Linking Climate Change with Ozone Loss over the US in Summer: New Instrument for the Detection of HCl in the Stratosphere

ES96 Spring 2016

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CHEMISTRY AND PHYSICS OF CLIMATE AND EARTH SYSTEM CHANGE

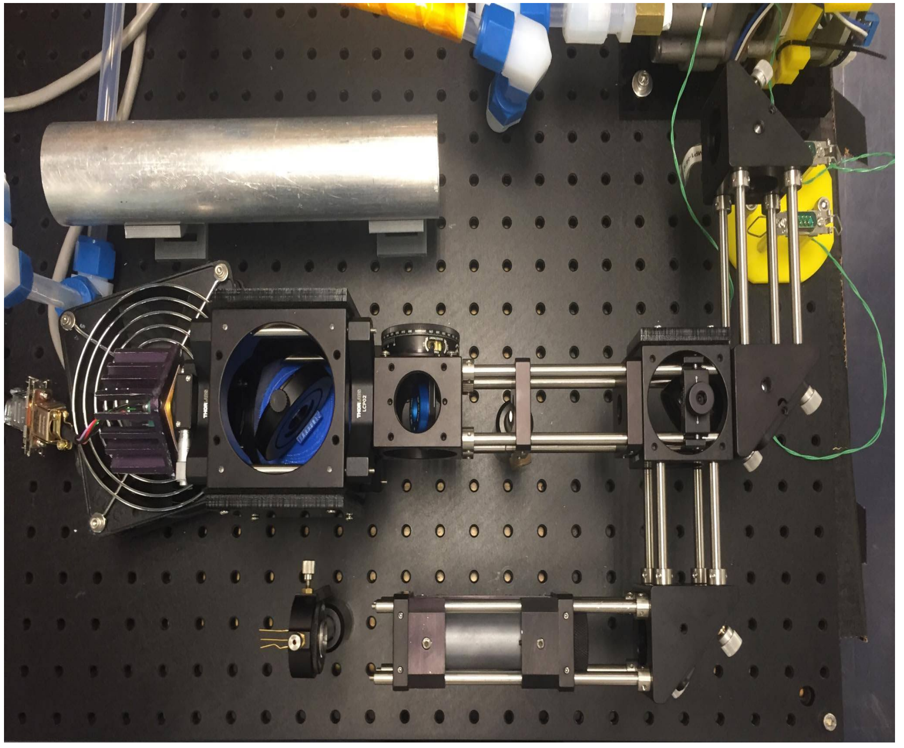
NASA

HCl Instrument

- **Measure HCl concentrations in the lower stratosphere:**
  - **50ppt accuracy**
  - **Precision of 10%**

- **Integrated Cavity Output Spectroscopy (ICOS)**

- **High altitude operation**



Overview

1. Scientific Context
2. System Overview
3. Design Details
   a. Laser
   b. Cavity
   c. Detector
   d. Pump
   e. System Wide Design
4. Next Steps

Scientific Context

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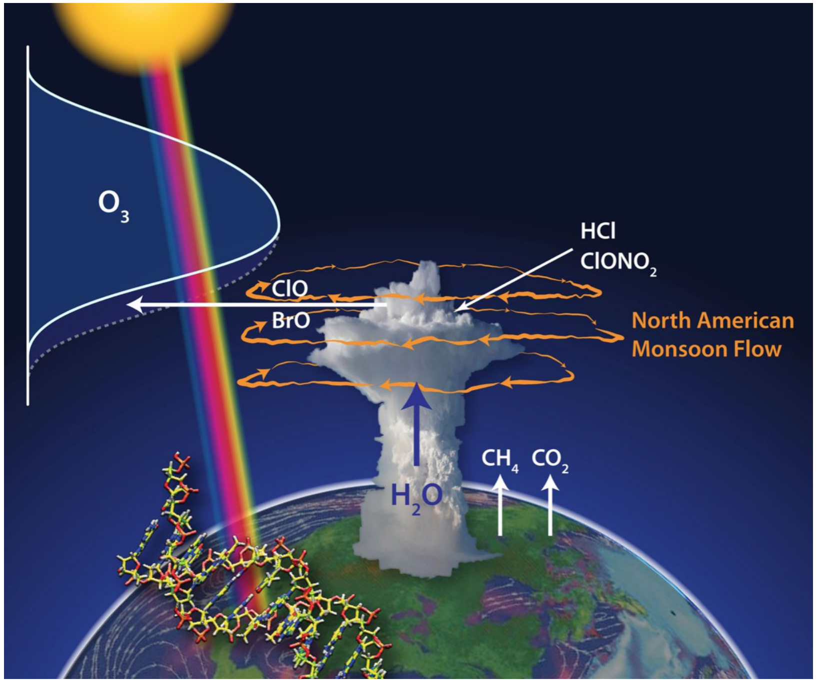
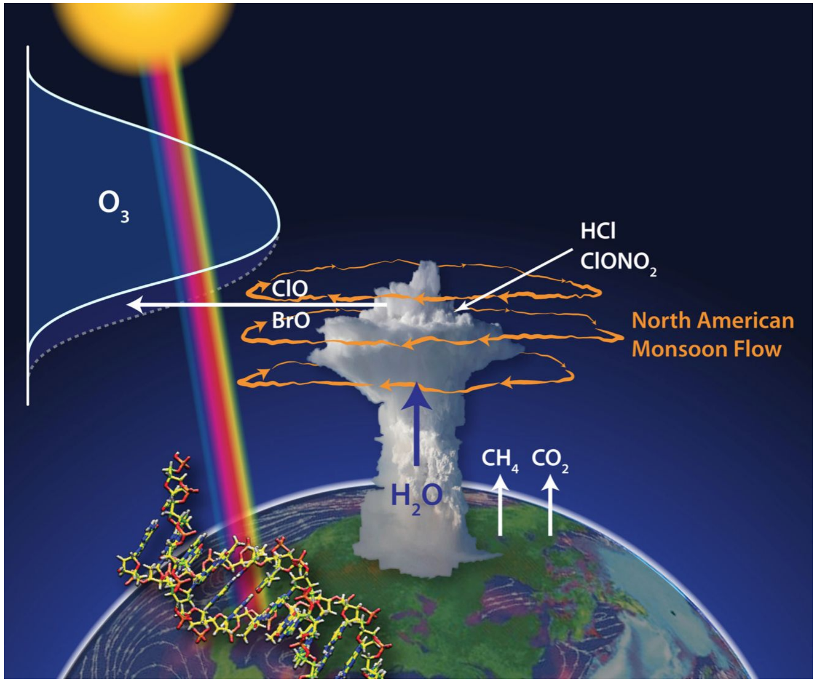
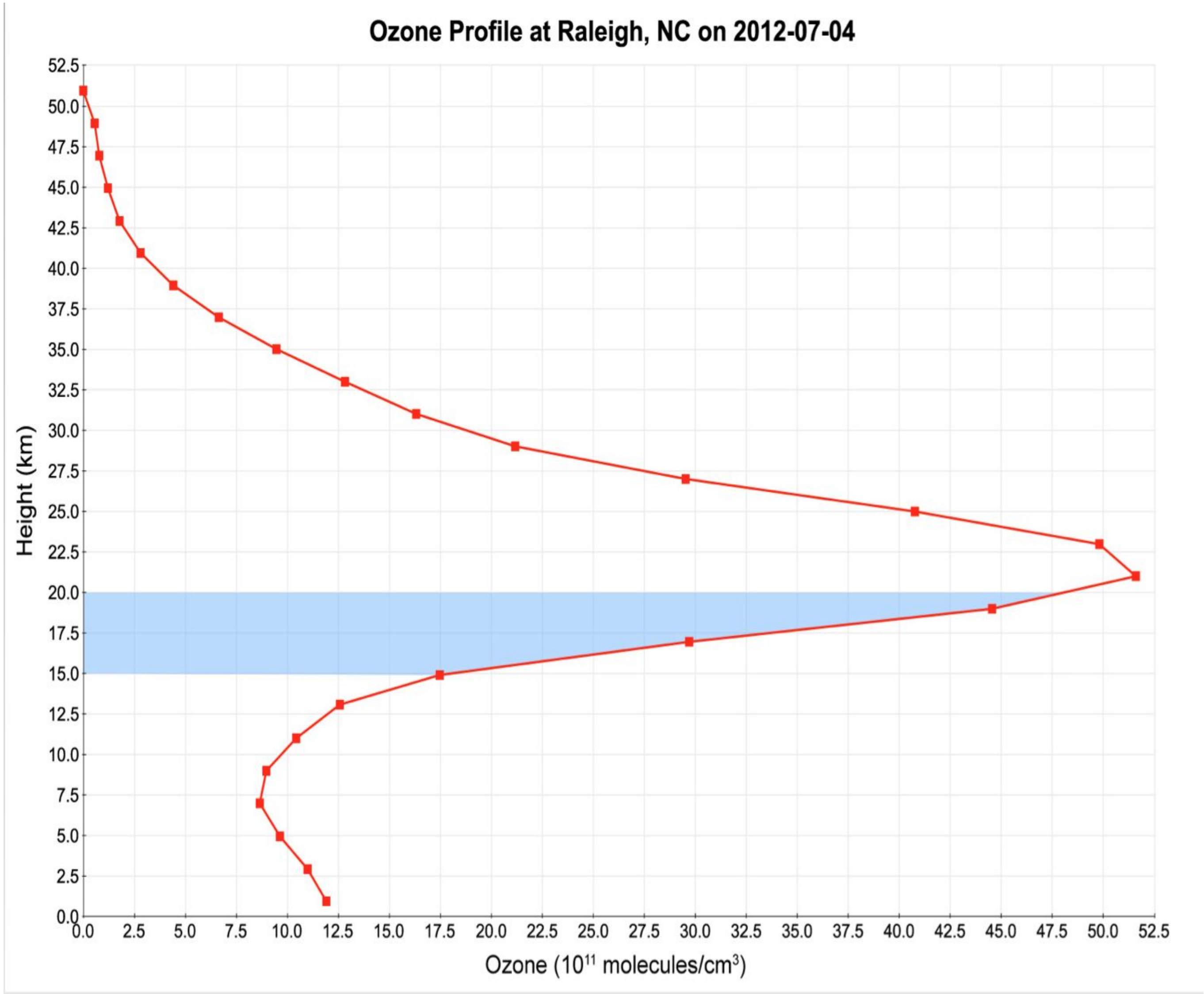


Scientific Context

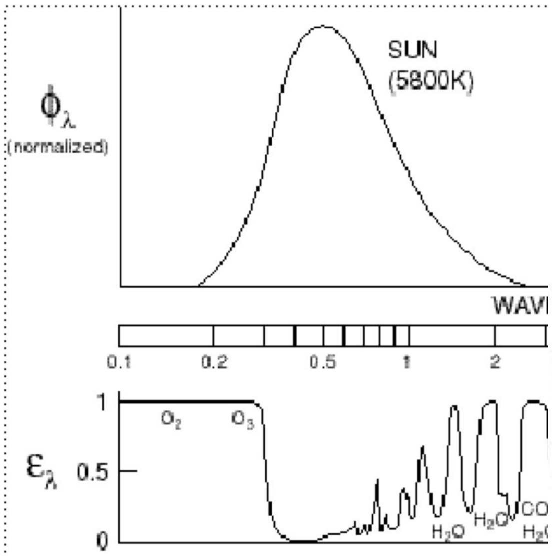
1. **Ozone**
2. HCl Effect on Ozone
3. Stratospheric Ozone Depletion in Central US
4. ASC^{5}ENA Proposal

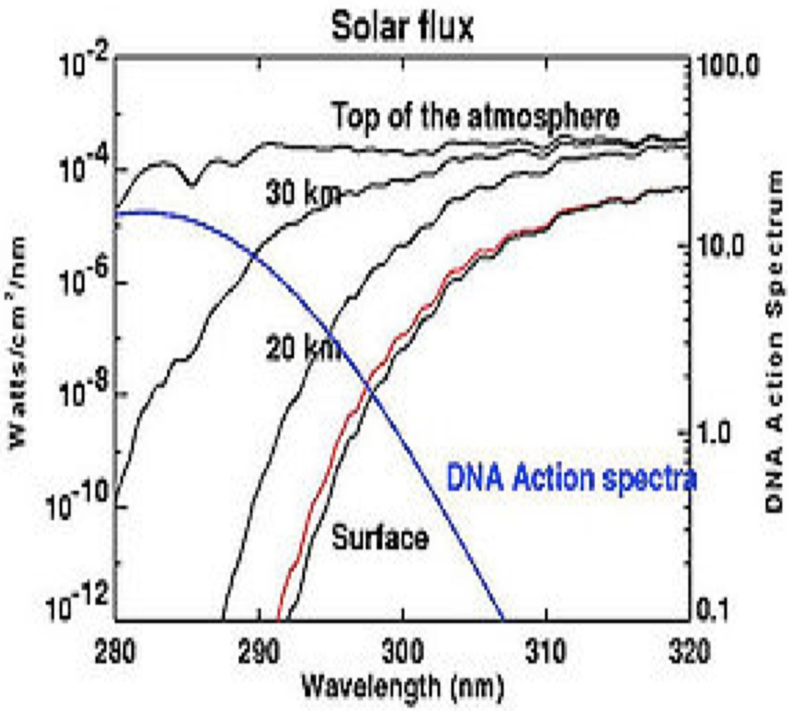


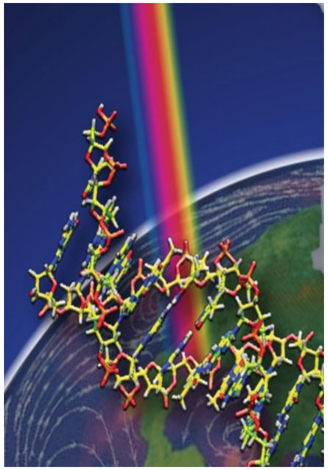
Location of Ozone over the US



Effect of Ozone



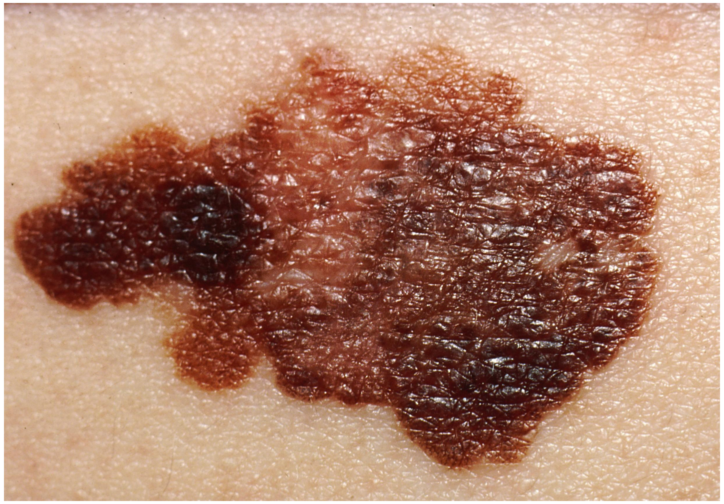




Why do we care?

1% decrease in ozone column

3% increase in skin cancer rates. **3,500,000** new skin cancer cases per year in the US



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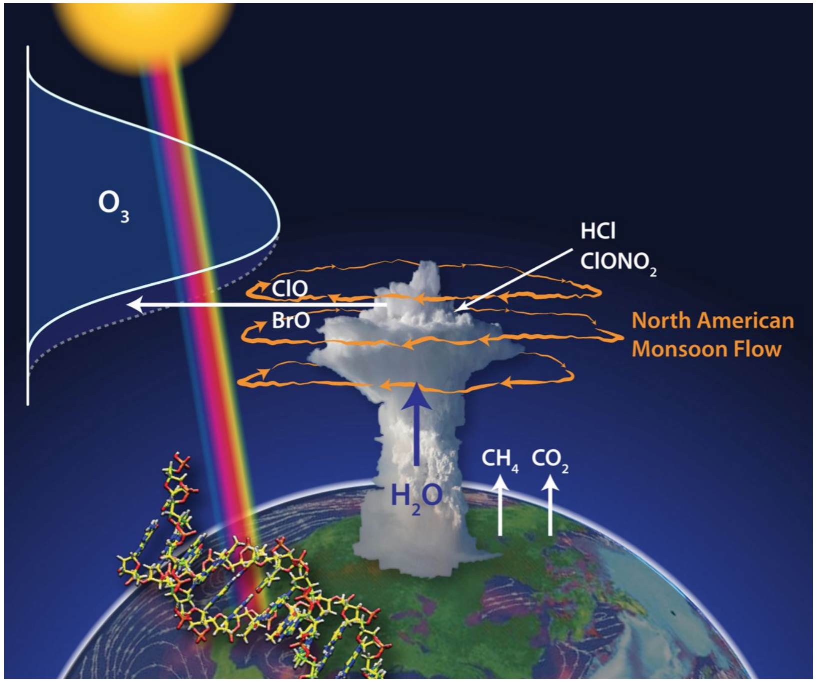

HCl Effect on Ozone

- HCl is a reservoir of inorganic chlorine in the atmosphere
- Presence of HCl in the atmosphere creates the potential for chlorine activation
- Chlorine activation occurs on particle surfaces

Activation of Chlorine Catalytic Cycle

$$ClONO_2 + HCl \rightarrow Cl_2 + HONO_2$$

$$ClONO_2 + H_2O \rightarrow HOCl + HONO_2$$

$$HOCl + HCl \rightarrow Cl_2 + H_2O$$

$$Cl_2 + h\nu \rightarrow 2Cl$$

HCl Effect on Ozone

- **Cl and Br act in catalytic cycles for the degradation of O_3**

$$2(Cl + O_3 \rightarrow ClO + O_2)$$
$$ClO + ClO + M \rightarrow ClOOCl + M$$
$$ClOOCl + hv \rightarrow Cl + ClOO$$
$$ClOO + M \rightarrow Cl + O_2 + M$$
$$\text{Net } 2O_3 \rightarrow 3O_2$$

$$BrO + ClO \rightarrow Br + Cl + O_2$$
$$Br + O_3 \rightarrow BrO + O_2$$
$$Cl + O_3 \rightarrow ClO + O_2$$
$$\text{Net } 2O_3 \rightarrow 3O_2$$

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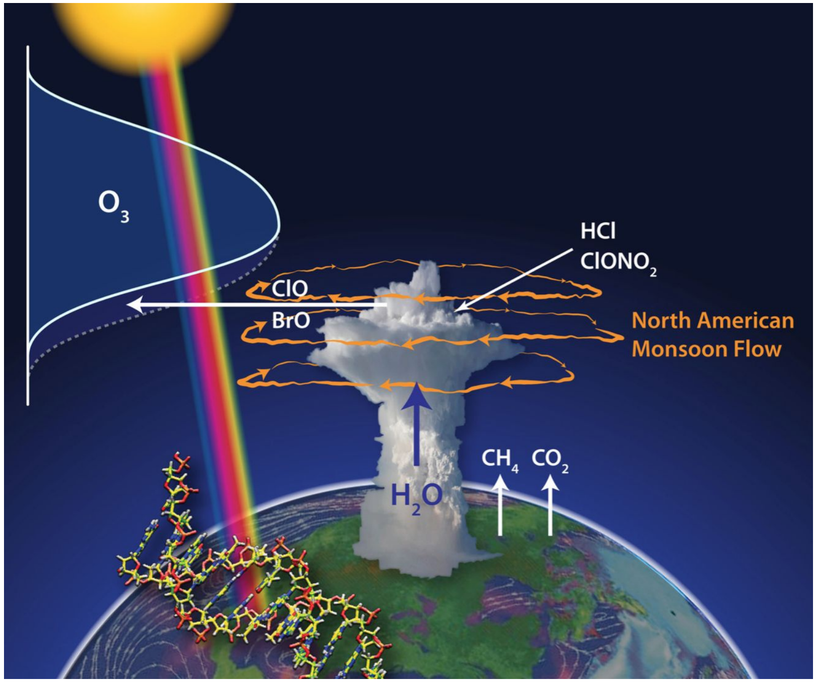
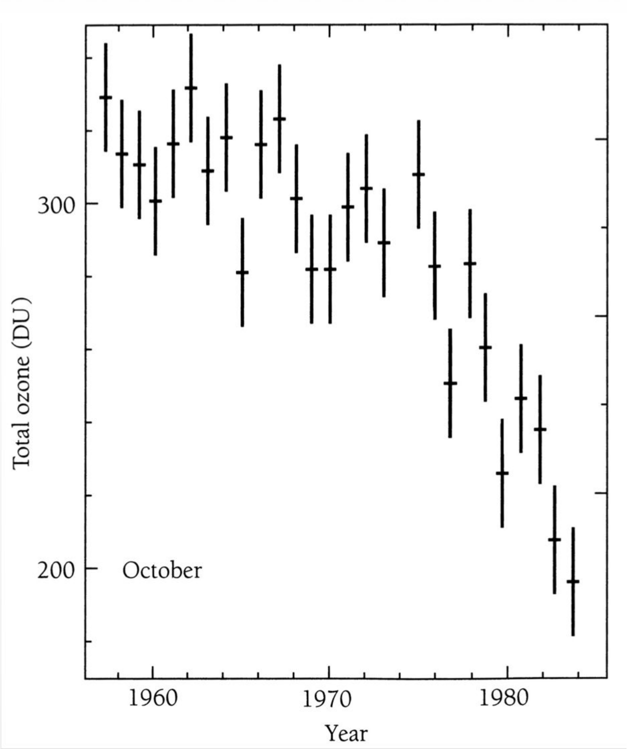
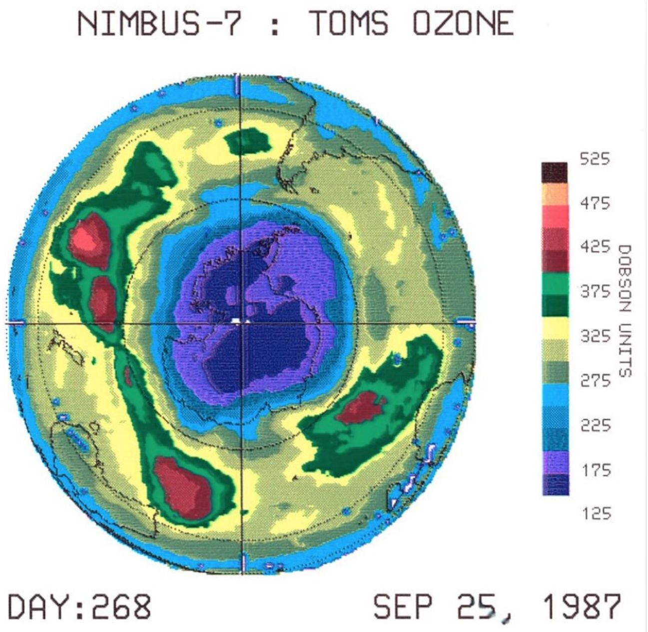


Antarctic Ozone Hole (1st noticed 1985)





- Ground based observations clarified by NASA satellite data

Antarctic Ozone Hole (1st noticed 1985)

$$ClO + ClO + M \rightarrow ClOOCl + M$$

$$ClOOCl + h\nu \rightarrow Cl + ClOO$$

$$ClOO + M \rightarrow Cl + O_2 + M$$

$$2(Cl + O_3 \rightarrow ClO + O_2)$$

$$\text{Net } 2O_3 \rightarrow 3O_2$$

$$BrO + ClO \rightarrow Br + Cl + O_2$$

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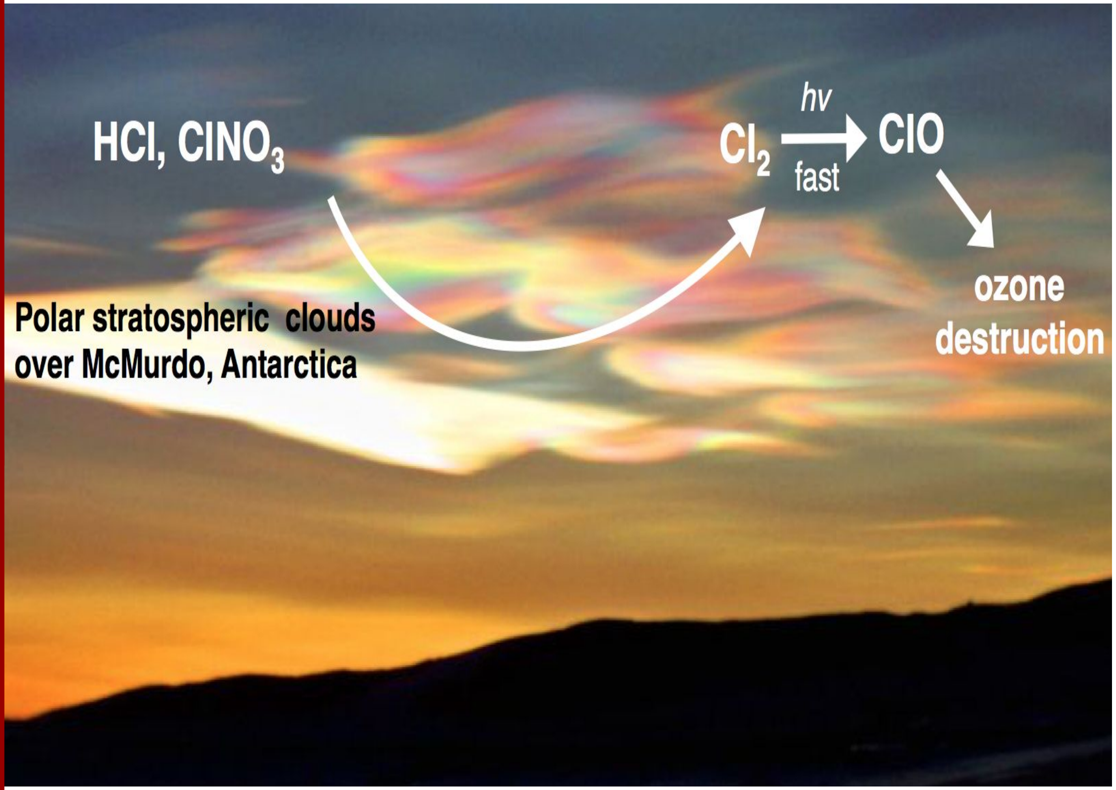
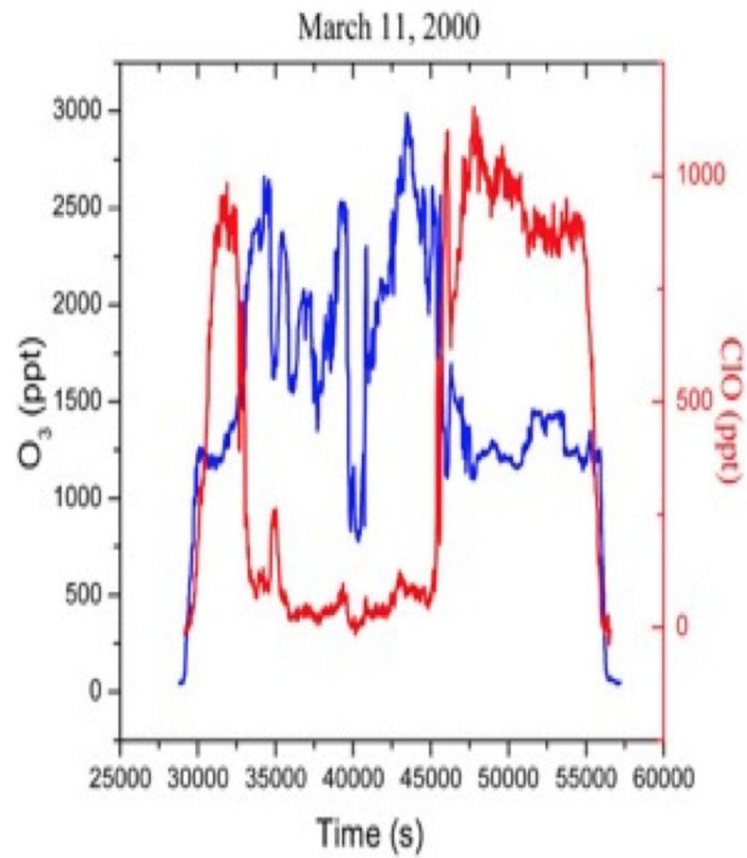
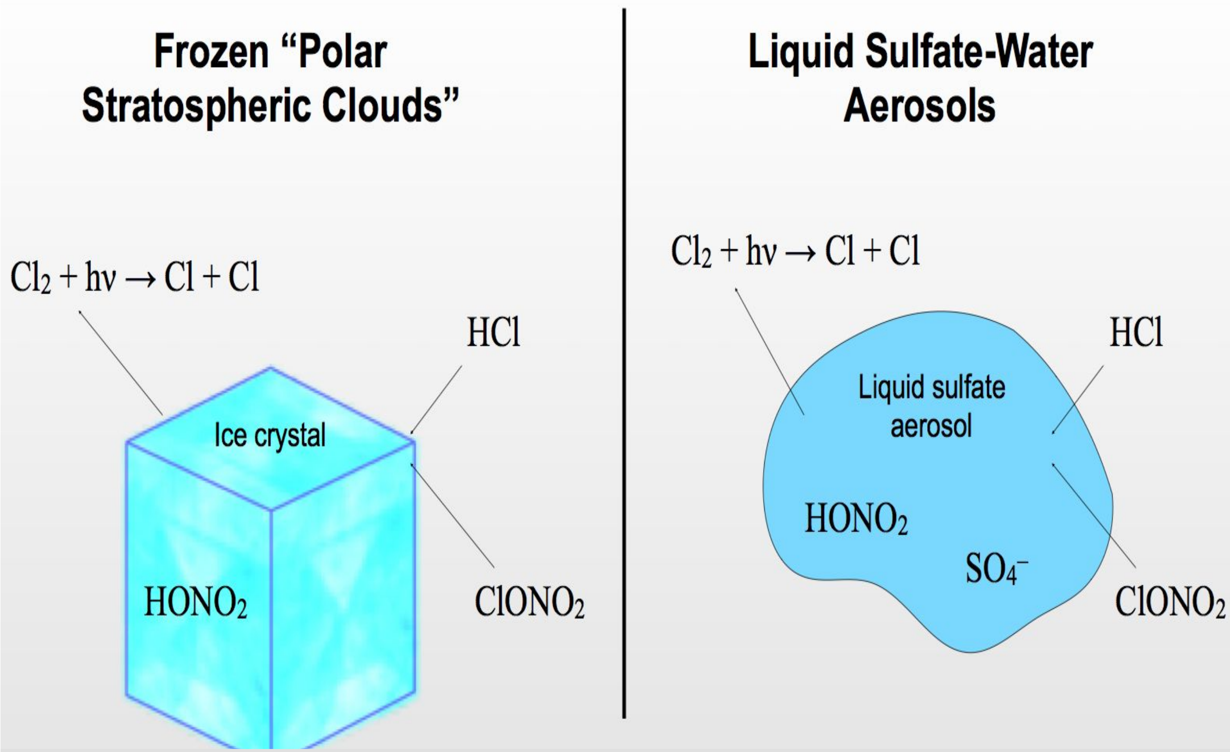


Arctic Ozone Depletion



Arctic Ozone Depletion



Result:

$$HCl + ClONO_2 \rightarrow Cl_2 + HONO_2$$

$$Cl_2 + h\nu \rightarrow Cl + Cl$$

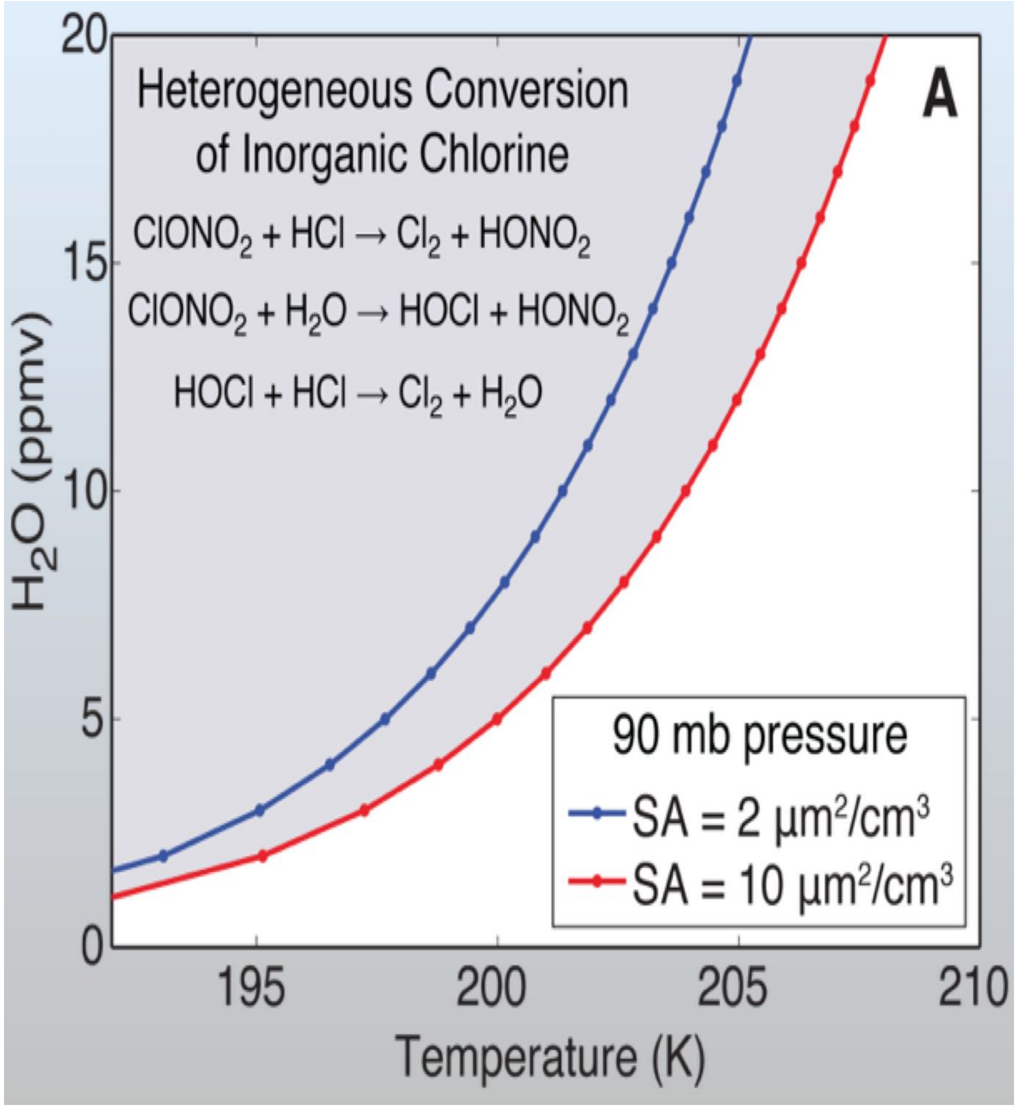
$$Cl + O_3 \rightarrow ClO$$

- Reaction also occurs on sulfate aerosols
- Sulfate aerosols are ubiquitous in the stratosphere

Conditions for ClO production

1. **Sulfate Aerosols**
2. Temperature
3. Water Vapour Concentration

- **Solar Radiation Management**
- **Volcanoes**



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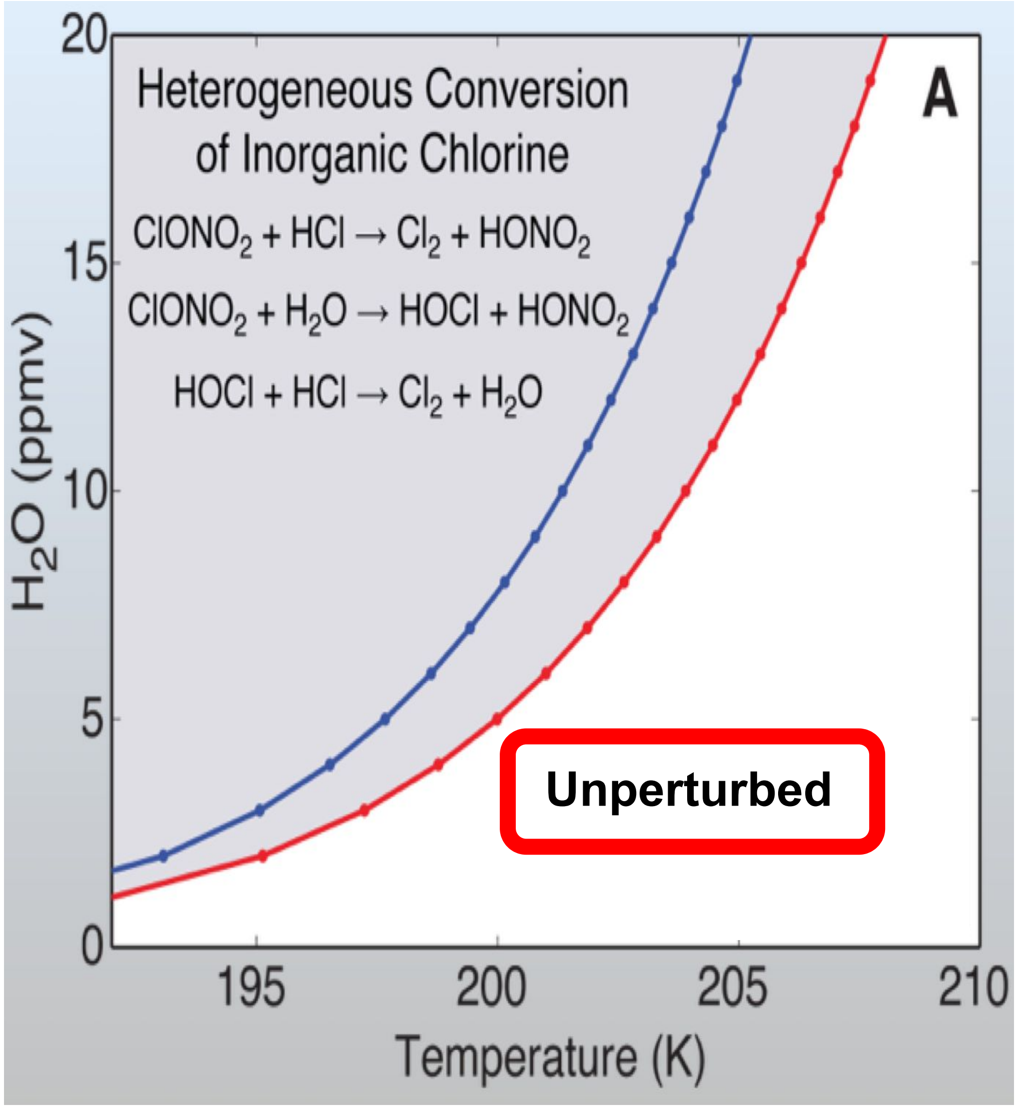

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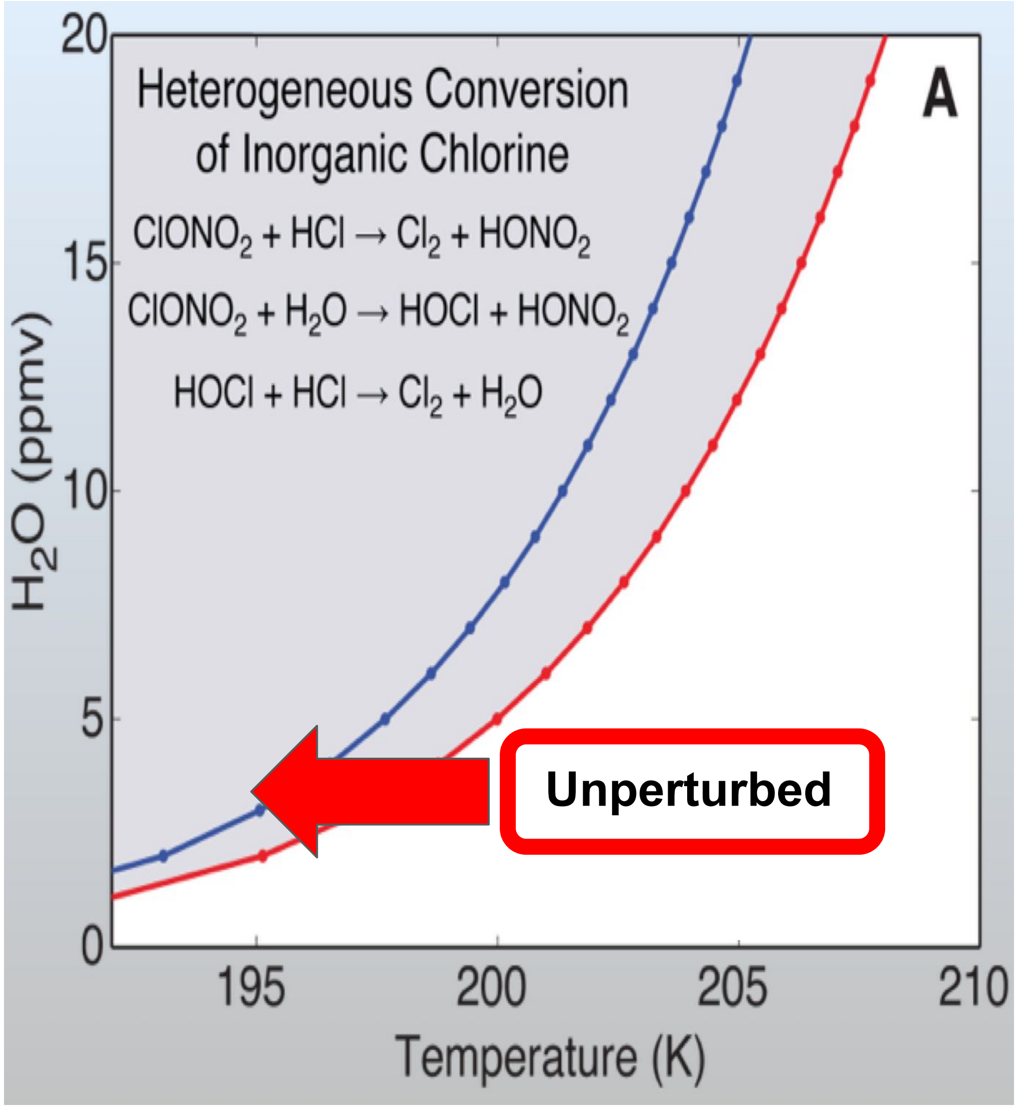

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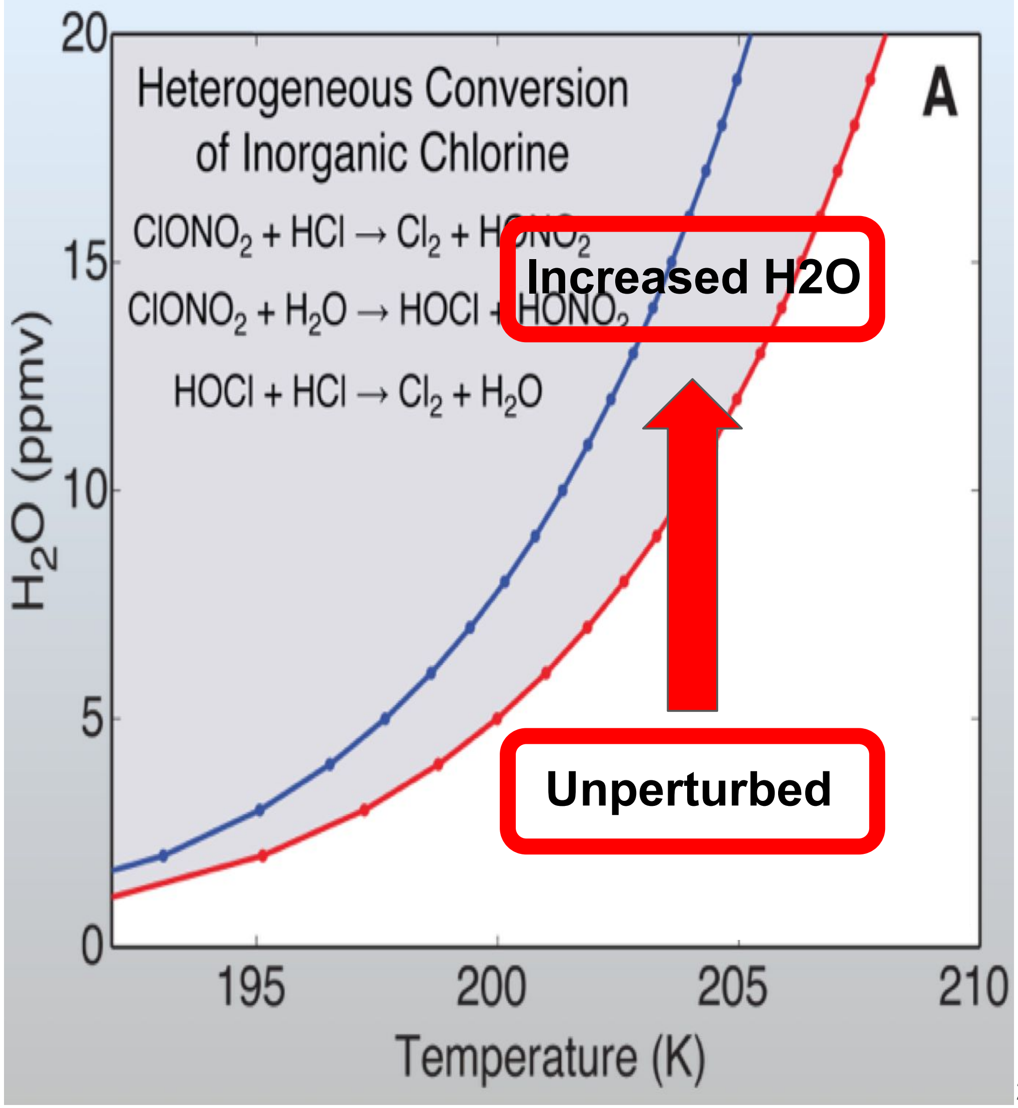

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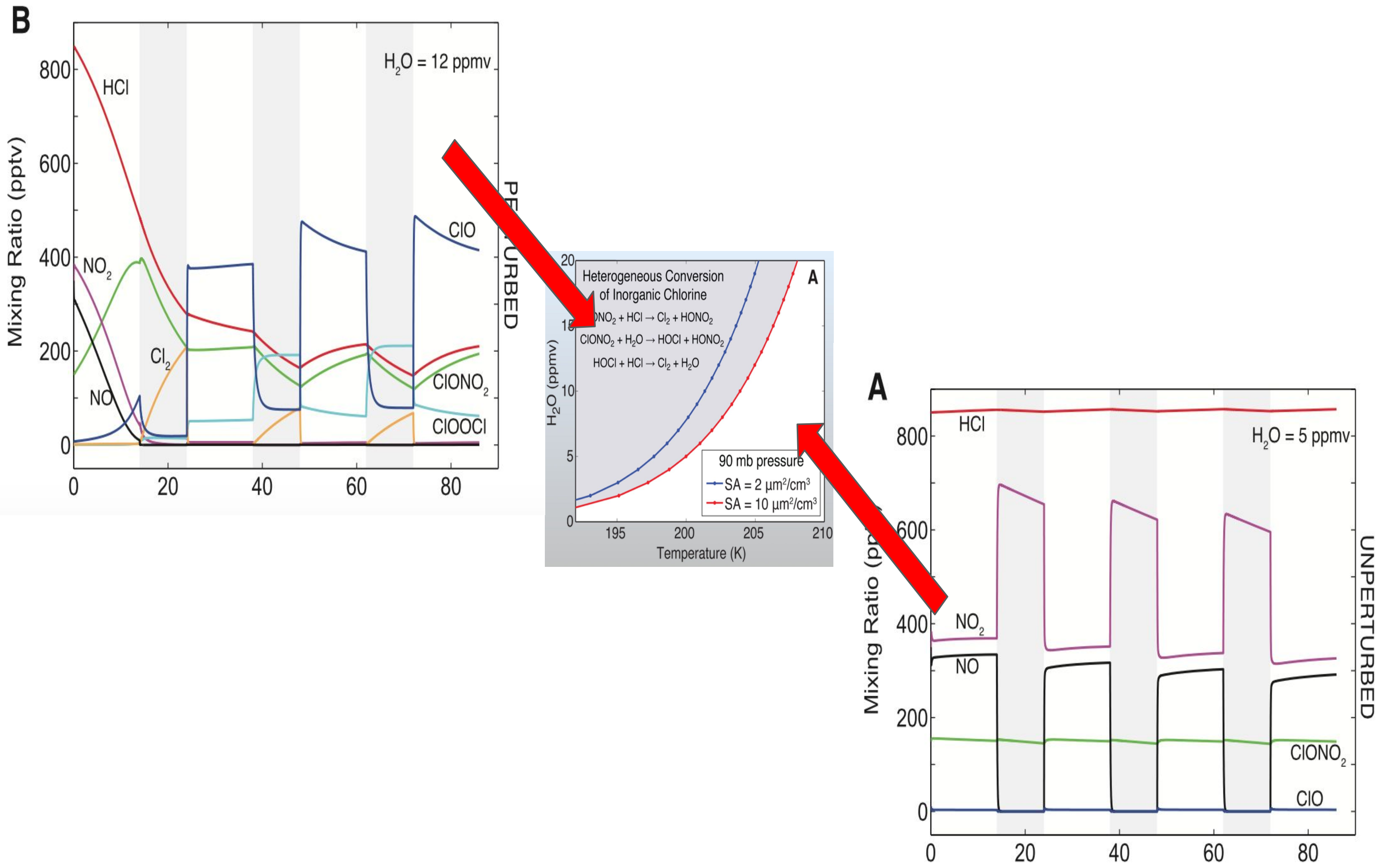

Conditions for ClO production

1. Sulfate Aerosols
2. Temperature
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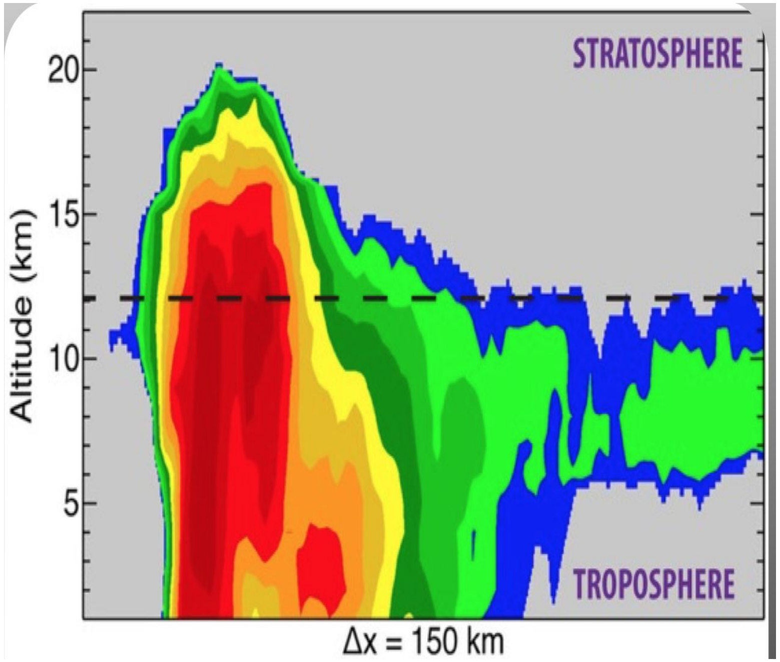
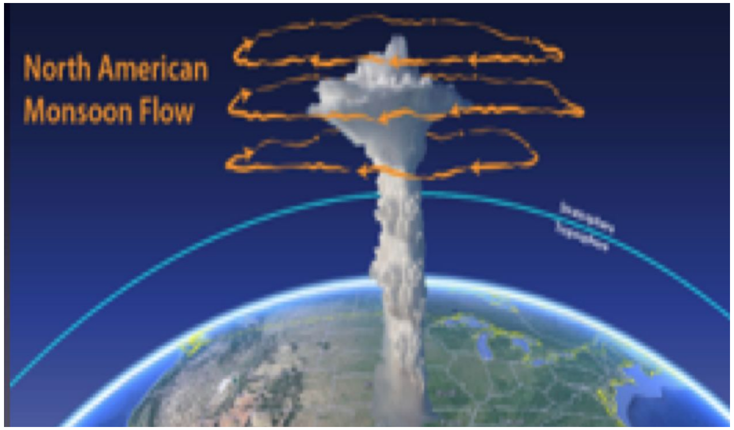
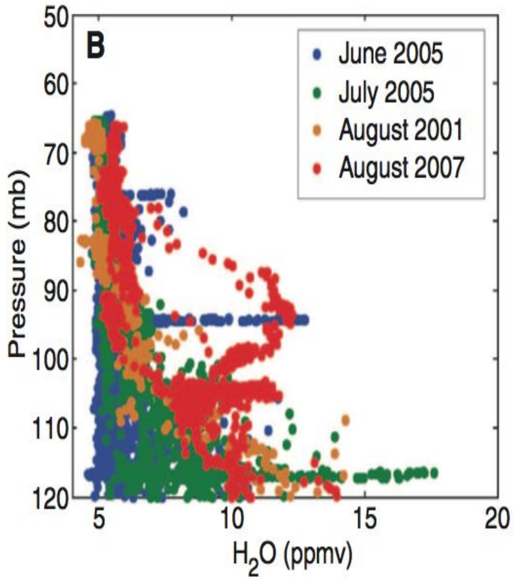
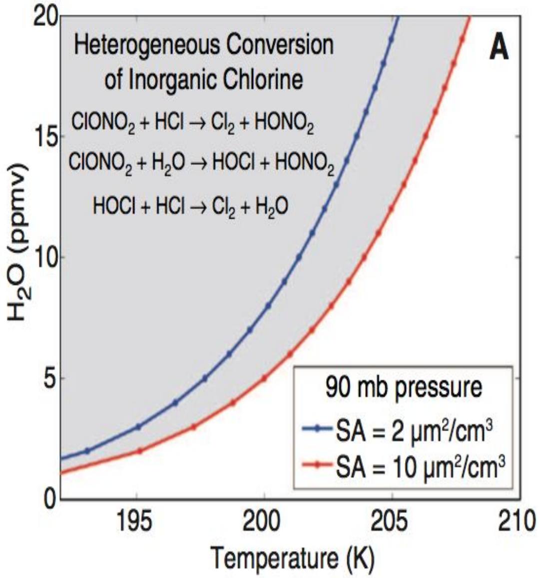
- Convective Storms
- Anticyclonic Monsoon Flow

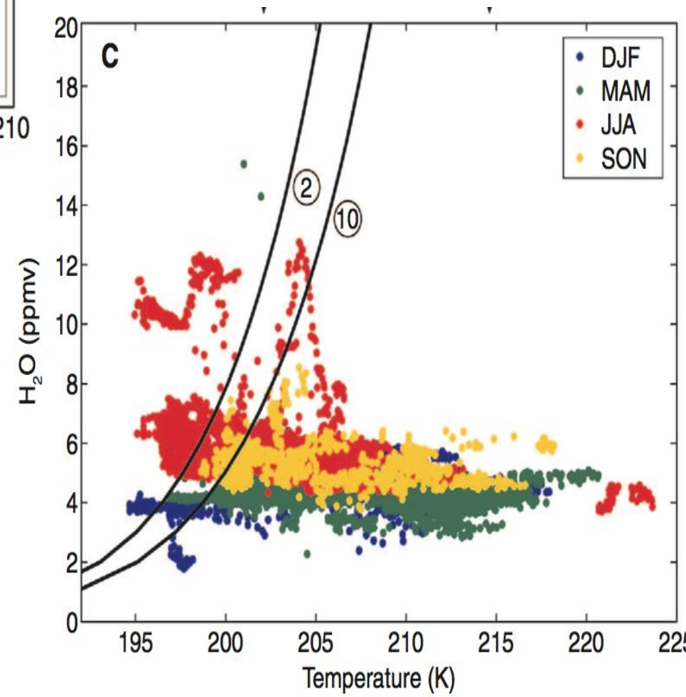




Observations







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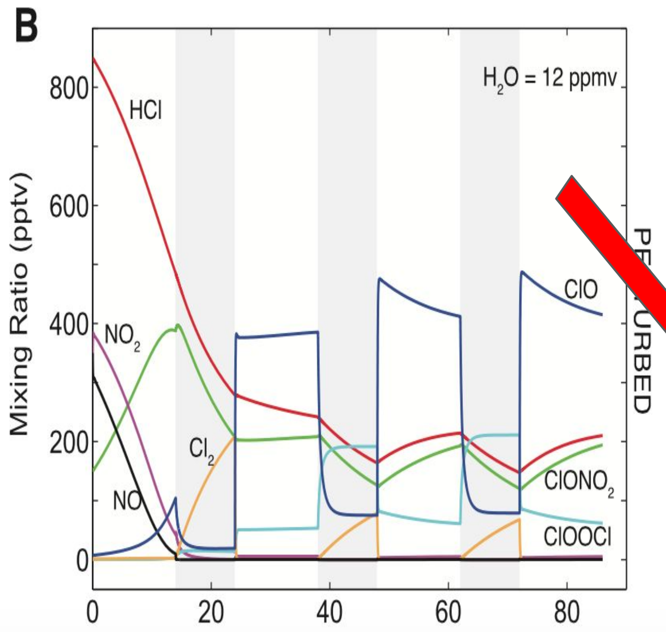

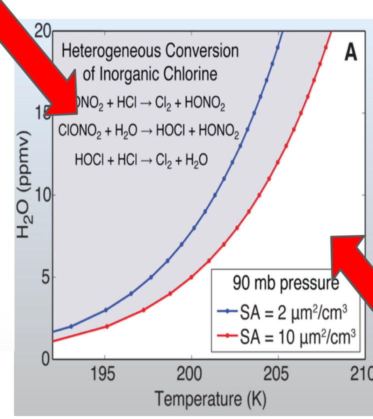

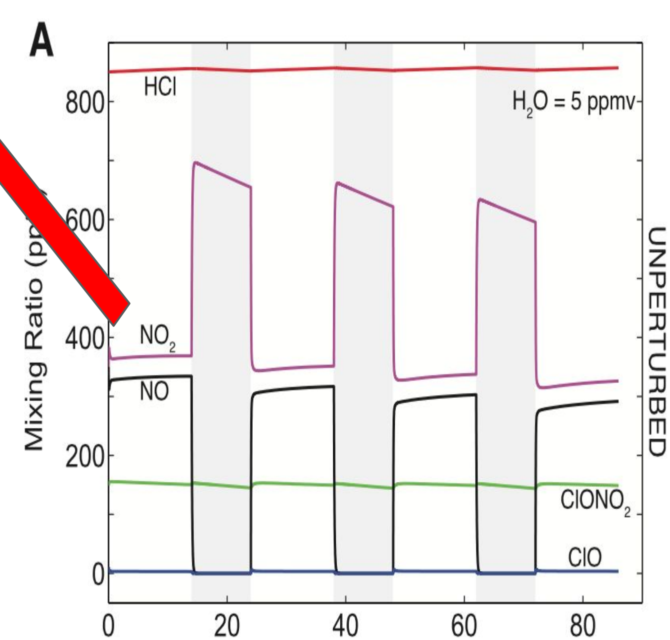

Goals:

1. Verify HCl concentrations in unperturbed conditions
2. Observe Cl activation over US in summer

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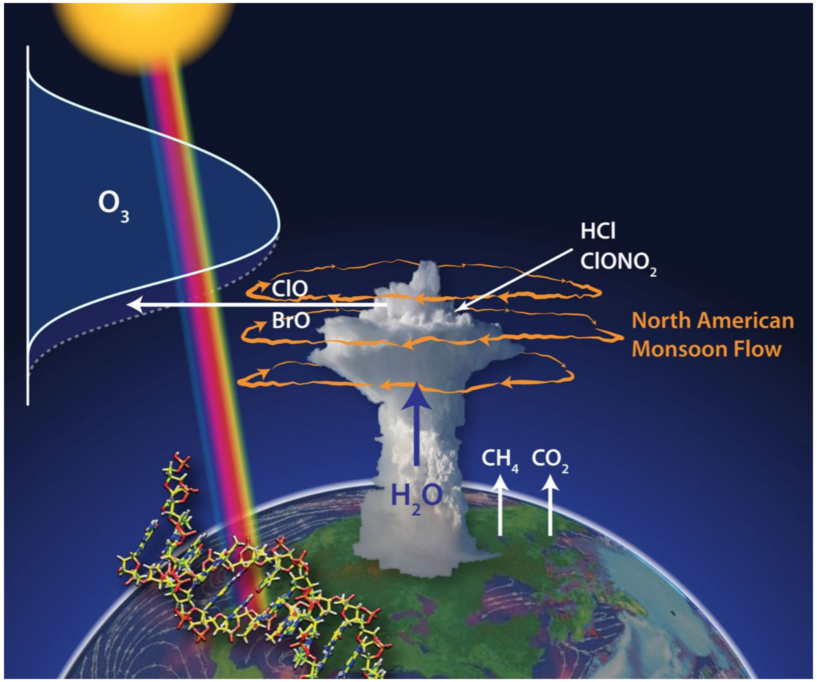
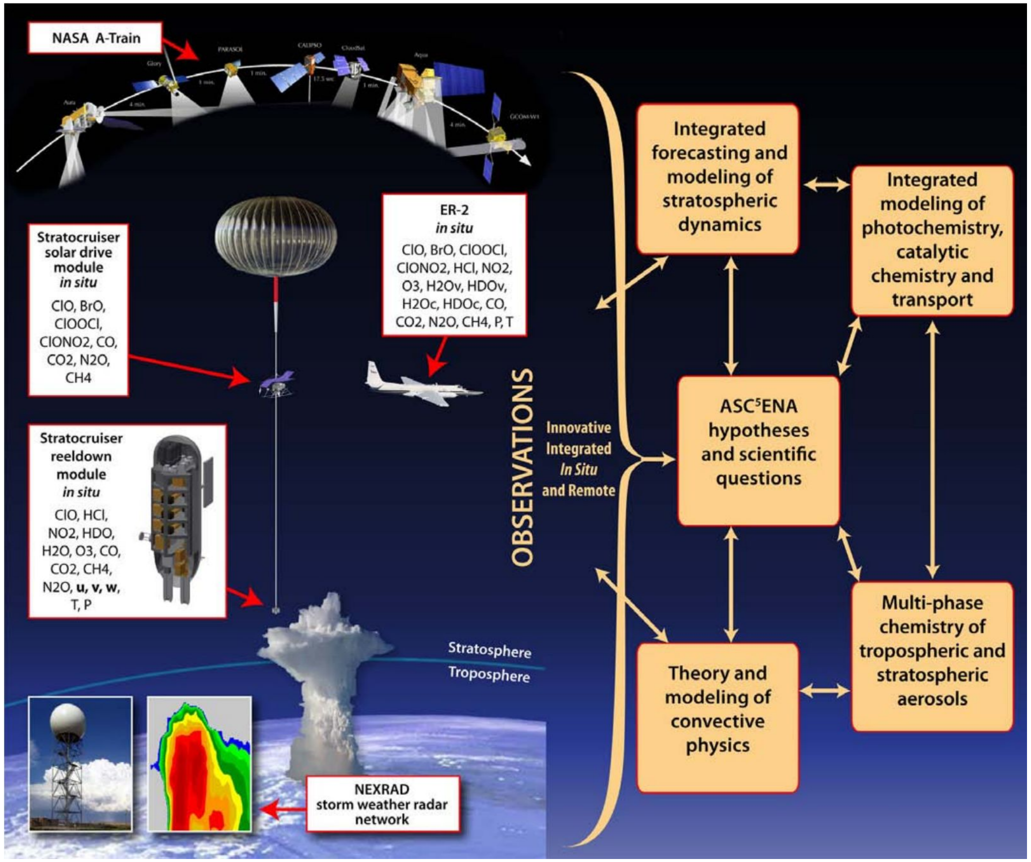


The Proposed Mission Outline

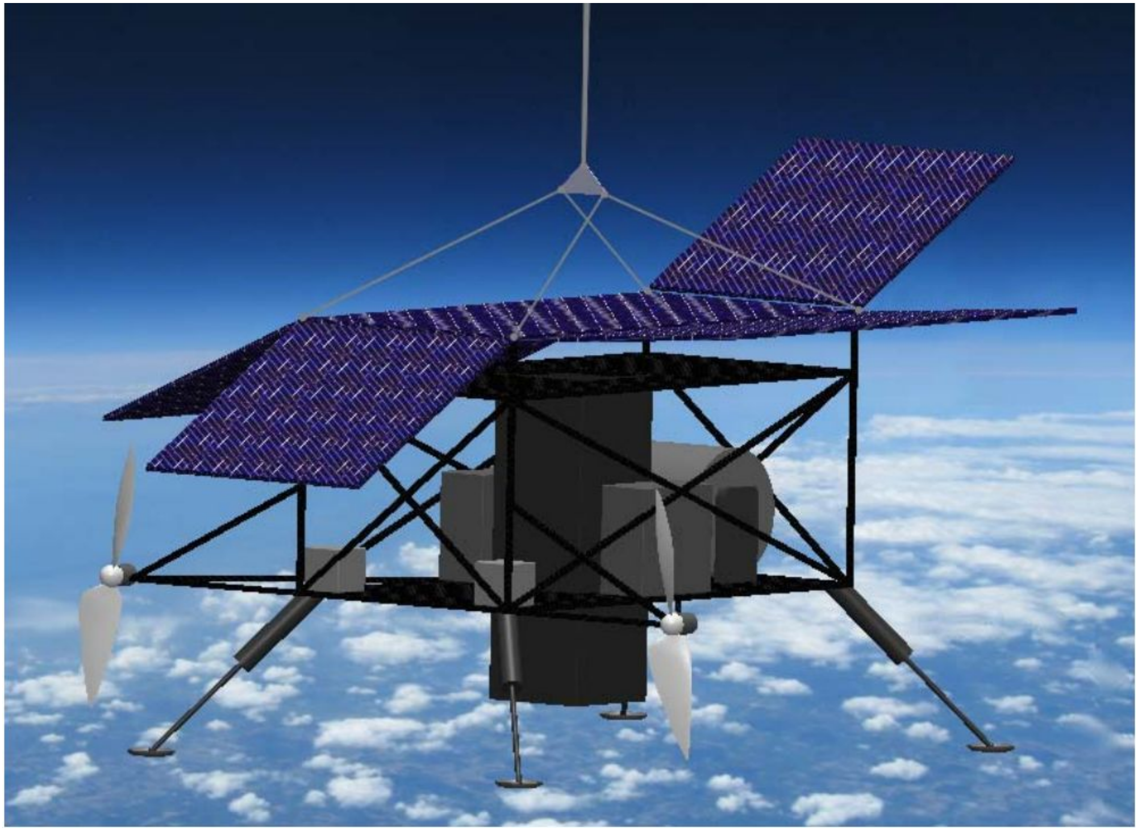
1. Long duration pumpkin balloon
2. Drive module
3. Suspended Payload

- 4-6 week mission
- Altitude of 20km



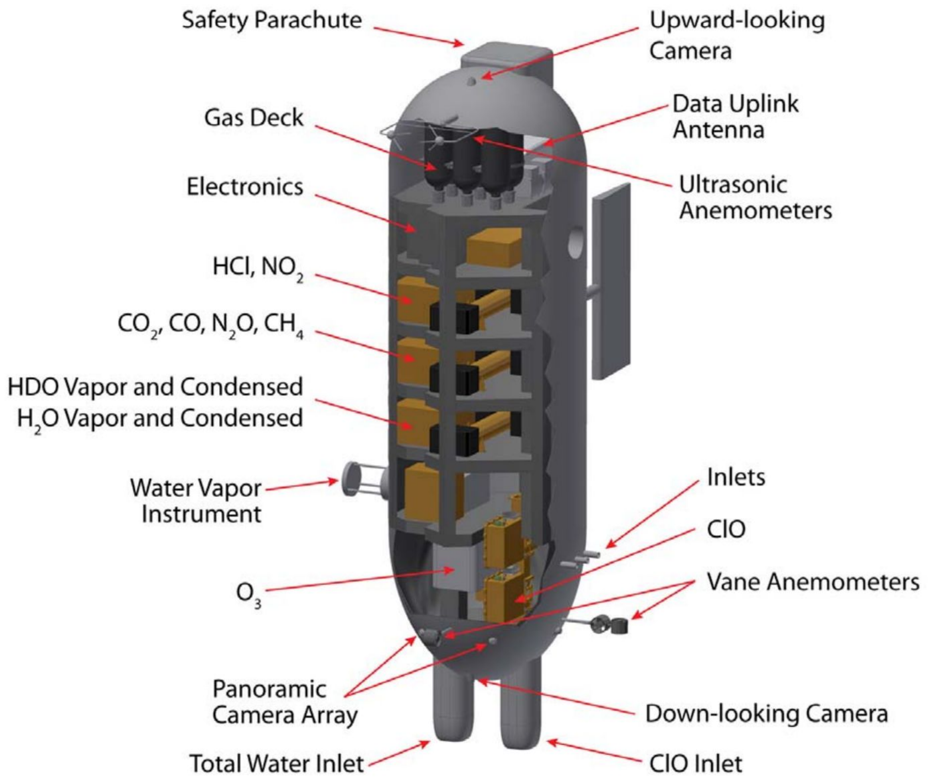
Stratocruiser Drive Module

- **Waypoint or heading navigation**
- **Range of 500km/day**
- **Speeds up to 8 m/s**
- **5.3kWh / 2.0kWh (Day/Night) of continuous power**



Stratocruiser Suspended Payload

- **Winch system lowers payload at 5-10 m/s for up to 10km**
- **200kg mass limit**
- **Data is sent via Iridium satellite data link to the Science Control Center**



System Overview

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   a. Laser
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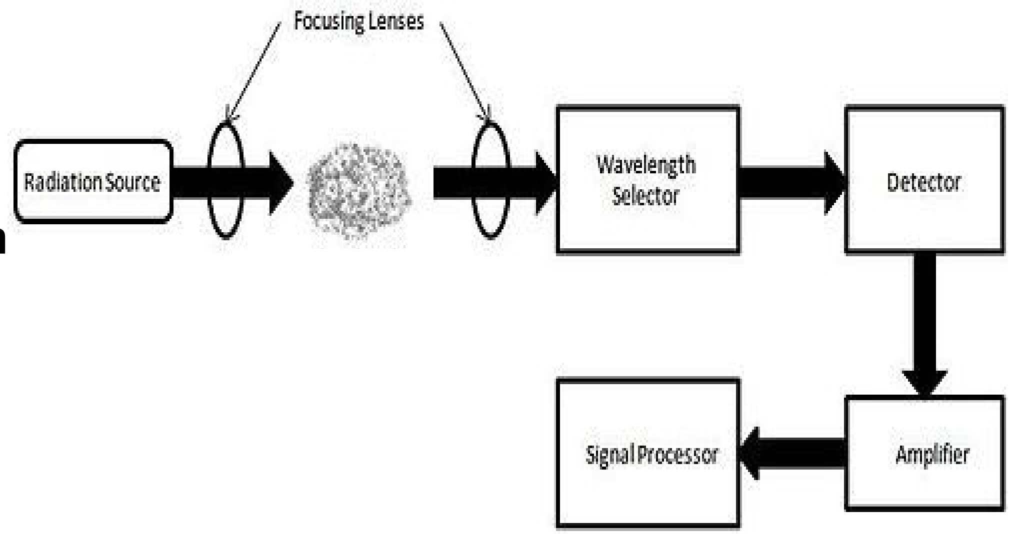
Integrated Cavity Output Spectroscopy (ICOS)

- **Specialized form of absorption spectroscopy**
- **Beer's Law:** $ln(I / I_o) = -n\sigma\ell$
  - ***n : concentration***
  - ***σ : absorption cross-section***
  - ***ℓ: path length***
- **∴ ↑ path length → ↑ absorption**
- **ICOS increases effective path length from 0.5 - 1m to >5km**
- **Highly sensitive - pptv**



A general example of an absorption spectroscopy system

System Diagram

Detector

Design Details

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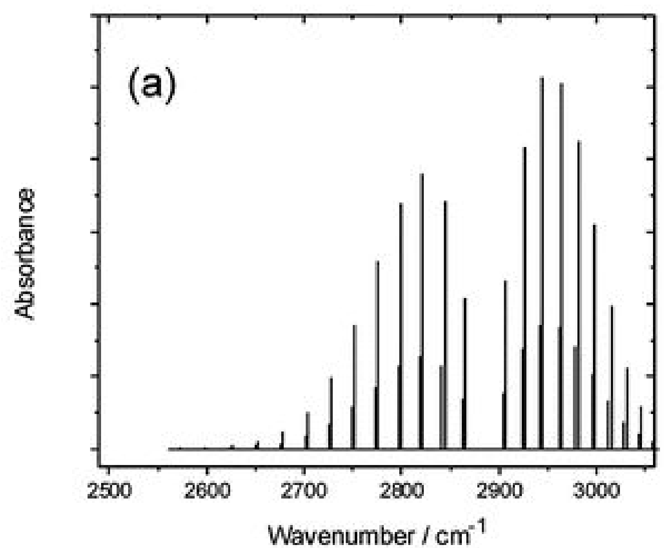
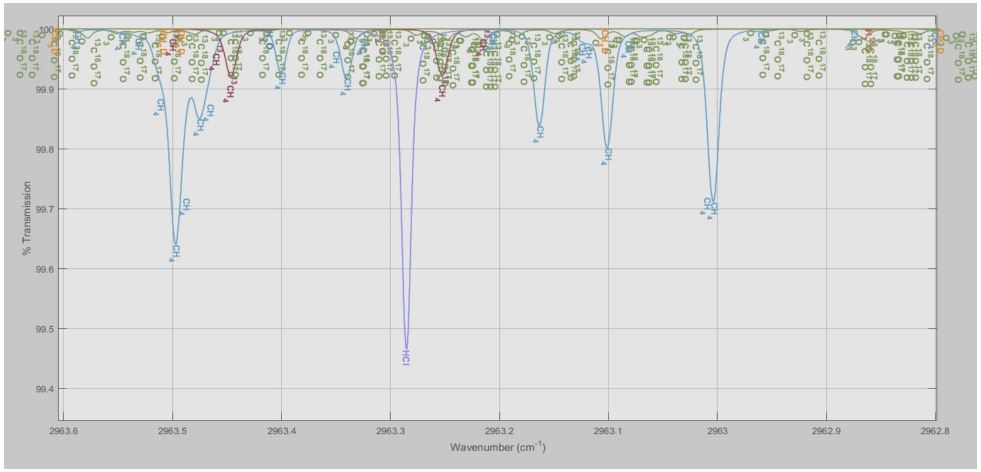
Laser System - Laser Specifications

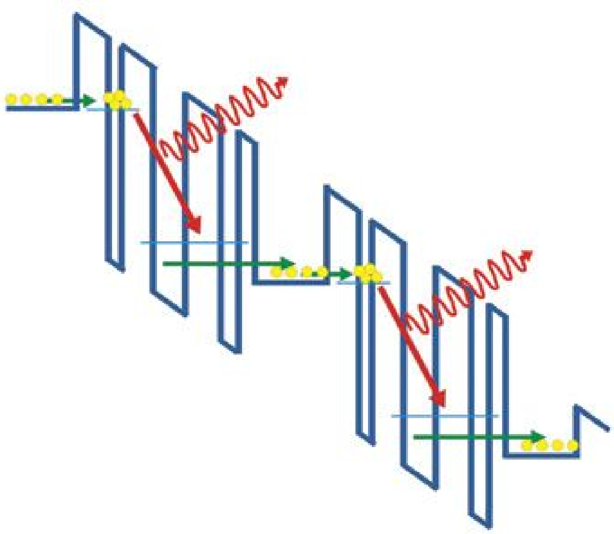
- **Wavelength Choice**
  - **Requires high resolution and separation from other peaks**
  - **Final decision: 3.375 µm (2963 cm^{-1})**

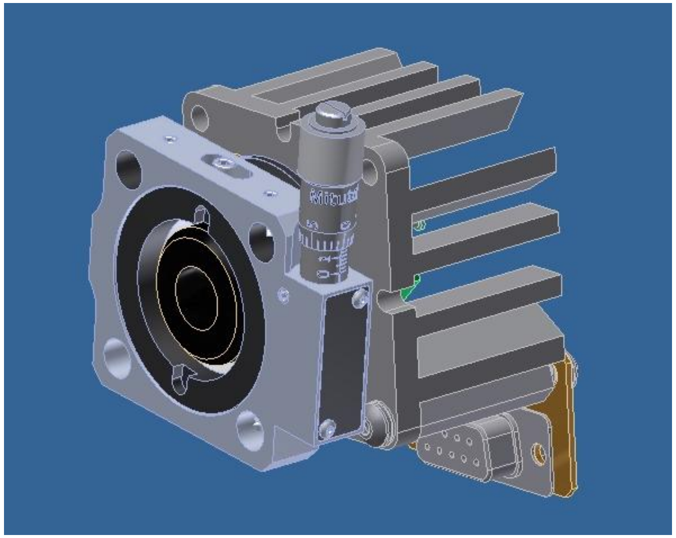




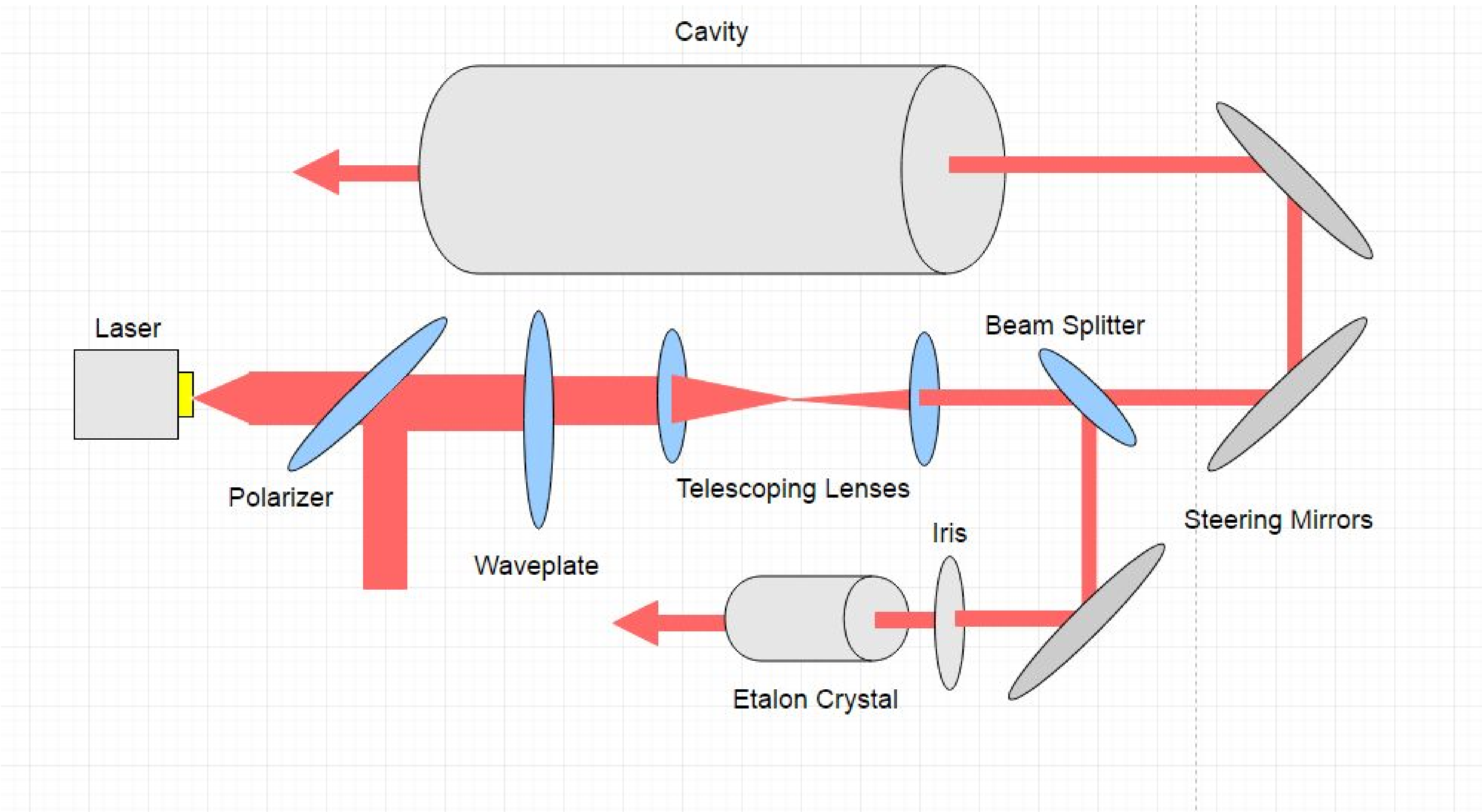
Laser System - Laser Specifications

- **Laser Choice - Interband Cascade Laser**
  - **JPL-ICL57 for final instrument**
  - **JPL-ICL58 for testing**



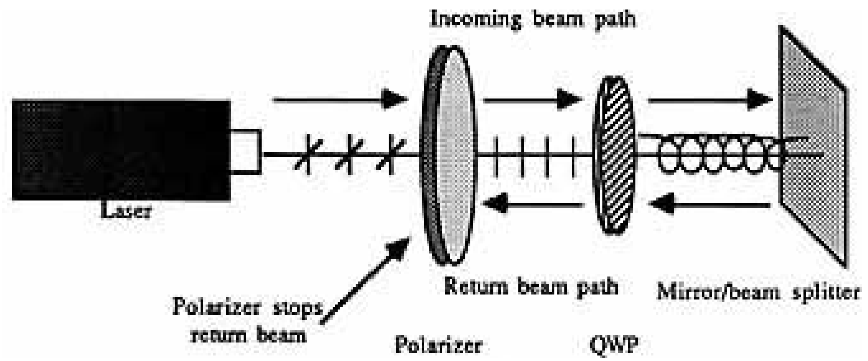


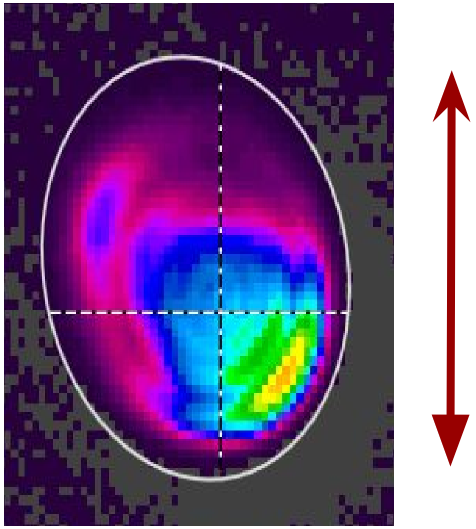
Laser System - Fore-Optics Diagram

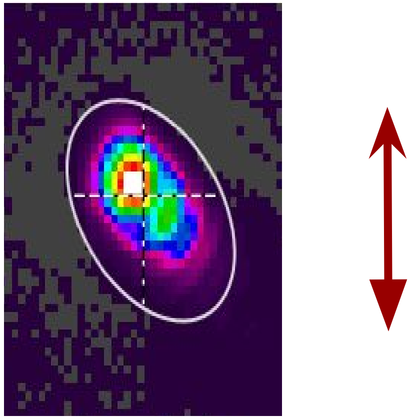


Laser System - Fore-Optics Specifications

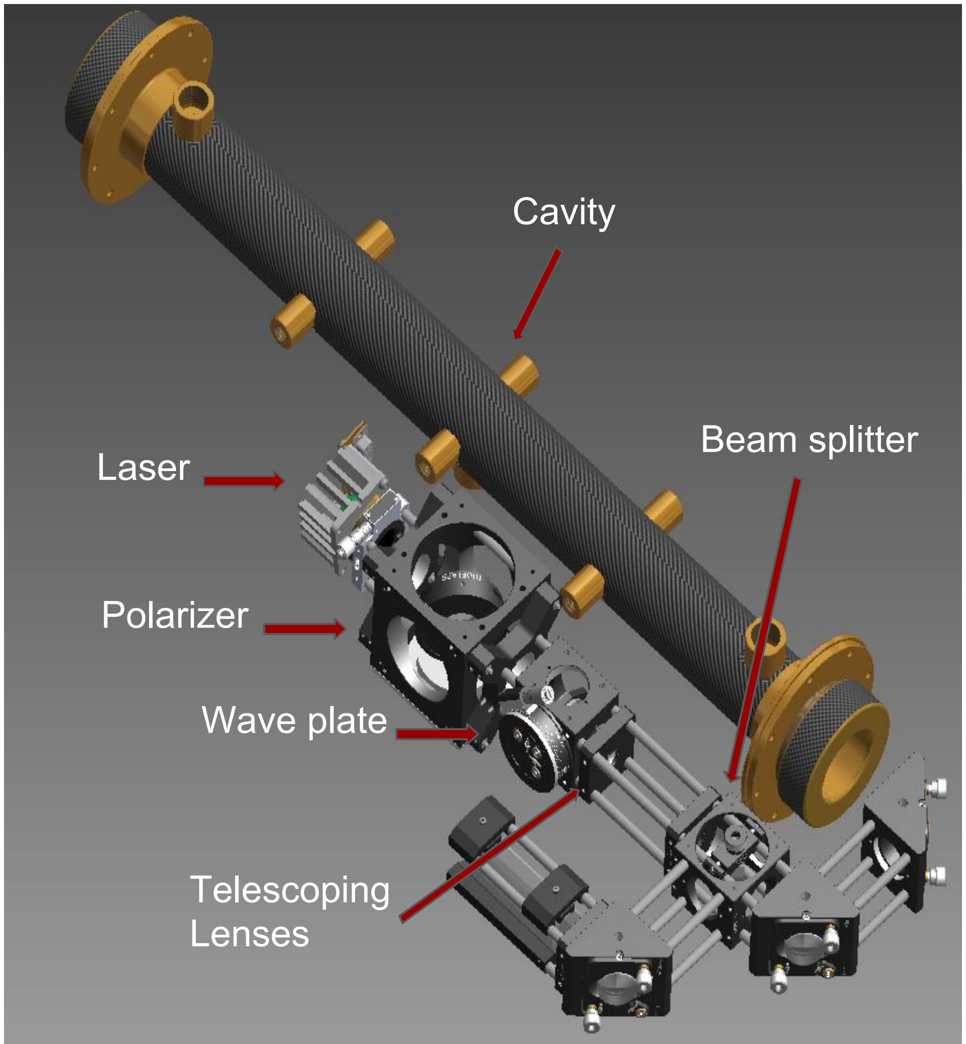
- Reduced interference into laser with wave plate and polarizer
- Reduced beam diameter for greater resolution in cavity



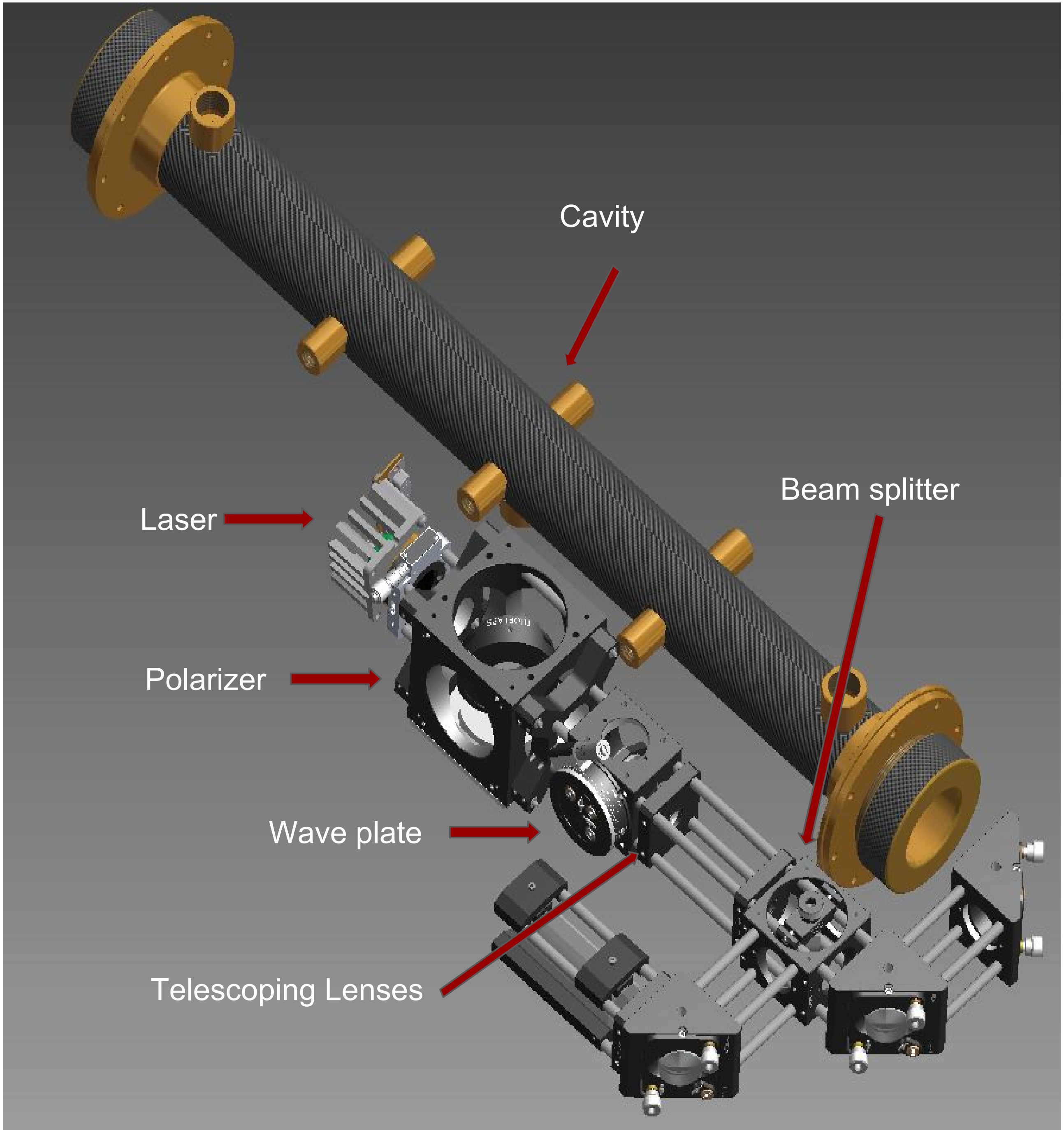




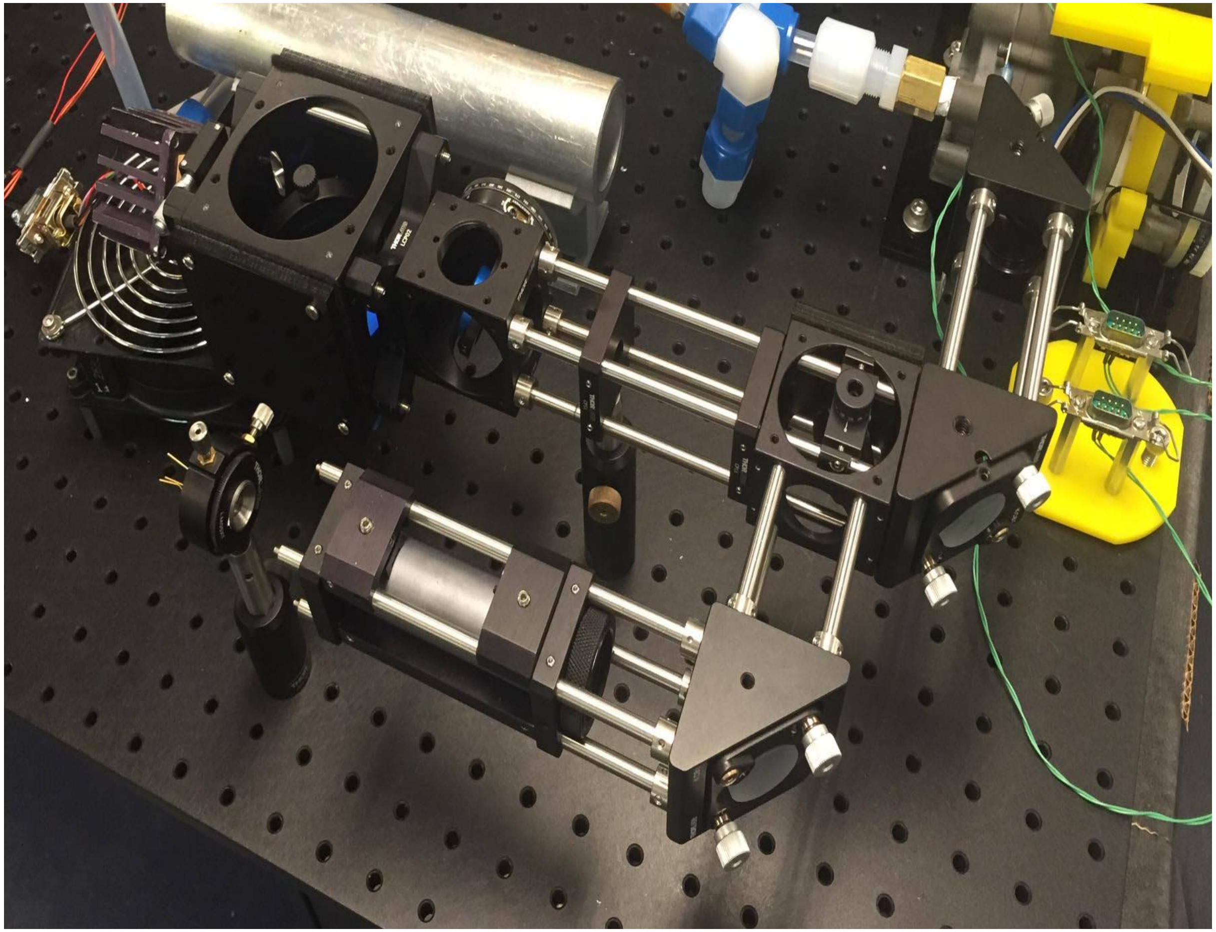
Laser System - Fore-Optics CAD Model



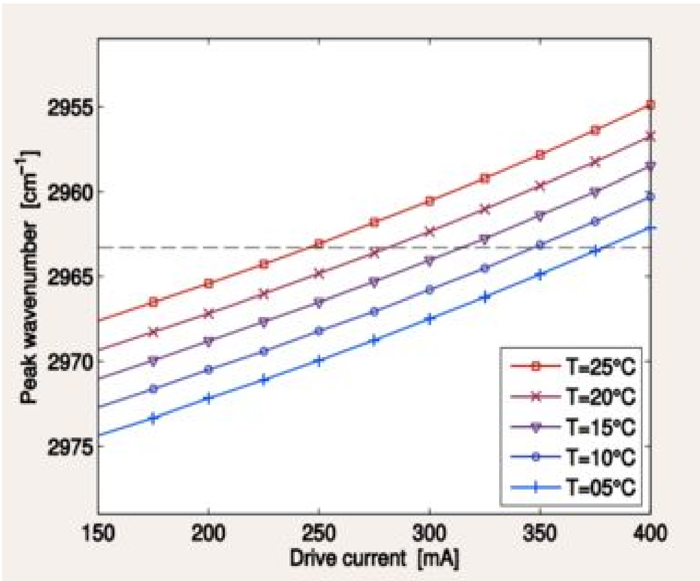
- **Modular cage system for easy assembly and change of components**
- **Individual rotation mounts for precision alignment control**
- **Stainless steel cage and single-point attachment to cavity for in-flight durability**

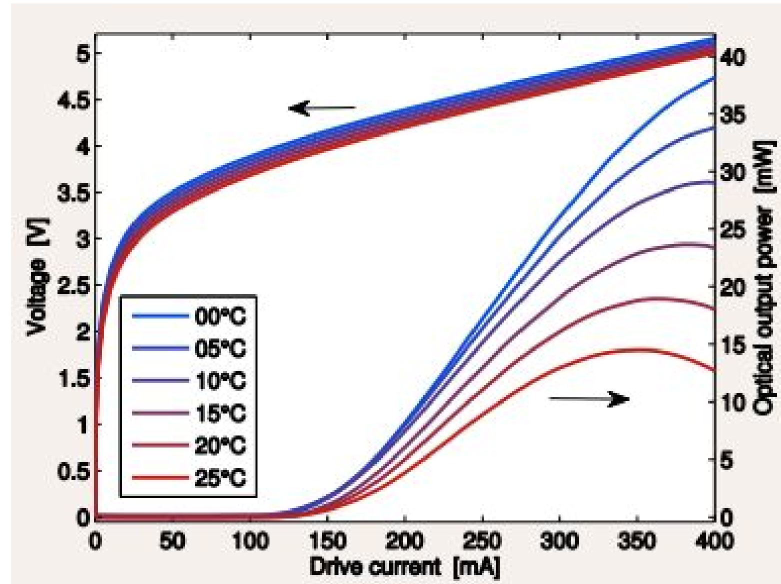

Cavity
Beam splitter
Laser
Polarizer
Wave plate
Telescoping Lenses

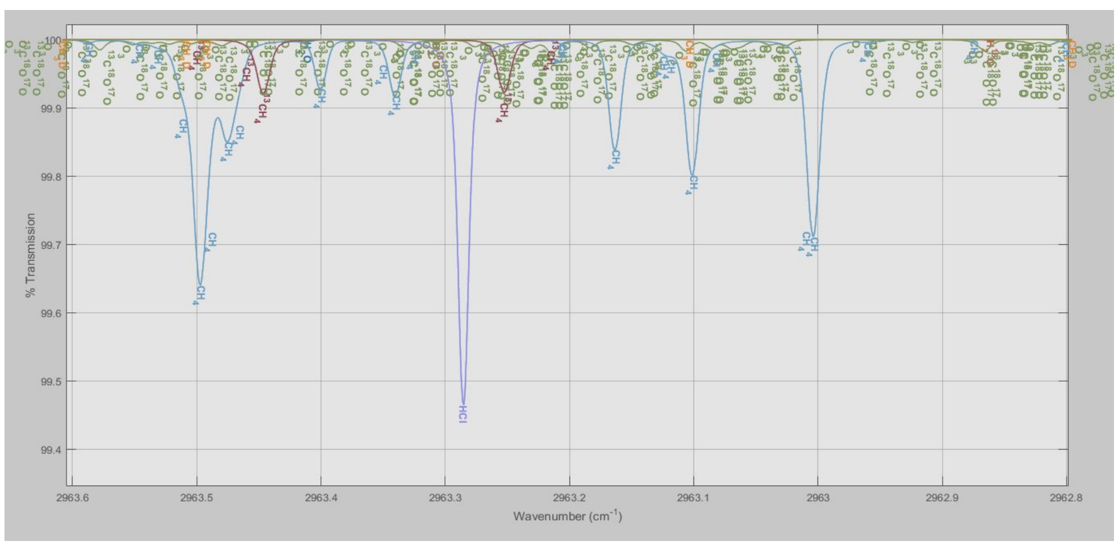
Laser System - Fore-Optics Assembly



Laser System - Laser Driver Overview





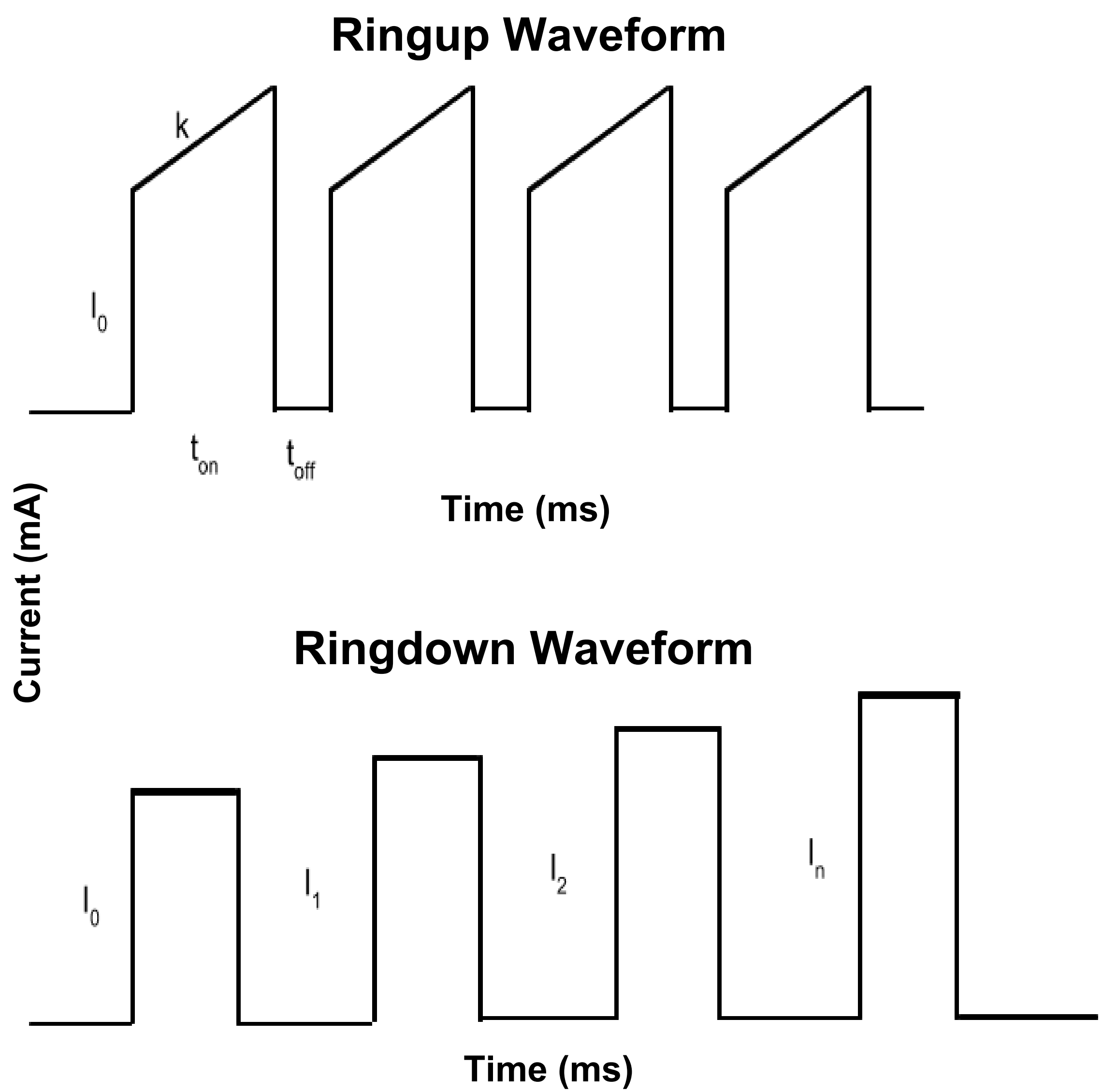


Laser System - Driver Waveforms

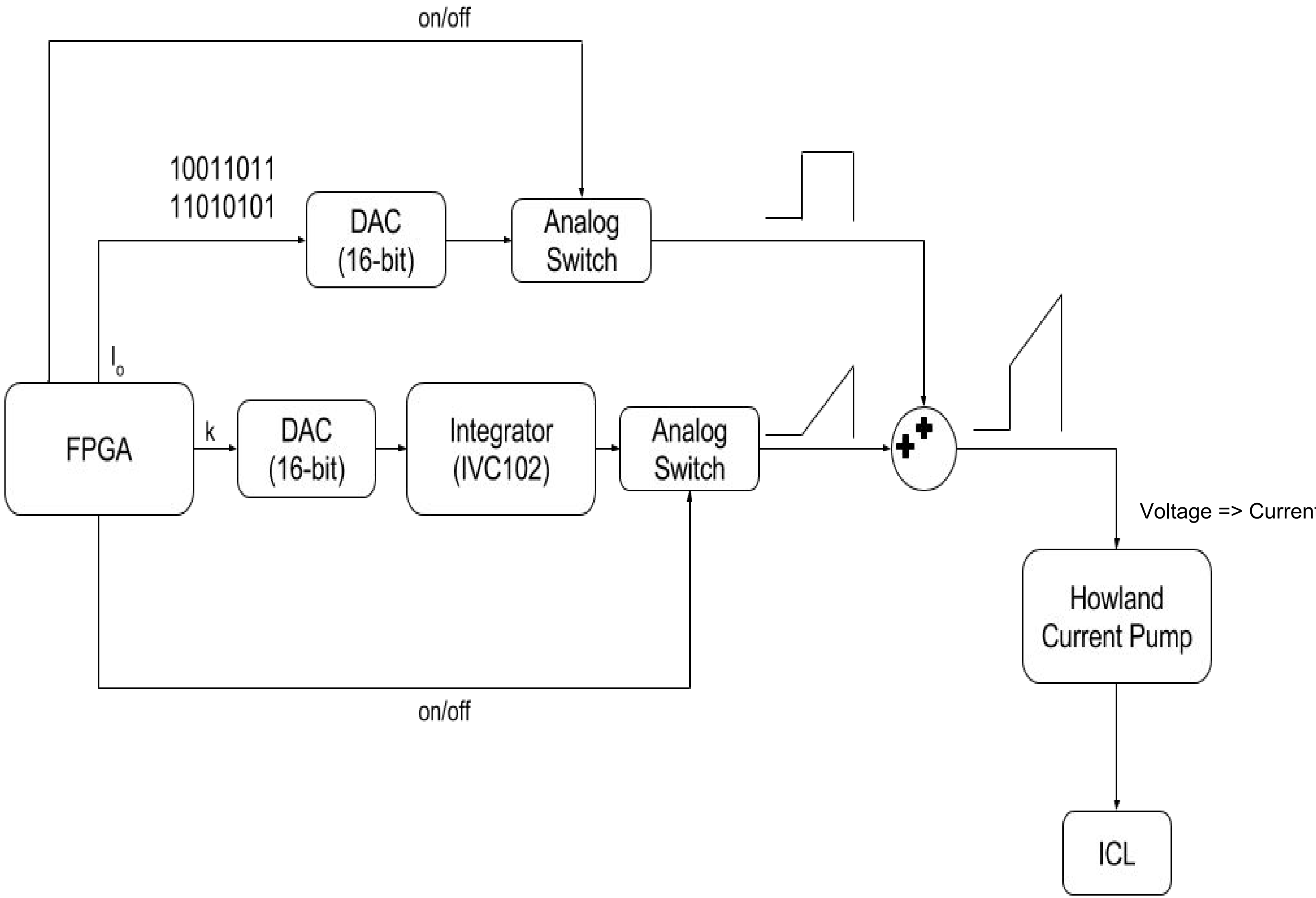
- Programmed by FPGA, and generated by laser driver.
- Current waveform sweeps across laser wavelengths.
- Ringdown waveform operates laser at single wavelengths.

- Frequency: 1kHz
- Rise/Fall Time: <1us

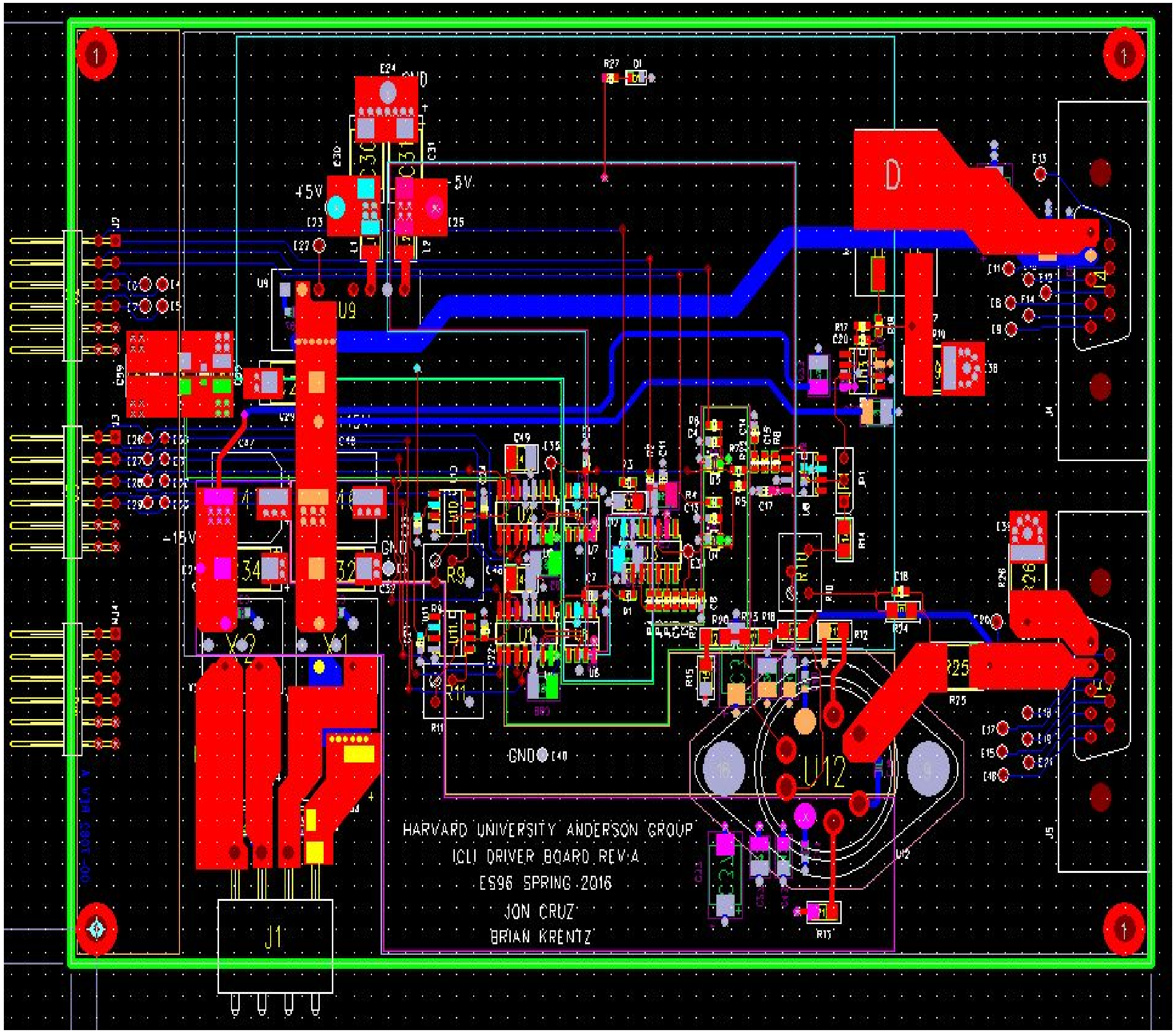
- ~50% duty cycle - ringdown waveform



Laser System - Driver Block Diagram



Laser System - Driver Board



Cavity

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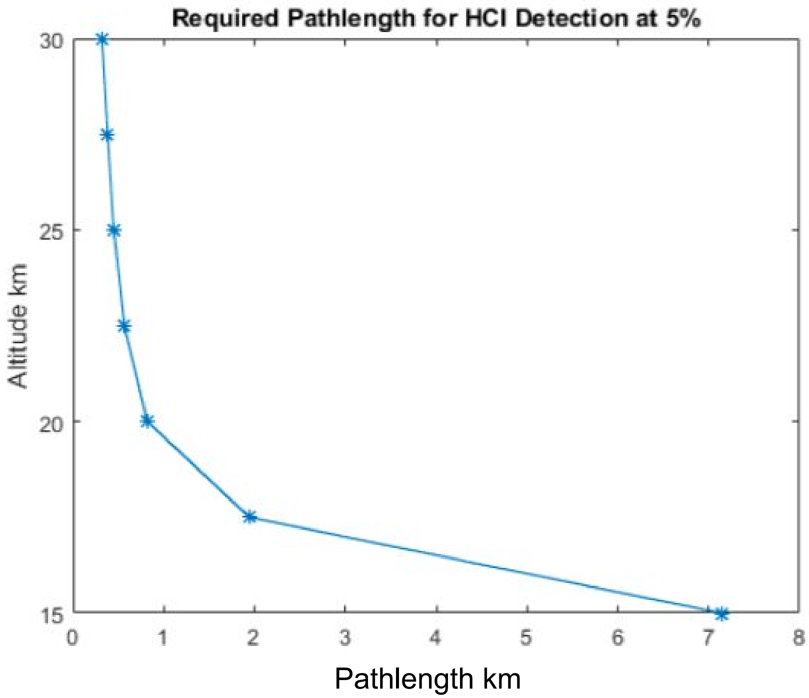
System Diagram - Cavity

Cavity - Objectives

- House the atmosphere sample in an airtight, thermally uniform environment
- Maintain relatively low cell volume
- Generate effective pathlength of several kilometers

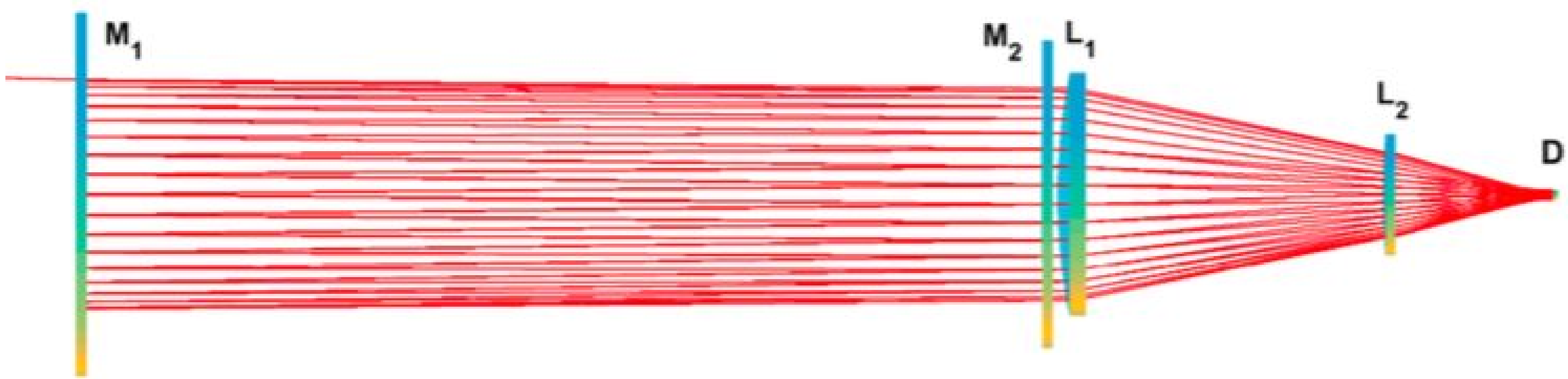


Cavity - Optical configuration

- **Integrated cavity output spectroscopy (ICOS)**
- **Two highly reflective mirrors**
- **Series of post cavity lenses focused onto a detector**

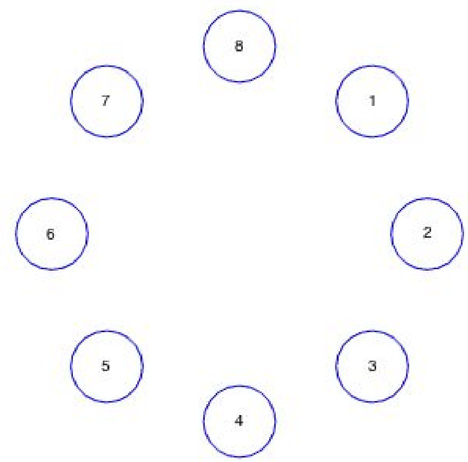
$$\ell' \cong \frac{\ell}{\mathrm{L}+\alpha}$$

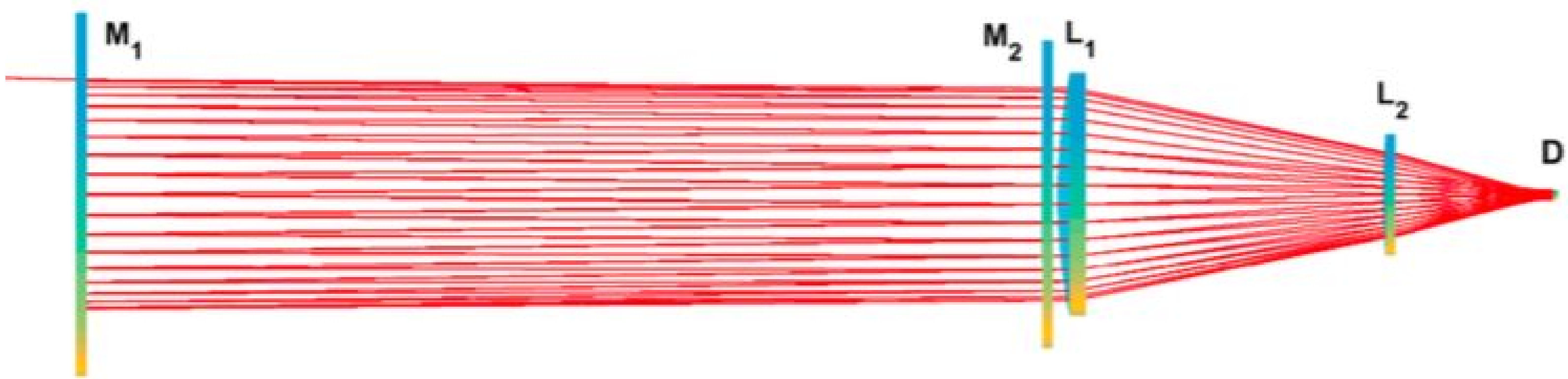
$$L = 1 - e^{-\ell/c\tau} \cong \ell/c\tau$$



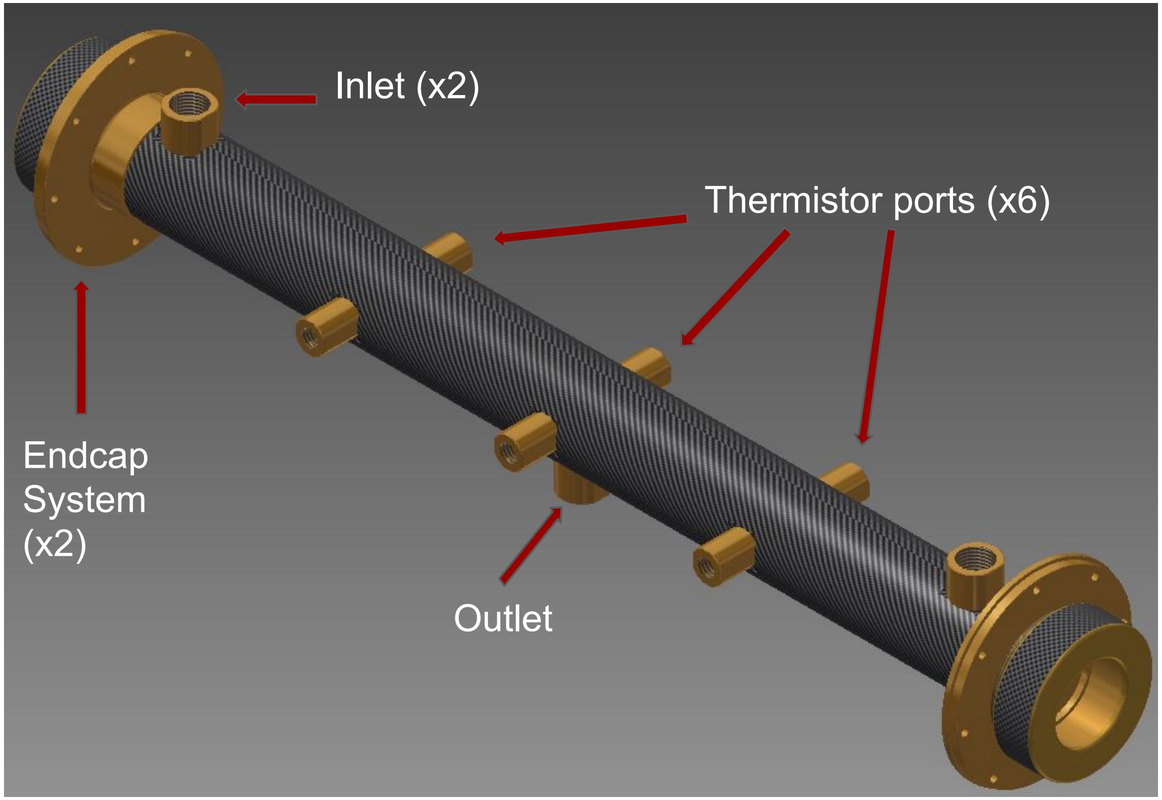
Cavity - Optical configuration

- Material: Zinc Selenide
- Mirror Loss: 60 - 1000 ppm
- M_1: 200 cm; 300cm
- M_2: 1000 cm; 400 cm
- Mirror diameter: 1.5in; 2in
- Volume: < 1 liter



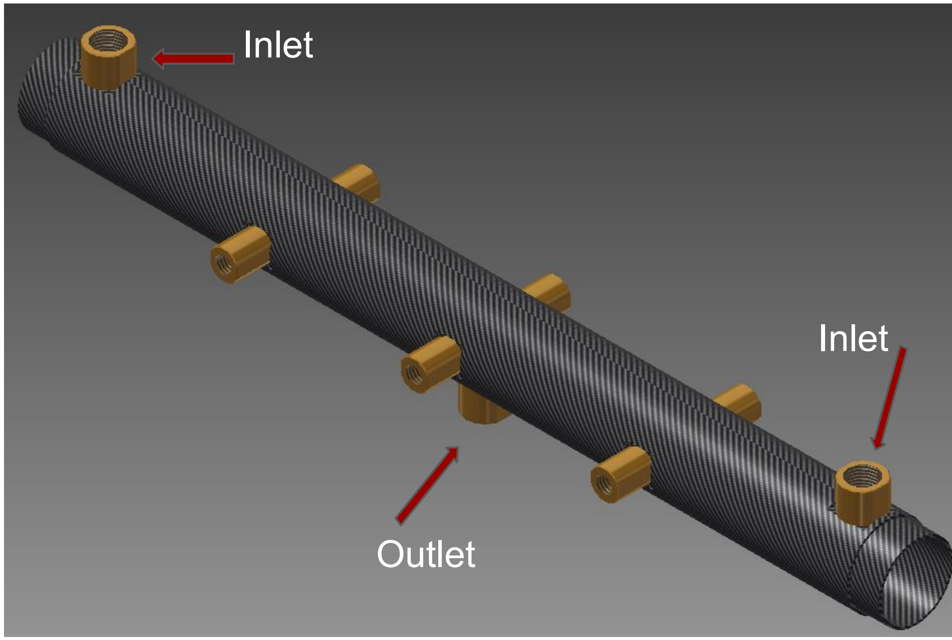


Cavity - Structure



- **Carbon-Fiber tube**
  - **Low mass**
  - **Low volume**
- **Cryogenic Epoxy**
  - **Non-reactive with HCl**
  - **-120° F to 120° F range**
- **T and P data for sample**

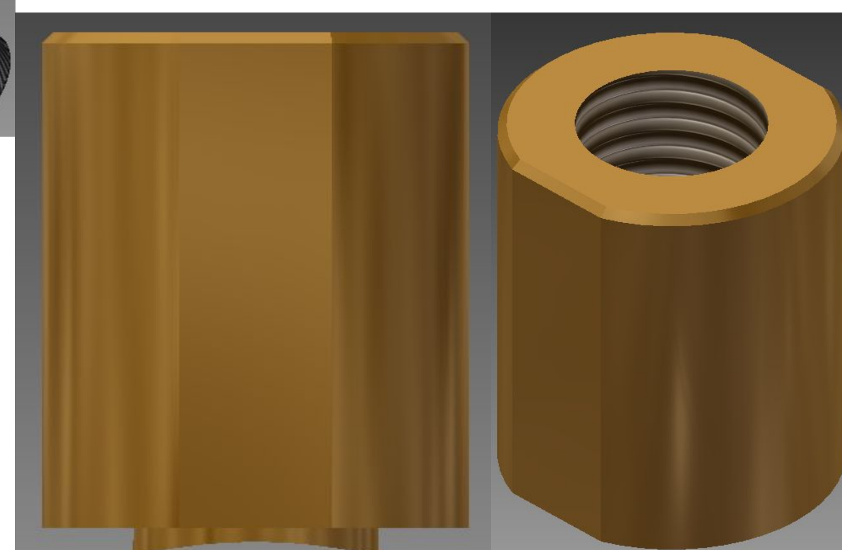
Cavity - Sensors & Ports



Cavity assembly:

- 2 inlets
- 1 outlet
- 6 in-cavity thermistor ports

Thermistor boss



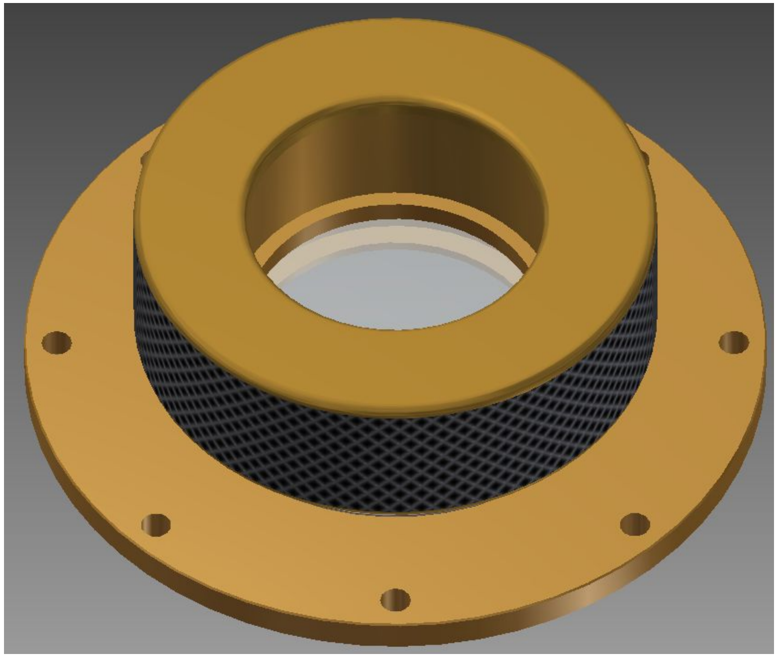
Temperature & Pressure Sensor

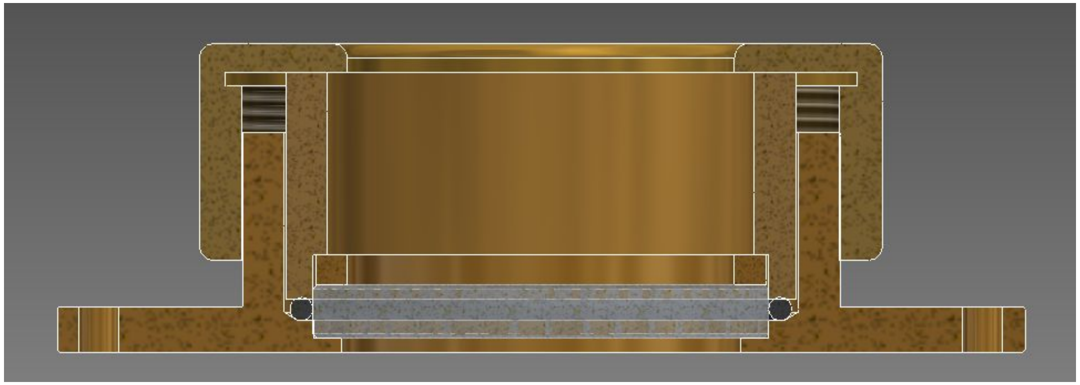
Thermistor housing

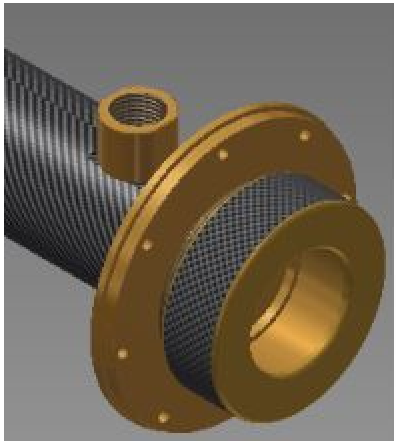
- **9 total thermistors in cavity**
  - **NTC 100KΩ 1% bead**
  - **6 along length of cavity**
  - **1 at each inlet and outlet**
- **1 thermistor on surface of cavity**
  - **Acts at temperature control for 2 thermofoil heaters**
- **1 pressure sensor located at outlet**
  - **Absolute pressure transducer, 0-5Vdc output, cable connection**
  - **Supply voltage: 10-30Vdc @ 10mA**

Pressure probe

End Cap System







Detector

1. Scientific Context
2. System Overview
3. Design Details
    a. Laser
    b. Cavity
    c. **Detector**
    d. Pump
    e. System Wide Design
4. Next Steps

System Diagram - Detector(s)

ICOS Detector Subsystem Diagram

Cooled Detector

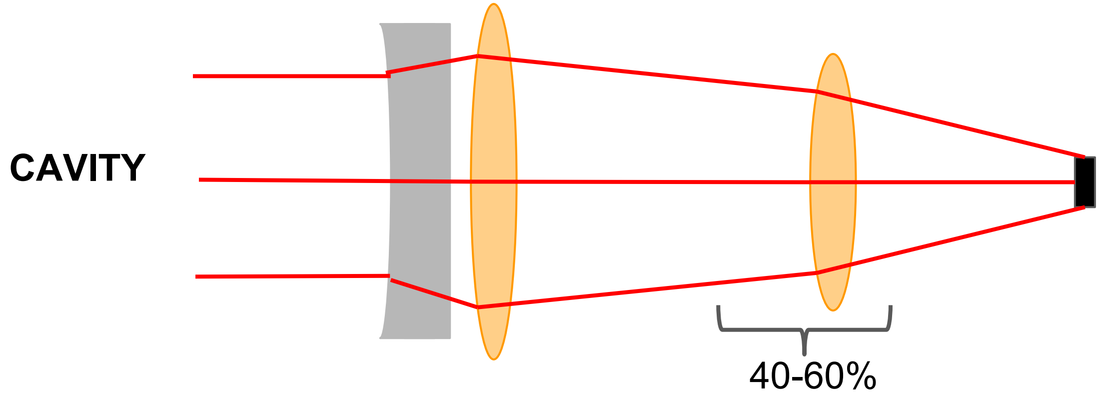
- Cooled Detector subsystems
  - Lenses
  - Detector + Cooling (integrated)
  - Pre-Amp
  - Heat sink/fan

- Etalon Detector subsystems
  - Etalon Crystal
  - Detector (uncooled)
  - Pre-Amp

Post-Cavity Lens Selection

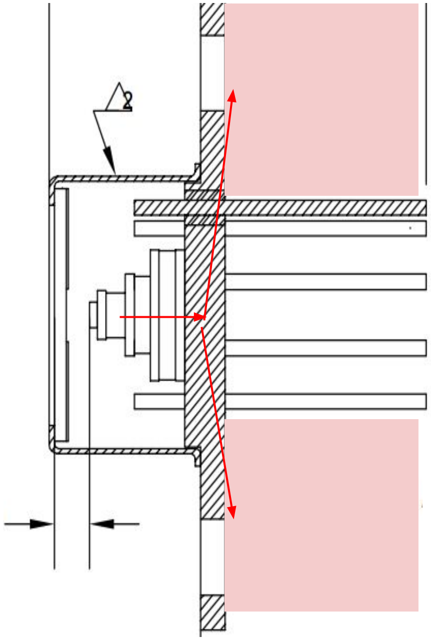
We selected three post-cavity lenses for more than a dozen potential configurations.

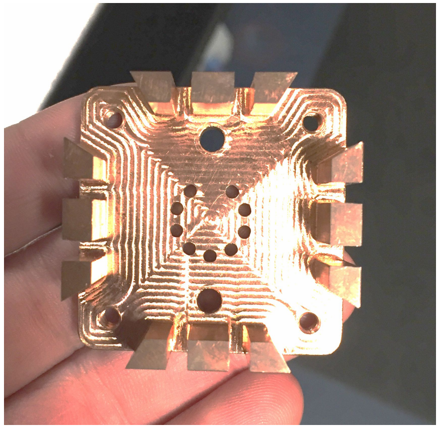
- ZC-PM-25-150
  - Zinc Selenide
  - Positive Meniscus
  - 25.4 mm diameter
  - 150 mm focal length
- ZC-PM-38-200
  - Zinc Selenide
  - Positive Meniscus
  - 38.1 mm diameter
  - 203 mm focal length
- ZC-PM-38-63
  - Zinc Selenide
  - Positive Meniscus
  - 38.1 mm diameter
  - 63.5 mm focal length



Detector Thermal Control

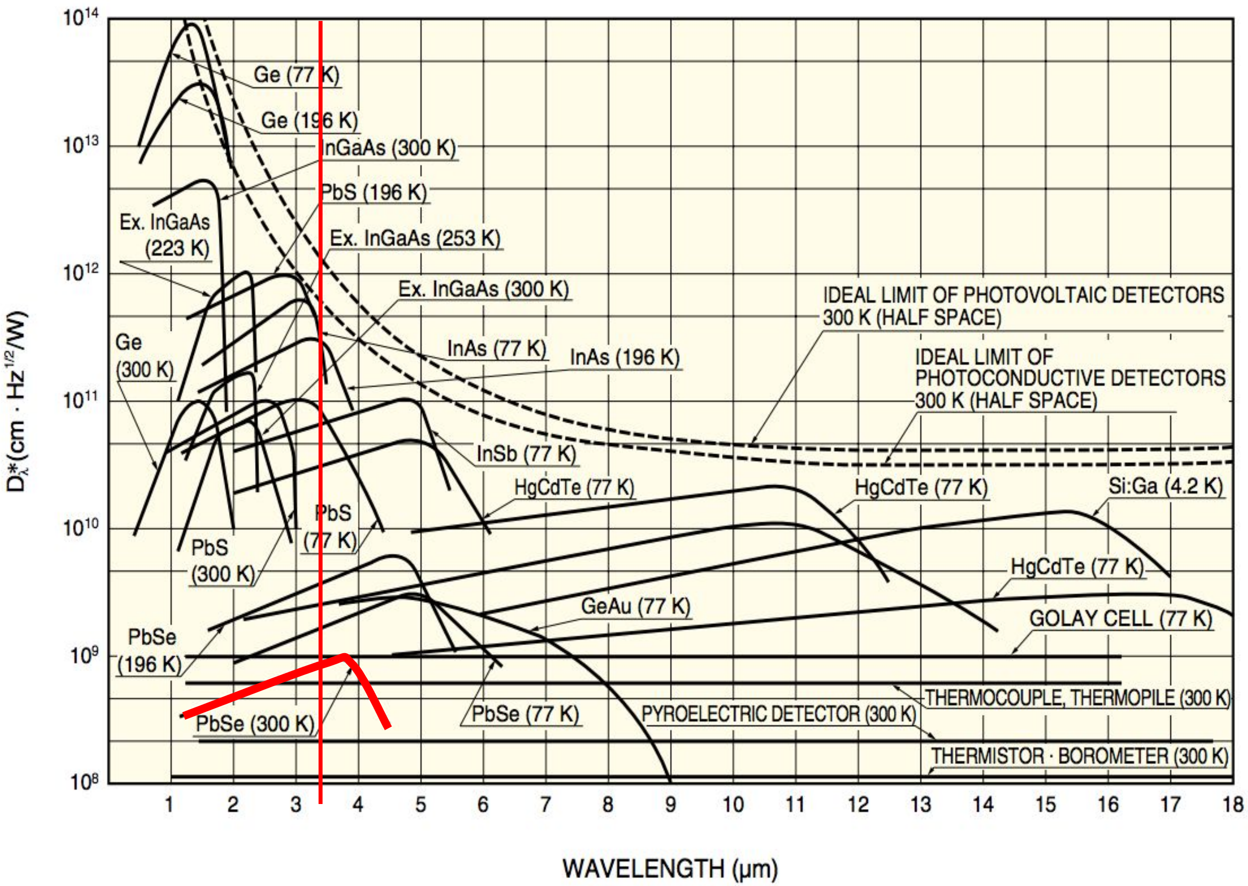
- Material
  - Copper
    - High Thermal Conductivity
    - Machinability
- Heat exchange
  - TEC
  - Overall Container
  - Detector Operating Temp
    - -75 °C





System Diagram - Etalon Detector (ED)

ED Design Criteria - Wavelength



Final Candidate:

- **PbSe uncooled 2mmx2mm**
- **Photoconductive detector from OptoDiode**
- **TO-5 Package, 3-pin pinout**
- **BXP-25**

ED Design Criteria - Time Constant

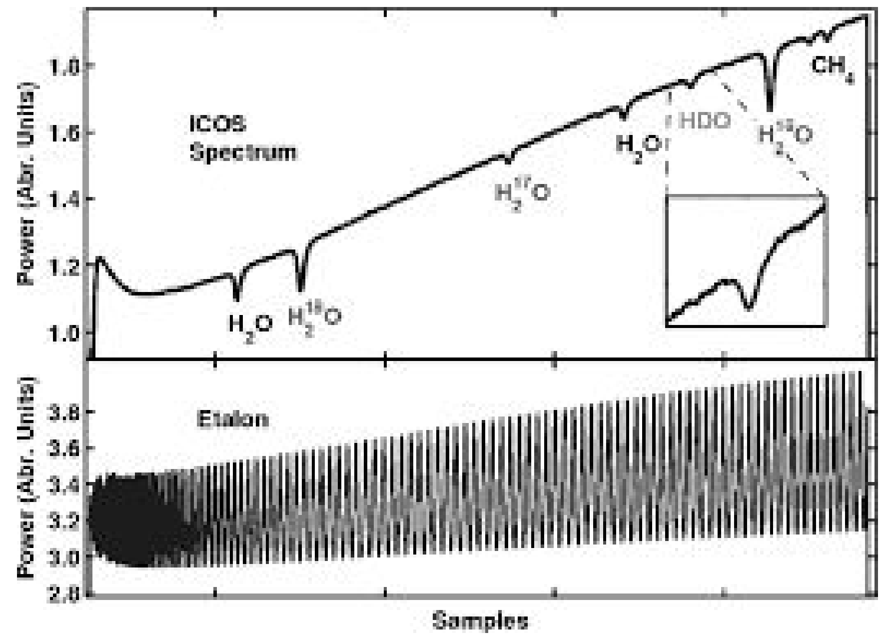
Time for 1 etalon fringe:

$$\frac{t_{full-sweep}}{\Delta\nu_{wavenumbers}} * FSR = \frac{t_{full-sweep}}{\Delta\nu_{wavenumbers}} * \frac{1}{2nL}$$

Assuming $1 cm^{-1}$ in 1ms, L = 7.62cm, n = 4,

t_{fringe} = 16μs

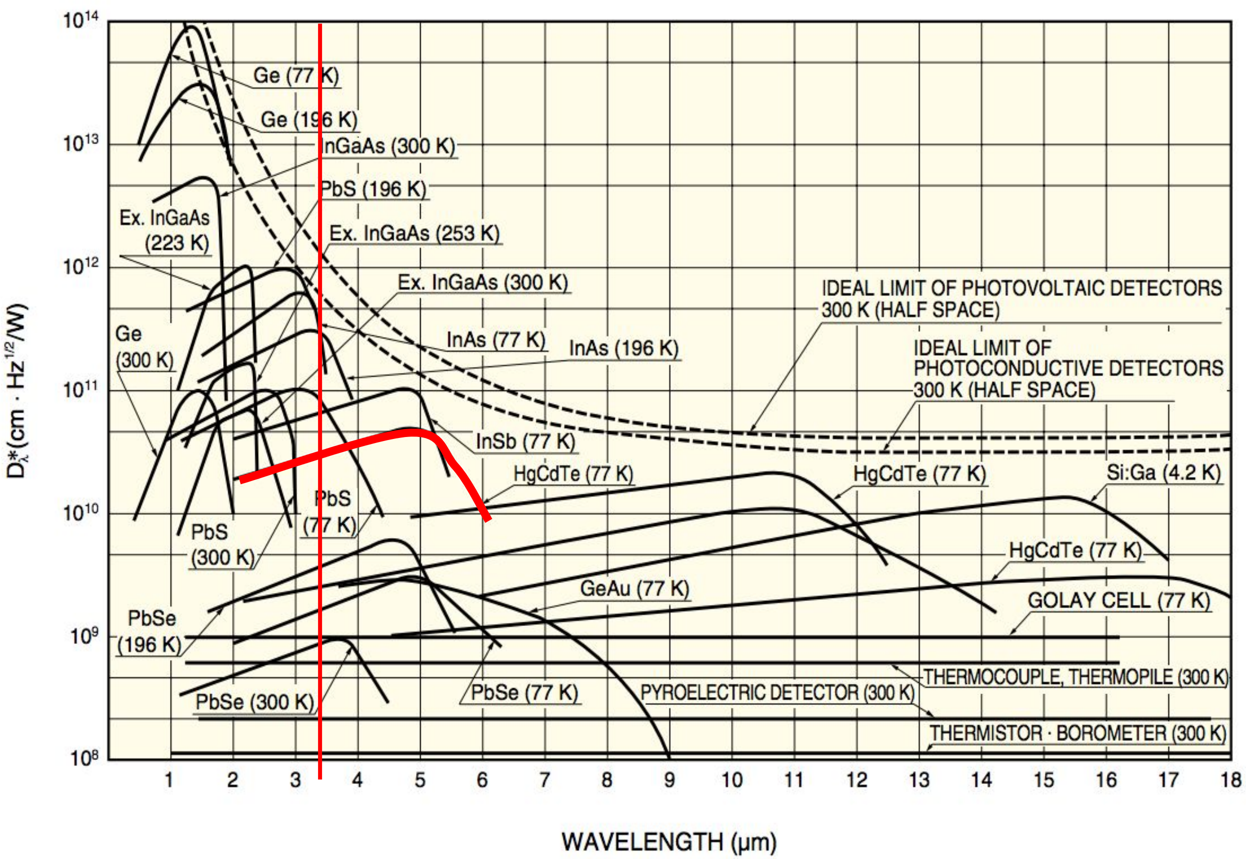
61 fringes per scan



A new cavity based absorption instrument for detection of water isotopologues in the upper troposphere and lower stratosphere. Sayres, David S. and Moyer, E. J. and Hanisco, T. F. and St. Clair, J. M. and Keutsch, F. N. and O'Brien, A. and Allen, N. T. and Lapson, L. and Demusz, J. N. and Rivero, M. and Martin, T. and Greenberg, M. and Tuozzolo, C. and Engel, G. S. and Kroll, J. H. and Paul, J. B. and Anderson, J. G., Review of Scientific Instruments, 80, 044102 (2009), DOI:http://dx.doi.org/10.1063/1.3117349

System Diagram - Cooled Detector (CD)

CD Design Criteria - Wavelength



Final Candidate:

- **HgCdTe 4-stage TEC-cooled 2mmx2mm**
- **Photoconductive detector from Infrared Associates**
- **TO-66 package, 8-pin pinout**
- **MCT-4.5-TE4-2.00**

CD Design Criteria - Time Constant

Ringdown Time - required time for laser beam to complete the full path length.

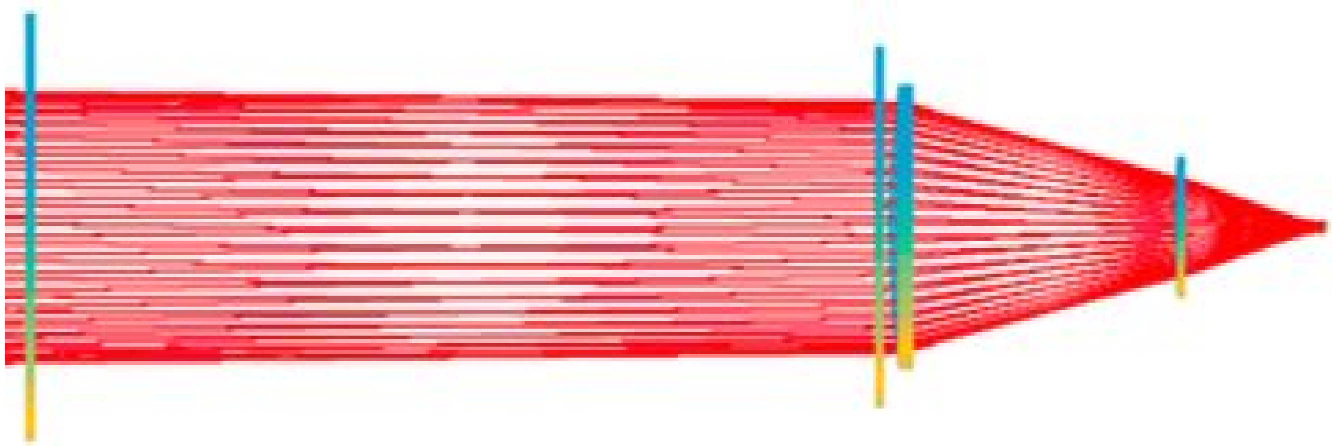
Effective Path Length - length of cell multiplied by number of passes of laser.

$$\ell_{path} = \ell_{cell}/L_{loss}$$

$$t_{ringdown} = \ell_{path}/c$$

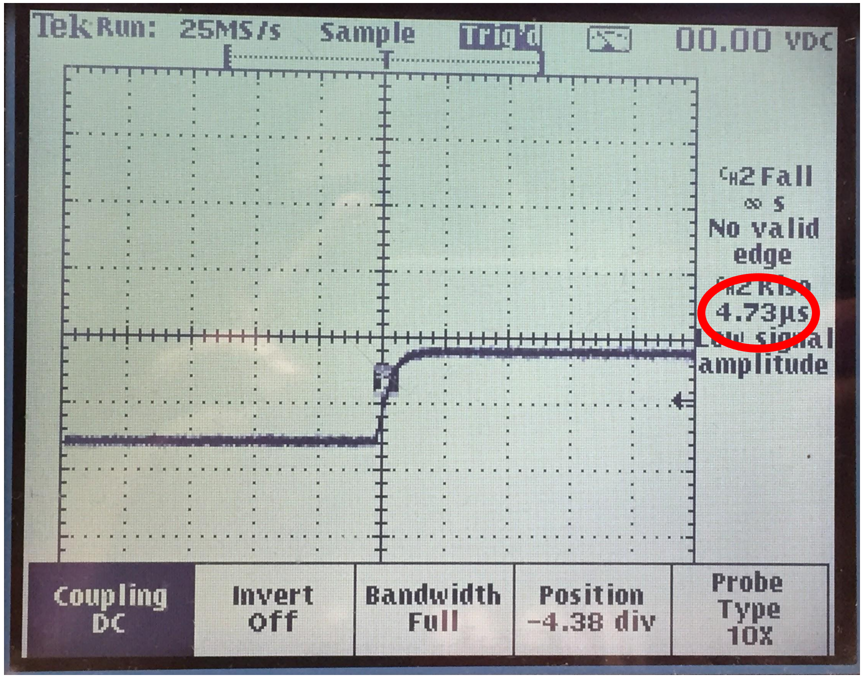
ℓ_{path} = effective path length
ℓ_{cell} = cell length
L_{loss} = 1 - Reflectivity

$$17\mu s < t_{ringdown} < 21\mu s$$

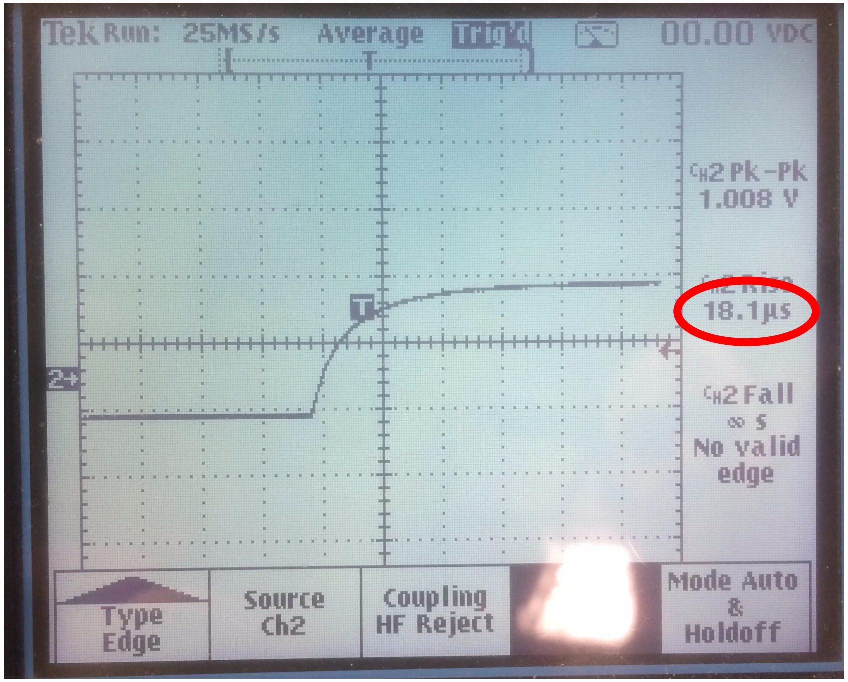


Detector Testing

Etalon Detector



Cooled Detector

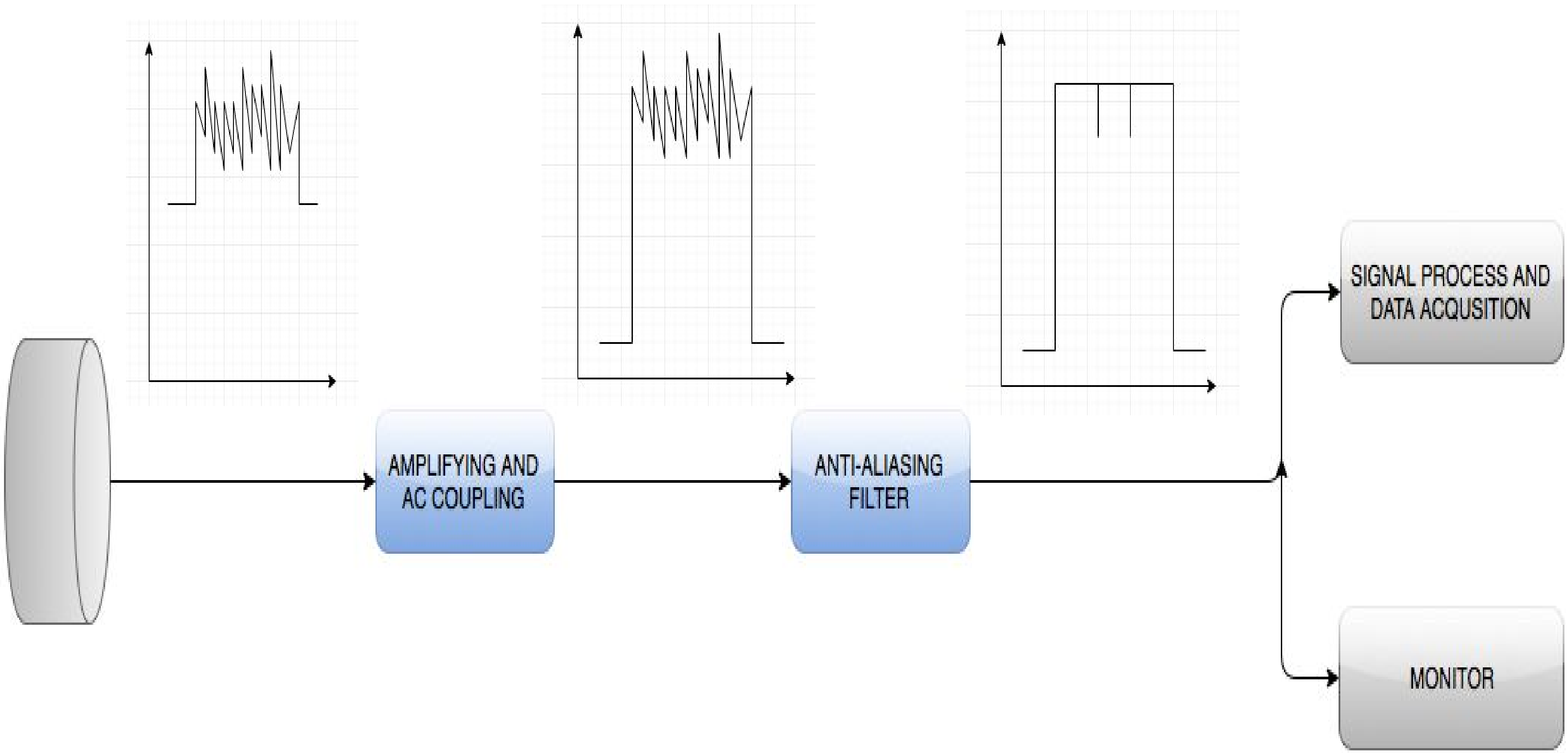


Pre-Amp

Why a pre-amp?

- Amplify detector signal
- Remove DC bias
- Remove noise picked up

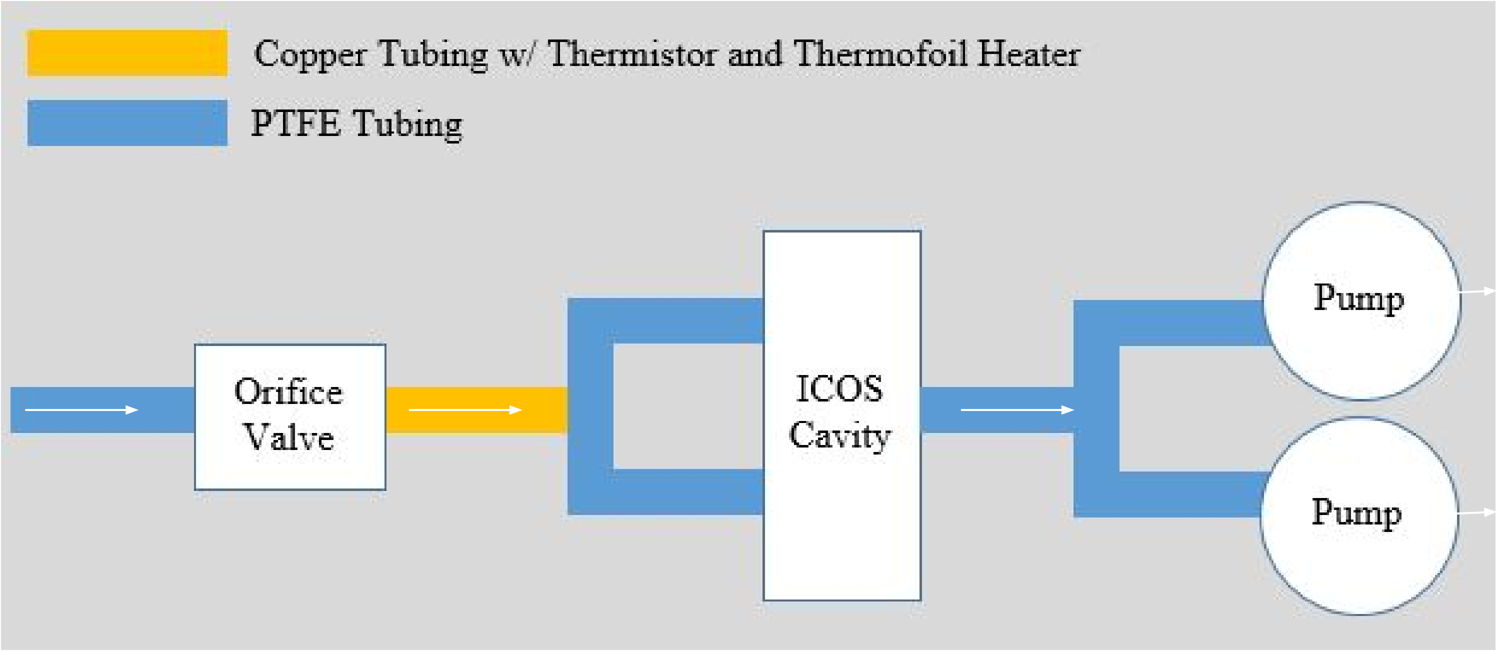
Pre-amp Block Diagram



Pump

1. Scientific Context
2. System Overview
3. Design Details
    a. Laser
    b. Cavity
    c. Detector
    d. **Pump**
    e. System Wide Design
4. Next Steps

Pump - Flow Setup



System Diagrams - Pumps

Pump - Requirements

Minimum Flow Rate	90 L/min
Vacuum Pressure	40 torr or 53 mbar
Max Pressure Differential	165 torr or 220 mbar
Max Power	500 W
Max Weight	10 kg

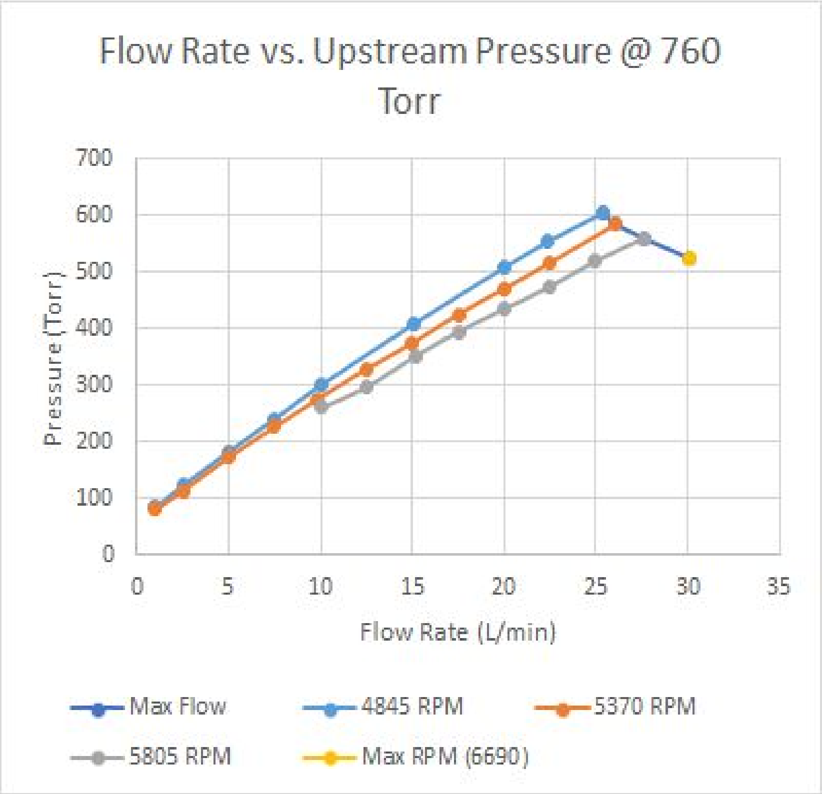
- **Flow Rate > 1.5 L/s = 90 L/min**
    - **Cavity volume of ~1L**
    - **1Hz sampling rate (at the minimum)**
- **Brushless DC Motor**
    - **prevents arcing**
- **Continuous flow for steady data sampling**

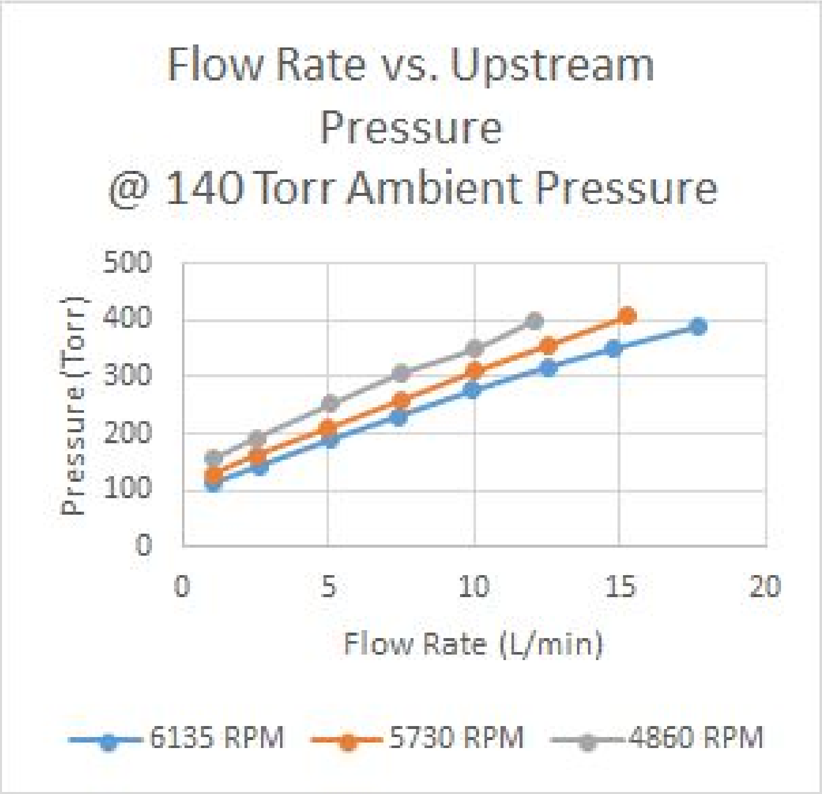
Pump - Selection

SVF-x-50

Pump	SVF-E0-50 (Scroll Labs)	T2-01 (Parker)	KNF N838 (Old Pump)
Pump Type	Scroll	Diaphragm	Diaphragm
# of pumps	2	2	1
Weight (kg)	1.0 (2.0 total)	1.38 (2.76 total)	3
Volume of Unit	0.968 (1.936 total)	1.78 (3.56 total)	1.5
Max Power Usage (W)	95±3 (190±6 total)	69 (138 total)	101
Vacuum Pressure (mbar)	≤1.0 (ultimate)	406 (differential)	90
Flow Rate/ Unit (S.L/min)	45	66	60
Price per Unit ($)	2590.00 (5180)	809.00 (1618.00)	--

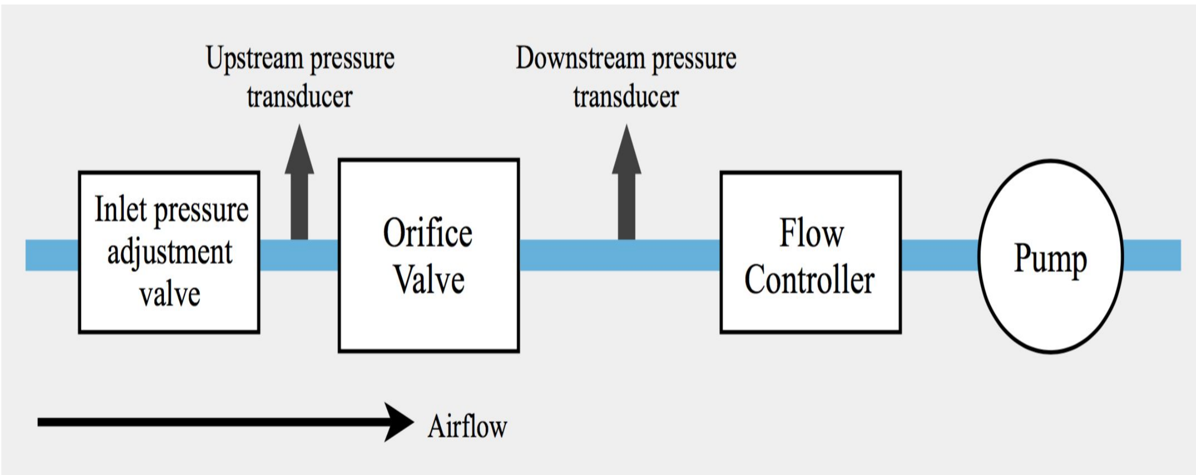
Pump - Pump Characterization

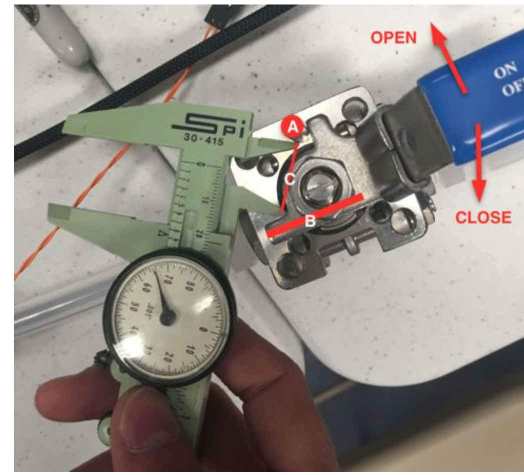


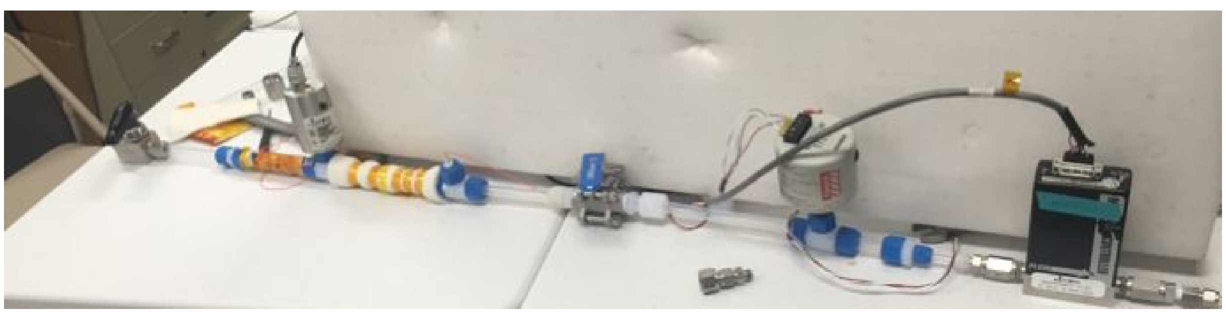


Pressure and Temperature Control

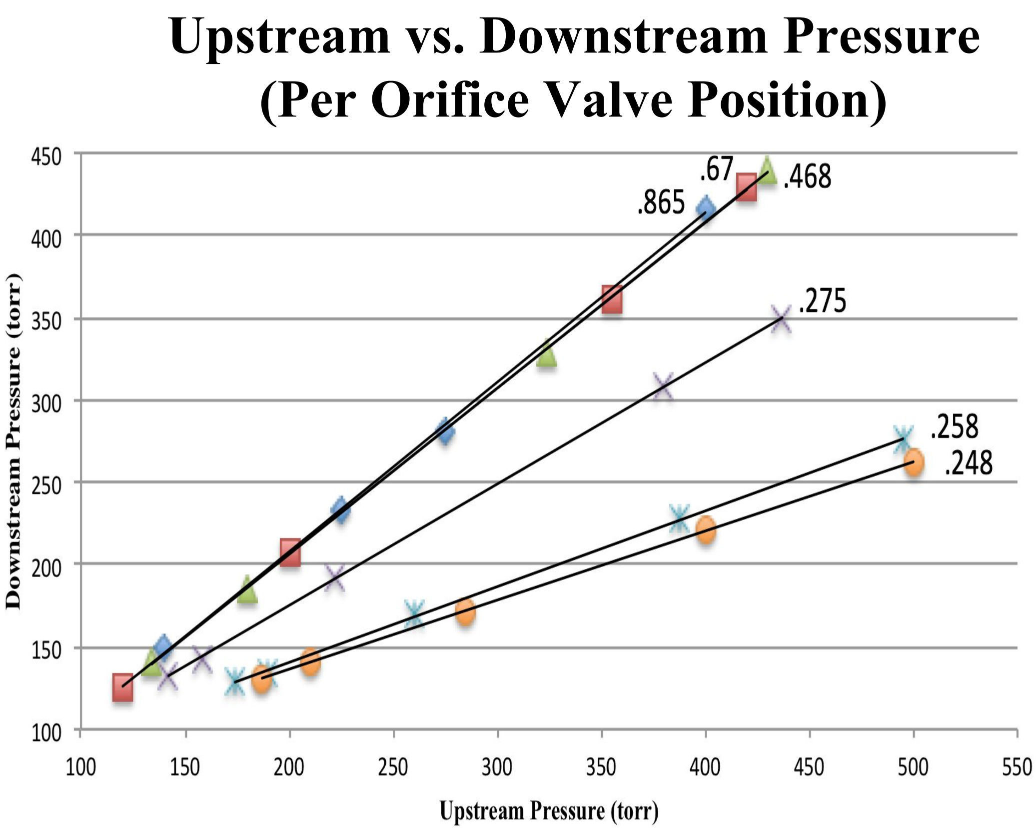
Pump - Orifice Valve Testing



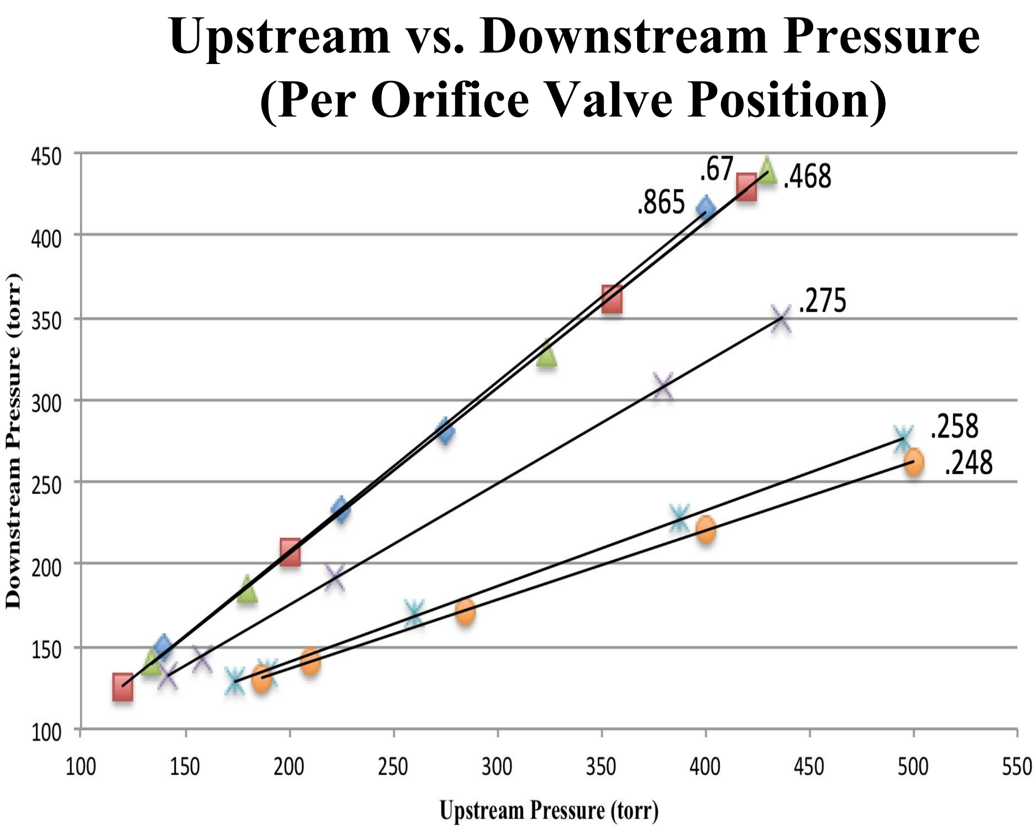


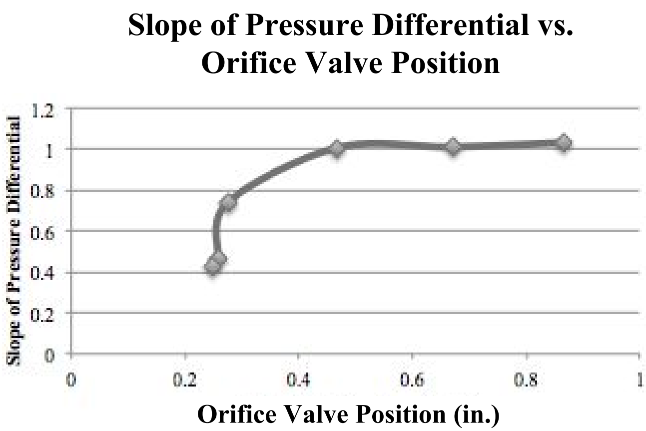


Pump - Orifice Valve Testing

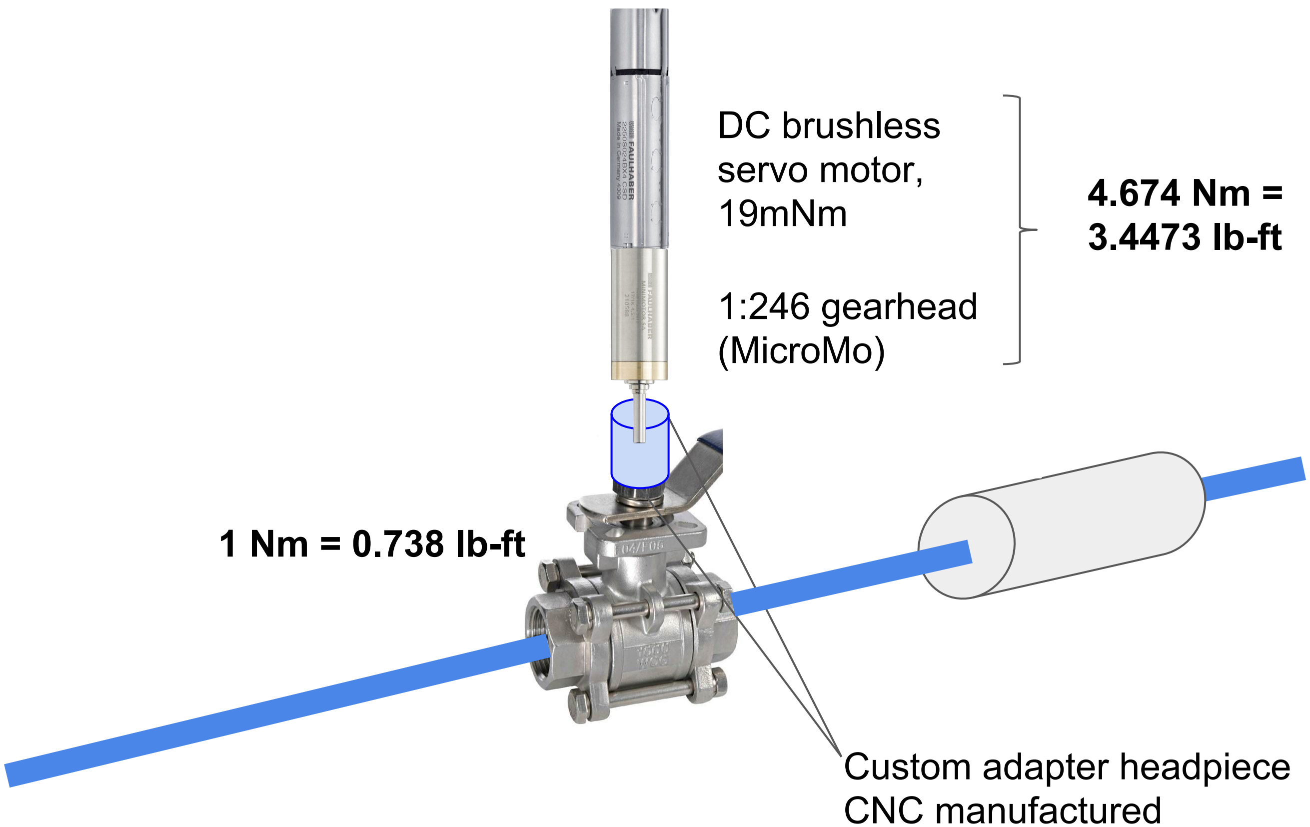


Pump - Orifice Valve Testing

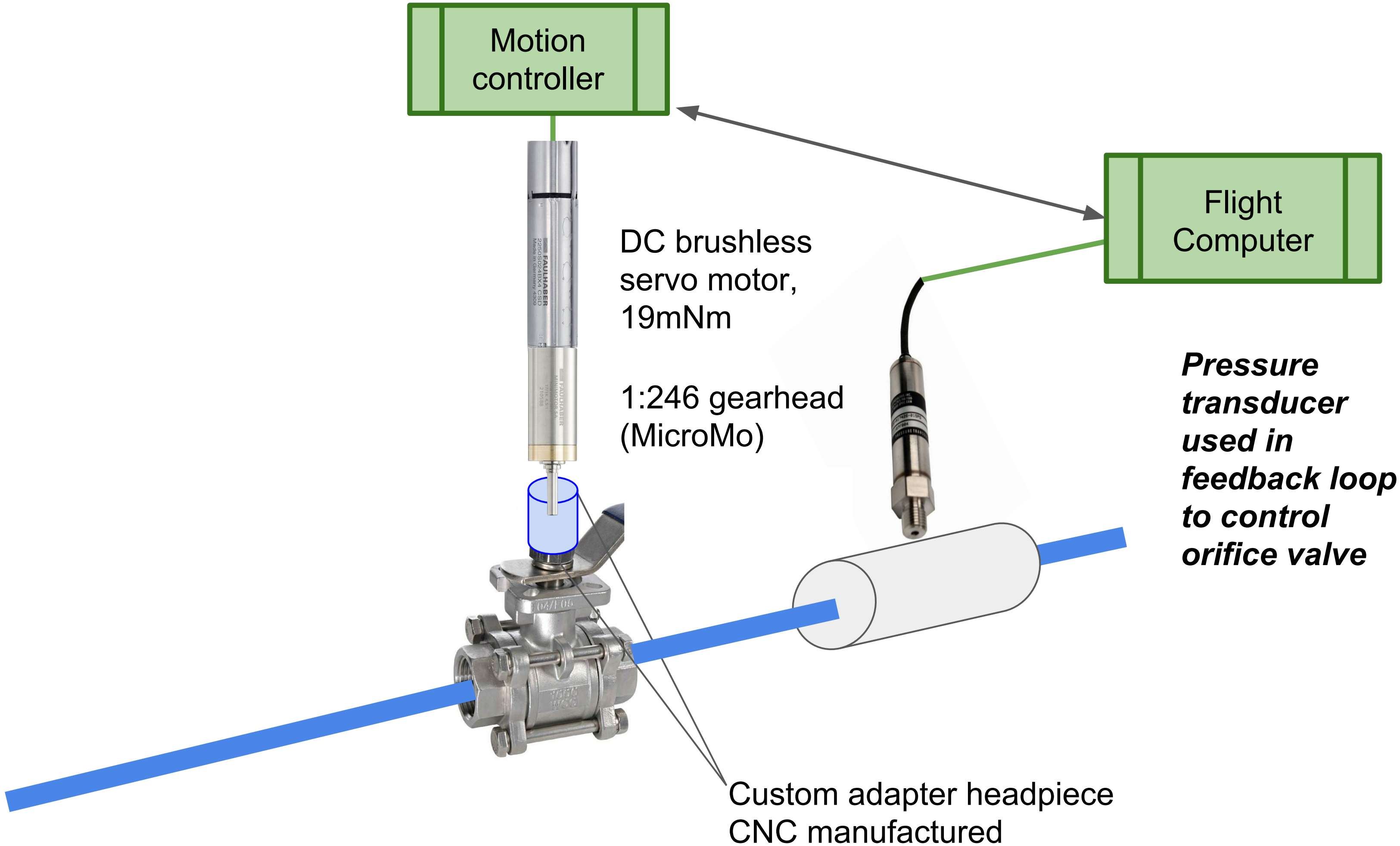




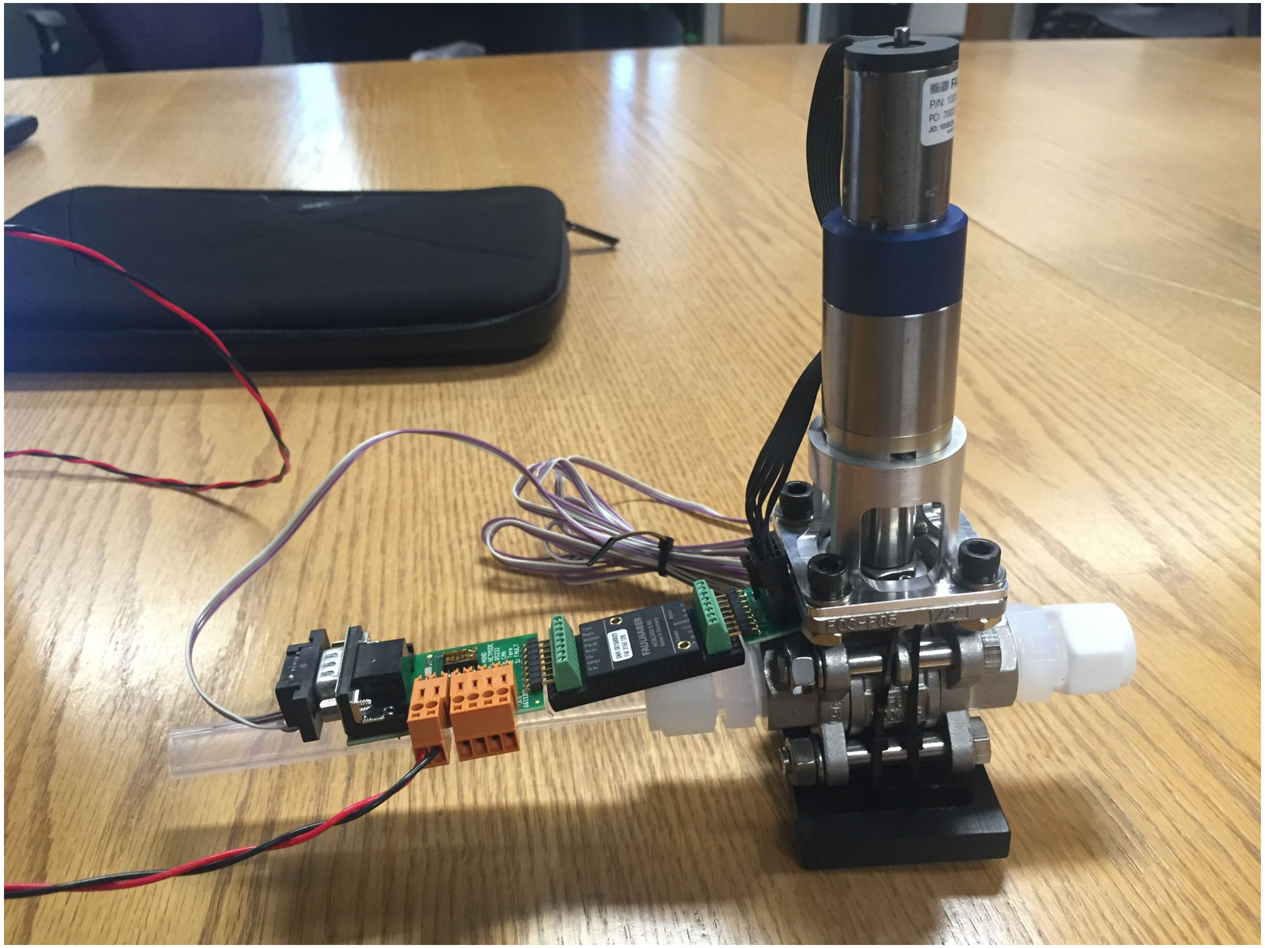
Pump - Orifice Valve Feedback



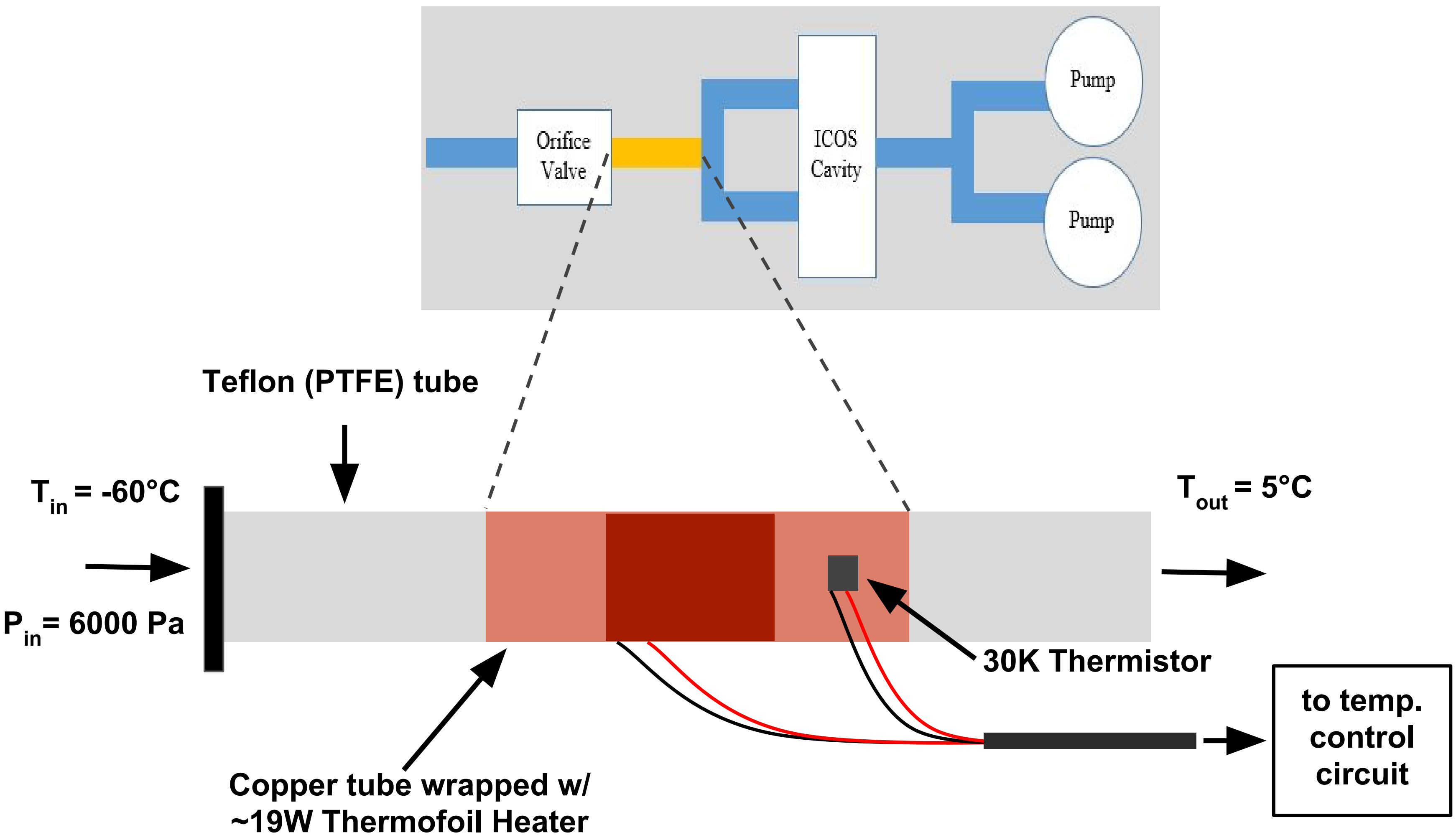
Pump - Orifice Valve Feedback



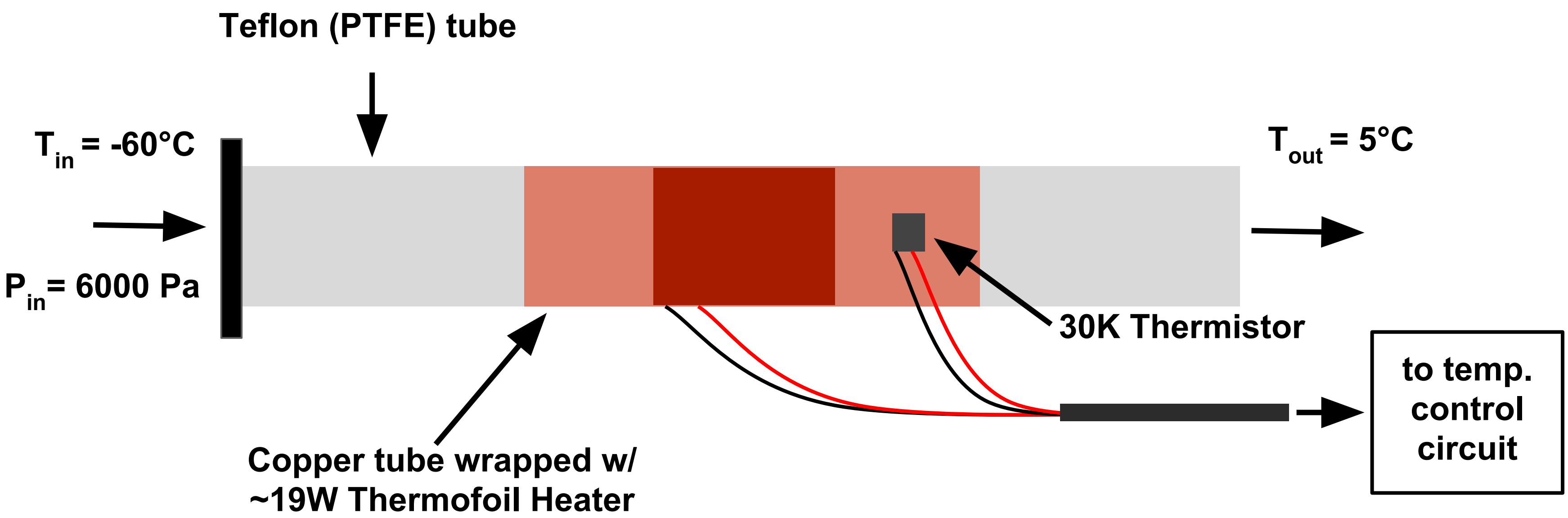
Pump - Orifice Valve Feedback



Pump - Air Temperature Control

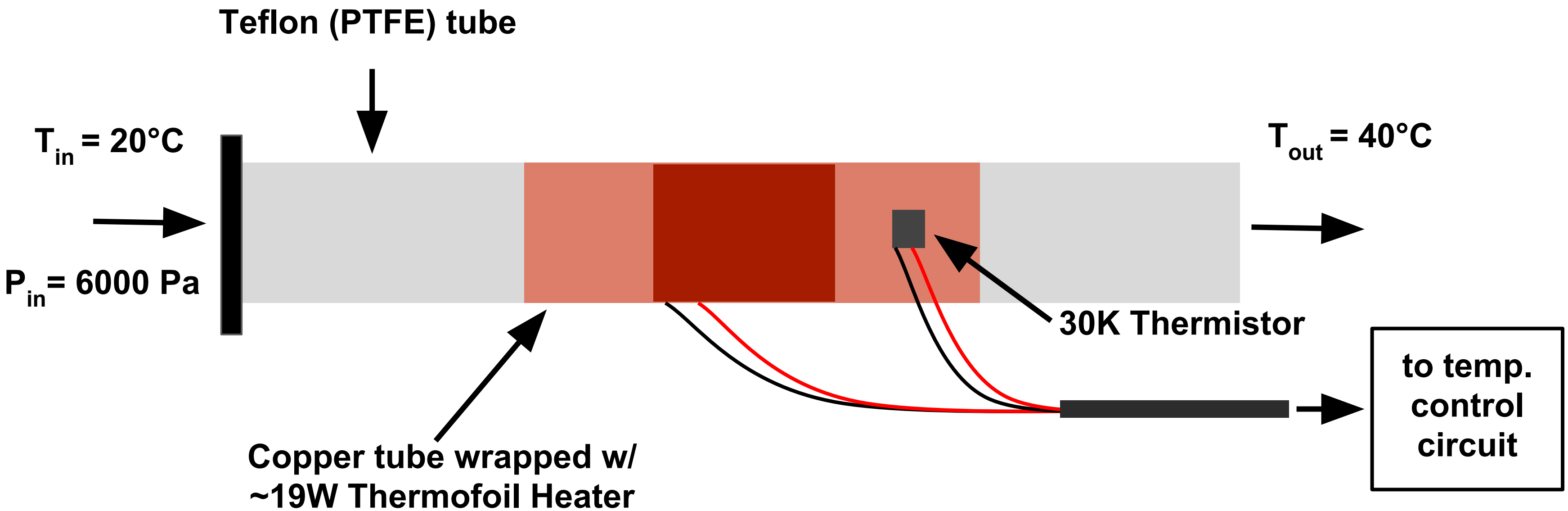


Pump - Air Temperature Control



2.0x0.5 in
@ 25 W/in^2

Pump - Air Temperature Control

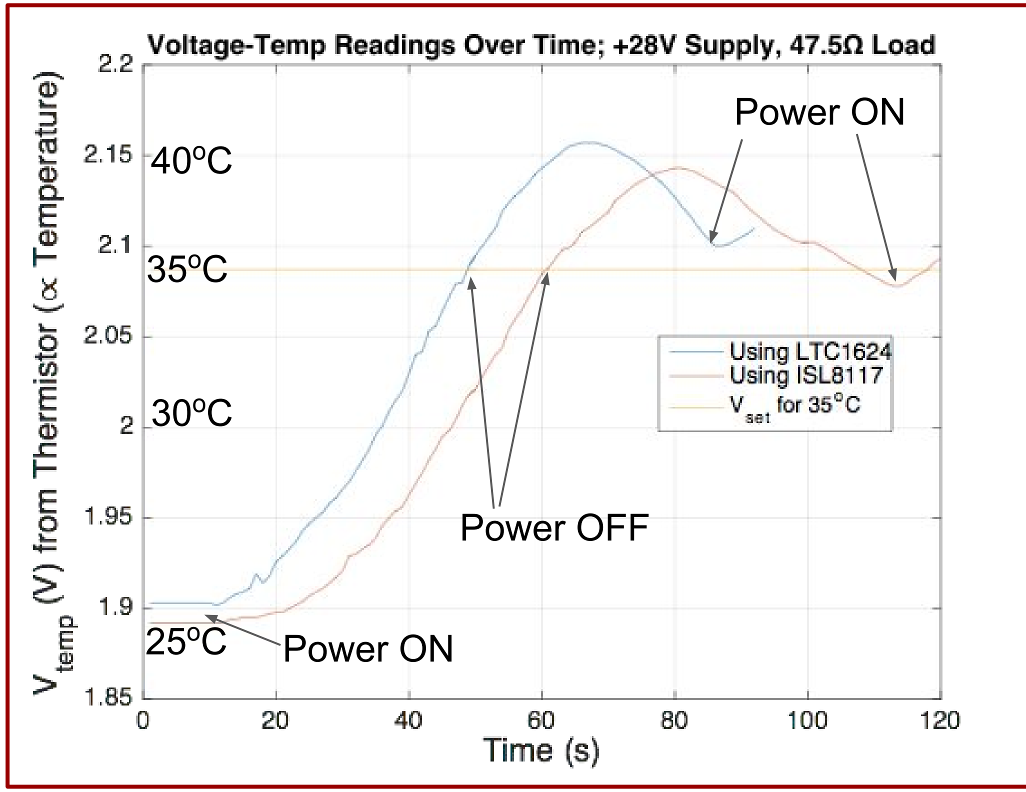


Testing indicates:
- The heater is powerful enough for our needs
- Cu tube ΔT = 101°C
- Downstream air ΔT is not pressure-dependent

2.0x0.5 in
@ 25 W/in²

Pump - Inlet Temperature Control

- Tested switching voltage regulators on the PI board using 47.5Ω power resistor load with thermistor attached
- ISL8117 showed improved performance over LTC1624 (older version)
  - Low power output when reading near set point, improved timing for ON
- Next steps: redesign board for more seamless integration of new chip, tune PID for full system



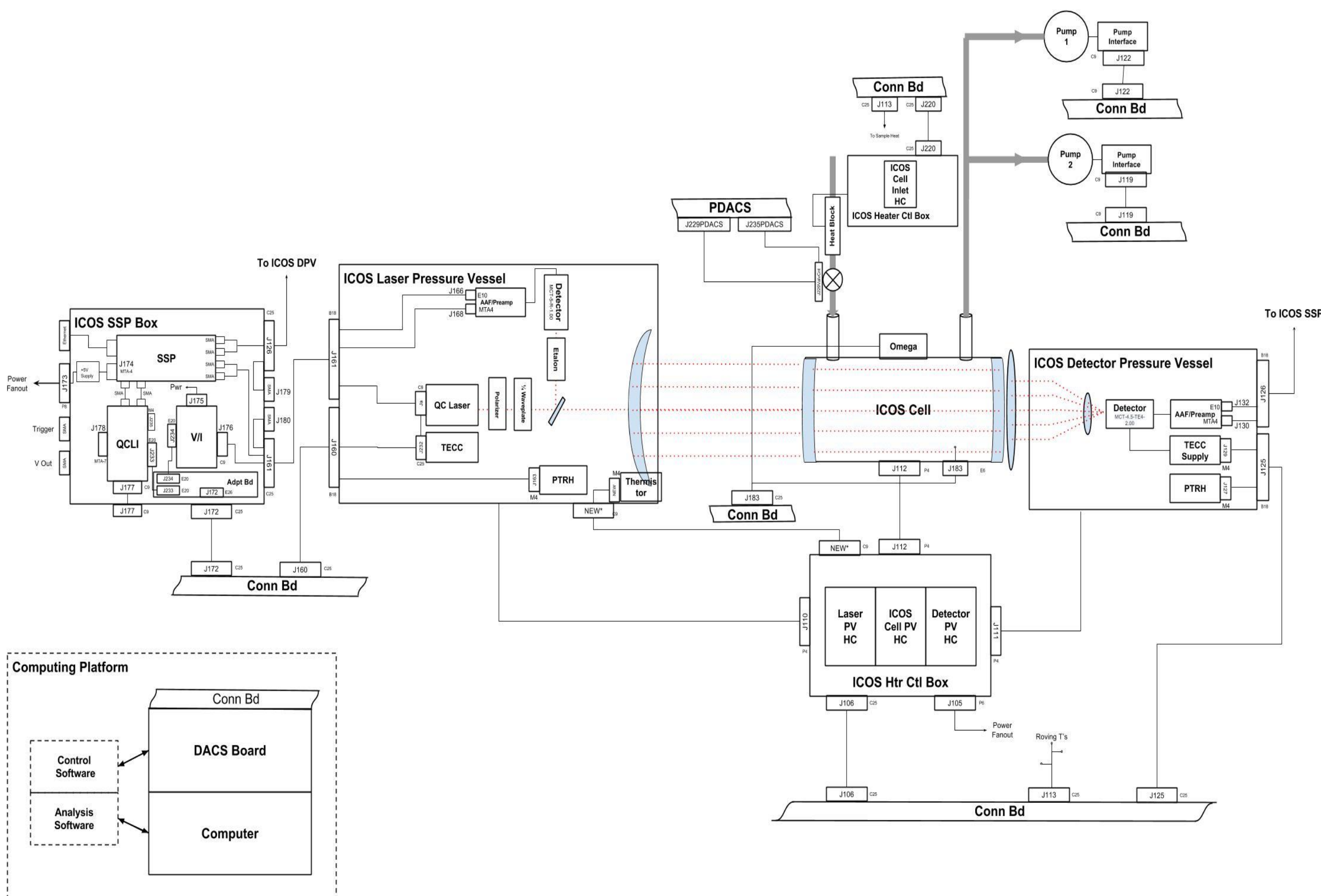
System Wide Design

1. Scientific Context
2. System Overview
3. Design Details
    a. Laser
    b. Cavity
    c. Detector
    d. Pump
    e. **System Wide Design**
4. Next Steps

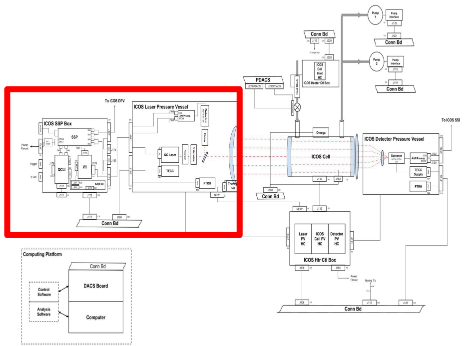
System Wide - Budgets

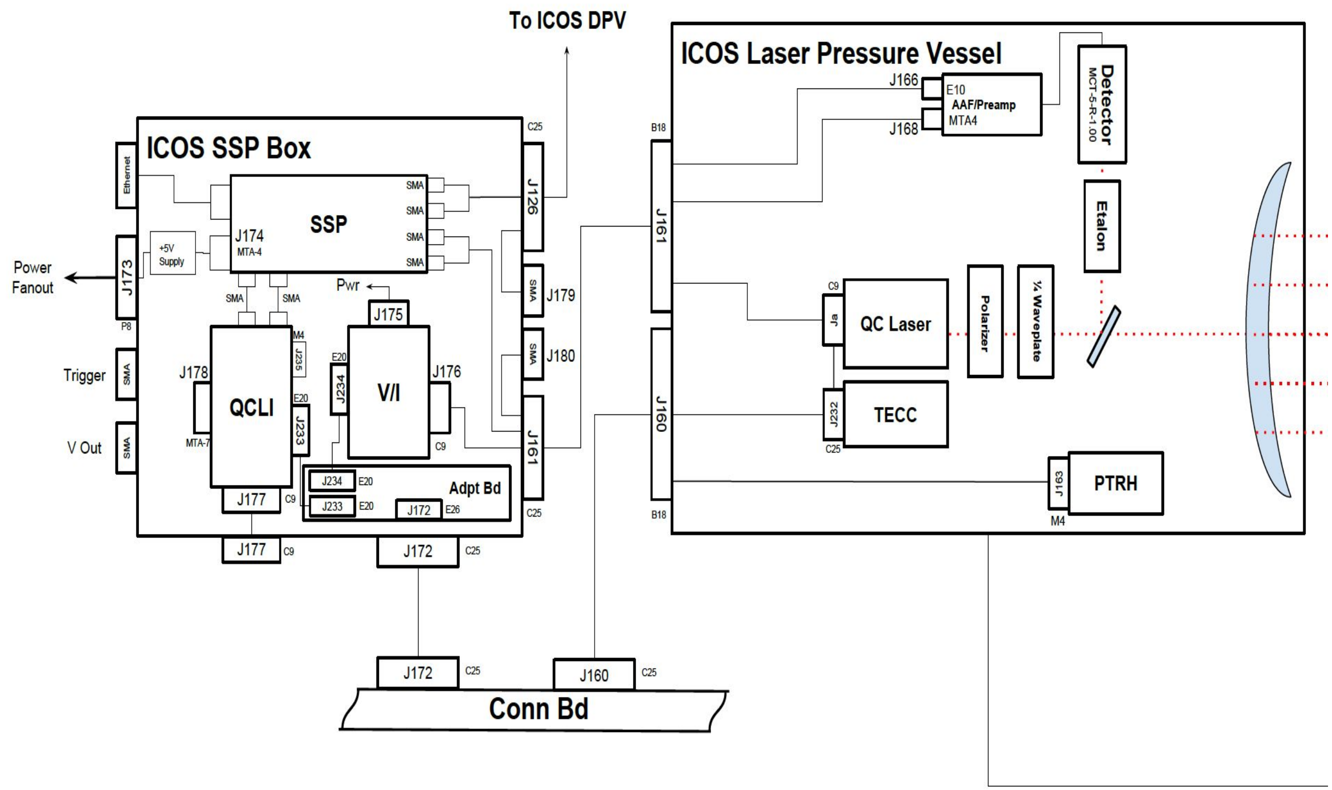
System	Power Est (W)	Mass Est (kg)	Volume Est (L)
Pump	215	3.10	2.26
Cavity	39	1.20	2.50
Laser (Driver)	1	0.23	0.02
Laser (Fore-optics)	0	2.27	8.85
Detector	1	2.60	4.56
Additional Housings	0	10.00	2.00
Total	256 (41 not incl pump)	19.40	20.19
Design Goals	<500 (60 not incl. pump)	<25 kg	<25 L

System Wide Interconnect Diagram

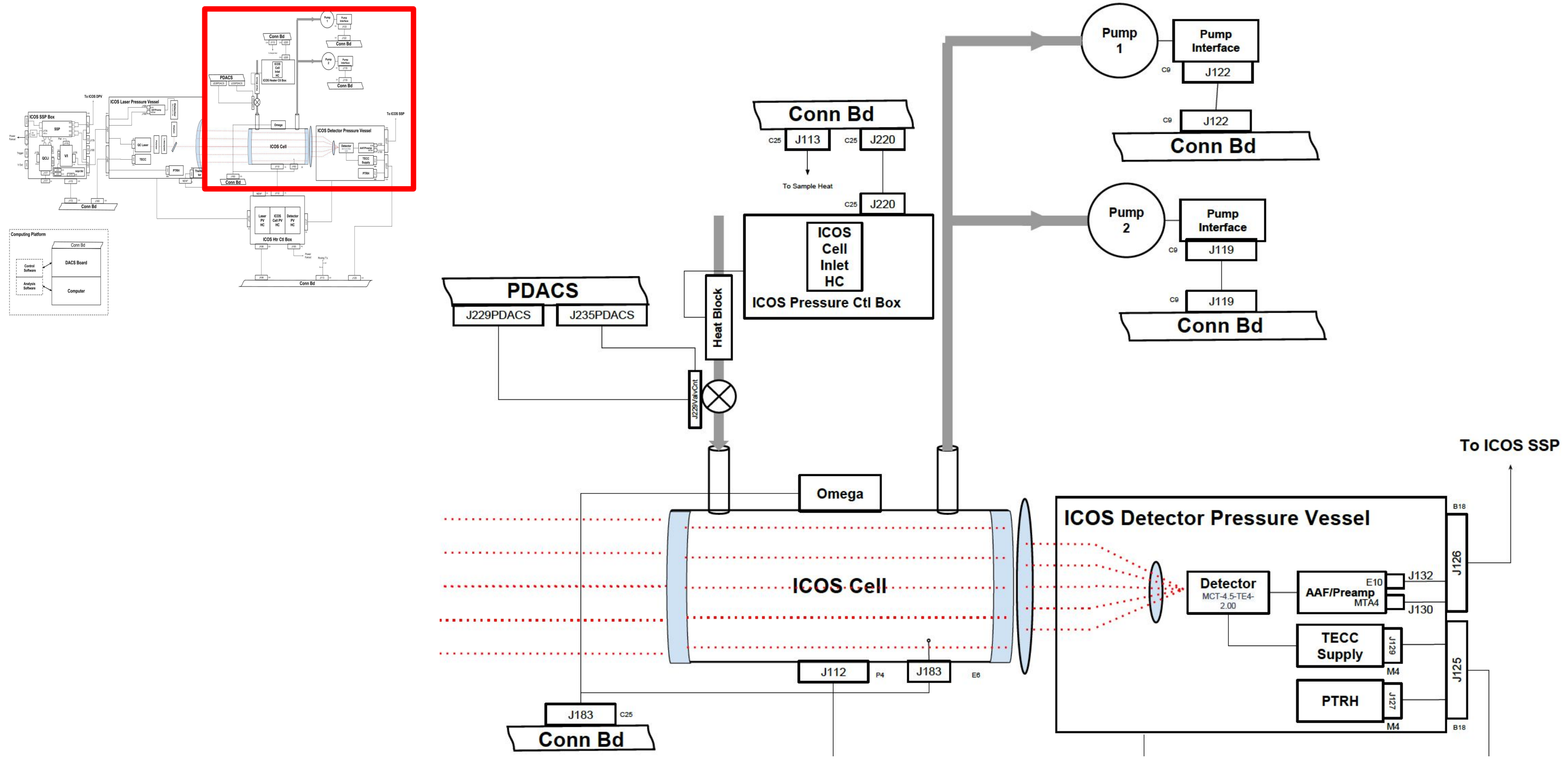


System Wide Interconnect Diagram





System Wide Interconnect Diagram



System Wide - Flight Computer

Hardware ⇄ **Software**

- Wires
- Connectors
- Connector Board
- DACS Board – Data Acquisition and Control System Board
- Computer

- Data Collector
- Telemetry Buffer
- Data Clients
  - TMCalgo – Data Analyser
  - Computer Displays
- Commands

Next Steps

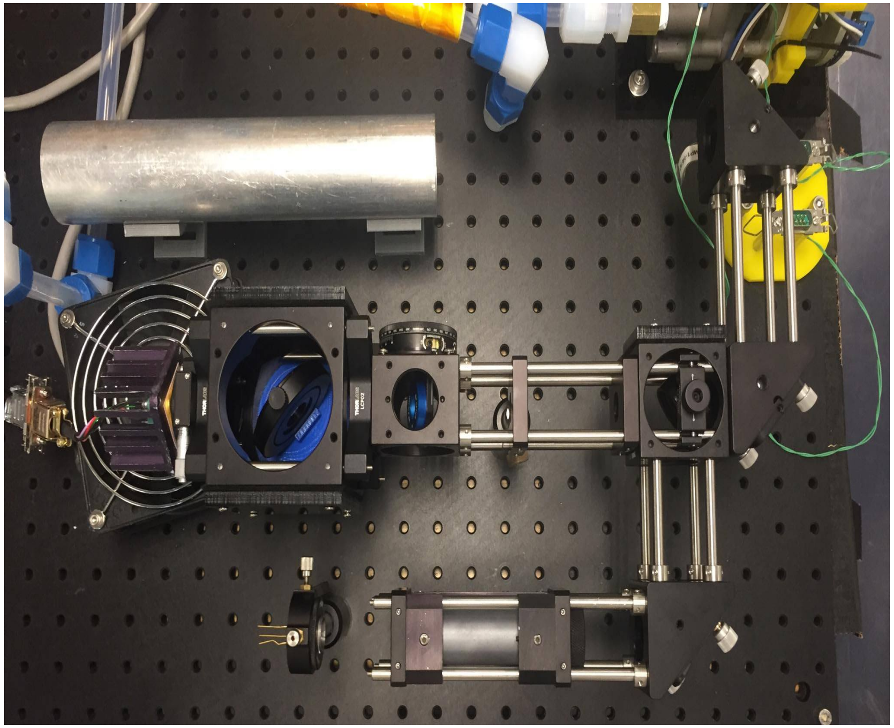
Improvements

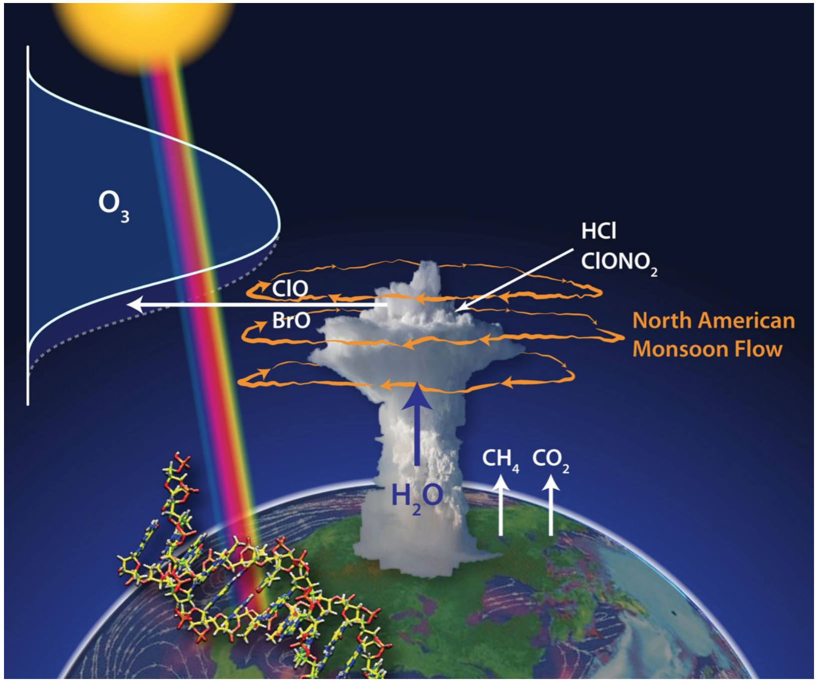
- *Pump*: lighter, smaller pump. Higher flow rate than older ICOS systems
- *Fore optics*: Now use independent mounting for all components, telescope to decrease mirror spotting, and a fully incorporated, minimized cage system for modularity and ease of assembly
- *Laser Driver*: simplified to one board, faster response time to voltage changes
- *Cavity*: smaller, reduced weight (hardware), updated locations of temperature probes
- *Simulation*: New MATLAB cavity script, refined ray tracing model
- *Sensing*: Pressure feedback loop for flow control
- *Detector*: Cheaper, faster etalon detector

Next Steps

- NASA Undergraduate Student Instrument Project (USIP)
- Summer 2016: Independent research (5 students)
- ES100 - Theses (8 students)
- ES96 - Spring 2017
- Spring/Summer 2017: NASA Balloon Flight for HCl and Ozone

HCl Detection Instrument





Acknowledgements

I. **ES96 Teaching Staff**
   A. **Professor Jim Anderson, Karena McKinney, Marco Rivero, Mike Greenberg, Norton Allen, Terry Martin**
II. **SEAS Teaching Labs Staff**
   A. **Maddie Hickman, Joe Huggard, Andreas Haggerty, Elaine Kristant**
III. **Machine Shop**
   A. **Mike McKenna**