



University of California at Irvine  
Combustion Summer School  
August 24, 2023



# Combustion research: past, present and future – ignition experiments

**Margaret Wooldridge**

Director, Institute for Energy Solutions at the University of Michigan

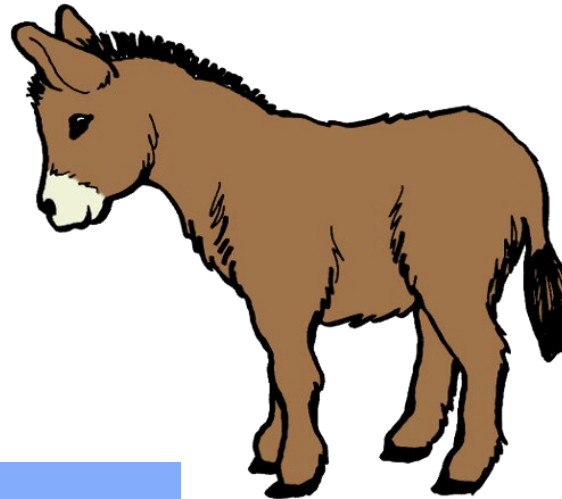
Walt J. Weber, Jr., Professor of Sustainable Energy,  
Environmental, and Earth Systems Engineering

Arthur F. Thurnau Professor,  
Departments of Mechanical and Aerospace Engineering,  
University of Michigan, Ann Arbor

- **The carrot (opportunities) and the stick (challenges) of ignition experiments**
- How we do it in the motor city – characteristics of ignition experiments in a rapid compression facility (RCF)
- A little bit of absorption theory
- The devil is in the details – application of laser absorption to RCF experiments
- Invitation to do consider laser experiments

# What motivates us?

- The carrot and the stick of interrogating ignition experir

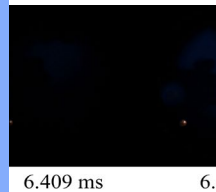


## Ignition studies:

- provide quantitative data on the reactivity of fuels
- provide quantitative data on the reaction pathways important during combustion
- provide quantitative data on fuel performance (efficiency and emissions)

## Ignition studies:

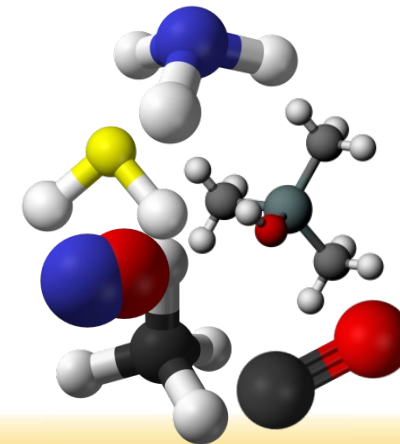
- are inherently transient
- span a broad range of temperatures (600-2000 K)
- span a broad range of pressures (5-100 atm)



1. How does ignition behavior apply to gas turbines and combustors and reciprocating engines?
  - Ignition pathways are the same as the reaction pathways found in flames in engines, combustors, boilers, etc. (*time = distance*)
  - Ignition/flame interaction behavior is critical to gas turbines and reciprocating engines - currently limiting efficiencies in reciprocating engine technology
2. Why do reaction pathway studies matter?
  - Too many blends and impurities to test them all... We need to develop reaction rate rules based on chemical structure
  - Ignition data provide higher fidelity metrics of our understanding of heat release rates, emissions, abnormal combustion, etc.



<https://www.youtube.com/watch?v=fo-LuonknfA>



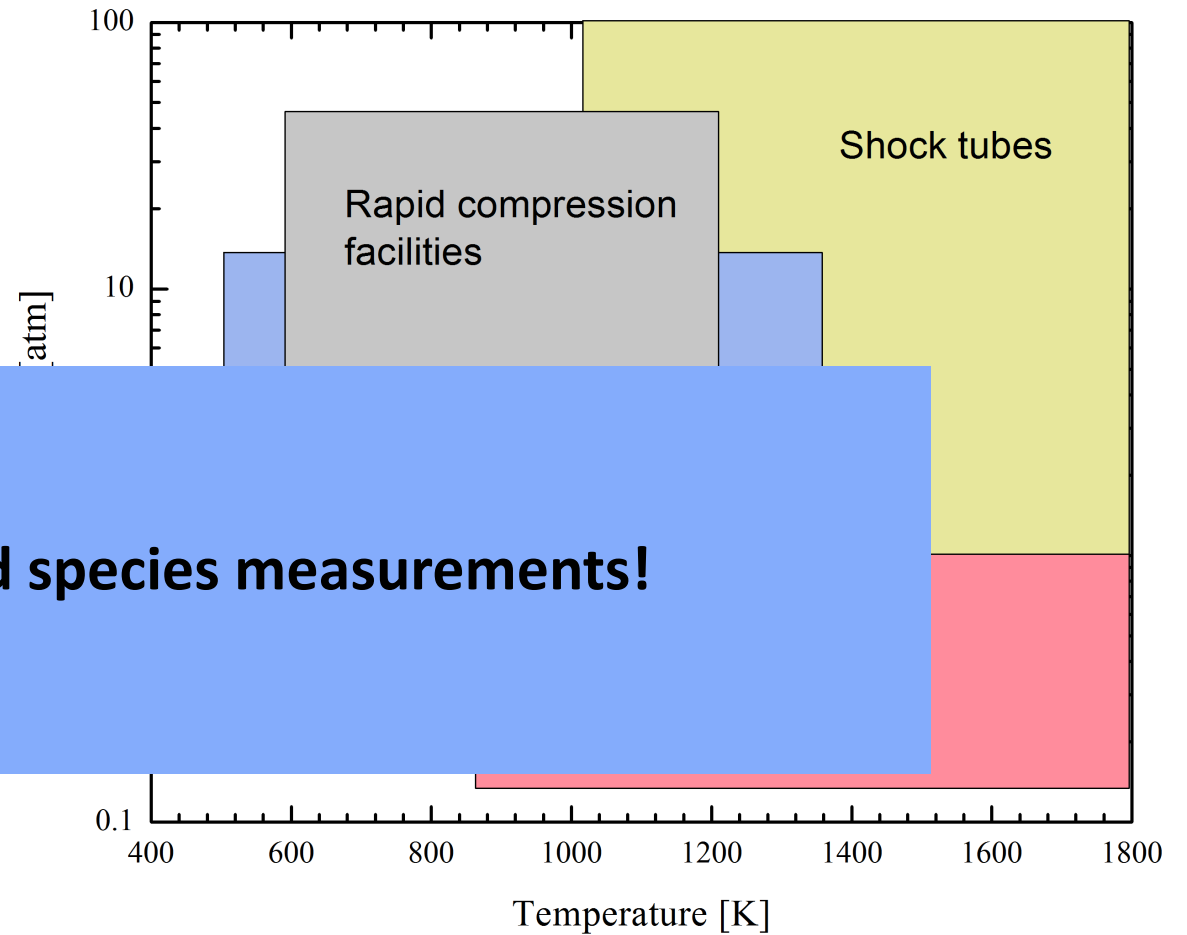
- **Research Approach:**

- Quantify ignition properties - which are critical to flame stability and engine phasing and therefore directly impact efficiency
- Quantify reaction pathways - which are critical to maximizing efficiencies and minimizing

**Technical A**

Use a rapid  
to create h  
pressure c  
The RCF si  
allowing u  
chemistry

**What is missing? Time resolved species measurements!**



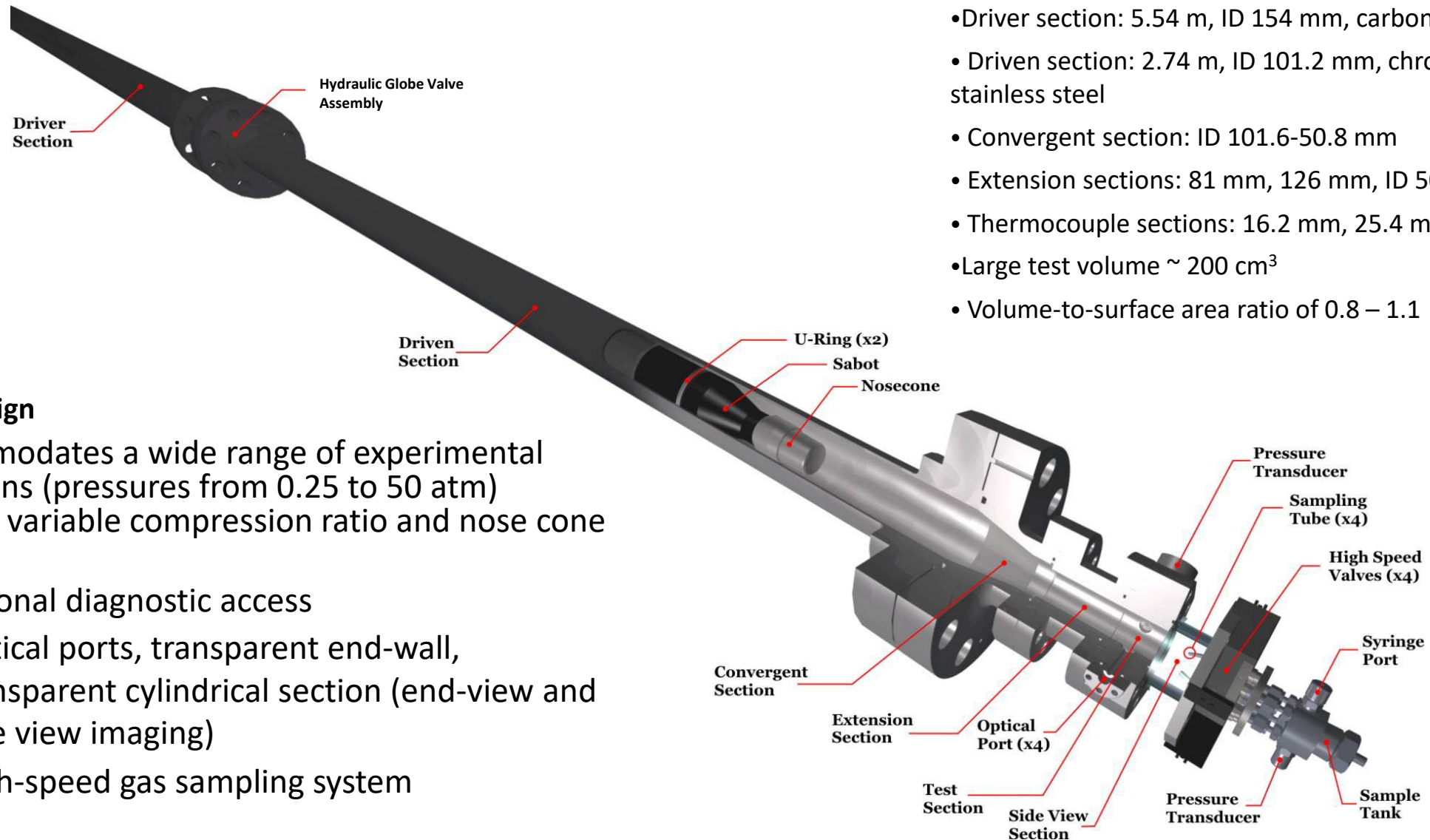
**We want high fidelity measurements that tell us how well we understand the reactivity and pathways of the fuel.**

We need this information to design, predict performance, and limit emissions in engines, combustors, furnaces, etc.

## Choose a new partner

- Share a description of your experimental platform(s) you are using for your doctoral work with your partner
- Explain why it is a good tool for your research topic

# The UM rapid compression facility



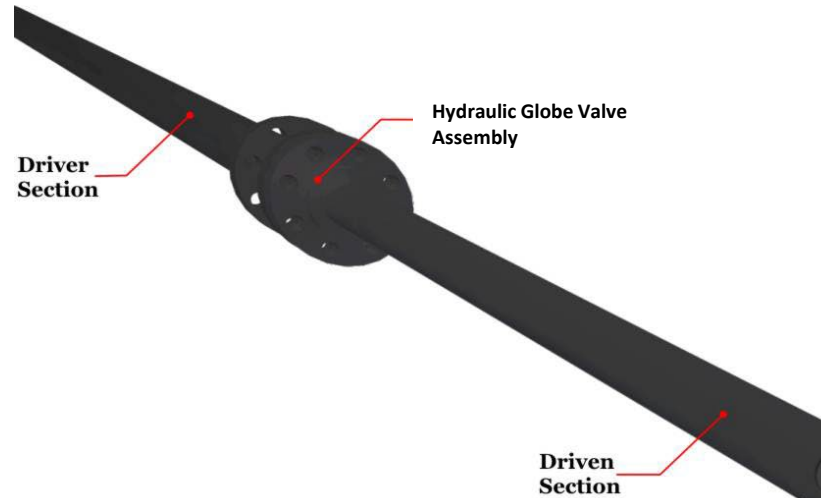
## UM RCF Hardware:

- Driver section: 5.54 m, ID 154 mm, carbon steel
- Driven section: 2.74 m, ID 101.2 mm, chromed and honed stainless steel
- Convergent section: ID 101.6-50.8 mm
- Extension sections: 81 mm, 126 mm, ID 50.8 mm
- Thermocouple sections: 16.2 mm, 25.4 mm, ID 50.8 mm
- Large test volume  $\sim 200 \text{ cm}^3$
- Volume-to-surface area ratio of 0.8 – 1.1

## UM RCF design

- Accommodates a wide range of experimental conditions (pressures from 0.25 to 50 atm) through variable compression ratio and nose cone design
- Exceptional diagnostic access
  - Optical ports, transparent end-wall, transparent cylindrical section (end-view and side view imaging)
  - High-speed gas sampling system

# The UM rapid compression facility



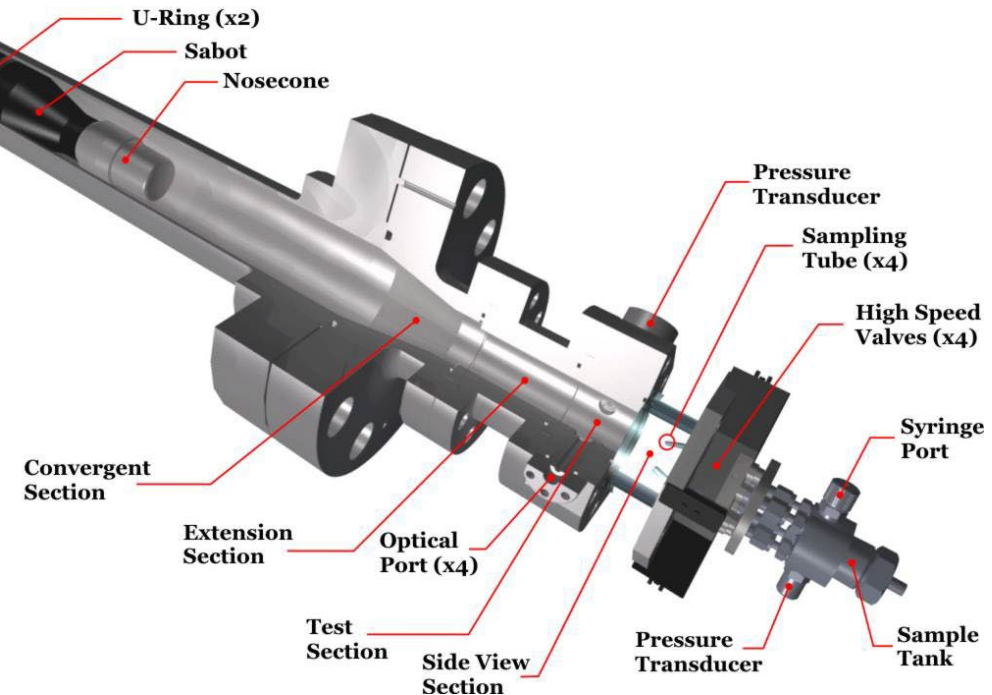
## UM RCF Hardware:

- Driver section: 5.74 m, ID 154 mm, carbon steel
- Driven section: 2.74 m, ID 101.2 mm, chromed and honed stainless steel
- Convergent section: 101.6 mm
- Extension sections: 81 mm, 126 mm, ID 50.8 mm
- Thermocouple sections: 16.2 mm, 15.4 mm, ID 50.8 mm
- Large test chamber: 1.5 cm<sup>3</sup>
- Volume-to-surface area ratio of 0.8 – 1.1

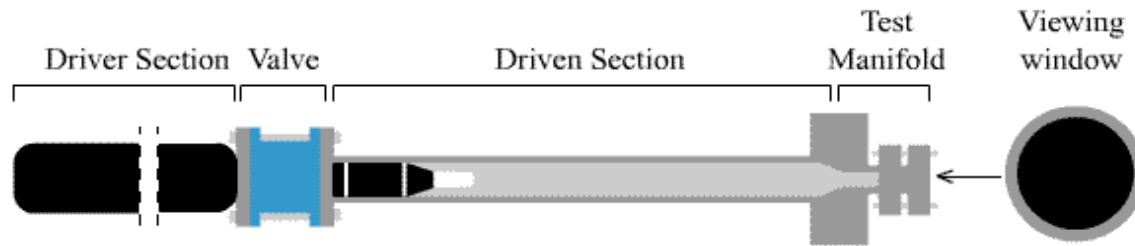
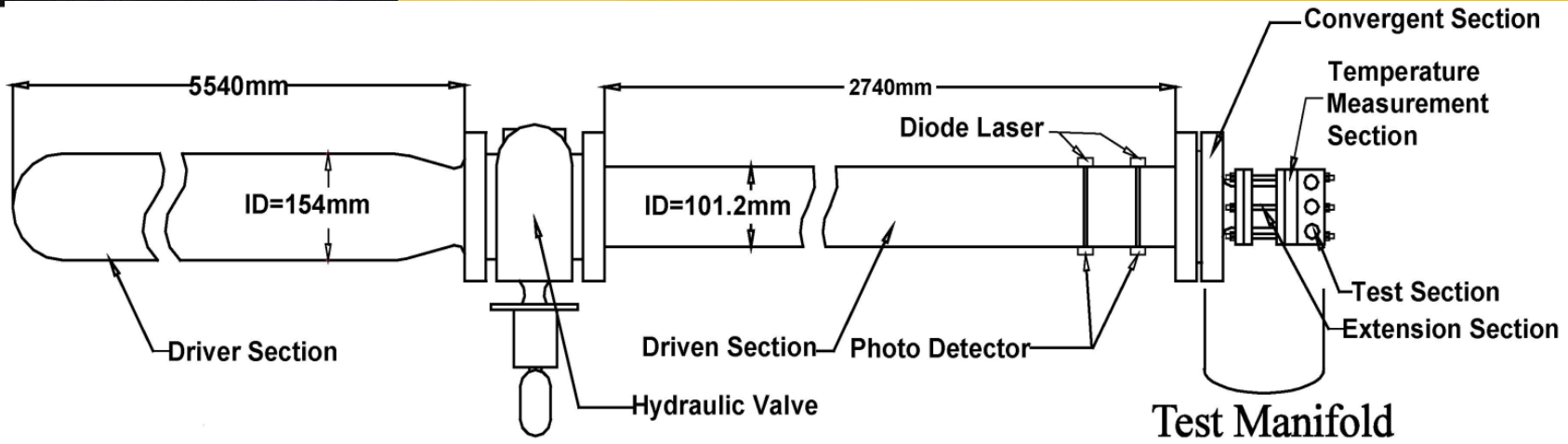
The RCF is essentially a single stroke engine with a free piston with a very low repetition rate (~4 cycles per day).

## UM RCF design

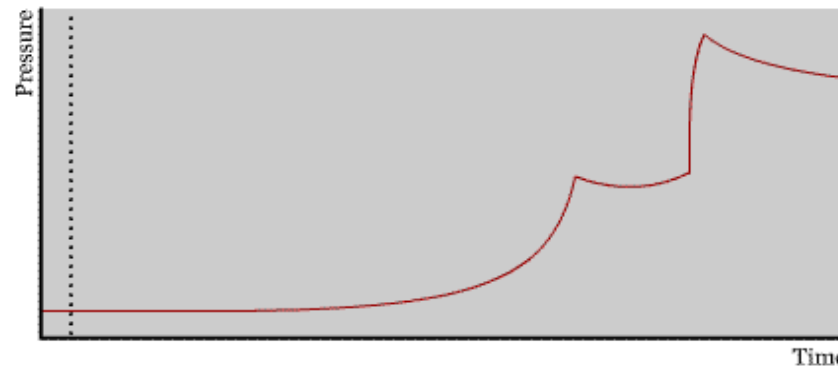
- Accommodates a wide range of experimental conditions (pressures from 0.25 to 50 atm) through variable compression ratio and nose cone design
- Exceptional diagnostic access
  - Optical ports, transparent end-wall, transparent cylindrical section (end-view and side view imaging)
  - High-speed gas sampling system



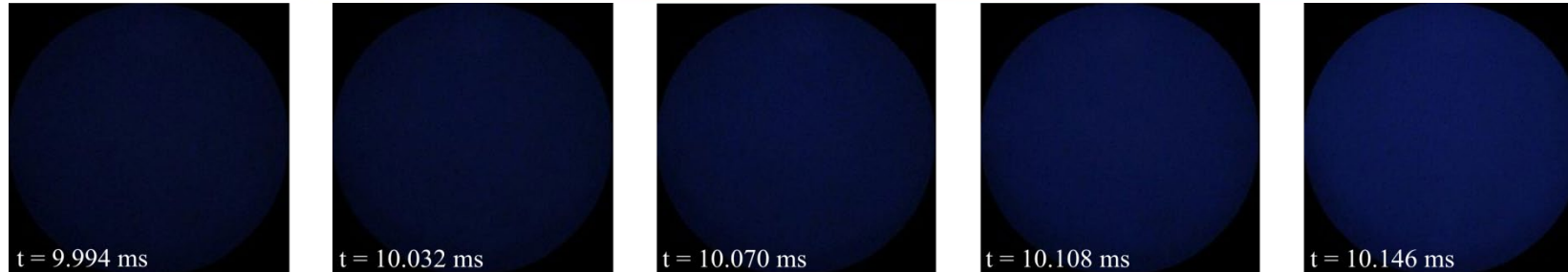




$$P_{eff} = \frac{1}{t_{dP} - t_{P_{max}}} \int_{t_{P_{max}}}^{t_{dP}} P dt$$

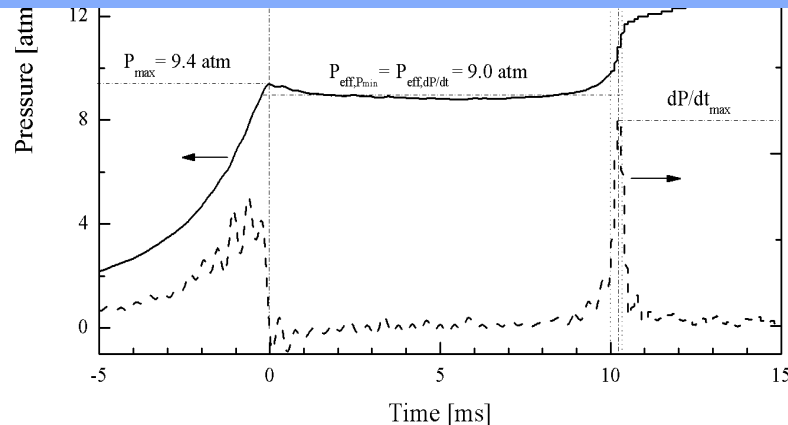


$$\int_{T_0}^{T_{eff}} \frac{\gamma}{\gamma - 1} d \ln T = \ln \left( \frac{P_{eff}}{P_0} \right)$$



We have **excellent radial and axial homogeneity!**  
**RCF experiments are well suited to line-of-absorption measurements.**

1. We measure **pressure**.
2. From pressure, we can estimate **temperature**
3. We want **species** time histories!
4. We can make those measurements physically ← gas sampling at discrete times
5. Or we can make those measurements non-intrusively – **laser absorption**



Pressure time history  
 $\phi = 0.30$ , inert/O<sub>2</sub> = 5.00,  
 $T_{\text{eff}} = 1020 \text{ K}$ ,  $P_{\text{eff}} = 9.0 \text{ atm}$

Walton, He, Zigler, Wooldridge, Atreya, 2007. "An experimental investigation of iso-octane ignition phenomena," *Combustion and Flame*, 150 (2007), 246-262.

The single most important equation in absorption spectroscopy.

$$I_\nu(L)/I_\nu^0 = \text{fractional transmission}$$

$$I_\nu(L)/I_\nu^0 = \exp(-k_\nu L)$$

$$\text{also } I_\nu(L)/I_\nu^0 = \exp(-k_\nu P \chi_i L)$$

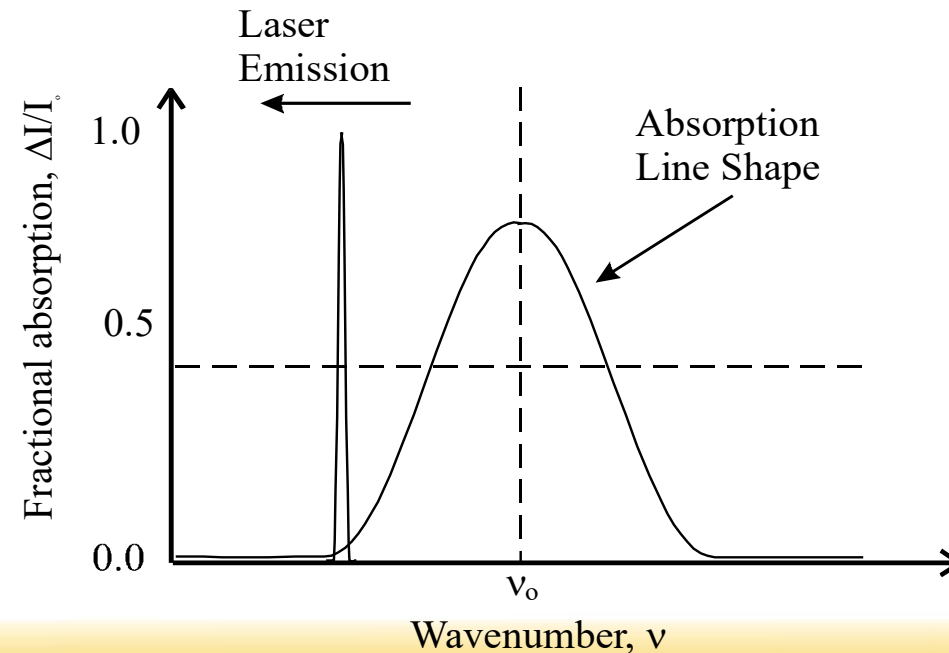
spectral intensity =  $I_\nu$

spectral intensity of source radiation =  $I_\nu^0$

path length through the absorbing media =  $L$

spectral absorption coefficient =  $k_\nu$ ,  $k_\nu$

\*There are caveats on where this is applicable, like when the source radiation intensity is much greater than the blackbody emission\



- *There are many forms of the equations for Beer's law.*
  - *Units are our friends, and can help!*
- The Einstein coefficients, integrated line strength, **S**; the oscillator strength, **f**; and the spectral absorption coefficient, **k<sub>v</sub>** are all related and are all fundamental properties of a molecule or atom.
- Watch the units to determine which parameter is being used. Beer's law was developed for absorption in optically thin media.

$$-\ln \frac{I(\nu)}{I_o} = k_{\nu,OH} L$$

$$-\ln \frac{I(\nu)}{I_o} = S_{lu} \phi(\nu) p \chi_{OH} L$$

$$-\ln \frac{I(\nu)}{I_o} = S_{lu} \phi(\nu) p_{OH} L$$

$\phi(\nu)$  = normalized line shape function

P = pressure

$\chi_{OH}$  = mole fraction of OH

$P_{OH}$  = partial pressure of OH

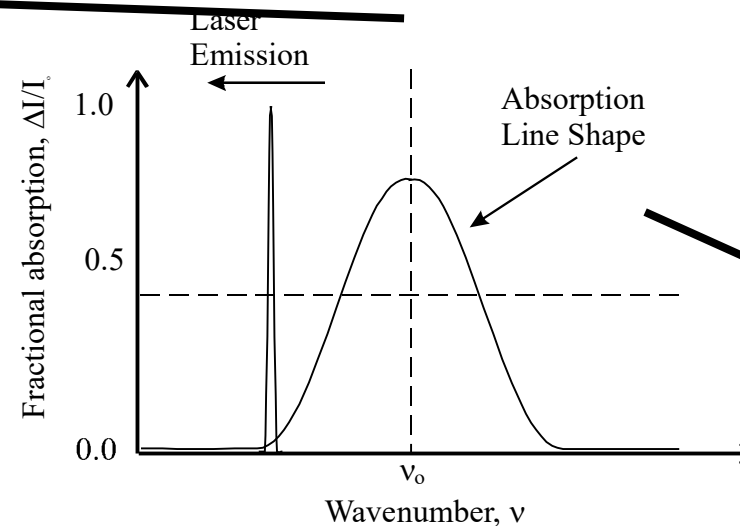
Several methods to choose from:

- Scanning wavelength ← fast frequency modulation spectroscopy
- **Fixed frequency ← maximum absorption at the resonant transition frequency**
- Single transition versus multiple transitions (multiplexed)
- etc.

$\chi_i$ ?

the smaller species, like **OH** (electronic transitions in the uv

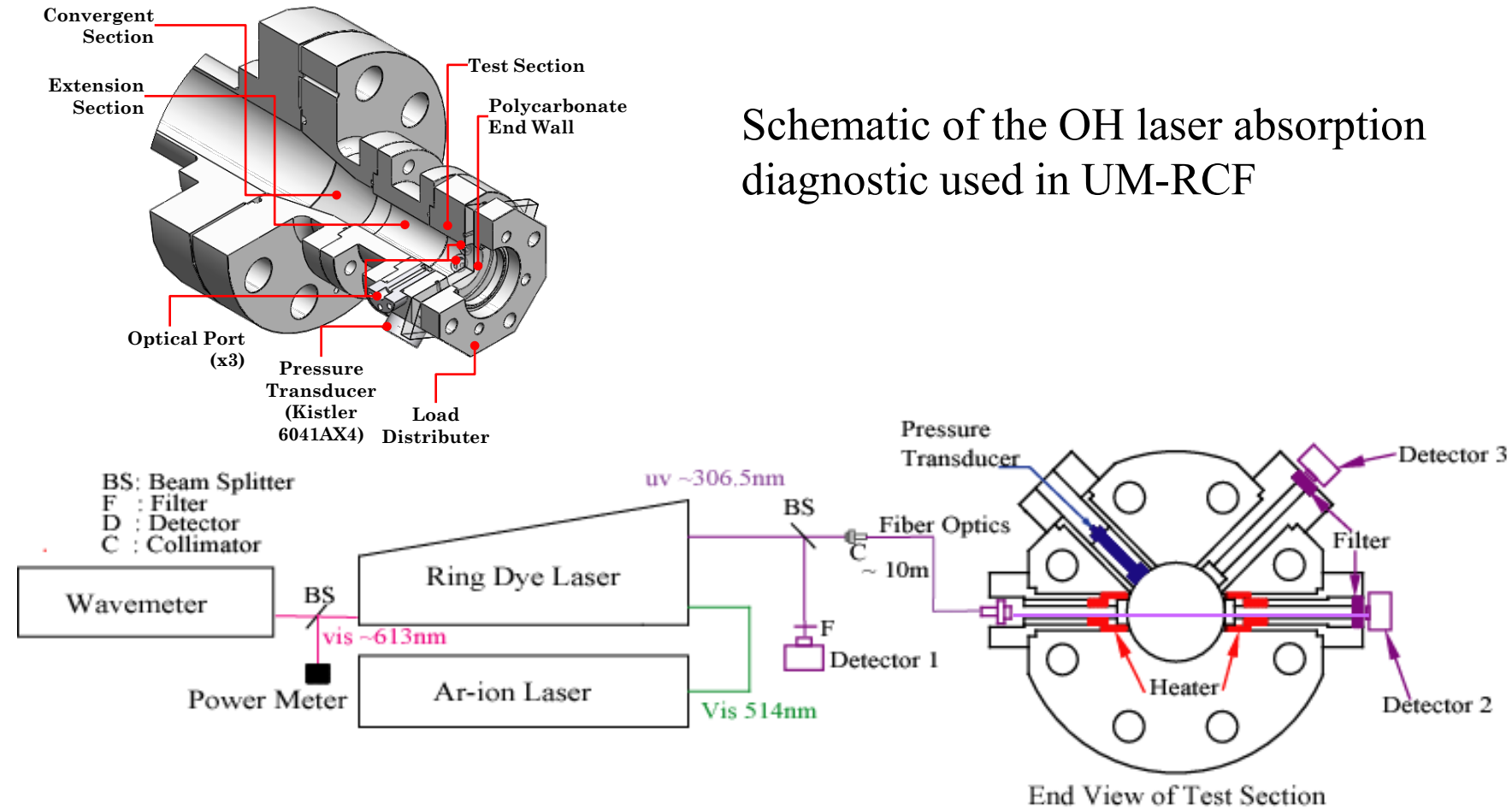
transitions of stables in the infrared e.g. 1.392  $\mu\text{m}$ )



**Let's focus on OH – the most important radical in low temperature (~1000 K) ignition**

$$-\ln \frac{I(\nu)}{I_o} = S_{lu} \phi(\nu) p \chi_{OH} L = k_{\nu} L$$

- Path averaged absorption is function of:
  - **Temperature** (via transition strength, Doppler broadening, and collisional broadening)
  - Absorbing species **mole fraction**
  - **Pressure** (via collision broadening and density of absorbing media)
  - Path length (fixed for the UM RCF = diameter)

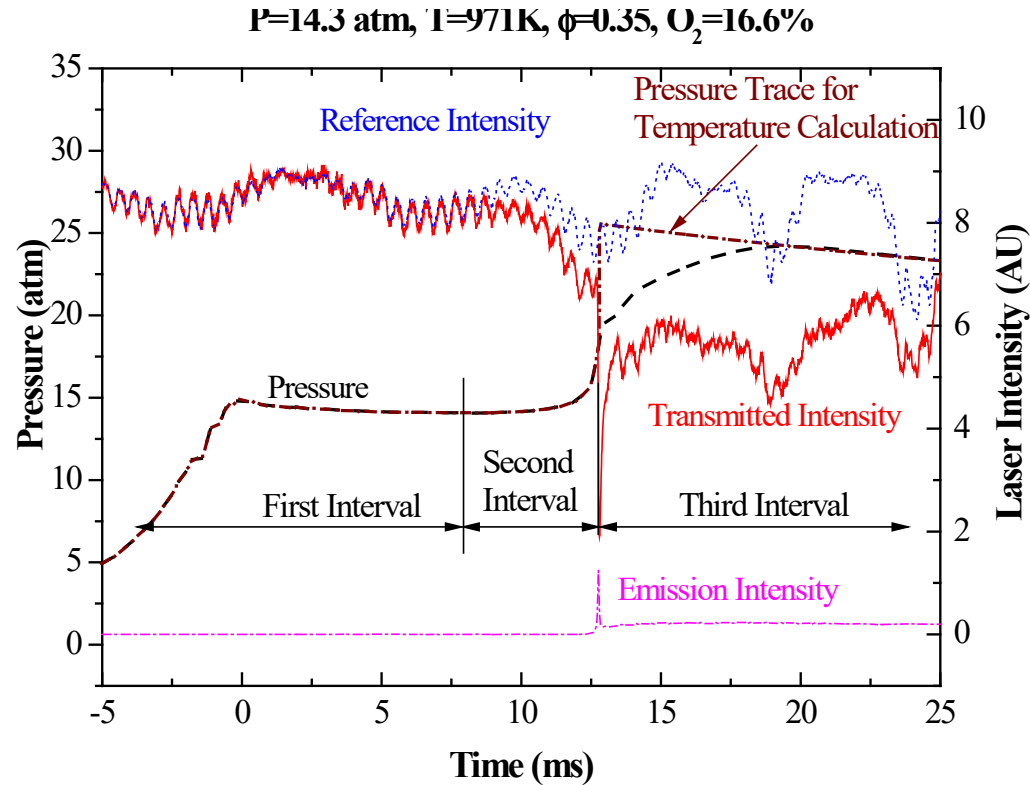


Schematic of the OH laser absorption diagnostic used in UM-RCF

Fixed-frequency, differential, narrow-line laser absorption

Laser : Intra-cavity doubled ring dye laser pumped with an Ar ion (now pumped with a solid state diode laser)

$R_1(5)$  transition of  $A^2\Sigma^+ \leftarrow X^2\Pi_1(0,0)$  ( $\nu_0 = 32606.56 \text{ cm}^{-1} / 306.687 \text{ nm}$ ).



Temperature calculated based on pressure data using three time intervals.

1. From the start of compression to the minimum P after EOC, use isentropic relations

$$\int_{T_o}^T \frac{\gamma}{\gamma - 1} d \ln T = \ln \left( \frac{P}{P_o} \right)$$

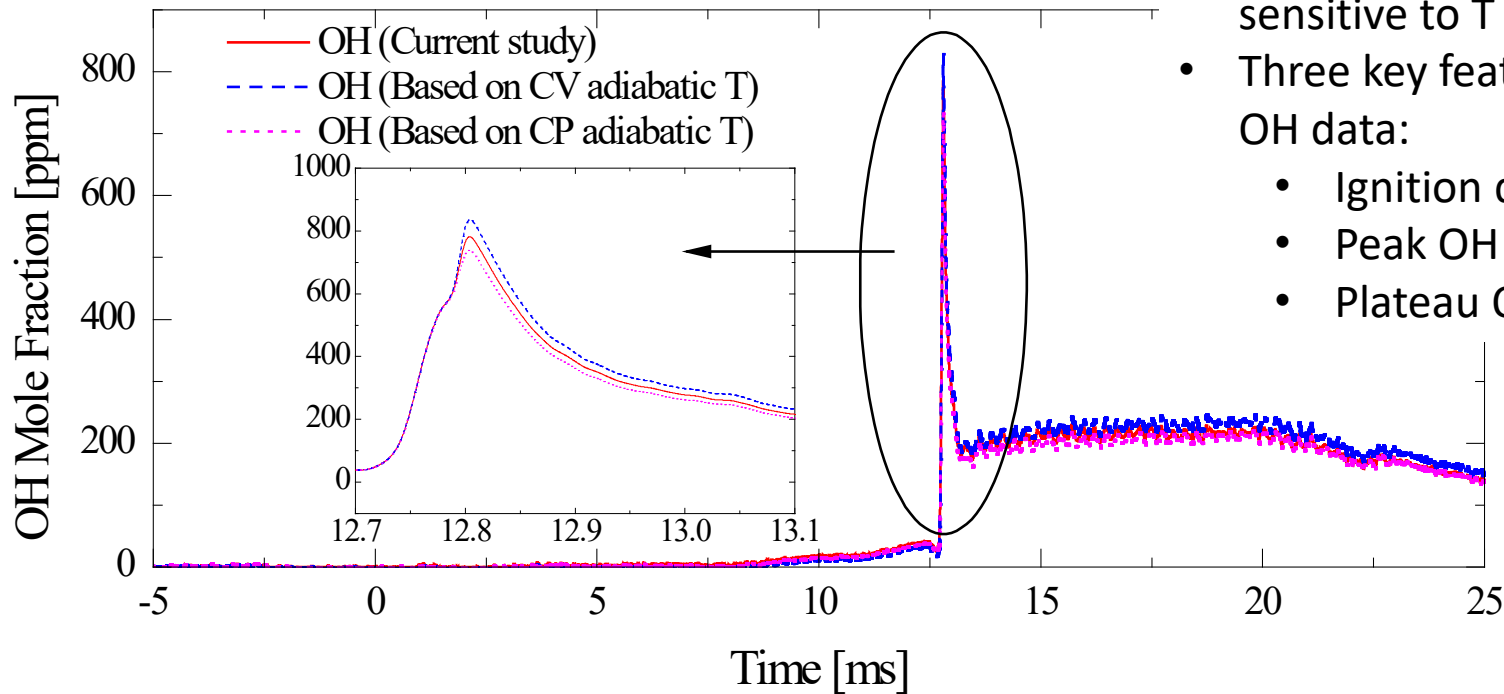
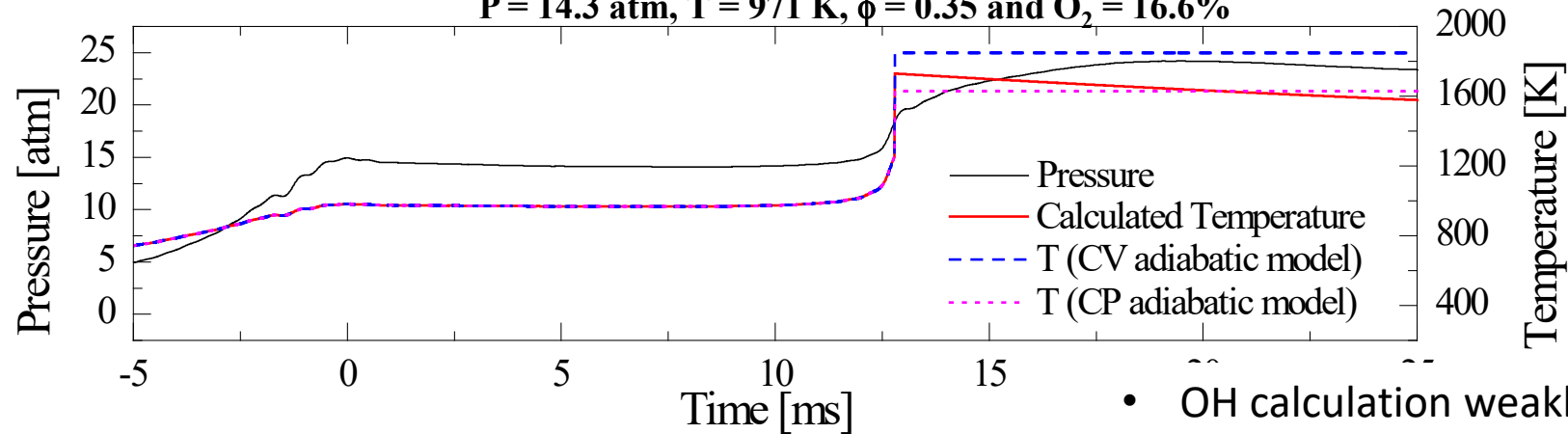
2. Use chemically reacting model for second and third intervals

$$\chi_{OH} = -\frac{1}{S(T)\phi_v PL} \ln \left( \frac{I}{I_o} \right)_v$$



# OH mole fraction time history

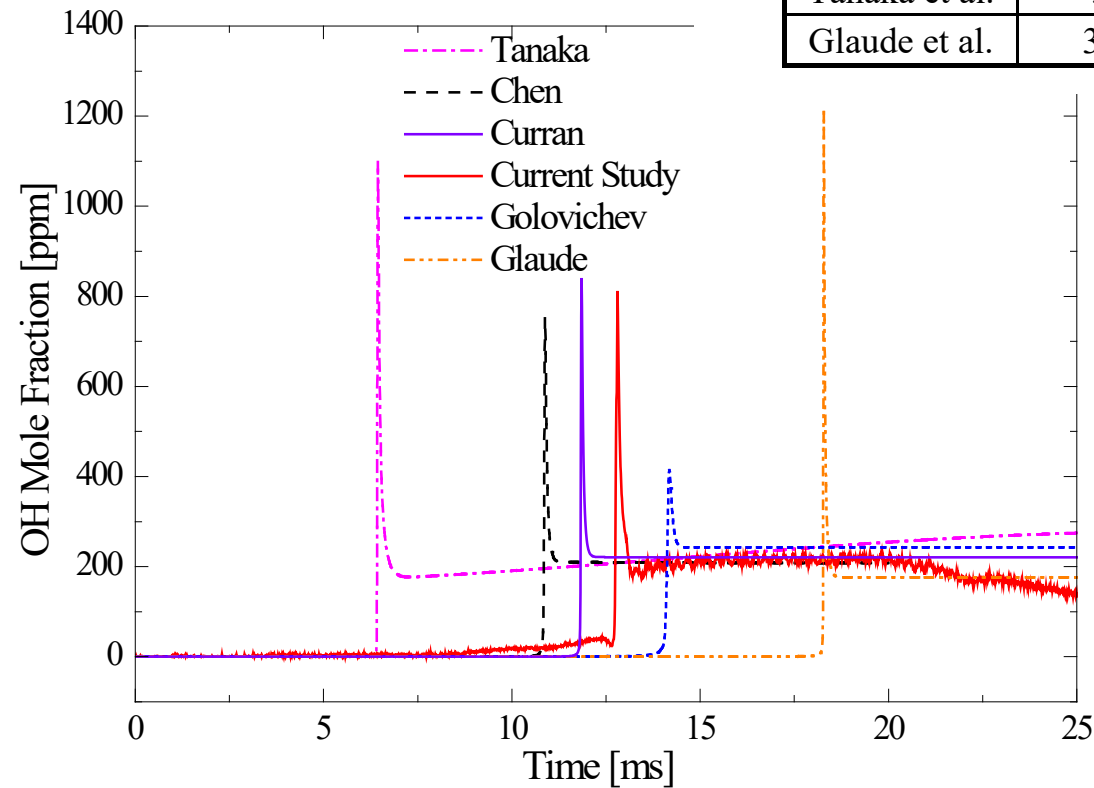
$P = 14.3 \text{ atm}$ ,  $T = 971 \text{ K}$ ,  $\phi = 0.35$  and  $O_2 = 16.6\%$



- OH calculation weakly sensitive to T model used!
- Three key features to all OH data:
  - Ignition delay time
  - Peak OH level
  - Plateau OH level

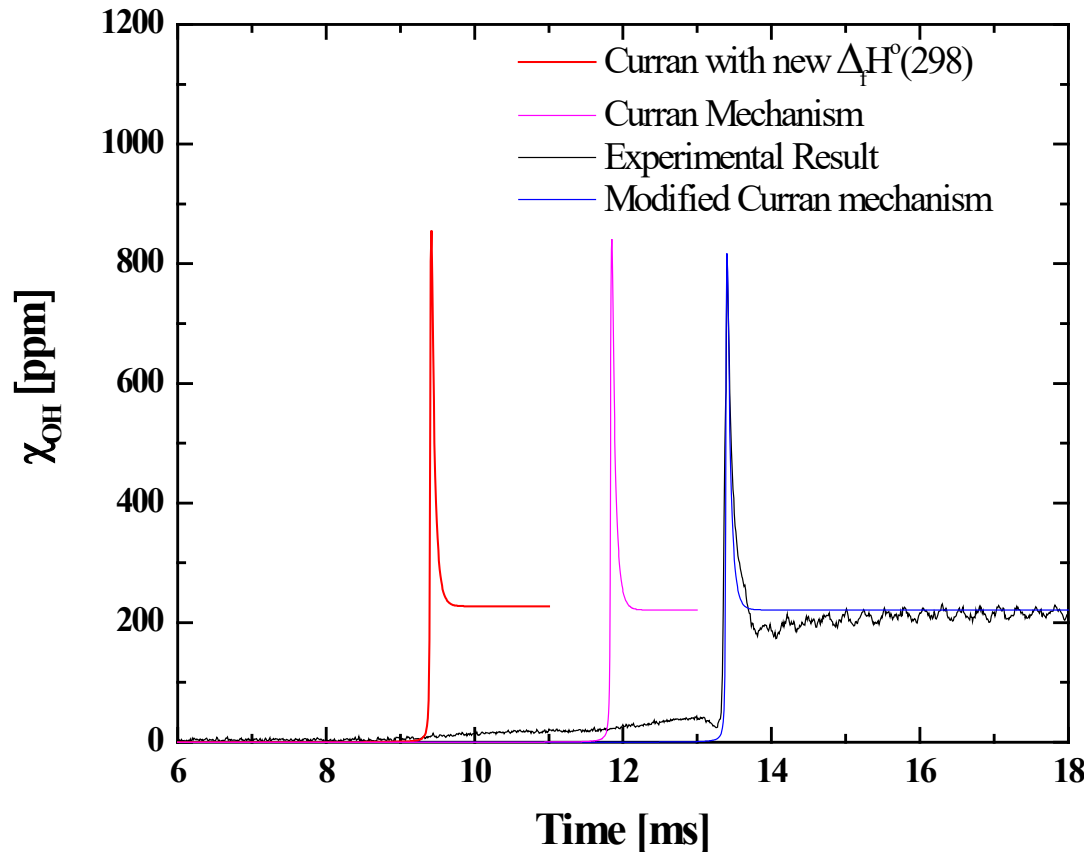
## 1. We can benchmark reaction mechanisms

	Number of Species	Number of Reactions	Mechanism Type
Curran et al	858	3606	Detailed
Chen	259	621	Skeletal
Golovichev	84	412	Skeletal
Tanaka et al.	38	61	Reduced
Glaude et al.	353	1481	Detailed



$P = 14.3 \text{ atm}$   
 $T = 971 \text{ K}$   
 $\phi = 0.35$   
 $O_2 = 16.6\%$

## 2. We can evaluate the effects of thermochemical data.

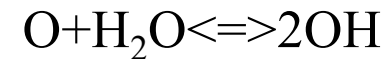


$P = 14.3 \text{ atm}, T = 971 \text{ K}, \phi = 0.35, O_2 = 16.6\%$

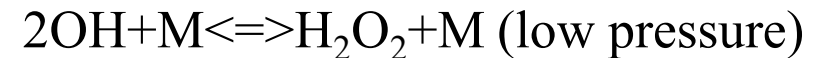
Use  $(\Delta H_f^o)_{298,OH}$  recommend by Herbon *et al.* in Curran thermodynamic data:

39.7 kJ/kg  $\longrightarrow$  7.3 kJ/kg

$\tau_{ign}$  is very sensitive to  $(\Delta H_f^o)_{298,OH}$   
6.5% change in  $(\Delta H_f^o)_{298,OH}$   
results in 20% decrease in  $\tau_{ign}$



A:  $2.97 \times 10^6$  ( $\downarrow$  by 10%)  $\longrightarrow$   $2.673 \times 10^6$



A:  $3.041 \times 10^{30}$  ( $\downarrow$  by 74%)  $\longrightarrow$   $0.7982 \times 10^{30}$

- 3. We can use the features to improve elementary rate coefficients
- 4. We can use trends with pressure to identify reactions governing ignition behavior

Reactions	$\tau$	Peak $\chi_{OH}$
$O+H_2O \rightleftharpoons 2OH$	—	↑
$CO+OH \rightleftharpoons CO_2+H$	↑	↓
$H+O_2 \rightleftharpoons O+OH$	↓	↑
$2OH+M \rightleftharpoons H_2O_2+M$	↓	—

## Sources of experimental uncertainties

Uncertainty Source	Direct Uncertainty	$U_i = \text{Uncertainty in } \chi_{OH}$
Absorption due to olefine molecular	3%	-8%
Laser source departure from resonant laser frequency	$\pm 0.05 \text{ cm}^{-1}$	3%
Peak temperature estimation	+150K/-100K	10%/-7%
Pressure oscillations, Pressure transducer linearity, and amplifier drift	$\pm 4\%$	0.5%
Path length	$\pm 1.0 \text{ mm}$	$\pm 2.5\%$
Spectroscopic parameters Various		$\pm 5\%$
<b>Combined uncertainty</b>		+12%/-12%

## Laser absorption spectroscopy can be...

- absolute and quantitative: does not require calibration\*
- accurate\*:  $\pm 5\%$  T (via OH),  $\pm 20\%$  T (via H<sub>2</sub>O),  $\pm 10\%$   $\chi_{OH}$ ,  $\pm 35\%$   $\chi_{H_2O}$
- sensitive\*\*:  $\sim 1\text{-}15$  ppm detectivity limit for OH,  $\sim 0.02\%\text{-}0.1\%$  detectivity limit for H<sub>2</sub>O
- robust: applicable in high T, high P, multi-phase flows
- *in situ*/non intrusive  $\leftarrow$  need optical access, *but/and* line-of-sight (path-averaged)
- good spatial resolution:  $< 0.5$  mm
- fast: with continuous laser source, the temporal resolution is limited by your detection and data acquisition methods ( $< 0.5$   $\mu\text{sec}$  with photodiodes)

\*depends on the accuracy of the absorption constants of the probe species

\*\*depends on the oscillator strength of the probe species, the source laser intensity and the interrogation conditions

**I encourage you to explore the possibilities!**

## With your partner

- Briefly, explain what diagnostics you are using in your experiments and why? For example, thermocouples for exhaust gas temperature. What are the sources of uncertainties in your experiments?



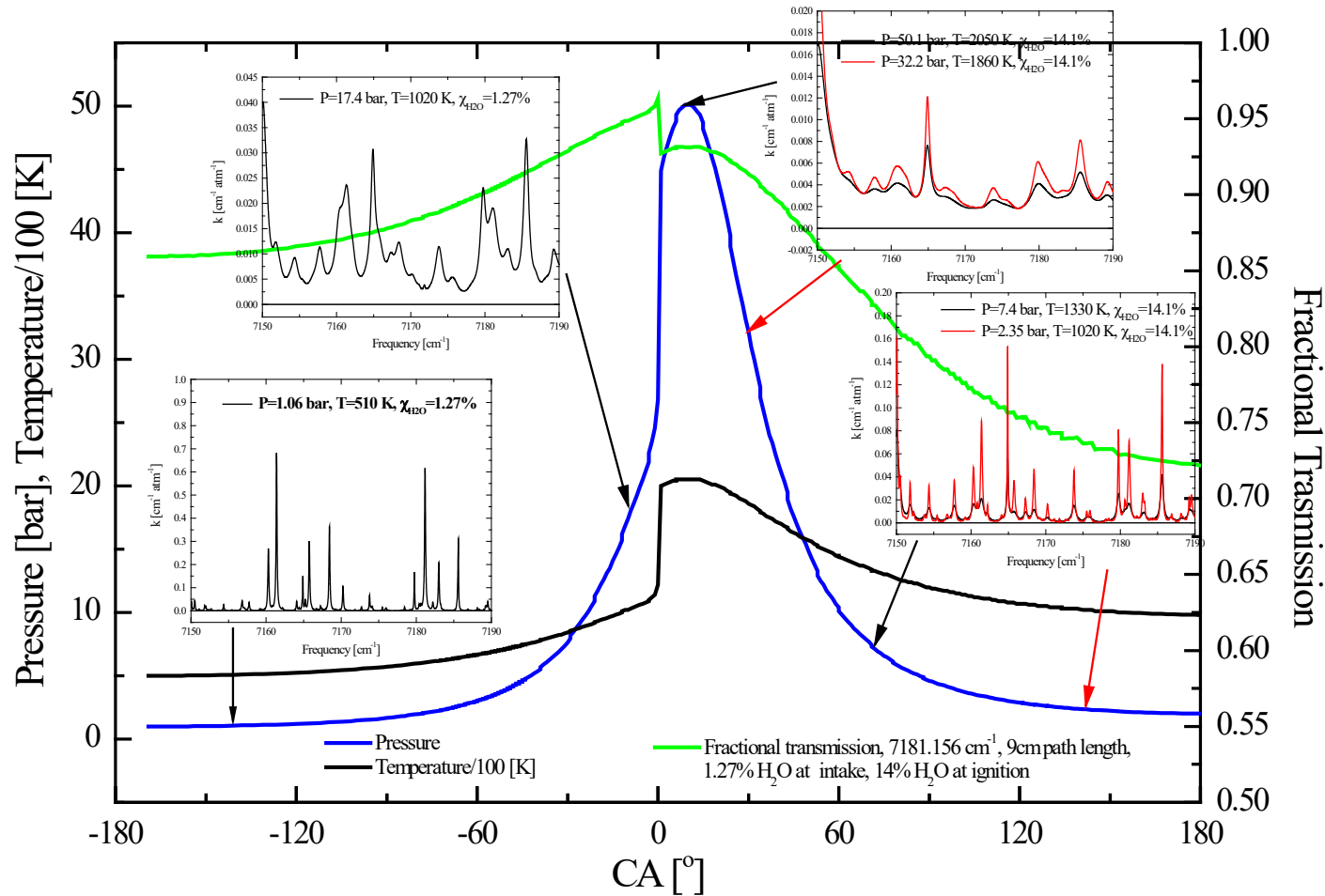
**combustion** LABORATORY

**Supplemental material**



# What to expect in a reciprocating engine?

Absorption and emission spectroscopy are difficult, but not impossible with gases at high pressures



$$-\ln \frac{I(\nu)}{I_0} = S_{lu} \phi(\nu) P \chi_{OH} L = k_\nu P \chi_{OH} L$$

$$k_\nu [\text{cm}^{-1} \text{atm}^{-1}] = S_{lu}(T) \phi(\nu)$$

$\phi(\nu)$  = normalized line shape function

$P$  = pressure

$\chi_{OH}$  = mole fraction of OH

$P_{OH}$  = partial pressure of OH

- So I know Beer's Law. So what?
- 1. Fractional absorption is “easy” to measure,
- 2.  $k_\nu$  is a function of many important combustion parameters, like  $P$ ,  $T$  and  $\chi_i$  (the mole fraction of the absorbing species)

# Absorption Spectroscopy Theory

Beer's Law: 
$$-\ln \frac{I(\nu)}{I_0} = S_{lu} \varphi(\nu) P \chi_{OH} L = k_v \boxed{P \chi_{OH}} L$$

Absorption Coefficient: 
$$k_v [\text{cm}^{-1} \text{atm}^{-1}] = S_{lu}(T) \varphi(\nu)$$

Integrated Line Strength: 
$$S_{lu}(T) = \frac{1}{8\pi c \nu_0^2} \frac{1}{kT} \frac{e^{-\frac{hcE''}{kT}}}{Q_{\text{int}}} A_{ul} (2J' + 1) (1 - e^{-\frac{hc\nu_0}{kT}})$$

Partition Function: 
$$Q_{\text{int}} = Q_{\text{elec}} Q_{\text{rot}} Q_{\text{vib}} = f(T)$$

Normalized Line Shape Function: 
$$\varphi(\nu) = \left( \frac{\ln 2}{\pi} \right)^{1/2} \frac{2}{\Delta \nu_{\text{Doppler}}} V(w, a)$$

Collisional Broadening: 
$$\Delta \nu_{\text{collision}} = \sum 2\gamma_{i,\text{ref}} \boxed{P_i(T/T_{\text{ref}})^{-n_i}}$$
$$\Delta \nu_{\text{Doppler}} = 3.581 \times 10^{-7} \nu_0 \sqrt{\boxed{T} / M}$$

Doppler Broadening: 
$$\boxed{a} = (\ln 2)^{1/2} \Delta \nu_{\text{collision}} / \Delta \nu_{\text{Doppler}}$$