



CASE WESTERN RESERVE  
UNIVERSITY EST. 1826

# Syngas and Hydrogen Combustion

Grant Number: DE-FG26-06NT42717

*Development of Comprehensive Detailed and Reduced Reaction Mechanisms for Syngas and Hydrogen Combustion*

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# Outline

- Objectives
- Scope of Work
- Experimental Facilities/Specifications
- Accomplishments to Date
- Laminar Flame Speeds of Moist H<sub>2</sub>/CO Mixtures with Preheat
- Uncertainty in Diffusion Coefficients
- Autoignition of Moist H<sub>2</sub>/CO Mixtures
- Reaction Kinetics of  $\text{HO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2$  :  
*ab initio* Study and Master Equation Modeling
- Concluding Remarks
- Future Work





# Objectives

- This project aims to develop the tools necessary for the design of future synthesis-gas and hydrogen (SGH) fueled combustion turbines.
  - Generate a detailed experimental database of SGH combustion at IGCC-like conditions.
  - Investigate fundamental chemical kinetics of  $\text{H}_2/\text{CO}/\text{O}_2/\text{N}_2/\text{H}_2\text{O}/\text{CO}_2$  at pressures, temperatures, and concentrations typical of SGH combustion in gas turbines
  - Develop detailed and reduced chemical mechanisms based on this database, capable of predicting  $\text{NO}_x$  formation during SGH combustion.





# Scope of Work

- Obtain benchmark experimental data for combustion characteristics of syngas
  - **Conterflow Burner Apparatus**
    - Laminar flame speeds and Extinction limits
  - **Rapid Compression Machine**
    - Ignition delays at elevated pressures
- Develop comprehensive and computationally-efficient chemical models
  - Assessment of available kinetic mechanisms
  - Theoretical calculations to determine critical rate constants
  - Mechanism optimization
  - Mechanism simplification and reduction





- **Counterflow Burner Apparatus**

- High temperature chemistry
- Laminar flame speed and extinction stretch rate measurements using DPIV
- Preheat up to 470 K

- **Rapid Compression Machine (RCM)**

- Low-to-Intermediate temperature chemistry
- Autoignition investigations
- Compressed pressure up to 50 bar
- Compressed temperature from 650 to 1100 K





# Reagent Purity Specifications

- For flame investigations:

Reagent	Purity	Supplier	Impurities
N <sub>2</sub>	99.98%	Praxair	
O <sub>2</sub>	99.98%	Praxair	
H <sub>2</sub>	99.995%	Praxair	O <sub>2</sub> <5 ppm, H <sub>2</sub> O<5 ppm
CO	99.50%	Praxair	O <sub>2</sub> <100 ppm, H <sub>2</sub> O<5 ppm, N <sub>2</sub> <4500 ppm, CO <sub>2</sub> <100 ppm, Ar<100 ppm, H <sub>2</sub> <100 ppm
H <sub>2</sub> O	Deionized Water	PTI Process Chemicals	

- For autoignition investigations:

Reagent	Purity	Supplier	Impurities
N <sub>2</sub>	99.98%	Praxair	
O <sub>2</sub>	99.993%	Praxair	H <sub>2</sub> O<3 ppm, N <sub>2</sub> <10 ppm, THC< 1 ppm, Ar<40 ppm
H <sub>2</sub>	99.995%	Praxair	O <sub>2</sub> <5 ppm, H <sub>2</sub> O<5 ppm
CO	99.998%	Matheson	O <sub>2</sub> <0.5 ppm, H <sub>2</sub> O<1 ppm, N <sub>2</sub> <10 ppm, CO <sub>2</sub> <3 ppm, H <sub>2</sub> <1 ppm, Fe(CO) <sub>5</sub> <0.5 ppm, THC as CH <sub>4</sub> <0.5 ppm
H <sub>2</sub> O	Deionized Water	PTI Process Chemicals	





- Autoignition of dry  $H_2/CO$  mixtures at elevated pressures in a rapid compression machine.
- Assessment of kinetics of syngas combustion at elevated pressures using global uncertainty analysis methods.
- Reaction kinetics of  $CO+HO_2$  – *ab initio* calculations.
- *Laminar flame speed determination of moist  $H_2/CO$  mixtures.*
- *Uncertainty in diffusion coefficients and syngas flame sensitivity.*
- *Preliminary experimentation on autoignition of moist  $H_2/CO$  mixtures at elevated pressures in a rapid compression machine.*
- *Reaction kinetics of  $HO_2+OH$  – ab initio calculations (in progress).*





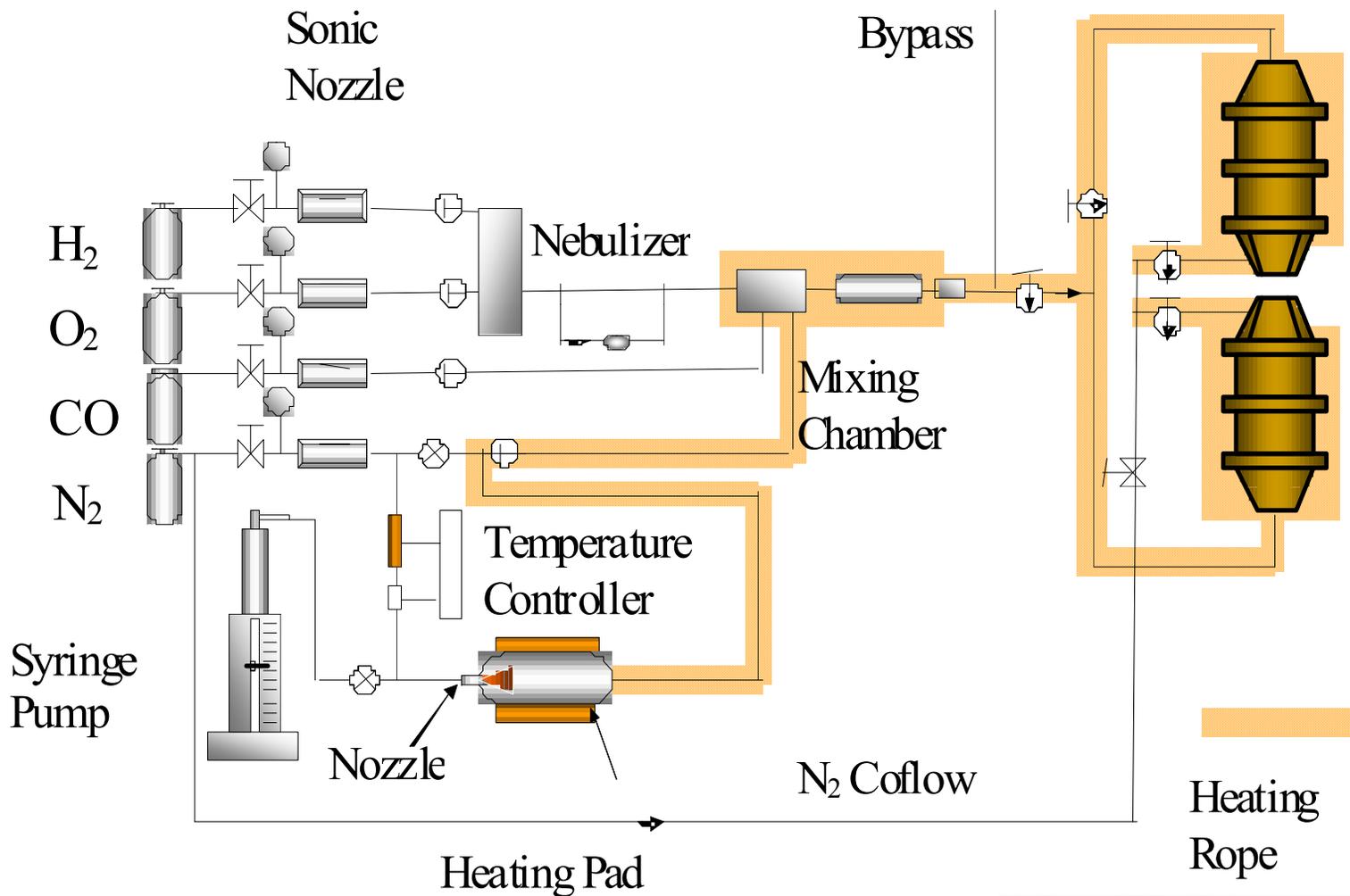
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# *Laminar Flame Speeds of Moist H<sub>2</sub>/CO Mixtures with Preheat*

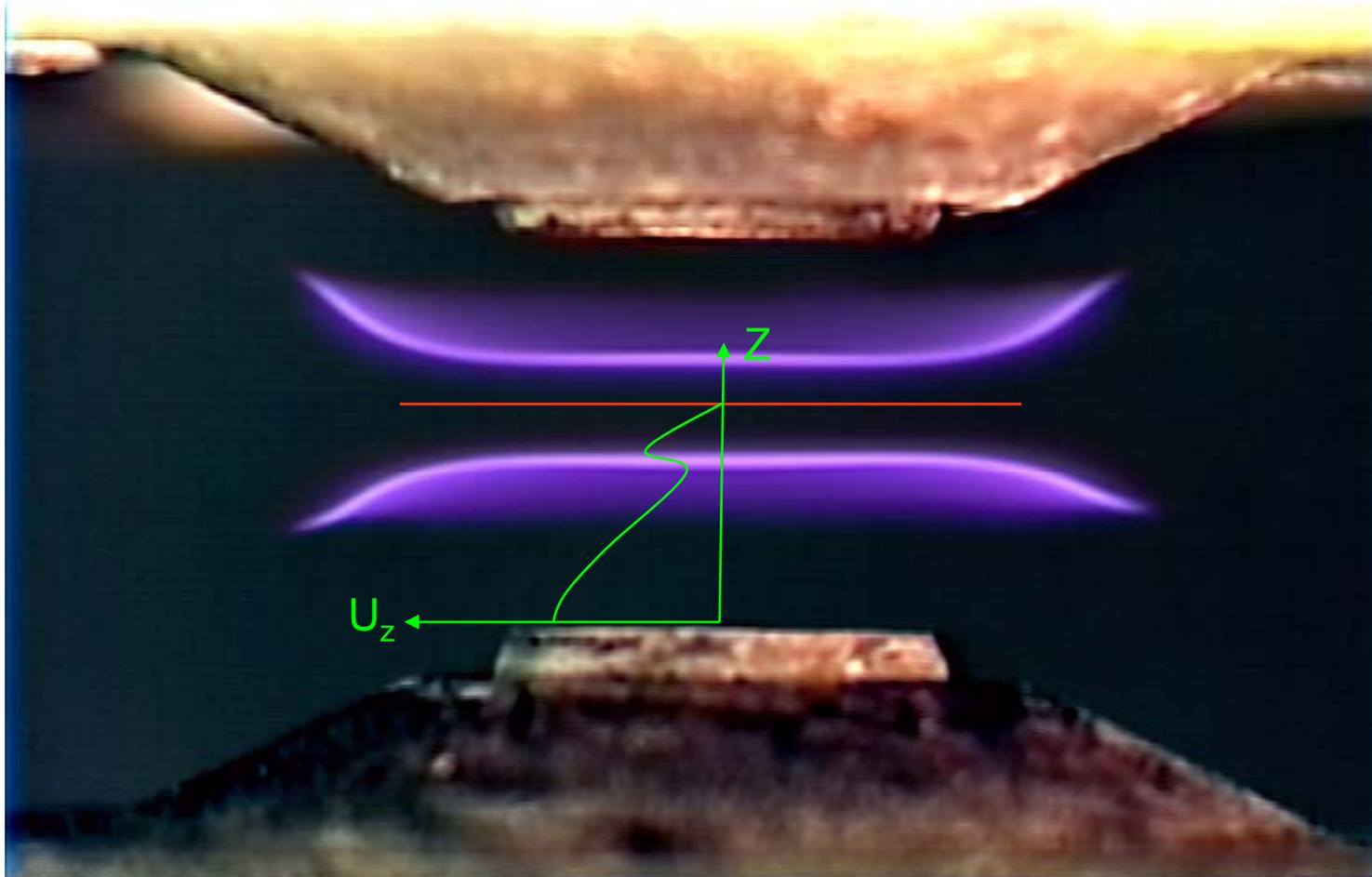


# Counterflow Twin-Flame Configuration



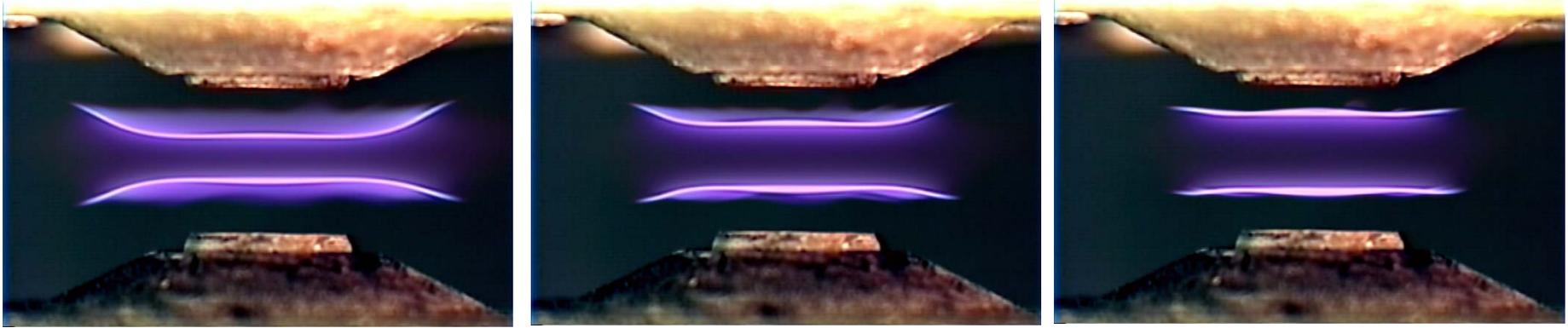


# Counterflow Twin Flames (1)





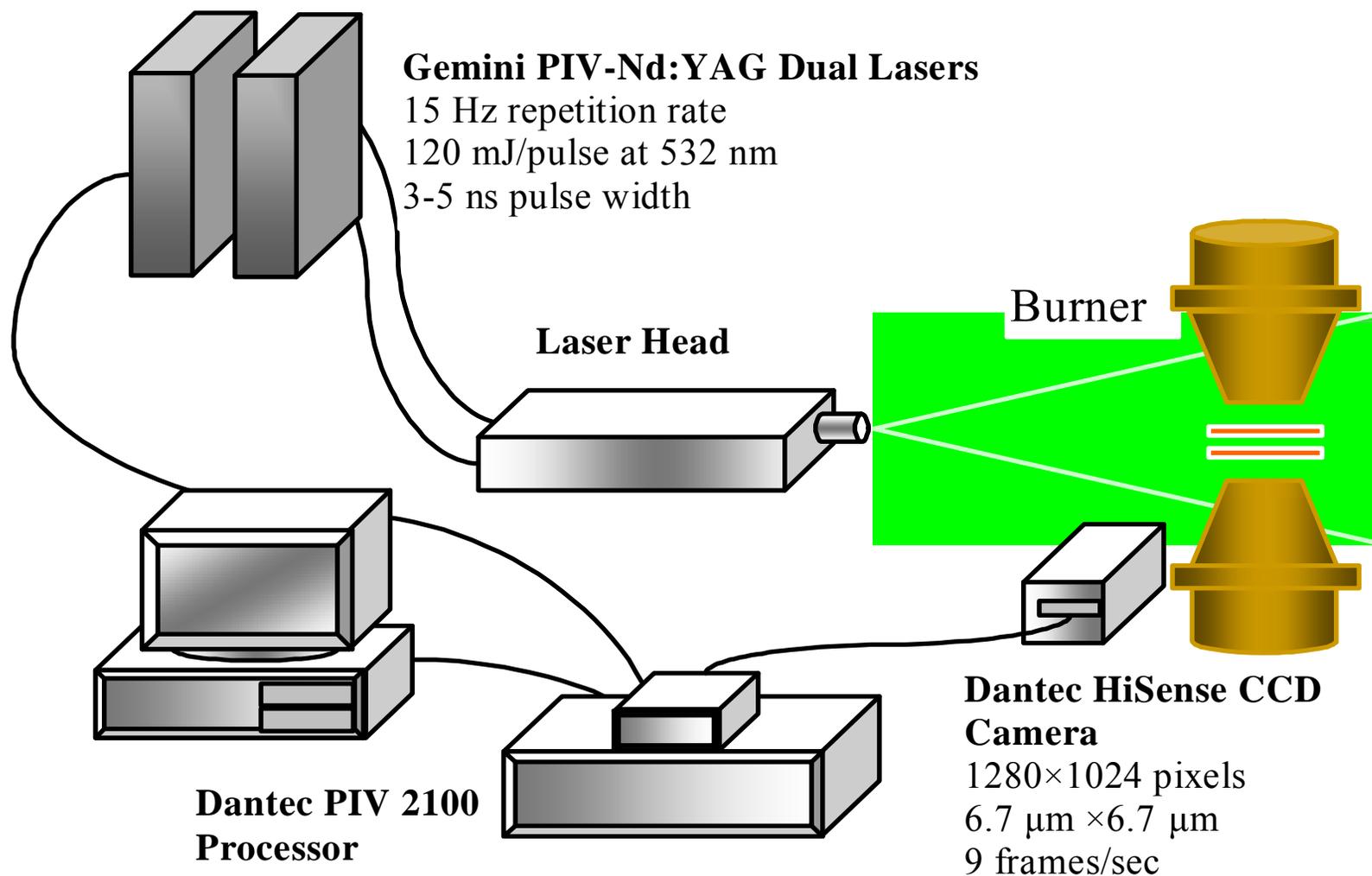
# Counterflow Twin Flames (2)



→  
Decreasing Stretch Rate  $\Rightarrow$  *laminar flame speed*

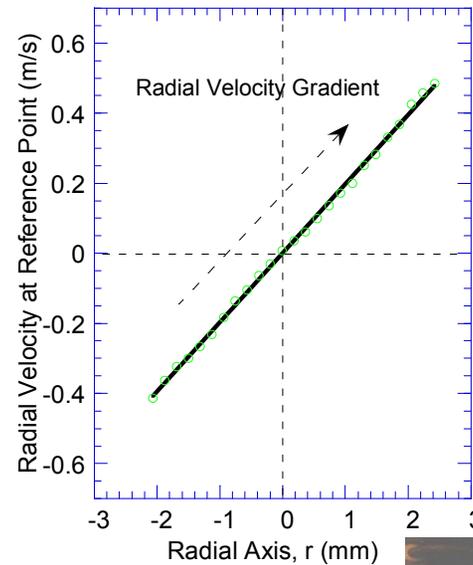
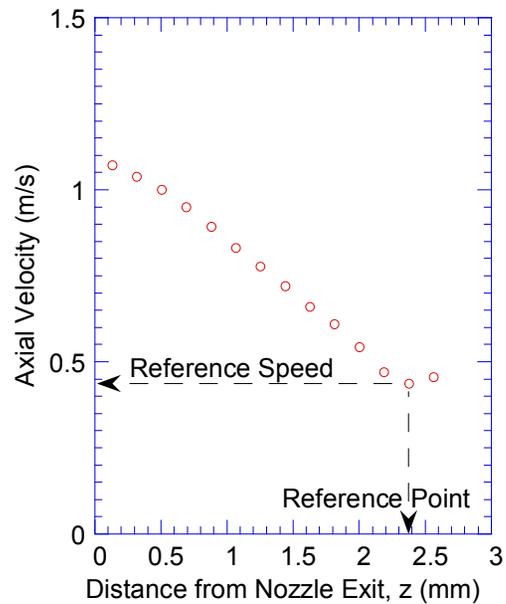
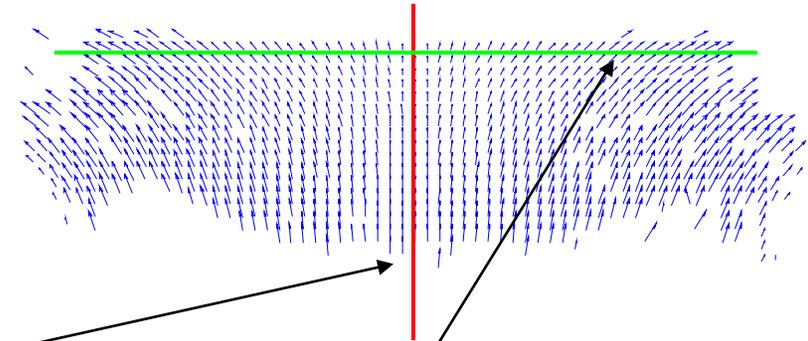
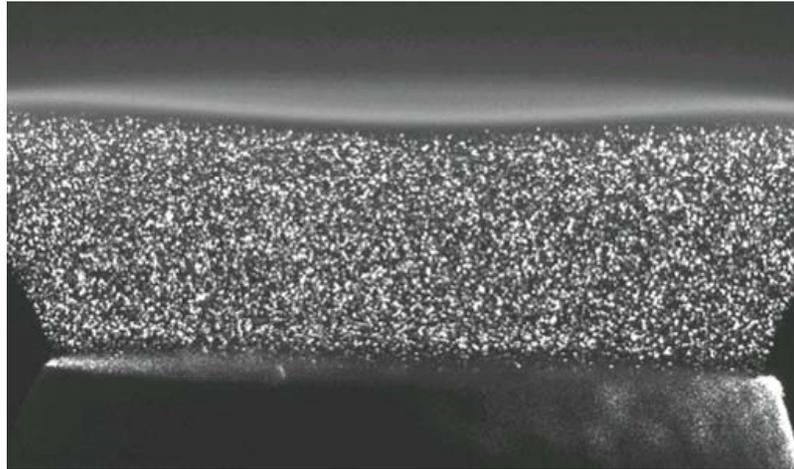
←  
*extinction stretch rate*  $\Leftarrow$  Increasing Stretch Rate

# DPIV System for Velocity Measurement





# DPIV Measurement

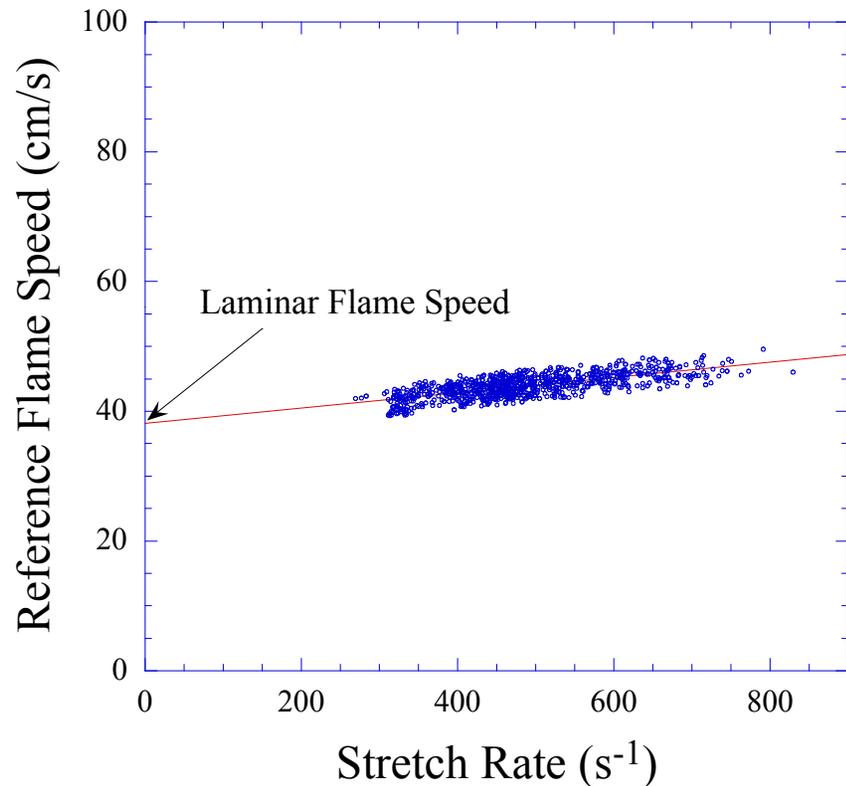


→ stretch rate

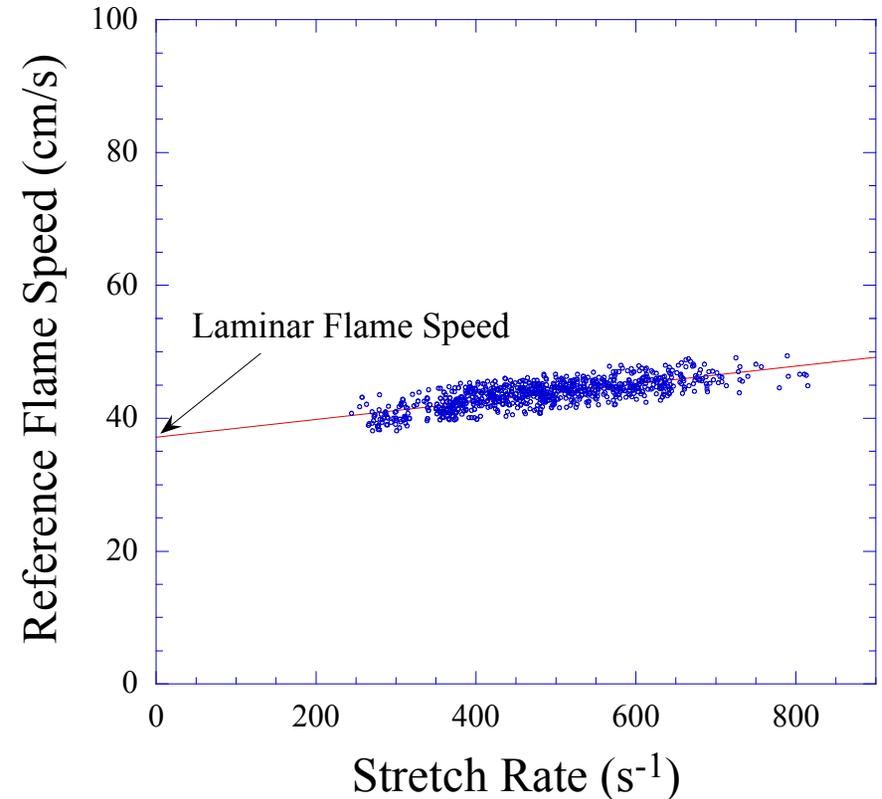


# Linear Extrapolation

$\phi=0.7, R_{CO}=0.95, \xi_{H_2O}=15\%, T_u=323\text{ K}$



$\phi=0.7, R_{CO}=0.95, \xi_{H_2O}=25\%, T_u=323\text{ K}$



$$\xi_{H_2O} = \{ [H_2O] / ([H_2] + [CO] + [H_2O]) \} \times 100\%$$

$$R_{CO} = [CO] / ([H_2] + [CO])$$





# Experimental Conditions

- Preheat temperature :  $T_u=323$  K
- Equivalence ratio:  $\phi=0.3 - 0.9$
- $H_2/CO$  molar ratio ( $R_{CO}=[(X_{CO})/(X_{H_2}+X_{CO})]$ ):
  - 5/95 (0.95)
  - 10/90 (0.90)
  - 15/85 (0.85)
  - 20/80 (0.80)
  - 50/50 (0.50)
- Moisture in fuel mixture ( $\xi_{H_2O}=[(X_{H_2O})/(X_{H_2}+X_{CO}+X_{H_2O})]\times 100\%$ ):
  - 0%
  - 7.5%
  - 15%
  - 25%
  - 35%





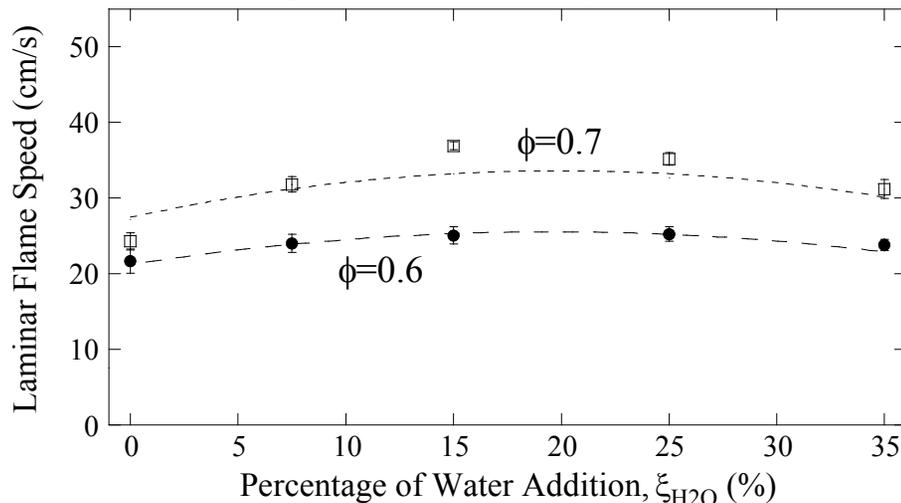
# Contamination of CO with $\text{Fe}(\text{CO})_5$

- Steel CO cylinders obtained from commercial suppliers are prone to contamination by iron pentacarbonyl,  $\text{Fe}(\text{CO})_5$ , over time.
  - CO can readily react at high pressure with metals present in steel to form carbonyls.
- In premixed flames,  $\text{Fe}(\text{CO})_5$  can reduce the burning velocity considerably (cf. Reinelt and Linteris, 1996; Babushok *et al.*, 1998; Rumminger *et al.*, 1999; Rumminger and Linteris, 2000; Williams and Shaddix, 2007).
- A “cold trap”,  $\frac{1}{4}$ ” $\times$ 20’ stainless steel tube coiled and immersed in dry ice (194.5 K), is used to condense out any possible presence of  $\text{Fe}(\text{CO})_5$  (melting point: 253 K).
- Comparison is made between measurements with and without the cold trap for CO rich case ( $R_{\text{CO}}=0.95$ ).
  - Laminar flame speed results obtained from both cases are close.
  - Difference is within the experimental uncertainty.
  - Negligible contamination effect for the present study.

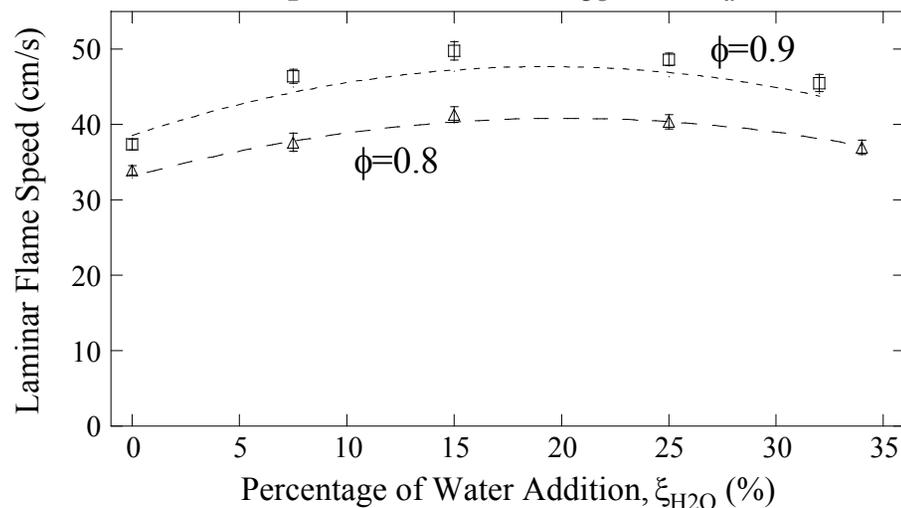


# Effects of Water Addition: $R_{CO}=0.95$

Moist H<sub>2</sub>/CO/Air Mixtures:  $R_{CO}=0.95$ ,  $T_u=323$  K



Moist H<sub>2</sub>/CO/Air Mixtures:  $R_{CO}=0.95$ ,  $T_u=323$  K

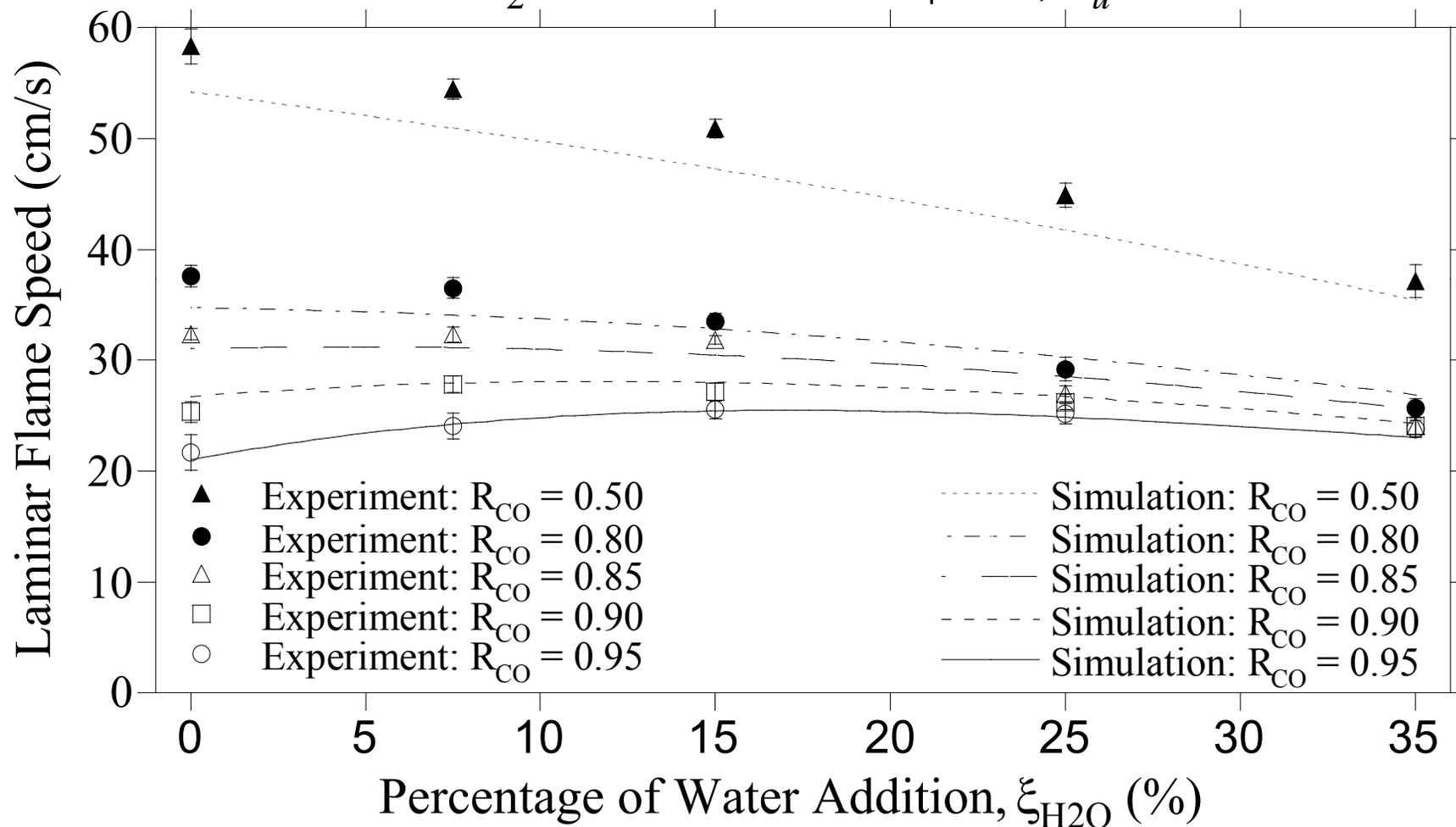


- Flame speed measurements for  $R_{CO}=0.95$ ,  $\xi_{H_2O}=0-35\%$ ,  $\phi=0.6-0.9$ ,  $T_u=323$  K
- Data exhibit a non-monotonic trend of flame speed with water addition
- Flame speed increased from  $\xi_{H_2O}=0$  to 15% then decreased from  $\xi_{H_2O}=15\%$  to 35%
- Computed laminar flame speed using the mechanism of Li *et al.* (2007) agree fairly well with the experiments



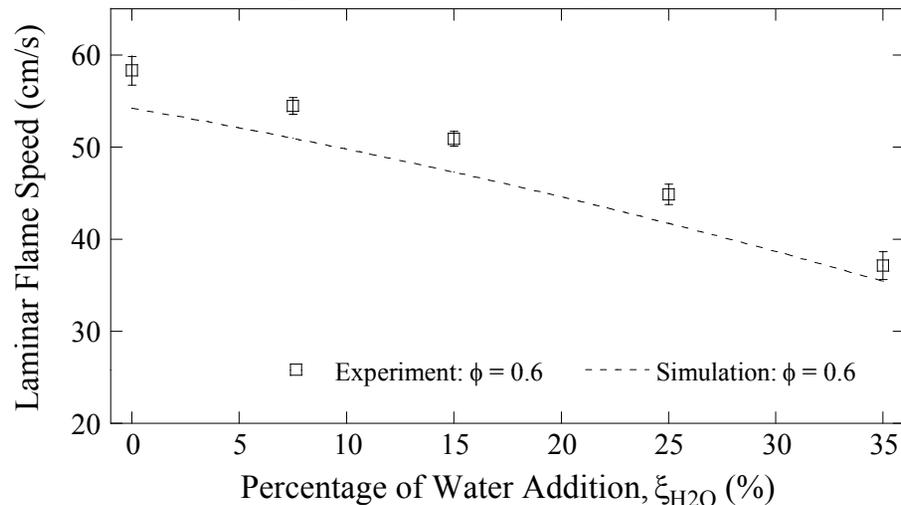
# Effects of H<sub>2</sub>/CO Ratio

Moist H<sub>2</sub>/CO/Air Mixtures:  $\phi=0.6$ ,  $T_u=323$  K

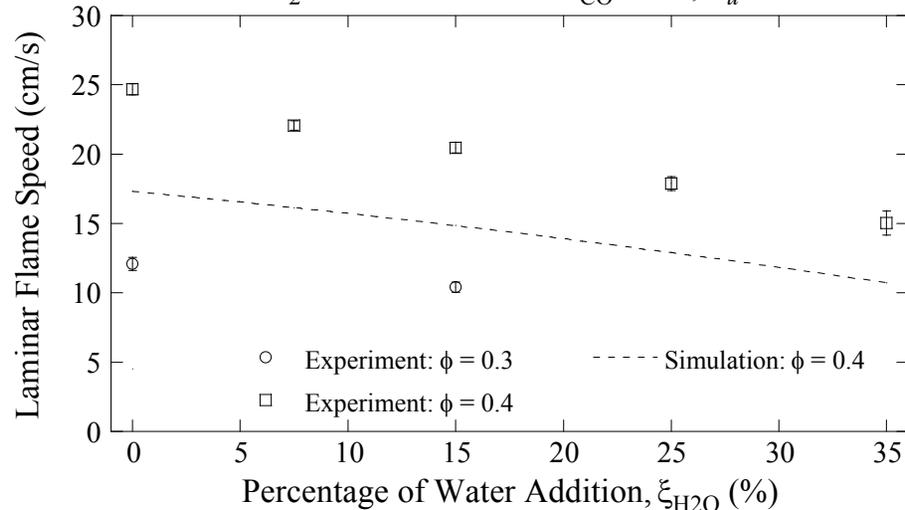


# Effects of Water Addition: $R_{CO}=0.50$

Moist  $H_2/CO/Air$  Mixtures:  $R_{CO}=0.50$ ,  $T_u=323$  K



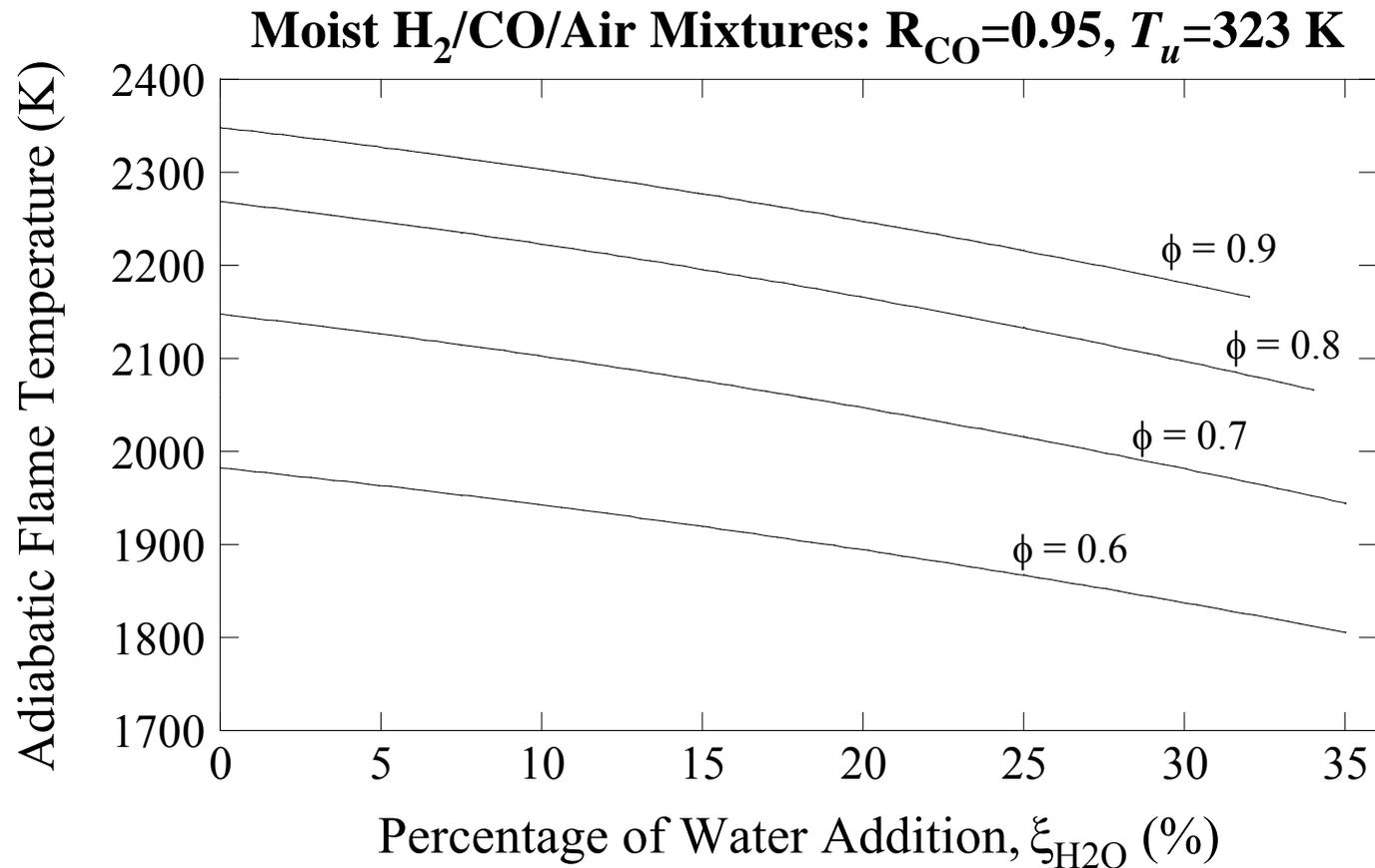
Moist  $H_2/CO/Air$  Mixtures:  $R_{CO}=0.50$ ,  $T_u=323$  K



- Flame speed measurements for –  $R_{CO}=0.50$ ,  $\xi_{H_2O}=0-35\%$ ,  $\phi=0.3-0.6$ ,  $T_u=323$  K
- Data exhibit a monotonic trend of flame speed with water addition
- Computed laminar flame speed using the mechanism of Li *et al.* (2007) agree fairly well with the experiments at  $\phi>0.5$ , but underpredicts at  $\phi<0.5$



# Thermal Effect of Water Addition



- Addition of water has a dilution effect
  - Explains the decrease of flame speed when water content is sufficiently high



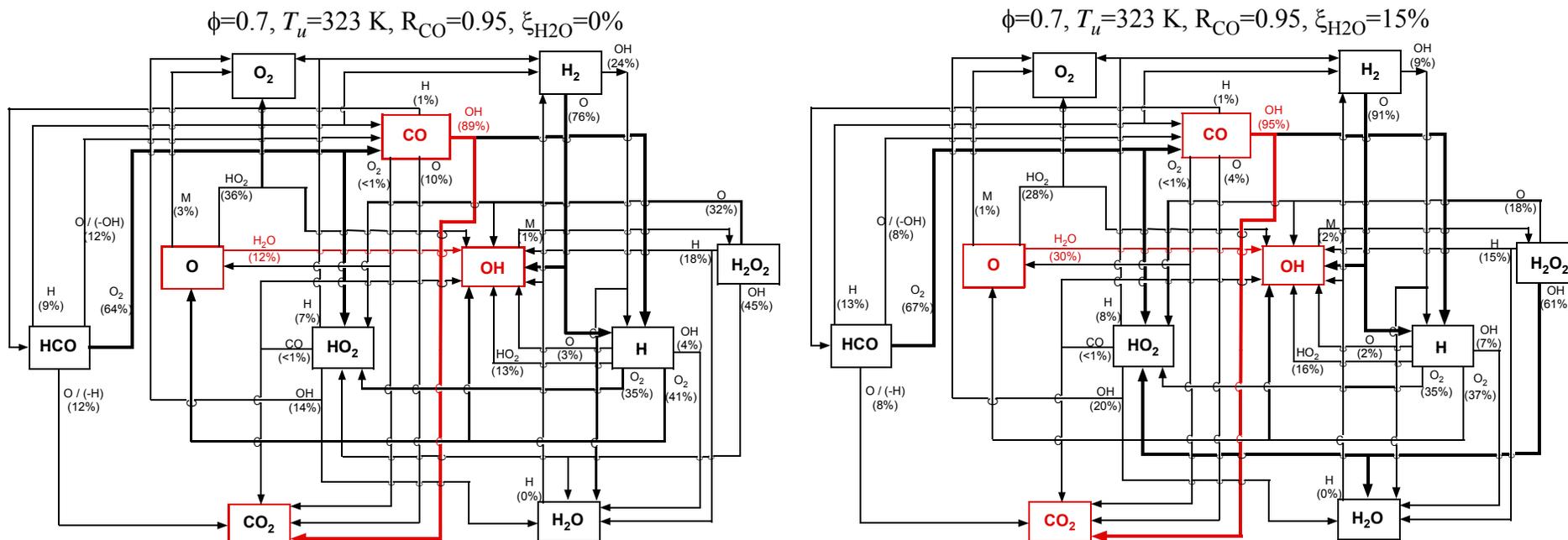


# Chemical Effect of Water Addition

- Water addition in the range of  $\xi_{\text{H}_2\text{O}} < 15\%$  is seen to promote flame propagation for the CO-rich mixtures ( $R_{\text{CO}} = 0.95$ ).
- Expected that a positive chemical effect due to water addition dominates for  $\xi_{\text{H}_2\text{O}} < 15\%$ .
- A detailed integral flux flow analysis is conducted using the mechanism of Li *et al.* (2007):
  - Integrated species consumption is calculated within the reaction zone of the flame.
  - Defined by the region between the locations upstream and downstream of the flame having less than or equal to 1% of the peak heat release rate.
- Comparison for  $\xi_{\text{H}_2\text{O}} = 0\%$  and  $\xi_{\text{H}_2\text{O}} = 15\%$  ( $\phi = 0.7$  and  $T_u = 323$  K):
  - $R_{\text{CO}} = 0.95$
  - $R_{\text{CO}} = 0.5$



# Flux Flow Analysis: $R_{CO}=0.95$



- Increase of OH production
  - Marked by increase in % O consumption (12% to 30%) through  $H_2O+O=2OH$
- Addition of  $H_2O$  increased the OH radical pool
  - Provides the ultimate consumption path of CO for CO rich case of  $R_{CO}=0.95$
- Consumption of CO through  $CO+OH$  increases
  - Marked by increase in % CO consumption (89% to 95%)
- Analysis for a pure CO case showed similar results



# Flux Flow Analysis: $R_{CO}=0.50$

- Flux Flow Analysis for  $\xi_{H_2O}=0\%$  and 15%:
  - Production of OH radicals through the reaction  $H_2O+O=2OH$  increases slightly (indicated by the change of percentage O consumption from 11% to 22 %).
- Comparison of species and temperature profiles:
  - Flame temperature is reduced by  $\sim 50$  K with  $\xi_{H_2O}=15\%$ .
  - Key radical profiles remain almost unchanged, except a slight reduction in the H radical pool.
  - Chemical effect is not very notable.
  - Negative thermal effect of water addition reduces laminar flame speed.
- Analysis for pure  $H_2$  case showed similar results.





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# *Uncertainty in Diffusion Coefficients*





# Background (1)

- As compared to fruitful advance of knowledge in reaction kinetics, little advance is made in transport processes and notably in the theory of diffusion of gaseous free radical species.
- An accurate description of various transport processes and rates is as important in combustion simulation as a quantitative knowledge of elementary reaction kinetics.
- The uncertainties of the transport parameters stem mainly from the difficulties to measure the viscosity, conductivity, and diffusivity of a free radical species.





## Background (2)

- Recent studies suggested that the diffusion coefficients of free radical species may be highly uncertain because of the formation of a transiently bound complex upon molecular collision.
- While transport uncertainties are apparent, it is not clear to what extent these uncertainties affect the predictions of laminar flame properties like the laminar flame speed.
- Goal: determine the sensitivity of flame speed predictions with respect to binary diffusion coefficients.





# Uncertainties in the Diffusion Coefficients and Flame Sensitivity

- Rigorous sensitivity analyses for representative syngas mixtures using a statistical factorial design.

Mixture	Levels			Test Mixtures			
	H <sub>2</sub>	CO <sub>2</sub>	H <sub>2</sub> O	H <sub>2</sub>	CO	CO <sub>2</sub>	H <sub>2</sub> O
<b>C1</b>	1	1	-1	<b>0.375</b>	<b>0.375</b>	<b>0.250</b>	<b>0.000</b>
<b>C2</b>	1	-1	-1	<b>0.500</b>	<b>0.500</b>	<b>0.000</b>	<b>0.000</b>
<b>C3</b>	-1	1	-1	<b>0.194</b>	<b>0.484</b>	<b>0.323</b>	<b>0.000</b>
<b>C4</b>	-1	-1	-1	<b>0.286</b>	<b>0.714</b>	<b>0.000</b>	<b>0.000</b>
<b>C5</b>	1	1	1	<b>0.281</b>	<b>0.281</b>	<b>0.188</b>	<b>0.250</b>
<b>C6</b>	1	-1	1	<b>0.375</b>	<b>0.375</b>	<b>0.000</b>	<b>0.250</b>
<b>C7</b>	-1	1	1	<b>0.145</b>	<b>0.363</b>	<b>0.242</b>	<b>0.250</b>
<b>C8</b>	-1	-1	1	<b>0.214</b>	<b>0.536</b>	<b>0.000</b>	<b>0.250</b>
<b>C9</b>	0	0	0	<b>0.323</b>	<b>0.462</b>	<b>0.115</b>	<b>0.100</b>

**Dry** (C1-C4)

**Wet** (C5-C9)

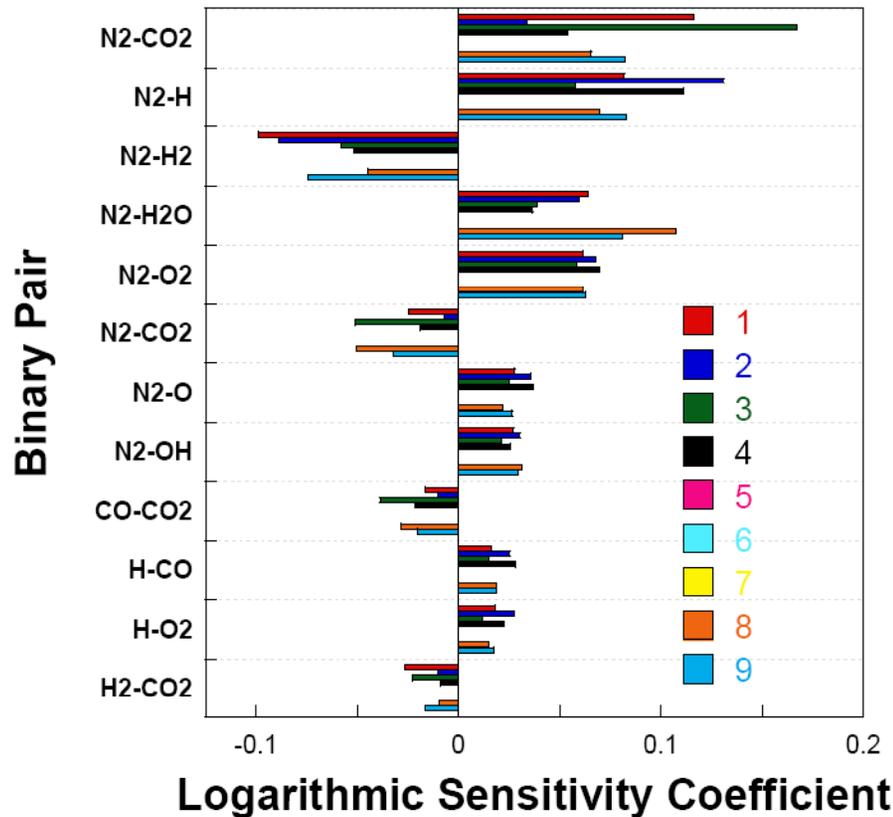
- Computations used USC-Mech II and USC updated binary diffusion coefficients for selected pairs ([http://ignis.usc.edu/Mechanisms/USC-Mech%20II/USC\\_Mech%20II.htm](http://ignis.usc.edu/Mechanisms/USC-Mech%20II/USC_Mech%20II.htm))



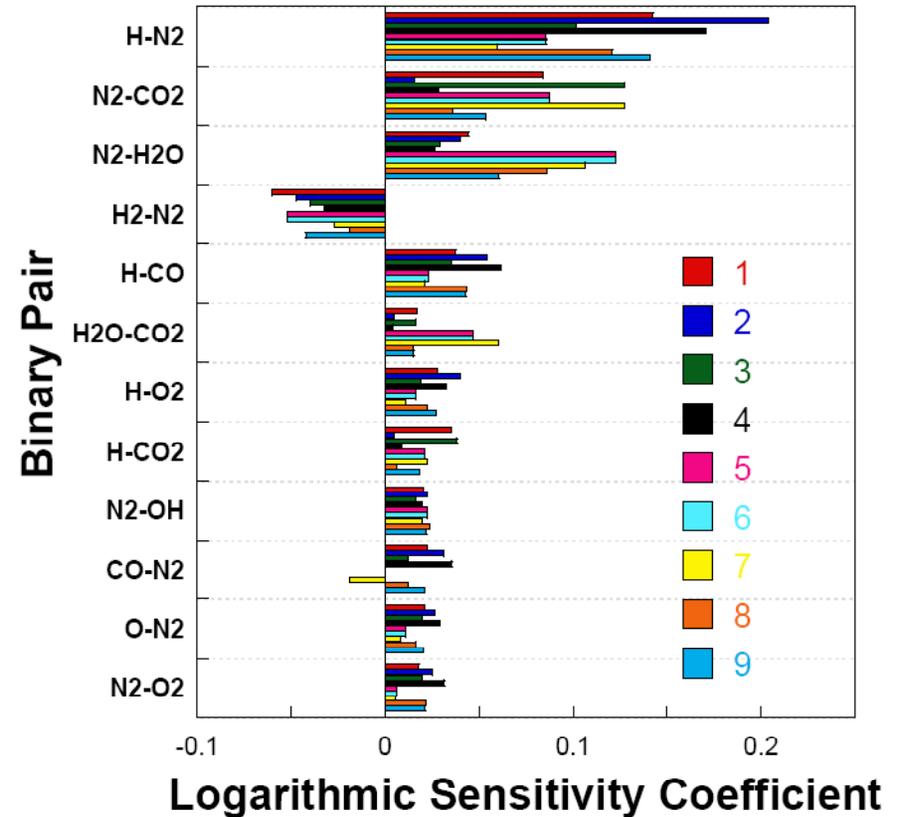
# Uncertainties in the Diffusion Coefficients and Flame Sensitivity

## Laminar Flame Speed of H<sub>2</sub>/CO/CO<sub>2</sub>/H<sub>2</sub>O-air Mixtures

$\phi = 0.7$



$\phi = 1.0$



- No drastic variations in the flame response to the binary diffusion coefficients over a representative range of syngas composition.
- The binary diffusivities of N<sub>2</sub>-CO<sub>2</sub>, N<sub>2</sub>-H<sub>2</sub>O, N<sub>2</sub>-O<sub>2</sub>, and N<sub>2</sub>-CO<sub>2</sub> may require further study.

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School of Engineering





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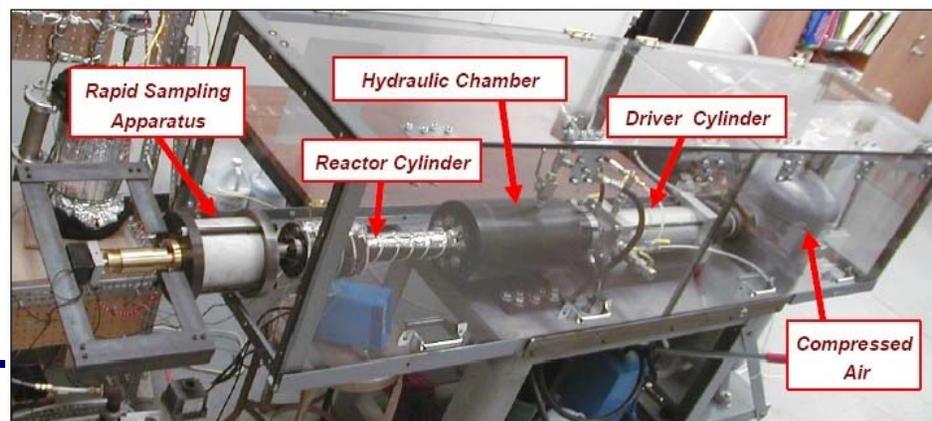
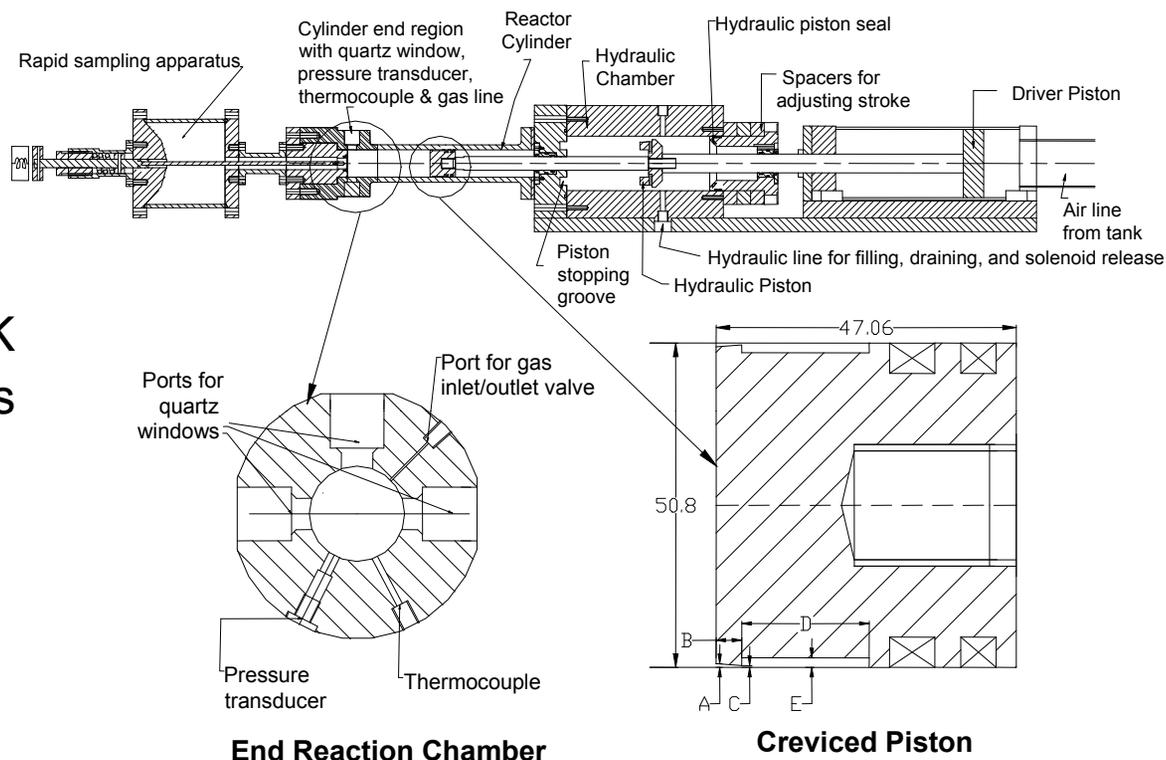
# *Autoignition of Moist H<sub>2</sub>/CO Mixtures*





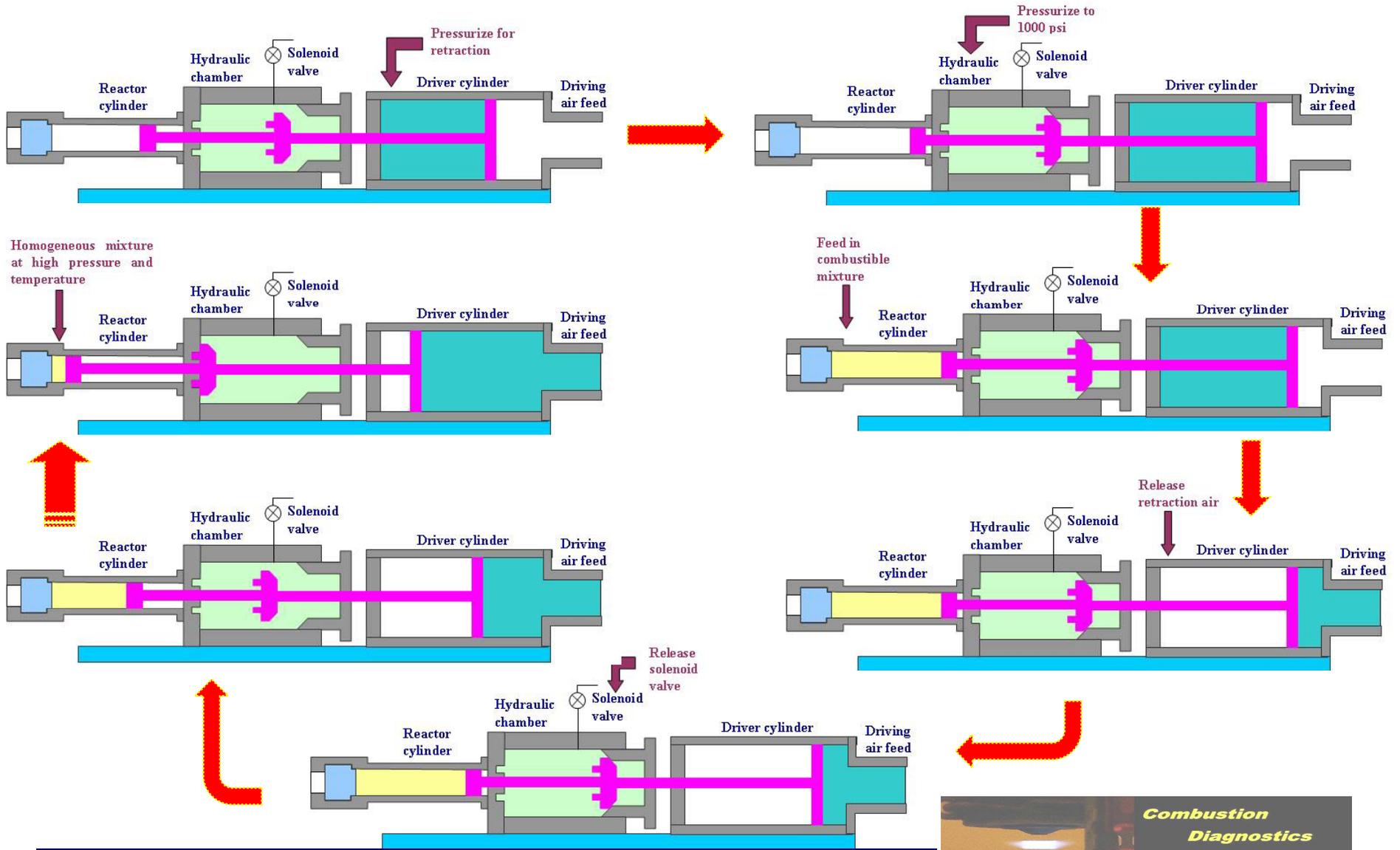
# Features of the Present RCM

- Adjustable stroke and clearance
- Fast compression ( $< 30$  ms)
- Compressed pressure up to 60 bar
- Temperature – 500 to 1100 K
- Elevated pressure condition is sustained up to 100 ms
- Optimized creviced piston for ensuring homogeneity of reacting mixture
- Optically accessible
- GC/MS and a fast sampling apparatus for species measurement
- Direct measurement of ignition delay
- Study of low-to-Intermediate temperature chemistry



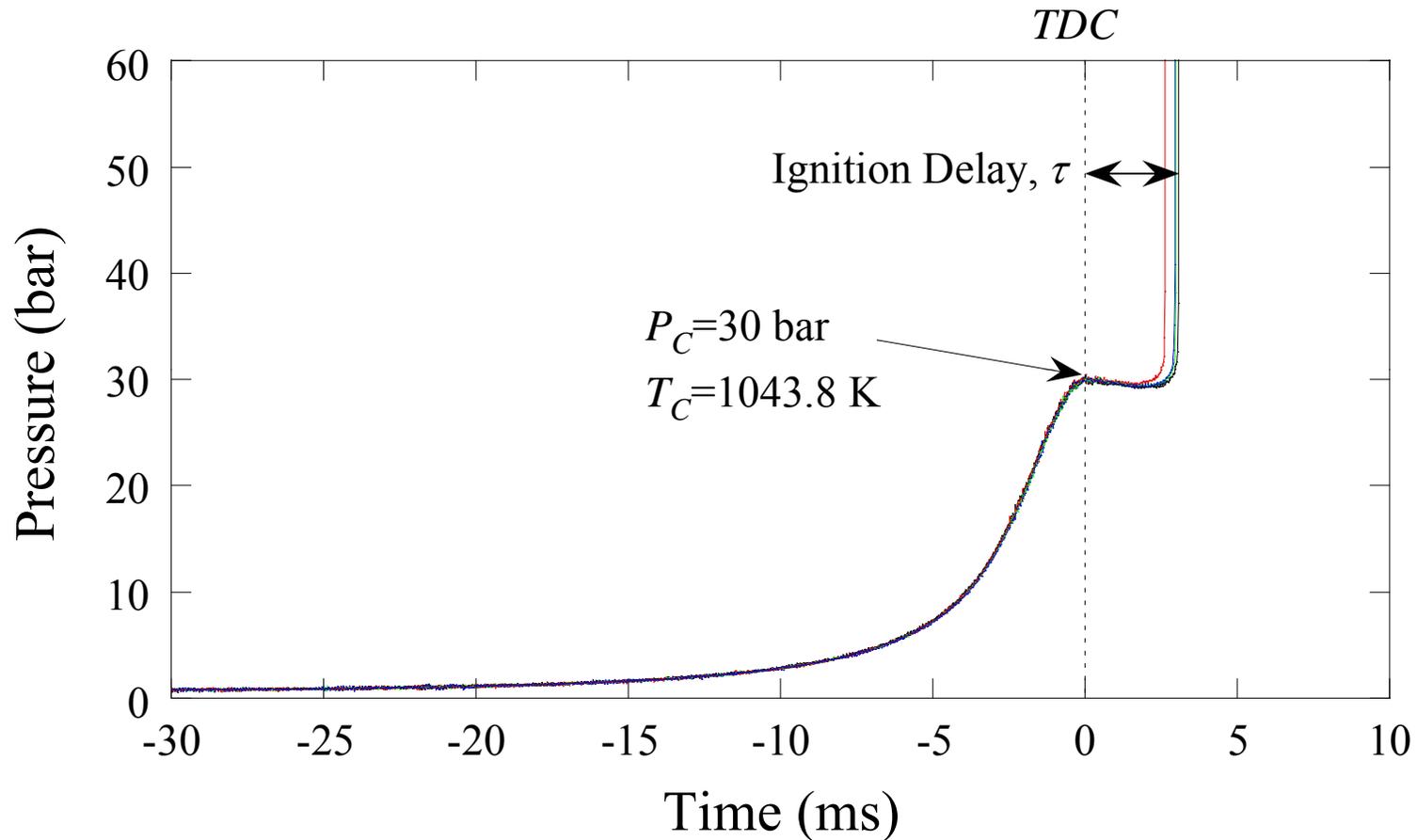


# RCM Operation





# Reproducibility



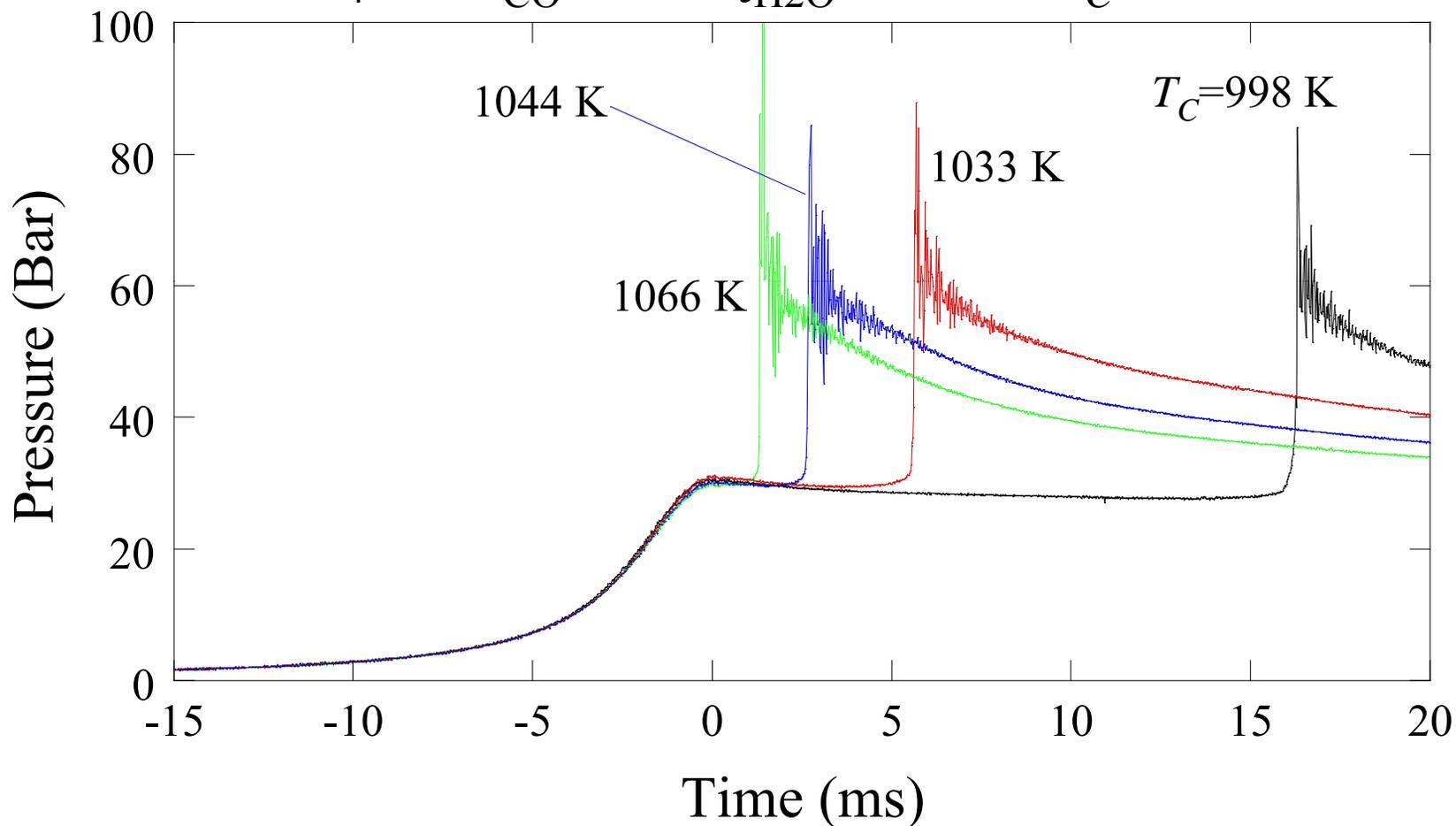
Molar composition:  $\text{H}_2/\text{CO}/\text{H}_2\text{O}/\text{O}_2/\text{N}_2/\text{Ar} = 2.5/10.0/2.5/6.25/15.625/63.125$

Initial conditions:  $T_0 = 300.9$  K and  $P_0 = 571.6$  Torr



# Moist H<sub>2</sub>/CO Ignition Delay

$\phi=1, R_{CO}=0.80, \xi_{H_2O}=16.7\%, P_C=30 \text{ bar}$



H<sub>2</sub>/CO/H<sub>2</sub>O/O<sub>2</sub>/N<sub>2</sub>/Ar=2.5/10.0/2.5/6.25/15.625/63.125





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# *ab initio Study and Master Equation Modeling*

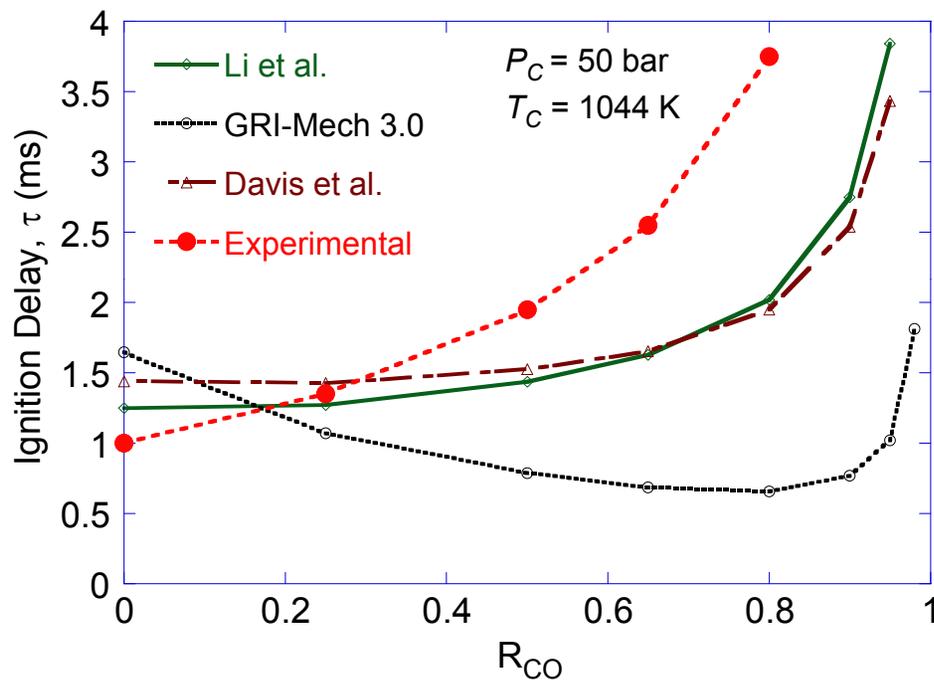
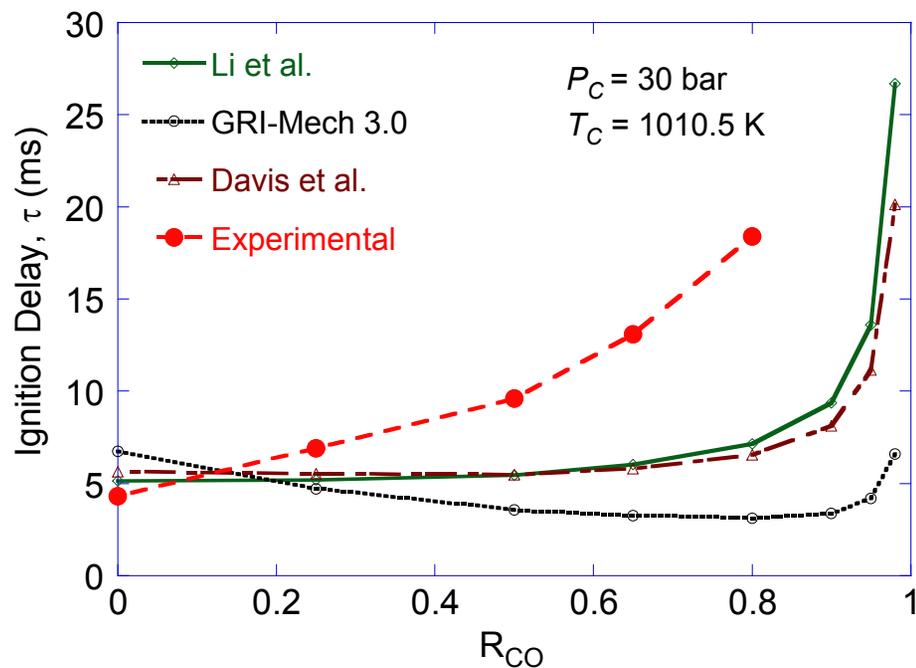




# Dry H<sub>2</sub>/CO Ignition Delay

- Existing mechanisms fail to describe the inhibition effect of CO addition.
- From mechanisms, inhibition effect of CO is not observed until it constitutes 80% of the total fuel mole fraction.

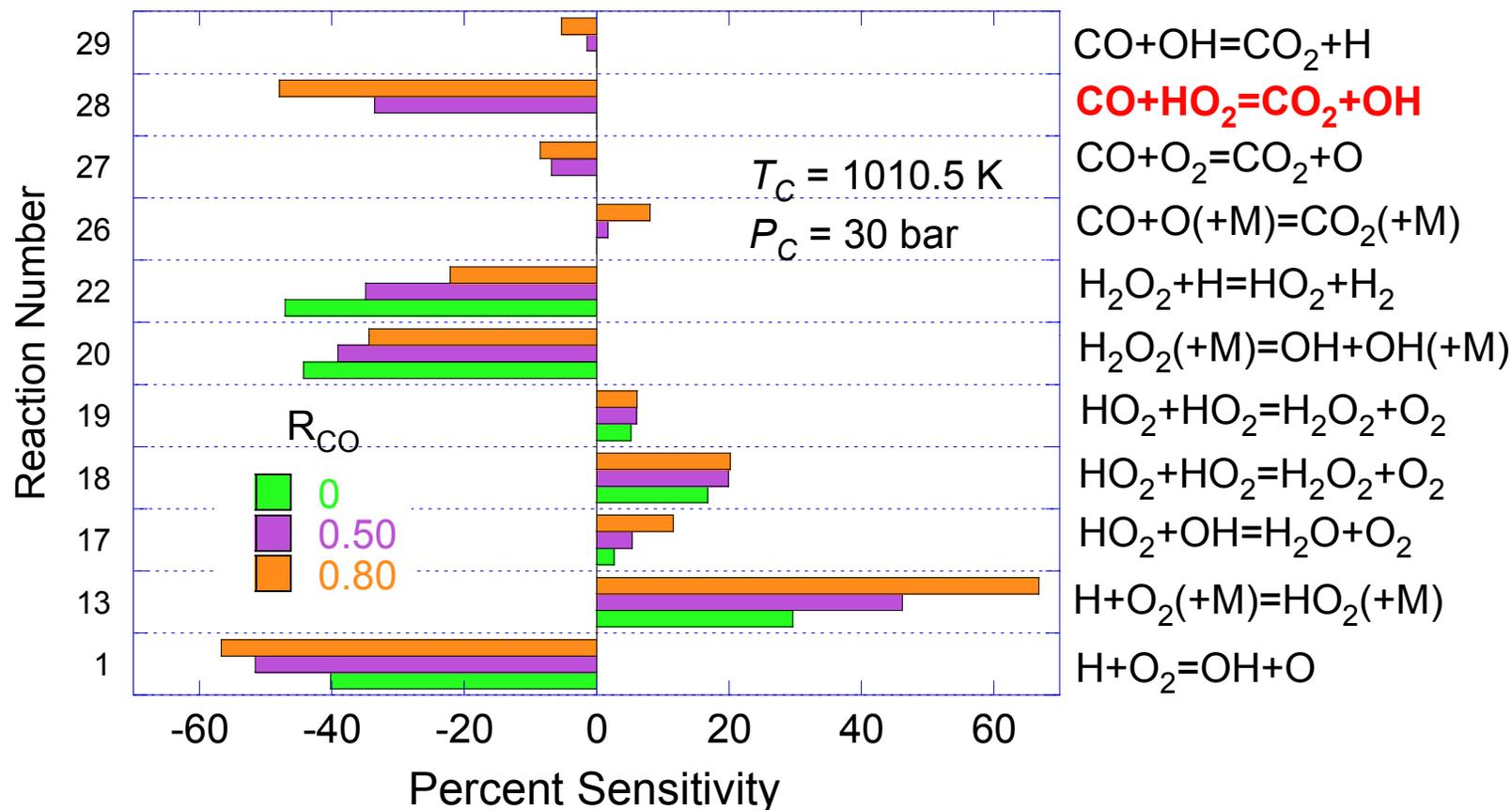
(H<sub>2</sub>+CO)/O<sub>2</sub>/N<sub>2</sub>/Ar=12.5/6.25/18.125/63.125



$$R_{CO} = [CO] / ([H_2] + [CO])$$



# “Brute Force” Sensitivity Analysis



**CO+HO<sub>2</sub>=CO<sub>2</sub>+OH** appears to be the primary reaction responsible for the mismatch of experimental and calculated ignition delays.



# Recommended Rate Constant

- Theoretical *ab initio* study and Master equation modeling supports lower rate value for  $\text{CO} + \text{HO}_2 = \text{CO}_2 + \text{OH}$ .

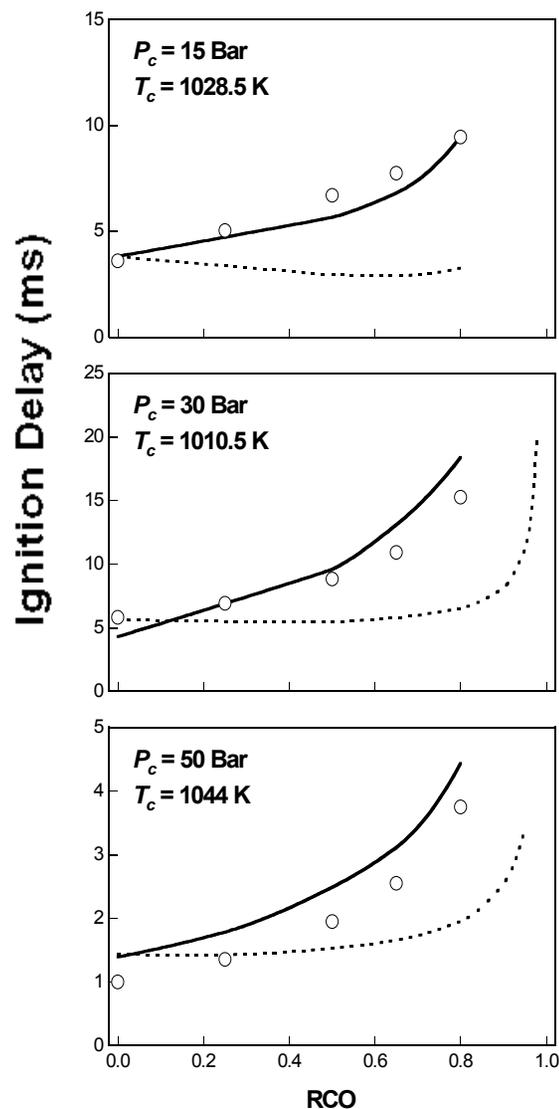
- Recommended rate expression:

$$k \left( \text{cm}^3 / \text{mol} \cdot \text{s} \right) = 1.57 \times 10^5 T^{2.18} e^{-9030/T}$$

( $300 \leq T \leq 2500$  K,  $P \leq 500$  atm)



# Modeling vs. RCM Experiments



Molar composition:  $(H_2+CO)/O_2/N_2/Ar$   
 $=12.5/6.25/18.125/63.125$ .

- Dashed lines: Model of Davis *et al.* (2005)
  - Solid lines: updated model.
1.  $CO+HO_2=CO_2+OH$  (this work)
  2.  $CO+OH=CO_2+H$  (Joshi and Wang)
  3.  $HO_2+OH=H_2O+O_2$  (Sivaramakrishnan *et al.*)



# Theoretical ab initio Study



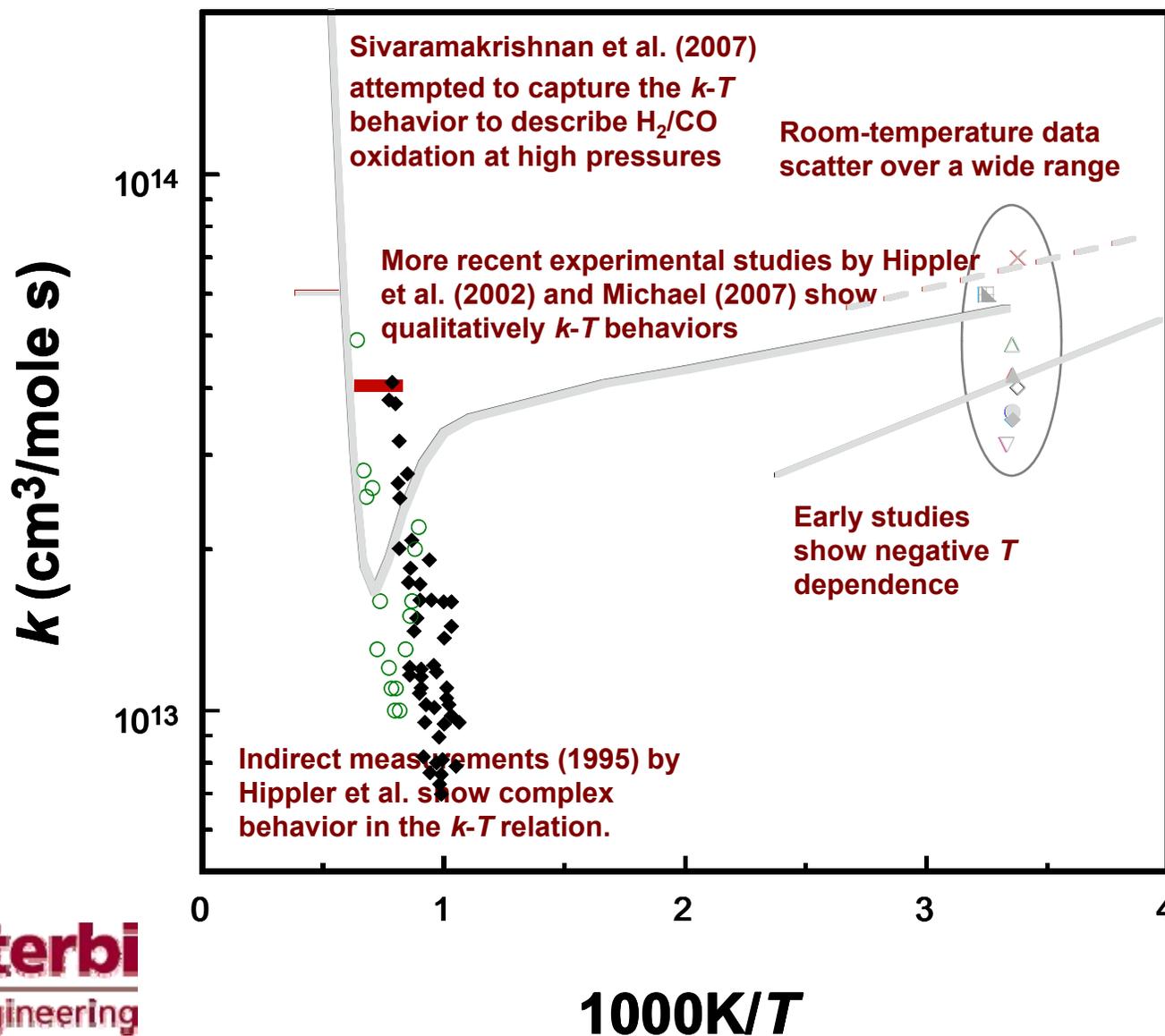
## The problem:

- A key reaction in high-pressure oxidation of CO-H<sub>2</sub> mixtures.
- The rate constant is highly uncertain.

## Objective:

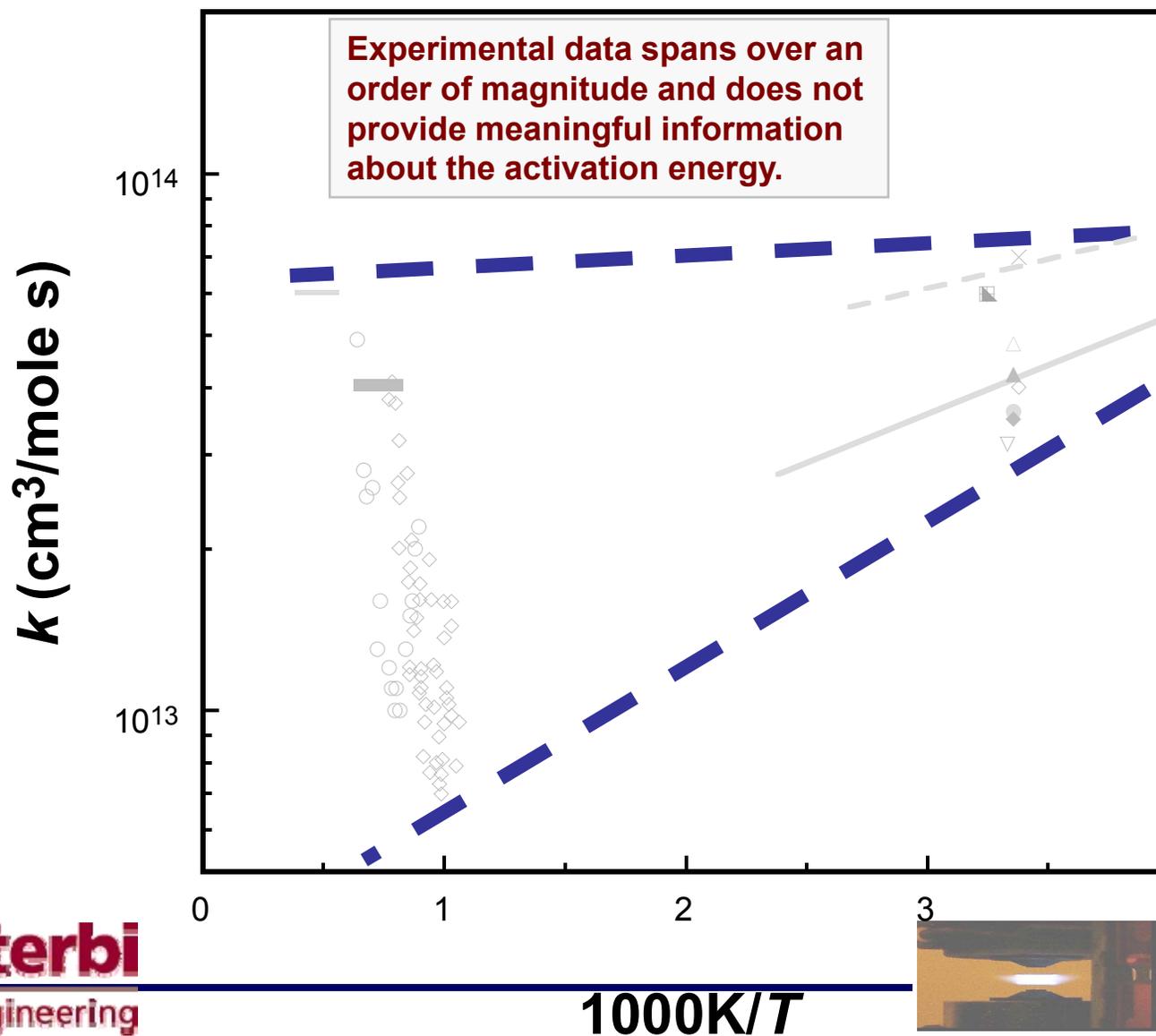
- To explore and quantify the potential energy surface for the reaction by ab initio methods (CBS-QBH and others).
- To determine its rate parameters through RRKM/VFTST/Master equation modeling with tunneling corrections.

# Theoretical ab initio Study

$$\text{HO}_2\bullet + \text{OH}\bullet \rightarrow \text{H}_2\text{O} + \text{O}_2$$


# Theoretical ab initio Study

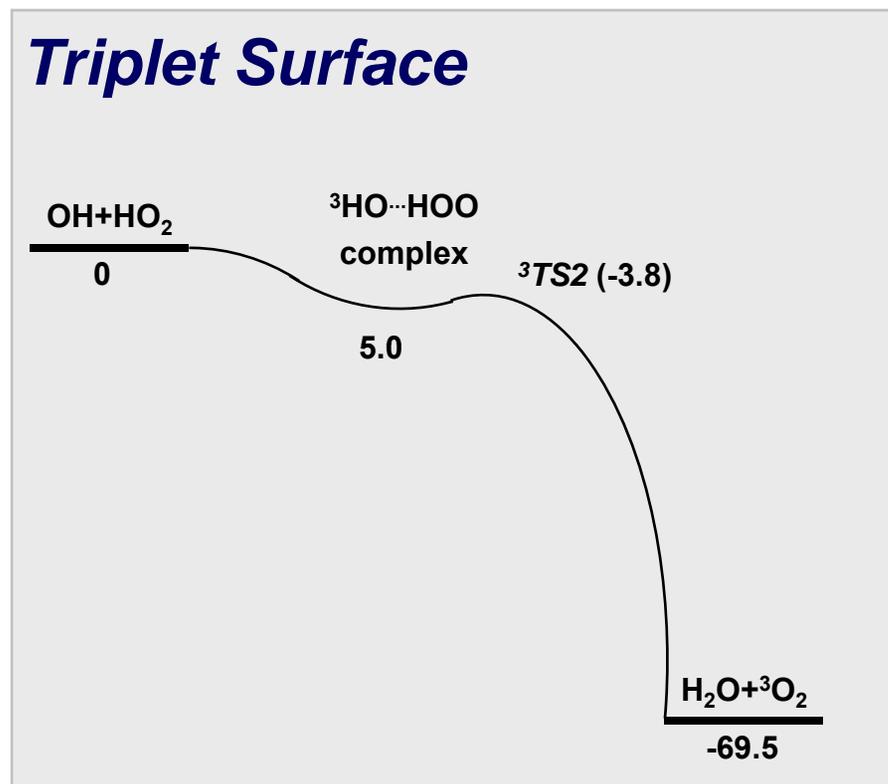
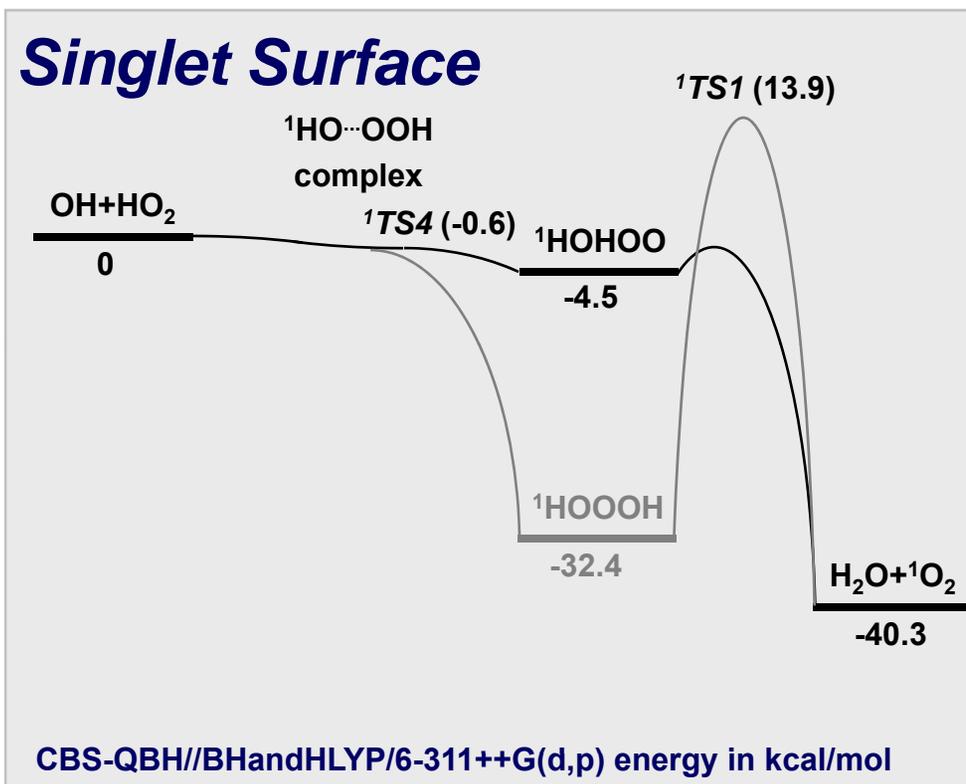
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## Preliminary Results



- The potential energy surface is quite complex for a relatively simple reaction.
- Reaction proceeds on both singlet and triplet surface without notable energy barrier.
- It is unclear (a) whether intersystem crossing can occur, and (b) what implication the singlet oxygen has on the reaction mechanism.
- Rate coefficient analysis is ongoing.



# Concluding Remarks

- For the CO-rich mixtures, laminar flame speed exhibits a non-monotonic behavior with water addition.
  - Lower percentages of water addition: positive chemical effect is much more pronounced than the negative thermal effect.
  - Beyond a certain value of water addition, negative thermal effect becomes dominant, leading to the reduction in laminar flame speed.
- Non-monotonic trend reduces with Increase in the  $H_2/CO$  ratio.
- Beyond a certain value of  $H_2/CO$  ratio, behavior is strictly monotonically decreasing with water addition.
  - Thermal effect completely dominates throughout the range of water addition
- Need extensive benchmark data of high fidelity for syngas and hydrogen combustion.





# Future Work

- Conduct further laminar flame speed measurements, with varying H<sub>2</sub>/CO ratio and additions of CO<sub>2</sub> and H<sub>2</sub>O.
- Obtain experimental data for extinction limits of various syngas flames using the counterflow burner configuration.
- Investigate effects of CO<sub>2</sub> and H<sub>2</sub>O addition on the autoignition of H<sub>2</sub>/CO mixtures using the rapid compression machine.
- Completing the master equation analysis for the rate constant of  $\text{HO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2$ , and finalize the reaction model of H<sub>2</sub>/CO combustion.

