Oxidative Catalytic Activity of Turbine Inlet Materials

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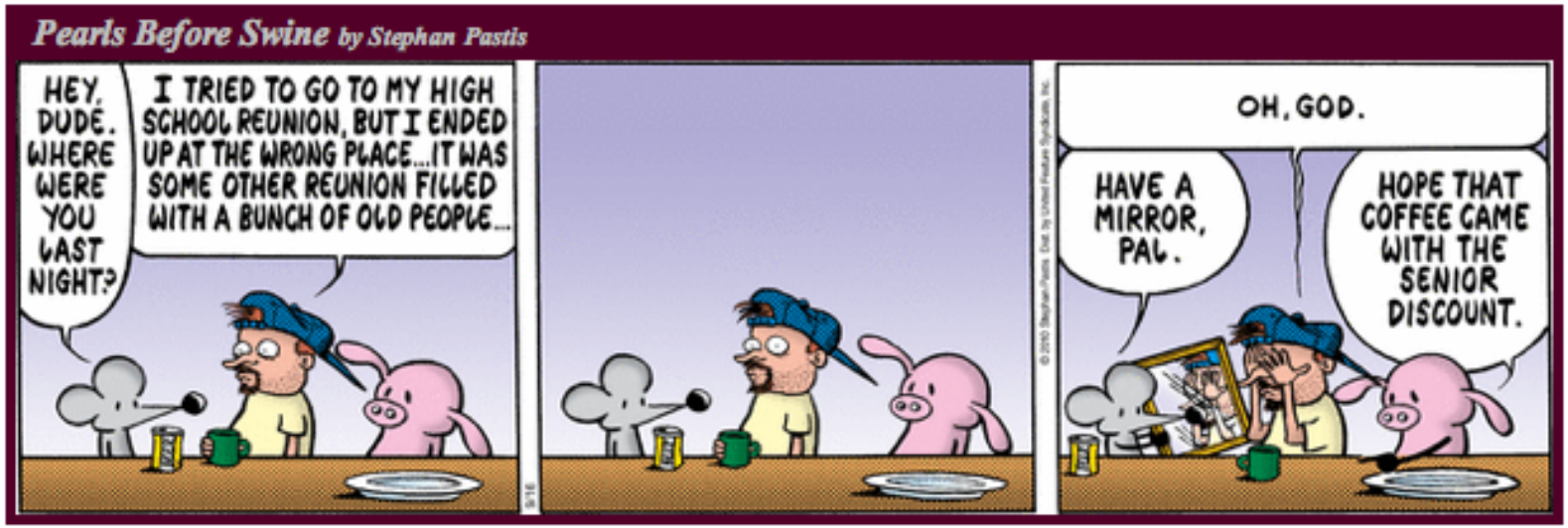
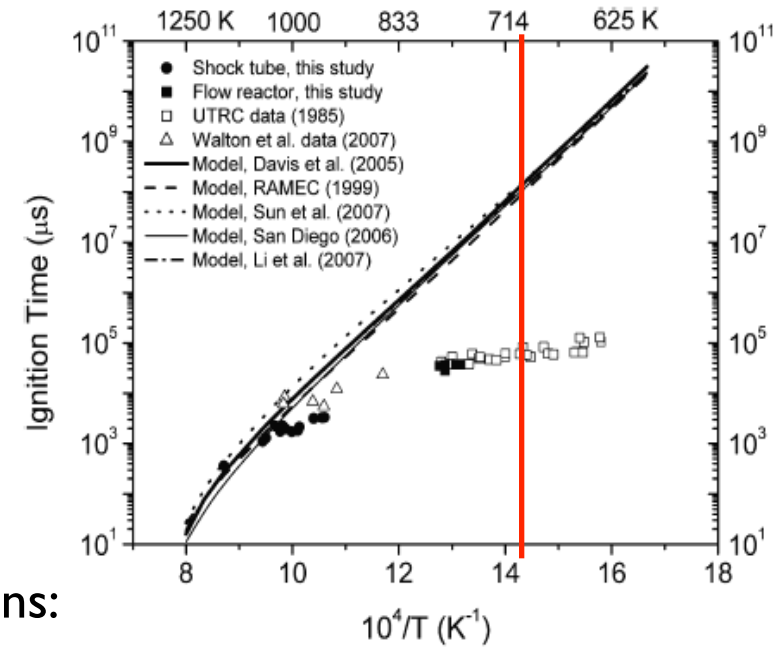
High School Reunion



Gas Turbine Need

- Improving Gas Turbine Technologies
  - Hydrogen-rich syngas
    - H_2, CO and CO_2
    - Reduce CO_2 emissions
    - Renewable fuels (biomass)



- Unexplained Discrepancy
  - Measured and predicted ignition delay at ideal gas turbine combustor inlet conditions:
    - 600-800 K and 10-20 bar
    - Important safety and reliability issue

- Our Target is understanding difference at 700K and 20 bar

Petersen et al. (2007)

Varatharajan et al. (2005)

Original Project Objectives

- Develop the necessary chemical kinetics information to understand the combustion of syngas and nearly pure hydrogen fuels at conditions of interest in gas turbine combustion.
- Explore high-pressure kinetics by making detailed composition measurements of combustion intermediates and products in a flow reactor using molecular beam/ mass spectrometry (MB/MS) and matrix isolation spectroscopy (MIS).
- Compare experimental data with calculations using existing mechanisms.
- Use theoretical methods to improve the predictability of existing mechanisms.

Review of the Known High P Low T Chemistry

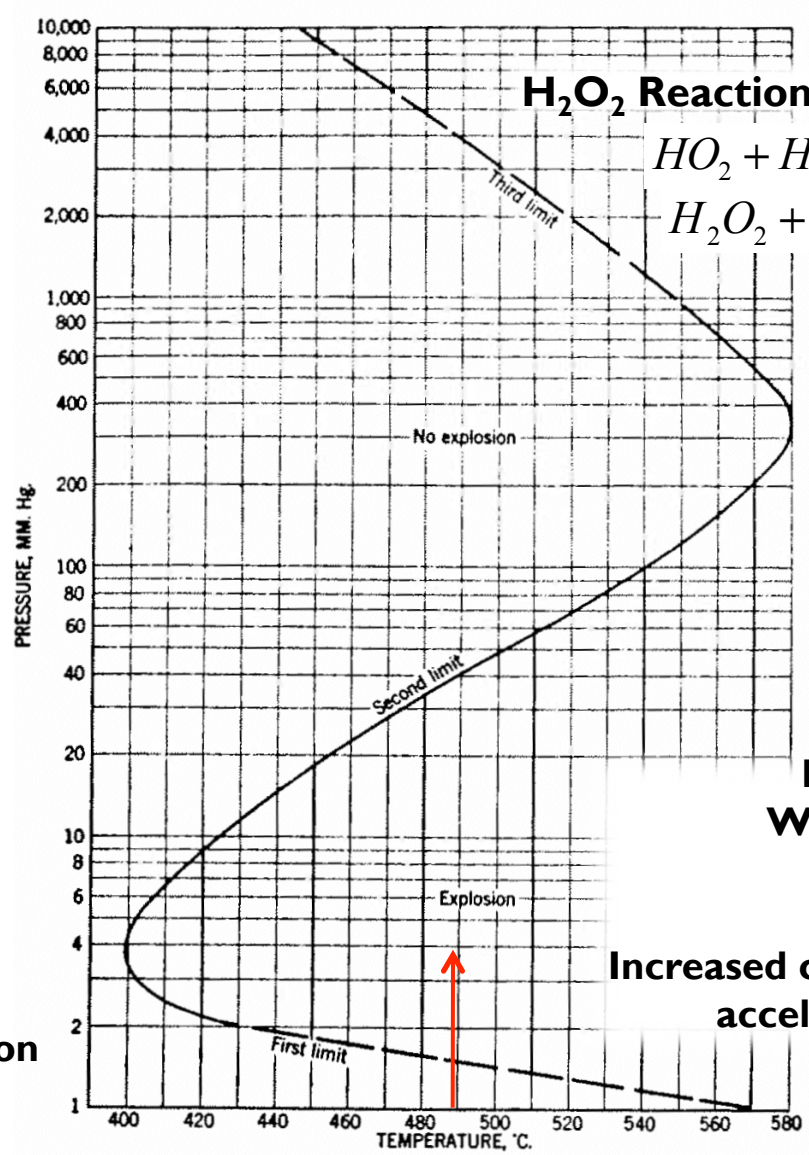
- Initiation is by slow bimolecular H_2 and O_2 dissociation reactions
- HOO is formed followed by HOOH
- HOOH dissociates to OH + OH providing chain amplification
- At 700K and 20 bar, the build up is slow > 50 sec under homogeneous condition.

Basic H_2/O_2 Chemistry

Three body recombination reactions increase
Result: Slow Combustion

$$H + O_2 + M \longleftrightarrow HO_2 + M$$

Radicals destroyed on vessel walls



H_2O_2 Reaction Increase Chain Branching:

$$HO_2 + H + M \rightarrow H_2O_2 + H + M$$

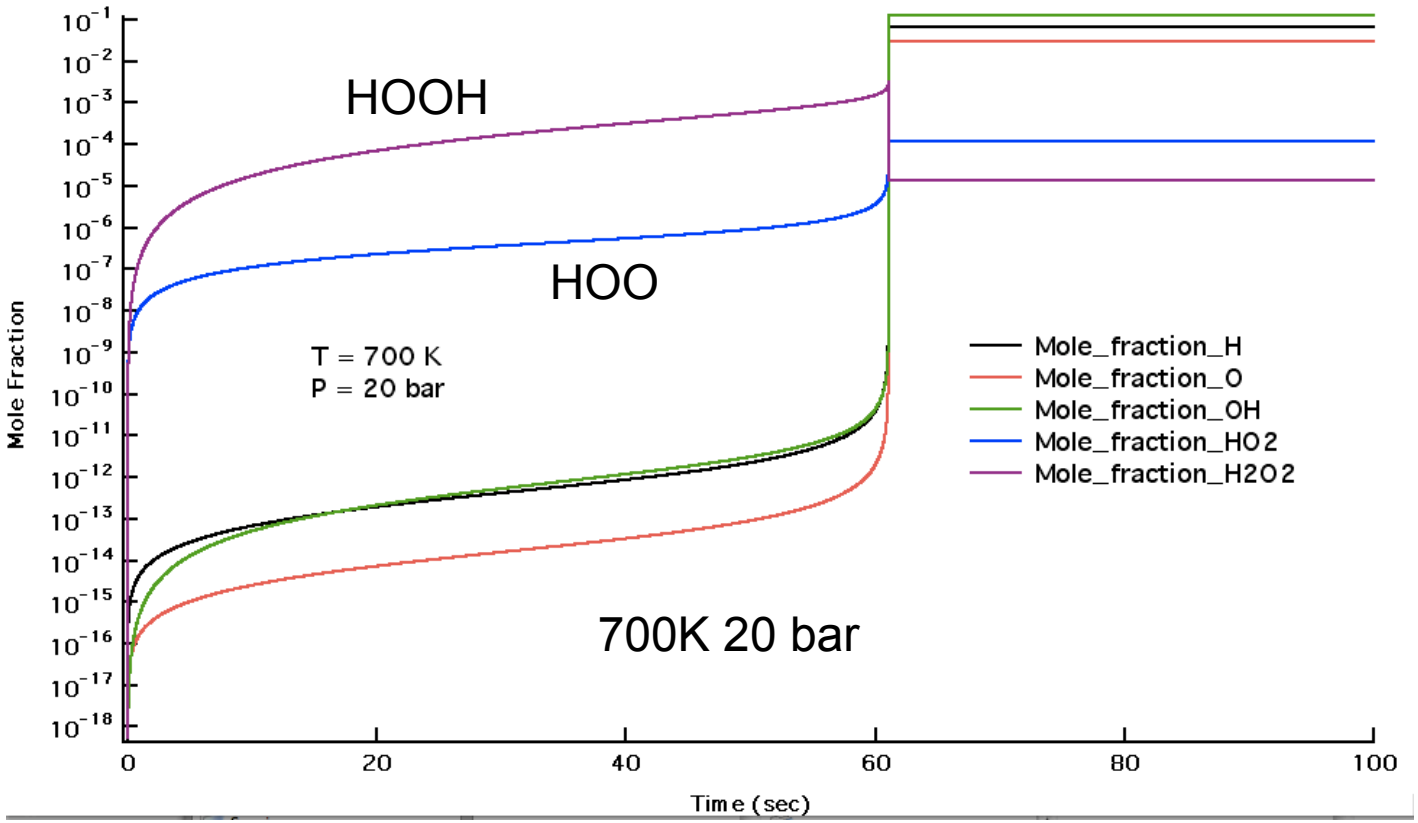
$$H_2O_2 + M \rightarrow OH + OH + M$$

Increased pressure:
Wall diffusion inhibited

Result:
Increased chain branching reactions and acceleration of reaction rate

Lewis and von Elbe,1961

Ignition Controlled by Peroxide Formation in Gas Phase at High Pressure

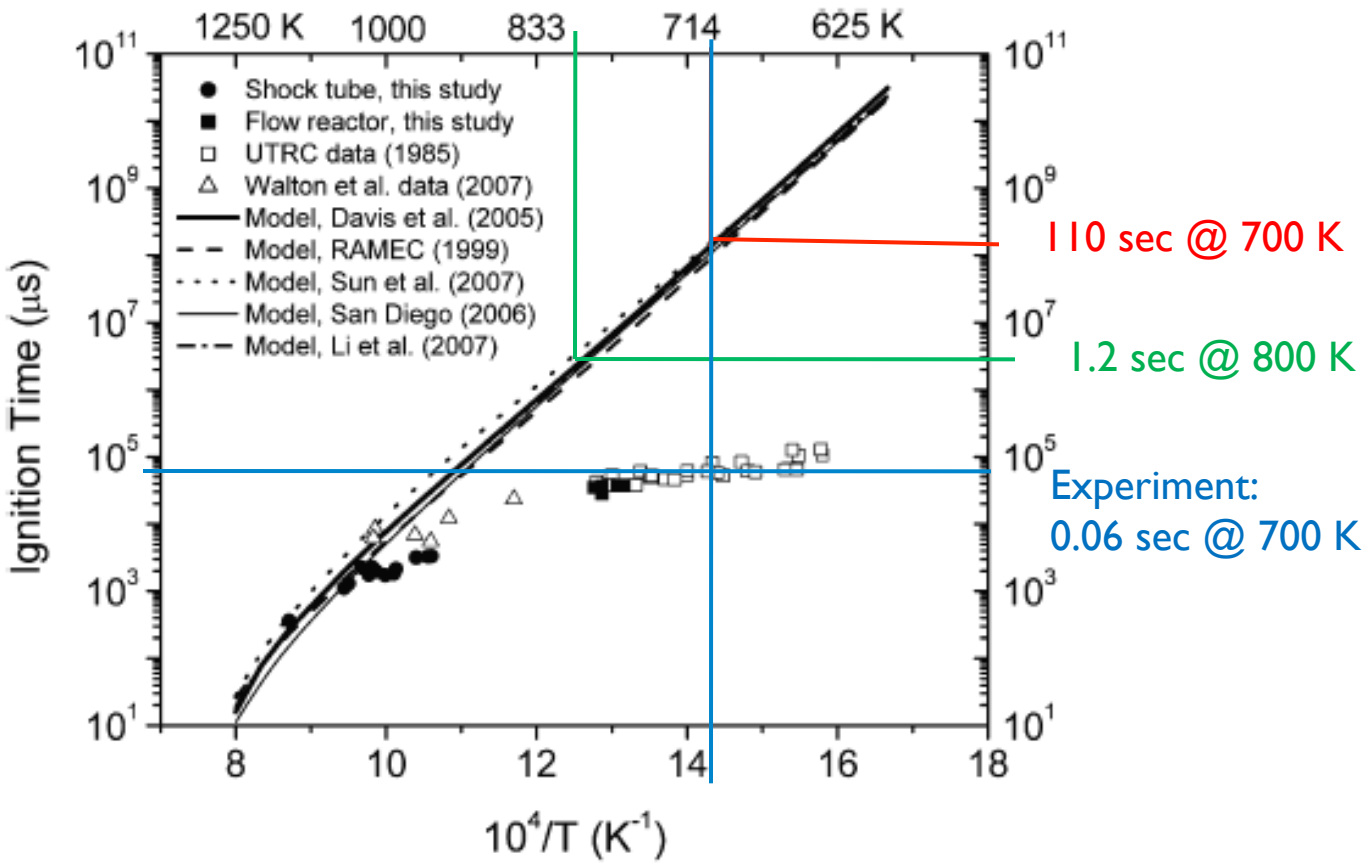


Possible Gas Phase Explanations for Fast Ignition

- Uncertainty in Reaction Rates
- Missing Species and/or Reactions
- Sensitizers
- Local Perturbations in Thermodynamic State
- Uncertainty in Flow Conditions

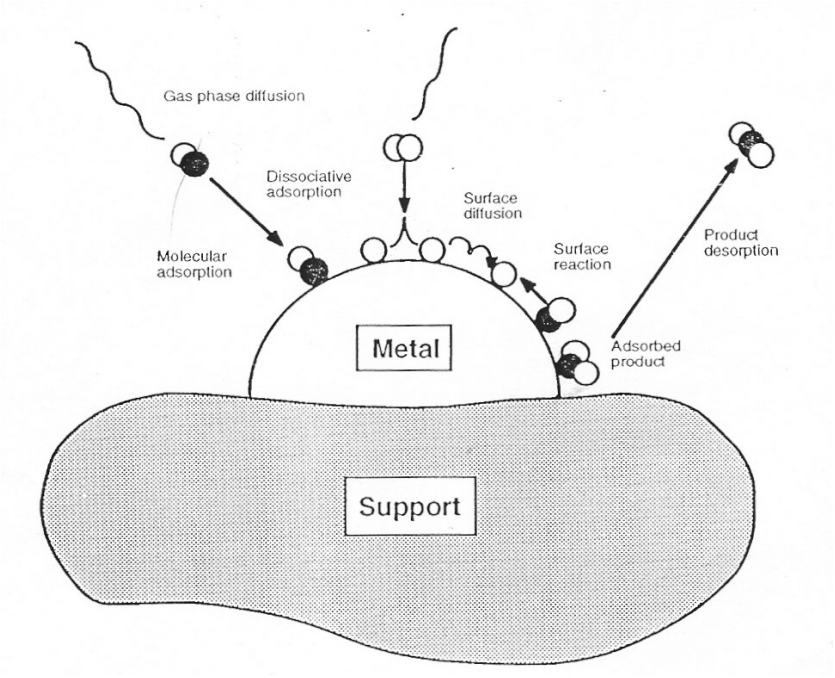
None of these can realistically explain the large departures observed at 700K and 20 bar.

Role of Small Perturbations



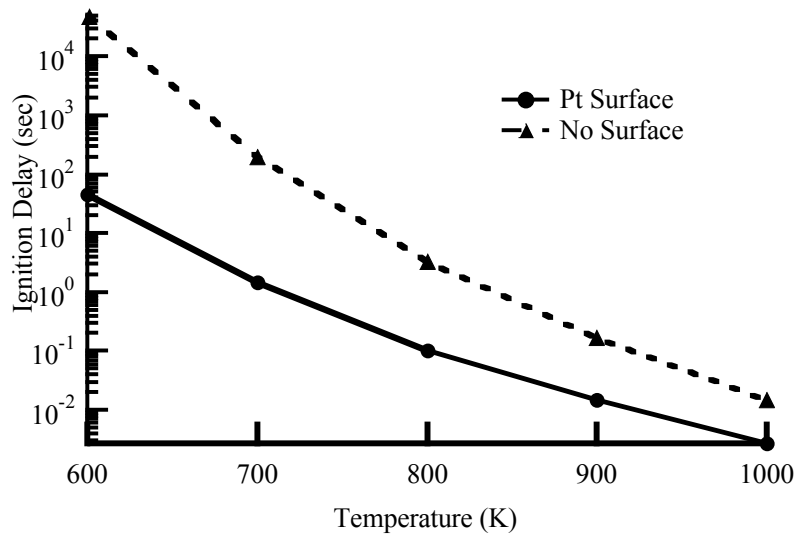
Hypothesis: Surface Catalysis

- Hypothesized that reactions can occur on suspended particles or reactor walls



Surface Catalysis

- Simulate with Known Platinum Surface Mechanism
  - Gas Phase $H_2/O_2/CO$ Mechanism: Li et al., 2004
  - Surface Mechanism: Raja et al., 2000



- Catalytic reactions can do the job.
  - But what about engineering materials?
  - And is mechanism realistic?

Typical Experimental Facilities

- Laboratory Experimental Reactor
  - Most likely stainless steel
- Gas Turbine Inlet/Combustor
  - High-temperature alloys (Inconels, Hastelloys) + oxide thermal barrier coatings
- More study is needed to understand catalytic effects of these materials

What does Literature Say?

- A great deal on empirical behavior of known catalysts - Pt, Ni, W, Ru, Pd etc.
- Deustschmann et al. H2/CH4/O2 on Pt.
- Dadayan et al./Zhu et al. H2/O2 on nickel similar to Pt mechanisms.
- However, not much on engineering materials.

Deutschmann et al., Catalysis Today 21, 461 (1994)

Dadayan et al., Kinetics and Catalysis 20, 795 (1979)

Zhu et al., J. Electrochem. Soc. 152 (2005)

One Exception for Inconel

- Bustamante et al., "High-Temperature Kinetics of the Homogeneous Reverse Water–Gas Shift Reaction," AIChE J. 50 (2004):

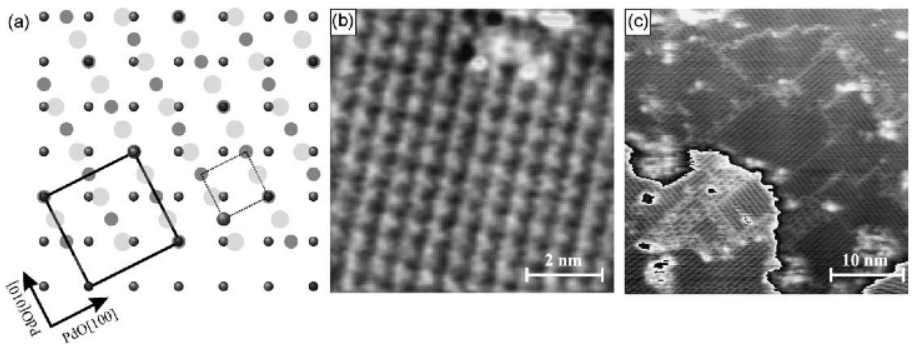
"Conversions attained in an Inconel® 600 reactor operating at comparable conditions were approximately two orders-of-magnitude greater than those realized in the quartz reactor. This dramatic increase in conversion suggests that the Inconel® 600 surfaces, which were depleted of nickel during the reaction, catalyzed the rWGSR."

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

Physics: Ni (Dadayan, etc.)

- O2 -> 2O(s) is chemi-adsorbed in "islands" as NiO
- H2 -> 2H(s) chemi-adsorbed?
- OH(s) formed at island boundaries
- H2O formation and release rate limiting step

E.I. Altman, R.E. Tanner / Catalysis Today 85 (2003) 101–111



Likely Surface Reactions

- H2/O2

$$H_2 + 2s \rightarrow H(s) + H(s)$$

$$O_2 + 2s \rightarrow O(s) + O(s)$$

$$H(s) + O(s) \rightarrow OH(s) + s$$

$$H(s) + OH(s) \rightarrow H_2O(s) + s$$

$$OH(s) + OH(s) \rightleftarrows H_2O(s) + O(s)$$

$$H + s \rightarrow H(s)$$

$$O + s \rightarrow O(s)$$

$$OH + s \rightleftarrows OH(s)$$

$$H_2O(s) \rightarrow H_2O + s$$

$$CO + s \rightleftarrows CO(s)$$

$$CO(s) + O(s) \rightarrow CO_2(s) + s$$

$$CO_2(s) \rightarrow CO_2 + s$$

$$CO(s) + s \rightleftarrows C(s) + O(s)$$

The Peroxide Question

- Could catalytic peroxide reactions be important at the short ignition delay times observed?
- Long entry lengths and/or slow moving recirculation zones might encourage peroxide growth.
- Combined with catalysis might enhance ignition.

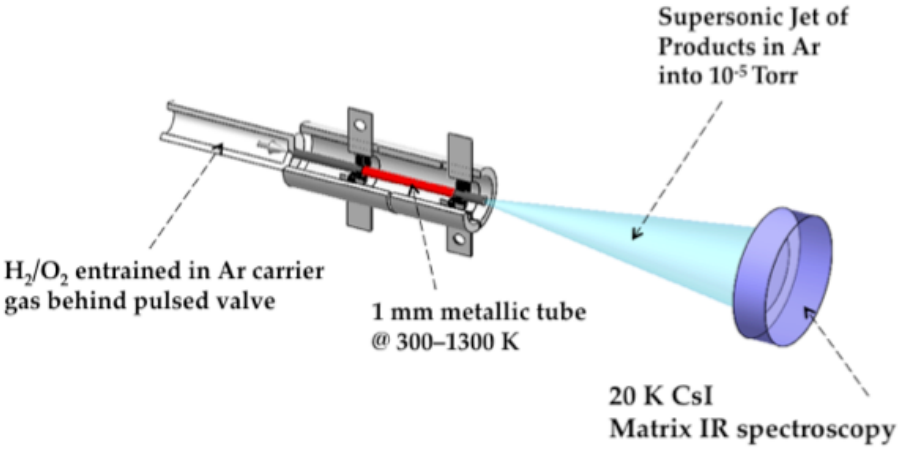
Epiphany

- At observed ignition delay times (<1sec), the gas phase formation of HO_2 and H_2O_2 likely unimportant.
- Ignition is dominated by two-body reactions that are started by surface chemistry
- Thus, low pressure surface chemistry experiments OK

Experimental Approach

- "Fancy" (high vacuum) surface science not really suitable for engineering materials
- Need approach more suited to realistic thermal conditions and materials
- Flow reactor of some kind

Our Approach - Pulsed High Temperature Miniature Reactor



Matrix isolation infrared spectroscopy diagnostics

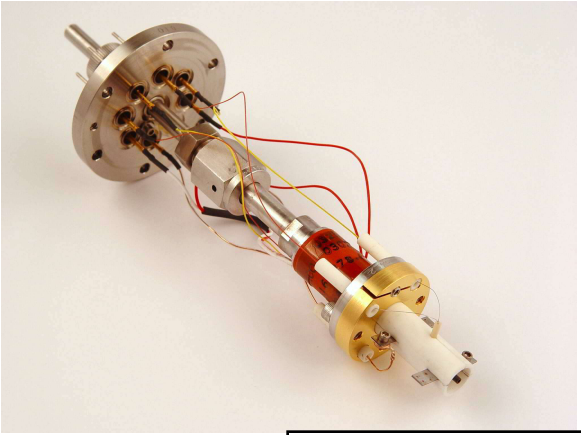
Use D_2 instead of H_2 to avoid water contamination

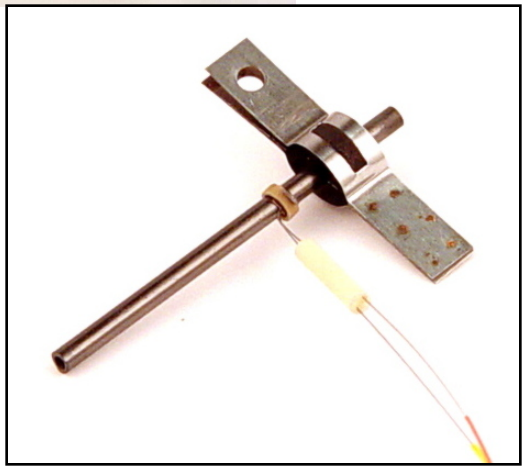
Matrix Isolation/IR:

Detect species with good IR vibrational bands

- H_2O, OH, HOO, HOOH, CO, CO_2 etc.
- Deuterated compounds - D_2O, OD, DHO etc.
- Not homogeneous diatomics: H_2, D_2, and O_2

Nozzle Assembly



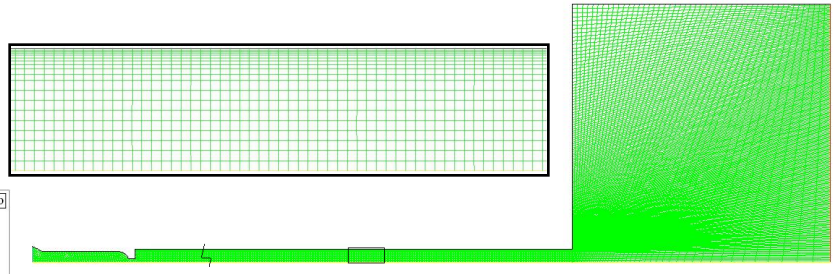


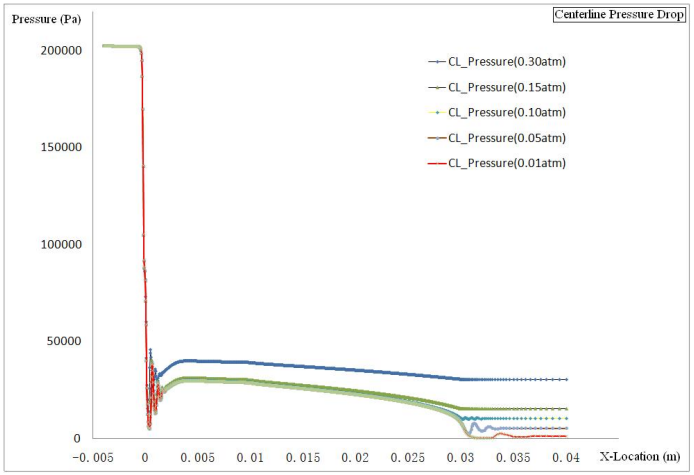
- Reactor is 3 cm long and 1 mm ID.
- Heated for last 2 cm up to 1500K.
- Residence times limited to ~ 2 cm/300-500 m/sec ~ 40-66 μsec.
- Choked at valve and downstream end due to Rayleigh/Fanno
- Under expanded jet means flow freezes in less than 1 ID.

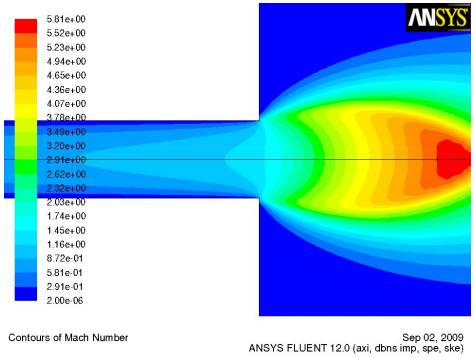
- "Chen Nozzle" originally described by Daniel W. Kohn, Horst Clauberg, and Peter Chen in Rev. Sci. Instrum. 63 (8), August 1992

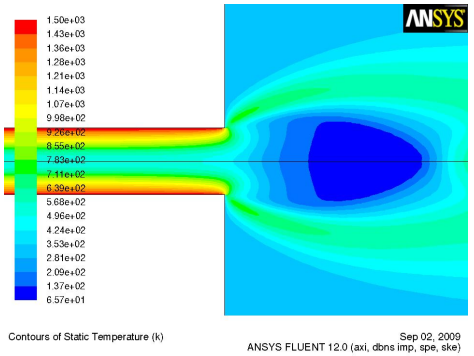
Reactor Flow Field

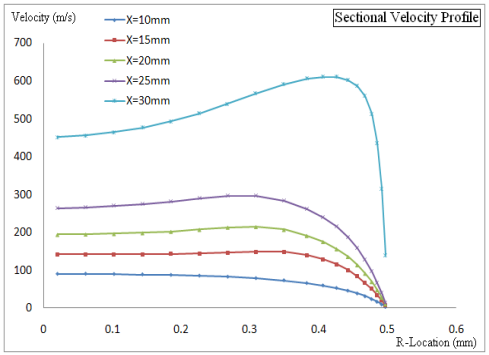
- CFD analysis



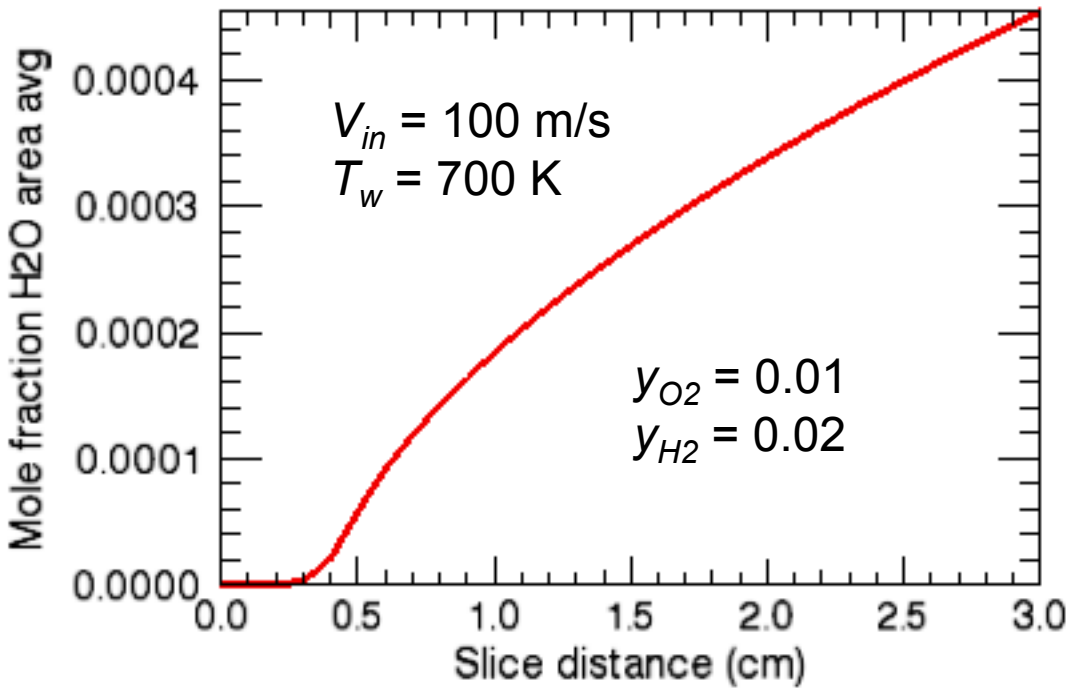






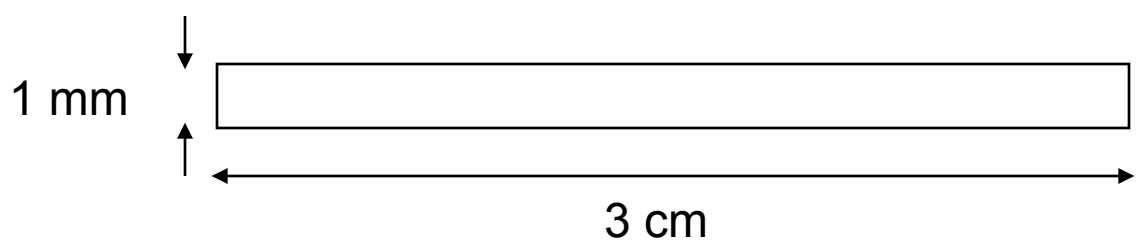


Should we see Reaction?



- Gas Phase H_2/O_2 Mechanism: Li et al., 2007
- Surface Ni Mechanism: Zhu et al., 2005
- 1% H2 0.5% O2 in Ar

No reaction w/o surface chemistry



Experimental Plan

- Explore early time surface reaction chemistry by varying surface properties and temperature.
- Materials:
  - Alumina
  - SiC
  - Stainless Steel (304)
  - High temperature alloys (Nickel, Inconel)
- Gases
  - Pure Ar
  - D_2, O_2, D_2O in Ar individually for calibration
  - $D_2 + O_2$ in Ar
- Conditions
  - $298 < T < 1500$ K

Data Analysis

- IR spectroscopy of deposited material on matrix
- Measure optical density as a function of frequency

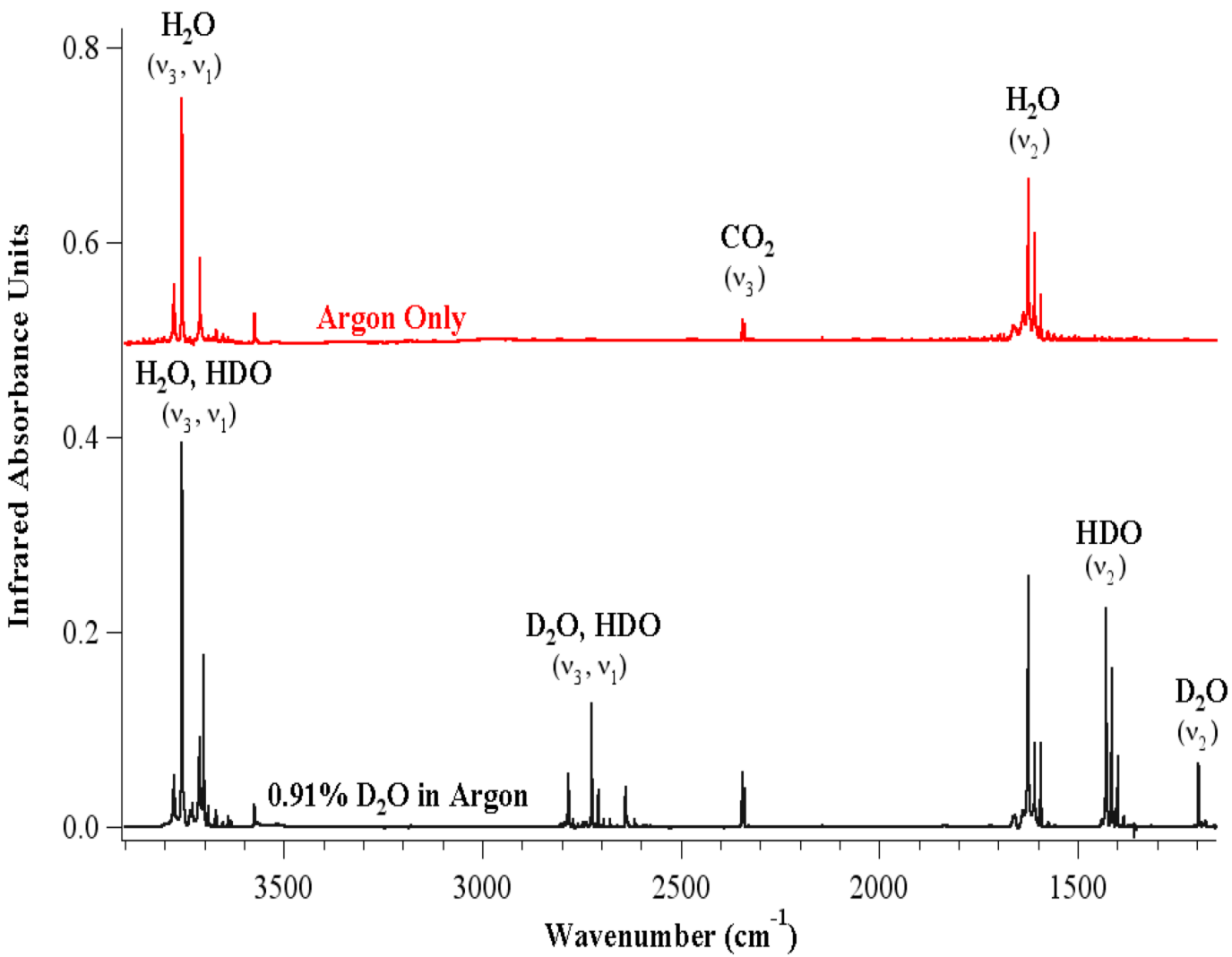
$$OD(v) = \log_{10}\left|\frac{I_0(v)}{I(v)}\right|$$

- Solve for number density

$$n_{\text{Total } D_2O} = \pi r^2 \ln(10)\left[\frac{1}{A_{D_2O}}\int_{D_2O} OD(v)\,dv + \frac{1}{2A_{HDO}}\int_{HDO} OD(v)\,dv\right]$$

- where $A \equiv \int \sigma(v)\,dv$

Why Deuterate?



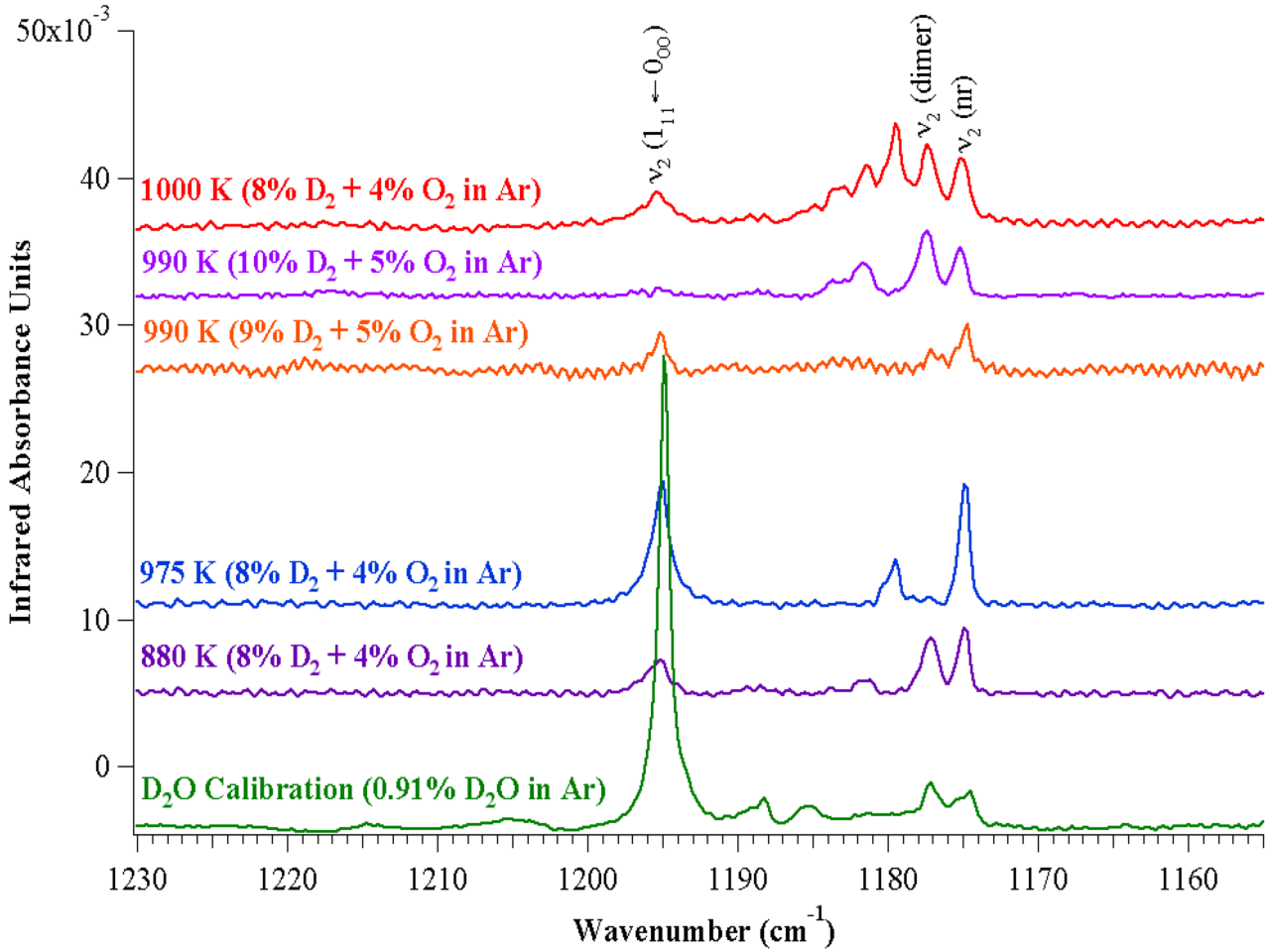
Experiments

- Calibration experiments with SiC and SS
- SiC and SS
  - No reaction observed on SiC
  - No reaction observed on SS
- Inconel and Nickel
  - Reaction observed on both

Nickel

- Did observe activity.
- It was noticed that the catalytic activity degraded with time.
- Likely due to oxygen poisoning.
- Reactivated by exposing with D_2 at high temperature.

Nickel


50x10^-3
40
30
20
10
0
Infrared Absorbance Units
1000 K (8% D2 + 4% O2 in Ar)
990 K (10% D2 + 5% O2 in Ar)
990 K (9% D2 + 5% O2 in Ar)
975 K (8% D2 + 4% O2 in Ar)
880 K (8% D2 + 4% O2 in Ar)
D2O Calibration (0.91% D2O in Ar)
ν2 (1_11 ← 0_00)
ν2 (dimer)
ν2 (nr)
1230
1220
1210
1200
1190
1180
1170
1160
Wavenumber (cm^-1)

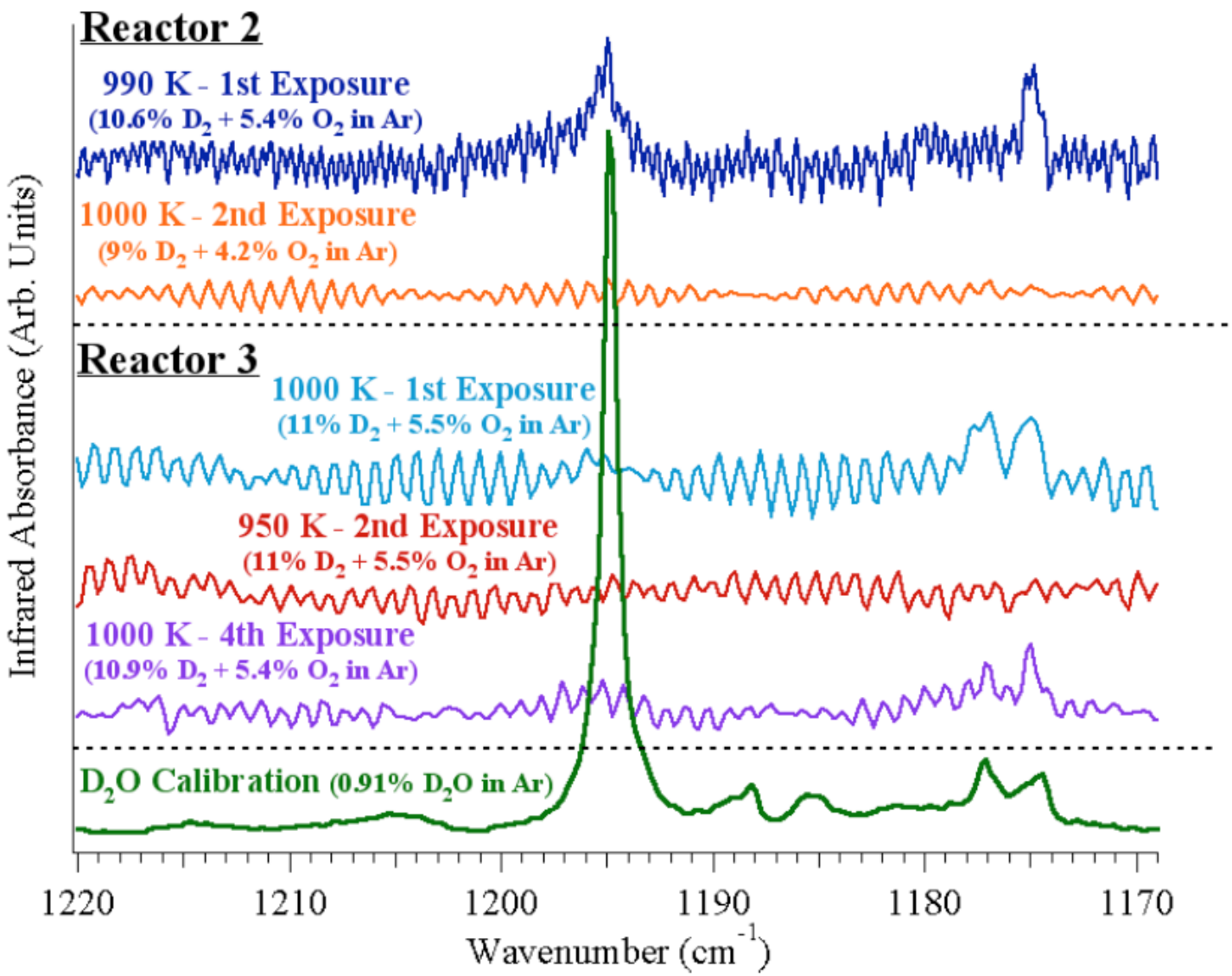
Nickel Results

	1000 K	975 K	880 K	990 K #1	990 K #2	Syngas-990K	
Amt of D_2	65	60	60	79	74	66	torr
Amt of O_2	32	30	30	39	43	34	torr
Amt of Ar (+CO)	680	700	700	690	697	714	torr
% D_2 in Mixture	8.37	7.59	7.59	9.78	9.09	8.11	%
Amt on Window	120	120	120	120	120	110	torr
Amt "D_2" on Window	10.04	9.11	9.11	11.73	10.91	8.92	torr
	3.88E+20	3.52E+20	3.52E+20	4.53E+20	4.21E+20	3.45E+20	molecules
n-D_2O (calc)	6.40E-06	4.16E-06	4.38E-06	5.69E-06	1.77E-06	3.23E-06	moles
	3.85E+18	2.51E+18	2.64E+18	3.42E+18	1.06E+18	1.95E+18	molecules
%-Conversion	**0.99**	**0.71**	**0.75**	**0.76**	**0.25**	**0.57**	%

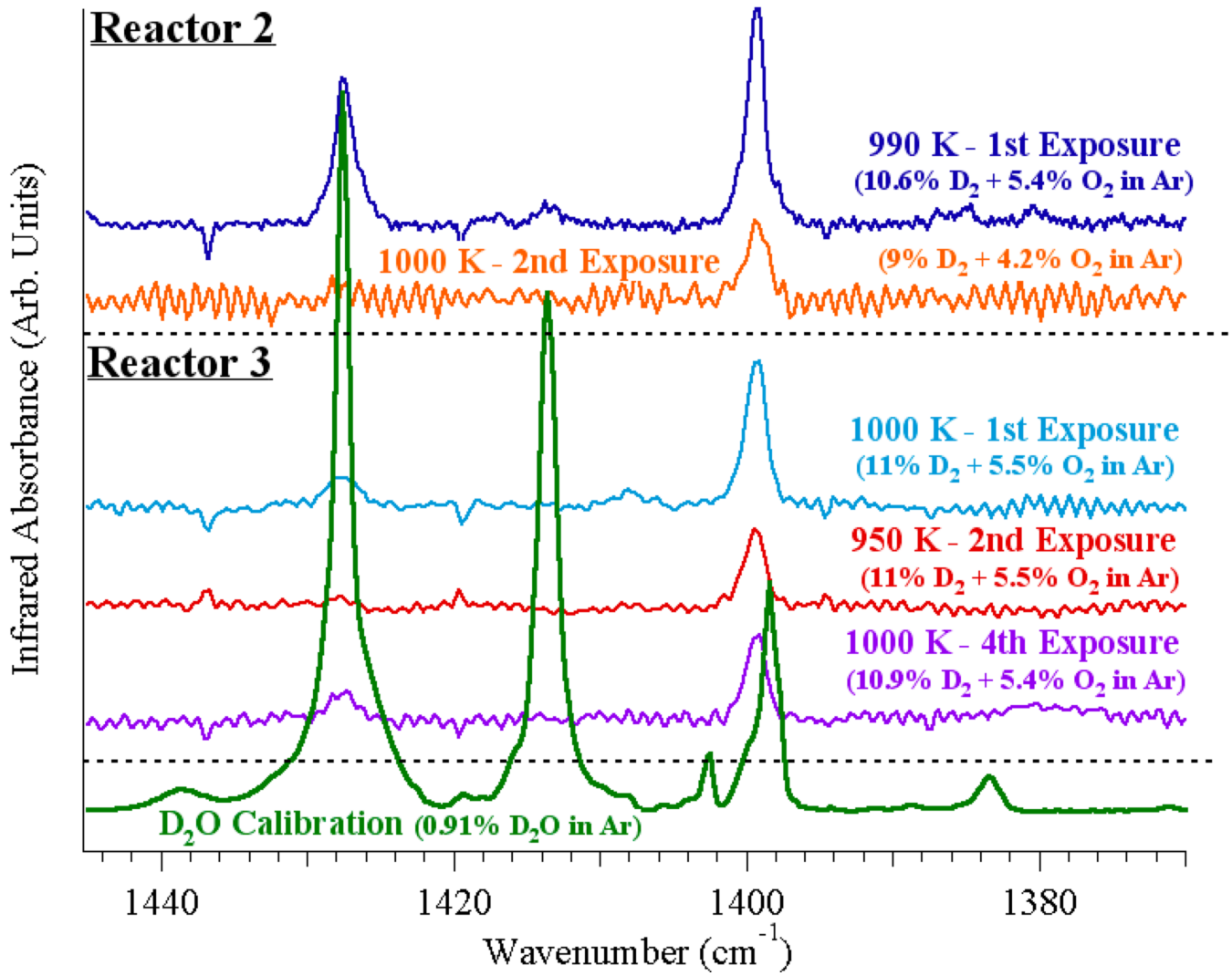
Inconel

- Observed about ¼ activity of Nickel.
- Also noted degradation with exposure and material variability.
- Carried out experiments in three different reactors.
- Not successful in reactivating.

Inconel – D_2O Band



Inconel – HDO Bands



Inconel Results

	Inconel 990 K	
Amt of D_2	90	torr
Amt of O_2	46	torr
Amt of Ar	714	torr
% D_2 in Mixture	10.59	%
Amt on Window	120	torr
Amt "D_2" on Window	12.7	torr
	4.9E+20	molecules
n-D_2O (calc)	2.3E-06	moles
	1.4E+18	molecules
%-Conversion	**0.28**	%
Estimated Error	$\pm$ 0.1%	

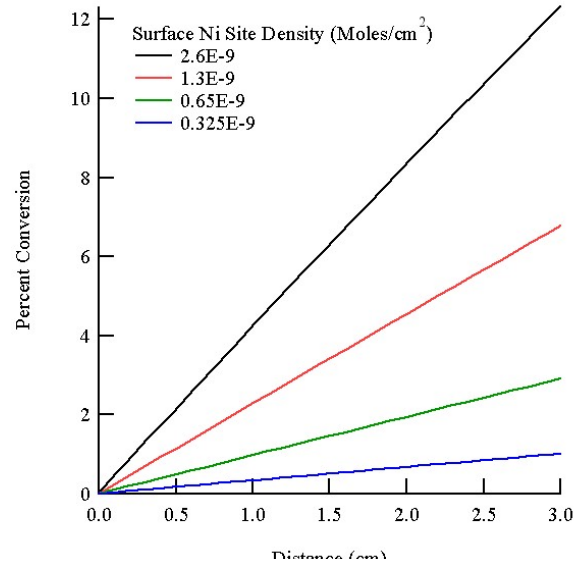
Summary of Experimental Results

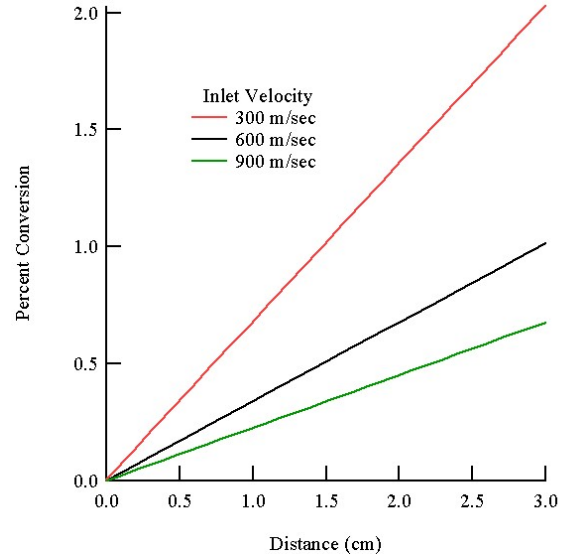
Nickel 200		Integrated Value	n-calc (molec/cm^3)	n-calc (mol/cm^3)	moles	Torr D_2	Torr O_2	Torr Ar (+CO)	% D_2 in Mixture	Torr on Window	Torr "D_2" on Window	Amt D_2 (molec)	n-D_2O calc (mol)	n-D_2O calc (molec)	%-Conv
1010 K	D_2O	0.0190	1.3E+19	2.2E-05	3.9E-06	65	32	680	8.4	120	10.0	3.9E+20	6.4E-06	3.9E+18	**0.99**
8.4% : 4.1% (D2O20025)	HDO	0.0408	1.7E+19	2.9E-05	5.0E-06										
975 K	D_2O	0.0181	1.3E+19	2.1E-05	3.7E-06	60	30	700	7.6	120	9.1	3.5E+20	4.2E-06	2.5E+18	**0.71**
7.6% : 3.8% (D2O20026)	HDO	0.0074	3.2E+18	5.2E-06	9.1E-07										
880 K	D_2O	0.0123	8.7E+18	1.4E-05	2.5E-06	60	30	700	7.6	120	9.1	3.5E+20	4.4E-06	2.6E+18	**0.75**
7.6% : 3.8% (D2O20028)	HDO	0.0303	1.3E+19	2.1E-05	3.7E-06										
990 K	D_2O	0.0126	9.0E+18	1.5E-05	2.6E-06	79	39	690	9.8	120	11.7	4.5E+20	5.7E-06	3.4E+18	**0.76**
9.8% : 4.8% (D2O20030)	HDO	0.0504	2.2E+19	3.6E-05	6.2E-06										
990 K	D_2O	0.0108	7.7E+18	1.3E-05	2.2E-06	66	34	714	8.1	110	8.9	3.4E+20	3.2E-06	1.9E+18	**0.57**
8.1% : 4.2% : 3.4% (syng0001)	HDO	0.0165	7.0E+18	1.2E-05	2.0E-06										
940 K	D_2O	0.0000	0.0E+00	0.0E+00	0.0E+00	54	43	725	6.6	120	7.9	3.0E+20	0.0E+00	0.0E+00	**0.00**
6.6% : 5.2% (D2O20031)	HDO	0.0000	0.0E+00	0.0E+00	0.0E+00										
990 K	D_2O	0.0068	4.9E+18	8.1E-06	1.4E-06	74	43	697	9.1	120	10.9	4.2E+20	1.8E-06	1.1E+18	**0.25**
9.1% : 5.3% (D2O20032)	HDO	0.0059	2.5E+18	4.2E-06	7.3E-07										
1000 K "Reactivated"	D_2O	0.0382	2.7E+19	4.5E-05	7.8E-06	67	46	601	9.4	150	14.1	5.4E+20	1.0E-05	6.1E+18	**1.12**
9.4% : 6.4% (D2O20033)	HDO	0.0374	1.6E+19	2.7E-05	4.6E-06										

Inconel 600		Integrated Value	n-calc (molec/cm^3)	n-calc (mol/cm^3)	moles	Torr D_2	Torr O_2	Torr Ar (+CO)	% D_2 in Mixture	Torr on Window	Torr "D_2" on Window	Amt D_2 (molec)	n-D_2O calc (mol)	n-D_2O calc (molec)	%-Conv
990 K	D_2O	0.0037	2.6E+18	4.4E-06	7.6E-07	90	46	714	10.6	120	12.7	4.9E+20	2.3E-06	1.4E+18	**0.28**
10.6% : 5.4% (D2O20034)	HDO	0.0247	1.1E+19	1.8E-05	3.0E-06										

Can We Predict These Results?

- Uncertainty
  - Measured conversion
  - Reaction mechanism and rates
  - Surface site density
  - Large material variability
  - Fluid mechanics





Summary

- There exists a large discrepancy in ignition delay at ideal gas turbine combustor inlet conditions (700 K and 20 bar)
- Several gas phase pathways explored to try to explain the discrepancy
  - None of the pathways seemed reasonable
- Catalytic wall effects considered.
  - Surface mechanisms examined and coupled with gas phase reaction mechanism
  - Adding surface reactions deceases ignition delay to range of observed experimental rates
- Experiments confirm catalytic activity of Inconel
- Modeling difficulties pose serious challenge