Species Time-Histories and Temperature Sensing at Elevated Pressures

Ronald K. Hanson

Dept. of Mechanical Engineering, Stanford University

- **Shock Tube Kinetics**
  - **Experimental Approach**
  - **Ignition Delay Times**
  - **Species Time Histories**
- **Temperature Sensing**
  - **Experimental Approach**
  - **CO_2-Based T Sensor**
  - **H_2O-Based T Sensor**
  - **Application Domains**

Some of the work presented here is unpublished. Please check with RKH/DFD before regarding the data as final or importing it into publications. We would also value feedback from team members regarding our data and how it might be modeled.

rkhanson@stanford.edu
dfd@stanford.edu

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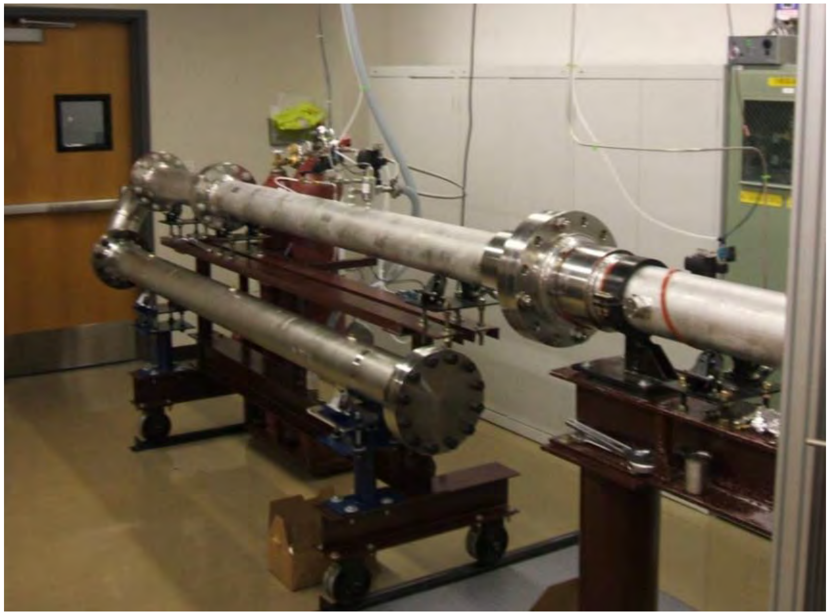
Shock Tube Kinetics: Experiment Types

Stanford STs provide access to pressures from 1 to 500+ atm

- **HP Ignition delay times provide global targets for engine models**

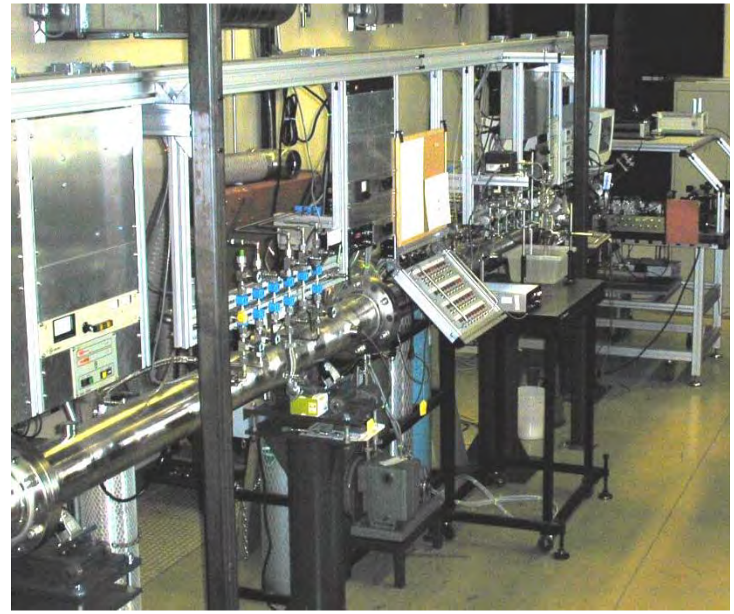
- **Species time-histories provide strong constraints on mechanisms**
  - **CW Laser absorption can provide species time-histories for: OH, CO, CO_2, CH_2O, H_2O, CH_3, CH_4, C_2H_4, MF, MeOH, NH_3, fuel, …**

- **Direct determination of elementary reaction rate constants**
  - **Provide *k* where estimates/theory are not sufficient**
  - **Provide access to high-pressure limit: k_∞**

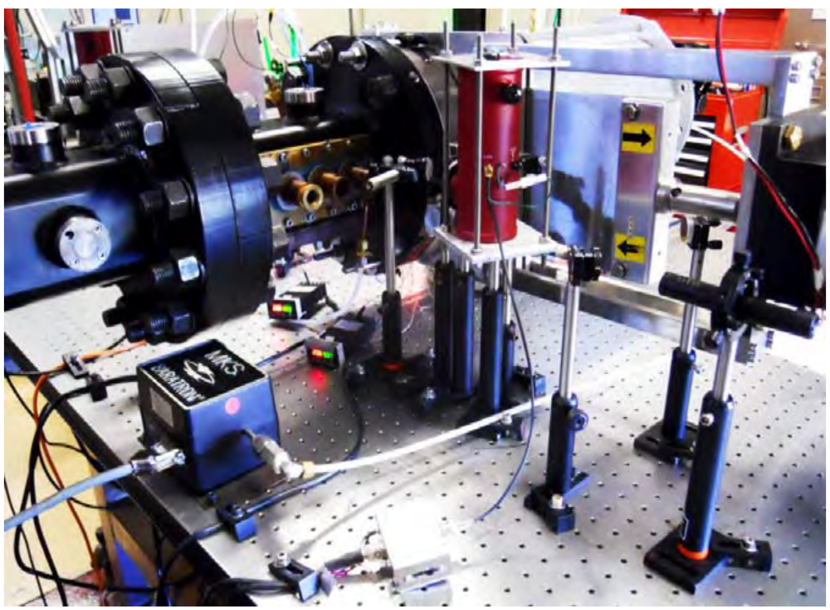


Kinetics Shock Tube 1 (30 atm)

Kinetics Shock Tube 2 (30 atm)



Experimental Approach



Aerosol Shock Tube (10 atm)

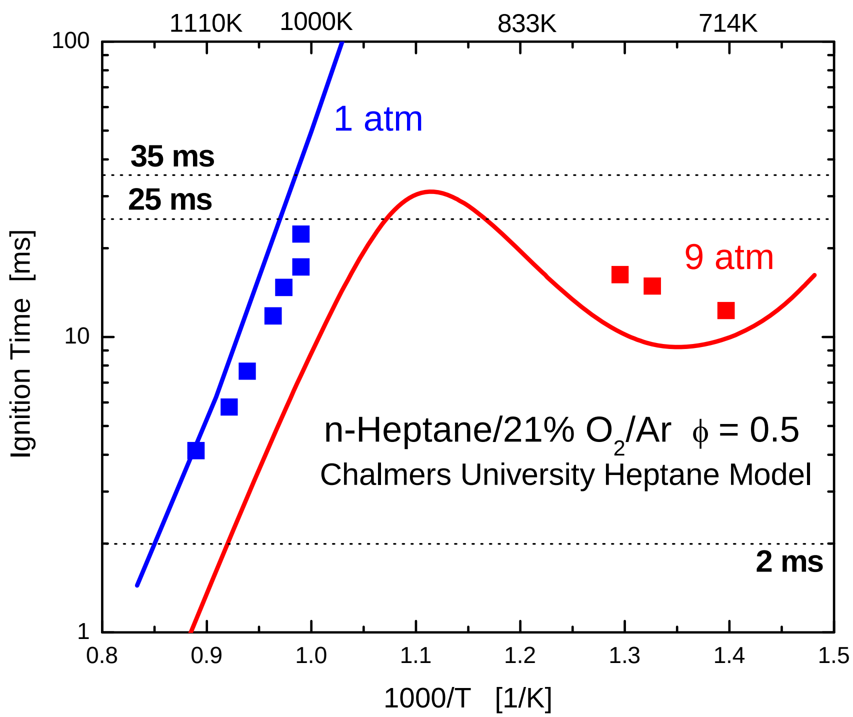
High Pressure Shock Tube (500 atm)

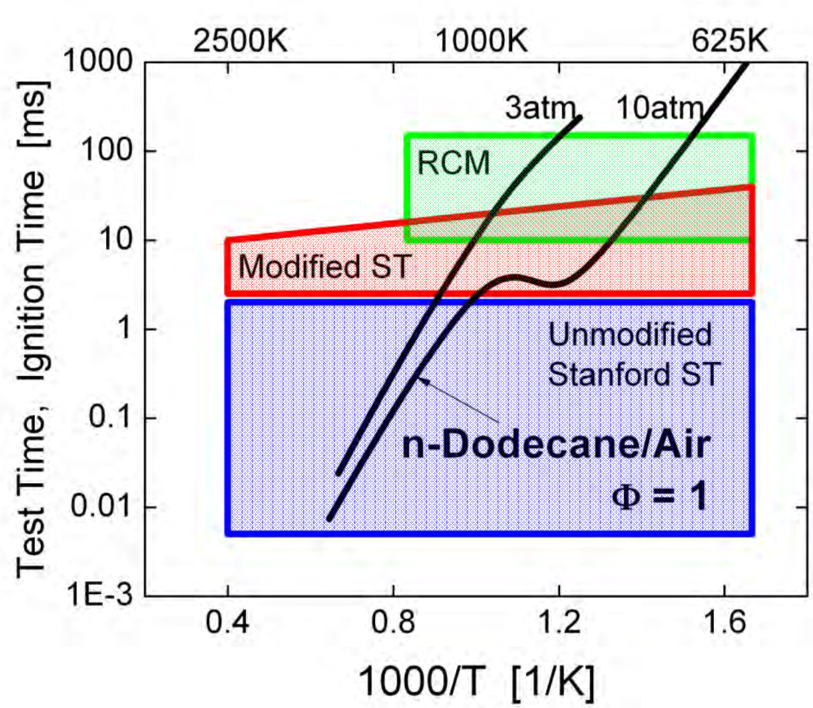
Advances in Shock Tube Methodology

- **Tailored driver gas/new driver geometry** provide extended test time for access to high P and low T
- **Driver inserts** provide highly uniform reflected shock conditions approaching constant U/V
- **Aerosol shock tube** provides access to low-vapor-pressure fuels
- **Gasdynamic modeling of shock tube flows** to account for facility effects and energy release

Access to High Pressure & Low Temperatures

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



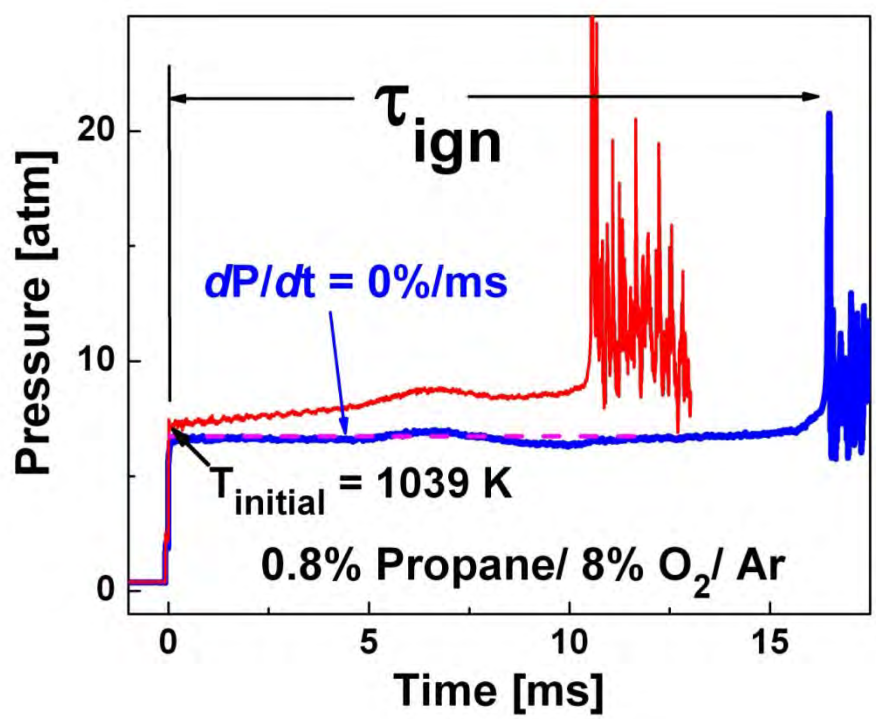


- Shock tubes now can overlap with RCMs

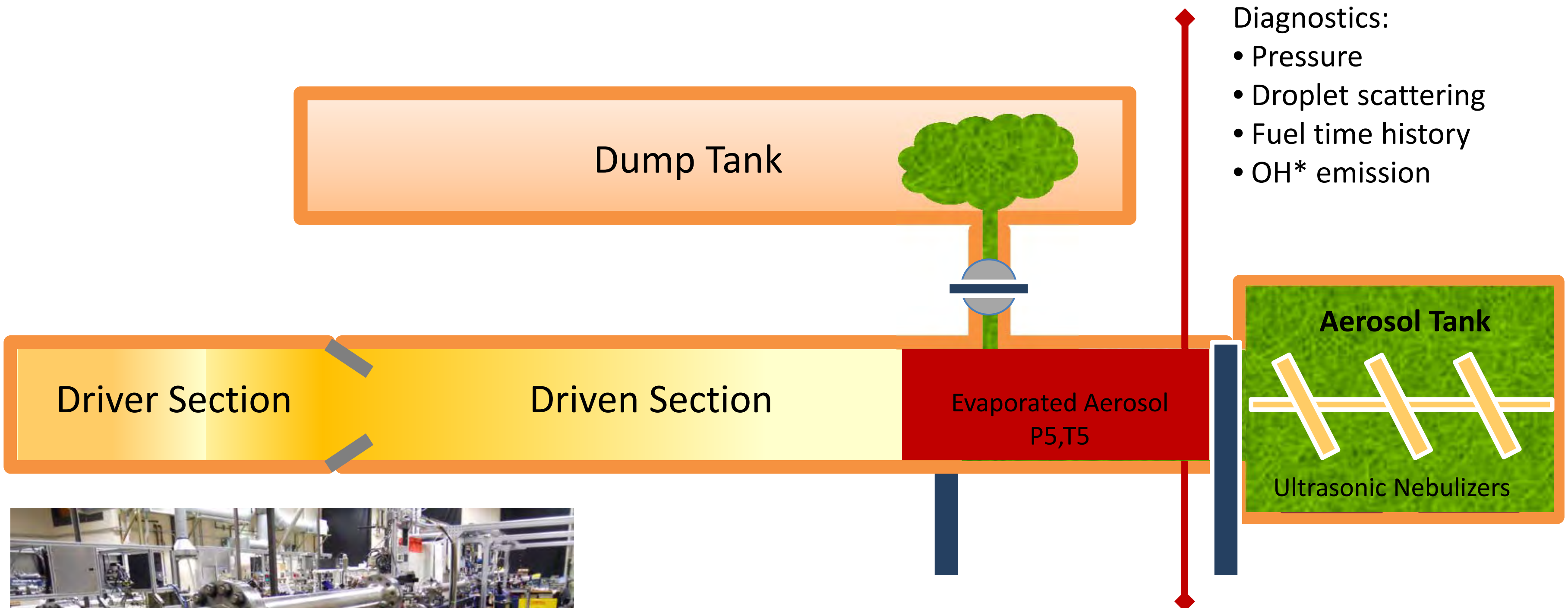
Improvement in Pressure & Temperature Uniformity

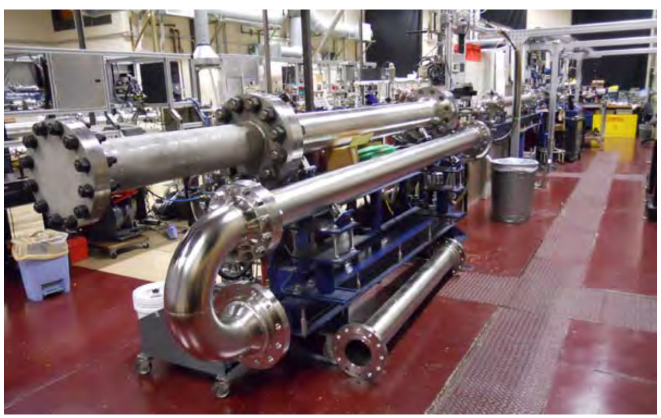
- **Problem:** Ignition delay times are artificially shortened by non-ideal facility effects!! dP/dt ≠ 0
- **Solution:** Driver Inserts
- **Results**: Near-ideal constant-volume performance!! dP/dt ≈ 0

dP/dt ≈ 0 for t > 17 ms



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 methyl esters, bio-diesel surrogates

Absorption Spectroscopy at High Pressures

Beer-Lambert Law (for absorption of monochromatic light)

- $T_\lambda = I/I_0 = \exp(-N_i\,\sigma\,L) = \exp\,(-\{X_iP/RT\}\,\sigma\,L)$
- $\mathbf{A}$ = absorption = $(1 - I/I_0) \sim \{X_iP/RT\}\,\sigma\,L$

At High Pressures

a) center of isolated lines $\sigma_{peak} \sim 1/\Delta\nu \sim T/P$

Hence $\mathbf{A} \sim X_iL$ **independent of P!**

b) broad spectral features $\sigma \approx$ constant

Hence $\mathbf{A} \sim X_iPL/T$ **increases with P!**

Current Laser Capabilities for Species Detection

for real-time, *in situ* sensing

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

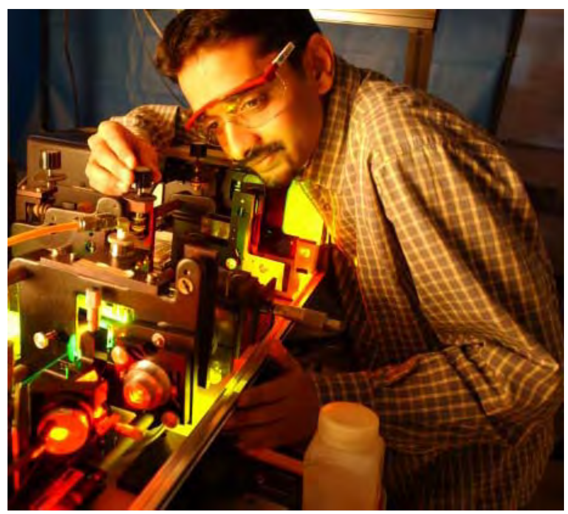
Visible

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

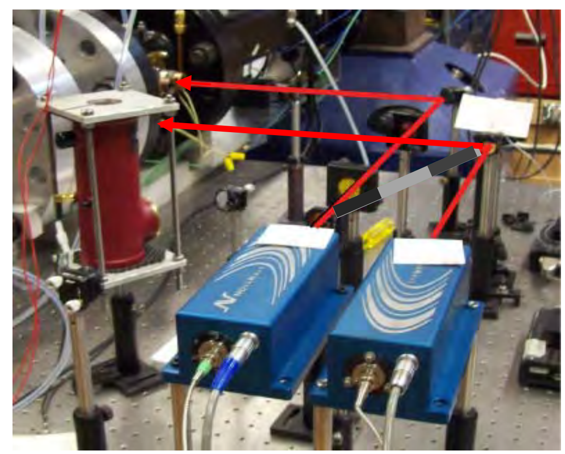
Infrared

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

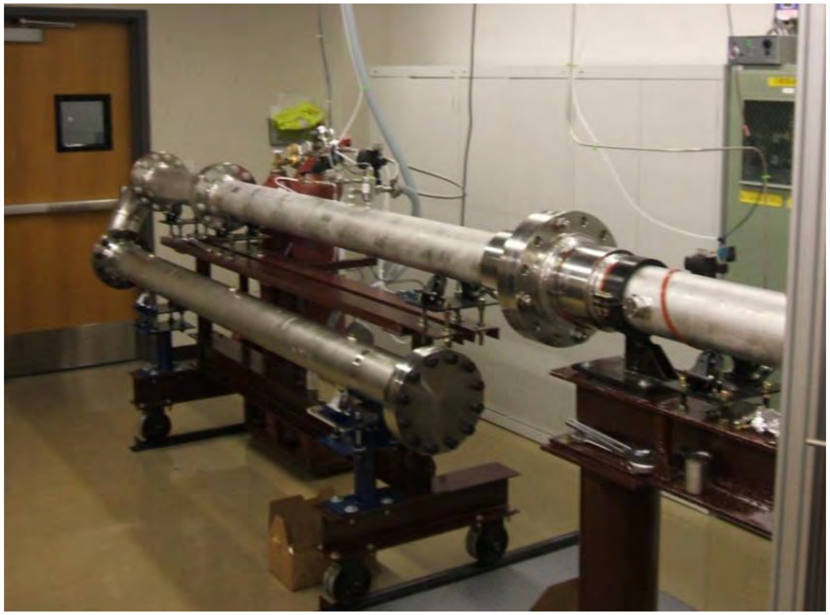
Coherent MIRA Ti-Sapphire

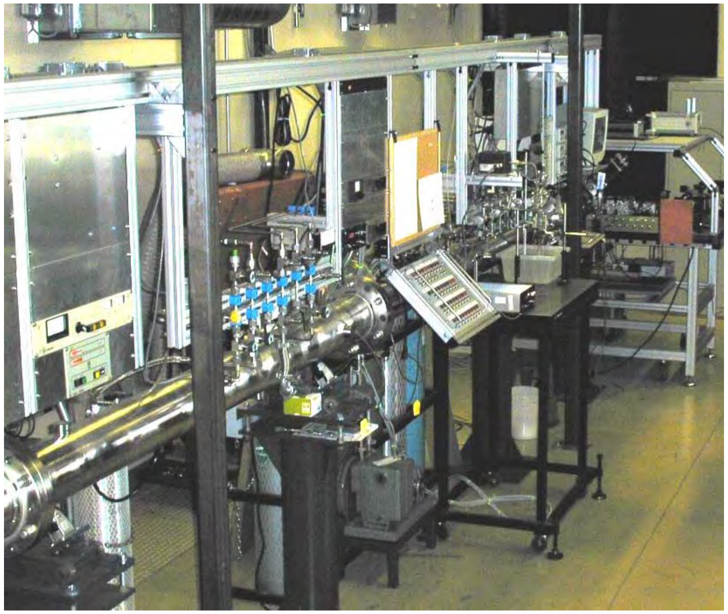


Spectra-Physics 380 Ring

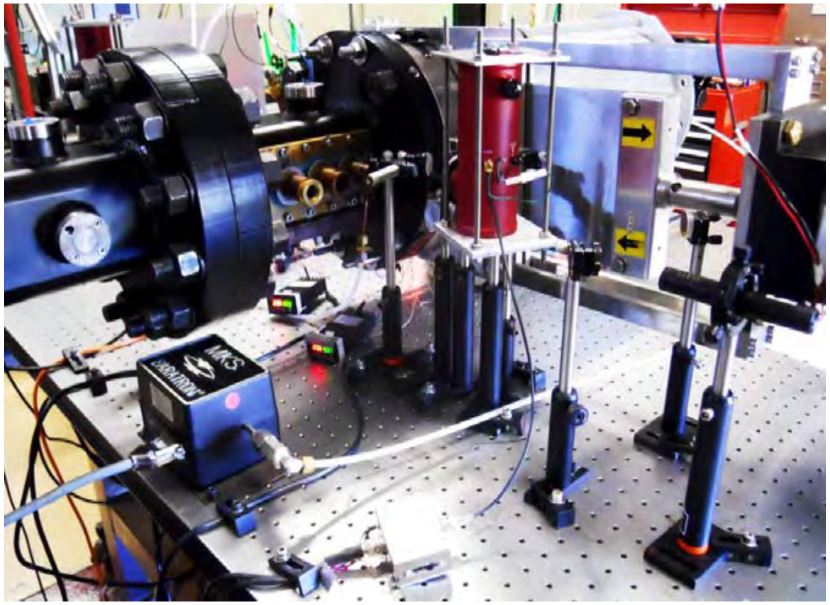


NovaWave Mid-IR DFG





HP Ignition Delay Time Data



Aerosol Shock Tube 10 atm

High Pressure Shock Tube 500 atm

HP Ignition Delay Time Data

2 Representative Examples

- **2-Butanol: 1-43 atm**
- **Methyl Oleate: 4-8 atm**

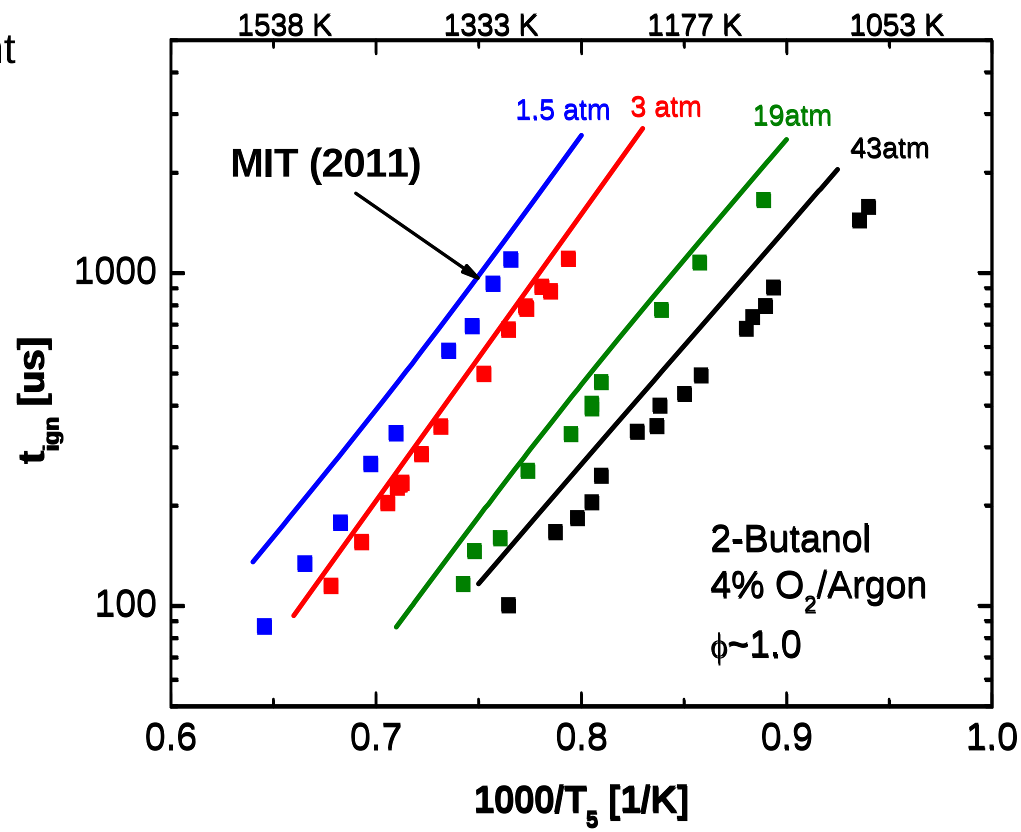
Ignition Delay Times:
2-Butanol Variation with Pressure in HPST

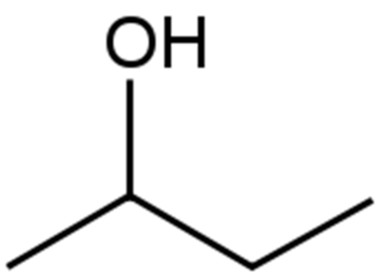
Very **low scatter** (± 5-10 %) consistent with uncertainty in T

Ignition delay times **scale approximately as $P^{-0.7}$**

MIT (2011) model P-dependence consistent with 2-butanol data

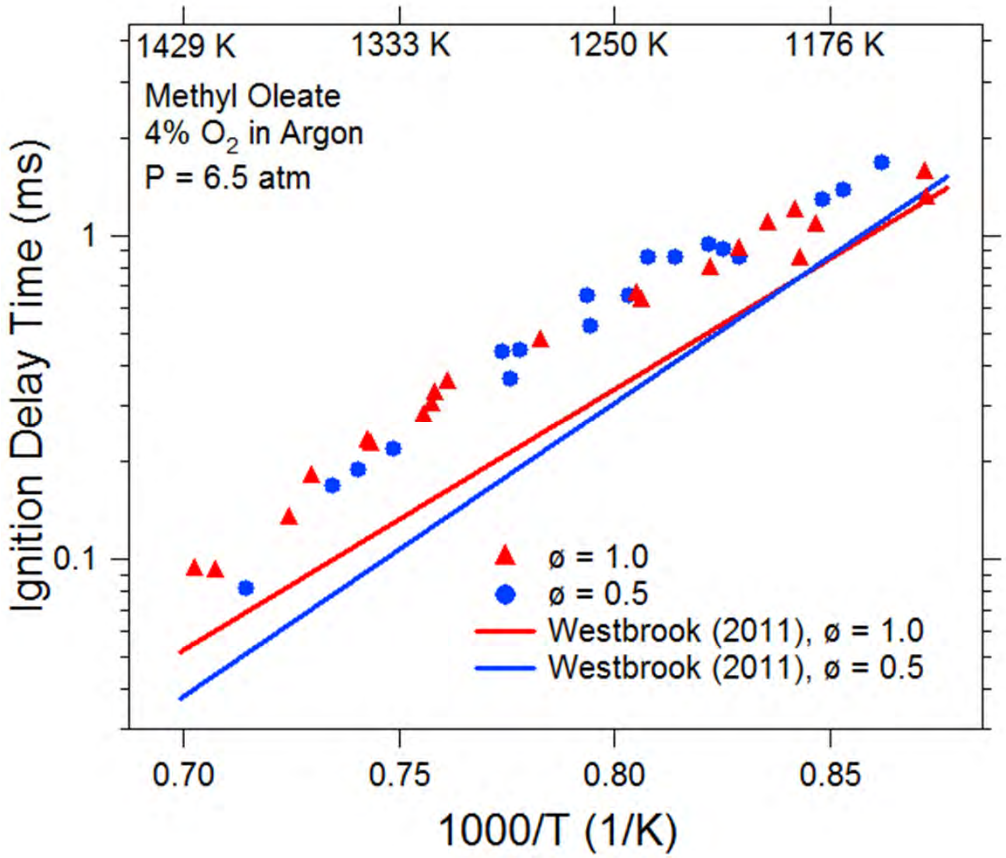
(but deviations larger than experimental uncertainty!)





2-Butanol

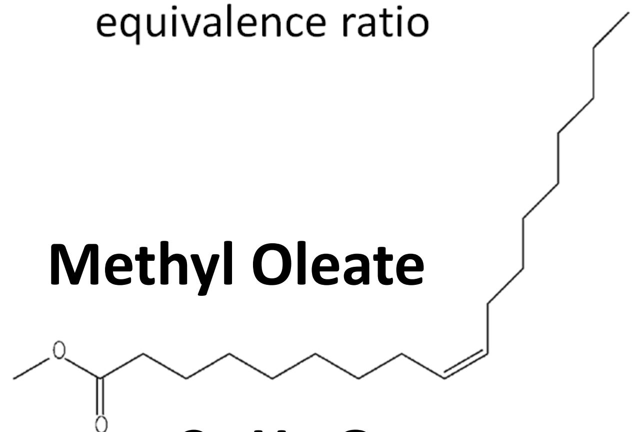
Ignition Delay Times: Methyl Oleate in Aerosol Shock Tube



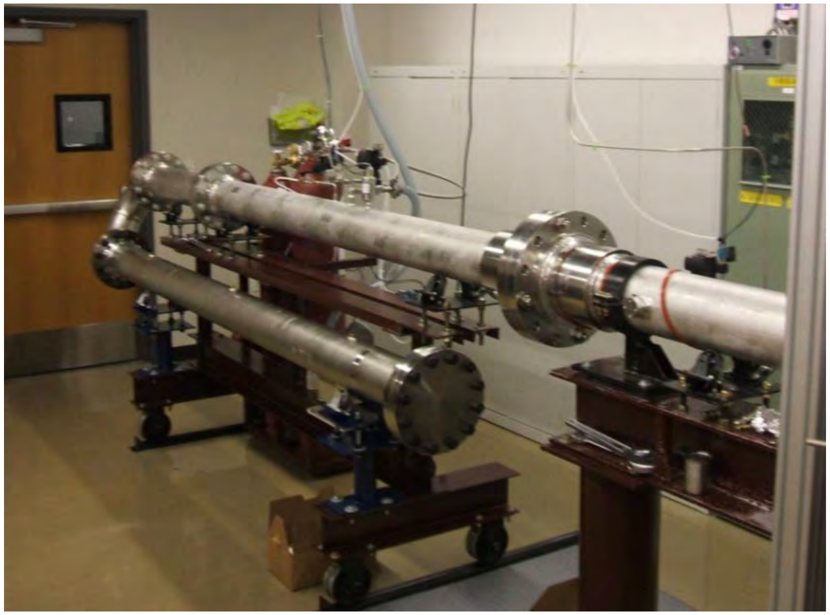
- Data reveal weak dependence on equivalence ratio

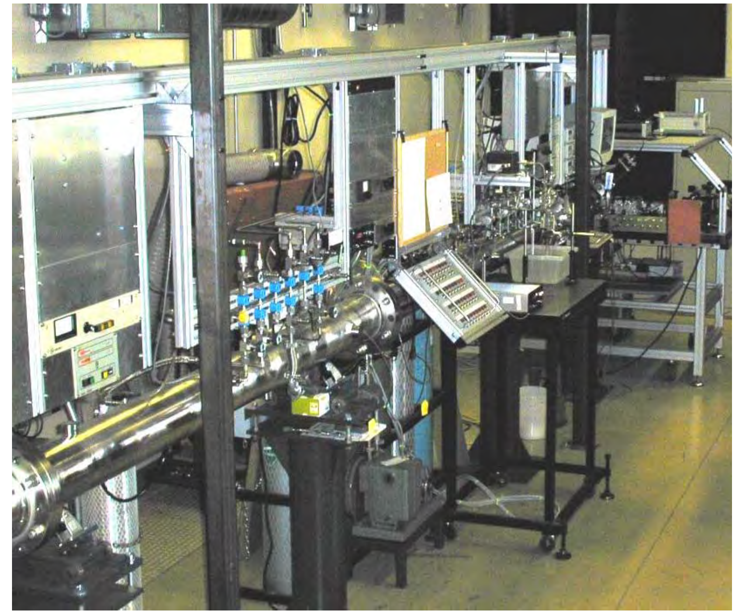
- **Westbrook model:**
- underestimates ignition delay times by about 50%
- But confirms weak dependence on equivalence ratio

Methyl Oleate

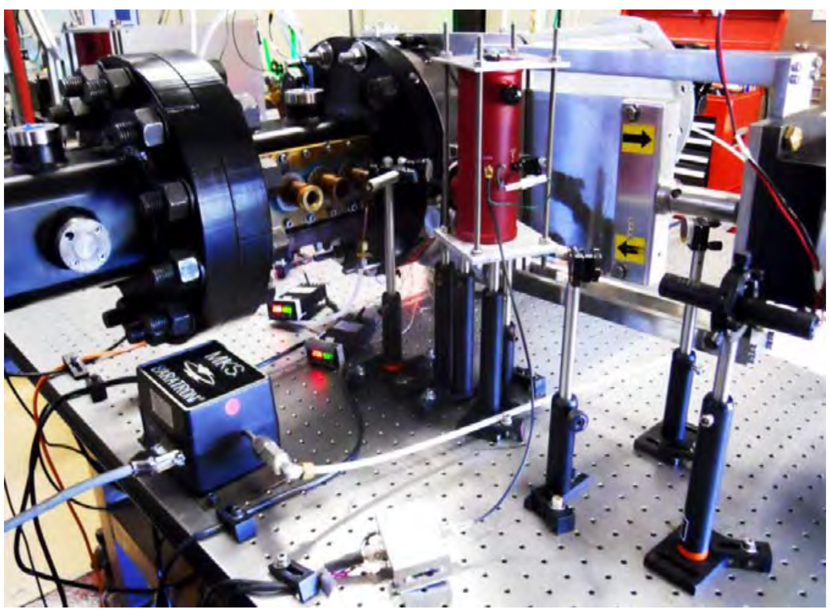


$C_{19}H_{36}O_2$





Species Time-History Data at High P



Aerosol Shock Tube 10 atm

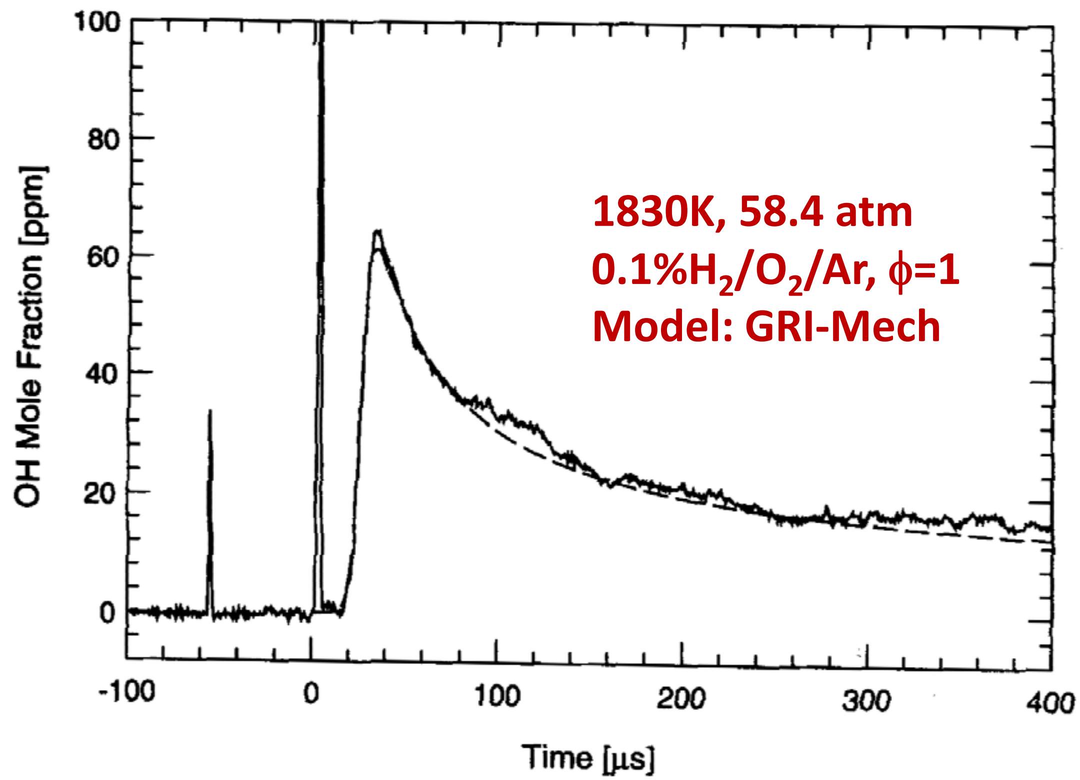
High Pressure Shock Tube 500 atm

Species Time-History Studies at Elevated Pressures

4 Representative Examples

- **OH species time-history during H_2/O_2 ignition** **(58 atm)**
- **OH species time-histories during jet fuel surrogate oxidation**:
  methylcyclohexane, n-dodecane, n-heptane **(17 atm)**
- **C_2H_4 and Fuel time-histories during jet surrogate pyrolysis**:
  n-dodecane, methylcyclohexane, iso-cetane **(15 atm)**
- **NO_2 emission time-histories during NO_2 pyrolysis**:
  Rate constant determination: $NO_2 \rightarrow NO+O$ **(380 atm)**

H_2/O_2 Ignition: OH Species Time-History

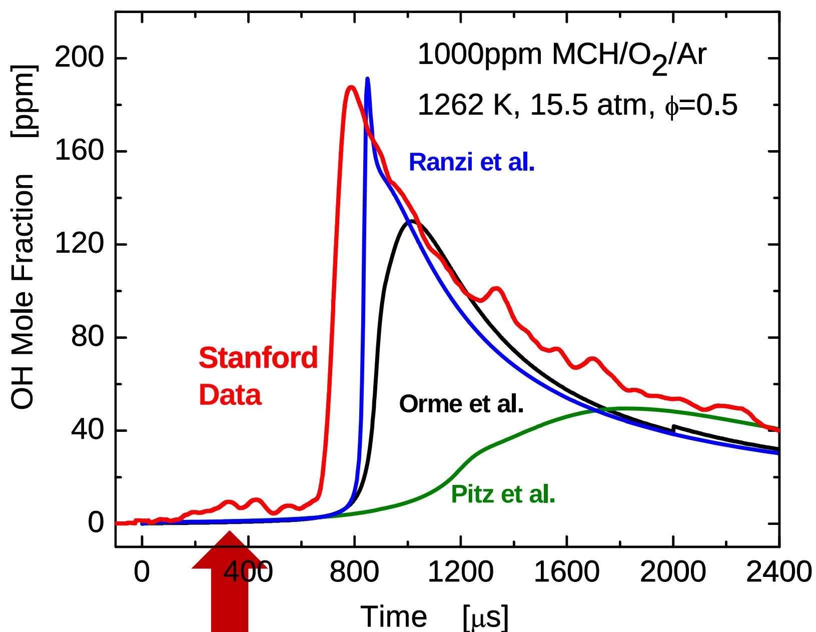


- **High-quality, ppm-level detection of OH**
- **Useful for spectroscopic parameters/HP kinetics**

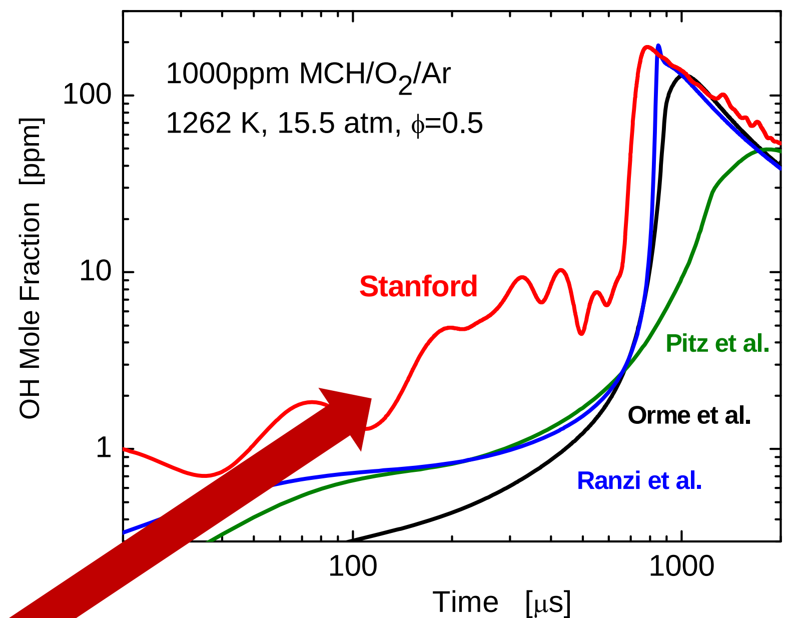
Davidson et al. 1996, JQSRT

Methylcyclohexane Oxidation: OH Time-History

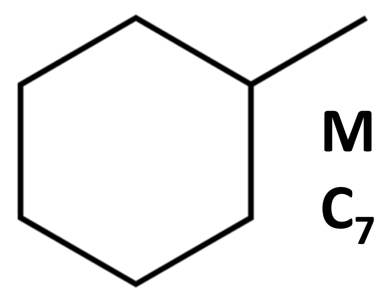
Linear Scale



Log Scale



Early-time OH formation revealed

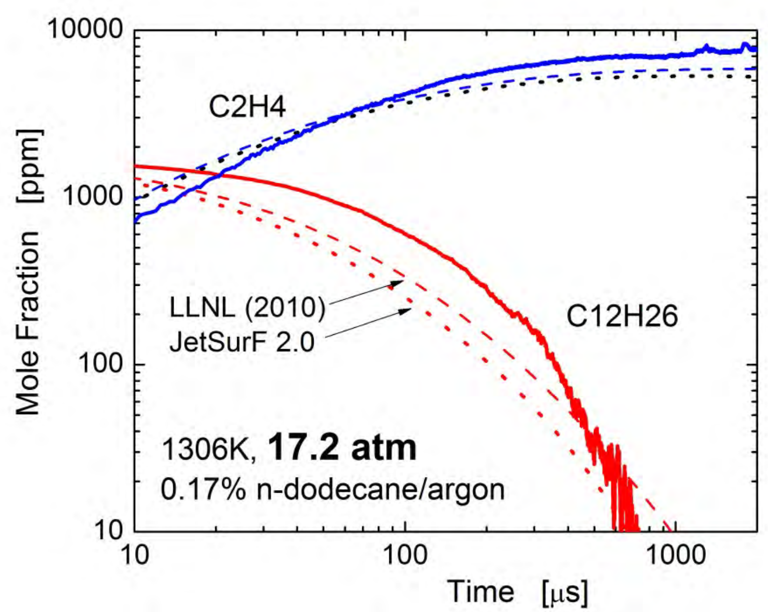


MCH

C_7H_{14}

- **Time-resolved speciation allows access to multiple phases of oxidation kinetics**

n-Dodecane Pyrolysis: Ethylene and n-Dodecane Time-Histories

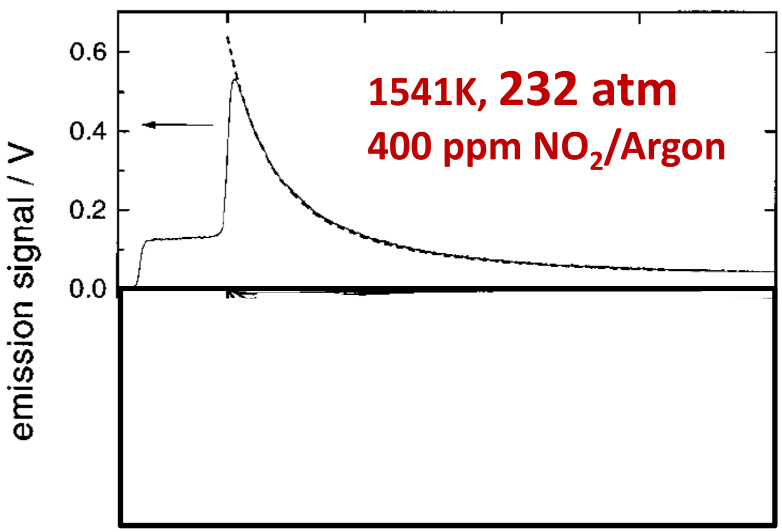


- IR laser absorption measurement
  - n-Dodecane (3.39 μm)
  - Ethylene (10.5 μm)
- C_2H_4 major contributor to carbon product balance
  - 78% conversion to C_2H_4
- Current n-alkane mechanisms do not capture time scales or ethylene yields at HP

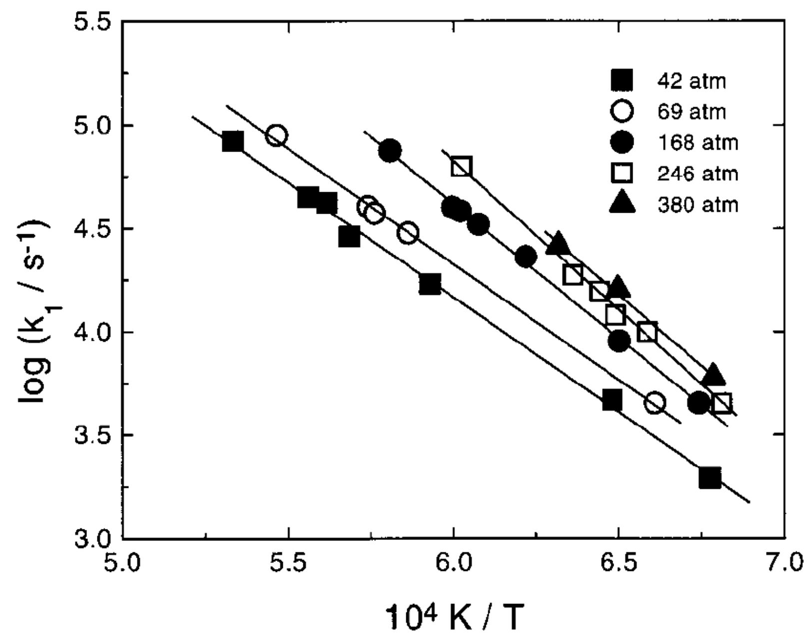
- **Species time-history measurements also provide access to direct measurement of elementary reaction rate constants!**

$NO_2 \rightarrow NO + O$
High-Pressure Rate Determination using IR Emission

IR Emission NO_2 Sensitivity



Arrhenius Plot



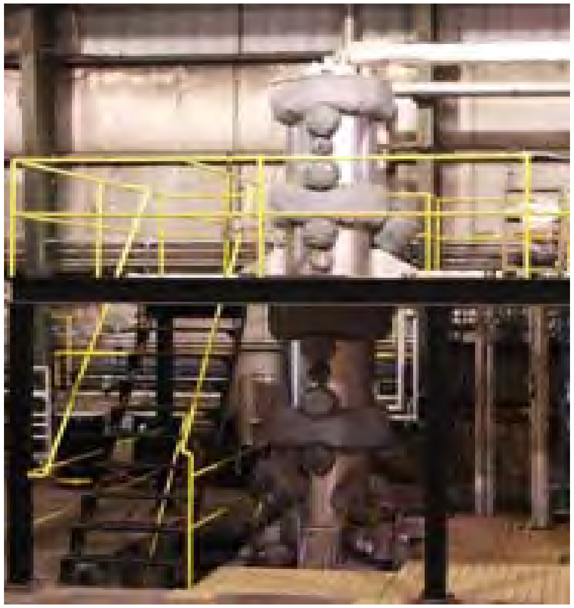
- Emission ~ N_i^* → improves with P!
- Real gas effects accounted for
- Sensitivity analysis shows NO_2 has strong sensitivity to title reaction

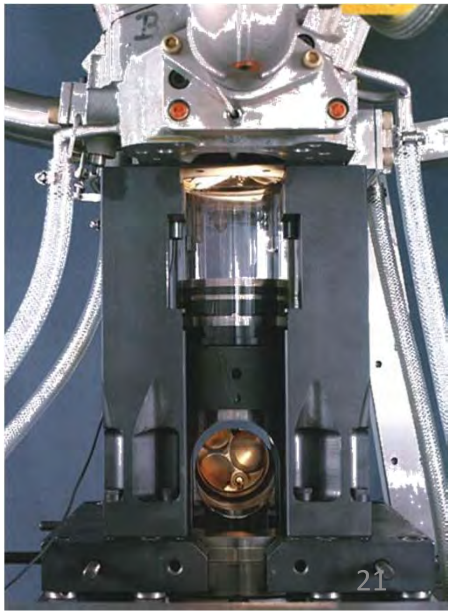
- Data obtained to 380 atm
- Then replotted for fall-off plot

Temperature Sensing

TDL sensors developed for variety of facilities and applications

- Shock tubes
- Coal gasifiers
- Engines





TDL Sensing at High Pressures

Issues/Challenges:

- Little spectrally-resolved absorption data at HP
- Absorption lineshape theory is inadequate at HP
- Diagnostic strategies needed for harsh environments
  e.g. multi-phase extinction

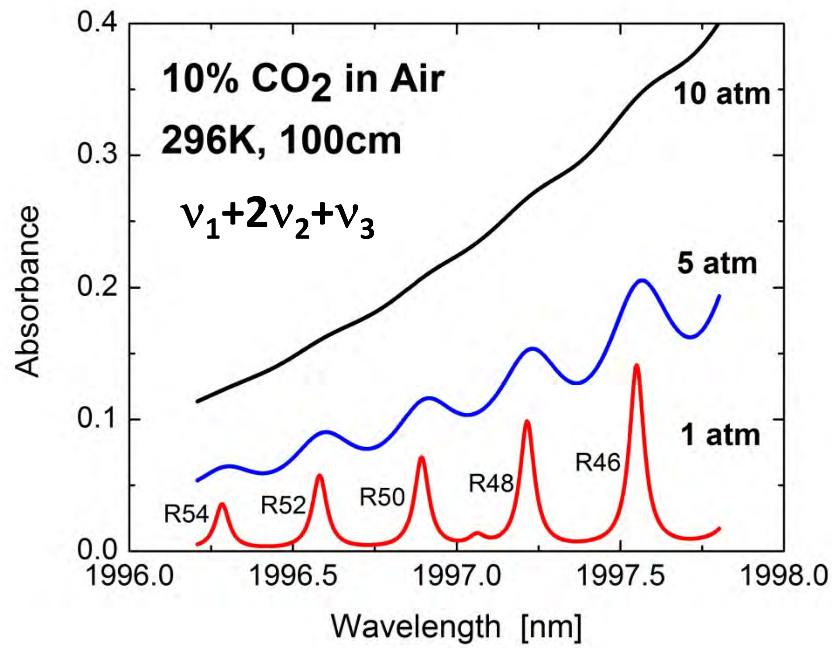
Strategies:

- 2f/1f WMS may provide a solution for moderate pressures (1-30 atm)
- Direct absorption of H_2O&CO_2 near 2.7μm for higher pressures (>30 atm)

3 Representative Examples:

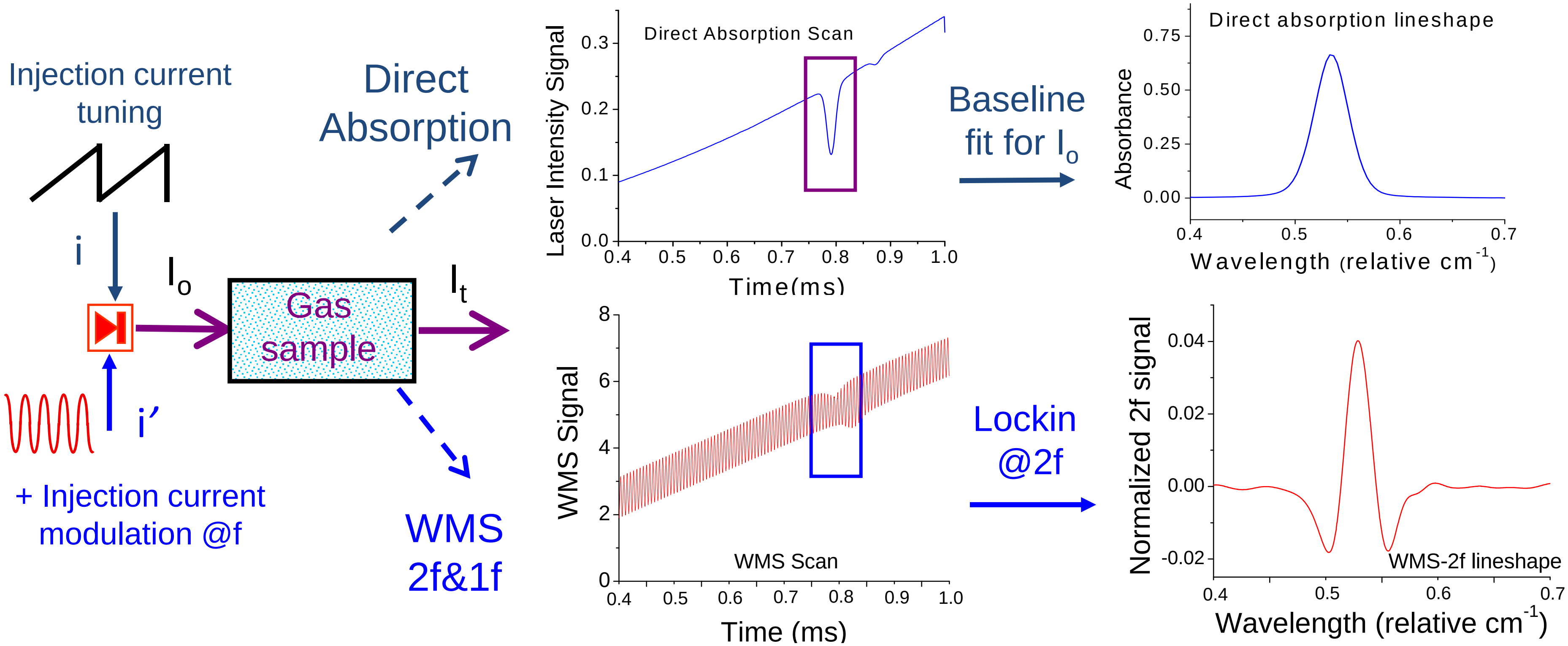
- **Temperature Sensing using CO_2**
- **Temperature Sensing using H_2O**
- **Simultaneous Species Time History and Temperature Sensing**

Problem: Spectral Character Changes with Pressure



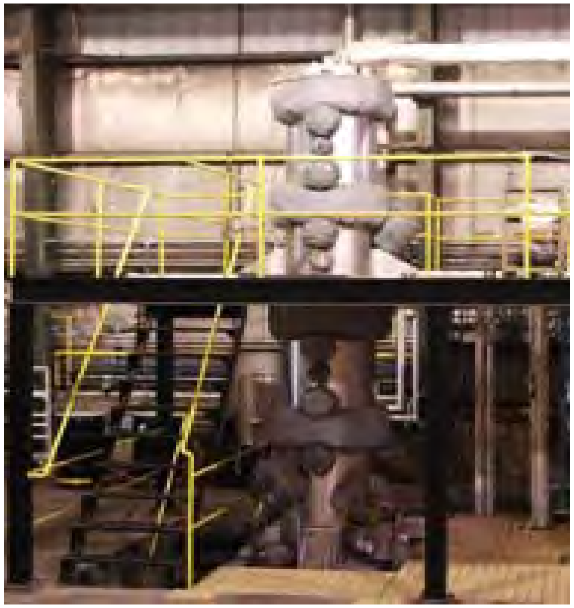
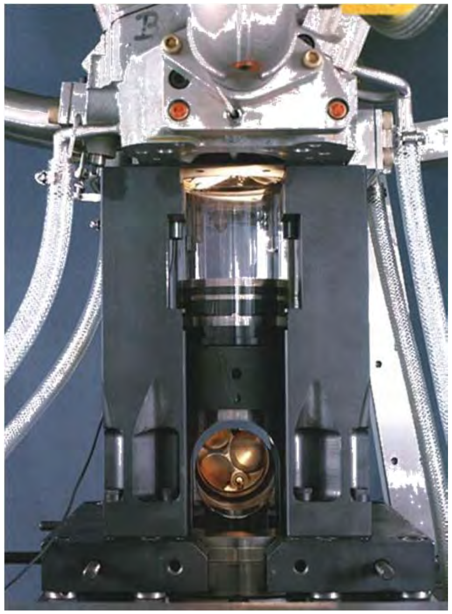
- Transitions broadened by collisions
- Transitions shifted by collisions
- Multiple absorption transitions blend; making species selectivity difficult
- Need for fundamental spectroscopy studies and "new diagnostic strategies"

Direct Absorption & Wavelength Modulation Spectroscopy



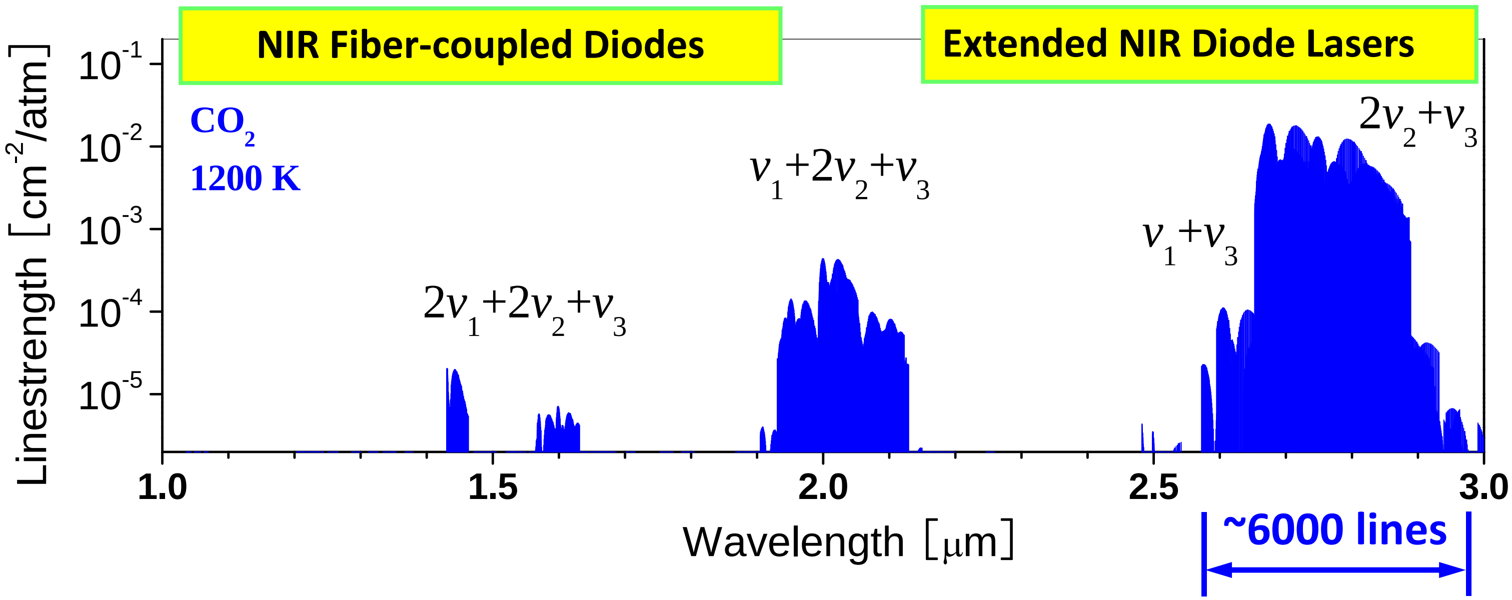
- **Direct Absorption: Simple, if absorption is strong enough**
- **WMS: More sensitive, especially for small signals**
  - Ratio of two WMS-*2f* signals provides T (same as direct absorption)
  - WMS also produces intensity modulation *@1f*
  - *Both 2f and 1f signals proportional to intensity; 2f/1f **independent** of optical losses*

High P Temperature Sensing Using CO_2

CO_2 Absorption

CO_2 Spectrum



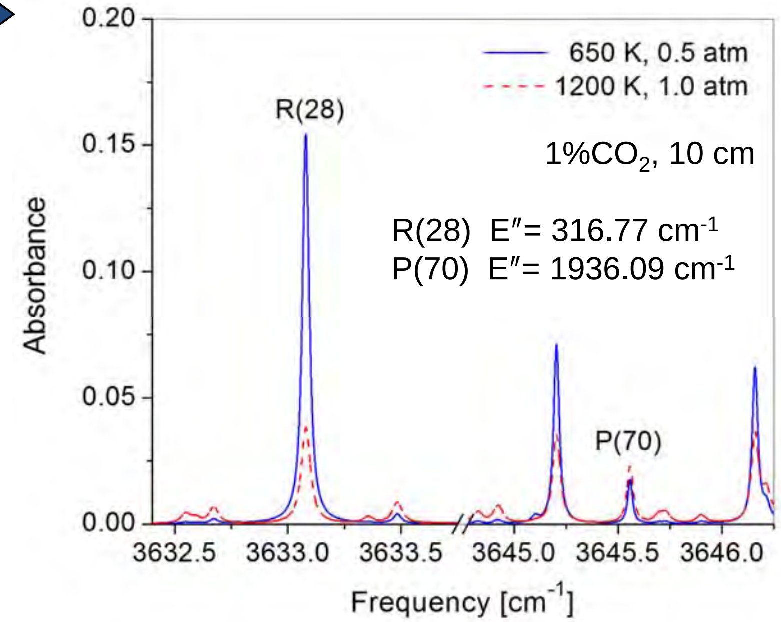
- 2.7μm CO_2 bands are 30× and 1000× stronger than bands at 2μm and 1.4μm
- Stronger absorption: shorter sensor paths, lower detection limits, higher sensitivity

➡ For T, use ratio of two optimal absorption lines!

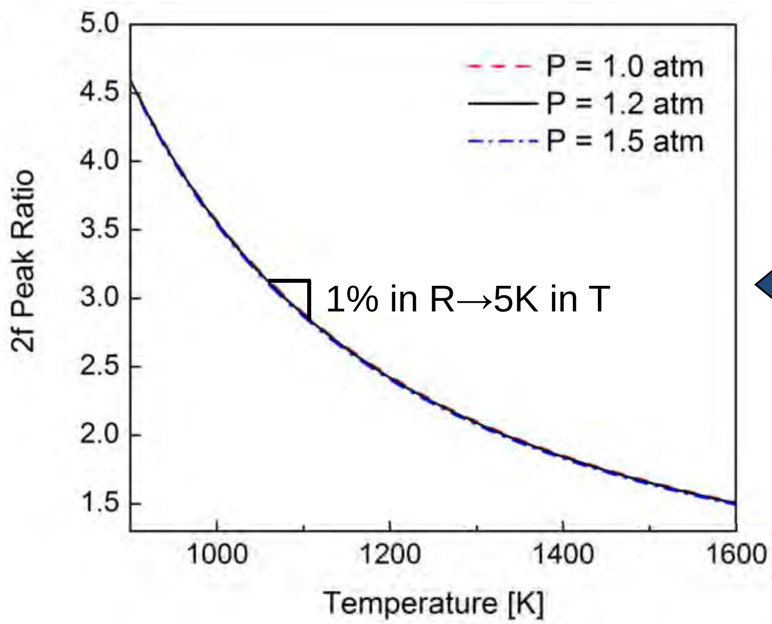
CO_2 T-Sensor Design

- **Optimal line-pair R(28) and P(70)**
  - Large line-strength S(T)
  - Isolated from neighboring lines
  - Well-separated lower state energy (E″)

CO_2 Line Selection

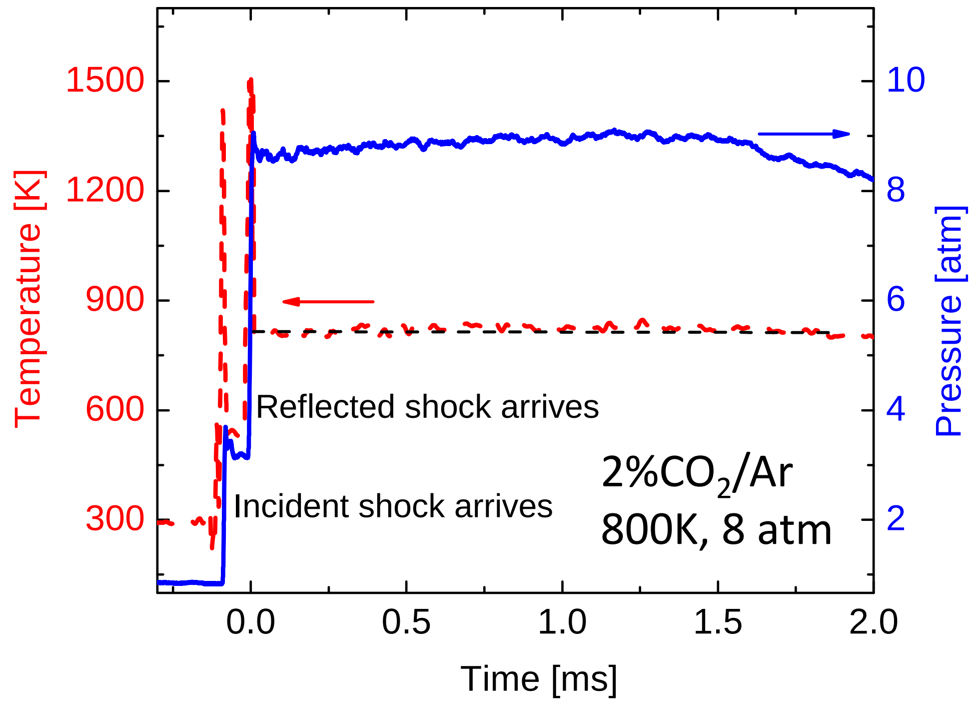


2f Ratio vs. Temperature



- **T inferred from measured 2f ratio**
- **Pressure influence is negligible**

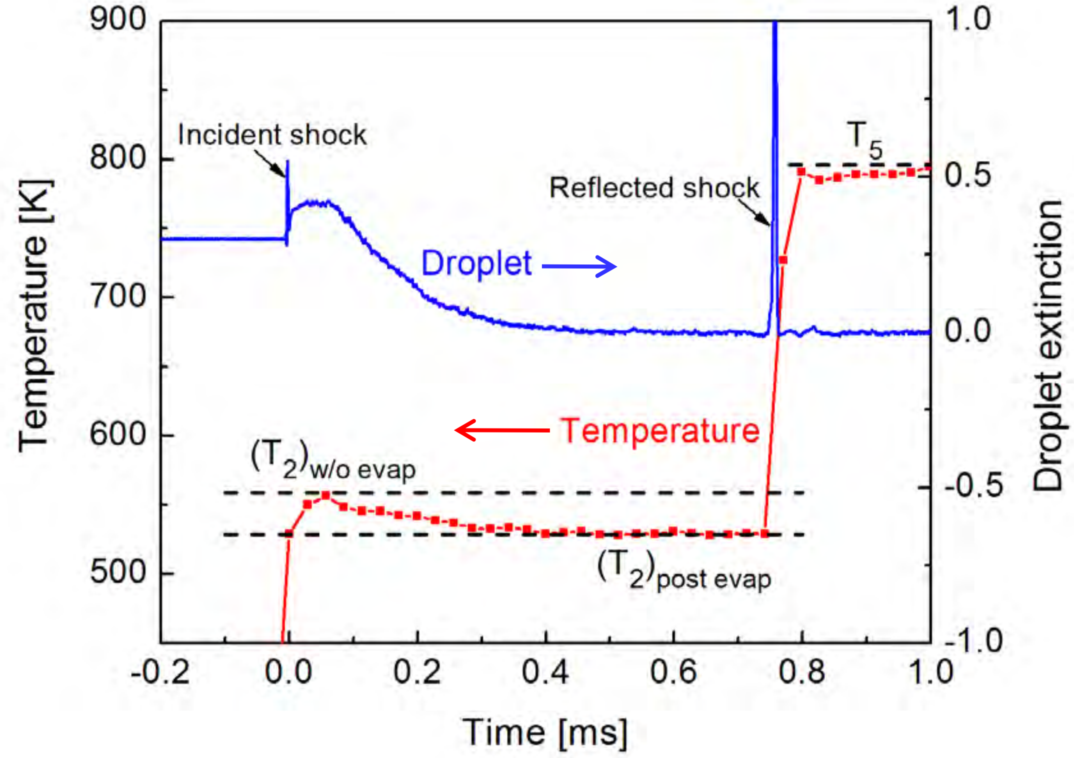
Shock Tube CO_2 Temperature Measurement: 8 atm



- **Sensor precision ~ 4K**
- **Shock tube attractive test bed for HP studies**
- **T measurement possible with CO_2 tracer or combustion products**
- **Successfully tested to 15 atm**

1f-Normalized WMS-2f for CO_2 with Particulate Scattering

Validated in Aerosol-Laden Gases

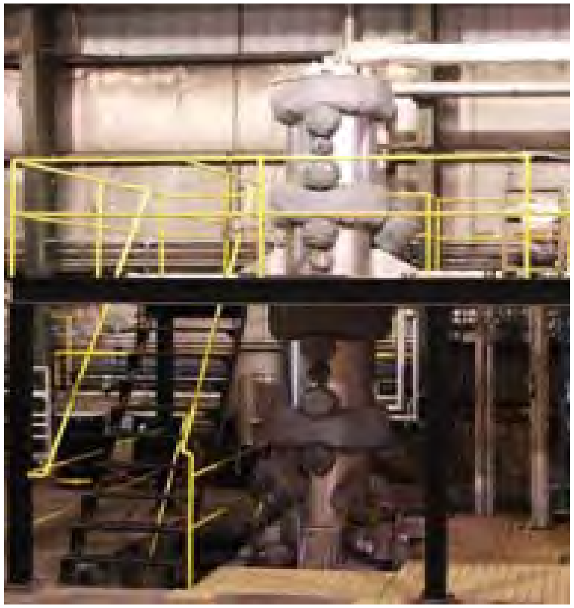


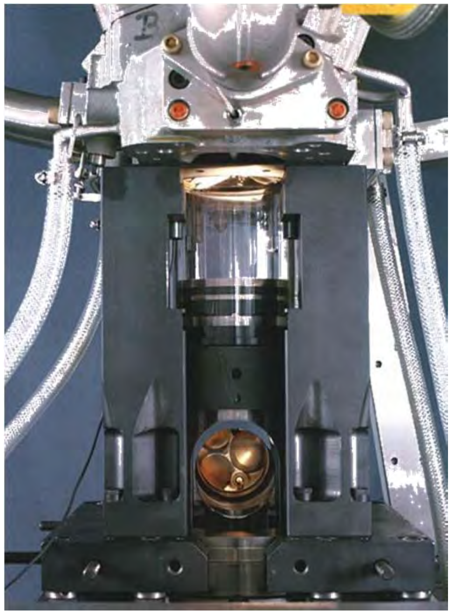
Aerosol shock tube:
2% CO_2 /Ar, 0.5 atm
w/ dodecane aerosol

- **2f/1f TDL sensor successfully measures T in presence of aerosol!**

Ren, Jeffries, Hanson, MS&T, 2010

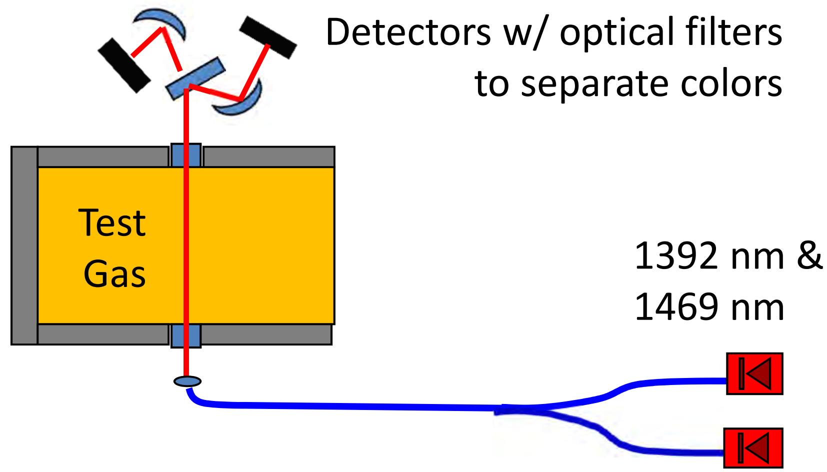
HP Temperature Sensing Using H_2O

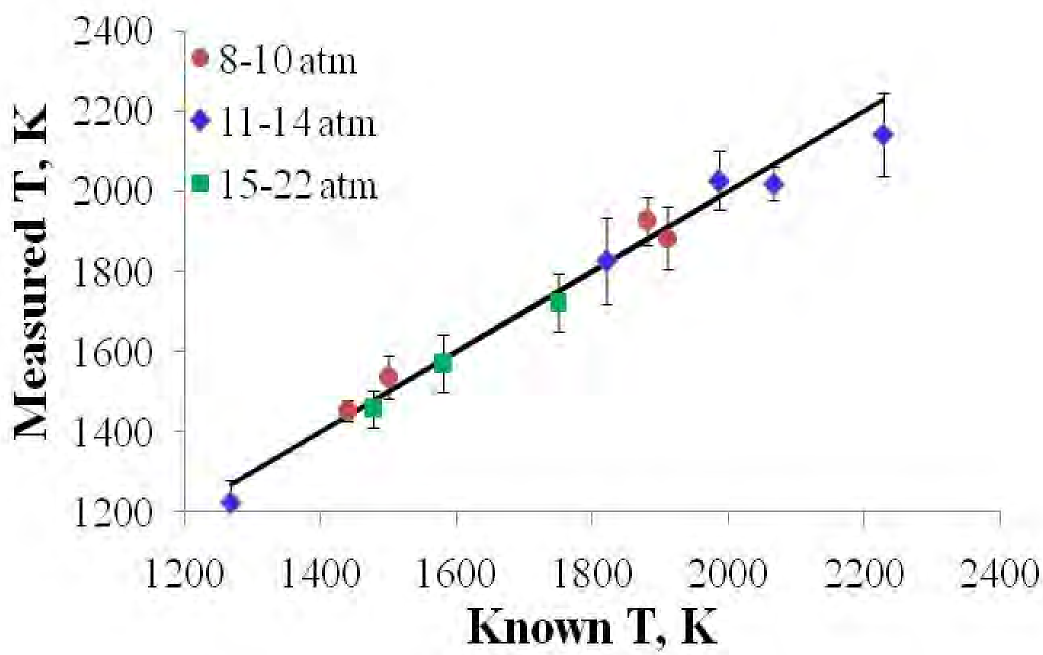




Temperature Diagnostic Validation in Shock Tube

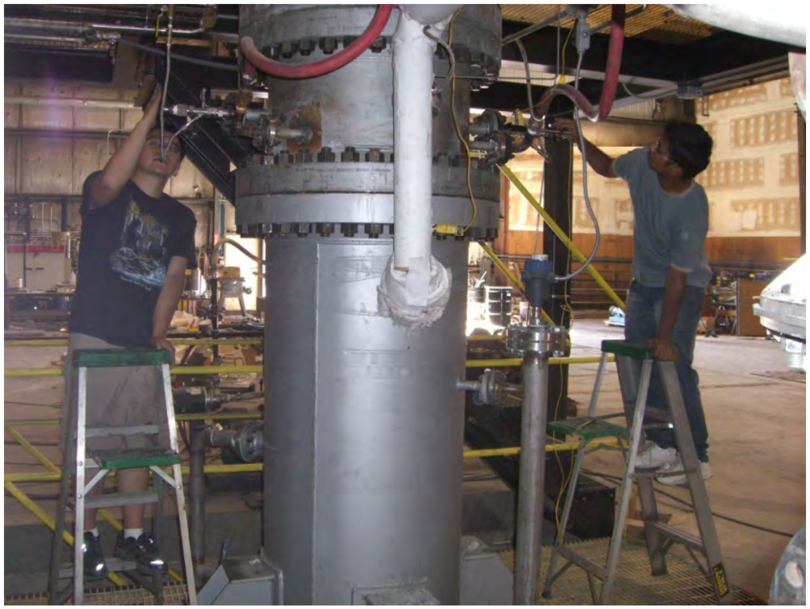
- **Two-wavelength T sensor**
- **Direct measurement of T using H_2O in shock tube**

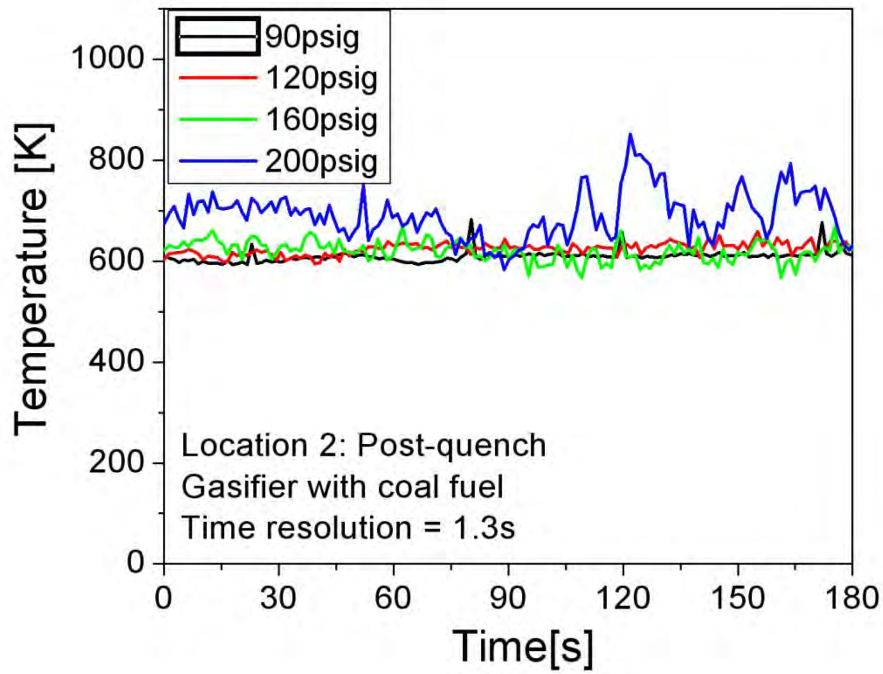




- **WMS Diagnostic validated to 22 atm and 2200 K**

Temperature in Gasifier: High P & Low Transmission

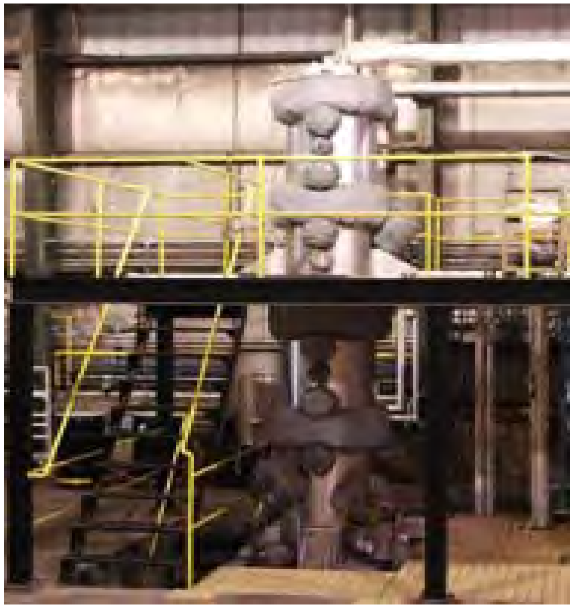
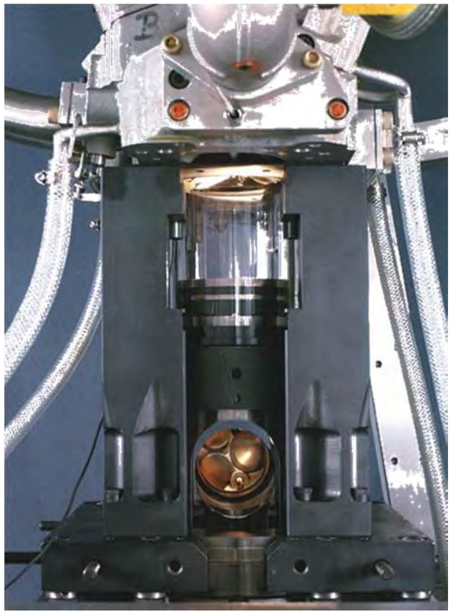




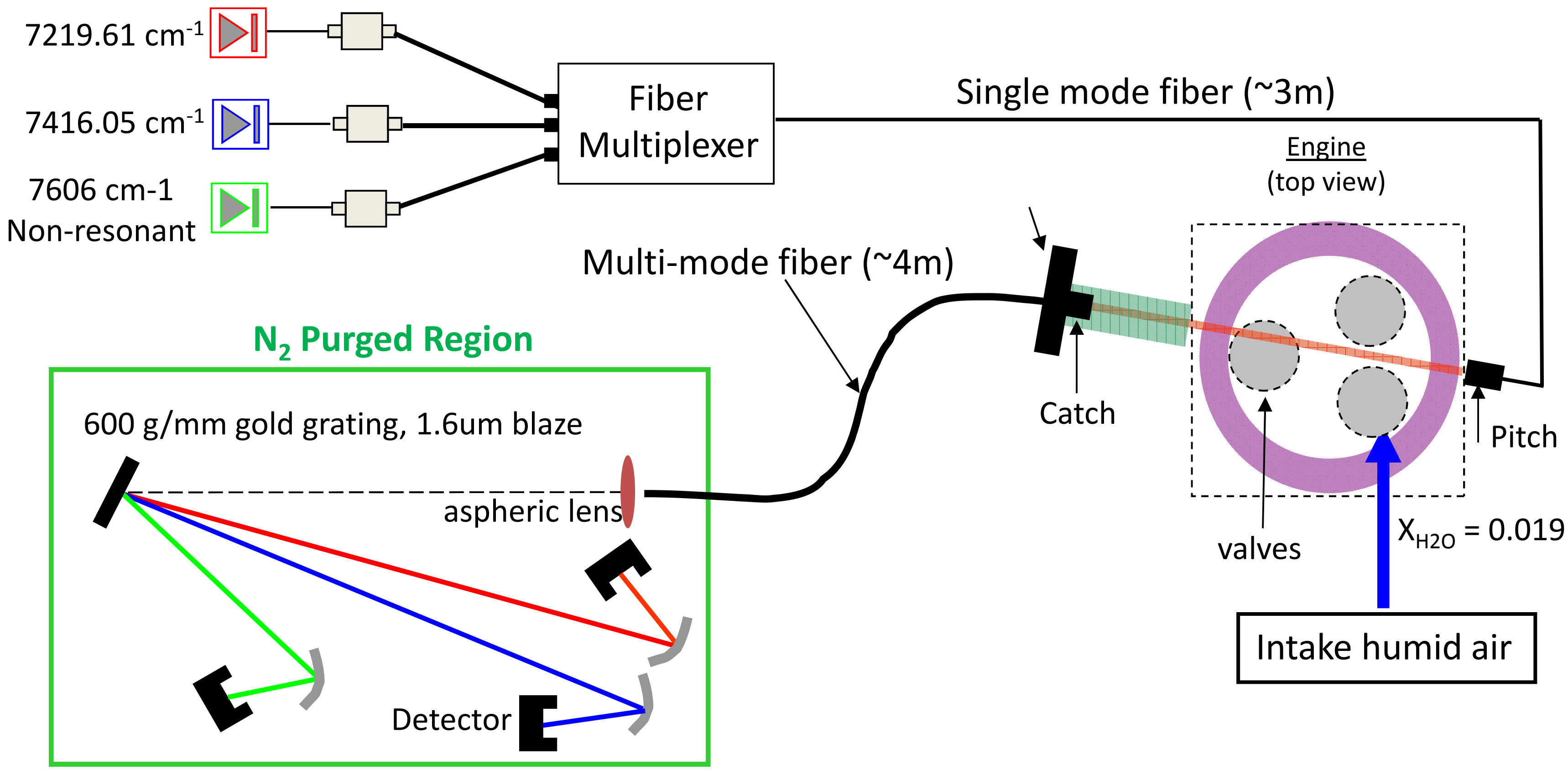
Sensor λ's: 7426cm^{-1}, BW = 13kHz
7466cm^{-1}, BW = 10kHz

- **High SNR, time-resolved measurements of T**
- **Normalized WMS enables T sensing even with transmission less than 0.1%**
- **Measured T at reactor pressures of 90, 120 and 160 psig stable**
- **Measured T at 200 psig identified instabilities (due to O_2 input flow)**

Simultaneous Species Time-History and Temperature Sensing

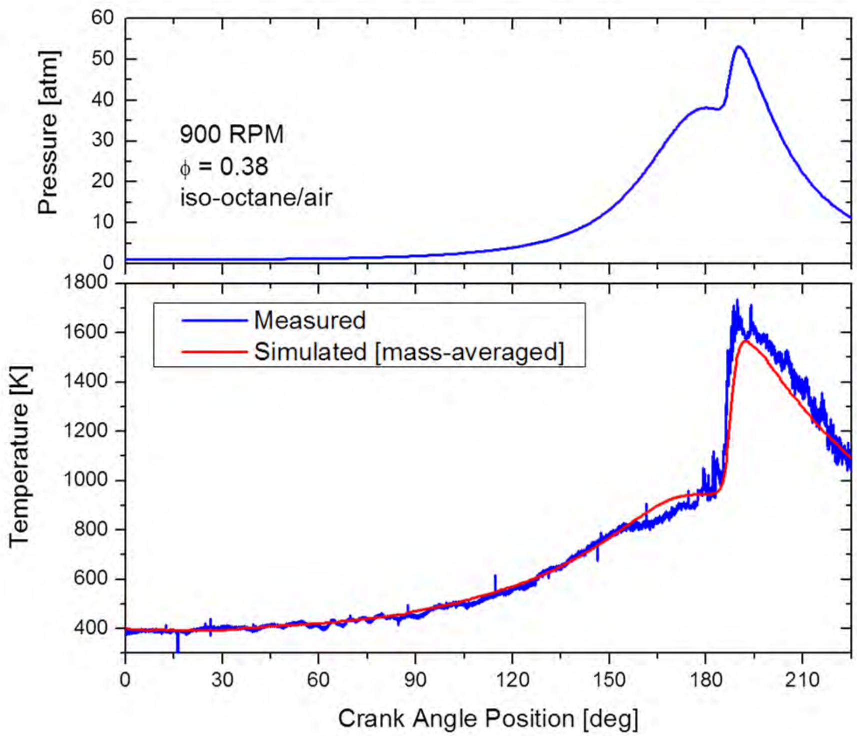
  

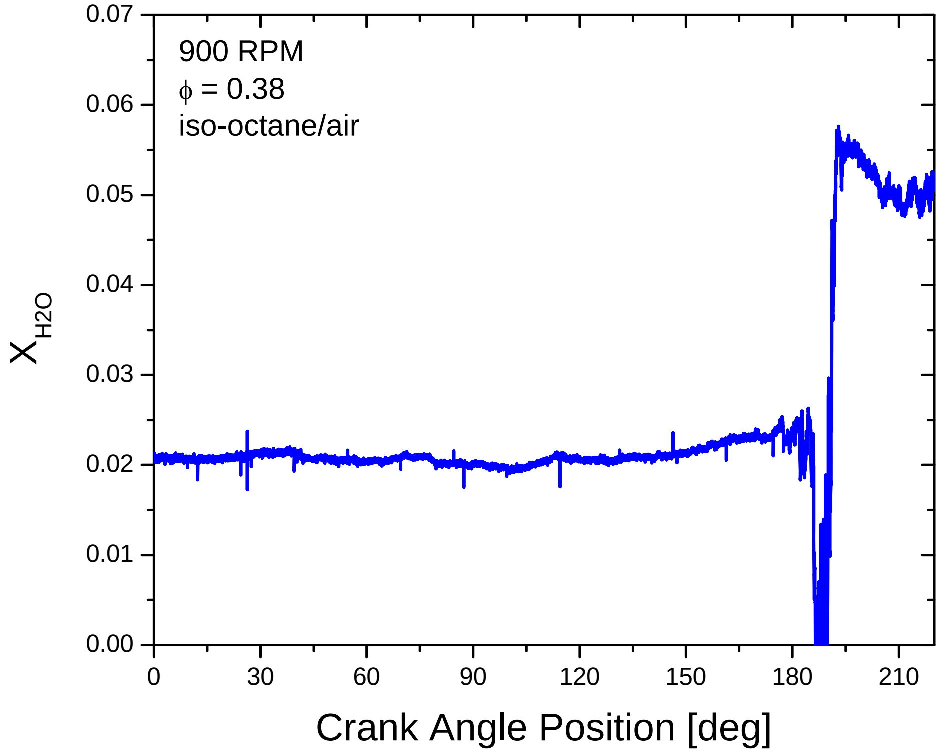
Cross-Cylinder TDL Sensor for Optical Engine



- **Portable, robust, noise resistant, fiber-coupled optical system**

Optical Engine Measurements at Sandia



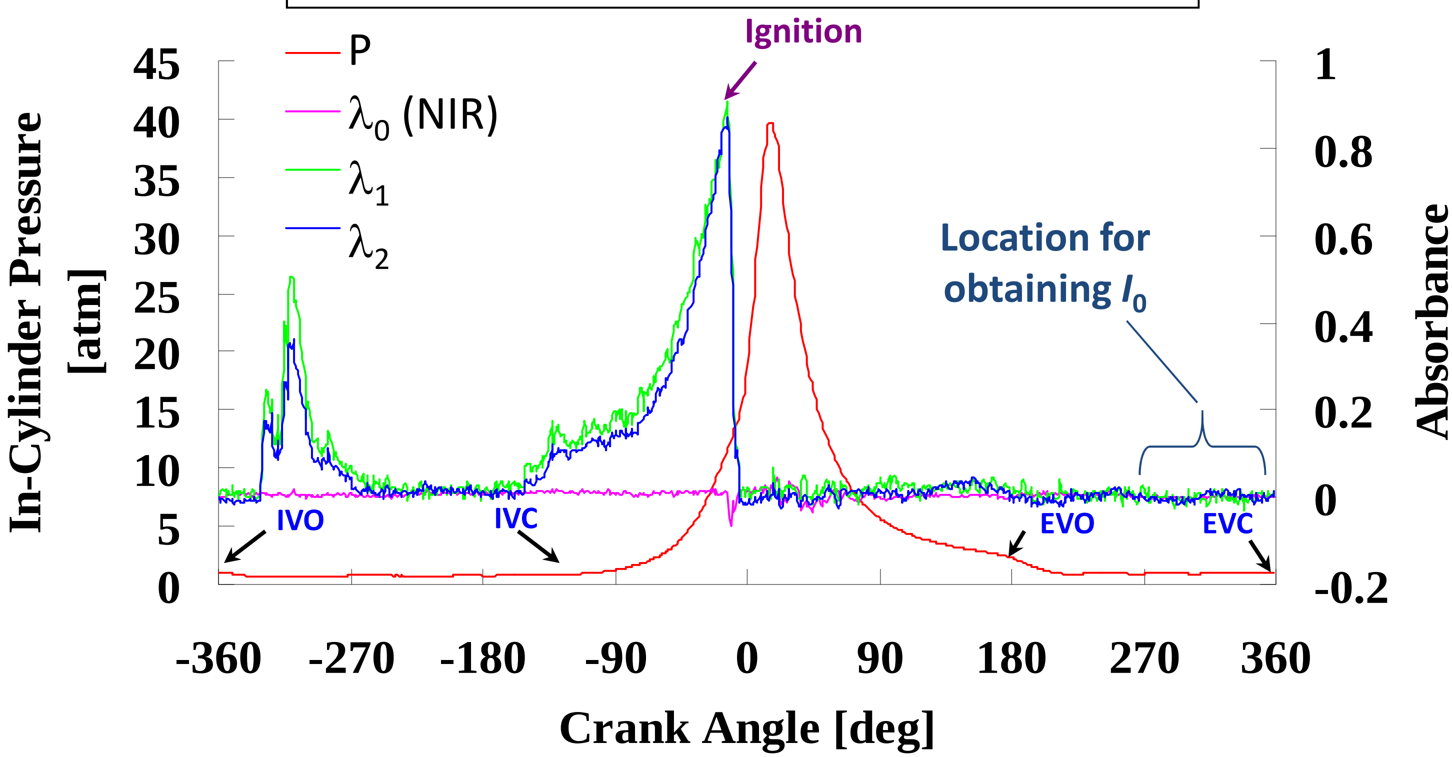


- 2-color temperature; extra colors can be used to quantify non-uniformities
- Water mole fraction from T and absorbance
- Can be used to evaluate combustion models/determine combustion efficiency

Dec et al., Sandia (2005)

IC-Engine Application: Crank-Angle-Resolved Fuel/T Sensing with the Spark Plug Probe

Example gasoline sensor measurement



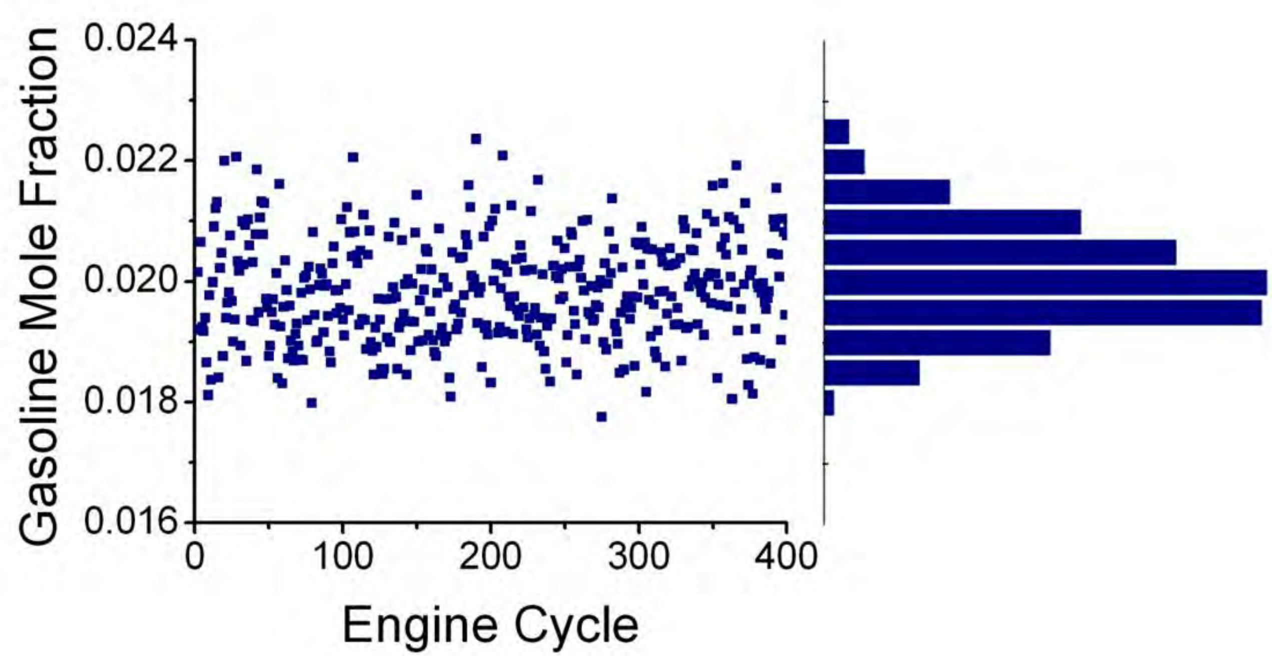
1200rpm
200kPa IMEP
Exhaust A/F=16.0
Ignition = -10º BTDC
Tw = Toil = 20ºC

- Single-cycle data from production engine
- High SNR with 5 mm probe gap!
- Sensor provides cycle-by-cycle results not available previously

Nissan North America (2007)

Cold Start Ignition Statistics

Peak fuel at ignition for 400 cold start cycles



- **High resolution quantifies small changes in fuel loading**
- **Sensor provides new tool to optimize MPI & DIG engines**

Jeffries, SAE, 2010
Sholes, SAE, 2010

Summary

- **Laser absorption well-suited to wide range of T & P**
  - **Provides species time-histories at HP**
- **WMS 2f/1f abs. allows measurement in harsh environments**
  - **Even with 0.1% transmission or multi-phase flows**
- **Need for quantitative studies of spectra at high P and T**
  - **Current studies underway in UV, Vis & IR**

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