Development of Detailed and Reduced Mechanisms for Surrogates of Petroleum-Derived and Synthetic Jet Fuels:

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Introduction

- **Advances in Shock Tube & Laser Methods**

Results

- **Direct Rate Measurements**
- **Ignition Delay Time Measurements**
- **Multi-Species Time-Histories**

MACCCR 3rd Annual Fuels Summit, Sept. 20–23, 2010

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

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: extend to multi-species time-histories

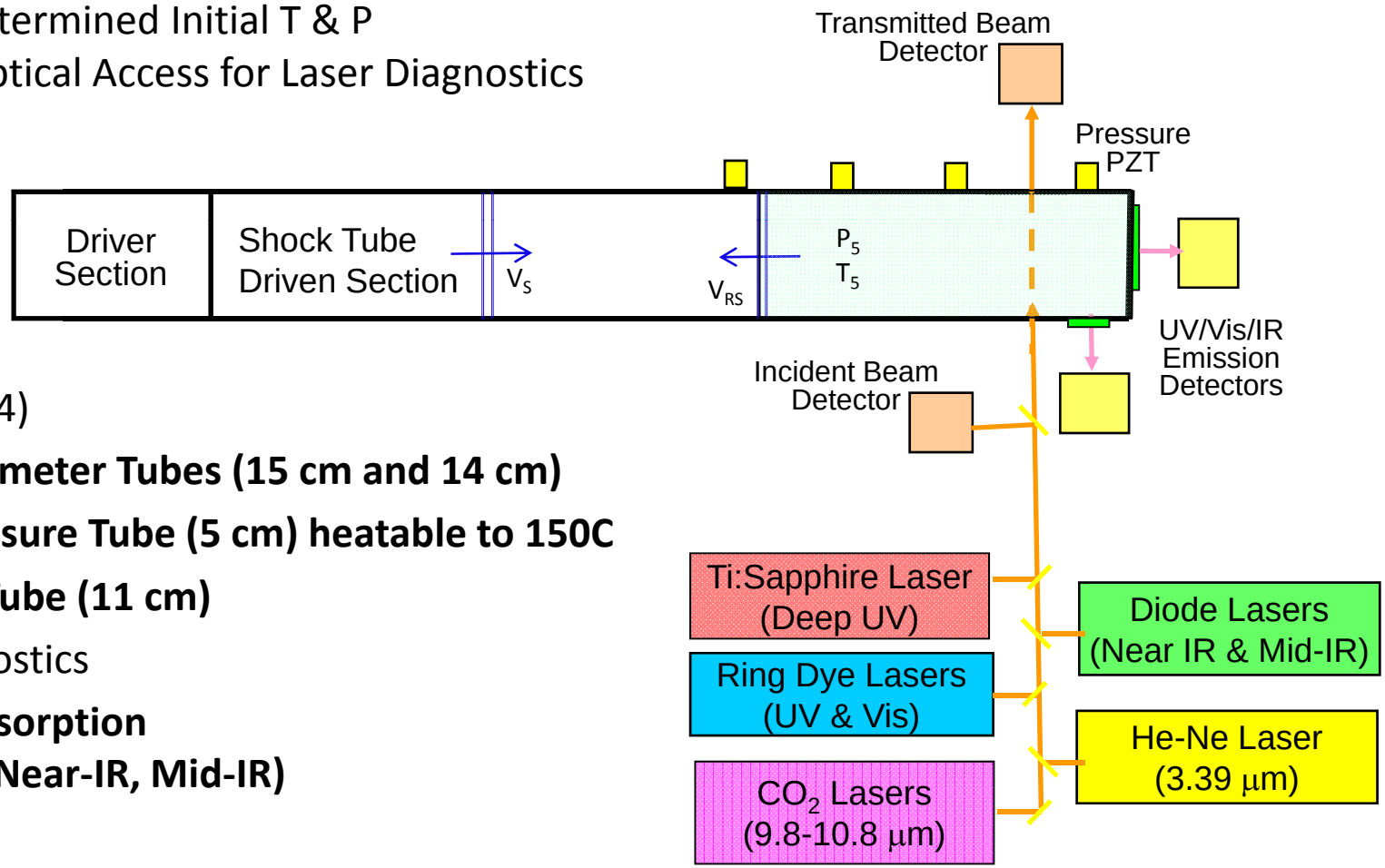
- cyclo-alkanes (CH, MCH, BCH): τ_{ign} at low pressures
- n-heptane oxidation: multi-species profiles

Year 3: n-alkanes, cyclo-alkanes and branched alkanes

- branched alkanes (2,4-DMP, 2,5-DMH): τ_{ign} at low pressure
- n-dodecane & MCH oxidation: 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 (UV, Vis, Near-IR, Mid-IR)**

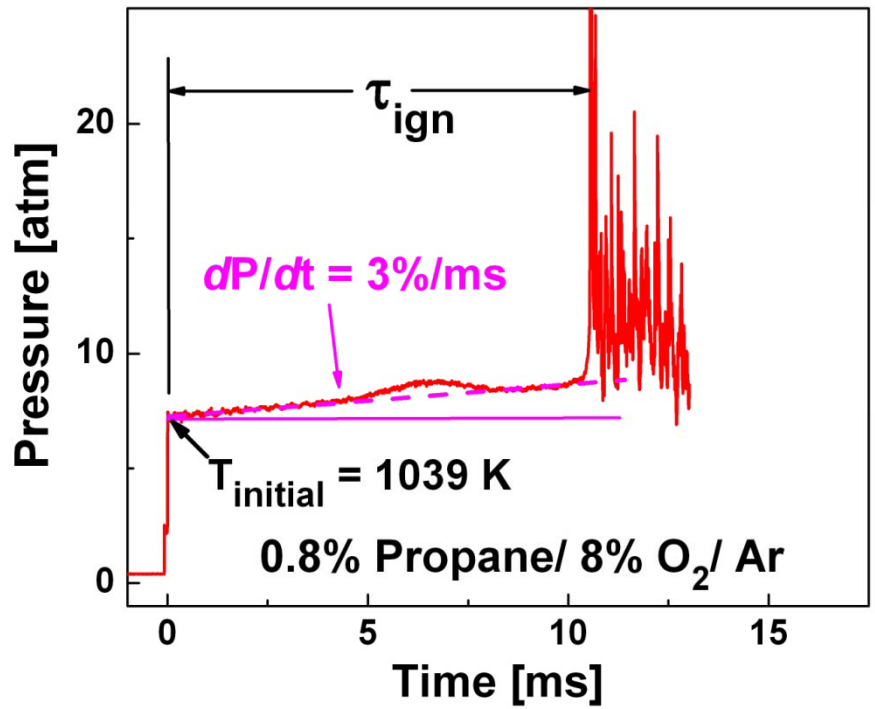
Advances in Shock Tube Methods

enabling higher-quality kinetics data

1. **Improvement in temperature uniformity**
   (to improve quantitative modeling)
2. **Extension of test time**
   (to access NTC regime)
3. **Aerosol fuel loading**
   (for study of low-vapor-pressure fuels)

1. Improvement in Temperature Uniformity

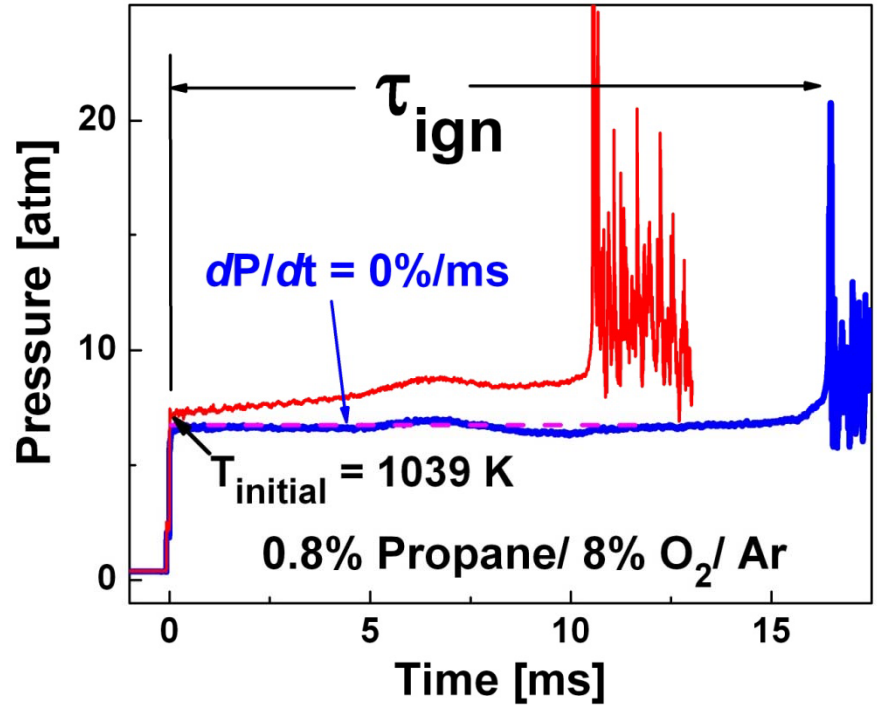
- **Non-ideal facility effects perturb flow conditions, i.e. dP/dt ≠ 0, dT/dt ≠ 0**
- **Ignition delay times are artificially shortened!!**
- **Solution: Driver Inserts**



- **Driver inserts modify flow to achieve uniform T and P at long test times**

1. Improvement in Temperature Uniformity

- **Result: Near-ideal constant-volume performance with dP/dt ~ 0, dT/dt ~ 0**

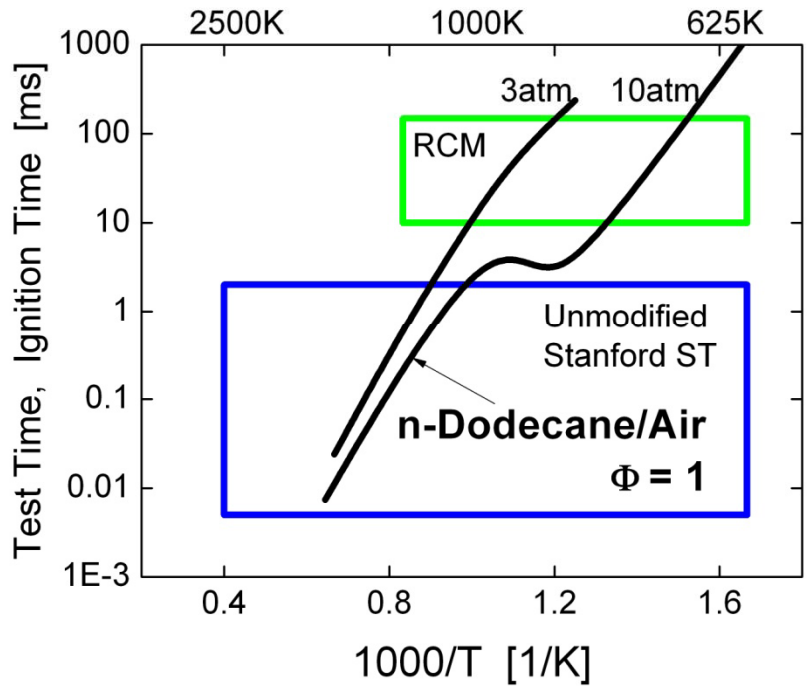


- **Driver inserts modify flow to achieve uniform T and P at long test times**

2. Extension of Test Time:

Access to Low Temperatures

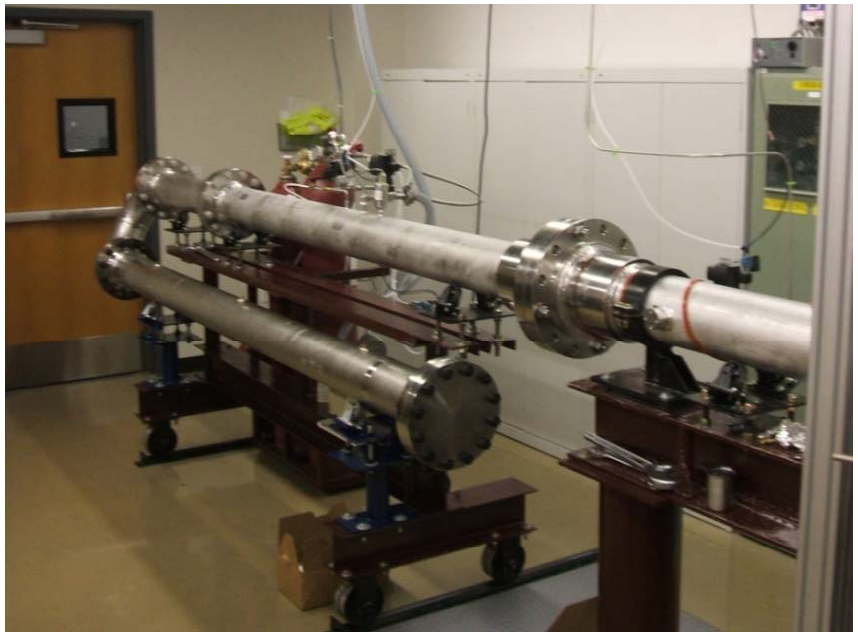
- Conventional shock tube operation: ~1-3 ms test time
- No overlap with RCM operation: ~10-150 ms test time



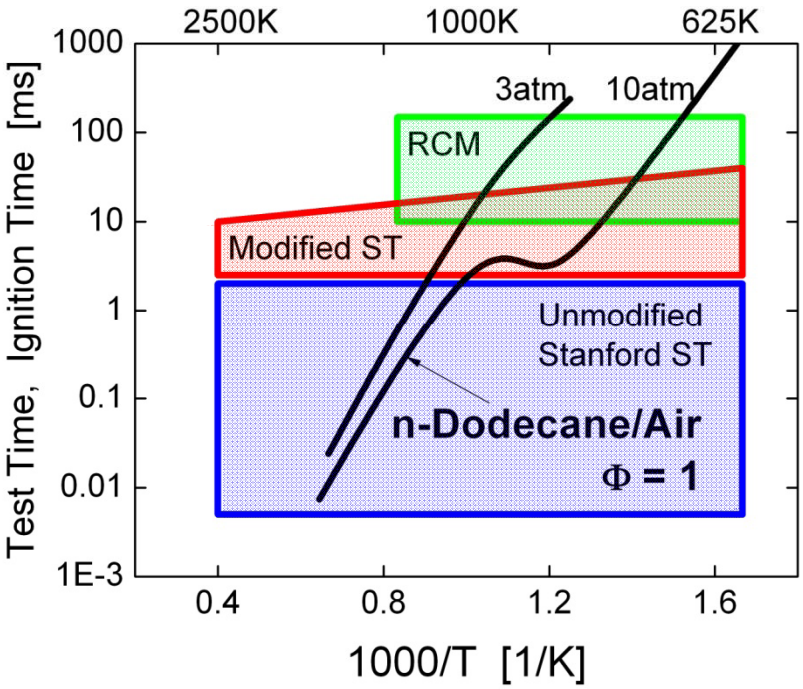
2. Extension of Test Time:

Access to Low Temperatures

- Longer driver length and tailored gas mixtures can provide longer test times (> 40 ms)

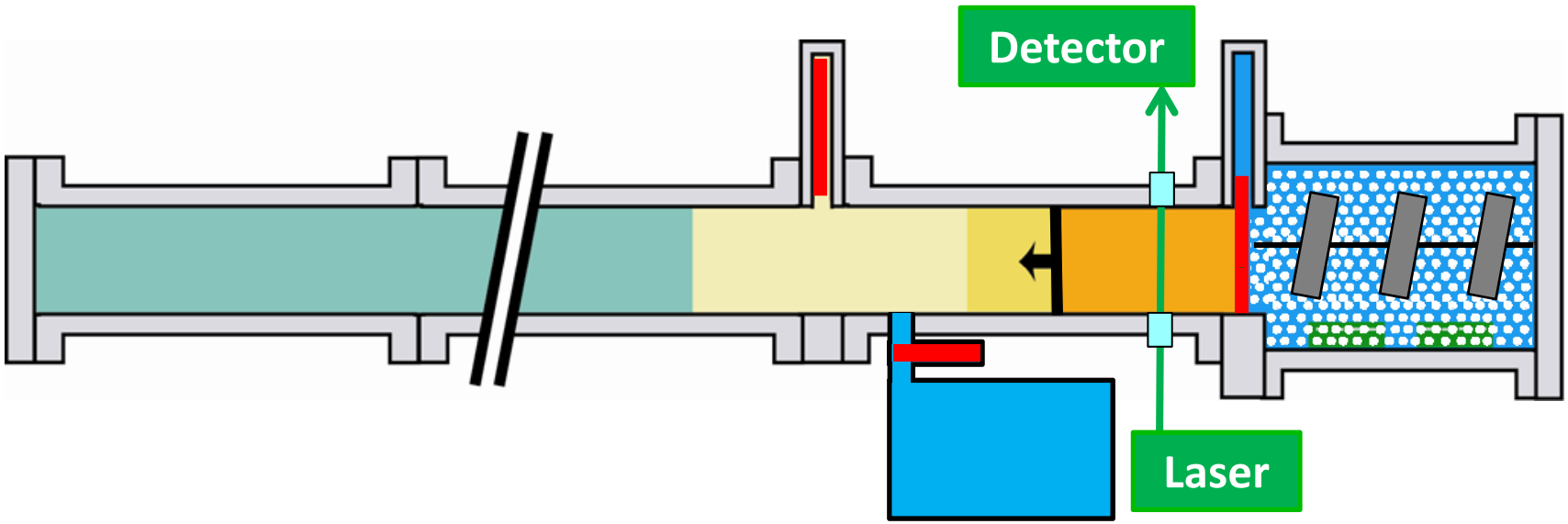


2x Driver Extension



- Shock tubes now can overlap with RCMs

3. Aerosol Shock Tube for Low-Vapor-Pressure Fuels

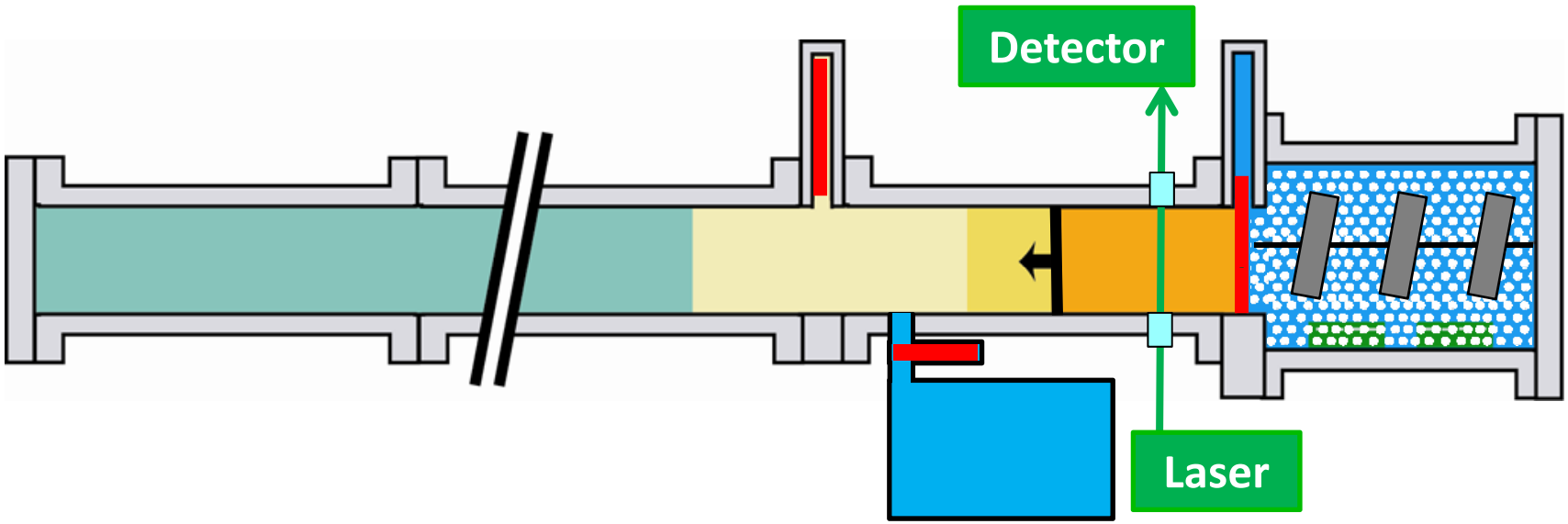


Three Step Operation:

1. Fill with fuel aerosol generated using nebulizers
2. Incident shock evaporates fuel droplets
3. Reflected shock heats gas-phase mixture→ T_5 & P_5

enables laser absorption measurement of chemistry

3. Aerosol Shock Tube for Low-Vapor-Pressure Fuels



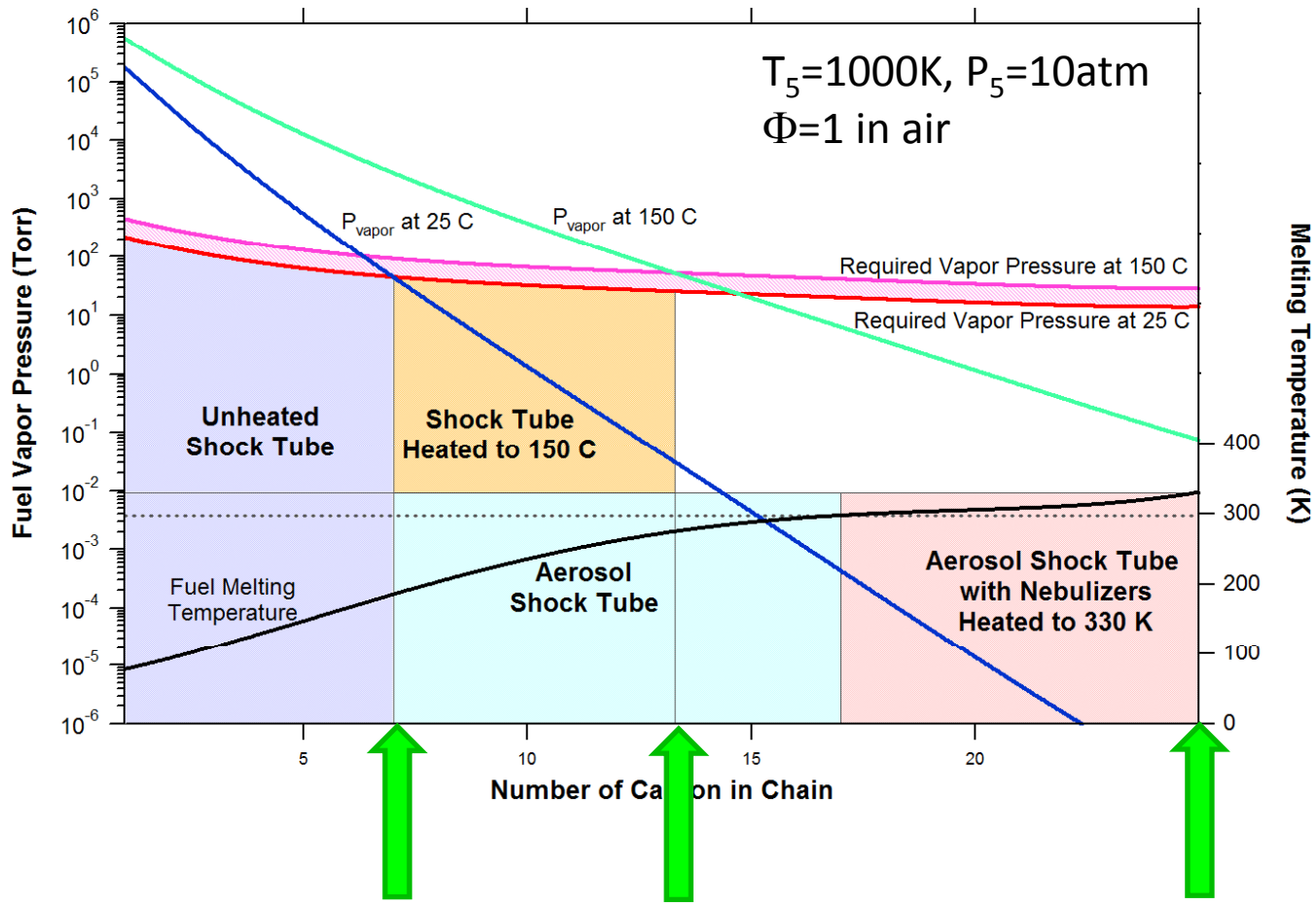
- Does not require heated shock tube
- Eliminates fuel cracking and partial distillation
- Provides access to low-vapor-pressure fuels:

  Jet fuel, diesel, bio-diesel surrogates

Aerosol Shock Tube Operation Regime

- **Unheated ST provides access up to C7 n-alkanes**
- **Heated ST provide access up to C14 (n-tetradecane)**
- **AST provides access up to large C25 n-alkanes**

Shock Tube Access to Fuels: Normal Alkanes



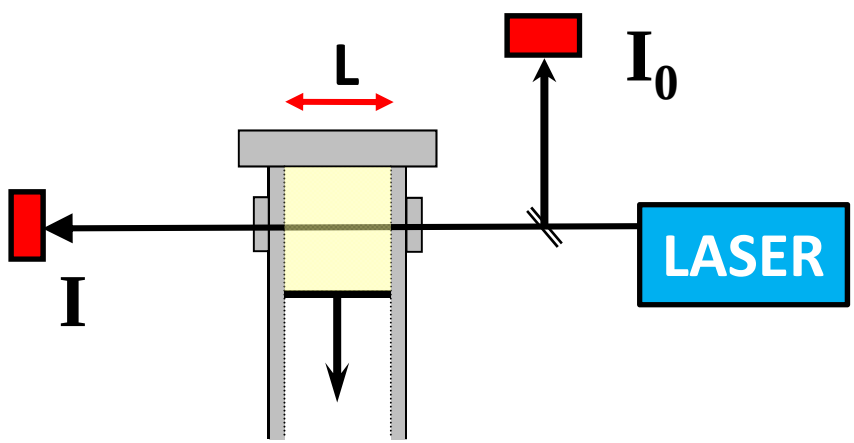
Advances in
Laser Absorption Diagnostics

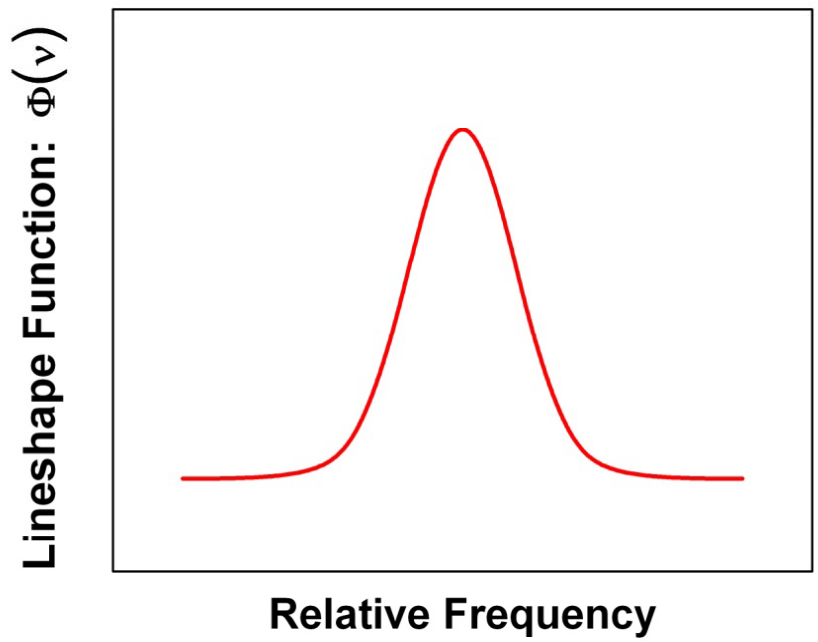
Laser Absorption Theory

- **Governing Equation: Beer-Lambert Law**

$$I/I_0 = \exp(-S_{lu}\,\Phi(\nu)\,X_{species}\,P_{total}\,L)$$

Line Strength **Line shape**



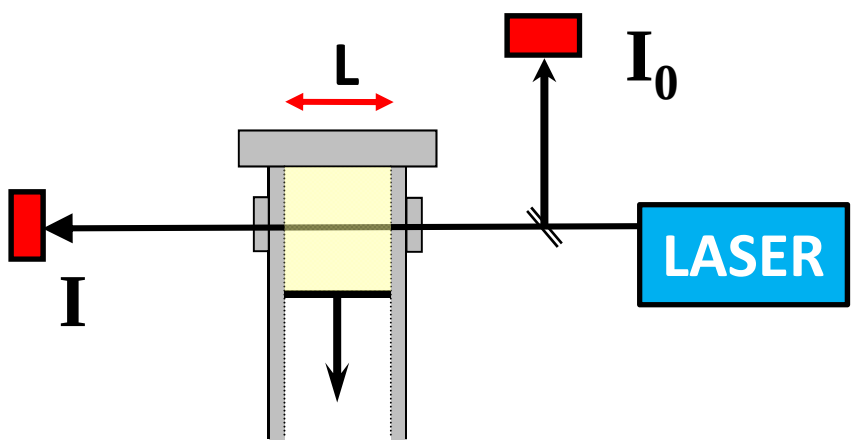


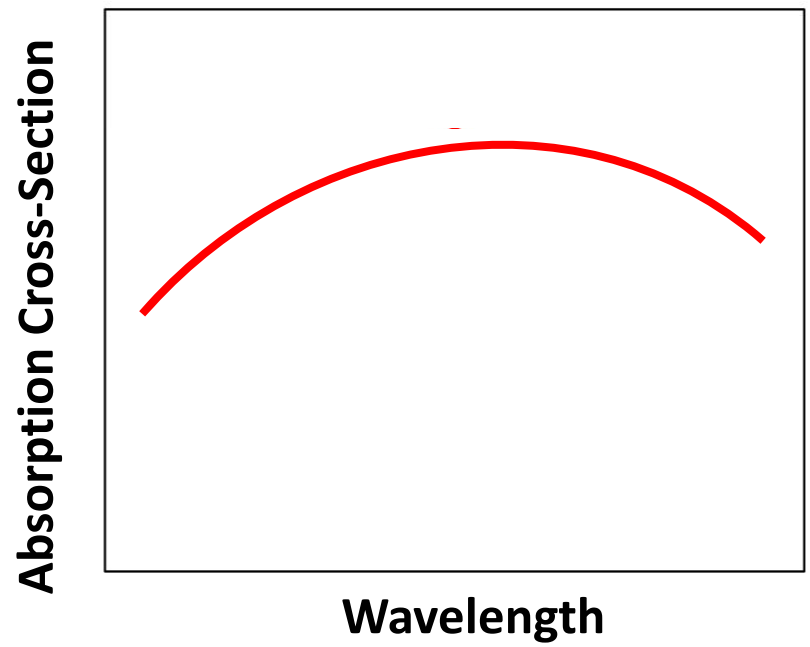
- **Quantitative absorption requires database for S and Φ for discrete lines**

Laser Absorption Theory

- **Governing Equation: Beer-Lambert Law**

$$I/I_0 = \exp(-S_{lu}\,\Phi(\nu)\,X_{species}\,P_{total}\,L) = \exp(-\sigma\,N_{species}\,L)$$





- **Requires database for σ for broad absorbers**
- **What species are accessible?**

Species Diagnostics Developed at Stanford :

Species and Wavelengths

Ultraviolet	
CH_3	216 nm
NO	225 nm
O_2	227 nm
HO_2	230 nm
OH	306 nm
NH	336 nm

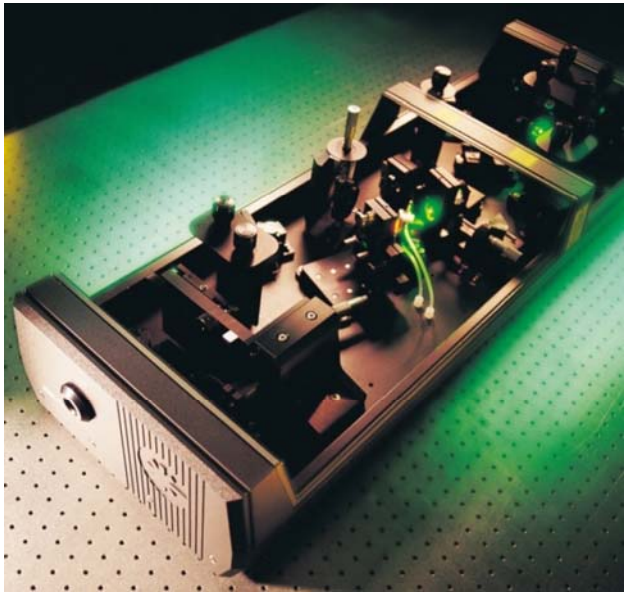
Visible	
CN	388 nm
CH	431 nm
NCO	440 nm
NO_2	472 nm
NH_2	597 nm
HCO	614 nm

Infrared	
CO	2.3 μm
H_2O	2.5 μm
CO_2	2.7 μm
Fuel	3.4 μm
NO	5.2 μm
C_2H_4	10.5 μm

Advances in the UV:

- Ultra-fast lasers used to extend tuning range (2009)

Coherent MIRA
Ti-Sapphire Ring Laser



Species Diagnostics Developed at Stanford :

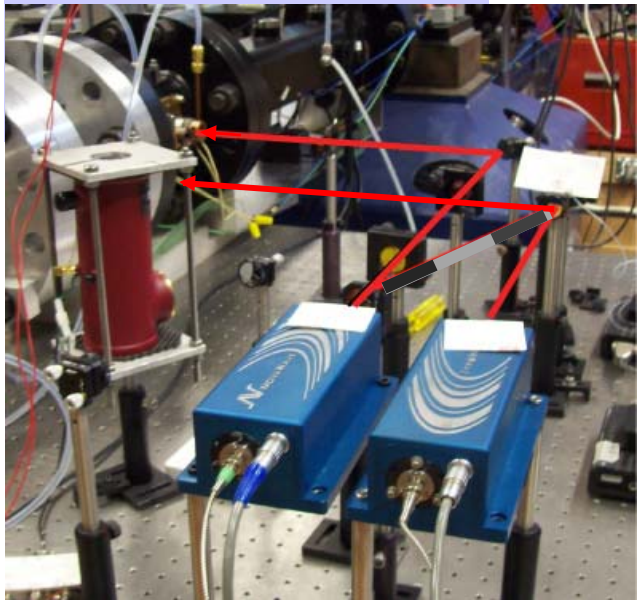
Species and Wavelengths

Ultraviolet		Visible		Infrared	
CH_3	216 nm	CN	388 nm	CO	2.3 μm
NO	225 nm	CH	431 nm	H_2O	2.5 μm
O_2	227 nm	NCO	440 nm	CO_2	2.7 μm
HO_2	230 nm	NO_2	472 nm	Fuel	3.4 μm
OH	306 nm	NH_2	597 nm	NO	5.2 μm
NH	336 nm	HCO	614 nm	C_2H_4	10.5 μm

Advances in the IR

- New diode lasers allow simple access to mid-IR (2007-10)

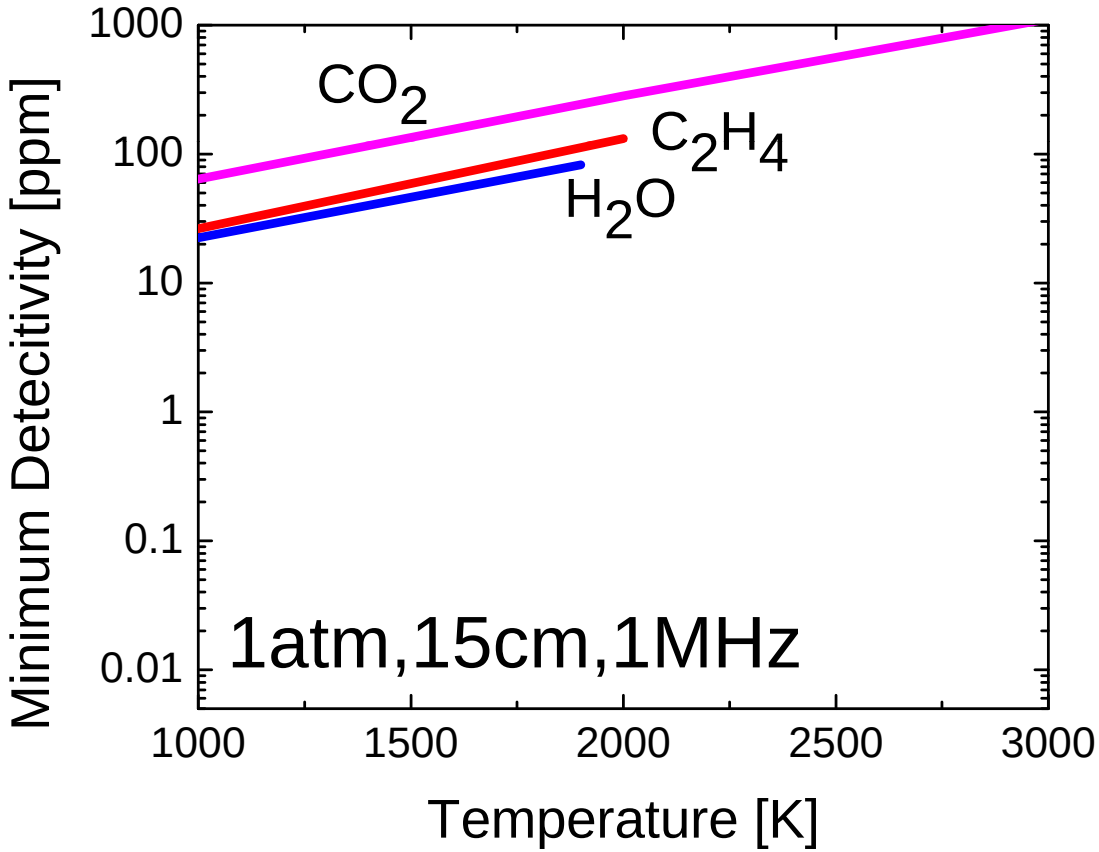
- CO_2 gas laser for C_2H_4



NovaWave Mid-IR Laser

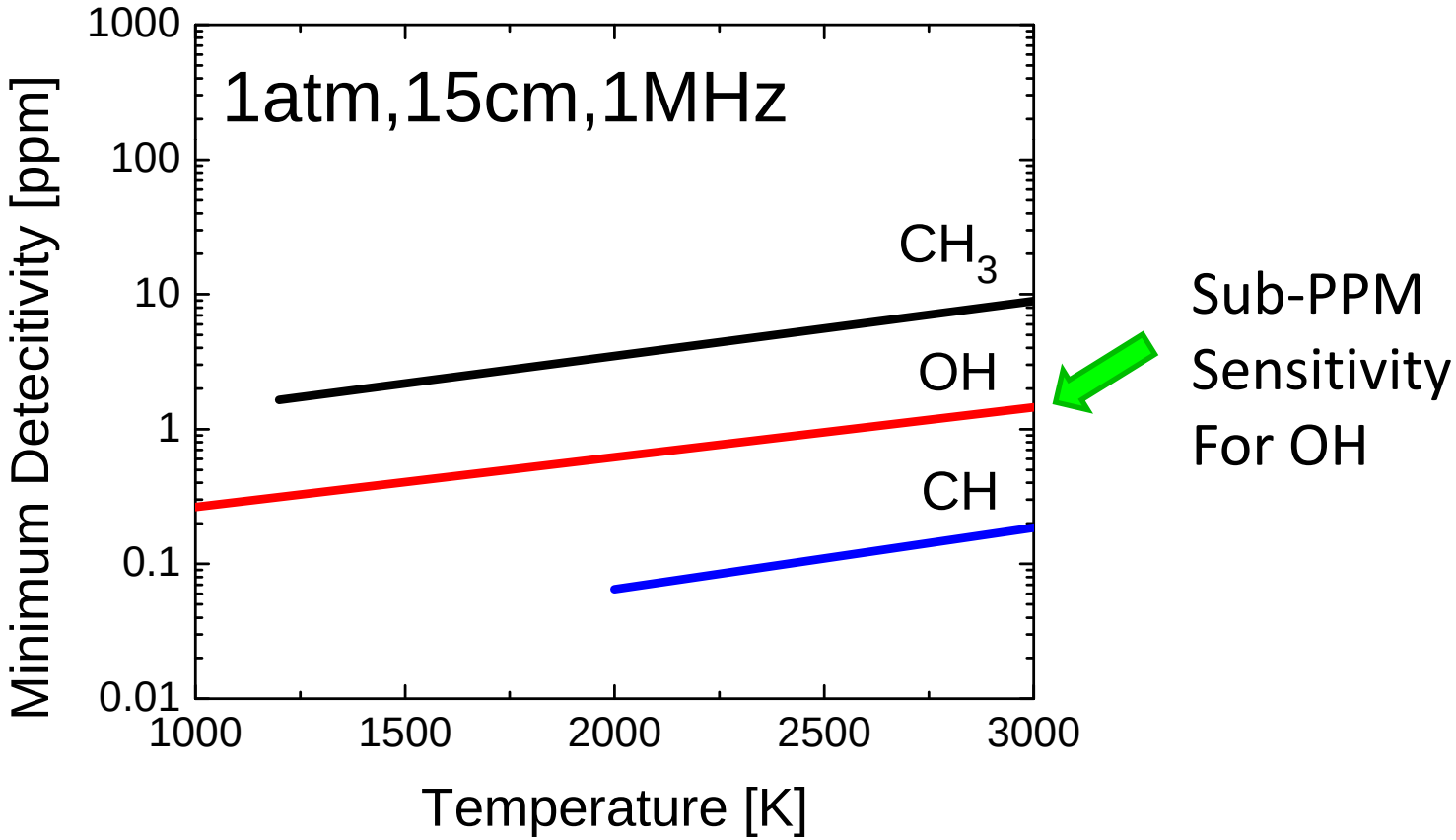
How sensitive are laser absorption diagnostics in shock tubes?

- **IR Transitions – Stable Molecules: 10-100's ppm**



How sensitive are laser absorption diagnostics in shock tubes?

- **UV-Vis Transitions – Radical Species: sub-ppm to ppm**



Results: 3 Types of Shock Tube/Laser Data

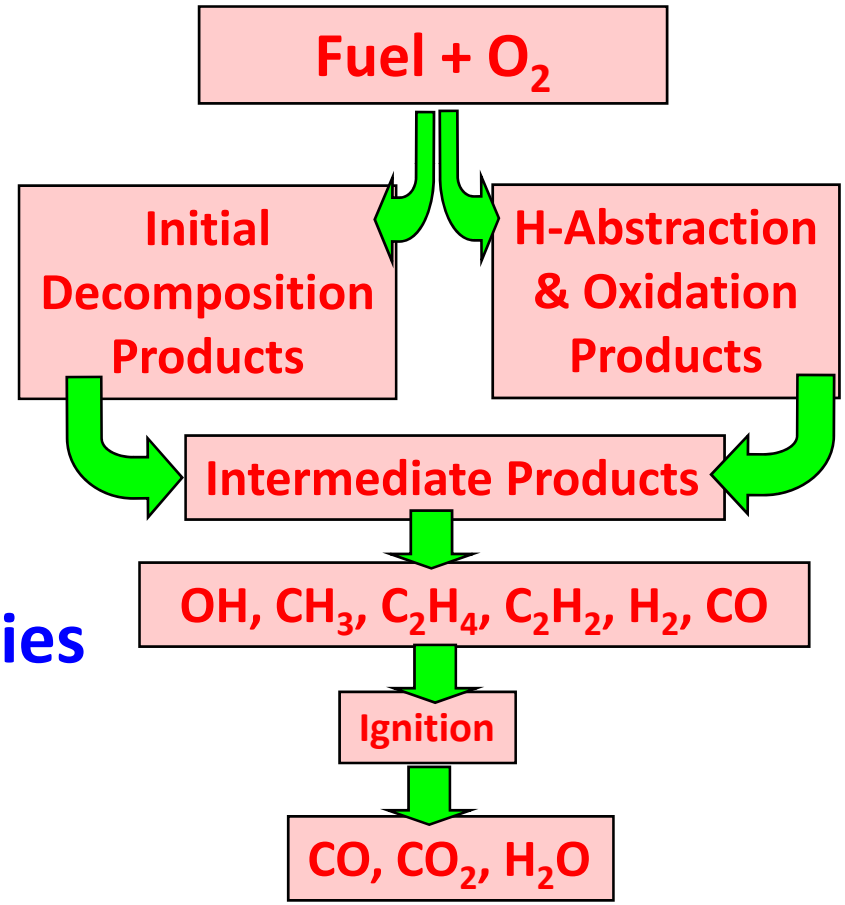
EXPERIMENT

1. Direct Study of Individual Rxn. Rate Constants

2. Global Kinetic Targets: Ignition Delay Times

3. Multi-Wavelength, Multi-Species Time-Histories

MODEL



1st Type of Data: Direct Studies of Individual Reaction Rate Constants

1. $OH + C_2H_4 \rightarrow H_2O + C_2H_3$
2. $OH + C_3H_6 \rightarrow H_2O + C_3H_5$
3. $OH + 1,3\text{-}C_4H_6 \rightarrow H_2O + C_4H_5$

Motivation: OH + alkene reactions strongly influence ignition delay times

Example 1: $OH + C_2H_4 \rightarrow H_2O + C_2H_3$

<u>3-Part Strategy</u>

1. **Fast OH source: TBHP (tert-butyl-hydroperoxide)**

   $TBHP \rightarrow OH + CH_3 + CH_3COCH_3$

2. **Pseudo-first-order removal**

   $C_2H_4 >> OH$

3. **Monitor OH using laser absorption**

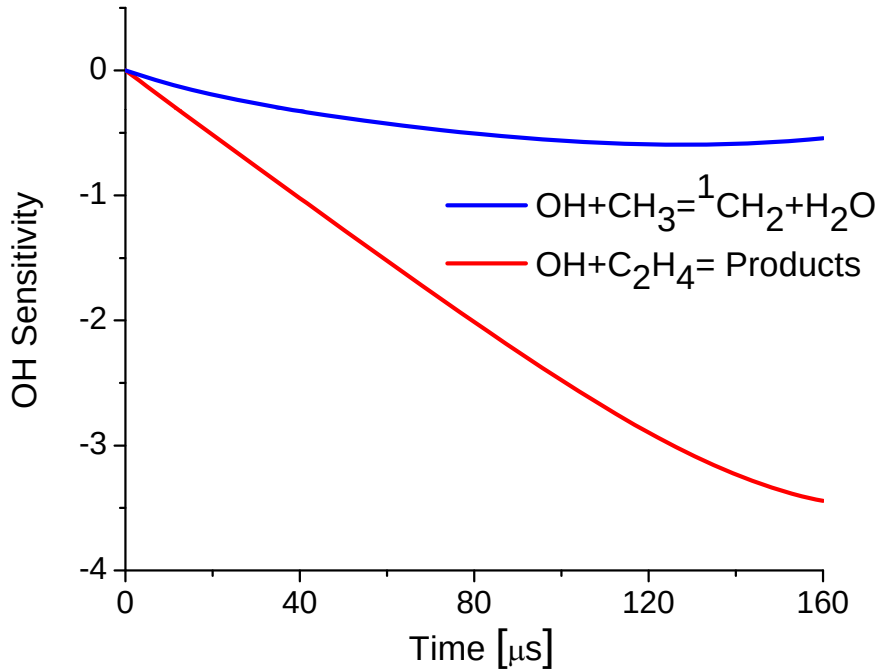
   ppm detection sensitivity

Example 1: $OH + C_2H_4 \rightarrow H_2O + C_2H_3$

Rate Measurement using OH Laser at 306 nm

Shock Conditions: 1201 K, 2.0 atm, 500ppm C_2H_4/23ppm TBHP/Ar

OH Sensitivity



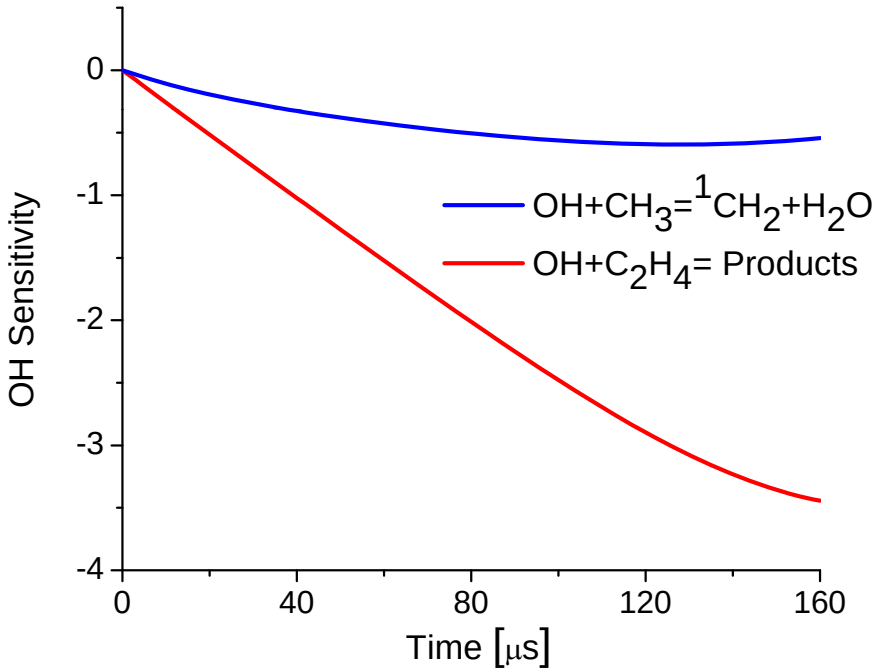
- **Reaction rate for $OH + C_2H_4$ dominates**

Example 1: $OH + C_2H_4 \rightarrow H_2O + C_2H_3$

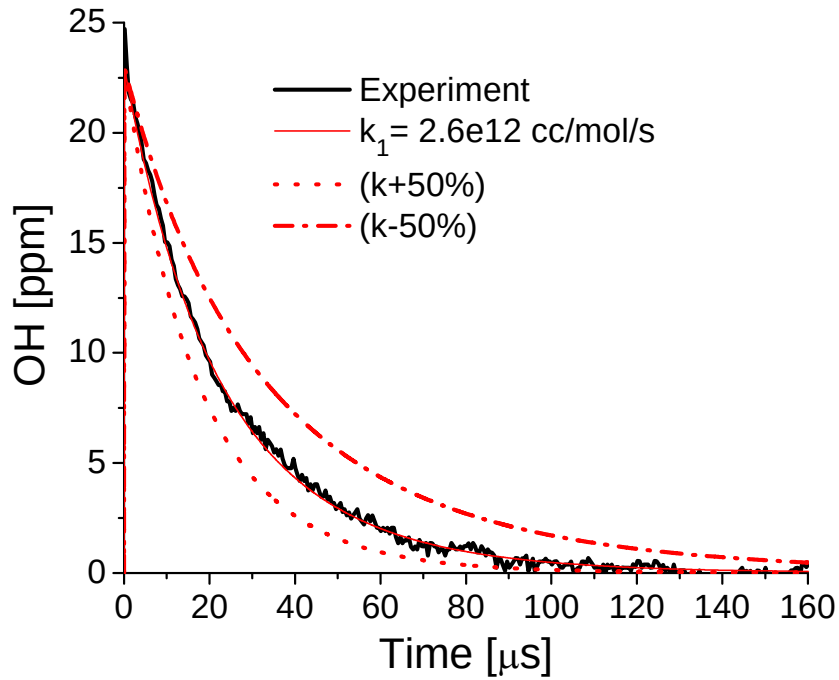
Rate Measurement using OH Laser at 306 nm

Shock Conditions: 1201 K, 2.0 atm, 500ppm C2H4/23ppm TBHP/Ar

OH Sensitivity



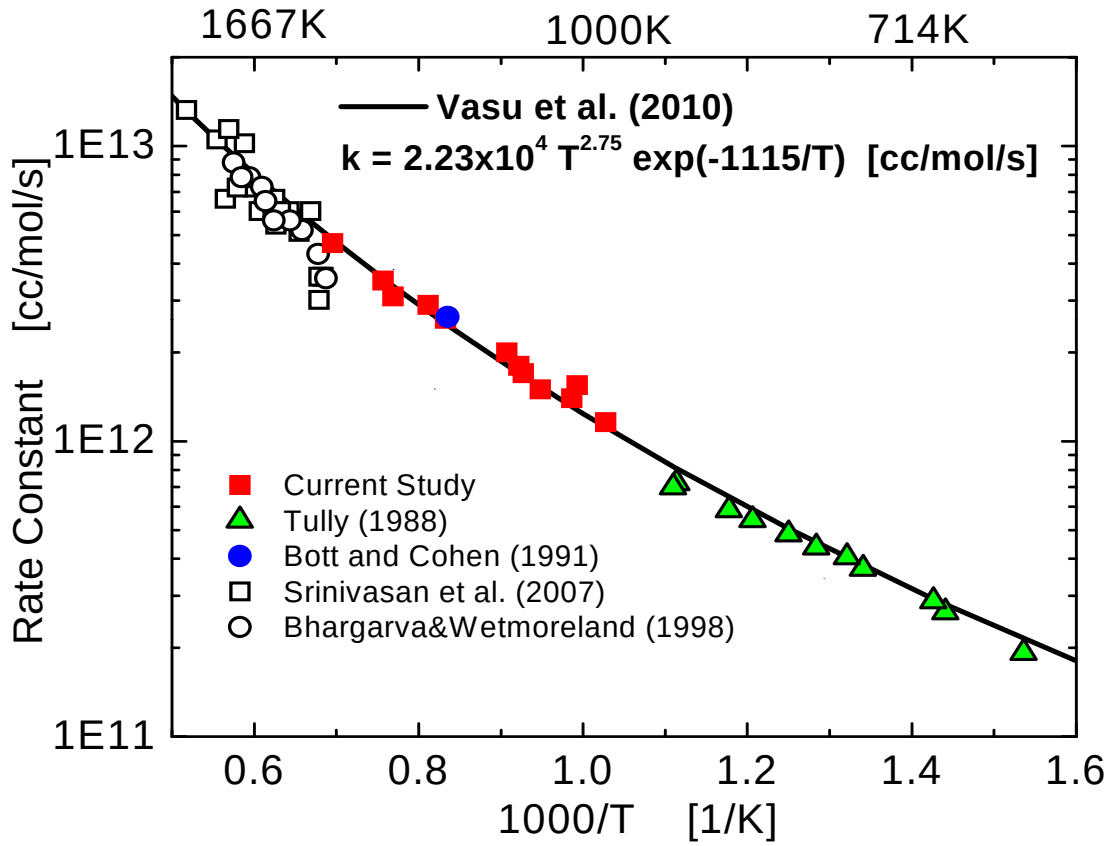
OH Time-History



- **precise determination of *k* (+/-20%)**

Example 1: $OH + C_2H_4 \rightarrow H_2O + C_2H_3$

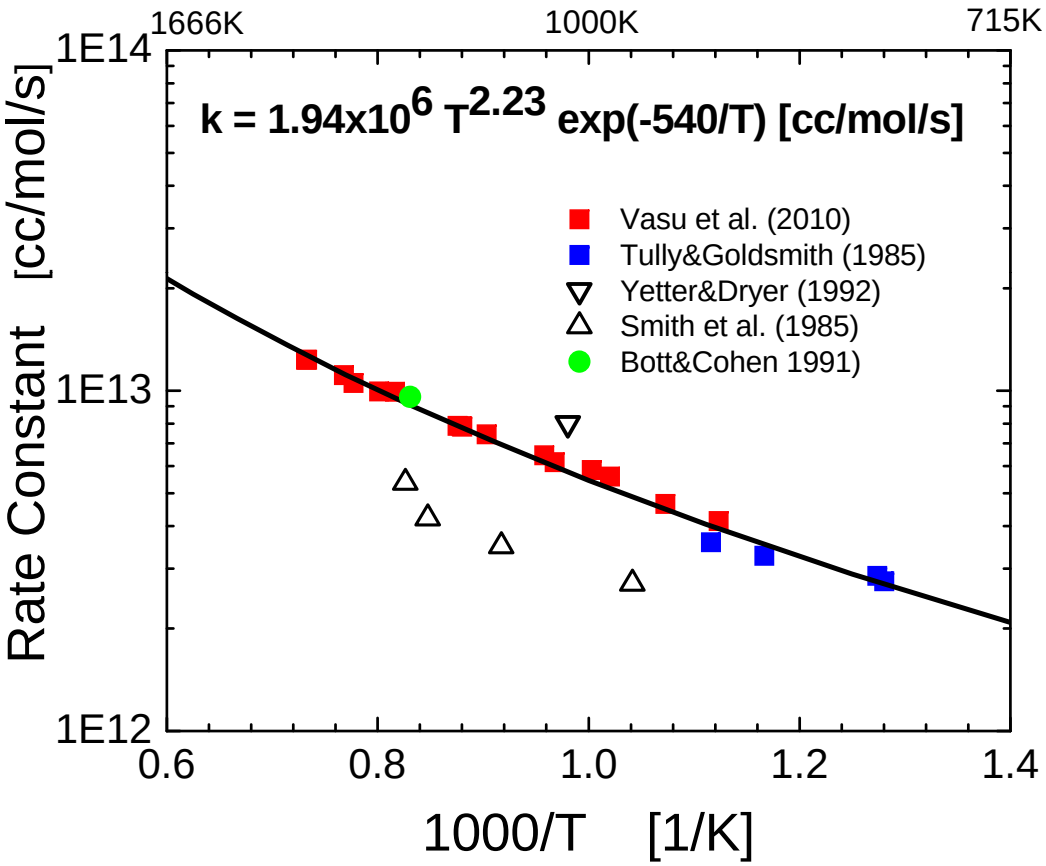
Results - Arrhenius Plot



- **High-quality, low-scatter data**
- **Unique coverage of 950-1400 K temperature range**
- **Good agreement with TST/tunneling model**

Example 2: OH + C_3H_6 → H_2O + C_3H_5

Results - Arrhenius Plot

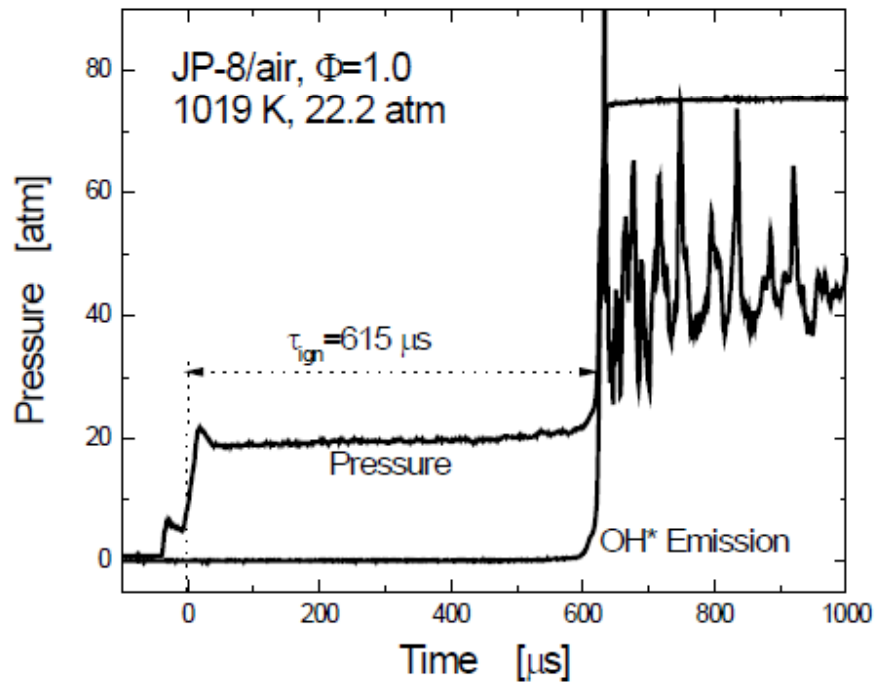


- **Good agreement with Tully & Goldsmith and Bott & Cohen**
- **Unique coverage of 950-1400 K temperature range**
- **Good agreement with TST/tunneling model**

2nd Type of Data: Jet Fuel Ignition Delay Times

- Overview of Previous Studies (ARO)
  1. Jet Fuel Ignition Delay Times
  2. JP-8/Jet-A Comparison
  3. τ_{ign} Pressure Dependence
  4. Performance of Available Models
- Studies of Individual Jet Fuel Surrogate Components (AF-IPT)

1. Jet Fuel Ignition Delay Times How are they measured?

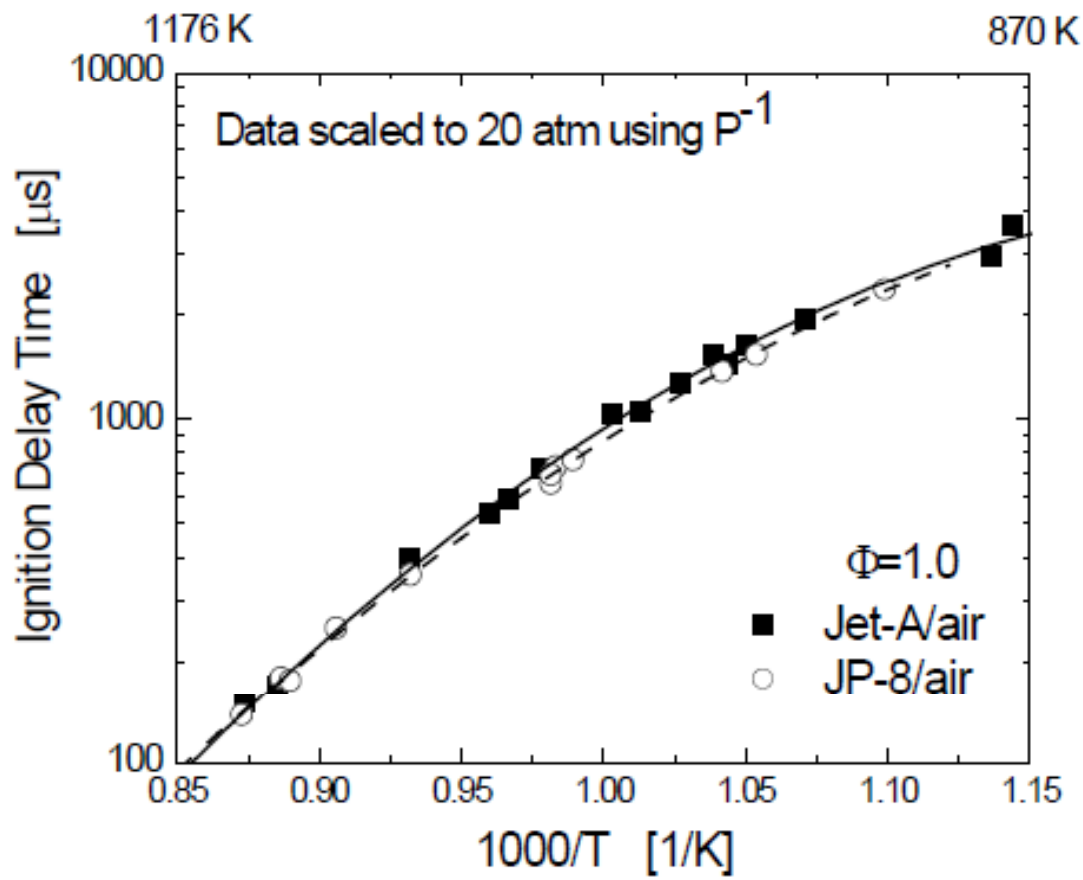


- **Ignition delay times measured using pressure and emission**
- **Shock tubes provide ignition delay time data over a wide temperature and pressure range**

2. Is there a Significant Difference between JP-8 and Jet-A?

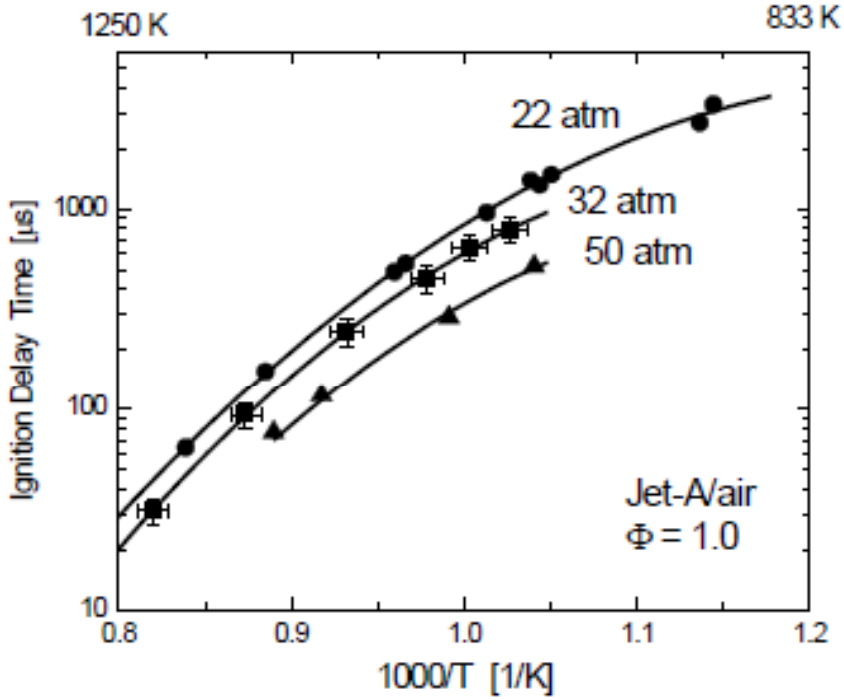
- **Ignition delay times similar for JP-8 (ARO) and Jet-A (POSF4658)**

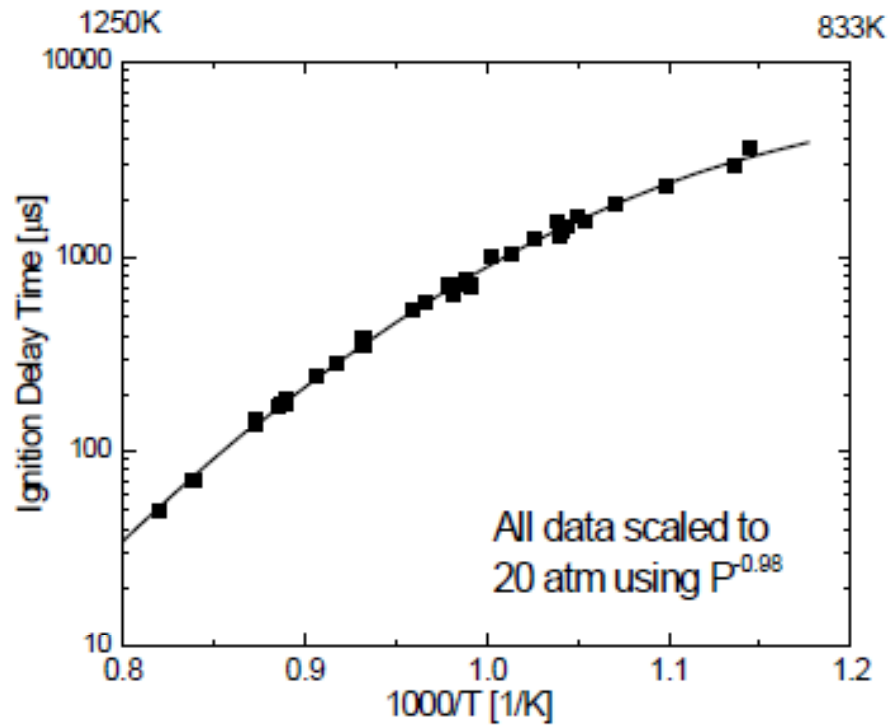
- **Open Question: Are there τ_{ign} variations with F-T fuels, S-8, bio-derived fuels?**



3. What is Pressure Dependence of Jet Fuel τ_{ign}?

Jet-A/Air, ϕ=1.0





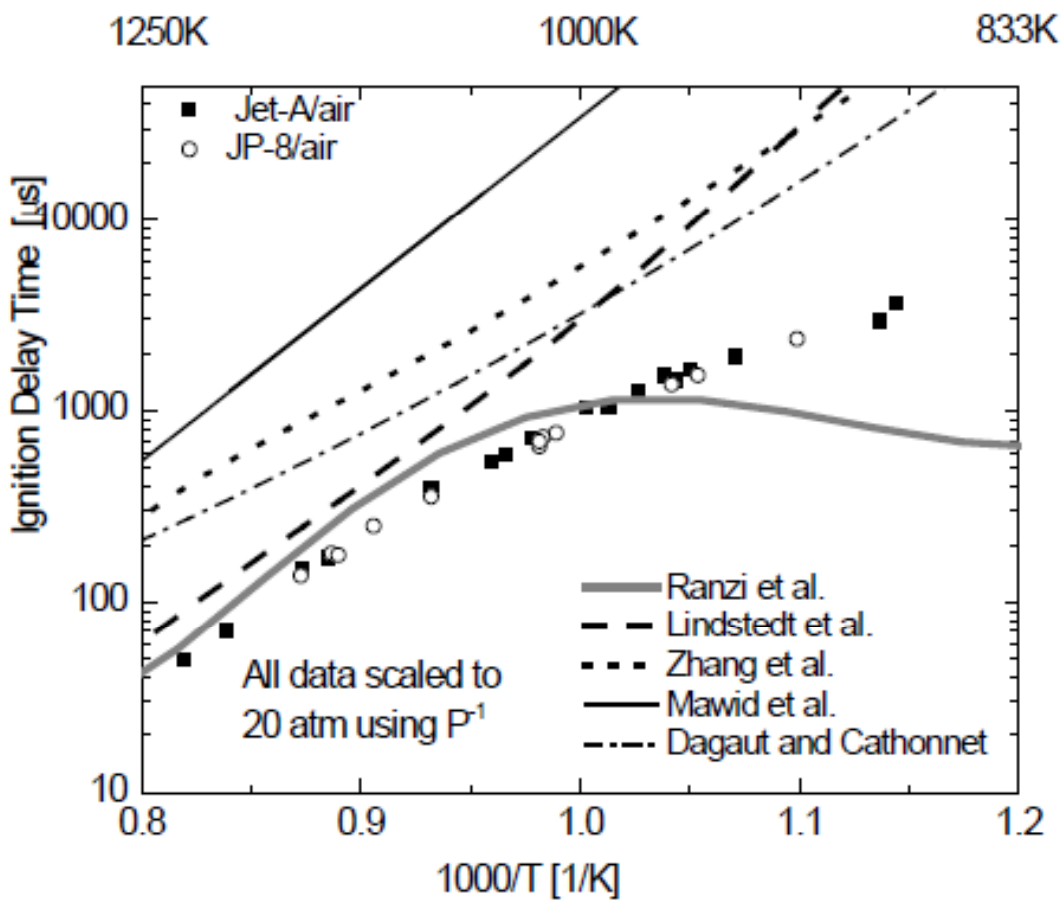
- **At high P (20-50atm): ignition delays scale as 1/P**

4. How do available models perform using multi-component surrogates?

- Violi #3 surrogate

MCH 10%
toluene 10%
benzene 1%
iso-octane 5.5%
n-dodecane 73.5%

- **Wide variability in model predictions at all temperatures**
- **Next step: study of individual surrogate component kinetics**



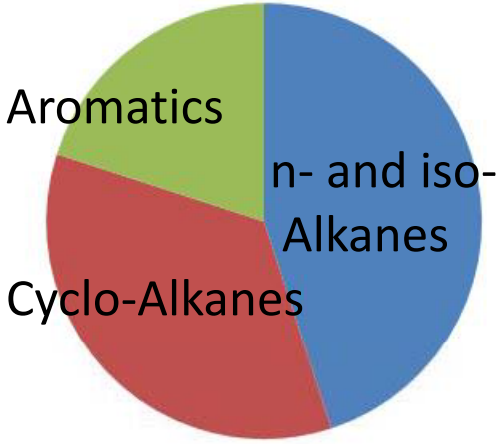
Studies of Individual Jet Fuel Surrogate Components:

Ignition Delay Times

n-Alkanes ⟵

cyclo-Alkanes

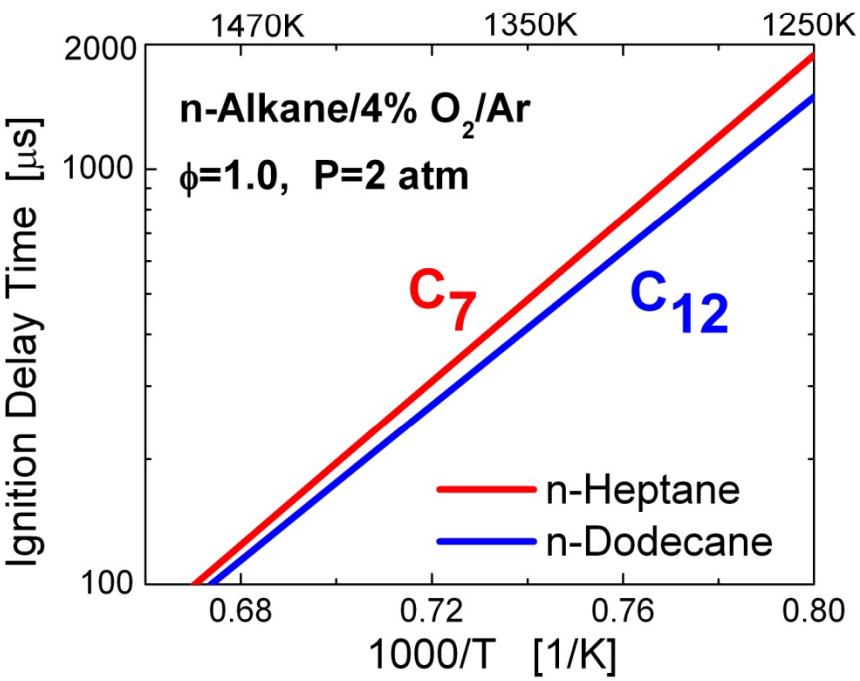
iso-Alkanes



JP-8 Composition

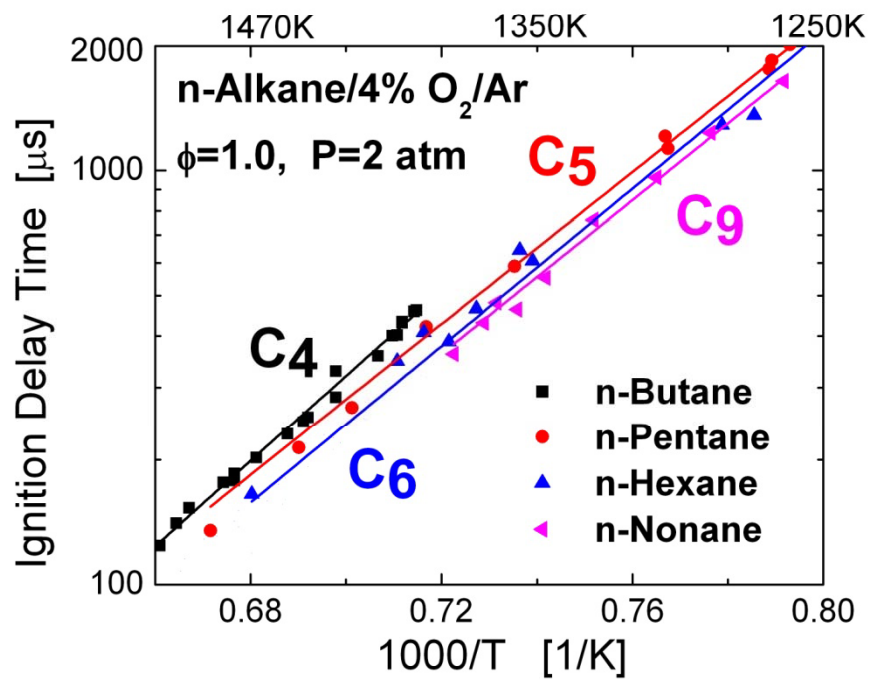
How Well Do n-Alkane Mechanisms for τ_{ign} Fit New High T Data: 1250-1500K, 2 atm?

Simulations



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

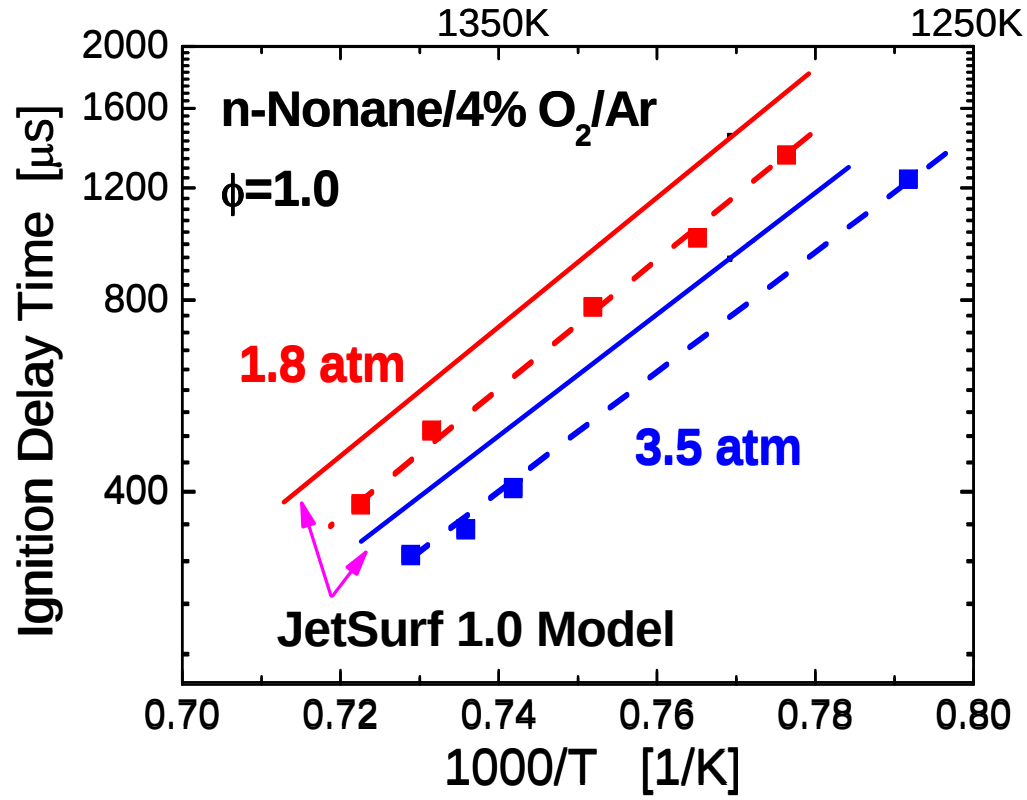
Experiment



- Shock tube experiments successfully confirm small variation of τ_{ign} with carbon #

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

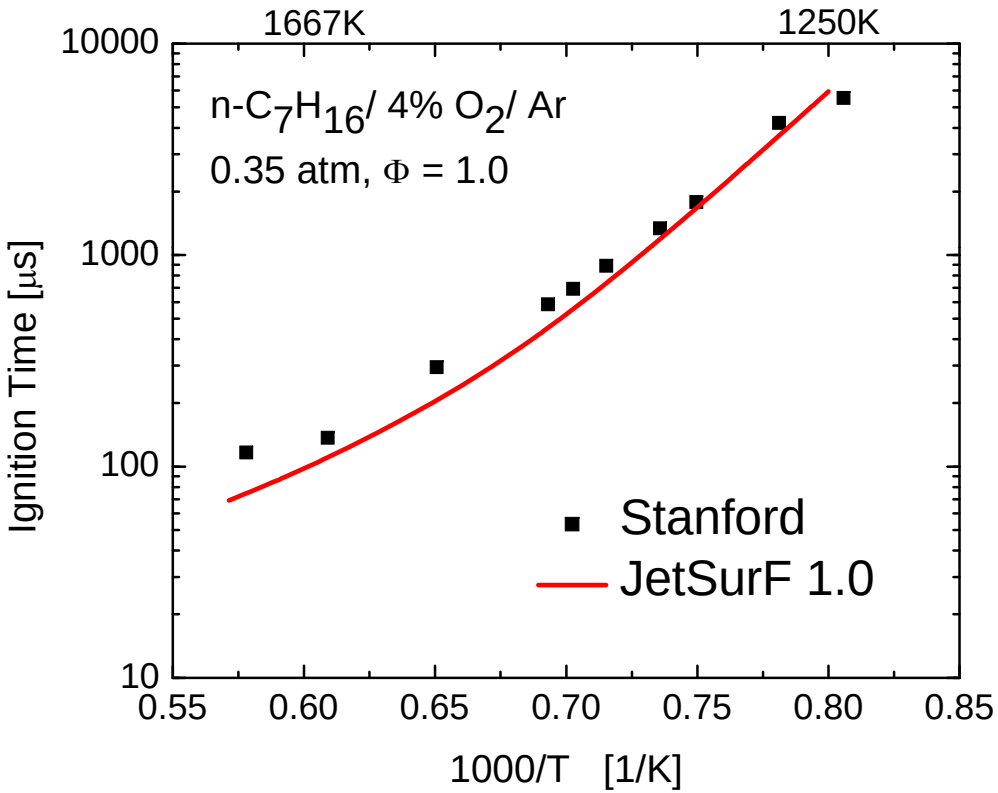
- **Experiment:**
  - τ_{ign} varies as $P^{-0.5}$
- **Current models:**
  - τ_{ign} varies as $P^{-0.67}$
  - Some difference in magnitude



- **Current interest in τ_{ign} delay at sub-atm pressures: high-altitude re-light problem**

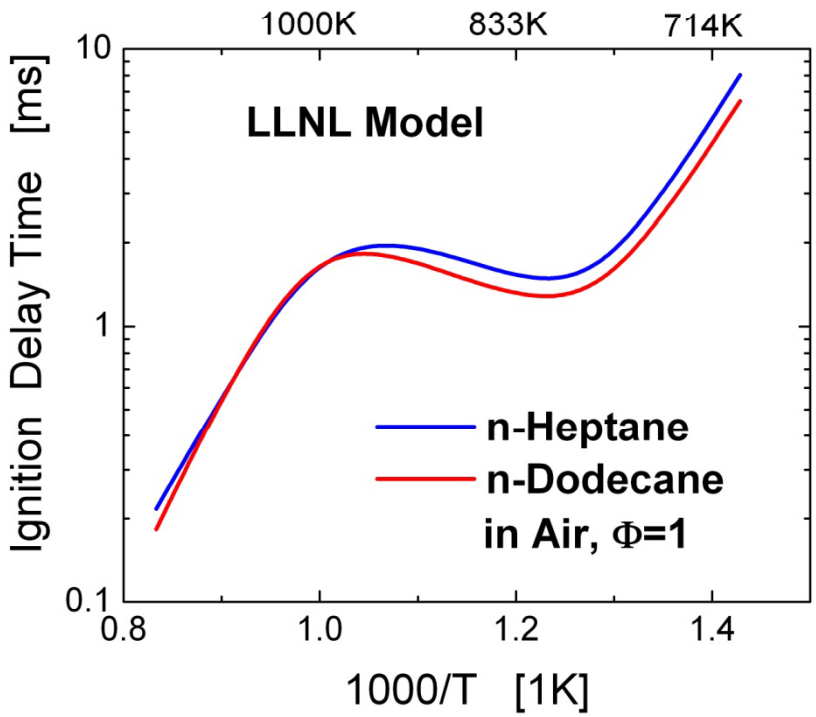
How Good are Models at Sub-Atm Pressure?
n-Heptane Ignition: 0.35 atm (8/2010)

- 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

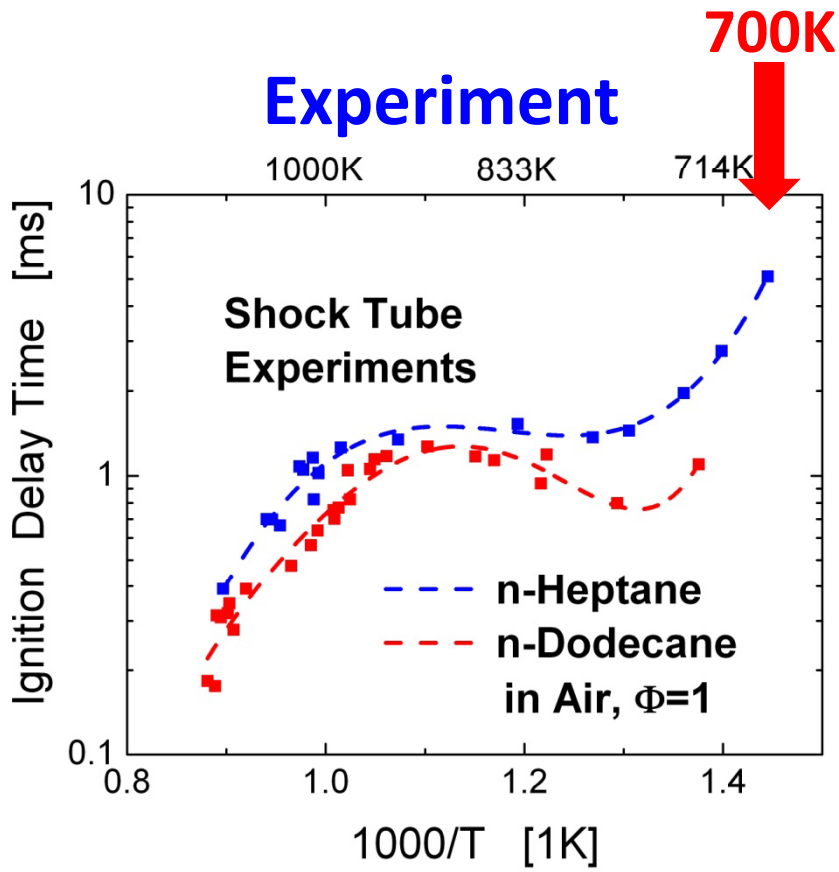


How Well Do n-Alkane Mechanisms for τ_{ign} Fit New Low T Data: 700-1000K, 20 atm?

Simulations



Experiment



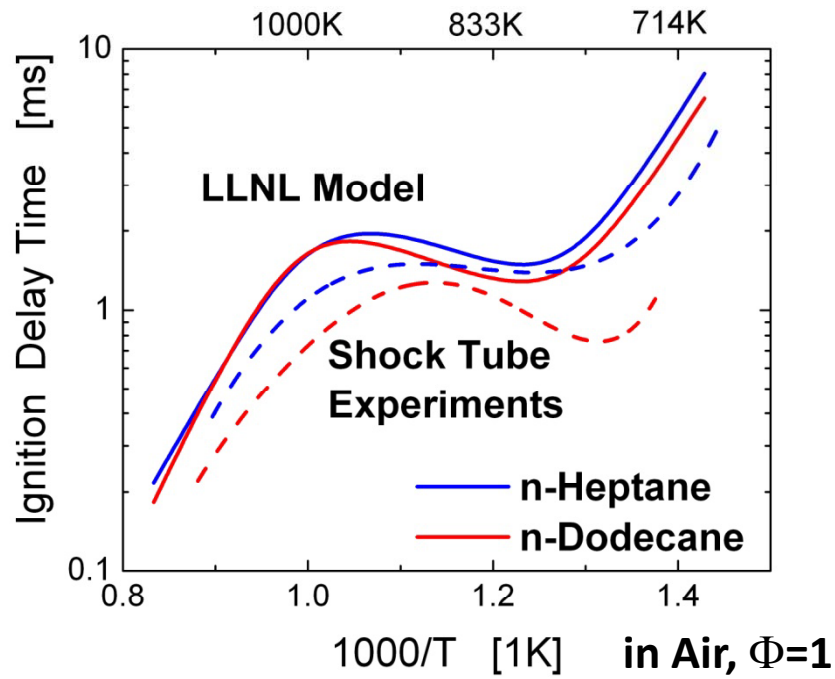
- Westbrook et al. (2009) predict NTC behavior with little variation with carbon #

- High pressure experiments can provide access to low T

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:

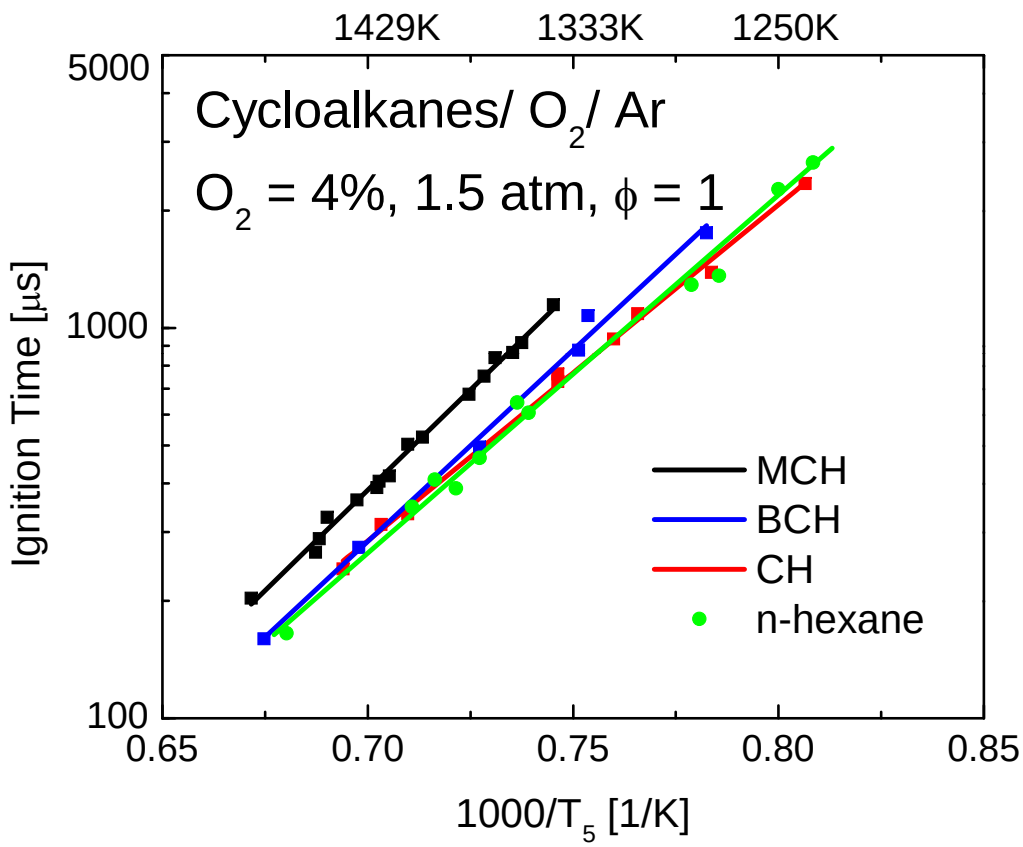
Ignition Delay Times

n-Alkanes

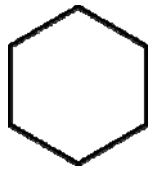
cyclo-Alkanes ⟵

iso-Alkanes

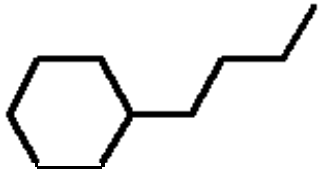
Cyclo-Alkane Ignition Delay Times: CH, BCH and MCH



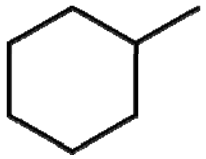
- Cyclohexane



- Butylcyclohexane



- Methylcyclohexane



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

Studies of Individual Jet Fuel Surrogate Components:

Ignition Delay Times

n-Alkanes

cyclo-Alkanes

iso-Alkanes ⟵

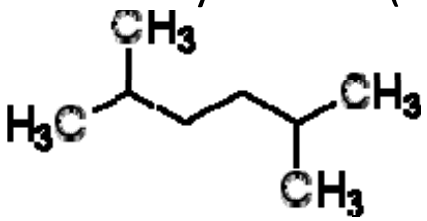
Iso-Alkanes

- Selection Criteria
  - Large carbon number
  - Dimethyl alkanes
  - End-to-end symmetry
  - Affordable

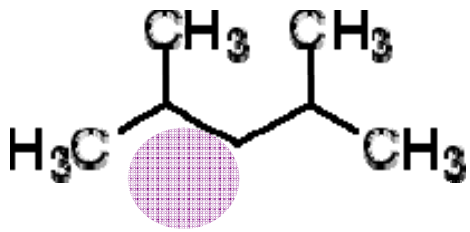
Current Studies

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

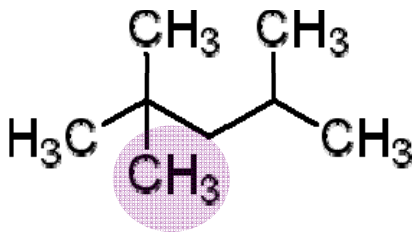
- 2,5-dimethylhexane (DMH)



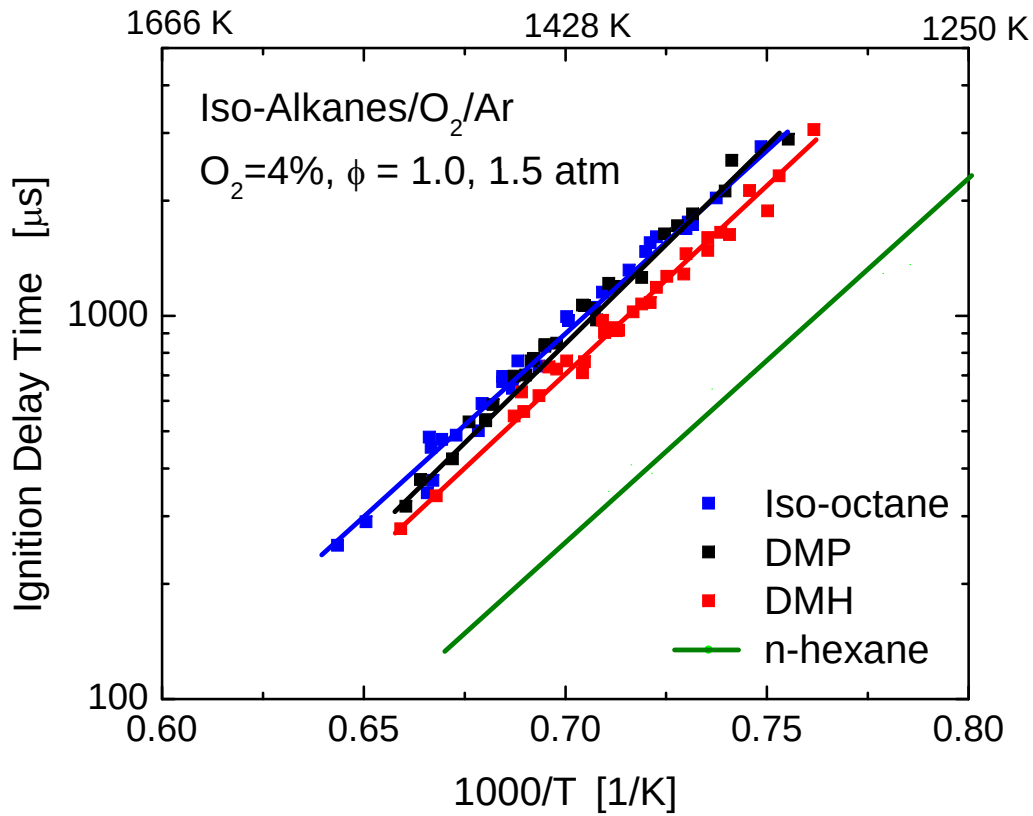
- 2,4-dimethylpentane (DMP)



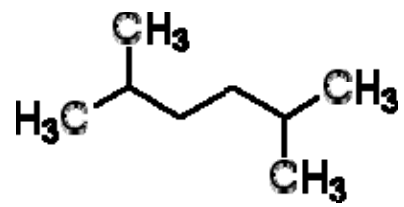
- 2,2,4-trimethylpentane (iso-octane)



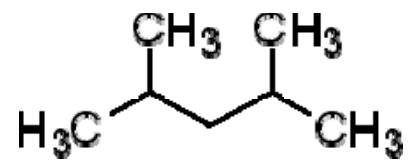
Iso-Alkanes: Initial Study



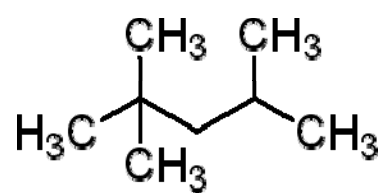
- 2,5-dimethylhexane (DMH)



- 2,4-dimethylpentane (DMP)



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



- ❑ All iso-alkanes **<u>much slower</u>** than n-hexane, (and thus most n-alkanes)
- ❑ Future Studies: Extend to larger hydrocarbons e.g., 2,7-dimethyloctane (T. Edwards)

3rd Type of Data: Multi-Species Time-Histories:

1. n-Heptane (2008)
2. n-Dodecane (2009)
3. Cyclo-Alkanes (2010)

3rd Type of Data: Multi-Species Time-Histories:

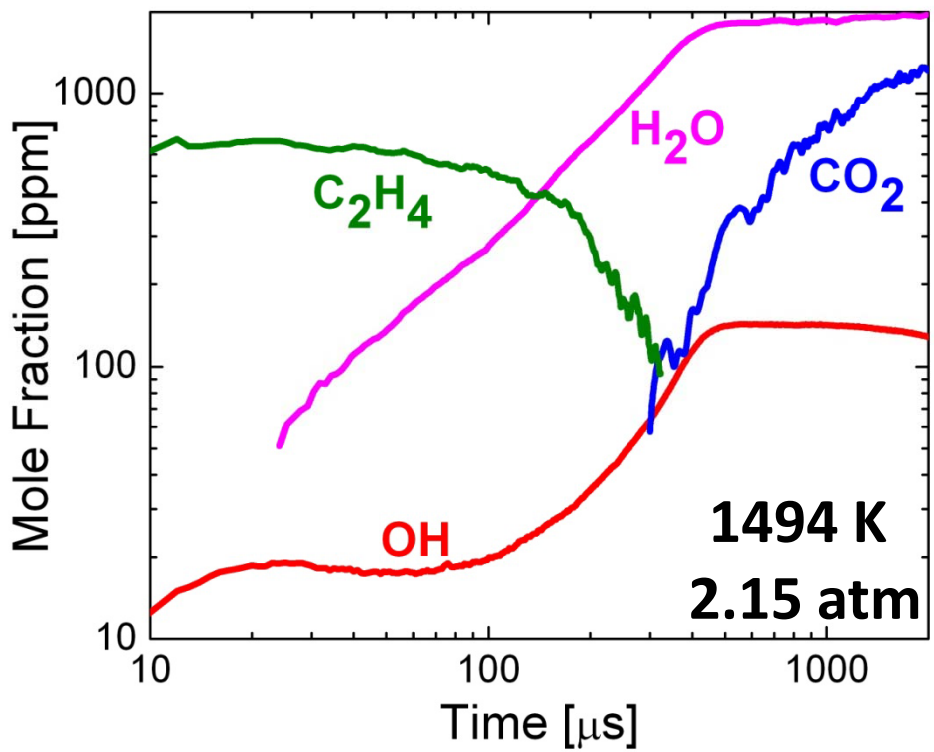
1. **n-Heptane (2008)**
2. n-Dodecane (2009)
3. Cyclo-Alkanes (2010)

Multi-Species Laser Absorption Data: n-Heptane Oxidation

- Fuel (Heptane)
- Radicals (OH)
- Stables (C_2H_4)
- Products (H_2O; CO_2)
- Temperature

- Unique data with high sensitivity and fast time response

300 ppm Heptane/O_2/Ar, ϕ=1

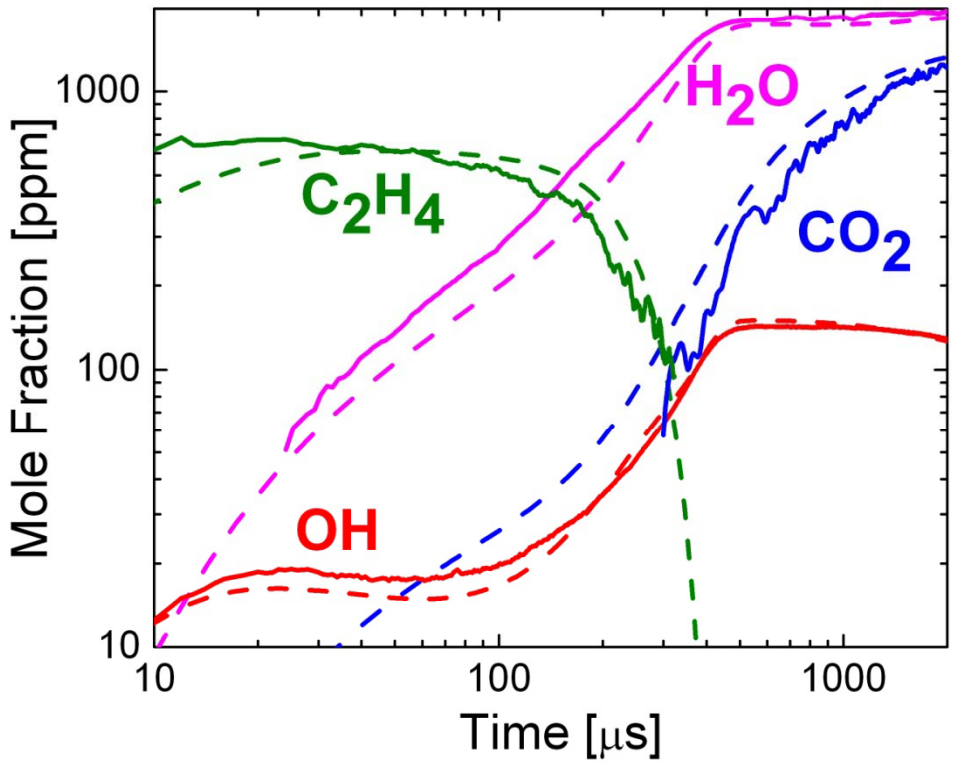


Davidson et al. (2010) C&F

Do Mechanisms Reproduce Multi-Species Data?
n-Heptane Oxidation

- **Earlier model captures overall behavior of all species, but …**
- **… availability of multi-species data enables improvement**

Dryer et al. (2007)



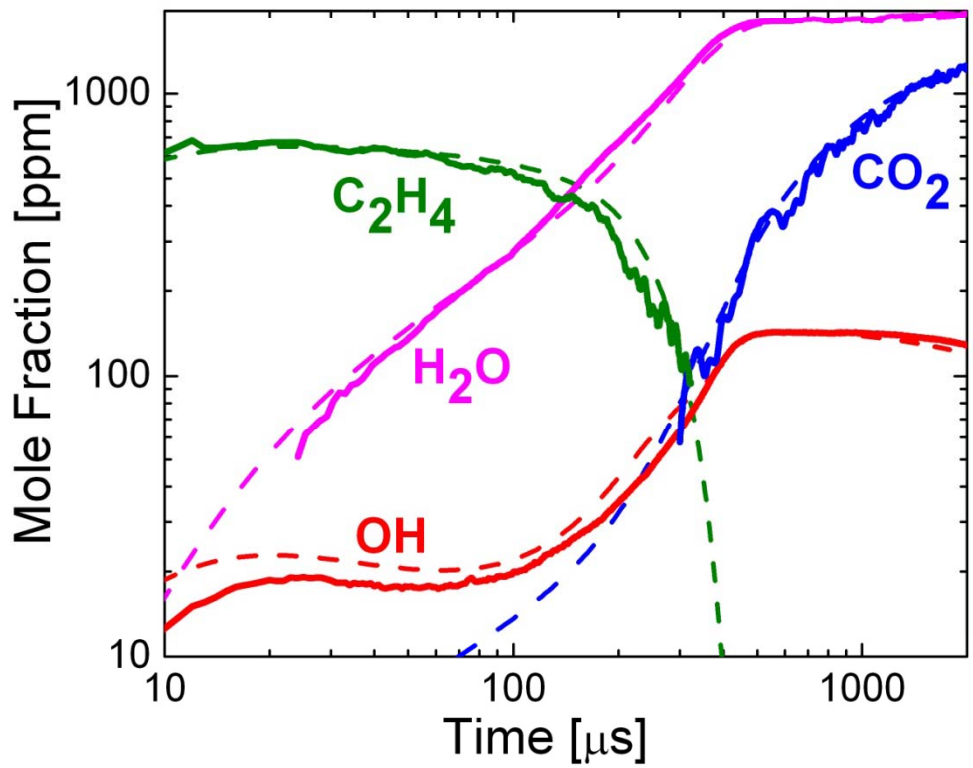
1494K, 2.15 atm
300ppm heptane, ϕ=1

Comparison of USC/JetSurF Mechanism
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?**

Sirjean et al./JetSurF 1.0 (2009)



1494K, 2.15 atm
300ppm heptane, ϕ=1

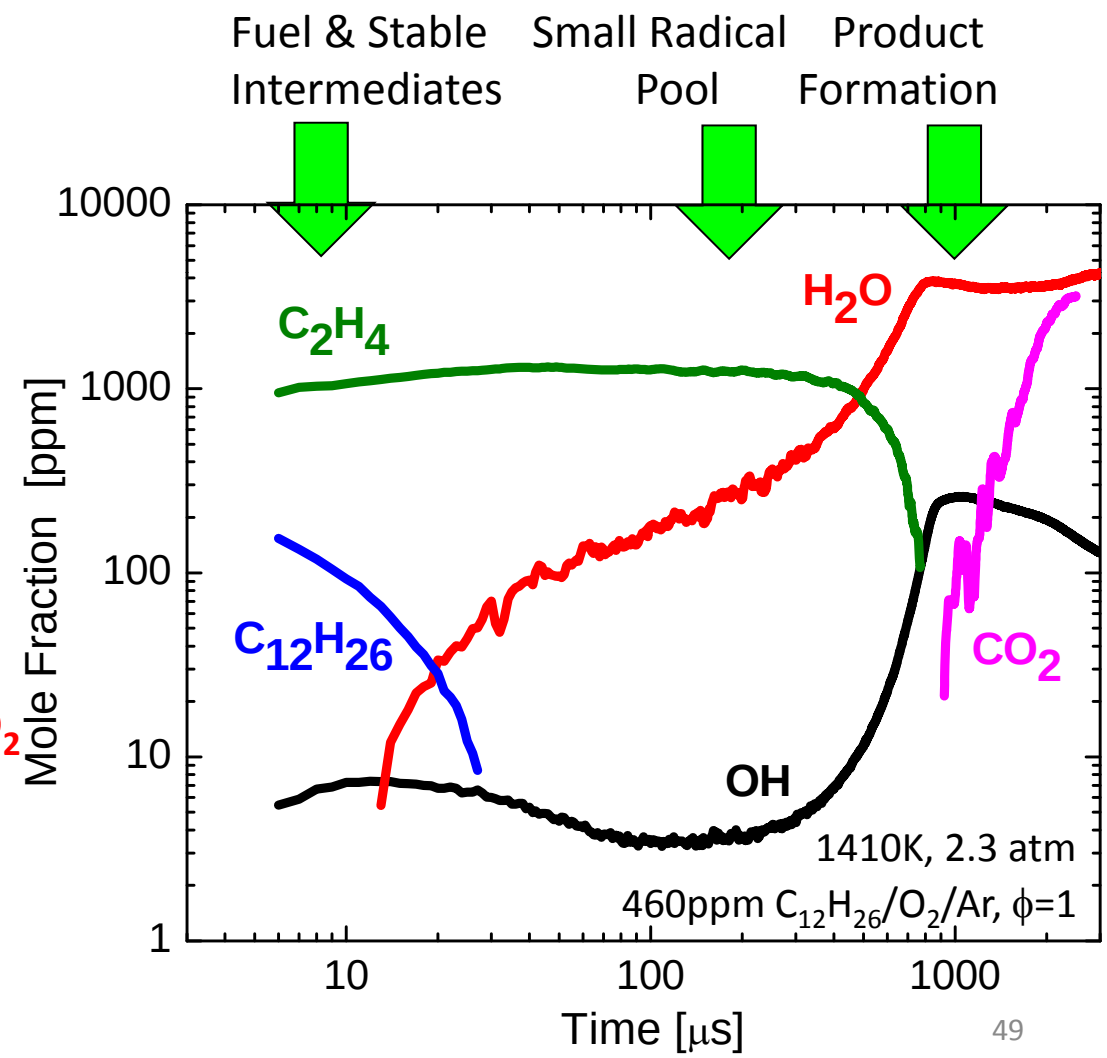
Multi-Species Time-Histories:

1. n-Heptane (2008)
2. **n-Dodecane (2009)**
3. Cyclo-Alkanes (2010)

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**

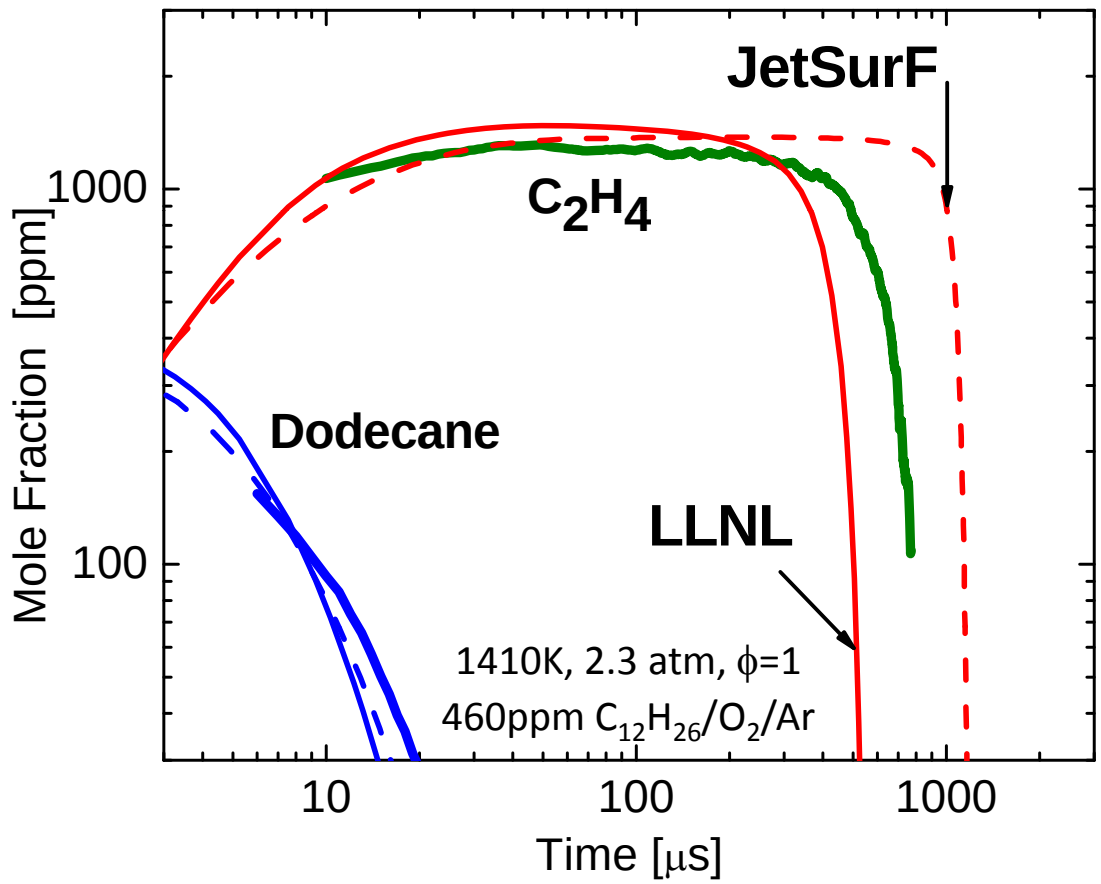


Comparison of N-Dodecane Data and Model:

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

- Good agreement with dodecane decomposition rate but …
- Ignition delay times not correct!
- C_2H_4 sensitivity analysis shows strong influence by the following reactions:

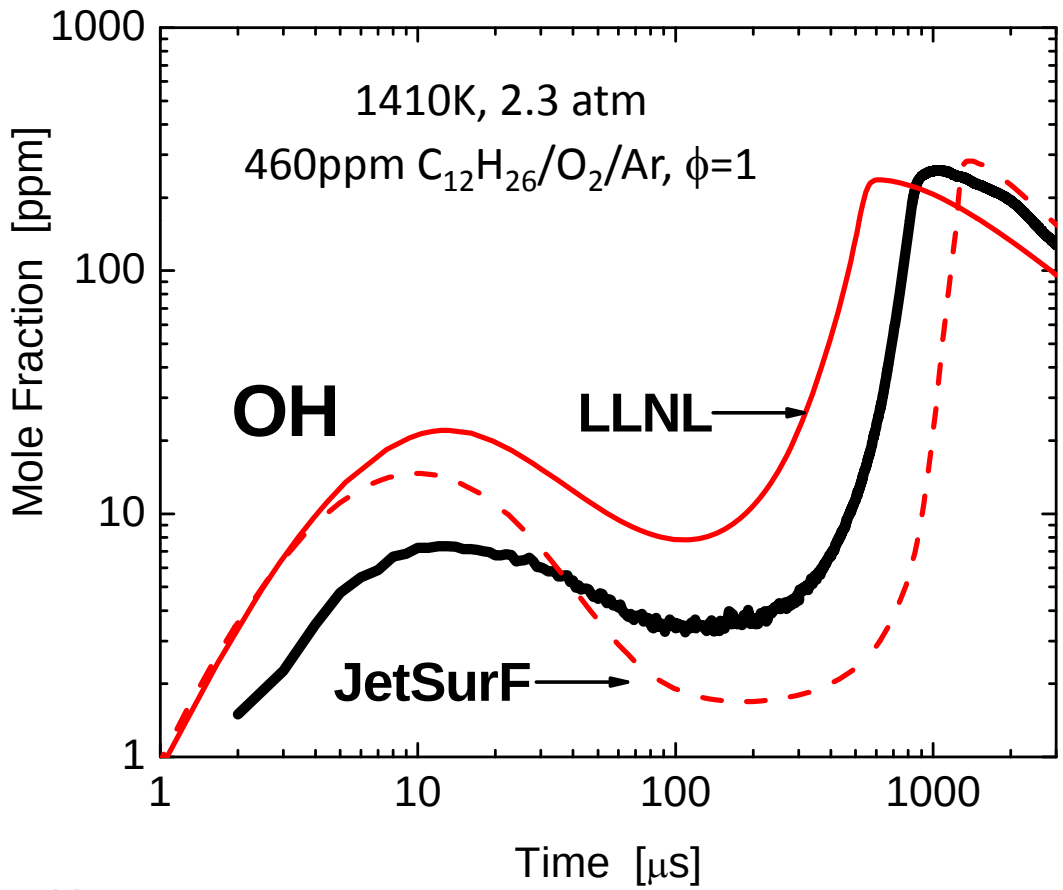
  $C_{12}H_{26} \rightarrow$ Products
  $C_3H_6 \rightarrow aC_3H_5+H$
  $C_3H_6+H \rightarrow aC_3H_5+H_2$



Comparison of N-Dodecane Data and Model:

Transient Radicals - OH

- Radical-formation peak and radical-scavenging minimum not captured accurately
- Large improvements needed in small-radical sub-mechanisms!
- OH sensitive to:
  $H+O_2 = OH+O$
  $aC_3H_5 = aC_3H_4+H$
  $C_3H_6 = aC_3H_5+H$
  $C_3H_6+H=aC_3H_5+H_2$



- **What about cyclo-alkanes?**

Multi-Species Time-Histories:

1. n-Heptane (2008)
2. n-Dodecane (2009)
3. **cyclo-Alkanes (2010)**

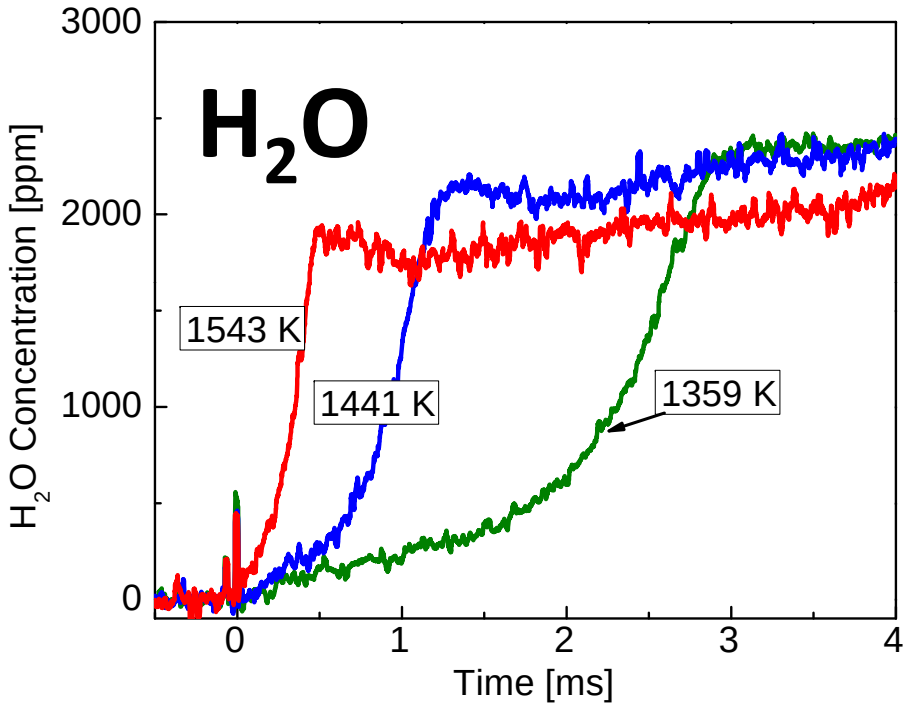
   cyclohexane

   methylcyclohexane

   butylcyclohexane

Cyclohexane Oxidation: Data and Model (2010)

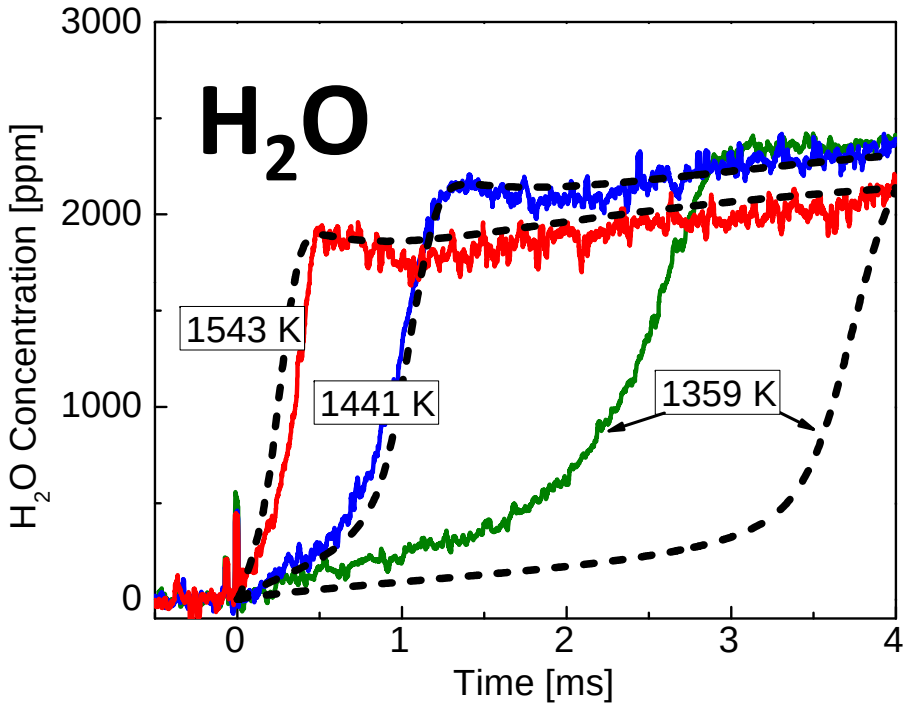
470 ppm/O_2/Ar, ϕ=1, 2.2 atm



- **First multi-species time-history measurements available for <u>cyclohexane</u>**

Cyclohexane Oxidation: Data and Model (2010)

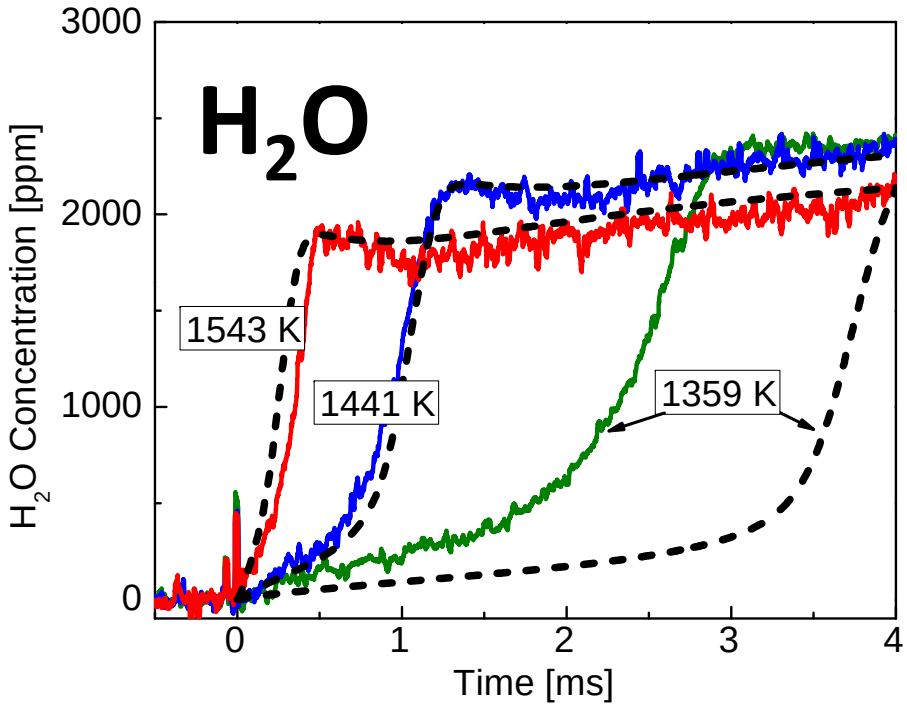
470 ppm/O_2/Ar, ϕ=1, 2.2 atm

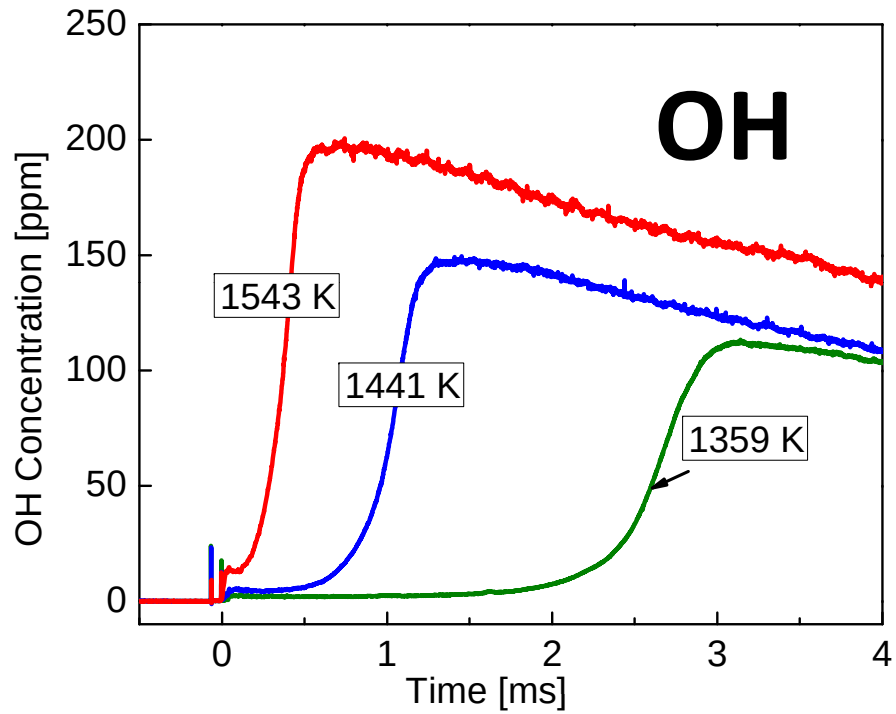


- **Good agreement of JetSurF 1.1 model and data for <u>cyclohexane</u> H_2O time-histories at high T; poor agreement at 1359K**

Cyclohexane Oxidation: Data and Model (2010)

470 ppm/O_2/Ar, ϕ=1, 2.2 atm

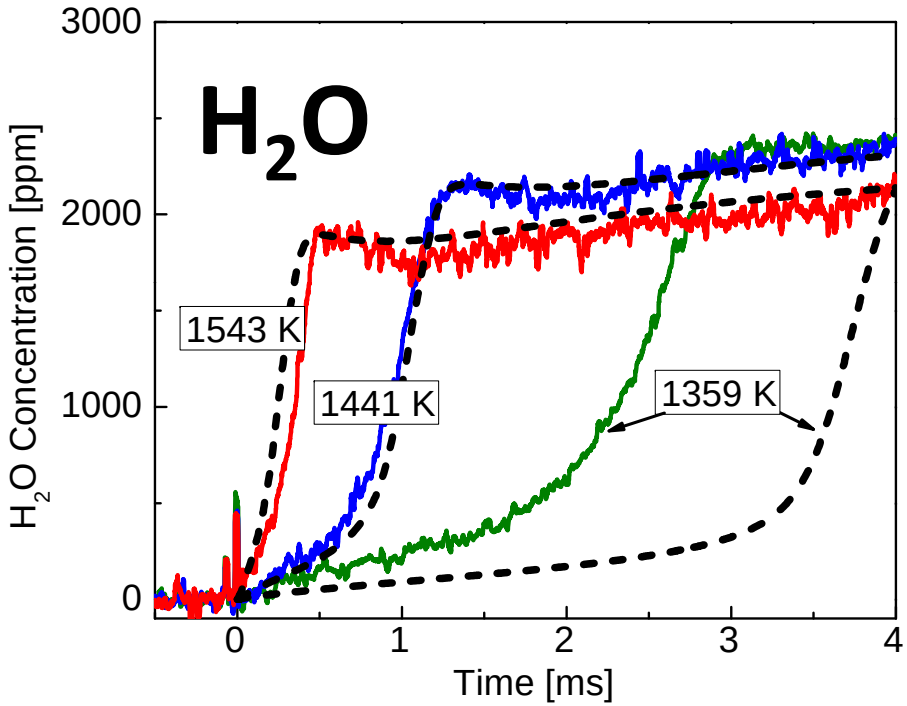


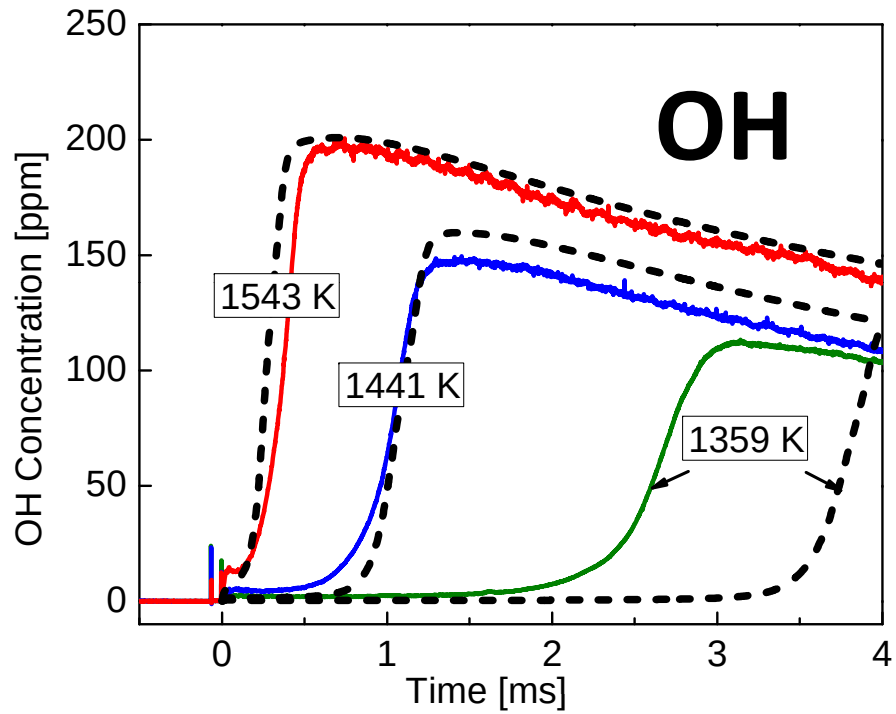


- **High-quality radical (OH) time-history data for <u>cyclohexane</u> simultaneous with H_2O data**

Cyclohexane Oxidation: Data and Model (2010)

470 ppm/O_2/Ar, ϕ=1, 2.2 atm

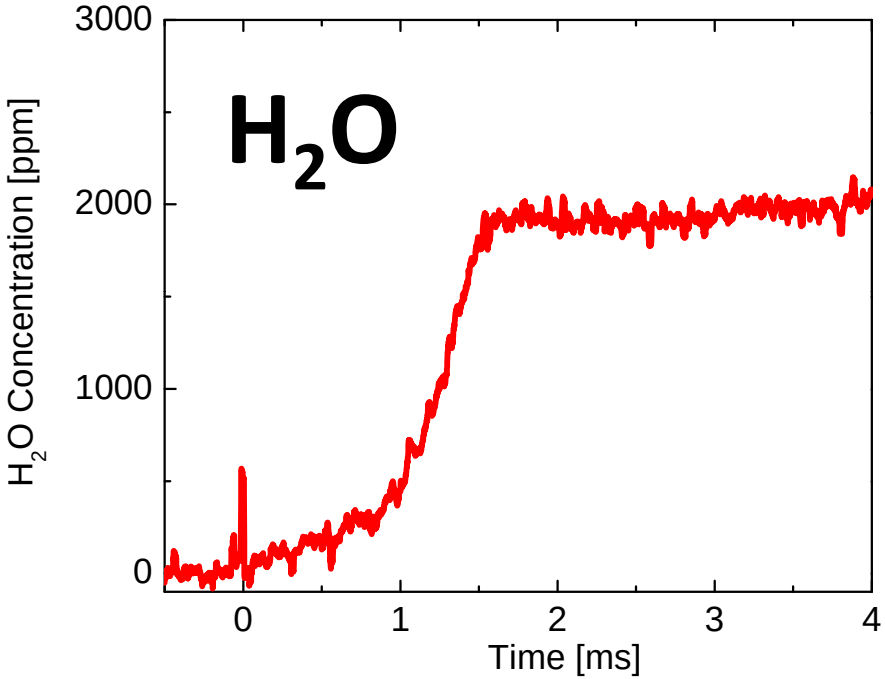




- **Good agreement of JetSurF 1.1 model and data for <u>cyclohexane</u> OH time-histories at high T, poor agreement at 1359K**

Methylcyclohexane Oxidation: Data and Models

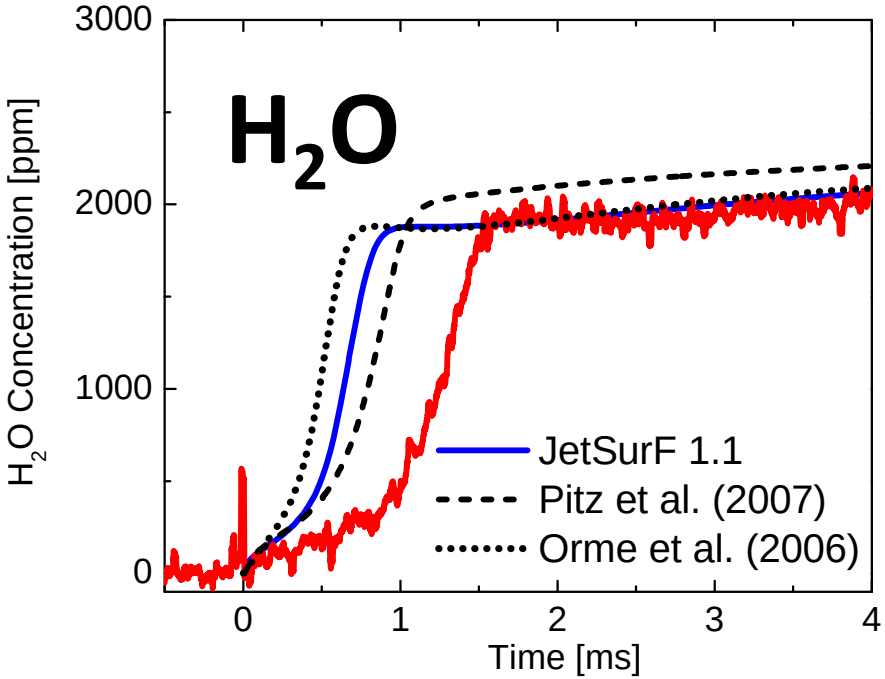
340 ppm/O_2/Ar, ϕ=1, 1435K, 2.2 atm



- **Multi-species time-history data available for <u>methylcyclohexane</u>**

Methylcyclohexane Oxidation: Data and Models

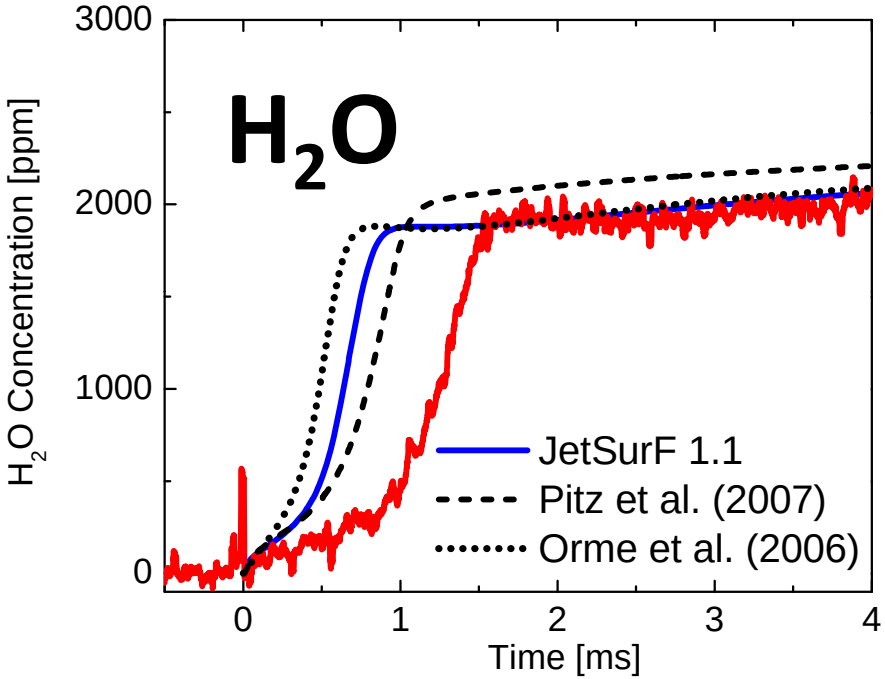
340 ppm/O_2/Ar, ϕ=1, 1435K, 2.2 atm

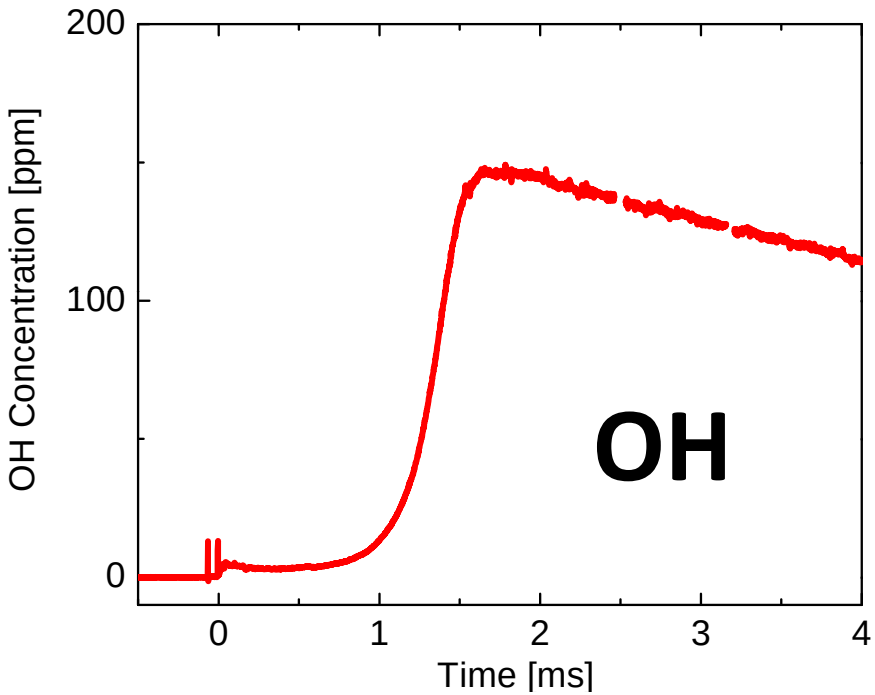


- **Wide variability between model simulations for <u>methylcyclohexane</u> H_2O time-histories**

Methylcyclohexane Oxidation: Data and Models

340 ppm/O_2/Ar, ϕ=1, 1435K, 2.2 atm

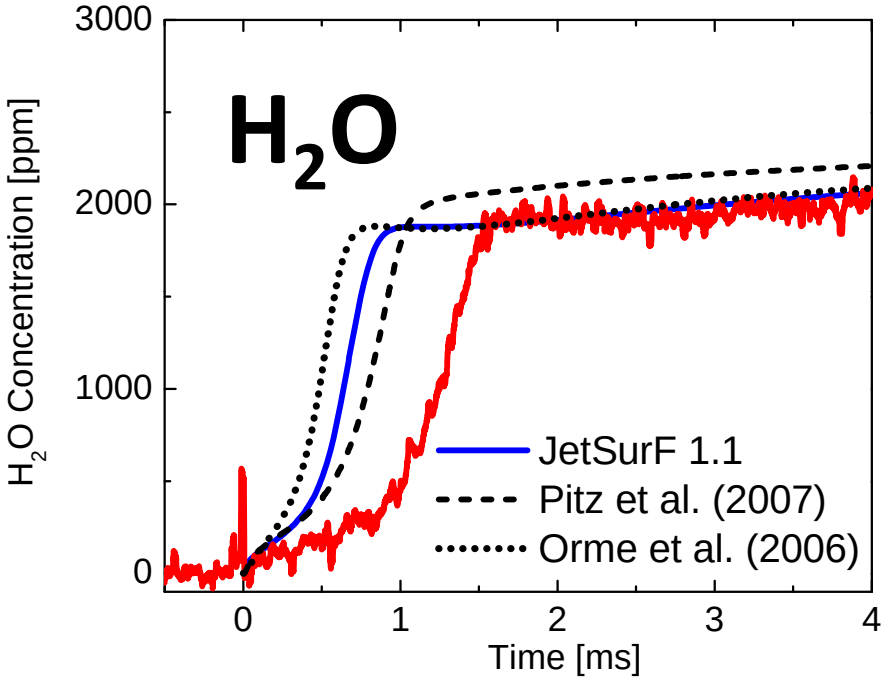


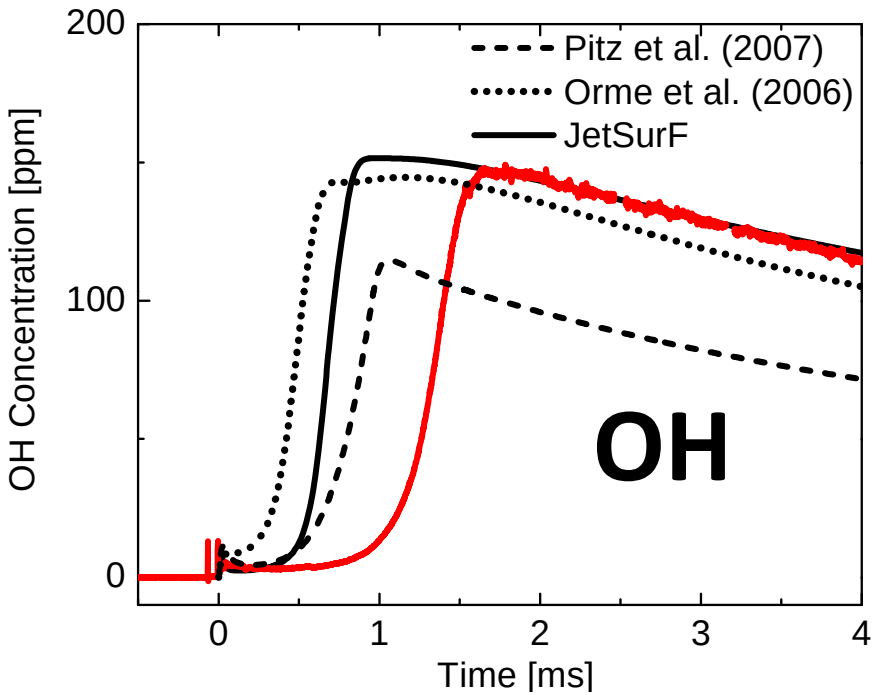


- **High-quality OH radical time-history data for <u>methylcyclohexane</u> simultaneous with H_2O data**

Methylcyclohexane Oxidation: Data and Models

340 ppm/O_2/Ar, ϕ=1, 1435K, 2.2 atm

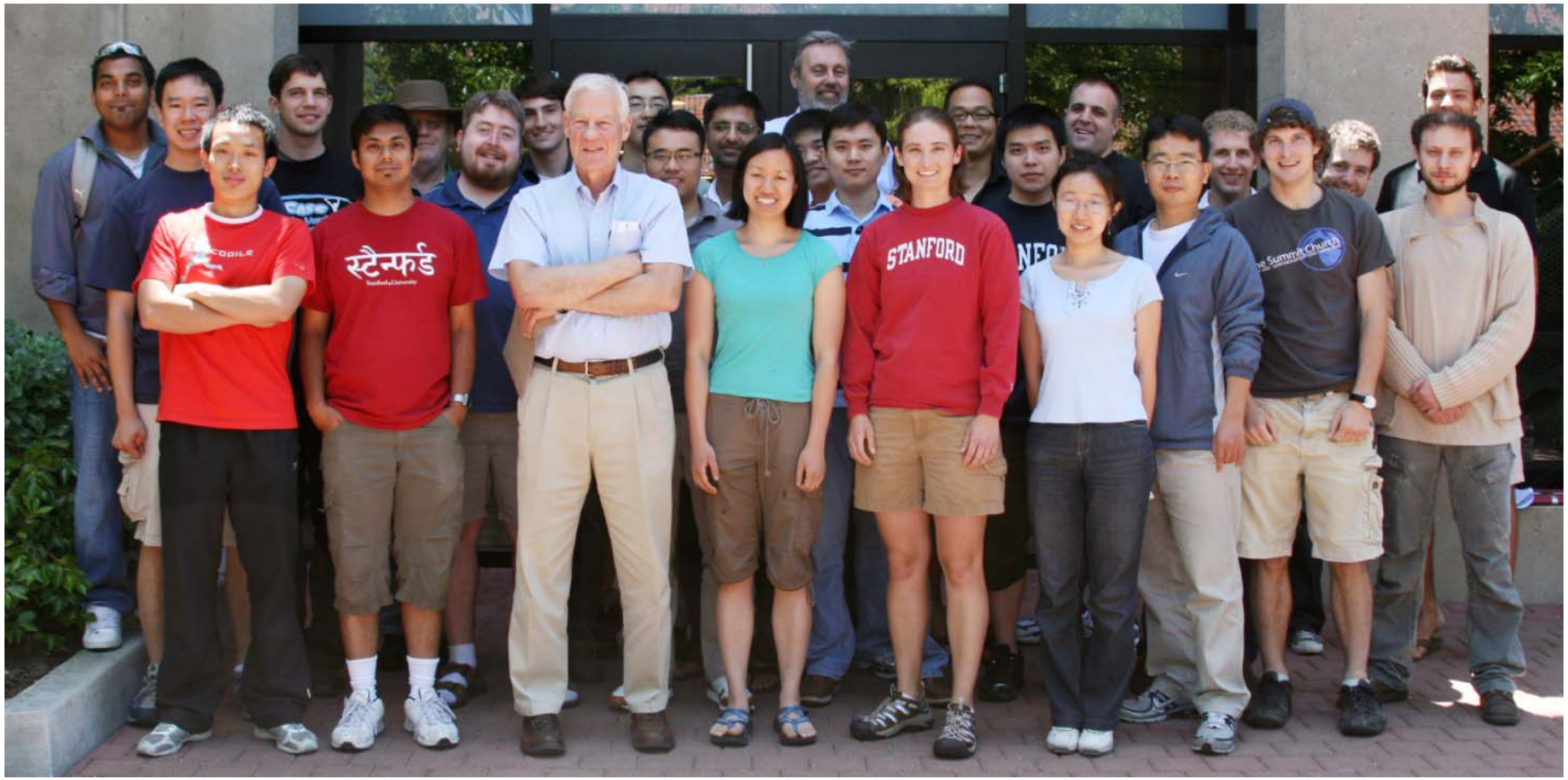




Wide current variability of model simulations for <u>methylcyclohexane</u> H_2O and OH time-histories

Future Plans

- **Extend multi-species time-history databases**
  - **Jet Fuel, Aromatics, n-dodecane in NTC**
- **Continue use of Stanford aerosol shock tube for low P_{vap} fuels**
  - **Jet Fuel surrogates**
- **Measure jet fuel surrogate ignition delay times**
  - **Low-pressure (sub-atmospheric) measurements**
  - **High-pressure measurements in NTC regime**
- **Develop new laser absorption diagnostics**
  - **CH_4, C_2H_4, C_3H_6, C_2H_5, …**

Acknowledgements

- **Visit Stanford website http://hanson.stanford.edu/ for Fundamental Kinetics Database Using Shock Tubes**
- **Thanks to our many shock tube and laser students**