Quantitative Laser Diagnostics for Combustion Chemistry and Propulsion

Lecture 12: Shock Tube Applications with Lasers

1. Laser Absorption Theory

2. Survey of Capabilities

3. Kinetics Applications:
   - Rate Constant Measurements
   - Multi-Species Time-Histories

4. New Species Diagnostics

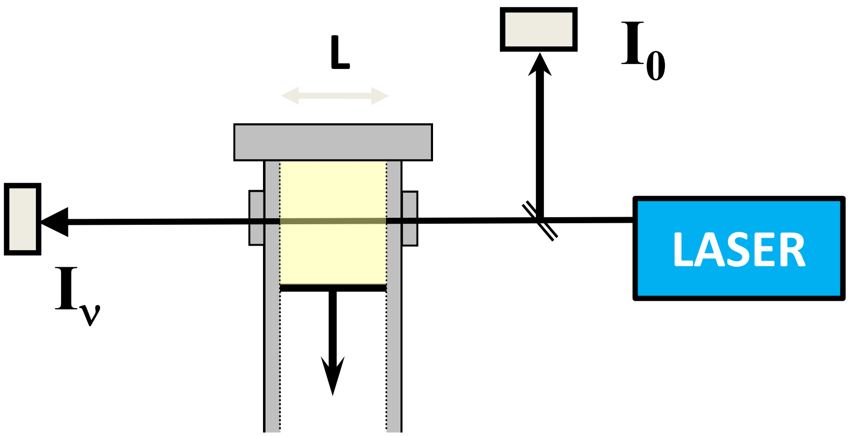
1. Laser Absorption Theory

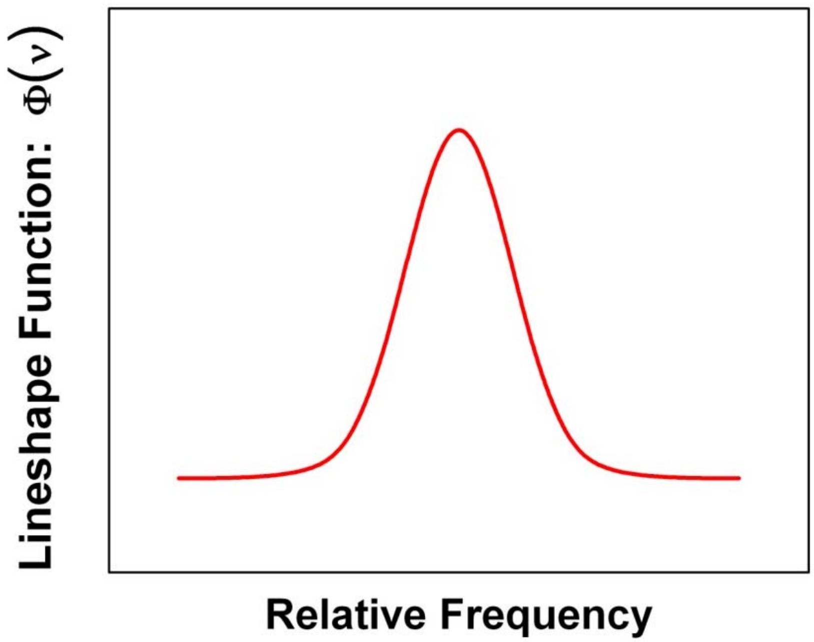
- **Governing Equation: Beer-Lambert Law**

$$I_\nu/I_0 = \exp(-S_{lu}\,\Phi(\nu)\,X_{species}\,P_{total}\,L)$$

Line Strength

Line shape





- **Quantitative absorption requires database for S, Φ**
- **What species have been measured?**

2. Survey of Capabilities:
Species and Wavelengths

Ultraviolet

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

Visible

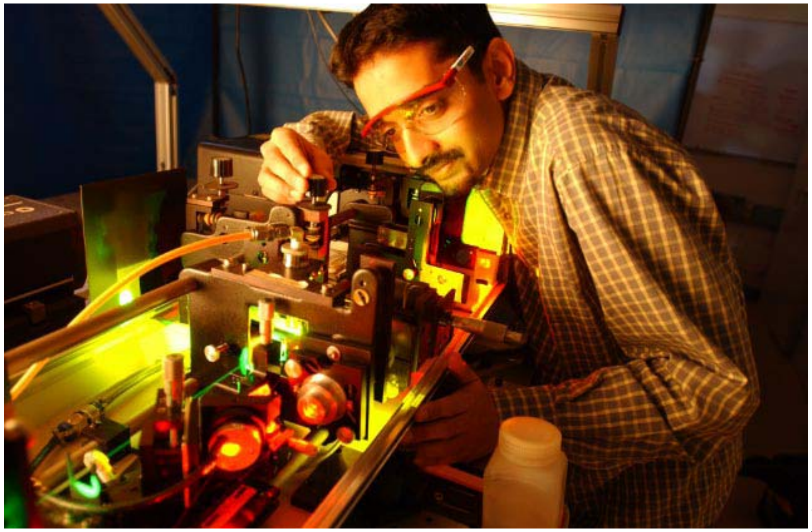
CN	388 nm
CH	431 nm
NCO	440 nm
NO_2	472 nm
NH_2	597 nm
HCO	614 nm

Infrared

CO	2.3 μm
H_2O	2.5 μm
CO_2	2.7 μm
Fuel/CH_2O	3.4 μm
NO	5.2 μm
C_2H_4	10.5 μm
C_3H_6/i-C_4H_8	11/11.3 μm

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

Spectra-Physics 380



2. Survey of Capabilities:
Species and Wavelengths

Ultraviolet		Visible		Infrared	
CH_3	216 nm	CN	388 nm	CO	2.3 μm
NO	225 nm	CH	431 nm	H_2O	2.5 μm
O_2	227 nm	NCO	440 nm	CO_2	2.7 μm
HO_2	230 nm	NO_2	472 nm	Fuel/CH_2O	3.4 μm
OH/CH_2O	306 nm	NH_2	597 nm	NO	5.2 μm
NH	336 nm	HCO	614 nm	C_2H_4	10.5 μm
				C_3H_6/i-C_4H_8	11/11.3 μm

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

Coherent MIRA
Ti-Sapphire Ring Laser

2. Survey of Capabilities:
Species and Wavelengths

Ultraviolet

CH_3	216 nm
NO	225 nm
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Infrared

CO	2.3 μm
H_2O	2.5 μm
CO_2	2.7 μm
Fuel/CH_2O	3.4 μm
NO	5.2 μm
C_2H_4	10.5 μm
C_3H_6/i-C_4H_8	11/11.3 μm

New lasers allow simple access to mid-IR

M^2 UV Ti:Sapp Laser

2. Survey of Capabilities:
Species and Wavelengths

Ultraviolet		Visible		Infrared	
CH_3	216 nm	CN	388 nm	CO	2.3 μm
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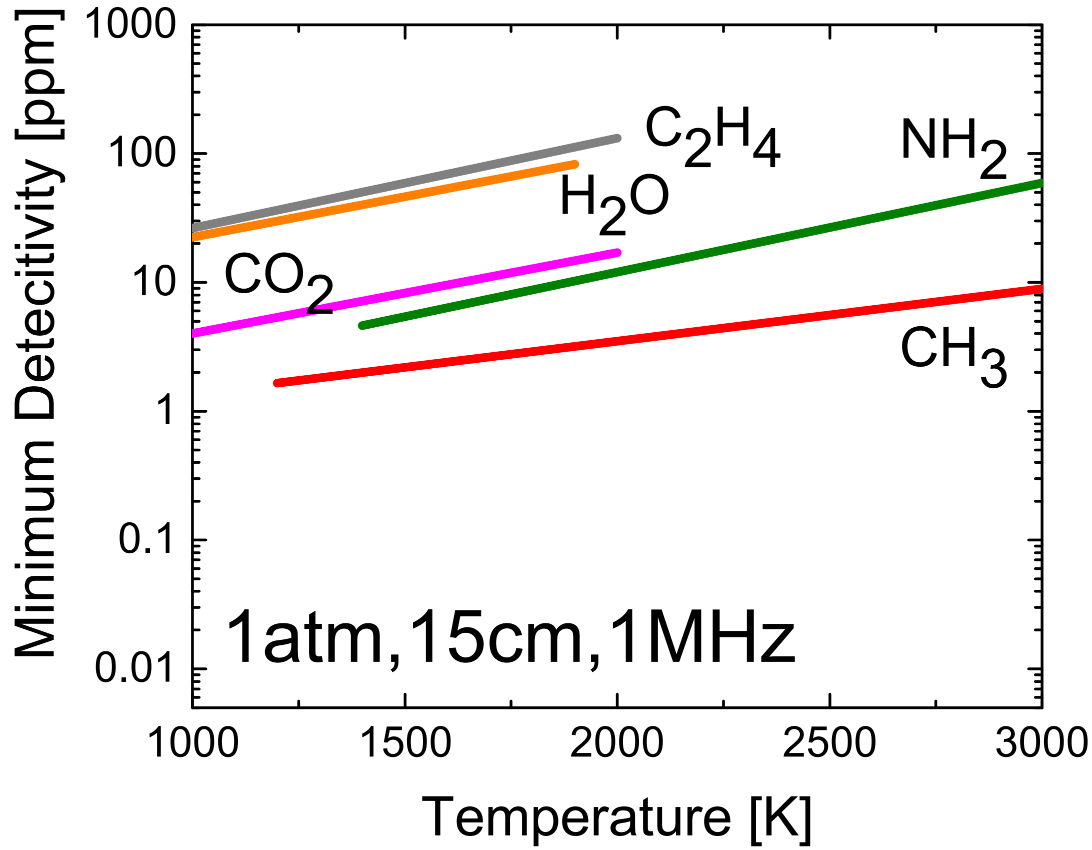
NH	336 nm	HCO	614 nm	C_2H_4	10.5 μm
				C_3H_6/i-C_4H_8	11/11.3 μm

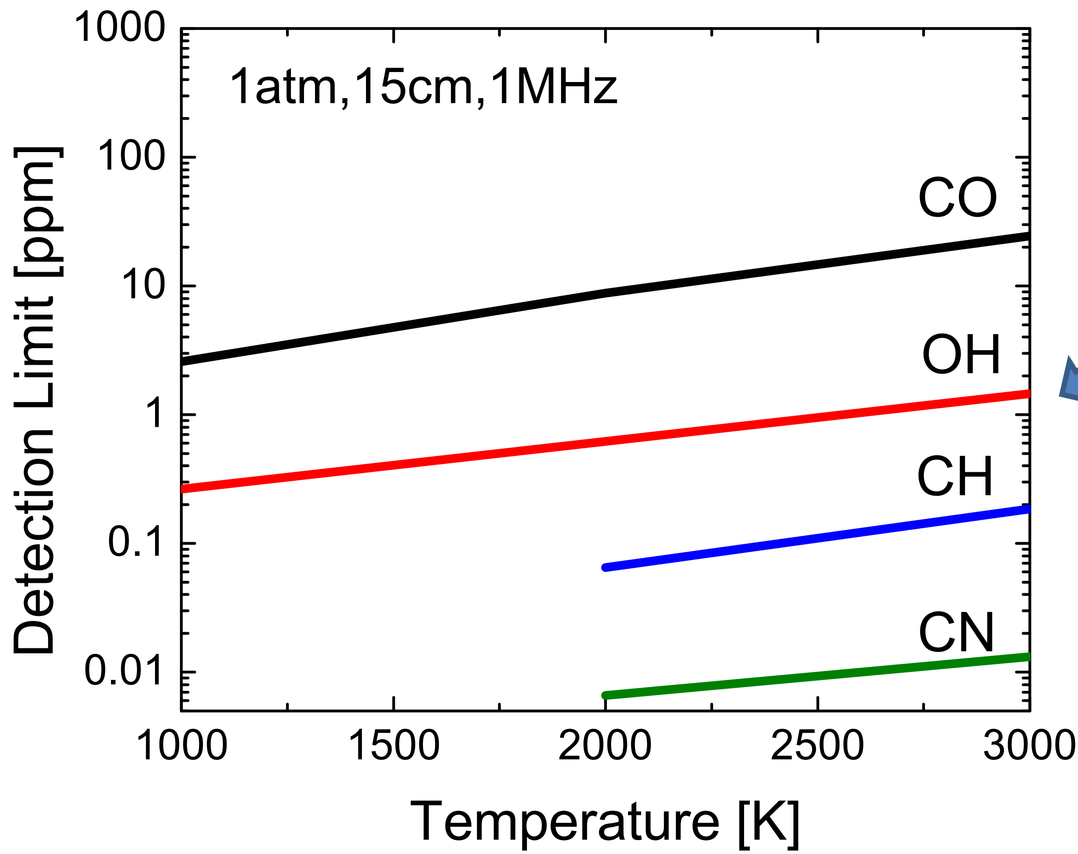
How sensitive are laser absorption diagnostics in shock tubes?

2. Laser Absorption Yields High Sensitivity
Representative Detection Limits: Large Molecules



- **Large molecules: 10-100’s ppm**

2. Laser Absorption Yields High Sensitivity
Representative Detection Limits: Diatomic Molecules



sub-ppm sensitivity for OH, CH, CN

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

3. Kinetics Applications

1. **Foundation Fuel Kinetics**

   $OH+H_2=H_2O+H$

2. **Methyl Ester Kinetics**

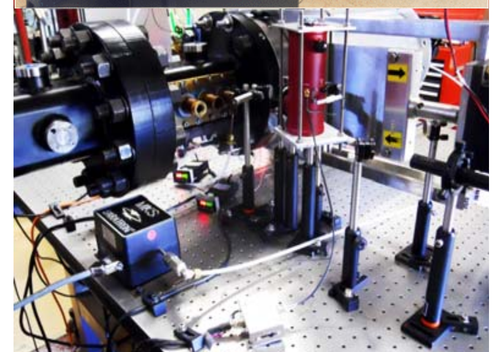
   ME+OH=Products

   Methyl Formate pyrolysis

3. **Butanol Isomer Kinetics**

   n-Butanol pyrolysis

   t-butanol+OH using isotopic labeling



3.1 Foundation Fuel Kinetics:

- **Recent Elementary Rate Constant Measurements using Shock Tube/Laser Absorption Methods**

- $H + O_2 = OH + O$
- $H_2O_2 + M = OH + OH + M$
- $OH + H_2O_2 = H_2O + HO_2$
- $OH + HO_2 = H_2O + O_2$
- $HO_2 + HO_2 = H_2O_2 + O_2$
- $CH_3 + HO_2 = \text{Products}$
- $C_2H_4 + M = C_2H_2 + H_2 + M$
- $OH + H_2 = H_2O + H$

3.1 Foundation Fuel Kinetics

How Do We Measure Individual Reaction Rates?
- Two-Step Process

1. **Design: use sensitivity analysis to kinetically isolate reactions**

2. **Execute: use shock tubes for step heating and laser absorption for species detection**

Example: $H + O_2 \xrightarrow{k} OH + O$

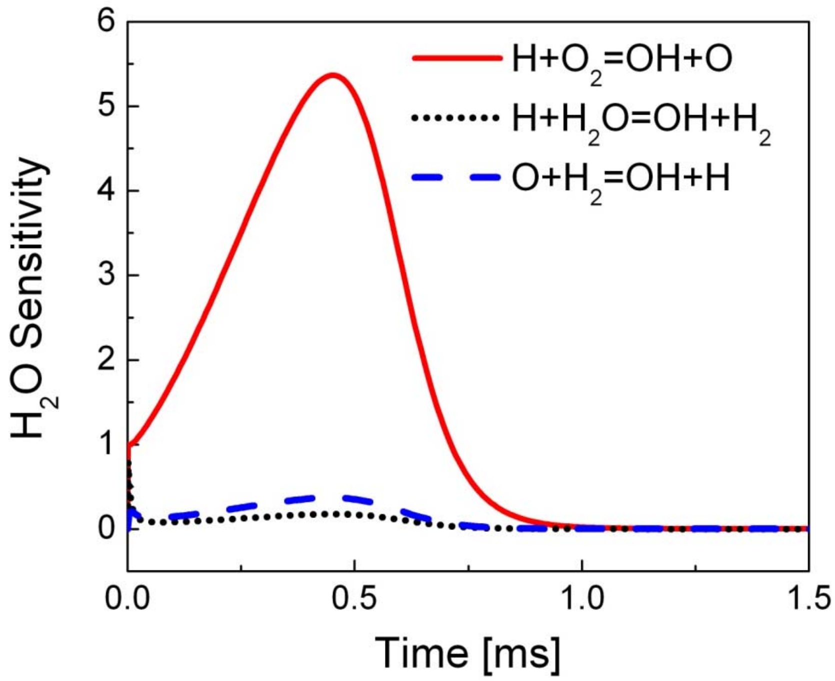
- **Accurate *k* values critical to combustion modeling**

3.1 Foundation Fuel Kinetics

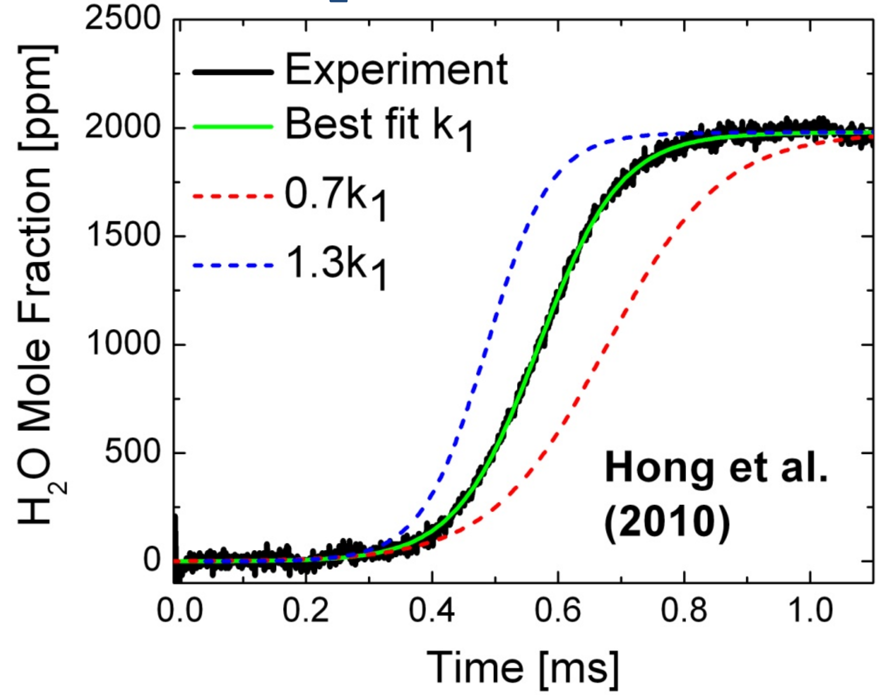
- **Example: $H + O_2 \rightarrow OH + O$**
  Rate Measurement using H_2O Laser at 2.55 mm

Shock Conditions: 1472 K, 1.8 atm, 0.1%O_2/0.9%H_2/Ar

H_2O Sensitivity



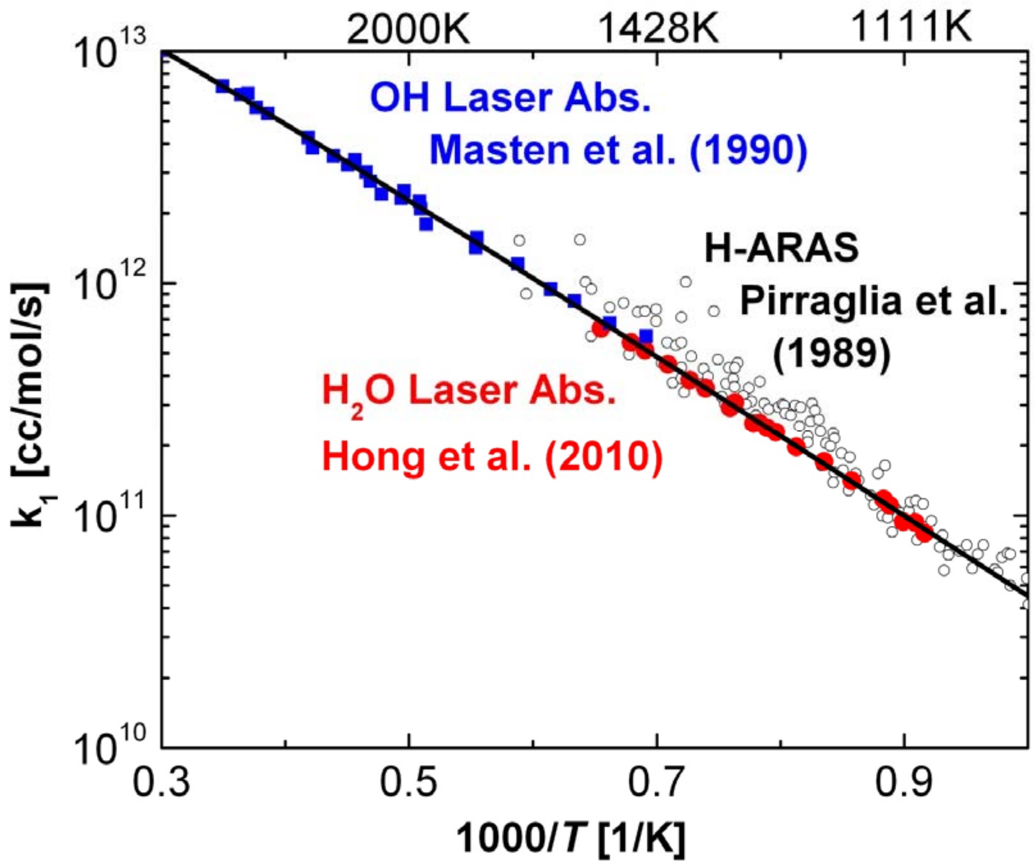
H_2O Time-History



- **H_2O time-history provides precise determination of k_1**

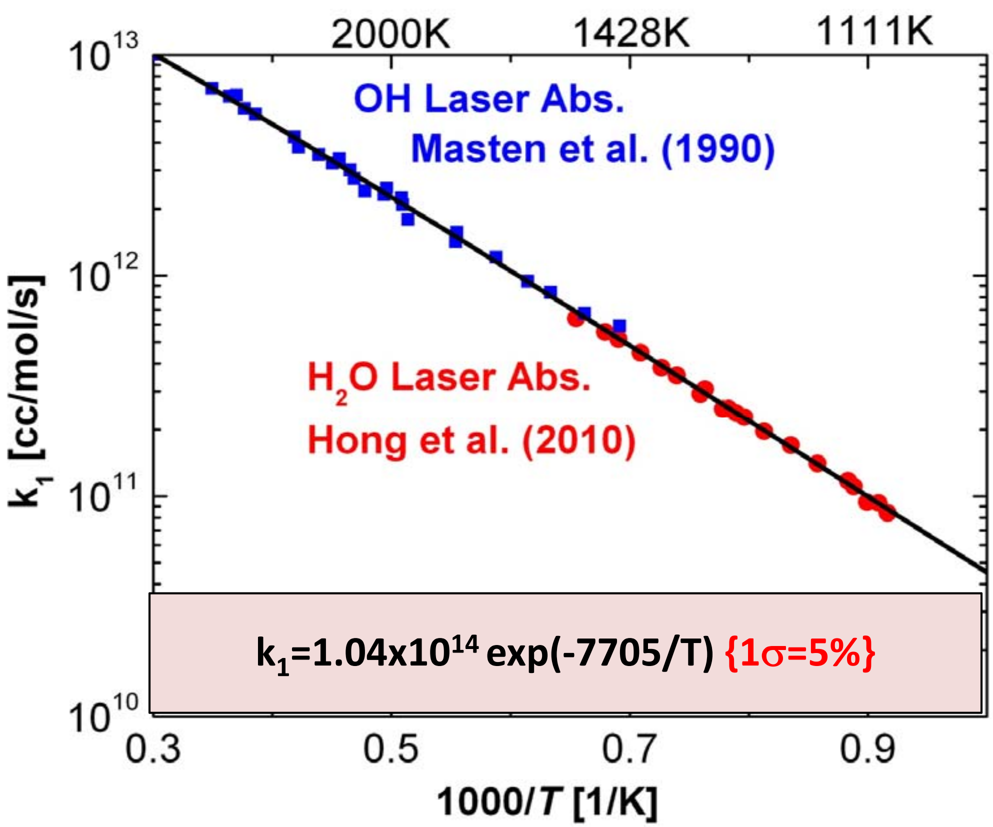
3.1 Foundation Fuel Kinetics

Arrhenius Plot: $H + O_2 \rightarrow OH + O$



3.1 Foundation Fuel Kinetics

Arrhenius Plot: $H + O_2 \rightarrow OH + O$



- Modern laser methods significantly reduce measurement uncertainty!

Next example: $OH + H_2 \rightarrow H_2O + H$

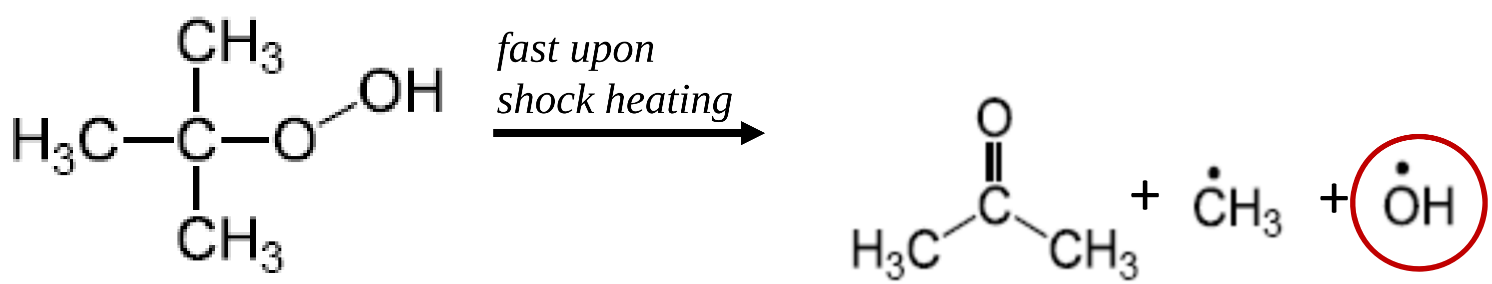
3.1 Foundation Fuel Kinetics

- **Elementary Reaction Rate Determination:**
  $OH + H_2 \rightarrow H_2O + H$

Motivation: **Large uncertainty in k_{OH+H2} gives large uncertainty in modeled H_2/air flame speeds**

Experimental Strategy: **Direct determination of rate constant**

- **Pseudo-first order experiment**
- **Fuel in excess**
- **TBHP used as a prompt OH precursor**
  - **Useful T range (850 to 1350 K)**
  - **Pioneered by Bott and Cohen (1984), also used at Argonne**

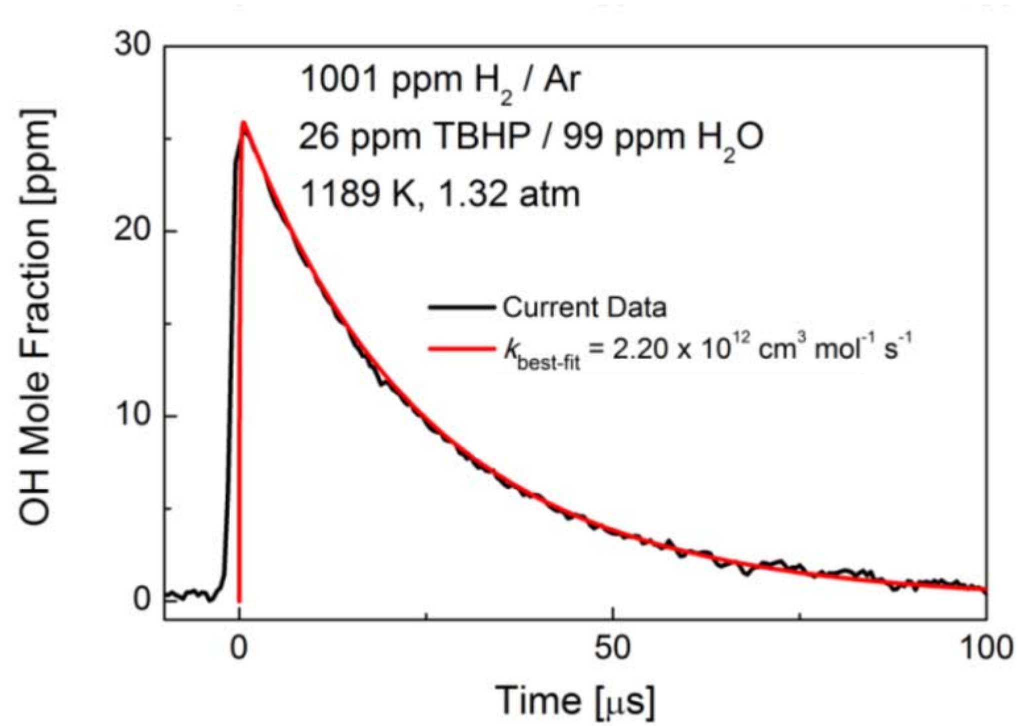


TBHP: tert-butylhydroperoxide

Acetone

3.1 Foundation Fuel Kinetics

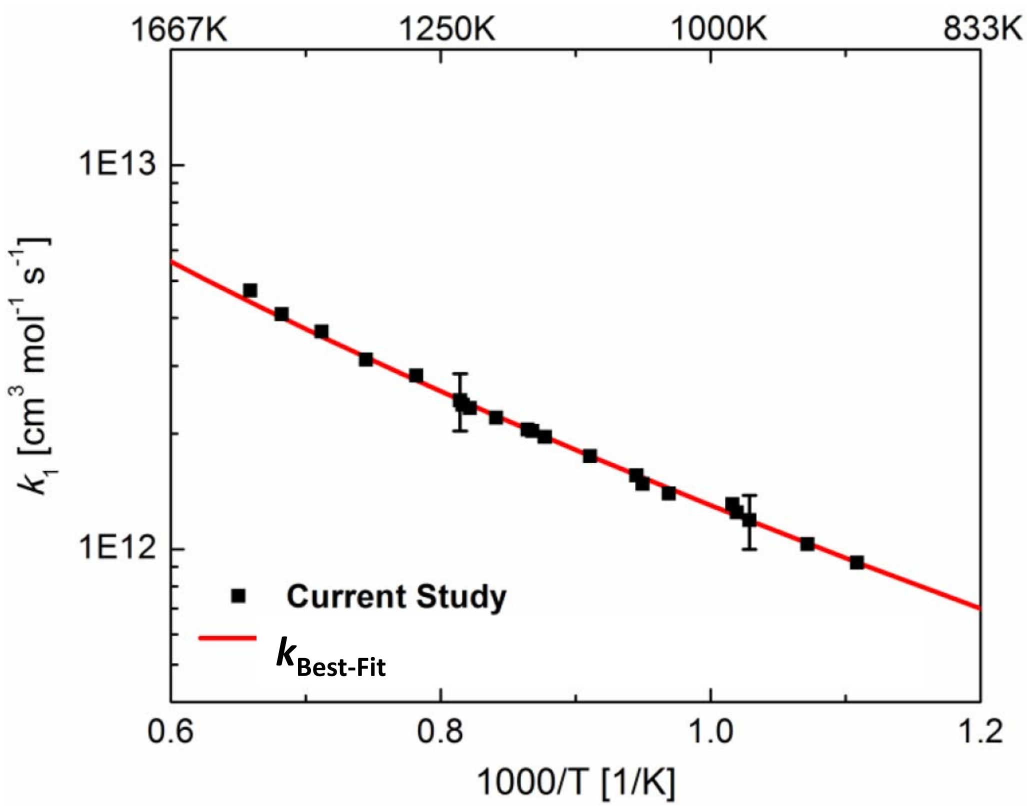
- **Representative OH Absorption Data**



- **High SNR data, ppm sensitivity**
- $k_{best\text{-}fit}$ **determined within 3-5%**

3.1 Foundation Fuel Kinetics

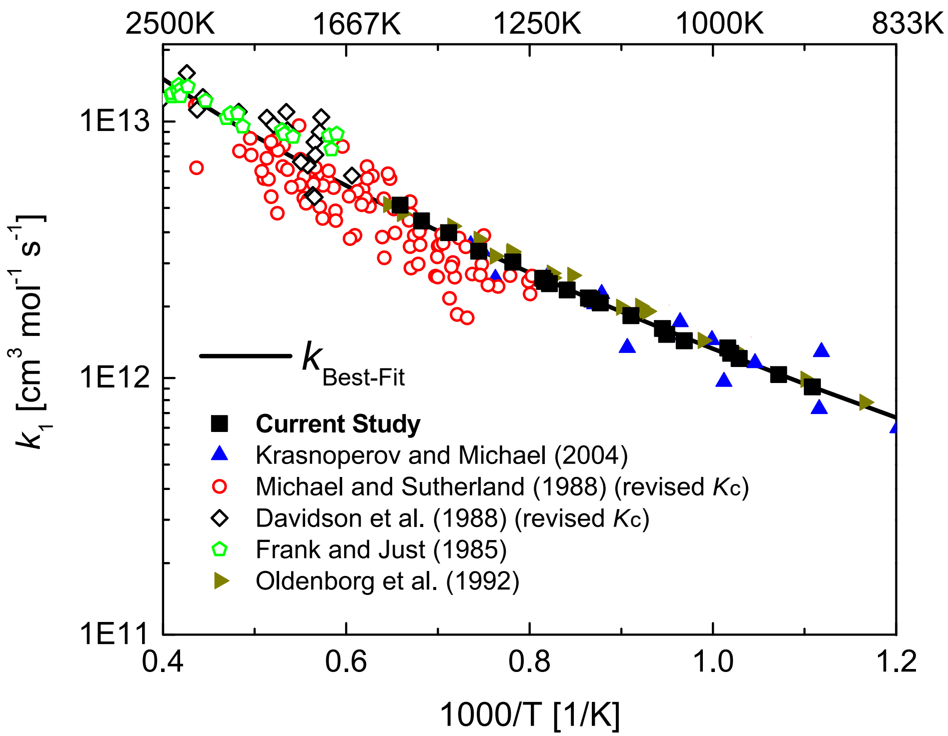
- **Arrhenius Plot: $OH + H_2 \rightarrow H_2O + H$**



- **Very low overall uncertainty in *k*: ±17% (2σ)**

3.1 Foundation Fuel Kinetics

- **Comparison with Past Work: $OH + H_2 \rightarrow H_2O + H$**



- **Excellent agreement with previous work, but uncertainty in *k* substantially reduced**

3.2 Methyl Ester Kinetics

1. Rate Constant Measurements

- OH + Methyl Formate
- OH + Methyl Acetate
- OH + Methyl Propanoate
- OH + Methyl Butanoate

Conducted as first-order experiments, with TBHP as source of OH

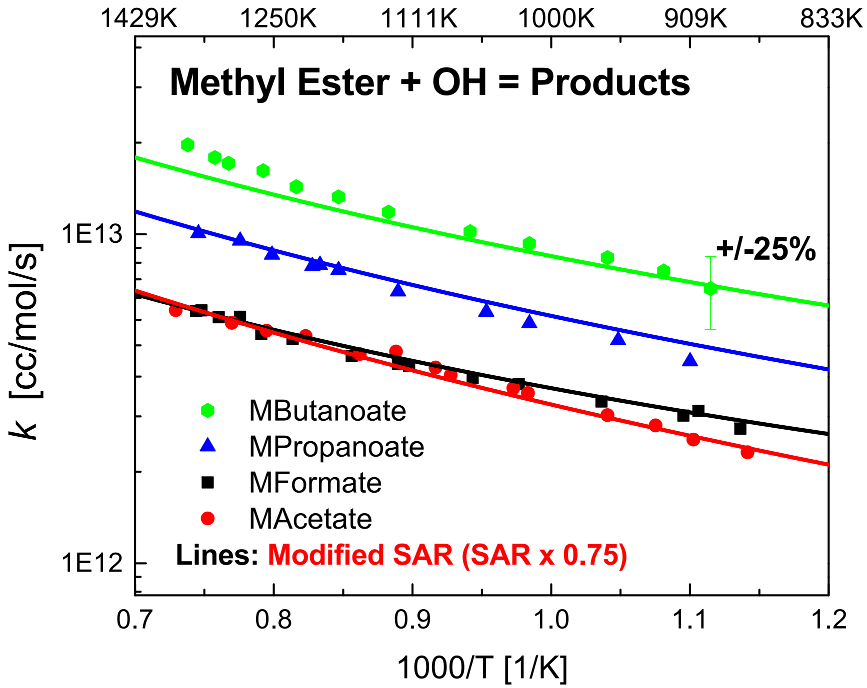
2. Methyl Formate Pyrolysis

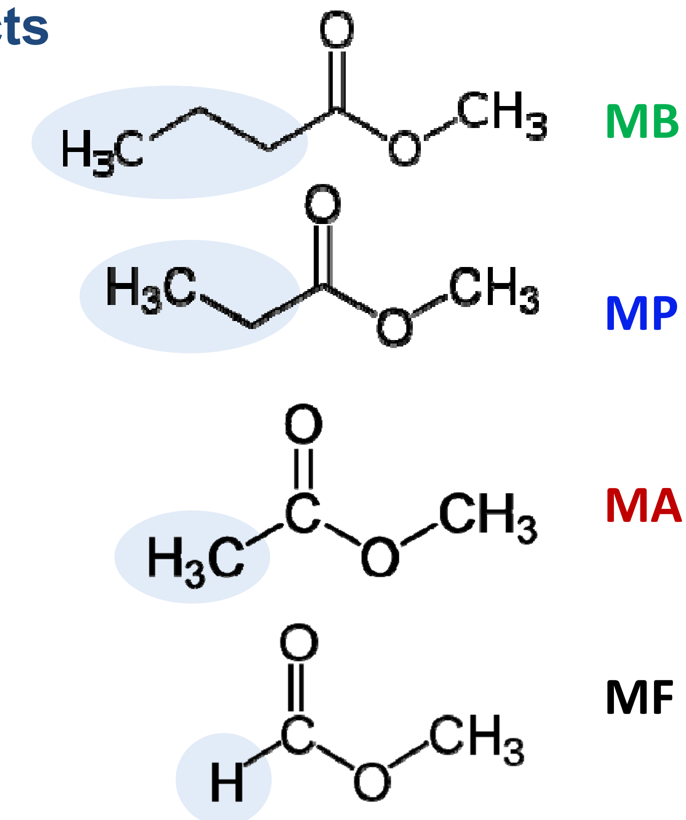
- Multi-species Data

MF, CH_3OH
CO, CH_4, CH_2O

3.2 Methyl Ester Kinetics

- **Summary: OH+Methyl Esters → Products**



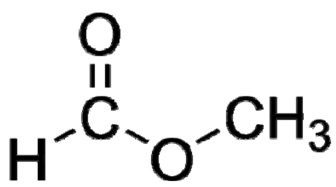


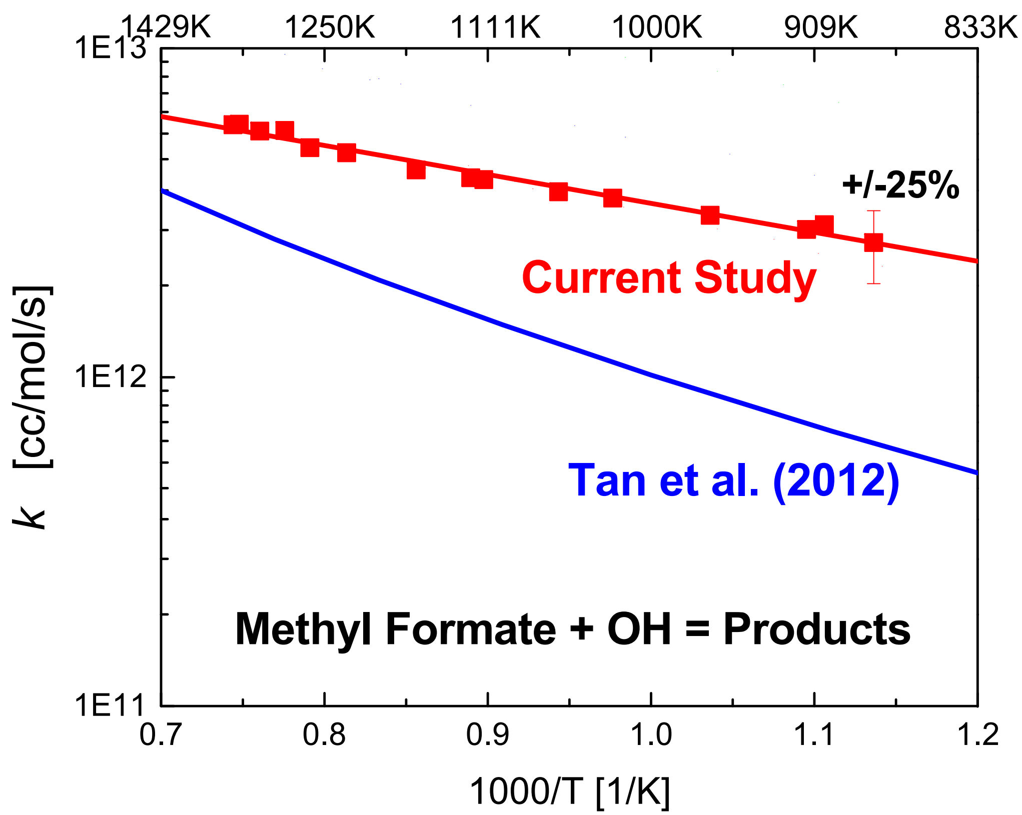
- **Low scatter data with ± 25% overall uncertainty**
- **Good agreement with modified SAR**

(Structure Activity Relationship)

3.2 Methyl Ester Kinetics

- **Comparison with Recent Quantum Calculations: Methyl Formate +OH → Products**

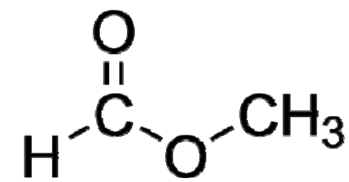


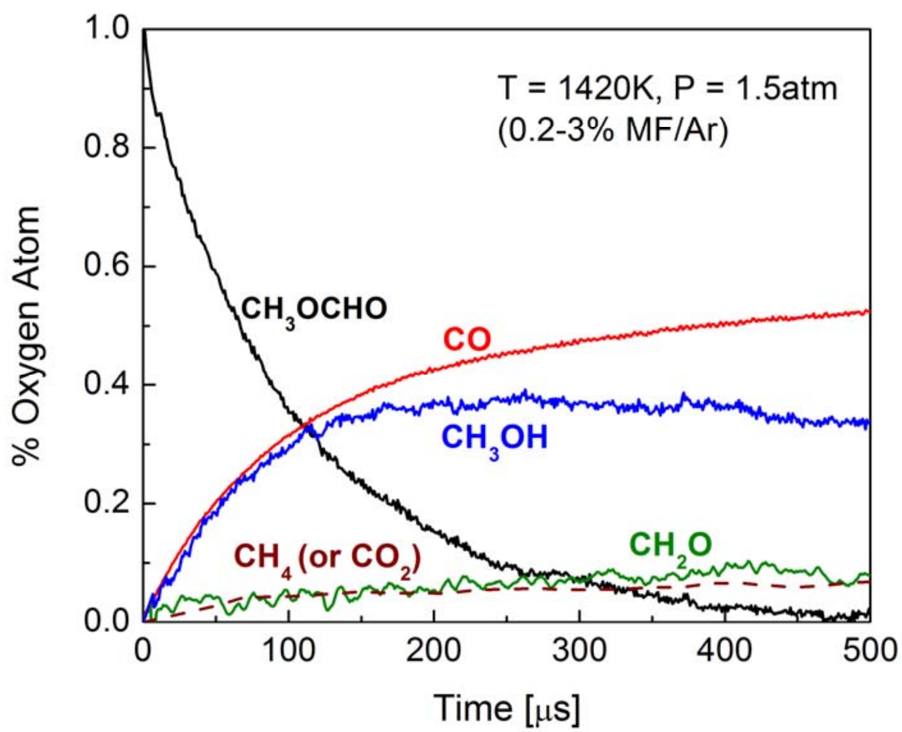


- **Shock tube/laser absorption rate 2-4x faster than calculation**
- **Confirms continuing value of high–accuracy experimental data**

3.2 Methyl Ester Kinetics

- **Methyl Formate Pyrolysis Kinetics:**
  Multi-Species Laser Absorption Data Can Provide Near-Complete Oxygen Balance





@ t = 300μs

% Oxygen balance:

5.5% in CH_3OCHO

34.8% in CH_3OH

44.9% in CO

5.8% in CO_2

7.2% in CH_2O

Total: >98%

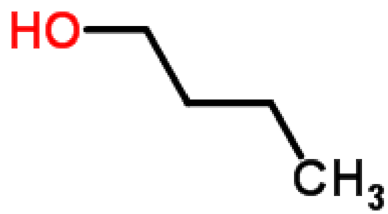
- **Laser data successfully tracks all major contributors to O-atom balance**
- **Atom balance provides important new validation tool for chemical models**

3.3 Butanol Isomer Kinetics

- **Two Studies of Butanol Kinetics**

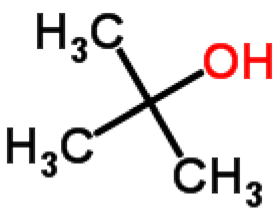
1. **n-Butanol Pyrolysis:**

   Challenge: Complex Pathways
   Solution: Multi-Species Time-Histories
   OH, CO, CH_4, H_2O, C_2H_4



2. **tert-Butanol + OH → Products**

   Challenge: Multiple Reaction Sites, OH Reformation
   Solution: Isotopic Labeling



3.3 Butanol Isomer Kinetics

- **OH+ tert-Butanol → Products**
  Use of Isotopic Labeling

- **Challenges:** **Multiple Reaction Sites, OH Reformation**

- **Solution:** **Isotopic labeling provides strategy to identify OH attack sites**

3.3 Butanol Isomer Kinetics

- **OH+ tert-Butanol → Products**
  Conventional Experiment using t-$C_4H_9{}^{16}OH$

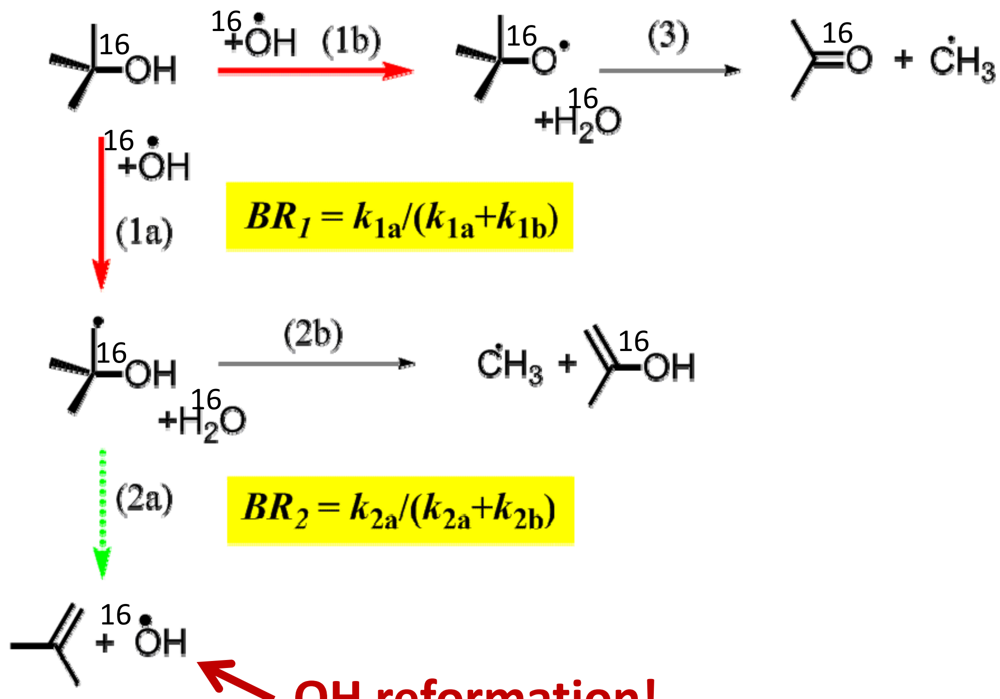
- Measurement of OH removal by t-$C_4H_9{}^{16}OH$ affected by OH reformation pathway

- Measurement gives

$$k_{1b} + k_{1a}(1-BR_2)$$

$$= (k_{1b}+k_{1a})(1-BR_1BR_2)$$

t-$C_4H_9{}^{16}OH$ + ^{16}OH



OH reformation!

3.3 Butanol Isomer Kinetics

- **OH+ tert-Butanol → Products**
  Conventional Experiment using t-$C_4H_9{}^{16}OH$

- Measurement of OH removal by t-$C_4H_9{}^{16}OH$ affected by OH reformation pathway

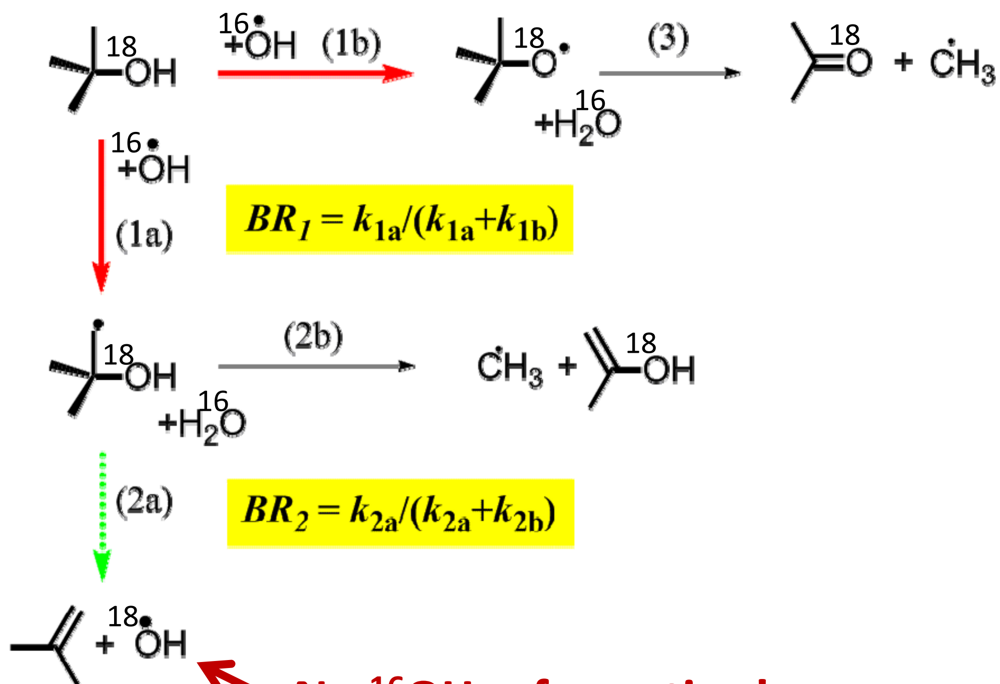
- Measurement gives

  $k_{1b} + k_{1a}(1\text{-}BR_2)$

  $= (k_{1b}+k_{1a})(1\text{-}BR_1BR_2)$

- **Measurement of ^{16}OH in t-$C_4H_9{}^{18}OH$ gives ($k_{1a}+k_{1b}$) with no ^{16}OH reformation**

t-$C_4H_9O^{18}H$ + ^{16}OH

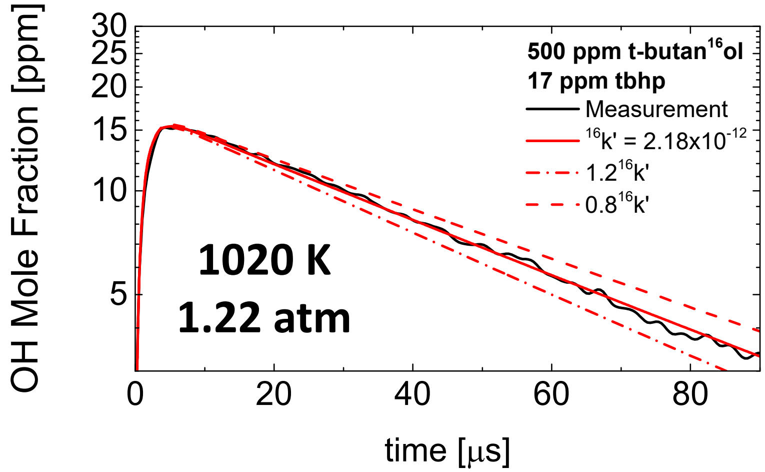


No ^{16}OH reformation!

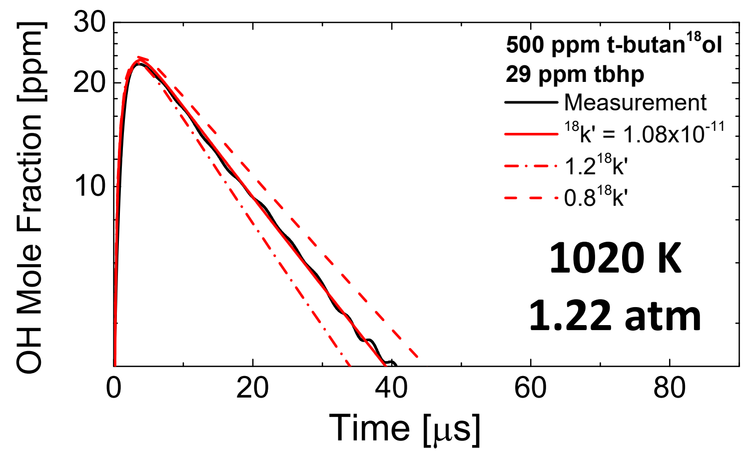
3.3 Butanol Isomer Kinetics

- OH Absorption Data for tert-Butanol (O^{16} & O^{18})

^{16}O-Butanol



^{18}O-Butanol



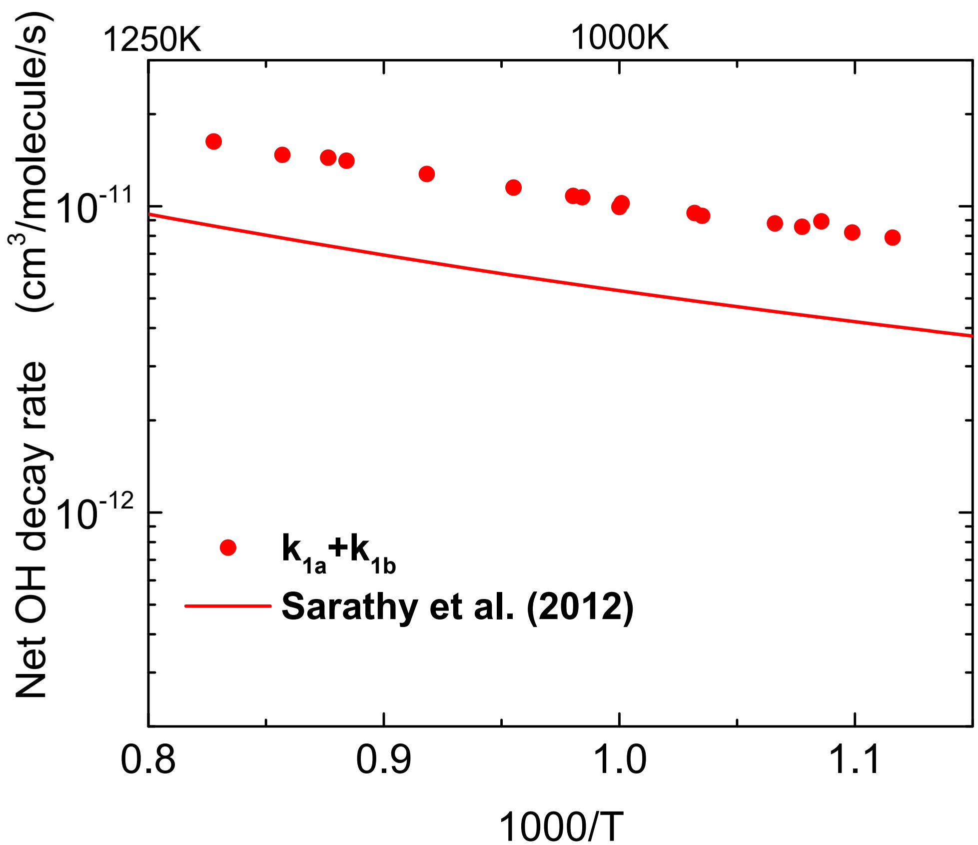
- Slow removal of OH during ^{16}O butanol pyrolysis
- Faster removal of OH during ^{18}O butanol pyrolysis

- **How do the rates compare?**

3.3 Butanol Isomer Kinetics

- **OH + tert-Butanol (O^{16} & O^{18})**

  Net OH Decay Rate due to Reaction with t-Butanol

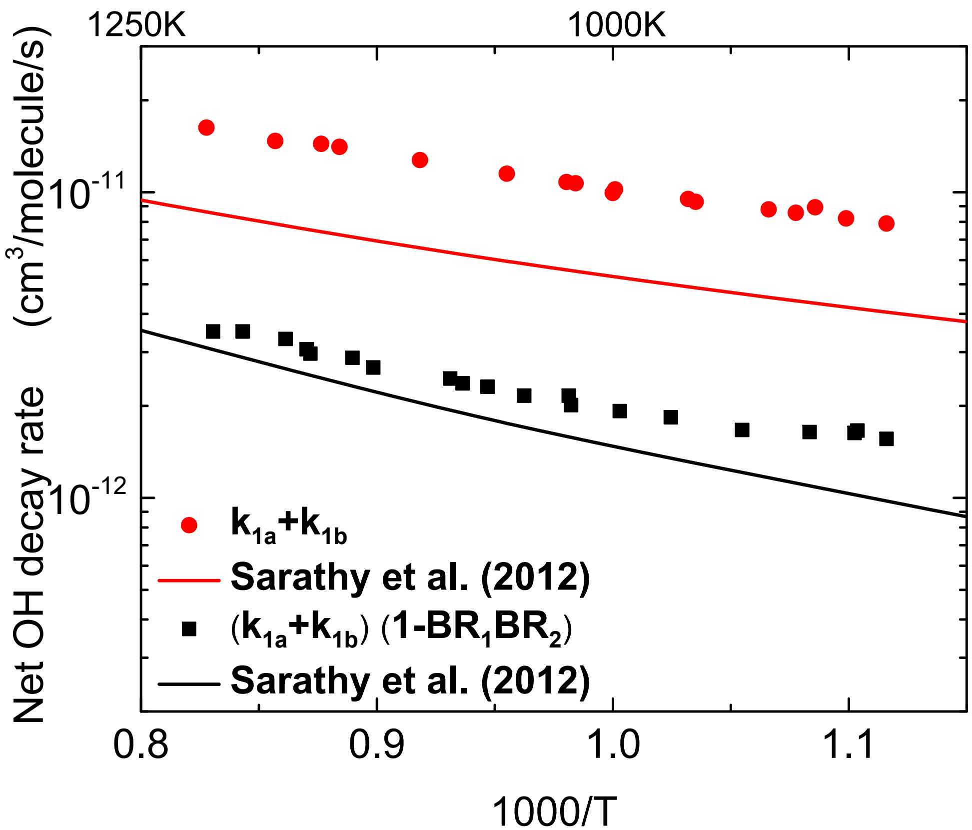


$k_{total} = (k_{1a}+k_{1b})$

Derived from t-$C_4H_9{}^{18}OH$

3.3 Butanol Isomer Kinetics

- **OH + tert-Butanol (O^{16} & O^{18})**
  Net OH Decay Rate due to Reaction with t-Butanol



$k_{total} = (k_{1a}+k_{1b})$
Derived from t-$C_4H_9{}^{18}OH$

$(k_{1a}+k_{1b})$ $(1\text{-}BR_1BR_2)$
Derived from t-$C_4H_9{}^{16}OH$

- **First direct determination of overall rate ($k_{1a}+k_{1b}$)**
- **Ratio ($^{18}O/^{16}O$ expts.) gives $(1\text{-}BR_1BR_2) = 0.2$**
- **Since $BR_1 = 0.95$, then $BR_2 = 0.8$ ($\pm$0.05)**

4. New Species Diagnostics

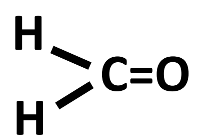
Recent Work:

1. **Aldehydes, e.g.: CH_2O, CH_3CHO**
2. **Alkenes, e.g.: iso-C_4H_8**
3. **Alkynes, e.g.: C_2H_2**
4. **Cavity Enhanced Absorption Spectroscopy (CEAS)**

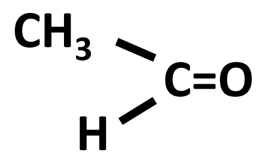
4. New Species Diagnostics - 1

- **Aldehyde Diagnostics**

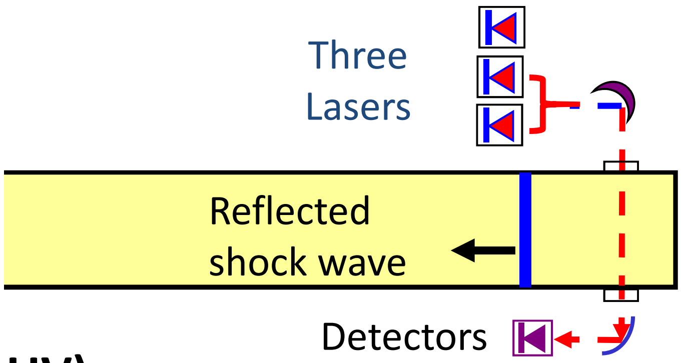
Motivation: Aldehydes provide critical information about first stages of hydrocarbon oxidation, especially oxygenated fuels



Formaldehyde



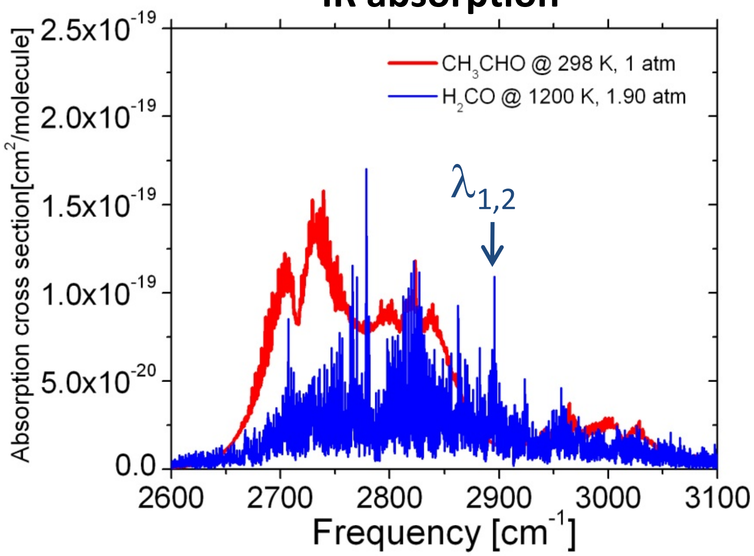
Acetaldehyde



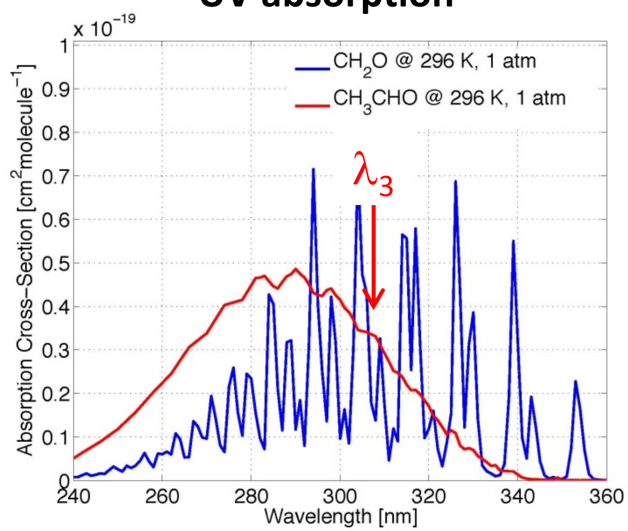
Challenge: Overlapping absorption spectra

Strategy: Three colors (λ_1 and λ_2 in IR, and λ_3 in UV)

IR absorption



UV absorption

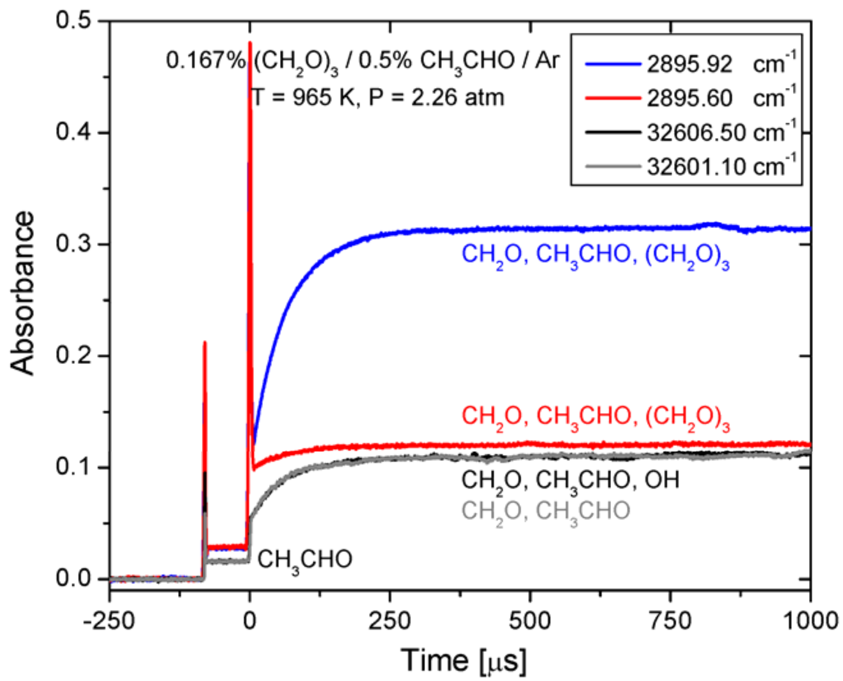


4. New Species Diagnostics - 1

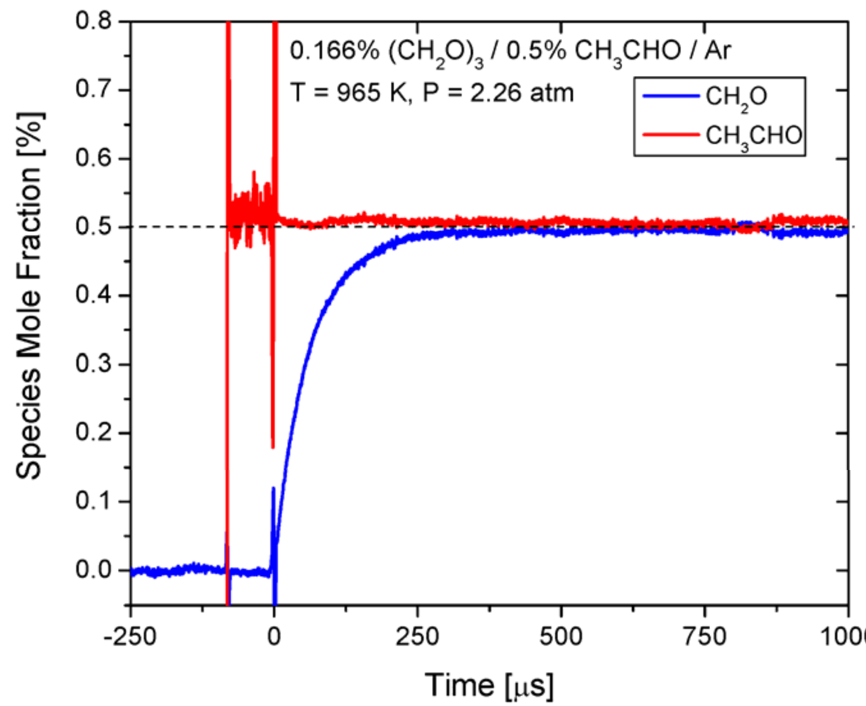
- **Validation Experiment: Simultaneous Measurement of Known CH_2O & CH_3CHO Concentrations**

- **Shock heat trioxane/acetaldehyde mixture**
- **Observe formaldehyde formation**
- **Recover correct CH_2O/CH_3CHO concentrations**

Measured Absorbance Time-Histories



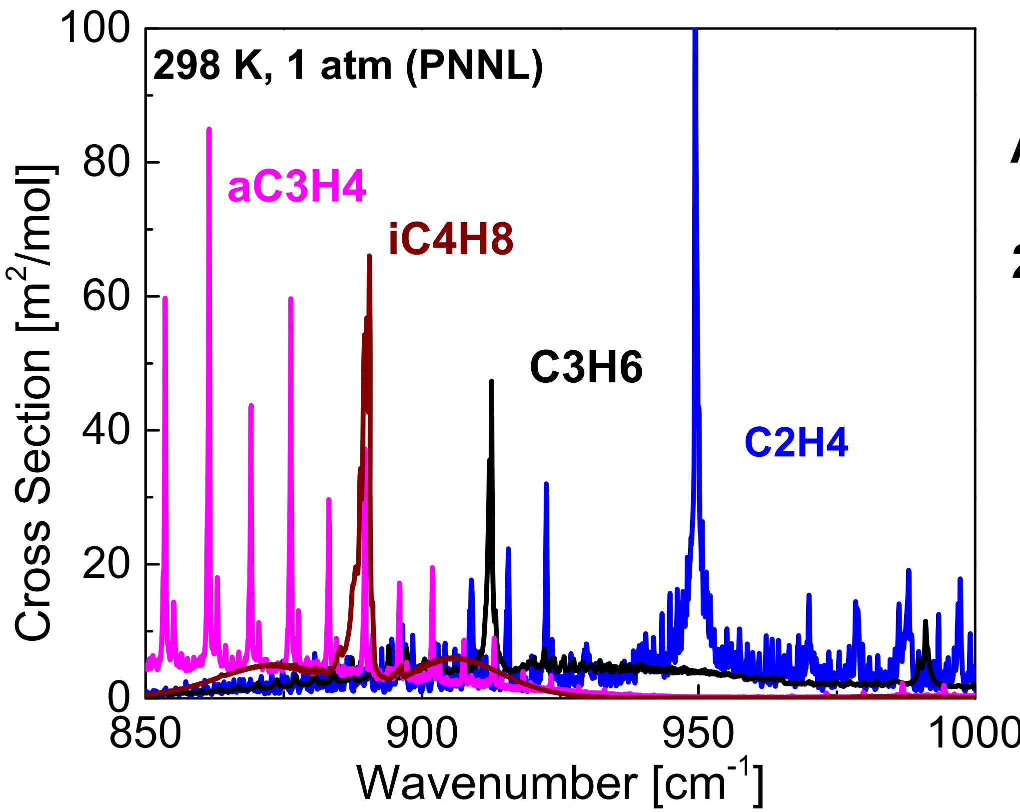
Aldehyde Concentration Time-Histories



- **Recovered dCH_2O/dt & plateau mole fractions: Success!**

4. New Species Diagnostics - 2

New Alkene Sensors: Far-IR Detection using QC Laser



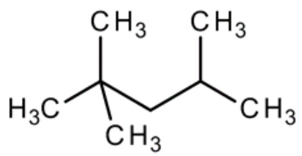
Absorption Spectra 298K, 1atm

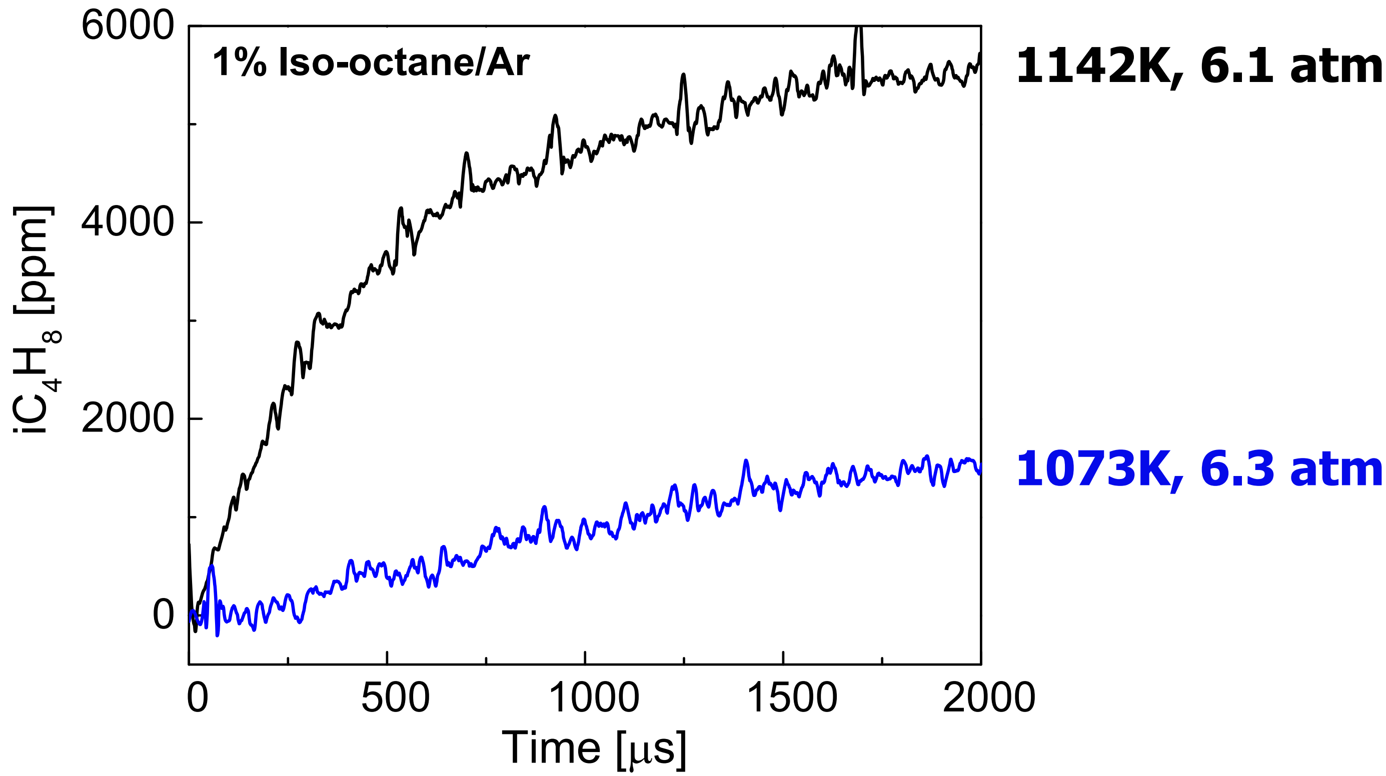
- **This spectral region holds high promise for multiple species: ethylene, propene, isobutene, …**

Example: isobutene, an important decomposition product of branched alkanes

4. New Species Diagnostics - 2

Iso-Octane Pyrolysis: First Detection of iso-Butene in Shock Tube

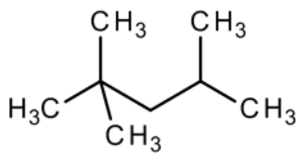


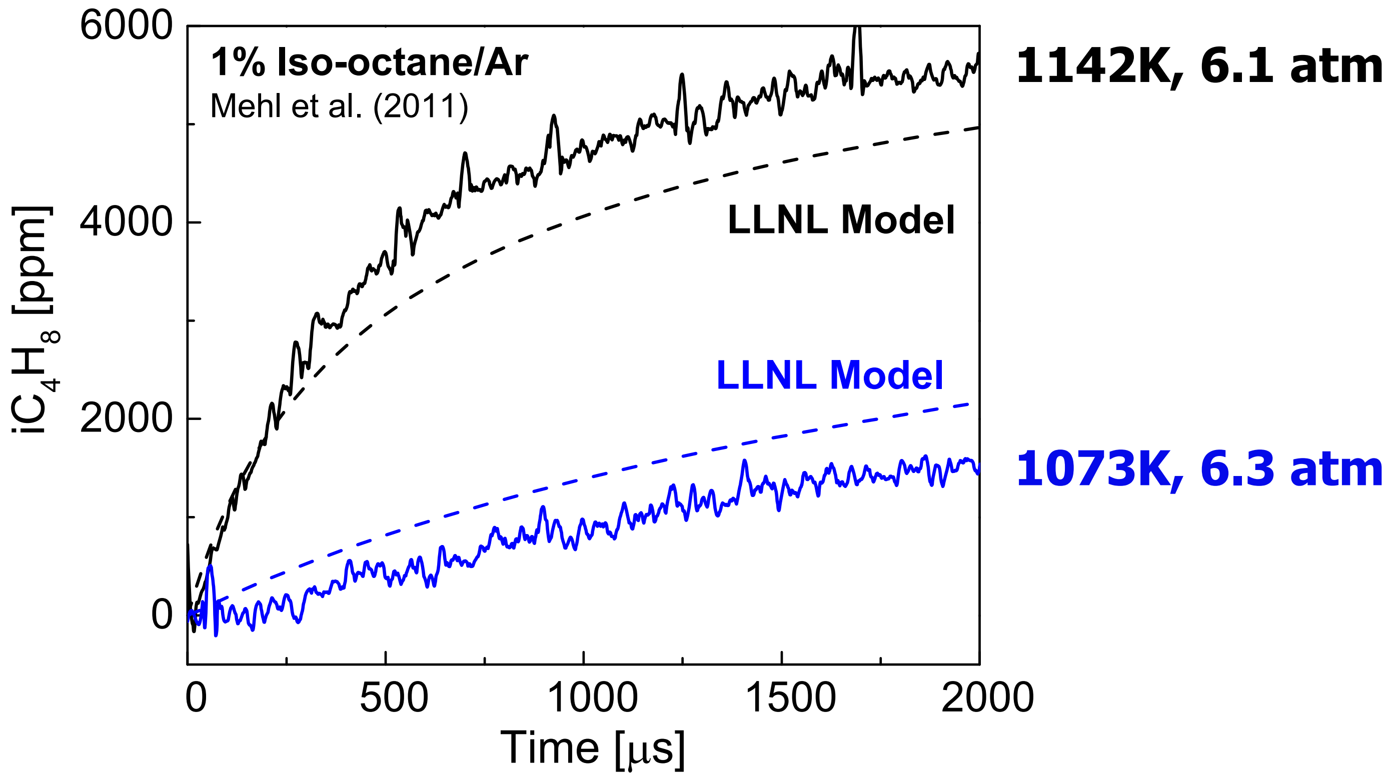


- **Data provide important test for iso-octane decomposition pathways**

4. New Species Diagnostics - 2

Iso-Octane Pyrolysis: Comparison with Modeling



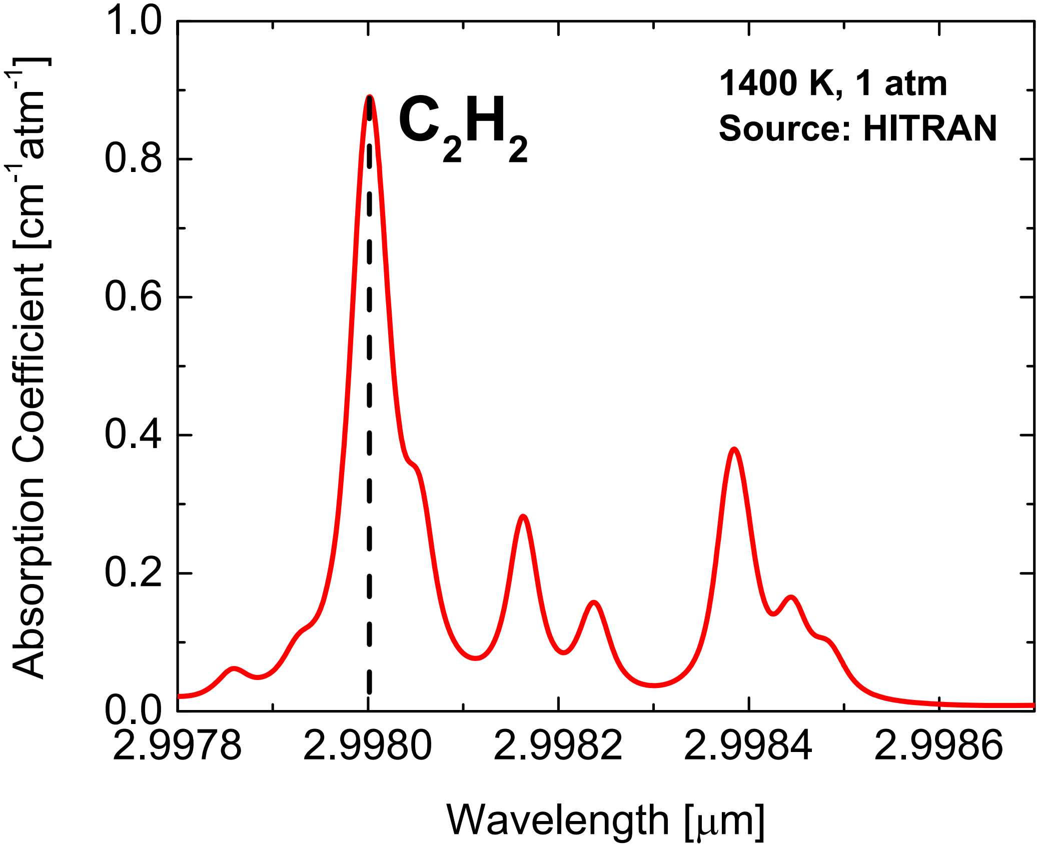


- **Data provide important test for iso-octane decomposition pathways**
- **Reasonable agreement with LLNL model!**

Next alkyne detection: acetylene

4. New Species Diagnostics - 3

New Alkyne Sensor: Acetylene Detection at 3 μm

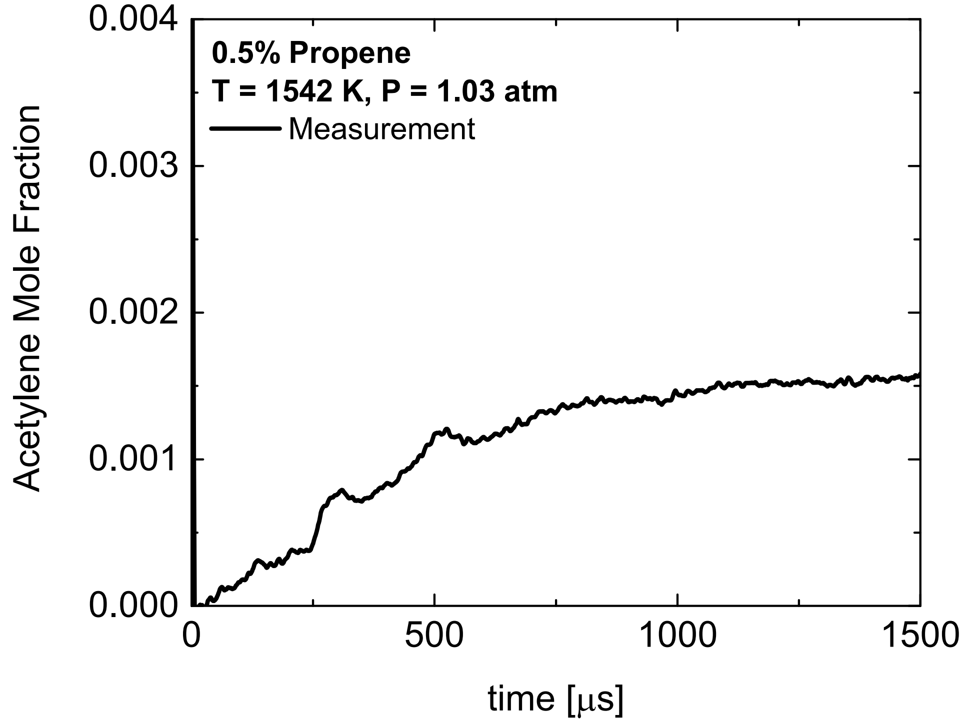


- **3 μm acetylene detection provides sensitive mid-IR detection**

Next: first application in propene

4. New Species Diagnostics - 3

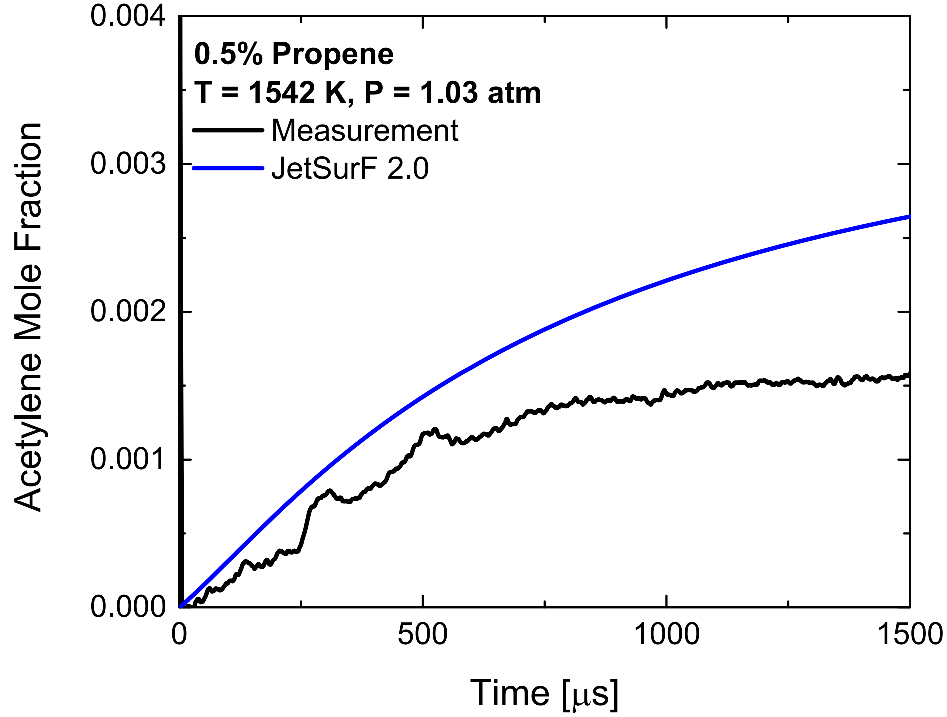
First Acetylene Measurements: Propene Pyrolysis



- **Data provide high-sensitivity acetylene time-histories for modeling**

4. New Species Diagnostics - 3

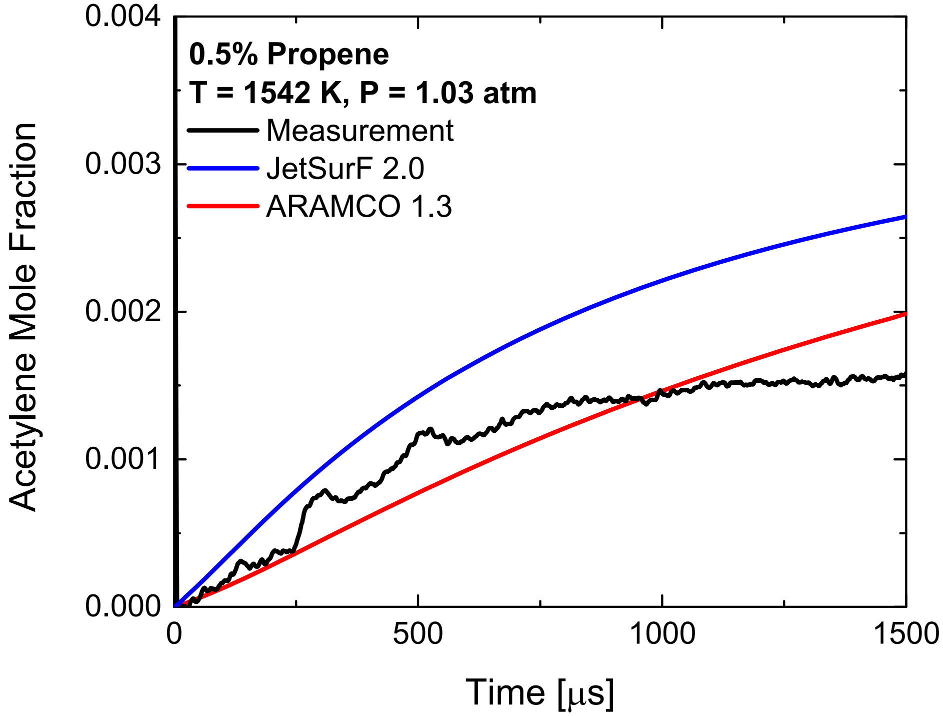
First Acetylene Measurements: Propene Pyrolysis



- **Data provide high-sensitivity acetylene time-histories for modeling**

4. New Species Diagnostics - 3

First Acetylene Measurements: Propene Pyrolysis



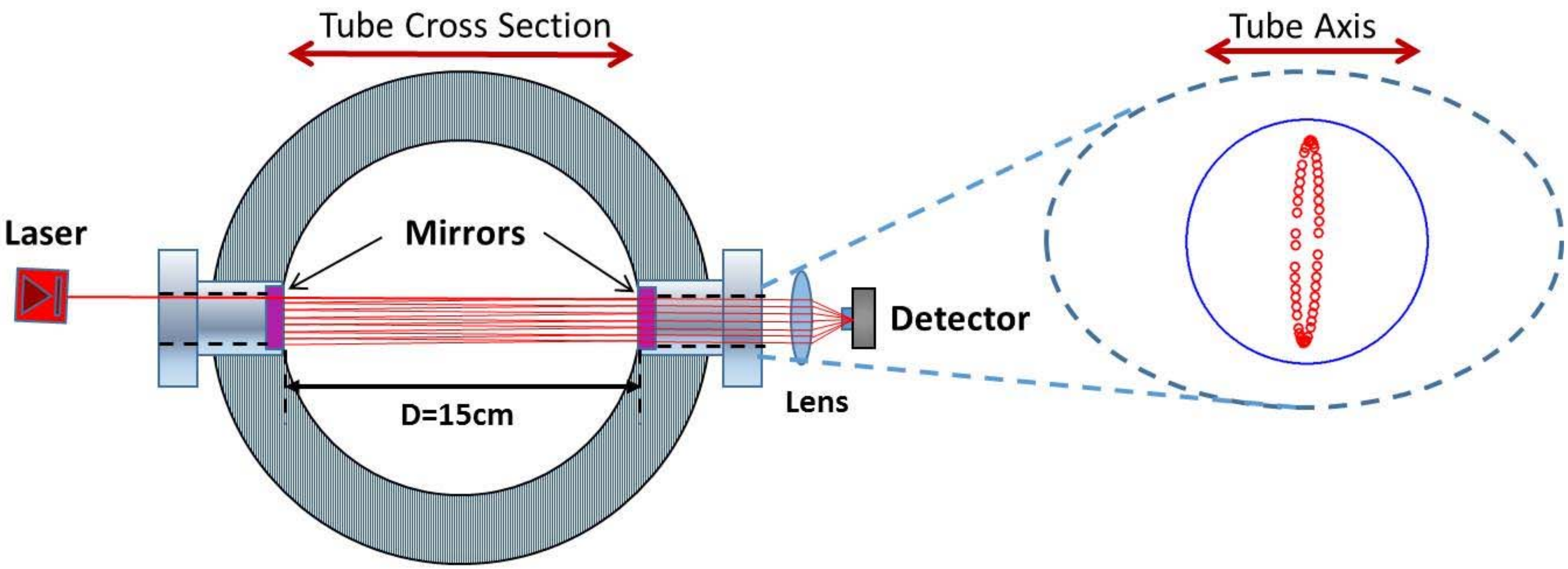
- **Data provide high-sensitivity acetylene formation rates**
- **Reveals significant difference between JetSurF, ARAMCO and data**
- **Wide applicability of diagnostic: soot formation, alkene pyrolysis. ...**

Next: Cavity Enhanced Absorption Spectroscopy (CEAS)

4. New Species Diagnostics - 4

Ultra-sensitive Species Detection:
Cavity-Enhanced Absorption Spectroscopy (CEAS) with TDL Source

- **Off-axis CEAS superior to traditional multipass**

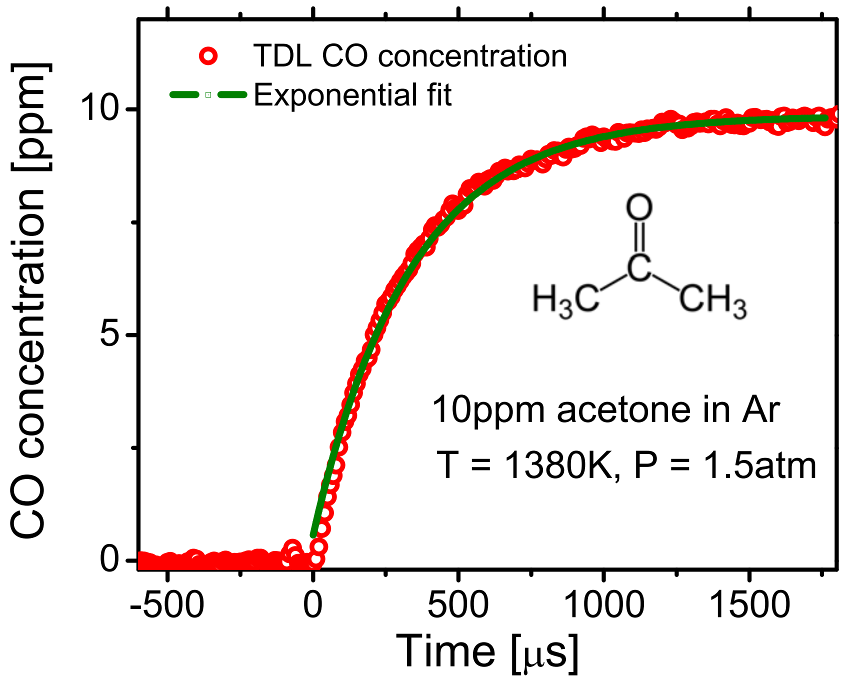


- **Cavity increases effective absorption path length, L_{eff}**
- **Variable gain via L_{eff} where $G=L_{eff}/D=R/(1-R)$ (10<G<1000 at low finesse)**
- **Off-axis insertion enables easy, robust alignment**

Example: Detection limits for CO using MIR source

4. New Species Diagnostics - 4

CO formation by acetone (10ppm) pyrolysis



- **First highly-diluted CO formation experiment**
- **Detection limit ~ 0.3ppm at 100kHz time resolution**
- **Data yield rate constant for acetone dissociation**

- **Demonstrates high CO sensitivity and good temporal resolution**
- **Further improvements: 10 – 100x in progress**

Summary:

Laser absorption & shock tubes are a frontier for combustion kinetics

Next: Three Lectures on Laser-Induced Fluorescence (LIF)

- Two level model
- More complex models
- Applications