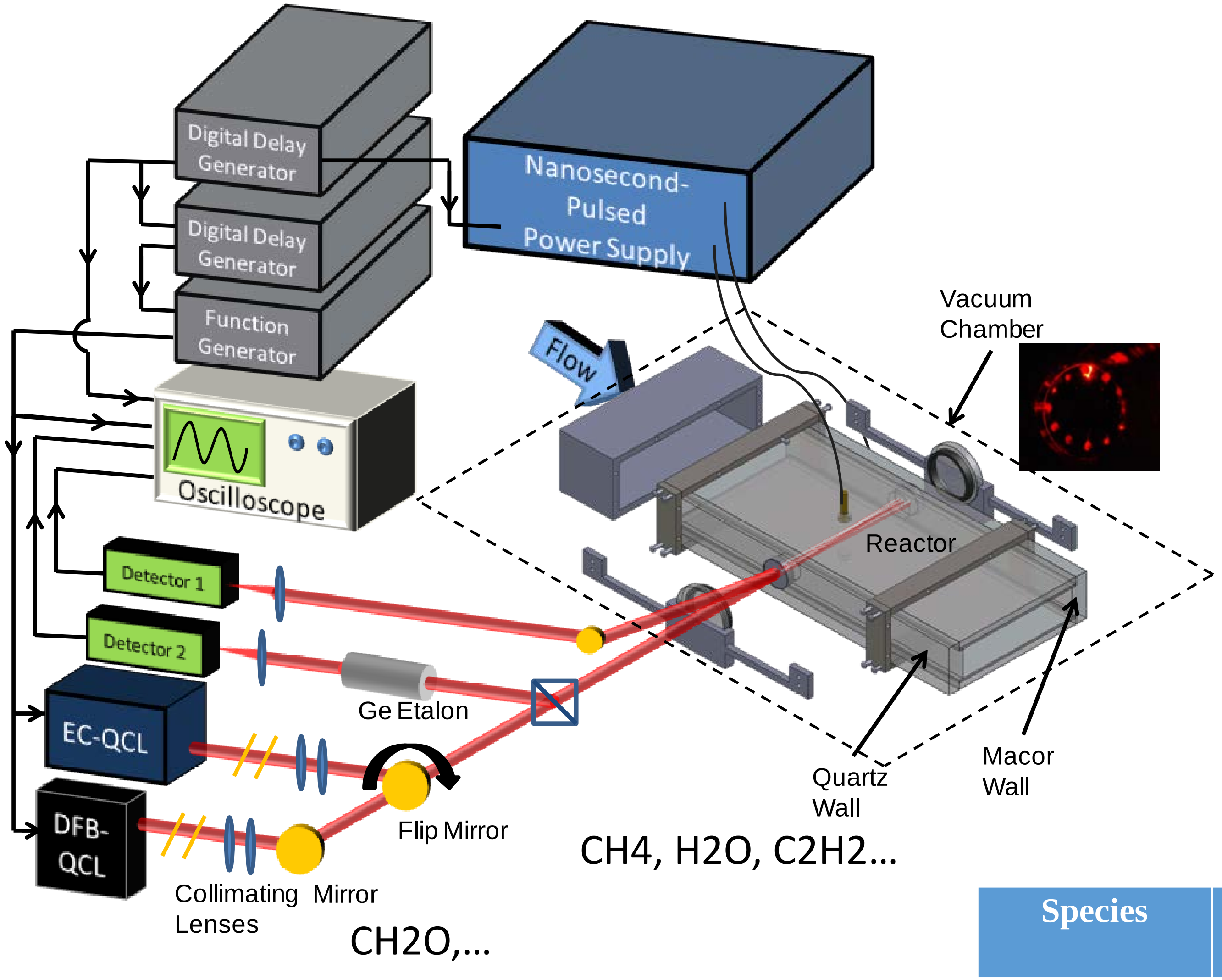
- Condition
  - Preheat gas temp.: 1050 K
  - Preheat gas O_2: 12%
  - Center burner vel.: 20 m/s
  - Center burner CH_4/N_2: 10%
  - Plasma reactor vel.: 5 m/s

Plasma reactor

- CH_4/air ratio: 0% and 3%

Shorter and wider reaction zone

3. In Situ time accurate Mid-IR LAS Diagnostics in plasma/flow reactors (CH4/O2)



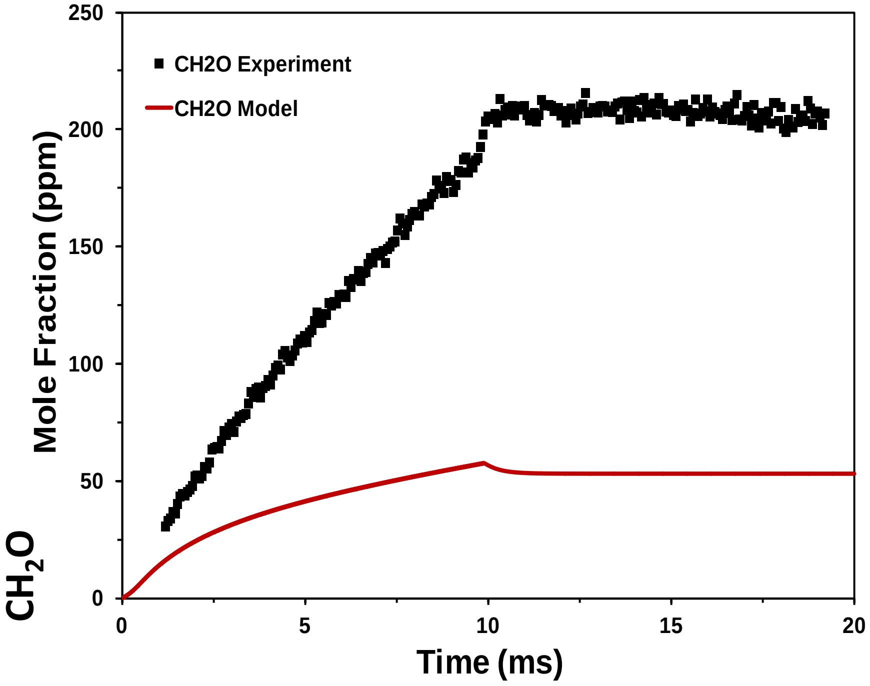
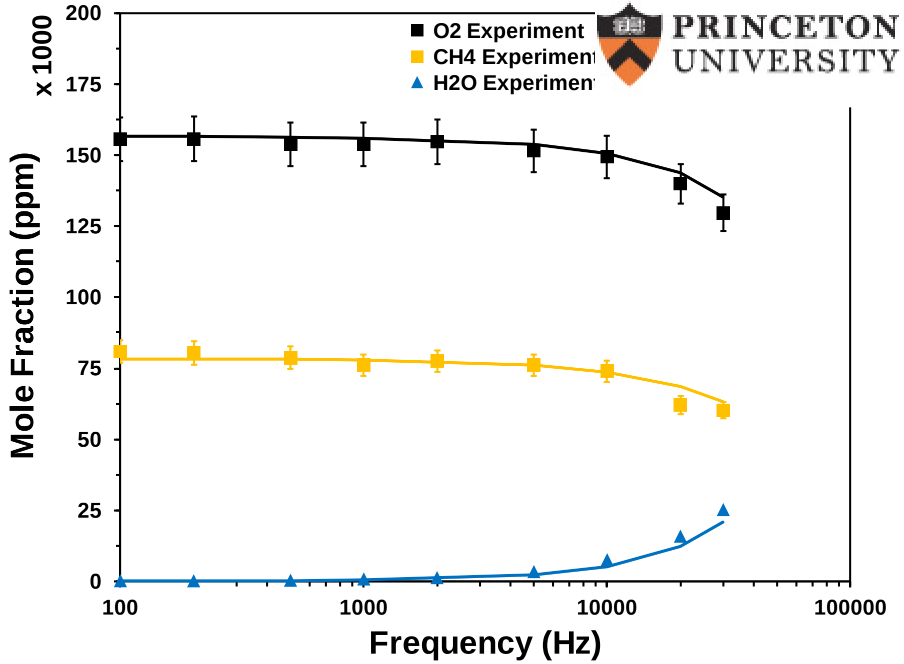


Fig. 1 CH_2O time history measurements and modeling of a 300 pulse burst at 30 kHz in a stoichiometric $CH_4/O_2/He$ with 75% dilution.

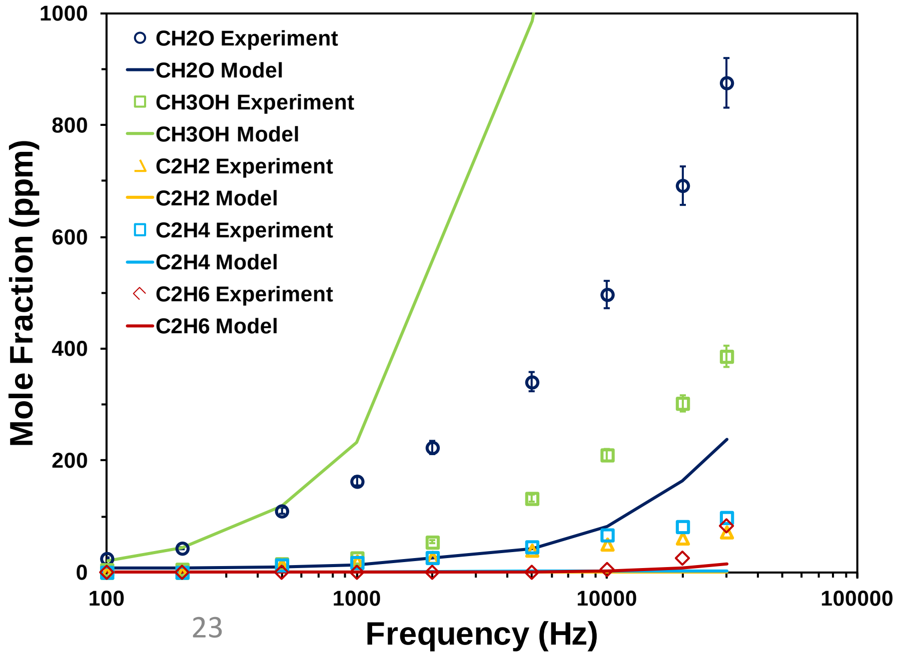
Species	Wavelength (nm)	Wavenumber (cm^{-1})	Line strength @ 300 K (cm/molecule)
CH_4/Temp	7442.91	1343.56	1.898×10^{-22}
	7442.52	1343.63	1.78×10^{-22}
CH_2O	5791.09	1726.79	6.47×10^{-20}

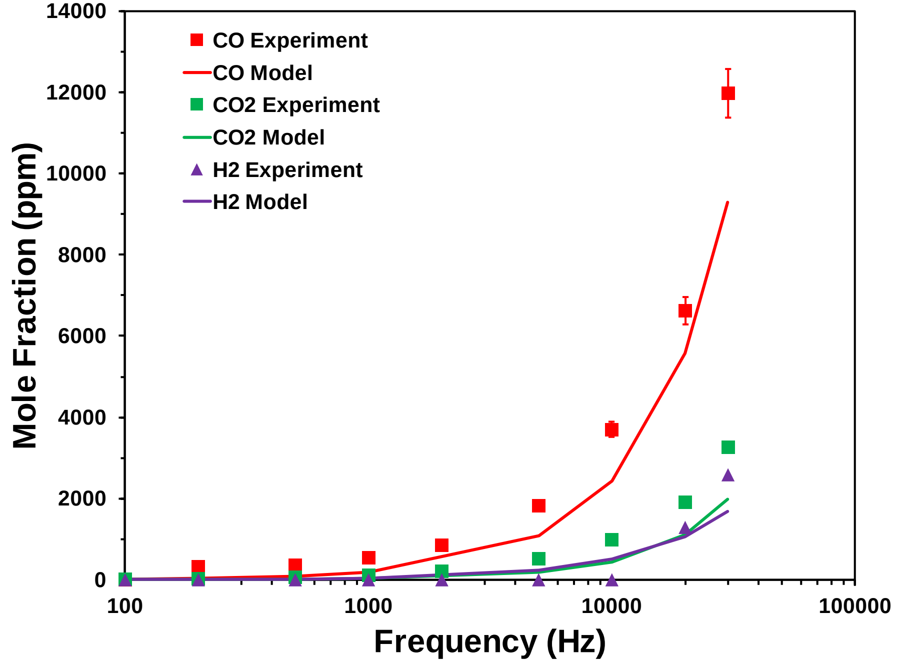
Continuous Plasma – $CH_4/O_2/He$

- Stoichiometric, 75% helium dilution, 30 kHz pulse rep. freq.
- Fuel consumption and major species agree well with model
- Disagreement with minor species



Intermediate species





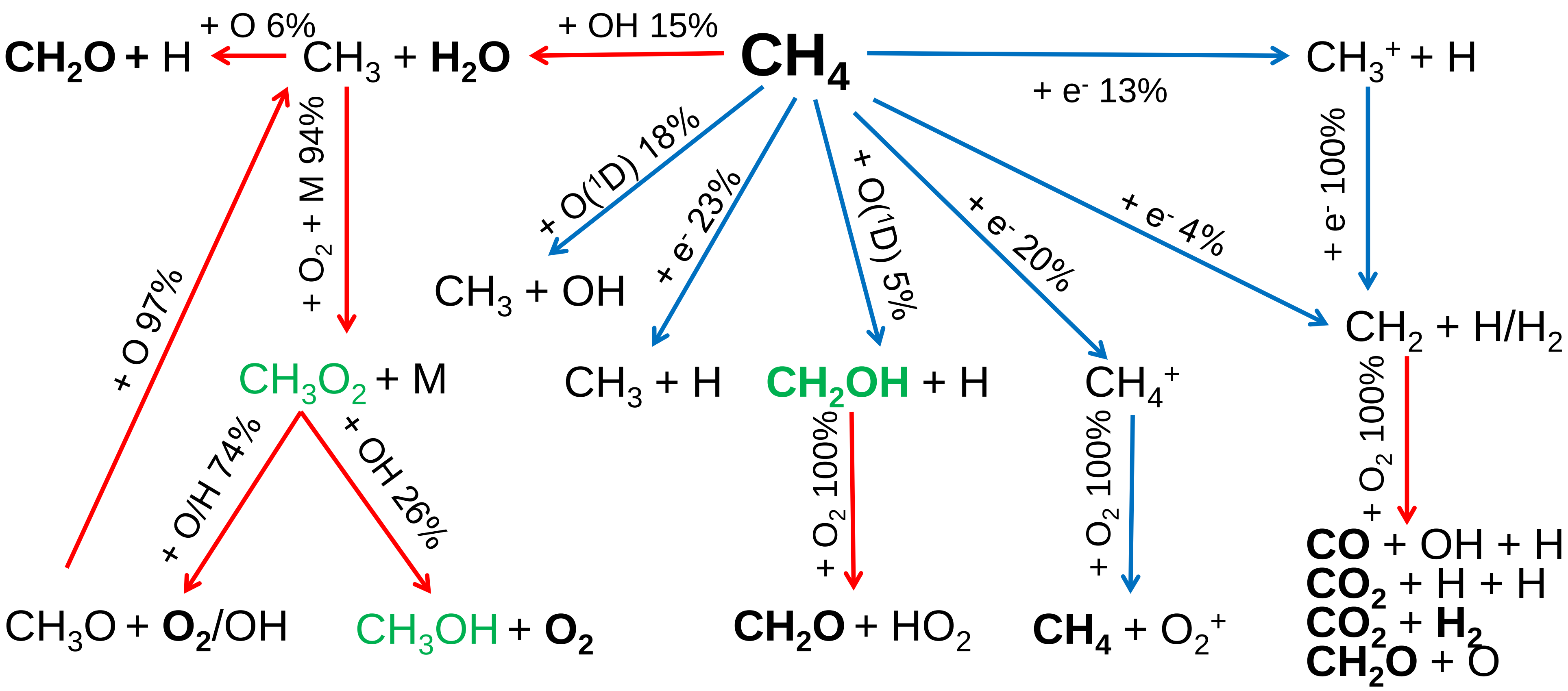


Figure 6: Path flux analysis of fuel consumption integrated over a single pulse period during continuous discharge at 30 kHz repetition frequency and steady state temperature conditions. Bold species represent those which are measured in Figure 5, red arrows refer to reactions from the combustion model, and blue arrows are from the plasma model.

Large uncertainty in low temperature oxidation pathways

In Situ Mid-IR Diagnostics and kinetic study in plasma/flow reactors (c2h4/o2)

In-situ Steady state species measurements

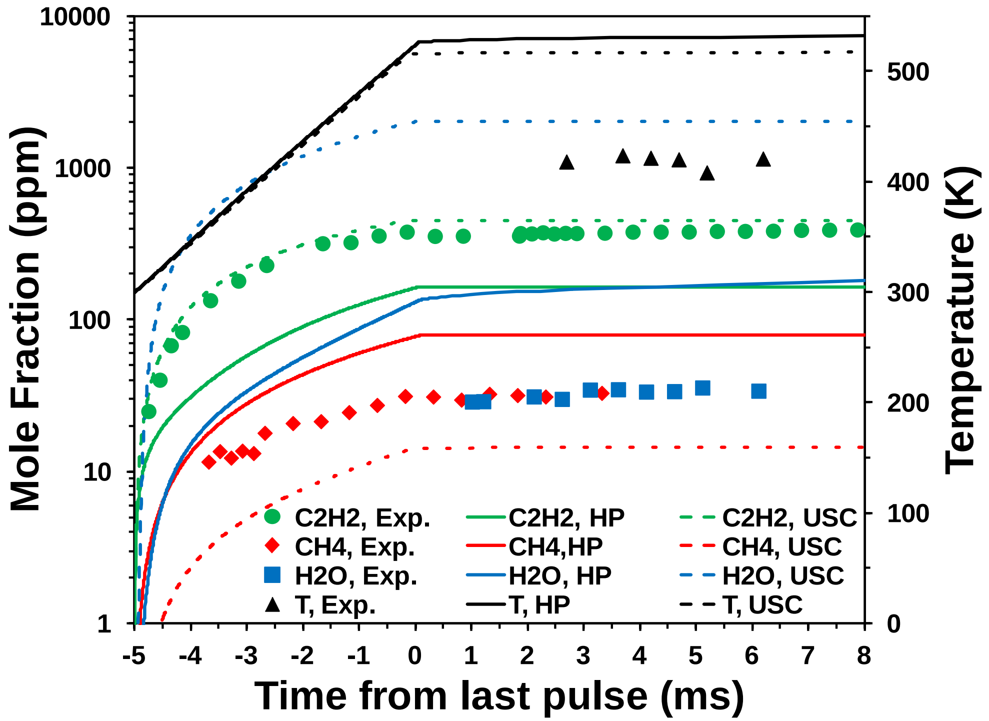
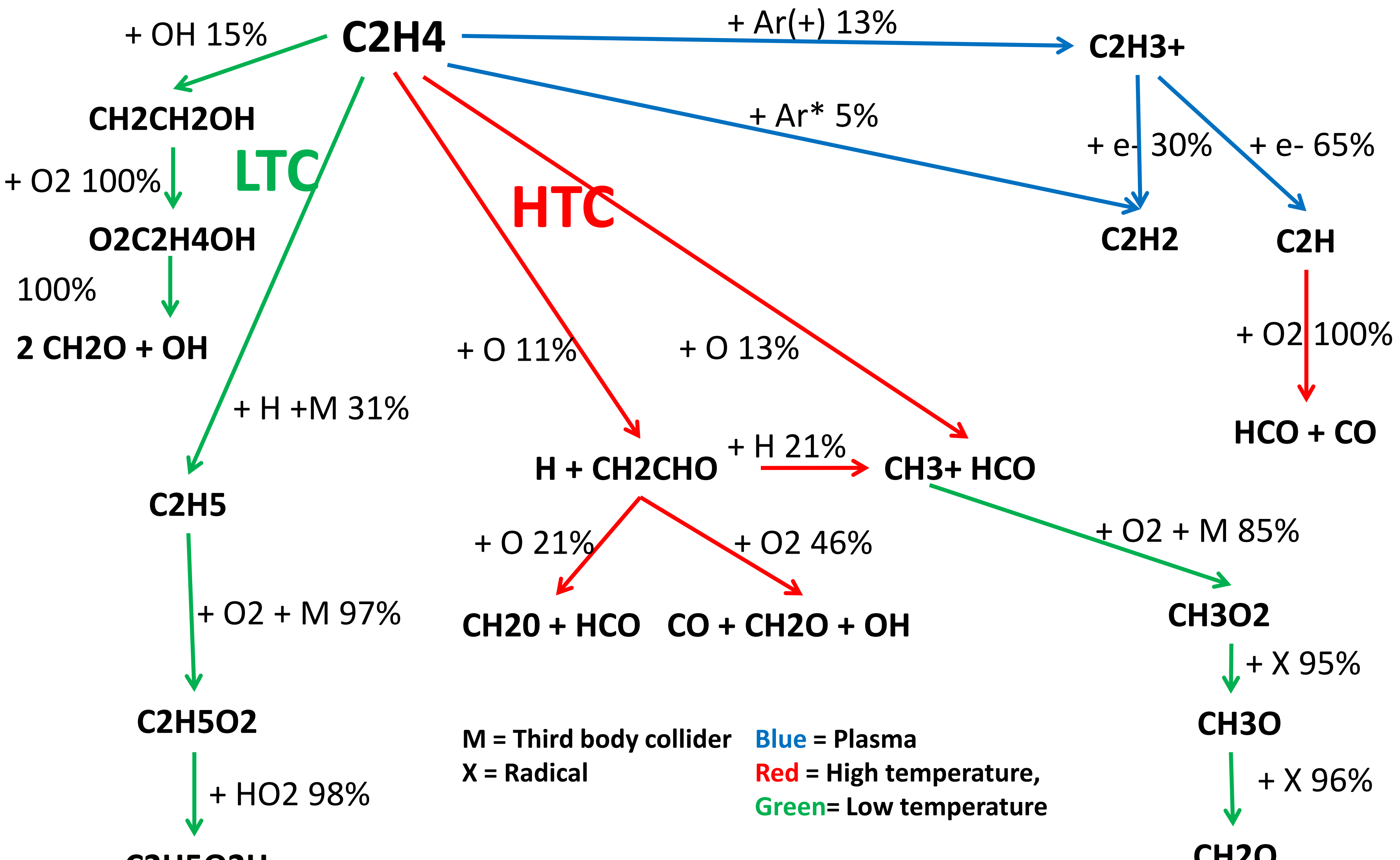


Fig. 2 Comparison of measured and predicted species (H2O, CH4, C2H2 formation in C2H4 oxidation: HP-Mech vs. USC Mech

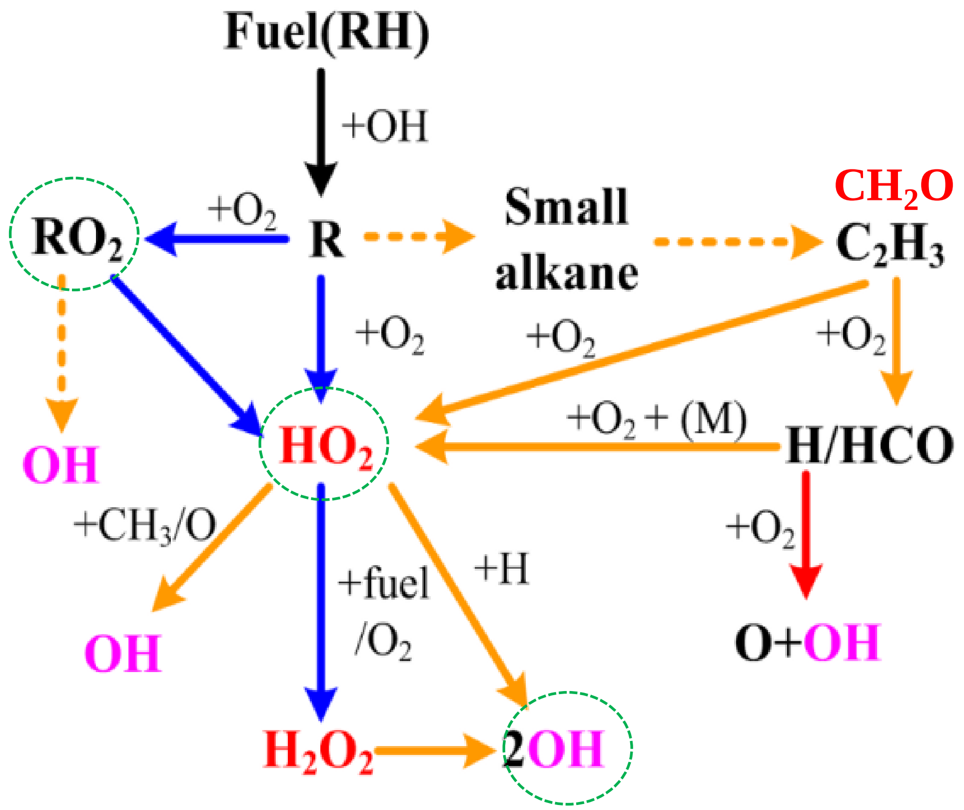
Ethylene Oxidation Pathways (C2H4/O2/Ar)



PAC activates C2H4 low temperature chemistry

Large uncertainty in low temperature oxidation pathways

Key reaction pathways in combustion kinetics at high pressure and low temperature: HO2/RO2



blue arrow: Below 700K;
yellow arrow: 700-1050 K;
red: above 1050K

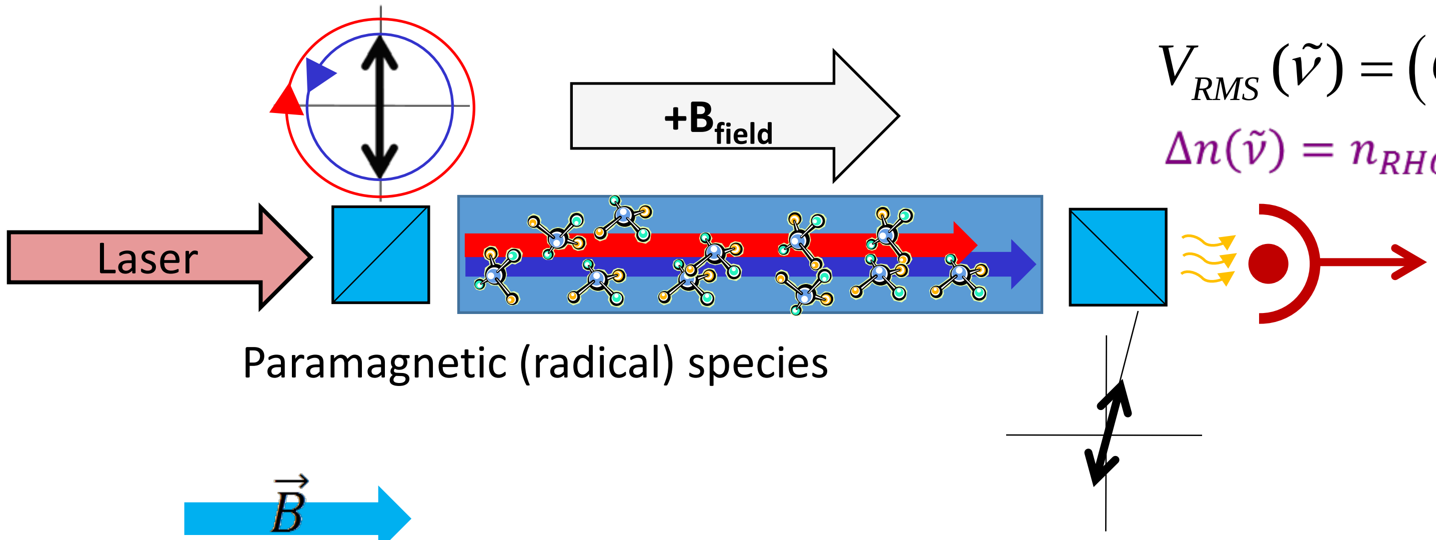
- Strong spectra overlap between HO2, H2O2, RO2 in UV and with H2O in mid-IR
- Unstable
- OH detection is limited by linebroading.

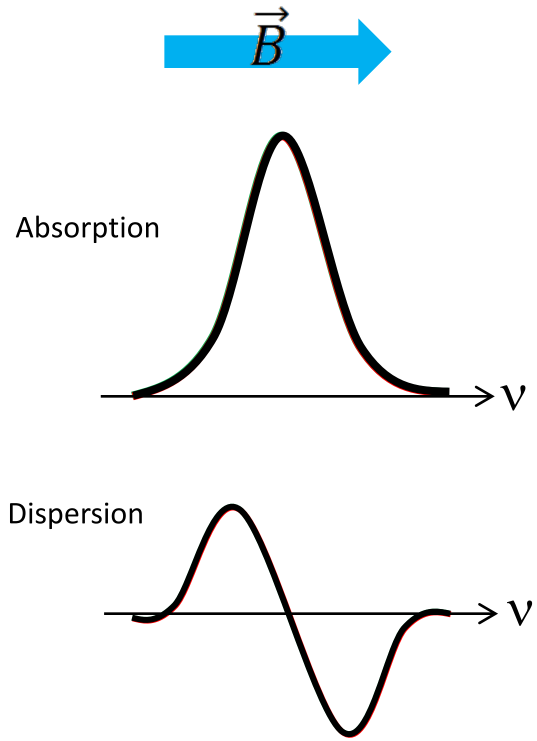
Bretfield et al., JPC letters, 2013.

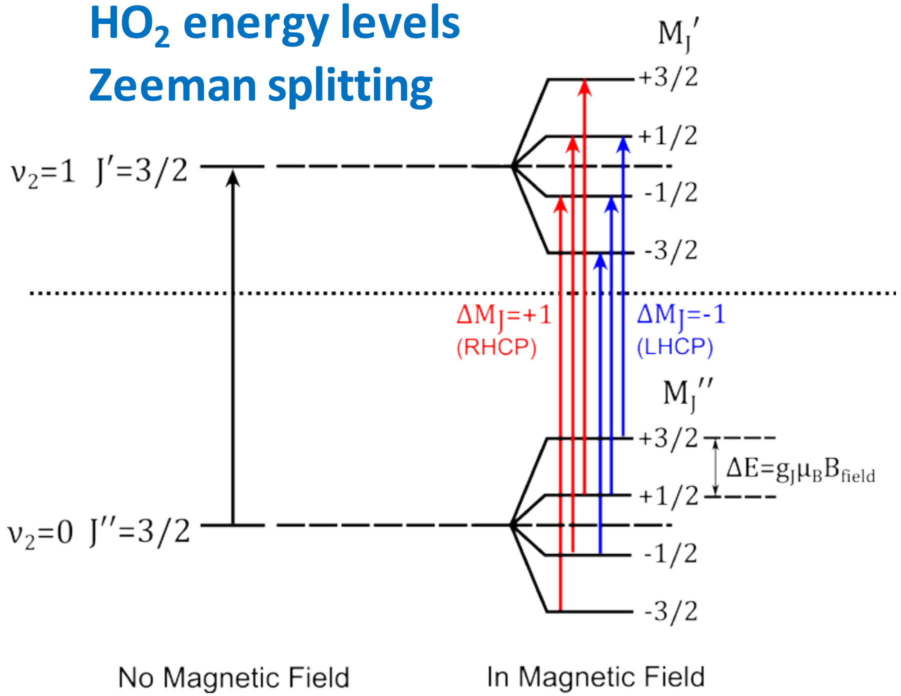
New diagnostics: HO_2/OH using mid-IR Faraday Rotational Spectroscopy

$$V_{RMS}(\tilde{\nu}) = \left(GP_0 \sin 2\theta\right)\Theta_{RMS}$$

$$\Delta n(\tilde{\nu}) = n_{RHCP}(\tilde{\nu}) - n_{LHCP}(\tilde{\nu})$$

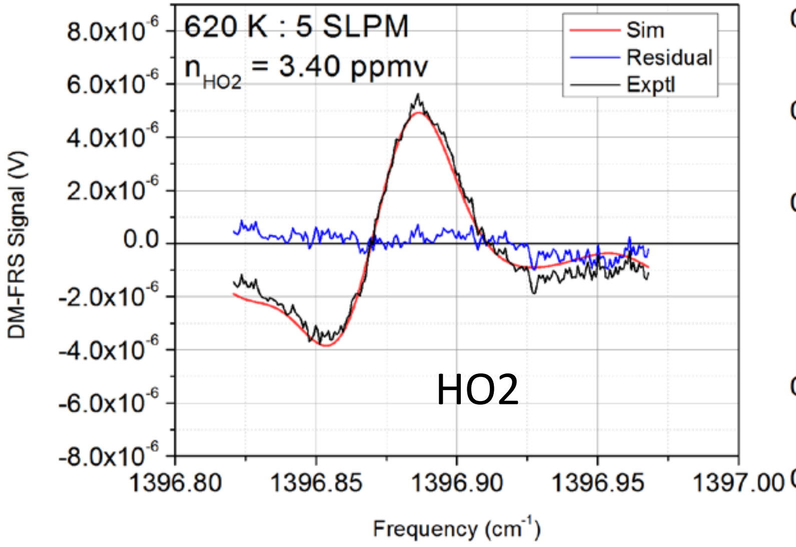


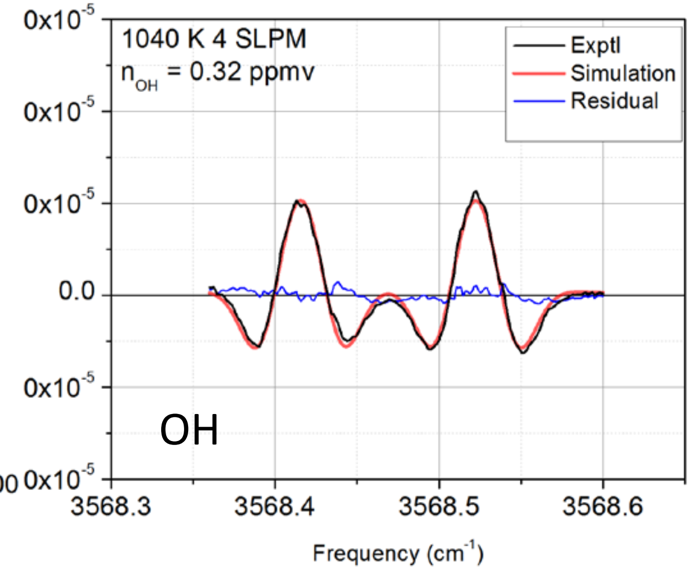




Experimental results: HO_2/OH measurements

Signal



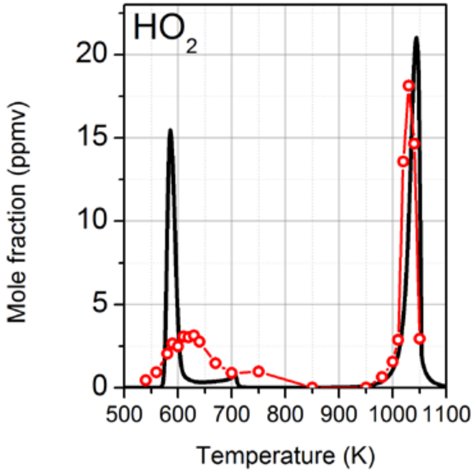


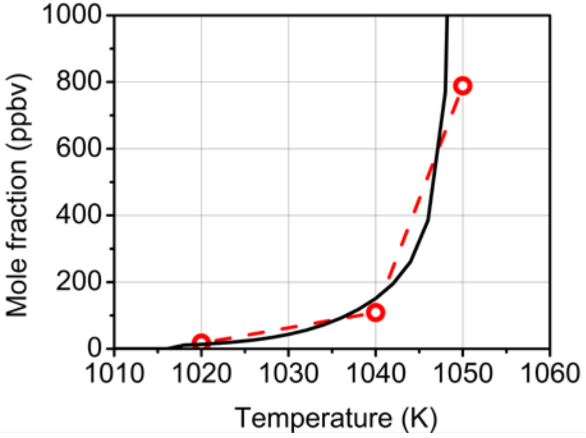
Sensitivity

σ detection limit $\approx$ 1 ppmv $/\sqrt{Hz}$

3σ detection limit = 20 ppbv $/\sqrt{Hz}$

DME flow reactor model validation





Implicatio

RO2→QOOH→O2QOOH uncertainty

HCO+O2=HO2+CO reaction uncertainty and HCO formation pathway?

Bremfield et al., 2013, JPC letters, 2013; Kurimoto et al. 2014

4. High Pressure Mechanism for Plasma Assisted Combustion (HP-Mech/plasma)

H2/H2O2/O3/CO/CH2O/CH3OH/CH4

- **Base mechanism: high pressure combustion mechanism: HP-Mech**

  H2/O2 sub-mechanism: Burke et al. 2012 (PU and ANL)

  CO/CH2O/CH3OH sub-mechanism: Labbe et al. 2014 (ANL and PU in CEFRC)

- **O3 sub-mechanism: (PU, Ombrello et al. 2010)**

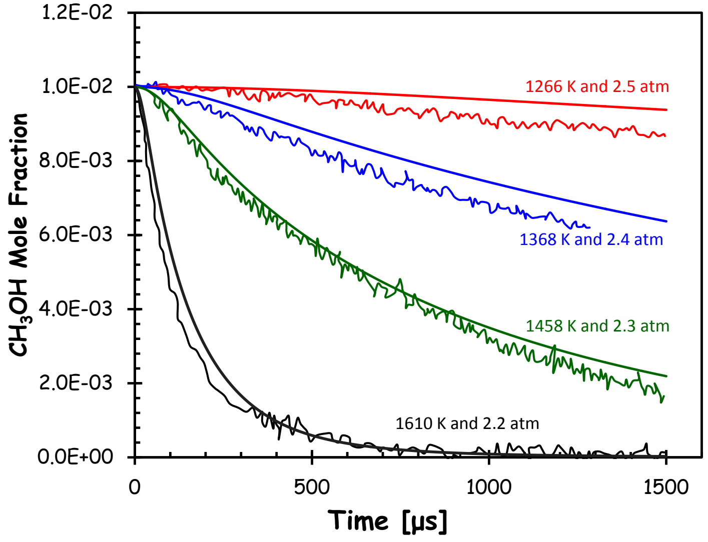
  O3 decomposition updated (J. Michael, 2013)

- **O(1D) reaction pathways**

  O(1D) + Fuels/N2/O2/CO/CO2/H2O/CH2O updated

- **O2(singlet) reaction pathways**

  O2(singlet) + Fuels/H/OH/CH3/H2/CH4 updated



- **NOx reaction pathways**

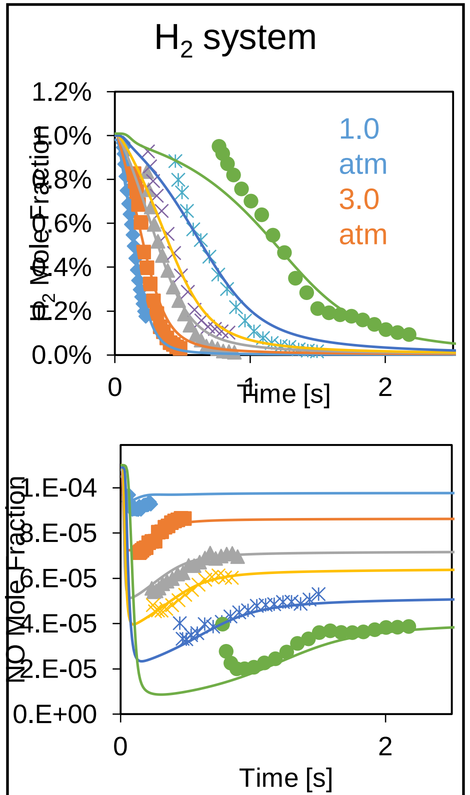
  Mueller et al., Intl. J. Chem. Kin. (1999), Vol. 31, pp. 705-724

  Allen et al., Combust. Flame (1997), Vol. 109, pp. 449-470

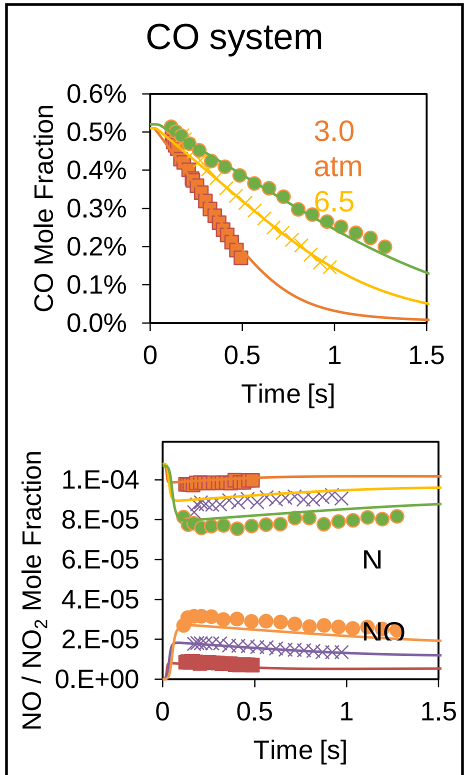
  Dean and Bozelli (2000, Gardiner ed.)

  Klippenstein, Stephen J.; Harding, Lawrence B.; Glarborg, Peter; Miller, James (2011)

Tests of NO_x chemistry in various fuel oxidation systems



T_{ini} = 807 K
1% H_2, 2% O_2, 108 ppm NO, balance N_2
Experimental measurements at various points in flow reactor (Mueller et al., 1999)



T_{ini} = 952 K
0.5% CO, 0.75% O_2, 0.5% H_2O,
108 ppm NO, balance N_2
Experimental measurements at various points in flow reactor (Mueller et al., 1999)

•Mueller et al., Int. J. Chem. Kin. 31 (1999), pp. 705-724

Collaborating with Richard Yetter, 2014

Plasma Modeling Tool Development

ZDPlasKin

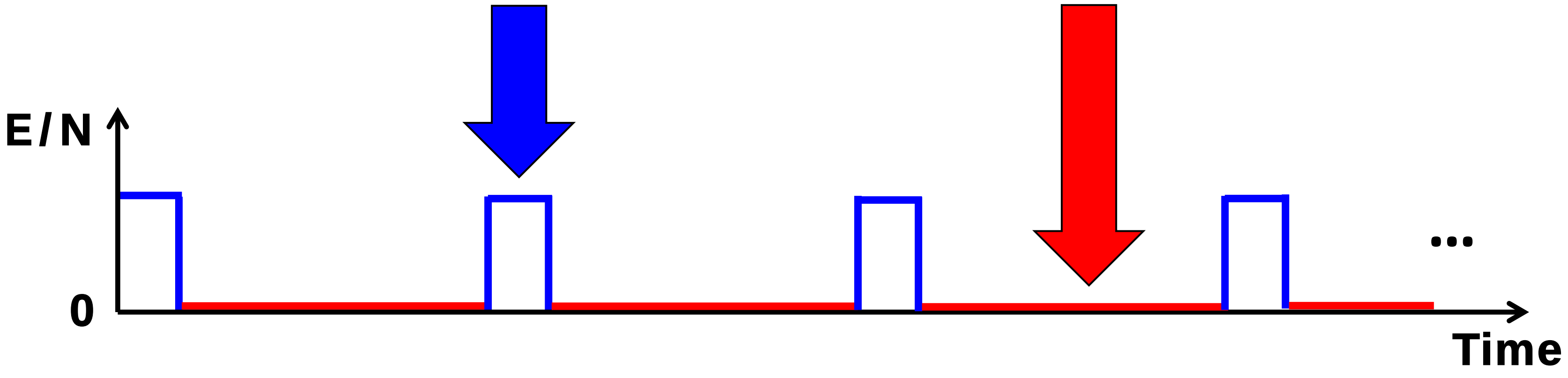
$$\frac{dN_i}{dt} = \sum_{j=1}^{j_{max}} Q_{ij}(t)$$

$$\frac{1}{\gamma - 1} k_B \frac{d(NT_{gas})}{dt} = P_{ext} - P_{elec} - P_{chem}$$

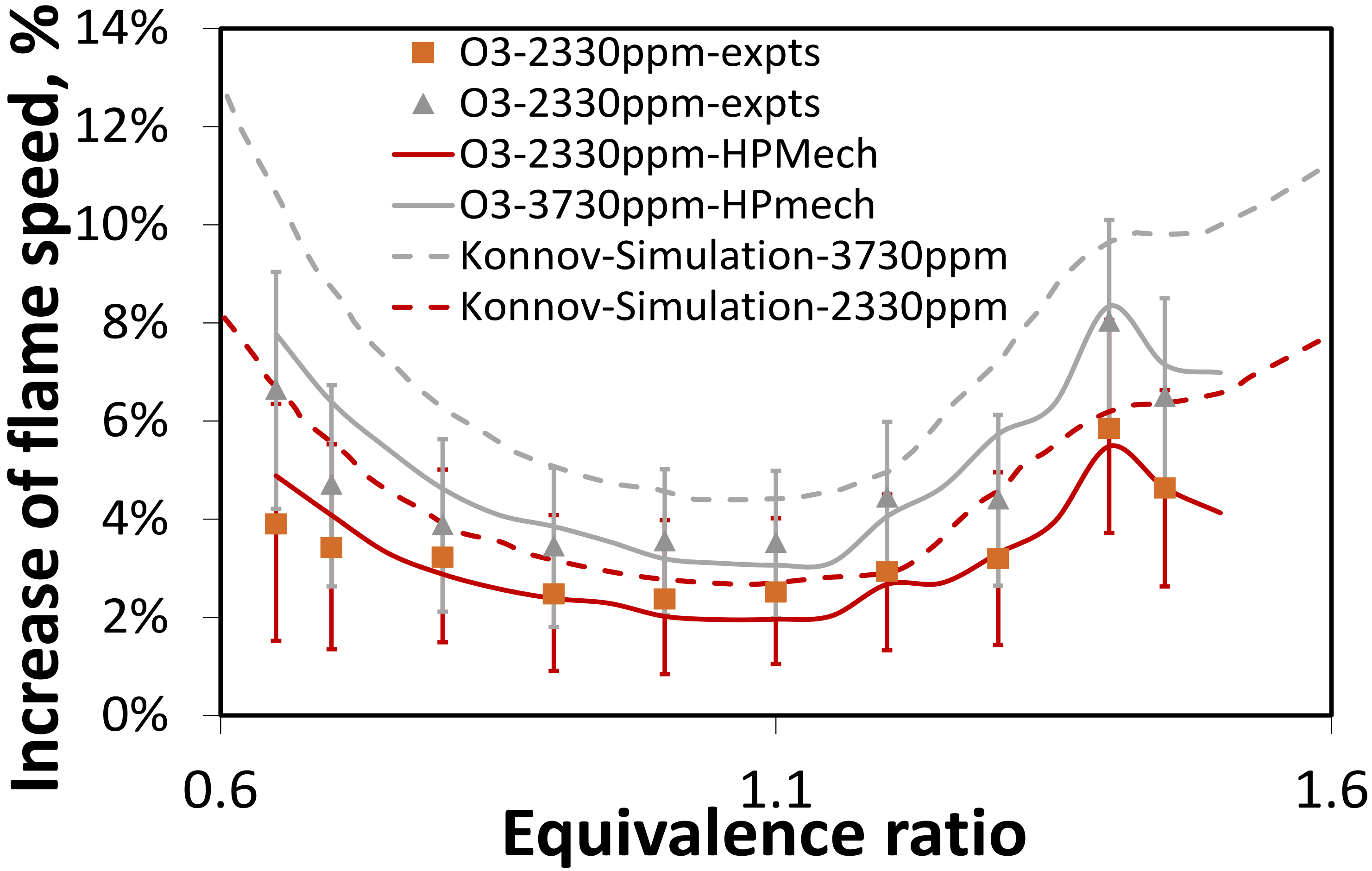
CHEMKIN II - SENKIN

$$\rho \frac{dY_k}{dt} = \omega_k W_k$$

$$\rho C_V \frac{dT}{dt} = -\sum_{k=1}^{K} e_k \omega_k W_k$$



HP-Mech/plasma validation: Ozone effect on flame speeds



Conclusions

1. This MURI program is a very exciting exploration of knowledge frontier.

2. Plasma activated Self-Sustaining diffusion and premixed Cool Flames & mild combustion were established for the first time. Creating exciting opportunities in engine and fuel applications.

3. Plasma has a strong kinetic effect in low temperature combustion. A direct ignition transition to flame without extinction limit was observed.

4. New diagnostic method (e.g. FRS) for in-situ and time accurate measurements of intermediate species and HO2 radicals was developed. Plasma active low temperature chemistry via CH2O and RO_2 is an important fuel oxidation pathway at low temperature.

5. Plasma combustion chemistry remains a big challenge, especially at low temperature. The existing plasma kinetic mechanism is not able to predict appropriately the plasma activated low temperature kinetics.

Publications and Awards:

Journal Publications

1. Ju, Y. and Sun, W., (2015), Plasma Assisted Combustion: Dynamics and Chemistry, **Progress of Energy Science and Combustion**, 2015.
2. Ju, Y. and Sun, W., (2015), Plasma Assisted Combustion: Challenges and Opportunities, **Combust. Flame**, 2015. Invited opinion paper.
3. Peng Guo; Timothy Ombrello, Sang Hee Won, Christopher A Stevens, John L Hoke, Frederick Schauer, Yiguang Ju, Schlieren Imaging and Pulsed Detonation Engine Testing of Ignition by a Nanosecond Repetitively Pulsed Discharge, submitted to **Combust. Flame**, 2015.
4. Lefkowitz, J.K., Uddi, M., Windom, B., Lou, G.F., Ju, Y. (2015), *In situ* species diagnostics and kinetic study of plasma activated ethylene pyrolysis and oxidation in a low temperature flow reactor, **Proceedings of Combustion Institute**, 35, 2015.
5. Won, S.H., Jiang, B., Diévart, P., Sohn, C.H., Ju, Y., (2015), Self-Sustaining n-Heptane Cool Diffusion Flames Activated by Ozone, **Proceedings of Combustion Institute**, 35, 2015
6. Brumfield, B., Sun, W., Wang, Y., Ju, Y., and Wysocki, G. (2014), Dual Modulation Faraday Rotation Spectroscopy of HO2 in a Flow Reactor, **Optics Letters**, Vol. 39, Issue 7, pp. 1783-1786 (2014).

Awards:

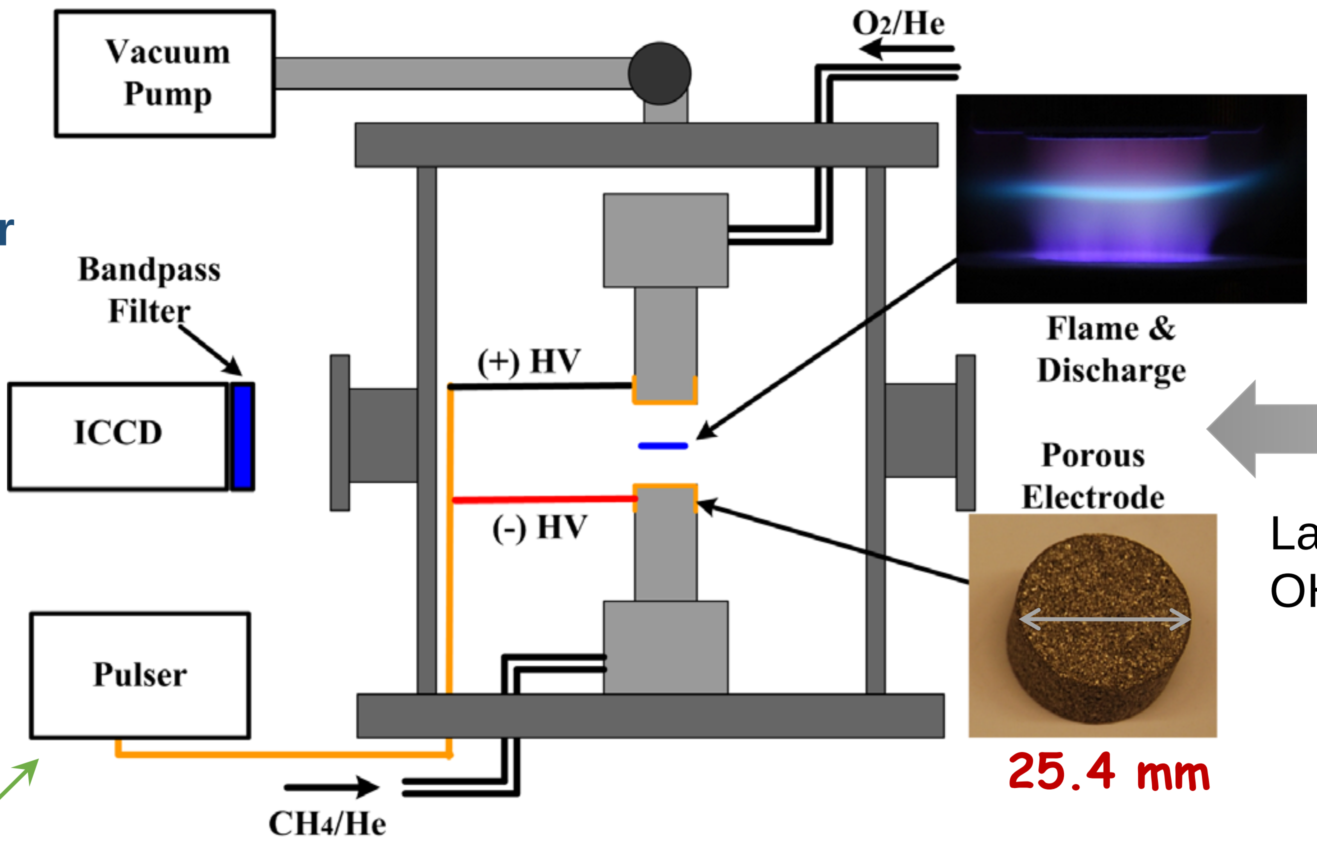
1. **Distinguished Paper Award** of the 35th International Symposium on Combustion: "Self-Sustaining n-Heptane Cool Diffusion Flames Activated by Ozone"
2. **Plenary Lecturer**, The 8th International Conference on Reactive Plasmas, Fukuoka, Japan, 2014.

5. Future research

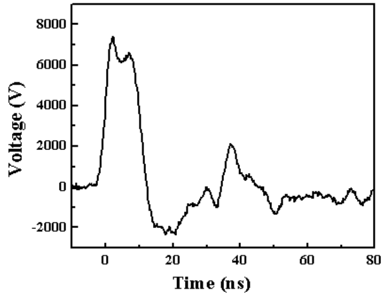
- **Plasma combustion kinetic mechanism development**
- **Time accurate species and plasma property measurements**
- **Low temperature Fuel oxidation kinetics involving O(1D), HO2, O3, O2(1Δ) in photolysis and flow reactor (0.1-2 atm)**
- **High pressure plasma assisted cool flames (1-10 atm)**

3. Plasma assisted low temperature combustion
Methane vs. Dimethyl ether (DME)

P = 72 Torr
f = 24 kHz



Laser beam
OH, CH_2O PLIF

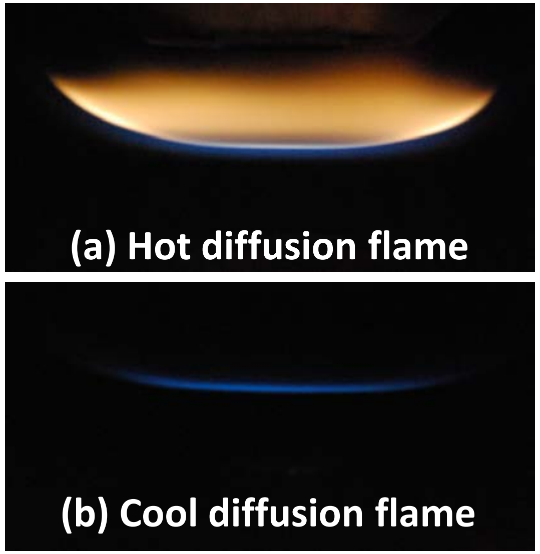


Peak Voltage = 7.8 KV

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

Power ~ 17 W (repetitive pulses)

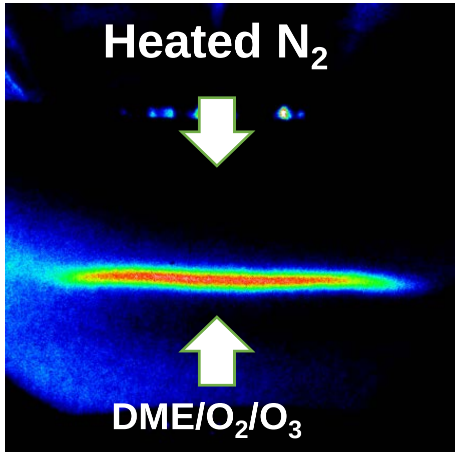
1. Plasma assisted *Cool Flames and Mild Combustion:*



N-heptane
Normal diffusion flame
T_f~1900 K

Cool diffusion flame
T_f~650 K

Fig. 1 Plasma assisted normal and cool diffusion flames



Direct chemi-luminescence image of cool premixed flame by ICCD camera for $DME/O_2/O_3$ mixture (φ = 0.104)

Fig.2 Plasma assisted cool premixed flame (DME)

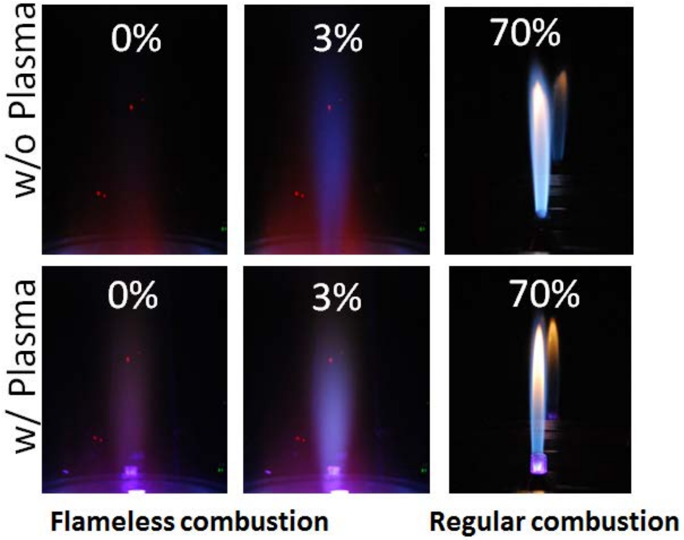
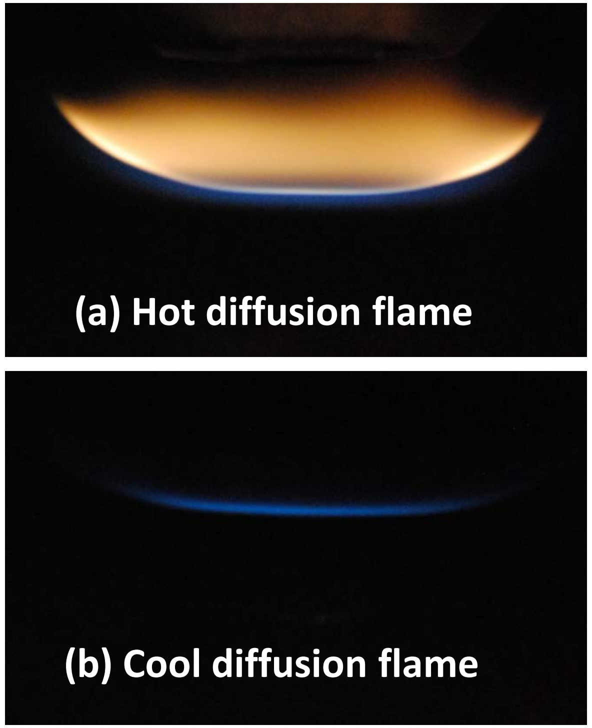


Fig.3 Plasma assisted mild combustion (methane diluted by N2)

1. Plasma activated *Cool Flames: n-heptane-air*



T_f~1900 K

T_f~650 K

Fig. 1 Hot and cool n-heptane diffusion flames at the same condition

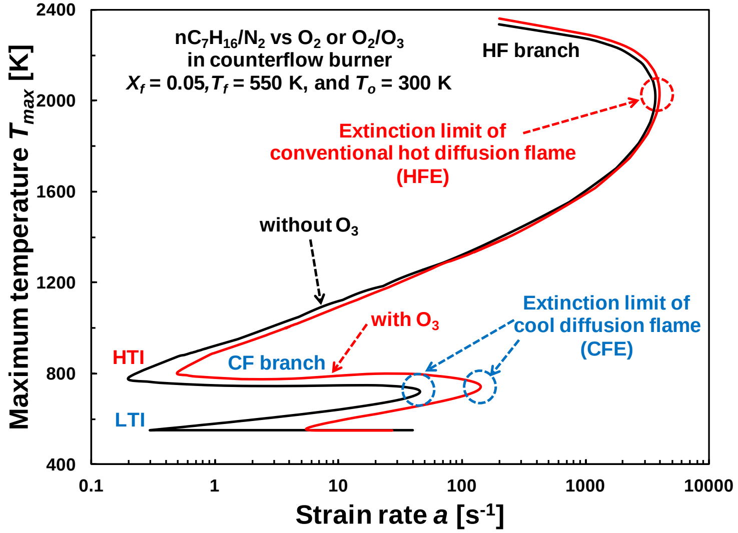


Fig. 2 Ozone (red line) extends the burning liit of cool flames

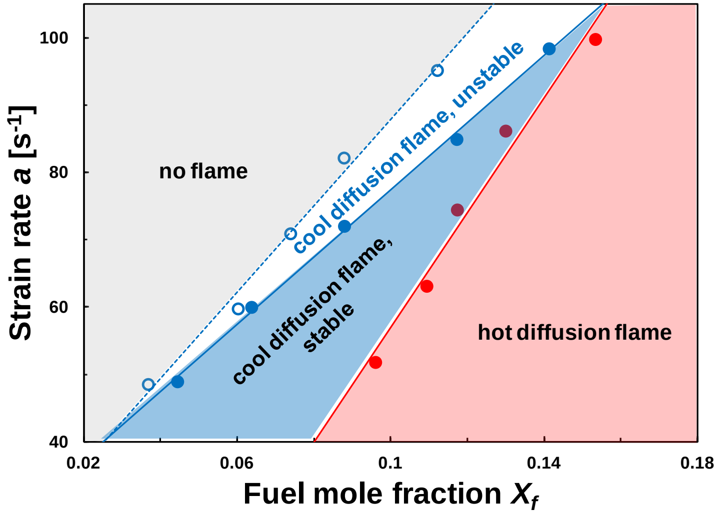
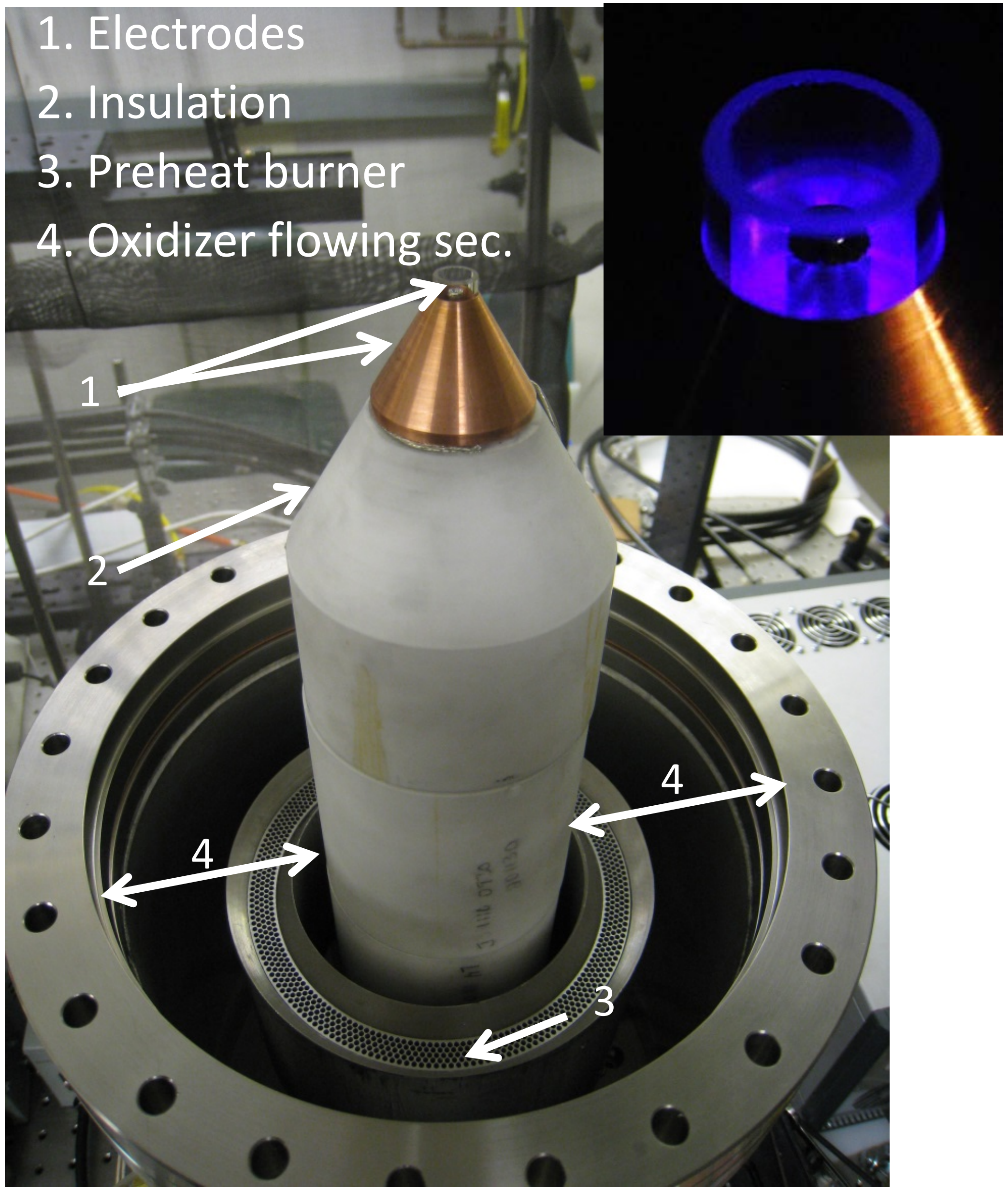


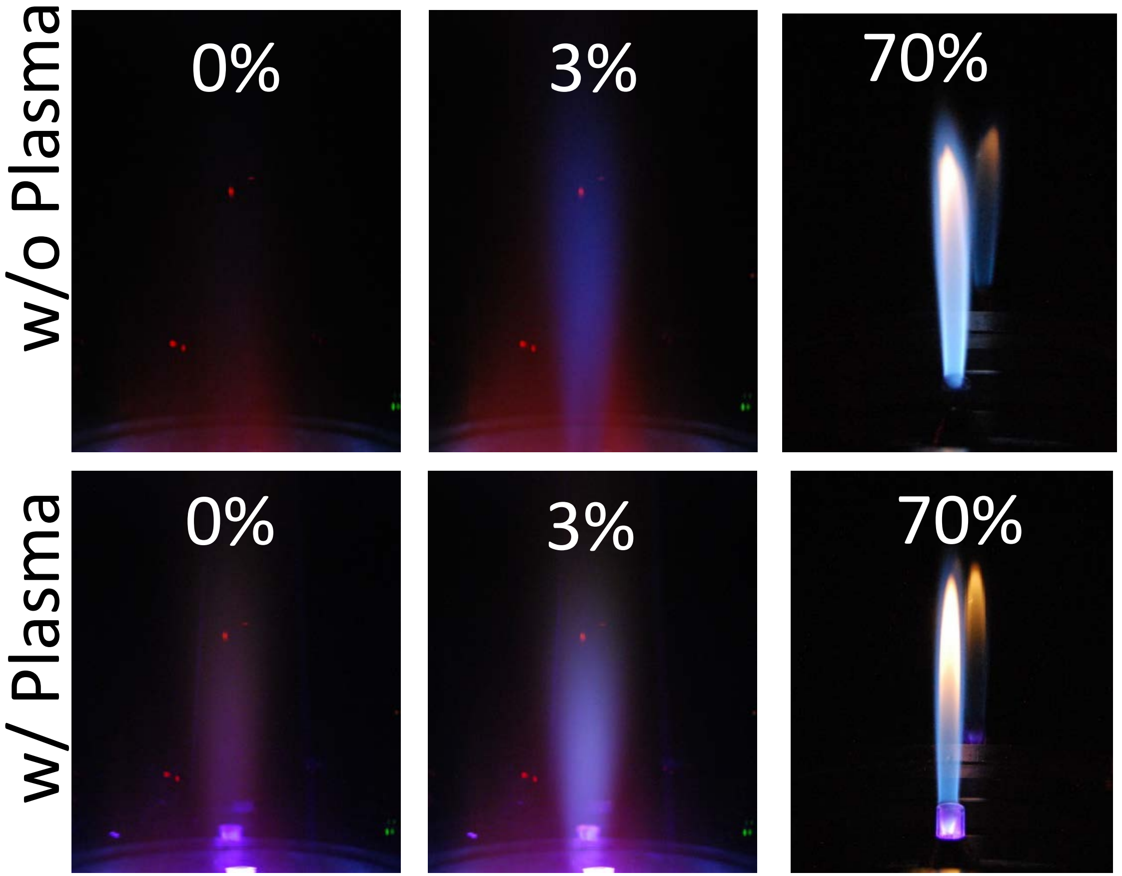
Fig. 3 Diagram of hot flame (pink), stable cool flame (blue), and unstable cool flame (white)

Plasma makes cool flame to be observed at 1 atm at 10 ms timescale.

2. Plasma assisted flameless (MILD) combustion



- Tested conditions
  - Preheat: 1050 K (including 12% O_2)
  - Center burner CH_4/N_2 and vel.: 10-70% and **5-40 m/s**
  - Flame structure change with CH4% in plasma reactor



Flameless combustion **Regular combustion**

3. In Situ Mid-IR Diagnostics and kinetic study in plasma/flow reactors

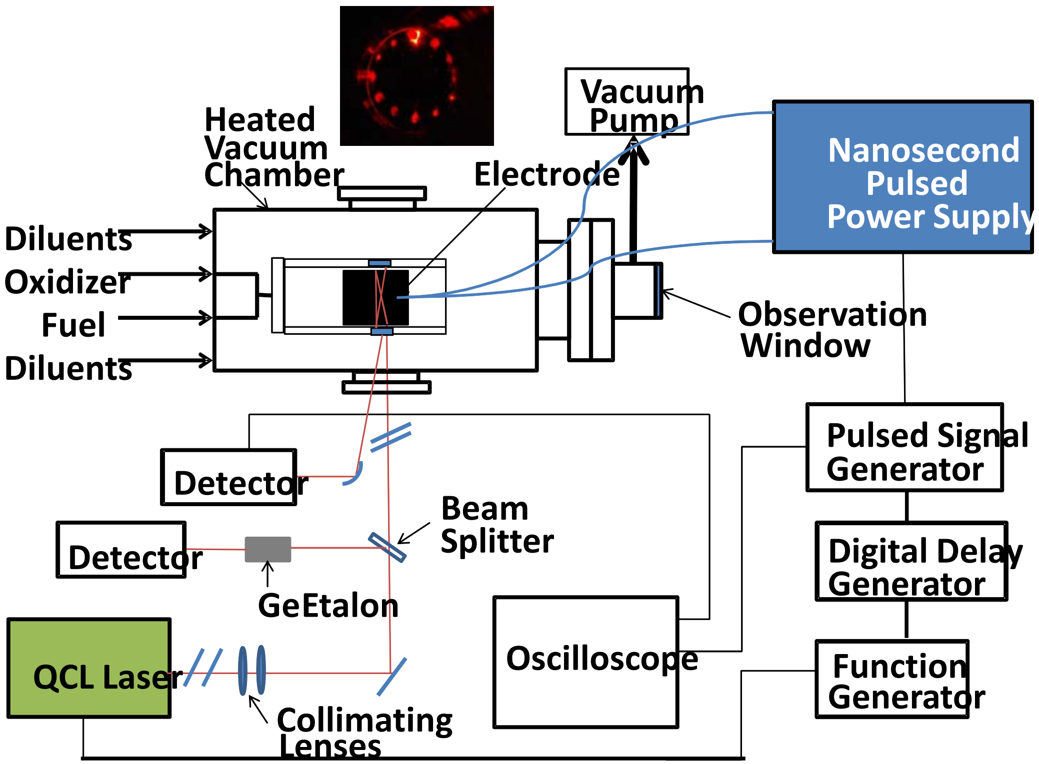


Fig. 1 Experimental setup of plasma reactor and IR-Herriot cell

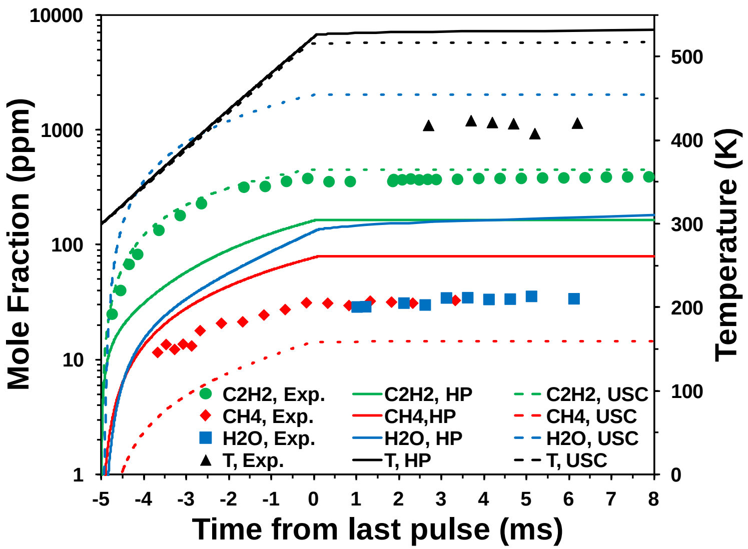


Fig. 2 Comparison of measured and predicted species (H2O, CH4, C2H2 formation in C2H4 oxidation: HP-Mech vs. USC Mech

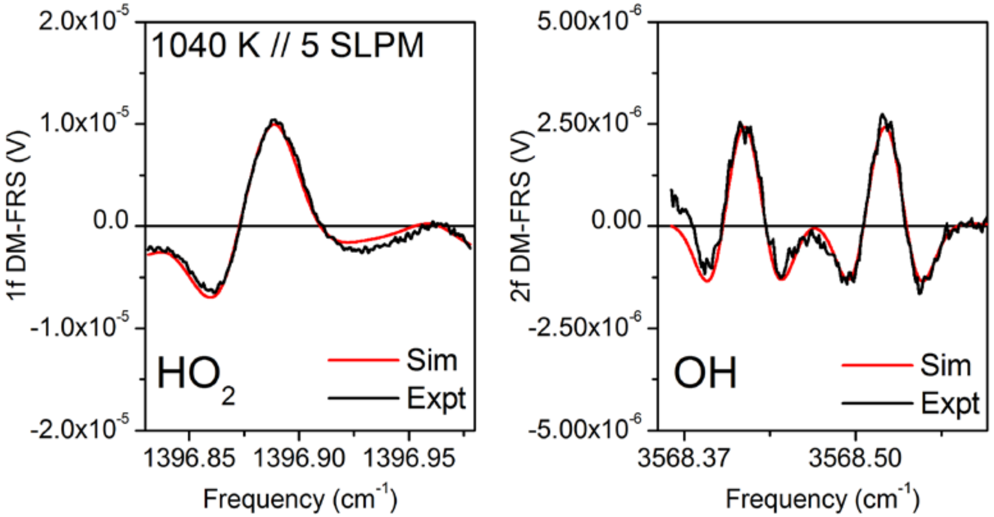


Fig. 3 OH and HO2 diagnostics in DME flow reactor by using Faraday rotational spectroscopy. Predicted and measured signals.

In situ diagnostics of H2O, CH4, C2H2, OH, and HO2 measurements were conducted by using mid-IR absorption and FRS.

4. Development of high pressure mechanism (HP-Mech) for plasma assisted combustion

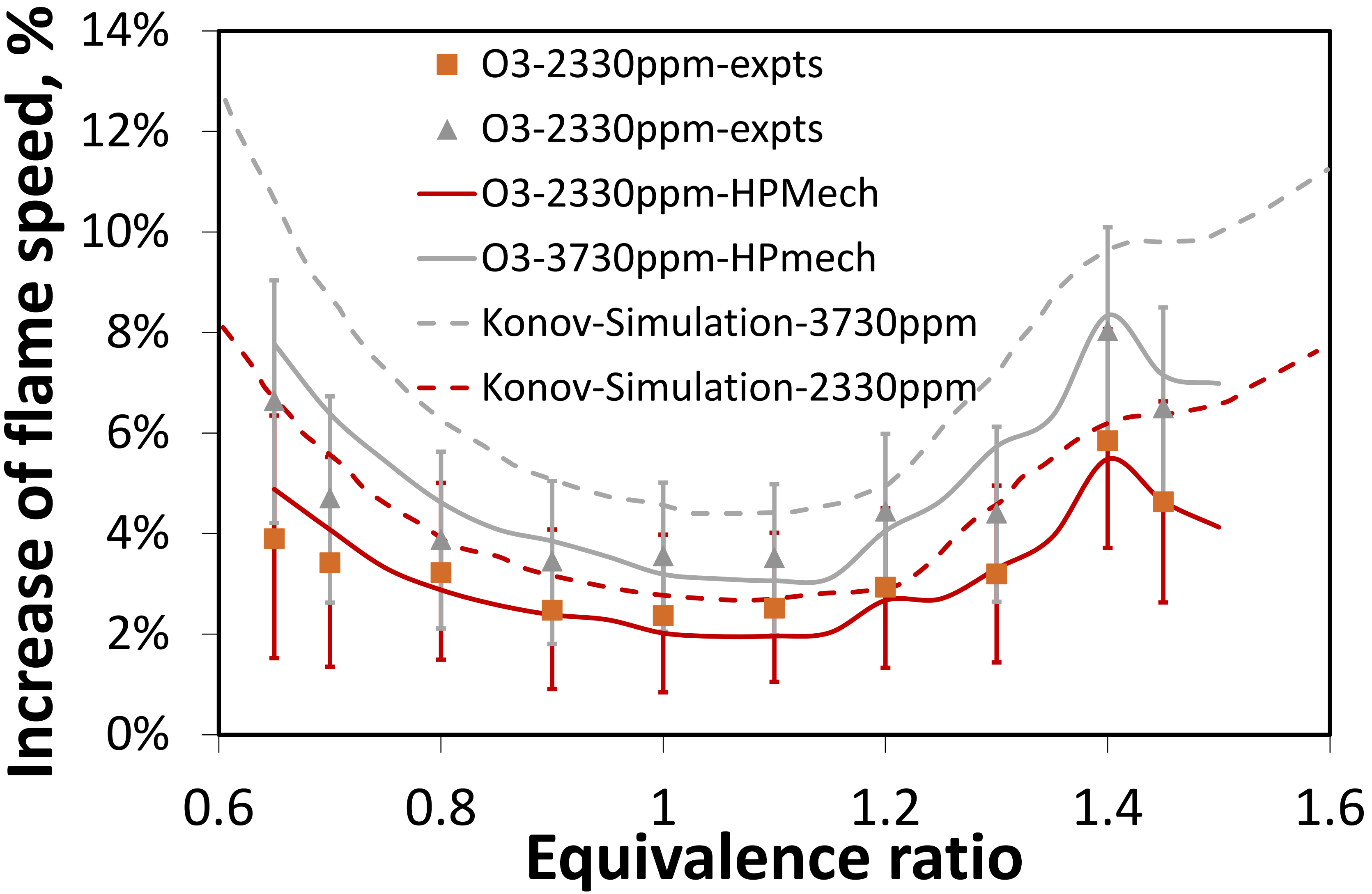


Fig.1 Comparison of predicted flame speed increase (percentage) by O3 addition in methane/air flame (HP-Mech vs. Konov)