Jet Fuel Surrogate Components: Shock Tube/Laser Absorption Measurements

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Ignition Delay Times
- **n-alkanes**
- **cyclo-alkanes**
- **branched alkanes**

Multi-Species Time-Histories
- **n-alkanes**
- **cyclo-alkanes**

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Stanford Objectives and Strategy

Extend and utilize modern shock tube/laser methods to establish a detailed, higher-quality kinetics database

Leading to:

Improved detailed mechanisms for jet fuels and jet fuel surrogates

Target Jet Fuel Surrogate Components:

n-alkanes, cyclo-alkanes, branched alkanes

Research Summary

Year 1: n-alkanes, ignition delay time (τ_{ign}) measurements

- n-alkanes (C5-C9): τ_{ign} at low pressures
- n-dodecane (C12): τ_{ign} at high pressures

Year 2: n-alkanes and cyclo-alkanes, multi-species time-histories

- cyclo-alkanes (CH, MCH, BCH): τ_{ign} at low pressures
- n-heptane oxidation: multi-species profiles

Year 3: n-alkanes and cyclo-alkanes, multi-species time-histories

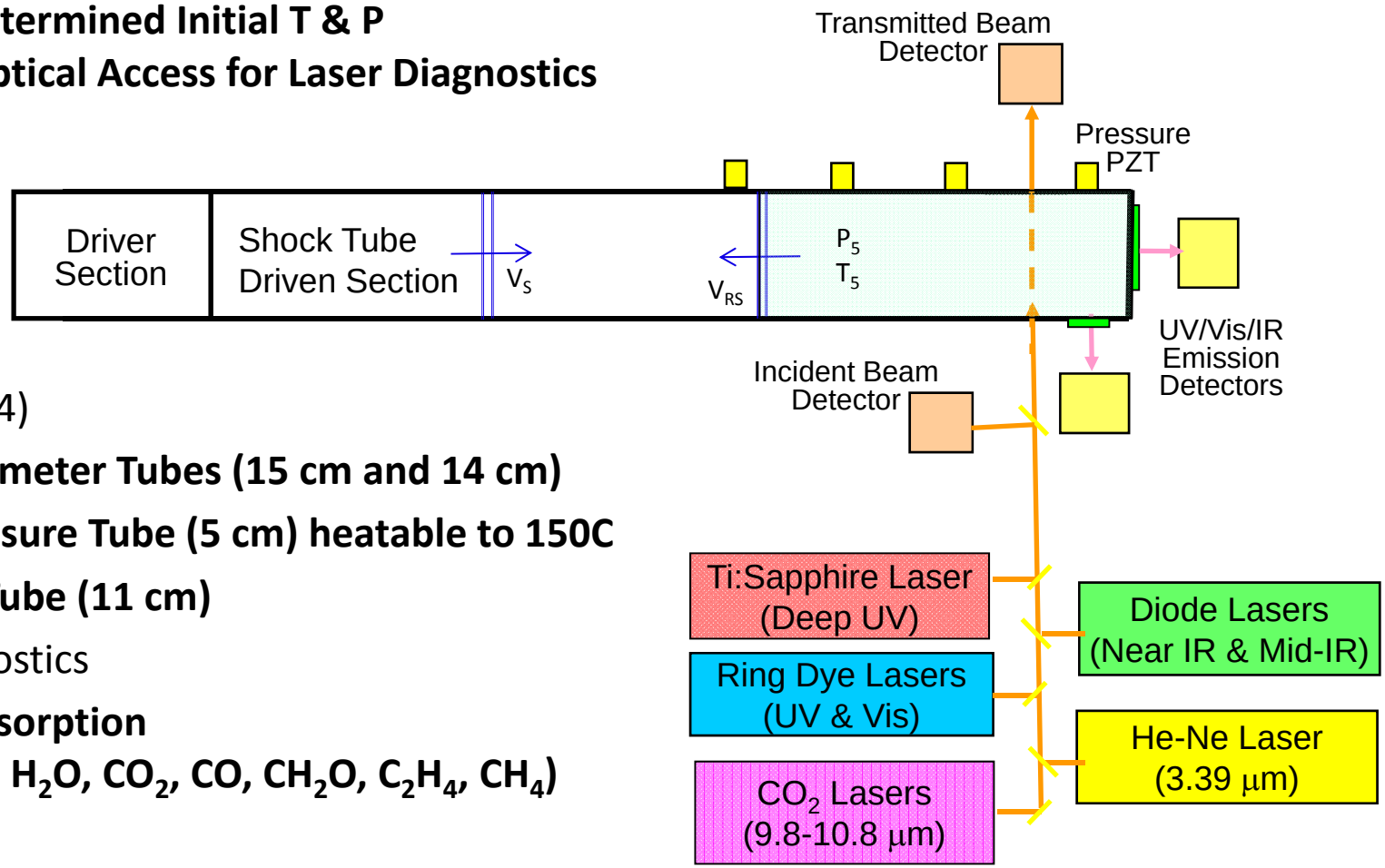
- n-dodecane & MCH oxidation: multi-species profiles

New Studies: di-methyl alkanes

- dimethyl-pentane, dimethyl-hexane, dimethyl-octane
- ignition delay times, multi-species profiles

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**
    (OH, CH_3, H_2O, CO_2, CO, CH_2O, C_2H_4, CH_4)

Studies of Individual Jet Fuel Surrogate Components

Ignition Delay Times
Multi-Species Time-Histories

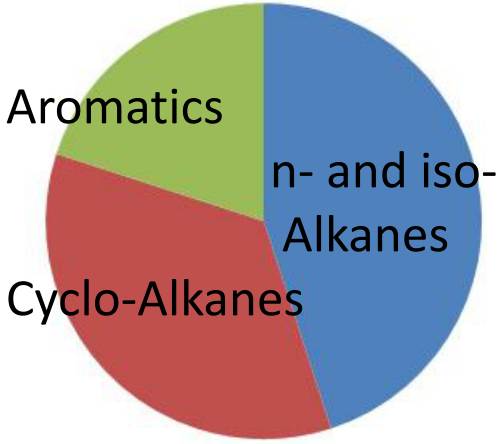
Studies of Individual Jet Fuel Surrogate Components

Ignition Delay Times

n-Alkanes

cyclo-Alkanes

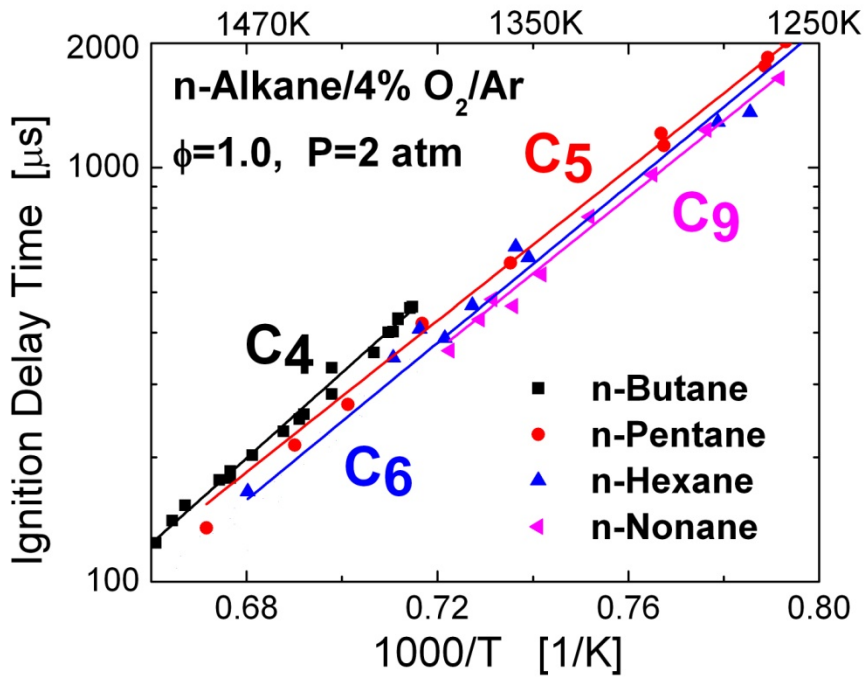
iso-Alkanes



JP-8 Composition

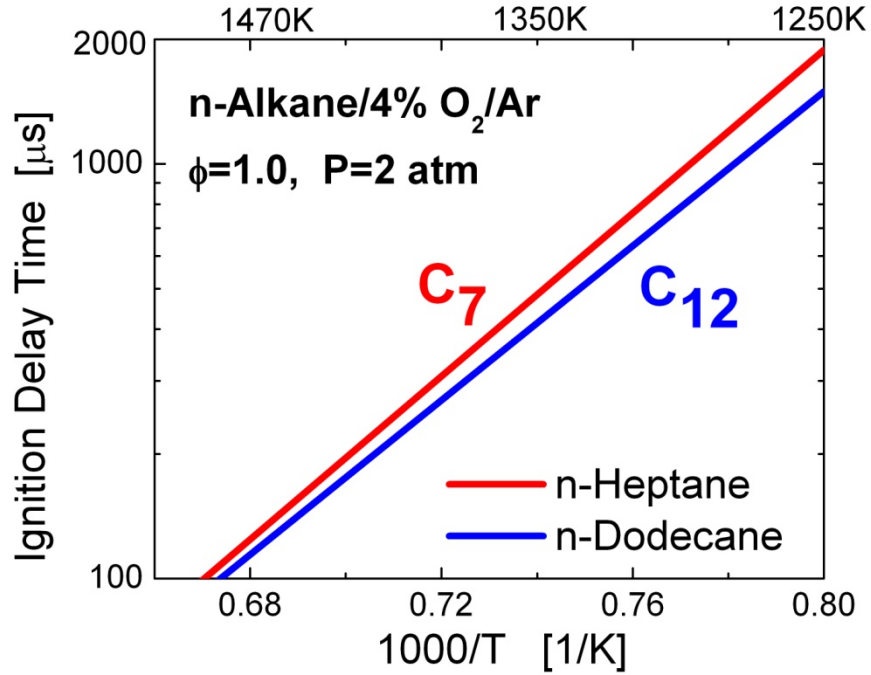
How Well Do n-Alkane Mechanisms for τ_{ign} Fit High T Data: 1250-1500K, 2 atm?

IPT Experiments



- Shock tube experiments show only small variation of τ_{ign} with carbon number

Simulations

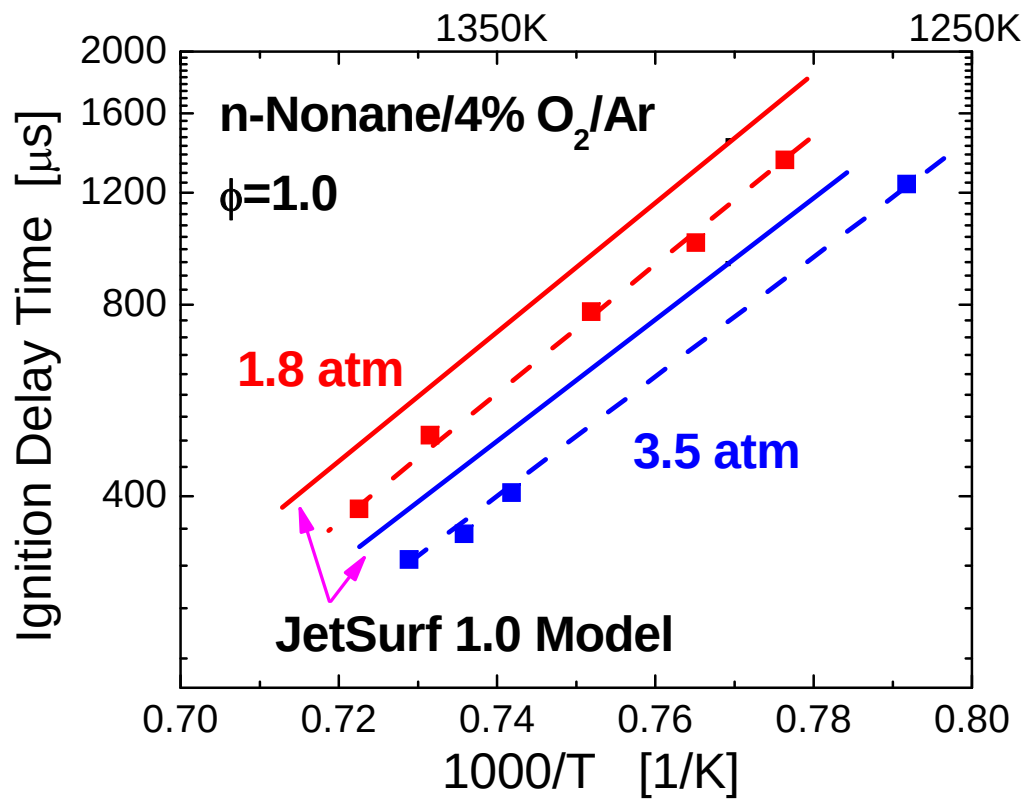


- Westbrook et al. (2009) predict small variation of ignition delay time with carbon number

How Good are Current Models at Low Pressure?
Example: n-Nonane Ignition Delay Times

- **Experiment:**
  - τ_{ign} varies as $P^{-0.5}$
- **JetSurF model:**
  - τ_{ign} varies as $P^{-0.67}$
  - Some difference in magnitude

IPT Experiments

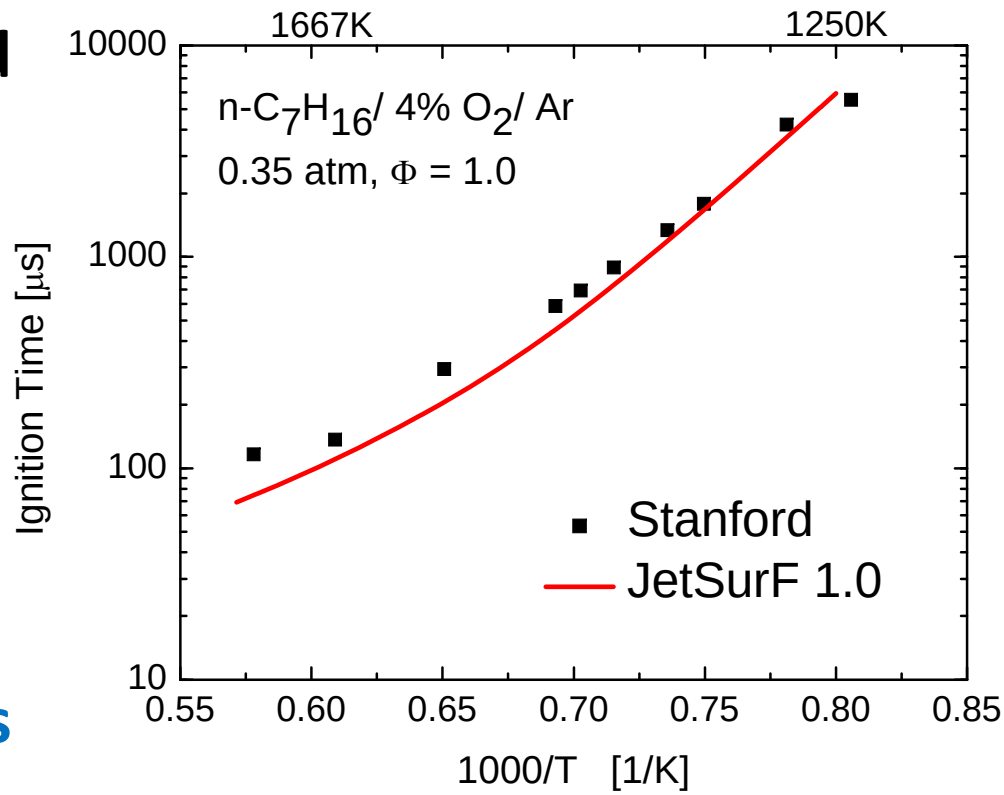


What about sub-atmospheric pressures?
High-altitude re-light problem?

How Good are Models at Sub-Atm Pressure?

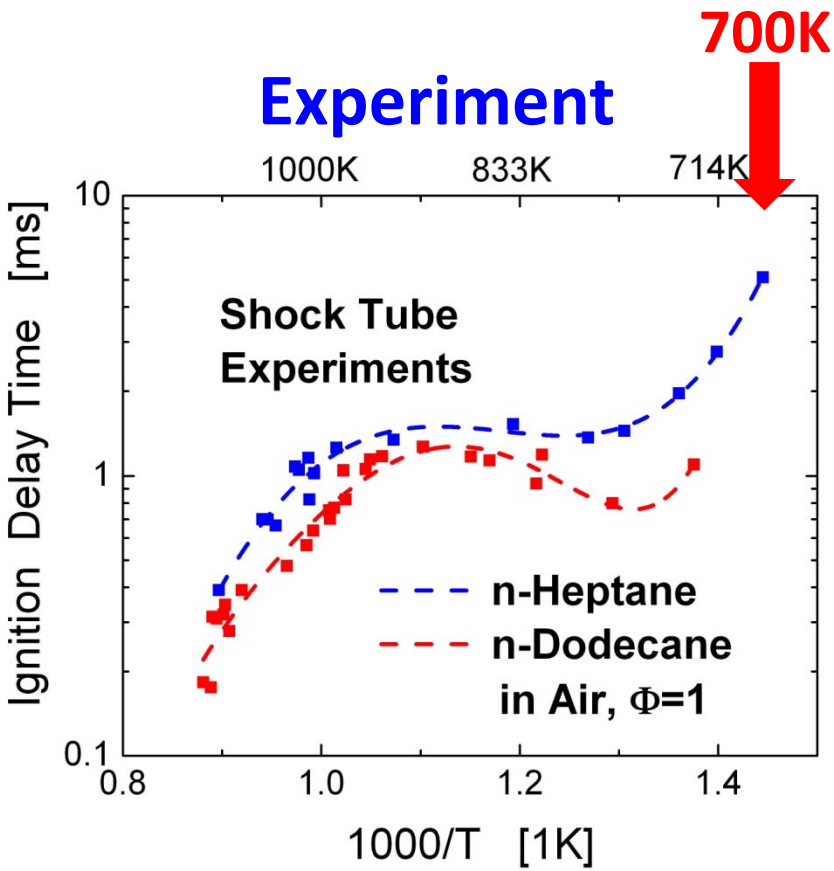
n-Heptane Ignition: 0.35 atm

- **n-Heptane data extended down to sub-atm**
- **Good agreement with JetSurF 1.0 below 1400K**
- **Future Work:**
  Extend sub-atm data to wider range of conditions and other fuels

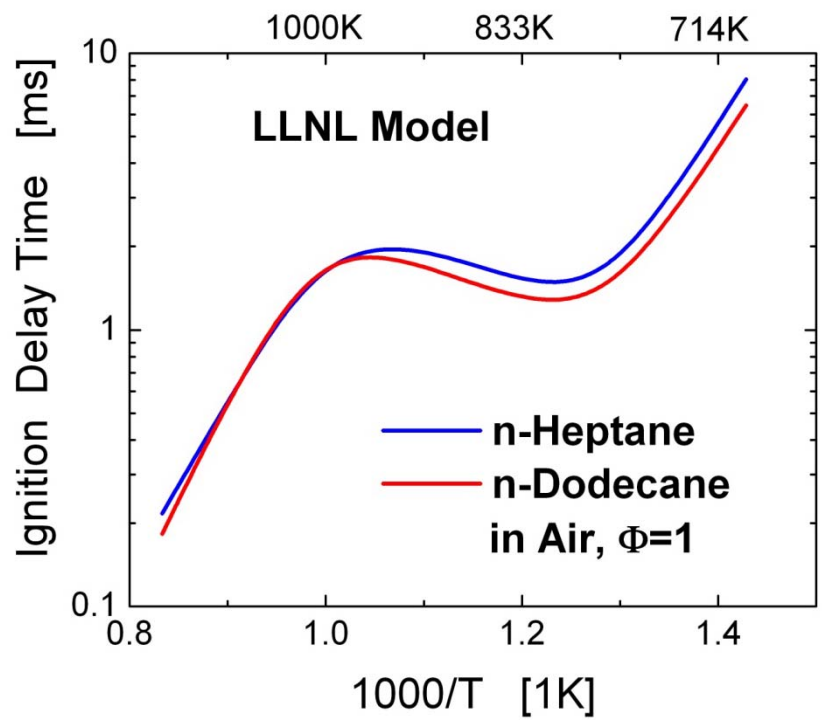


How Well Do n-Alkane Mechanisms for τ_{ign} Fit Low T Data: 700-1000K, 20 atm?

Experiment



Simulations

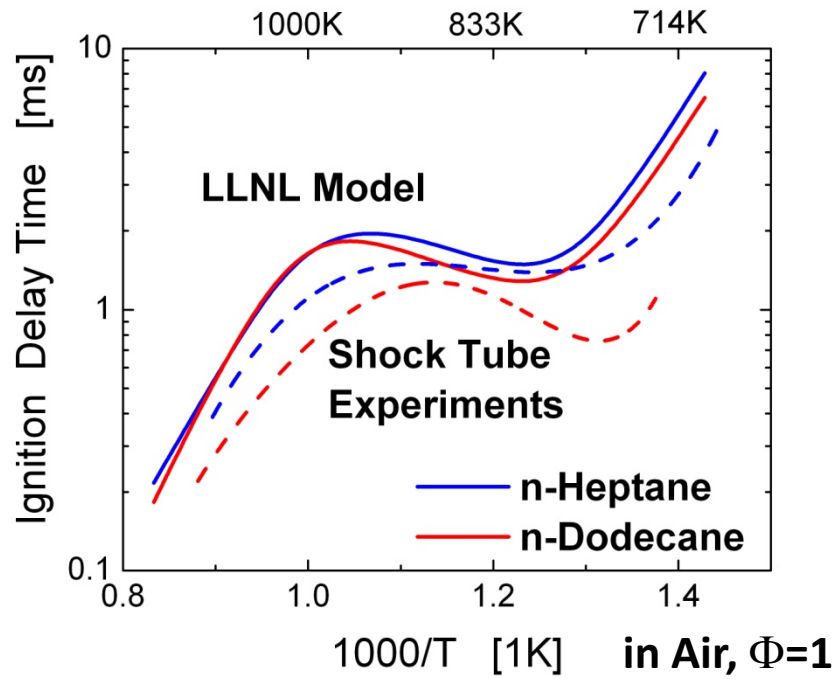


- **High pressure experiments provide access to low T**
- **Westbrook et al. (2009) predict NTC behavior with little variation with carbon number**

Direct Comparison of Simulation and Experiment Low Temperature: 700-1000K, 20 atm

- **High pressure shock tube data reveal larger variation with carbon # than predicted by simulations**

→ Conclusion: critical need for additional experiments at low T and high P



Studies of Individual Jet Fuel Surrogate Components:

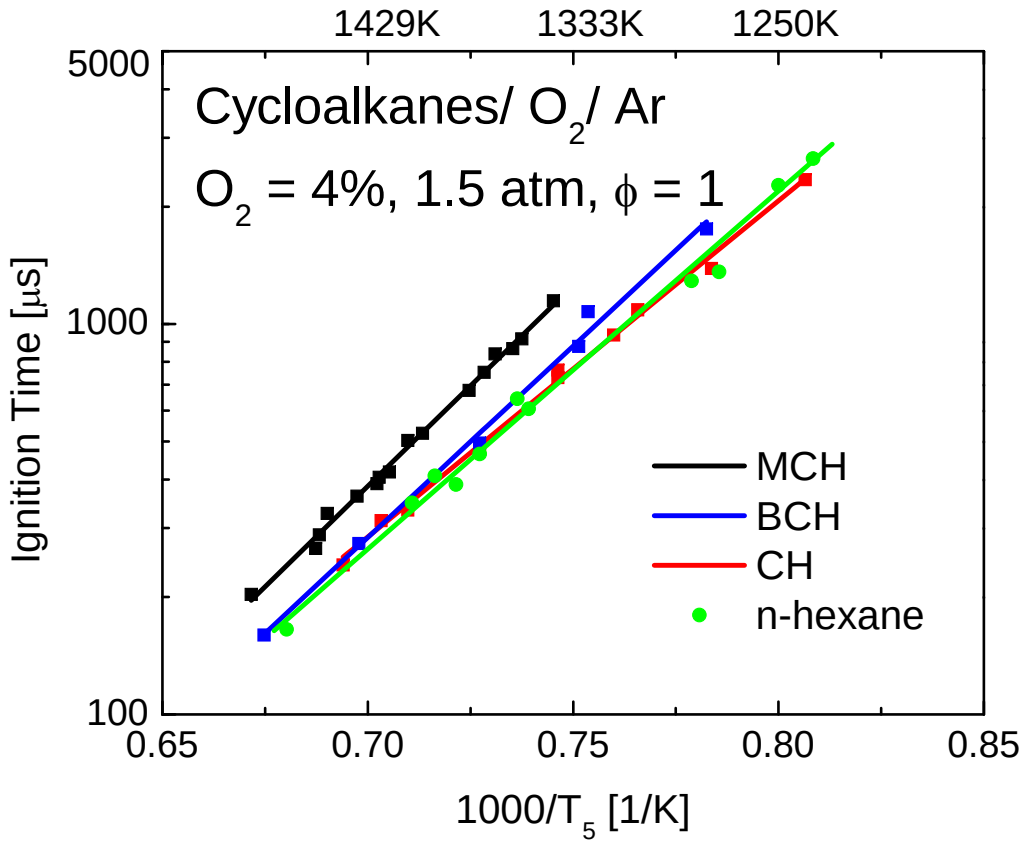
Ignition Delay Times

n-Alkanes

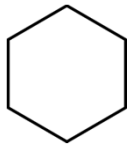
cyclo-Alkanes ⟵

Branched Alkanes

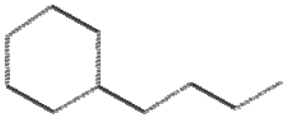
Cyclo-Alkane Ignition Delay Times: CH, BCH and MCH



- **Cyclohexane**

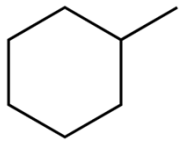


- **Butylcyclohexane**



- **N-Hexane**

- **Methylcyclohexane**



- **CH and BCH ignition delay times similar to n-hexane**
- **But MCH ignition distinctly slower than BCH, CH and n-hexane**

Studies of Individual Jet Fuel Surrogate Components:

Ignition Delay Times

n-Alkanes

cyclo-Alkanes

Branched Alkanes ⟵

Branched Alkanes

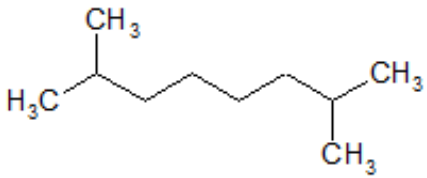
Major components of synthetic jet fuels

Completed Studies

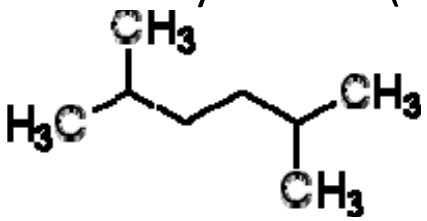
- 2,5-dimethylhexane (DMH)
- 2,4-dimethylpentane (DMP)
- 2,2,4-trimethylpentane (iso-octane)

Current Studies

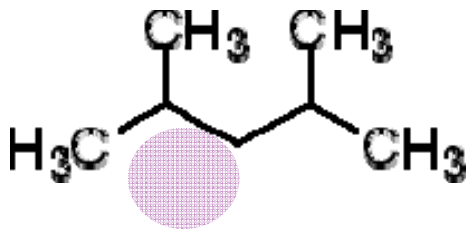
- 2,7-dimethyloctane (DMO)



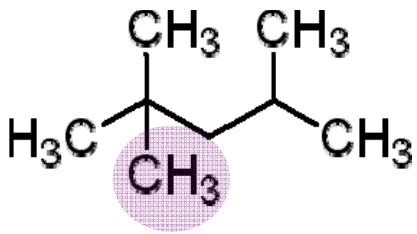
- 2,5-dimethylhexane (DMH)



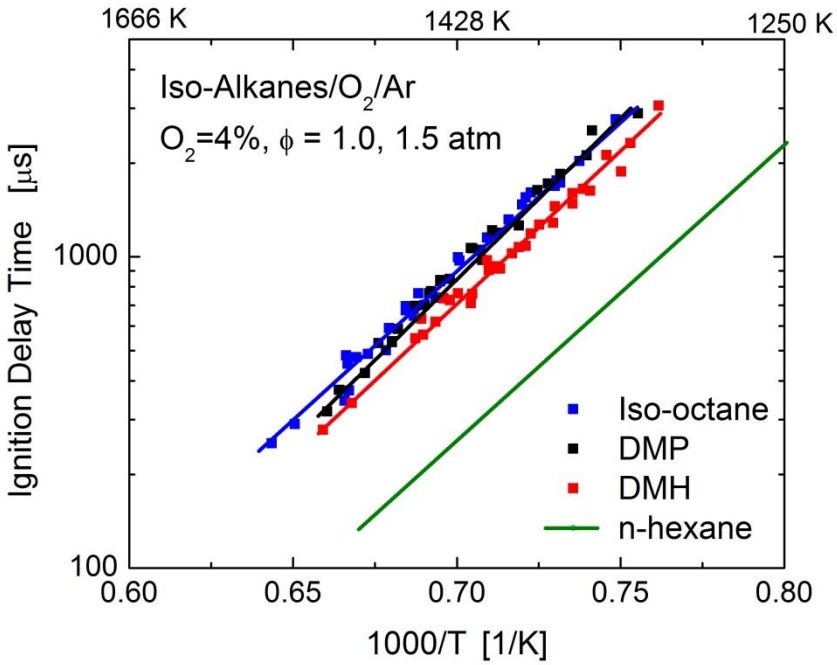
- 2,4-dimethylpentane (DMP)



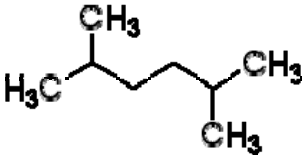
- 2,2,4-trimethylpentane (iso-octane)



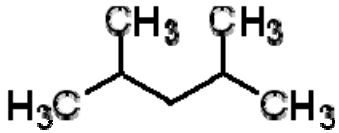
Branched Alkanes: Low Pressure Study



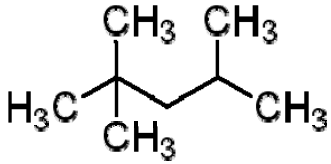
- **2,5-dimethylhexane (DMH)**



- **2,4-dimethylpentane (DMP)**



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

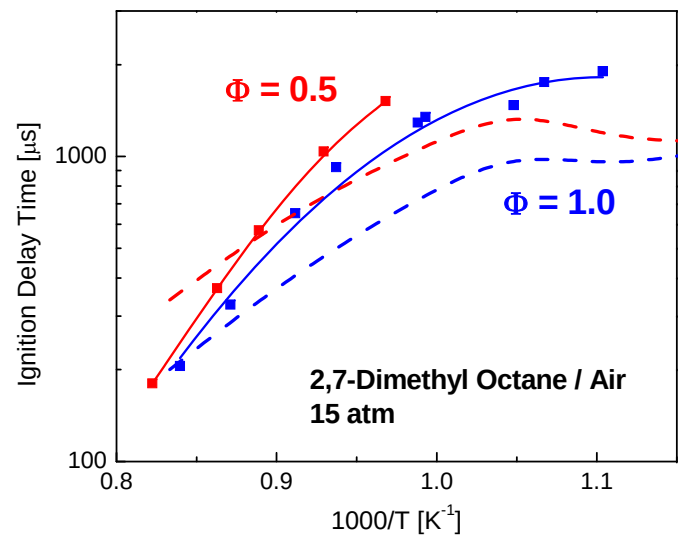


- **n-hexane**

- ❑ dimethyl/trimethyl alkanes have **similar** τ_{ign}
- ❑ All iso-alkanes **<u>much slower</u>** than **n-hexane**, (and thus most n-alkanes)

2,7-Dimethyl Octane: HP Ignition Delay Times

- **First high pressure τ_{ign}**
  15 atm, 900-1200 K
  approaches NTC regime
- **Variation with Φ**
  weak variation at high T
- **MIT/RMG generated model**
  710 reactions, 108 species
  first effort captures NTC
- **Influence of Carbon #**
  DMO very similar to DMH
  (2,5-dimethyl hexane)



Need for species time-history data!!

Studies of Individual Jet Fuel Surrogate Components

Multi-Species Time-Histories

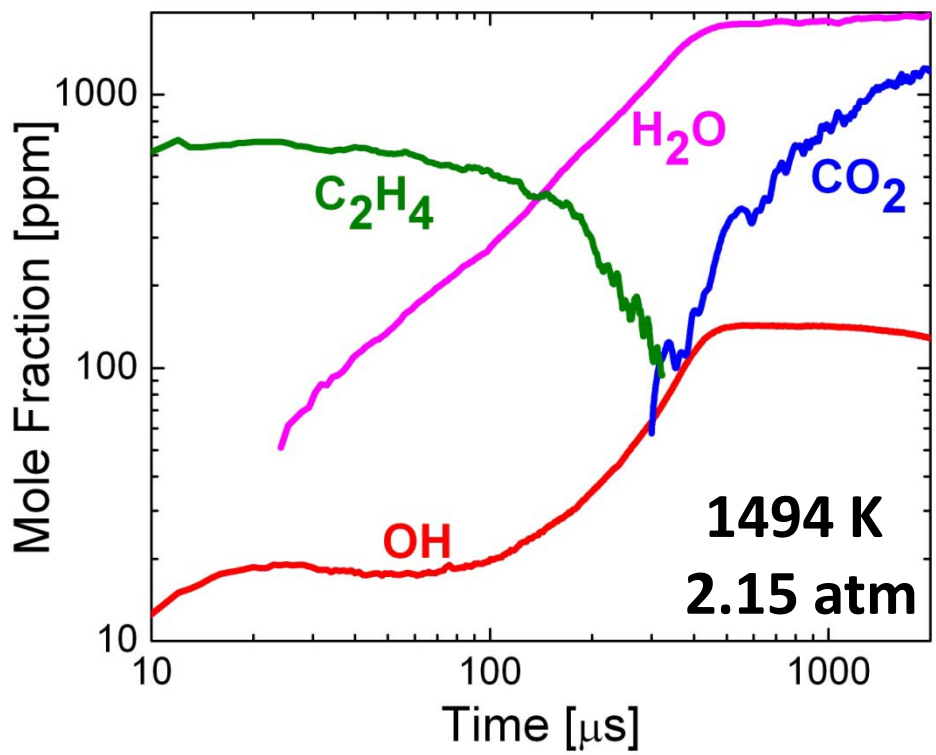
n-Heptane
n-Dodecane
Cyclo-Alkanes

Multi-Species Laser Absorption Data: n-Heptane Oxidation

- Radicals (OH)
- Stables (C_2H_4)
- Products (H_2O; CO_2)

- Unique data with high sensitivity and fast time response

300 ppm Heptane/O_2/Ar, ϕ=1



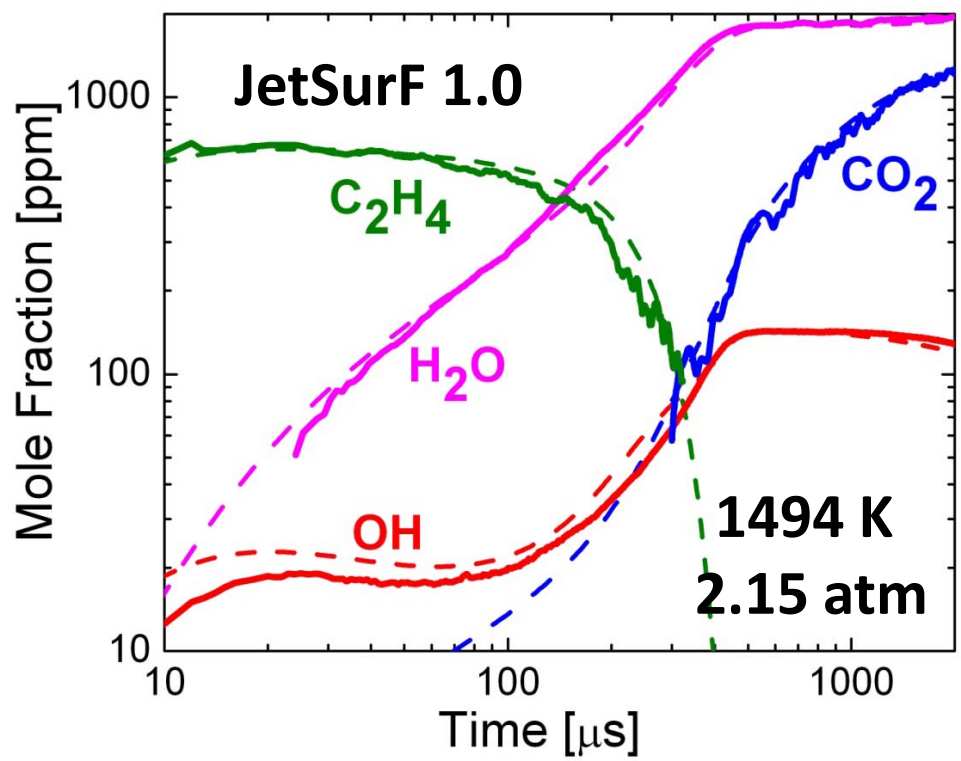
How does JetSurF compare with measurement?

Comparison with JetSurF Model
n-Heptane Oxidation

- Current model in excellent agreement with multi-species data
- Illustrates impact of multi-species data
- Further work needed on radical reactions

- What about larger n-alkane fuels?

300 ppm Heptane/O_2/Ar, ϕ=1



Studies of Individual Jet Fuel Surrogate Components

Multi-Species Time-Histories

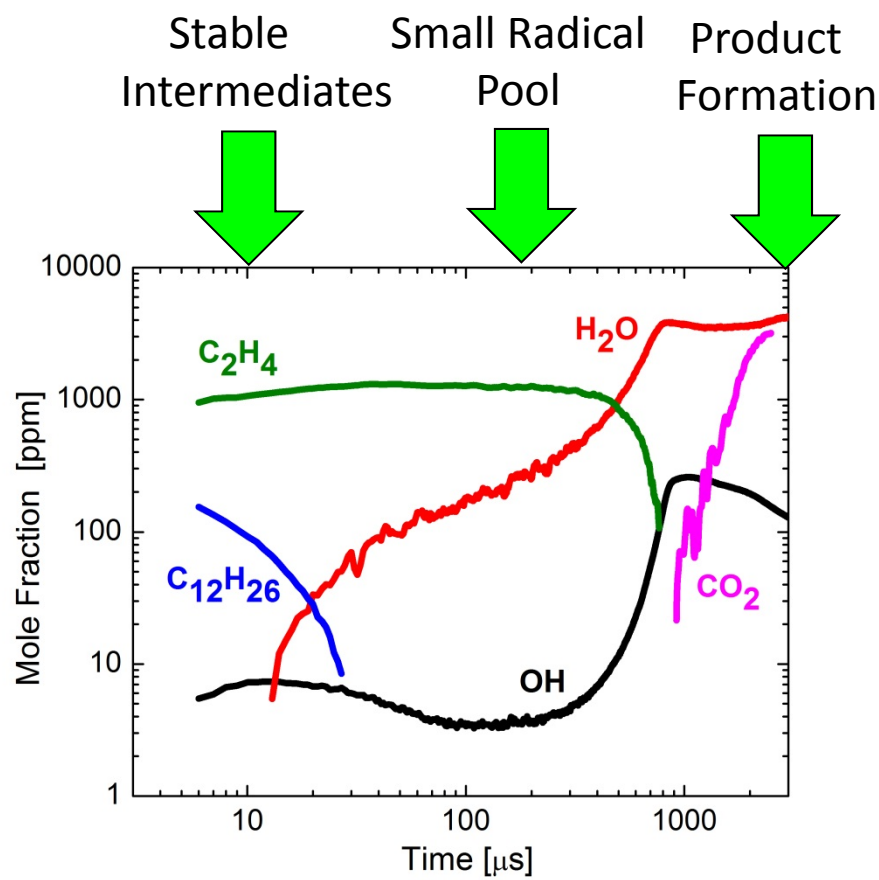
n-Heptane

n-Dodecane

Cyclo-Alkanes

Representative Multi-Species Time-History Data: N-Dodecane Oxidation

- **First multi-species campaign for n-dodecane oxidation**
- **Fuel: n-Dodecane**
- **Stable intermediates: C_2H_4**
- **Small radical pool: OH**
- **Combustion products: H_2O, CO_2**



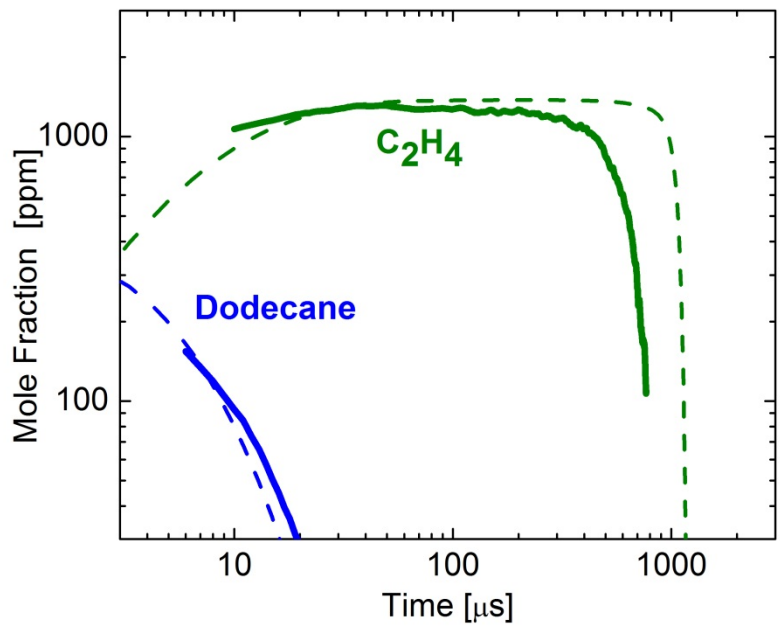
1410K, 2.3 atm
460ppm $C_{12}H_{26}/O_2/Ar$, ϕ=1

Comparison of N-Dodecane Data and JetSurF

Fuel (n-Dodecane) and Intermediate Products (Ethylene)

- Good agreement with dodecane decomposition rate
- Fair agreement with C_2H_4 plateau, but …
- Ignition delay times are slightly long

JetSurF 2.0



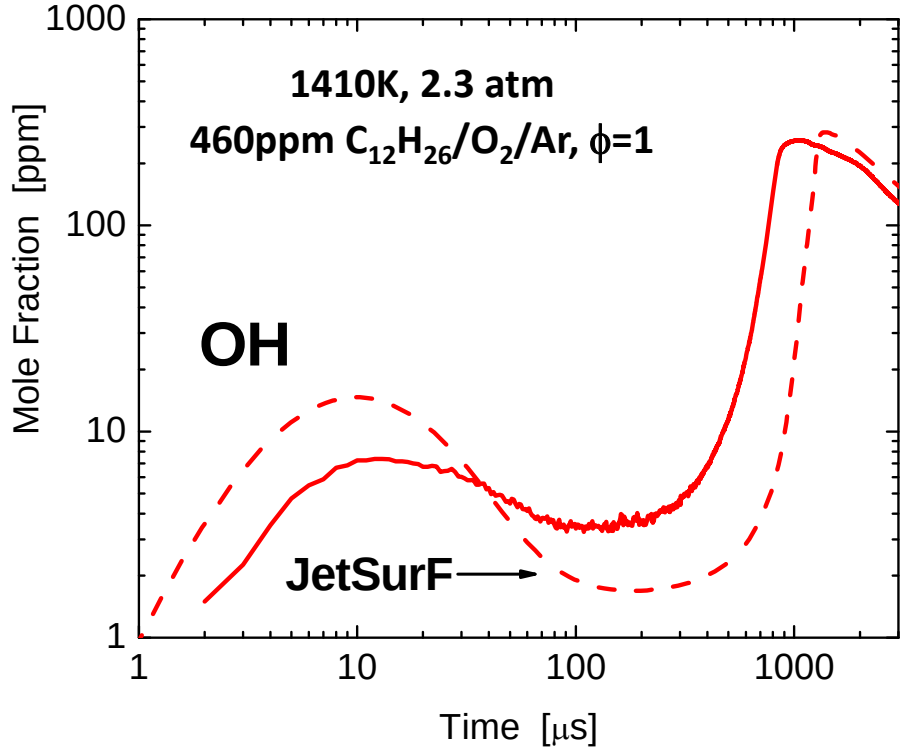
1410K, 2.3 atm

460ppm $C_{12}H_{26}/O_2/Ar$, ϕ=1

Comparison of N-Dodecane Data and Model:

Transient Radicals - OH

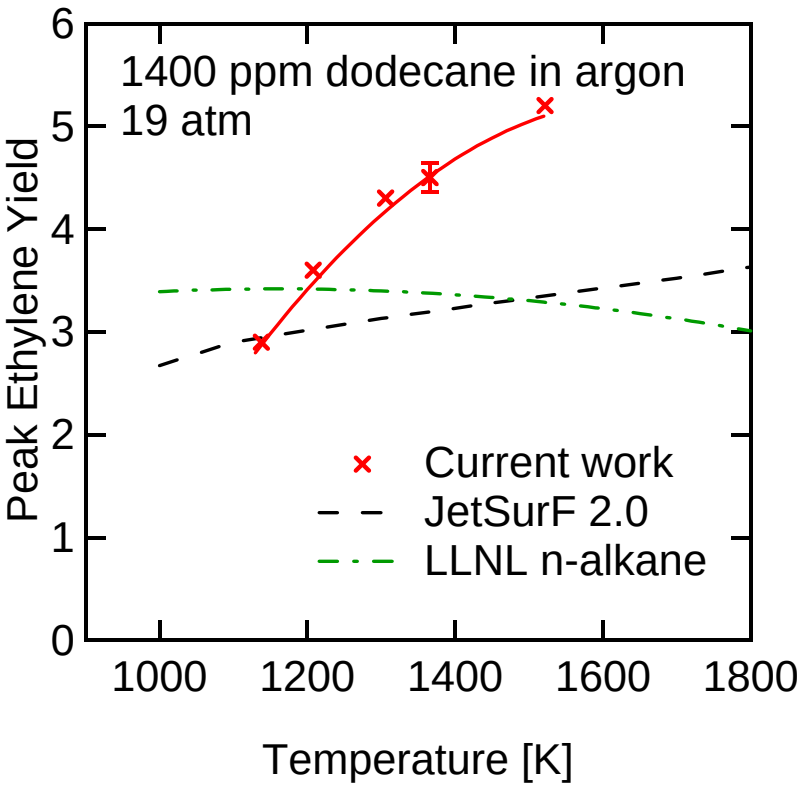
- **Radical-formation peak and radical-scavenging minimum not captured accurately**
- **Improvements needed in small-radical sub-mechanisms!**



- **What can we learn from n-dodecane pyrolysis?**

Ethylene Yields during n-Dodecane Pyrolysis

- **Ethylene yields measured at 19 atm during pyrolysis***
- **Data courtesy M. Billingsley AF-ERC (2011)**
- **Data reveal significant differences from model predictions**



- **Refinement needed in n-dodecane models at HP!**

Multi-Species Time-Histories

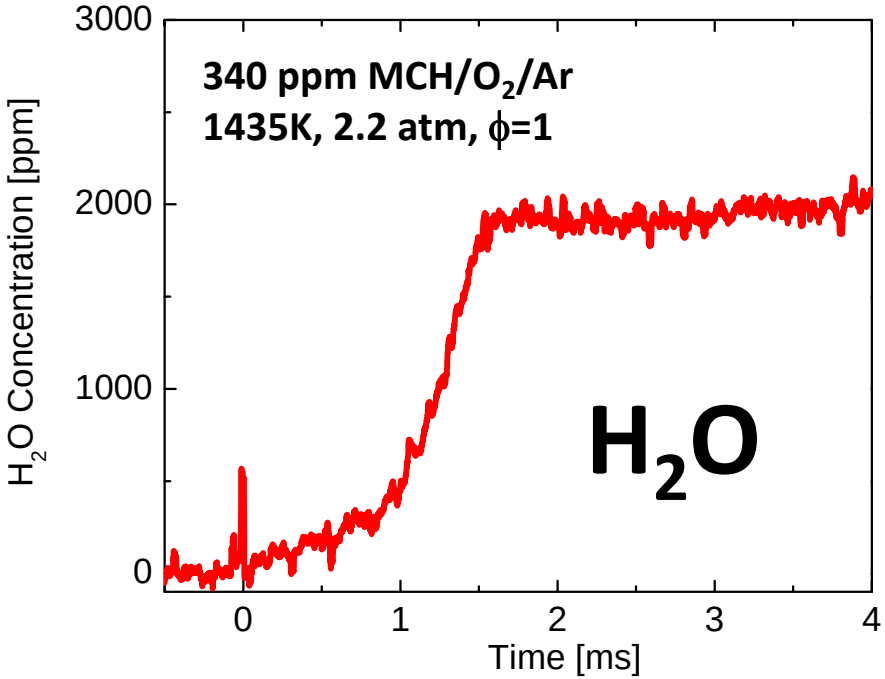
n-Heptane

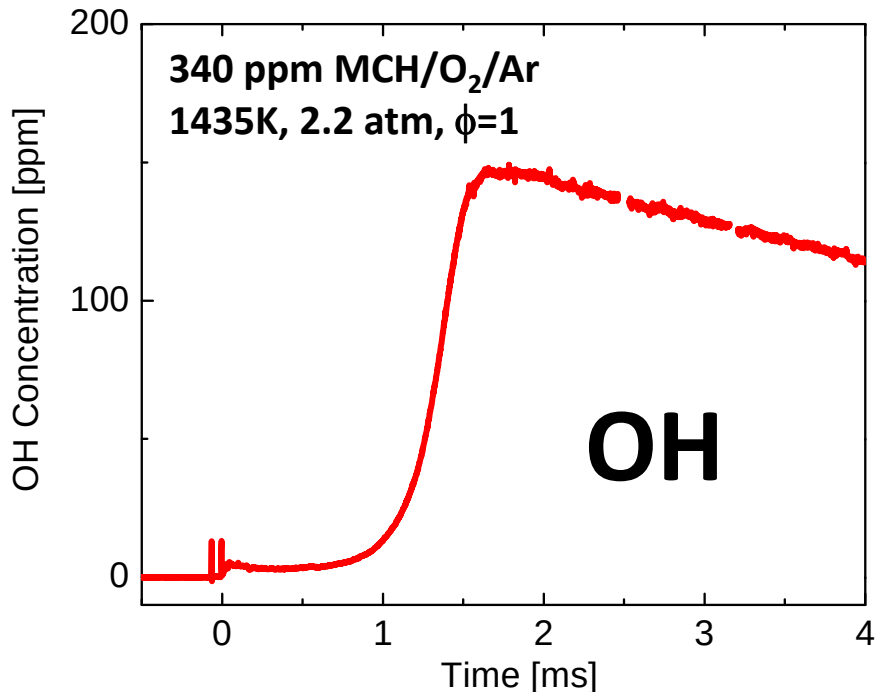
n-Dodecane

cyclo-Alkanes

- **cyclohexane**
- **methylcyclohexane** ⟵
- **butylcyclohexane**

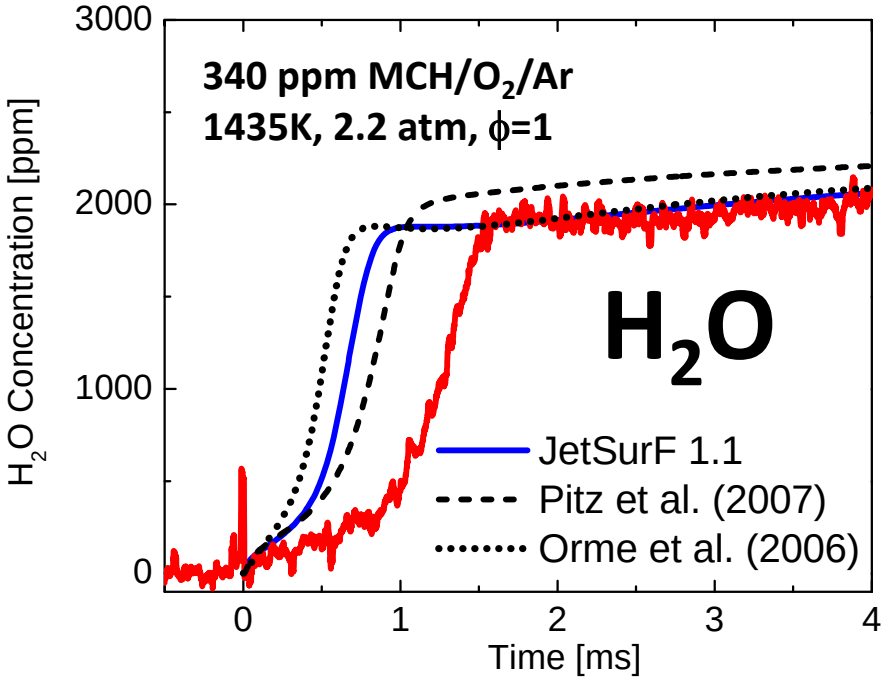
Methylcyclohexane Oxidation
Multi-Species Time Histories: H_2O, OH

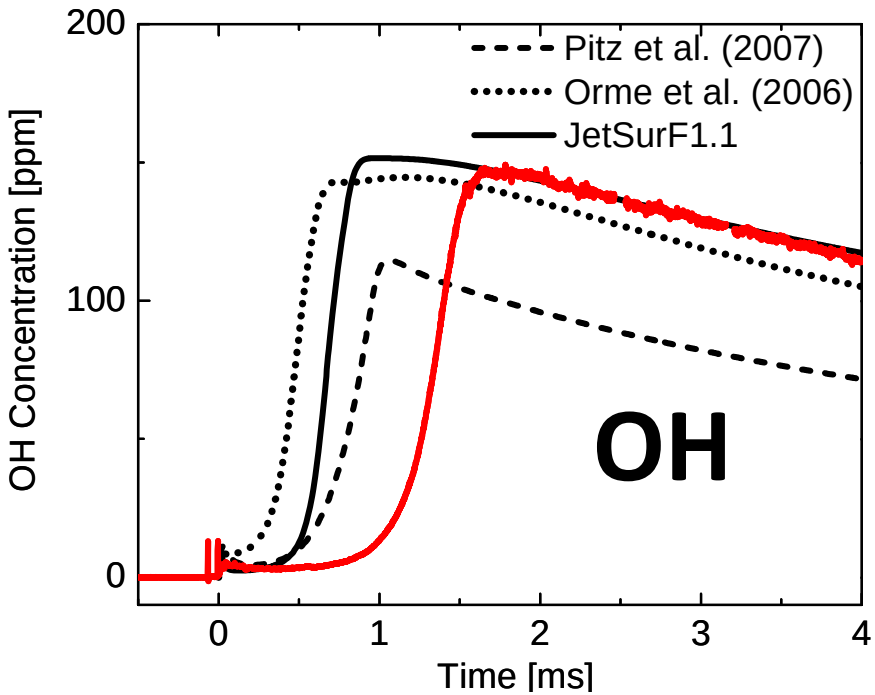




- **Time-history data available for CH, MCH and BCH**

Methylcyclohexane Oxidation Comparison with Models

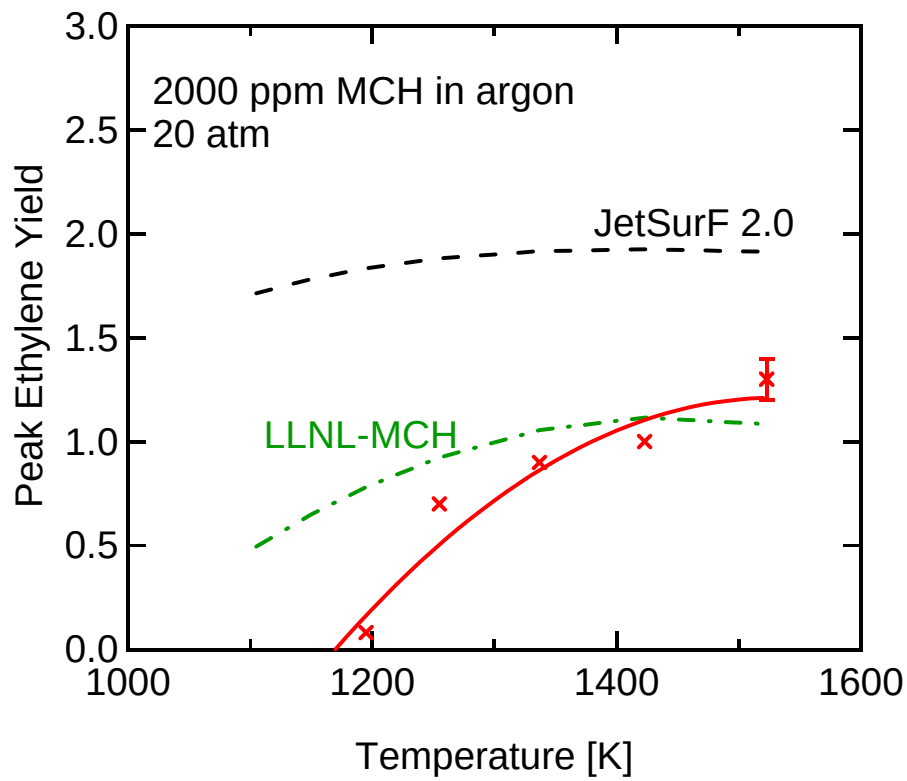




- **JetSurf/Orme capture post-ignition H_2O plateau levels**
- **JetSurf captures post-ignition OH plateau level**
- **Wide variability between model simulations for <u>methylcyclohexane</u> H_2O and OH time-histories**

MCH Decomposition: C_2H_4 Yields

- **Ethylene yields measured at 20 atm during MCH pyrolysis**
- **Data courtesy M. Billingsley AF-ERC (2011)**
- **Data reveal significant differences from model predictions**



- **Refinement needed in cyclo-alkane models!**
  - **Particularly in fuel decomposition pathways!**

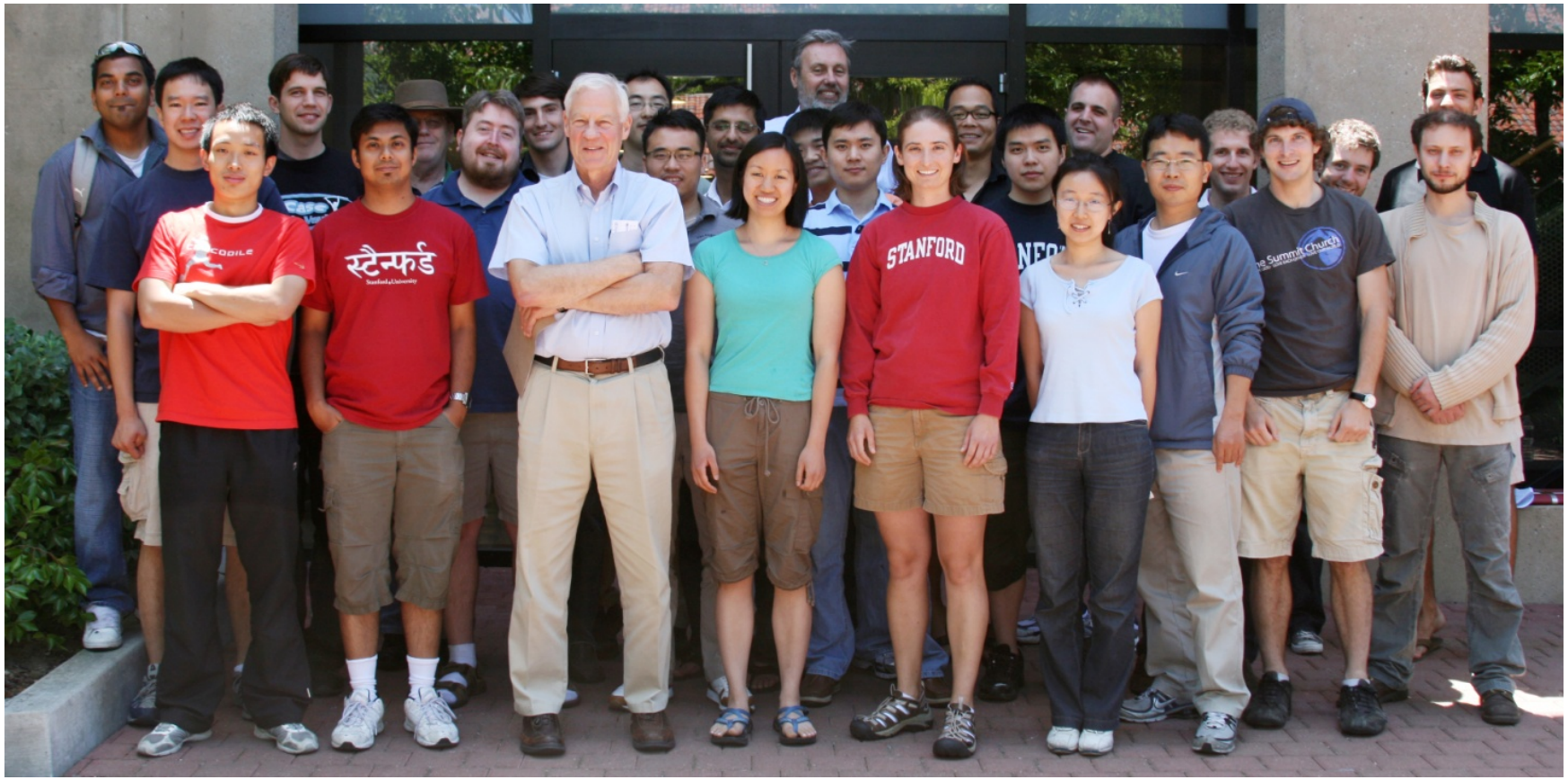
Summary

- **Fundamental shock tube kinetic database now available:**
  - **Ignition delay times, species time-histories**
  - **n-alkanes, cyclo-alkanes, iso-alkanes**

- **Next Step: Dimethyl Alkanes**
  - **Full ignition delay time study**
  - **Multi-species time-history study**
  - **Close collaboration with modelers**

Acknowledgments

- **Work supported by AF-IPT**
- **Pyrolysis work supported by AF-ERC**
- **Thanks to our many shock tube and laser students**



Stanford Flow Reactor Studies

C. T. Bowman and S. Banerjee

- **Flow Reactor Test Conditions**: **n-dodecane, 1 atm, 1150K, lean to rich (Φ = 0.8-1.5)**
- **Typical Reaction Time Scales: 35 - 40 ms**
- **Carbon Balance: +85% at all axial locations; +95% downstream**
- **Time Zero: Zwietering mixing/reaction model:**
  - single mixing parameter determined experimentally by inert tracer injection;
  - model validated using a single-step elementary reaction with well-known kinetics
    -(concerted elimination reaction of ethyl chloride)
- **Flow Reactor Diagnostics: GC, NDIR, PMA, Thermocouple**
  - **GC: C1-C4 stable HC intermediates, C1, C2 aldehydes, H_2, CO, CO_2, O_2**
  - **NDIR: CO, CO_2; PMA: O_2; NDIR and PMA allow a cross check on GC data**

- **Key Observations:**
  - **fair agreement with JetSurf 2.0**
  - **predicted reaction time scales are too slow (by about 20%)**

- **Next Step: currently running at elevated pressures 2 & 4 atm**