Shock Tube Studies of Liquid Fuel Combustion Kinetics

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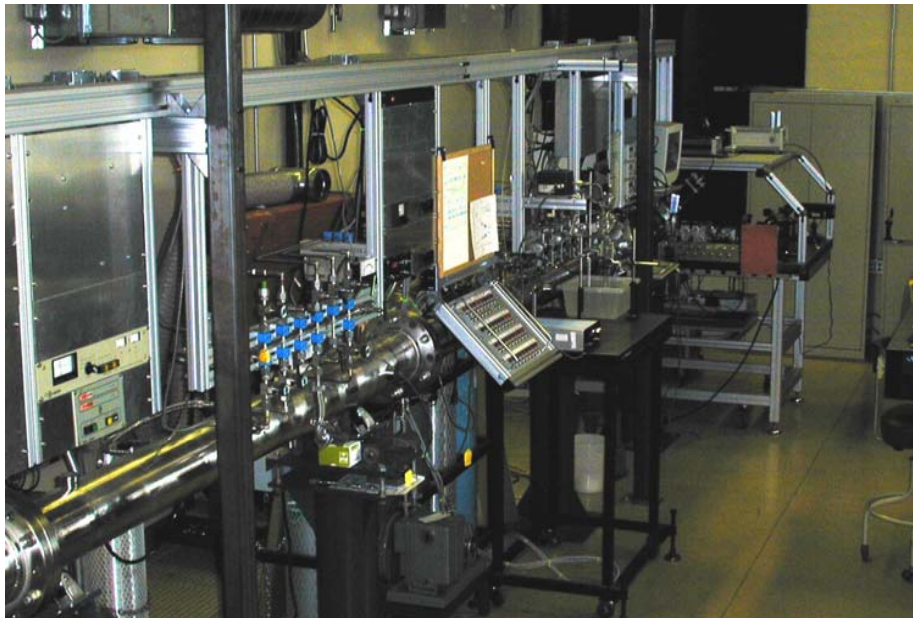
Objective:

Improve knowledge of combustion kinetics of vaporized liquid fuels relevant to the Army – through use of advanced shock tube and optical diagnostics



Work supported by the ARO Core program
Dr. Ralph Anthenien: Contract Monitor

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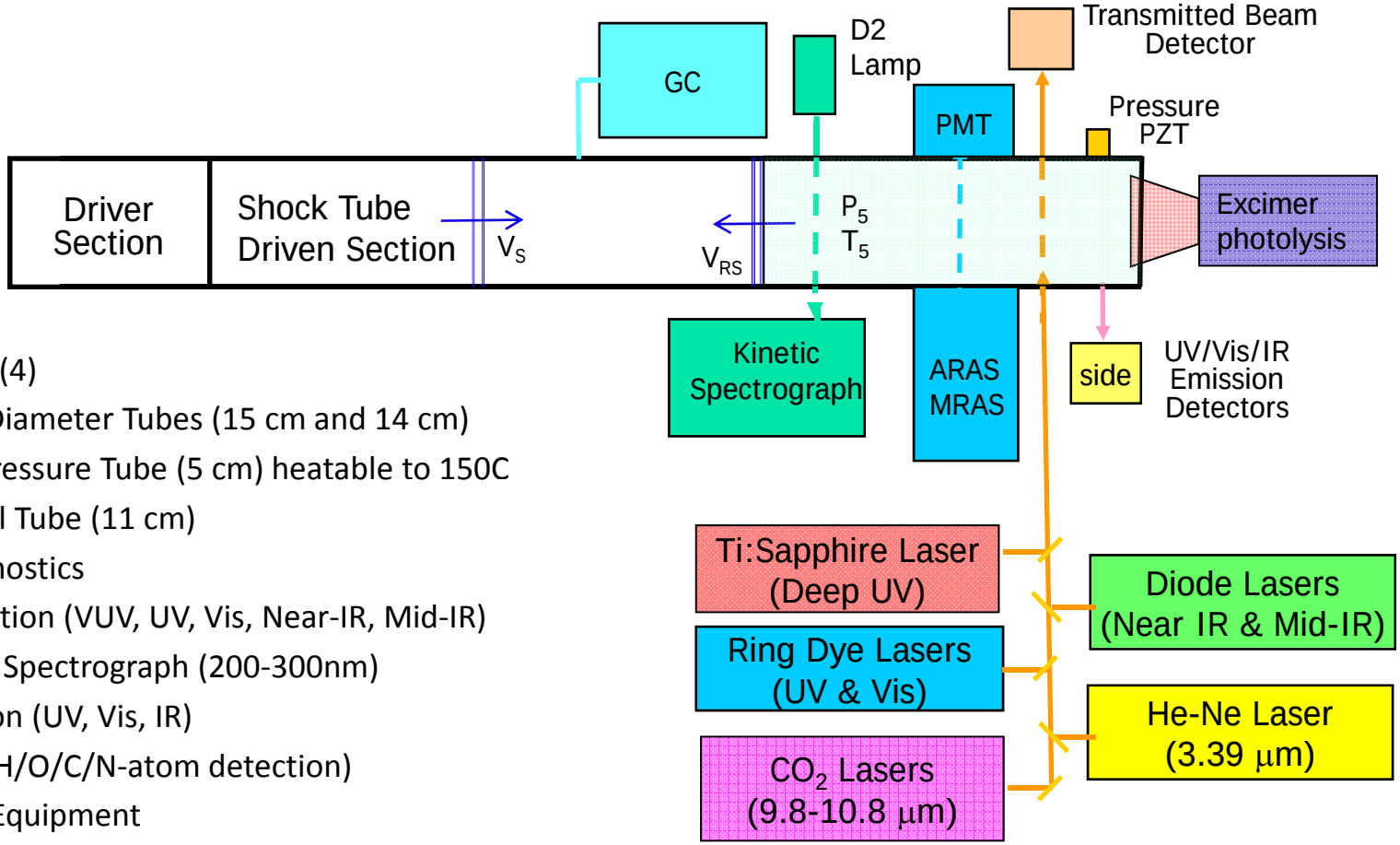
Outline of Topics

1. Development of second-generation aerosol shock tube and its application to *n-dodecane* and *diesel* ignition
2. Ignition measurements of cyclic jet fuel surrogate components: *toluene* and *methylcyclohexane (MCH)*
3. Extension of the operating regime and capabilities of conventional shock tubes
4. Successful resolution of apparent discrepancy in low-T *propane* ignition delay times

Stanford Shock Tube & Laser Facilities

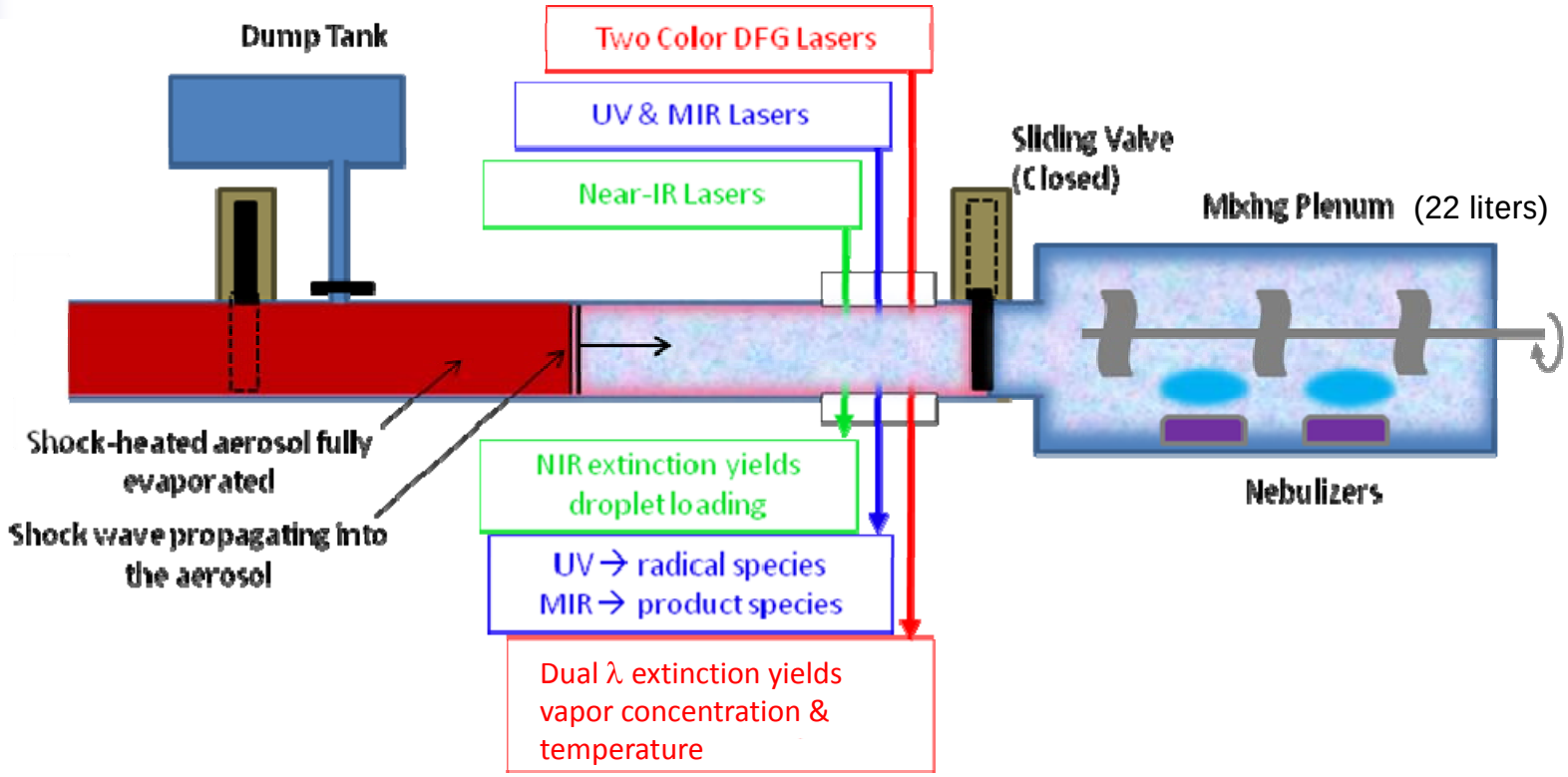


- Shock Tubes (4)
  - Large Diameter Tubes (15 cm and 14 cm)
  - High Pressure Tube (5 cm) heatable to 150C
  - Aerosol Tube (11 cm)
- Optical Diagnostics
  - Absorption (VUV, UV, Vis, Near-IR, Mid-IR)
  - Kinetic Spectrograph (200-300nm)
  - Emission (UV, Vis, IR)
  - ARAS (H/O/C/N-atom detection)
- Supporting Equipment
  - Gas Chromatography for *in situ* Fuel Analysis
  - Excimer Photolysis for Radical Production

Topic 1: Development of Second-Generation Aerosol Shock Tube (AST 2)

- First-generation aerosol shock tube (AST 1)
  - Turbulence-based filling method – some limitations on fuel loading range, uniformity and reproducibility
- Second-generation aerosol shock tube (AST 2)
  - New plug-flow-based aerosol delivery system allows partial ST filling
  - Improved spatial uniformity of the aerosol by pre-mixing test mixture
  - Greater range of aerosol (i.e. fuel) loadings
- Recent work
  - Fuel 1: N-Dodecane
  - Fuel 2: Diesel (DF-2)

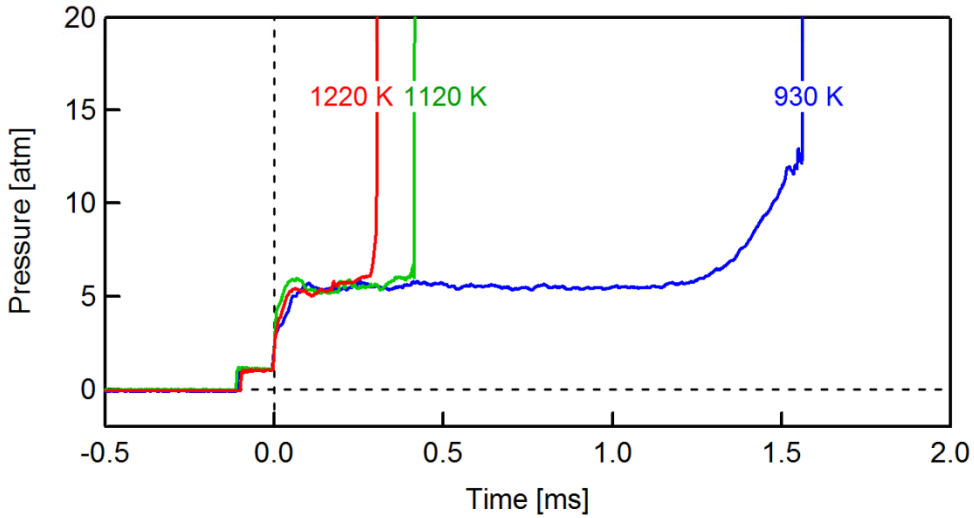
Second-Generation Aerosol Shock Tube: Experimental Schematic

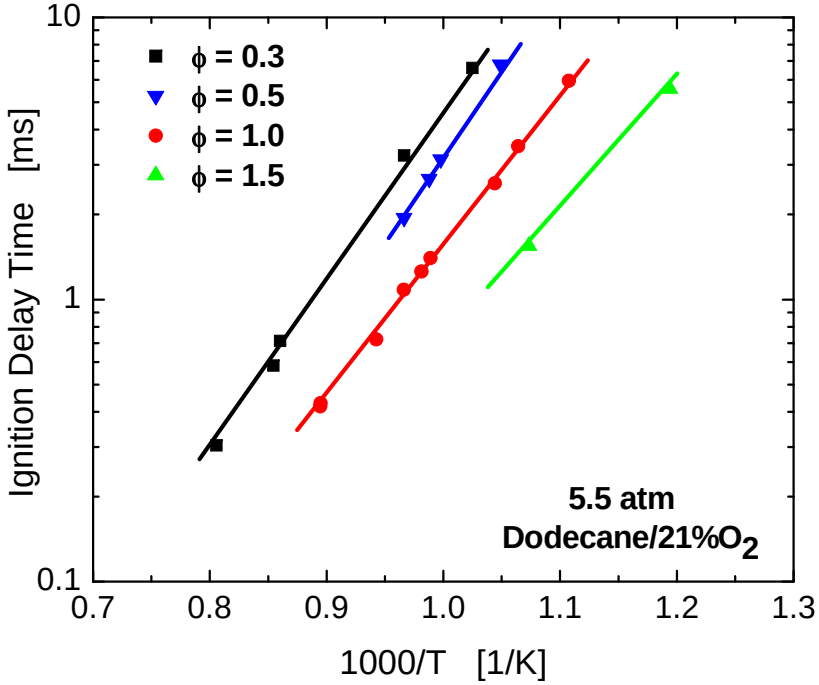


- New aerosol loading scheme uses two large ST gate valves, mixing plenum and dump tank; plug flow loading
- Laser diagnostics (UV to MIR) provide fuel loading, uniformity measure, and species concentration time-histories

Fuel: N-Dodecane
Ignition Delay Time Measurements

$C_{12}H_{26}$/21% O_2/Ar, ϕ=0.5, 5.5 atm

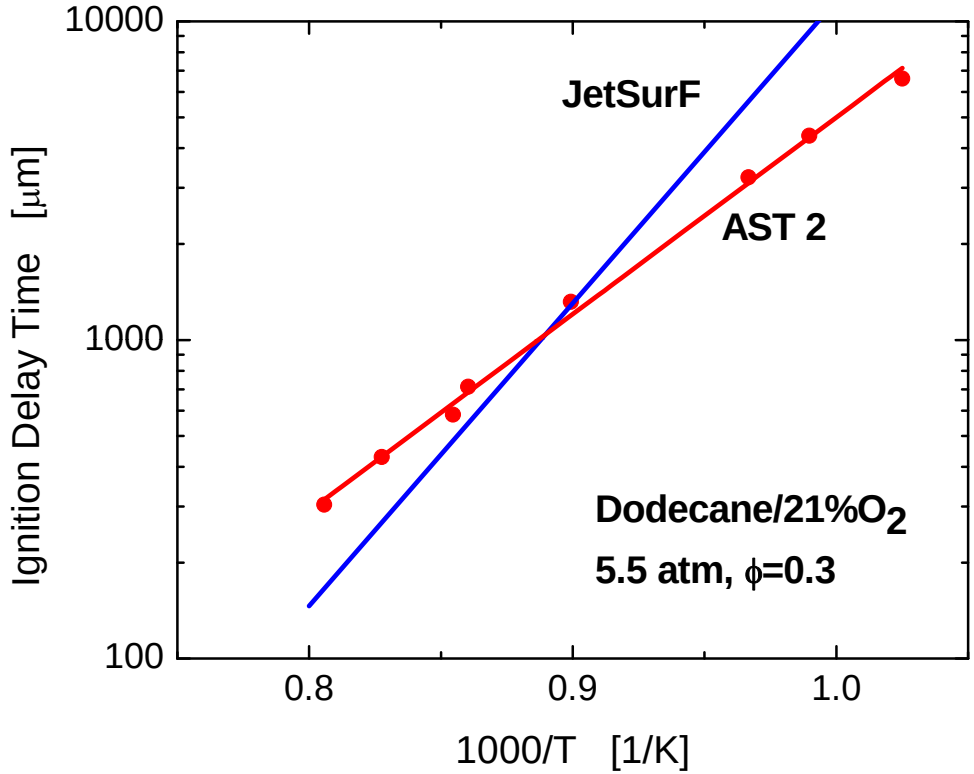




- Quiescent shock tube behavior, similar to conventional gas-phase ST
- Low-scatter ignition delay time data
- Wide range of fuel loading (ϕ = 0.3 to 1.5 in equivalent air)

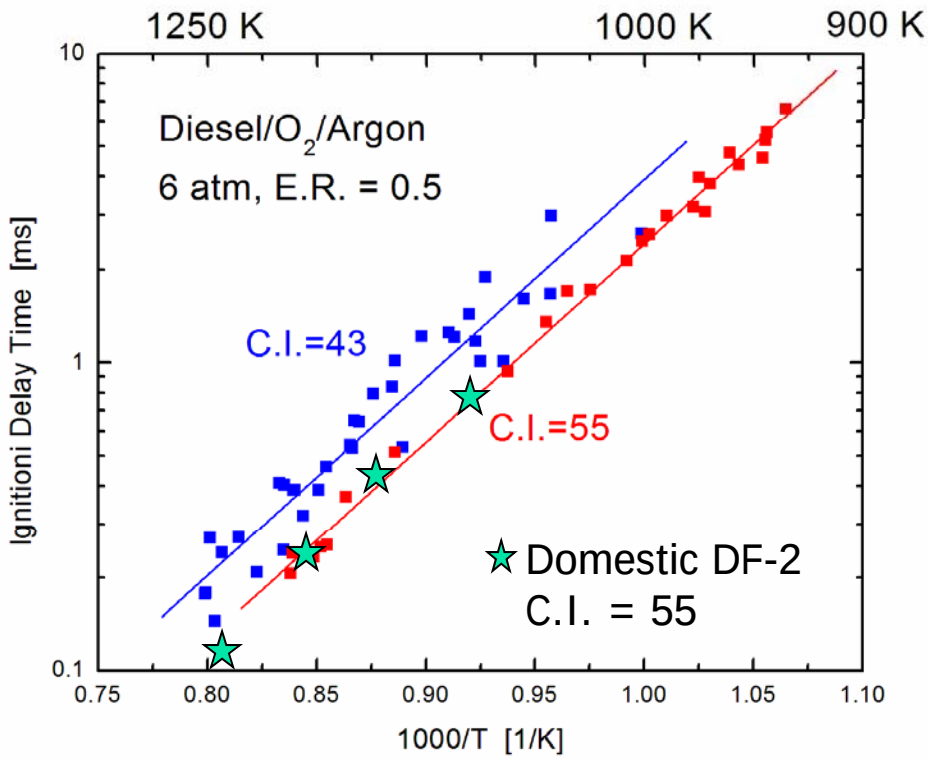
Fuel: N-Dodecane
Comparison with JetSurF Model

- JetSurF model predictions are only in "general agreement" with high-P, low-T ignition delay time data
- Further work needed to expand range of data (P,T,Φ)



❑ AST 2 can provide unique vapor-phase data for low-vapor-pressure fuels in support of mechanism development and validation

Fuel: Diesel (DF-2)
Ignition Delay Time Measurements



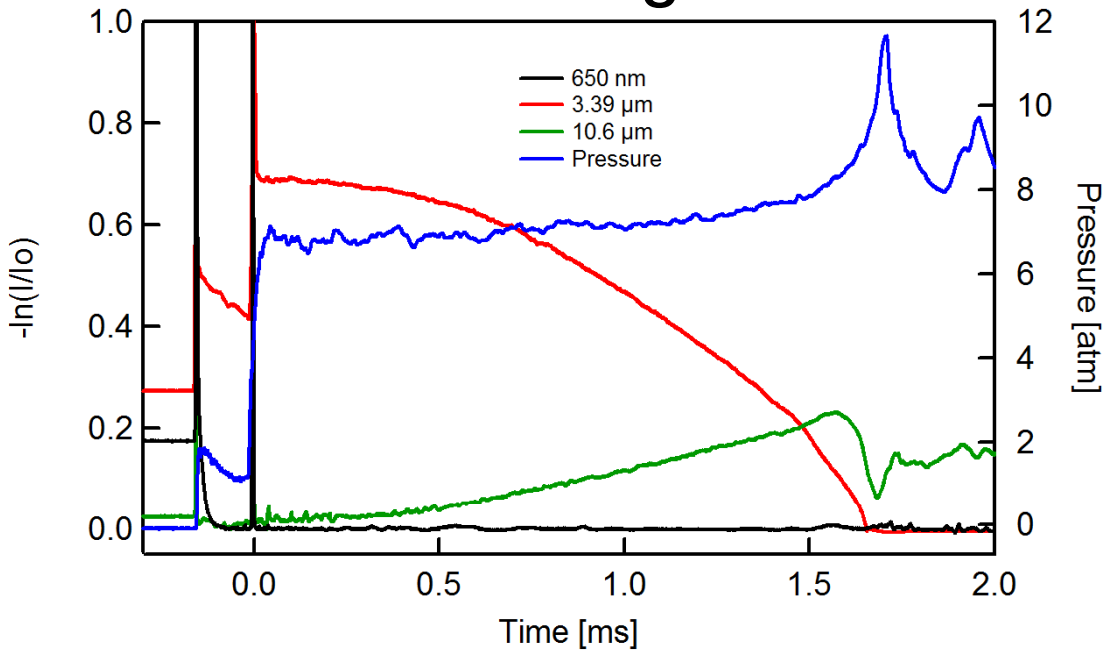
- New diesel ignition data (domestic DF-2, C.I.=55) in excellent agreement with previous Stanford study
- Low scatter measurements allow better quantification of ignition time variation with fuel variation (e.g. composition, Cetane Index)

- Next Step: - acquire data over wider range of conditions (T,P, mixture, Φ)
  - investigate jet fuel surrogates (including bio-derived fuels)

Fuel: Diesel (DF-2)

First AST 2 Application of Multi-Species Laser Absorption Strategy

Diesel Ignition



Reflected Shock Conditions: 1092K, 7.6 atm, 0.19% Diesel (DF-2), 21% O_2

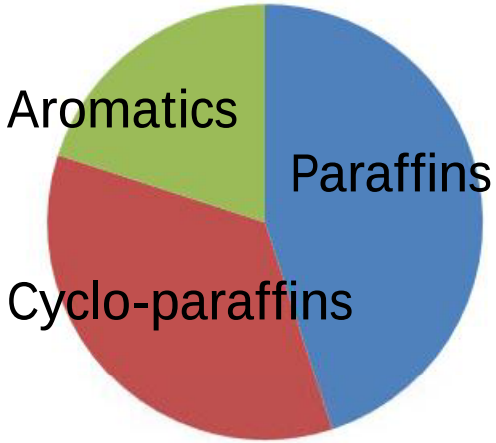
- Multi-species laser absorption measurements provide new chemical kinetic targets for diesel surrogate comparison
- Multi-Wavelength Diagnostics:
  - 650 nm: droplet extinction
  - 3.39 µm: fuel concentration
  - 10.6 µm: ethylene

- Multi-species data provides time histories for fuel decomposition and stable intermediates (C_2H_4)

Topic 2: Cyclic Jet Fuel Surrogate Components

- High-quality ignition and species data needed for primary surrogate jet fuel components:
  - paraffins (n-dodecane)
  - cyclo-paraffins (methylcyclohexane/MCH)
  - aromatics (toluene)

- Critical need for low-intermediate T data
- Current targets:
  - MCH: 60 atm, 700-1100 K
  - Toluene: need to resolve ST/RCM ignition time differences near 1000K



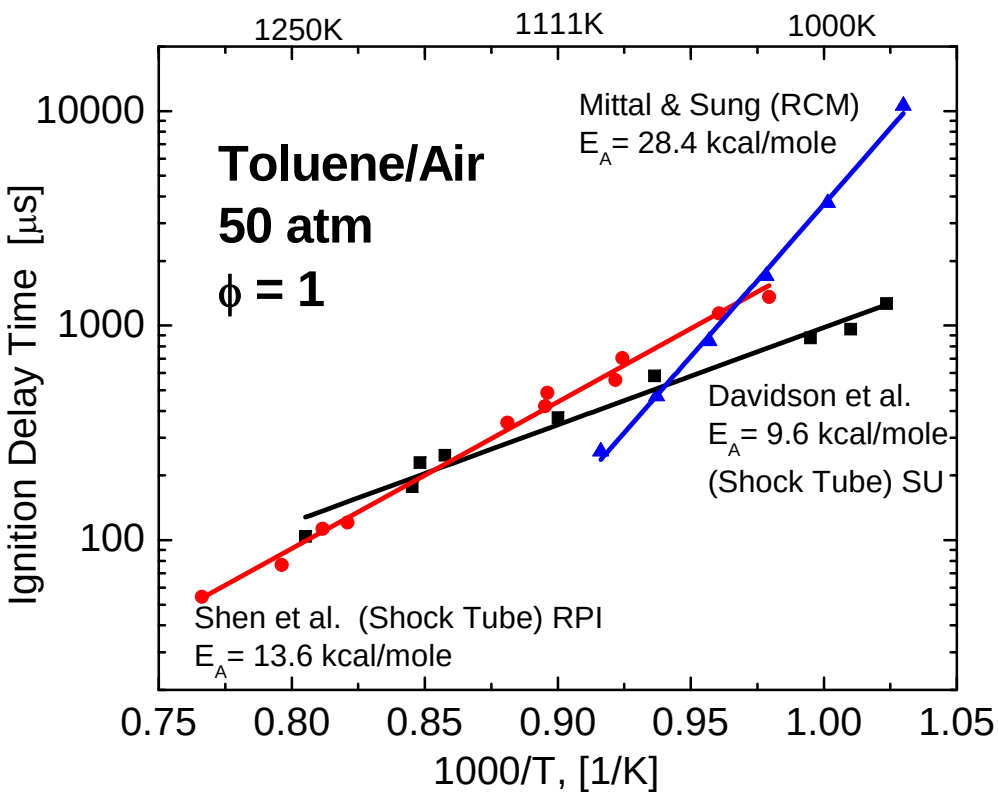
JP-8 Composition

Ignition Measurements of Jet Fuel Surrogate Components: Toluene

- Development/refinement of surrogate jet fuel mechanisms requires reliable ignition data for toluene at engine-relevant conditions

- The Problem: Recent ST and RCM studies of toluene ignition show differing trends at intermediate temperatures (900-1200 K) and high pressures (near 50 atm)

- The Need: Establish reliable data base for τ_{ign}, especially at T< 1050K



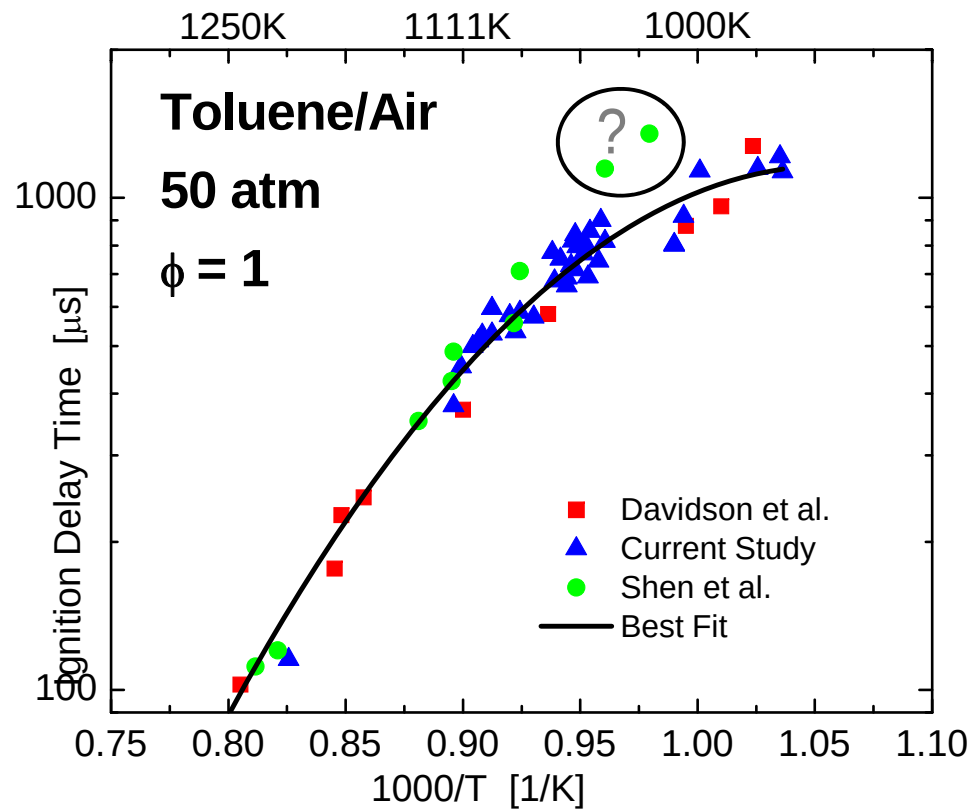
New Shock Tube Ignition Delay Time Measurements: Toluene

- To address this discrepancy we have measured ignition delay times for toluene/air mixtures ϕ = 1.0, 50 atm, 966-1211 K

- New measurements in good agreement with the previous Stanford study (Davidson 2005)

- Some variation in pressure time-histories with different fuel loading protocol, but no difference in ignition times

- New data also consistent with work by Shen (except for their two lowest T pts)



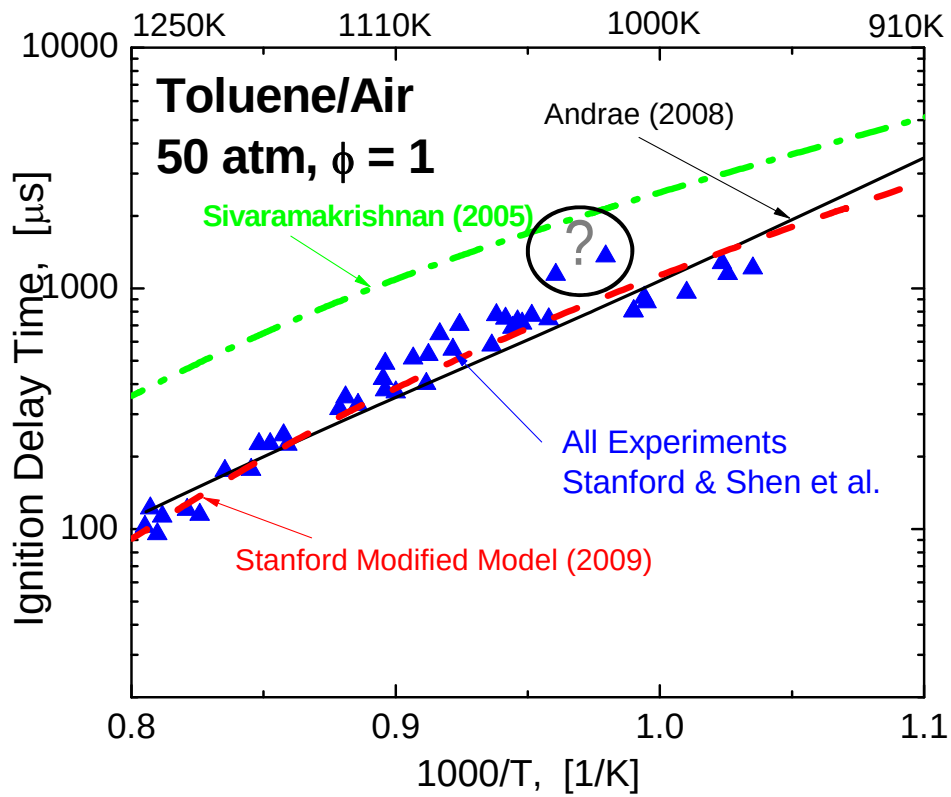
Toluene Ignition Delay Time Measurements: Comparison with Models

- General agreement with Andrae et al. (2008) model
- Shorter experimental times than predicted by Sivaramakrishnan (2005), but mechanism employs older rates for key reactions → Stanford Modified Model

- Stanford Modified Model uses updated rates for:

$H+O_2=O+OH$	(GRI)
$Tol+H=C_6H_5CH_3$	(Baulch)
$Tol+H=C_6H_5CH_2+H_2$	(Stanford)
$Tol+H=C_6H_6+CH_3$	(Baulch)
$Tol+O_2=C_6H_5CH_2+HO_2$	(Stanford)
$Tol+OH=C_6H_5CH_2+H_2O$	(Seta)
$Benzyl+C_6H_5CHO= Tol+C_6H_5CO$	(Bounaceur)

- Good agreement with Stanford Modified Model
- Next step: acquire data at lower temperatures (<1000 K) to guide model development



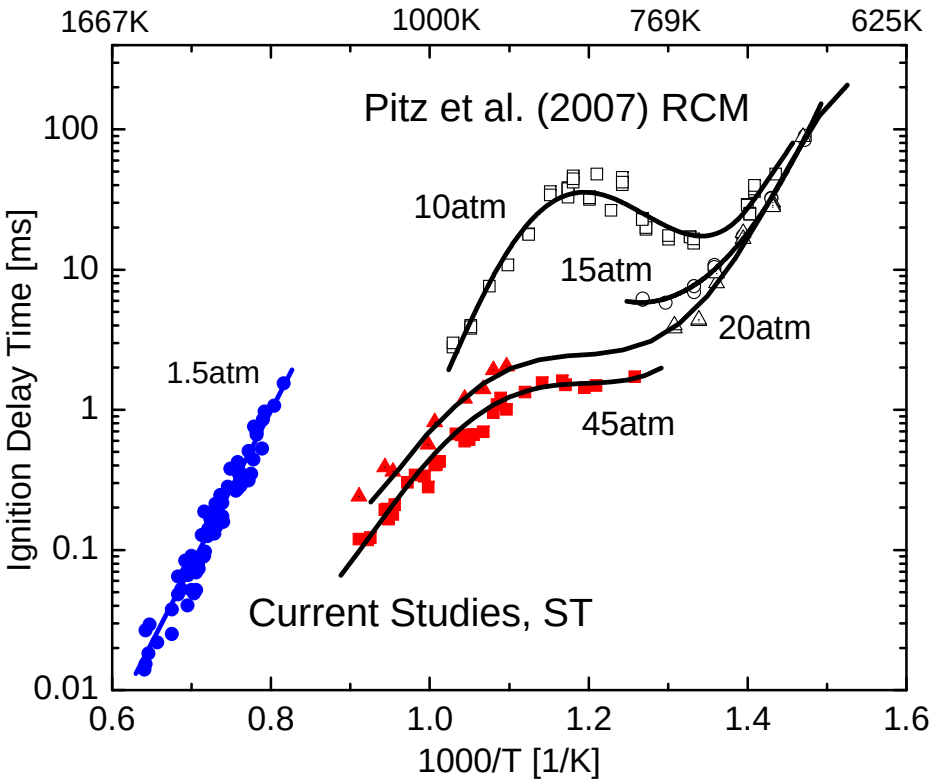
Ignition Measurements of Jet Fuel Surrogate Components: Methylcyclohexane (MCH)

- Cyclo-alkane (naphthenes) are important chemical class present in jet fuel; ignition time and species data needed for this component

- Current study provides extended temperature and pressure range of data (P=1.5, 20 and 45 atm)

- 20 atm shock tube measurements appear to extrapolate smoothly to RCM measurements

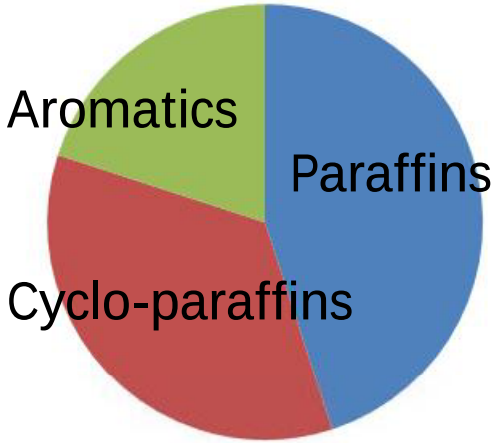
- Next Step:
  Testing and refinement of multi-component surrogates and models



Cyclic Jet Fuel Surrogates Components: Summary

- High-quality ignition and some species time-history data now available for surrogate jet fuel components:
  - paraffins (n-dodecane)
  - cyclo-paraffins (methylcyclohexane/MCH)
  - aromatics (toluene)

- Next Steps:
  - Low-T data needed for toluene
  - Additional species time-history data needed for all components (especially at low T)



JP-8 Composition

Topic 3: Extension of Conventional Shock Tube Capabilities

- Opportunities/Needs to extend/improve shock tube operating regime

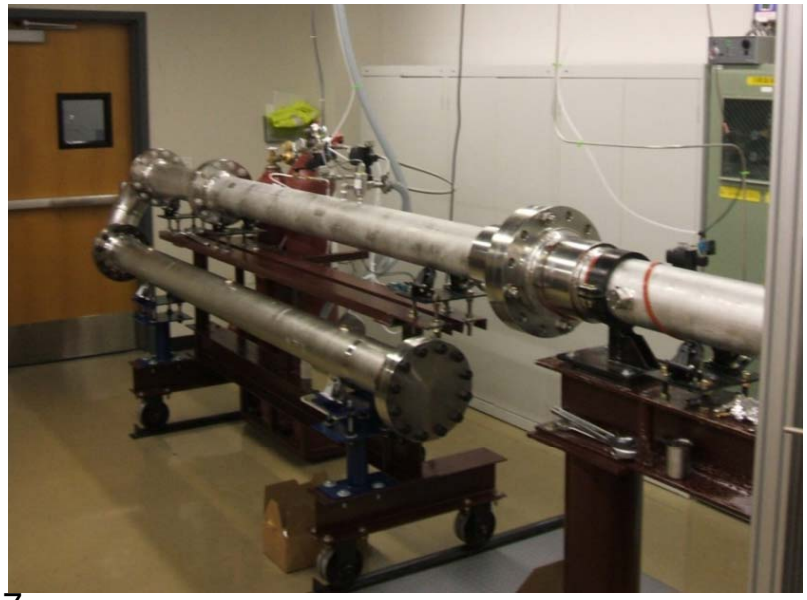
- Stanford strategy:
  A. Extend test time using tailored gases and longer driver
  B. Use driver inserts to correct for dP/dt during RS experiments
  C. Measure T directly using WMS CO_2 laser absorption
  D. Use CHEMSHOCK gasdynamic model to correct for changing test conditions

Strategy A: Use Driver Extension & Tailored Mixtures to Extend Test Time

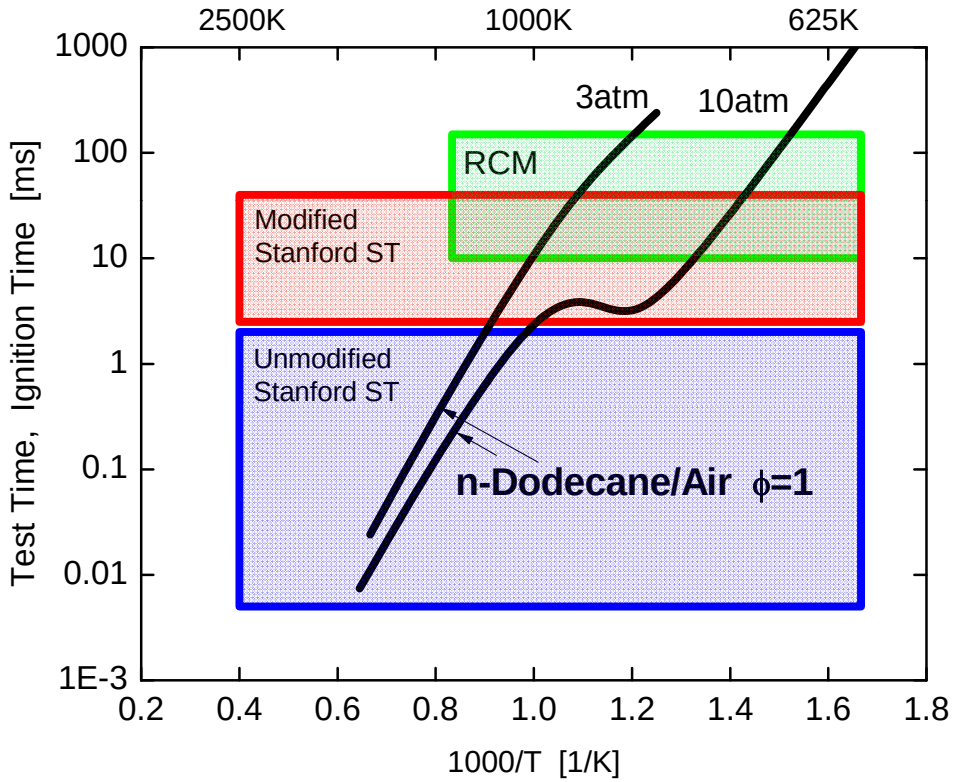
Motivation

- Critical need to overlap ST and RCM test times to resolve τ_{ign} modeling differences
- Have achieved > 40 ms!

Shock Tube with Driver Extension

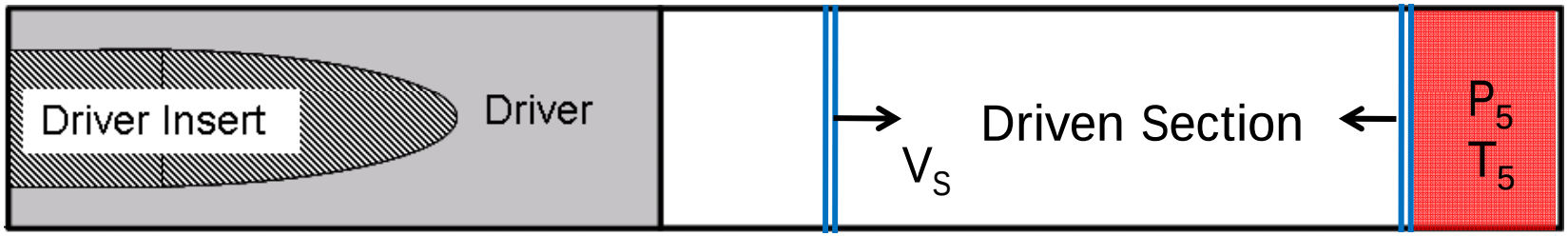


Facility Test Time



(Facility modifications funded by ARO)

Strategy B: Use Driver Inserts to Improve Uniformity of Reflected Shock Test Conditions

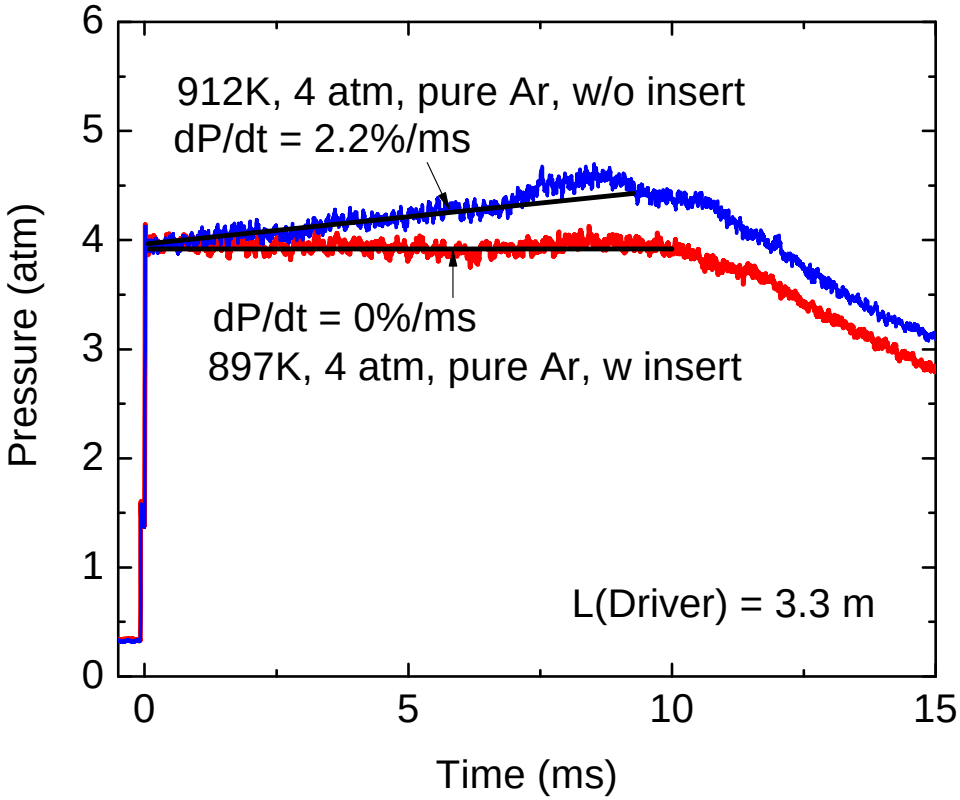


The Problem: Boundary layers and attenuation of V_S cause slow variations in P_5, T_5 with time

The Solution:

(1) Driver inserts: compensates for non-ideal variation in pressure (dP/dt)

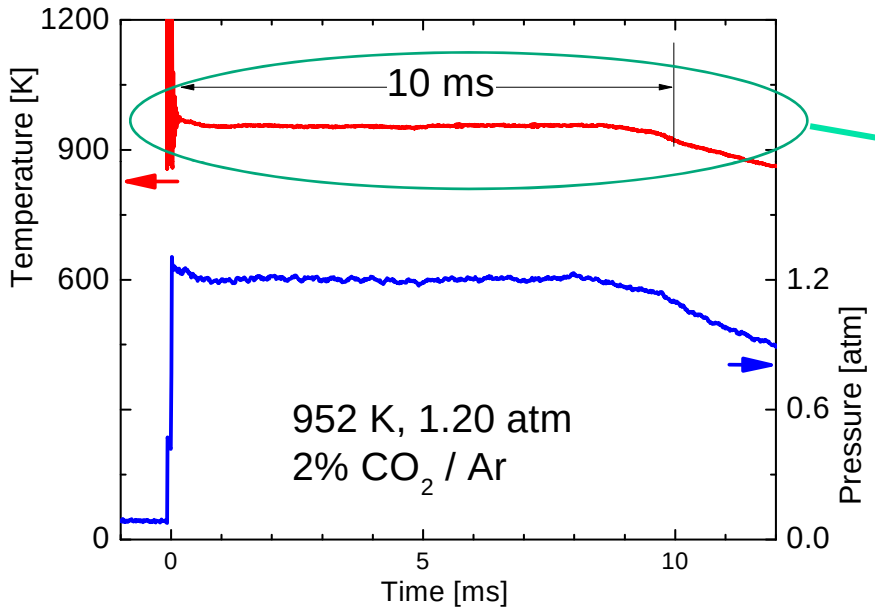
(2) Confirm uniformity with new sensitive T diagnostic



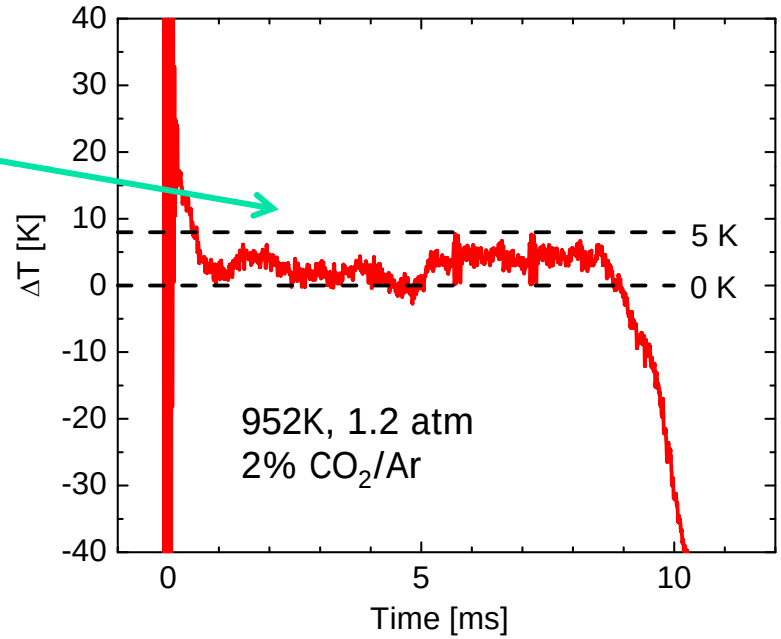
Strategy C: Confirm Uniformity using New High-Sensitivity T Diagnostic

Reflected Shock T, P Histories

(uses tailoring+insert, short driver)



Detail of T-History



- Direct measurement of T using wavelength modulation spectroscopy (WMS) of CO_2 at 2.7μm provides validation of highly uniform temperature over long test times ($\Delta T < \pm 3K$)

(T-diagnostic developed under AFOSR support)

Strategy D: Application of new reacting flow model: CHEMSHOCK

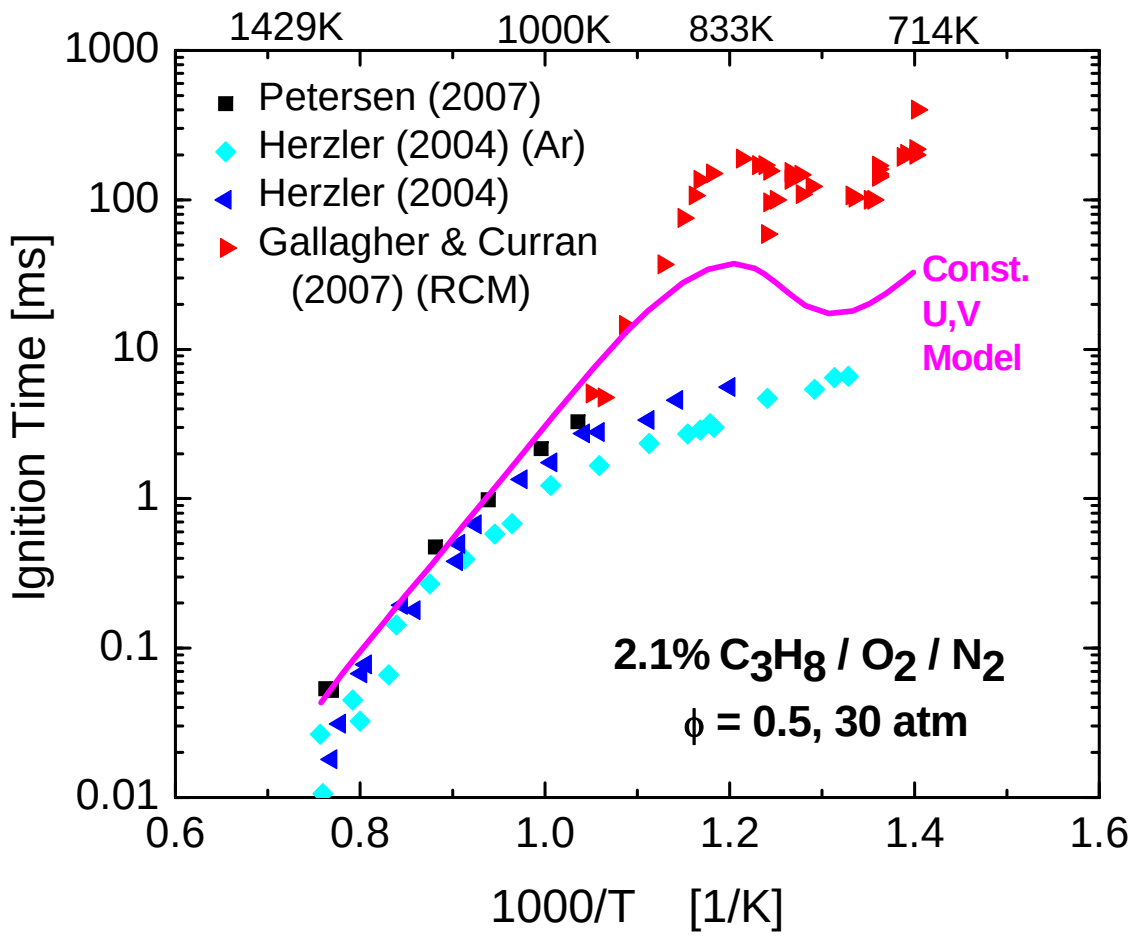
- Testing/validation of new high-fidelity reaction mechanisms with shock tube data demands both high-quality data and more accurate shock tube reactive gasdynamic models

➔ Improved model, CHEMSHOCK

- Uses CHEMKIN plus measured pressure instead of using traditional assumption of constant U,V
- Enable simulation of the temporal evolution of T and species concentrations behind reflected shock waves with chemical reaction and energy release
- Demonstrated successfully with low T ignition of hydrogen and propane
- Work in progress to extend CHEMSHOCK to allow simulation of the temporal *and spatial* variation of non-uniform (1-D) reflected-shock flowfields, including facility effects, as well as, chemical energy release

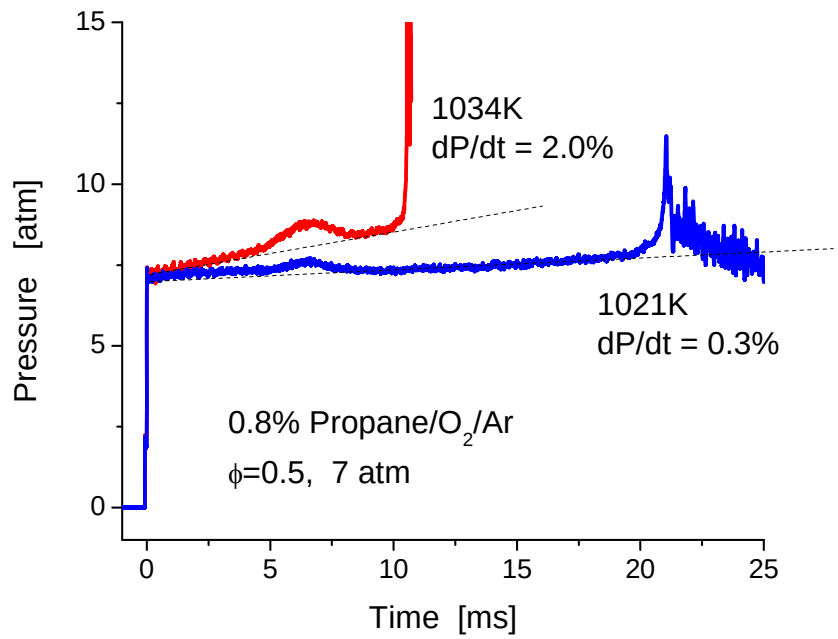
Topic 4: Resolution of Low-T Propane Ignition Delay Time Discrepancy

- Low T propane ignition time data for ST and RCM both inconsistent with const. U,V
- Herzler (2004) and Petersen (2007) show strong "NTC-type" behavior below 1000 K
- **Stanford strategy:** measure propane ignition times at 6 & 60 atm using new ST techniques and interpret using CHEMSHOCK model

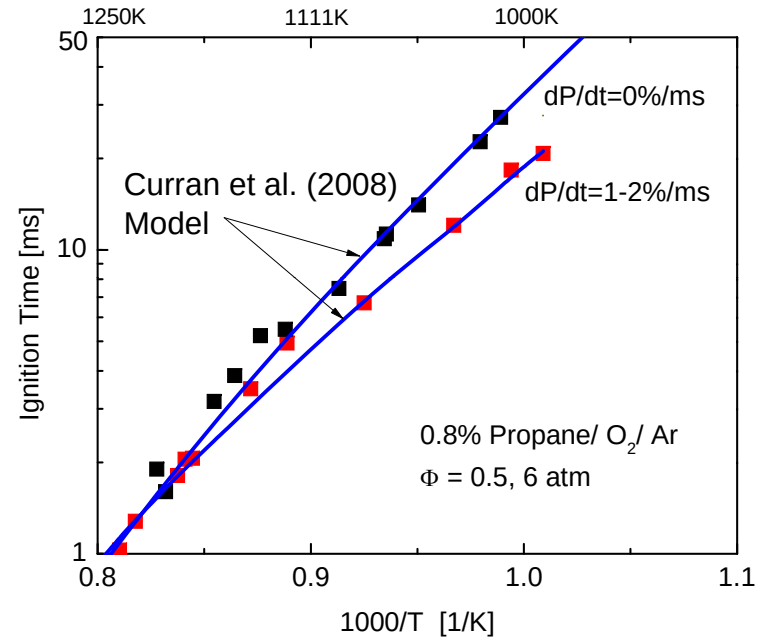


Use of Driver Inserts to Maintain Uniform P and T during Reflected Shock Wave Experiments: **6 atm**

Propane Ignition: Low P



Comparison with Model



- Experiments performed with and without driver inserts
  - Without driver insert dP/dt = 1-2%/ms (requires CHEMSHOCK model)
  - With driver inserts dP/dt = ~0%/ms (can use traditional constant U,V model)
- **Primary conclusion**: Same mechanism (Curran et al. 2008) successfully simulates all low P data! No discrepancy between detailed propane mechanisms and low T ST data.

Future Work

- Ignition chemistry at low temperatures (NTC): Species time-histories and ignition delay times
  - Fuels: Toluene, n-Dodecane
  - Species Monitored: OH, C_2H_4, H_2O, CO_2, fuel, benzyl

- Application of AST 2: Practical, Synthetic and Bio-derived Jet Fuels
  - Fuels: S-8, Large (bio-oil derived) Methyl Esters

Acknowledgements

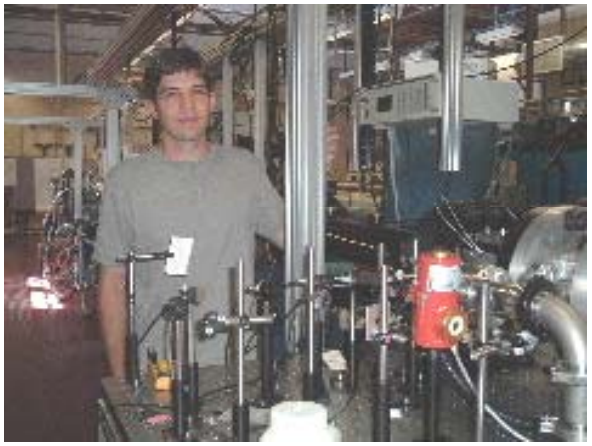
- Visit Stanford website http://hanson.stanford.edu/ for

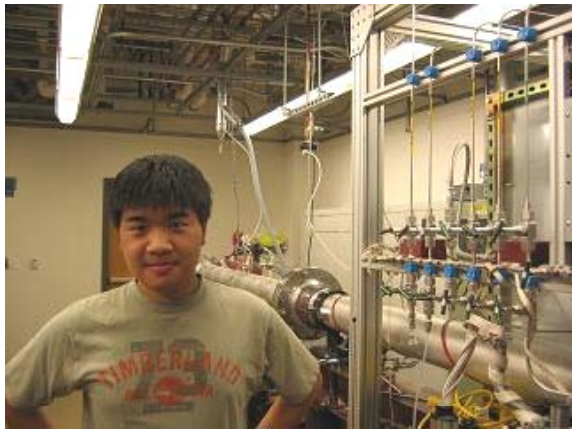
  Fundamental Kinetics Database Using Shock Tubes; Vol. 1: Ignition Delay Times, Vol. 2: Concentration Time Histories, Vol. 3: Reaction Rate Measurements

- Work supported by:

  ARO Core Program for Basic and Applied Scientific Research (Contract Monitor: Dr. Ralph Anthenien)

- Our Shock Tube and Laser Jockies





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