Measurements of Elementary Rate Constants, Ignition Delays and Species Histories in Shock Tubes

R. K. Hanson, D. F. Davidson
Stanford University

1st International Workshop on Flame Chemistry
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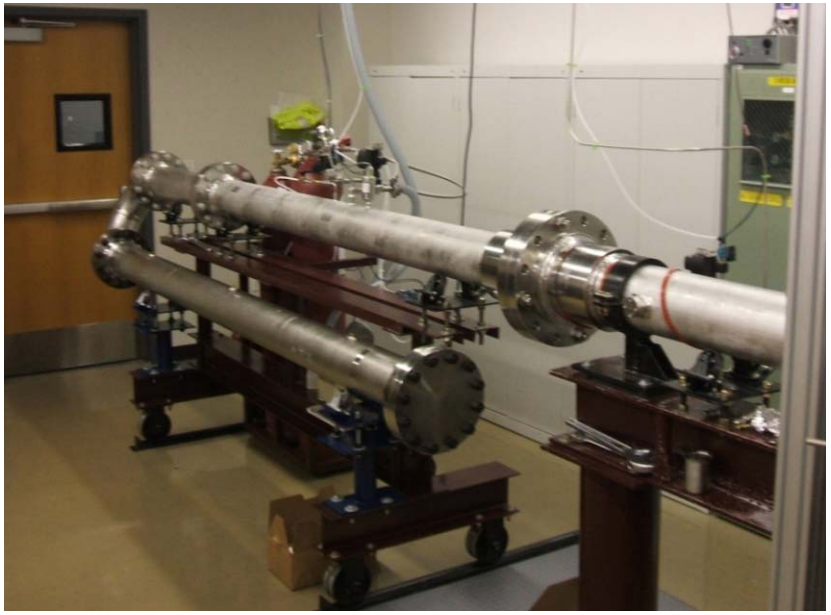
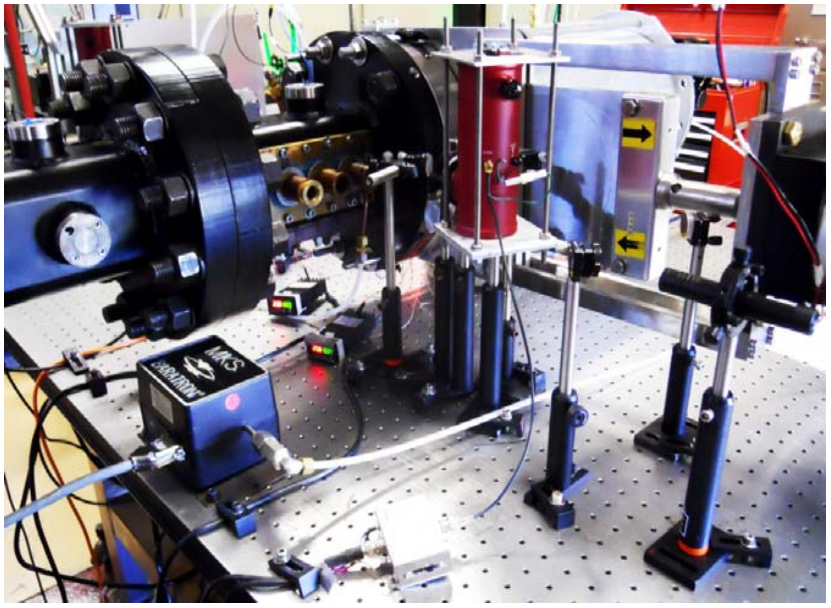
- Shock Tube/Laser Approach
- Advances in Methodology
- Elementary Reaction Rate Studies
- Multi-Species Time-Histories



Kinetics Shock Tube 1 (30 atm)

Kinetics Shock Tube 2 (30 atm)

Stanford Shock Tubes

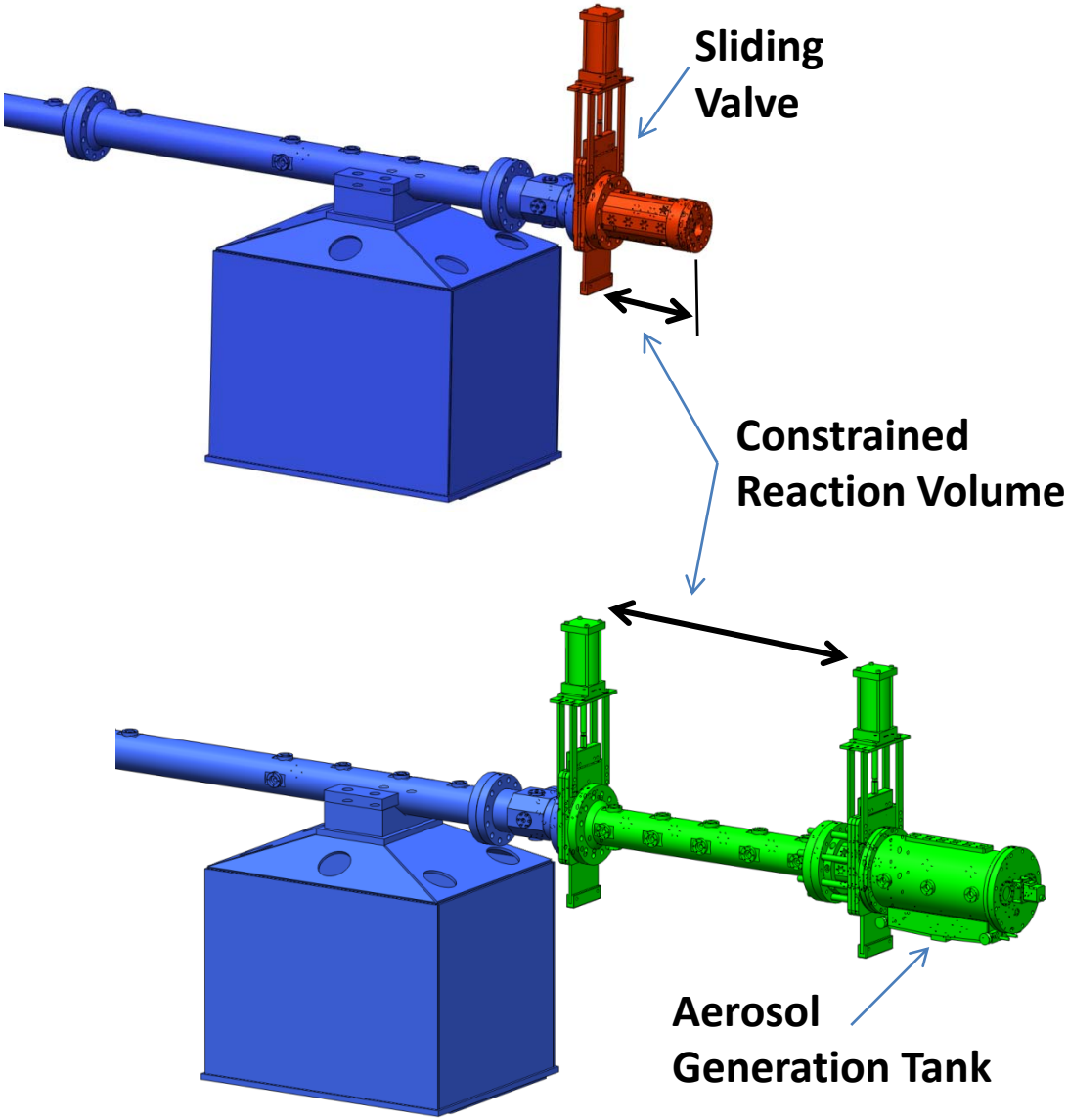


Aerosol Shock Tube (10 atm)

High Pressure Shock Tube (500 atm)

New Constrained Reaction Volume (CRV) Facility

2 Configurations

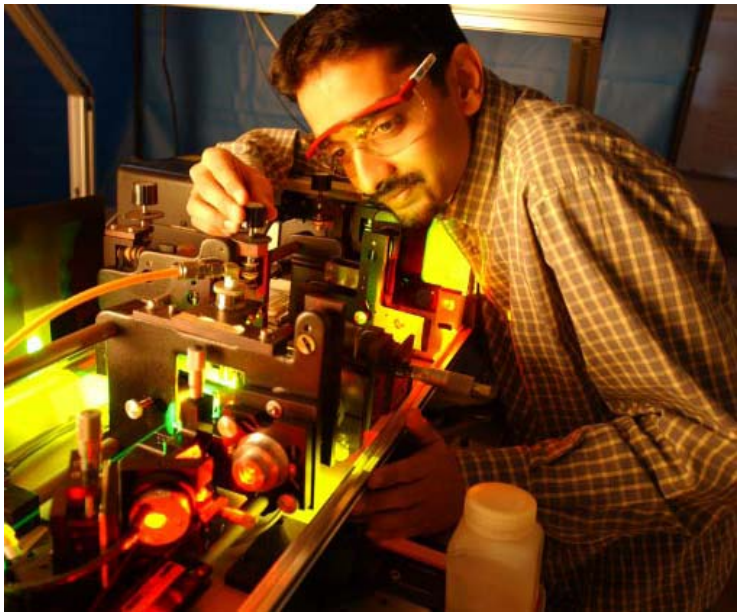


CRV-1

Gas-Phase Experiments to 100 atm

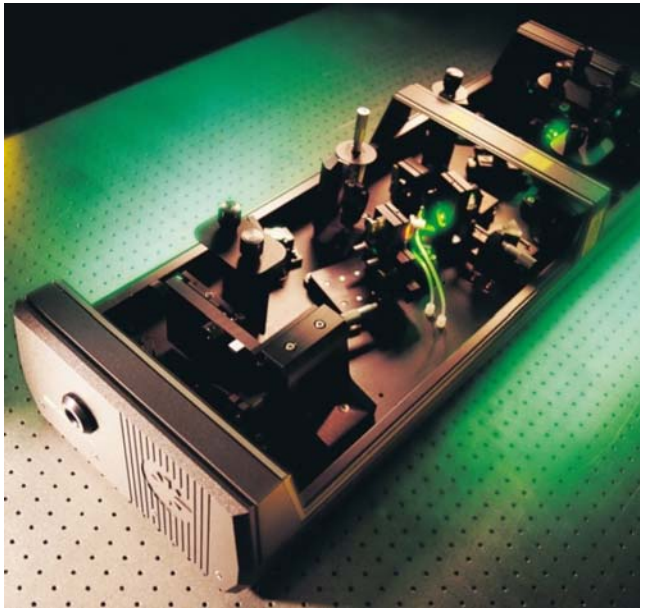
CRV-2

Aerosol Experiments to 100 atm



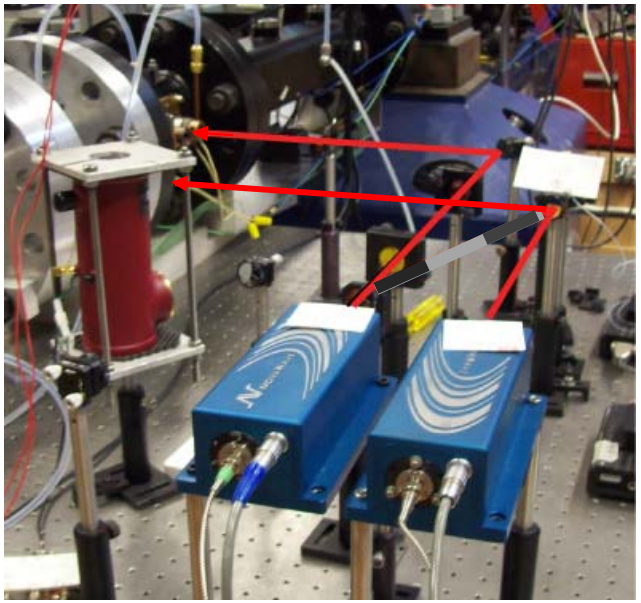
First use of tunable dye lasers in shock tubes (1982)

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



Stanford Laser Diagnostics

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



Ultraviolet

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

Visible

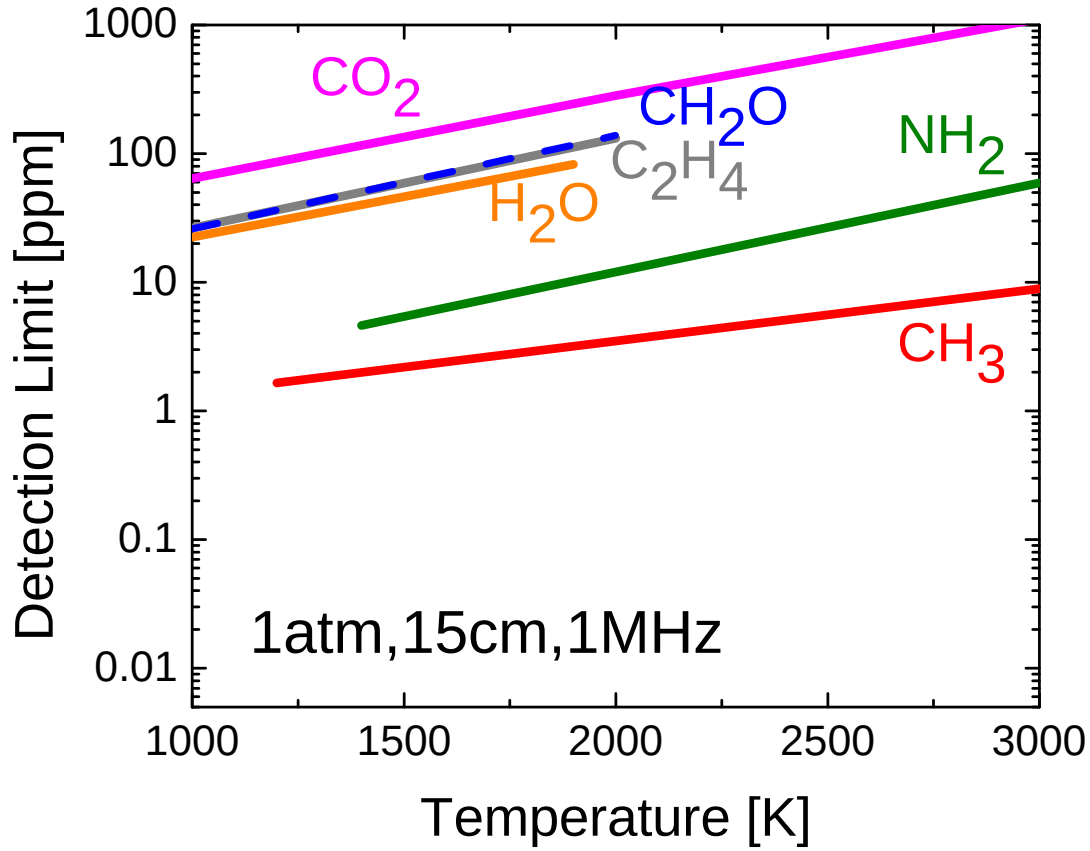
CN	388 nm
CH	431 nm
NCO	440 nm
NO_2	472 nm
NH_2	597 nm
HCO	614 nm

Infrared

H_2O	2.5 μm
CO_2	2.7 μm
CH_4	3.4 μm
CH_2O	3.4 μm
CO	4.6 μm
NO	5.2 μm
C_2H_4	10.5 μm

Laser Absorption Yields High Sensitivity

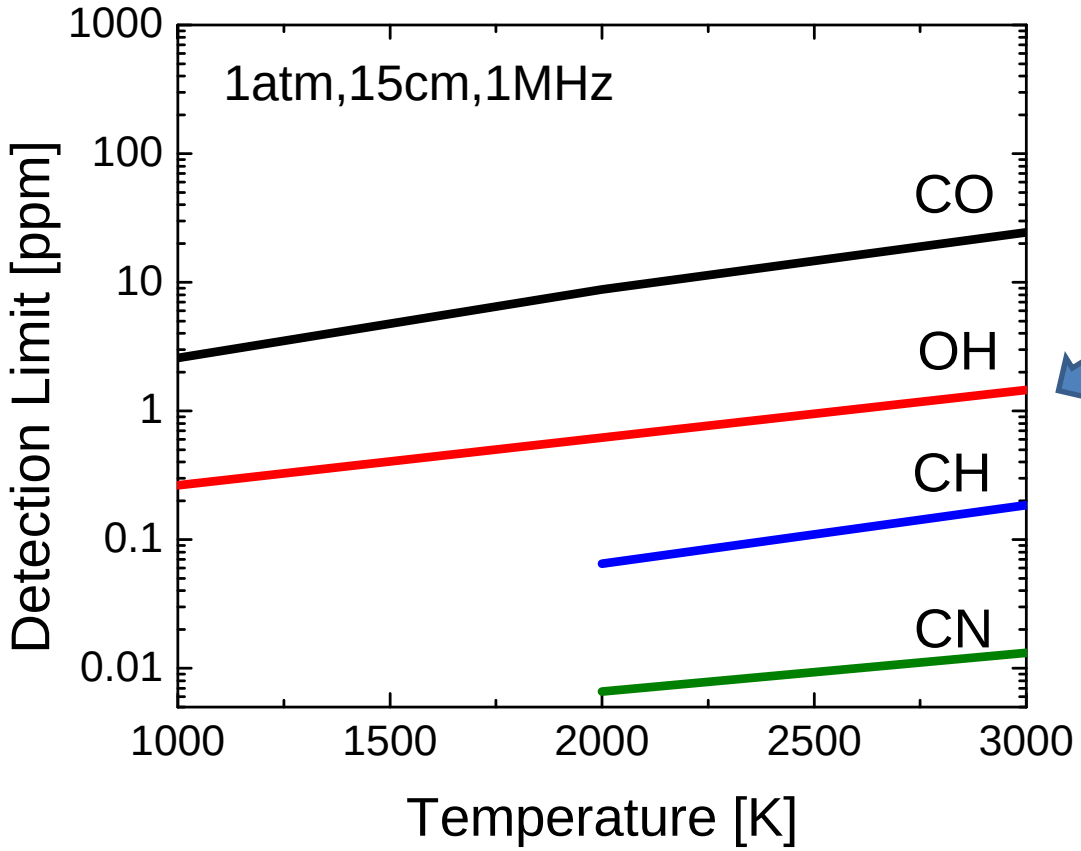
Representative Detection Limits: Polyatomic Molecules



- **Polyatomic molecules @ 1500K: 2-200 ppm**

Laser Absorption Yields High Sensitivity

Representative Detection Limits: Diatomic Molecules



sub-ppm sensitivity for OH, CH, CN

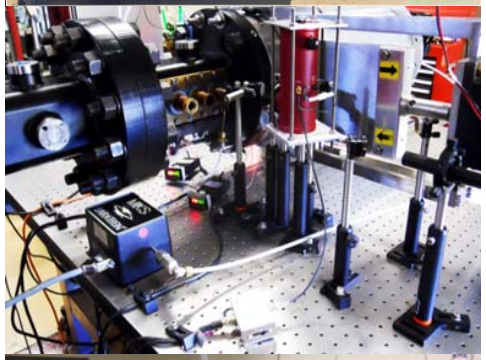
- **Diatomic molecules @ 1500K:**
  - **sub-ppm detectivitiy for UV absorbers**
  - **ppm detectivity for IR absorbers**

Advances in Shock Tube Methodology

1. **Improved uniformity with driver inserts**

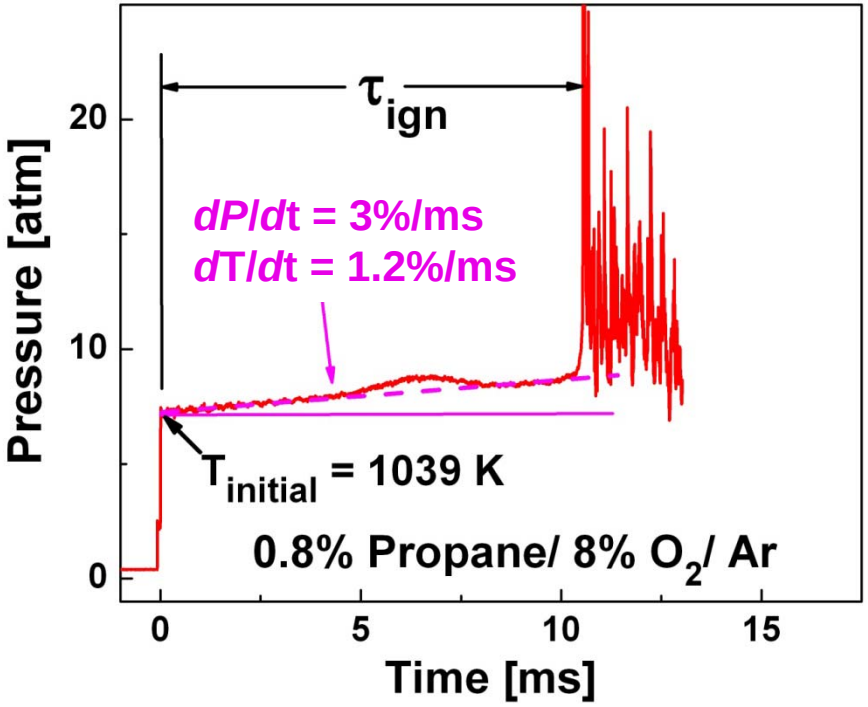
2. **Longer test times with tailored gas mixtures & extended driver**

3. **Reactive gas modeling: problem and solutions**



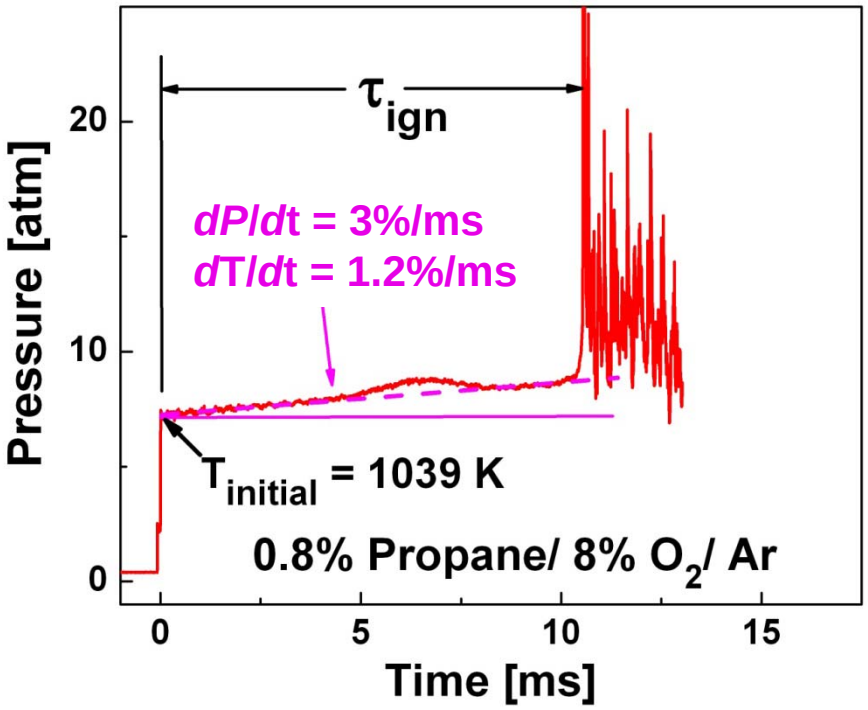
Improvement in Reflected Shock Temperature Uniformity Using Driver Inserts

- **Conventional shock tube operation can provide near-ideal uniform flows for 1-3 ms**
- **But, boundary-layers and attenuation induce dP/dt and dT/dt at longer times**



Improvement in Reflected Shock Temperature Uniformity Using Driver Inserts

- **These effects reduce ignition delay times relative to Constant P case**
- **Solution: Driver Inserts**

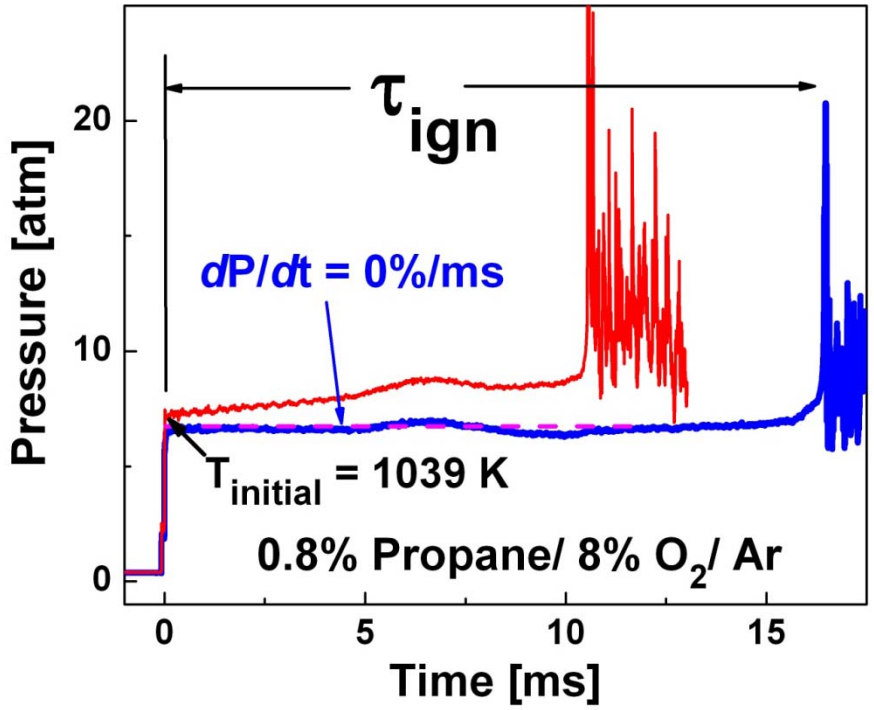


- **Driver inserts modify flow to achieve uniform T and P at long test times**

Improvement in Reflected Shock Temperature Uniformity Using Driver Inserts

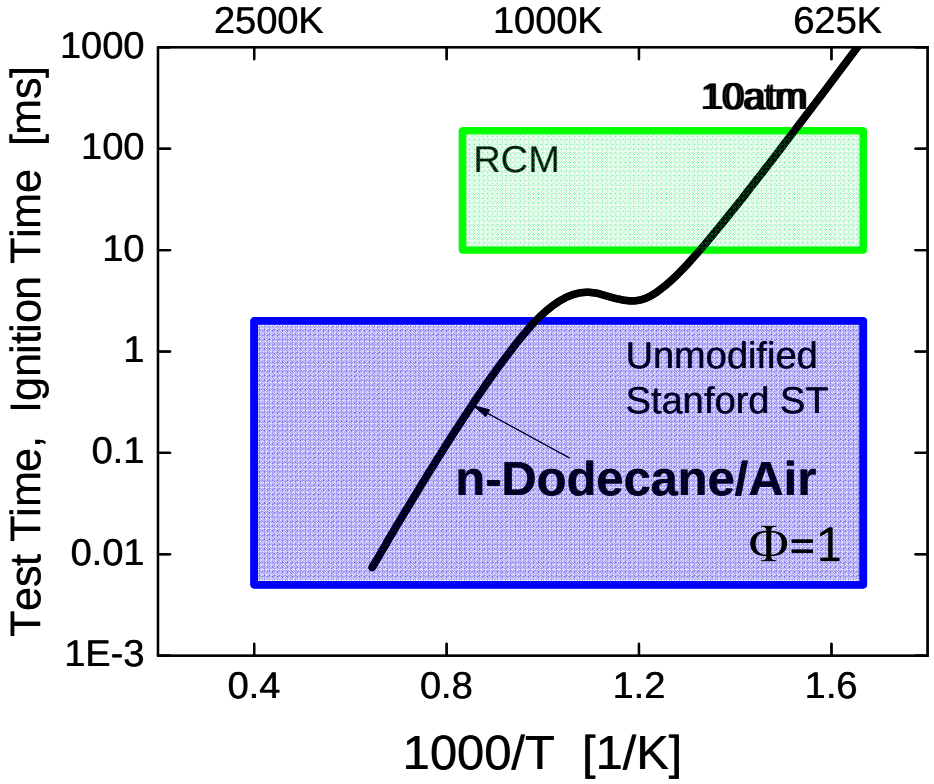
- **Result: dP/dt = 0 prior to ignition**

→ **Proper τ_{ign} for comparison with Constant P simulations**



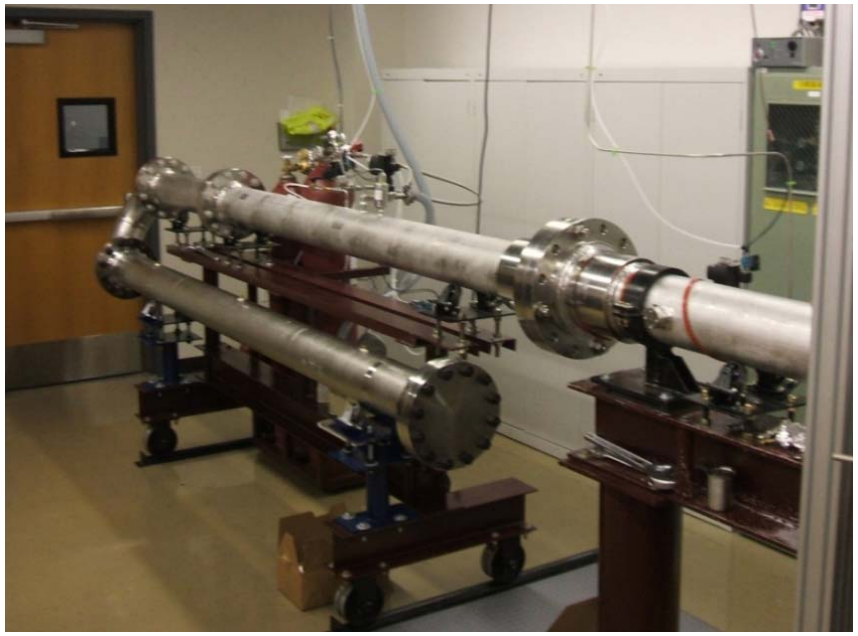
Longer Test Times Achievable with Tailored Gas Mixtures & Extended Driver Sections

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

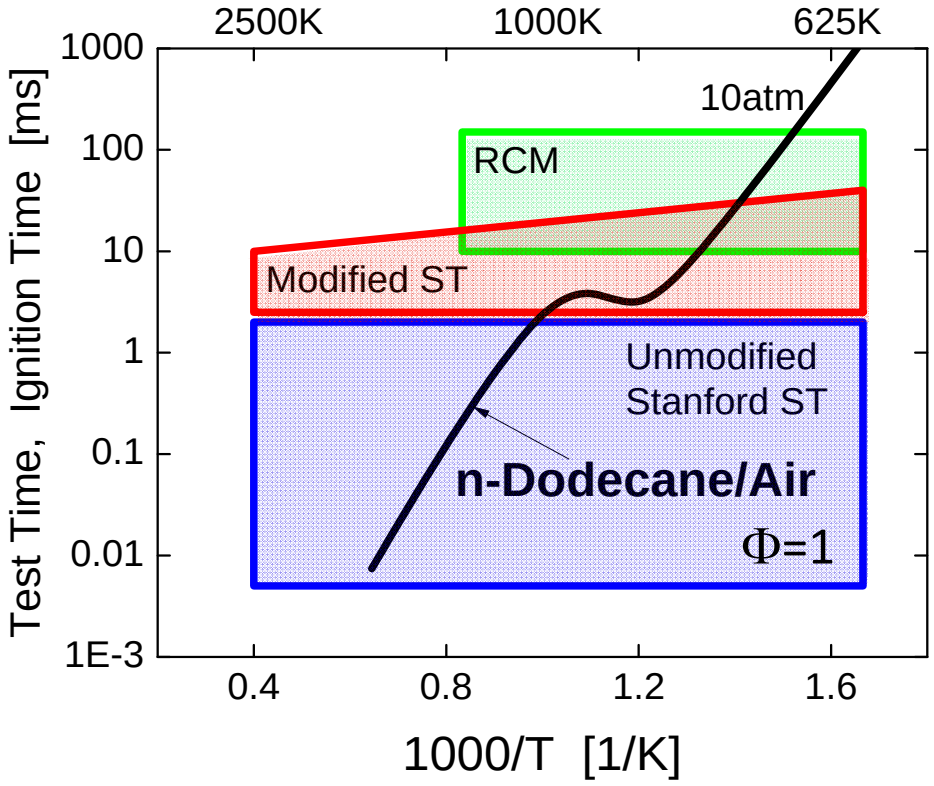


Longer Test Times Achievable with Tailored Gas Mixtures & Extended Driver Sections

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



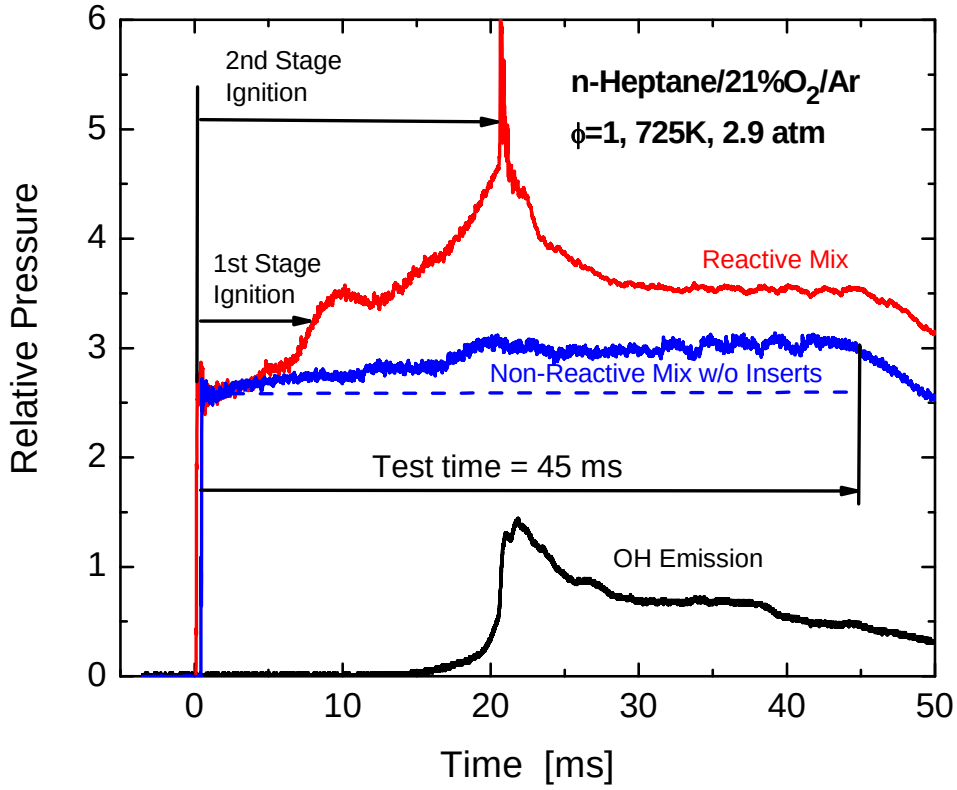
2x Driver Extension



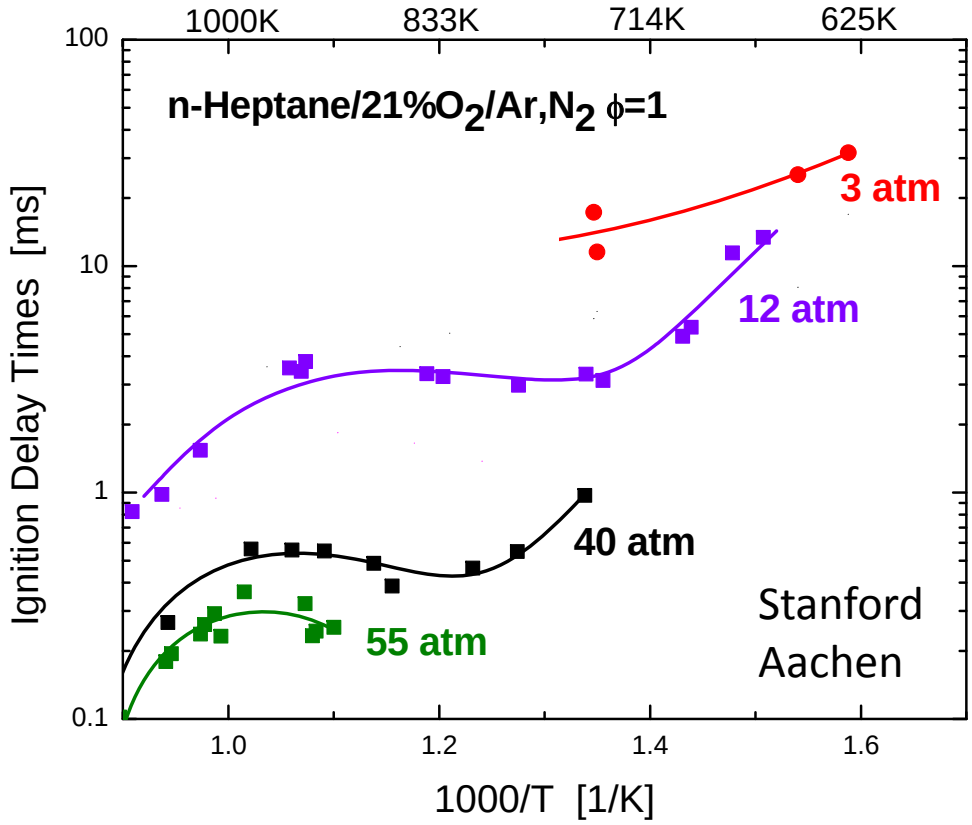
- **Shock tubes now can overlap with RCMs**

First Use of Long Test-Time Facility: Low Pressure n-Heptane Ignition in the NTC regime

- **Test time = 45 ms at 725K**
- **Enables first low-pressure (~3 atm) n-heptane ignition data in NTC regime**
- **Clear evidence of 2-stage ignition: τ_1 = 8 ms, τ_2 = 20 ms**
- **Next step: add driver inserts to remove *d*P/*d*t & *d*T/*d*t**
- **How do the 3 atm data compare to high P data?**

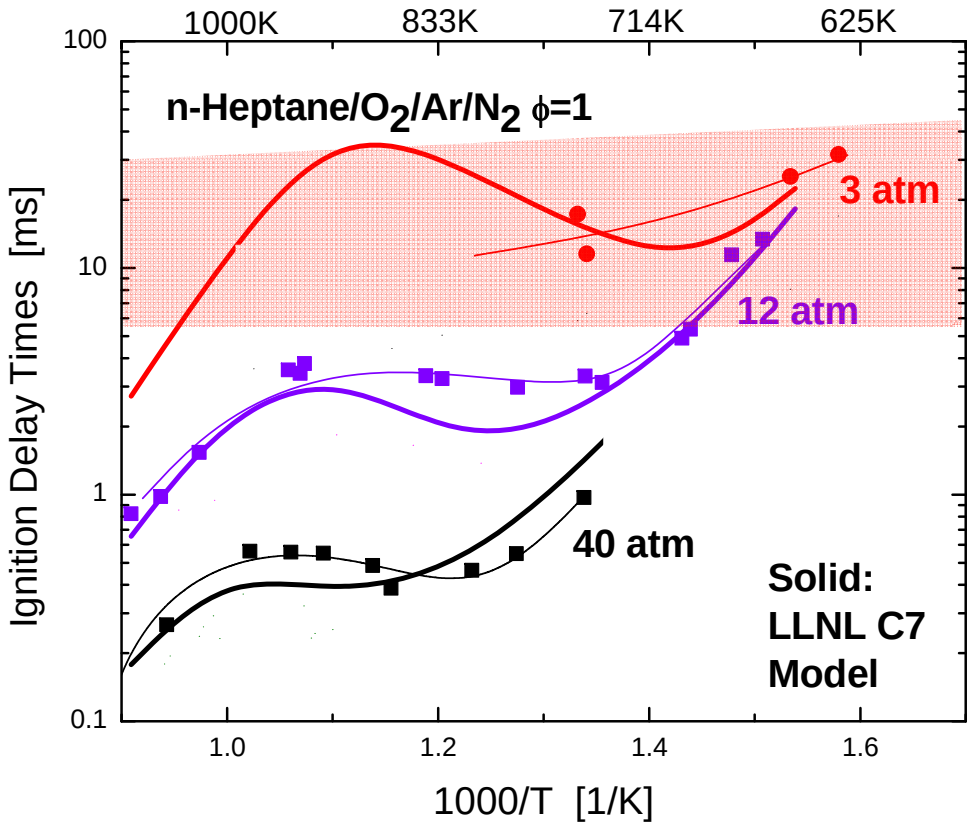


Low-Pressure, Low-Temperature Studies: New Results for n-Heptane in the NTC Regime



- Previous 12-55 atm data
- New 3 atm data
- How do measurements compare with current models?

Low-Pressure, Low-Temperature Studies: NTC Heptane, Comparison with Model



- LLNL C7 (2000) model performs reasonably well at high P
- Further tests needed at low P
- Reveals value of long test time experiments

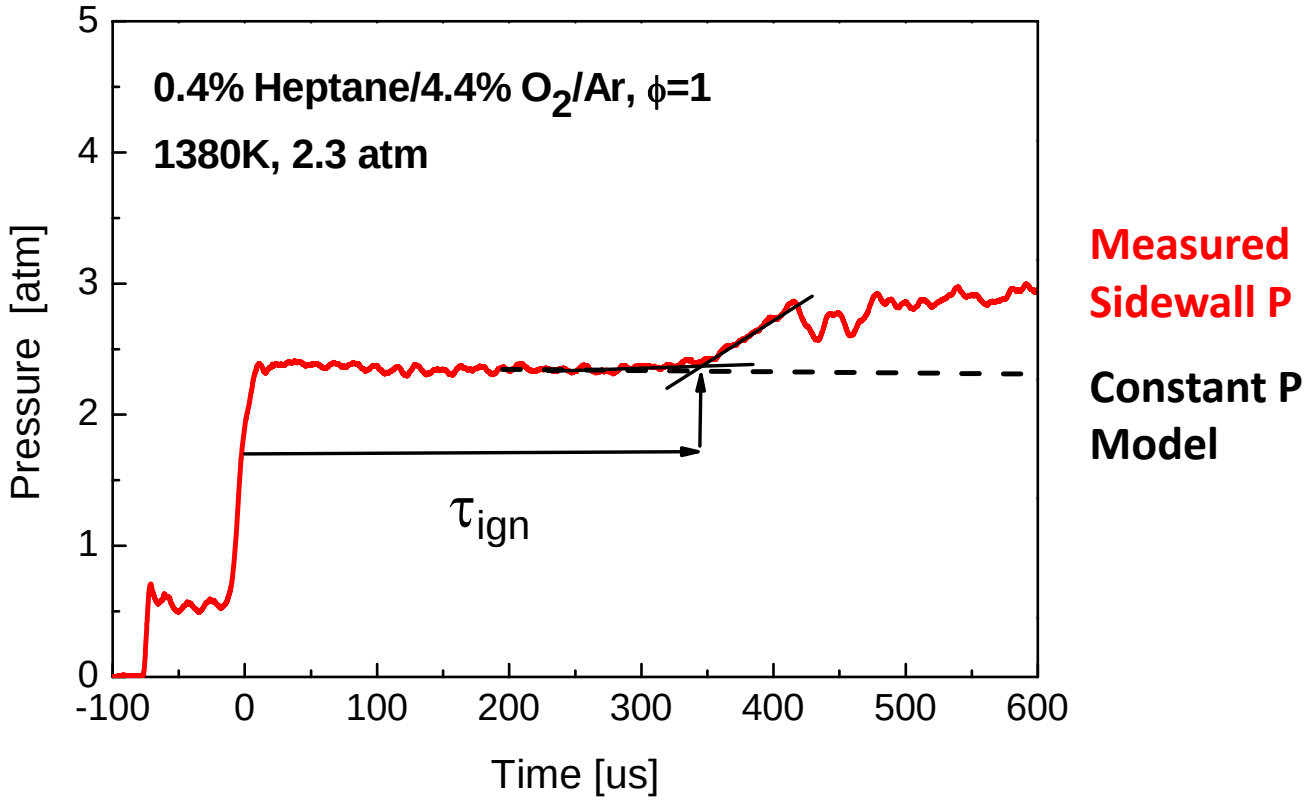
Reactive Gasdynamics Modeling: A Problem

- **Most current reflected shock modeling assumes Constant-Volume or Constant-Pressure**

But:

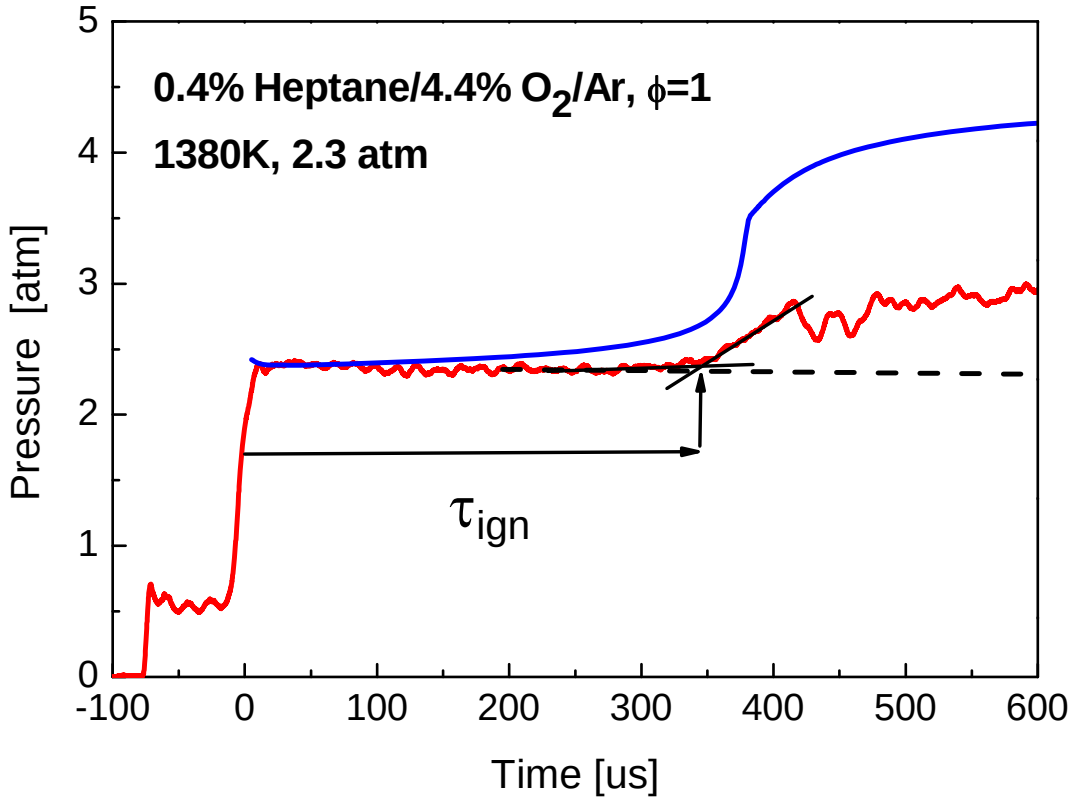
- **<u>Exothermic</u> energy release during oxidation or <u>endothermic</u> cooling during pyrolysis changes T & P behind reflected shocks**
  → not a Constant-V or Constant-P process!
- **Example: Heptane Ignition**

Effect of Energy Release on P Profiles: n-Heptane Oxidation



- **How does this compare with models?**
- **Not a constant P process!**

Effect of Energy Release on P Profiles: n-Heptane Oxidation



Constant V Model

Measured Sidewall P

Constant P Model

- How does this compare with model?
- Not a constant P process!
- Not a Constant-V process, even for 0.4% fuel!
- So how can entire process be modeled?

3 Proposed Solutions to Enable Modeling through Entire Combustion Event

1. **Minimize fuel loading to reduce exothermically- or endothermically-driven T and P changes**
   - enabled by high-sensitivity laser diagnostics

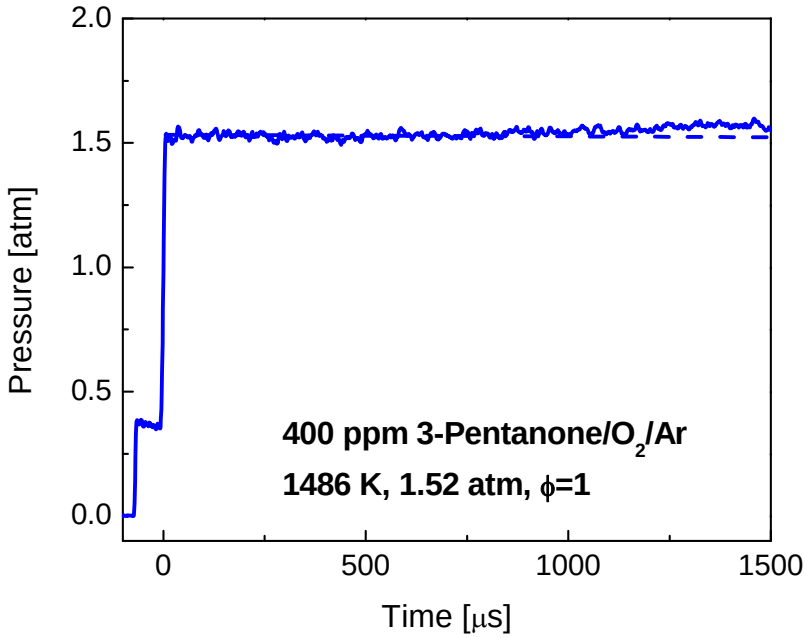
2. **Modified gasdynamics modeling to account for P and T change during combustion**
   - work in progress (but computationally intensive: 1-D, 3-D)

3. **Use new constrained reaction volume concept to minimize pressure perturbations**
   - enables constant P (or specified P) modeling

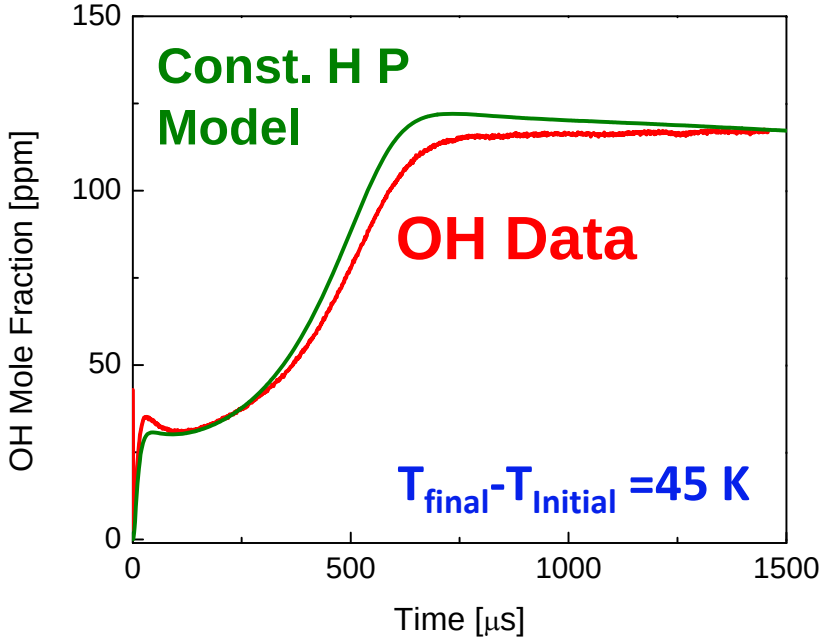
Examples: **1) Use of dilute reactive mixtures**
2) Use of constrained reaction volume

Example 1: Benefit of Dilute Mixtures
3-Pentanone Oxidation

Low Fuel Loading Experiment

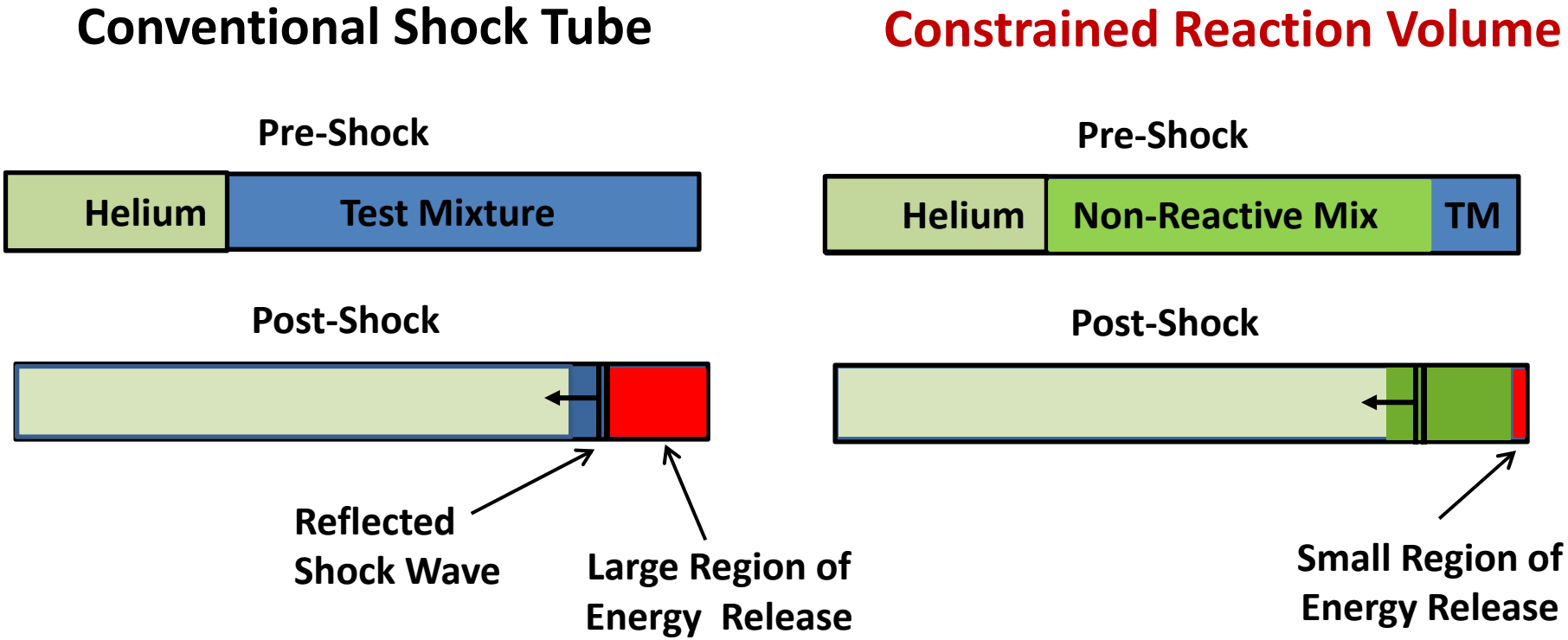


OH Mole Fraction



- Pressure nearly constant throughout experiment
- Good agreement between Constant H,P model and expt.
- Model successfully includes temperature change

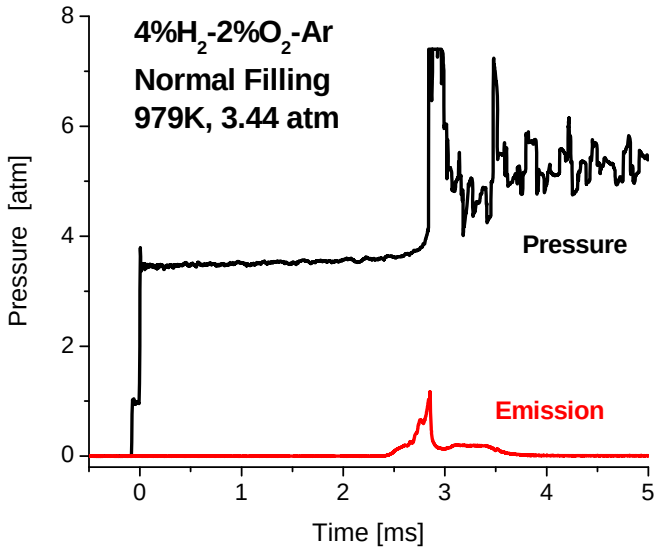
Example 2: Constrained Reaction Volume Approach
Hydrogen Ignition at 950 K



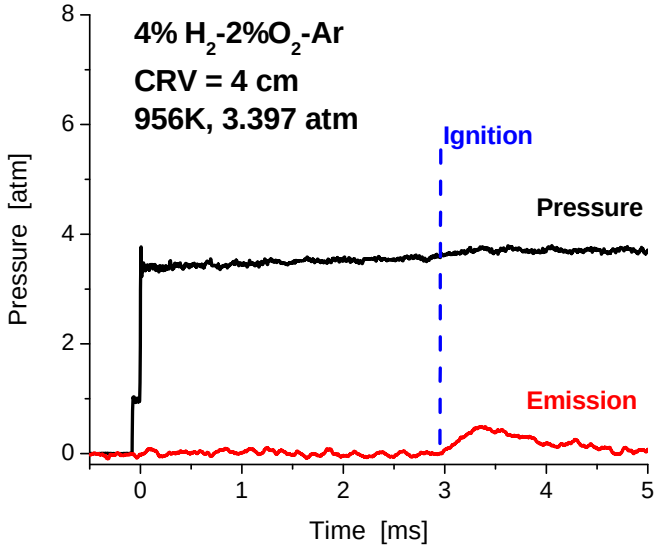
- Large reaction volume gives large energy release → ΔP & ΔT
- CRV gives reduced energy release → near-constant P

Example 2: Constrained Reaction Volume Approach Hydrogen Ignition at 950 K

Conventional Shock Tube



Constrained Reaction Volume



- **Conventional ST exhibits large pressure change!**
- **CRV pressure nearly constant throughout experiment!**
- **Allows kinetics modeling through ignition and combustion!**

Elementary Reaction Rate Determinations

Goal

Near-direct determination of rate constants for specific reactions

Examples

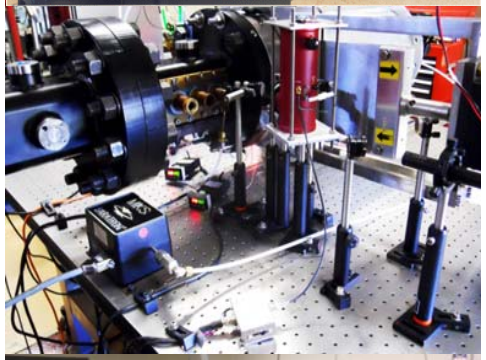
OH + ketones:

acetone, 2-butanone, 2- & 3-pentanone

OH + alkanes

OH + butanol isomers

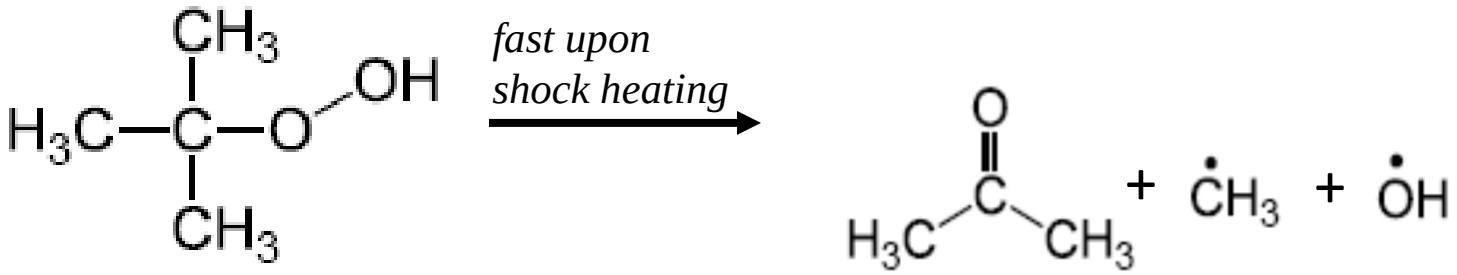
OH + methyl esters



Experimental Strategy

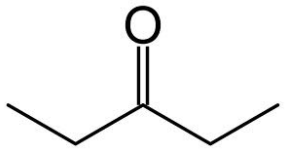
- **TBHP used as a prompt OH precursor**
  - **Useful T range (850 to 1350 K)**
  - **Pioneered by Bott and Cohen (1984)**
  - **Also used at Argonne**

- **Fuel in excess, pseudo-first order experiment**

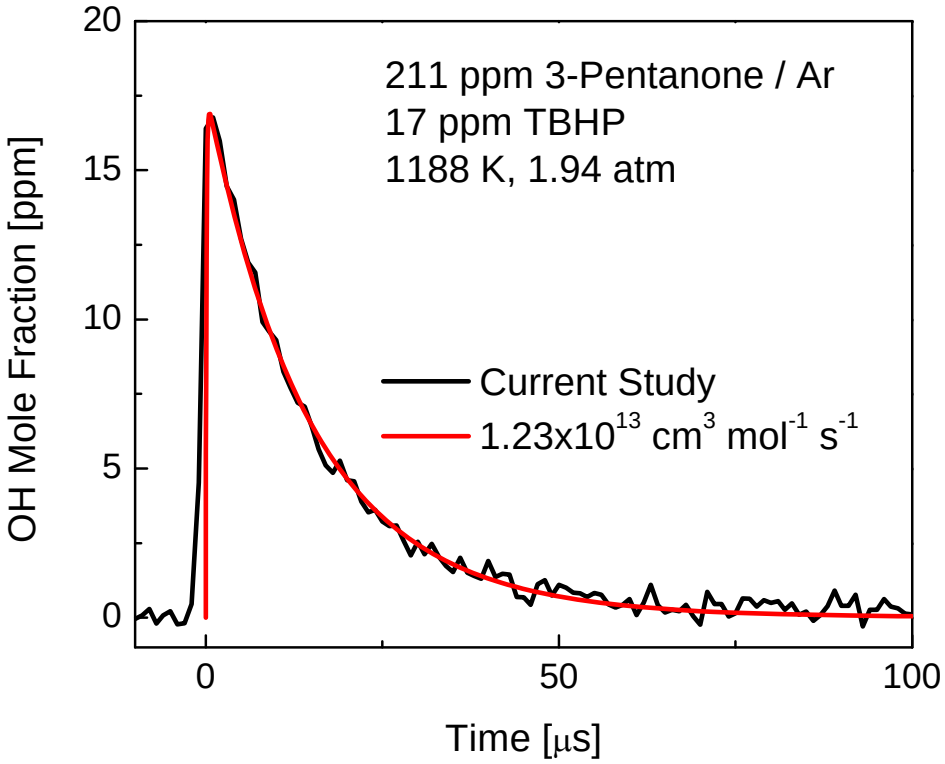


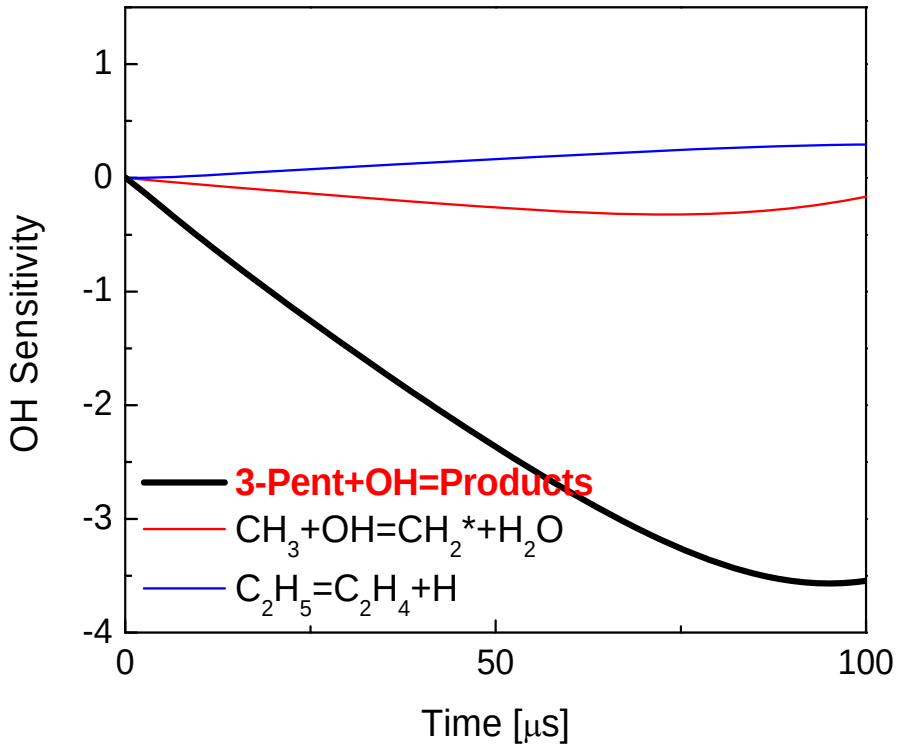
tert-butylhydroperoxide

Acetone



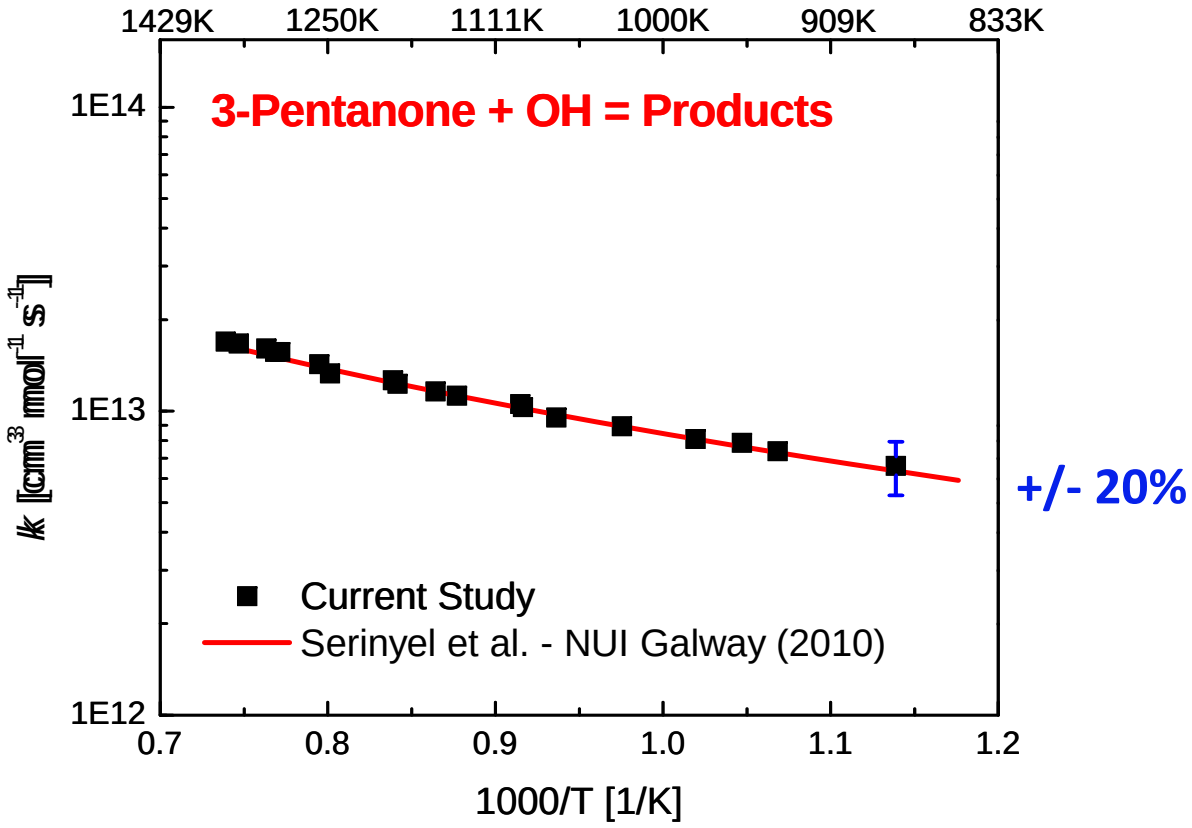
Representative 3-Pentanone+OH Data: 1188 K and 1.94 atm





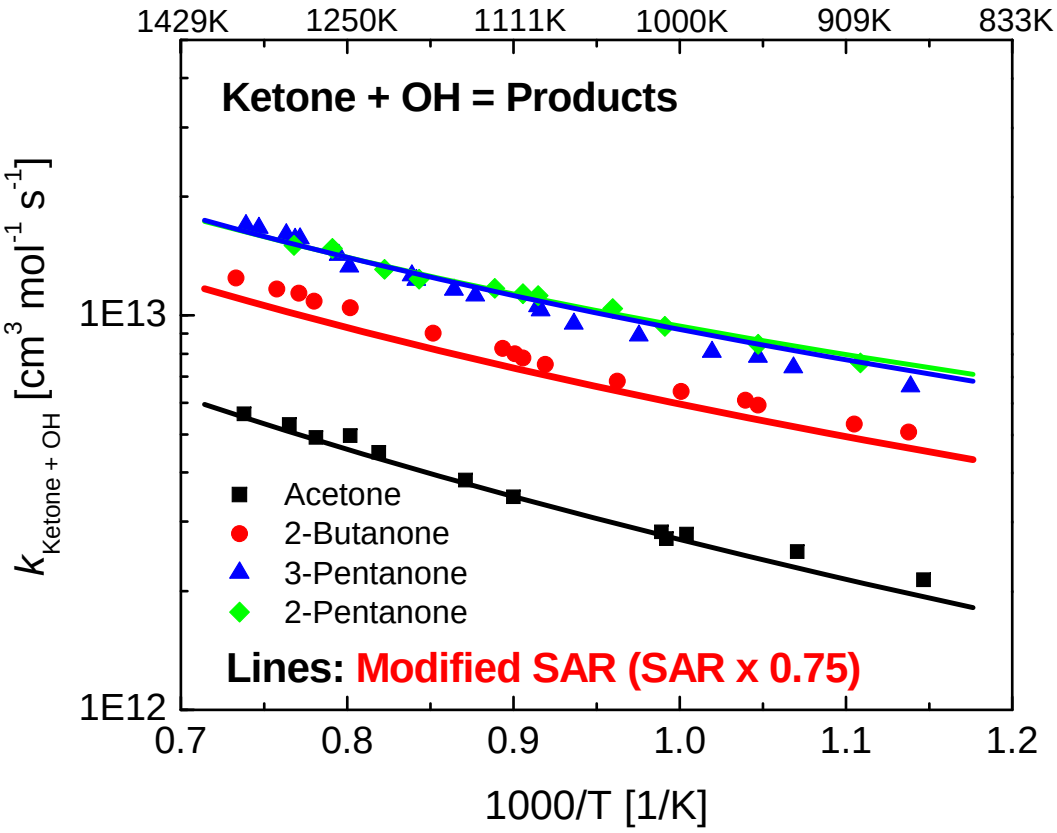
- **High-quality data allows high-precision comparison with model**
- **Sensitivity analysis confirms pseudo-first order behavior**
- **Near-direct determination of reaction rate constant!**

Results for 3-Pentanone + OH → Products



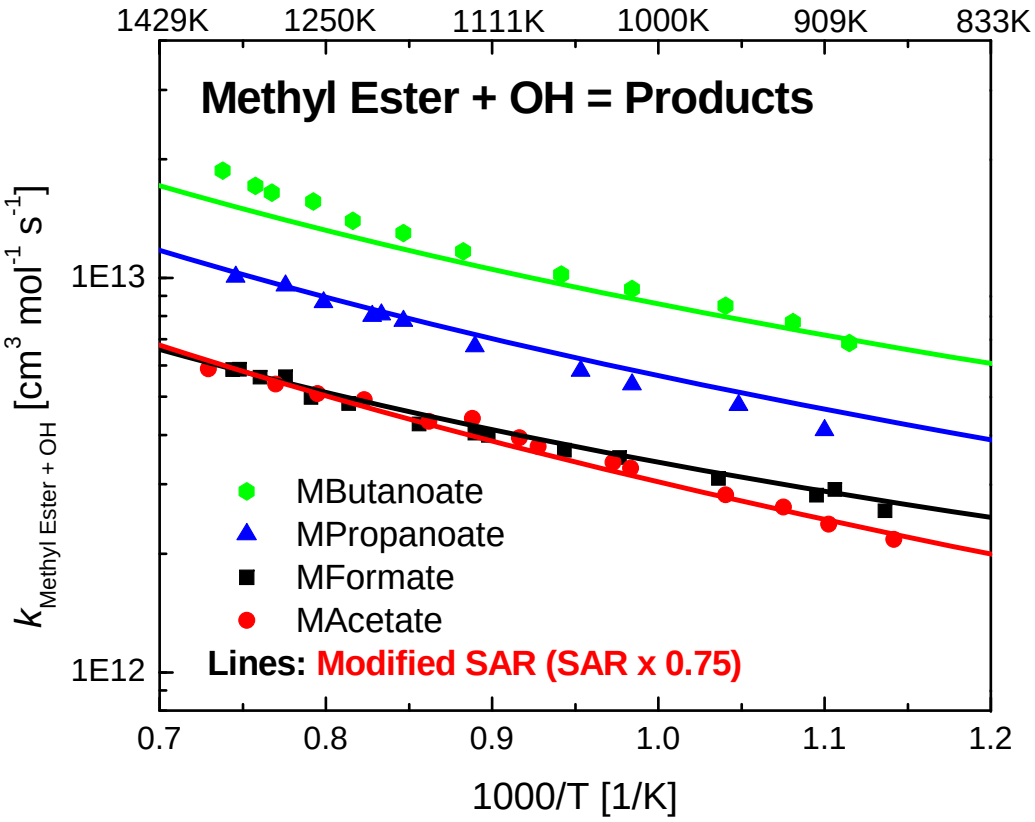
- **No other high temperature data available**
- **NUI model (Serinyel et al.) in excellent agreement**

Summary: OH+Ketones→Products



- **How do data compare with Structural Activity Relationship (SAR) model?**
- **Data agree within 25% with SAR-estimated rate constants**
- **Similar measurements performed with methyl esters**

Summary: OH+Methyl Esters → Products



- **Data agree within 25% with SAR-estimated rate constants**
- **Current work: OH + aldehydes, alcohols**

Multi-Species Time-Histories

Motivation

Multi-species provide greater constraint on mechanism refinement/evaluation

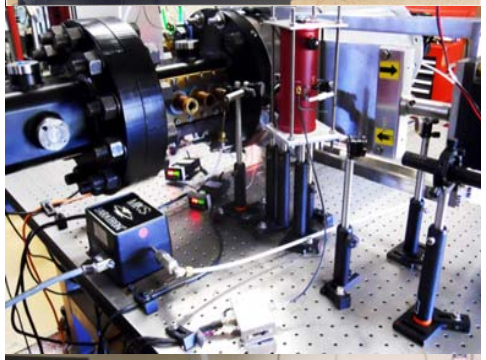
Recent Work

Ketones: Acetone, Butanone, 3-Pentanone

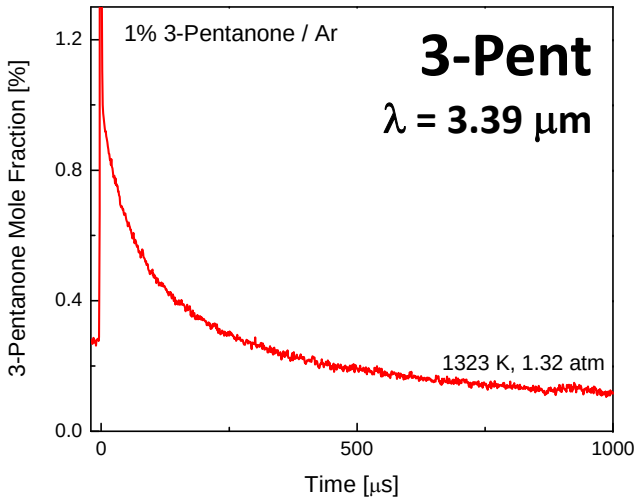
Alcohols: 1-, 2-, tert-,& iso-Butanol

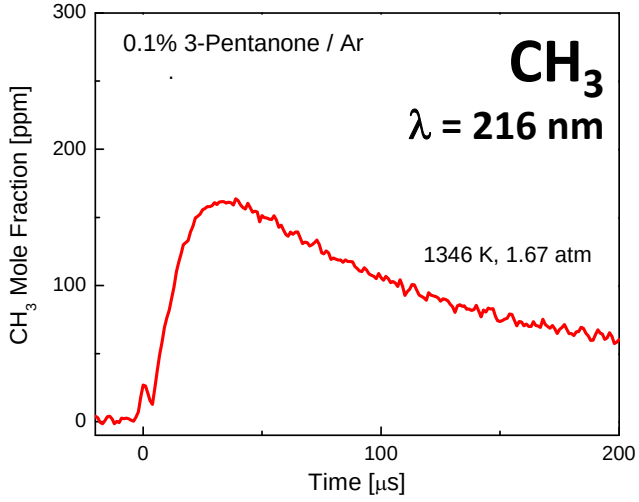
Alkanes: n-Hexadecane

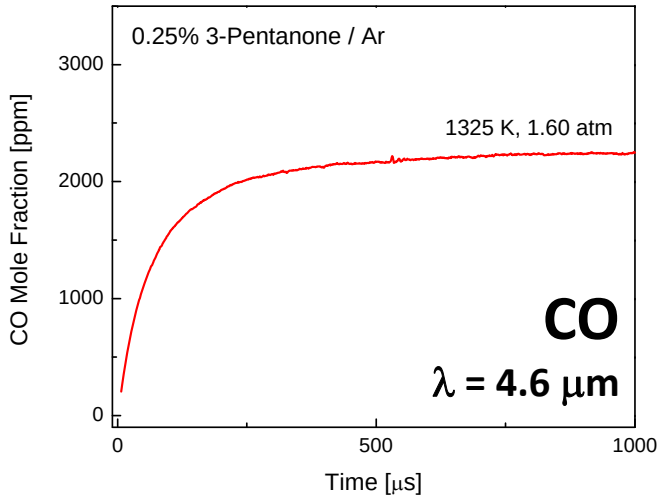
Esters: Methyl Formate, MA, MP, MB, EP

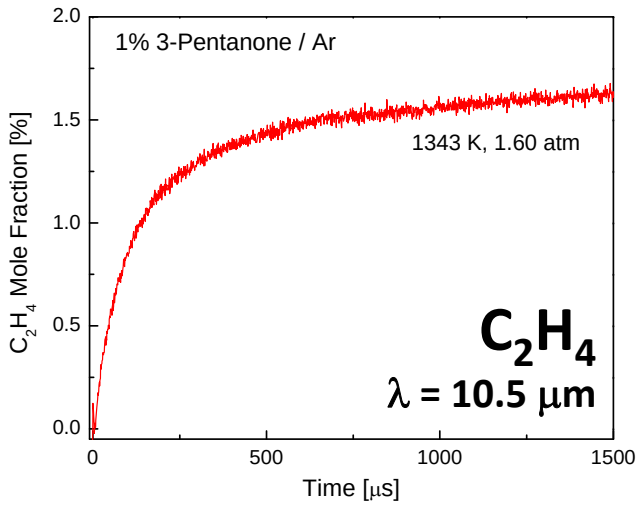


Multi-Species Approach: 3-Pentanone Pyrolysis



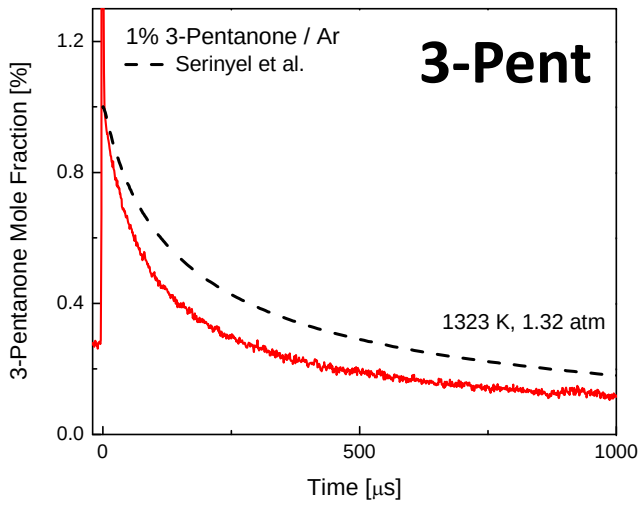


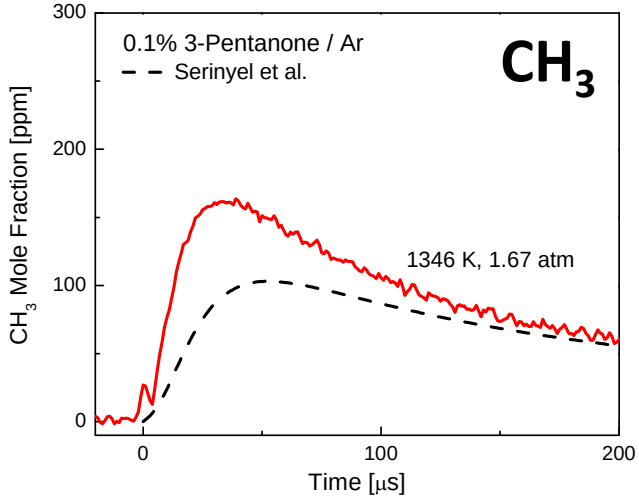


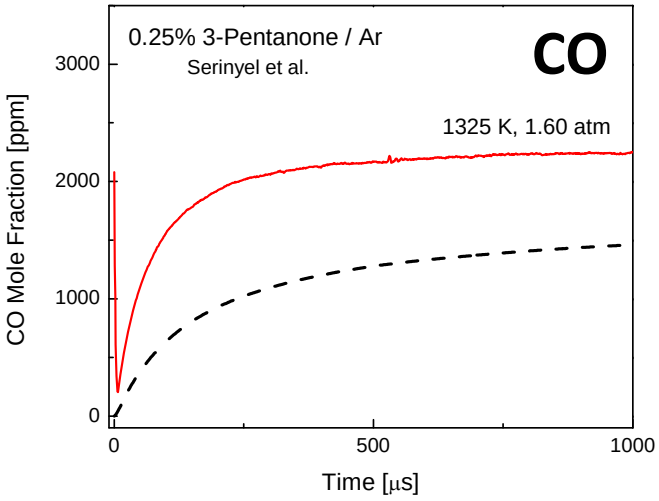


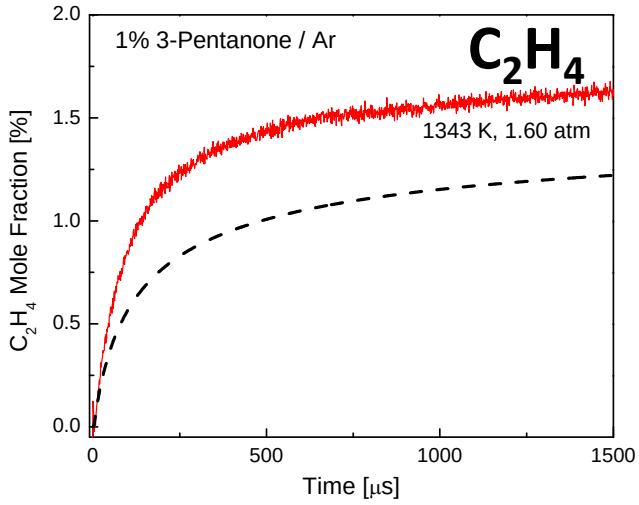
Excellent SNR, high sensitivity data

Comparison with Serinyel et al. (2010) Galway NUI





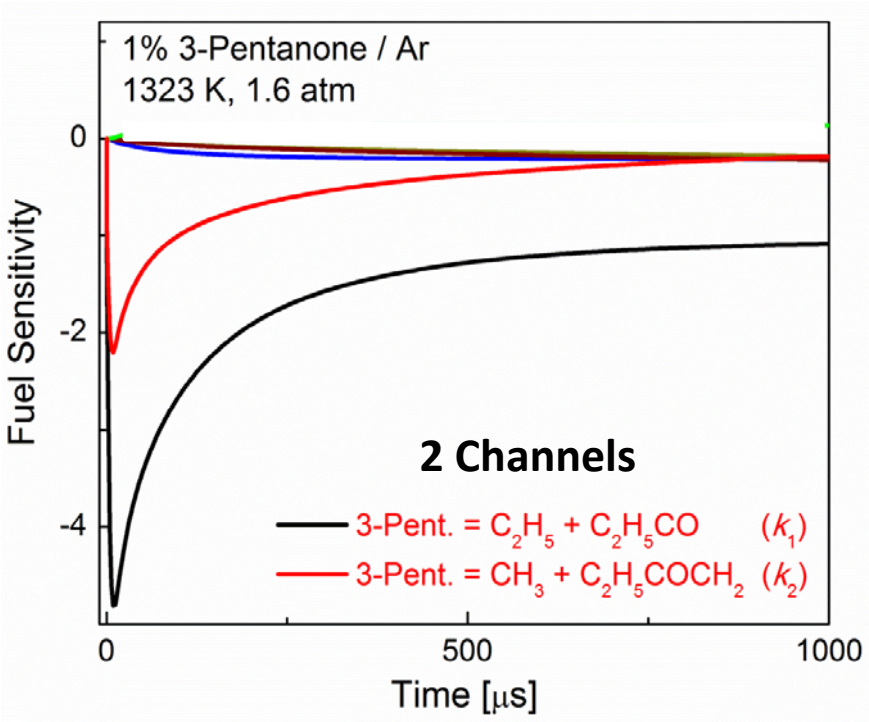




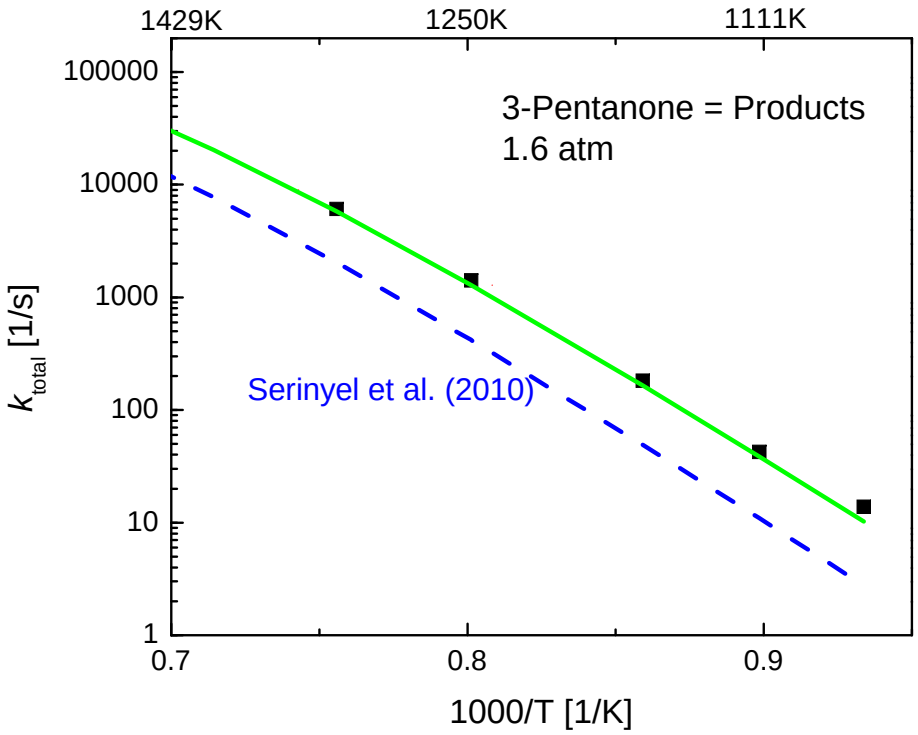
Two Differences: 1) 3-P decomposition rate; 2) CO/C_2H_4 yields

3-P Data Enables Revision of Decomposition Rate

3-Pentanone Sensitivity



Arrhenius Plot: 3-Pent → Products

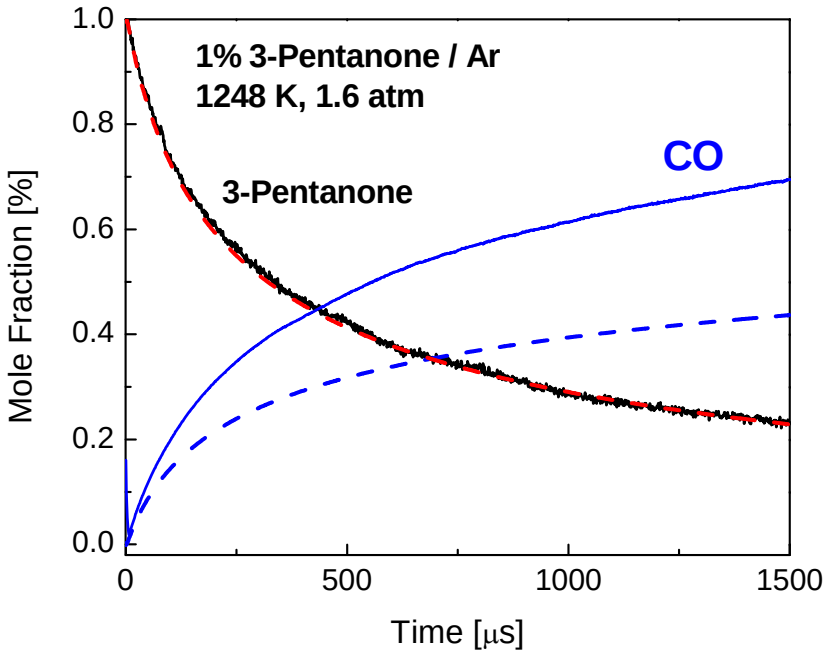


- 3-P data show strong sensitivities to $k_1 + k_2$

- Revised k_{total} 3.5x Serinyel et al. rate
- CO yields still not correct!

CO Yield Resolved through Use of O-Atom Balance

3-P and CO data yield total O-atoms



O-atom concentration at 1.5 ms

Laser Absorption

3-Pentanone:	23%
CO:	69%
Sum:	92%

Simulation (with new k_1+k_2)

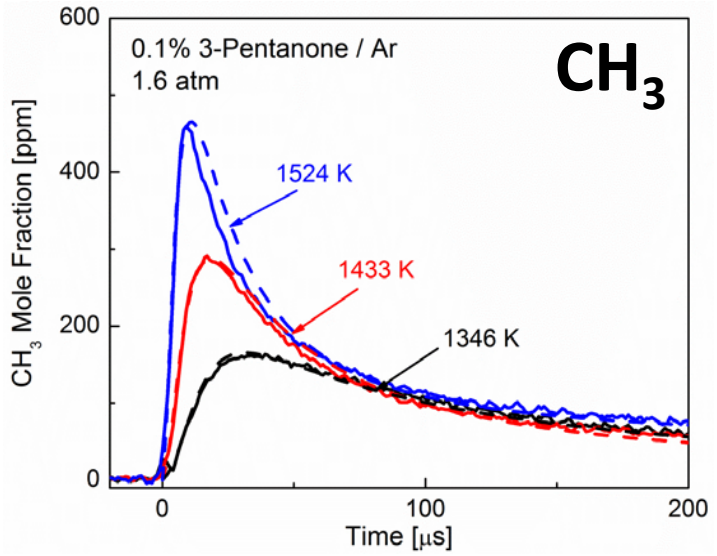
3-Pentanone:	23%
CO:	43%
CH_3CHCO:	27%
Sum:	93%

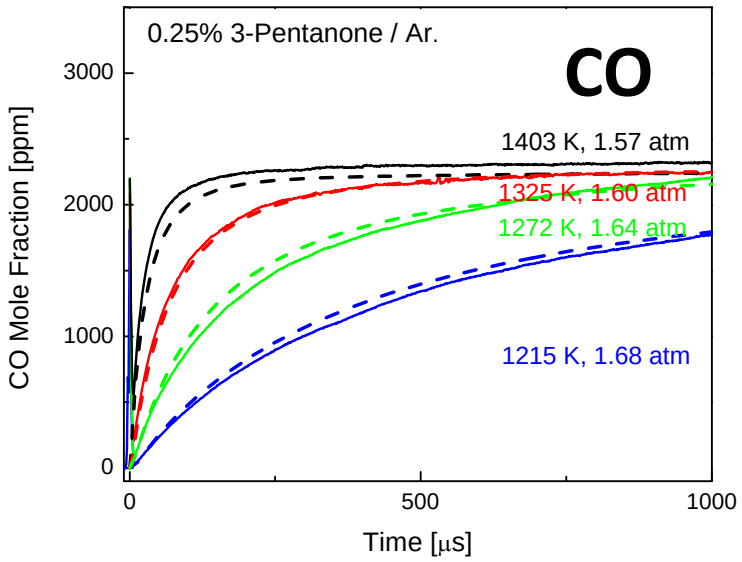
- Model underpredicts CO and overpredicts methyl ketene
- Why? Methyl ketene decomposition pathway missing in mechanism
- Introduce $CH_3CHCO \rightarrow C_2H_4 + CO$ (assume *k* the same as ketene decomp.)

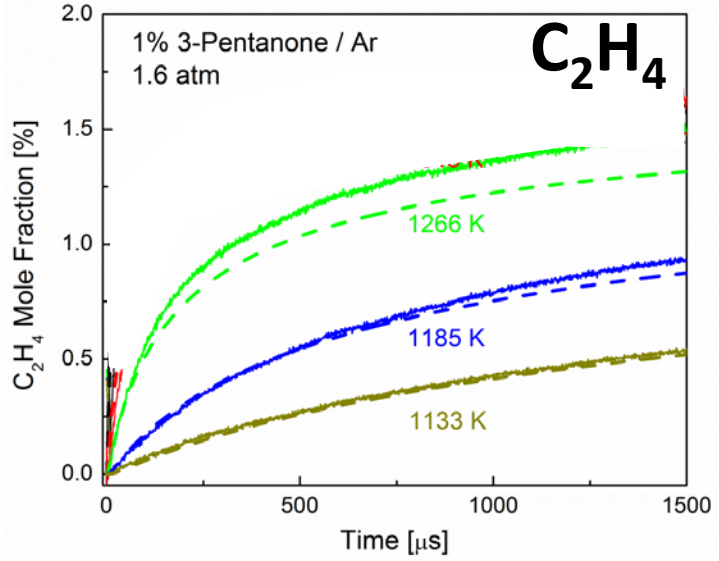
Revised Model Improves 3-P Simulations

Final Modifications to Serinyel et al. 3-Pentanone Mechanism

- **Revised decomposition rate: 3-pentanone → products**
- **Additional reaction: methylketene → C_2H_4 + CO**







- **Good agreement with 3-P, CH_3, CO, and Low-T C_2H_4 time-histories**

Ongoing Work

- **Diagnostics development & spectroscopy:**
  - **aldehydes (CH_2O, CH_3CHO)**
  - **alkyl radicals (C_2H_5)**
  - **methyl esters (methyl formate)**
  - **Alkenes (C_3H_6, C_4H_8)**

- **Continued improvement of shock tube methods:**
  - **constrained reaction volume**

- **Direct measurement of elementary reactions:**
  - **OH + oxygenates (aldehydes, ethers, alcohols)**
  - **decomposition of oxygenates**
  - **CH_3, HO_2 reactions with HC**

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