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Molten Salt Reactor PROGRAM

On-line Monitoring for MSR Off-Gas Treatment: Molecular Approach

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PNNL

Annual MSR Campaign Review Meeting April 16-18 2024

PNNL-SA-196932

In-line and On-line Monitoring

Sensors directly in or on the process

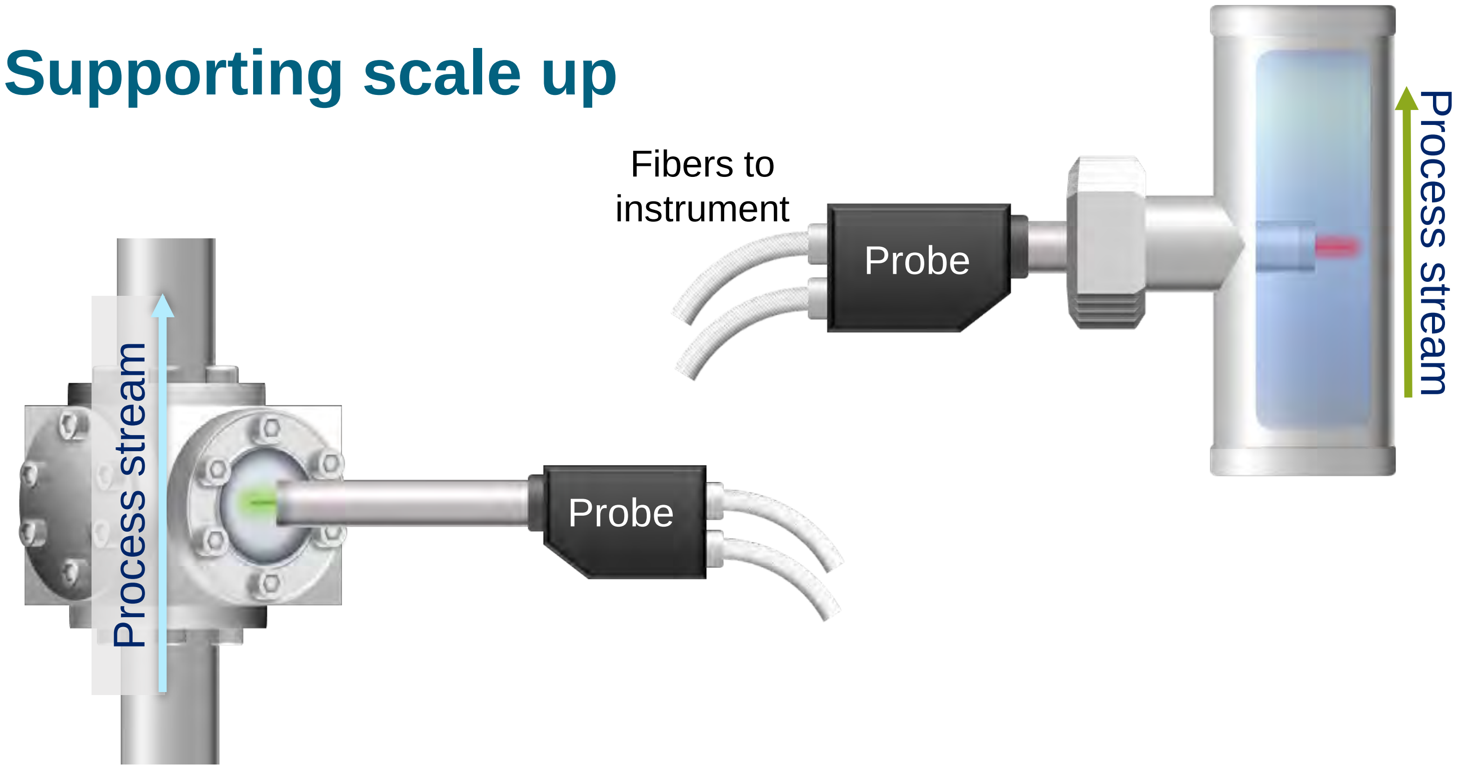
In situ and real-time analysis of a given process or system

Fundamental characterization

Efficient process design

Safe and cost-effective deployment

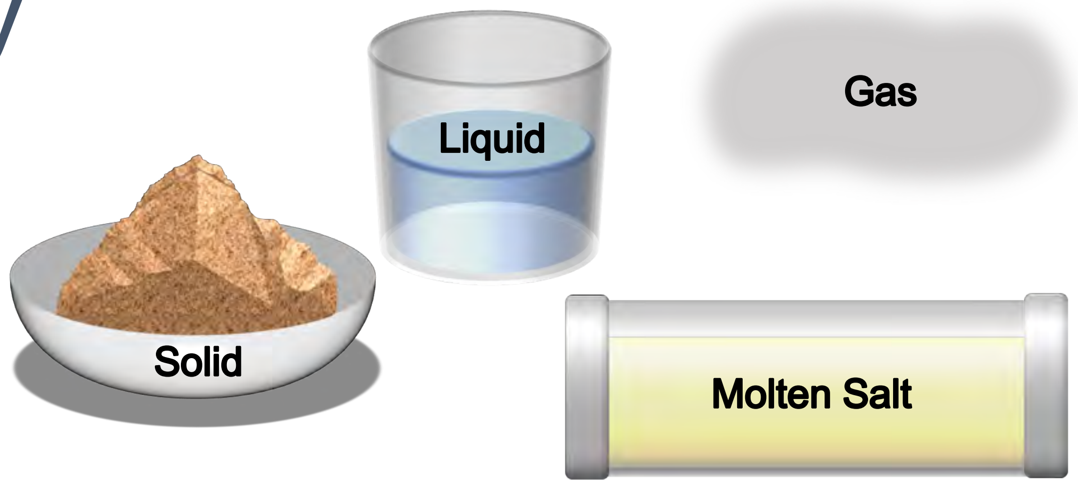
Supporting scale up



Chemical Characterization: Optical Spectroscopy

- Provides chemical information
  - Identification and quantification
  - Oxidation state
  - Molecular and elemental species
- Highly mature technology
- Simplistic integration
- Robust and versatile

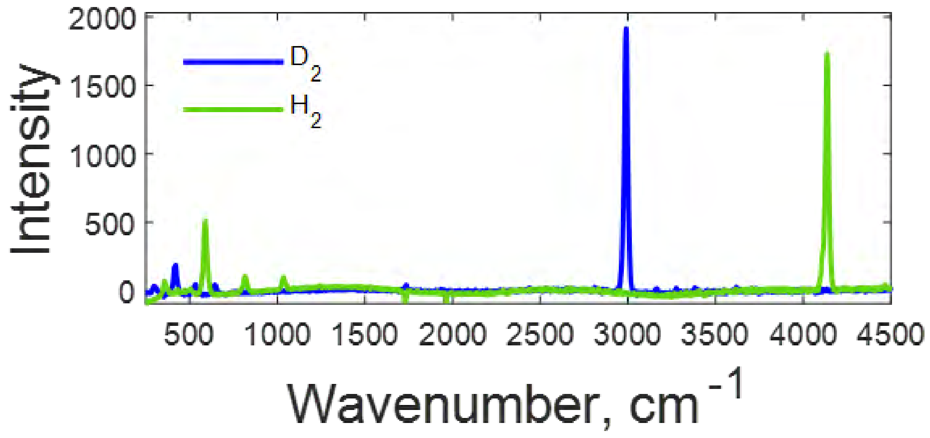
System matrix

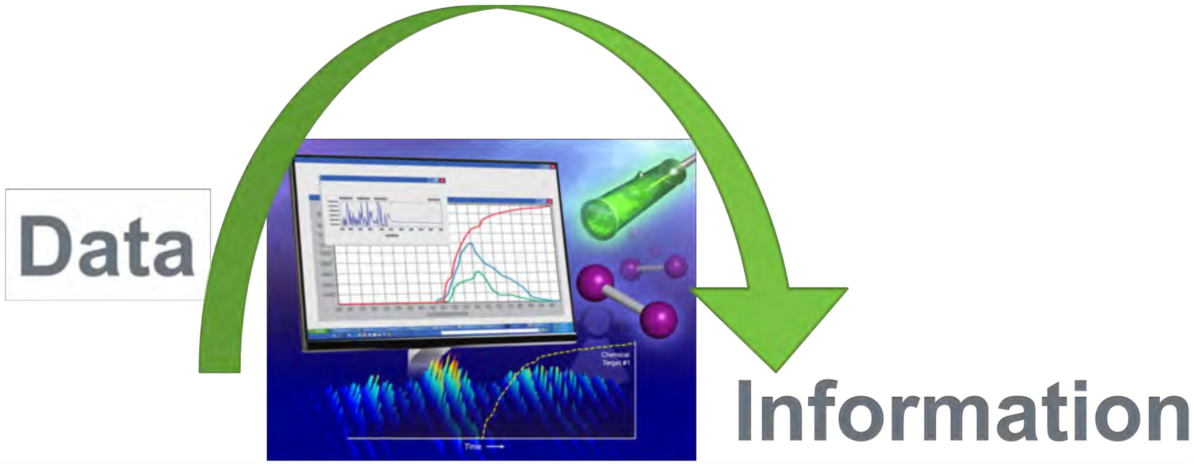


System scale

The Two-Pronged Challenge: Monitoring Harsh and Complex Chemical Systems

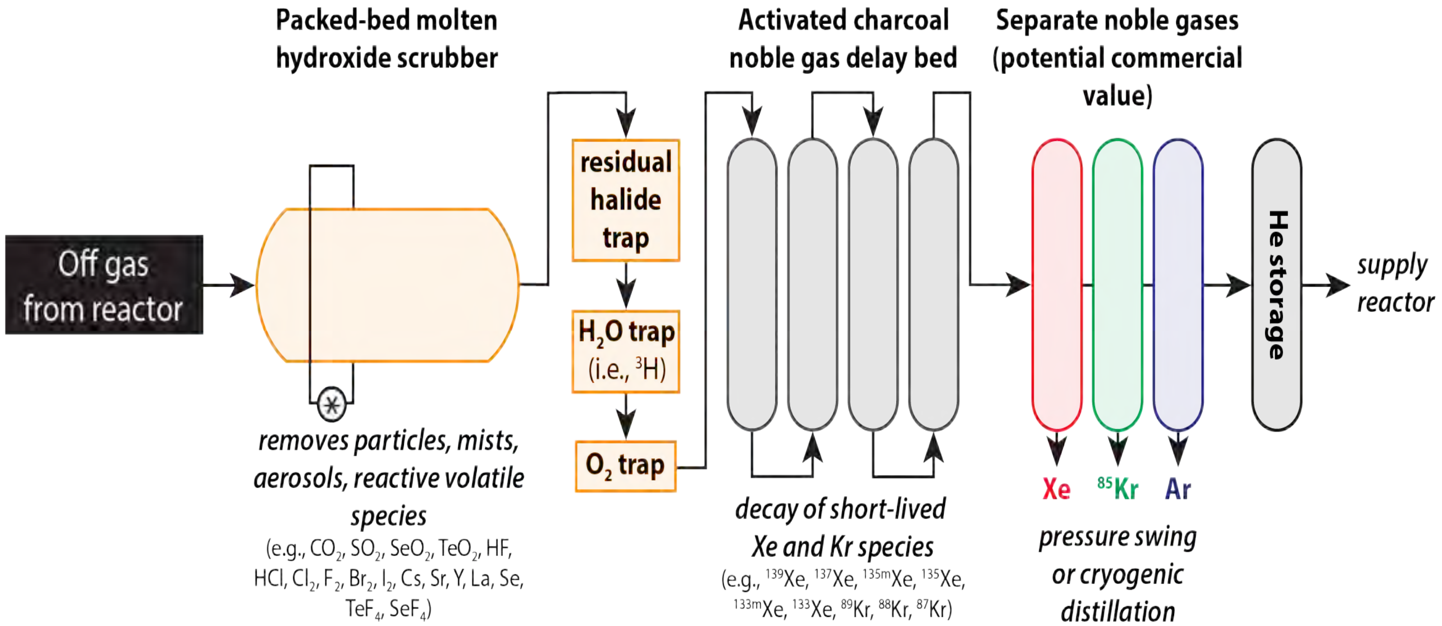
- Sensor development
  - Overcoming COTS (commercial off the shelf) limitations to build sensors that can survive:
    - Highly corrosive systems
      - HF gas, molten salts
    - High temperature systems
      - Molten salts
    - Radiation
  - Improve sensitivity and limit of detection for low signal targets
    - Hydrogen isotopes: e.g. H_2, D_2, T_2
- Making smart sensors
  - Building autonomous tool kits that can accurately identify and quantify chemical targets using spectral data





Systems of Focus

- Building tools to support development and demonstration of off-gas treatment systems
  - Informed development
  - Better, faster, safer, and cost-effective deployment



Mcfarlane, J.; Ezell, N.; Del Cul, G.; Holcomb, D. E.; Myhre, K.; Chapel, A.; Lines, A.; Bryan, S.; Felmy, H. M.; Riley, B. *Fission Product Volatility and Off-Gas Systems for Molten Salt Reactors*; Oak Ridge National Lab.(ORNL), Oak Ridge, TN (United States): 2019.

Interlaboratory Collaboration

- Building and demonstrating applications throughout the treatment process

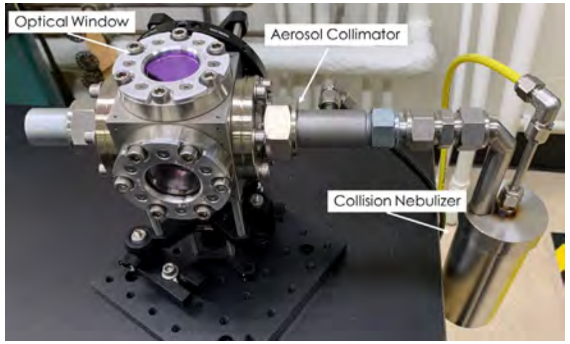
- Collaborating with additional teams to create comprehensive characterization/control strategies

- Aiming to provide key features such as mass balance

Molecular

PNNL team

Atomic



ORNL team
Hunter Andrews
Joanna Mcfarlane
Kevin Robb

FY24 Project Overview

- **M3RD24PN0602041: Demonstrate application of optical monitoring tools for demonstration on gas stream**
  - Due 9/30/24
  - Milestone is on schedule

- **Progress to date:**
  - Designing and testing improved gas measurement cell
  - Manuscript on hydrogen isotope measurements accepted by Analytical Chemistry
  - Continued collaboration with ORNL to test sensors in salt loop
  - Preparing for onsite demo at ORNL

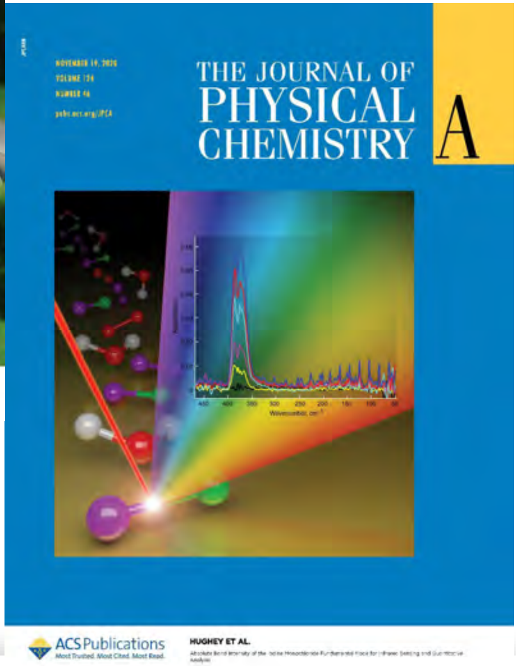
Improving Gas Cell Design

- Past focus has been on using COTS sensors and instrumentation
- Demonstration on a wide range of key targets
    - Iodine species (gas and molten salt phases)
    - Hydrogen gas species (gas phase)

Felmy, H. M.; Clifford, A. J.; Medina, A. S.; Cox, R. M.; Wilson, J. M.; Lines, A. M.; Bryan, S. A., On-Line Monitoring of Gas-Phase Molecular Iodine Using Raman and Fluorescence Spectroscopy Paired with Chemometric Analysis. *Environ Sci Technol 2021, 55, 6, 3898–3908.*

Adan Schafer Medina, Heather M. Felmy, Molly E. Vitale-Sullivan, Hope E. Lackey, Shirmir D. Branch, Samuel A. Bryan, and Amanda M. Lines
ACS Omega 2022 7 (44), 40456-40465.
DOI: 10.1021/acsomega.2c05522

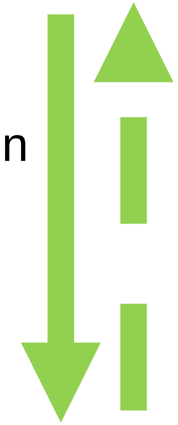
Hughey, K. D.; Bradley, A. M.; Tonkyn, R. G.; Felmy, H. M.; Blake, T. A.; Bryan, S. A.; Johnson, T. J.; Lines, A. M., Absolute Band Intensity of the Iodine Monochloride Fundamental Mode for Infrared Sensing and Quantitative Analysis. *J Phys Chem A 2020, 124* (46), 9578-9588.

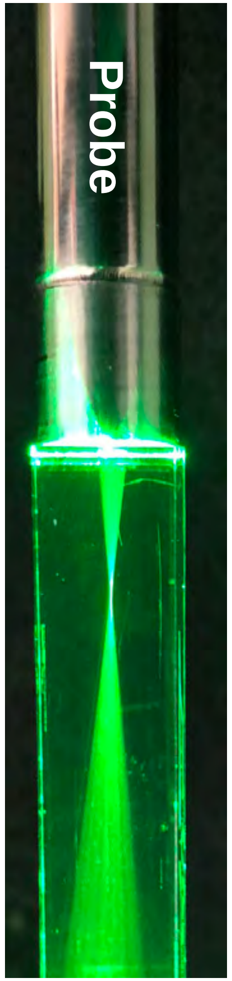


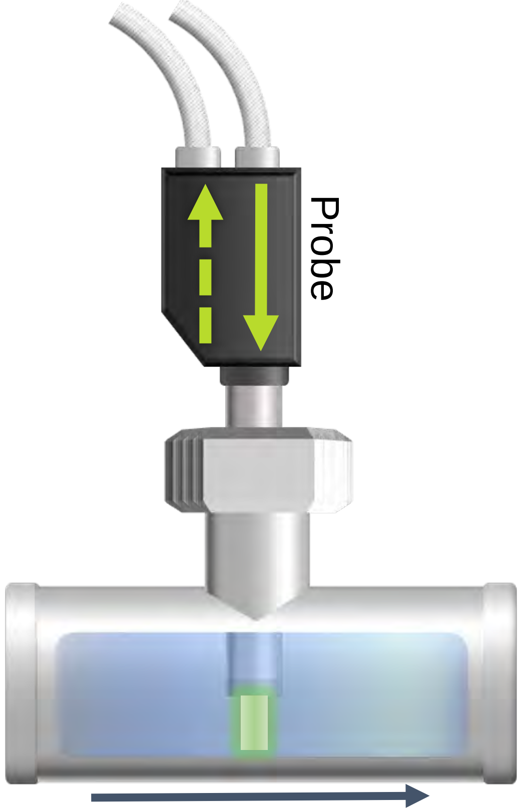
Probe Details

- Typically, Raman spectroscopy relies on 180° backscatter

- Measurement of molecular, polyatomic species including several key targets in the gas phase

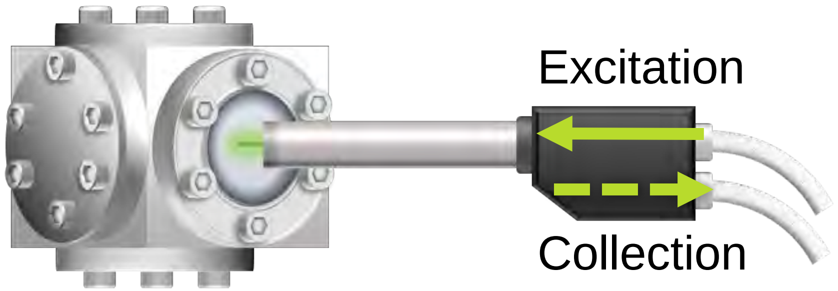


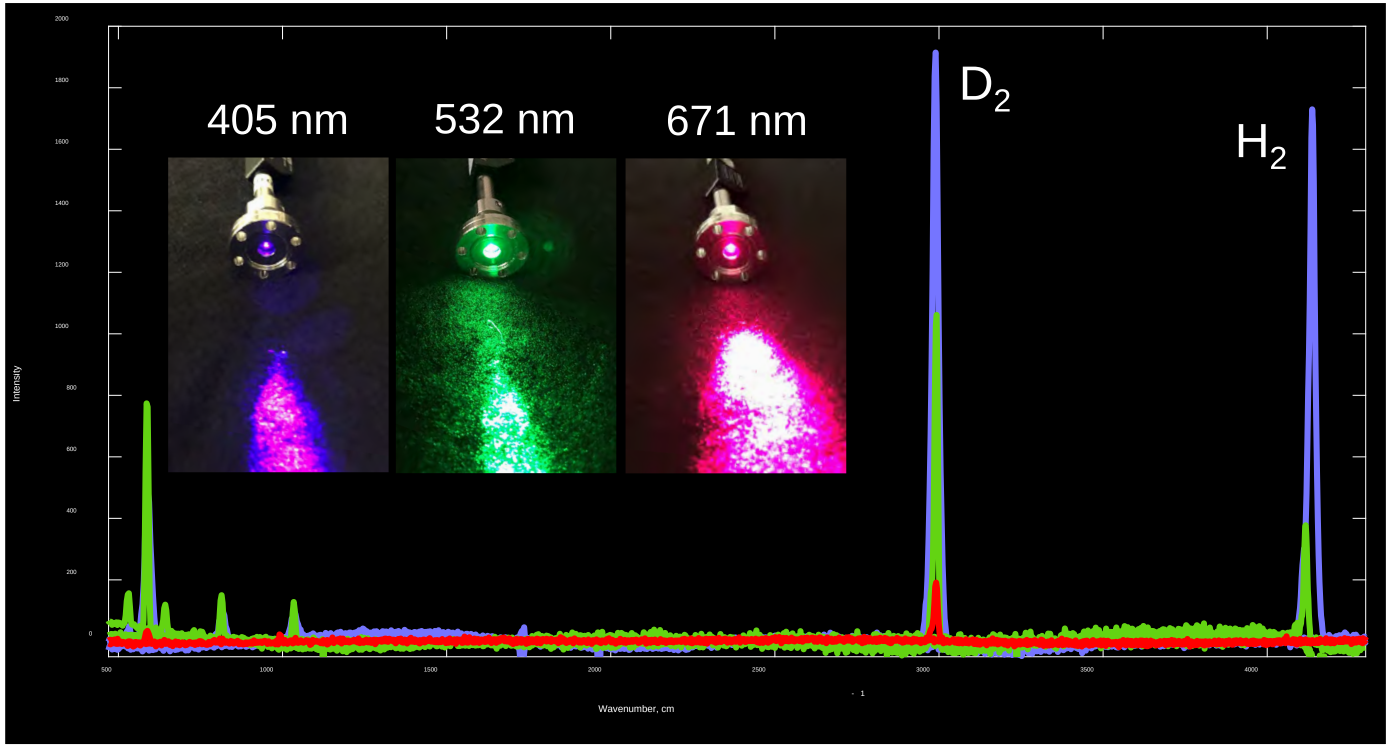




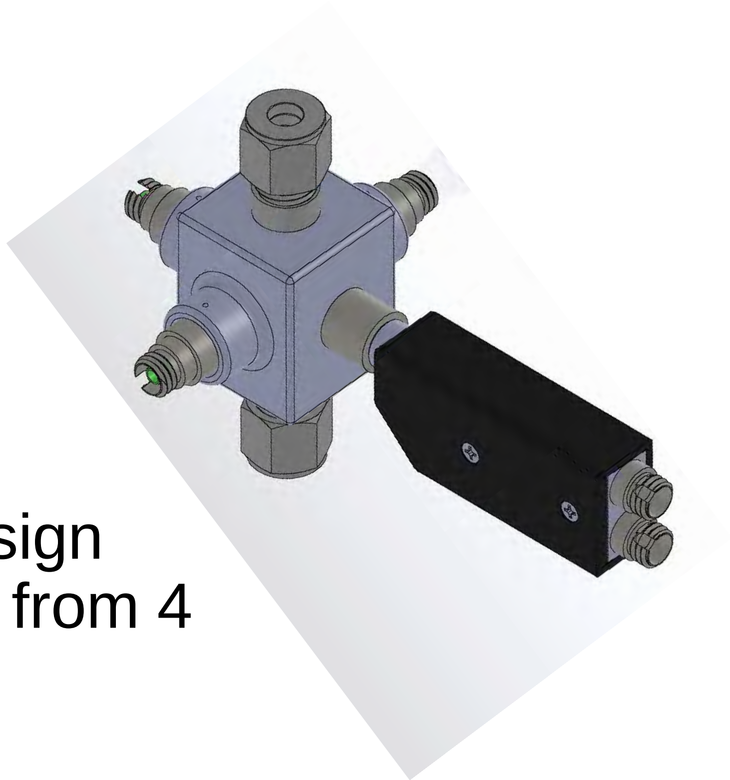
Improving Gas Cell Design

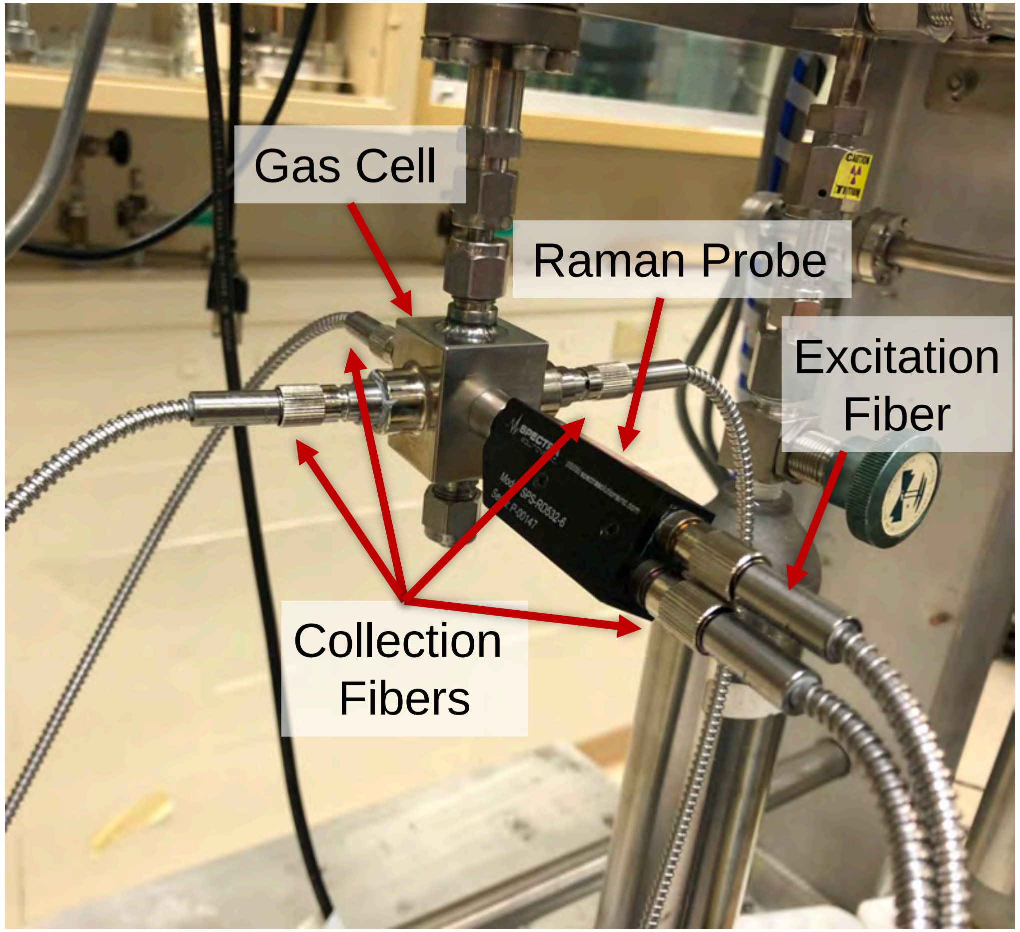
- First gas cell design consisted of optical window on gas line
- Application to hydrogen isotopes





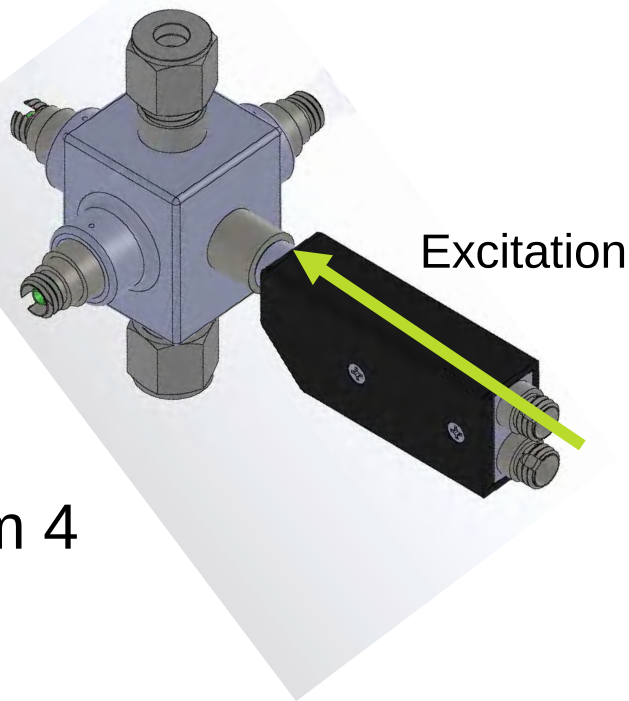
Improved Gas Cell

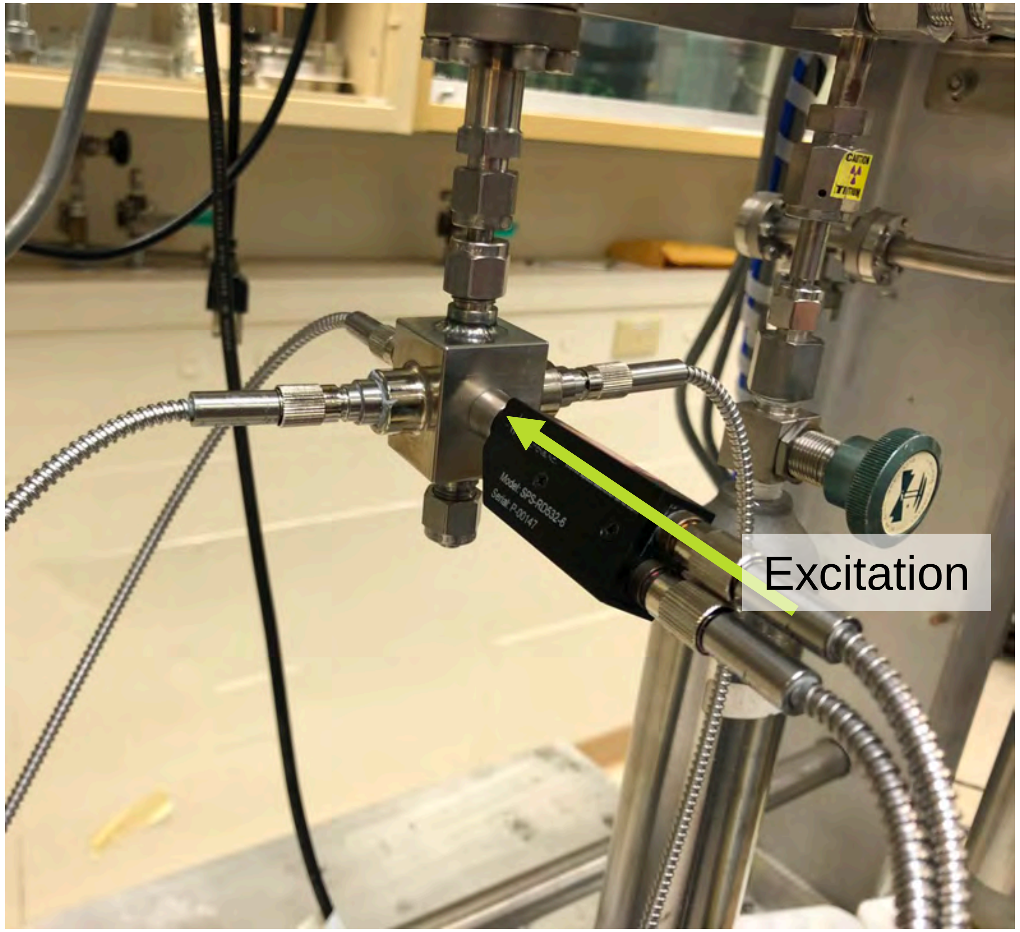




- New gas cell design combines signal from 4 collection ports

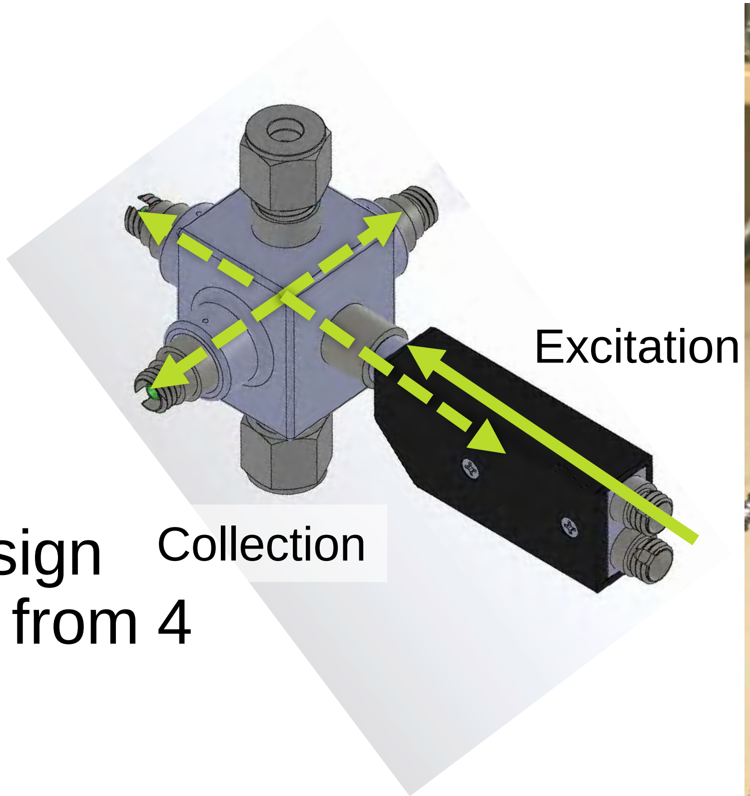
Improved Gas Cell

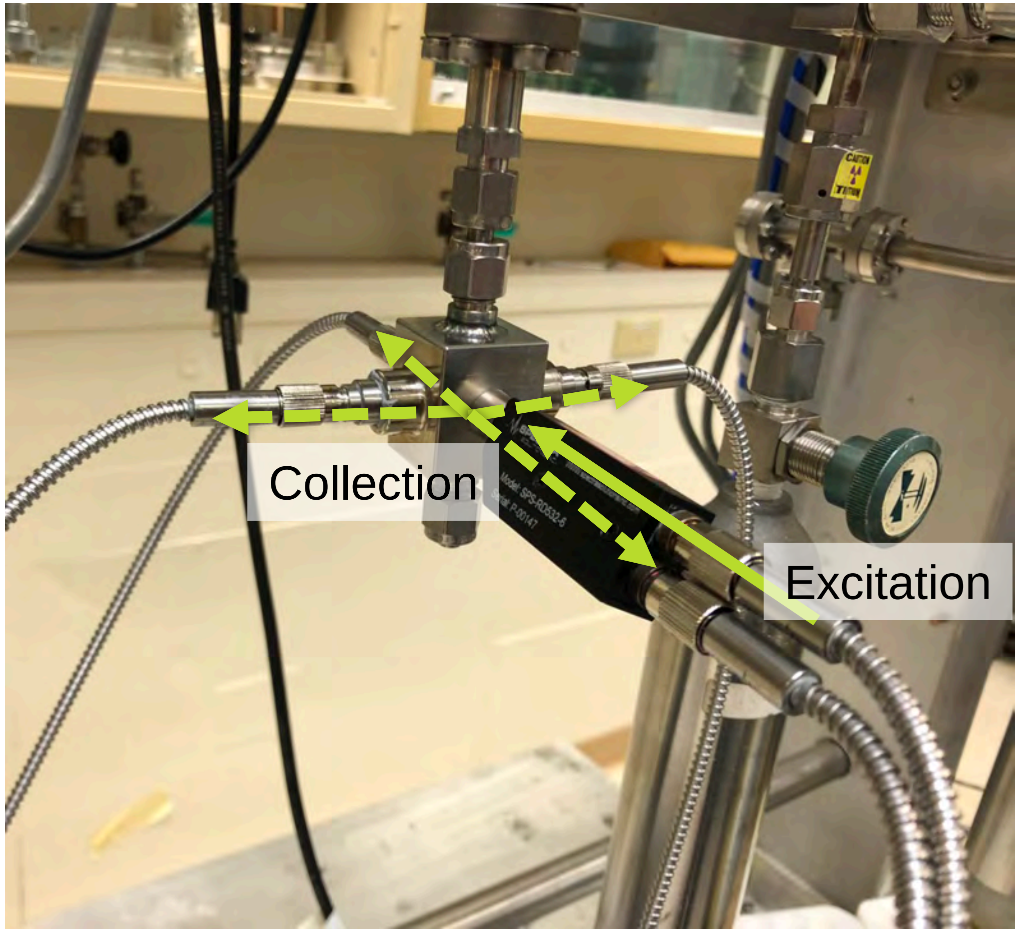




- New gas cell design combines signal from 4 collection ports

Improved Gas Cell

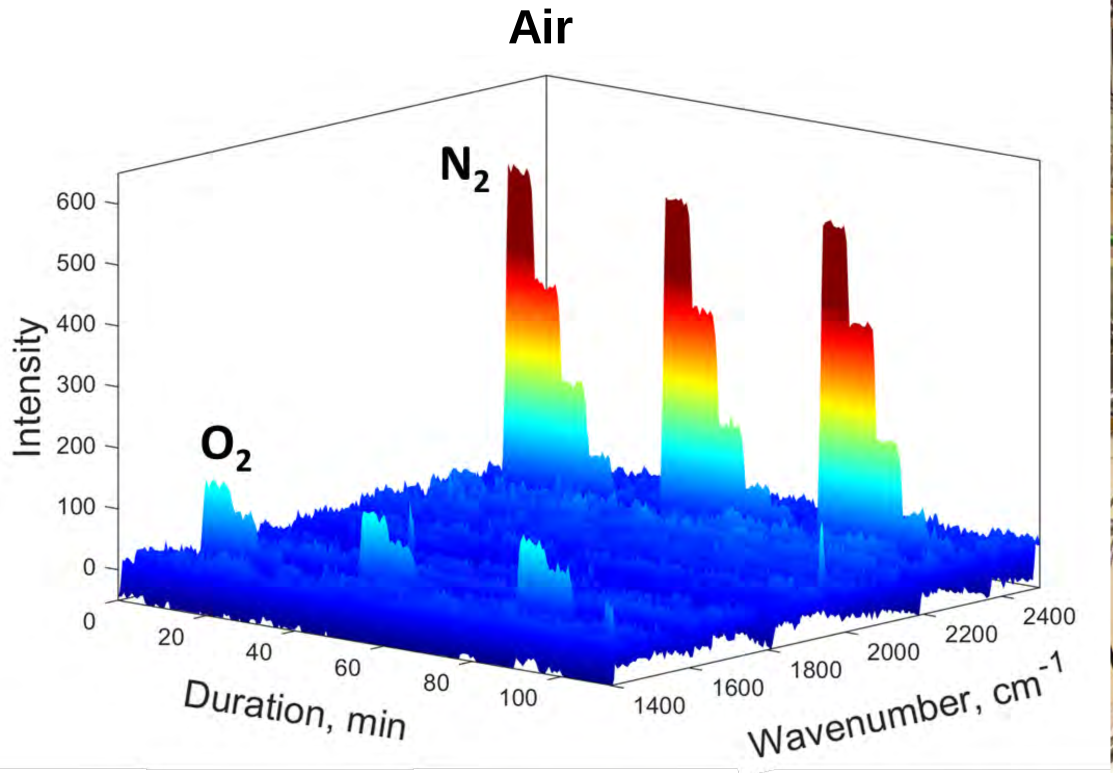




- New gas cell design combines signal from 4 collection ports

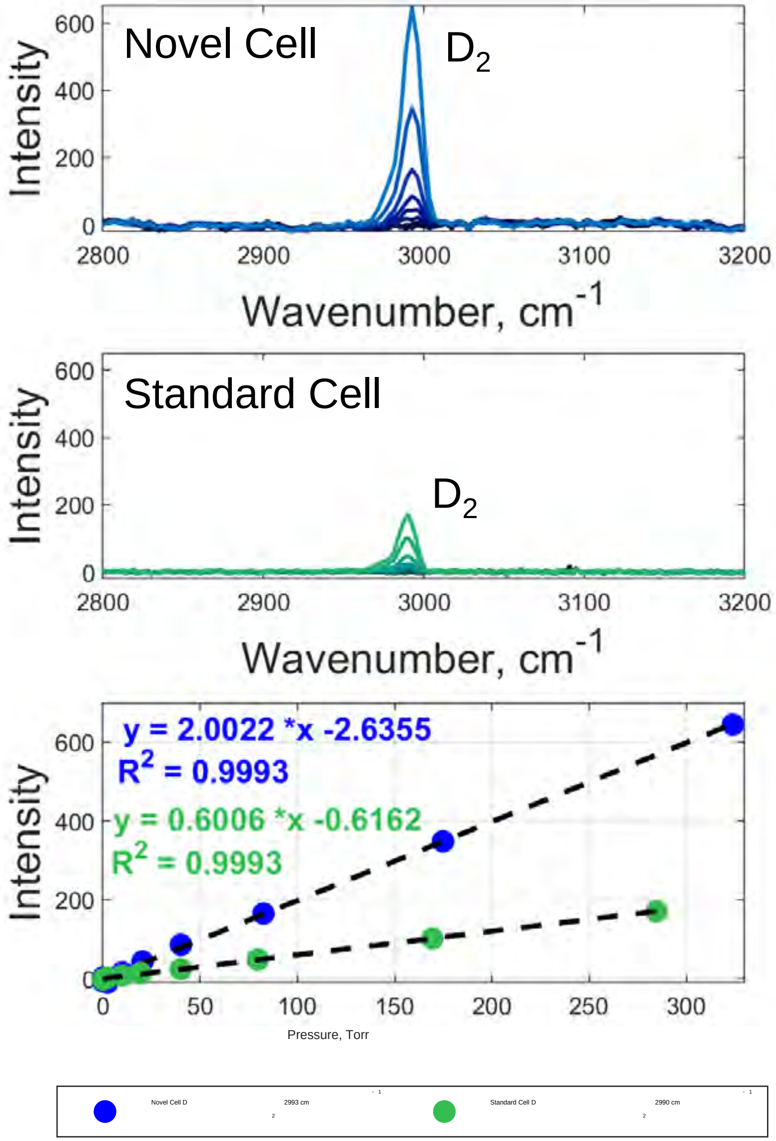
Improved Gas Cell

- Tested the new gas cell on standards to compare sensitivity
- Integration of summer student Alyssa Espley (now post-bachelor) into experimental work



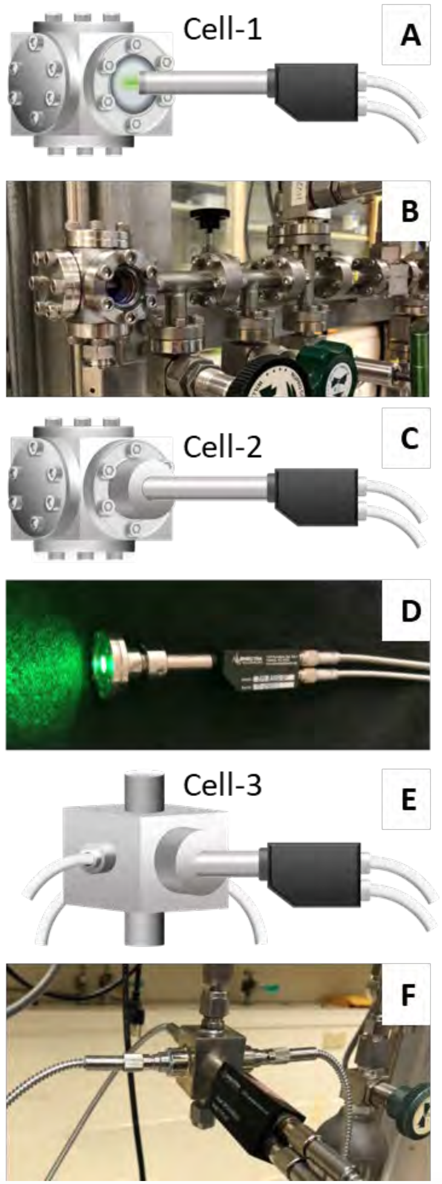
Improved Gas Cell

- Testing sensitivity
  - 3x higher signal with new gas cell
- Tie into building smart sensors
- Chemometric modeling
- Real-time and autonomous analysis of complex data



Application to Hydrogen Isotopes

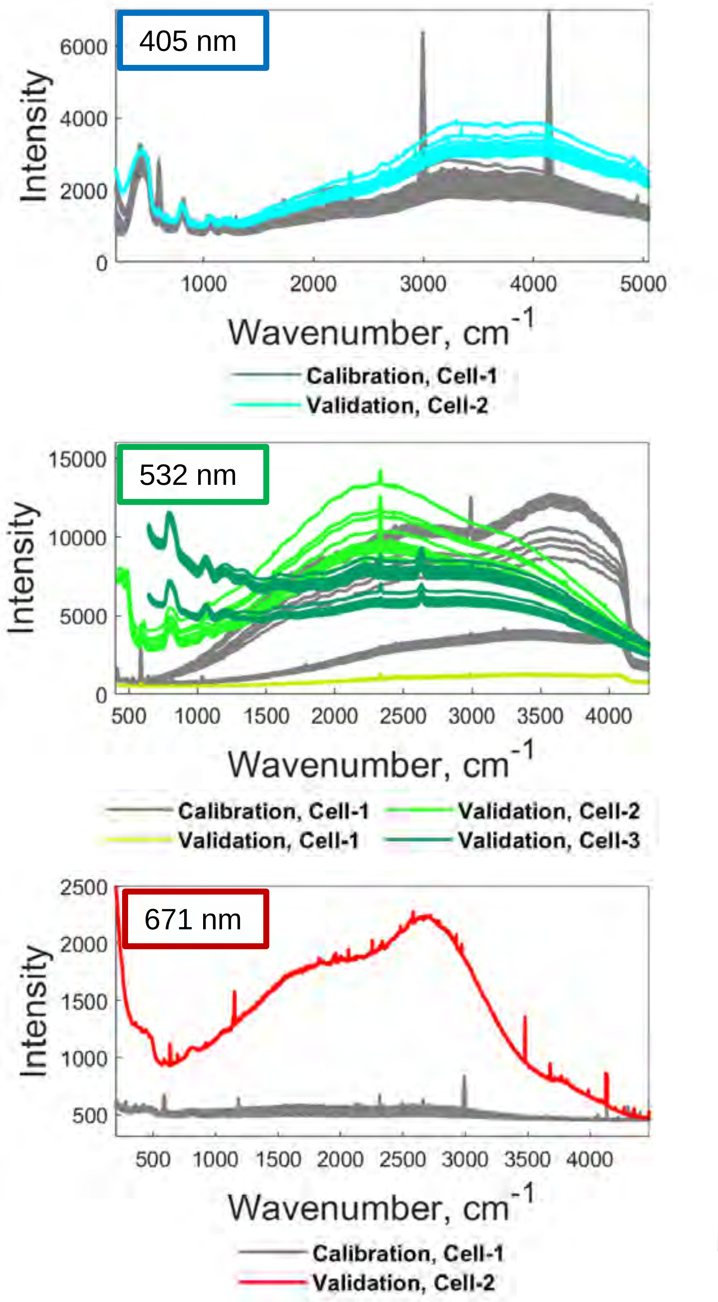
- Manuscript:
  - H_2 and D_2 Raman measurements across multiple systems
    - Multiple gas cells tested
    - 3 excitation wavelengths (405, 532, 671 nm)
  - Application of chemometric models to multiple systems
    - Different gas cells and instrumentation
  - Accepted for publication in Analytical Chemistry



Felmy, H. M.; Cox, R. M.; Espley, A. F.; Campbell, E. L.; Kersten, B. E.; Lackey, H. E.; Branch, S. D.; Bryan, S. A.; Lines, A. M. Quantification of hydrogen isotopes utilizing Raman spectroscopy paired with chemometric analysis for application across multiple systems. *Analytical Chemistry* **2024**, *Accepted April 10th, 2024*.

Application to Hydrogen Isotopes

- Complex spectral data encountered
  - Differences in measurement cells used
  - Raman probe alignment
  - Integration time differences
  - Instruments used
- Different instrumentation required calibration transfer
  - Axis alignment
  - Accounting for detector differences



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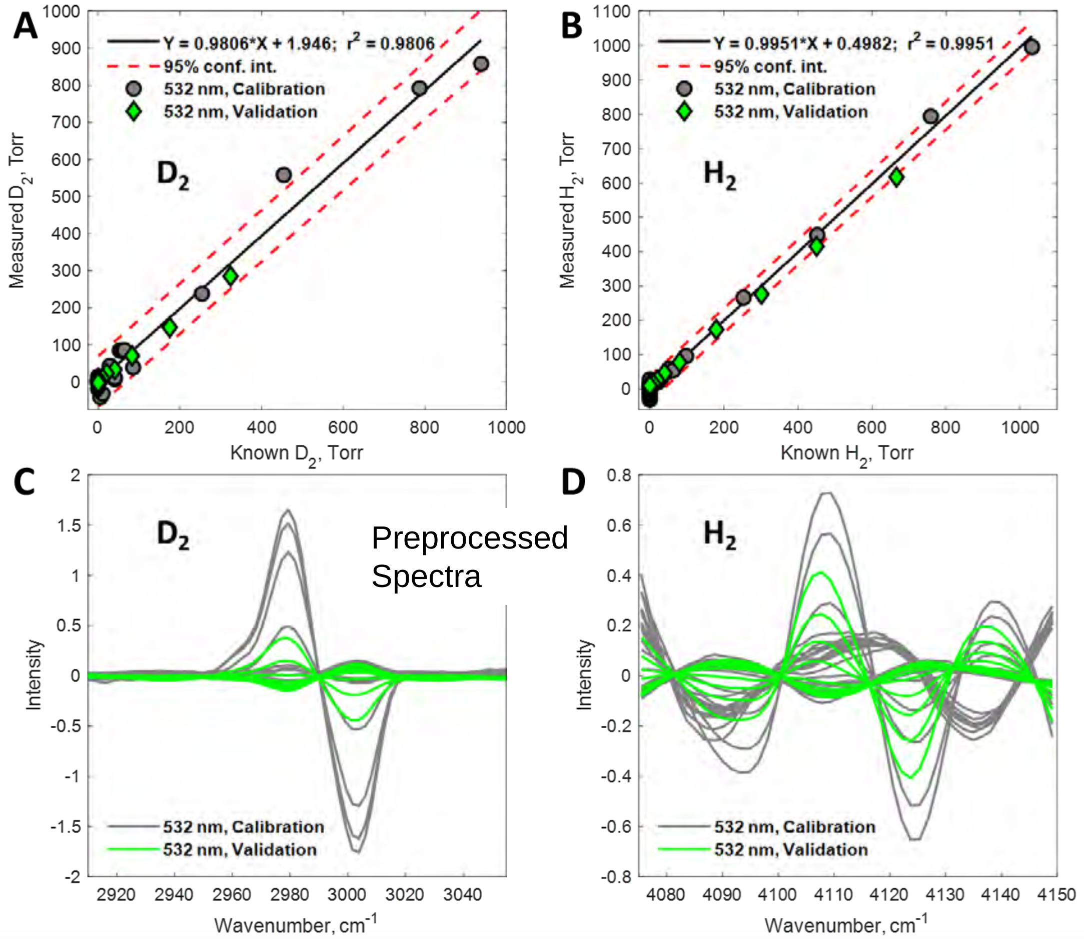
Application to Hydrogen Isotopes

- Chemometric models collected on one system applied to other systems
  - Spectral preprocessing required, included normalization and application of a 1st derivative
- Successfully applied models collected on first gas cell design to new cell
  - Quantification of H_2 and D_2



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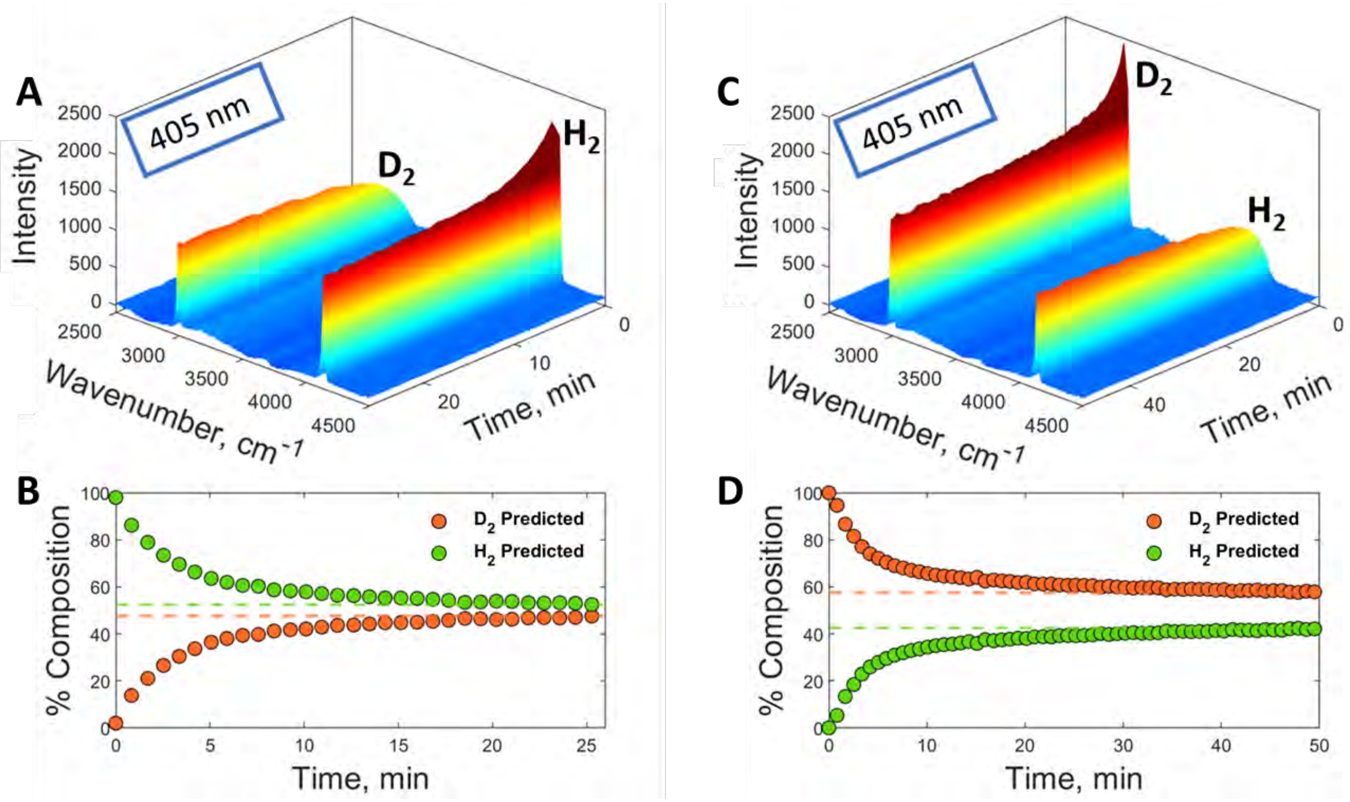
Application to Hydrogen Isotopes

- Application to gas mixing
  - Continuous data collection
  - Model predicted gas composition
- Models can be applied in real time
  - Can predict concentrations or gas pressures for multiple analytes simultaneously



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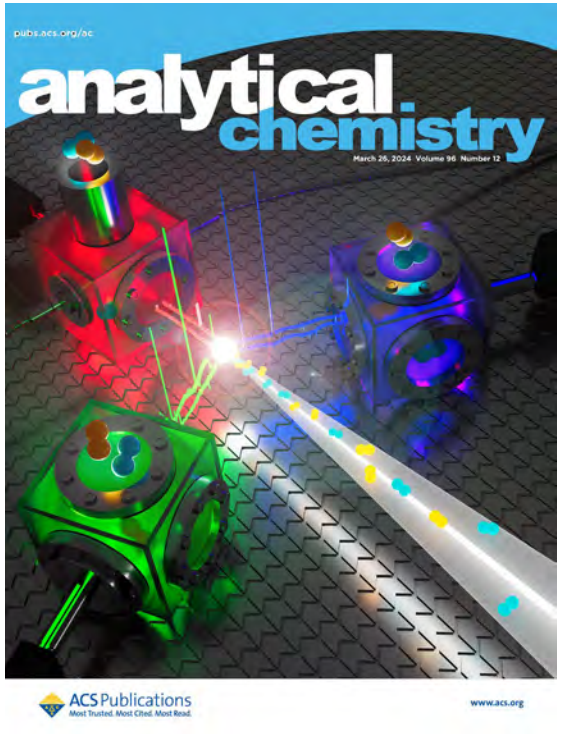
Highlights on Impacts and Advancements

- **Paper accepted**
  - Felmy, H. M.; Cox, R. M.; Espley, A. F.; Campbell, E. L.; Kersten, B. E.; Lackey, H. E.; Branch, S. D.; Bryan, S. A.; Lines, A. M. Quantification of hydrogen isotopes utilizing Raman spectroscopy paired with chemometric analysis for application across multiple systems. Analytical Chemistry 2024, Accepted April 10th, 2024.

    →With journal cover graphic



- **New Raman instrument on order with vendor to further improve sensitivities for gas phase species**

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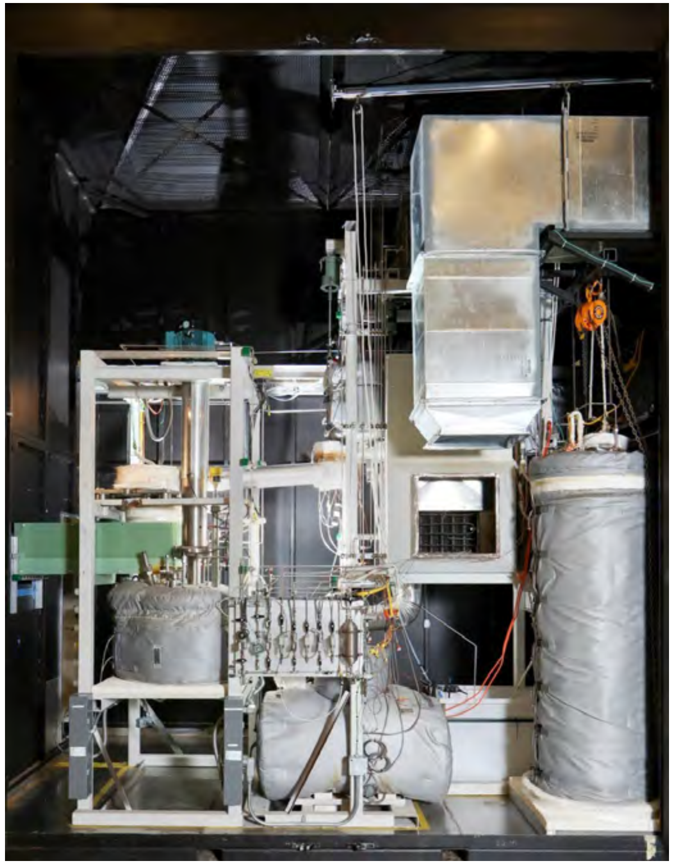
Testing Probe Materials in LSTL

- Ongoing testing of materials performance when exposed to conditions within the LSTL (liquid salt test loop)

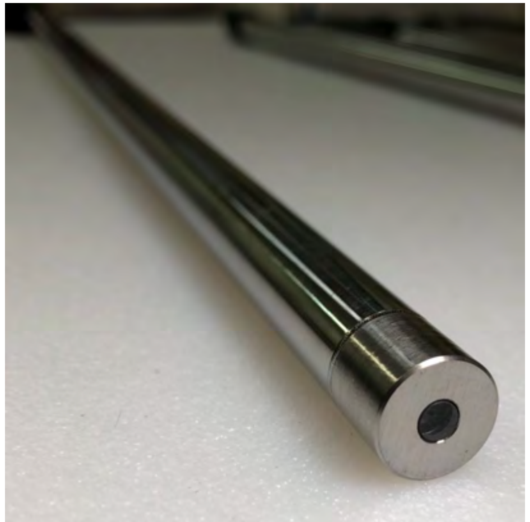
- **Big thank you to ORNL team**



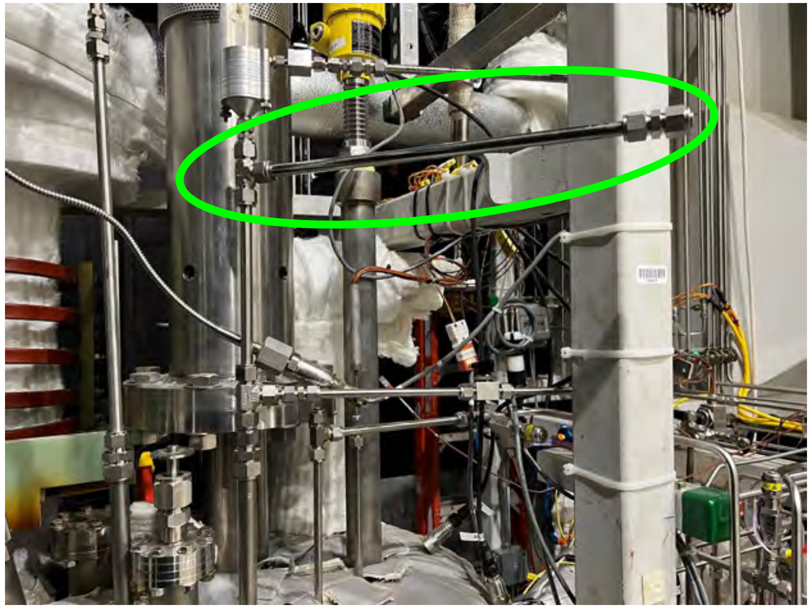
Testing Probe Materials in LSTL

1^{st} Probe Tested

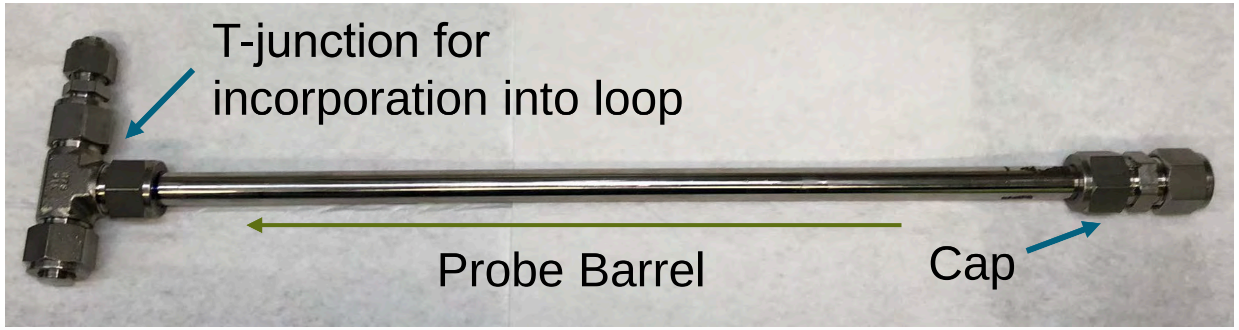
Before incorporation into salt loop



- **Salt loop testing**
  - Probe barrel Swaged into loop
  - No visual degradation after testing



After incorporation into salt loop

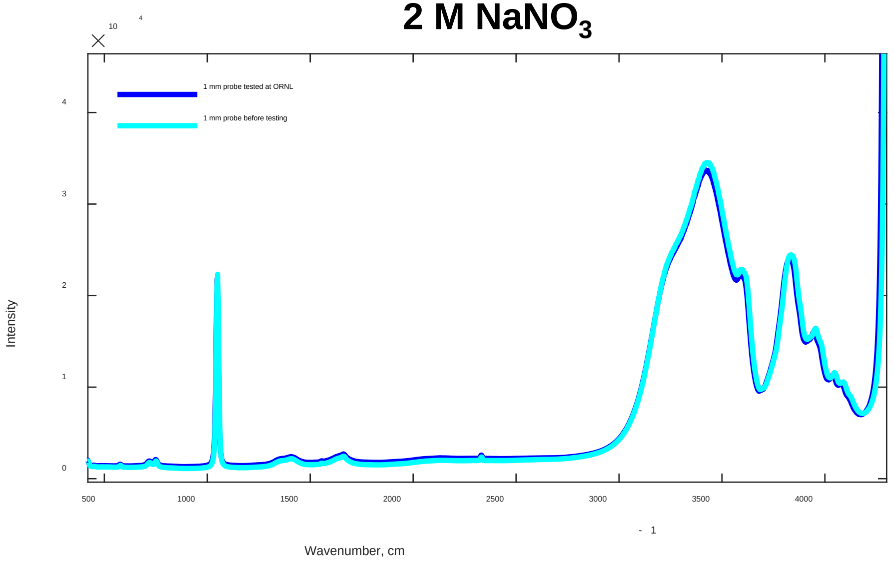


Testing Probe Materials in LSTL

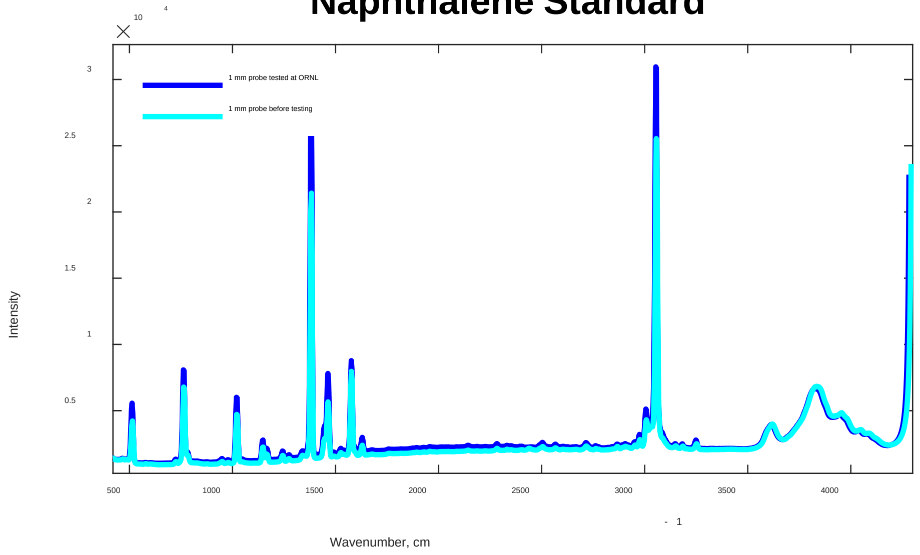
- Visually, probe appears in excellent condition after exposure in LSTL
- Raman data suggests comparable signal after incorporation into loop
- Minimal materials degradation/impacts to performance

1st Probe Tested

2 M $NaNO_3$



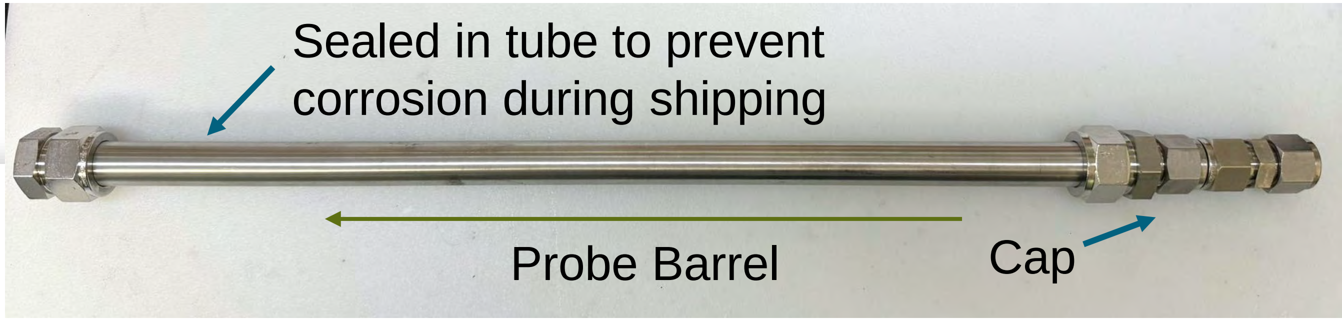
Naphthalene Standard



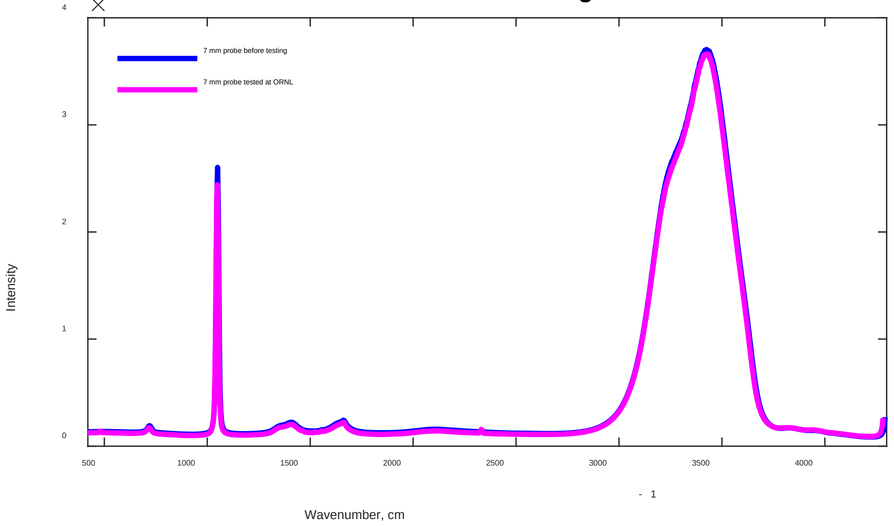
Testing Probe Materials in LSTL

- **Salt loop testing**
  - Probe barrel Swaged into loop
  - Corrosion and heat damage visible on exterior of probe
  - No significant impact to probe performance

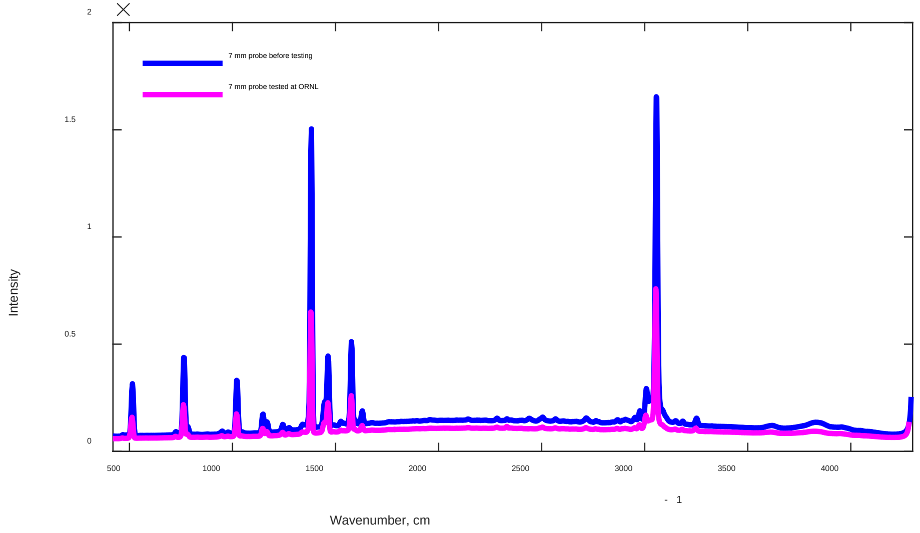
2nd Probe



2 M $NaNO_3$



Naphthalene Standard



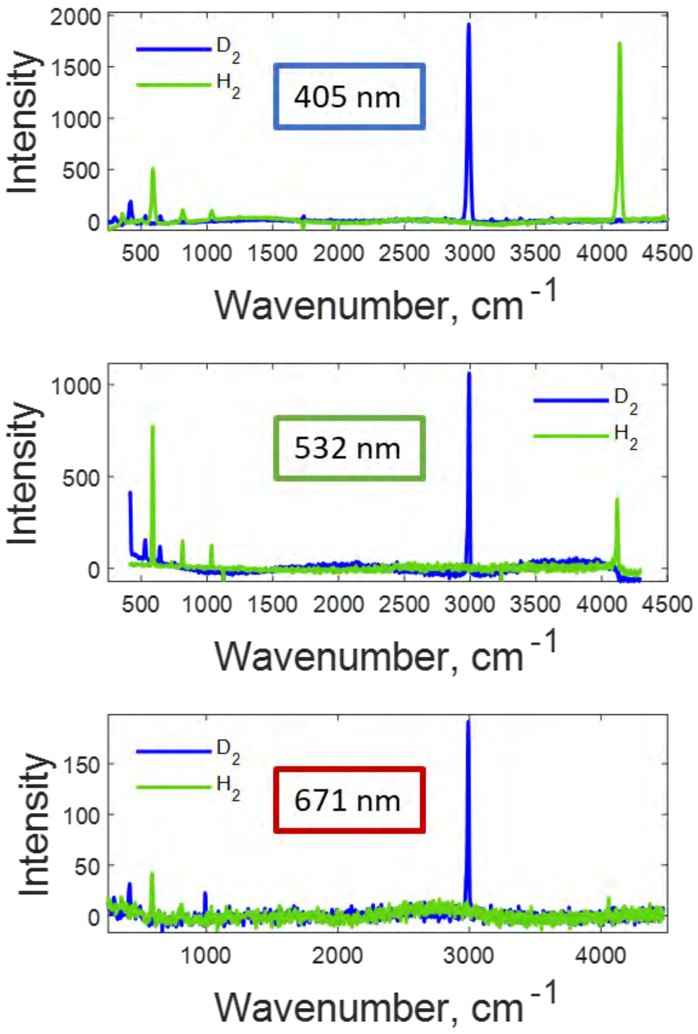
Preparing for Onsite Demo at ORNL

- Instrument on order
  - 405 nm excitation
  - Improved detector design
  - Multitrack
    - Allows for multiple simultaneous measurement locations
    - Compatible with new gas cell design

  → Improve sensitivity

- Documentation examples
  - EPR (Electronic Prep and Risk)
  - ORMP (Off-site Risk Management Plan)
  - SME (Subject Matter Expert) sign off on instrumentation
  - Lab Assist activity (PNNL safety documentation)

Increasing sensitivity



Highlights

- **Presentations**
  - ACS NORM June 28-30

- **Publications**
  - Felmy, H. M.; Cox, R. M.; Espley, A. F.; Campbell, E. L.; Kersten, B. E.; Lackey, H. E.; Branch, S. D.; Bryan, S. A.; Lines, A. M. Quantification of hydrogen isotopes utilizing Raman spectroscopy paired with chemometric analysis for application across multiple systems. Analytical Chemistry 2024, Accepted April 10th, 2024.

- **Student involvement**
  - Bethany Kersten: PhD intern, now post-doc at ANL
  - Alyssa Espley: SULI student, now post bachelors

Summary

- **Sensors and instrumentation tailored to off-gas targets**
  - Successful testing of redesigned gas cell to H_2, D_2, N_2, and O_2
    - Improved sensitivity over original cell design
  - Procurement of new Raman instrument
- **Hydrogen isotope journal manuscript accepted for publication**
  - Demonstration of calibration transfer method to multiple cell designs and instrumentation
- **Characterization of Raman probes integrated into LSTL**
  - Probes survived harsh conditions of salt loop
    - No significant change in probe performance
- **Continuing to prepare for on-site demo at ORNL**

Conclusions

- **On-line monitoring is a powerful tool that can support:**
  - More efficient design and testing of chemical processes
    - e.g., off-gas treatment
  - Informed transitions during scale up
  - Safer, optimized, and affordable deployment of processes
- **Optical sensors can provide complex chemical information**
  - PNNL is collaborating with other labs to build comprehensive tool kits

Future Opportunities

- **Testing of new instrumentation**
- **Full demo of Raman monitoring within ORNL salt loop**
- **Building and integrating on-line monitoring tools to support other aspects of gas treatment**
    - e.g., Gas capture with MOFS

Acknowledgements

PNNL Team:

Amanda Lines
Sam Bryan
Heather Felmy
Shirmir Branch
Hope Lackey
Adan Schafer Medina
Richard Cox
Emily Campbell
Brian Riley

ORNL Team:

Joanna Mcfarlane
Hunter Andrews
Kevin Robb

Students/visiting faculty/guests:

Prof. Gilbert Nelson (C. Idaho)
Job Bello (Spectra Solutions Inc.)
Alyssa Espley
Molly Vitale-Sullivan (SULI)
Andrew Clifford
Bethany Kersten

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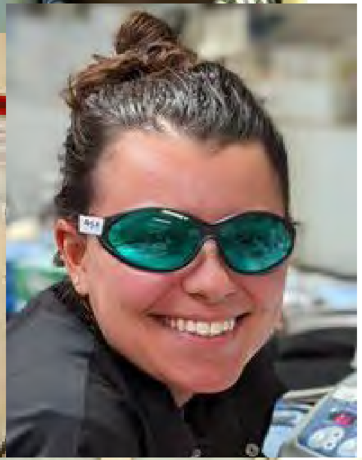

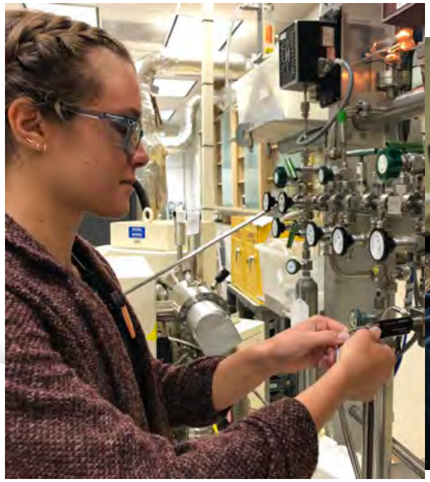

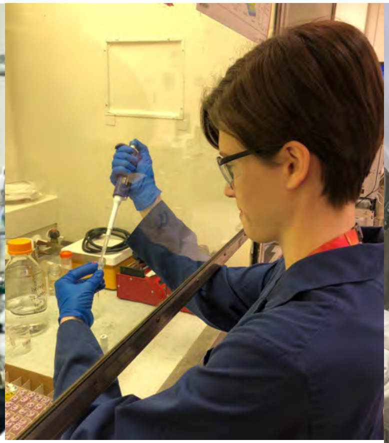

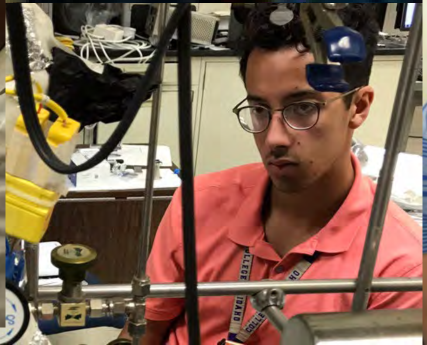

Thank you

Email Address:
heather.felmy@pnnl.gov

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