Fundamental Kinetics Database for Jet Fuel Surrogates: Shock Tube/Laser Absorption Measurements

Fuel Summit at USC, September 15-17, 2009

R. K. Hanson, D. F. Davidson
Department of Mechanical Engineering
Stanford University

- Objectives/Facilities
- Kinetics Database Experiments
  - Ignition Delay Times
  - Multi-Species Time-Histories
  - Comparisons with JetSurF
- Future Work

Work supported by AF-IPT Program
Julian Tishkoff: contract Monitor

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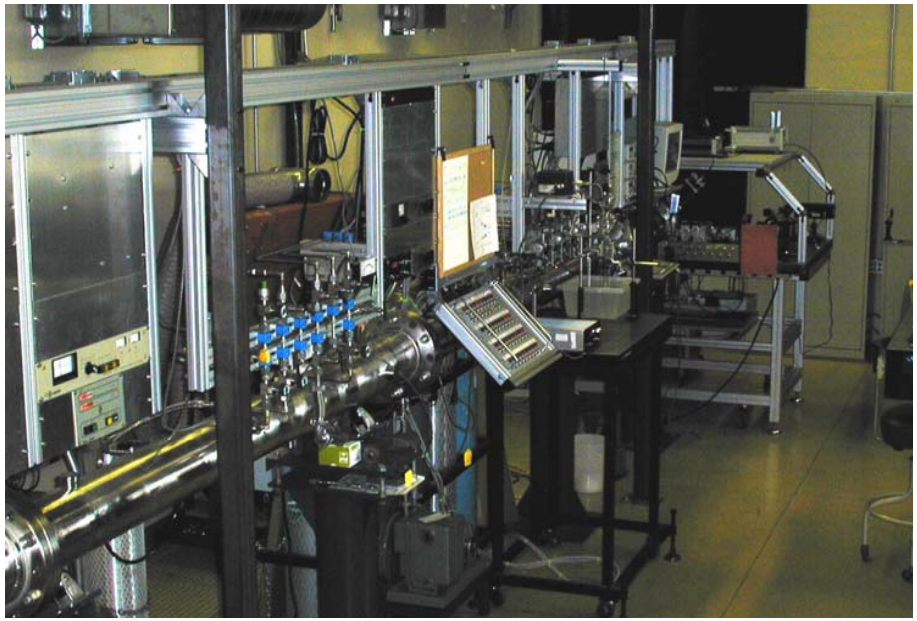

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Long-Term Objectives

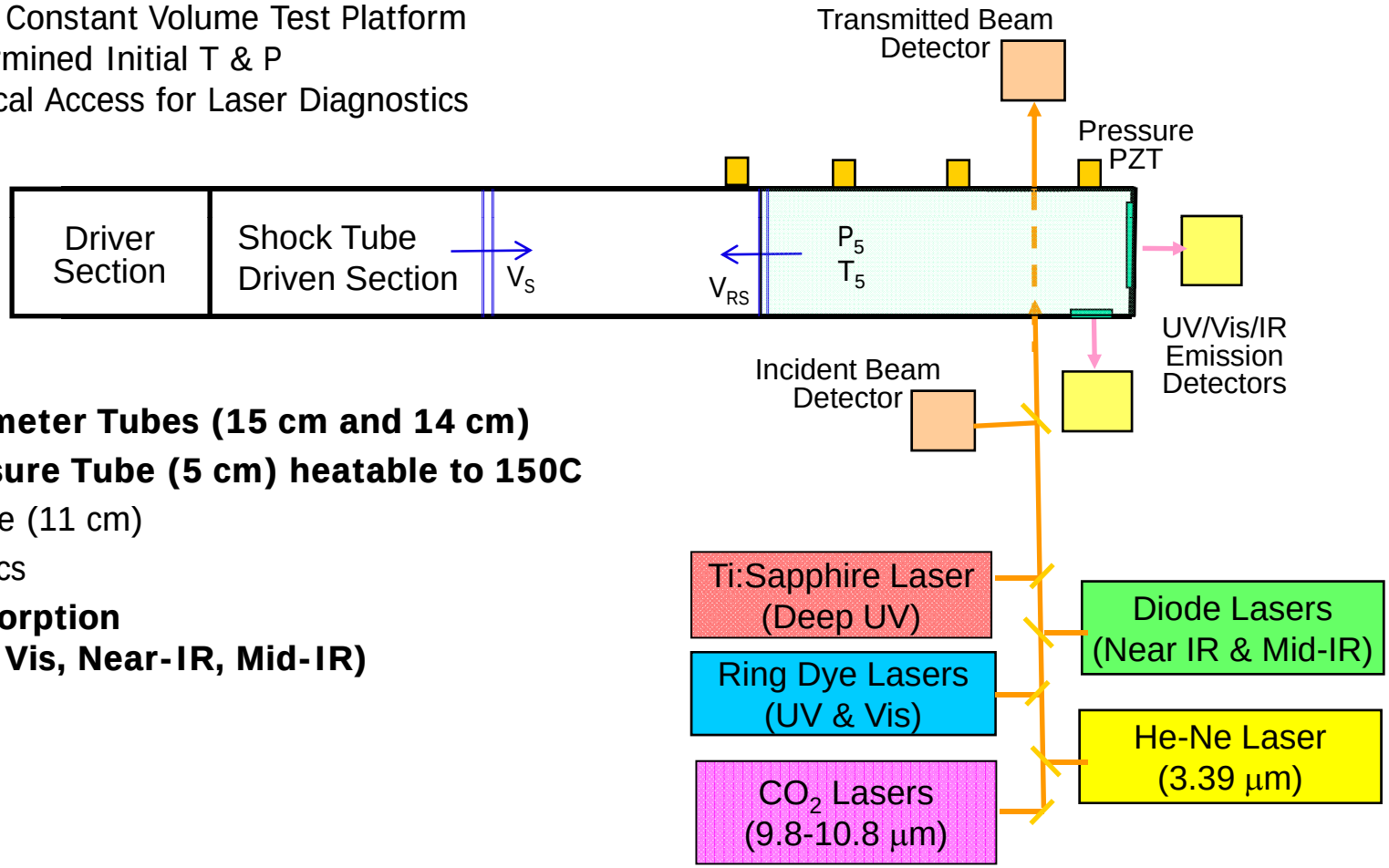
- To develop improved detailed mechanisms for jet fuel surrogates through a *collaborative research effort* by the AF-IPT team

➔ Stanford contribution: Fundamental kinetics database for jet fuel surrogates using shock tube/laser absorption measurements; includes data for ignition delay times and multi-species concentration time-histories

➔ Stanford contribution: Improve knowledge of specific elementary reaction rates through *targeted* experiments (indirect and direct)

Stanford Shock Tube & Laser Facilities

- Advantages of Shock Tubes
  - Near-Ideal Constant Volume Test Platform
  - Well-Determined Initial T & P
  - Clear Optical Access for Laser Diagnostics



- Shock Tubes (4)
  - **Large Diameter Tubes (15 cm and 14 cm)**
  - **High Pressure Tube (5 cm) heatable to 150C**
  - Aerosol Tube (11 cm)
- Optical Diagnostics
  - **Laser Absorption (VUV, UV, Vis, Near-IR, Mid-IR)**

4

Topic 1: Ignition Delay Times - Current Status

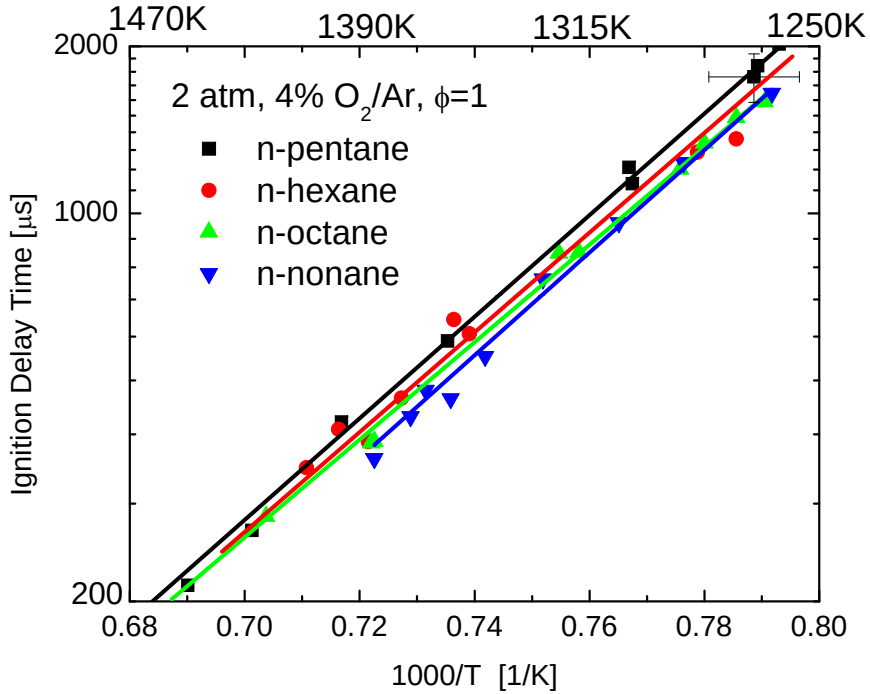
- Surrogate Fuels Studied
  - Year 1: Large normal alkanes
    - n-pentane, n-hexane, n-octane, n-nonane
  - Year 2: n-dodecane, cyclo-alkanes,
    - n-dodecane ($C_{12}H_{26}$)
    - cyclohexane (CH), methylcyclohexane (MCH), butylcyclohexane (BCH)

- Goal: High-quality dataset for jet fuel surrogates over a uniform range of conditions:

  4% O_2, ϕ=0.5-1.0, 1.5-3.0 atm, 1200-1600 K

$C_4 – C_9$ N-Alkane Ignition (Year 1)

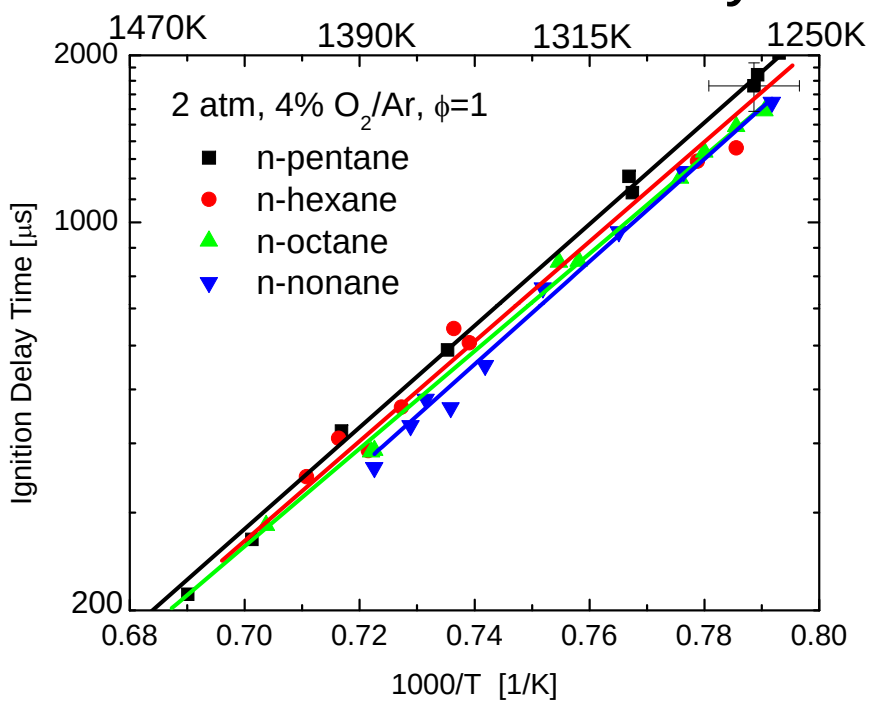
Stanford ST Study



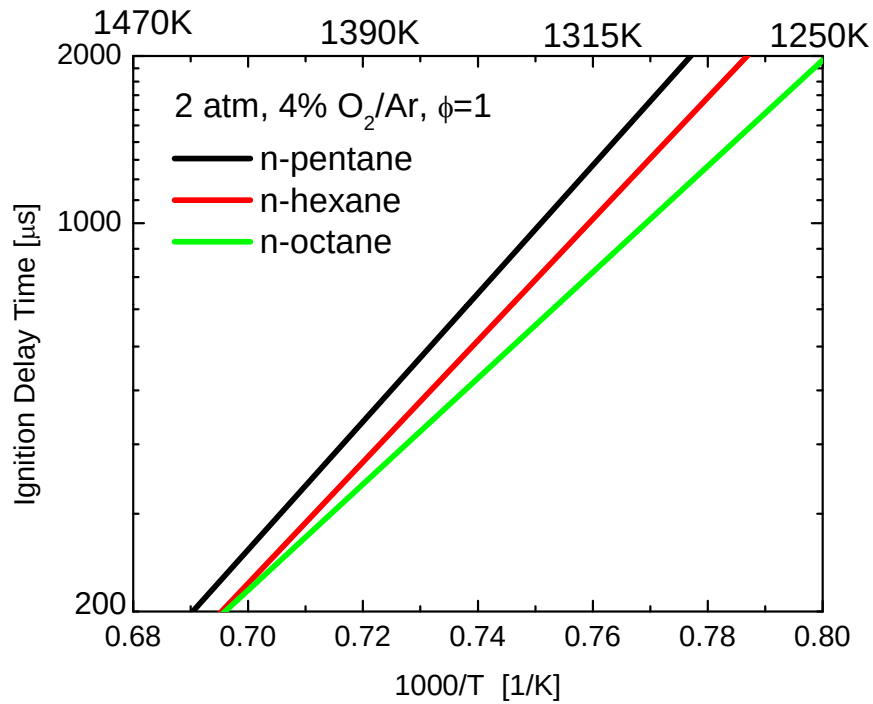
- Achieve goal of high-quality, low scatter data
- Well-defined values for E_A
- Small systematic variation of ignition delay time with carbon no. ($\tau_{ign} \sim C\#^{-0.4}$)

$C_4 – C_9$ N-Alkane Ignition (Year 1)

Stanford ST Study



JetSurF 0.2 Model

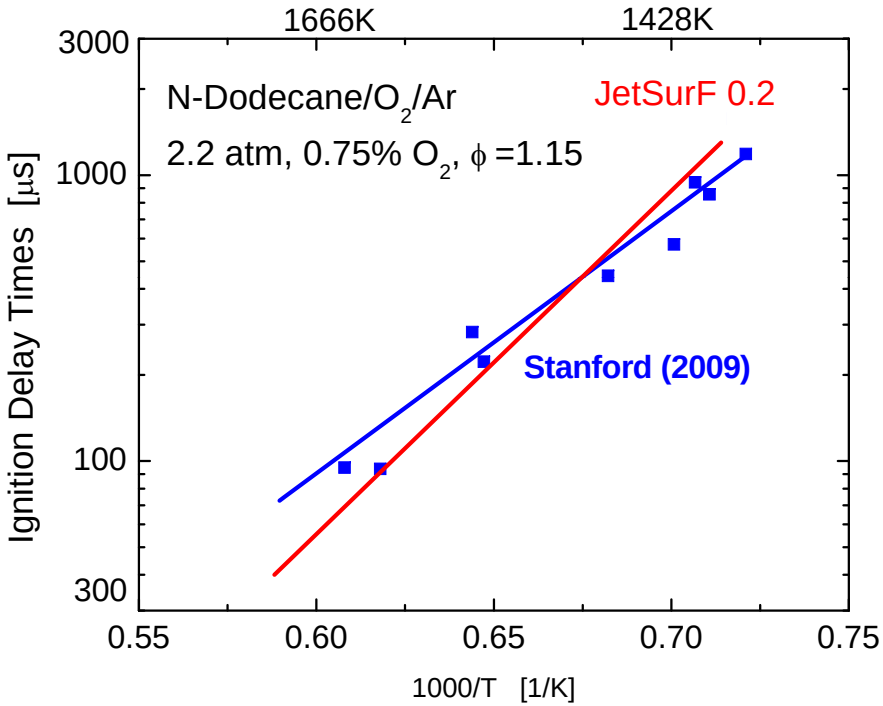


- Achieve goal of high-quality, low scatter data
- Well-defined values for E_A
- Small systematic variation of ignition delay time with carbon no. ($\tau_{ign} \sim C\#^{-0.4}$)
- JetSurF 0.2: some differences from experiment (but within USC uncertainty limits)

  ➔ SU data will facilitate JetSurF 1.1 model refinements, especially at low T

N-Dodecane ($C_{12}H_{26}$) Ignition (Year 2)

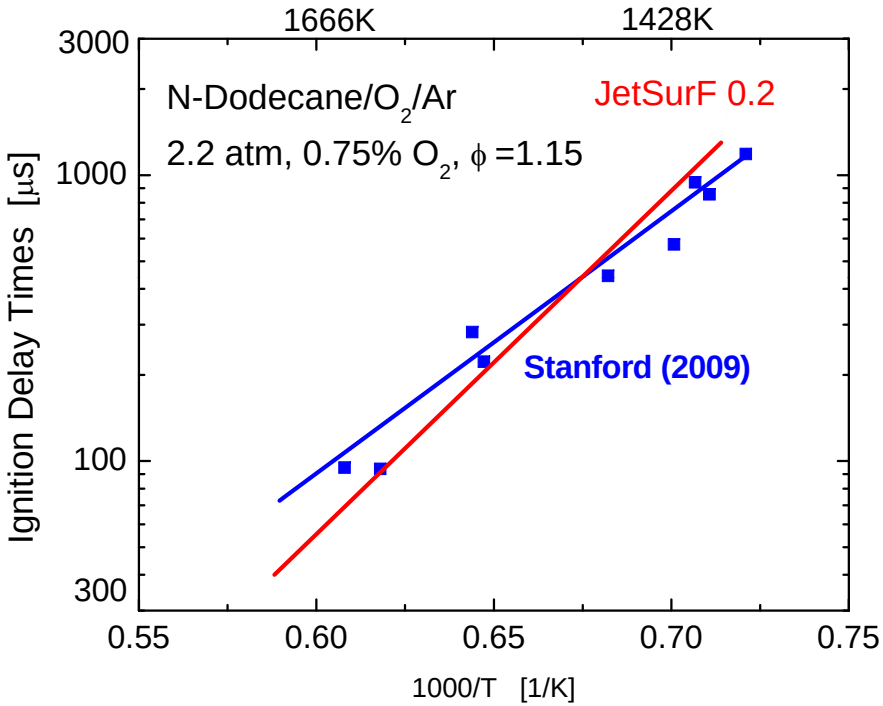
Low P, High T



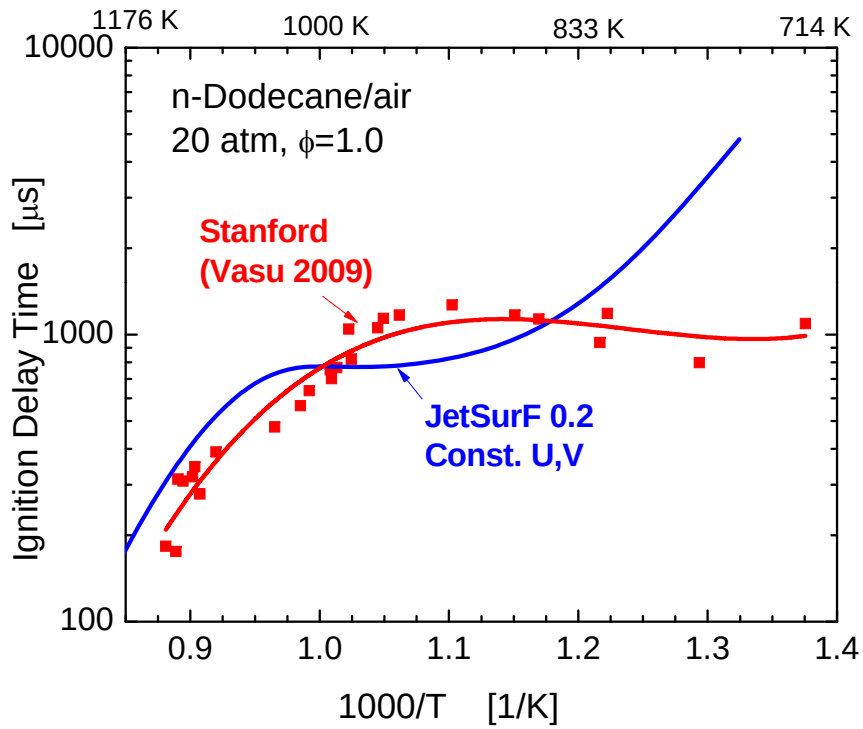
- Low P, High T: JetSurF 0.2 agrees with data at T ~1500 K, but overpredicts E_A

N-Dodecane ($C_{12}H_{26}$) Ignition (Year 2)

Low P, High T



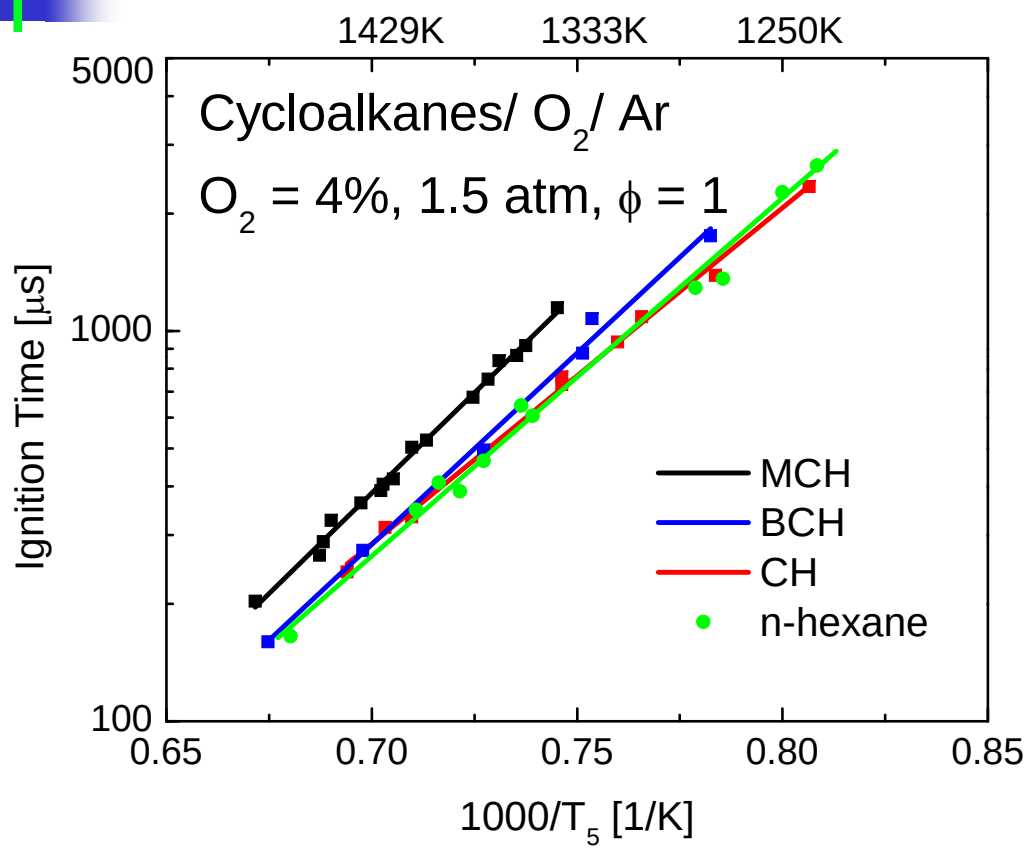
High P, Low T



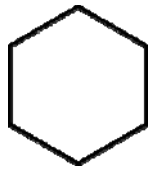
- Low P, High T: JetSurF 0.2 agrees with data at T ~1500 K, but overpredicts E_A
- High P, Low T: JetSurF 0.2 agrees with data near 1000 K, slightly overpredicts τ_{ign} at high T and varies widely from data at T<800K

  ➔ SU data will provide useful targets for refinements to JetSurF, especially at low T

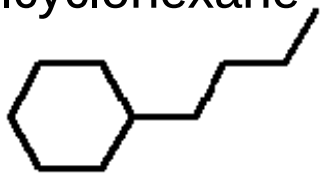
Cyclo-Alkane Ignition (Year 2): Relative Ignition Delays for CH, BCH and MCH



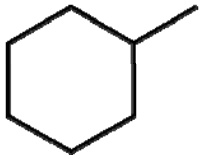
- Cyclohexane



- Butylcyclohexane



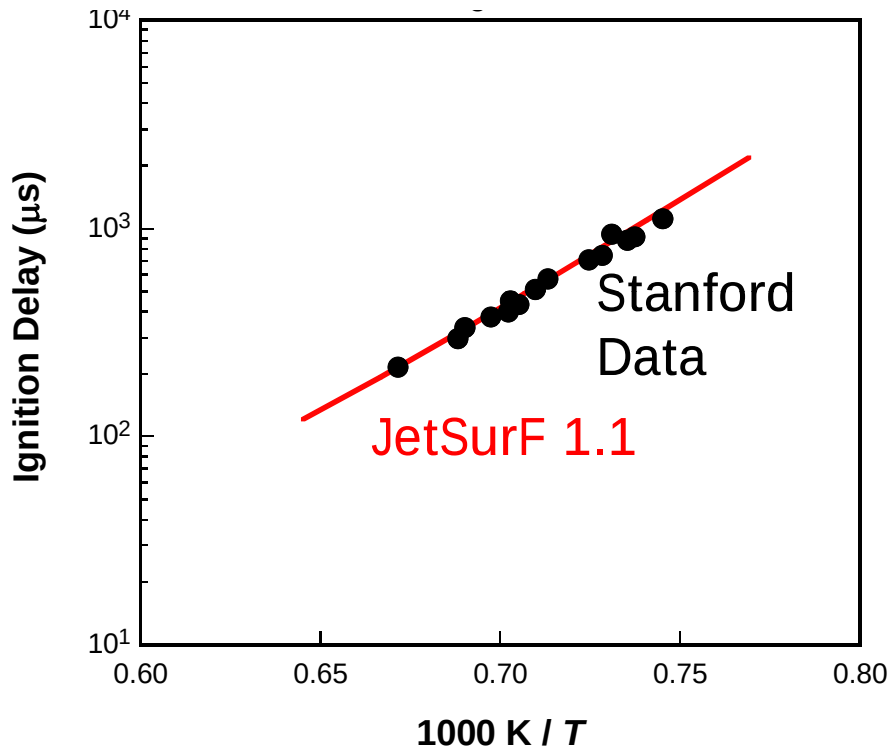
- Methylcyclohexane



- CH and BCH ignition delay times similar to n-hexane
- MCH ignition distinctly slower than BCH and CH
- Variation in ignition times can provide insight to decomposition pathways

Methylcyclohexane: Comparison with JetSurF 1.1 Model

MCH/4%O_2/Ar, 1.5 atm, ϕ=1.0



- Excellent agreement between JetSurF 1.1 and Stanford data for τ_{ign} and E_A at ϕ = 1.0

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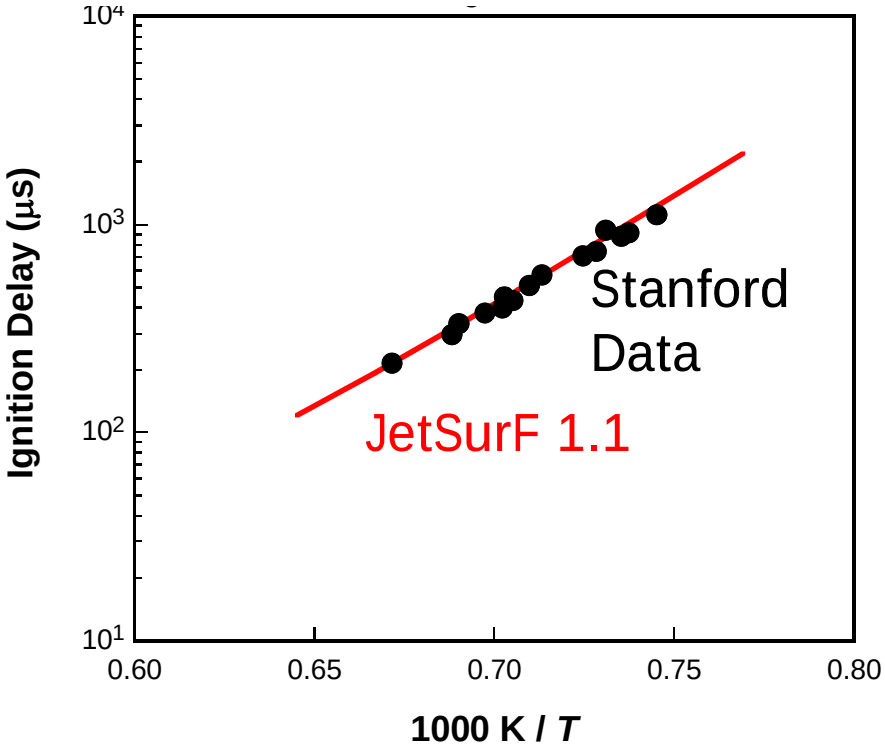
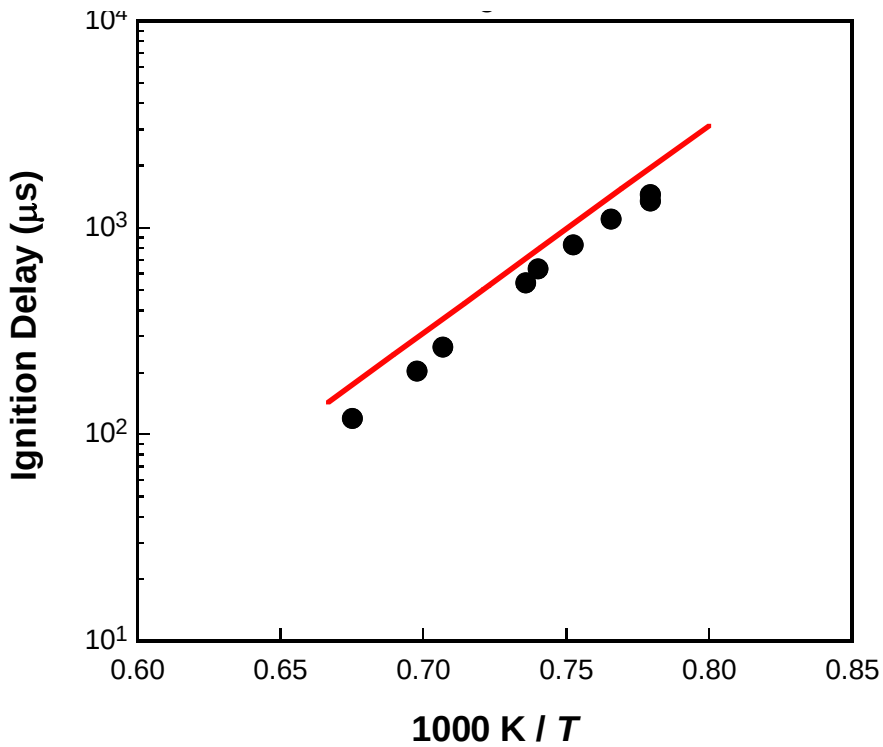


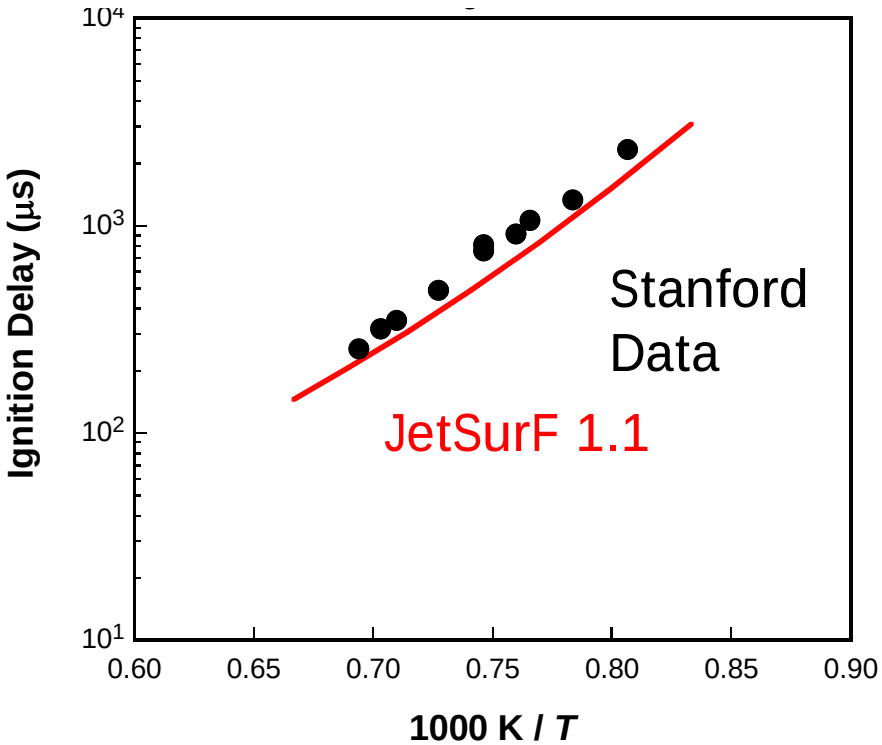
MCH/4%O_2/Ar, 1.5 atm, ϕ=0.5



- Excellent agreement between JetSurF 1.1 and Stanford data for τ_{ign} and E_A at ϕ = 1.0
- Relatively good agreement at ϕ = 0.5; but model slightly overpredicts τ_{ign}

Cyclohexane: Comparison with JetSurF 1.1 Model

CH/4%O_2/Ar, 1.5 atm, ϕ=1.0



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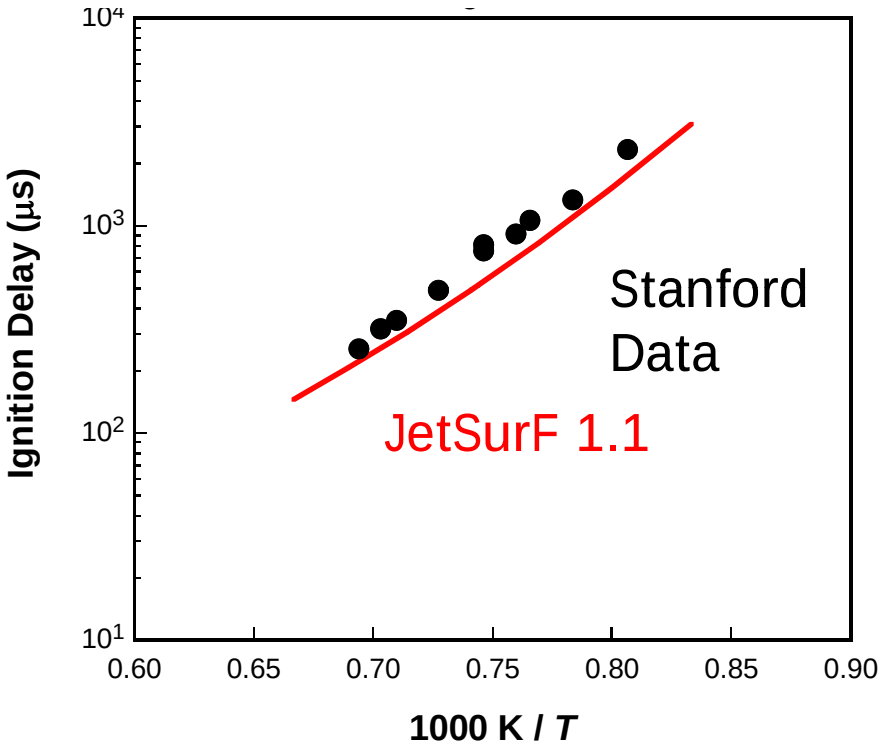
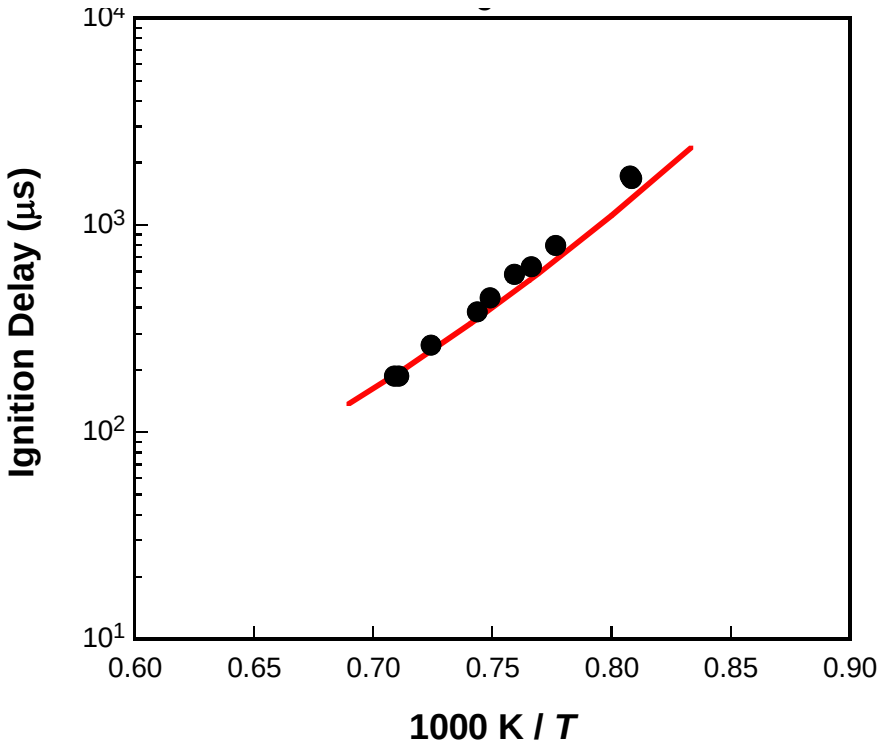


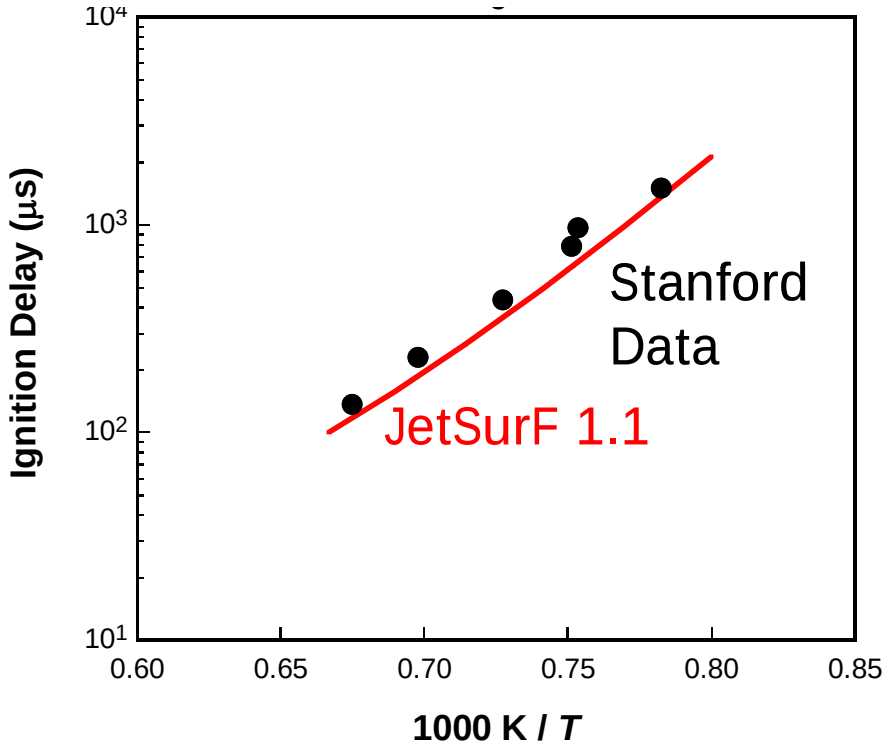
CH/4%O_2/Ar, 1.5 atm, ϕ=0.5



- Relatively good agreement between JetSurF 1.1 and Stanford data, but model slightly underpredicts τ_{ign} at ϕ = 1.0
- Very good agreement at ϕ = 0.5

Butylcyclohexane: Comparison with JetSurF 1.1 Model

BCH/4%O_2/Ar, 1.5 atm, ϕ=0.83



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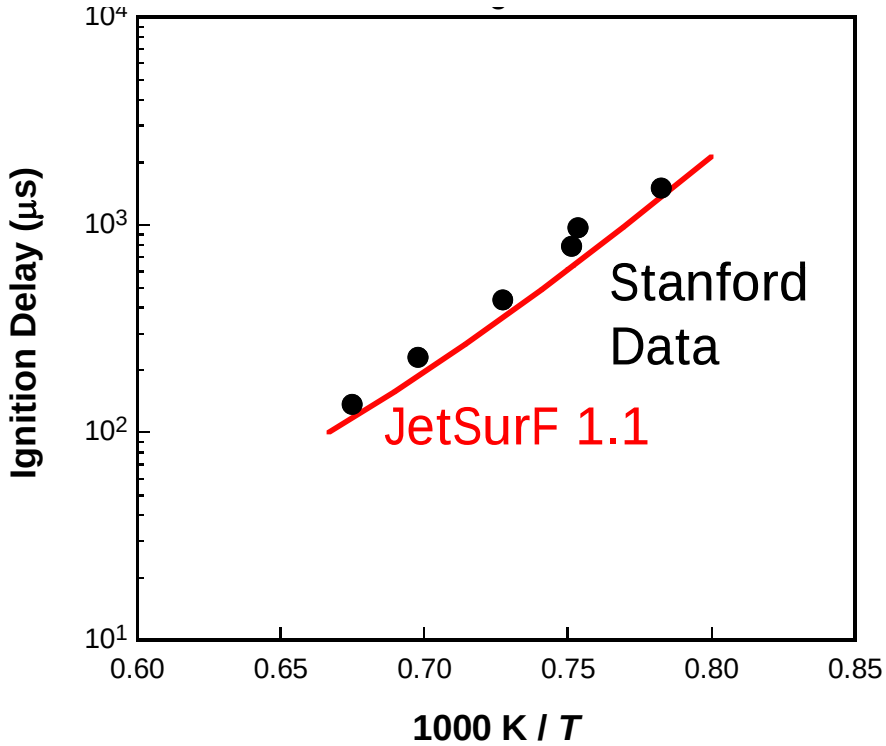
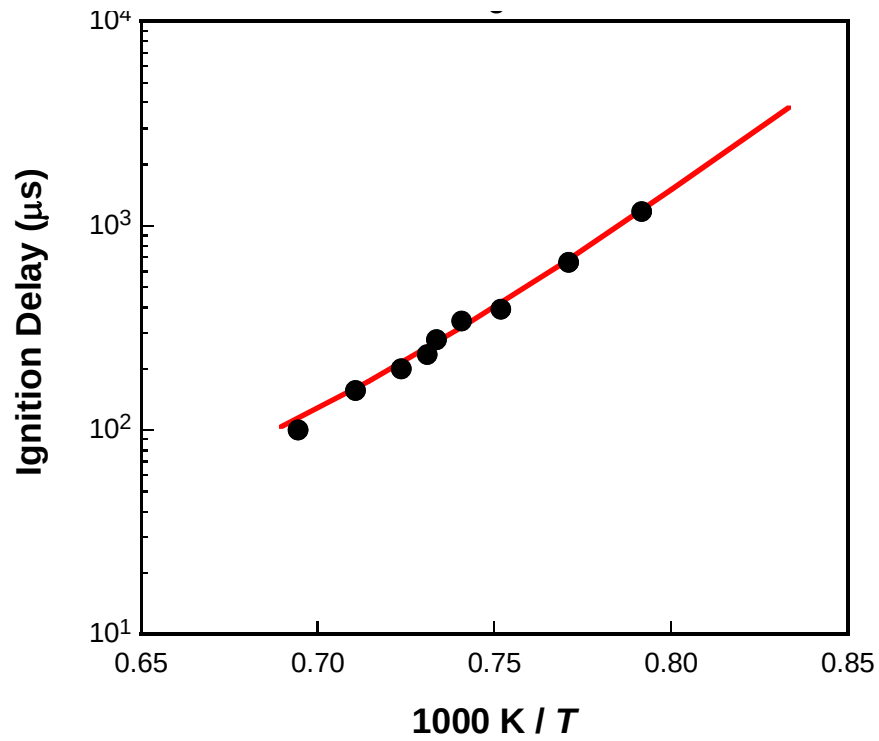


BCH/4%O_2/Ar, 1.5 atm, ϕ=0.45



- Good agreement between JetSurF 1.1 and Stanford data, but model slightly underpredicts τ_{ign} at ϕ = 0.83
- Excellent agreement at ϕ = 0.45!

Ignition Delay Times - Summary

- High-quality τ_{ign} dataset now available for key jet fuel surrogates at high T:
  - Large normal alkanes (C_5-C_{12})
    - n-pentane, n-hexane, n-octane, n-nonane, n-dodecane
  - Cyclo-alkanes
    - Cyclohexane, methylcyclohexane, butylcyclohexane
- Next Step: branched alkanes (year 3)

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JetSurF
← Some room for improvement

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JetSurF

🡐 Some room for improvement

🡐 Agrees well with data

- Next Step: branched alkanes (year 3)

Topic 2: Multi-Species Time-Histories – Current Status

- Surrogate Fuels Studied:
  - N-Heptane
  - N-Dodecane
  - Methylcyclohexane (MCH)

- Standard Conditions:
  - P = 2 atm
  - Φ = 1.0
  - T = 1250-1650K
  - X_{fuel} = 300-500 ppm

- Goal: develop multi-species database for oxidation and pyrolysis systems with time-histories of several key species: fuels, radicals, stable intermediates, products, and temperature

Multi-Species Diagnostics Methods

Currently In Use

- Fuels/Alkanes : C_7H_{16} (3.39 μm)
- Stable Intermediates/Alkenes: C_2H_4 (10.57 μm)
- Small Radicals: OH (306 nm)
- Products: H_2O, CO_2 (2.5, 2.7 μm)

In Development

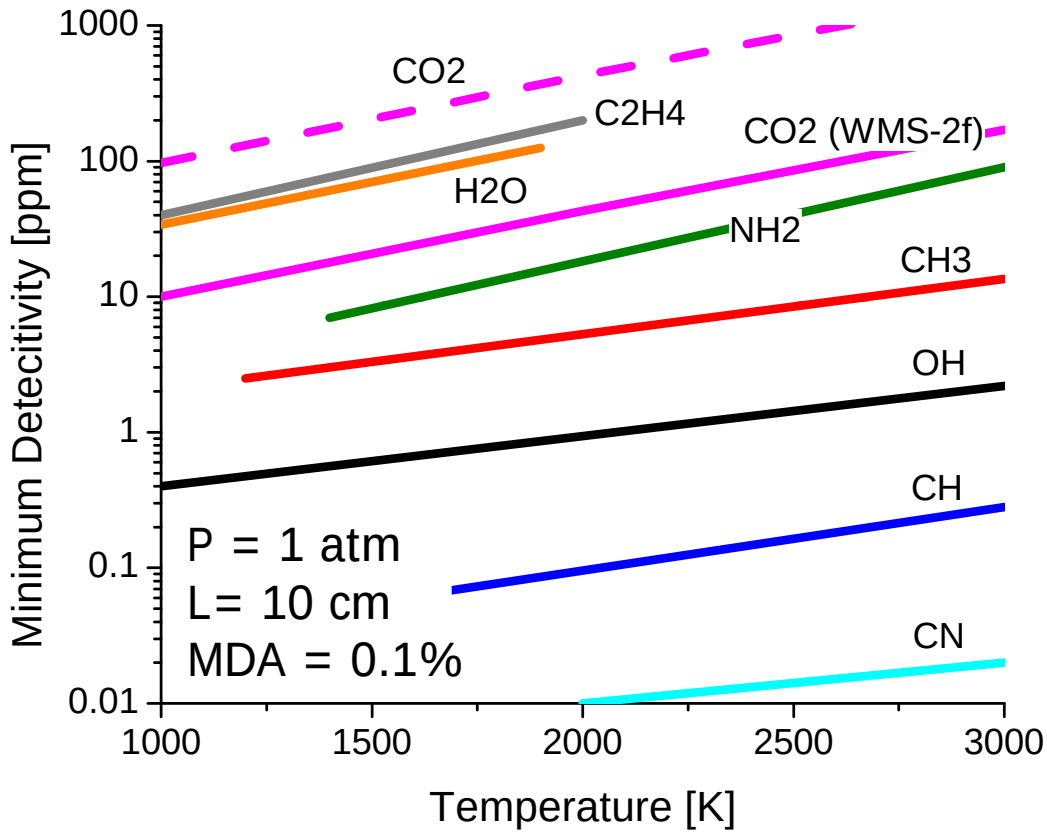
- Alkyl Radicals: CH_3, C_2H_5 (216 & 245 nm)
- Peroxide Species: HO_2/H_2O_2 (225 & 240 nm)
- Alkanes: Methane, Ethane, Propane (3.4 μm)
- Alkenes: propene, butene (11 μm, 3 μm)

➔ First multi-species application to jet fuel surrogate oxidation: n-heptane, n-dodecane, methylcyclohexane

Diagnostic development funded by other programs (mostly AFOSR)

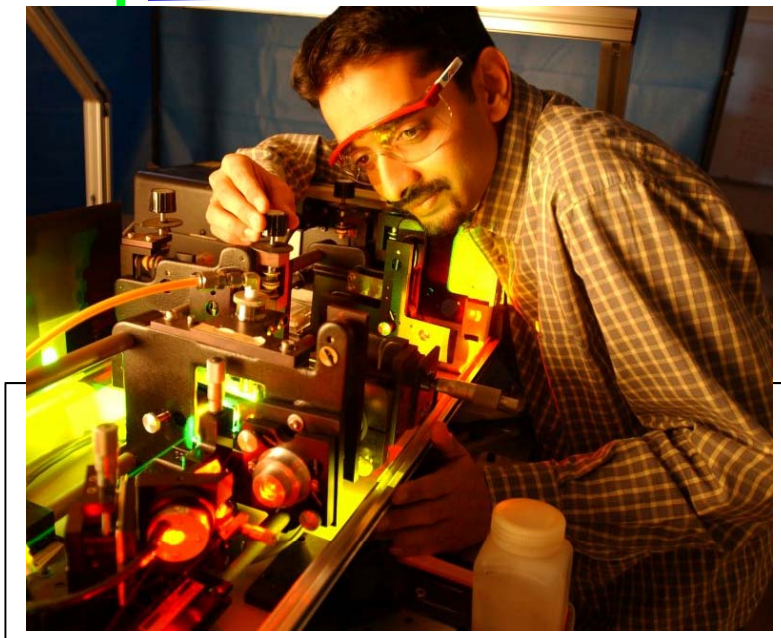
Laser Absorption Systems: Minimum Detectivity

- Ring-dye lasers with second harmonic generation (SHG): radical species
- Pulsed (ps) Ti:Sapphire laser with second (SHG), third (THG) and fourth (FHG) harmonic generation: radical species
- Distributed feedback (DFB) diode lasers: H_2O, CO_2, and T
- Difference-frequency-generation (DFG) diode lasers: HC fuels
- IR gas lasers: HC fuels (3.39 μm) and C_2H_4 (10.57 μm)



➔ ppm and 10's of ppm sensitivity available for species detection

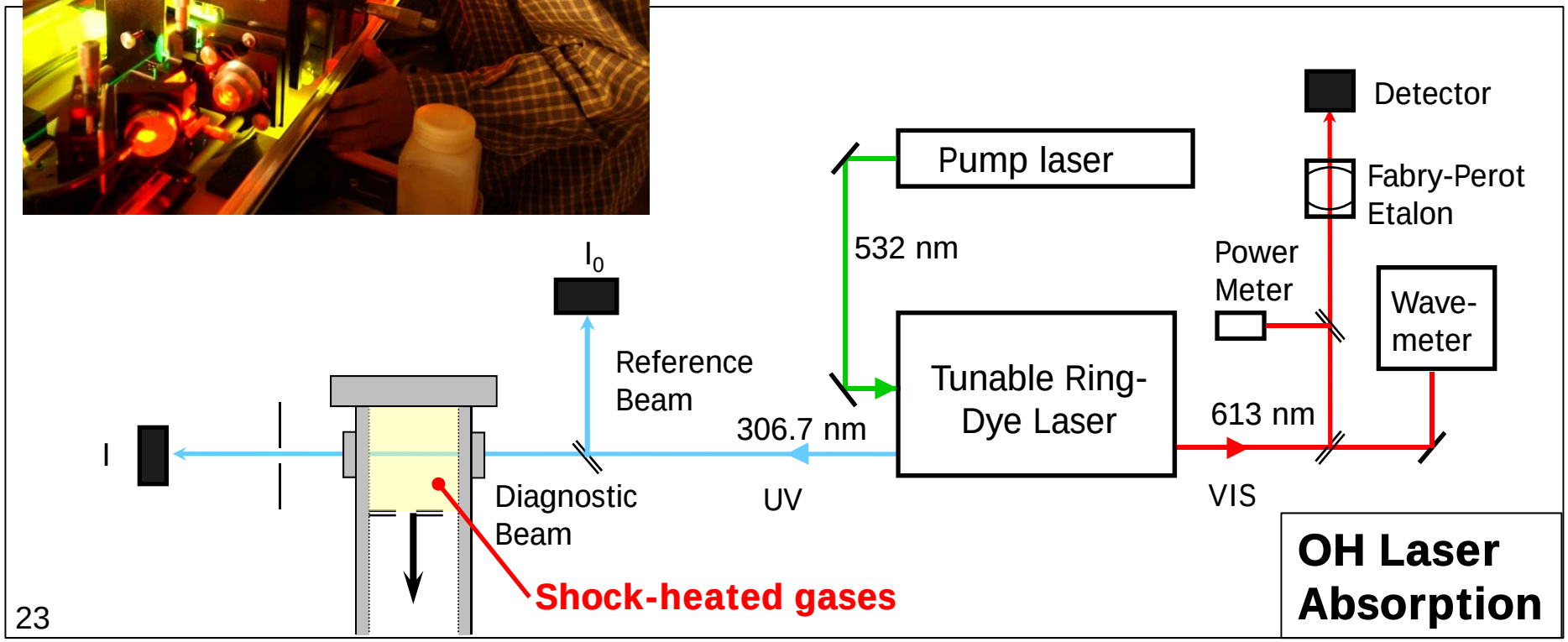
Example Experimental Setup: Ring Dye Laser for OH, CH, NH_2



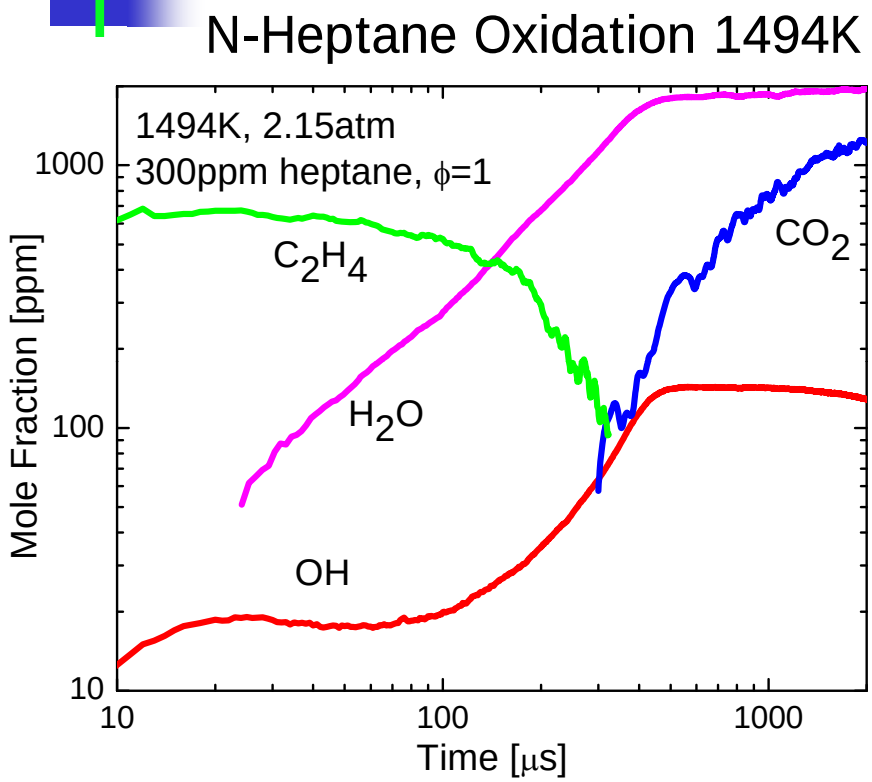
Beer-Lambert Law:

$$(I/I_0) = \exp\{-S(T)\,\Phi(T,P,x_i)\,P\,X_i\,L\}$$

Spectral parameters S & Φ determined at Stanford



Multi-Species Time-Histories: n-Heptane Oxidation

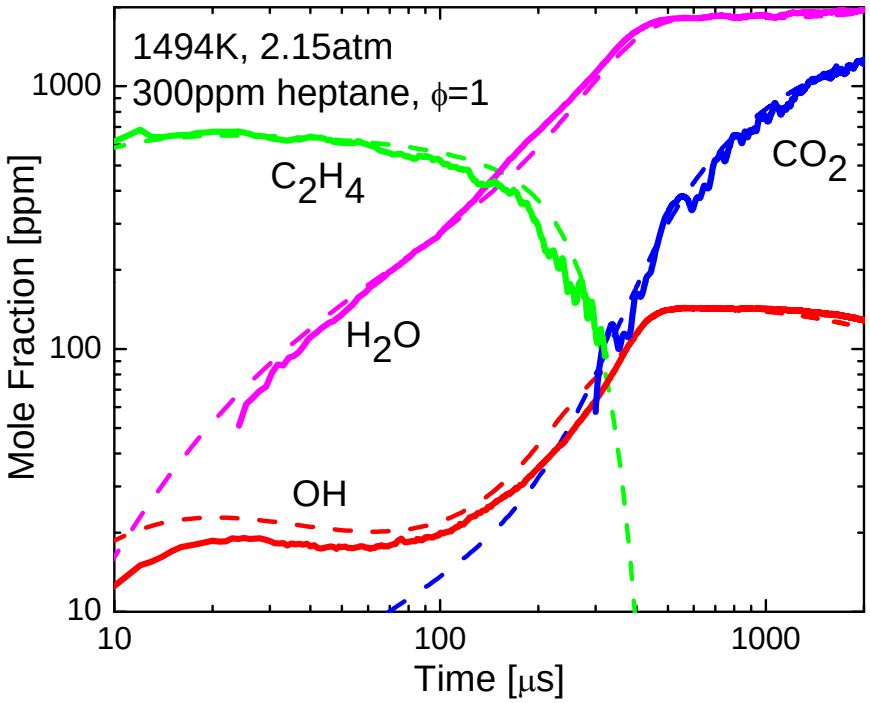


- First test of multi-species strategy:
- N-Heptane mechanism well-developed
- High SNR data
- Excellent shock-to-shock repeatability (± 10K)
- Optimized fuel concentration selection allows useful data over entire ignition process (two orders of magnitude coverage in species concentration)

- Successful application of multi-species method to n-heptane
- Enables evaluation (and refinement) of model sub-mechanisms: e.g. decomposition pathways, induction time, exponential radical growth

Relative Performance of Well-Established Models for n-Heptane Oxidation

JetSurF 0.2 (2008)



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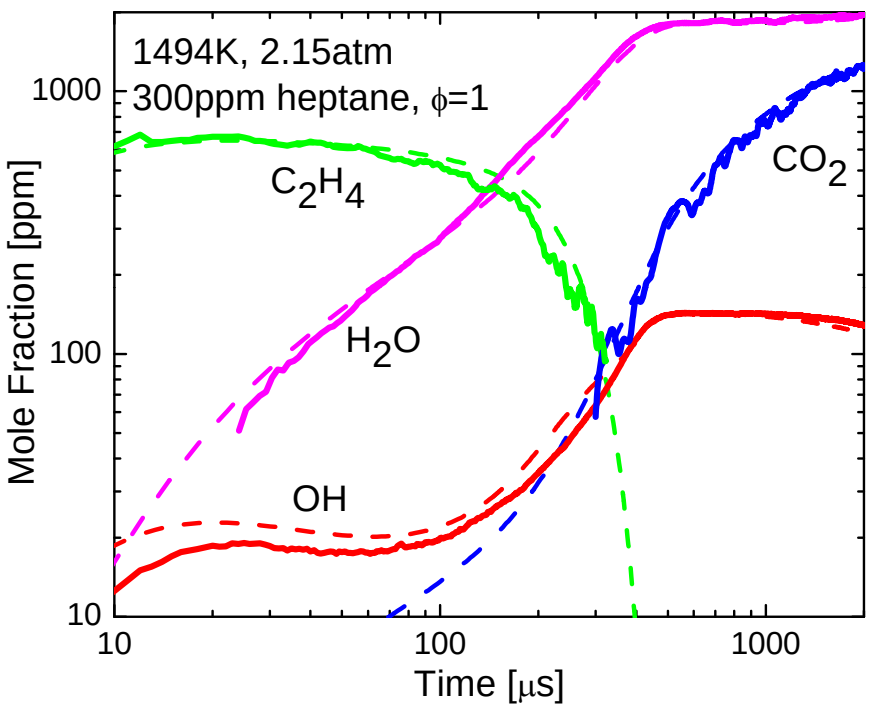
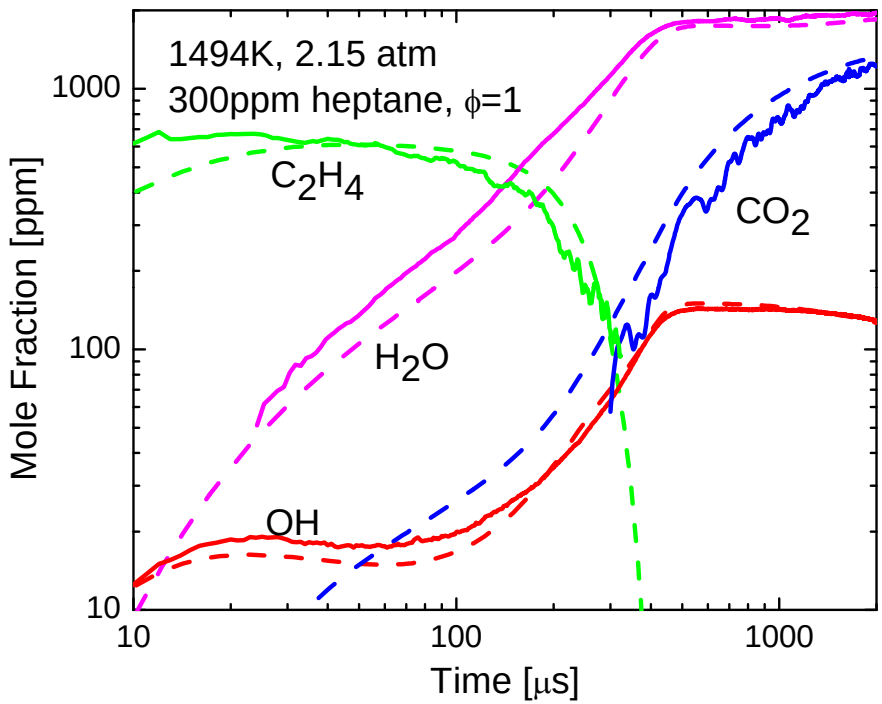


Chaos et al. (2007)



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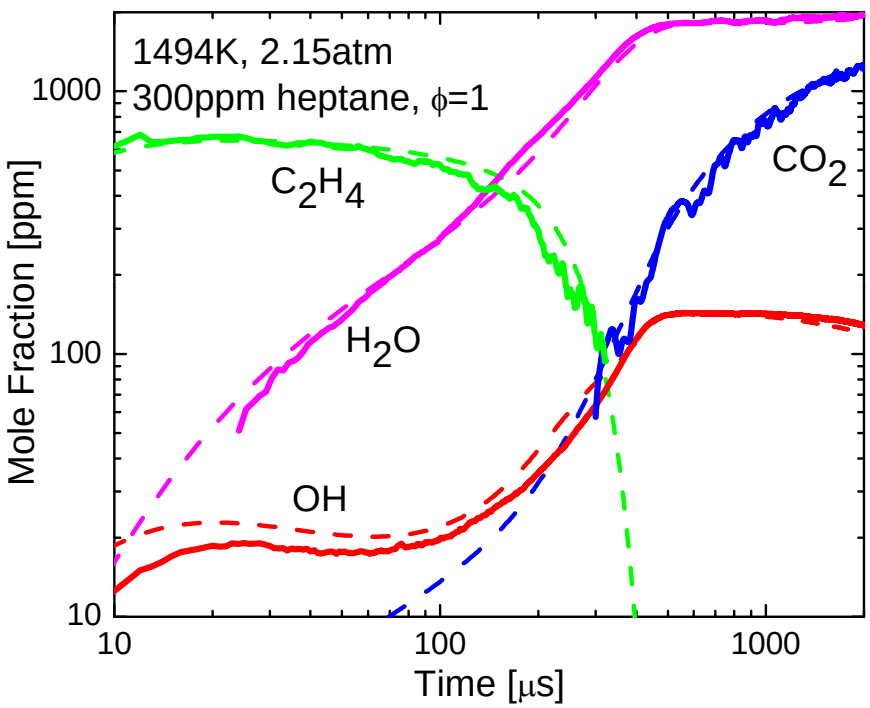

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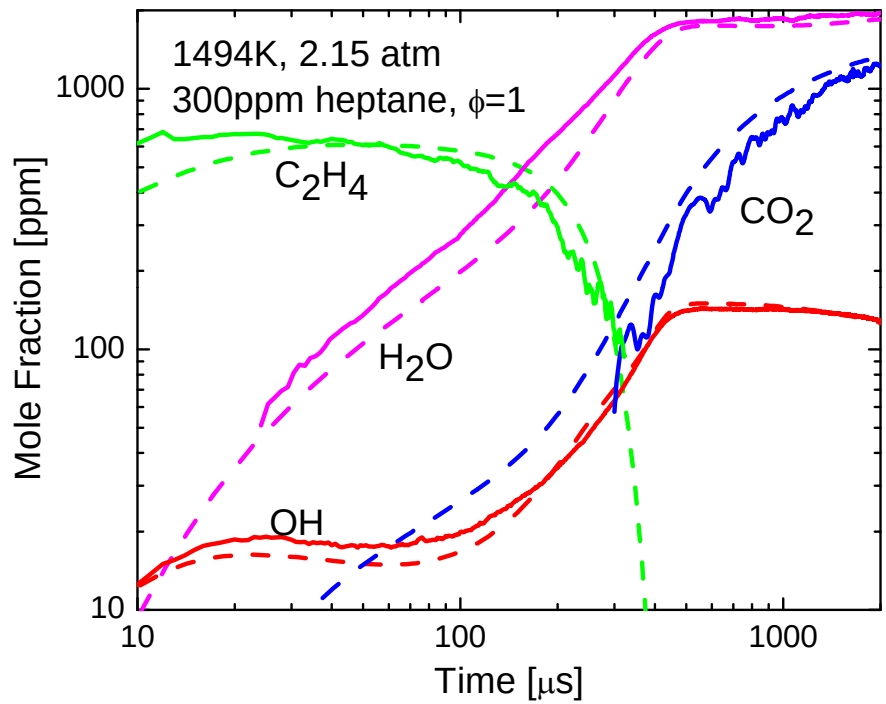
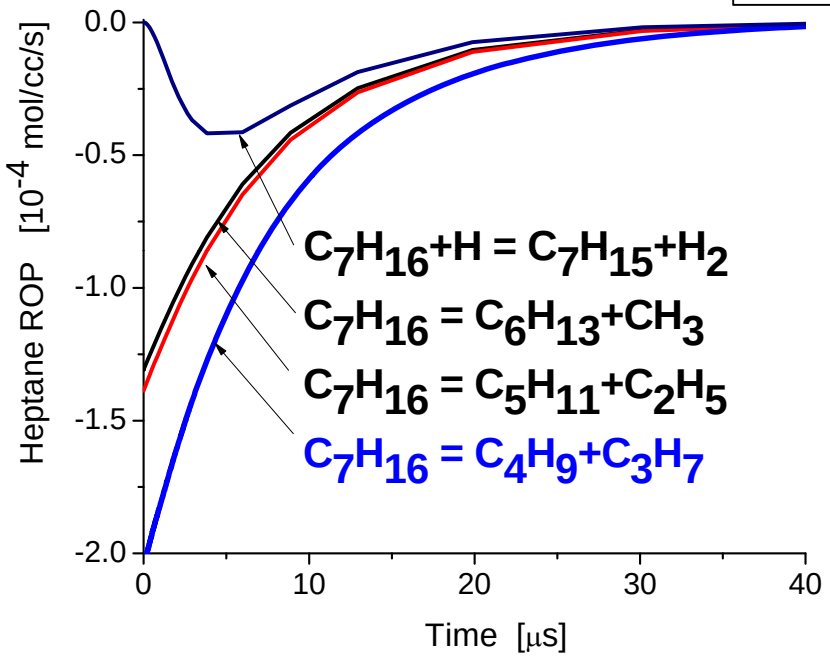


- Both models perform well, but multi-species time-history data is sufficiently accurate to enable some refinements in both mechanisms
- Kinetic analyses (*e.g. rate of production and sensitivity*) provide critical links from data to model, and guide mechanism refinement

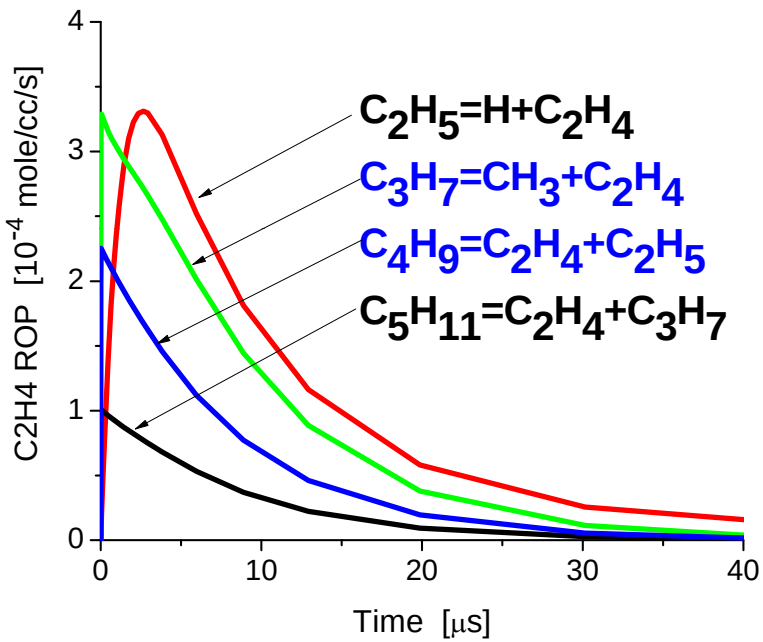
Example: Heptane Decomposition Kinetic Analysis

1500K, 2 atm, ϕ=1
300ppm heptane

Heptane ROP



Ethylene ROP



- ROP shows that primary n-heptane decomposition pathway (Dryer 2006) is: n-heptane → $C_4H_9+C_3H_7$
- Ethylene formed by secondary alkyl radical decomposition (C_2H_4 ROP)
- Large ethylene yields (2 C_2H_4 per C_7H_{16}) predicted by recent mechanisms confirmed with Stanford laser absorption data

Modeling using Dryer (2006)

Multi-Species Time Histories - Summary

- High-quality, multi-species datasets now available for oxidation of key jet fuel surrogates:

  N-Heptane
  N-Dodecane
  Methylcyclohexane

- Next Steps:
  - Expand range (T, P, mixtures) of experiments
  - Measure additional intermediate species, including:

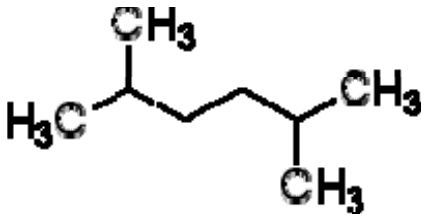
    simple alkanes (methane, ethane)
    higher alkenes (propene, butene)

Future Work (Year 3): Iso-Alkanes

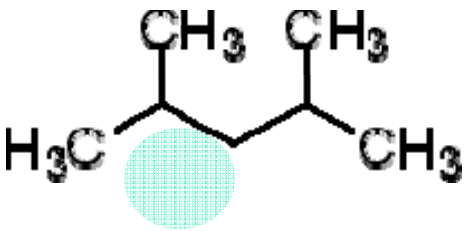
- Need for branched alkane surrogate candidates
  - End-to-end symmetry?
  - Dimethyl alkane?
  - Large carbon number??
  - Economical??

- Potential candidates:
  - 2,5-dimethylhexane (DMH)
  - 2,4-dimethylpentane (DMP)
  - 2,2,4-trimethylpentane (iso-octane) allows for comparison with DMP

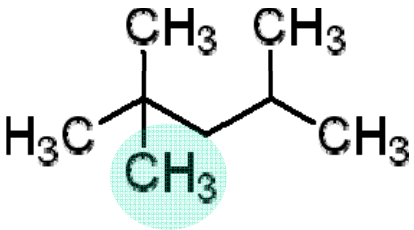
- 2,5-dimethylhexane



- 2,4-dimethylpentane



- 2,2,4-trimethylpentane (iso-octane)



Stanford Program Summary/Plans:

Achievements:

- Measured ignition delay times (n-alkanes, cyclo-alkanes, branched alkanes)
- Measured multi-species time-histories (fuel, OH, C_2H_4, H_2O, CO_2) in decomposition and oxidation of 3 jet fuel surrogates (n-heptane, n-dodecane, MCH)

Next Steps:

- Expand range of databases (T, P, mixtures)
- Multi-species measurements of branched alkanes (e.g. di-methyl alkanes) and aromatics (e.g. toluene)
- Apply new IR diagnostics methods to measure methane, ethane, higher alkenes in pyrolysis/oxidation of targeted fuels

Acknowledgements

- Visit Stanford website http://hanson.stanford.edu/ for

  Fundamental Kinetics Database Using Shock Tubes, Vol. 2: Concentration Time Histories

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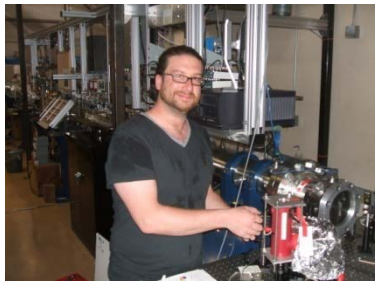
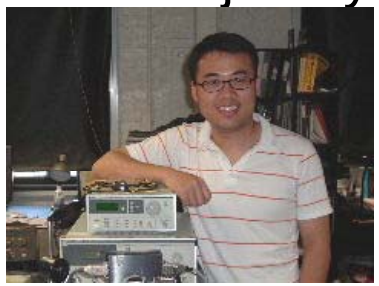
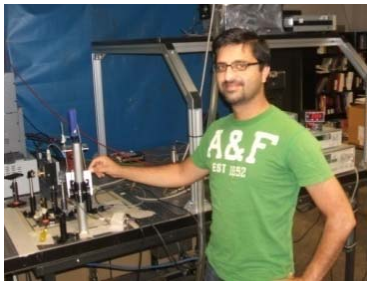
- Thanks to our four laser jockeys:



Dr. G. Pilla (C_2H_4)



Z. Hong (H_2O)



A. Farooq (CO_2)

R. Cook (OH)