Experiments on Low-Temperature Combustion

Development of a Stabilized Cool Flame Platform & Faraday Rotation Spectroscopy Diagnostic for In-Situ Measurement of HOx Radicals

2nd Flame Chemistry Workshop

San Francisco

2 - 3 August 2014

Sang Hee Won and Brian Brumfield (Joseph Lefkowitz)

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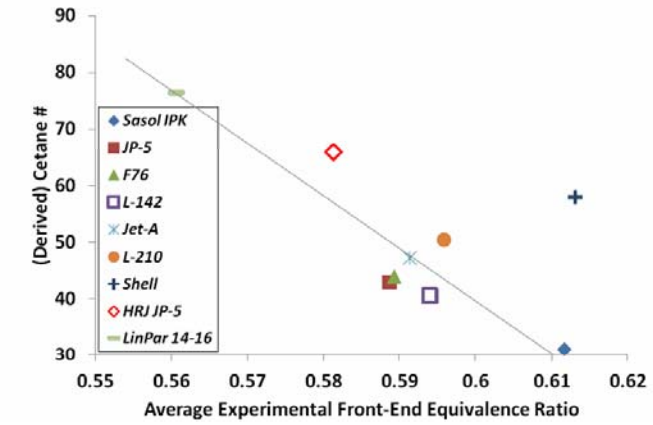
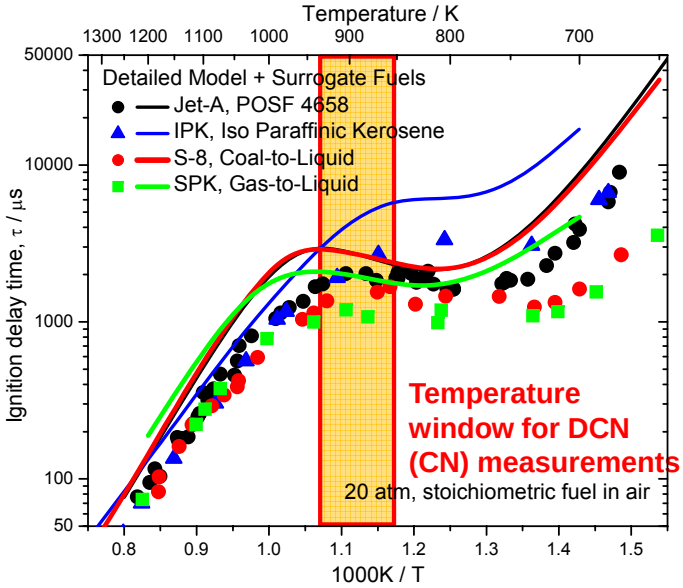
PULSE

Introduction

- **Take-home messages from the 1st Flame Chemistry Workshop**
  - What is the definition of flame chemistry?
    - Chemical kinetics constrained by transport
  - Development of well-defined experimental platforms
    - Extend ability to access **low temperature chemistry (LTC)**
    - Advanced laser diagnostic technique
- **Recent advanced engines**
  - Operate at low to intermediate temperature at higher pressure conditions
  - Near-limit combustion behaviors tend to be correlated with LTC

LBO test by Med Colket (UTRC)[3]





1) H. Wang, M. A. Oehlschlaeger, Fuel 98 (2012) 249-258.
2) S. H. Won, et al., "Comparative Evaluation of Global Combustion Properties of Alternative Jet Fuels," *51th AIAA Aerospace Sciences Meeting*, Grapevine, Texas (2013).
3) Med Colket, 2013 MACCCR meeting

Motivations

1. Experimental platform for cool flame
   - To stabilize LTC-driven flame

2. Development of FRS technique
   - Quantifying the LTC related species

Development of a Stabilized Cool Flame Platform

2nd Flame Chemistry Workshop
San Francisco
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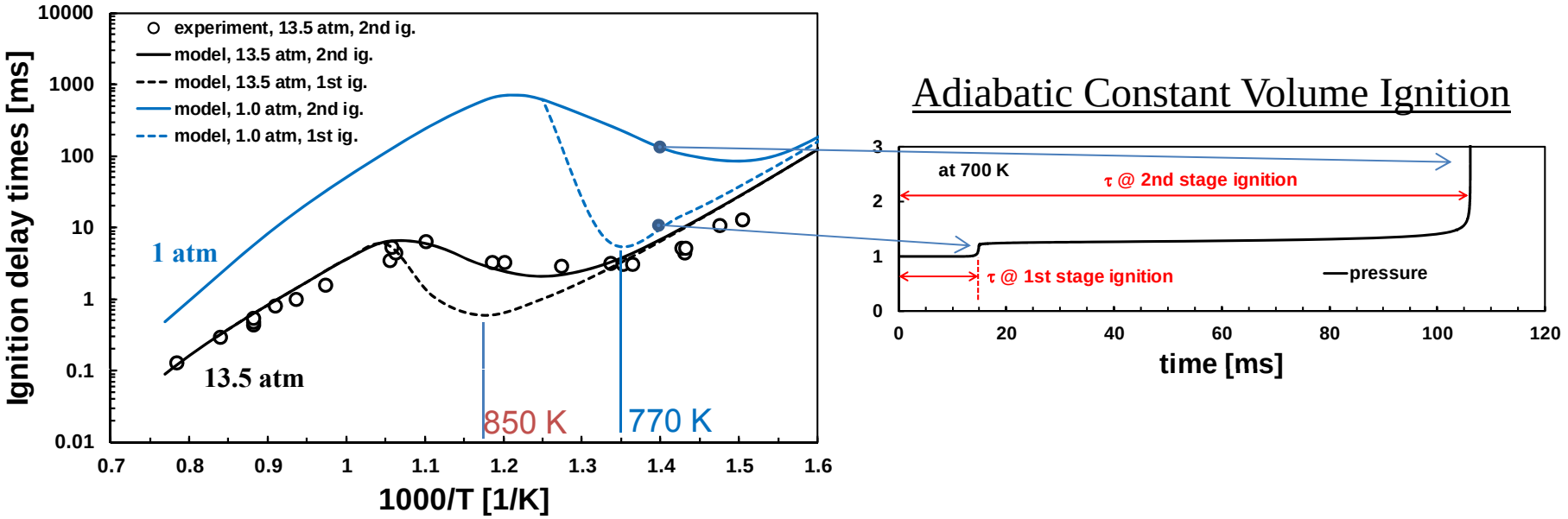
Challenges to Stabilize LTC-Driven Flames

- Induction chemistry at low temperature is very slow
  - Inability to initiate the radical pool (RH + X = R + HX)
  - Very sensitive to molecular structure
- **Then, how to shorten the induction chemistry?**

- Cool flames; mostly observed in premixed configuration
  - Flow reactor, jet-stirred reactor, etc..
- **Is it possible to observe cool flames in diffusive configuration ?**



1) H. J. Curran, P. Gaffuri, W. J. Pitz, C. K. Westbrook, Combust. Flame 114 (1998) 149-177.

Hints from Recent Studies

Zero-Gravity Experiment[1,2]

- Observed cool diffusion flame in a droplet combustion
- **Cool flame exists in diffusive configuration!**

1) V. Nayagam et al., Combust. Flame 159 (2012)
2) T. I. Farouk, F. L. Dryer, Combust. Flame 161 (2014)
3) W. Sun, S. H. Won, et al, Proc. Combust. Inst. 34 (2013)
4) T. Ombrello, S. H. Won, et al., Combust. Flame 157 (2010)
5) T. M. Vu, S. H. Won, et al., Combust. Flame 161 (2014)

Hints from Recent Studies

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- Observed cool diffusion flame in a droplet combustion
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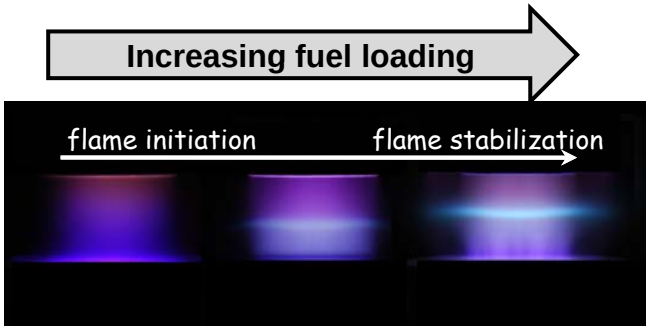
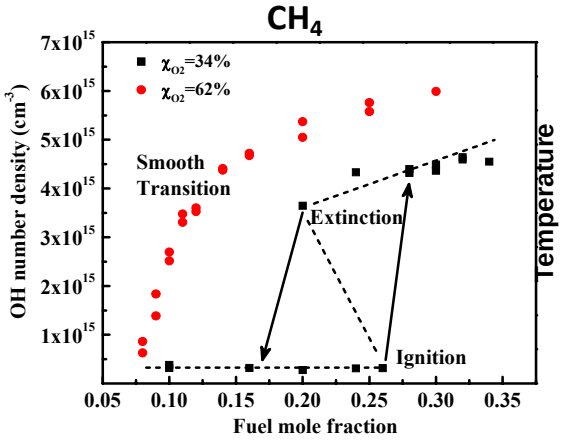
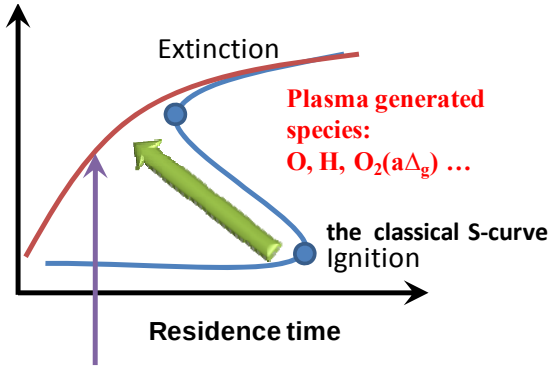
Plasma-Assisted Combustion[3-5]

- **Initiation of radical pool can be accelerated by Plasma**
- Enhancing flame ignition, propagation speed, and stabilization
- Electronically excited species and **ozone**, etc.



Low pressure counterflow diffusive configuration with nano-second pulsed discharge[3]



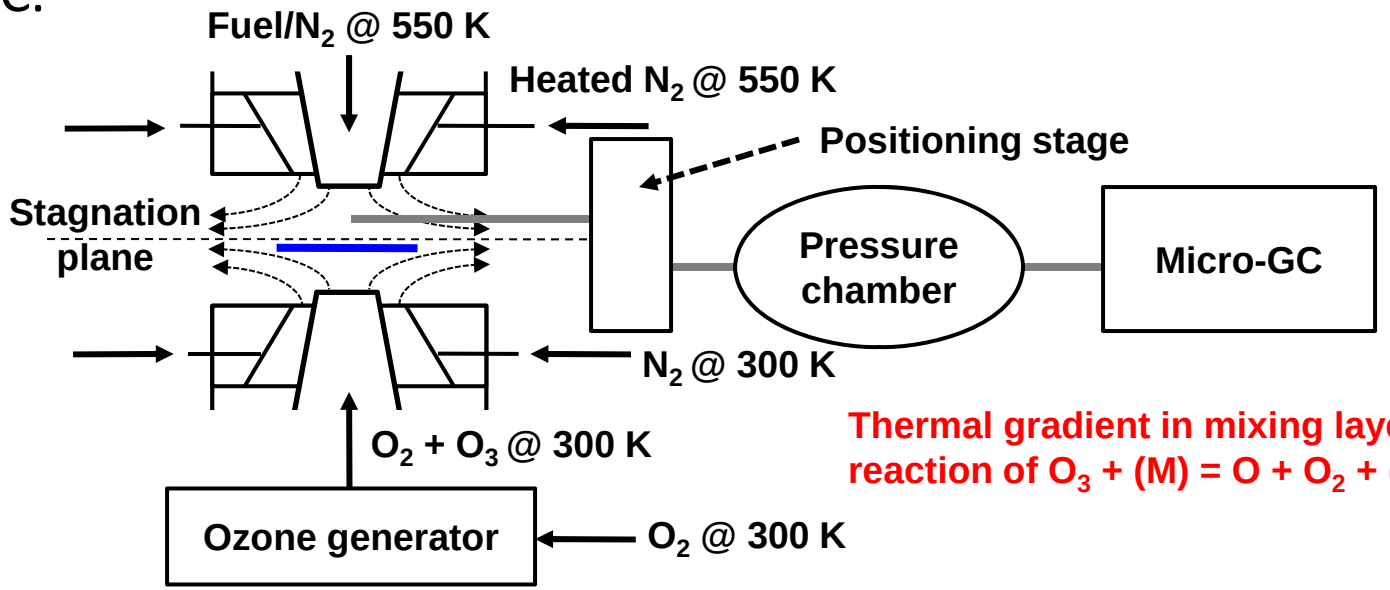


New combustion regime

1) V. Nayagam et al., Combust. Flame 159 (2012)
2) T. I. Farouk, F. L. Dryer, Combust. Flame 161 (2014)
3) W. Sun, S. H. Won, et al, Proc. Combust. Inst. 34 (2013)
4) T. Ombrello, S. H. Won, et al., Combust. Flame 157 (2010)
5) T. M. Vu, S. H. Won, et al., Combust. Flame 161 (2014)

Experiments

- 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]



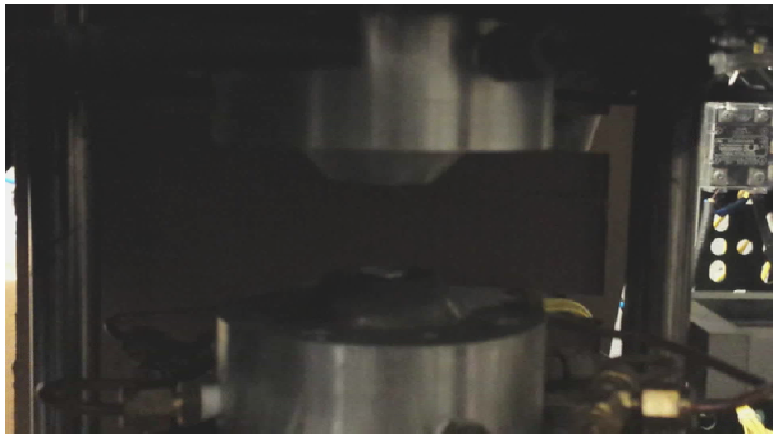
Thermal gradient in mixing layer initiates reaction of $O_3 + (M) = O + O_2 + (M)$

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

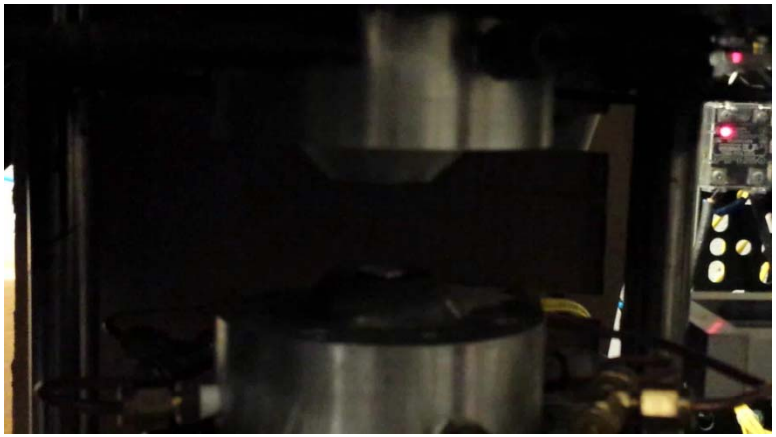
Initiation of Cool Diffusion Flames

- Procedure to initiate a cool diffusion flame
  1) Setting nitrogen (fuel side) and oxygen (oxidizer side) flow rates
  2) Turning on the ozone generator
  3) Flowing fuel (n-heptane) to fuel side

Lower fuel mole fraction:
Cool diffusion flame

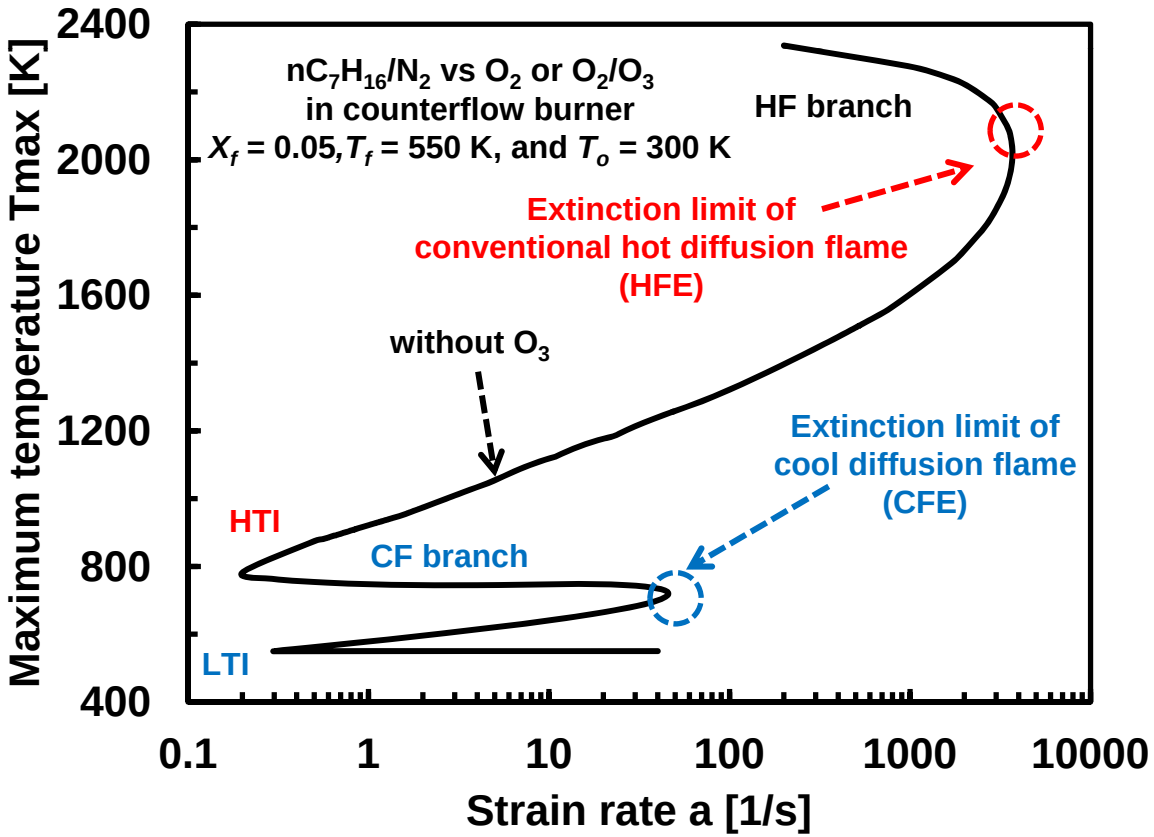


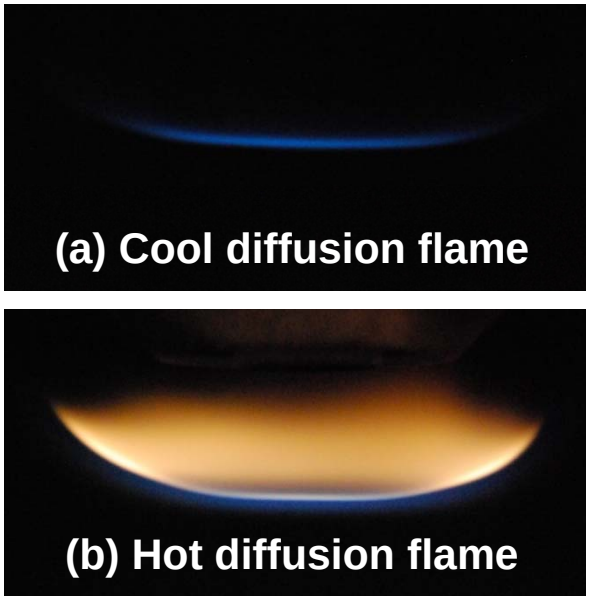
Higher fuel mole fraction:
Hot diffusion flame



Initiation of Cool Diffusion Flames

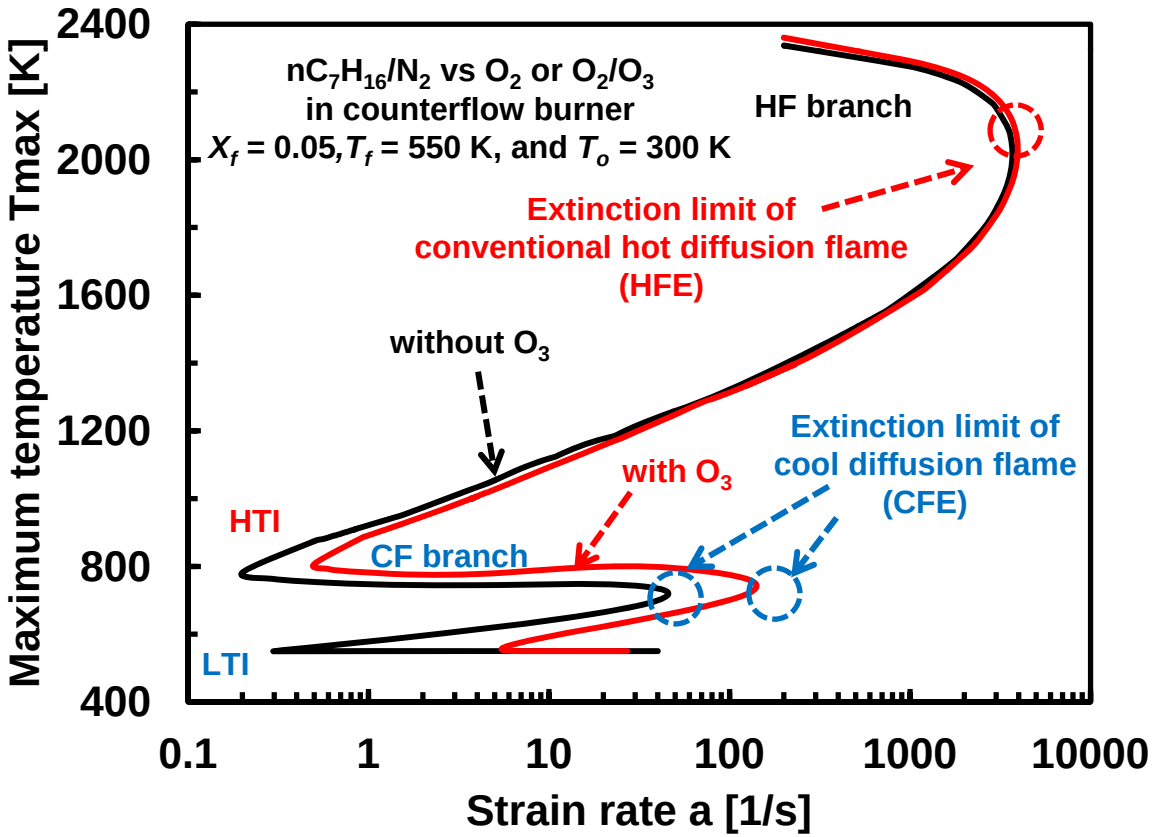
- Existence of cool diffusion flames in counterflow configuration with n-heptane
  - cool flame regime exists regardless of addition of ozone
  - .

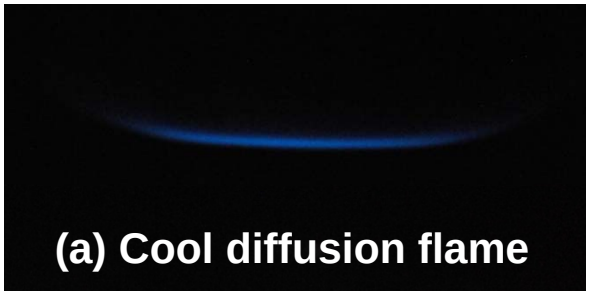




Initiation of Cool Diffusion Flames

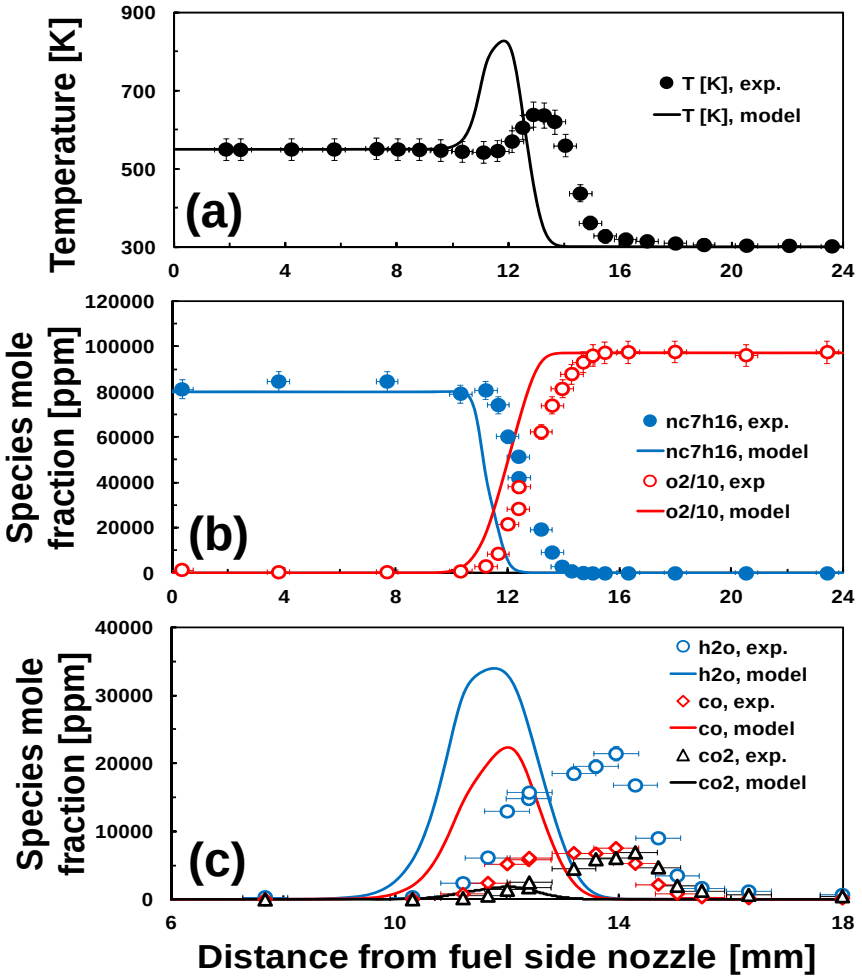
- Existence of cool diffusion flames in counterflow configuration with n-heptane
  - cool flame regime exists regardless of addition of ozone
  - Addition of ozone extends cool flame regime.





Speciation Profiles

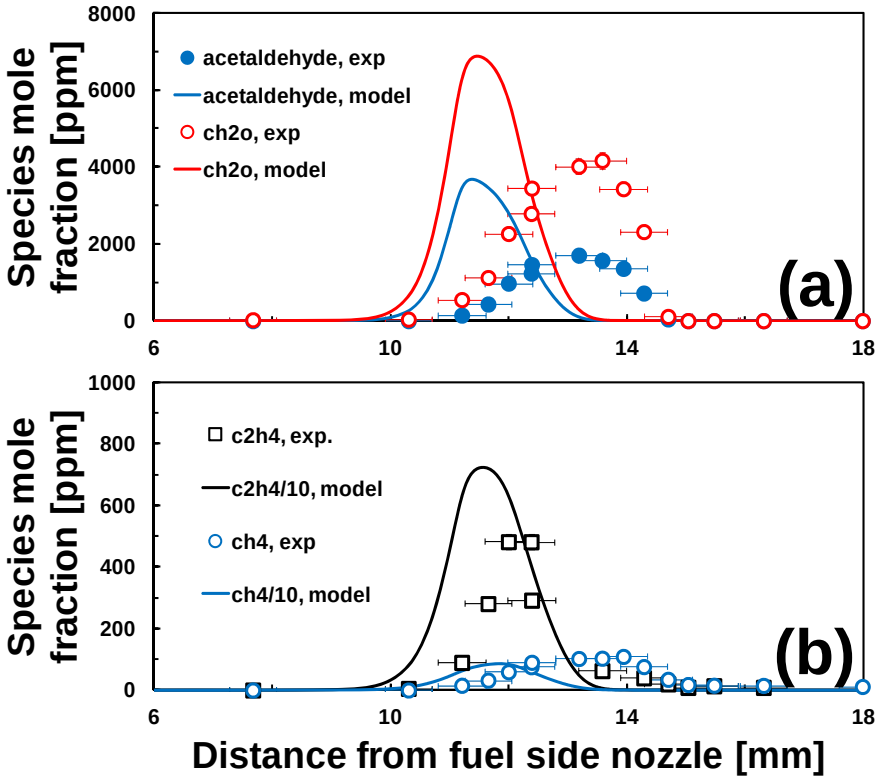
- Temperature measurements
  - Over-estimation of heat release in model prediction
- Failure to predict the flame position.
  - Boundary conditions were tested previously.[1]
  - Consistent even without putting sampling probe or thermocouple.

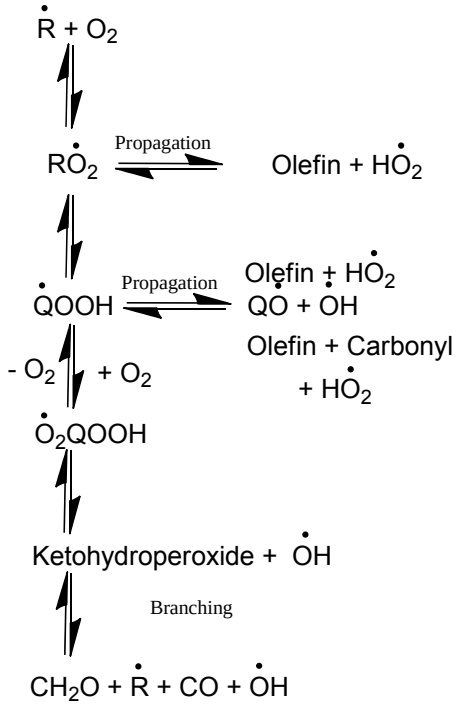


1) J. K. Lefkowitz, S. H. Won, et al., Proc. Combust. Inst. 34 (2013)

Speciation Profiles

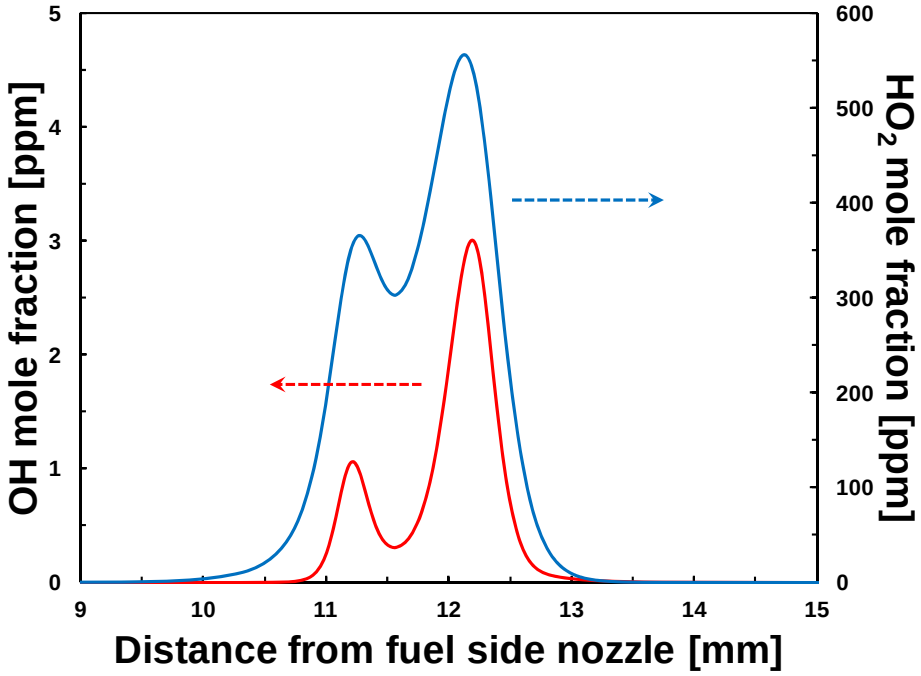
- Reasonable prediction of acetaldehyde and CH_2O
- Significant over-estimation of C_2H_4 and CH_4 formation
  - Factor of 10.

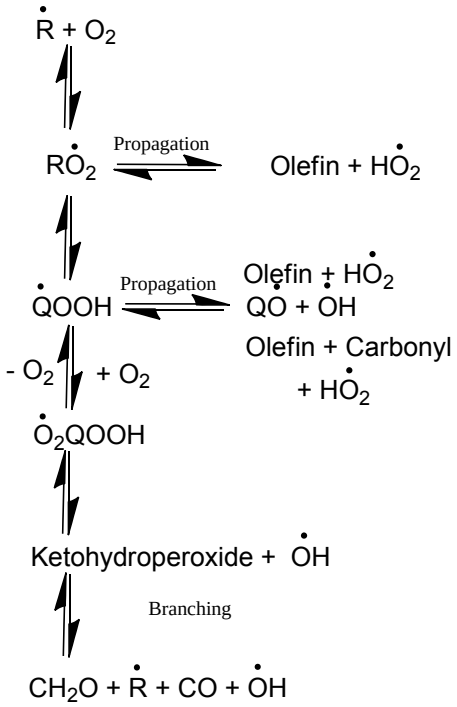




Quick Summary

- Well-defined experimental platform of cool flames for LTC study
- Speciation profiles revealed deficiency of kinetic model at cool flame regime
  - Over-prediction of small hydrocarbon species (CH_4, C_2H_4, etc.)
- **Sophisticated diagnostic techniques** might be able to point out
  - Origin of model over-prediction: low temperature chain branching vs. propagation reaction pathways





Faraday Rotation Spectroscopy Diagnostic for In-Situ Measurement of HO_x Radicals

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Joseph Lefkowitz[2], Xueliang Yang[2], Yiguang Ju[2],

Gerard Wysocki[1]

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[2] Mechanical and Aerospace Engineering Department, Princeton University, Princeton NJ

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Challenges w/ LTC HOx Measurements

- General challenges with radical quantification
  - Wall quenching
  - Spectral Interference

- Species specific complications
  - OH
    - Present at low concentrations (<1 ppmv)
    - Difficult to quantify via LIF *in situ*

  - HO_2
    - Not detectable via LIF (photo-fragmentation LIF* is possible)

- Fluorescence Assay by Gas Expansion (FAGE)†

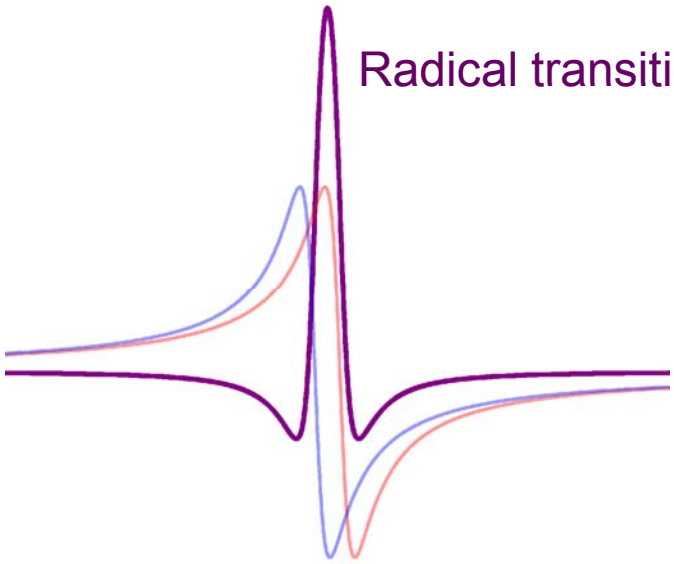
*Johansson, O.; Bood, J.; Li, B.; Ehn, A.; Li, Z. S.; Sun, Z. W.; Jonsson, M.; Konnov, A. A.; Aldén, M.: *Combust. Flame* **2011**, *158*, 1908-1919

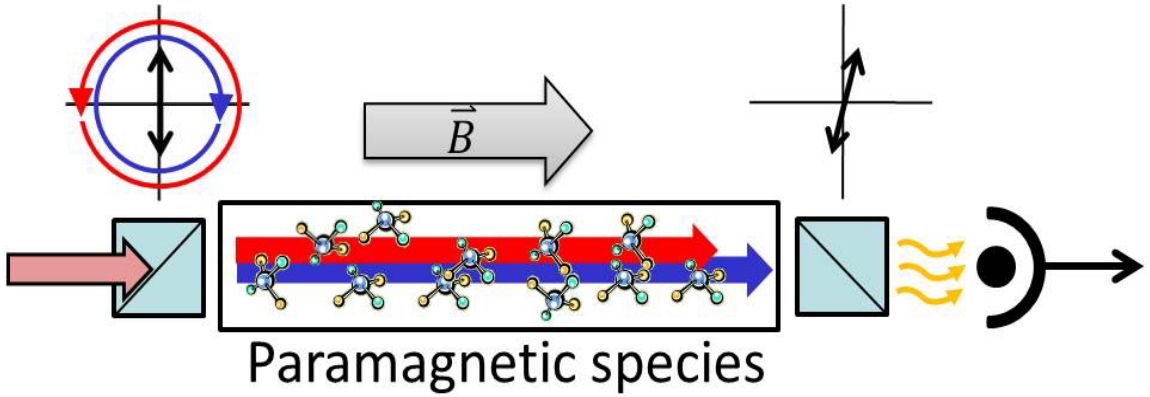
† Blocquet, M.; Schoemaecker, C.; Amedro, D.; Herbinet, O.; Battin-Leclerc, F.; Fittschen, C.: *Proc. Natl. Acad. Sci. U.S.A* **2013**, *110*, 20014-20017

Faraday Rotation Spectroscopy (FRS)

- Apply Magnetic Field → Zeeman Splitting → Faraday Effect
- Polarization rotation → Linear Polarizer → Intensity Variation

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



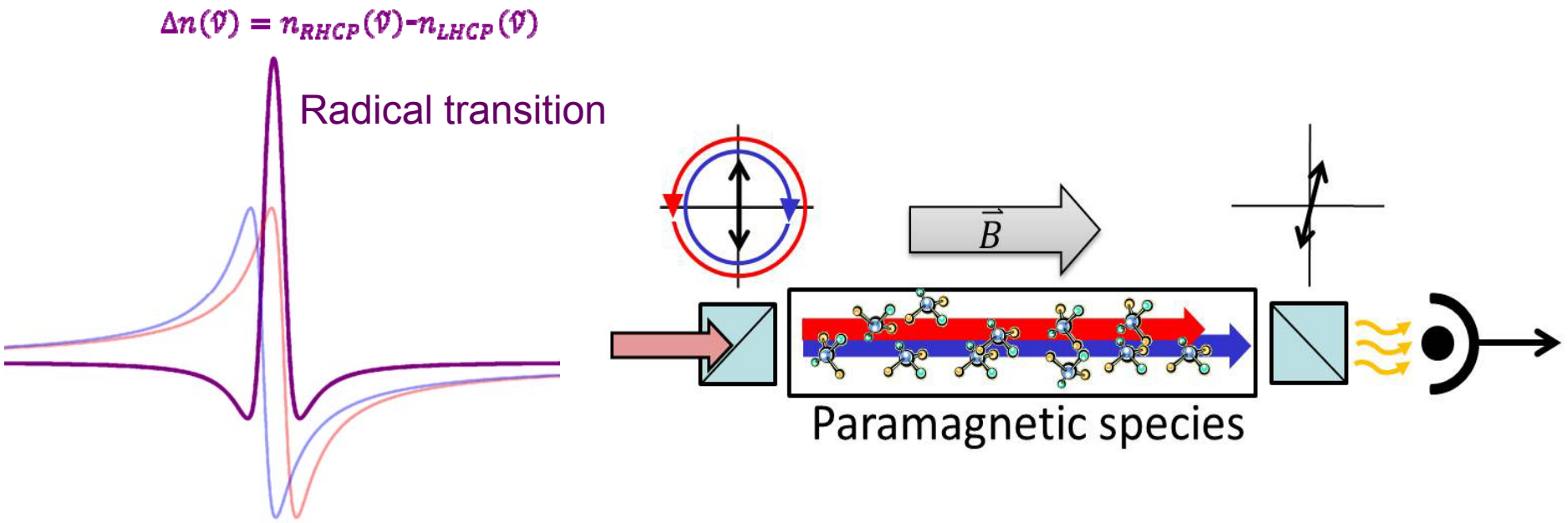


- Sample modulation by varying magnetic field (AC-FRS)*
- Strong suppression of absorption signals from non-radicals
- Zero background technique

* Litfin, G.; Pollock, C. R.; Curl, J. R. F.; Tittel, F. K.: *J. Chem. Phys.* **1980**, *72*, 6602-6605.
Brumfield, B.; Sun, W.; Ju, Y.; Wysocki, G.: *J. Phys. Chem. Lett.* **2013**, *4*, 872-876

Faraday Rotation Spectroscopy (FRS)

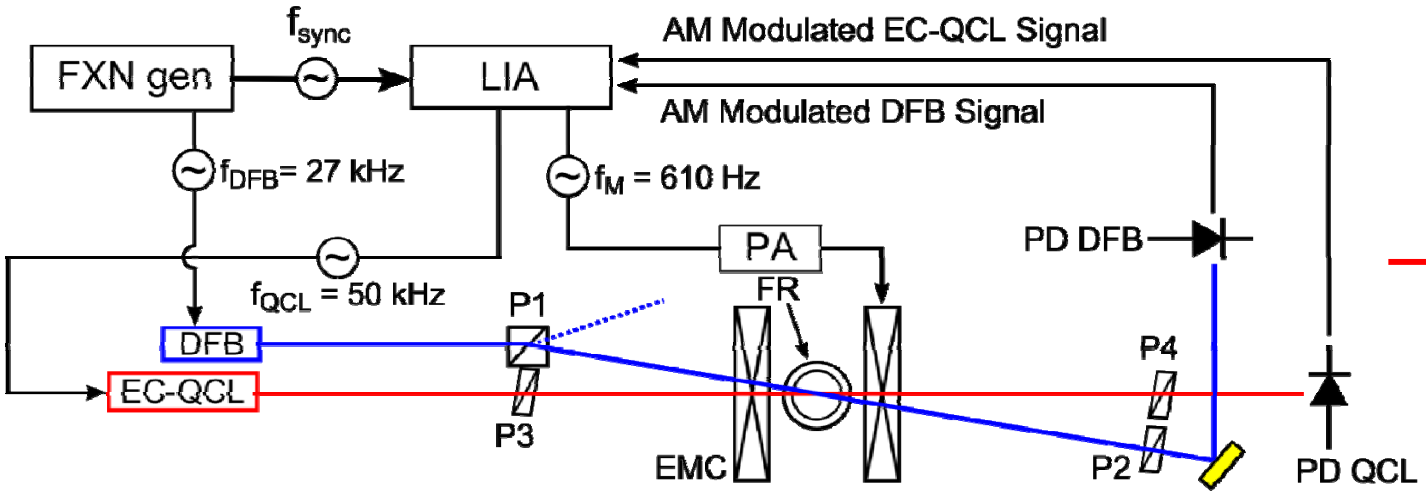
- Apply Magnetic Field → Zeeman Splitting → Faraday Effect
- Polarization rotation → Linear Polarizer → Intensity Variation

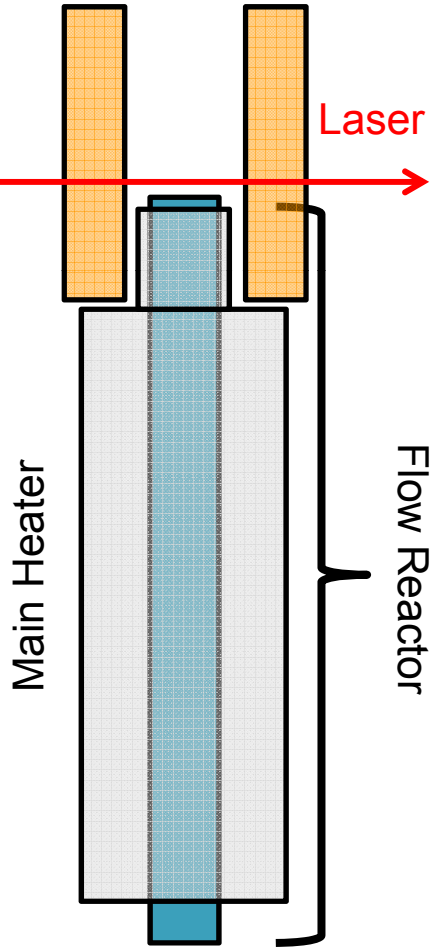


- Marginal increase in experimental complexity from TDLAS

  (polarizers, 1-2 lock-in amplifiers, magnetic coil)

Experimental Demonstration of FRS

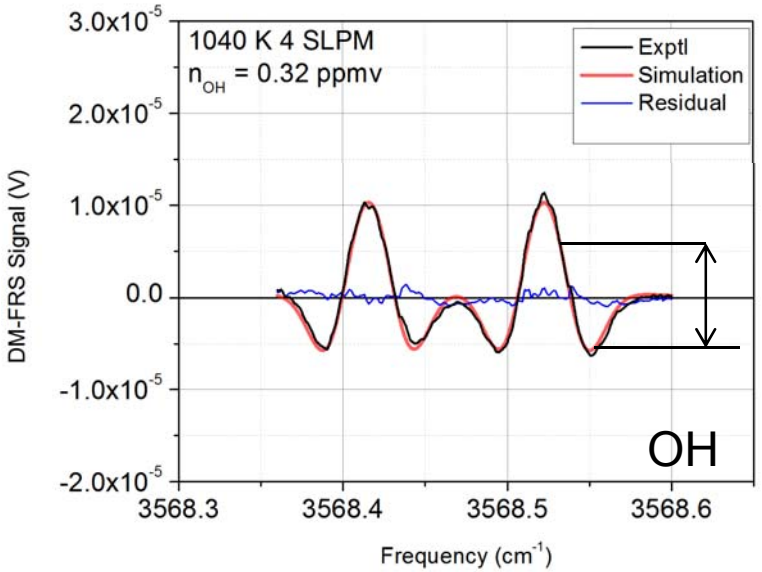


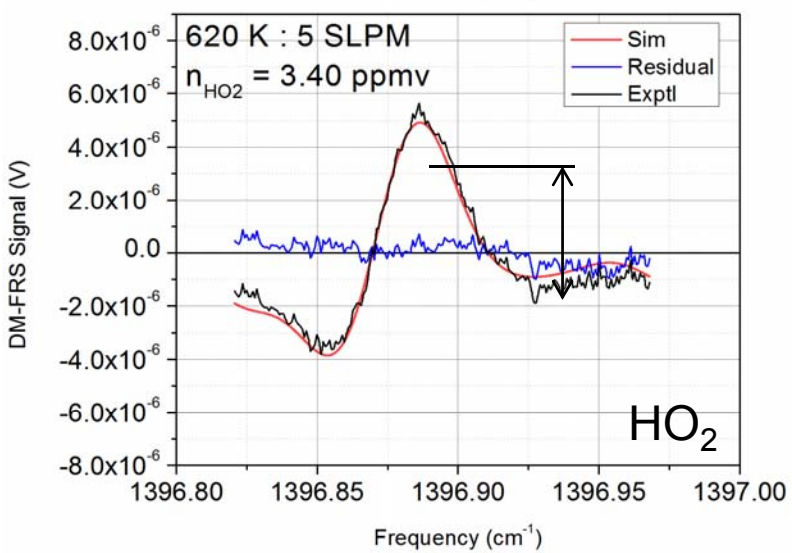


- Target OH (2.8 μm) and HO_2 (7.1 μm)
- 1.7 cm optical path from reactor opening
- Measure 2 mm from exit
- Laser wavelength + magnetic field modulation→ DM-FRS*
  - Detect HO_2 at $1f_L \pm f_M$ (1f DM-FRS)
  - Detect OH at $2f_L \pm f_M$ (2f DM-FRS)

* Brumfield, B.; Sun, W.; Wang, Y.; Ju, Y.; Wysocki, G.: *Opt. Lett.* **2014**, *39*, 1783-1786

Example DM-FRS Spectra

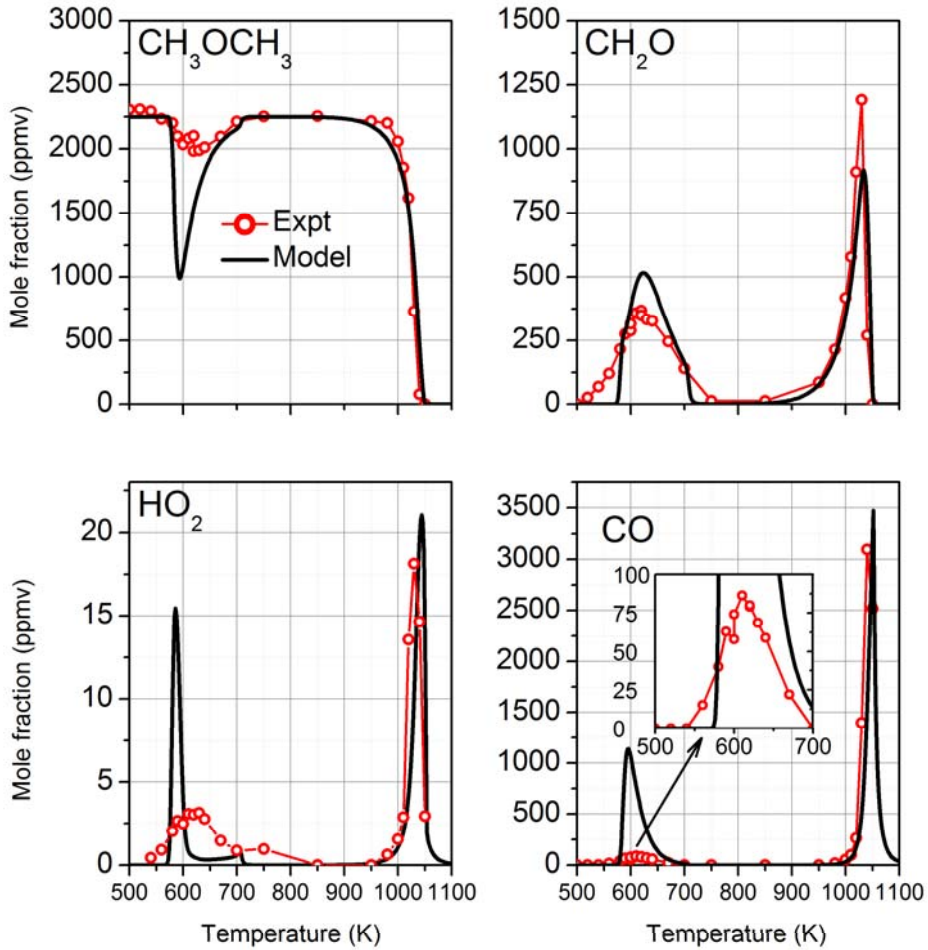


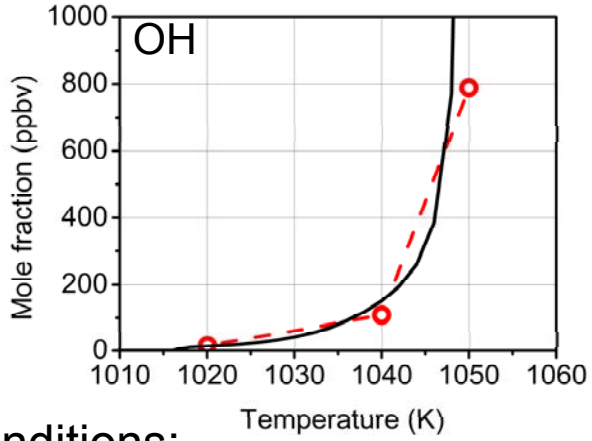


- FRS spectral model (w/ HITRAN parameters)*
- OH detection
  - Θ_{NEA} = 1.94x10^{-8} rad/$\sqrt{Hz}$
  - Ultimate limit (quantum shot-noise) = 8x10^{-9} rad/$\sqrt{Hz}$
  - 3σ detection limit = 20 ppbv /$\sqrt{Hz}$ **(single point peak-to-baseline)**
  - Equivalent to 8x10^{-8} /$\sqrt{Hz}$ fractional loss
- For HO_2 detection
  - Θ_{NEA} = 1x10^{-8} rad/$\sqrt{Hz}$
  - Ultimate limit = 1.5x10^{-9} rad/$\sqrt{Hz}$
  - 3σ detection limit ≈ 1 ppmv /$\sqrt{Hz}$
  - Equivalent to ~1x10^{-6} /$\sqrt{Hz}$ fractional loss
- Accuracy limited by systematic uncertainties

* Brumfield, B.; Sun, W.; Wang, Y.; Ju, Y.; Wysocki, G.: *Opt. Lett.* **2014**, *39*, 1783-1786

Observed Species Profiles





- Conditions:
  - Composition: 0.96/0.0375/0.00225 $He/O_2/CH_3OCH_3$
  - Plug-flow residence time: 0.45 to 0.2 seconds
- DME,CH_2O, and CO measured with gas chromatography
- OH/HO_2 concentrations consistent with model †
- Observed low-reactivity ~600 K similar to prior measurements*

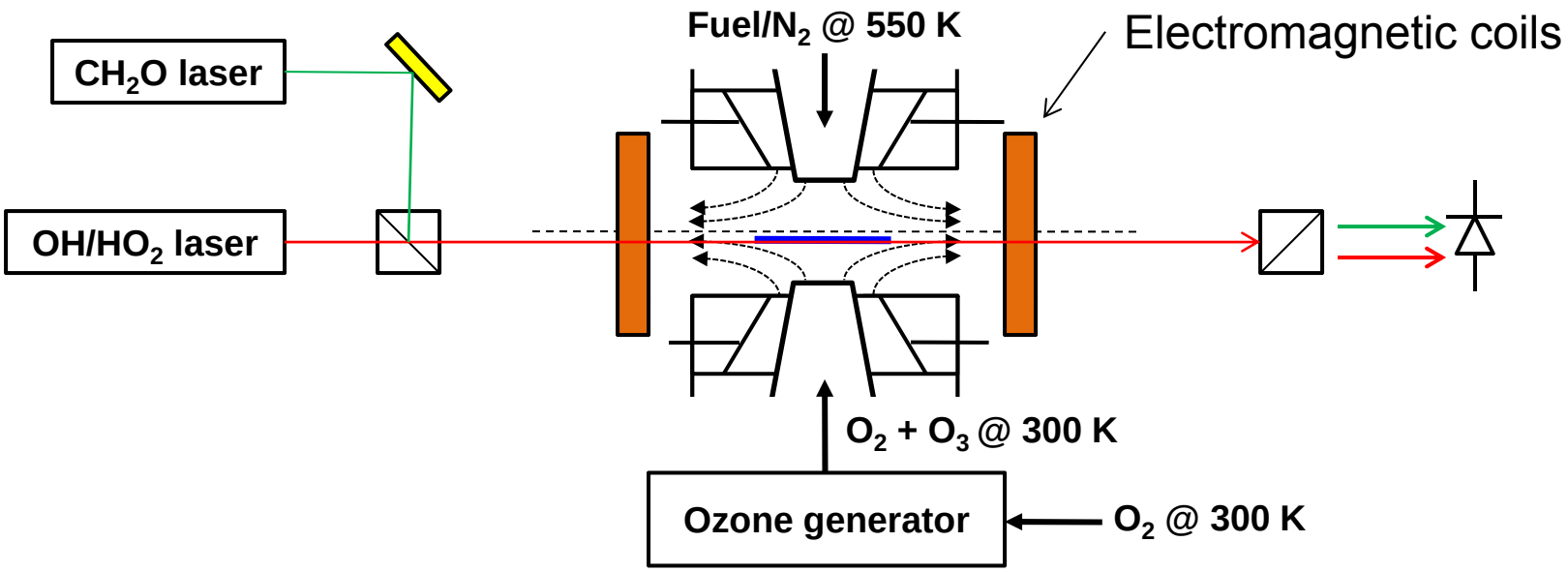
† Zhao, Z.; Chaos, M.; Kazakov, A.; Dryer, F. L.: *Int. J. Chem. Kinet.* **2008**, *40*, 1-18

* Brumfield, B.; Sun, W.; Ju, Y.; Wysocki, G.: *J. Phys. Chem. Lett.* **2013**, *4*, 872-876

Kurimoto, N.; Brumfield, B.; Yang, X.; Wada, T.; Diévart, P.; Wysocki, G.; Ju, Y.: *Proc. Combust. Inst., in Press*

DOI: 10.1016/j.proci.2014.05.120

Proposed Future Work



- Merge FRS diagnostic with cool flame platform
- Employ mid-IR absorption diagnostic for CH_2O quantification
- Potential to spatially profile cool flame
- Use LIF imaging to extract absolute concentration profile

Extension of FRS technique

- Applicable to many other small radical species
- Relevant to combustion and atmospheric chemistry studies
- Many potential targets;
  - CH, CH_2, CH_3, NO*, $NO_2^{\dagger}$, HCO, HCN etc…

*Wang, Y.; Nikodem, M.; Wysocki, G.: *Opt. Express* **2013**, *21*, 740-755
† Zaugg, C. A.; Lewicki, R.; Day, T.; Curl, R. F.; Tittel, F. K.: **2011**, 79450O-79450O-7

Conclusion

- Develop a experimental platform to study cool flame chemistry
- Significant disagreement from observed vs. predicted speciation profiles using existing n-heptane mechanism
- Quantification of HOx would aid in constraining kinetic model
- FRS has been demonstrated to provide sensitive and selective measurements of HOx
- Combination of platform with diagnostic will provide insight into LTC chemistry

Acknowledgements

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