Shock Tube/Laser Absorption Studies of Army-Relevant Fuels

ARO Contract # W911NF-10-1-0125

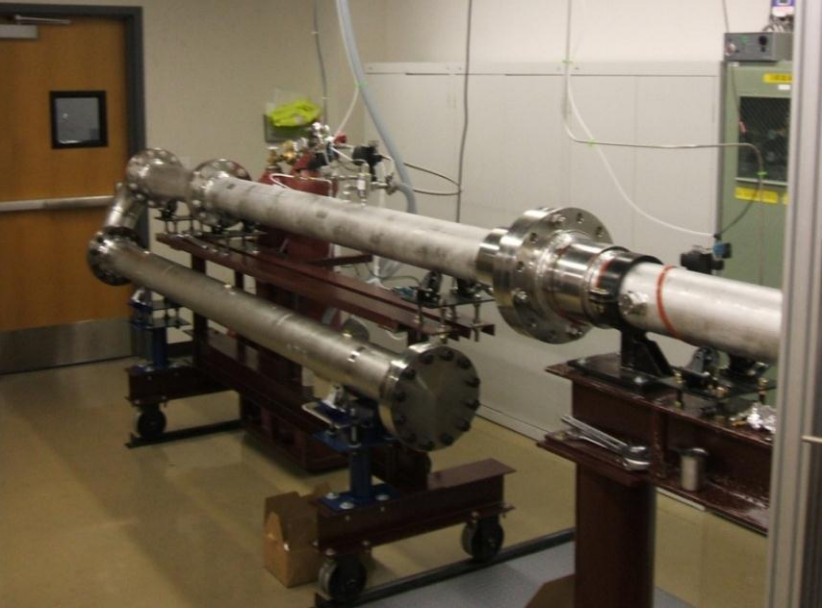
Ronald Hanson, Daniel Haylett and David Davidson

Dept. of Mechanical Engineering, Stanford University

- **Experimental Approach**
- **Ignition Delay Times**
  - **n-Alkanes (C10-C16), Diesel**
- **Multi-Species Time-Histories**
  - **n-Hexadecane, Diesel**

MACCCR 4th Annual Fuels Summit

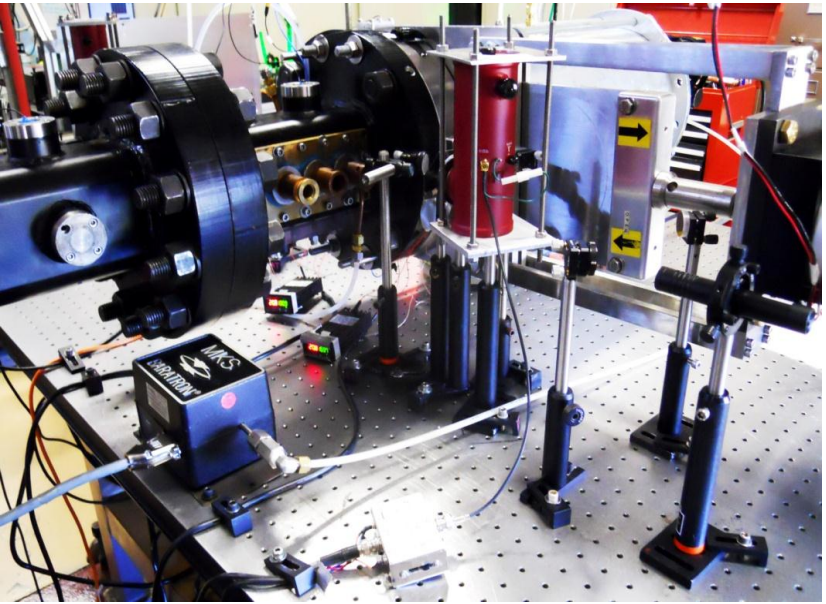
September 19-21, 2011



Kinetics
Shock Tube
20 atm

Kinetics
Shock Tube
20 atm

Experimental Approach



Aerosol
Shock Tube
10 atm
→100 atm

High Pressure
Shock Tube
500 atm

Types of Shock Tube Experiments

- **Ignition delay times provide global targets**
- **Species time-histories provide strong constraints on mechanisms**
  - **Current laser absorption capability includes: OH, CO, CO_2, CH_2O, H_2O, CH_3, CH_4, C_2H_4, fuel, NH_2, NH_3, MMH, …**

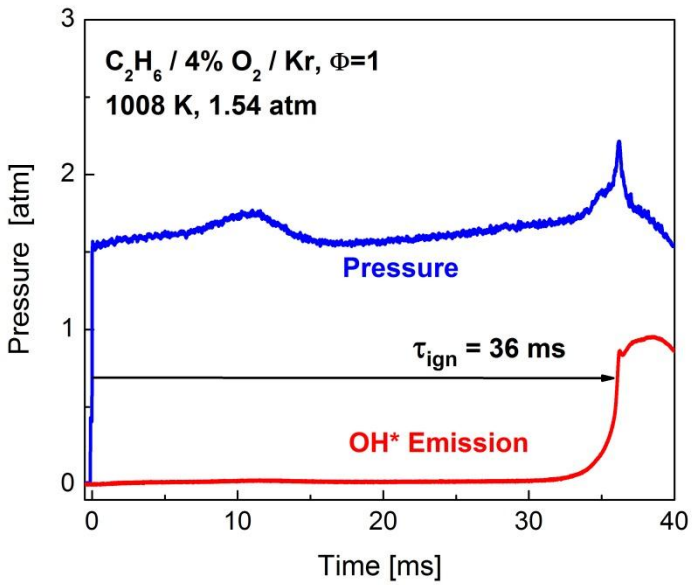
Goal: High-quality databases which motivate continued development of shock tube and laser techniques

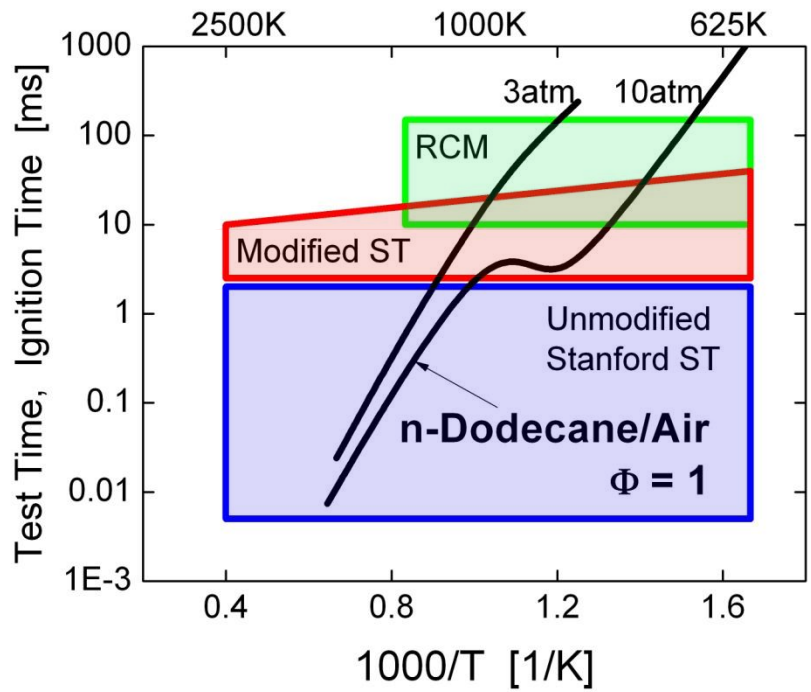
Advances in Shock Tube Methodology

- **Tailored driver gas/new driver geometry provide extended test time for access to low T**
- **Driver inserts provide highly-uniform reflected shock conditions approaching constant U/V**
- **Aerosol shock tube provides access to low-vapor-pressure fuels**

Access to Low Temperatures (and High P)

- Longer driver length and tailored gas mixtures can provide longer test times (> 40 ms)
- Shock tubes now can overlap with RCMs

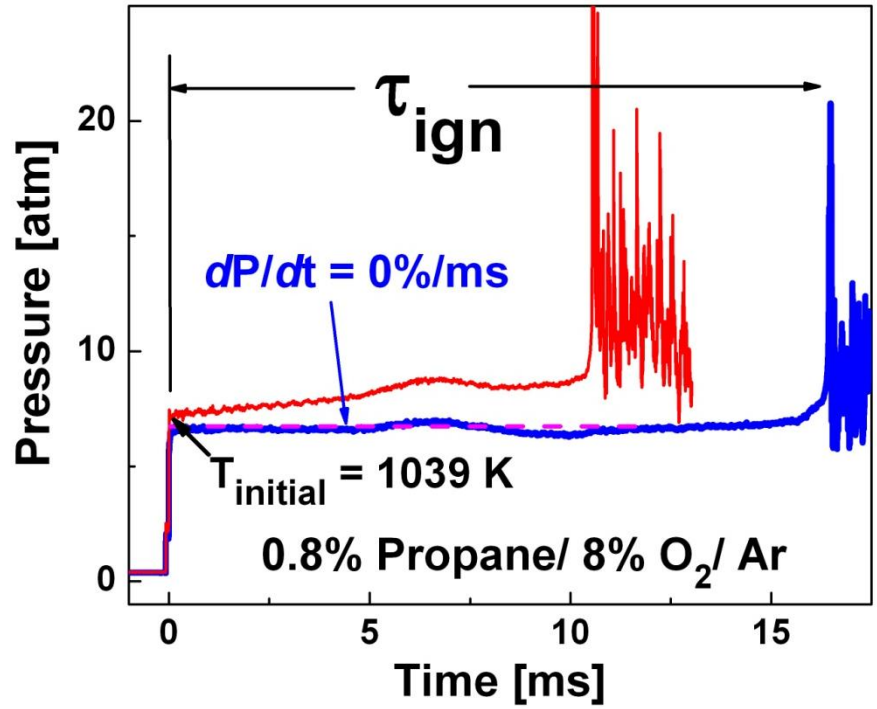




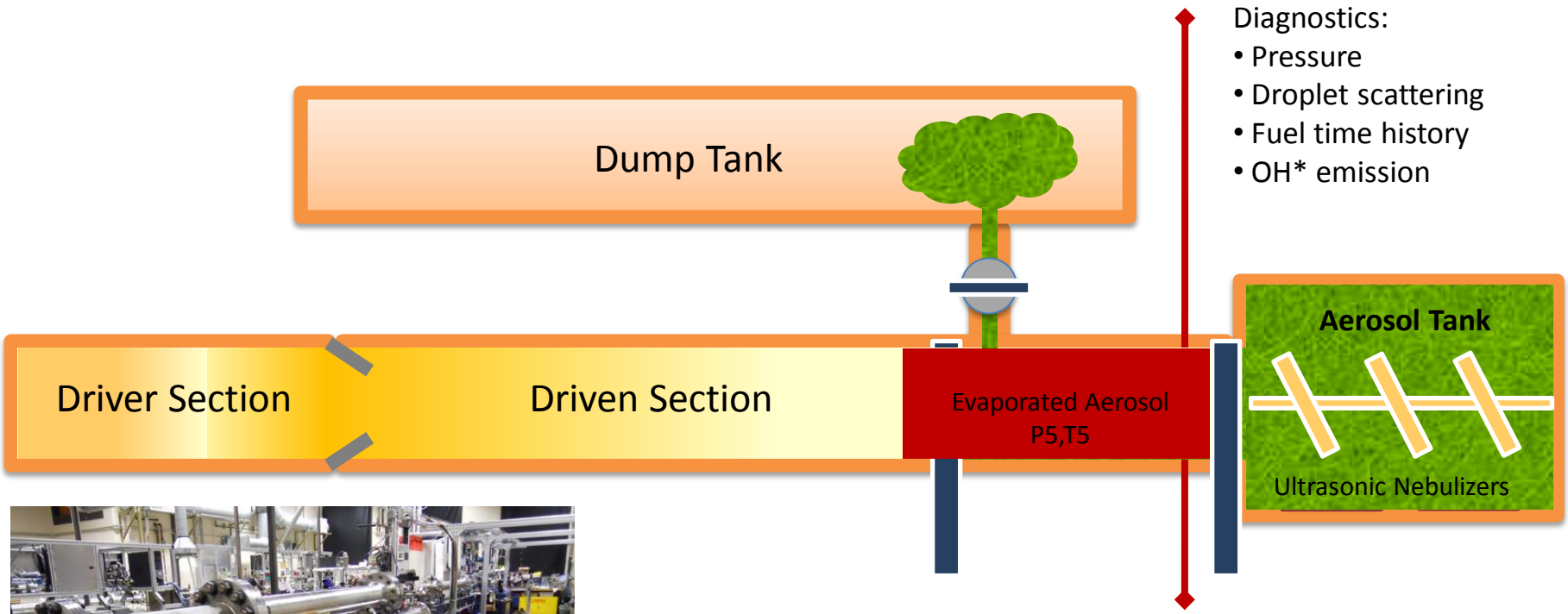
- Long shock tube test-times possible for NTC studies

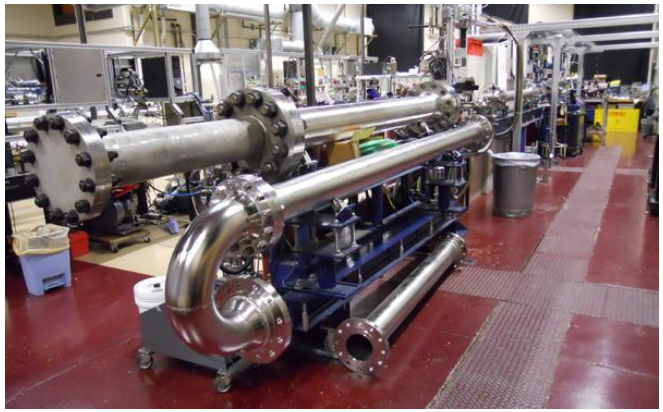
Improvement in Pressure & Temperature Uniformity

- **Problem**: Ignition delay times are artificially shortened by non-ideal facility effects!! dP/dt ≠ 0
- **Solution**: Driver Inserts
- **Results**: Near-ideal constant-volume performance!! dP/dt ≈ 0



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:**
  large jet fuel surrogate components

Current Laser Capabilities
for Multi-Species Time-Histories

Ultraviolet

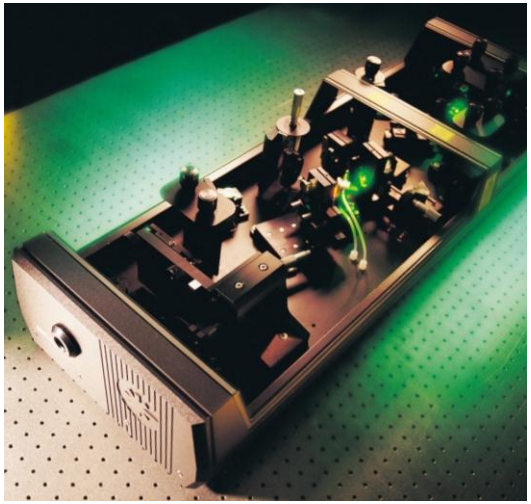
CH_3	216 nm
NO	225 nm
O_2	227 nm
HO_2	230 nm
CH_2O	305 nm
OH	306 nm
NH	336 nm

Visible

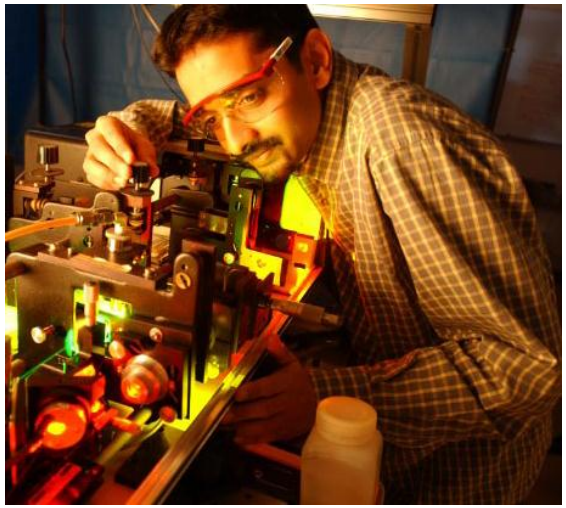
CN	388 nm
CH	431 nm
NCO	440 nm
NO_2	472 nm
NH_2	597 nm
HCO	614 nm

Infrared

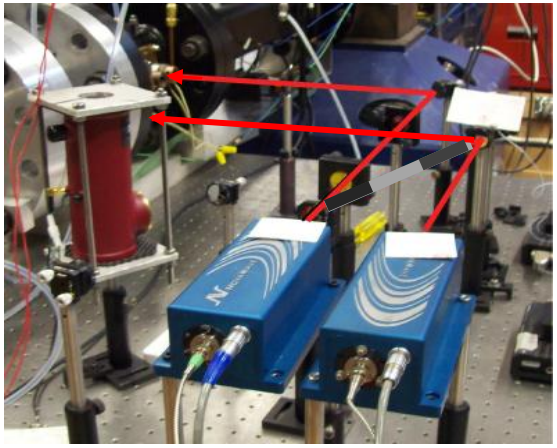
H_2O	2.5 μm
CO_2	2.7 μm
Fuel	3.4 μm
CO	4.6 μm
NO	5.2 μm
MF, MeOH	9.2, 9.7 μm
NH_3, MMH	9.6, 10.2 μm
C_2H_4	10.5 μm



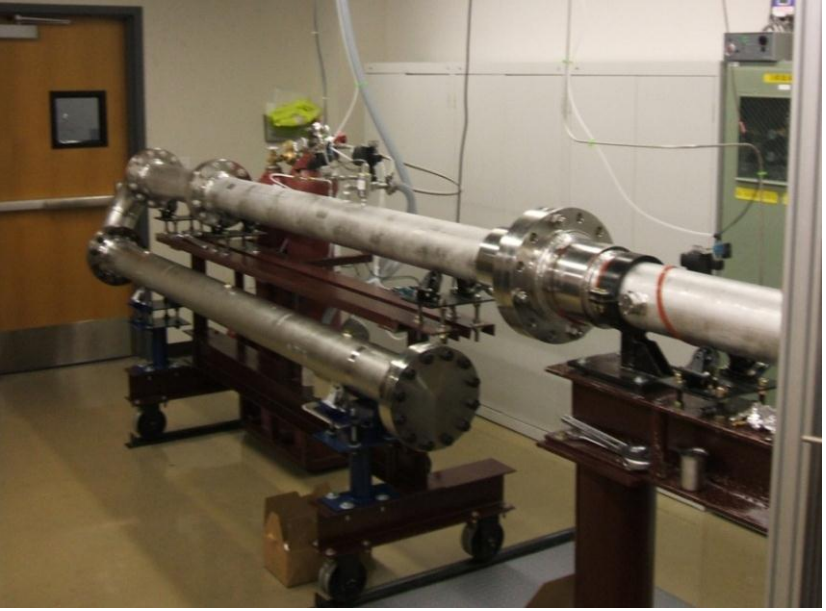
Coherent MIRA Ti-Sapphire



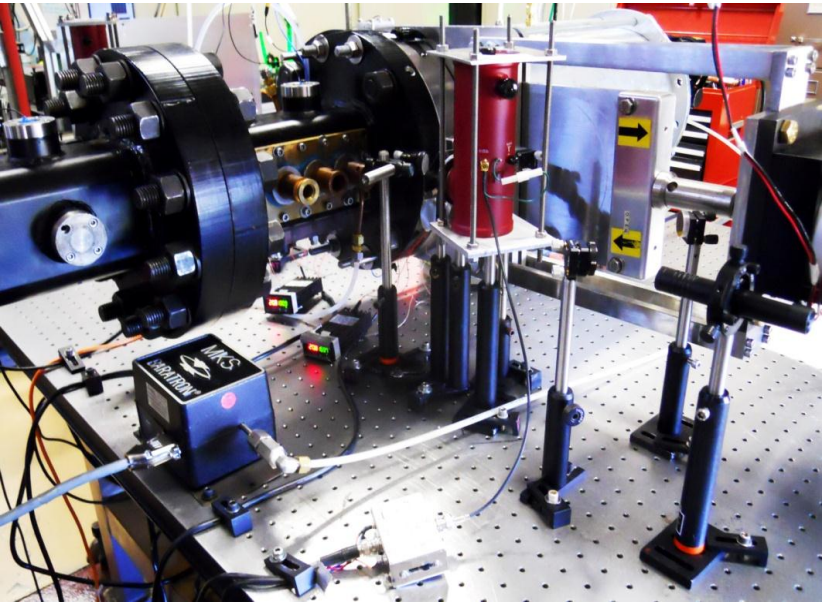
Spectra-Physics 380 Ring



NovaWave Mid-IR DFG



Ignition Delay Times



Aerosol Shock Tube

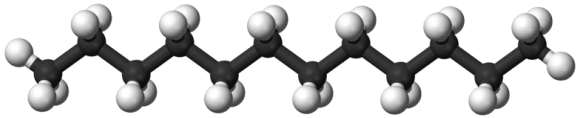
Ignition Delay Time Studies: 4 Fuels Studied

- n-Decane ($C_{10}H_{22}$) jet fuel surrogate component
- n-Dodecane ($C_{12}H_{26}$) jet fuel surrogate component
- n-Hexadecane ($C_{16}H_{34}$) Diesel primary reference fuel
- Diesel ($C_{12}H_{23}$) DF-2

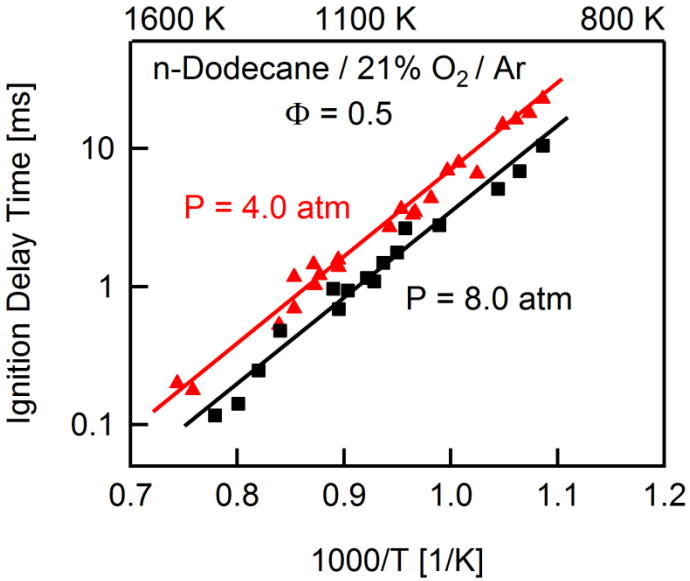
n-Dodecane Ignition Delay Times

- **Single-component jet fuel surrogate**
- **Low vapor pressure ≈ 1 torr**
- **Heated ST requires ≈ 80C**

n-Dodecane $C_{12}H_{26}$

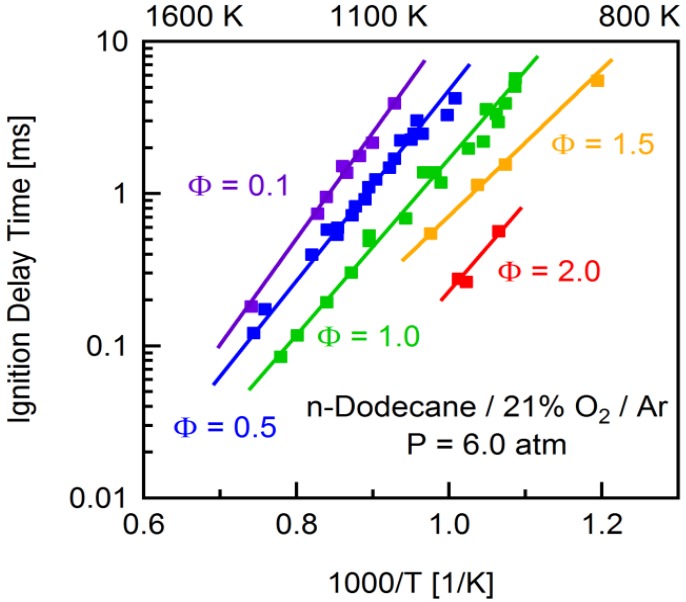


Pressure Dependence



Ignition delay time scales as $P^{-0.9}$

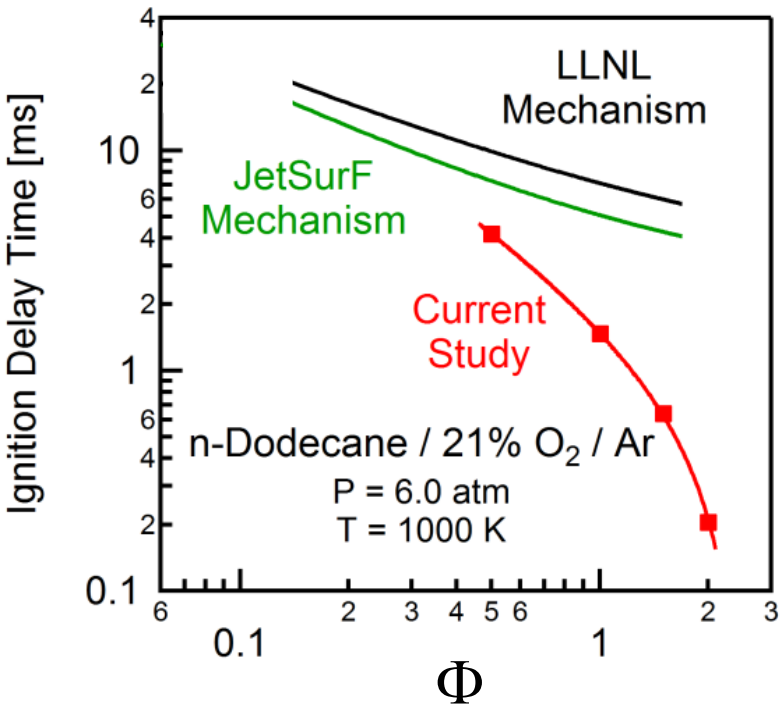
Equivalence Ratio Dependence



Can models replicate Φ dependence?

n-Dodecane Φ Dependence: Model Comparison

Experiment and Models

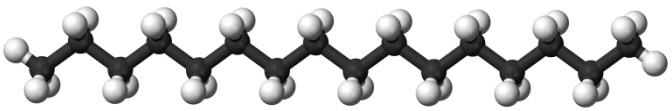


- **Measurement shows strong variation with Φ**
- **Models fail to capture dependence at high Φ**

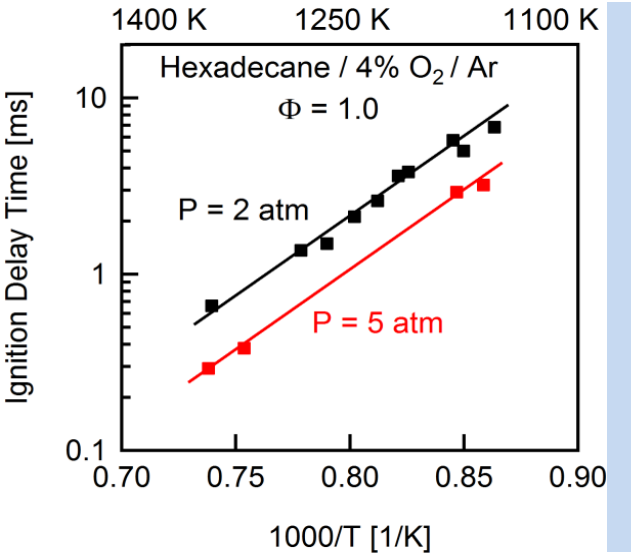
n-Hexadecane Ignition Delay Times

- **Diesel primary reference fuel**
- **Very low vapor pressure ≈ 1 mtorr**
- **Heated ST method problematic**

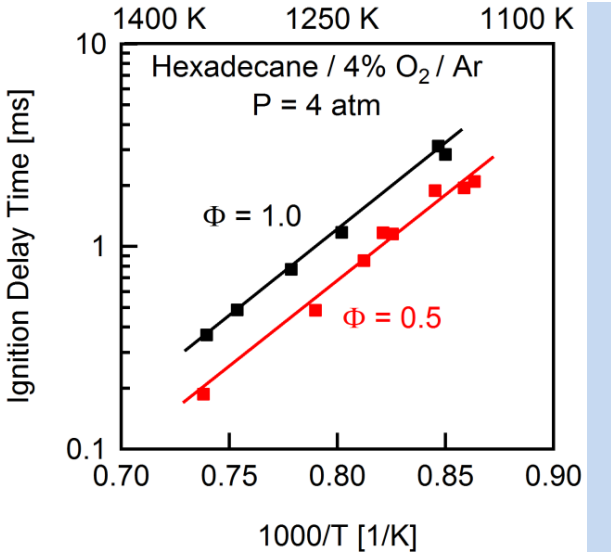
n-Hexadecane $C_{16}H_{34}$



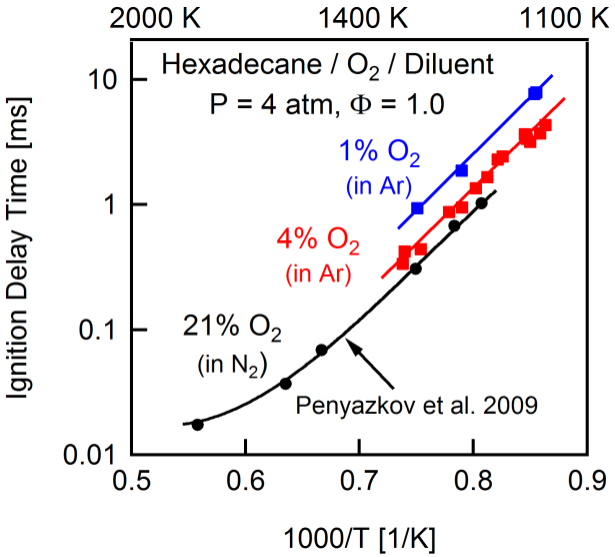
Pressure Dependence



Equivalence Ratio



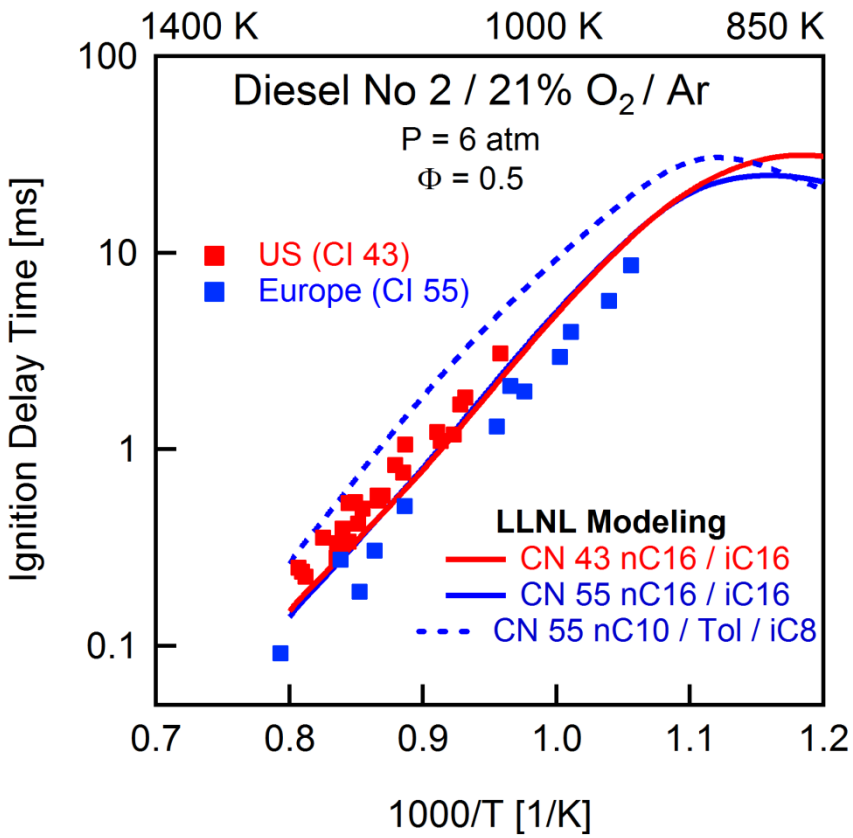
O_2 Dependence



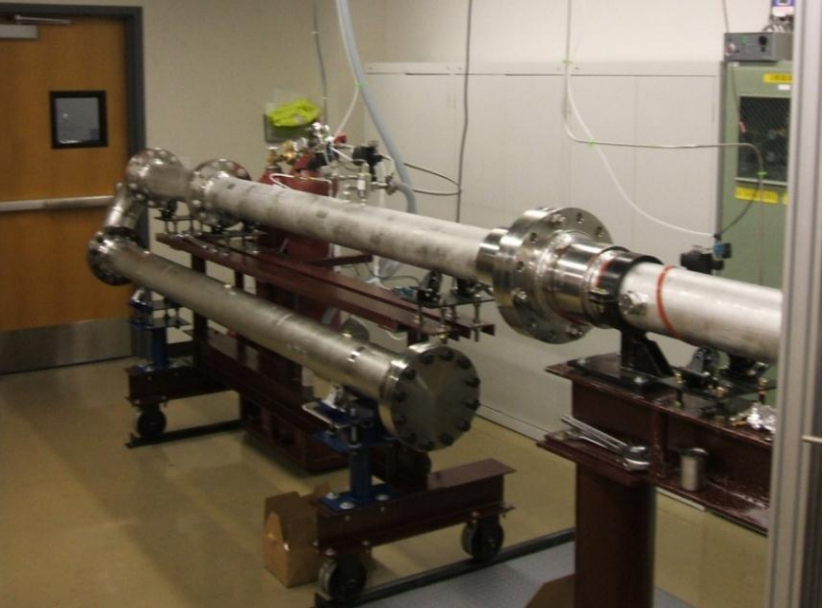
AST Measurement $\tau \sim P^{-0.73}$ $\tau \sim \Phi^{0.82}$ $\tau \sim X_{O2}^{-0.54}$

LLNL Mechanism $\tau \sim P^{-0.70}$ $\tau \sim \Phi^{0.55}$ $\tau \sim X_{O2}^{-0.74}$

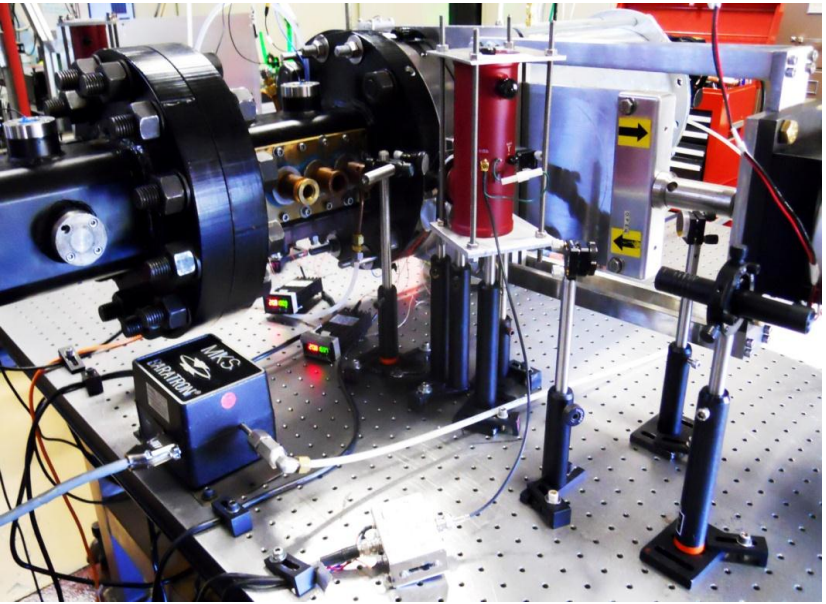
Diesel Ignition Delay Times



- **First purely gas-phase diesel ignition delay time data**
- **Ignition times shorten with increasing Cetane Number (CN)**
- **N16/I16 surrogate simulations show no High T CN dependence**
- **Multi-component surrogates capture some CN dependence**



Species Time-Histories



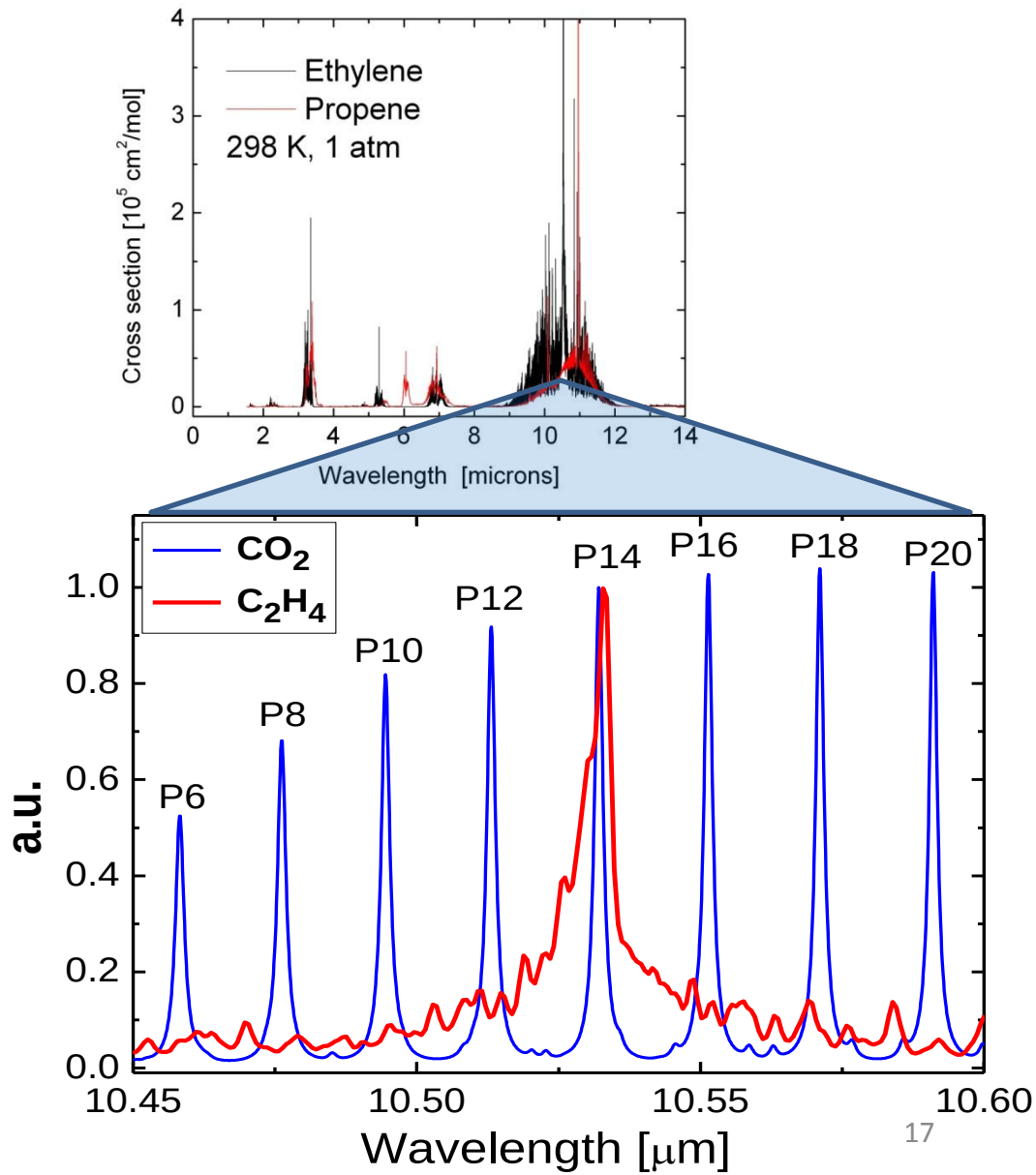
Aerosol Shock Tube

Recent Advances in Species Sensing

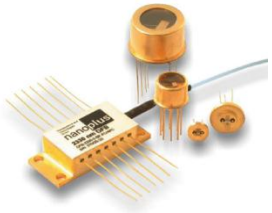
- C_2H_4 10.5 μm
- CO_2 2.7 μm
- H_2O 2.5 μm
- CO 4.7 μm
- CH_2O 305 nm, 3.4 μm

CO_2 Gas Laser: Ethylene Sensor

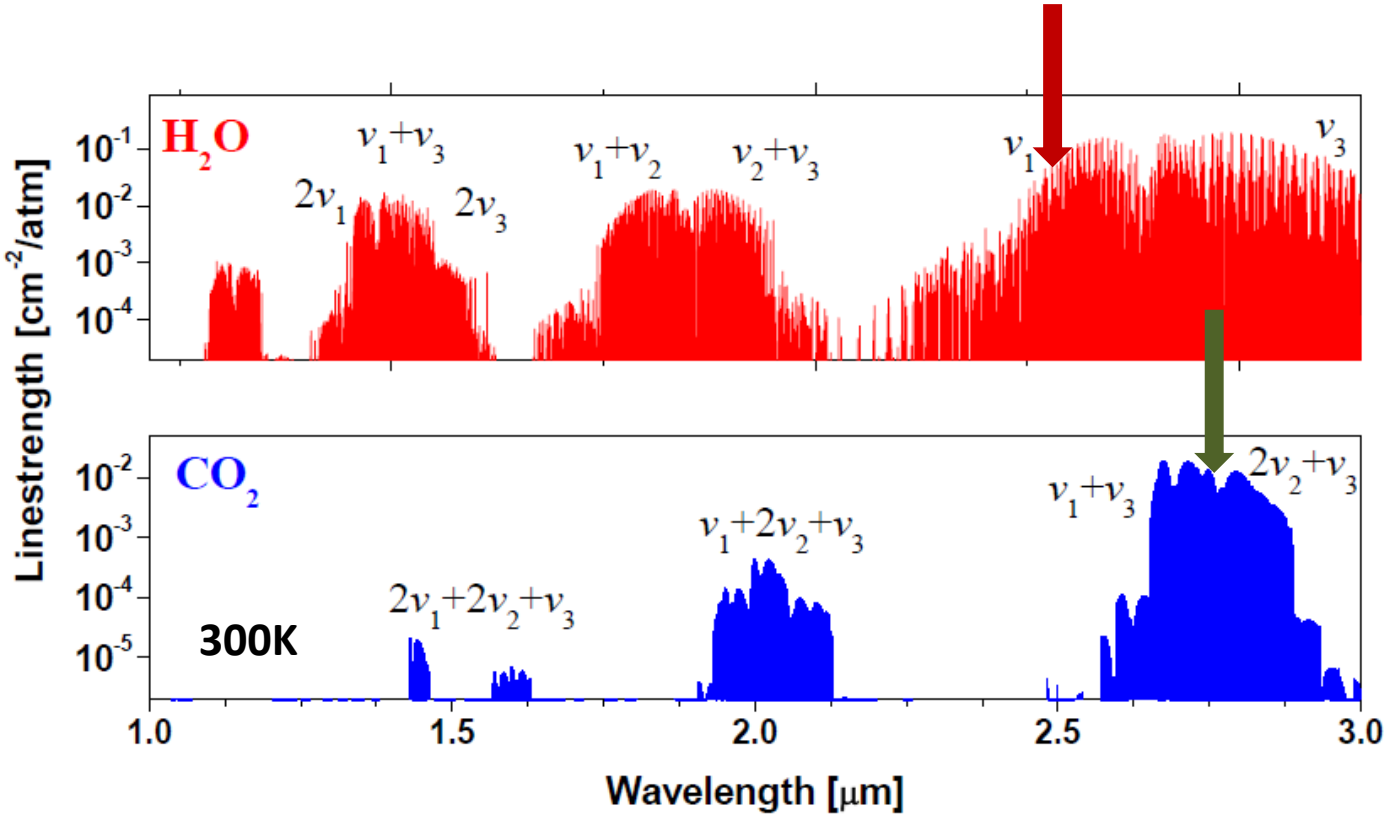
- Fortuitious overlap of **P14 CO_2 gas laser emission line** with strong C_2H_4 absorption feature at 10.53 microns
- Quantitative determination of C_2H_4 concentration possible using **Beer-Lambert law**



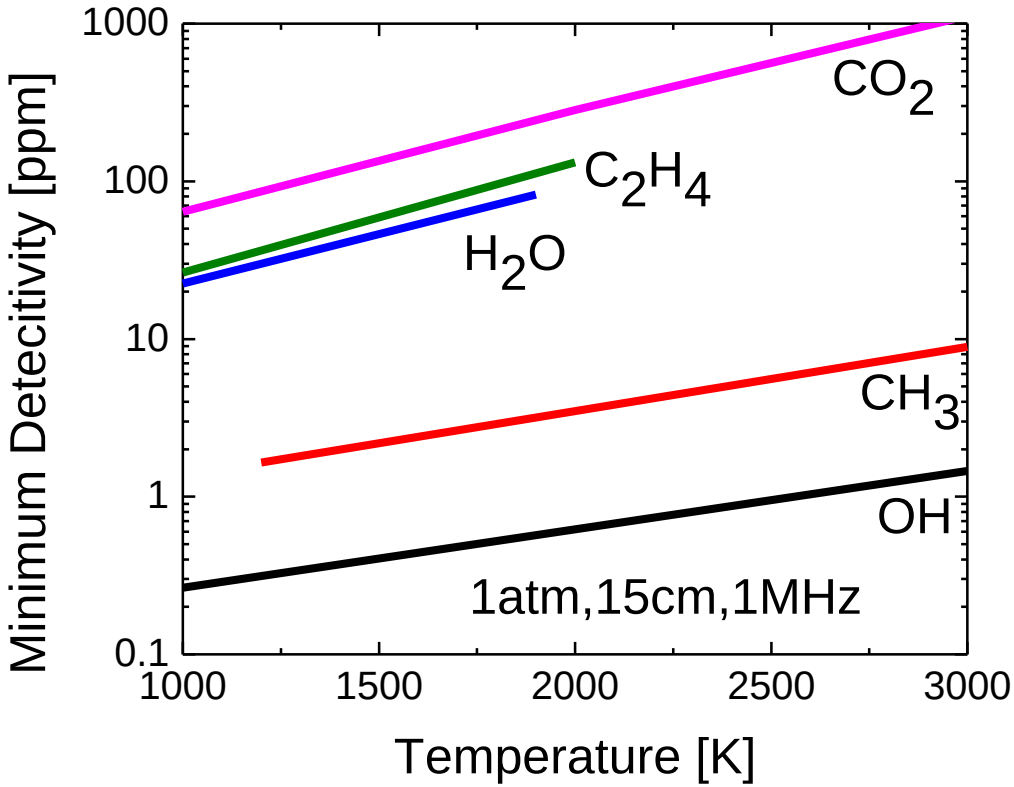
H_2O and CO_2 Diagnostics



- **Distributed feedback (DFB) laser diodes give access to strong IR absorption features near 2.7 µm**
  - **Water: 2.511 µm**
  - **Carbon Dioxide: 2.752 µm**



Minimum Detectivity Chart



- **Laser absorption provides ppm sensitivity**

  sub-ppm for OH to ~50 ppm for H_2O/C_2H_4

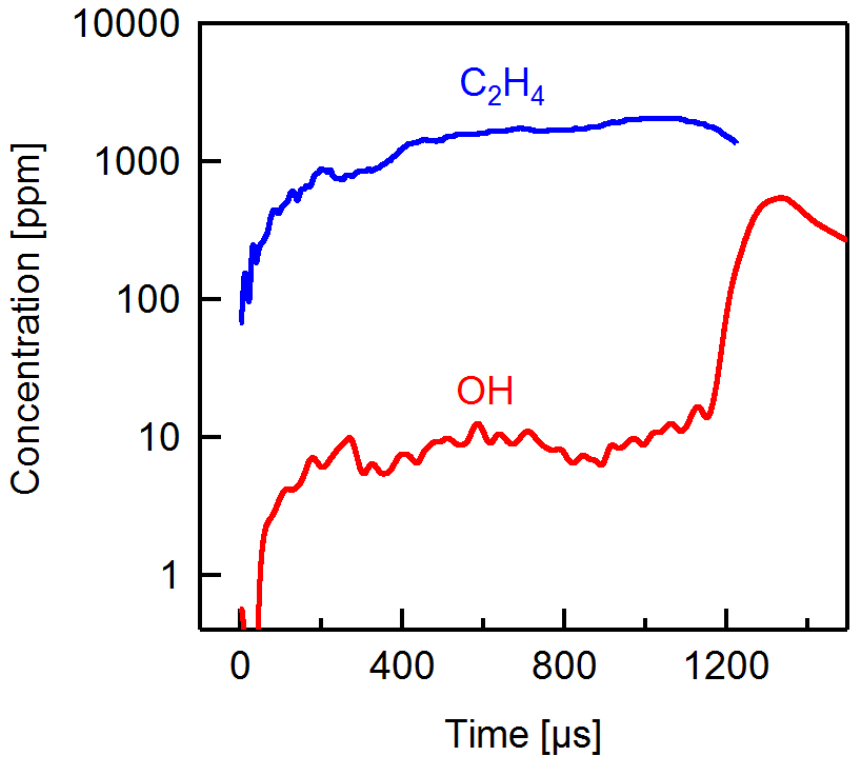
Recent Multi-Species Time-History Studies in Stanford Aerosol Shock Tube

- **Diesel oxidation: two species time-histories**
  OH, C_2H_4 simultaneously

- **N-Hexadecane oxidation: six species time-histories**
  Fuel, H_2O, CO_2, CH_4, OH, C_2H_4 simultaneously

Diesel Oxidation: OH and C_2H_4

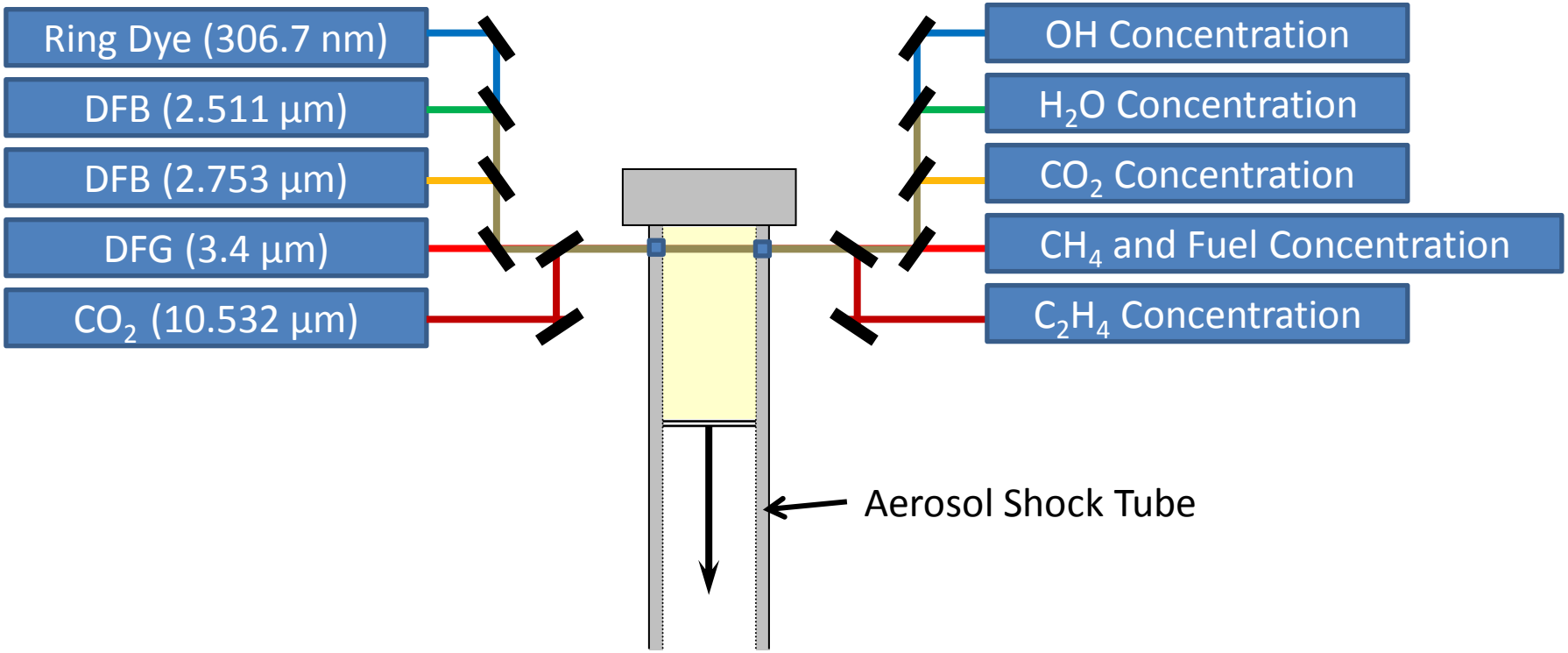
- **First species time-history measurements for Diesel fuel**
- **LLNL (2009) model**
  - **Ethylene yield is under-predicted**
  - **OH pre-ignition plateau strongly under-predicted**
  - **does a good job with ignition time but…**
  - **Reveals need for continued model refinement**



1228 ppm Diesel (CN=43) /O_2/Ar
Φ=0.5, 1198K, 6.7 atm

n-Hexadecane Oxidation: Multi-Wavelength Shock Tube Setup

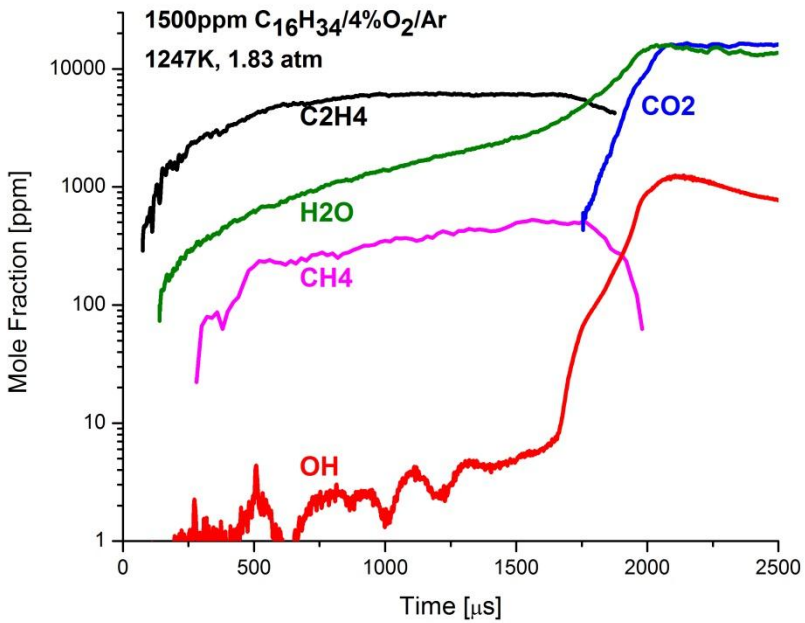
- **6 Simultaneous Species Time-Histories (UV to IR lasers)**



Hexadecane Oxidation:
Multi-Wavelength Laser Absorption Data

- **First multi-species time-history measurements in n-hexadecane!**
  - **Intermediates: C_2H_4, CH_4**
  - **Products: H_2O, CO_2**
  - **Radicals: OH**

- **Excellent SNR**



How does data compare with current models?

Hexadecane Oxidation:
Comparison with LLNL (2010) Model

LLNL (2010) Model

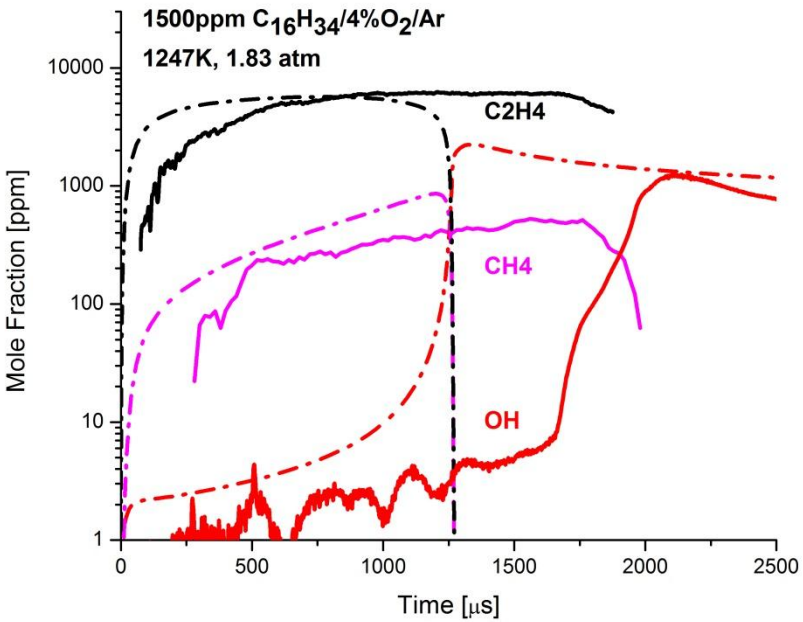
LLNL model:

- predicts C_2H_4 yield

- over-predicts CH_4

- over-predicts OH plateau

- shorter ignition delay time

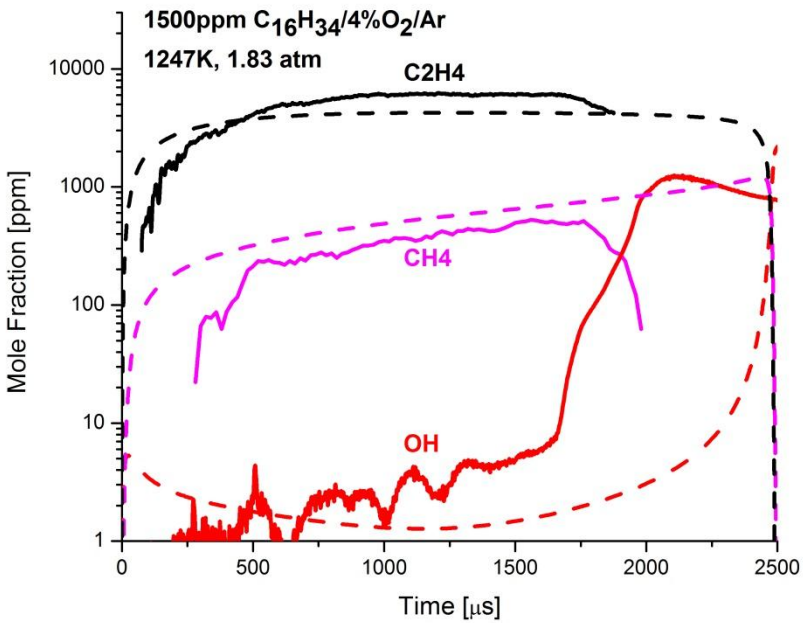


Hexadecane Oxidation:
Comparison with Ranzi (2011) Model

Ranzi (2011) Model

Ranzi model:

- under-predicts C_2H_4 yield
- over-predicts CH_4
- under-predicts OH plateau
- longer ignition delay time



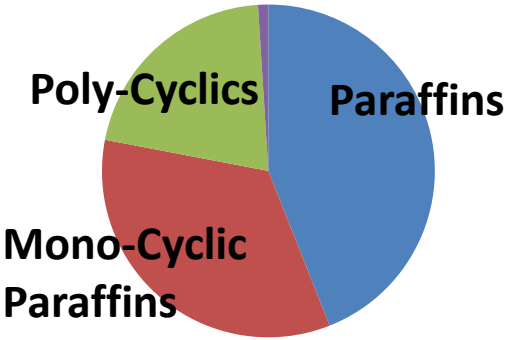
- **Multi-species data reveals need for model refinement for large fuel surrogate components!**

Summary

- Aerosol Shock Tube enables study of low-vapor-pressure fuels
- Multi-species time-histories for OH, C_2H_4, CH_4, CO_2, H_2O, Fuel
- New data provide unique kinetic targets and …
- Reveal need for further model refinement

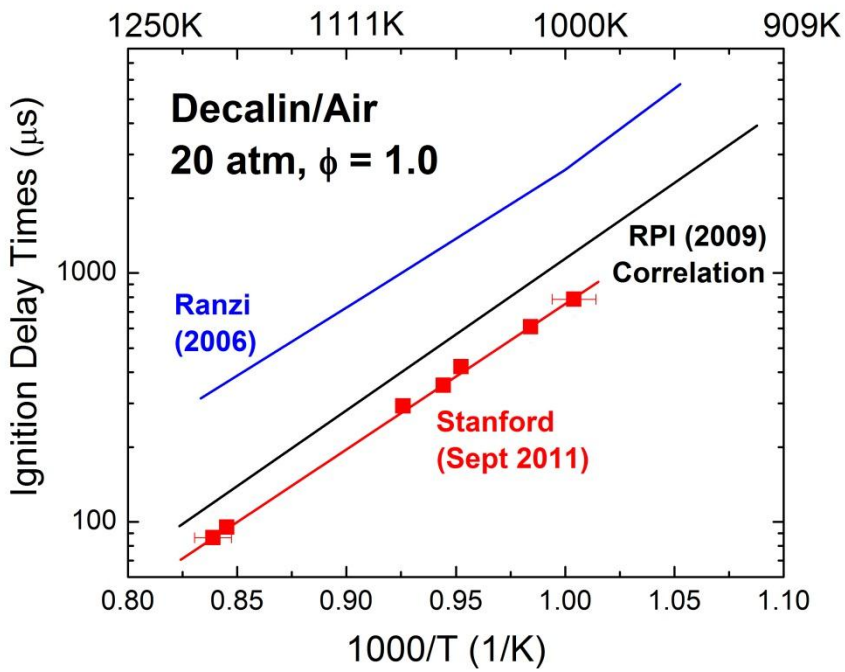
- Next Step:
  - Lower temperatures: into NTC regime
  - High Pressure Aerosol Shock Tube (100 atm)
  - Extend to poly-cyclic species

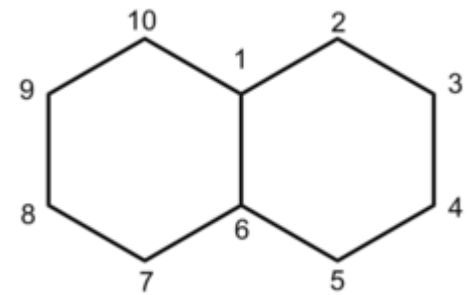
- Initial Results: Decalin



RP-1, Billingsley (2010)

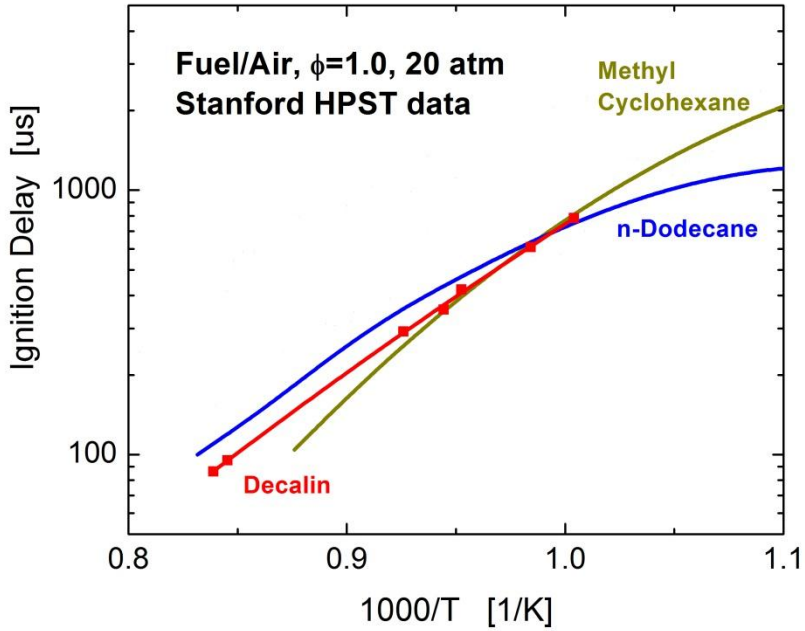
Decalin Ignition Delay Times

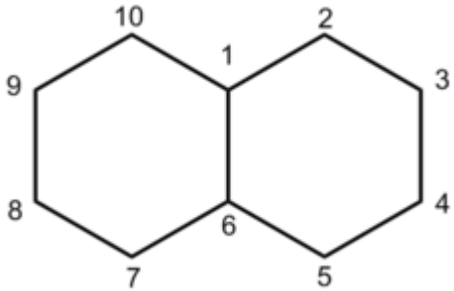




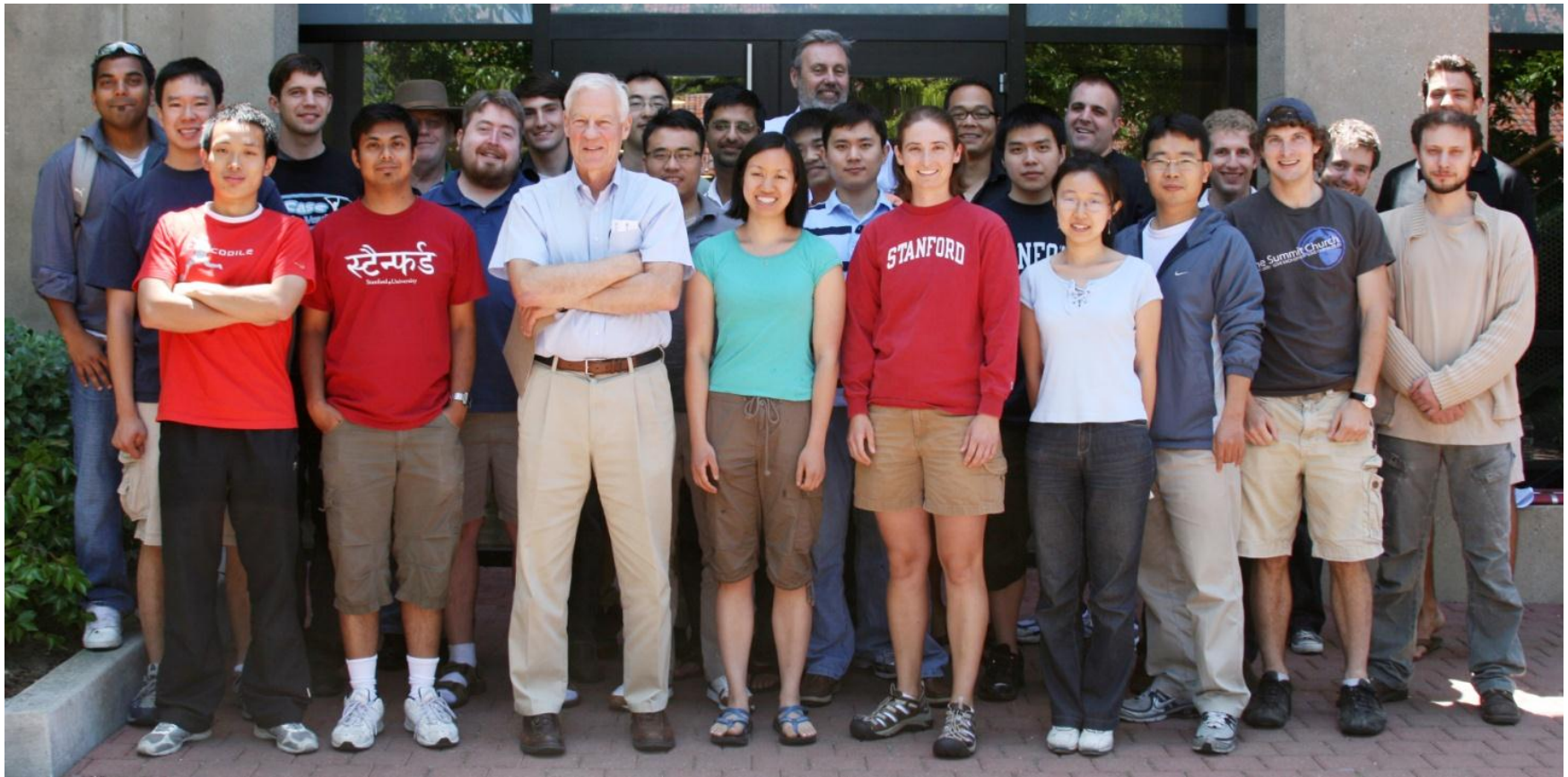
- **New decalin/air 20 atm shock tube measurements**
- **Some variation from RPI correlation**
- **Ranzi model (machine-generated) over-estimates τ_{ign}**
- **Next step: - extend measurements in P, T, and Φ space**
  - multi-species time-histories

Comparison of Jet Fuel Surrogate Components





- **Paraffins: n-dodecane**
- **Mono-cyclic paraffins: methyl cyclohexane**
- **Poly-cyclics: decalin**
- **Need: full database for all major surrogate components:**
  Ignition delay times, species time-histories, elementary reaction rates

Acknowledgements

- **Work supported by ARO**
- **Thanks to our many shock tube and laser students**