Progress Report

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Metal oxide sensing materials integrated with high-temperature optical sensor platforms for real-time fossil fuel gas composition analysis

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Program Overview

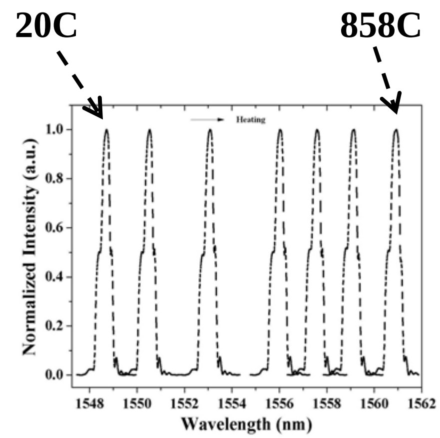
- University Coal Research Program
- Starting September 2010 (18-Months)
- Two Key Components:
  - Development of High-Temperature Sensor Platforms
  - Integration and Application of Functional Metal Oxide for Gas Sensing
- Three fiber sensor platform techniques
- Five journal publications
- Two industrial collaborations

Research Overview

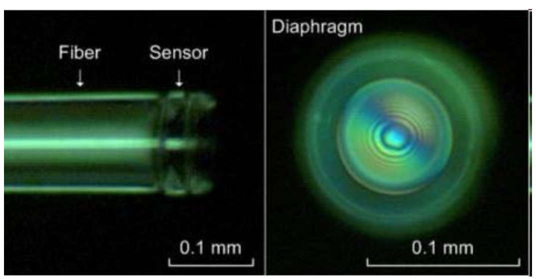
- **Point fiber sensor for high-T**
  - High performance high-T FBG point sensor (>800C) at $20/sensor
  - Chemical regenerative process
  - Integration with SnO_2 on D-Shaped fiber for NH_3 sensing
- **Distributed fiber chemical sensor**
  - First-ever demonstration of distributed fiber chemical sensing
  - Rayleigh-scattering OFDR technique
  - 1-cm spatial resolution
  - Integration with Pd/PdH for H_2 sensing
- **Coherent Anti-Stokes Raman (CAR) sensor**
  - One-laser pulse CARS measurement using temporal pulse shaping
  - Integration with hollow-core fiber
  - >1000 enhancement beyond spontaneous Raman
  - Aiming for CO_2 and C_2H_6 measurement

Topic I: Point Fiber Sensor for high-T

- Current State of the Art
  - Single-mode F-P interferometer on the fiber tip
  - Fiber Bragg grating in single-mode fiber by the ultrafast laser fabrication
- Challenge
  - Packaging is key (Expensive and difficult)
  - Poor spectral performance
  - **Expensive**

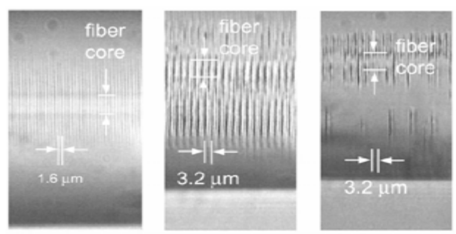


F-P Sensor



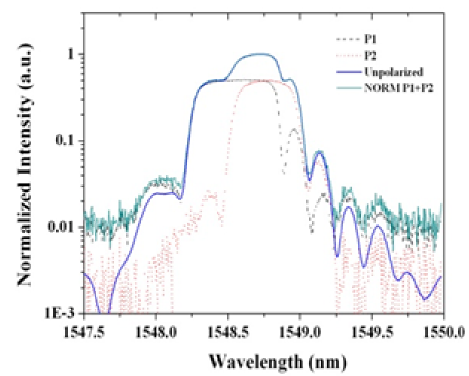
Dr. Wang's group at VT

Type II FBG



Type I IR 125 fs grating	Type II IR 125 fs grating	Type II IR 1.6 ps grating

CRC Canada



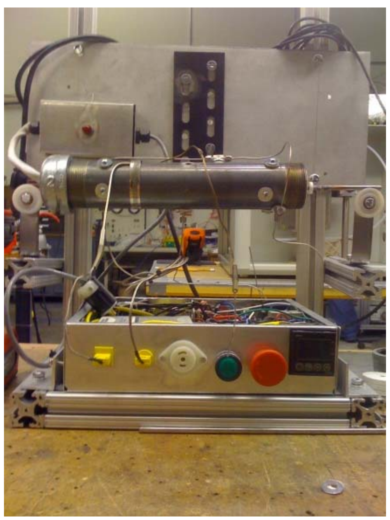
Technique: Chemical Regenerative Process

- Turn a dollar commercially off-shelf fiber Bragg grating ($20) into a high-temperature sensors beyond 800C.
- **Extended this process to air-hole microstructural fibers, expand capability of fiber sensor beyond only temperature or strain measurements**.
  - Specially laser fabrication equipment for high-T grating fabrication no longer needed!
  - Cost of high-T sensors could come down drastically!
  - Parameters that sensor can measure drastically expanded (due to the air-hole microstructural fibers.

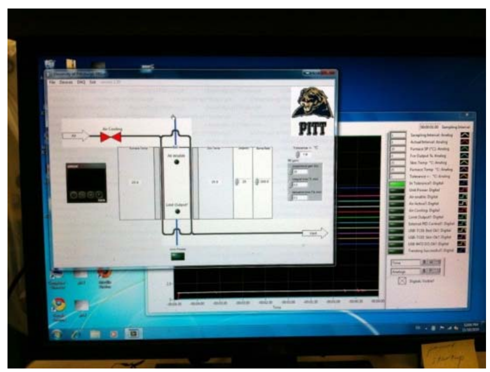
Process: Chemical Regenerative Process

- A Strong Type I FBG in optical fiber by UV laser.
- Rapid thermal annealing to anneal UV-induced defect.
  - Customer furnace development
- Stress induced on the fiber core-cladding interface during defect erasure.

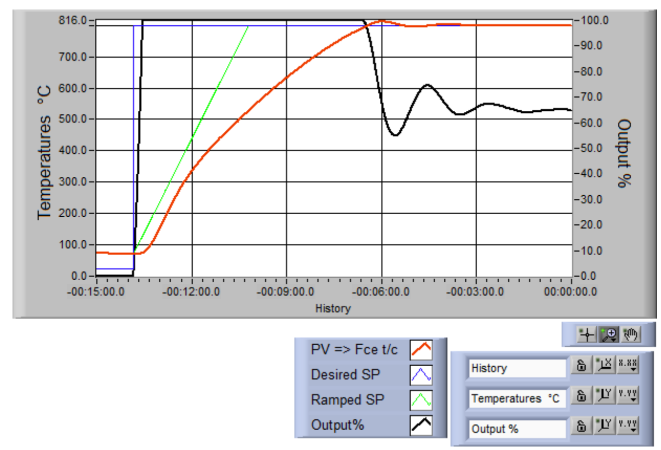
Miniaturized Furnace



Control Software

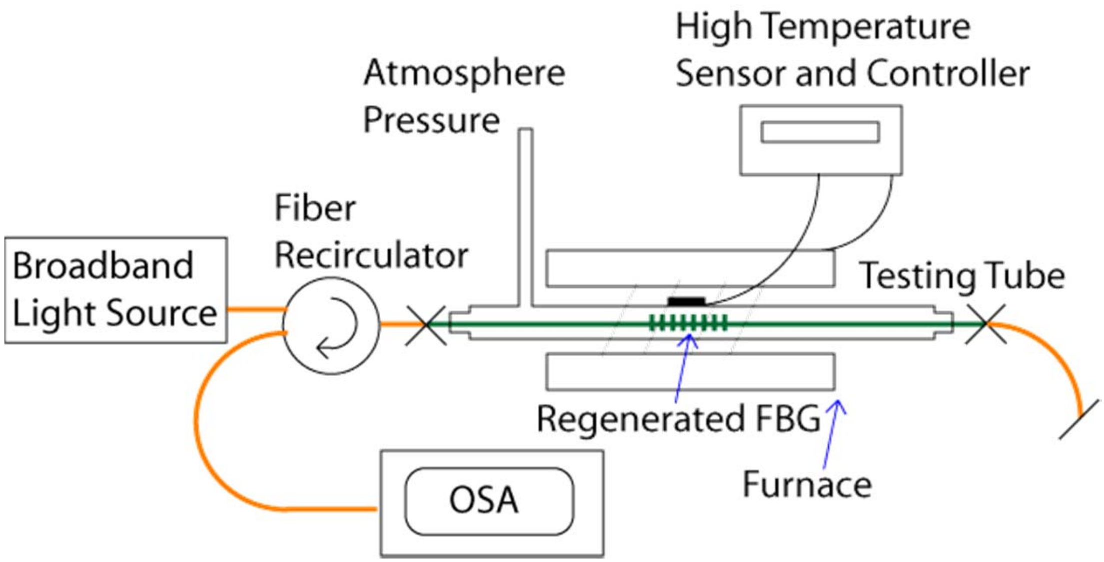


Sample Run

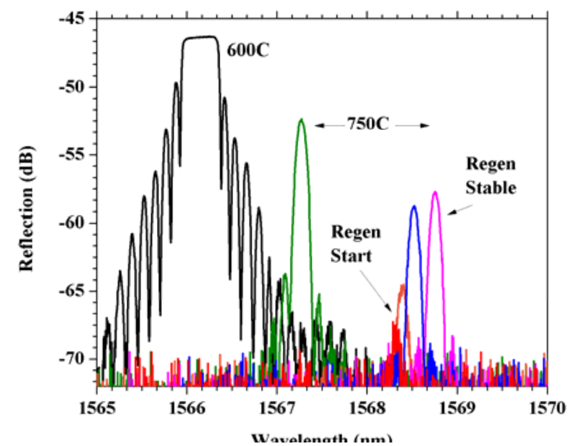


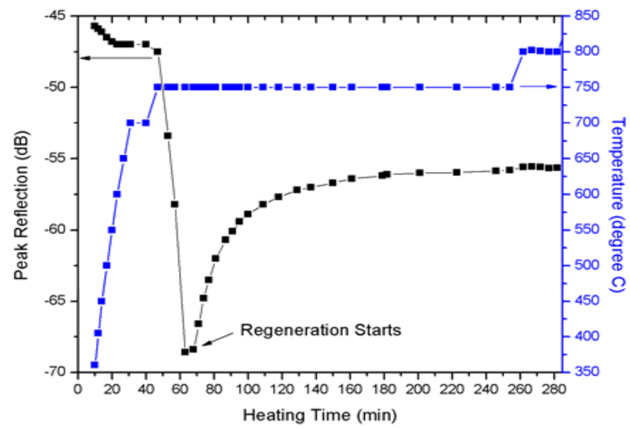
Process: Chemical Regenerative Process

Experimental Setup

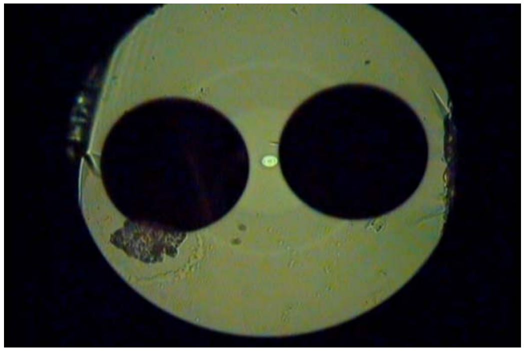


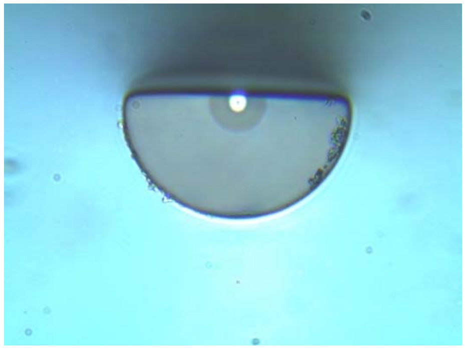
Typical Regenerative Process





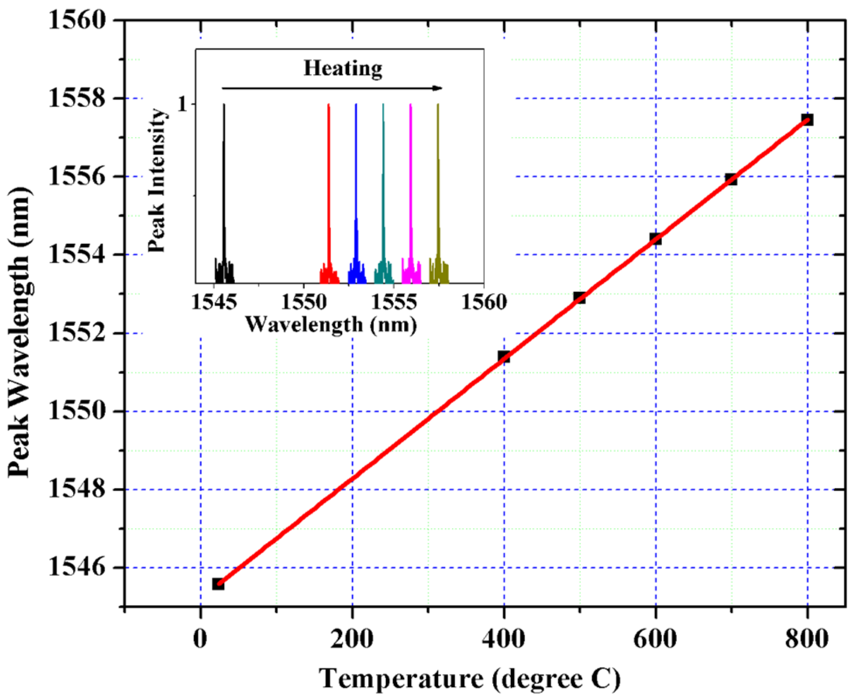
Fibers Used for this work



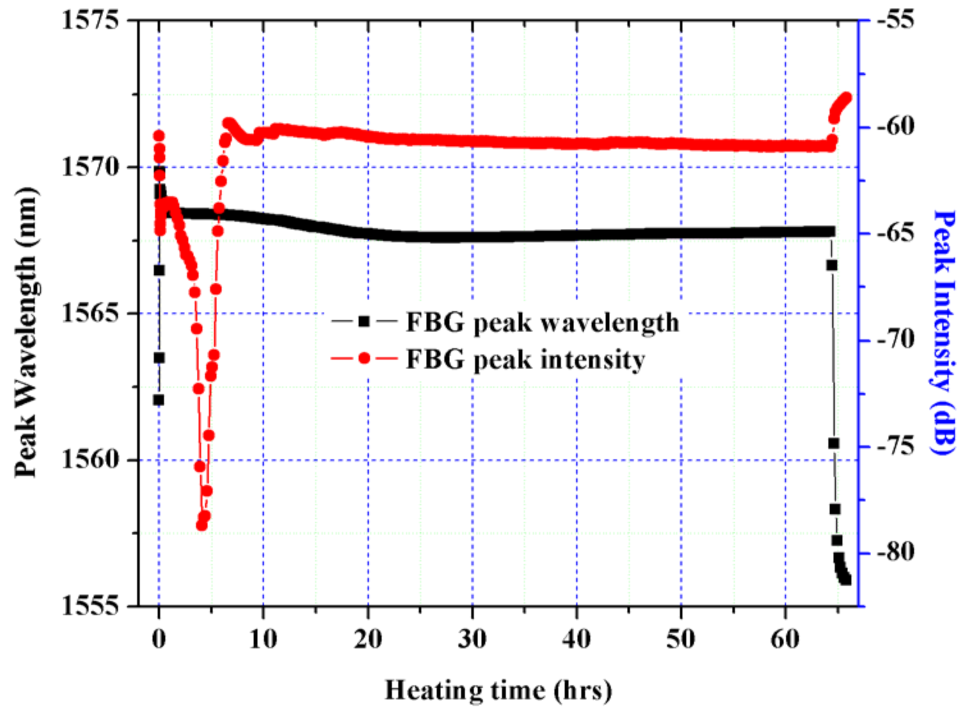


Regenerated Grating in Twin-hole Fiber

Temperature Cycles



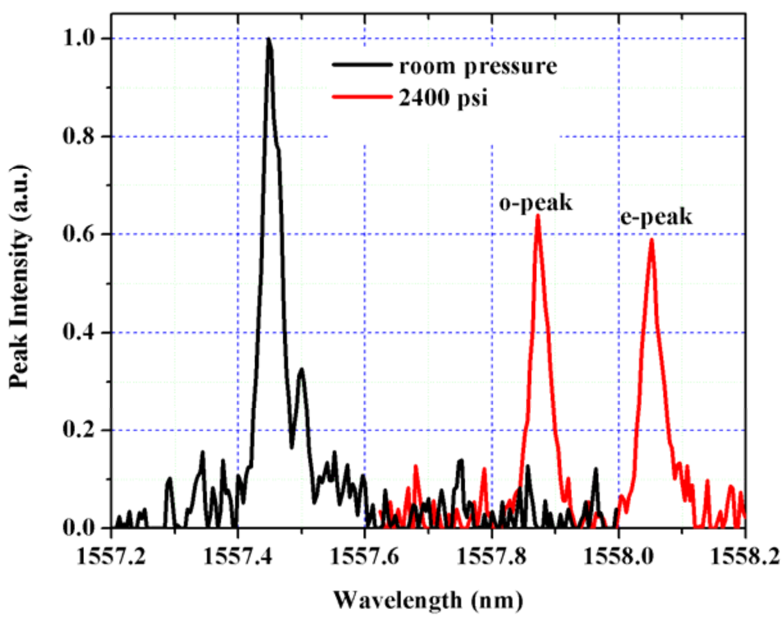
Stability Testing



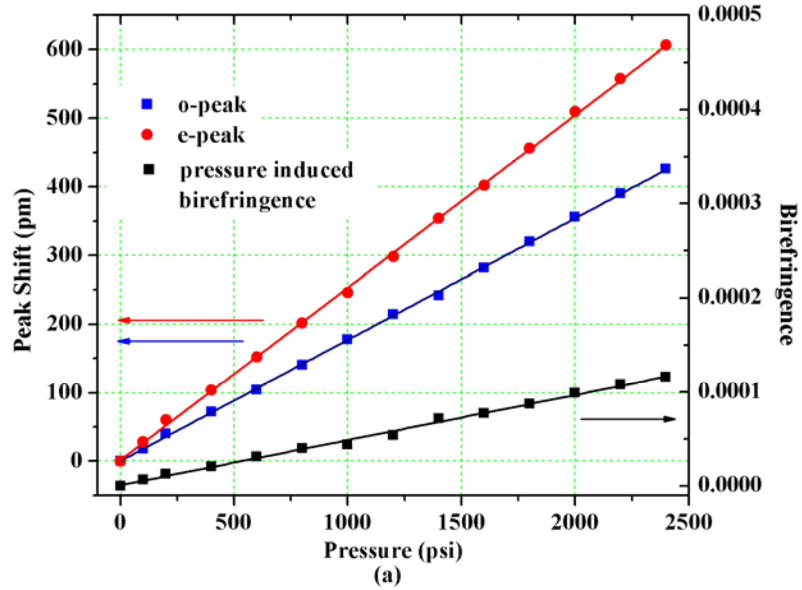
High-T Thermal Drift: 0.013 K/hour (Best case)
0.045 K/hour (Worse)

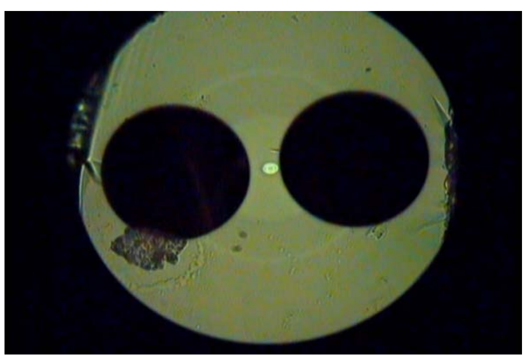
Regenerated Grating in Twin-hole Fiber

Pressure Test

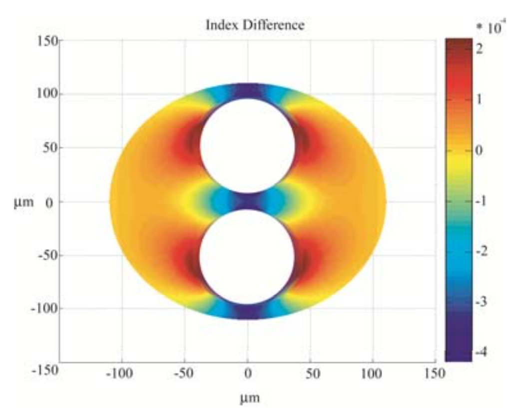


Pressure Testing



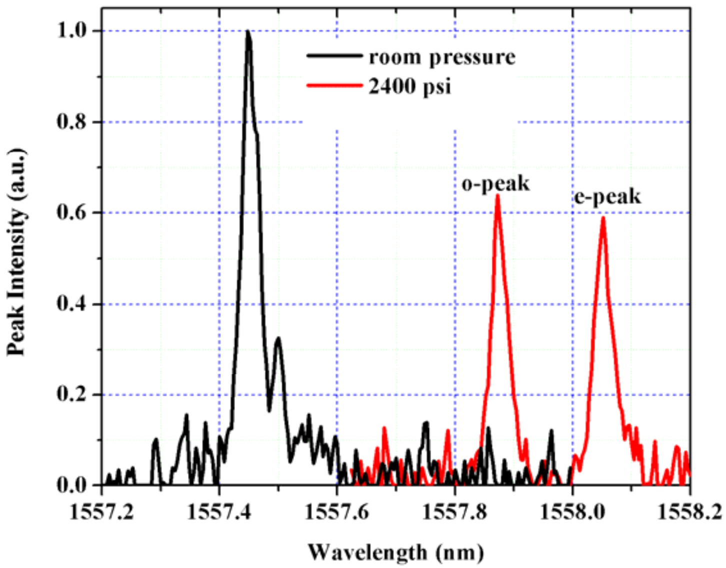


FEA Simulation

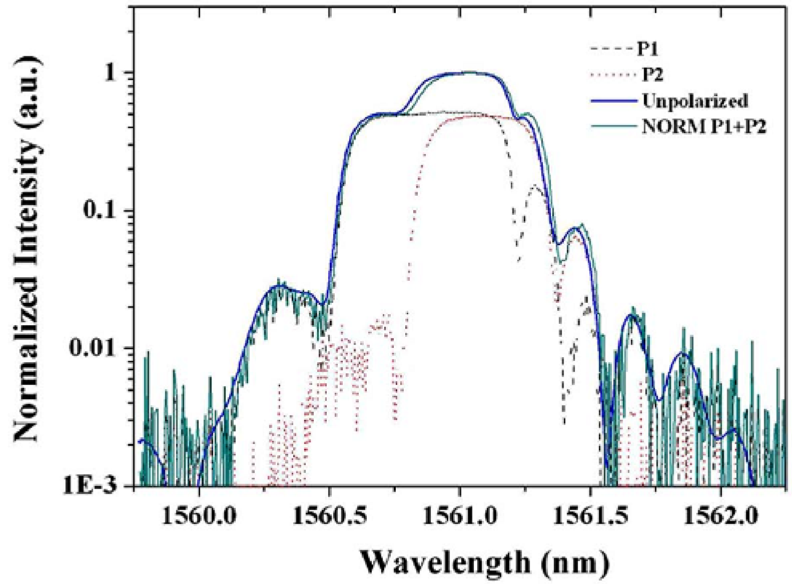


Regenerated Grating in Twin-hole Fiber

Regenerative FBG



Ultrafast Laser FBG



Simultaneous Measurement of T and P

$$\begin{pmatrix}\Delta\lambda_o \\ \Delta\lambda_e\end{pmatrix} = 1.532 \times 10^{-2}\Delta T + \begin{pmatrix}2.521 \times 10^{-4} - 9.185 \times 10^{-8}\Delta T \\ 3.526 \times 10^{-4} - 1.232 \times 10^{-7}\Delta T\end{pmatrix}\Delta P$$

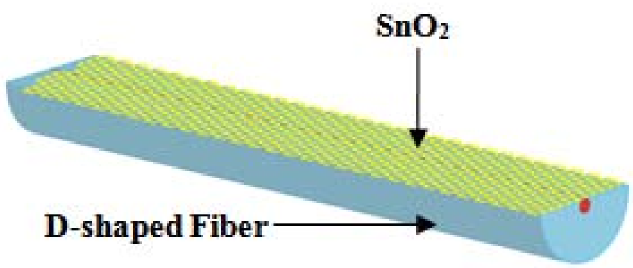
$$\Delta\lambda_{o,e} = \lambda - 1545.25nm$$

$$\Delta T = T - 0°C$$

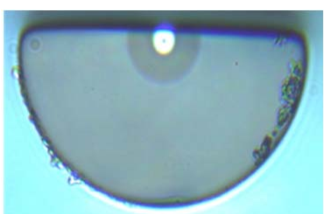
$$\Delta P = P - 0psi$$

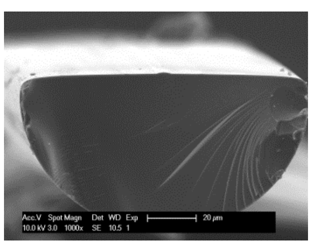
High-T Chemical Sensing

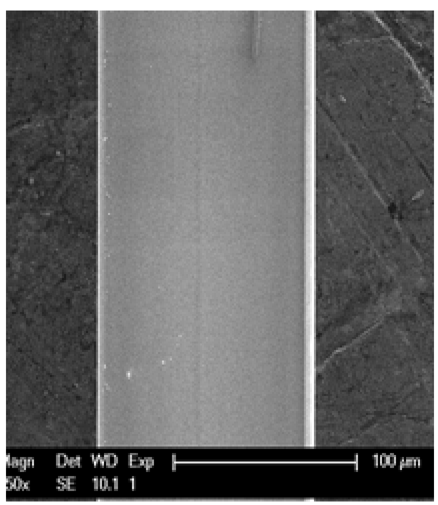
D-Shaped Fiber



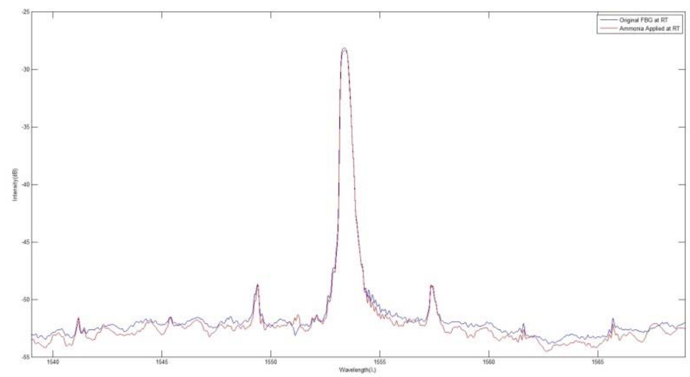
SnO_2 Dip Coating







5ppm Ammonia Testing



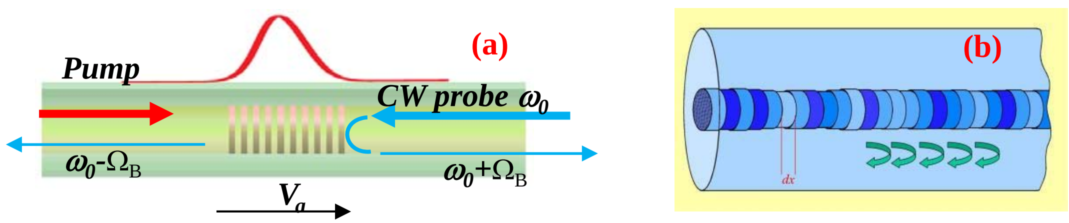
- Oxide-coated FBG stable up to 800C
- Metal Oxide Coating: TiO_2, SnO_2, ZnO_2
- Gas under tests: NH_3
- Testing Range: <1 ppm
- Oxide coating need optimization
- NETL Collaborator: Paul Ohodnicki

Progress Update: high T FBG sensors

- Success in sensor platform development
  - FBG sensors with superior spectral characteristics at high T
  - Demonstrate high-T stable FBG sensor derived from standard single-mode fiber
  - Low cost
  - Potential commercialization
  - >1000C operation possible using silica-core fiber
- Successful fiber coating development
  - SnO_2, TiO_2, and ZnO_2
  - Integration with D-shaped fiber
  - Coated FBG successfully regenerated at 700C
- Fiber sensor testing
  - NH_3, NO_x
  - Sensor response need optimization

Topic II: Distributed Fiber Sensor

- Current State of the Art
  - Brillouin Scattering – OTDR
    - Sub-meter resolution
    - Limited to Temperature and Strain measurement (0.1C and 1 $\mu\varepsilon$)
    - Long distance (up to km)
  - Rayleigh Scattering – OFDR
    - mm- resolution
    - Limited to Temperature and Strain measurement (0.1C and 1 $\mu\varepsilon$)
    - ~100 meter distance



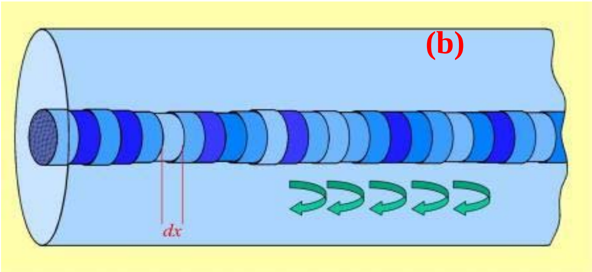
Schematic illustration of Brillouin scattering and (b) Rayleigh scattering.

Technique: Active Distributed Fiber Sensor

- Expand Rayleigh scattering distributed sensing beyond T measurement
- Active fiber sensing scheme for environmental adapability.
- Air-hole microstructural fiber for multi-parameter measurement
- Functional coating on-fiber for chemical sensing with –cm resolution

Rayleigh Scattering and OFDR

Rayleigh Scattering



$$\alpha\,(z)_{Rayleigh} = \frac{8\pi}{3\lambda^4}[n(z)^8 p^2](kT_f)\beta$$

OFDR Scheme

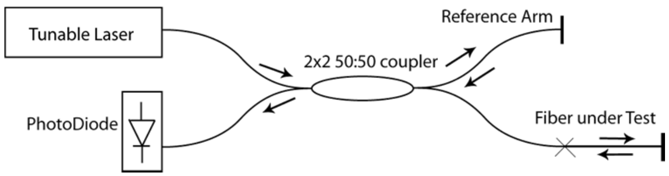
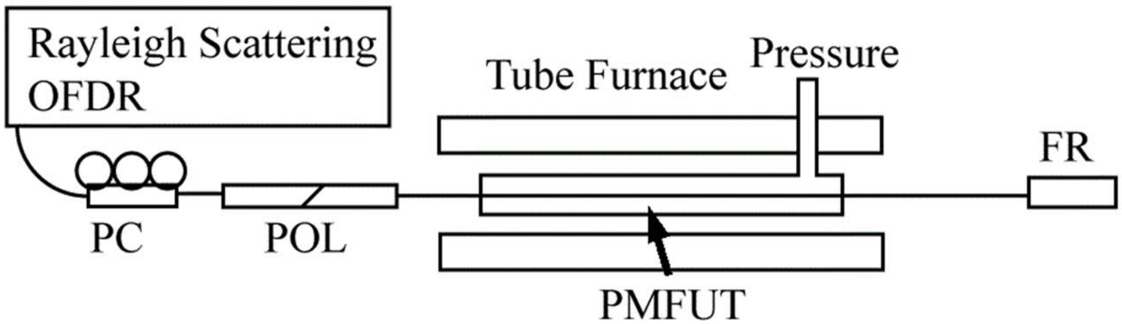
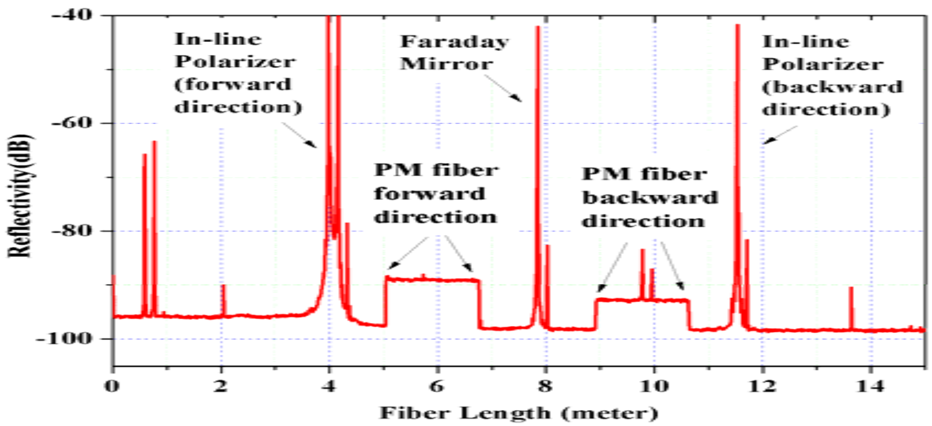


Fig. 3: Schematic sketch illustration of the OFDR operation principle [20].

- ✓ **Optical Frequency Domain Reflectometry (Swept-Wavelength Interferometry) for Sub-mm spatial resolution over tens of meters**
- ✓ **In-fiber Rayleigh scattering highly sensitive to local perturbation**
- ✓ **All-temperature operation**
- ✓ **Further Functionality improvement possible**
- o **Cost, Response Time, Cross Talk**

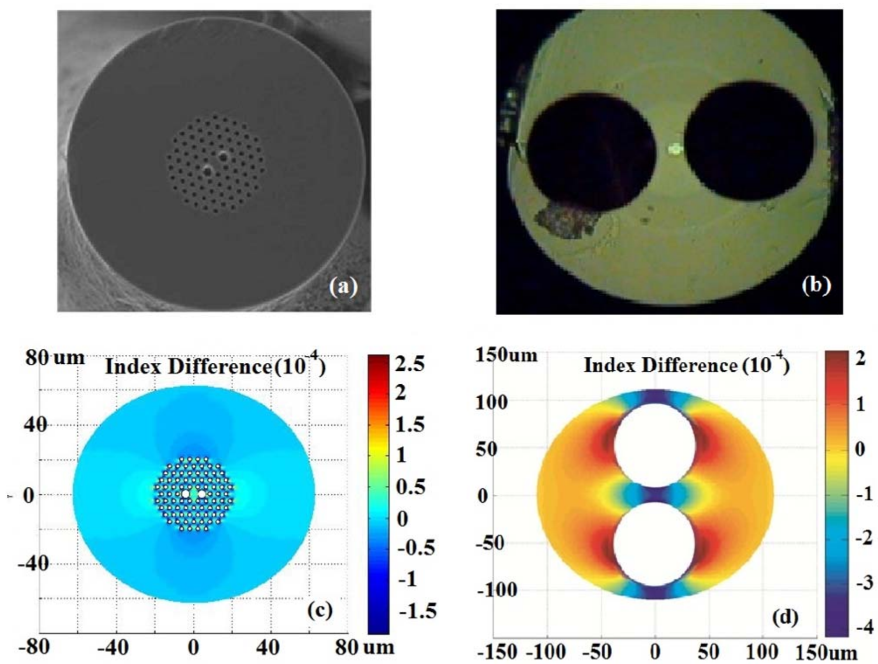
Distributed Pressure Measurement

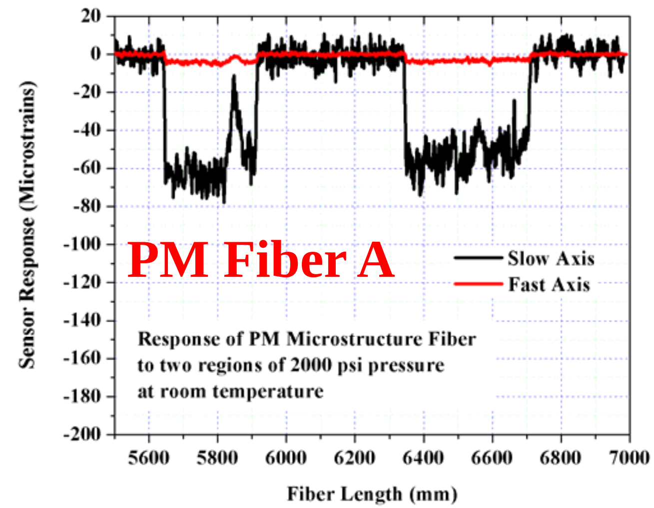


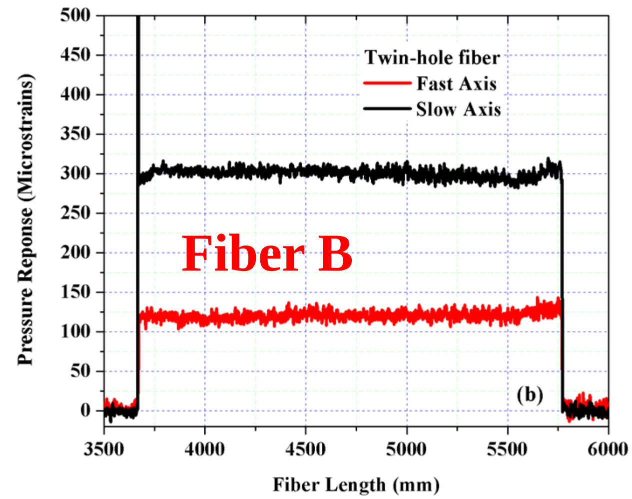


OFDR Measurement Results
Two-Hole Fibers: 2000 psi

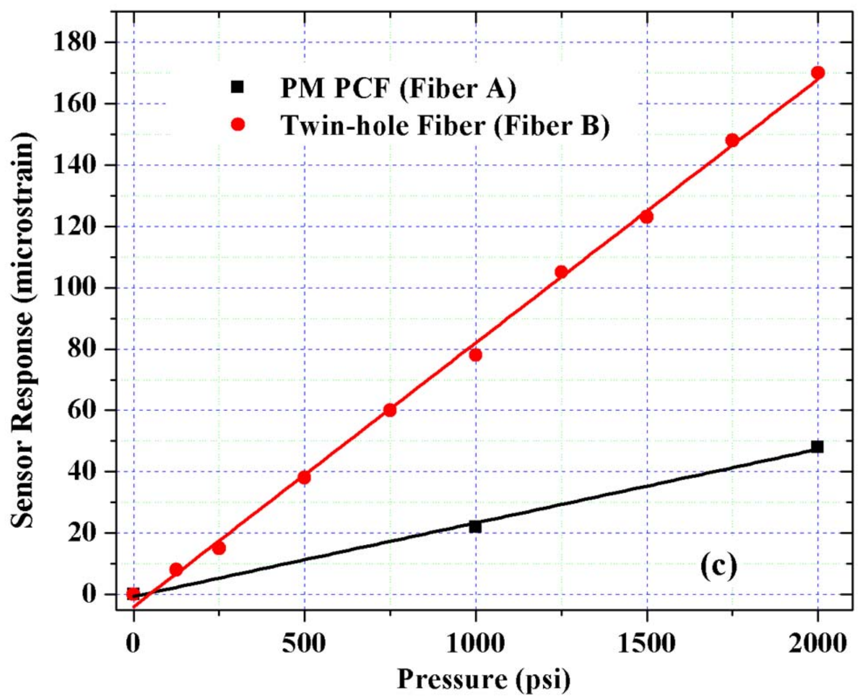
PM Fiber A | **Two-Hole Fiber B**



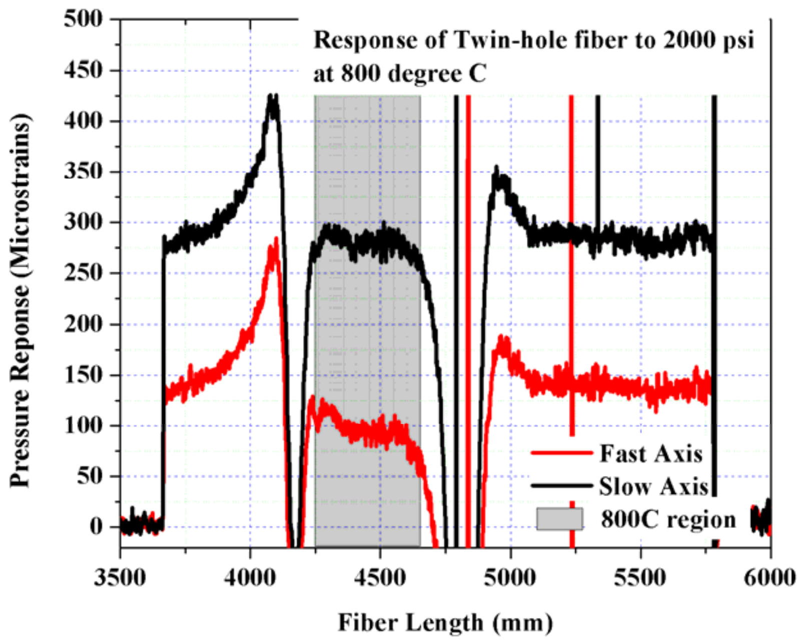


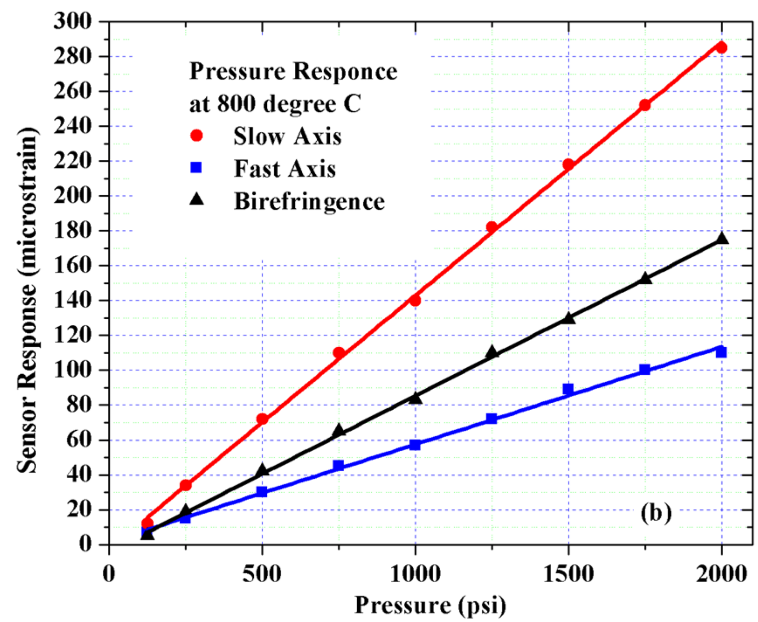


OFDR Measurement Results Room Temperature



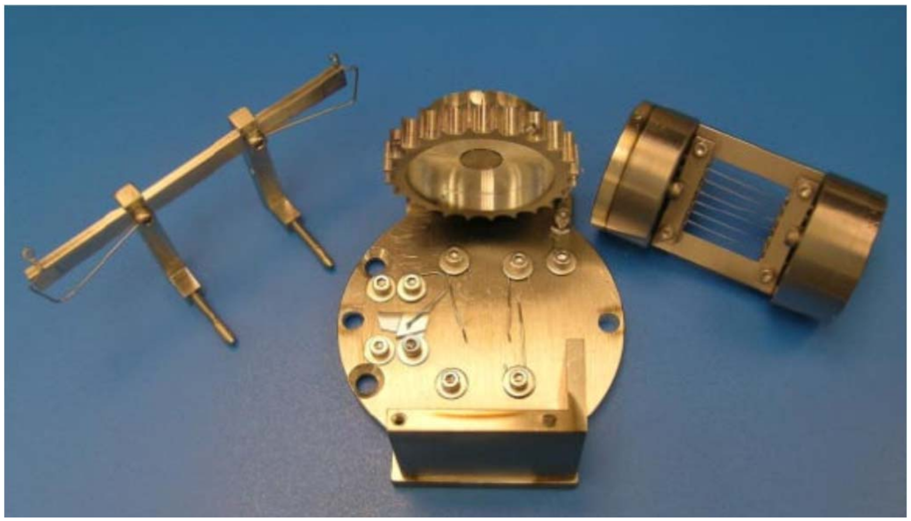
OFDR Measurement Results Two-Hole Fibers at 800C

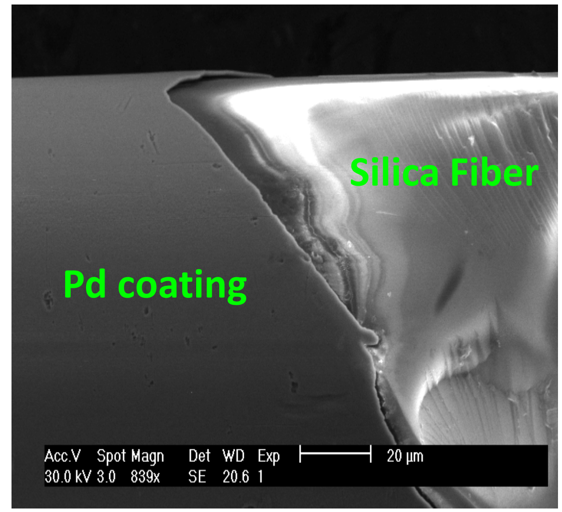


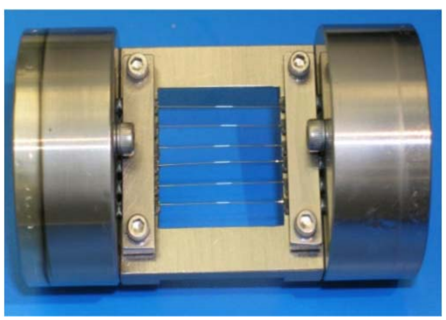


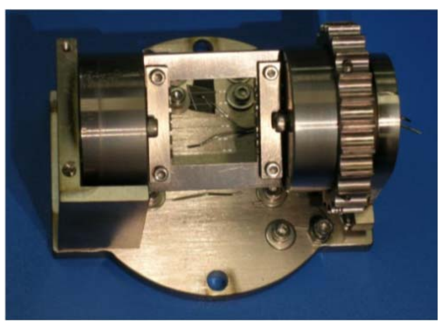
Distributed Hydrogen Sensing

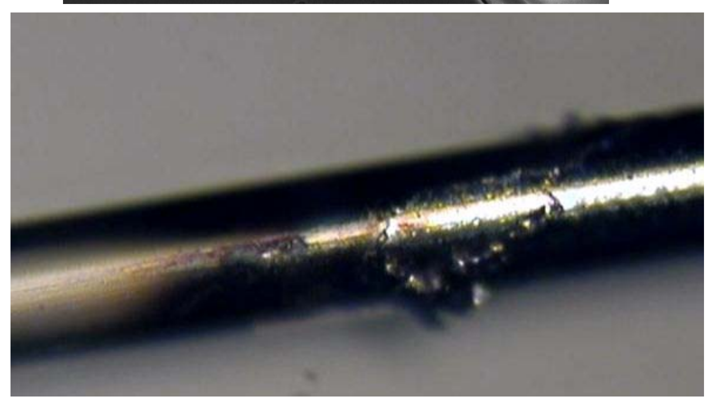
Sputtering Coating of Pd on fiber



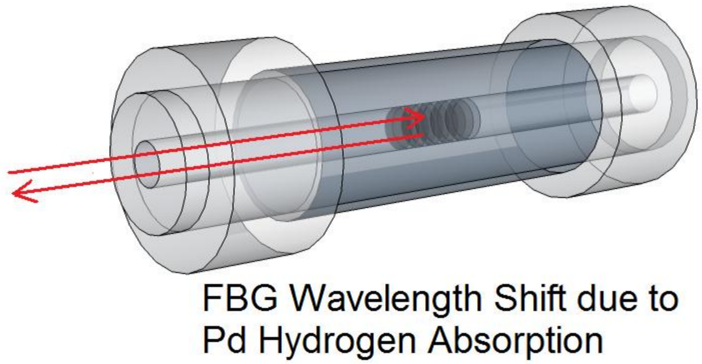


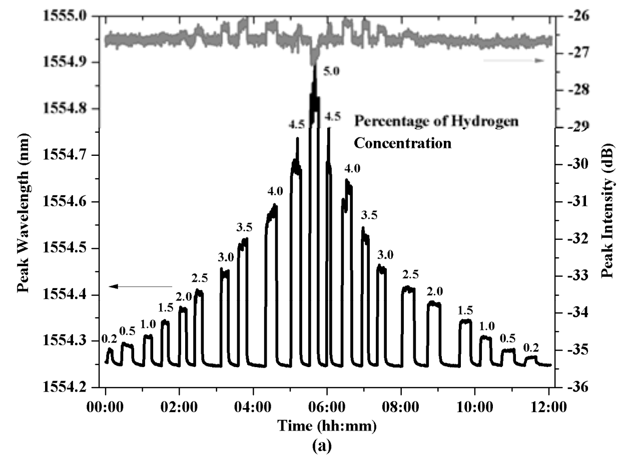


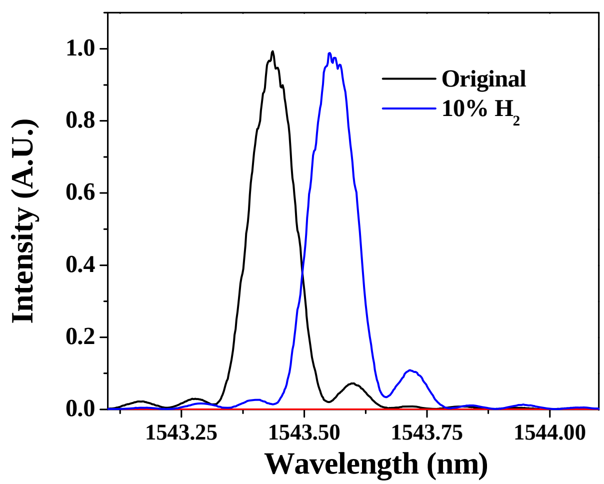


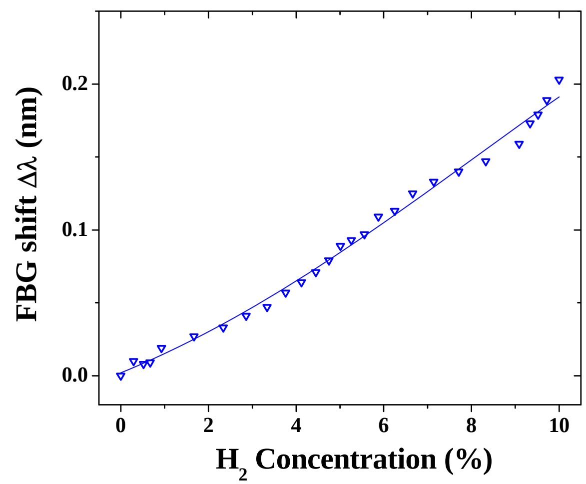


Chemical Sensing: H2 sensing Case using FBG

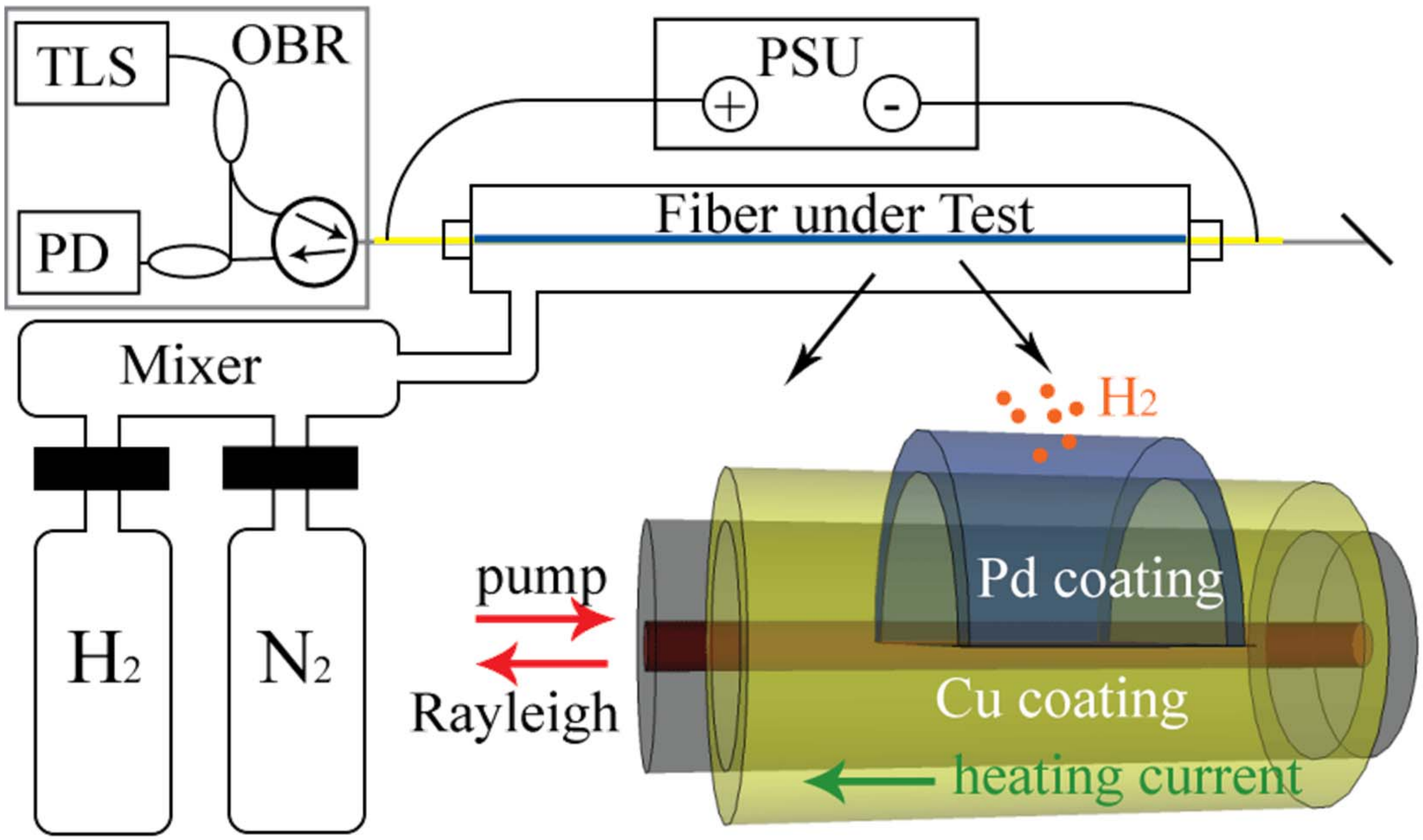




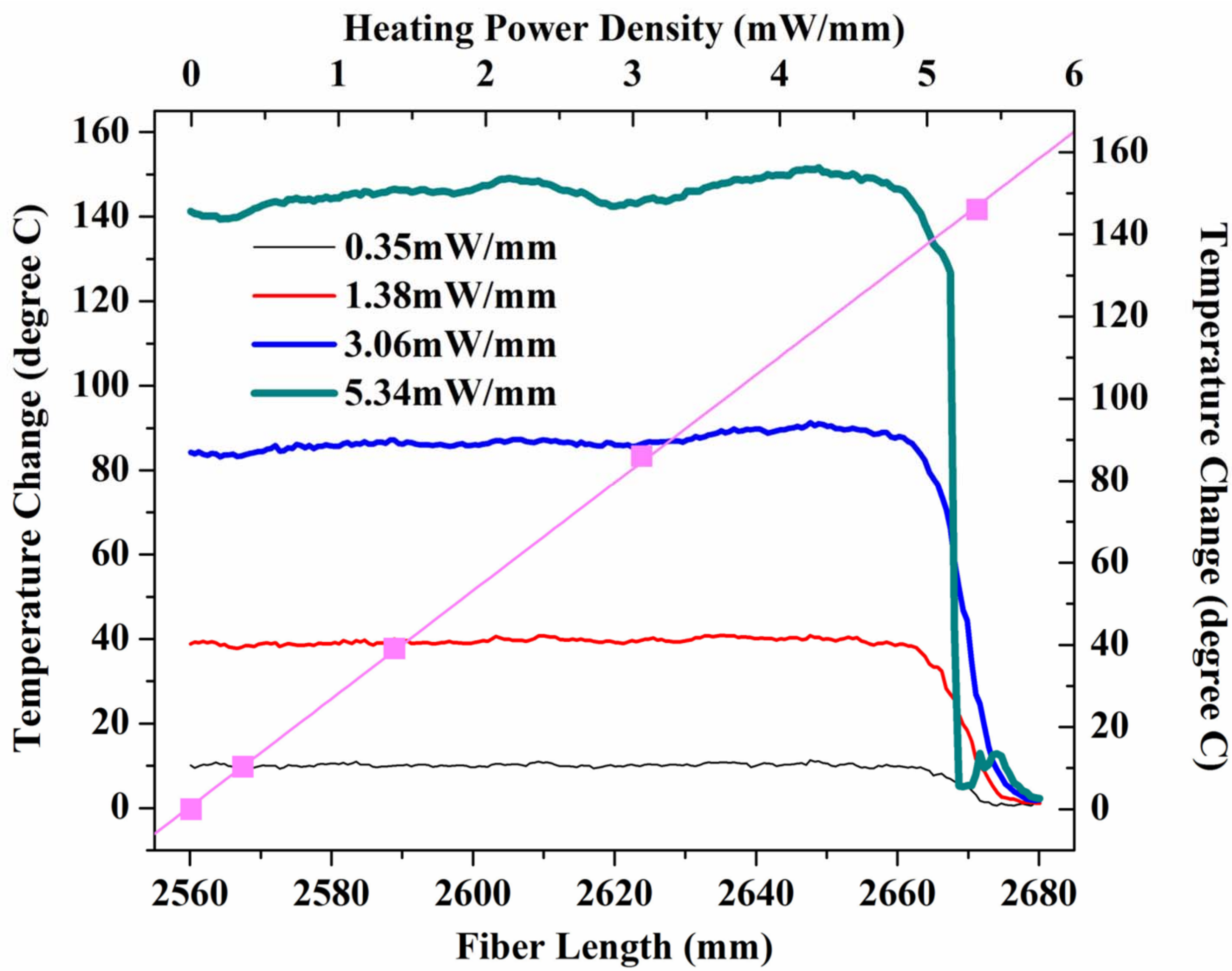




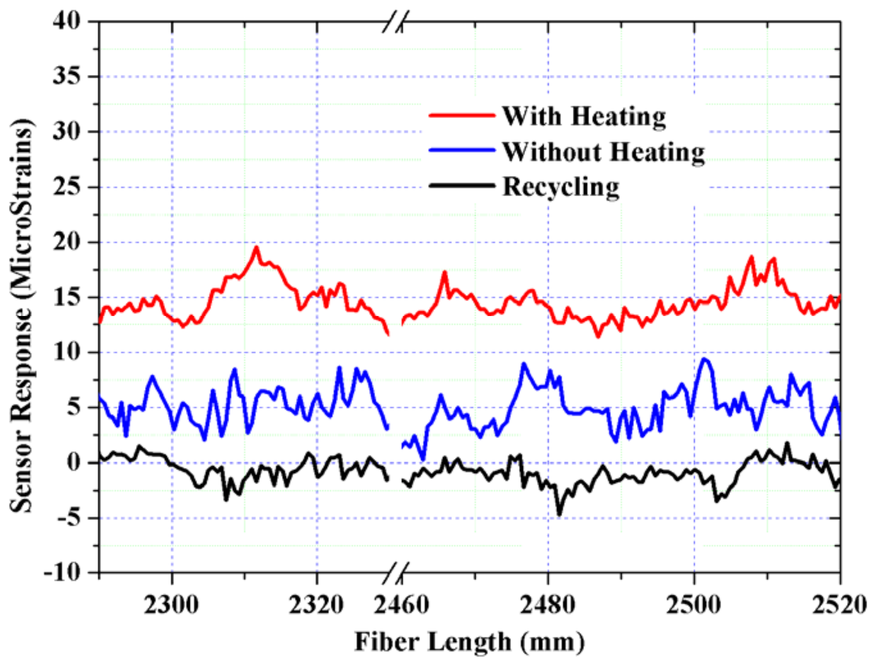
Distributed Chemical Sensing

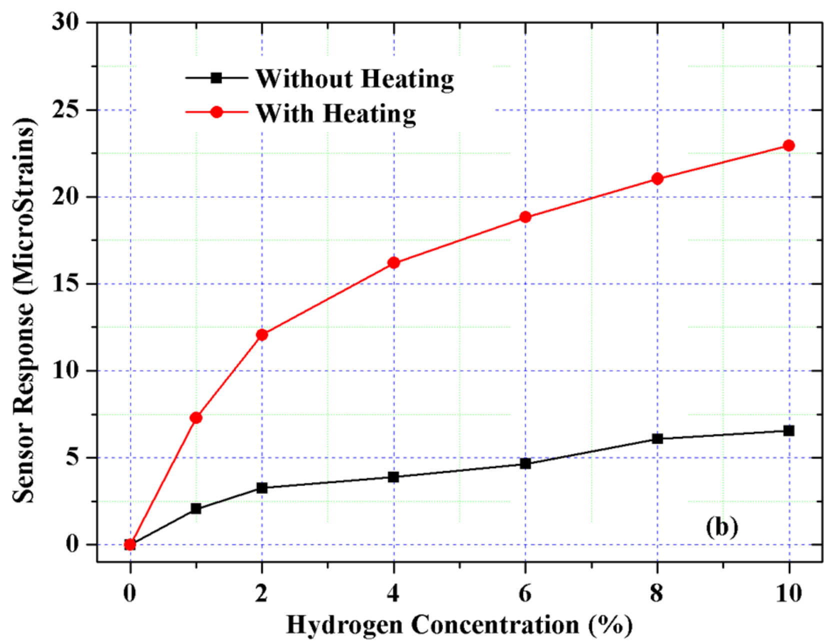


Heating of on-fiber Pd Coating to Speed up sensor performance



Distributed Sensor Response (10% hydrogen)

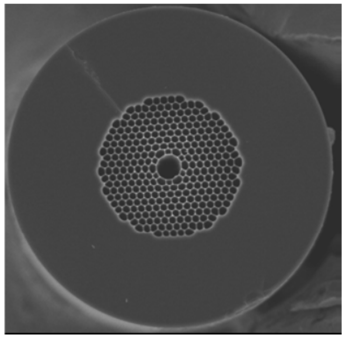


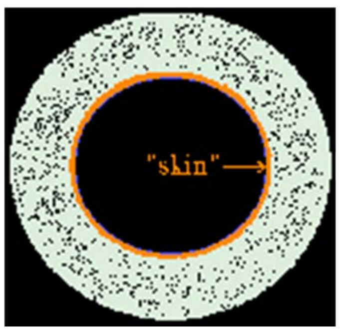


Progress Update: Distributed Sensing

- Distributed Fiber Sensing Beyond T and Strain Measurements
  - Demonstration of distributed pressure sensing
  - Demonstration of distributed chemical sensing
  - Spatial resolution of 1-cm achieved
  - High temperature capability demonstrated at 800C
  - >1000C operation possible (depends on fiber)
- Further development
  - Improve distributed chemical measurement distance > 1 km
  - Enhance sensitivity and response time
  - Expand distributed measurement species

Topic III: CARS Chemical Sensors

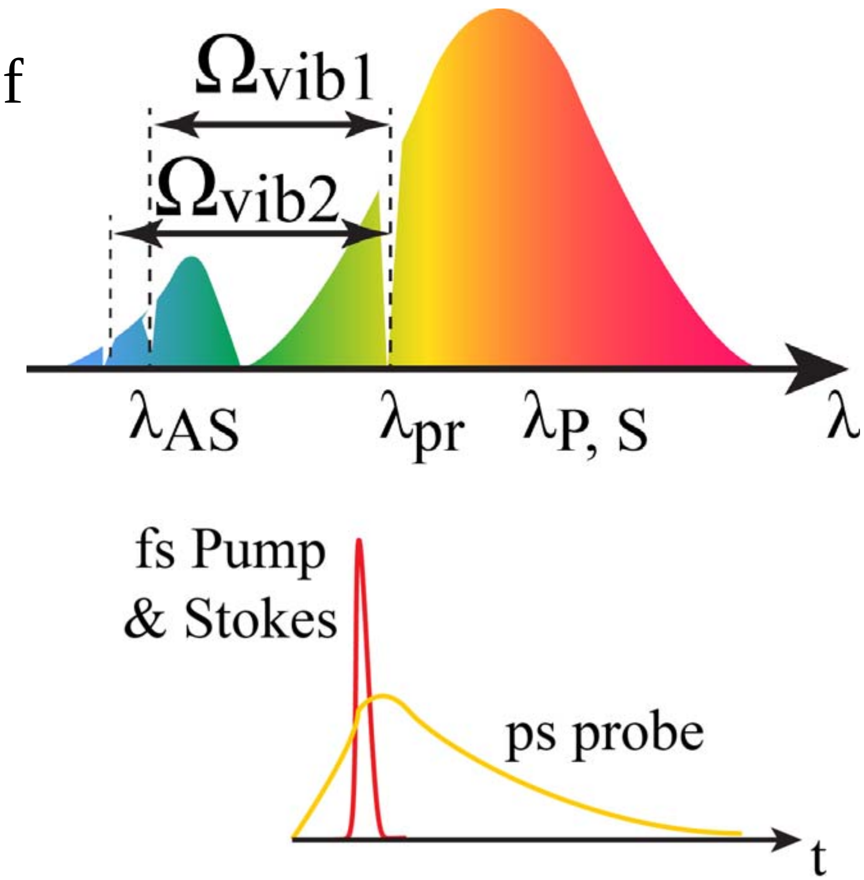




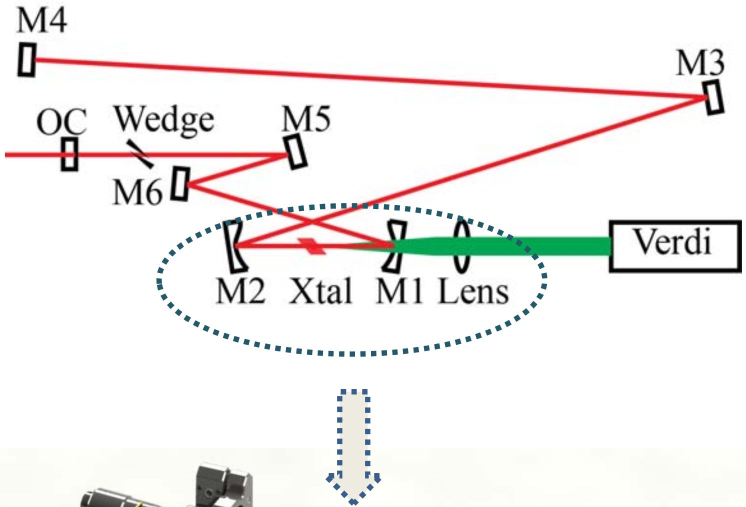
- Current State-of-the-Art
  - Spontaneous Raman spectroscopy in hollow core fibers
  - Sensitivity enhancement by spatial confinement
  - Gas exchange hampers the response time and sensitivity ("residual gas issue")
- Coherence Anti-Stokes Raman
  - Enhance signal up to 10^5
  - Reduce the length of hollow-core fiber from ~ meter to ~ cm
  - Single-beam CARS for easy optical measurement
  - Use of broadband ultrafast lasers for multi-gas measurement

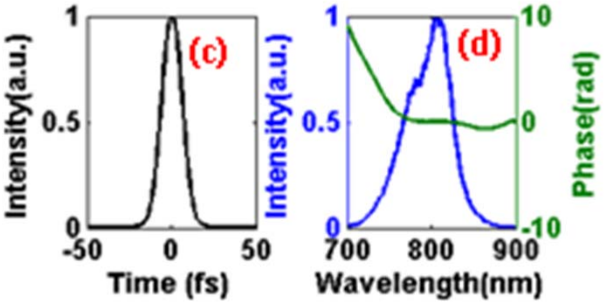
Single Beam CARS

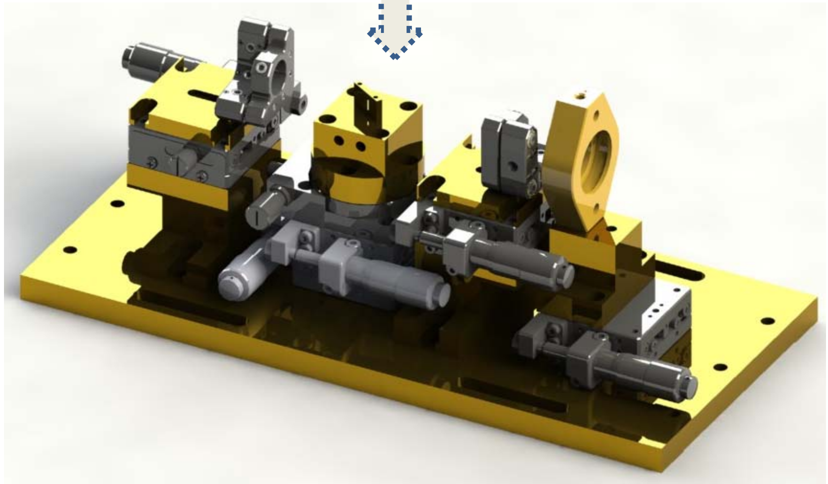
- Eliminate the need of alignment of multiple beams
- No need for accurate time-delay control
- Broadband spectrum provide wide range of available resonant energy levels.
- Single-shot multiplexible measurements
- Combine with hollow-core fiber spatial confinement for ultimate enhancement



Broadband Laser Development

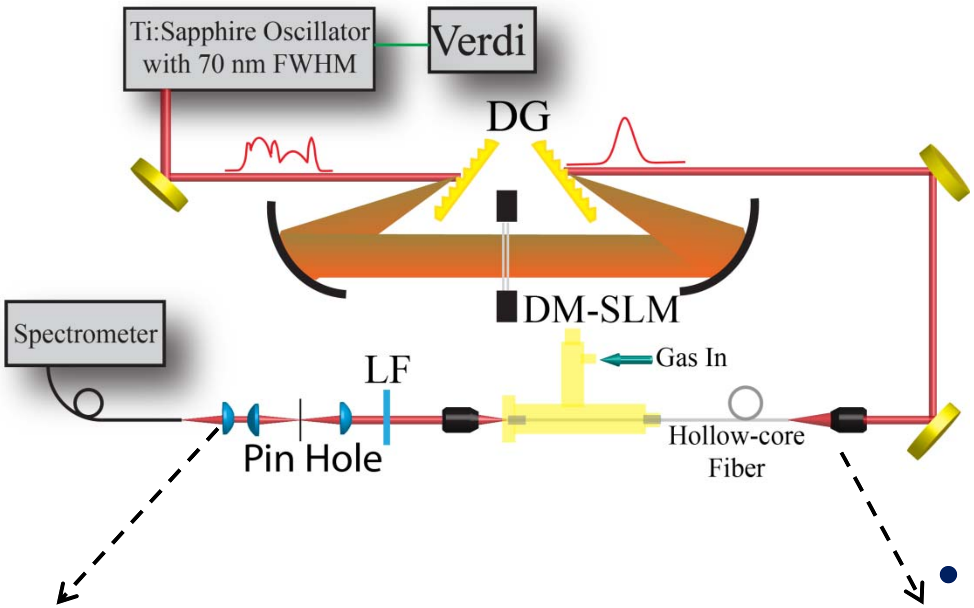




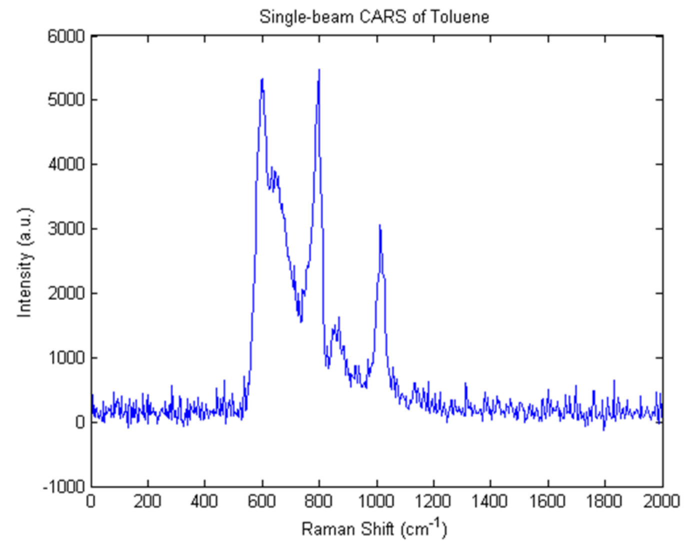


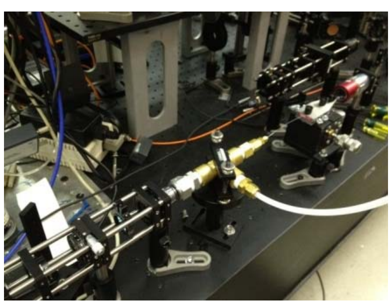
- Ti:Sapphire laser
- Chirped mirror technology
- Laser Bandwidth 1100 cm^{-1}
- Pulse duration down to ~10 fs

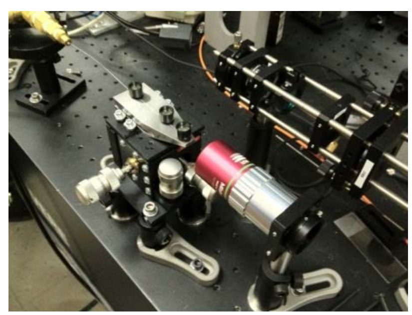
Experimental Setup



Toluene CARS



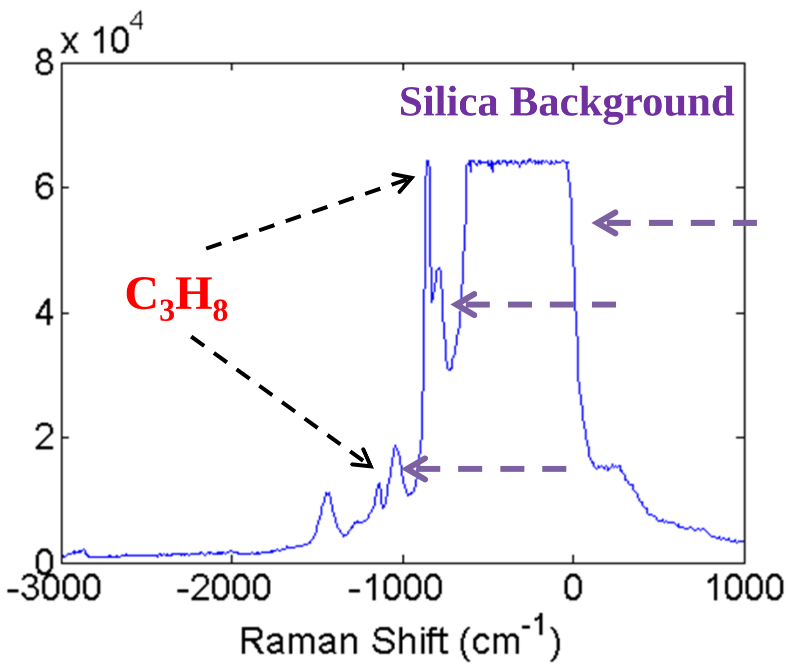




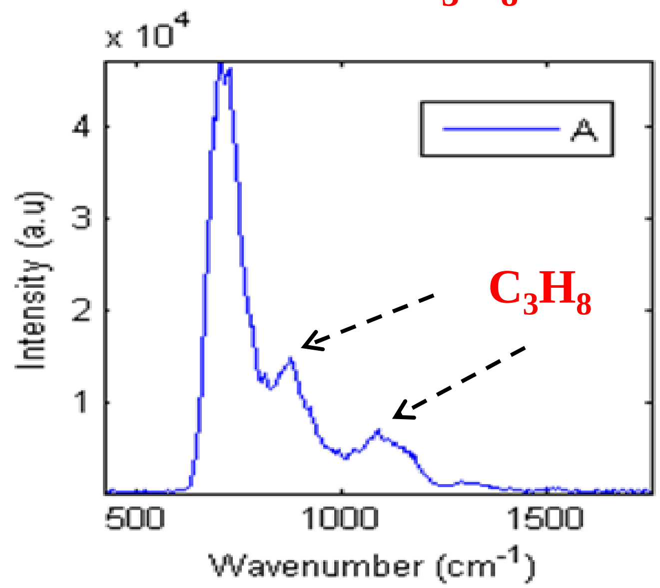
- Spatial light modulator pulse shaper
- Background-free detection
- **PCF as gas cell**
- Intended Gas: CO_2 and C_3H_8

Experimental Setup

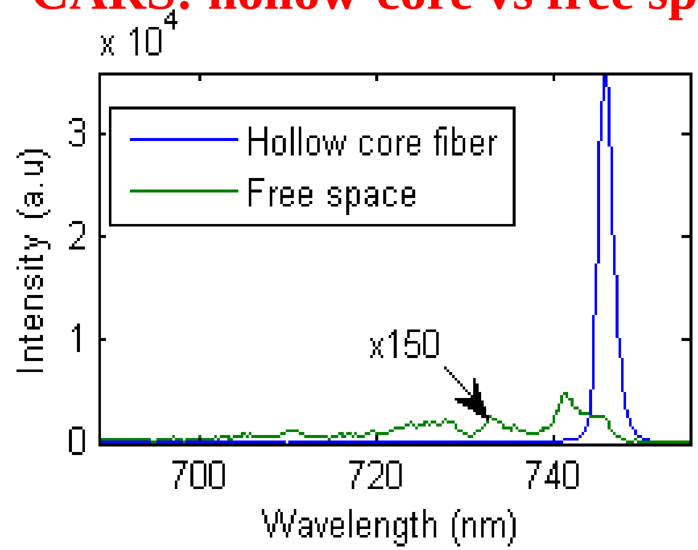
Spontaneous Raman: C_3H_8



CARS: C_3H_8



CARS: hollow-core vs free space



- Spontaneous Raman: 200-mW, 776-nm single wavelength, 10s integration.
- CARS: 20 mW (70 nm bandwidth, 0.3 s integration)
- Hollow core scheme see 150 time enhancement on CARS signal

Progress Update: Raman

- CARS in hollow core fibers
  - Successful development of custom ultrafast laser with wide bandwidth
  - Complete construction of gas sensing set up
  - Confirmed signal enhancement using CARS vs. spontaneous process
  - Confirmed CARS signal enhanced by hollow-core fibers
- Further development (in this program)
  - Optimization of phase match condition inside PCF
  - Complete all gas measurement (CO_2 and C_3H_8)
  - Data process