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Syngas and Hydrogen Combustion: Ignition and Flame Propagation

Grant Number: DE-FG26-06NT42717

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

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USC
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MICHIGAN

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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 $H_2/CO/O_2/N_2/H_2O/CO_2$ 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 NOx formation during SGH combustion.

Scope of Work

- Obtain benchmark experimental data for combustion characteristics of syngas
  - **Conterflow Burner Apparatus**
    - Laminar flame speeds
    - Extinction limits
    - Flame structure
  - **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

Accomplishments - Year 1

- 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.
- 3 journal publications and 1 under review.
- Preliminary experimentation on autoignition of wet H_2/CO mixtures at elevated pressures in a rapid compression machine.
- Preliminary experimentation to determine combustion characteristics of wet H_2/CO mixtures in a counterflow configuration.

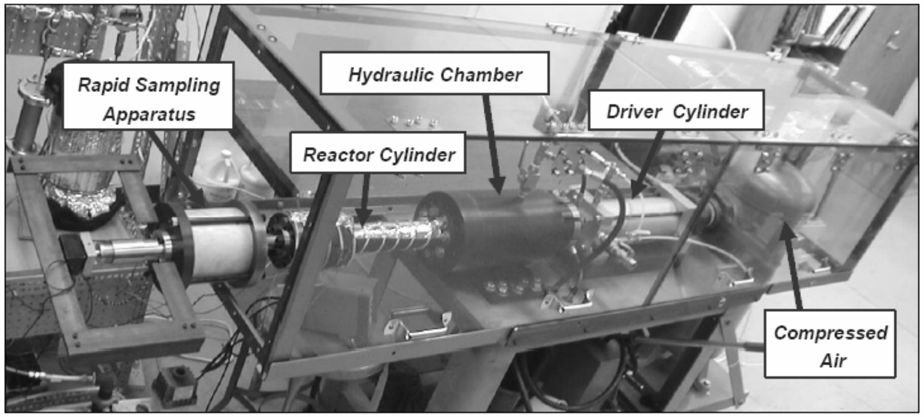
Outline

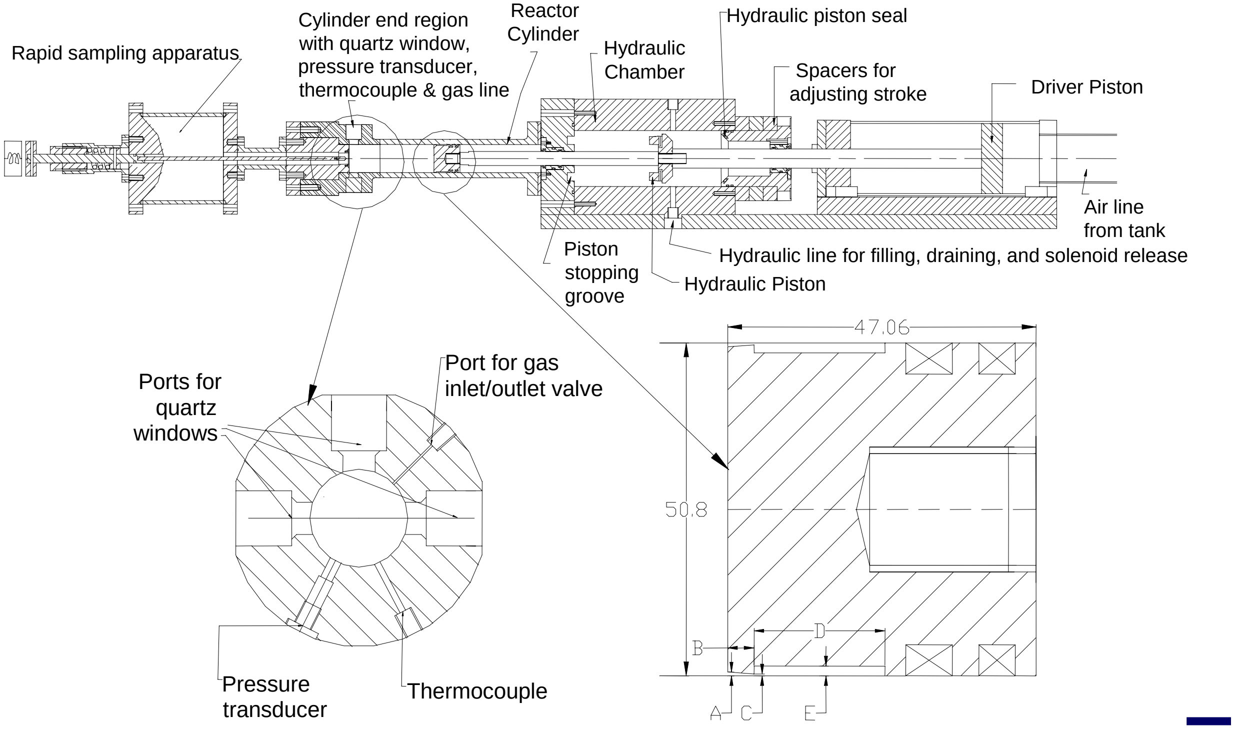
- Autoignition of Dry H_2/CO Mixtures
  - Characterization of Rapid Compression Machine
  - Ignition Delay Results
  - “Brute Force” Sensitivity Analysis
  - Global Uncertainty Analysis
- Reaction Kinetics of $CO+HO_2 \rightarrow CO_2 + OH$: *ab initio* Study and Master Equation Modeling
- Laminar Flame Speeds of Wet H_2/CO Mixtures with Preheat
  - Counterflow Burner Apparatus
  - Preliminary Results
- Conclusions
- Future Work

Autoignition of Dry H_2/CO Mixtures

High-Pressure Ignition and Oxidation

Rapid Compression Machine (RCM)





End Reaction Chamber

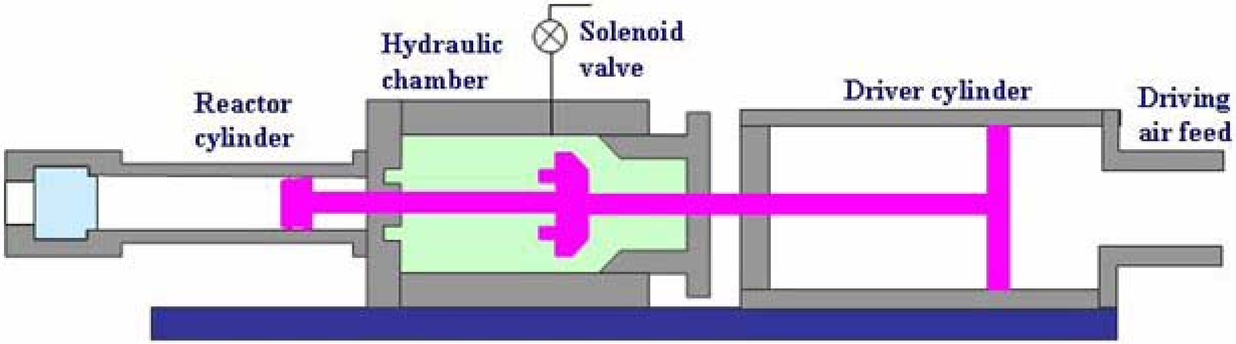
Creviced Piston

Features of the Present RCM

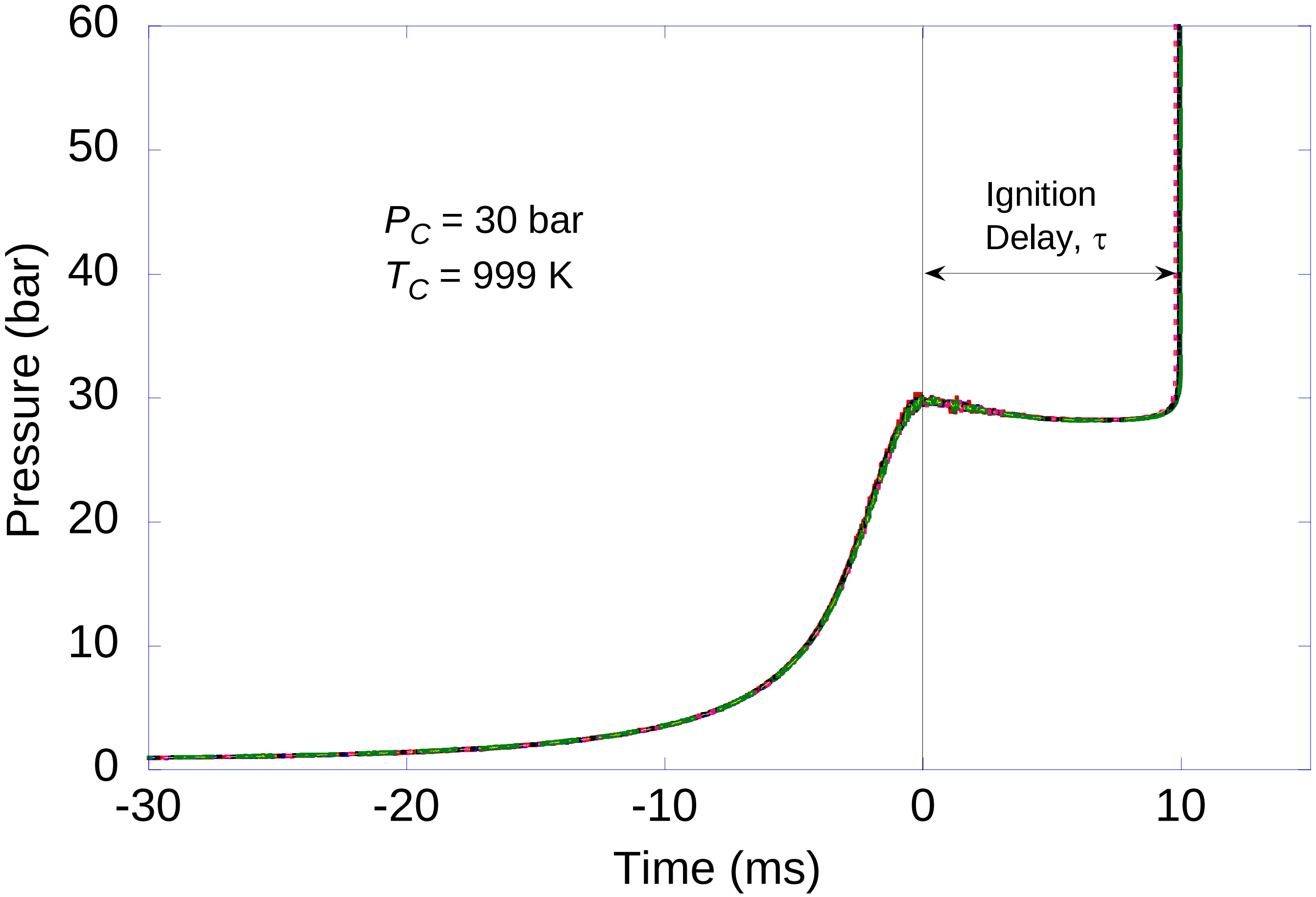
- RCM simulates a single compression stroke of an engine
  - simple and relatively easy to operate
- Adjustable stroke and clearance
- Fast compression (< 30 ms)
- Compressed pressure up to 60 bar
- Temperature – 500 to 1100 K
- Elevated pressure condition is sustained up to 100 ms
- Optimized creviced 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

- Pneumatically driven
- Hydraulically actuated and stopped



Reproducibility

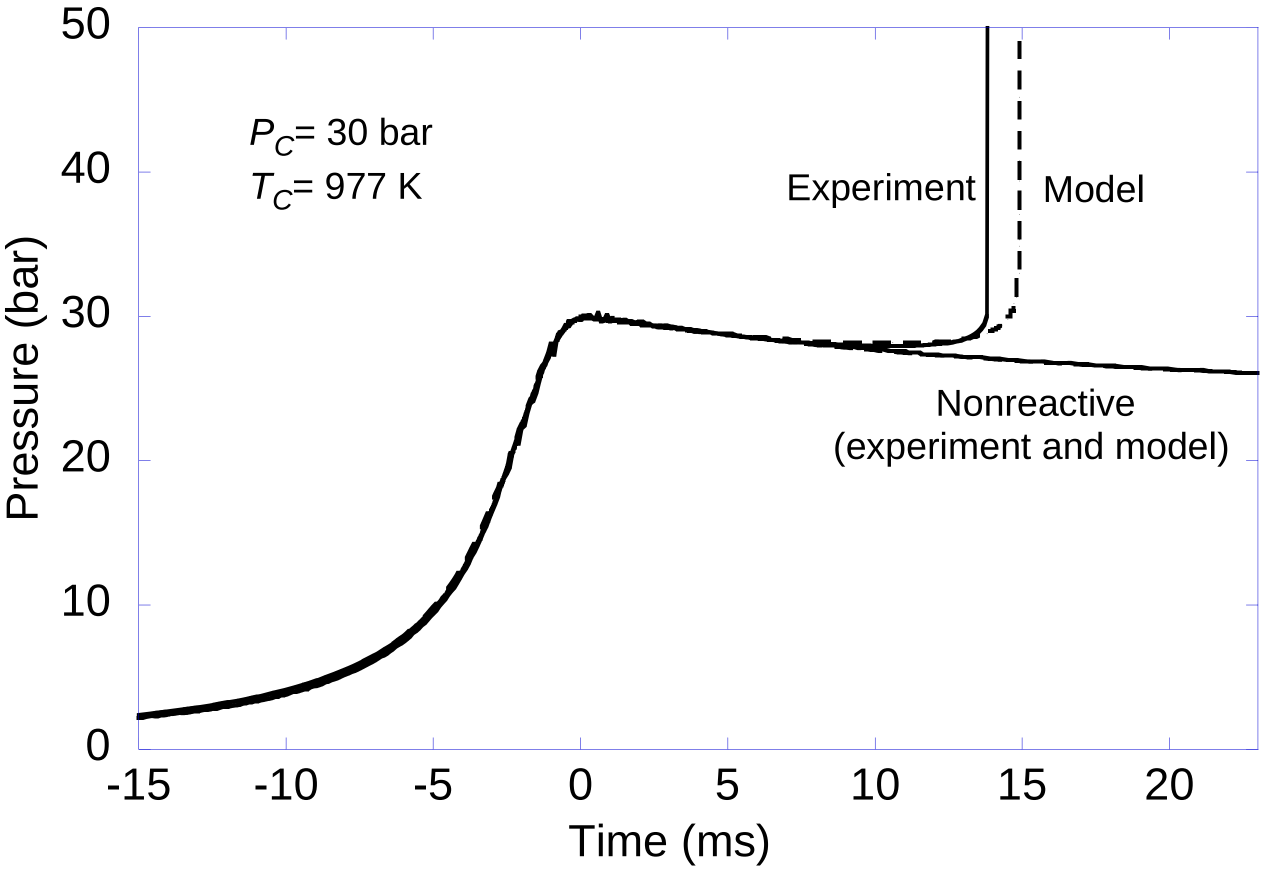


Molar composition: $H_2/CO/O_2/N_2/Ar$ = 9.375/3.125/6.25/18.125/63.125

Initial conditions – T_0 = 298.7 K and P_0 = 661 Torr

Comparison of RCM Experiment and Model

Simulation using CHEMKIN and SENKIN – with volume specified as a function of time in a homogeneous adiabatic system.



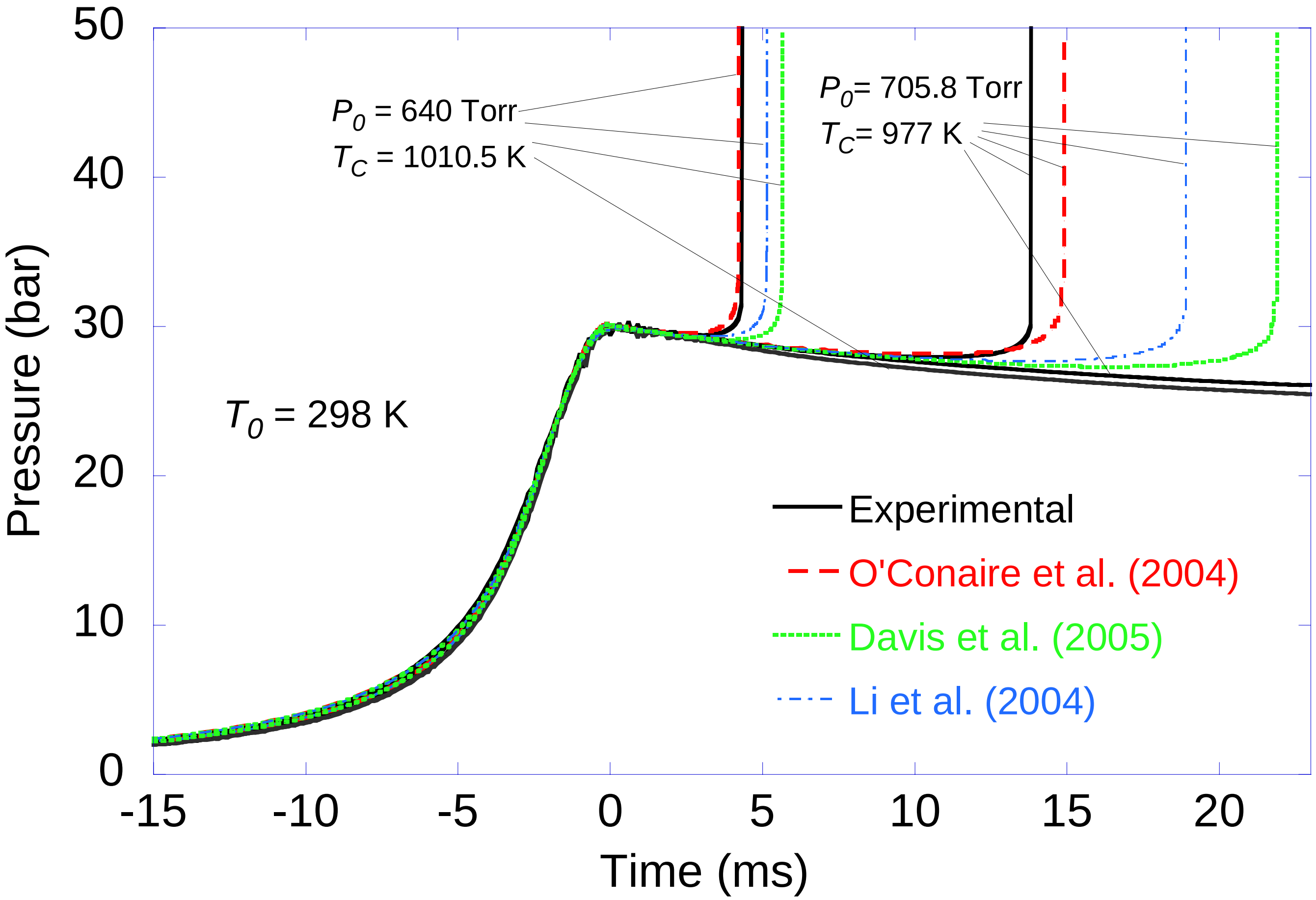
Dry H_2/CO Experiments − Specifications

- Temperature (T_C): 950 – 1100K
- Equivalence ratio (ϕ): 0.36 – 1.6
- Pressure (P_C): 15 − 50 bar
- R_{CO}=[CO]/([H_2]+[CO]): 0 – 0.80

Mixture #	ϕ	R_{CO}	H_2	CO	O_2	N_2	Ar
1	1.0	0	12.5%	0%	6.25%	18.125%	63.125%
2	1.0	0.25	9.375%	3.125%	6.25%	18.125%	63.125%
3	1.0	0.50	6.25%	6.25%	6.25%	18.125%	63.125%
4	1.0	0.65	4.375%	8.125%	6.25%	18.125%	63.125%
5	1.0	0.80	2.5%	10%	6.25%	18.125%	63.125%
6	0.36	0.25	6.667%	2.222%	12.345%	14.418%	64.348%
7	0.72	0.25	6.667%	2.222%	6.173%	21.586%	63.352%
8	1.0	0.25	6.667%	2.222%	4.444%	23.600%	63.067%
9	1.3	0.25	6.667%	2.222%	3.419%	24.782%	62.910%
10	1.6	0.25	6.667%	2.222%	2.777%	25.511%	62.823%

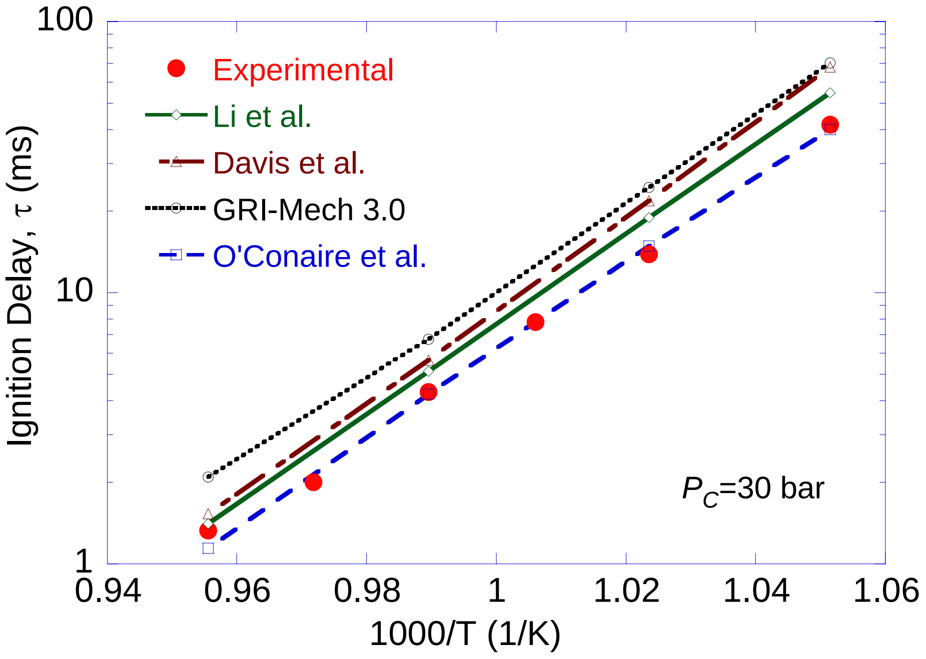
Hydrogen Ignition Delay (1)

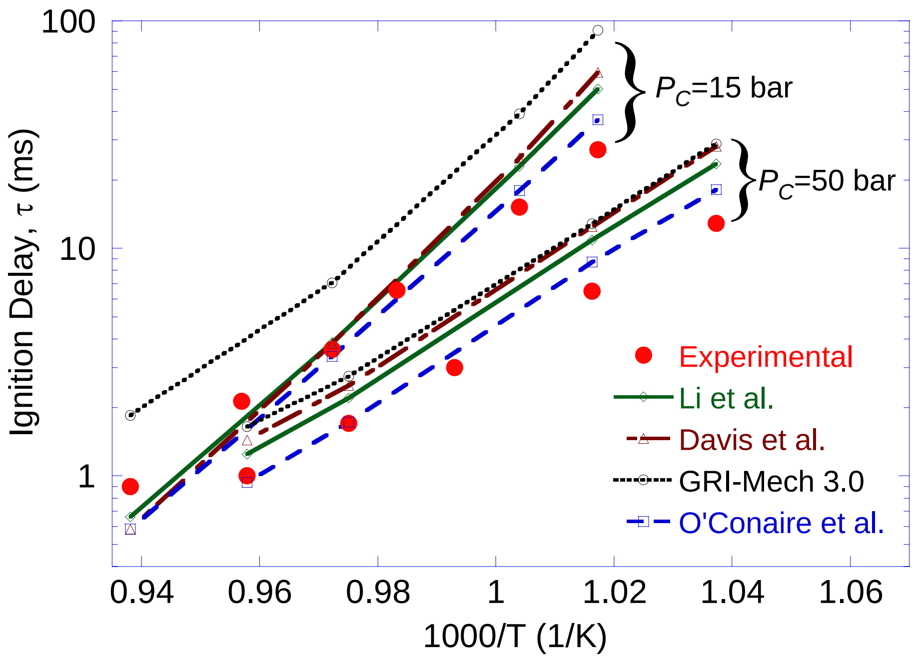
- Stoichiometric hydrogen mixtures ($H_2/O_2/N_2/Ar$ = 2/1/2.9/10.1)



Hydrogen Ignition Delay (2)

- $H_2/O_2/N_2/Ar = 12.5/6.25/18.125/63.125$





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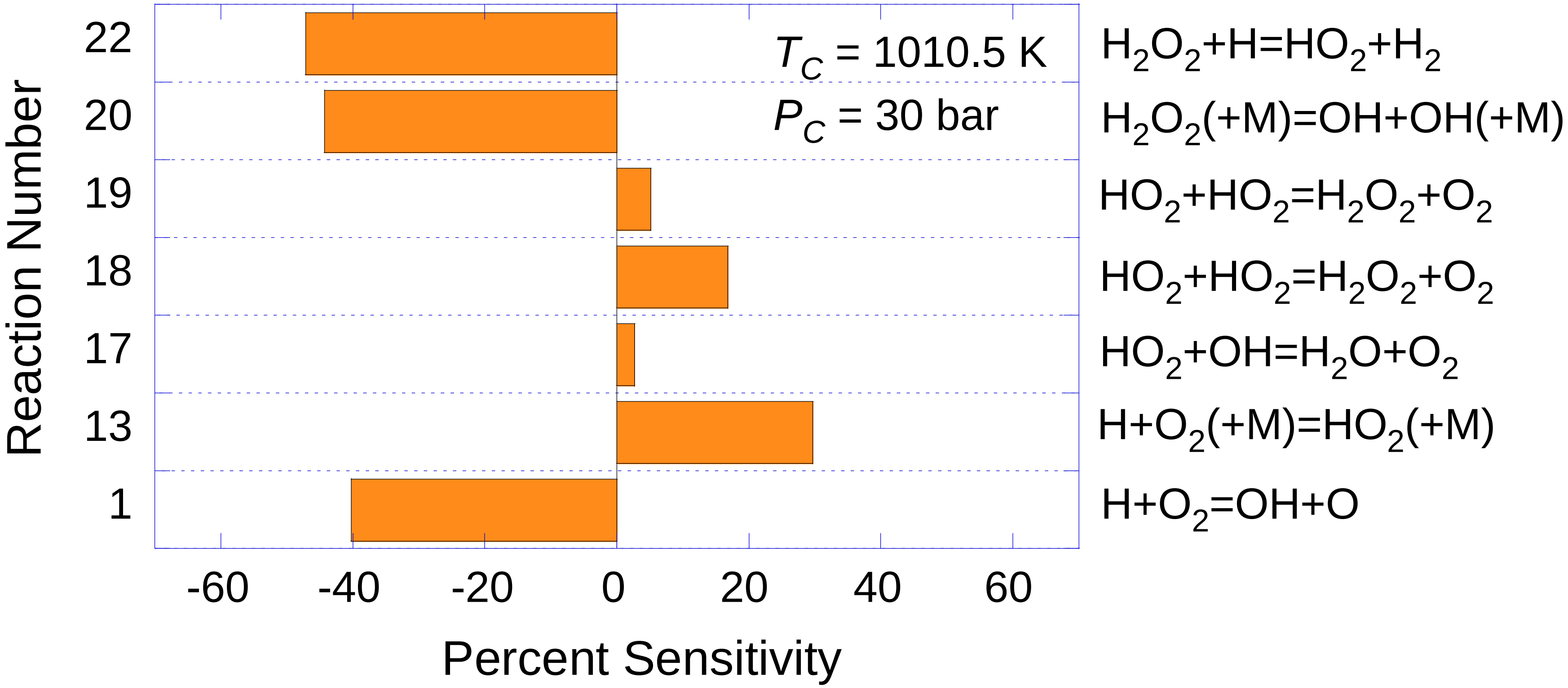
“Brute Force” Sensitivity Analysis



Reactions involving formation and consumption of HO_2 and H_2O_2 are important.

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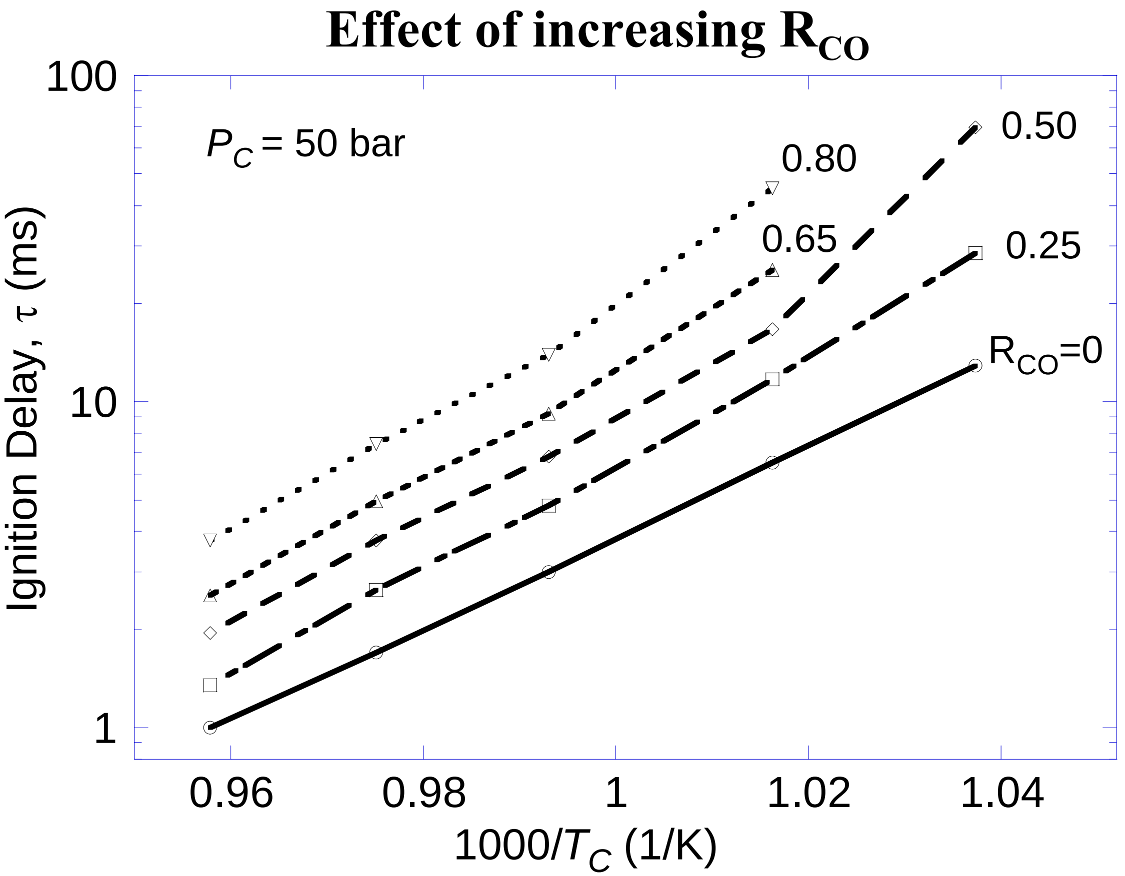
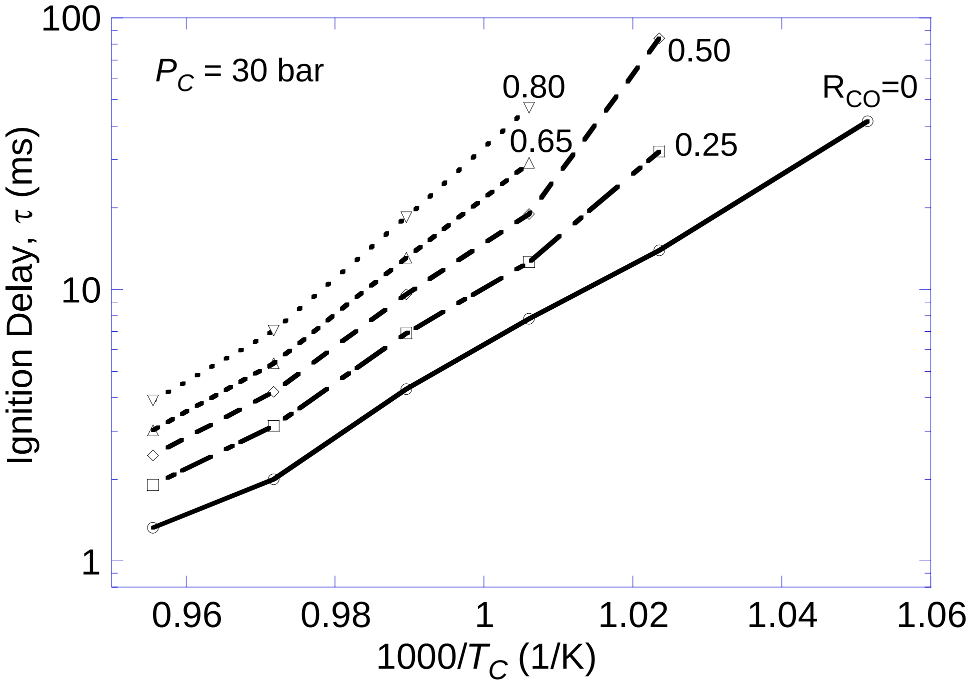
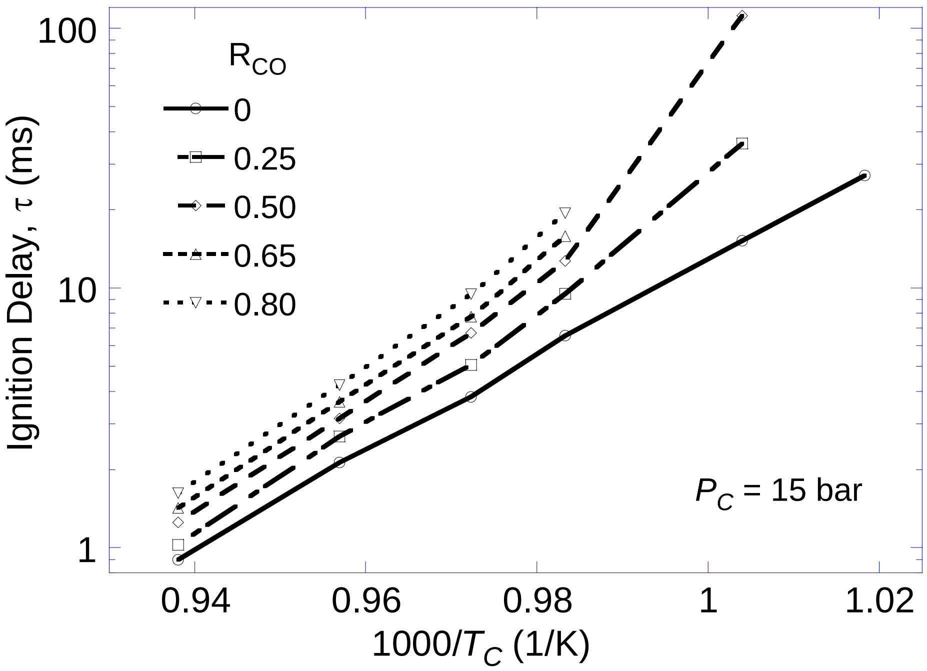
H_2/CO Ignition Delay (1)



Replacement of even small amounts of H_2 with CO leads to an inhibition of autoignition.

H_2/CO Ignition Delay (2)

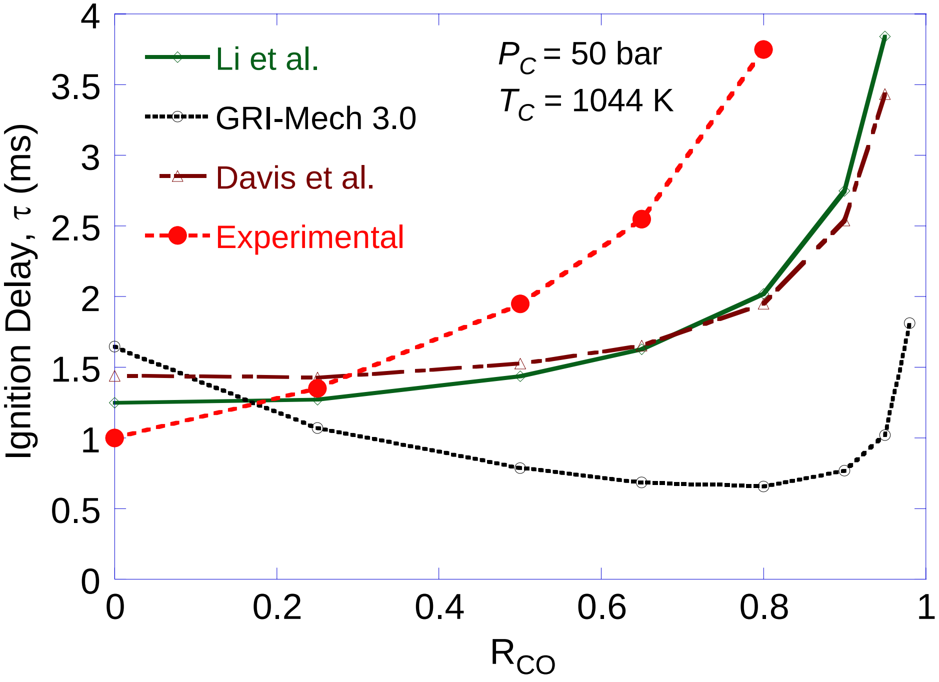


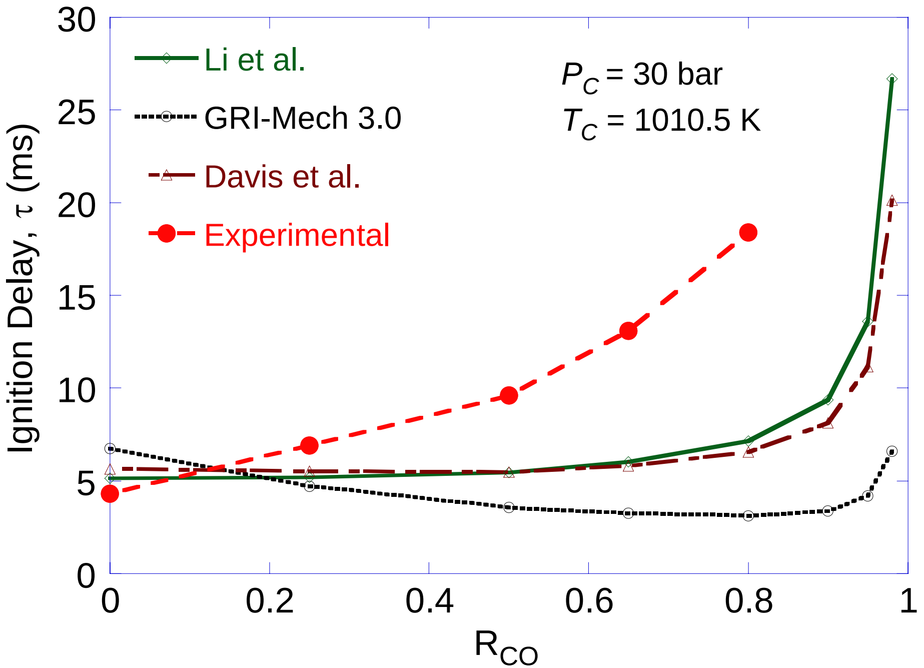


The inhibition effect of CO addition is seen to be much more pronounced at higher pressures.

H_2/CO Ignition Delay (3)

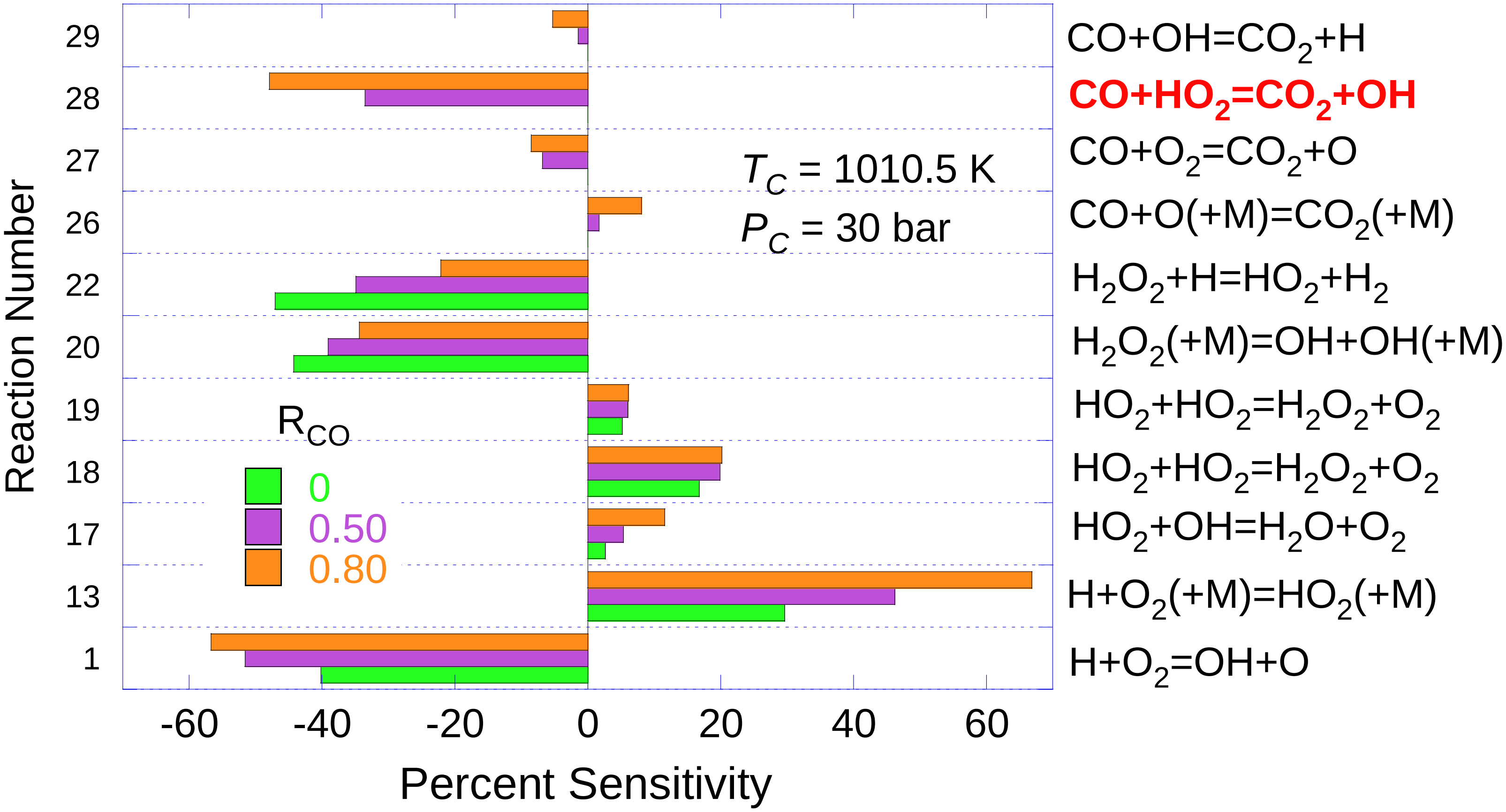
- Existing mechanisms fail to describe the inhibition effect of CO addition.
- From mechanisms, inhibition effect of CO is not observed until it constitutes 80% of the total fuel mole fraction.





$(H_2+CO)/O_2/N_2/Ar = 12.5/6.25/18.125/63.125$

“Brute Force” Sensitivity Analysis



CO+HO$_2$=CO$_2$+OH appears to be the primary reaction responsible for the mismatch of experimental and calculated ignition delays.

Global Uncertainty Analysis

- “Brute force” local sensitivity analysis is a useful linear analysis, but this cannot reveal interactions between kinetic parameter values.
- Uncertainties have to be assigned to all relevant parameters and the response to variations within the assigned ranges must be tested.
- Global, non-linear, uncertainty analysis which simultaneously considers variations in all kinetic parameters is required to interpret the origins of the discrepancy (e.g. Morris-one-at-a-time and Monte-Carlo methods).

in collaboration with Prof. J. F. Griffiths, University of Leeds

Morris Analysis (1)

- The overall importance ranking of reactions is determined by the absolute mean perturbation of the predicted ignition delay across all simulations when rate parameters are varied in a prescribed way within their ranges of uncertainty.
- The standard deviation reflects non-linear effects, i.e. the extent to which the sensitivity of the ignition delay may change if other parameters are adjusted.

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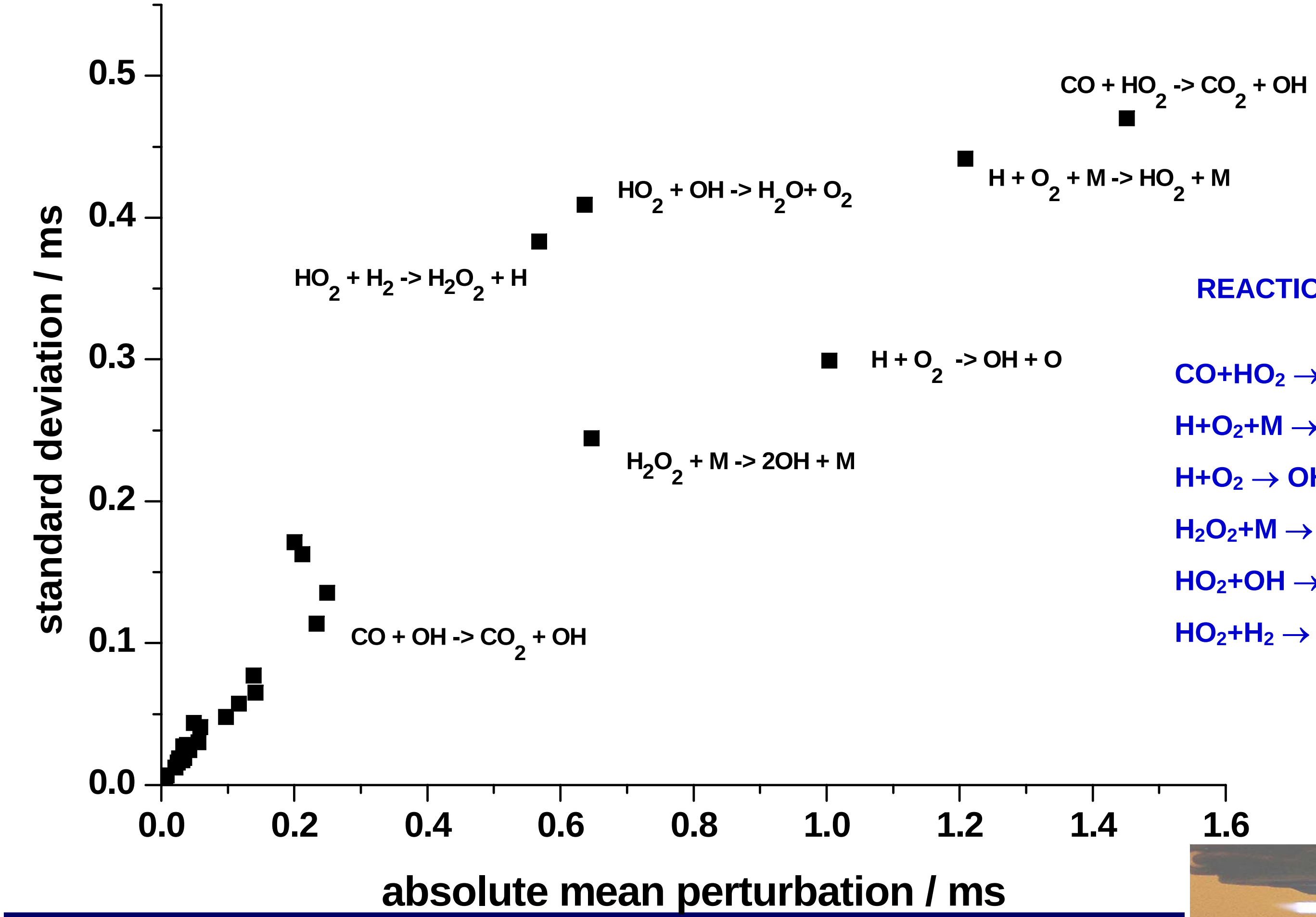
Morris Analysis (2)

0.8CO + 0.20H_2 at 50 bar and1040 K using 76 irreversible reaction scheme (Davis *et al.*, 2005)



REACTION	Range of log A (cm molecule s)
$CO+HO_2 \rightarrow CO_2+OH$	(-10.702 → -9.902)
$H+O_2+M \rightarrow HO_2+M$	(-11.272 → -10.871)
$H+O_2 \rightarrow OH+O$	(-7.207 → -7.507)
$H_2O_2+M \rightarrow 2OH+M$	(19.146 → 19.546)
$HO_2+OH \rightarrow H_2O+O_2$	(-10.905 → -9.905)
$HO_2+H_2 \rightarrow H_2O_2+H$	(-19.667 → -19.047)

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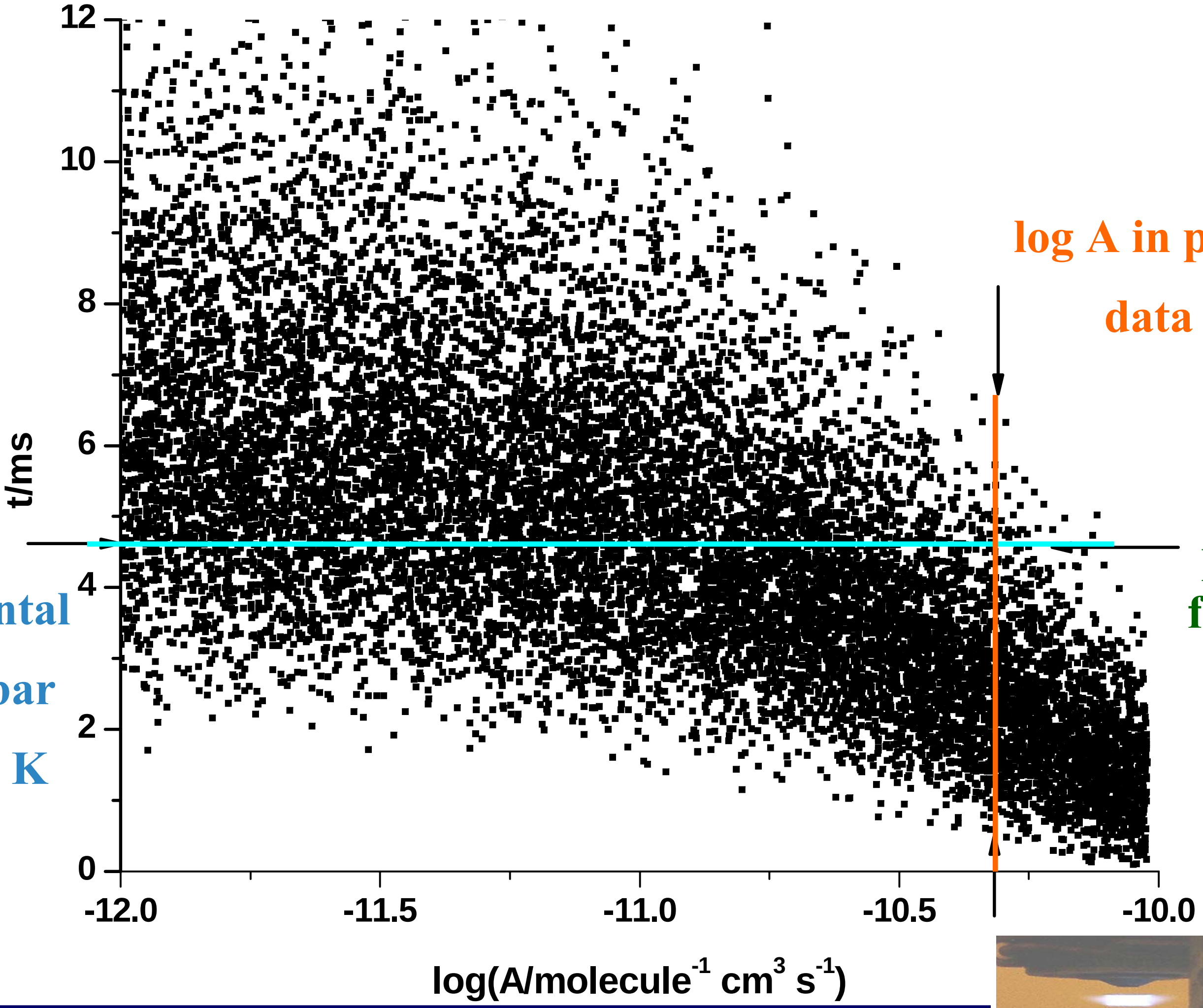
Monte Carlo Analysis (1)

Significance of k of $CO+HO_2$ in predicting ignition delay



log A in primary

data set

The experimental value for t_{ign} is predicted in only a few cases regardless of all other parameter values

Experimental

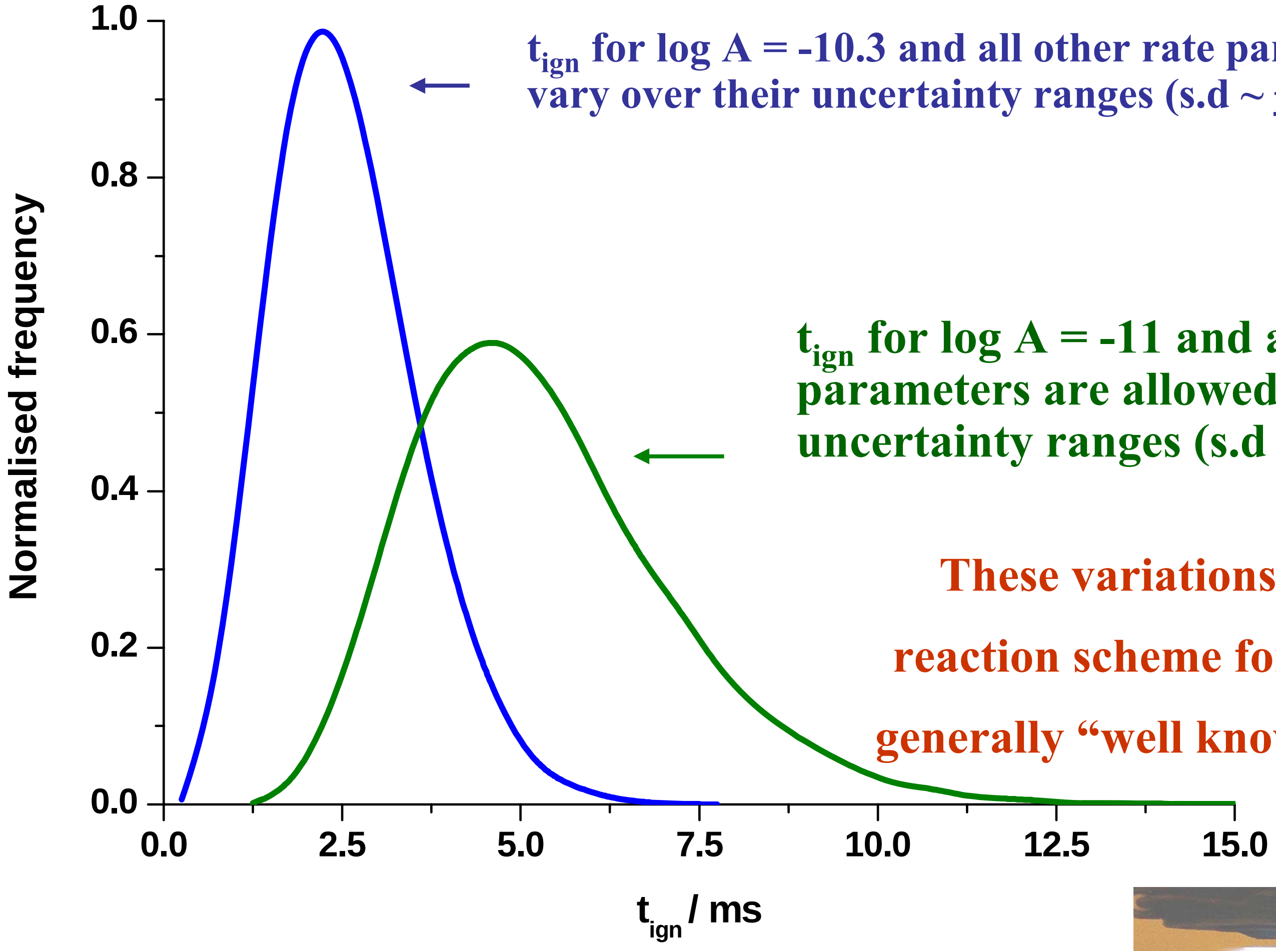
t_{ign} at 50 bar

and 1040 K

This is why we think k for $CO + HO_2$ is wrong.

Monte Carlo Analysis (2)

Relationship of various values of k of $CO+HO_2$ with predicted ignition delays



t_{ign} for log A = -10.3 and all other rate parameters are allowed to vary over their uncertainty ranges (s.d ~ ± 60%)

t_{ign} for log A = -11 and all other rate parameters are allowed to vary over their uncertainty ranges (s.d ~ ± 40%)

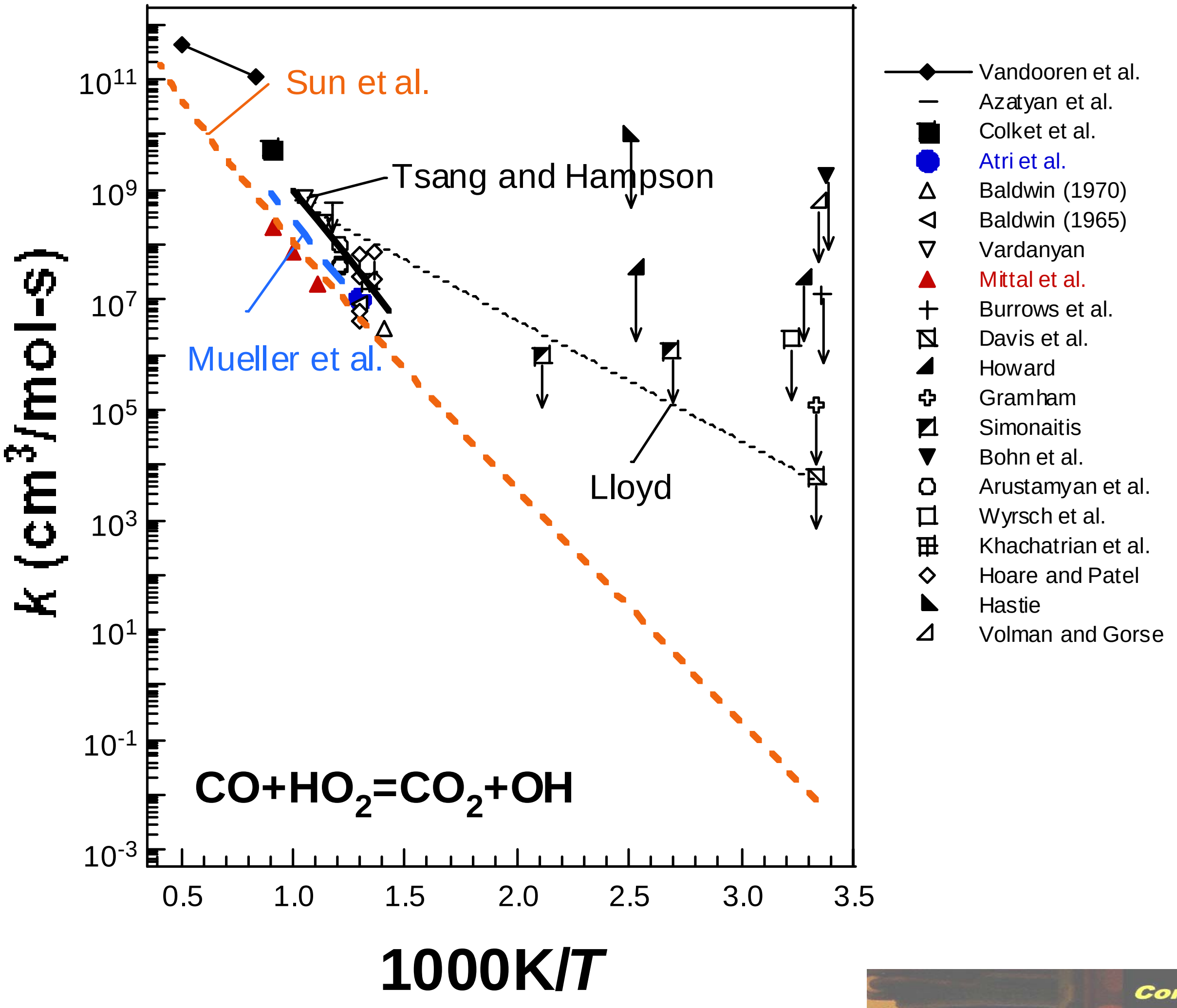
These variations arise even in a 76 reaction scheme for which the data are generally “well known”. BE WARNED!

Conclusions from Global Uncertainty Analysis

- The currently accepted parameter values for $CO + HO_2$ are obviously not right.
- Log A < -11 would fix it but the present analysis does not permit us to do more than indicate that the overall reaction rate is too fast.
- This constraint arises from the uncertainty in other rate parameters that gives the scatter in the predicted ignition delays – which is problem for any model validation using ignition delay data.
- Corrected parameters cannot be generated for this reaction solely from ignition delay evaluations
- Direct experimental or theoretical approaches are required to determine the rate parameters.

Reaction Kinetics of
$CO+HO_2 \rightarrow CO_2 + OH$
ab initio Study and Master Equation Modeling

Motivation (1)



Motivation (2)

- Prior theoretical efforts are insufficient to ensure an accurate rate coefficient.
- In all cases, the hindered internal rotations in the HOOC•O adduct and the critical geometries were inadequately treated.
- The complexity of the potential energy surface due to the *trans*- and *cis*-conformers and their mutual isomerization was not considered.
- In addition, the calculations of the potential energy barriers may not be sufficiently reliable to obtain accurate rate constant values.

Approach

- A more detailed analysis of the potential energy surface of $CO+HO_2$ reaction using several high-level quantum chemistry methods.
- Our best estimates for the saddle point energies are then incorporated in transition state theory simulations that consider the full complexity of the hindered rotational motions.
- Furthermore, the possibility of collisional stabilization and the dissociation of the adduct back to $CO + HO_2$• along the *trans* pathway is examined via master equation simulations.

Quantum Chemistry Calculation

- CCSD(T)/CBS energy (Halkier, 1998)

$$E_{\mathrm{CCSD(T)/CBS}} \approx E_{\mathrm{CCSD(T)/cc\text{-}pVQZ}} + \underbrace{\frac{27}{37} \times \left[E_{\mathrm{CCSD(T)/cc\text{-}pVQZ}} - E_{\mathrm{CCSD(T)/cc\text{-}pVTZ}} \right]}_{\textbf{Basis set correction}}$$

- FCC/CBS energy (He, 2000)

$$E_{\mathrm{FCC/CBS}} \approx E_{\mathrm{CCSD(T)/CBS}} + \underbrace{\frac{1}{5} \times \left[E_{\mathrm{CCSD(T)/cc\text{-}pVTZ}} - E_{\mathrm{CCSD/cc\text{-}pVTZ}} \right]}_{\textbf{Configuration Interaction truncation error}}$$

- Energies (kcal/mol) at 0 K relative to CO + HO_2•

Products/ transition state	G3B3	CCSD(T)/ cc-pVTZ	CCSD(T)/ cc-pVQZ^a	CCSD(T)/ CBS	FCC/CBS	Literature value
CO_2+OH	-63.3	-59.9	-61.0	-61.8	-61.7	-61.6±0.1
HOOC•O	6.3	8.1	7.2	6.5	6.0	
TS1	18.3	18.8	18.3	17.9	17.3	
TS2	12.0	14.4	13.4	12.7	11.8	
TS3	19.3	19.9	19.3	18.9	18.2	
TS4	15.5	17.2	16.4	15.8	15.3	
HC•O+O_2	33.3	33.1	33.7	34.1	34.0	33.6±0.1

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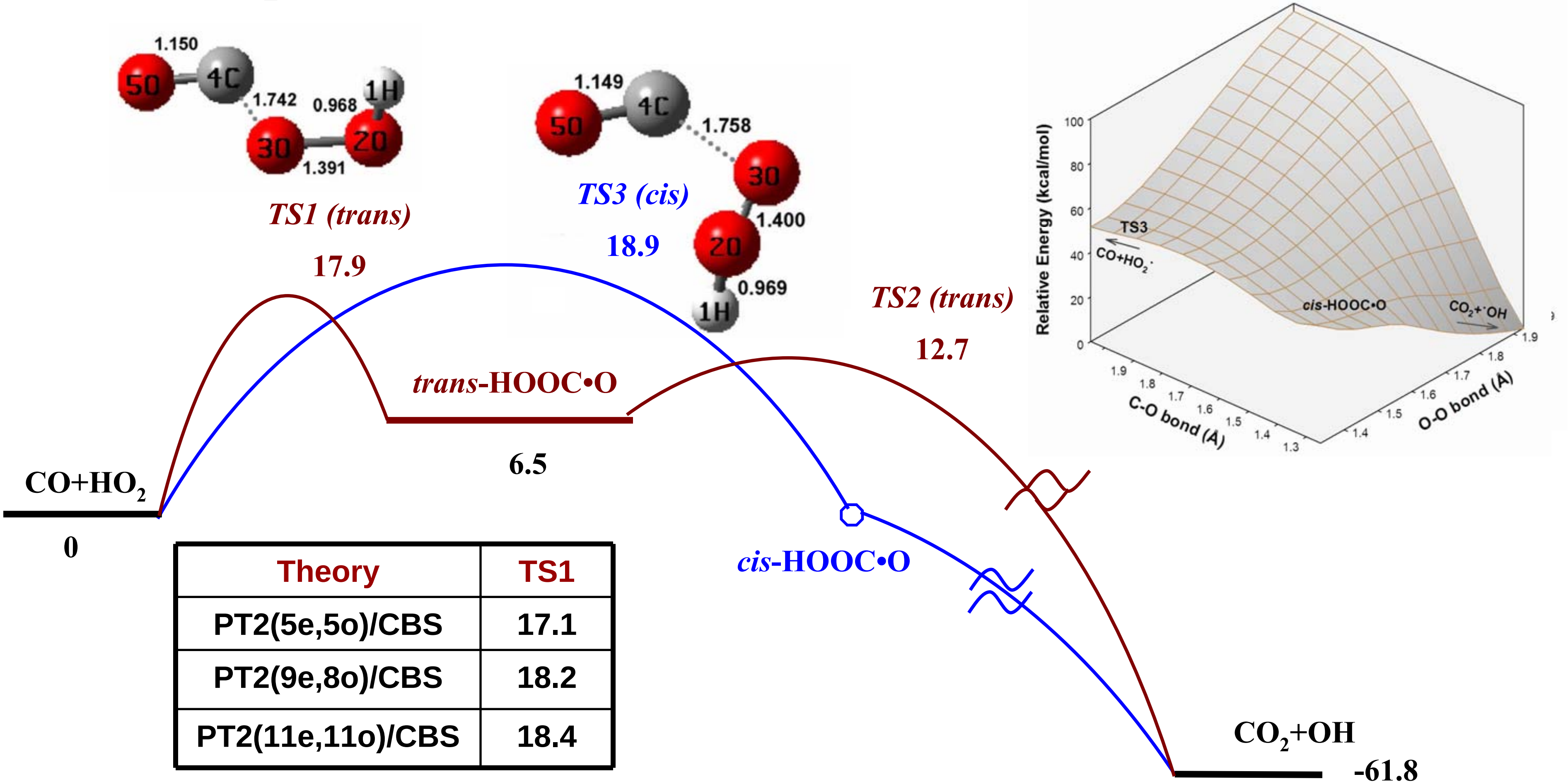
Potential Energy Surface

- CO+HO_2→products (CCSD(T)/CBS//CCSD(T)/cc-pVTZ, kcal/mol)



Theory	TS1
PT2(5e,5o)/CBS	17.1
PT2(9e,8o)/CBS	18.2
PT2(11e,11o)/CBS	18.4

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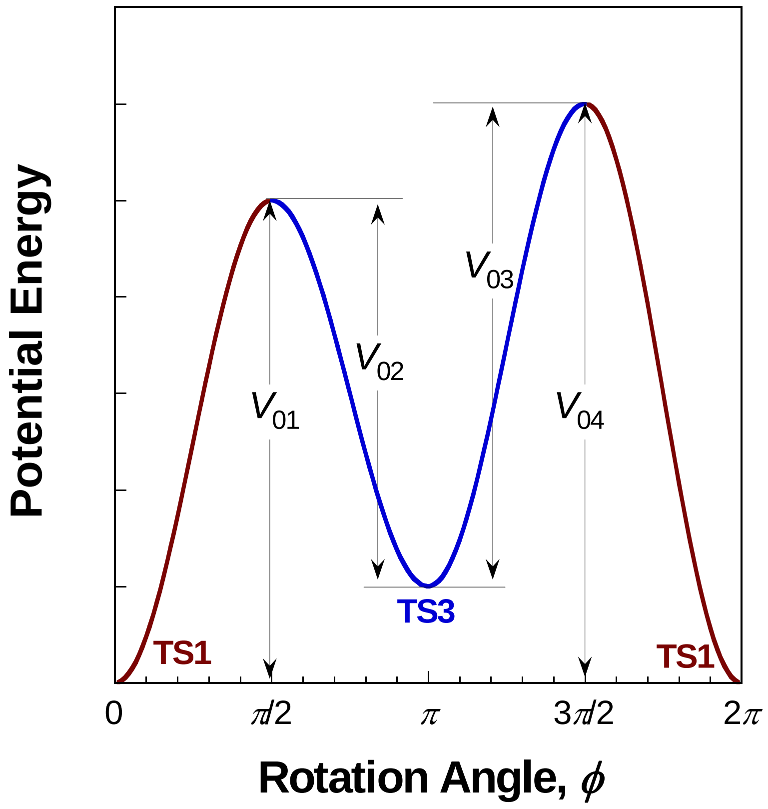
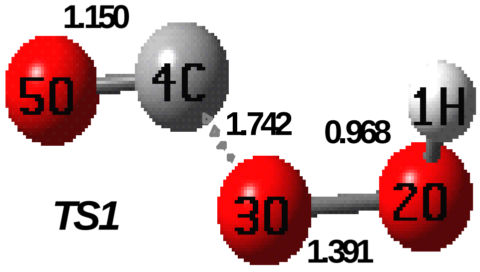
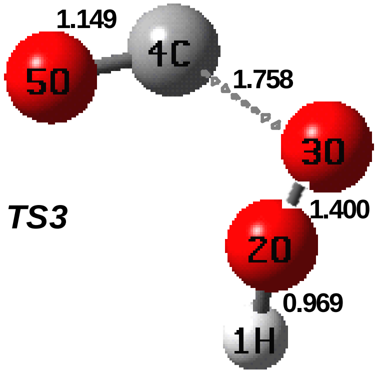
Internal Rotation

- Asymmetric characteristics
- TS1↔TS3







$$Q_h(T)=\frac{1}{2\pi}\left(\frac{\pi k_B T}{B}\right)^{1/2}\sum_{i=1}^{4}\int_{(i-1)\pi/2}^{i\pi/2} d\phi\, e^{-V/k_B T}$$

Density of States

- Hindered internal rotation contributions

$$\rho_h(E)=\rho_{h1}(E)+\rho_{h2}(E)+\rho_{h3}(E)+\rho_{h4}(E)$$

$$\rho_{h1}(E)=\begin{cases}\dfrac{K\left(\sqrt{\dfrac{E}{V_{01}}}\right)}{2\pi\sqrt{BV_{01}}} & \text{for } 0<E<V_{01}\\[2ex] \dfrac{K\left(\sqrt{\dfrac{V_{01}}{E}}\right)}{2\pi\sqrt{BE}} & \text{for } E>V_{01}\end{cases}$$

$$\rho_{h2}(E)=\begin{cases}\dfrac{K\left(\sqrt{\dfrac{E-(V_{01}-V_{02})}{V_{02}}}\right)}{2\pi\sqrt{BV_{02}}} & \text{for } 0<E-(V_{01}-V_{02})<V_{02}\\[2ex] \dfrac{K\left(\sqrt{\dfrac{V_{02}}{E-(V_{01}-V_{02})}}\right)}{2\pi\sqrt{B\left[E-(V_{01}-V_{02})\right]}} & \text{for } E-(V_{01}-V_{02})>V_{02}\end{cases}$$

$$\rho_{h3}(E)=\begin{cases}\dfrac{K\left(\sqrt{\dfrac{E-(V_{01}-V_{02})}{V_{03}}}\right)}{2\pi\sqrt{BV_{03}}} & \text{for } 0<E-(V_{01}-V_{02})<V_{03}\\[2ex] \dfrac{K\left(\sqrt{\dfrac{V_{03}}{E-(V_{01}-V_{02})}}\right)}{2\pi\sqrt{B\left[E-(V_{01}-V_{02})\right]}} & \text{for } E-(V_{01}-V_{02})>V_{03}\end{cases}$$

$$\rho_{h4}(E)=\begin{cases}\dfrac{K\left(\sqrt{\dfrac{E}{V_{04}}}\right)}{2\pi\sqrt{BV_{04}}}, & \text{for } 0<E<V_{04}\\[2ex] \dfrac{K\left(\sqrt{\dfrac{V_{04}}{E}}\right)}{2\pi\sqrt{BE}}, & \text{for } E>V_{04}\end{cases}$$

- Total density of states $\rho(E)=\int_0^E \rho_h(E)\,\rho_{vr}(E-\varepsilon)\,d\varepsilon$

Treatment of the Moment of Inertia

- At lower level approximation

$$I^{(2,n)} = \frac{I_L{}^{(1,n)} I_R{}^{(1,n)}}{I_L{}^{(1,n)} + I_R{}^{(1,n)}}$$

- At higher level approximation (East and Radom, 1997)

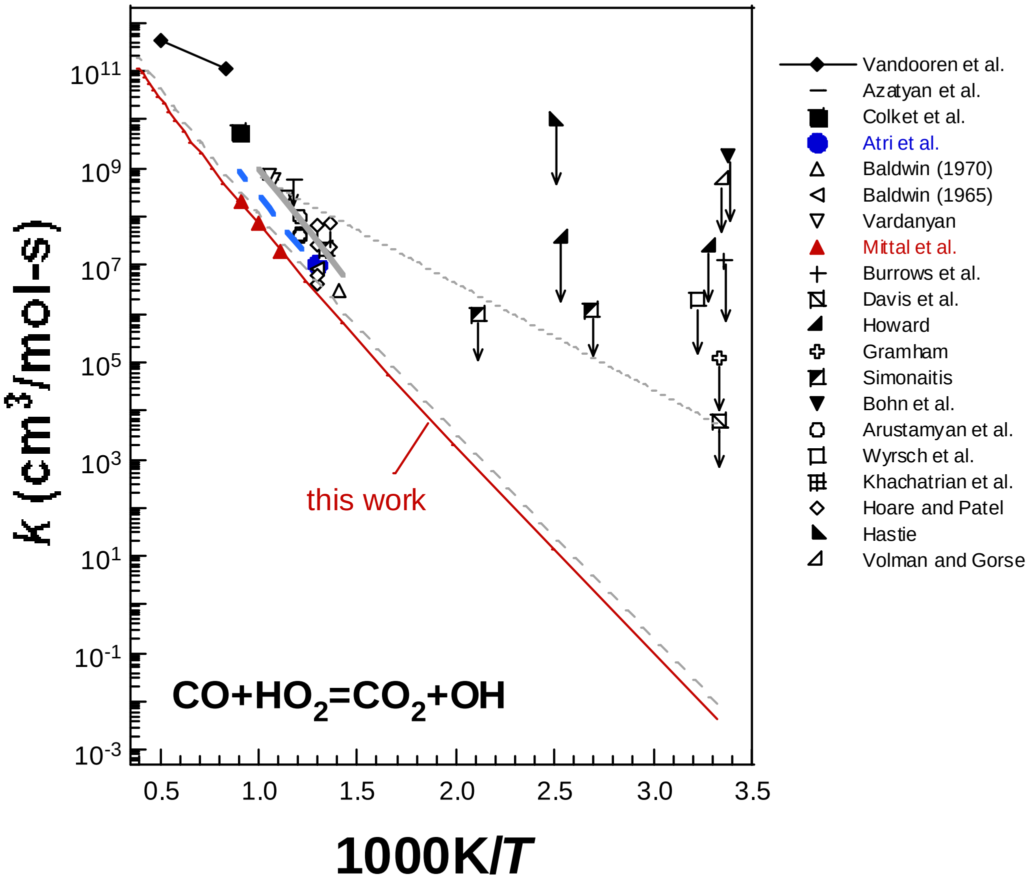
$$I^{(3,4)} = I^{(1,1)} - \sum_{i=1}^{3} \left[\frac{(\alpha_{iy} U)^2}{m_L + m_R} + \frac{\beta_i{}^2}{I_i} \right]$$

Results (1)

- Effects of internal rotor and I treatment on k (cm^3/mol·s)

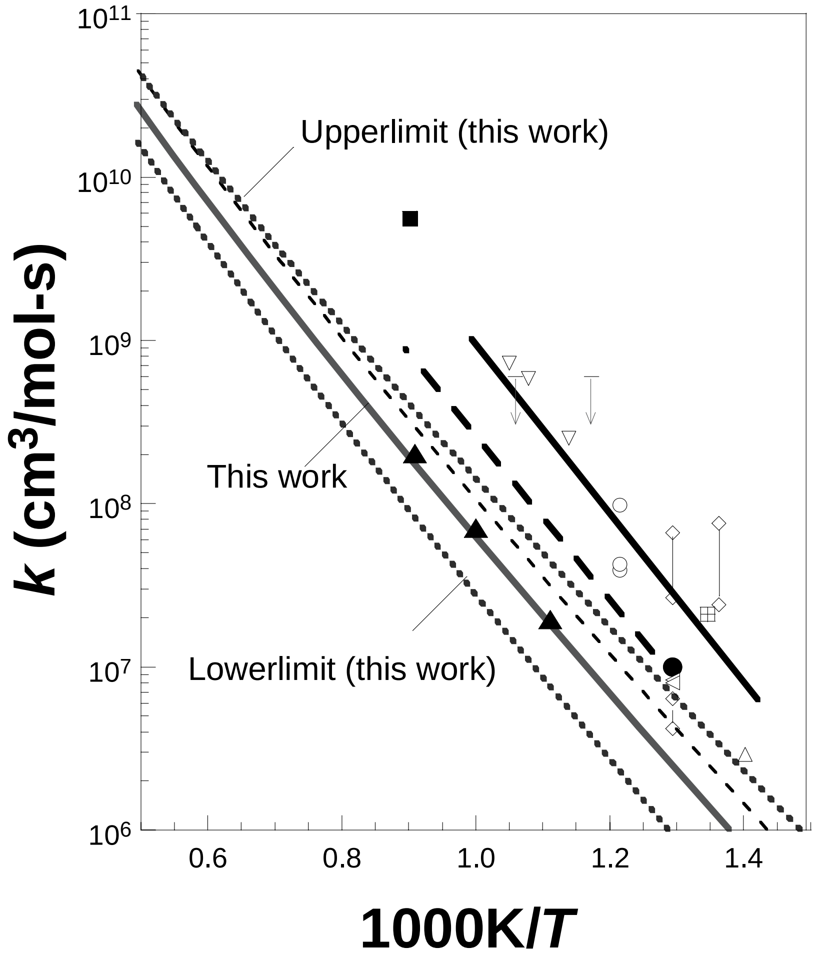
T(K)	Harmonic oscillator	Free rotor with $I^{(3,4)}$	Hindered rotor		
			$I^{(2,1)}$	$I^{(2,3)}$	$I^{(3,4)}$
500	2.1×10^{3}	3.8×10^{4}	2.9×10^{3}	1.5×10^{3}	1.7×10^{3}
1000	$\mathbf{5.6\times10^{7}}$	$\mathbf{6.1\times10^{8}}$	$\mathbf{1.1\times10^{8}}$	6.3×10^{7}	$\mathbf{6.5\times10^{7}}$
1500	2.6×10^{9}	2.1×10^{10}	5.5×10^{9}	3.4×10^{9}	3.2×10^{9}
2000	2.2×10^{10}	1.4×10^{11}	4.7×10^{10}	2.9×10^{10}	2.7×10^{10}
2500	8.8×10^{10}	4.6×10^{11}	1.9×10^{11}	1.2×10^{11}	1.1×10^{11}

Results (2)



- No pressure dependence up to 500 atm.
- Supports the notion advanced in RCM studies that the literature rate values are too large.

Uncertainty Analysis



Sources of Uncertainty:

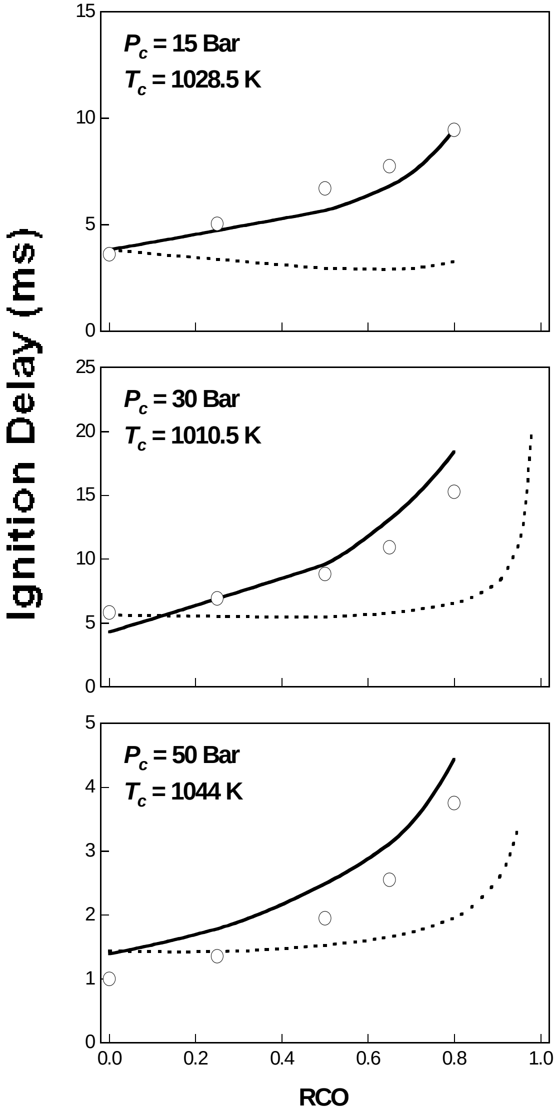
- TS1, TS3 barrier: ± 1 kcal/mol
- Internal rotation barrier: ± 1 kcal/mol
- State counting: 50%

Rate constant Uncertainty:

- 300 K, a factor of 8;
- 1000 K, a factor of 2;
- 2000 K, a factor of 1.7.

- **The error bars reject almost all of the rate values reported in earlier studies.**

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.*)

Summary

- The current theoretical analysis supports lower rate value for $CO+HO_2=CO_2+OH$.

- Recommended rate expression:

$$k\left(\mathrm{cm}^3/\mathrm{mol}\cdot\mathrm{s}\right)=1.57\times10^5T^{2.18}e^{-9030/T}$$

(300≤T≤2500 K, P≤ 500 atm)

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Laminar Flame Speeds of Wet H_2/CO Mixtures with Preheat

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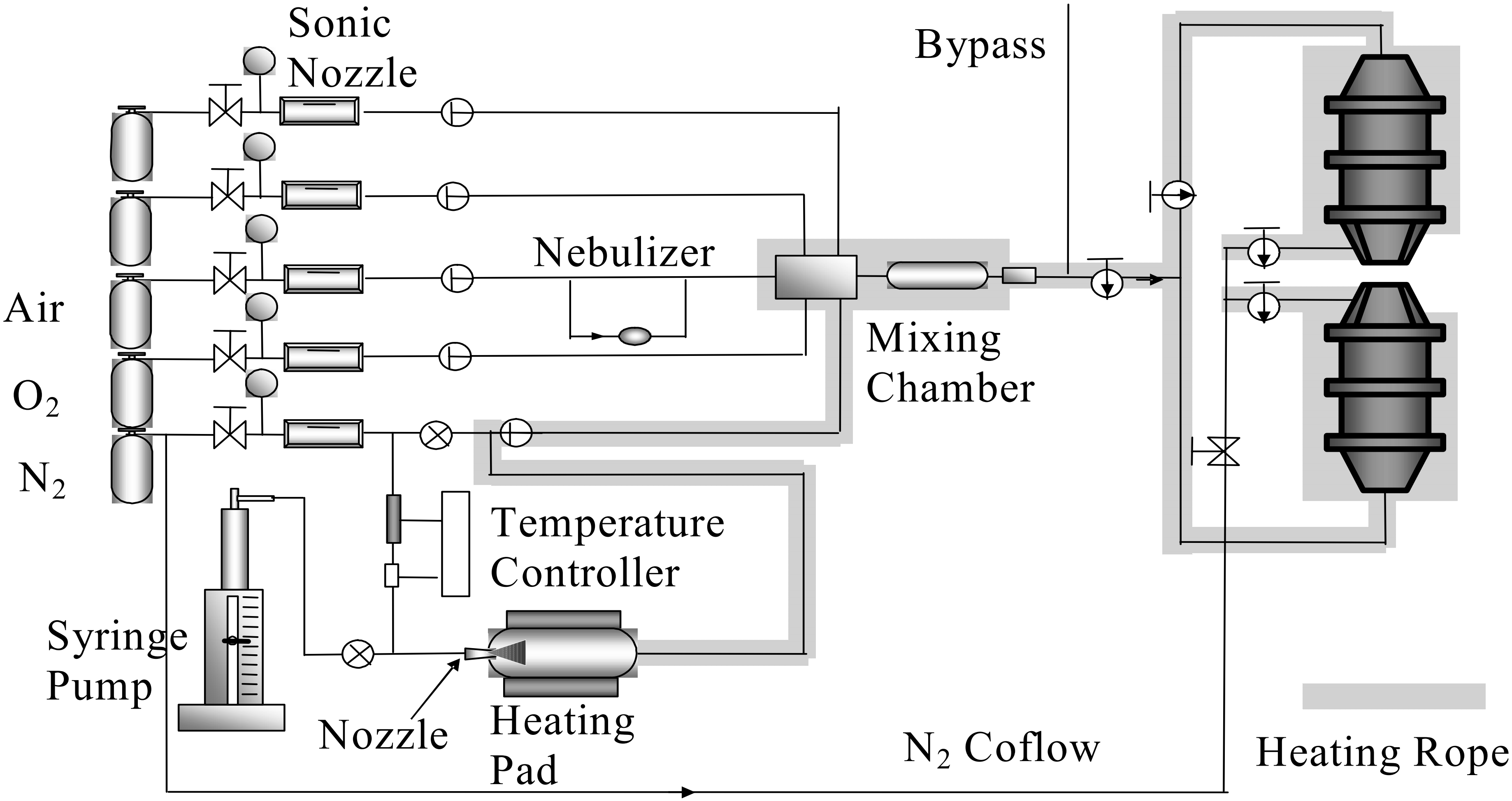
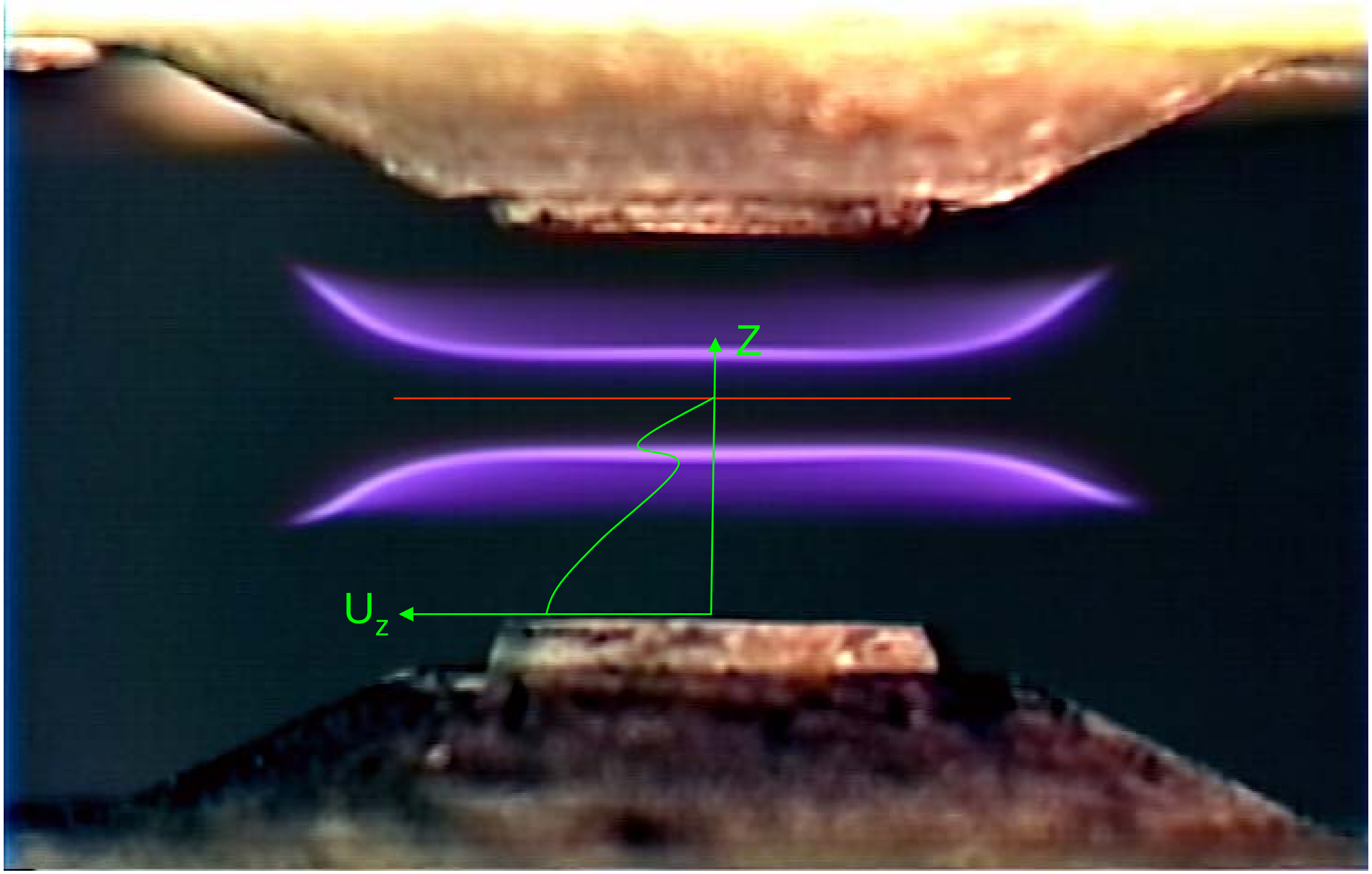
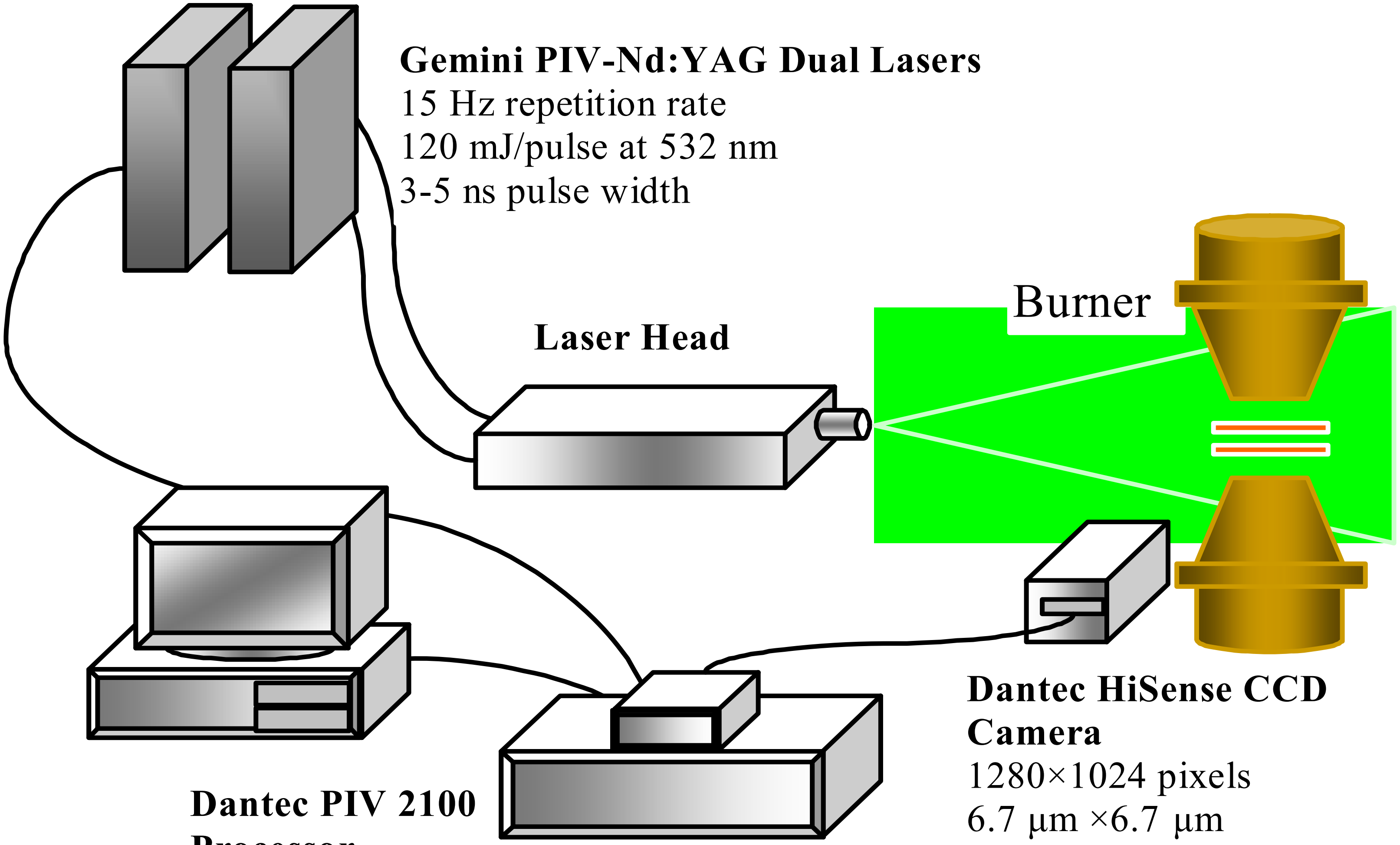
Counterflow Twin-Flame Configuration



Counterflow Twin Flames



DPIV System for Velocity Measurement



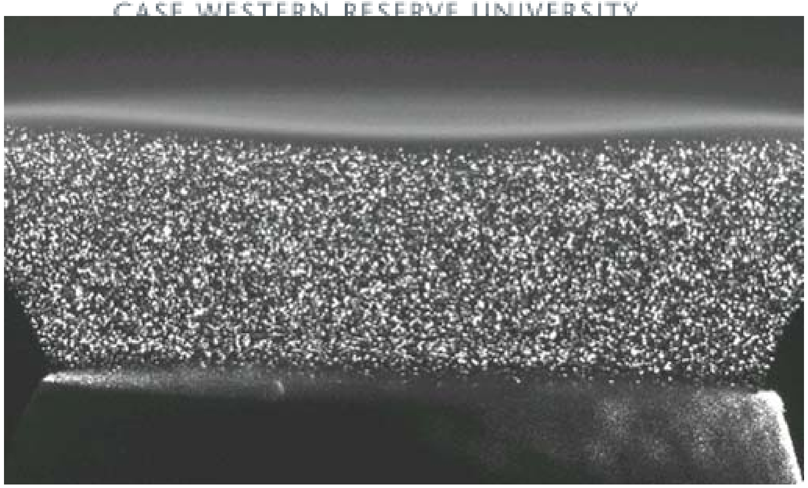
Gemini PIV-Nd:YAG Dual Lasers
15 Hz repetition rate
120 mJ/pulse at 532 nm
3-5 ns pulse width

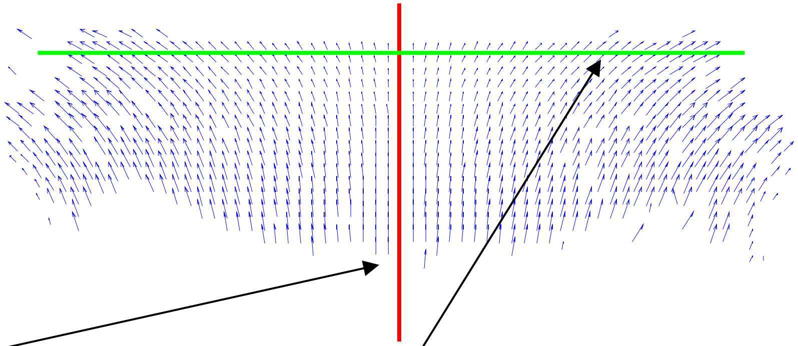
Laser Head

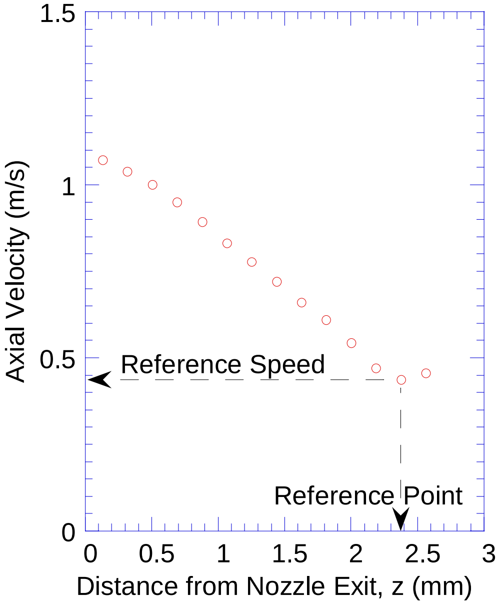
Dantec HiSense CCD Camera
1280×1024 pixels
6.7 µm ×6.7 µm
9 frames/sec

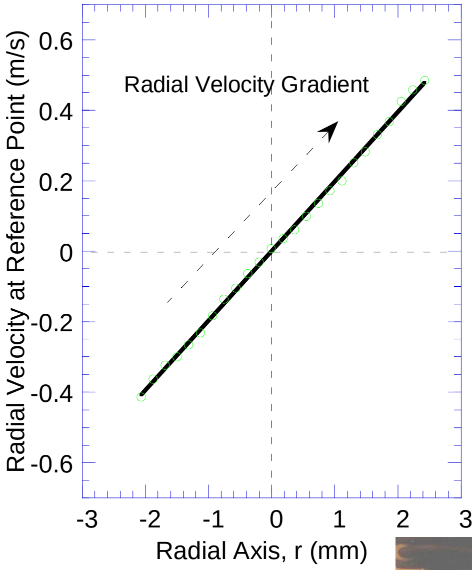
Dantec PIV 2100 Processor

DPIV Measurement





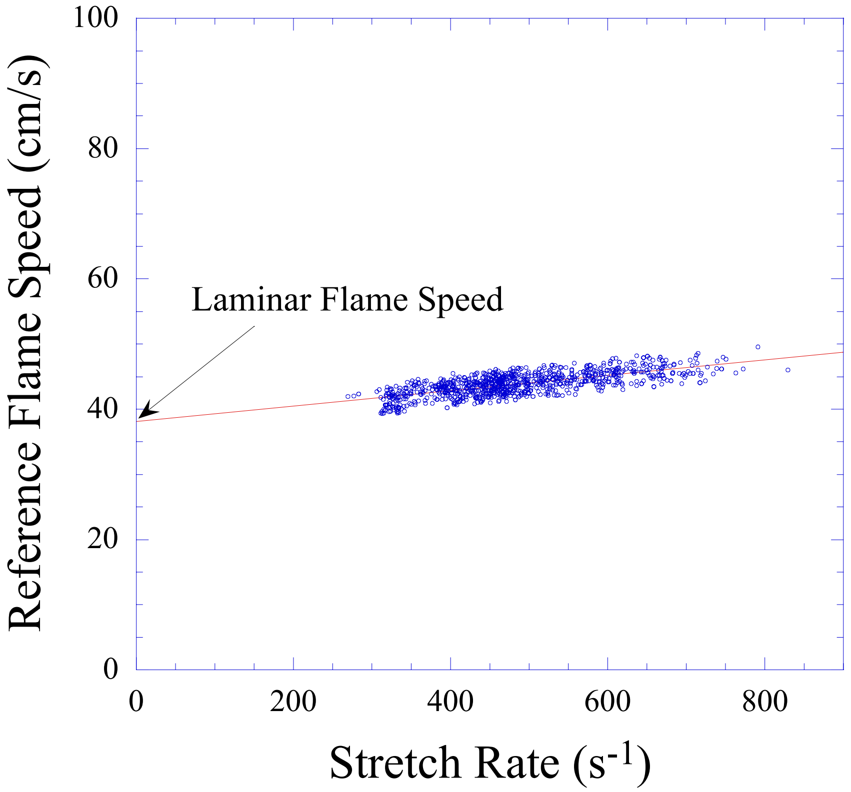




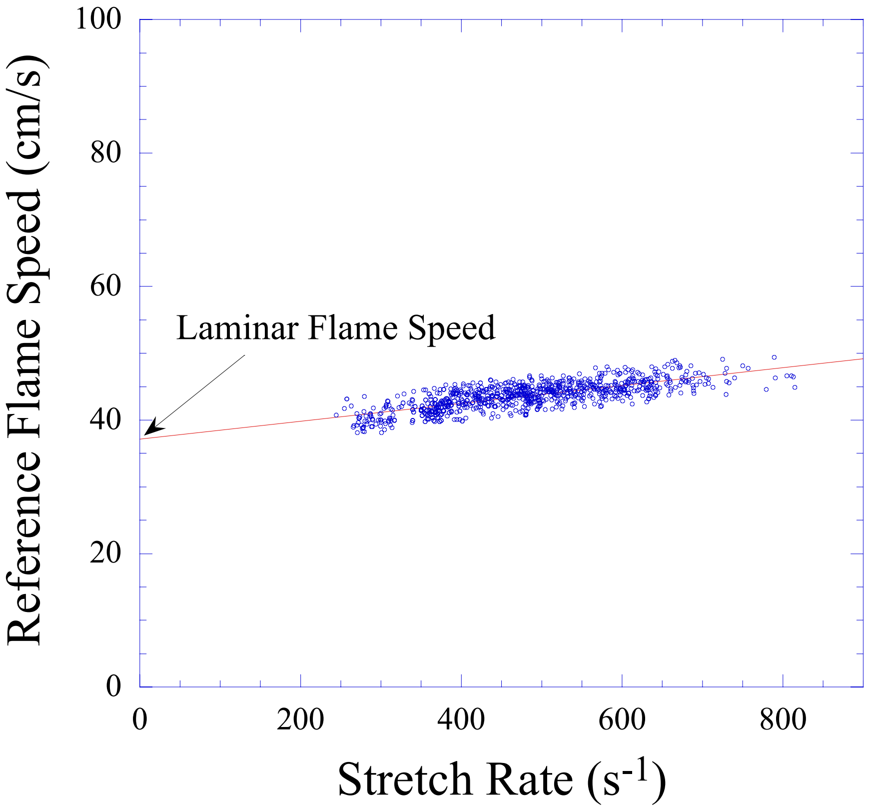
➔ stretch rate, K

Linear Extrapolation

ϕ=0.7, R_{CO}=0.95, ξ_{H2O}=15%, T_u=323 K



ϕ=0.7, R_{CO}=0.95, ξ_{H2O}=25%, T_u=323 K



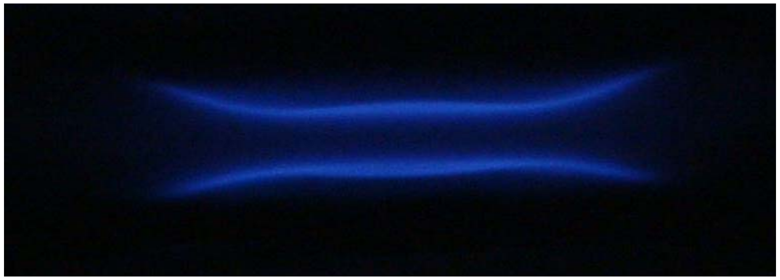
$$\xi_{H2O}=[H_2O]/([H_2]+[CO]+[H_2O])$$

Effect of Water Addition on Flame Propagation

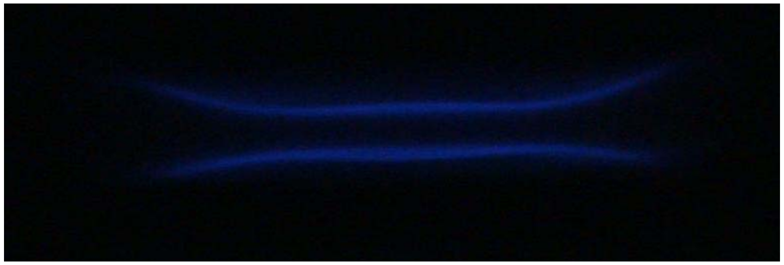
Fixed Volumetric Flow Rate

$\phi=0.7$, $R_{CO}=0.75$, $T_u=323$ K

$\xi_{H2O}=0\%$



$\xi_{H2O}=25\%$

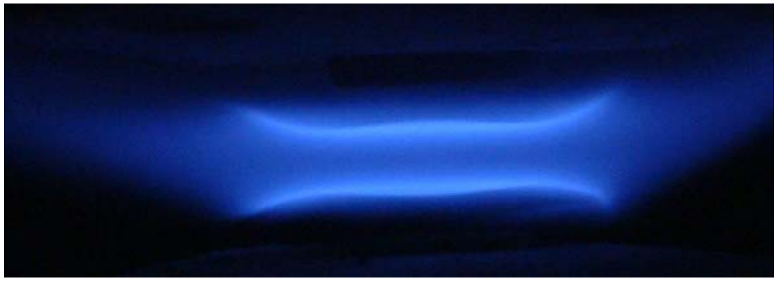


laminar flame speed <u>decreases</u> with increasing ξ_{H2O}

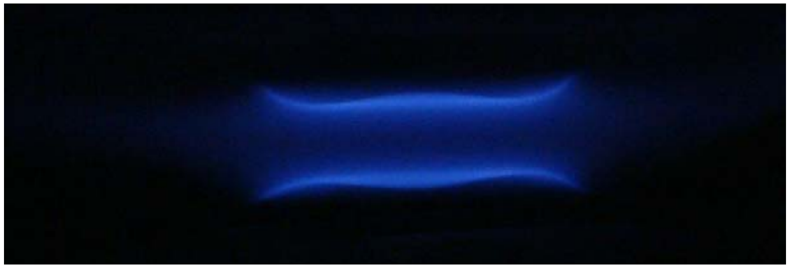
Fixed Volumetric Flow Rate

$\phi=1.3$, $R_{CO}=0.95$, $T_u=323$ K

$\xi_{H2O}=0\%$



$\xi_{H2O}=25\%$



laminar flame speed <u>increases</u> with increasing ξ_{H2O}

Conclusions

- Need comprehensive detailed and reduced mechanisms for syngas and hydrogen combustion.
- Discrepancies between simulations and the newly obtained experimental data are discussed.
- Comparison of experimental and computational results will enable the re-evaluation and optimization of current mechanisms.
- The lack of accurate/meaningful experimental data has in the past hampered the progress in the development of kinetic mechanism.
  - Need extensive benchmark data of high fidelity.

Future Work

- Obtain detailed experimental data for combustion characteristics of SGH mixtures using rapid compression machine and counterflow burner.
  - Effects of CO_2 and H_2O addition on the autoignition of H_2/CO mixtures.
  - Measurements of laminar flame speeds and strain-induced extinction limits of premixed SGH flames.
- Assess kinetic mechanism against the newly acquired experimental data, thereby enabling re-evaluation and optimization of rate constants and mechanism.
- Conduct *ab initio* quantum chemistry calculation and master equation modeling for certain key reactions, including $HO_2+HO_2 \rightarrow H_2O_2+O_2$ and $HO_2+OH \rightarrow H_2O+O_2$.
  - Notable influence on SGH oxidation rates under high-pressure, low-to-intermediate temperature conditions.
  - Complex temperature and pressure dependences that cannot be easily resolved through mechanism optimization.

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