

Plasma Assisted Combustion: Flame Regimes and Kinetic Studies

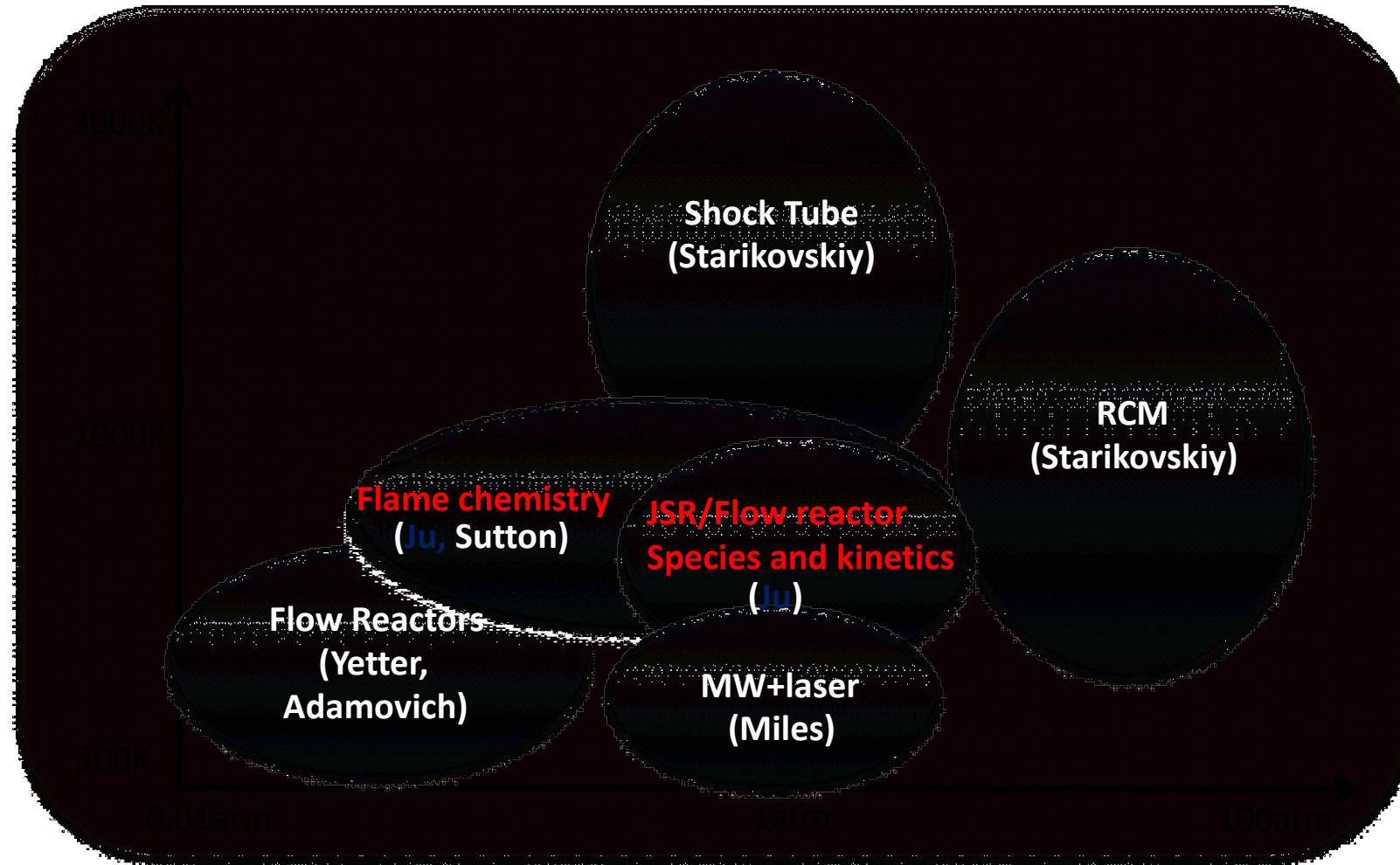
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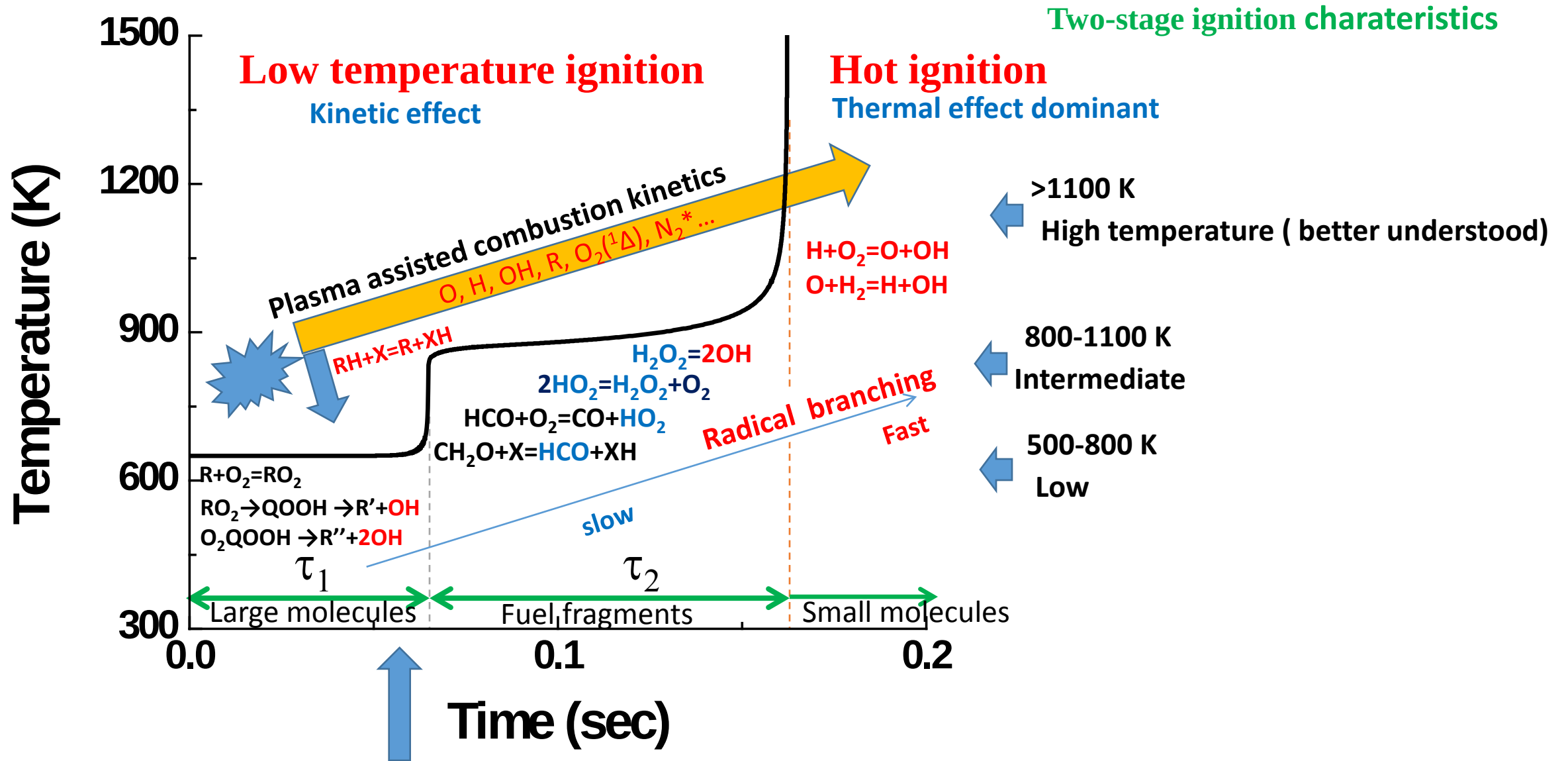
MURI Facility Summary and collaborative team structure



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

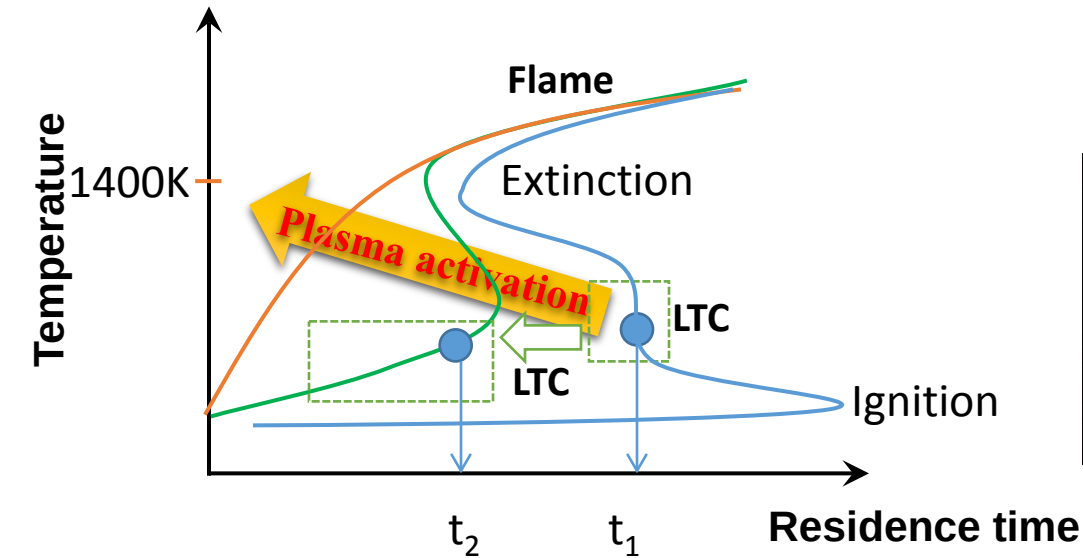
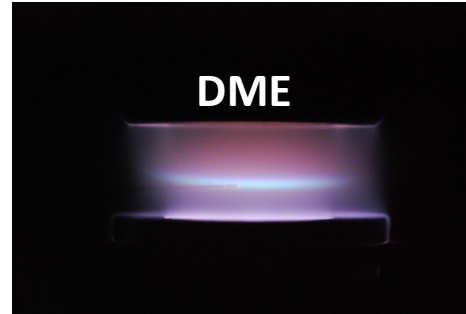


Plasma has more kinetic enhancement effect in lower temperature combustion
However, poorly studied and understood...

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

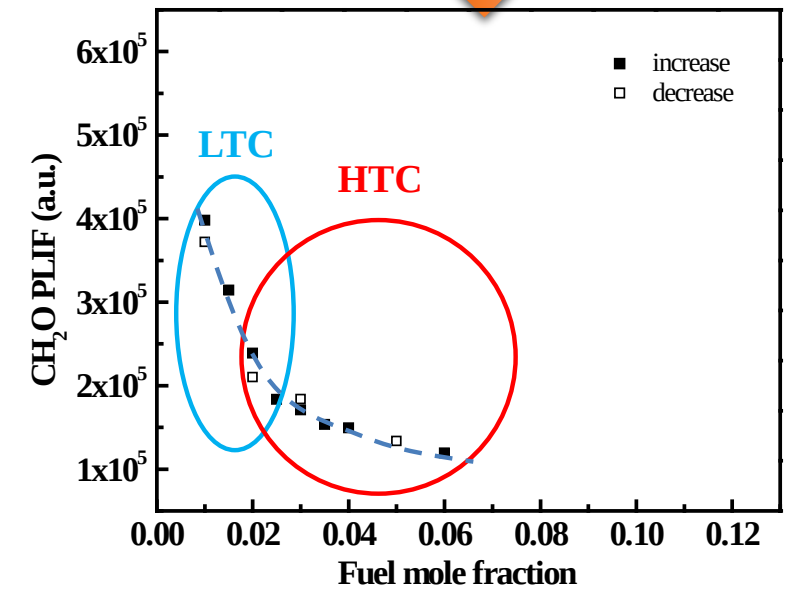
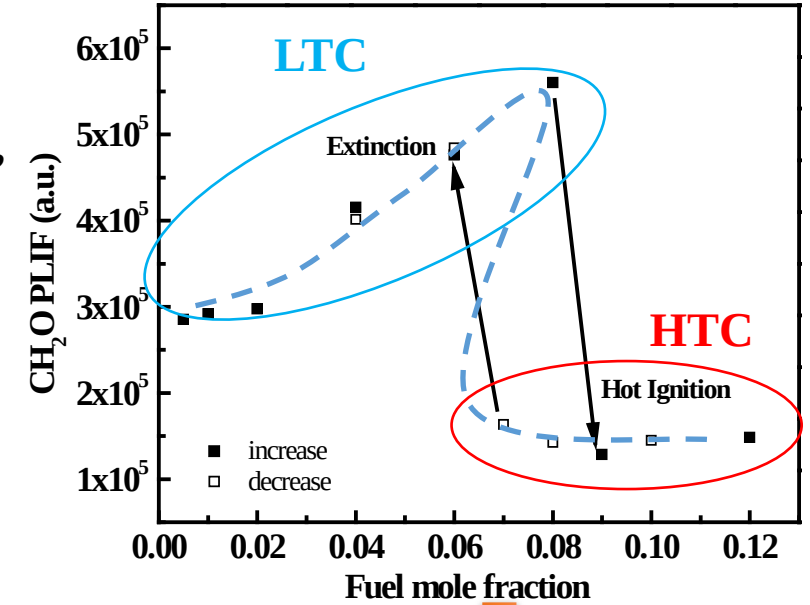
Plasma assisted low temperature

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

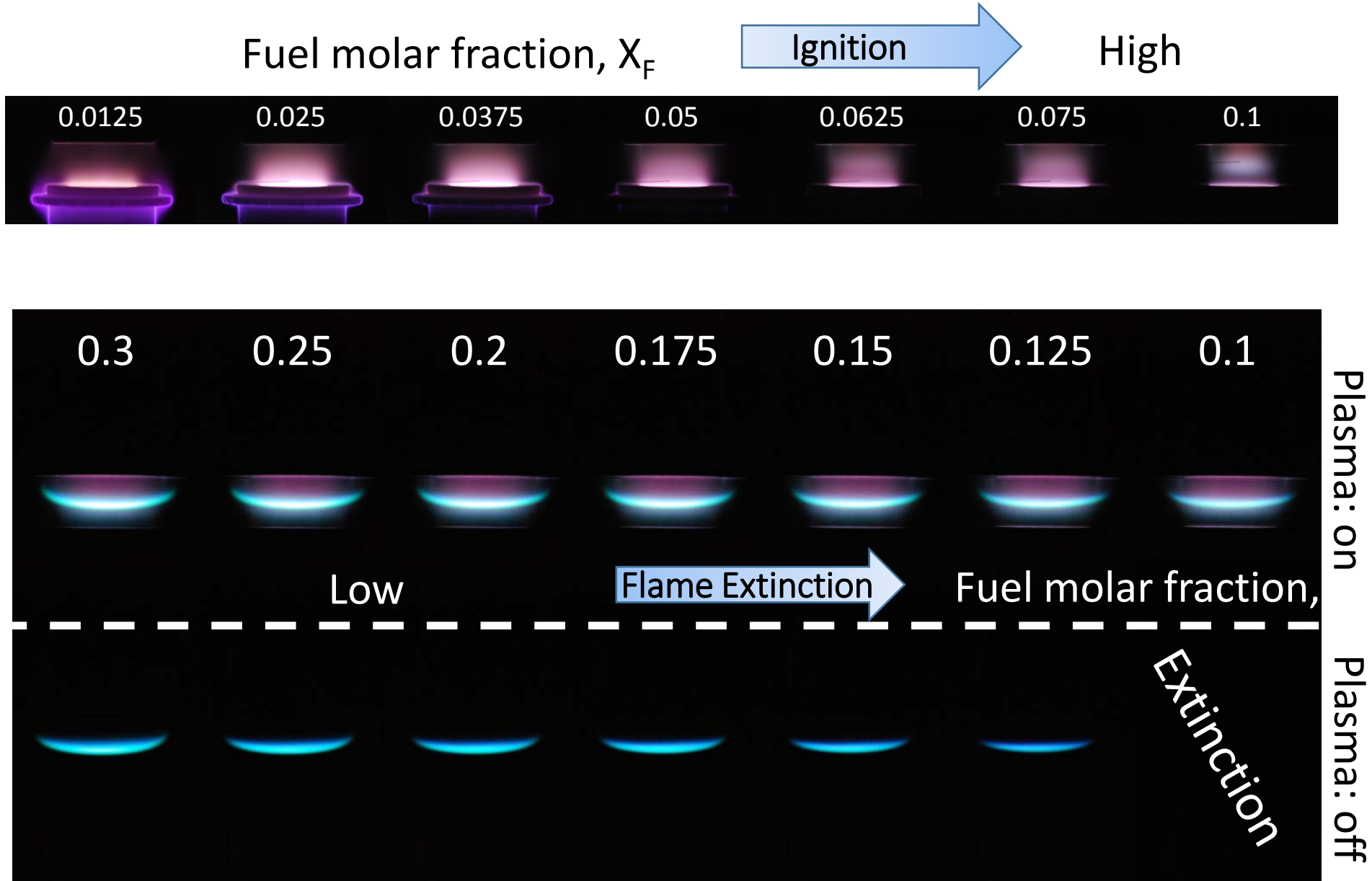


$t_2 \ll t_1$
 So it occurs in ms or even
 without an extinction limit!

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

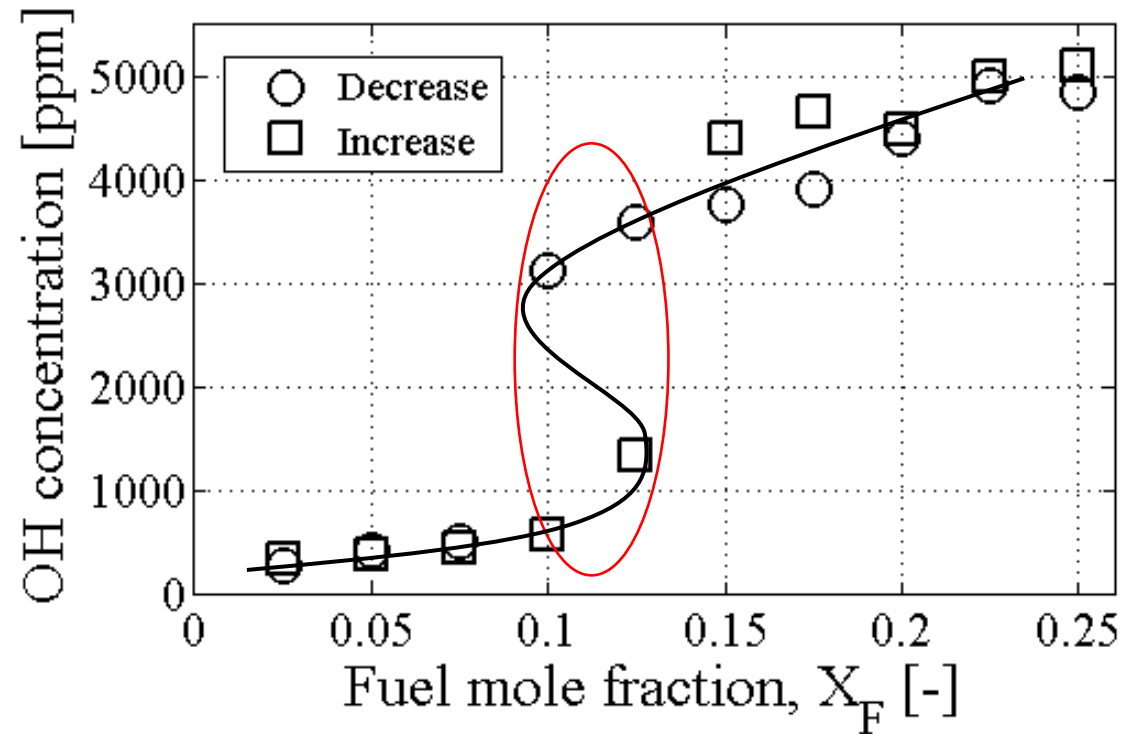


1.1 Plasma activated low temperature combustion: n-heptane



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

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



Flame

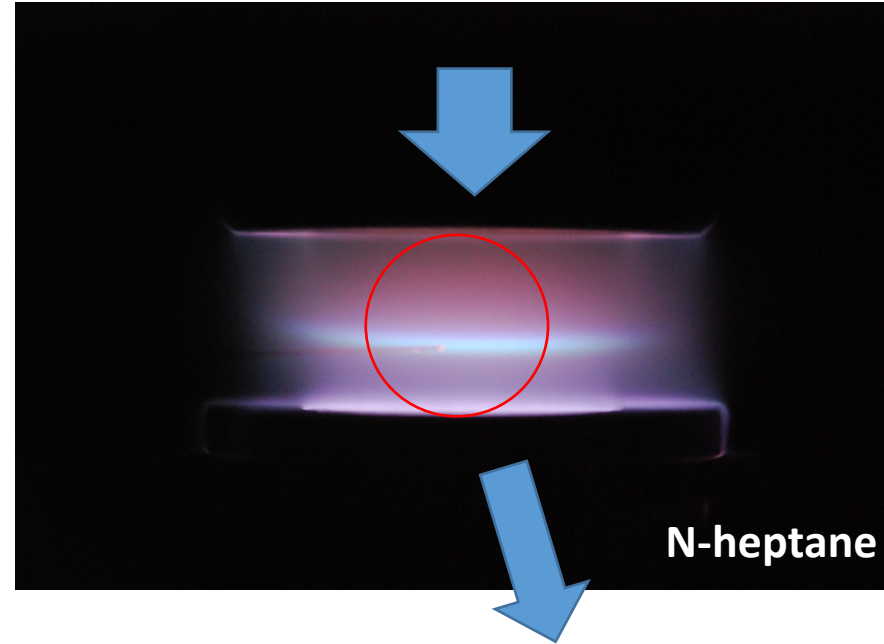
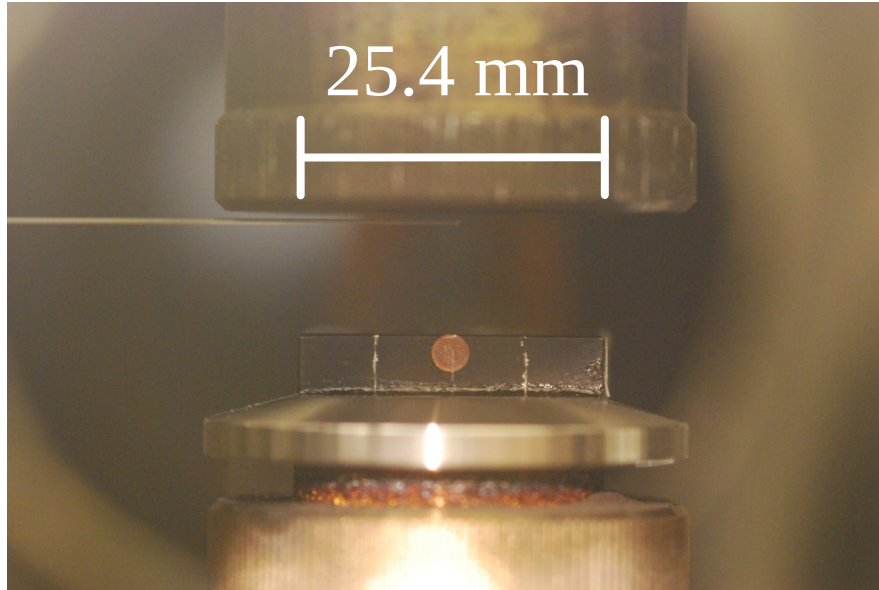


Ignition



- 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



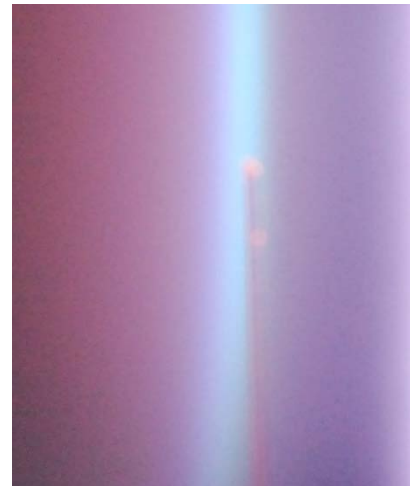
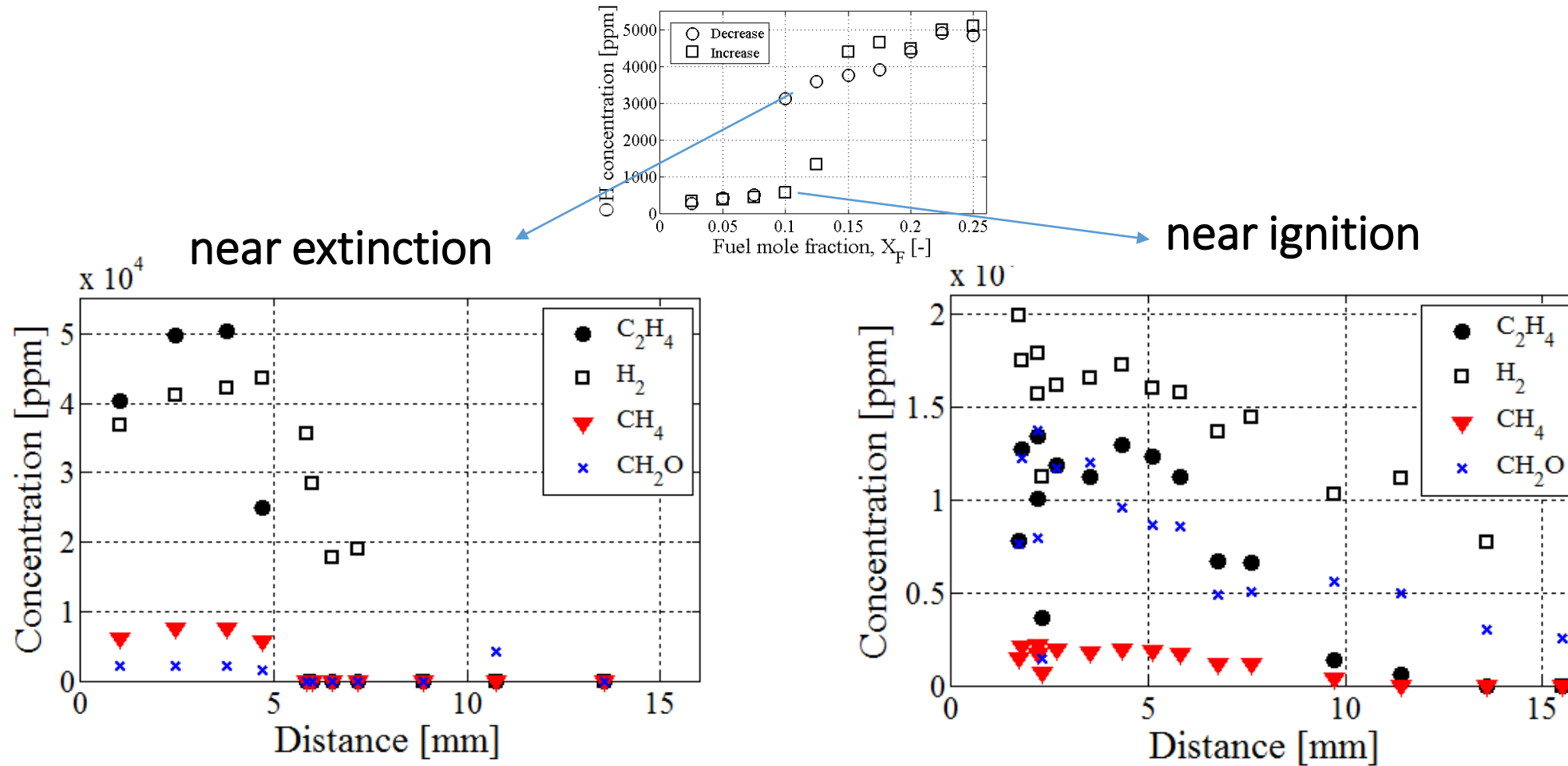
- Probe O.D.: 363 μm
- Adjust position (Vert. & horiz.)
- Negligible influence on the flame



Species distribution near ignition and extinction

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

Providing validation targets

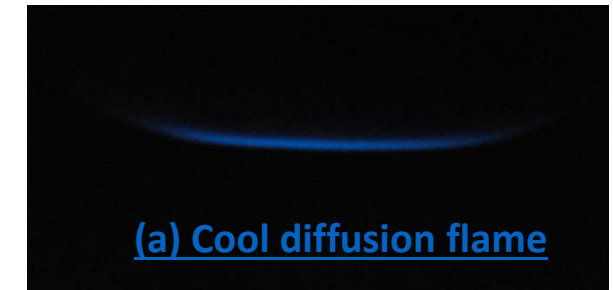
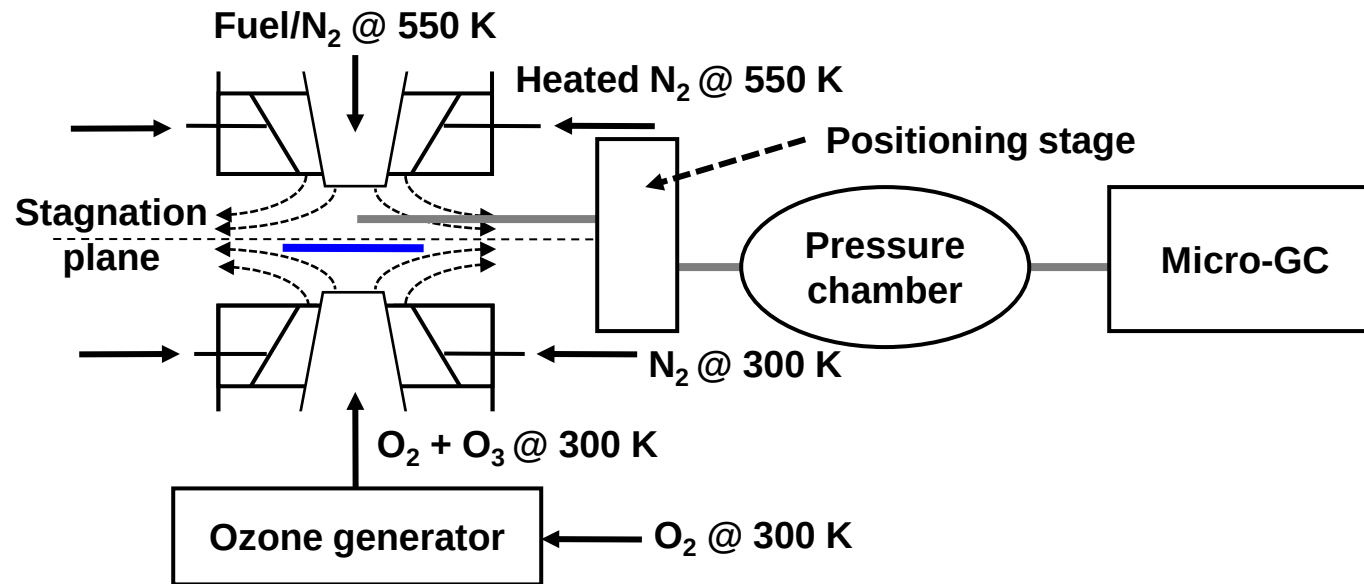


High temperature chemistry

Low temperature chemistry

1.2 Experimental study of plasma assisted **diffusional cool flames**

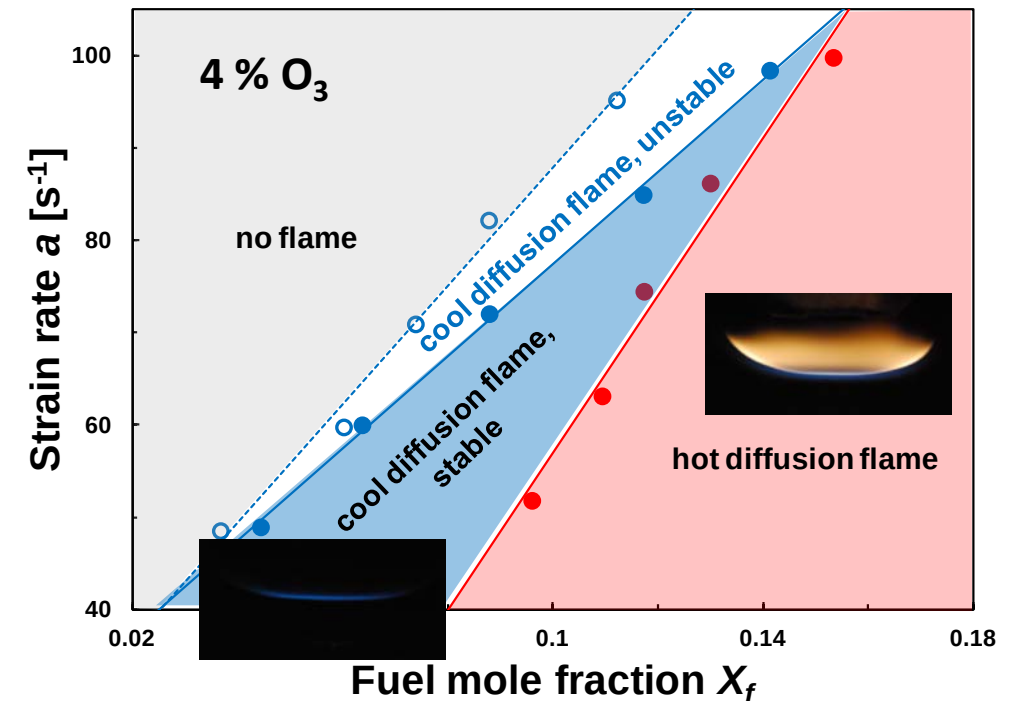
- A heated counterflow burner integrated with vaporization system¹
 - n-heptane/nitrogen vs. oxygen/ozone
- Ozone generator (micro-DBD) produces 2- 5 % of ozone in oxygen stream, depending on oxygen flow rate
- Speciation profiles by using a micro-probe sampling with a micro-GC.²



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

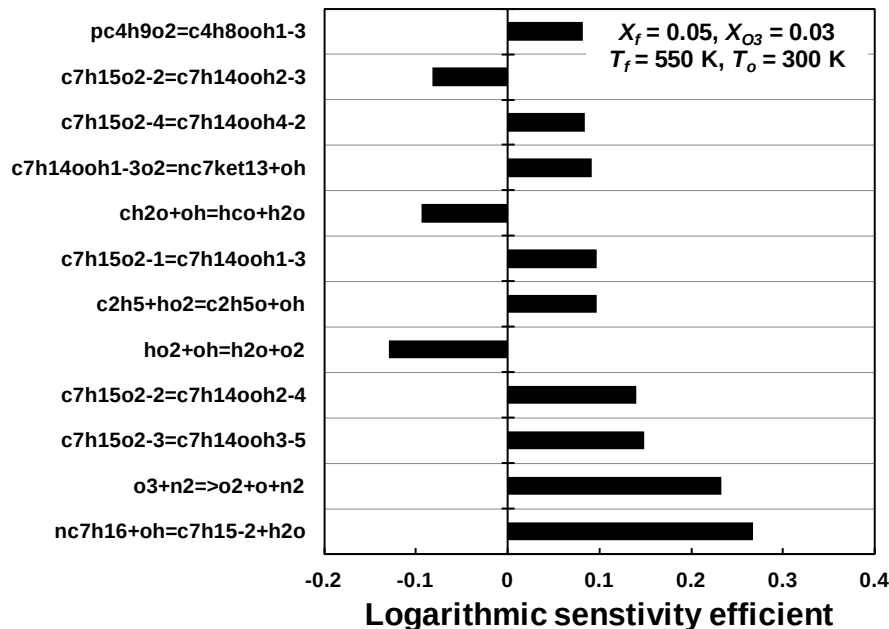


Cool flames extends the auto-ignition limit!

Sensitivity Analysis near Extinction

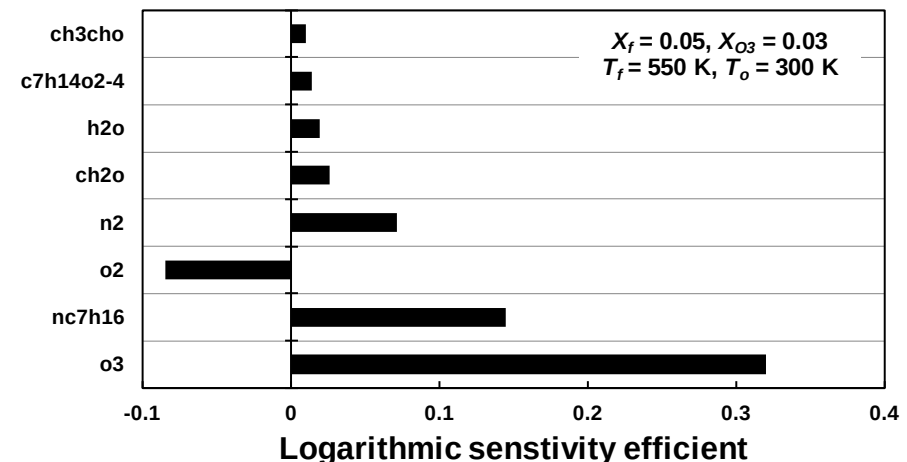
Reactions

- Importance of low temperature chemistries
 - RH + OH (~ 15% heat production)
 - R + O₂ reactions (~40%)
 - QOOH reactions
 - HO₂ reactions



Transport

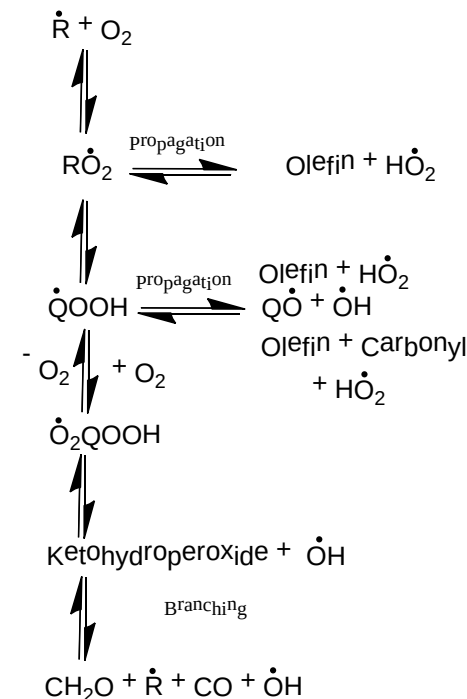
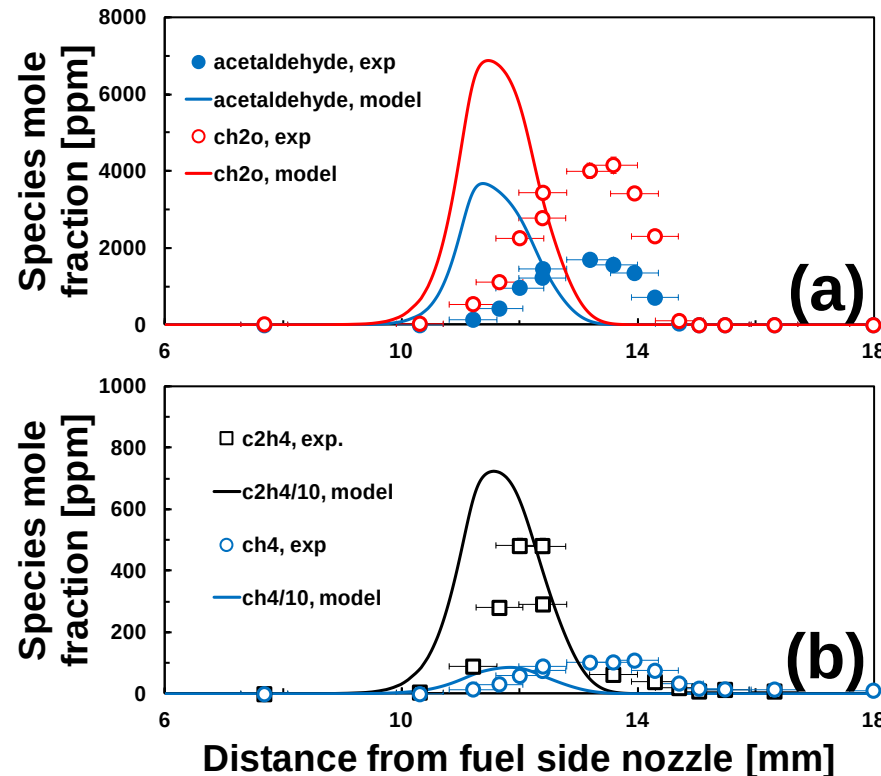
- Very sensitive to ozone diffusion
 - O₃ + N₂ → O₂ + O + N₂ for initiation of radical pool.
 - Thus, fuel diffusion is important as well.
- Strong sensitivity to CH₂O
 - Indicator of low temperature reactivity¹



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

Speciation Profiles and validation of kinetics

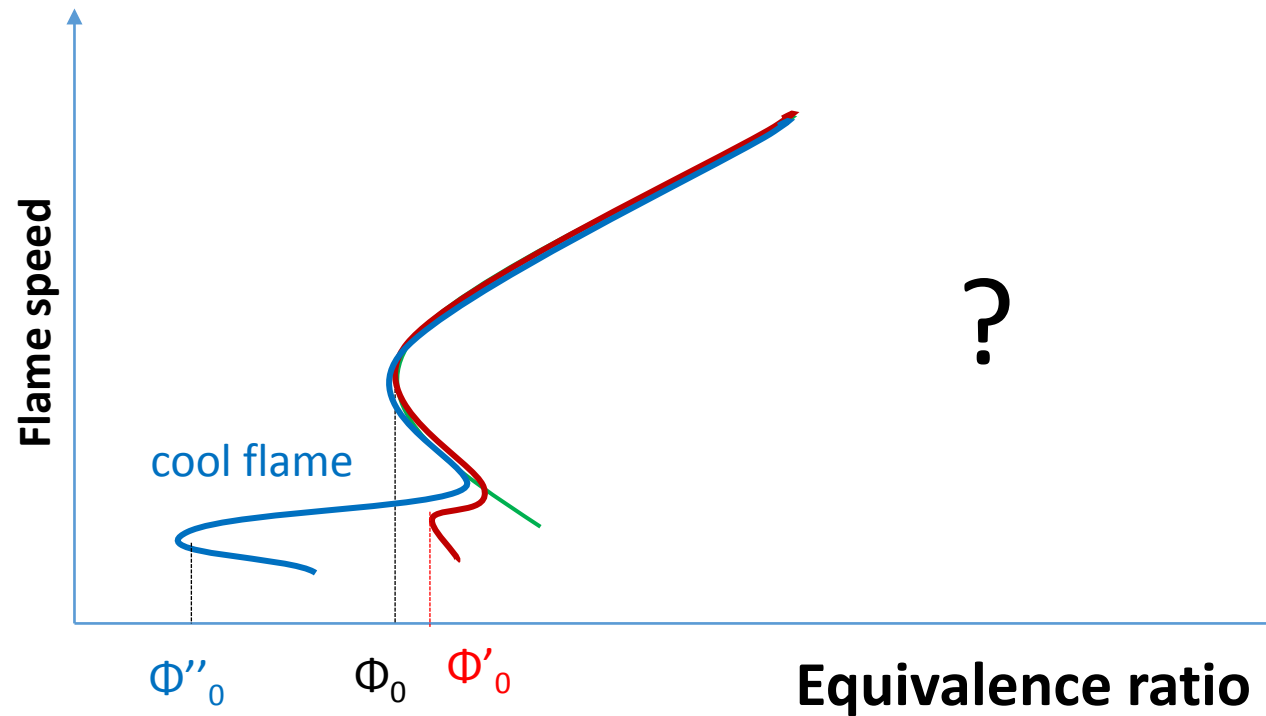
- Reasonable prediction of acetaldehyde and CH_2O
- Significant over-estimation of C_2H_4 and CH_4 formation
 - Factor of 10.



1.3 Plasma assisted premixed cool flames

- Lean Flammability Limit:

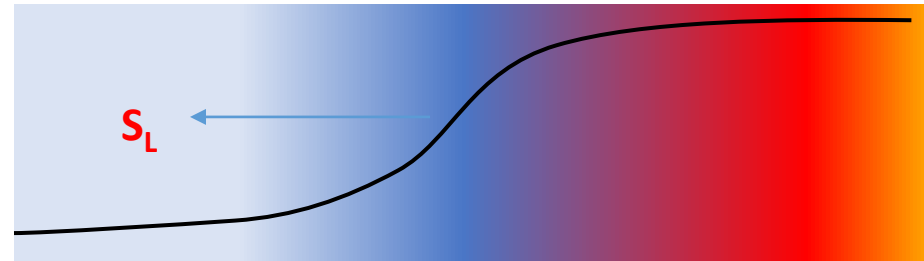
Normal flame vs. cool flame



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

- **Geometry**

1D freely propagating flames



- **Mixture and Kinetic model**

Fuel: Dimethyl ether **Oxidizer= $(1-x)\text{O}_2 + x\text{O}_3$, $x=0 - 0.1$, $p=1 \text{ atm}$**

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)

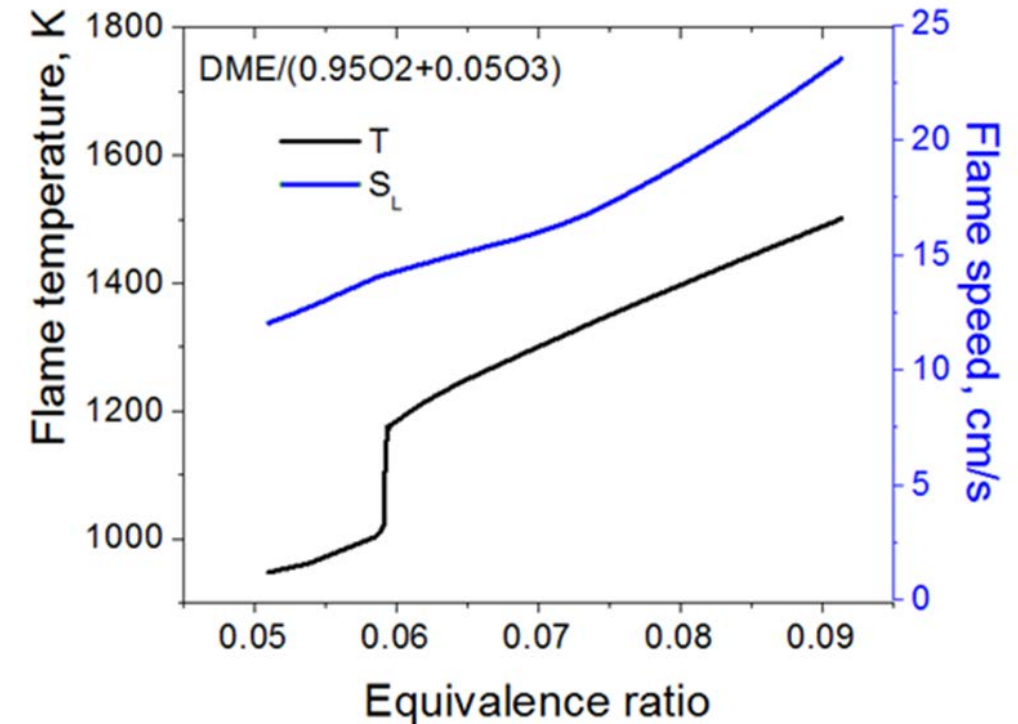
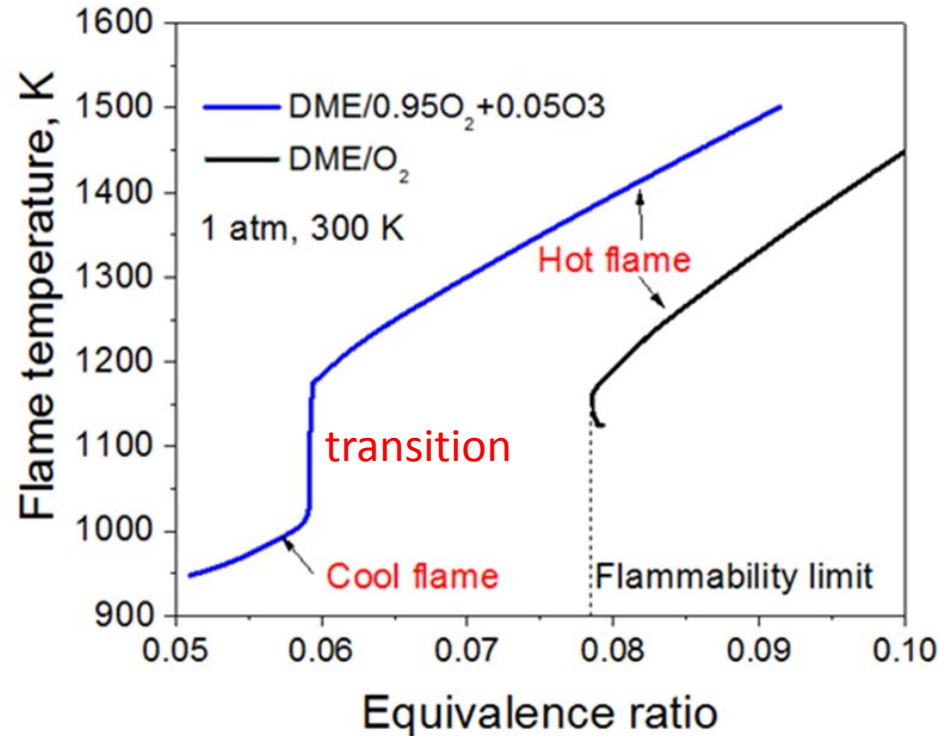
- **Numerical method**

Modified Chemkin with arc-continuation method

Radiation (Optically thin model for CO_2 , H_2O , CO , CH_4)

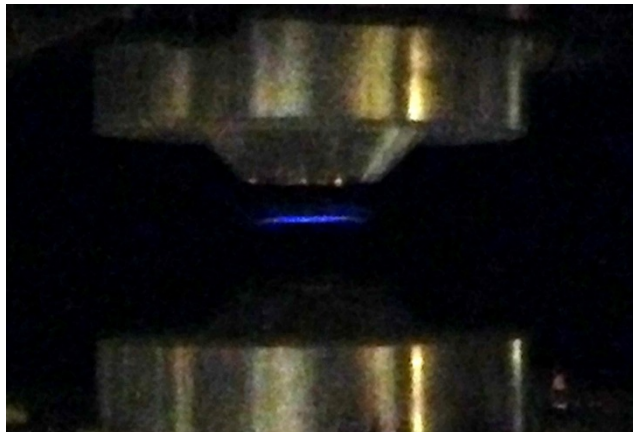
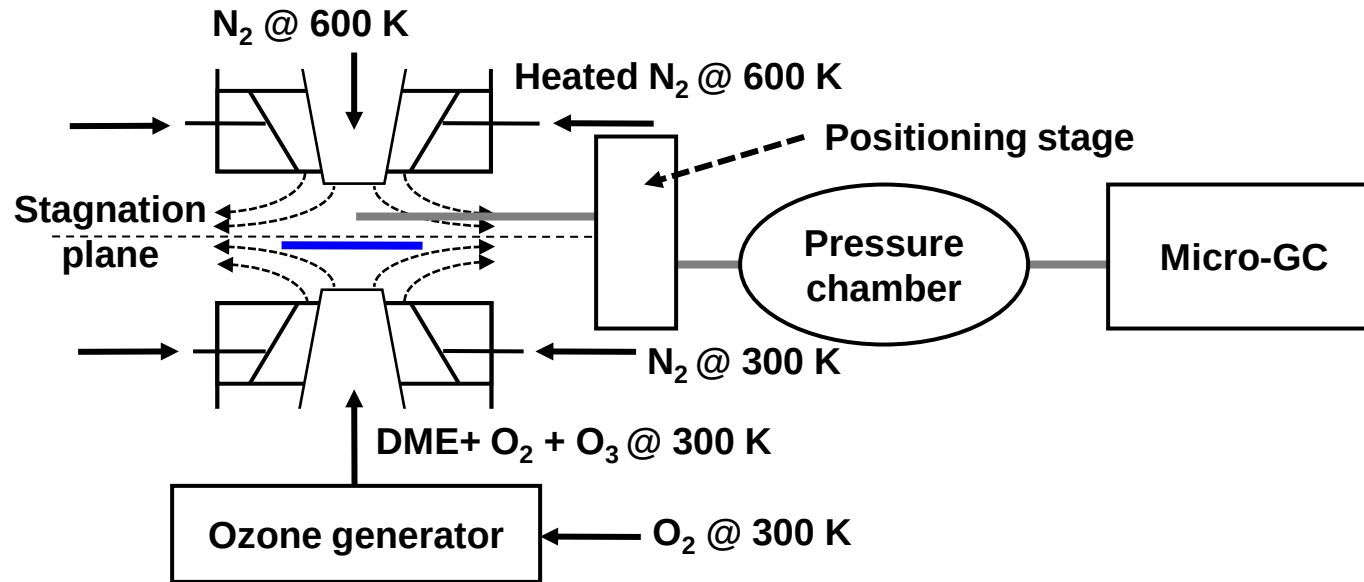
Ju et al. *JFM*, 1997

- Lean Flammability Limit Extension by formation of cool flames



- Lean limit of $\phi = 0.078$ 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)

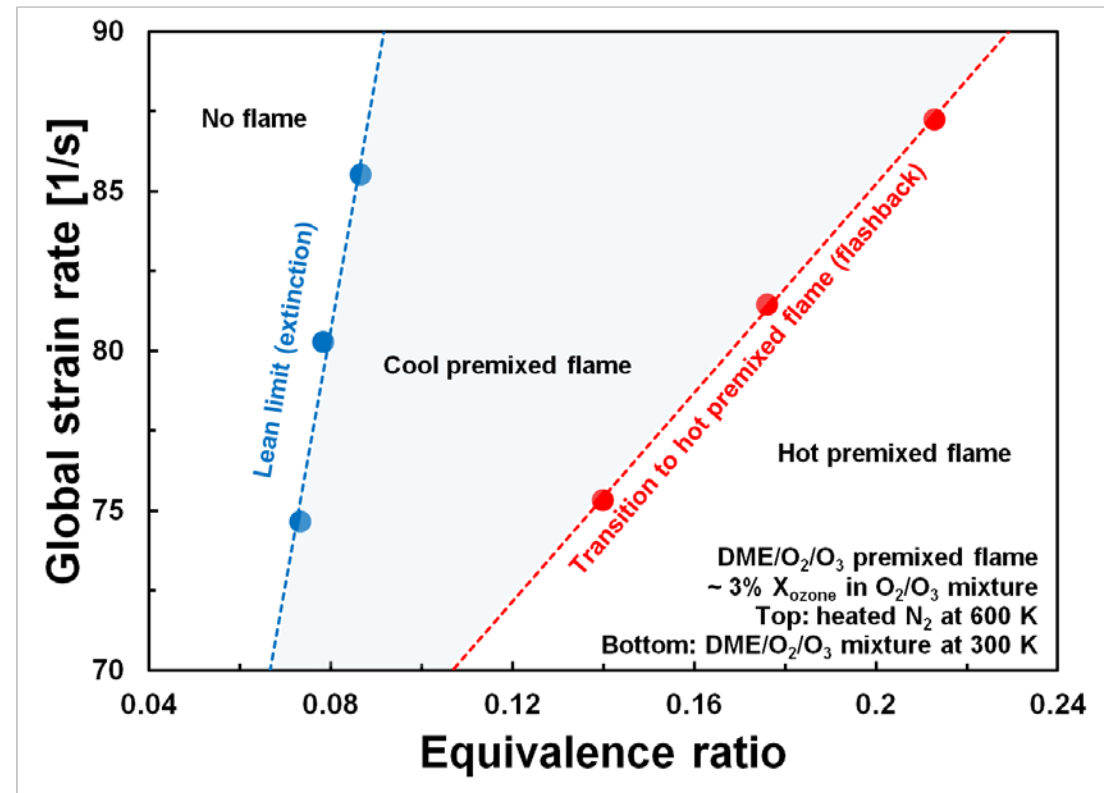
Experimental observation of premixed cool flames



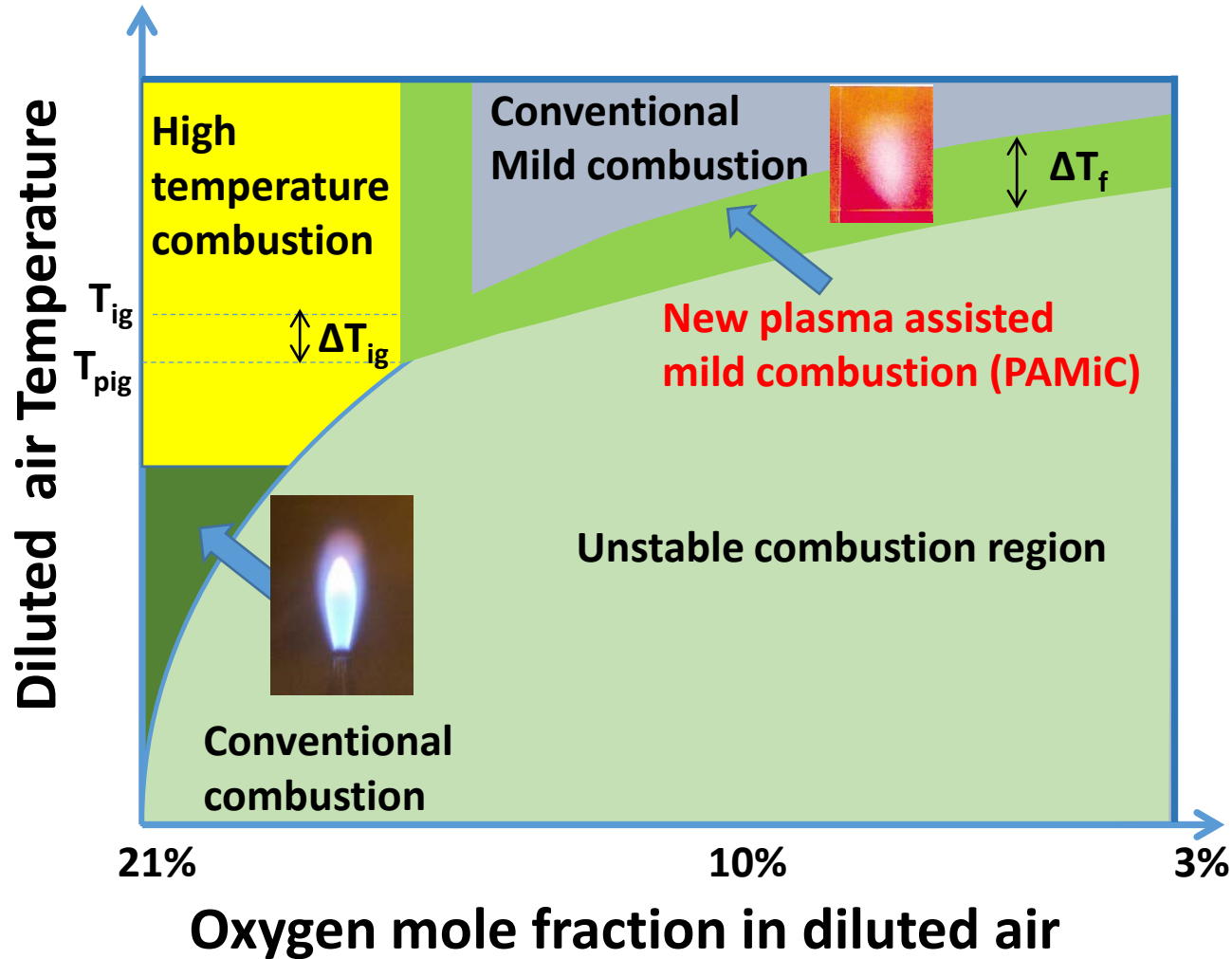
- Temperature of N_2 = 600K
- Temperature of DME/ O_3 / O_2 = 300 K
- Strain rate = 80 s^{-1}
- Ozone concentration: 3%

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}

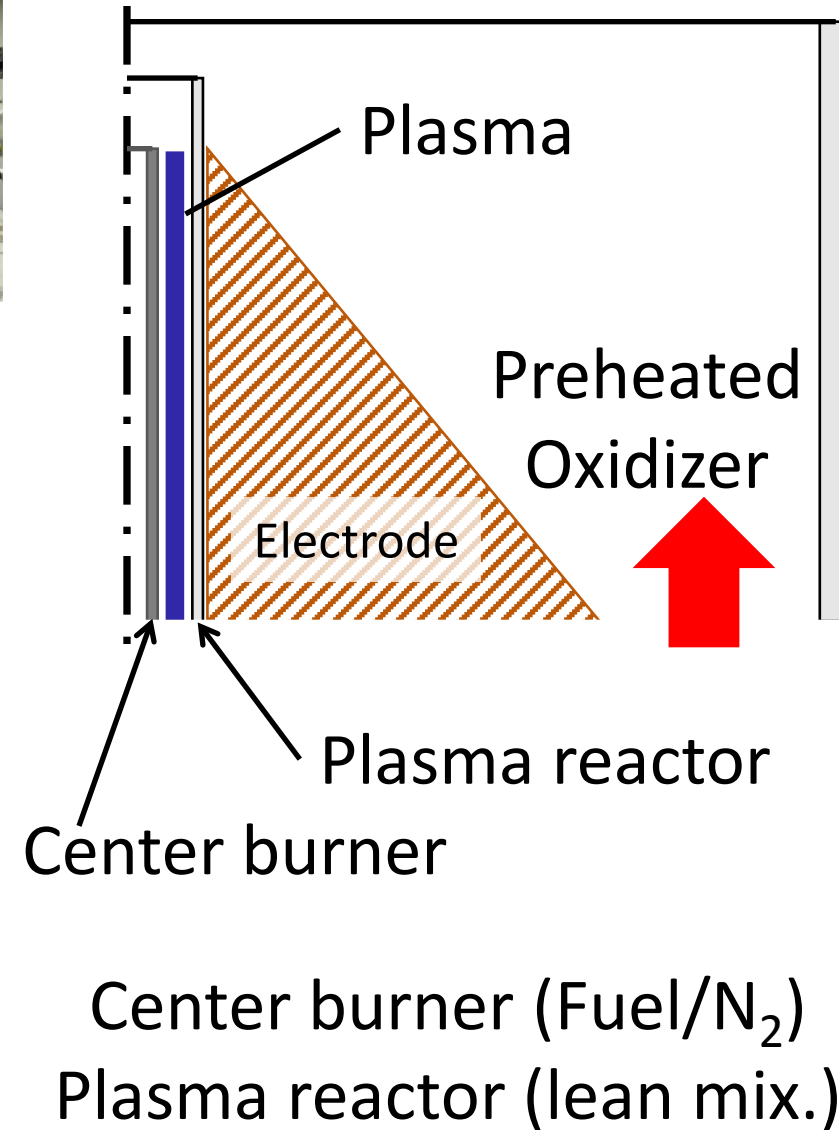
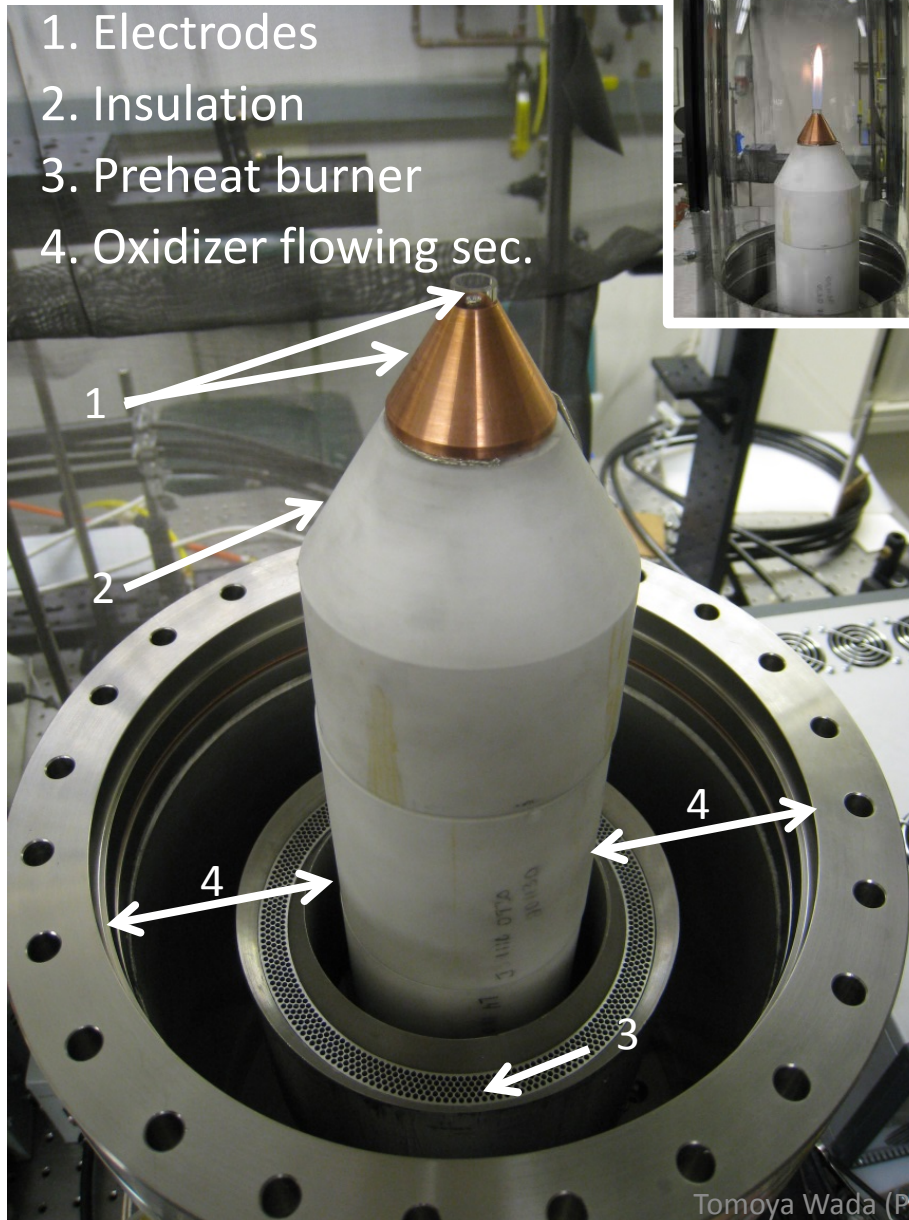


2. Plasma assisted mild combustion

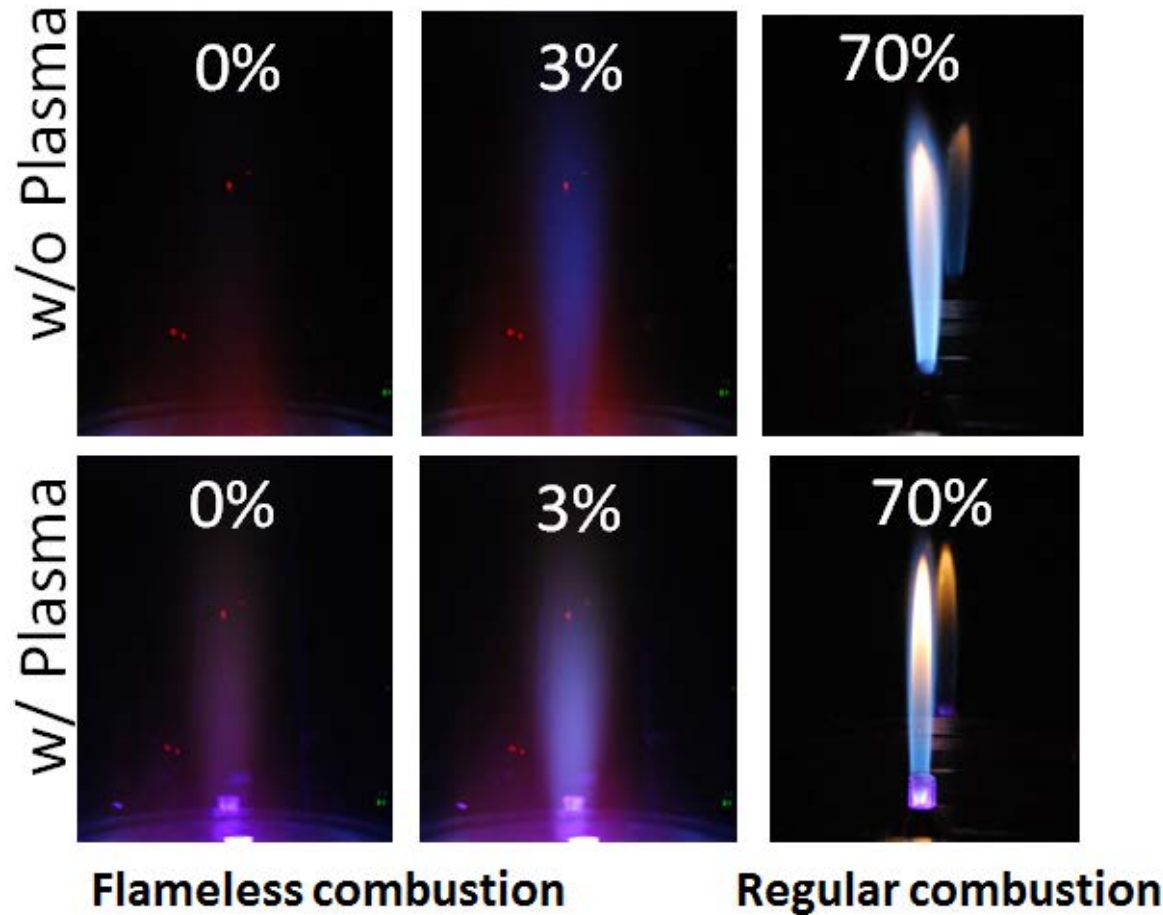


Can plasma extend the boundary of mild combustion to lower temperature?

Mild combustion: co-axial burner



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)

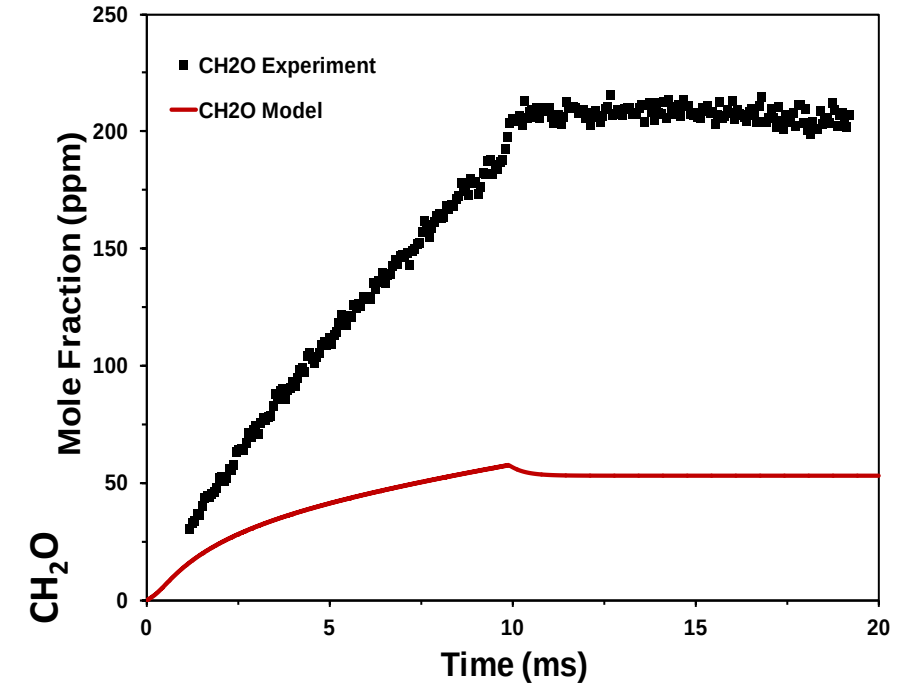
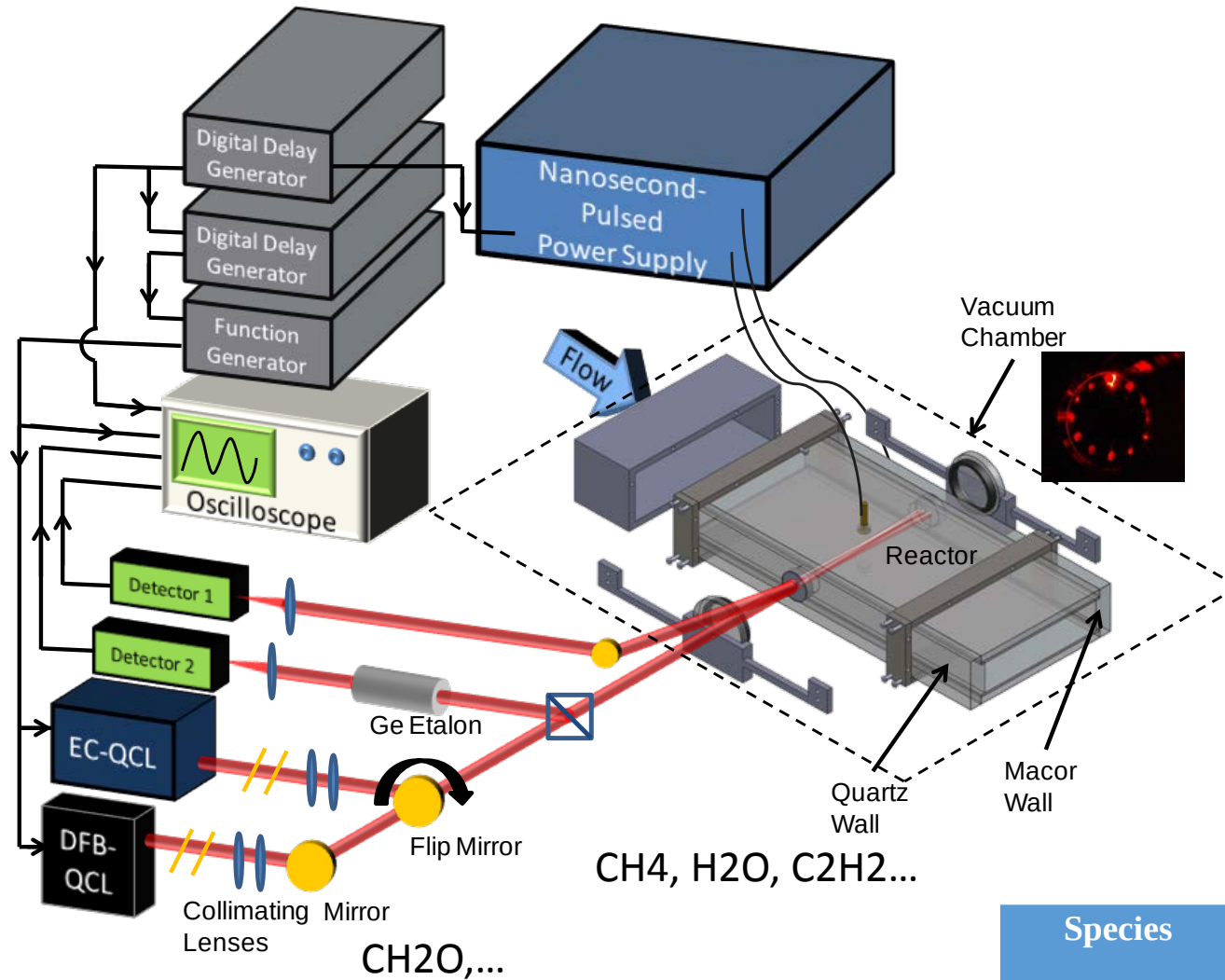


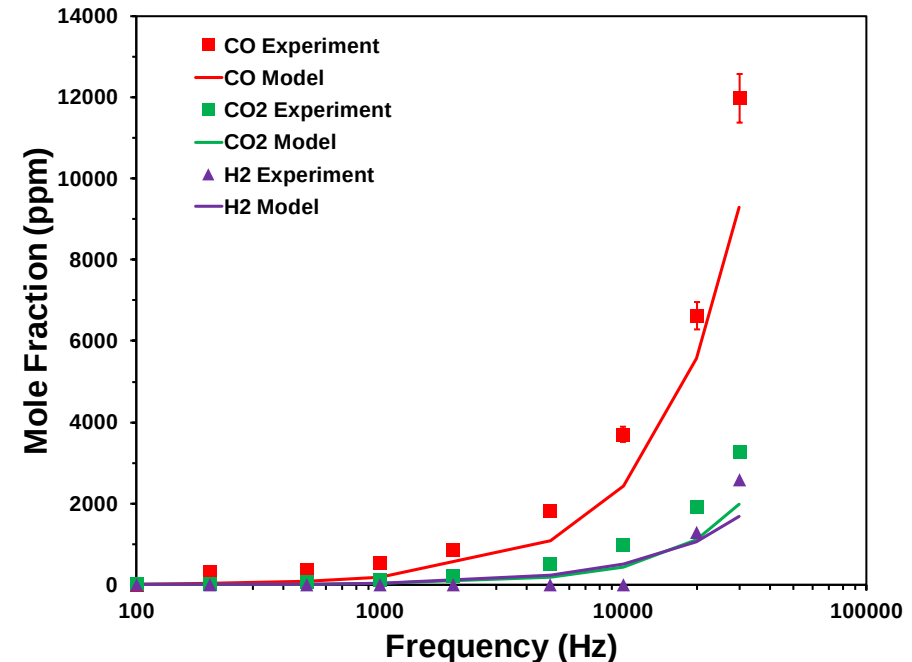
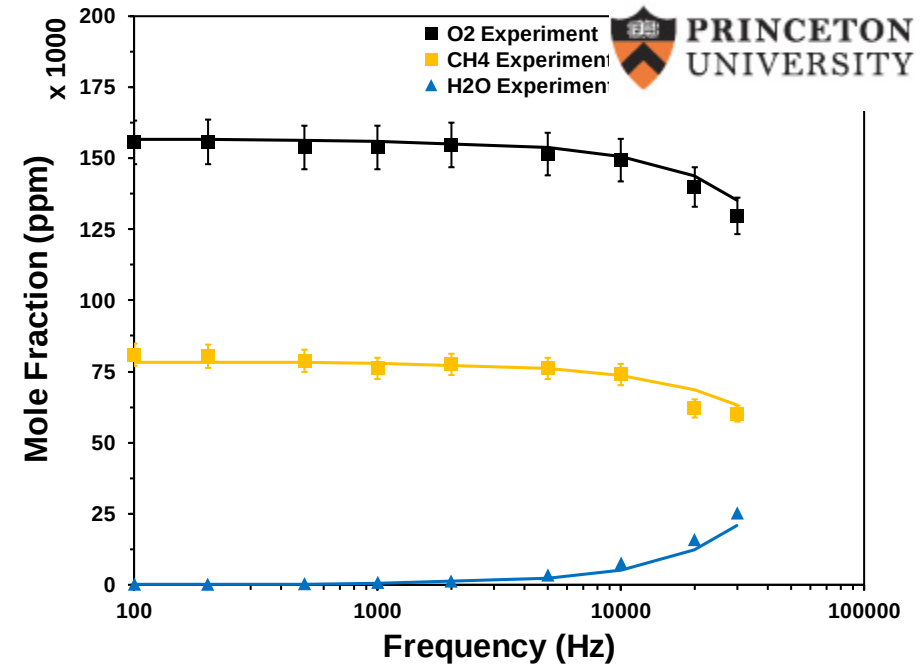
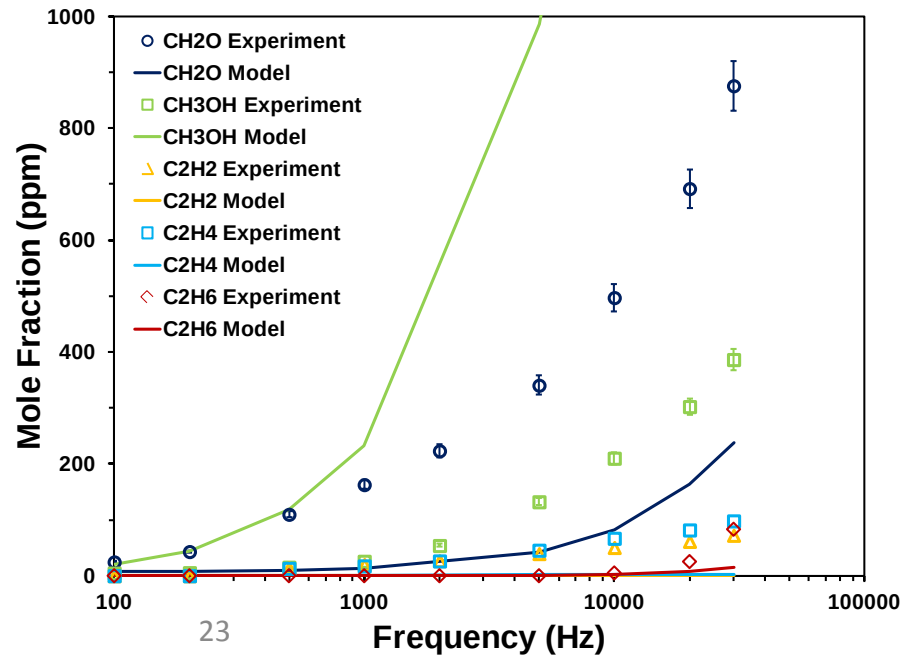
Fig. 1 CH₂O time history measurements and modeling of a 300 pulse burst at 30 kHz in a stoichiometric CH₄/O₂/He with 75% dilution.

Species	Wavelength (nm)	Wavenumber (cm ⁻¹)	Line strength @ 300 K (cm/molecule)
CH ₄ /Temp	7442.91	1343.56	1.898x10 ⁻²²
	7442.52	1343.63	1.78x10 ⁻²²
CH ₂ O	5791.09	1726.79	6.47x10 ⁻²⁰

Continuous Plasma – CH₄/O₂/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



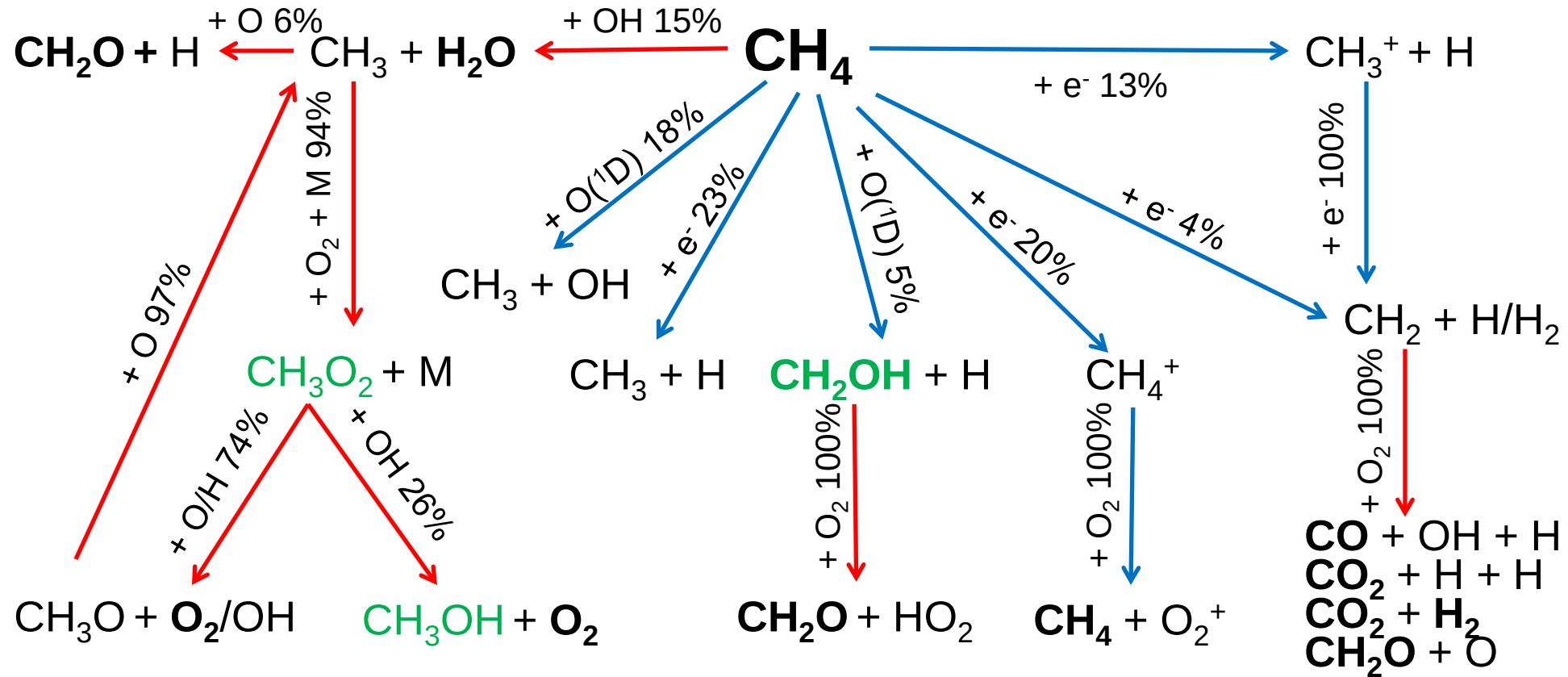


Figure 6: Path flux analysis of fuel consumption integrated over a single pulse period during continuous discharge at 30 kHz repetition frequency and steady state temperature conditions. Bold species represent those which are measured in Figure 5, red arrows refer to reactions from the combustion model,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

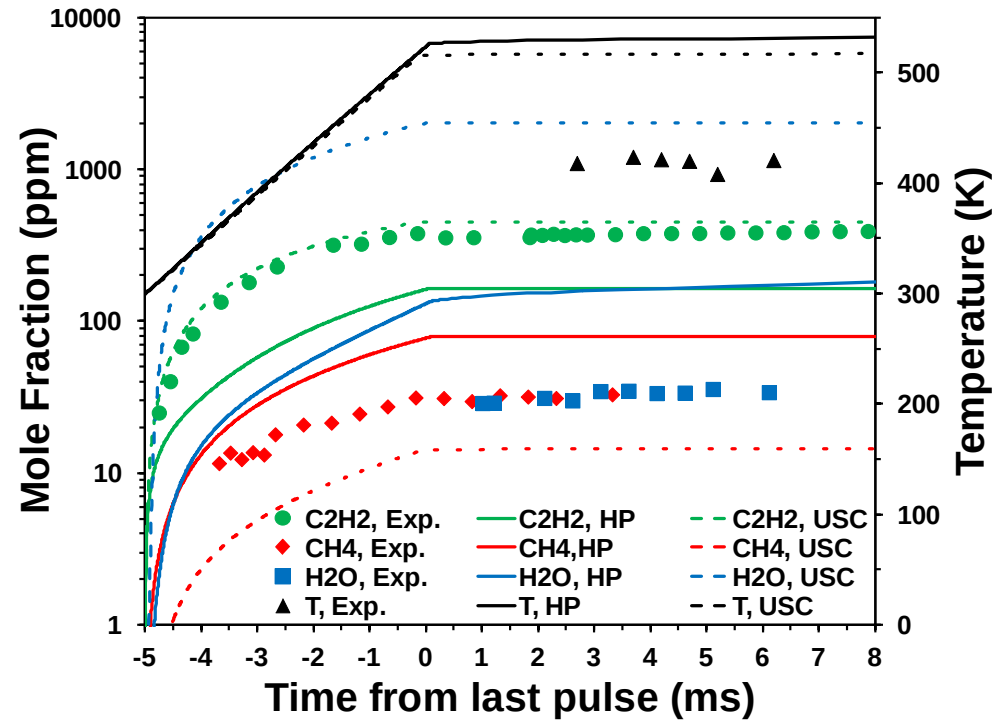
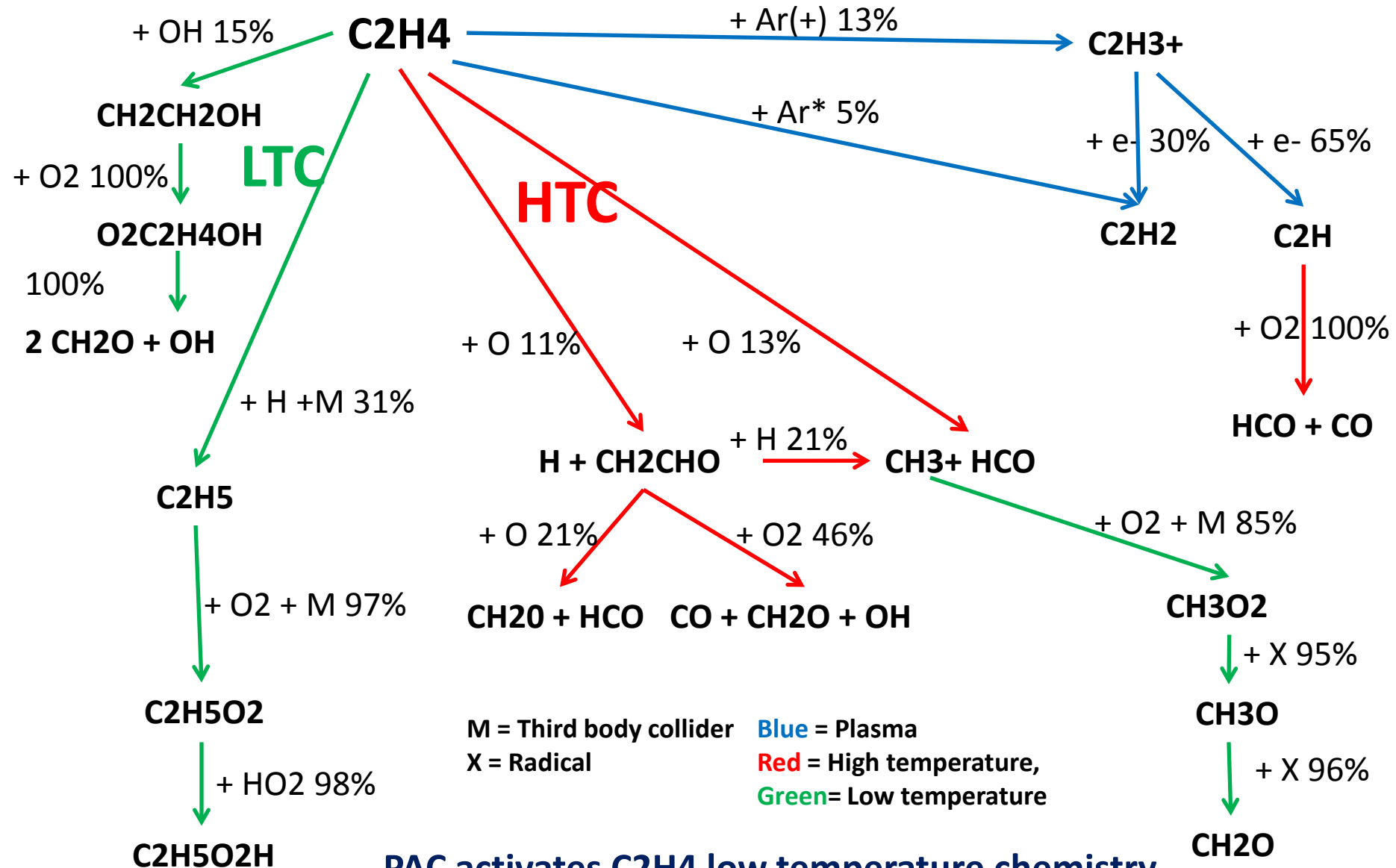


Fig. 2 Comparison of measured and predicted species (H2O, CH4, C2H2 formation in C2H4 oxidation: HP-Mech vs. USC Mech

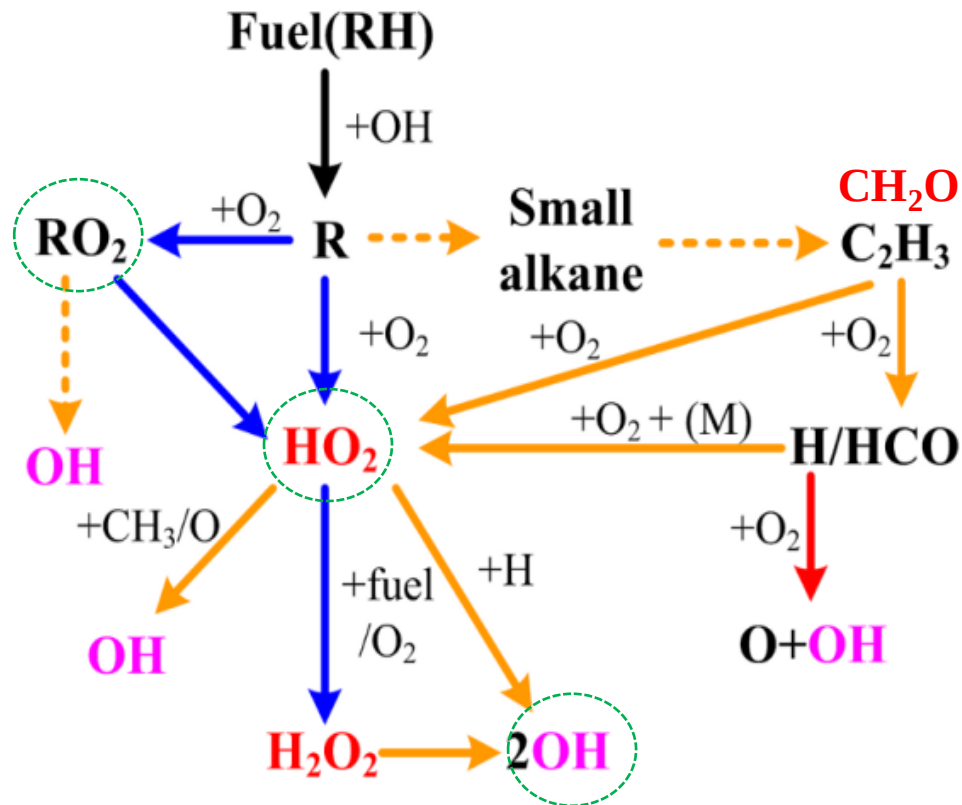
Ethylene Oxidation Pathways (C₂H₄/O₂/Ar)



PAC activates C₂H₄ low temperature chemistry

Large uncertainty in low temperature oxidation pathways

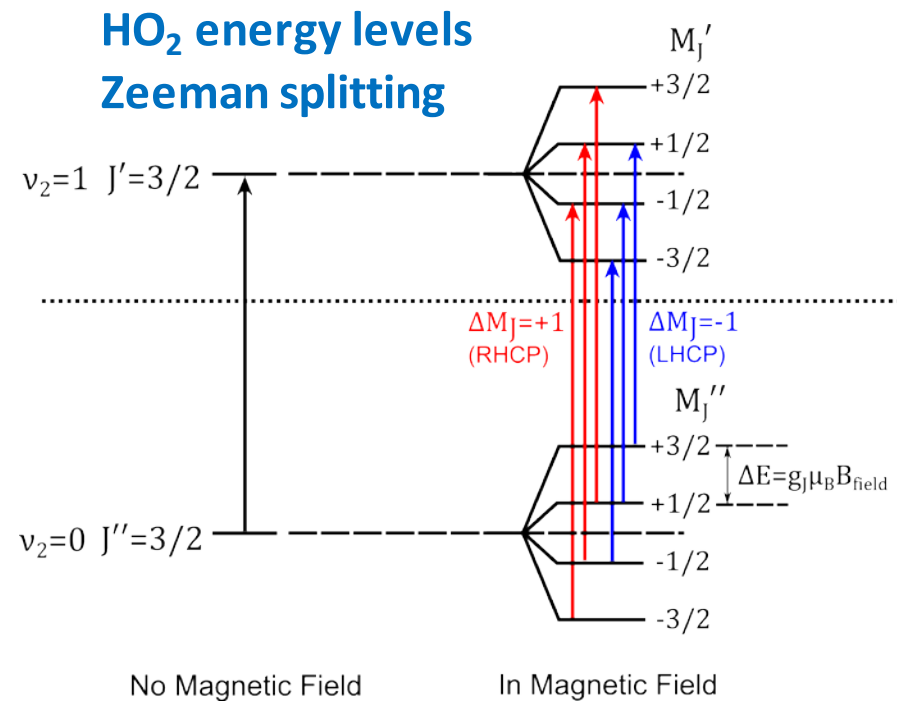
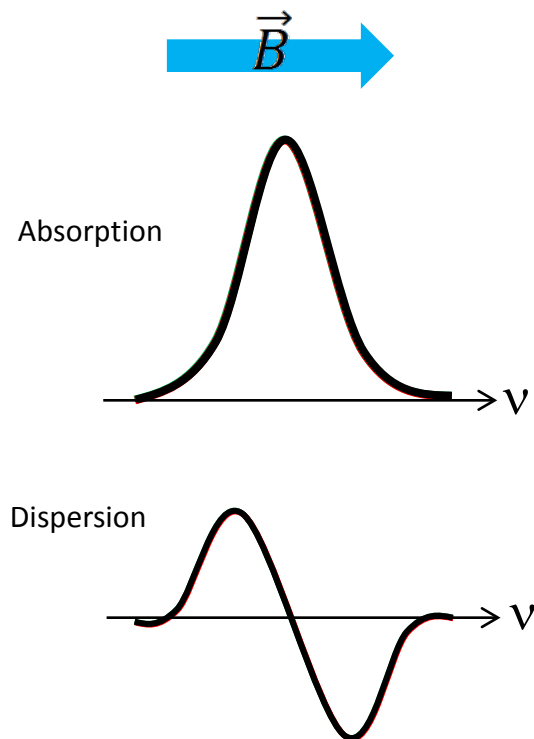
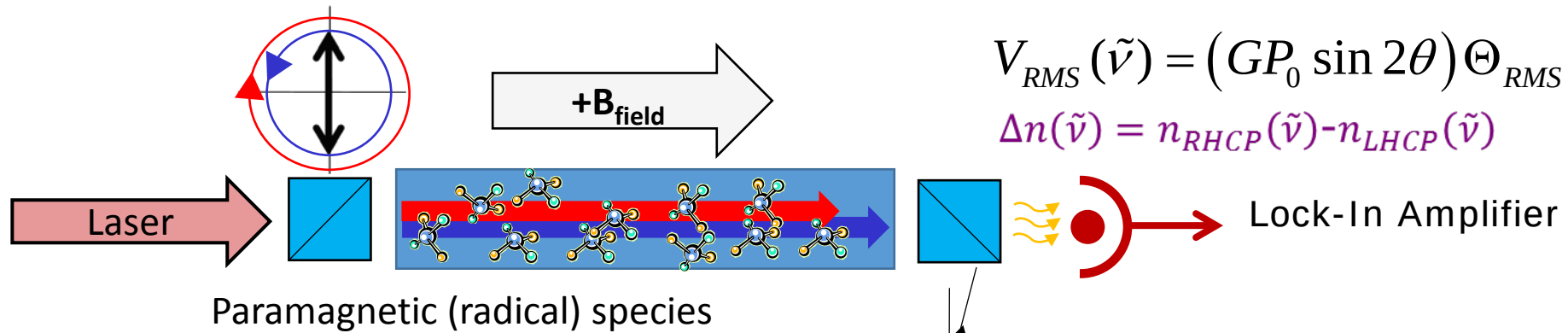
Key reaction pathways in combustion kinetics at high pressure and low temperature: HO₂/RO₂



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 linebroadening.

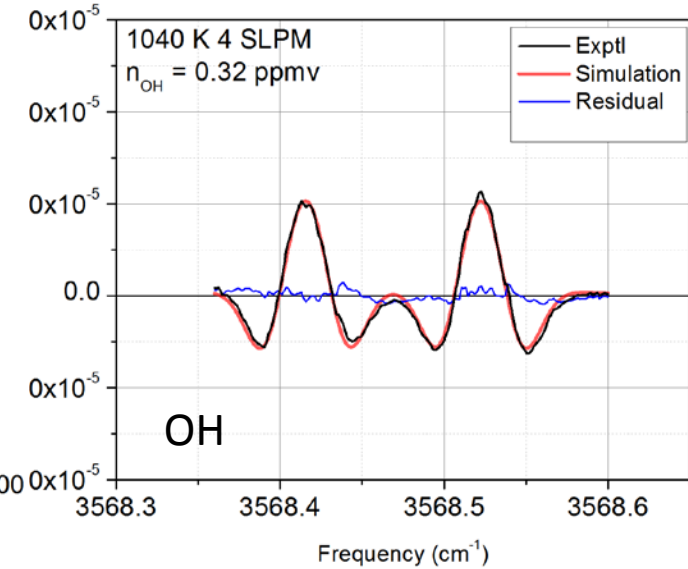
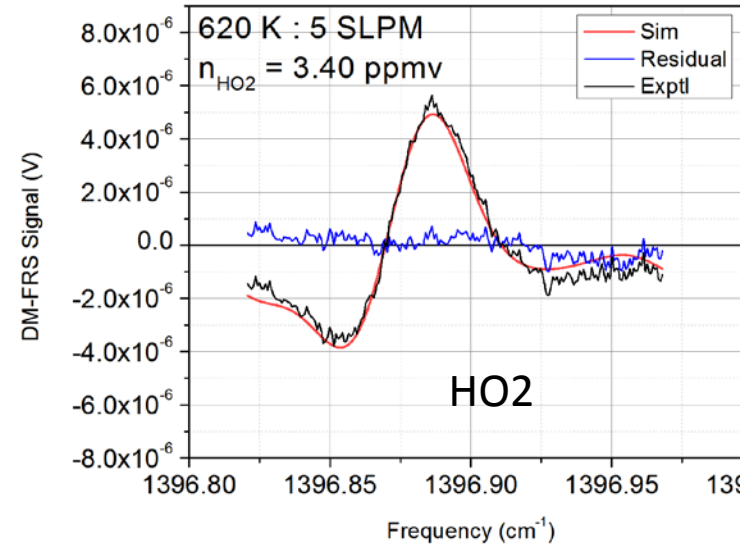
New diagnostics: HO₂/OH using mid-IR Faraday Rotational Spectroscopy



Experimental results: HO₂/OH measurements

Signal

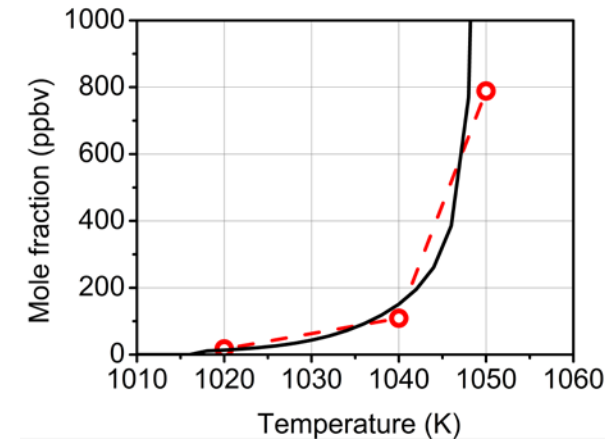
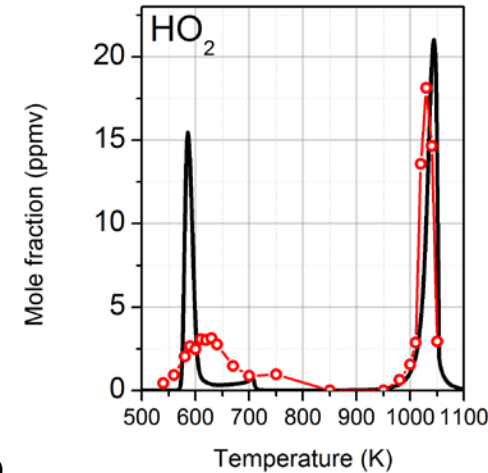
Sensitivity



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

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

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

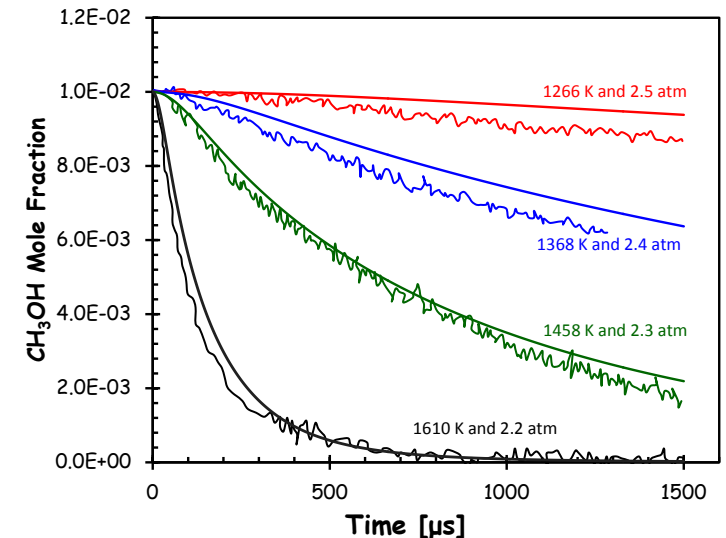
- NO_x reaction pathways

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

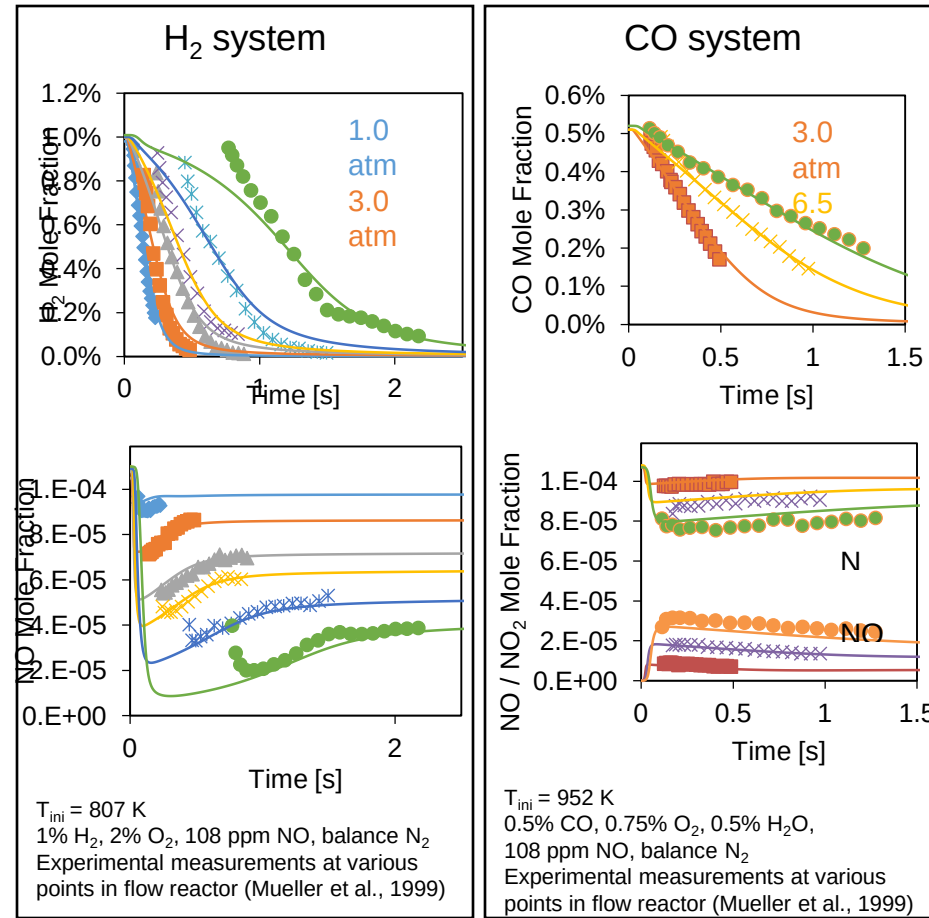
Allen et al., Combust. Flame (1997), Vol. 109, pp. 449-470

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



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

Plasma Modeling Tool Development

ZDPlasKin

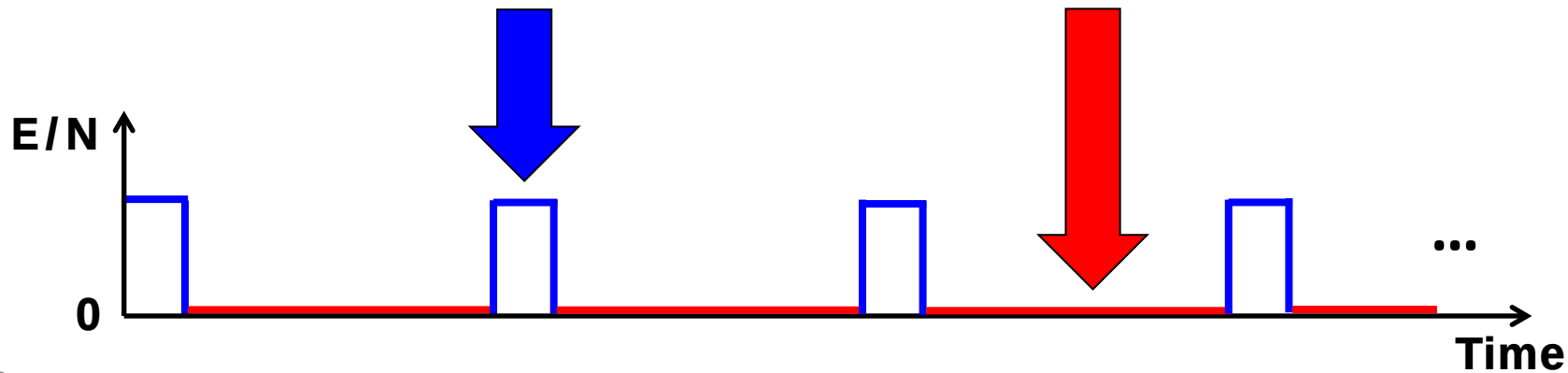
$$\frac{dN_i}{dt} = \sum_{j=1}^{j_{max}} Q_{ij}(t)$$

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

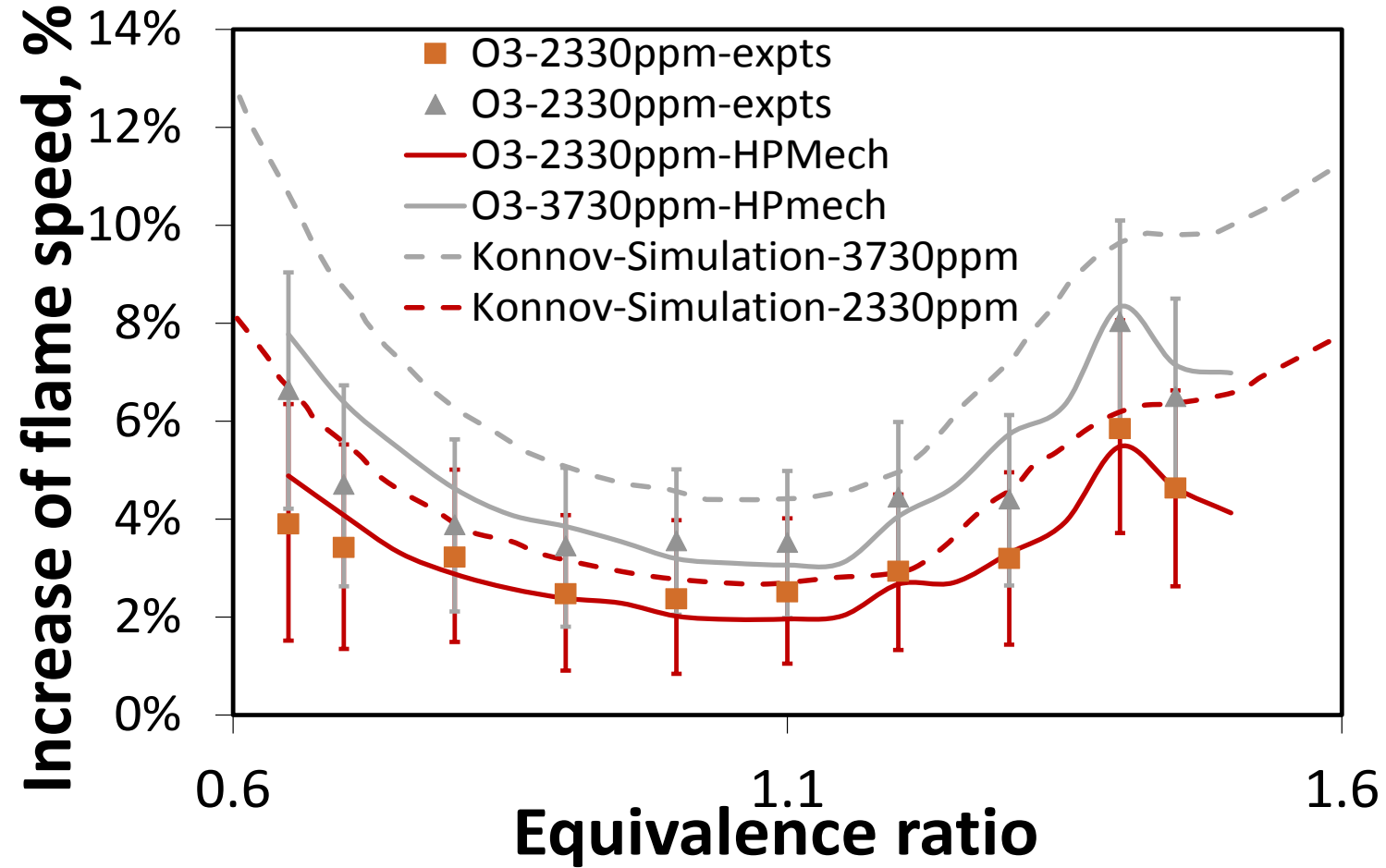
CHEMKIN II - SENKIN

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

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



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 RO₂ 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., Diévert, P., Sohn, C.H., Ju, Y., (2015), Self-Sustaining n-Heptane Cool Diffusion Flames Activated by Ozone, **Proceedings of Combustion Institute**, 35, 2015
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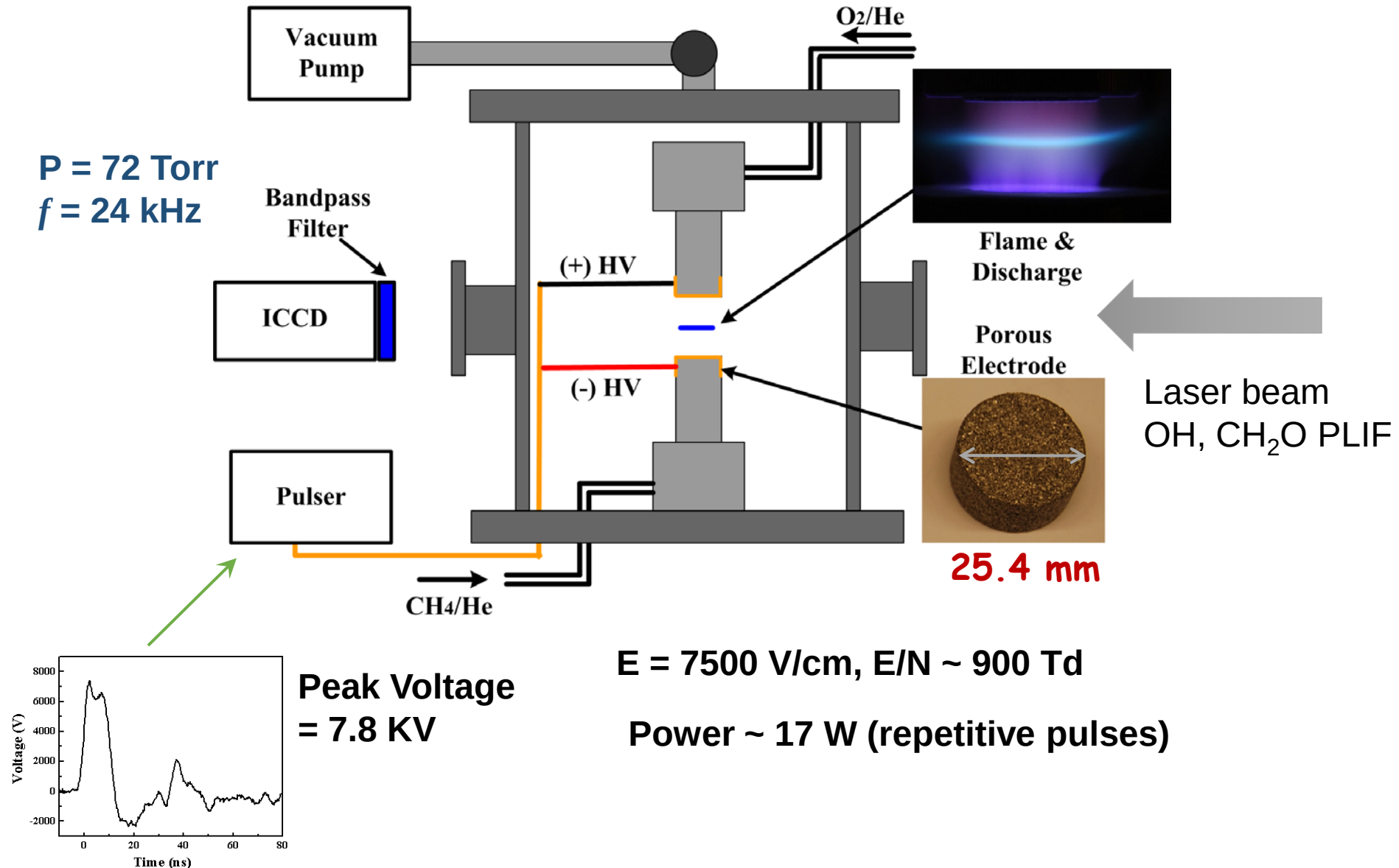
Awards:

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 $O(1D)$, HO_2 , O_3 , $O_2(1\Delta)$ in photolysis and flow reactor (0.1-2 atm)
- High pressure plasma assisted cool flames (1-10 atm)

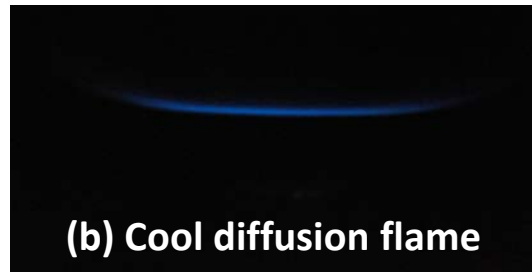
3. Plasma assisted low temperature combustion Methane vs. Dimethyl ether (DME)



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

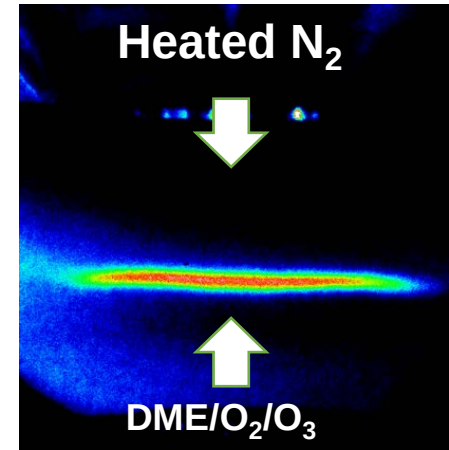


N-heptane
Normal diffusion flame
 $T_f \sim 1900$ K



Cool diffusion flame
 $T_f \sim 650$ K

Fig. 1 Plasma assisted normal and cool diffusion flames



Direct chemi-luminescence image of cool premixed flame by ICCD camera for DME/O₂/O₃ mixture ($\phi = 0.104$)

Fig.2 Plasma assisted cool premixed flame (DME)

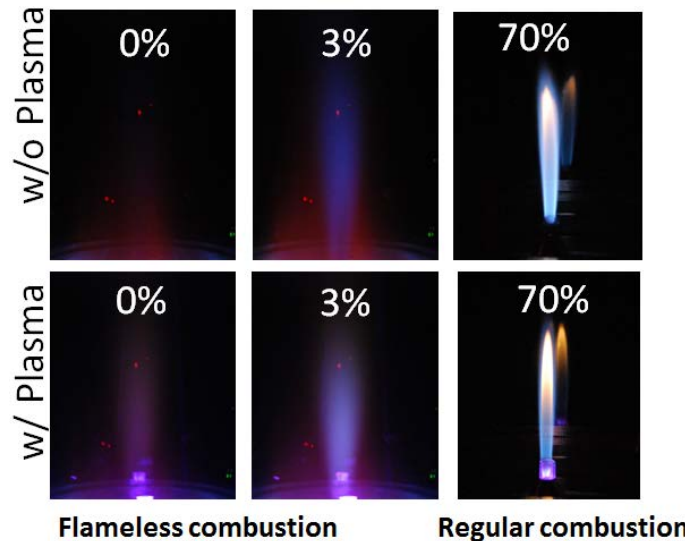
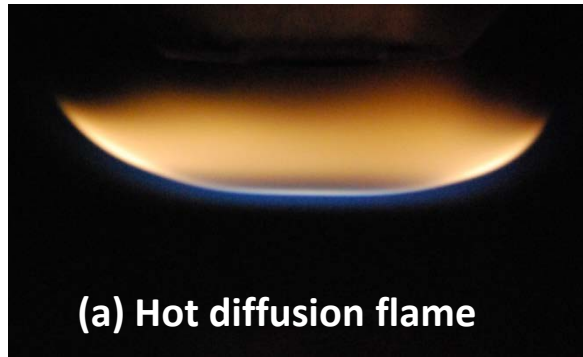
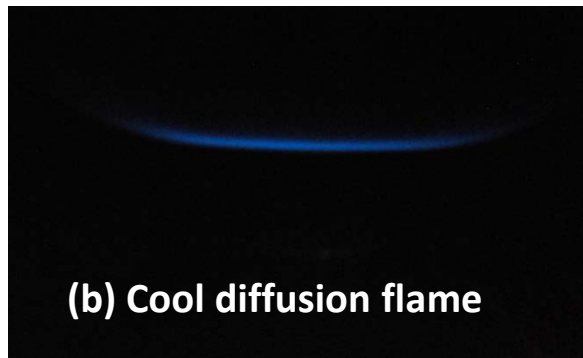


Fig.3 Plasma assisted mild combustion (methane diluted by N₂)

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



$T_f \sim 1900$ K



$T_f \sim 650$ K

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

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

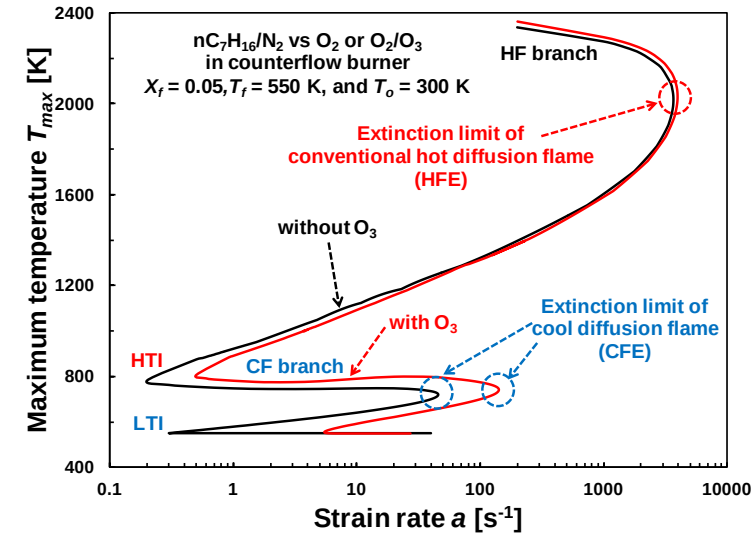


Fig. 2 Ozone (red line) extends the burning limit of cool flames

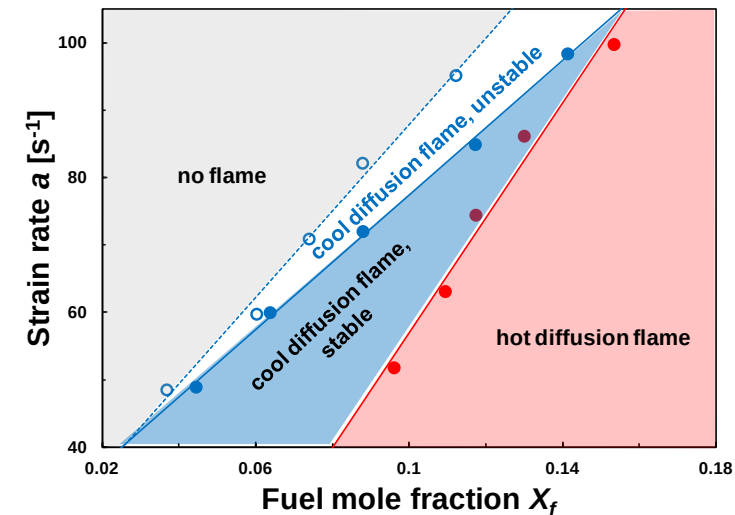
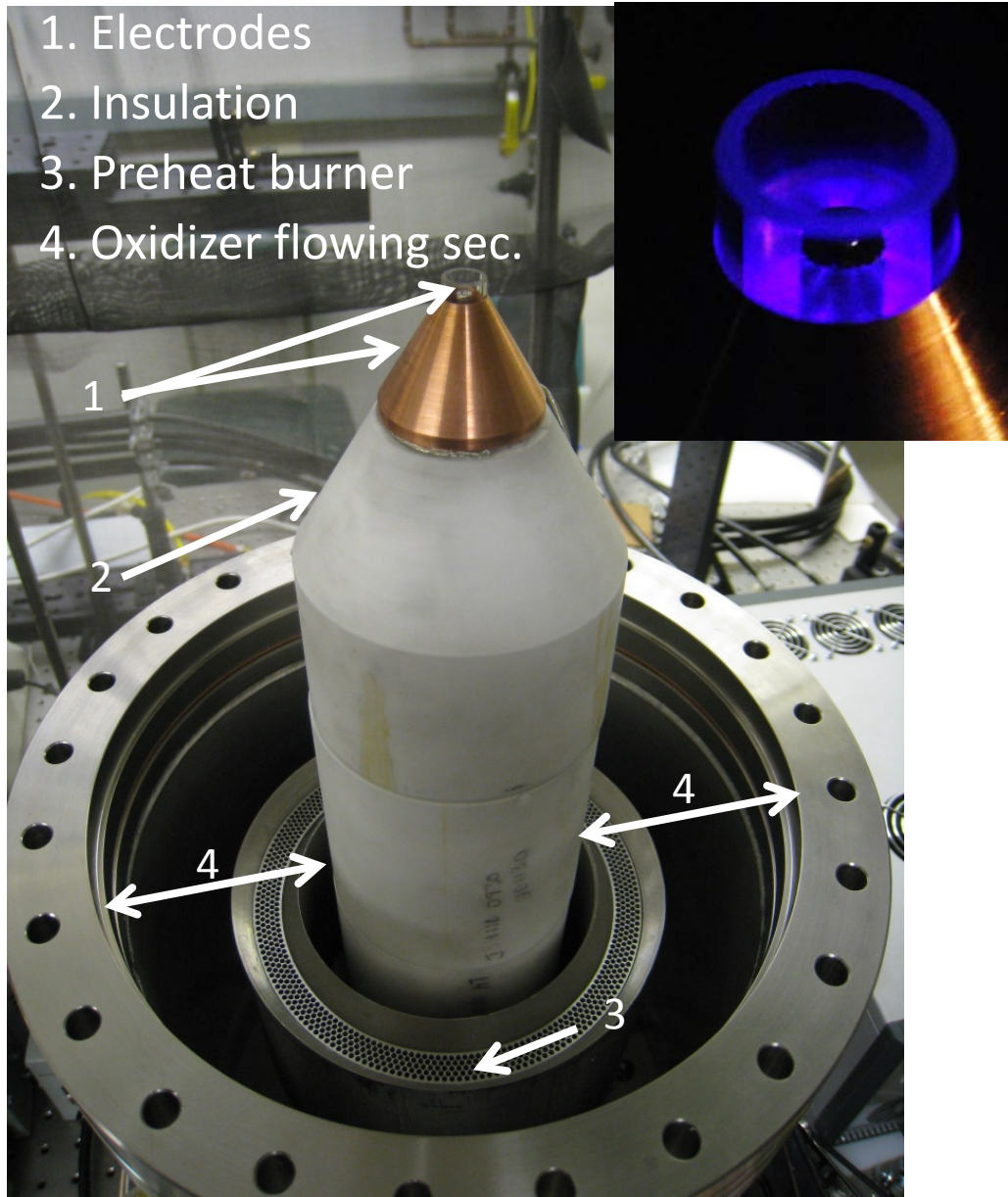


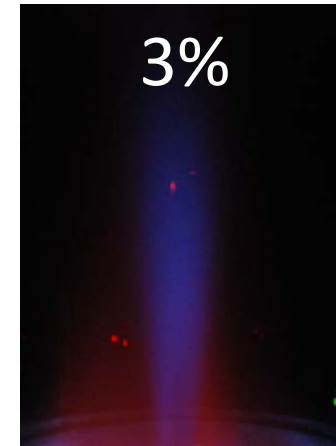
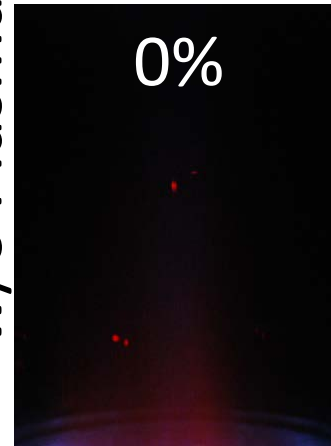
Fig. 3 Diagram of hot flame (pink), stable cool flame (blue), and unstable cool flame (white)

2. Plasma assisted flameless (MILD) combustion

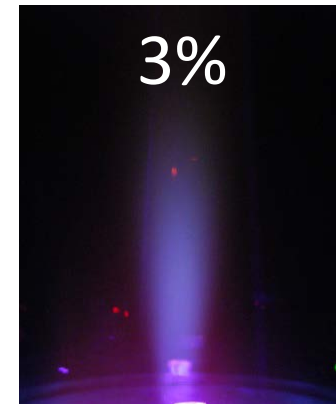


- Tested conditions
 - Preheat: 1050 K (including 12% O₂)
 - Center burner CH₄/N₂ and vel.: 10-70% and **5-40 m/s**
 - Flame structure change with CH₄% in plasma reactor

w/o Plasma



w/ Plasma



Flameless combustion

Regular combustion

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

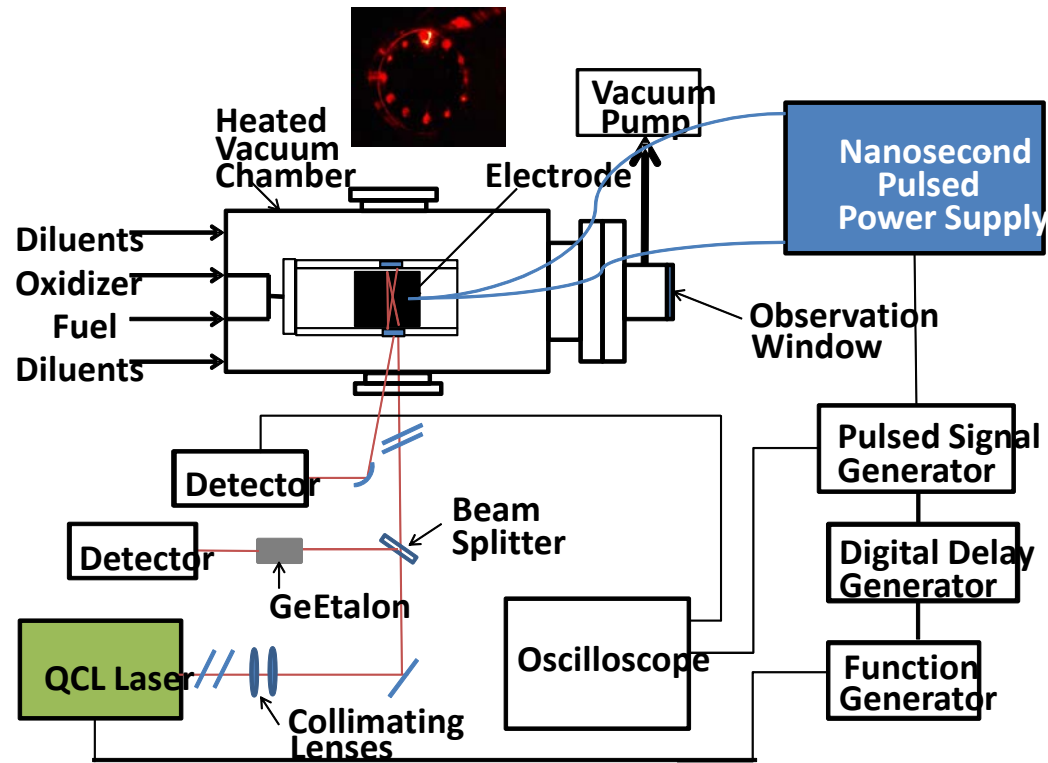


Fig. 1 Experimental setup of plasma reactor and IR-Herriot cell

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

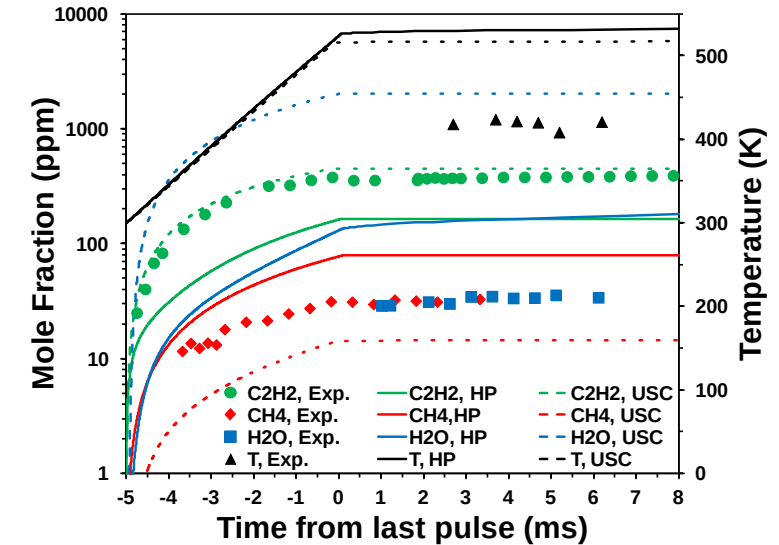


Fig. 2 Comparison of measured and predicted species (H₂O, CH₄, C₂H₂ formation in C₂H₄ oxidation: HP-Mech vs. USC Mech

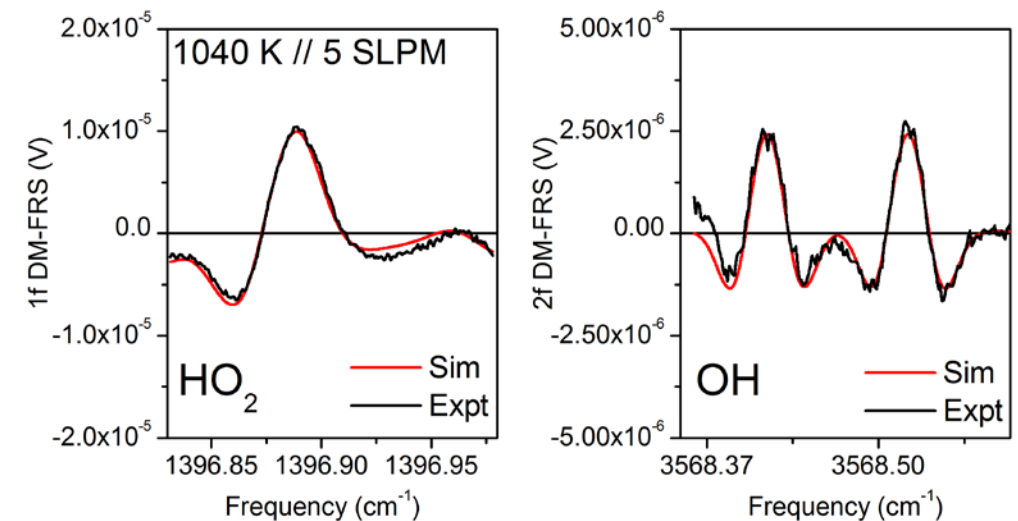


Fig. 3 OH and HO₂ diagnostics in DME flow reactor by using Faraday rotational spectroscopy. Predicted and measured signals.

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

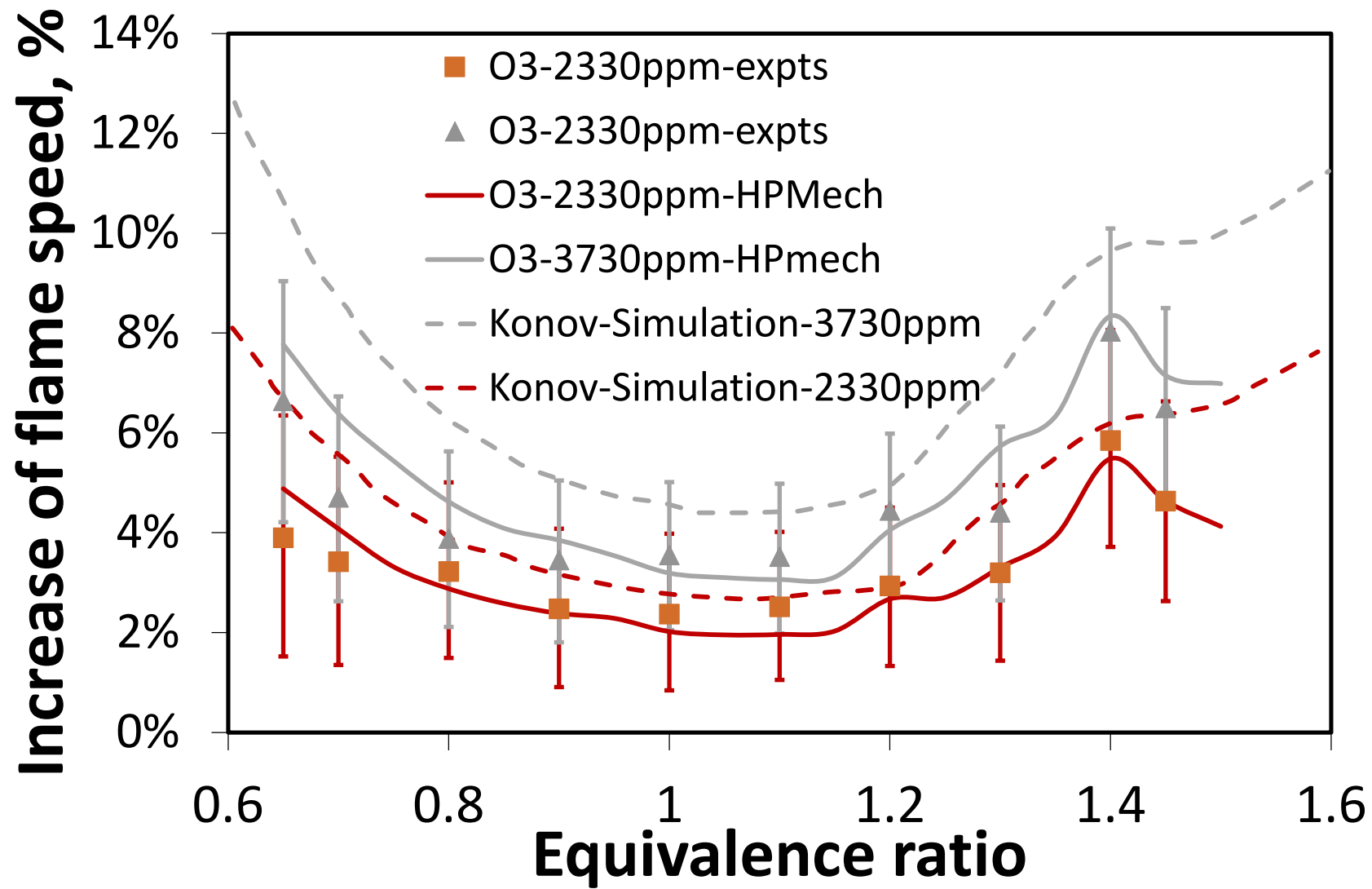


Fig.1 Comparison of predicted flame speed increase (percentage) by O₃ addition in methane/air flame (HP-Mech vs. Konov)