Raman Spectroscopy for the On-Line Analysis of Oxidation States of Oxygen Carrier Particles

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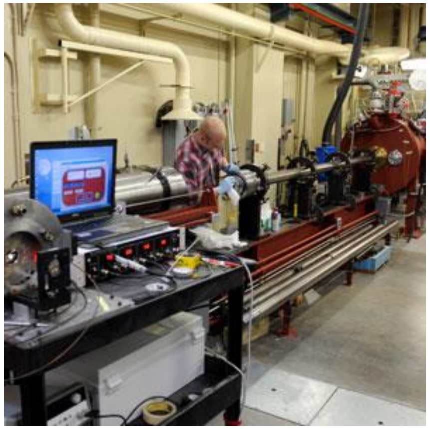
Outline

1. Who are we?
2. Motivation
    a. Fossil fuels and CO_2 capture
    b. Chemical Looping Combustion
3. Goal, Objectives, and Vision
4. Background – Raman spectroscopy
5. Team & Assignments
6. Tasks
7. Gantt Chart
8. Milestones

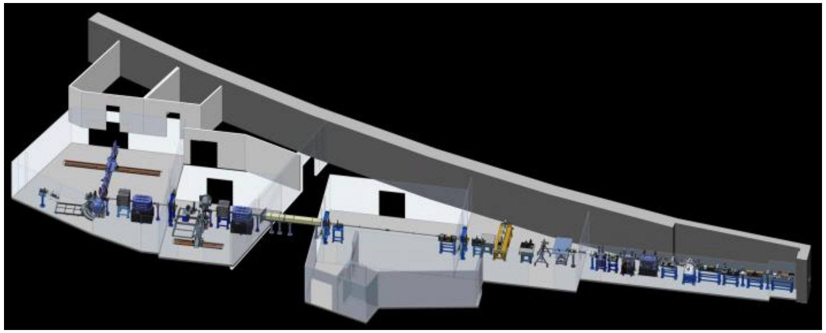
Institute for Shock Physics

Focus: Materials under Extreme Conditions

- **ISP (Pullman, WA)**
  - National resource in shock wave and static high pressure.
  - Fundamental research related to national security



- **DCS (Argonne National Lab)**
  Dynamic compression science



- **ASL (Spokane, WA)**
  Focused on solving problems and providing solutions for government agencies and industry

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Eilers Group

Optical Materials and Spectroscopy for Applications under Extreme Conditions

Team:

Hergen Eilers, Ph.D. Physics	Optical materials and spectroscopy
Ray Gunawidjaja, Ph.D. MSE	Synthesis, Processing
Benjamin Anderson, Ph.D. Physics	Optics
Natalie Gese, M.S. Chemistry	Synthesis, Processing
Michelle Warter, Ph.D. Phys. Chem.	Gas-phase Spectroscopy
Steven Livers, M.S. Mech. Eng.	Instrumentation support
John Kirtley, Ph.D. Chemistry	Spectroscopy, Chemistry
Victoria Leichner, Chemistry	undergraduate student (junior)
Jason Trader, Phys/Math/CS	undergraduate student (senior)

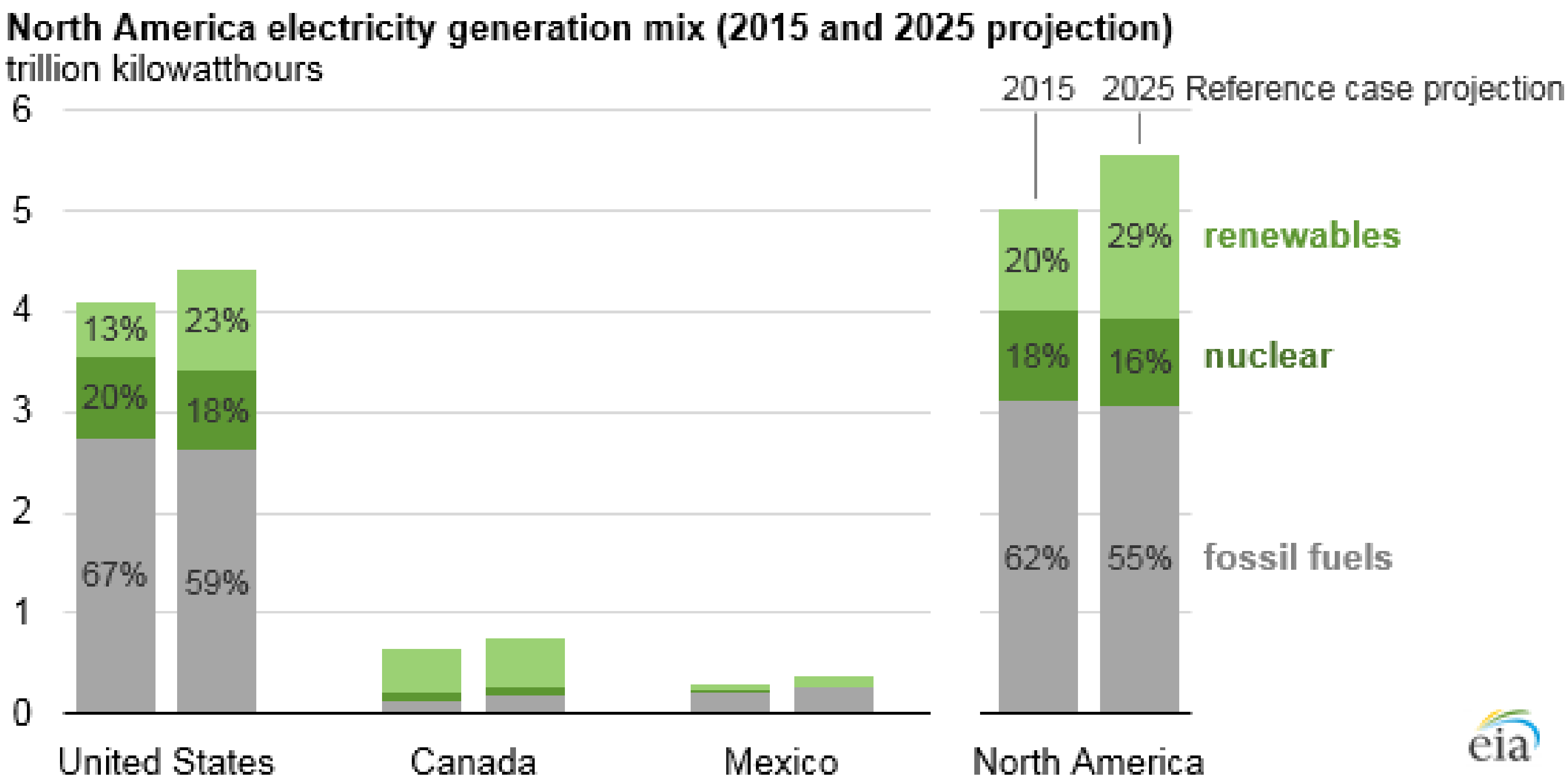
Complementary skills and expertise to address wide range of problems and provide solutions for customers

Current Projects

1. Temperature sensors for use in explosions (DTRA)
2. Temperature sensors for use in heterogeneous materials (AFOSR)
3. Temperature sensors for arson/fire investigations (NIJ)
4. Chemical reactions of CWA simulants under extreme heating (DTRA)
5. Development of biodegradable hydraulic fluids (Avista)
6. Raman spectroscopy for analysis of oxygen carrier particles (DOE/NETL)

Focus is on sensing of physical parameters and on identification of materials and chemical reactions

Fuel Consumption



http://www.eia.gov/todayinenergy/detail.cfm?id=27332, accessed 9/19/16

Fossil fuels are expected to remain the main source for electricity generation

CO_2 Capture

Motivation

- Improve CO_2 capture during fossil fuel combustion

Conventional combustion:

- Air is source of oxygen
- High concentration of nitrogen complicates CO_2 capture

Generate oxygen

- Expensive

Chemical Looping Combustion:

- Provides oxygen via oxidation-reduction cycling
- Uses oxygen carrier particles
- Eliminates large cost associated with generating oxygen

Wang, et al., "Chemical-Looping Combustion and Gasification of Coals and Oxygen Carrier Development: A Brief Review," Energies 2015, 8, 10605
"DOE/NETL Advanced Combustion Systems: Chemical Looping Summary," July 2013, DOE/NETL
J. C. Fisher II, "Oxy(gen) combustion and Chemical Looping Combustion," DOE/NETL

Chemical Looping Combustion

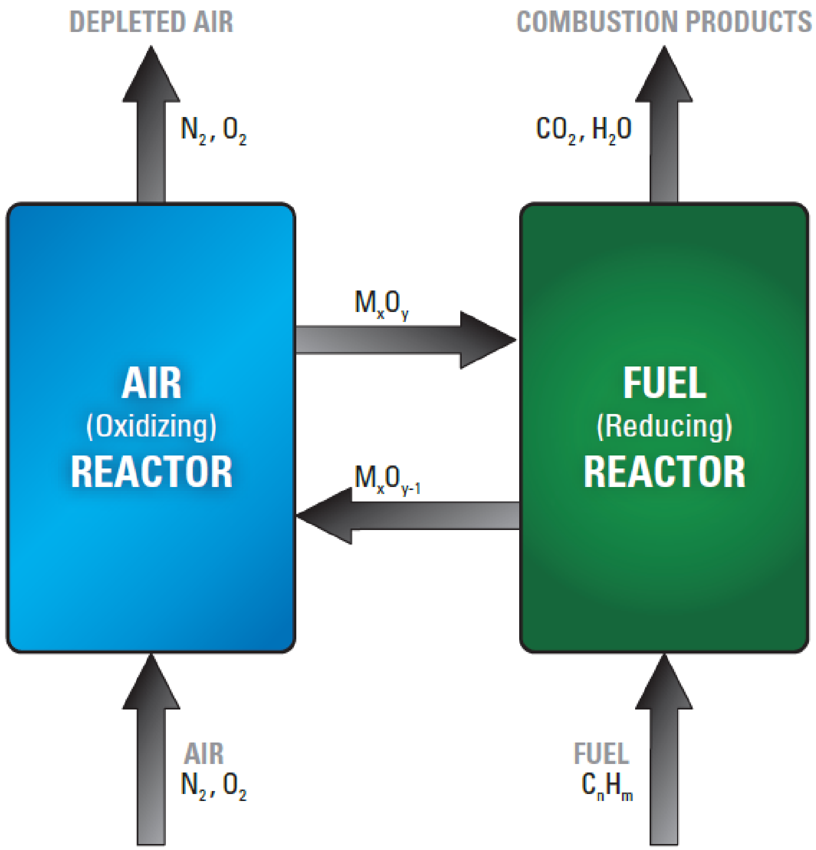


Figure 2: Two Reactor CLC Process

CLC generates CO_2, H_2O (can be condensed), and heat

"DOE/NETL Advanced Combustion Systems: Chemical Looping Summary," July 2013, DOE/NETL

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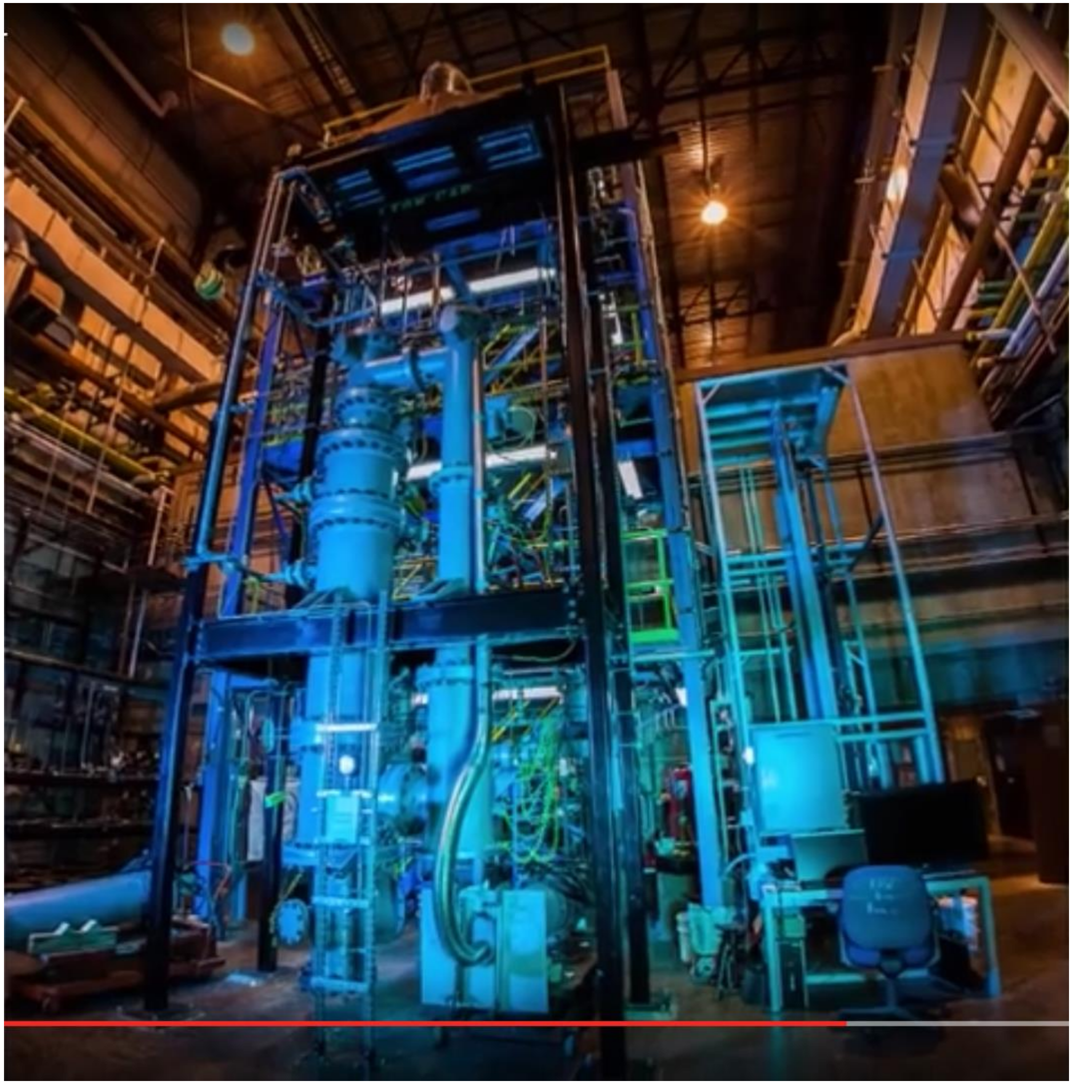
NETL Chemical Looping Reactor



https://www.youtube.com/watch?v=1r1VrtKB-AM, accessed 9/20/16

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Oxygen Carriers

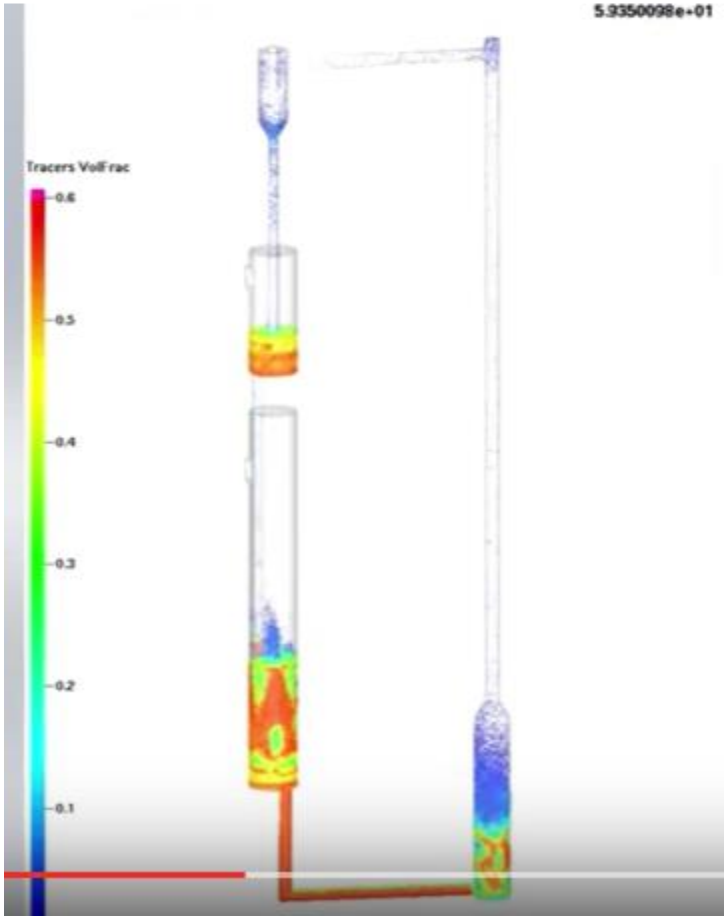
Examples:
- CuO/Cu_2O
- $Fe_2O_3/Fe_3O_4/Fe_{0.945}O$
- $Mn_2O_3/Mn_3O_4/MnO$
- $CaSO_4/CaS$

Desired properties include:
- High conversion efficiency
- High reactivity
- Low agglomeration
- Long lifetime
- Low cost
- Low environmental impact

https://www.netl.doe.gov/newsroom/labnotes/labnotes-archive/01-2014, accessed 9/26/16

J. C. Fisher II, "Oxy(gen) combustion and Chemical Looping Combustion," DOE/NETL

Online (in-situ) Characterization



https://www.youtube.com/watch?v=1r1VrtKB-AM, accessed 9/26/16

Conditions, including:

- Temperatures: 800 °C – 1000 °C
- Pressures: ~ 10 atm
- Particles constantly moving

Need to identify oxidation state

- Standoff/remote sensing
- Single-shot measurements

Need for diagnostic measurement technique

Goal, Objectives, and Vision

Goal:
Develop a sensor for the on-line analysis of the oxidation state of oxygen carrier particles and demonstrate its feasibility.

Objectives:
(1) Set up and test a time-gated Raman spectroscopy system in combination with a pressurized high-temperature sample chamber.

(2) Optimize operating parameters of the Raman spectroscopy system and measure the high-temperature spectra of oxygen carriers.

(3) Develop an analysis procedure, including statistical modeling and multivariate calibration, for the interpretation of the Raman spectra.

Long-term Vision:
Monitoring system that can easily be integrated into different types of CLC systems and provide feedback for process control.

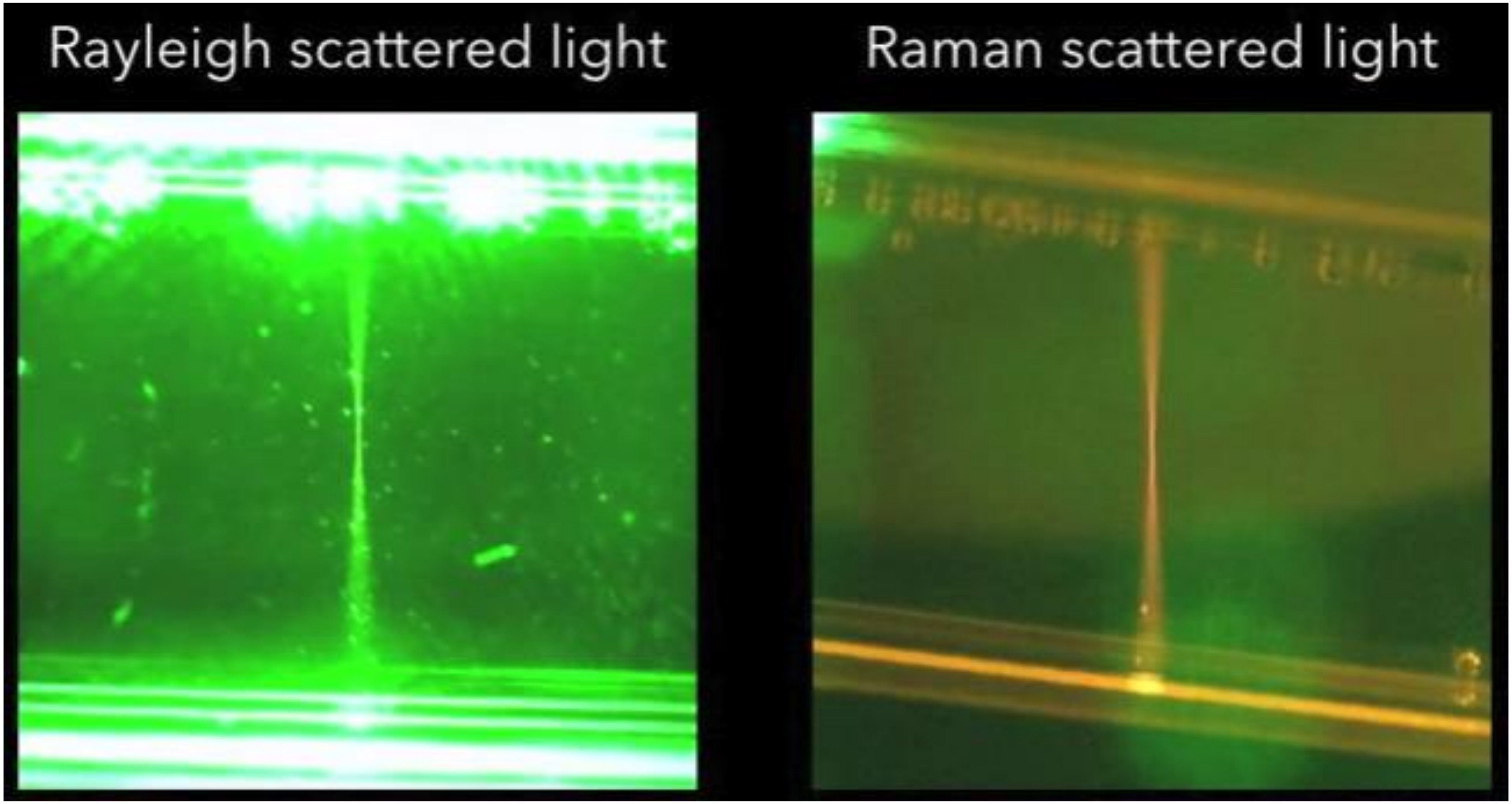
Raman Spectroscopy

- Widely used for the detection/identification of materials.
- Demonstrated for standoff/remote single-shot applications.

https://www.sciaps.com/raman-spectrometers/, accessed 9/30/16

Raman spectroscopy wide used and proven technique

Raman Spectroscopy



https://www.youtube.com/watch?v=TyKmhI_kFgY, accessed 9/26/16

Weak effect: ~1 in 10^7 photons is inelastically scattered

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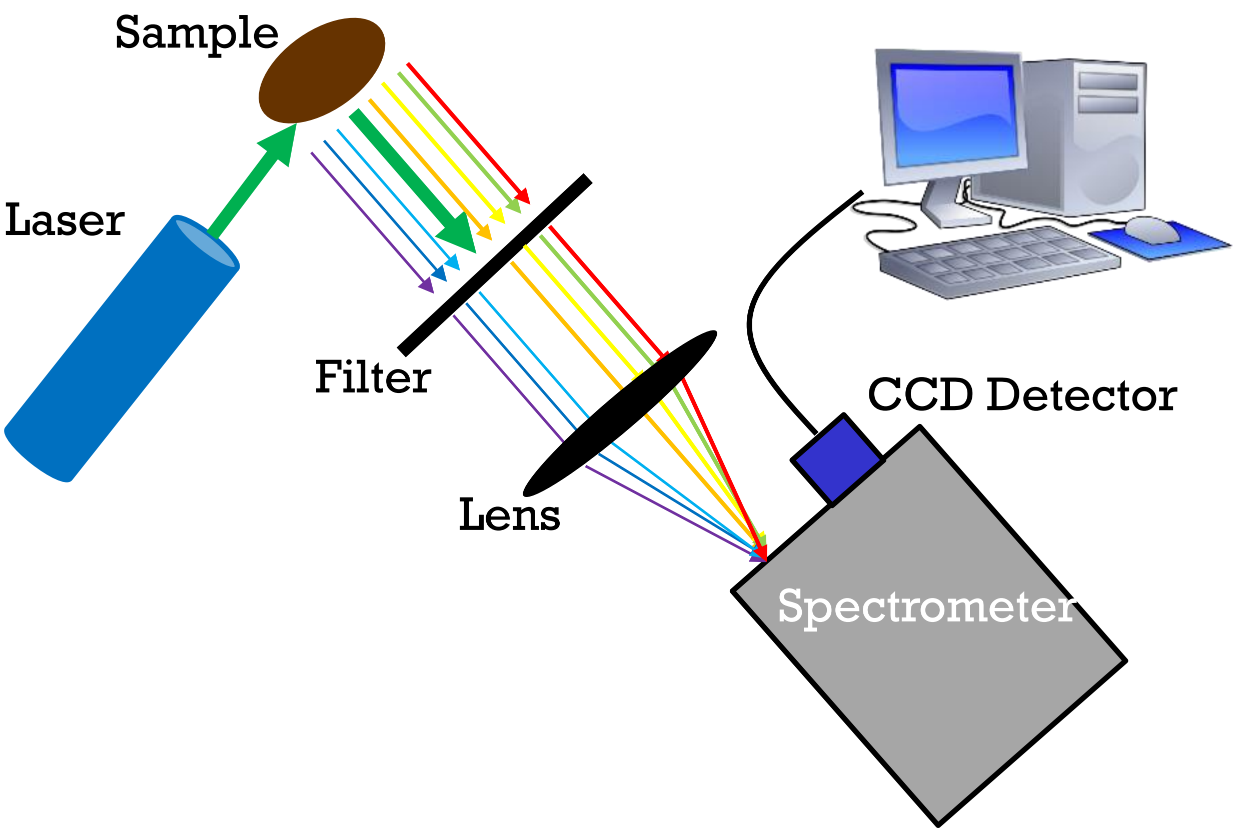
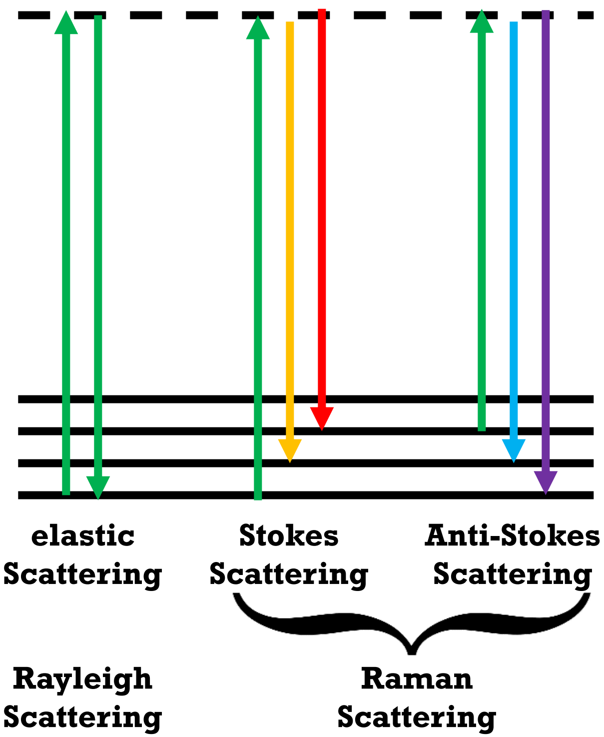
Raman Spectroscopy

$$\text{scattering} \propto \left(\frac{1}{\lambda}\right)^4$$





Provides unique vibrational information

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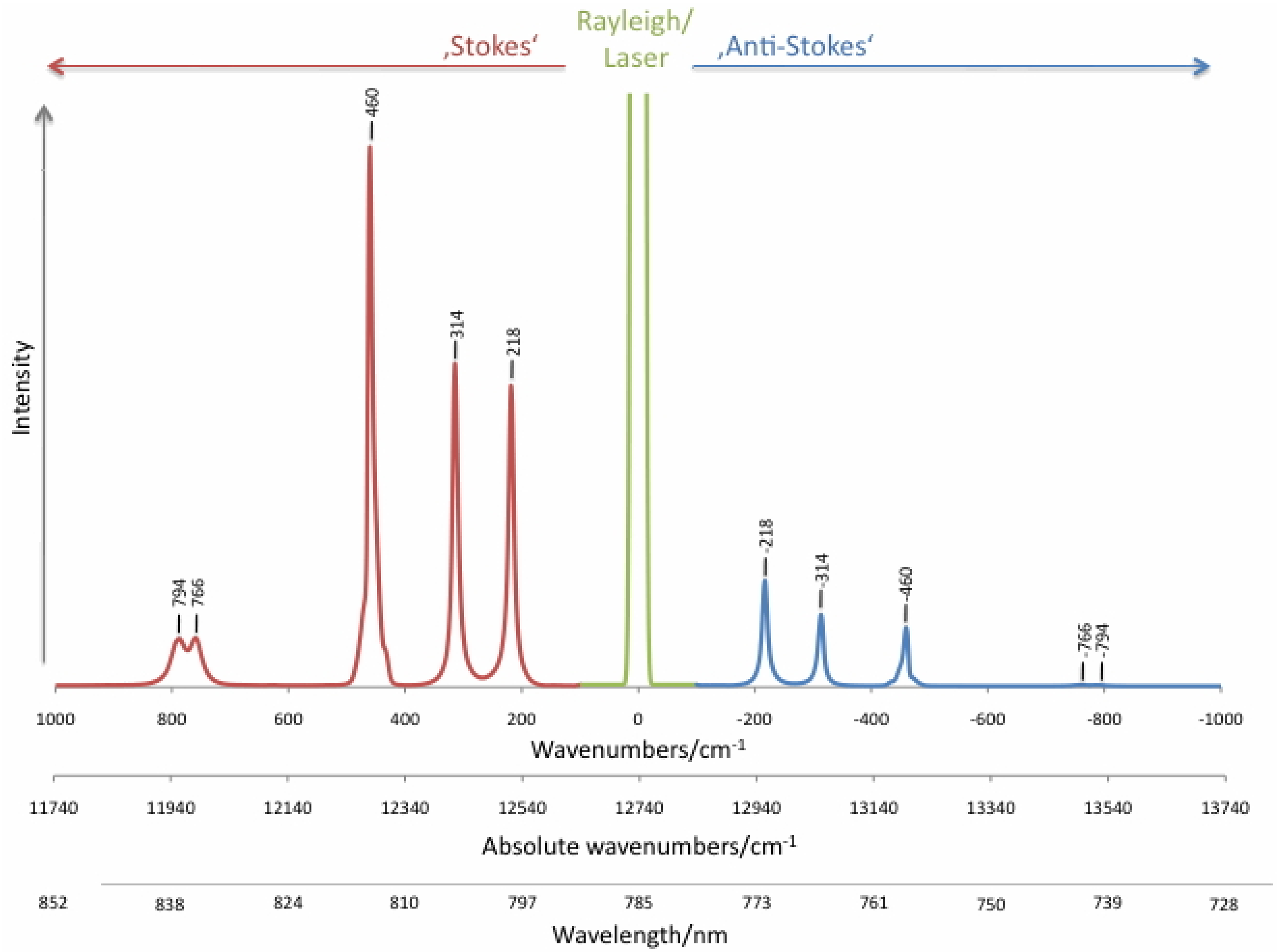
Raman Spectrum



www.raman.de

Frequency, FWHM, and Peak Area are typical parameters being extracted from Raman spectra

Raman Analysis

- **Heat known materials (e.g., Fe_2O_3, Fe_3O_4) to high temperature (e.g., 800 °C, 900 °C, and 1000 °C) and measure Raman spectra.**
- **Perform Inverse calibration (determine composition and temperature):**

$$x = \alpha_0 + \alpha_1 R_1 + \alpha_2 R_2 + \cdots + \alpha_h R_h$$

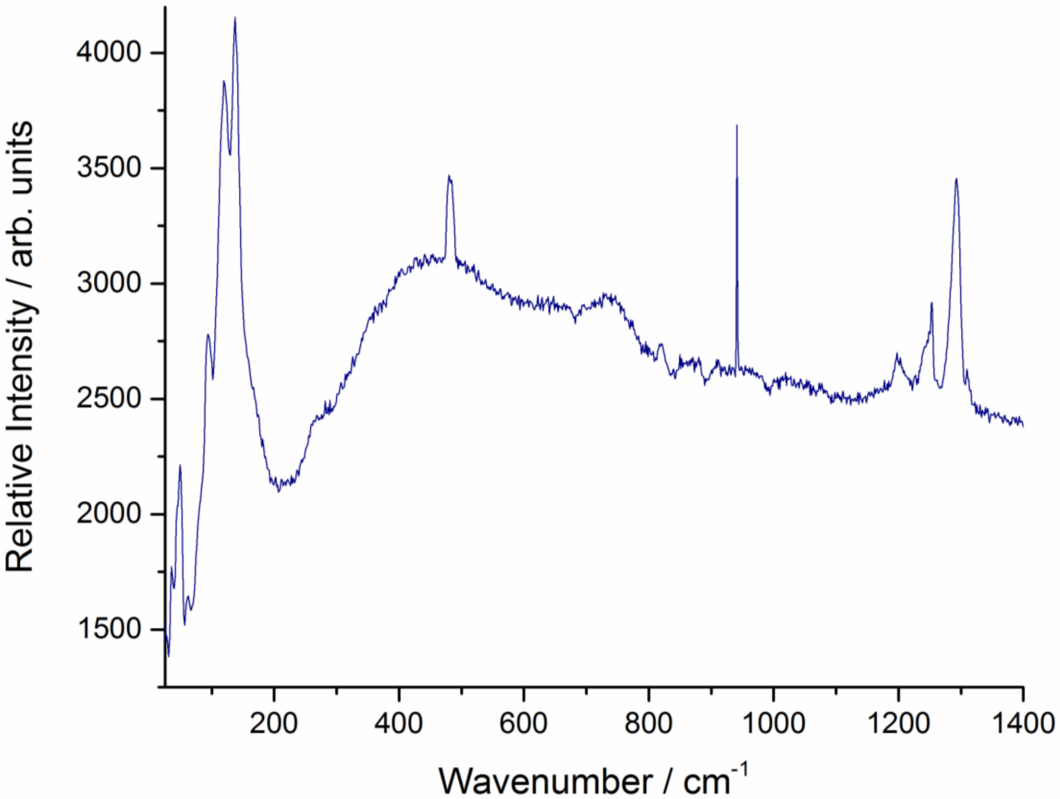
$$T = \beta_0 + \beta_1 R_1 + \beta_2 R_2 + \cdots + \beta_k R_k$$

x: Composition (e.g., mol% Fe_2O_3)
T: Temperature
α_i, β_i: fitting parameters
R_i: subsets of the Raman parameters (frequency; FWHM; area)

Yields T and x in the form of linear combinations of the Raman parameters

1. Li, H., et al. "Feasibility Study of Using High-Temperature Raman Spectroscopy for On-Line Monitoring and Product Control of the Glass Vitrification Process," Energy", PNNL/DOE 1998.
2. Piepel, G. F., et al. "Statistical Modeling of Raman Spectroscopy data from high-temperature glass melts for on-line monitoring of temperature and composition." Quality Engineering 2001, 13, 667-677

Raw CZT Raman Spectrum



Processing:

- Instrumental transfer function
  - Filters
  - Spectrometer
  - Detector
  - Other optical elements
- Background:
  - Fluorescence
  - Blackbody
  - Cosmic radiation
  - Stray light
  - Laser fluctuation
- Multi-peak fitting
  - Peak position
  - FWHM
  - Peak area

Raman spectra require various corrections

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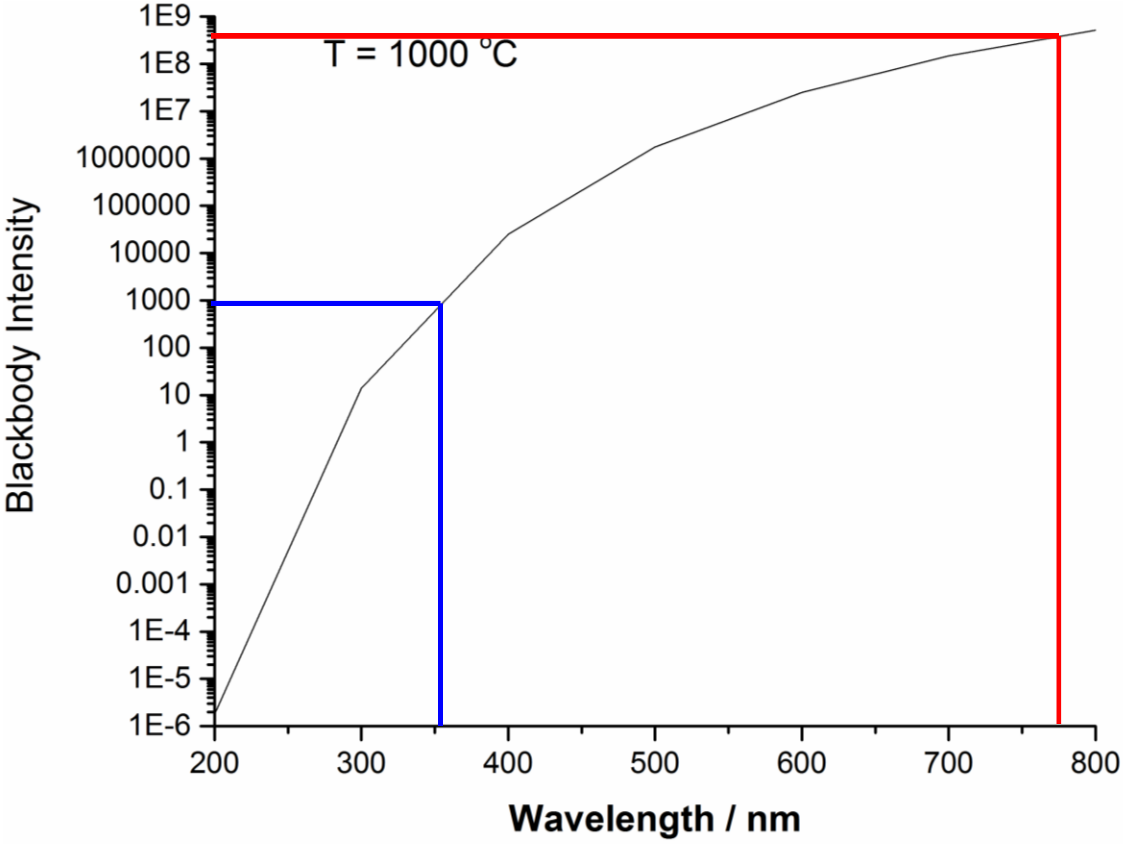
Blackbody Radiation at 1000 °C



$$I_\lambda = \frac{2hc^2}{\lambda^5\left(e^{\left(\frac{hc}{\lambda kT}\right)} - 1\right)}$$

Using 355 nm instead of 785 nm reduces background by more than 5 orders of magnitude

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Pulsed Laser & Gated Detection

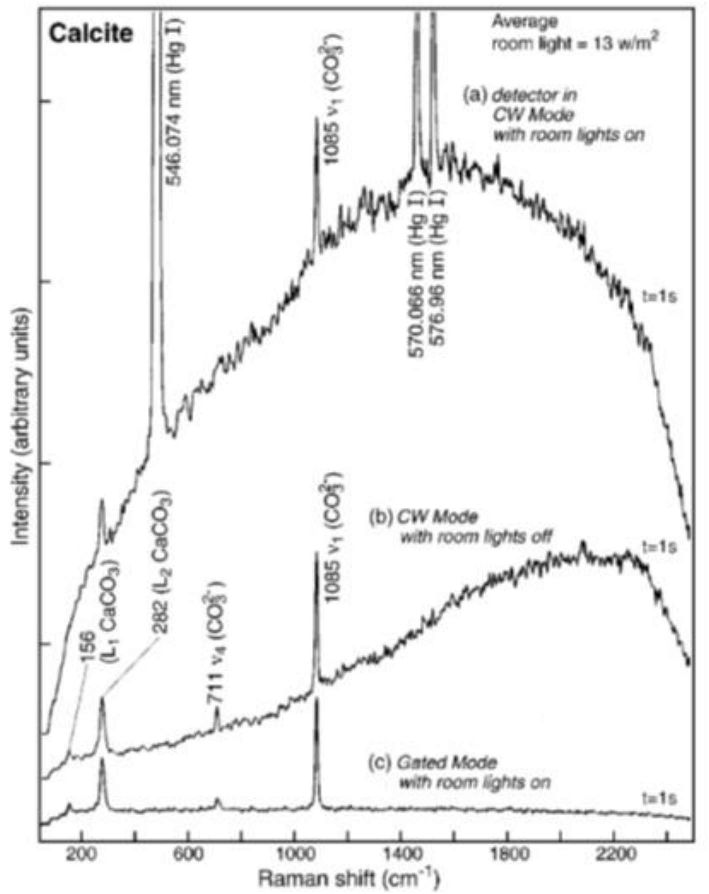

Fig. 2. Raman spectra of a calcite sample at 10 m distance with the fiber coupled system, integration time = 1 s. (a) CW mode with room lights on; (b) CW mode with room lights off and (c) spectrum in the gated mode with room lights on. Laser: 532 nm, 35 mJ pulse^{-1}, 20 Hz; slit 100 µm.

A. K. Misra, et al., *Spectrochim Acta A* **2005**, *61*, 2281

<u>Pulsed Laser</u>:
- Larger number of signal photons vs. background signal

<u>Gated Detection</u>:
- Reduction of background signal

Enhanced S/N

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Remote Raman

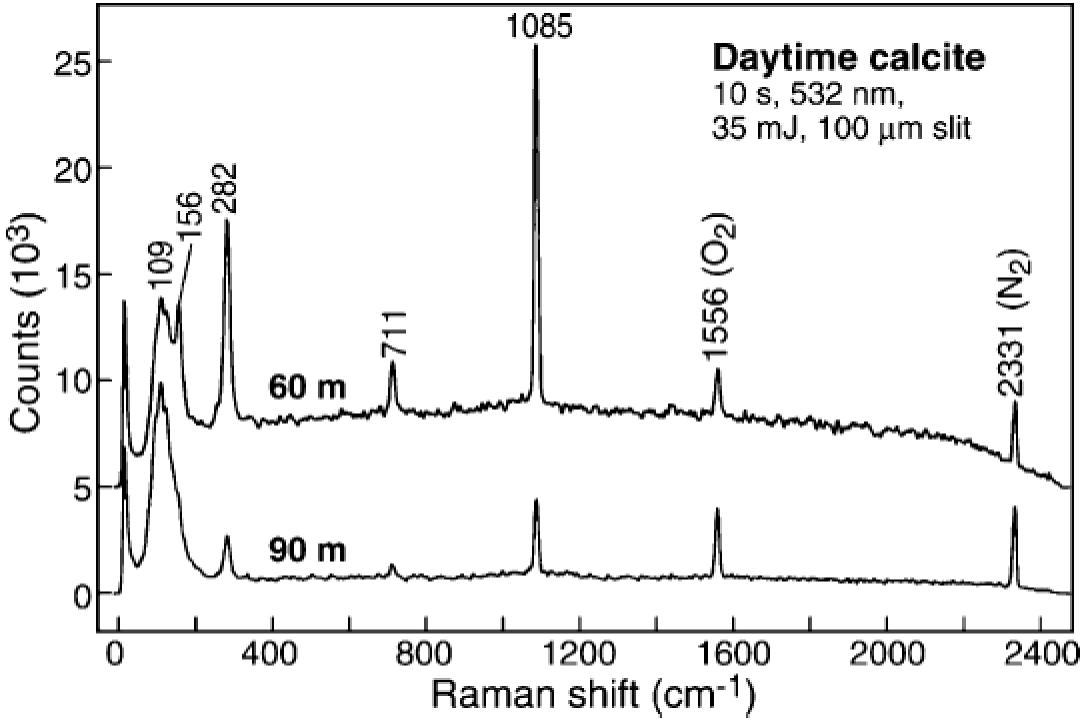

Fig. 9. Raman spectra of calcite at 60 m and 90 m distances measured during daylight using coaxial geometry with 10 s integration time in gated mode. Laser: 532 nm, 35 mJ pulse^{-1}, 20 Hz; slit 100 µm.

A. K. Misra, et al., *Spectrochim Acta A* **2005**, *61*, 2281

Raman demonstrated over long distances

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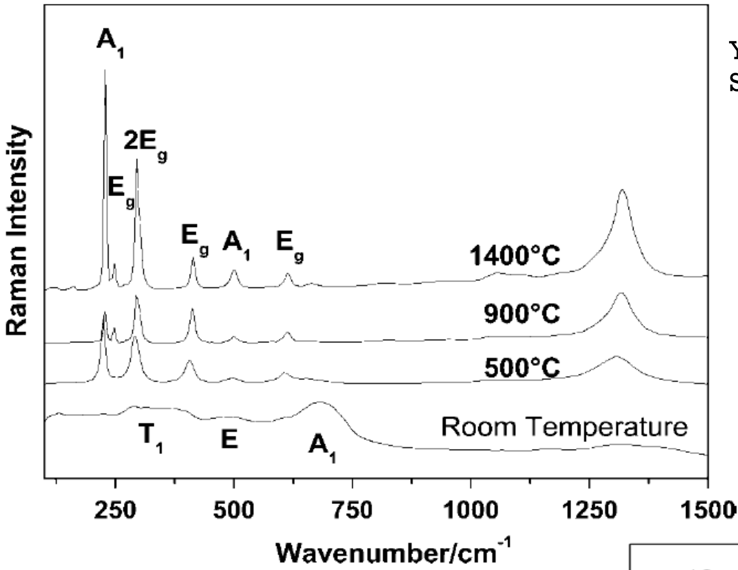
Example Raman Spectra

γ-Fe_2O_3 prepared at different temperatures



Y. El Mendili, et al., J. Raman Spec., 42, 239 (2011)

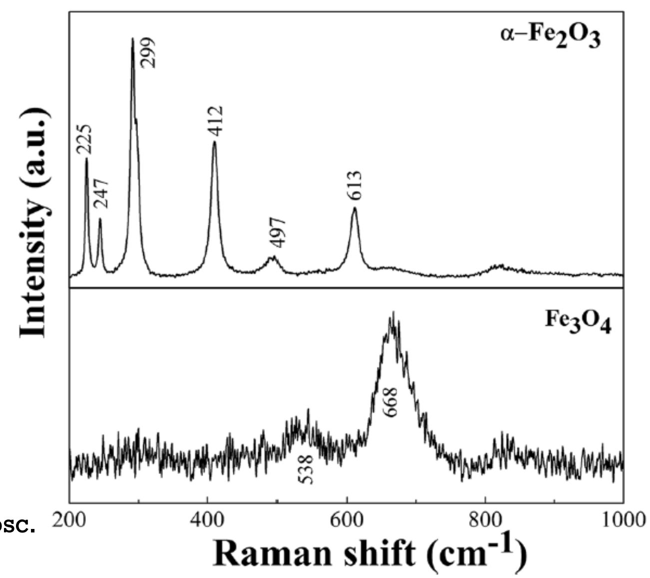
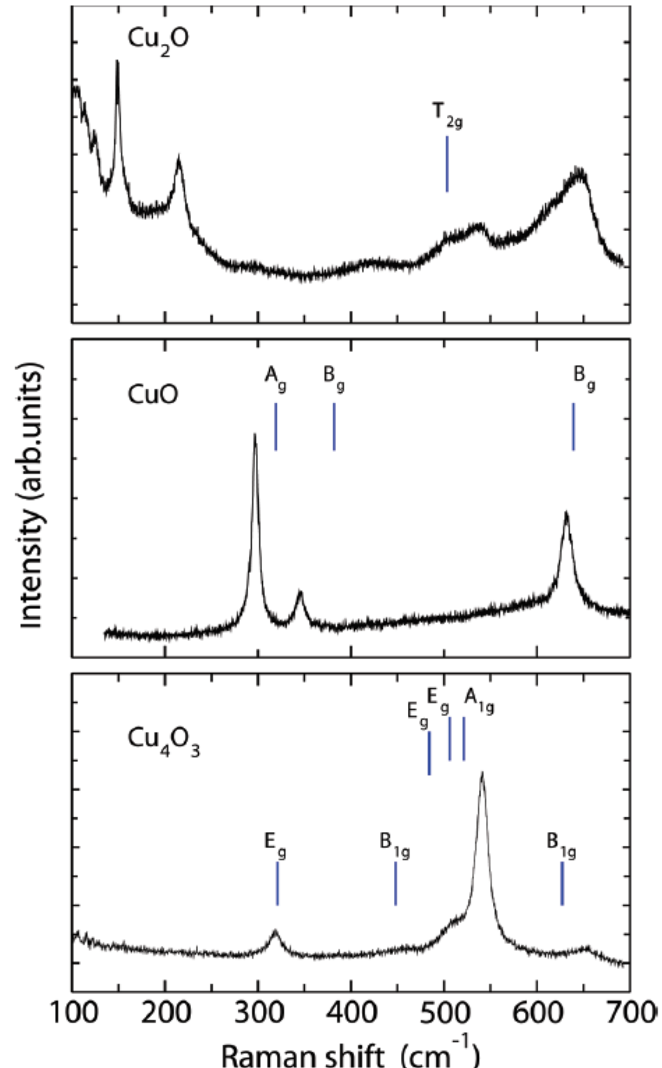


Figure 2 Raman spectra of α-Fe_2O_3 hexagonal plates and Fe_3O_4 polyhedral particles.

J.-F. Lu and C.-J. Tsai, Nanosc. Res. Lett. 9, 230 (2014)



L. Debbichi, et al., *J. Phys. Chem. C 116*, 10232 (2012)

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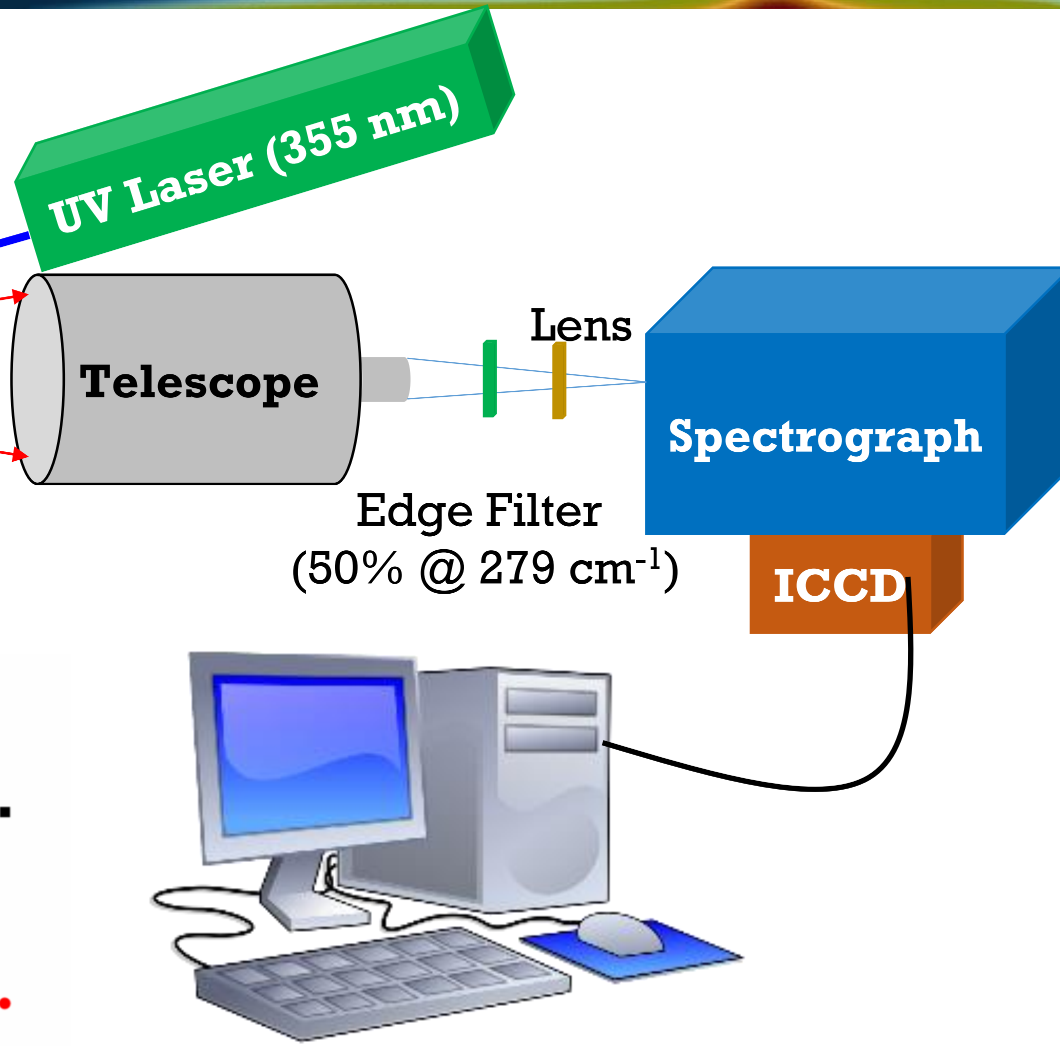
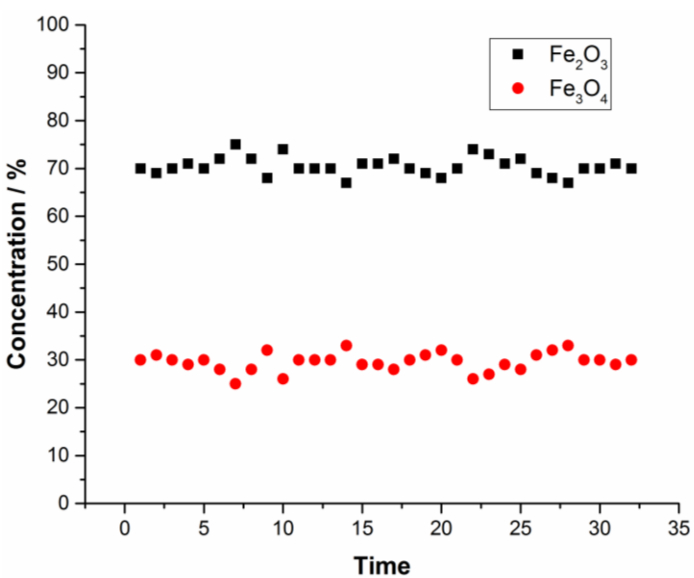
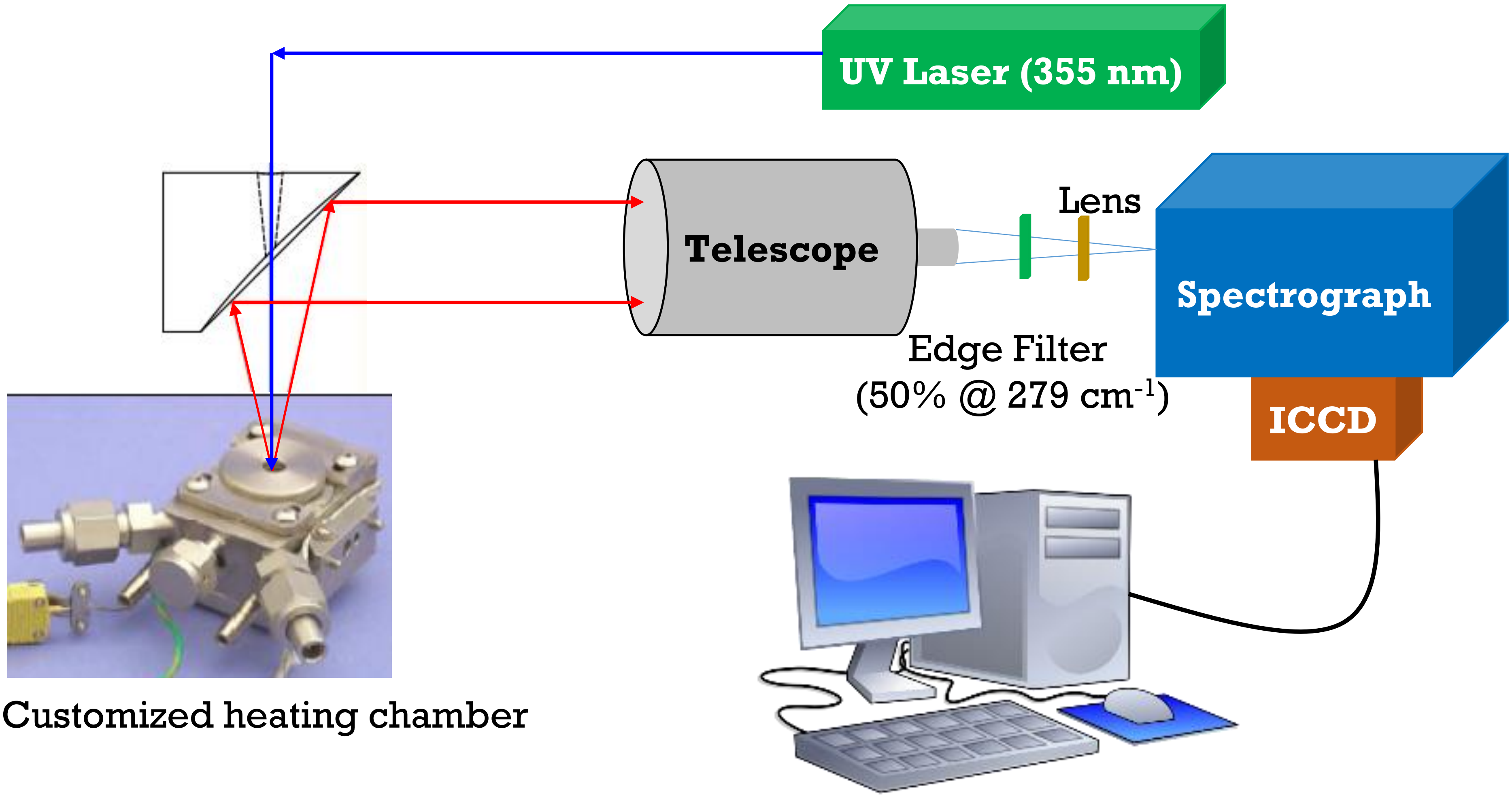
Envisioned Field Setup

Hot metal oxide (800 °C – 1000 °C)





Initial Laboratory Setup



Customized heating chamber

Calibration measurements on well-defined samples

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Team & Assignments

Project Team:

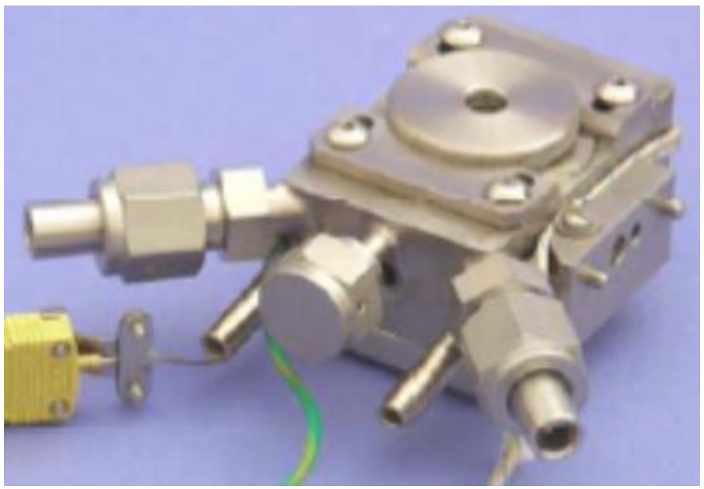
- Hergen Eilers, Ph.D. Physics PI
  - General oversight
  - Designing sample chamber
  - Setting up Raman system for pulsed UV measurements
- John Kirtley, Ph.D. Chemistry Postdoctoral associate
  - Optimizing Raman setup
  - Making Raman measurements
  - Analyzing Raman data
- Victoria Leichner, Chemistry Student
  - Currently learning about relevant scientific issues
  - Helping with design of sample chamber
  - Helping with Raman measurements
  - Helping with analysis of Raman data

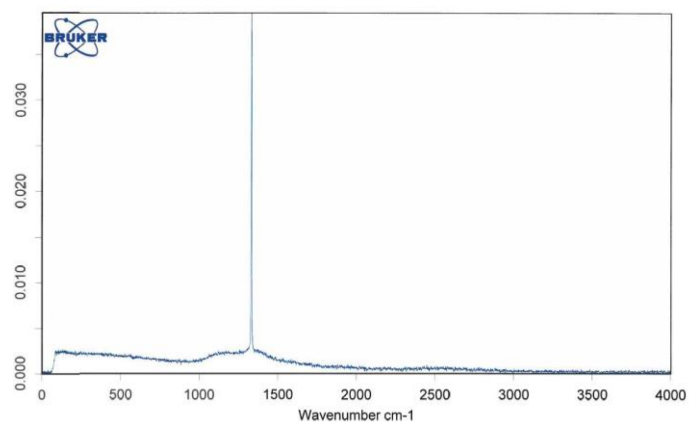
Tasks

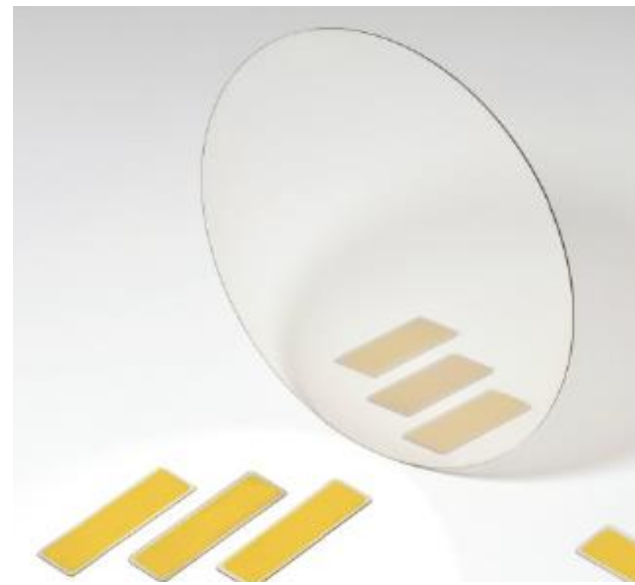
1.0 – Project Management and Planning

2.0 – Time-gated Raman spectroscopy system

2.1 – Design and build custom sample chamber



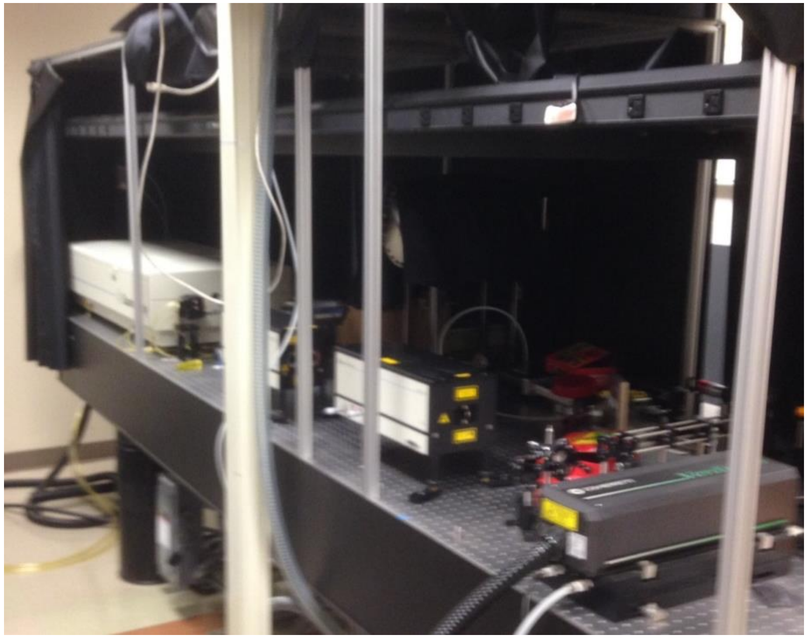




http://www.diamond-materials.com/downloads/diamond_optical_windows.pdf

Tasks

2.2 – Set up Raman spectroscopy system



3.0 – Experimental parameter optimization

Optimize S/N for single-shot measurements

(laser wavelength, gate delay, gate width, etc.)

Tasks

4.0 – Analysis procedure

4.1 – Pre-processing steps

Corrections for instrumental response, background, temperature, etc.

4.2 – Statistical modeling and multivariate analysis

Identify best approach for determining the oxidation state of the oxygen carrier particles.

4.3 – Automated analysis procedure

Automate pre-processing and analysis steps for quick analysis and feedback.

5.0 – Raman system demonstration

Blind tests on oxygen carrier particles

Gantt Chart

Year	1				2			
Quarter	1	2	3	4	5	6	7	8
Task 1.0 – Project Management and Planning *Start: Month 1 End: Month 24*								
Task 2.0 – Time-gated Raman spectroscopy system *Start: Month 1 End: Month 8*								
Subtask 2.1 – Custom sample chamber *Start: Month 1 End: Month 5*		A						
Subtask 2.2 – Raman spectroscopy system design *Start: Month 2 End: Month 8*			B					
Task 3.0 – Experimental parameter optimization *Start: Month 7 End: Month 12*					C			
Task 4.0 – Analysis procedure *Start: Month 7 End: Month 21*								
Subtask 4.1 – Pre-processing steps *Start: Month 7 End: Month 16*						D		
Subtask 4.2 – Statistical modeling and multivariate analysis *Start: Month 13 End: Month 20*							E	
Subtask 4.3 – Automated analysis process *Start: Month 13 End: Month 21*								F
Task 5.0 – Raman system demonstration *Start: Month 22 End: Month 24*								G

A, B, …,G refer to the milestones listed in section C.

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Milestones

ID	Budget Period	Title	Completion (end of month)
A	Year 1	High-temperature sample chamber available	5
B	Year 1	Completed high-temperature Raman spectroscopy setup	8
C	Year 1	Optimized measurement parameters	12
D	Year 2	Identified and implemented all pre-processing steps	16
E	Year 2	Completed statistical modeling and multivariate analysis	20
F	Year 2	Completed automated analysis procedure	21
G	Year 2	Demonstrated feasibility	24

SUCCESS CRITERIA AT DECISION POINTS

1. End of month 12: Experimental Raman spectroscopy system for high-temperature measurements operational.
2. End of month 21: Automated analysis process operational.
3. End of month 24: Demonstrated high-temperature Raman spectroscopy system on a minimum of three blind samples.

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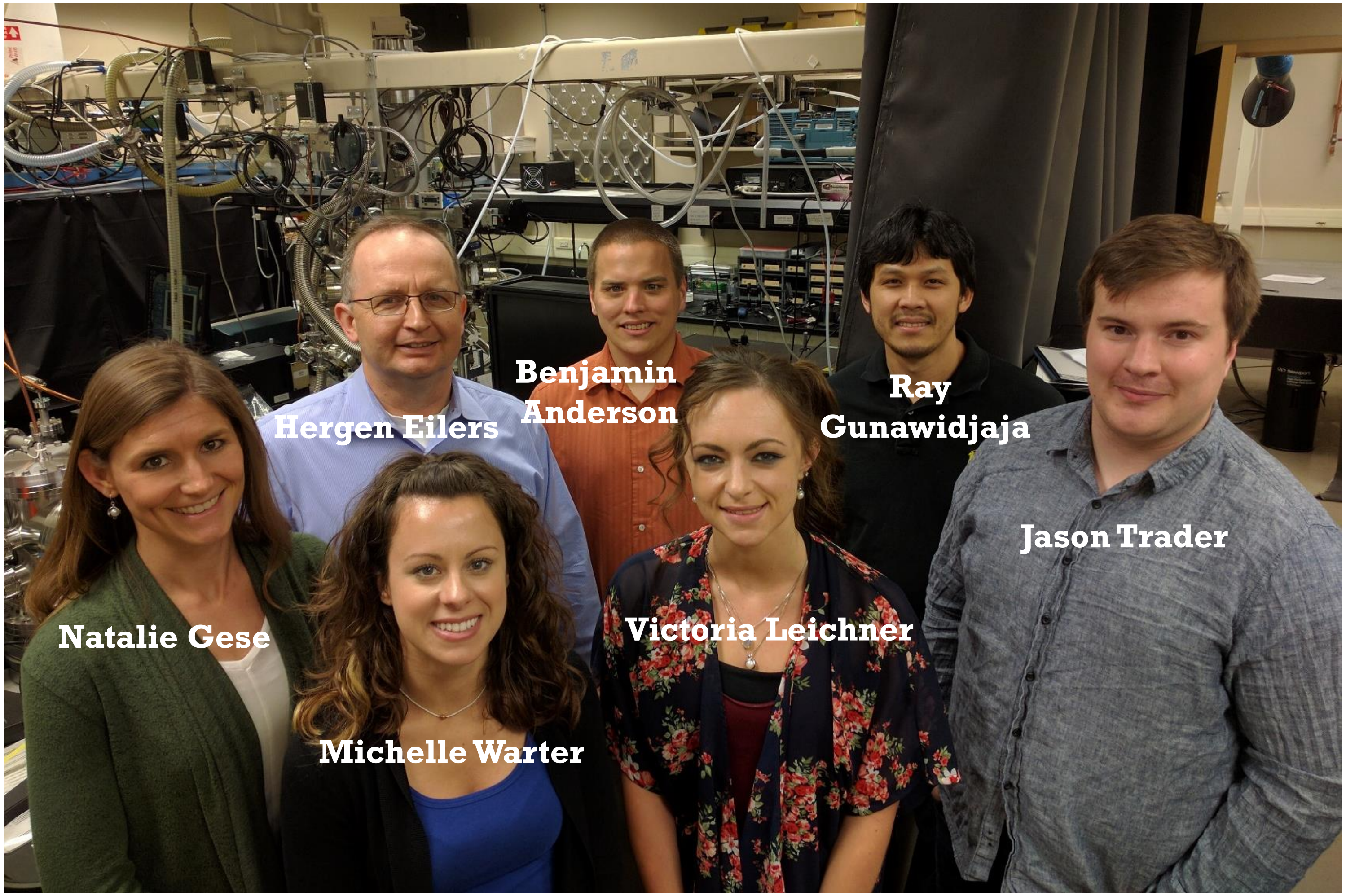
Questions?



Thanks to DOE/NETL and Dr. Jessica Mullen