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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 2-4 May 2023

In- On-line Monitoring

Sensors directly in or on the process

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

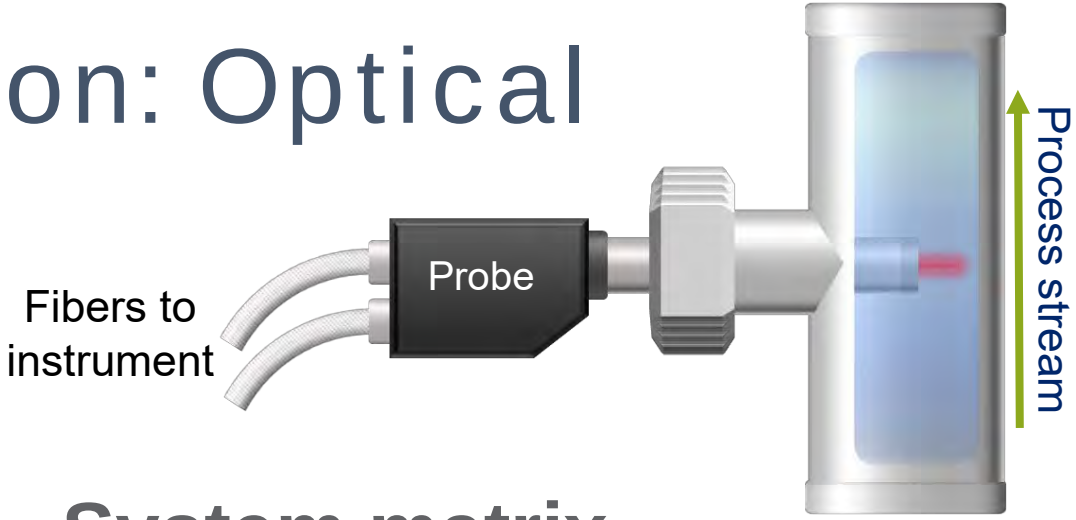
Fundamental characterization

Efficient process design

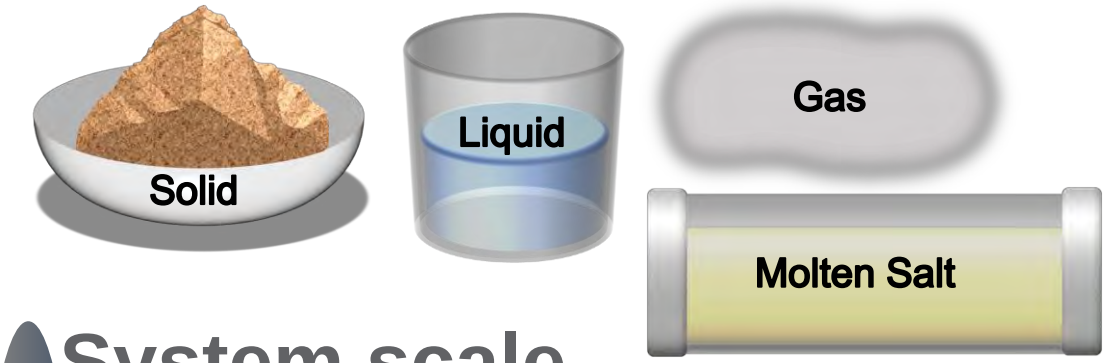
Safe and cost-effective deployment

Chemical Characterization: Optical Spectroscopy

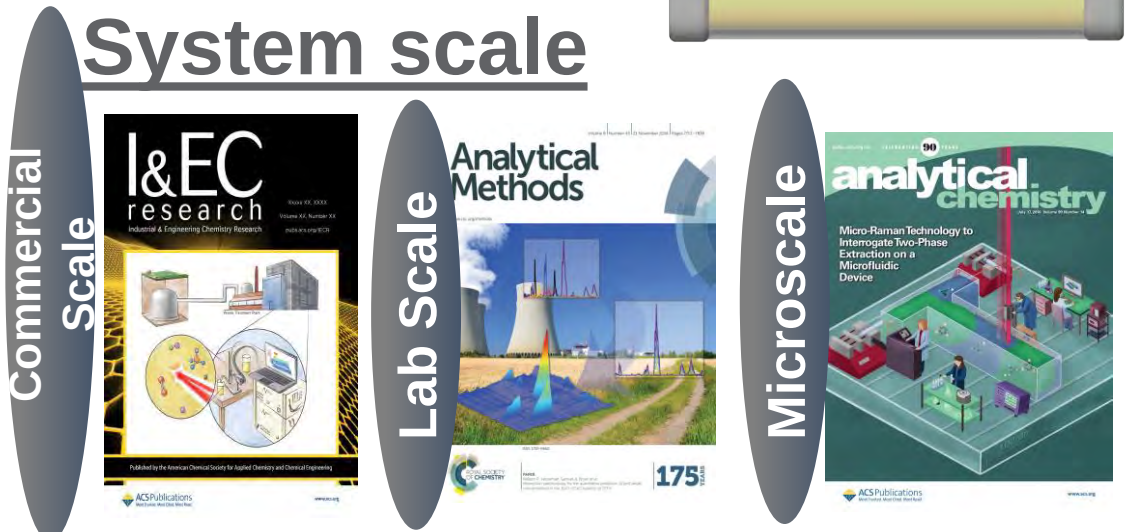
- Provides chemical information
  - Identification and quantification
  - Oxidation state
    - Essential information for control of systems
  - Molecular and elemental species
    - Essential information to control general system behavior
- Highly mature technology
- Simplistic integration
- Versatile



System matrix

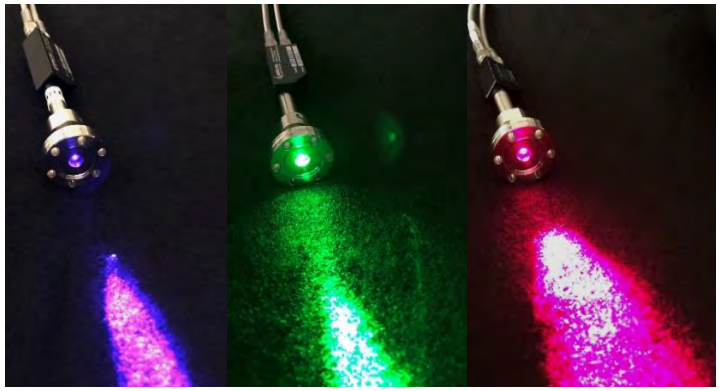


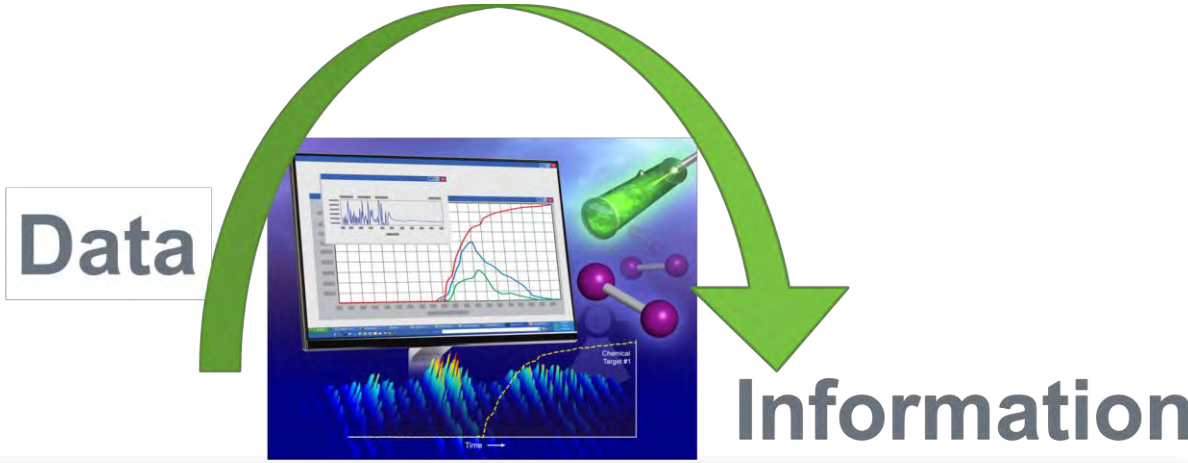
System scale



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

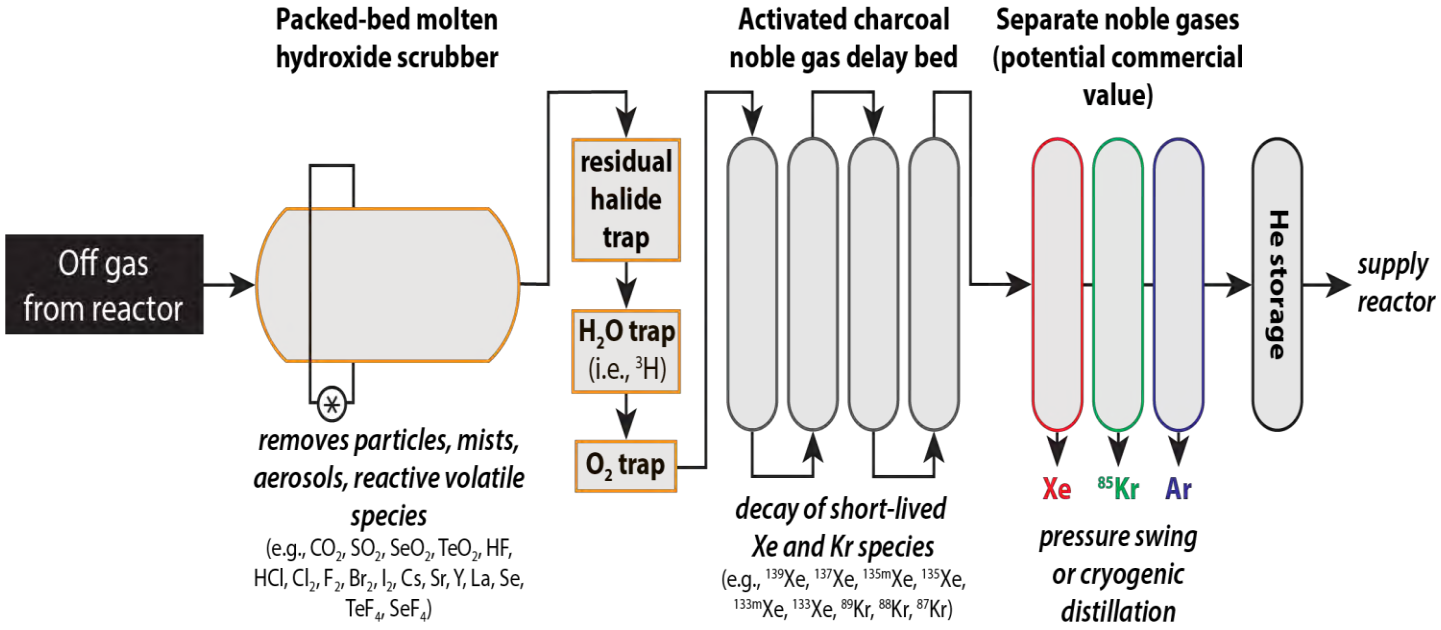
- **Probe development**
  - Overcoming COTS (commercial off the shelf) limitations to build sensors that can survive:
    - Highly corrosive systems (HF gas, molten salts)
    - High temperature systems (molten salts)
    - Radiation
- **Making smart sensors**
  - Building autonomous tool kits that can parse interfering fingerprints and accurately identify and quantify chemical targets





Systems of Focus

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

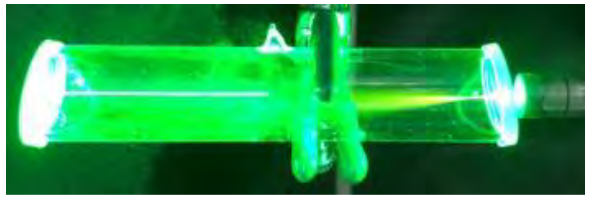


Mcfarlane, J.; Ezell, N.; Del Cul, G.; Holcomb, D. E.; Myhre, K.; Chapel, A.; Lines, A.; Bryan, S.; Felmy, H. M.; Riley, B. *Fission Product Volatility and Off-Gas Systems for Molten Salt Reactors*; Oak Ridge National Lab.(ORNL), Oak Ridge, TN (United States): 2019.

Interlab Collaboration

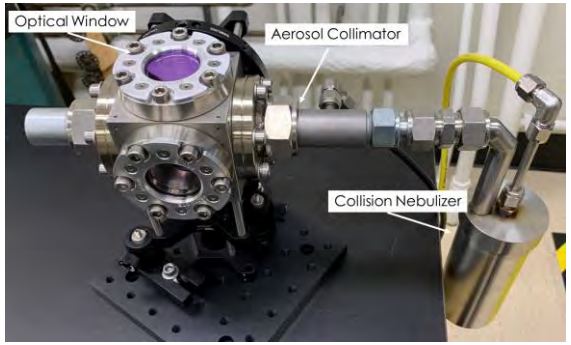
- **Building and demonstrating applications throughout the treatment process**
- **Collaborating with additional teams to create comprehensive characterization/control strategies**
- **Aiming to provide key features such as mass balance**

Molecular



PNNL team

Atomic



ORNL team
K Myhre
H Andrews

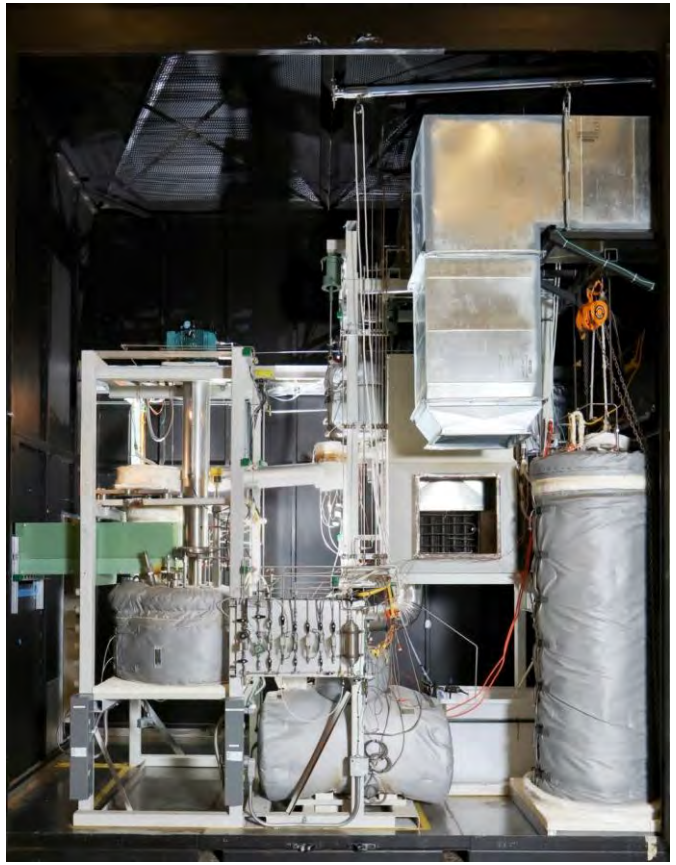
FY23 Project overview

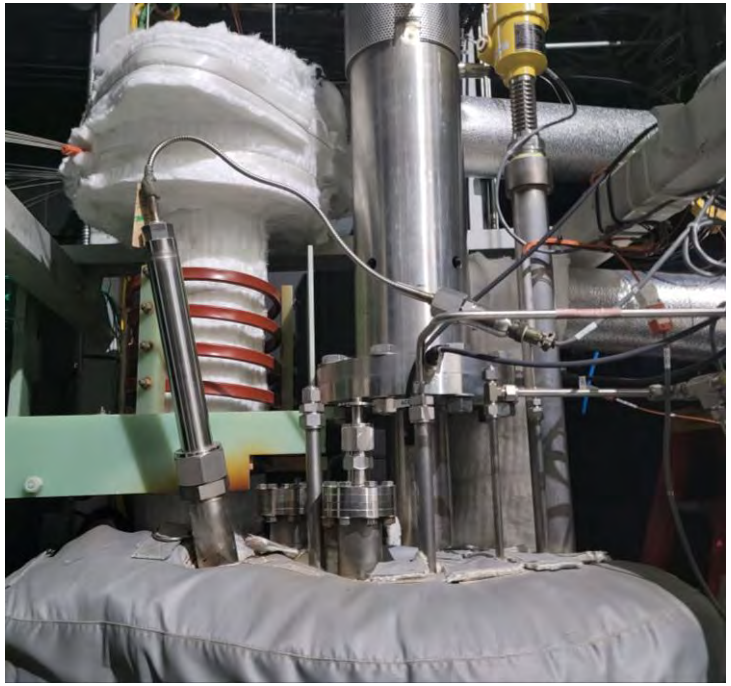
- **ActivityRD-23PN0602072 Complete testing of Raman probes from LSTL run**
  - On schedule (received one probe back for characterization)

- **M3RD-23PN0602071 Designing a gas cell for improved limits of detection- Due 9/30/23**
  - Milestone is on schedule

Testing Probe Materials in LSTL

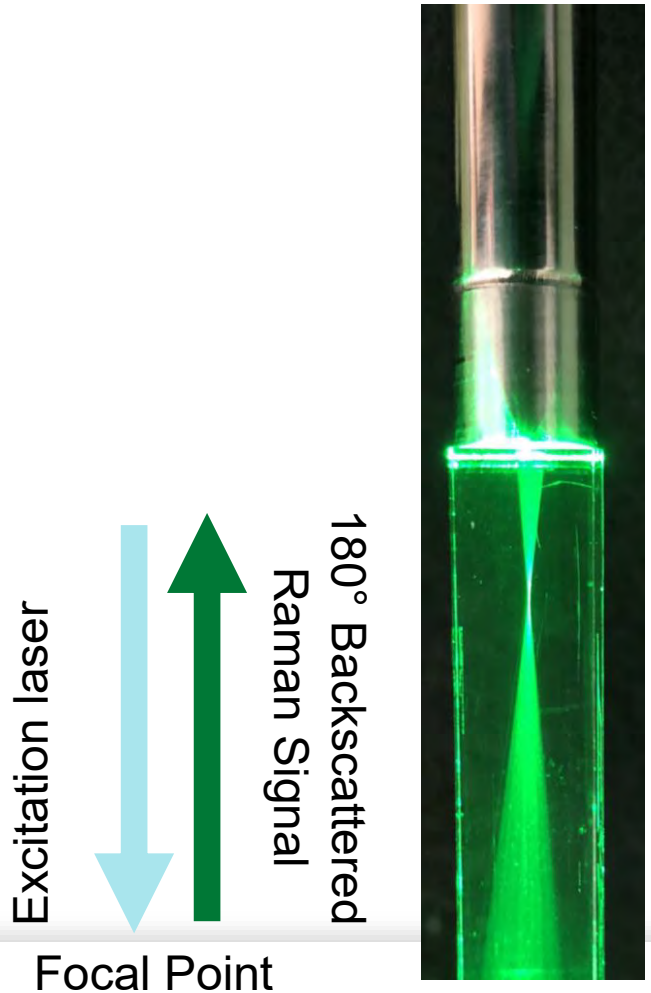
- **Goal: test materials performance when exposed to conditions within the LSTL**
- **Big thank you to ORNL team**





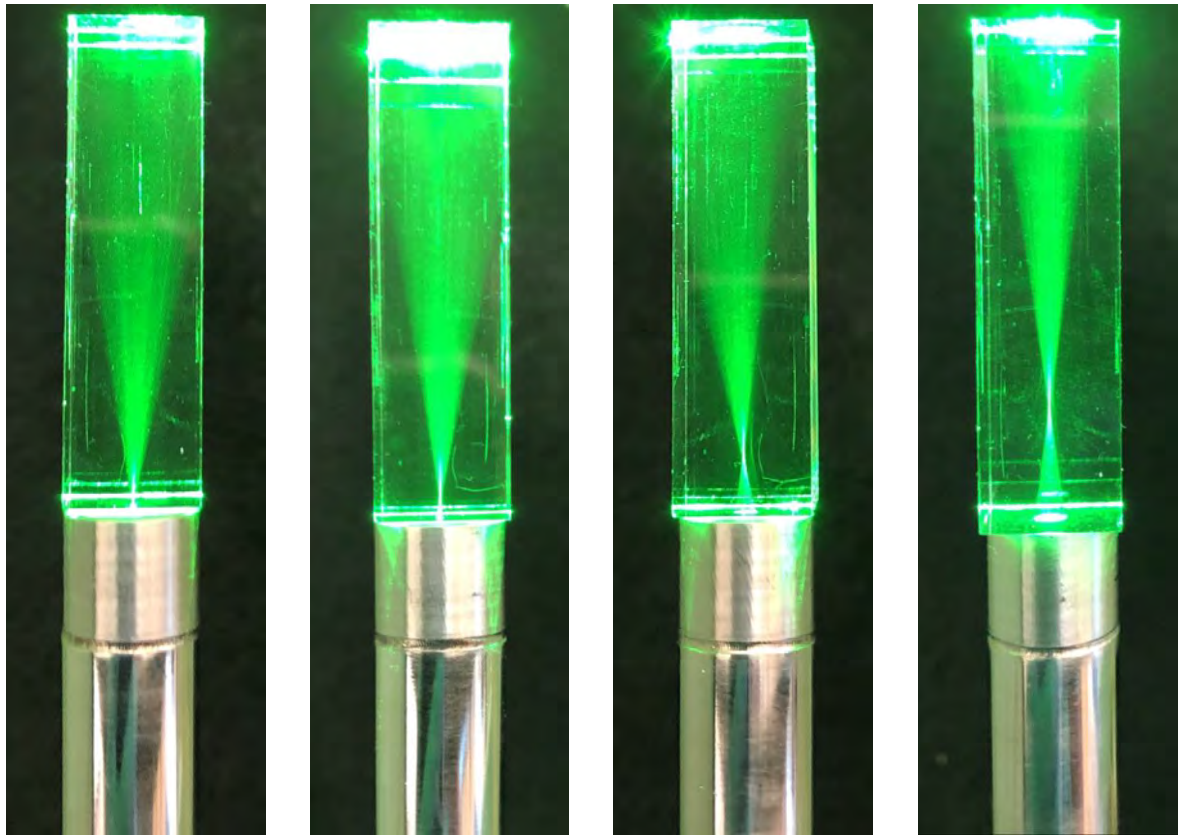
Probe Details

- **Utilizing Raman spectroscopy which relies on 180° backscatter**
- **Ideal for molecular, poly atomic species including several key targets in the gas phase**

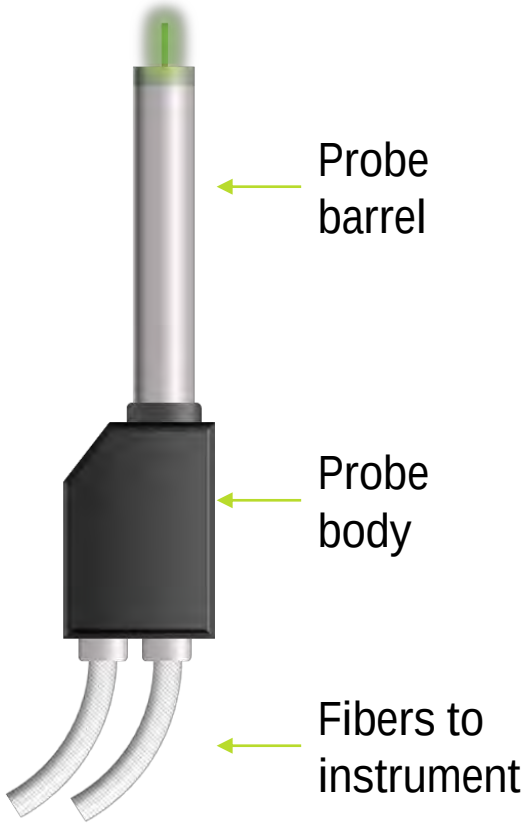


Probe Details

- **Testing multiple probes in multiple locations**
- **Probe specs specialized for each location**

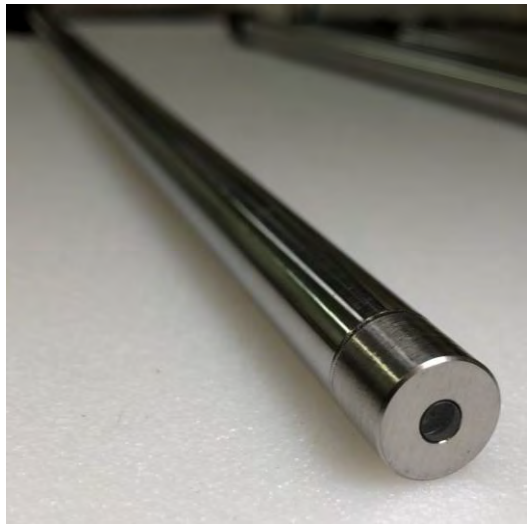


Focal Length: 1 mm 2 mm 5 mm 7 mm

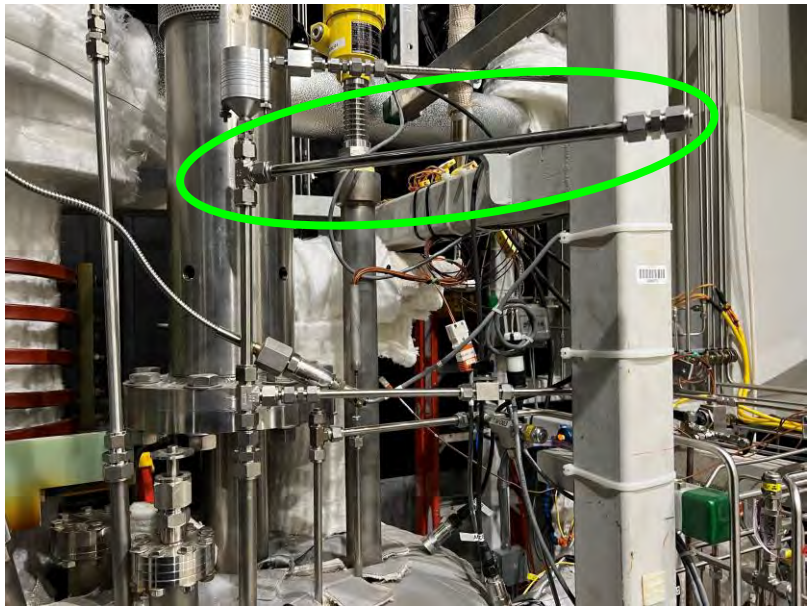


Testing Probe Materials in LSTL

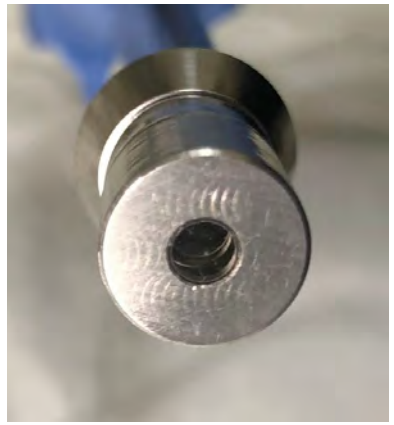
Before incorporation into salt loop

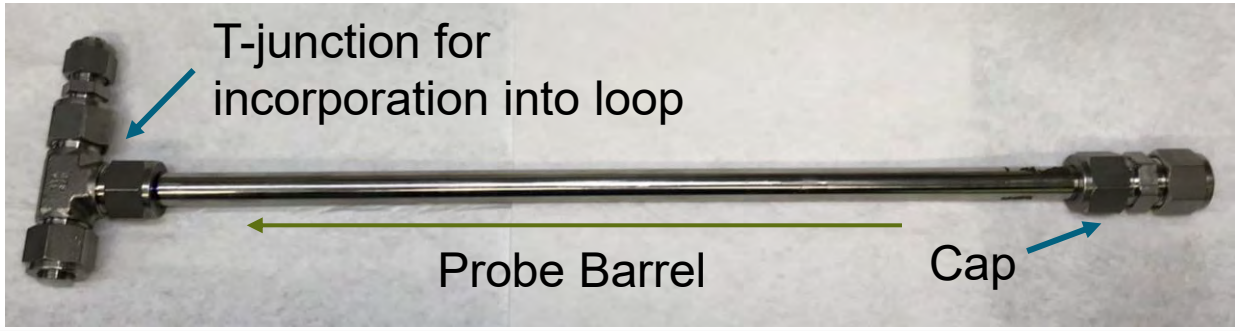


- **Salt loop testing**
  - Probe barrel swaged into loop
  - No visual degradation after testing



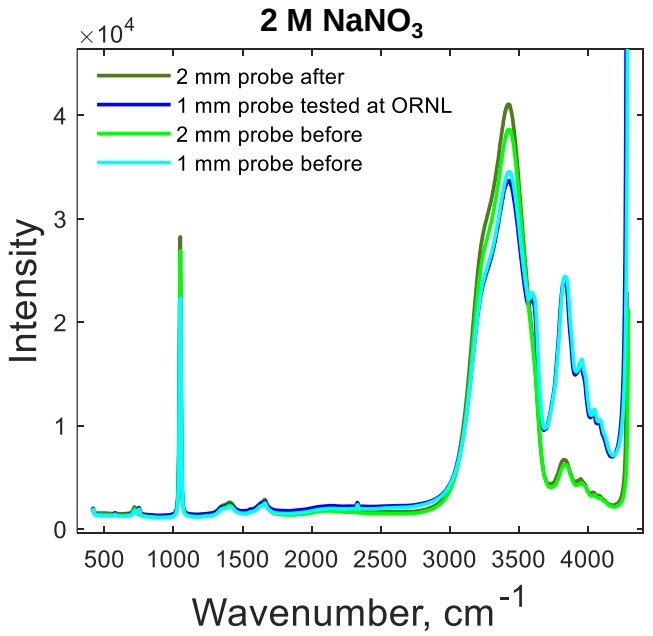
After incorporation into salt loop

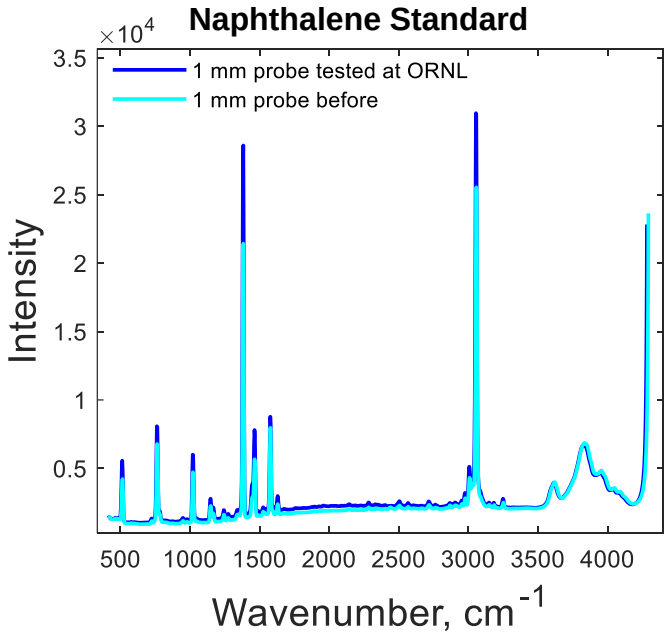




Testing Probe Materials in LSTL

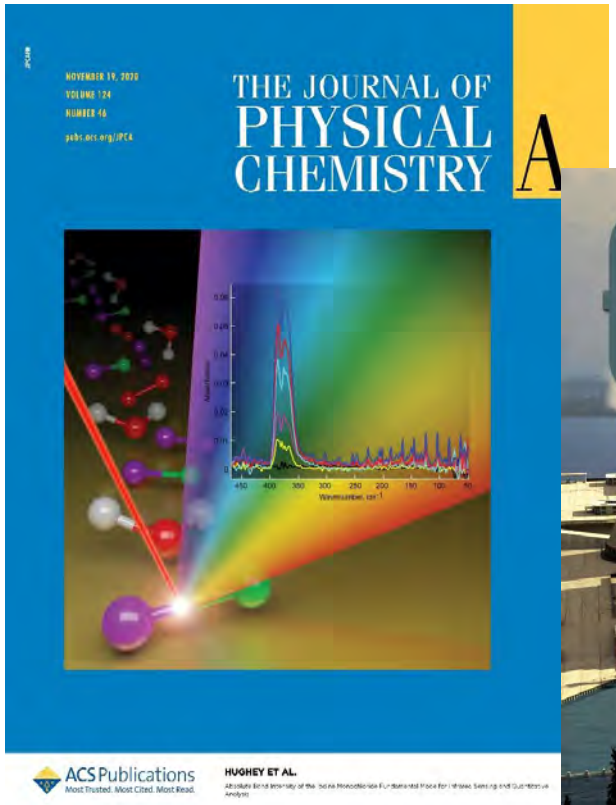
- **Visually, probe appears in excellent condition after exposure in LSTL**
- **Raman data suggests comparable signal after incorporation into loop**
- **Minimal materials degradation/impacts to performance**





Building a Better Gas Cell

- **Prepping probes to characterize multiple targets of interest**
- **Much of the focus up to now has been on using COTS sensors to build smart sensors or demonstrate on a wide range of key targets**



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.

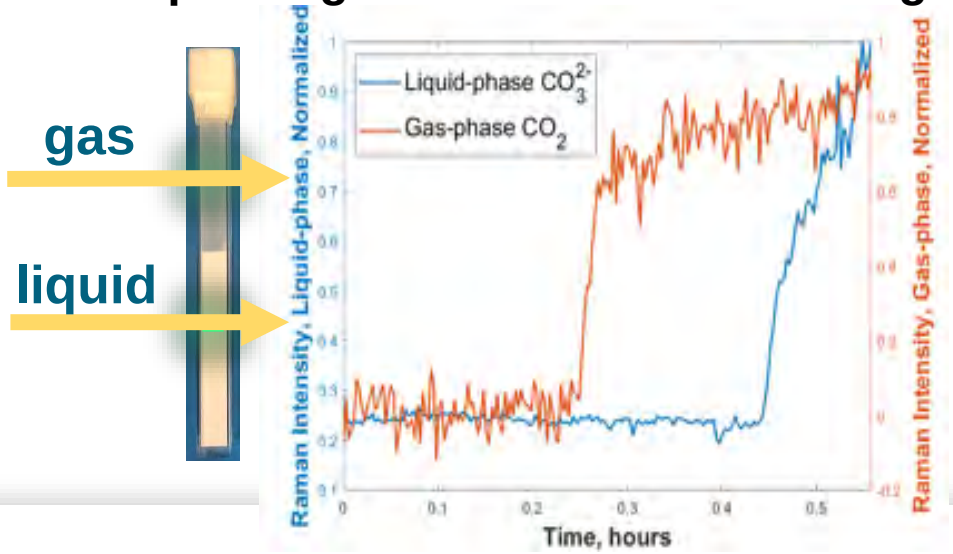
Felmy, H. M.; Clifford, A. J.; Medina, A. S.; Cox, R. M.; Wilson, J. M.; Lines, A. M.; Bryan, S. A., On-Line Monitoring of Gas-Phase Molecular Iodine Using Raman and Fluorescence Spectroscopy Paired with Chemometric Analysis. ***Environ Sci Technol*** *2021, 55, 6, 3898–3908.*

Building a Better Gas Cell

- **Expanded to look at the NaOH scrubber**
- **Dual-phase monitoring**
- **Recent publication which also made cover graphic**
- **Student involvement**

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

Dual-phase gas-NaOH melt monitoring



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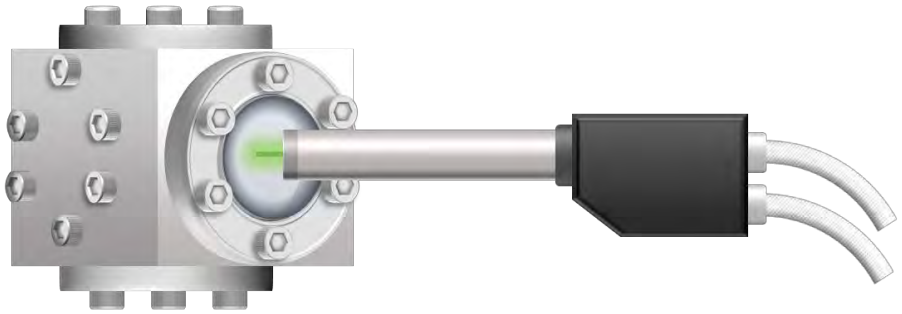
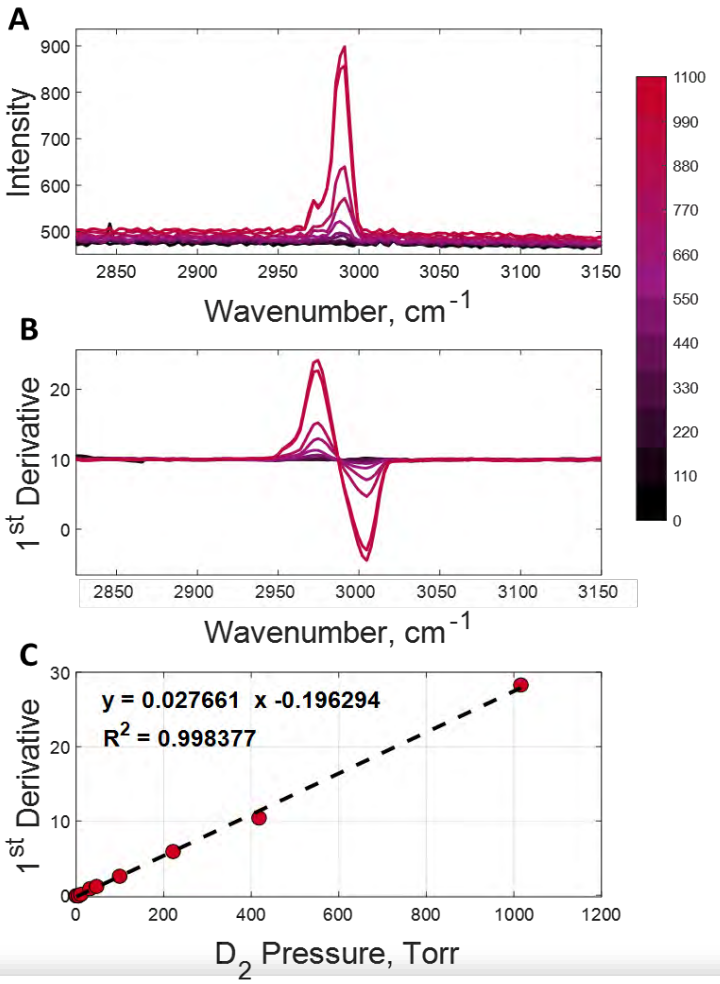
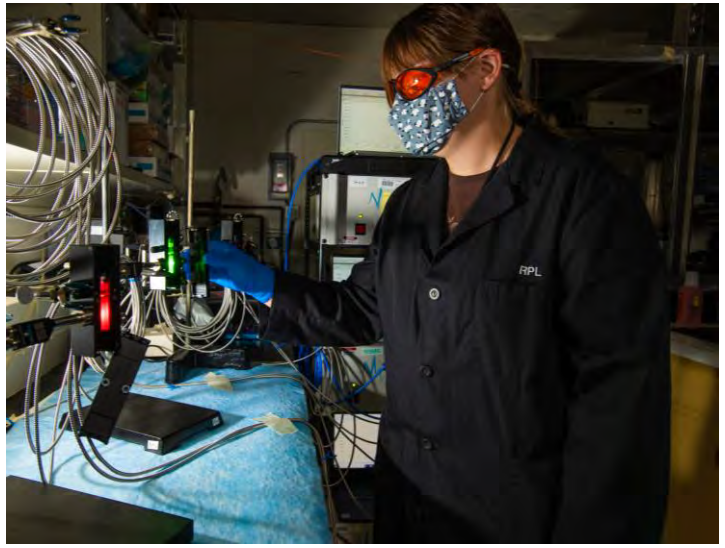
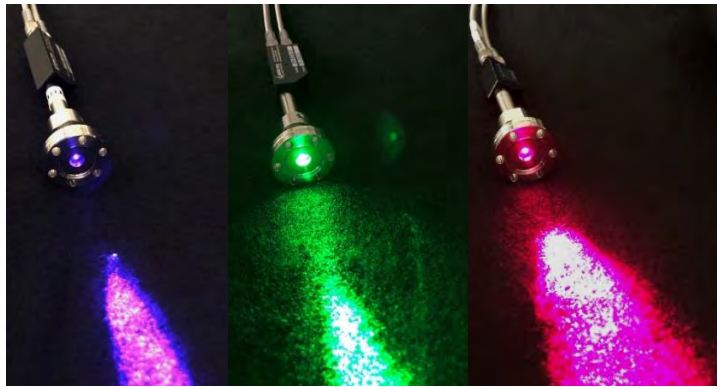
Building a Better Gas Cell

- **Expansion to H isotopes**
- **Raman can identify and quantify speciation and**



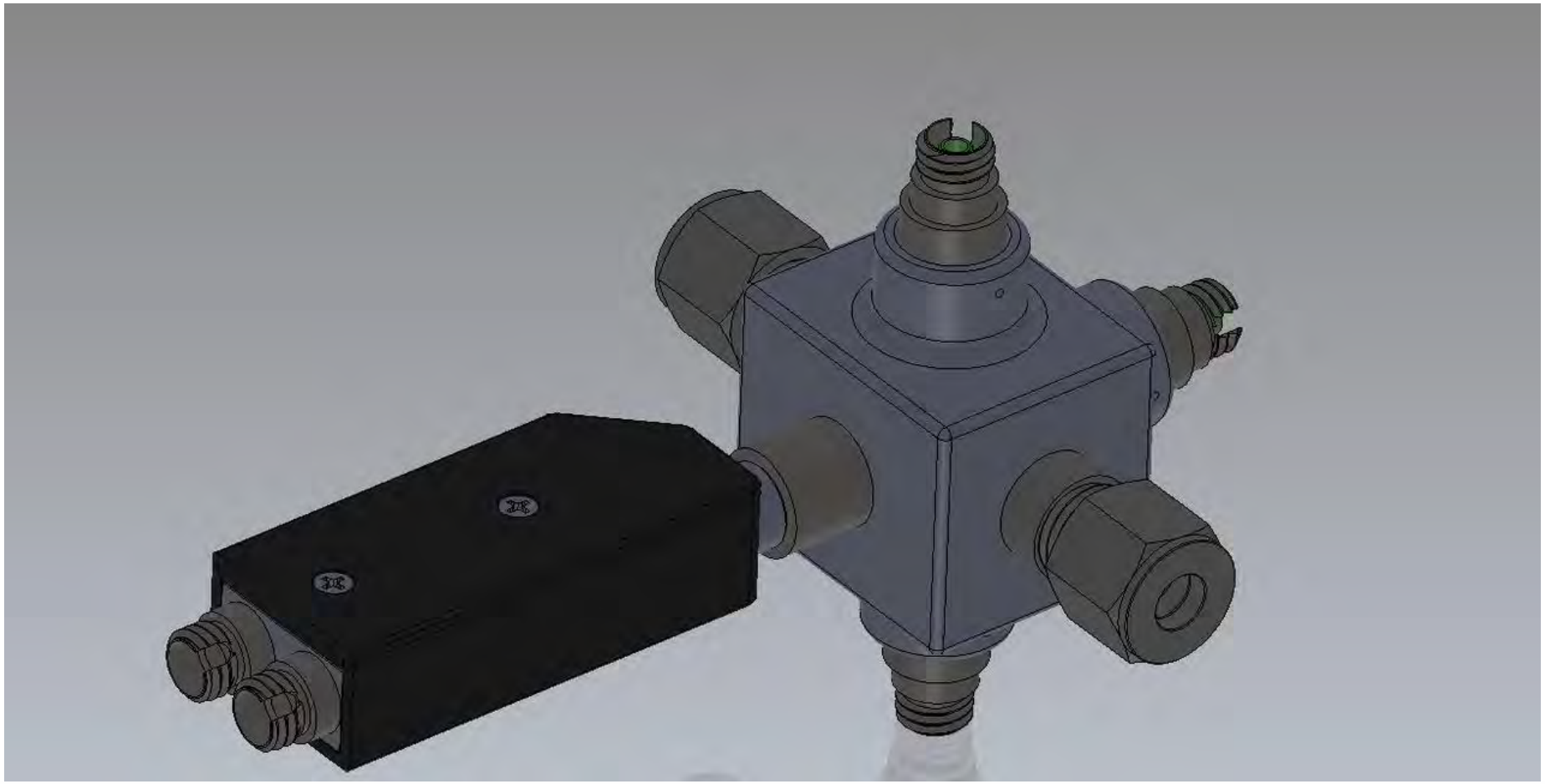






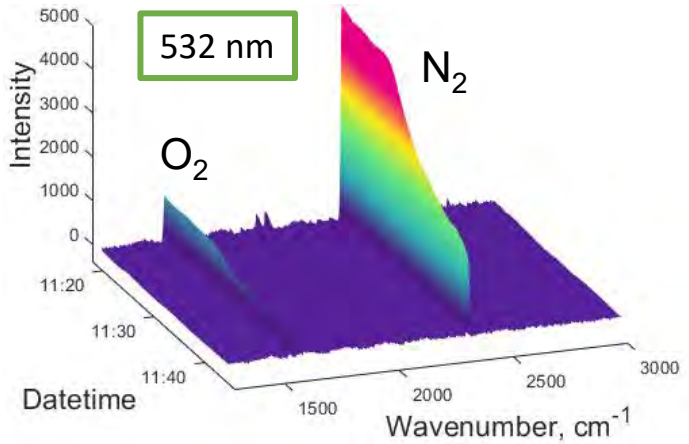
405 nm 532 nm 671 nm

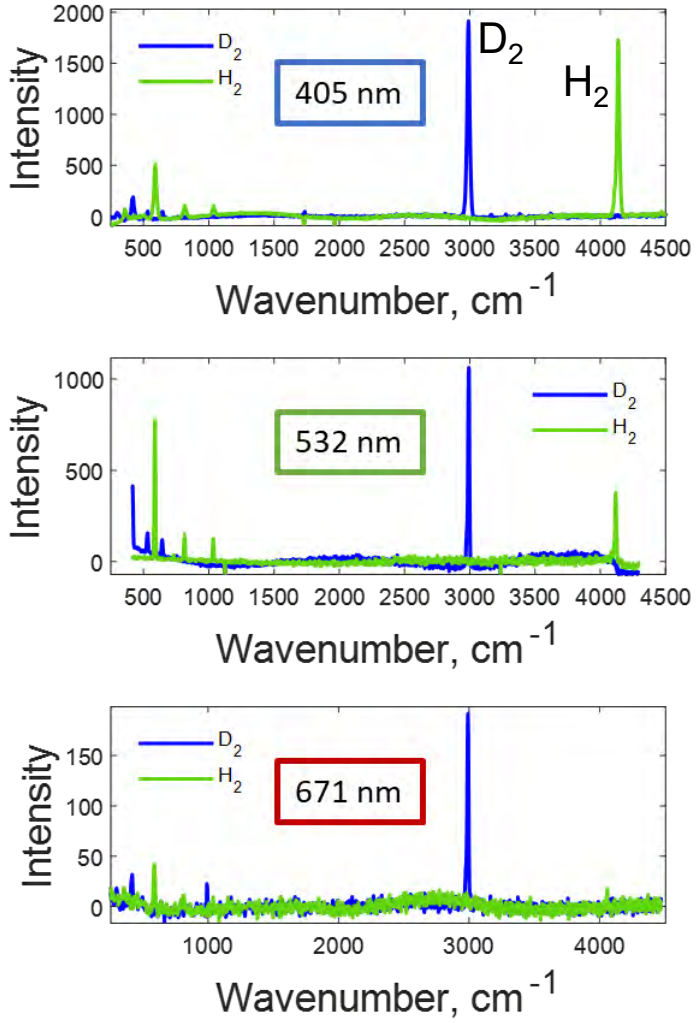
Building a Better Gas Cell



Building a Better Gas Cell

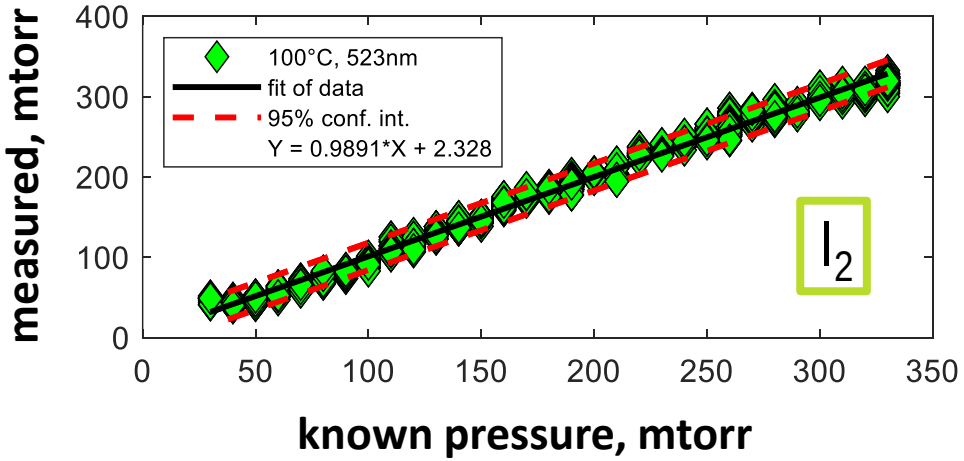
- **Testing the new gas cell on standards to compare limits of detection**
- **Integrate summer student into planned experimental work**

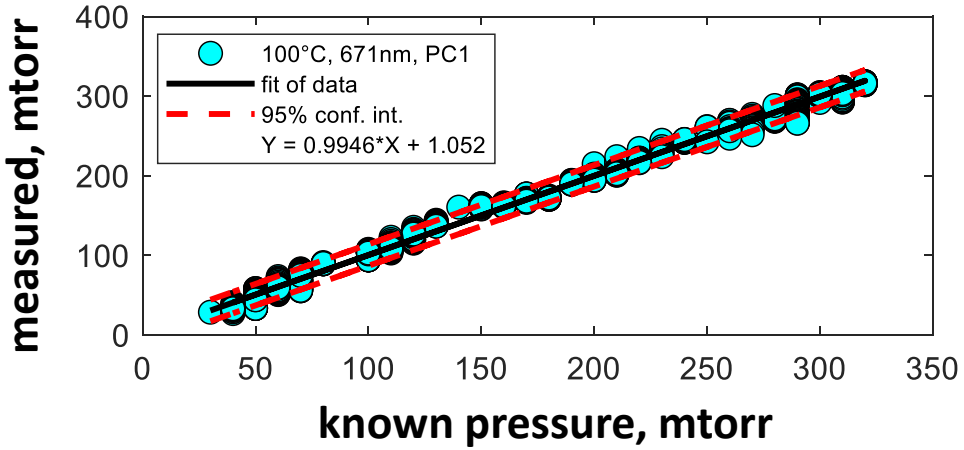


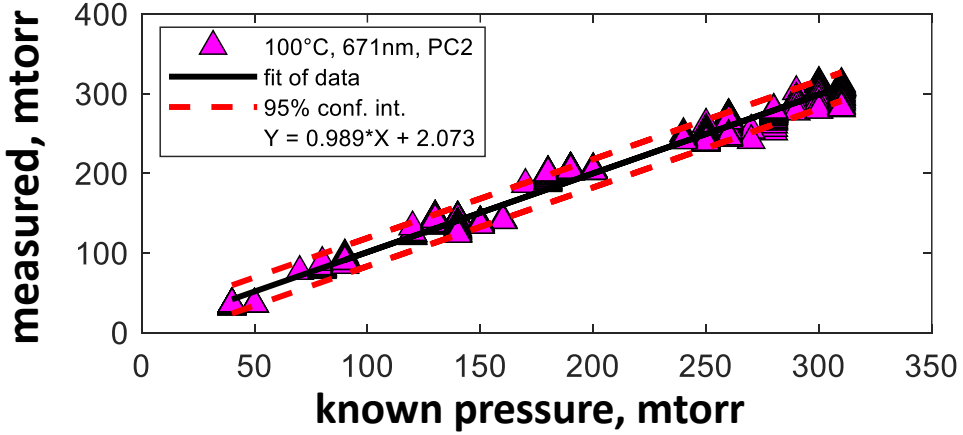


Building a Better Gas Cell

- **Tie into building smart sensors**
- **Chemometric modeling**
- **Real-time and autonomous analysis of complex data**







Highlights

- **Presentations**
  - Virtual Workshop on Optical Sensors for Energy Applications March 2-3
  - ACS NORM June 28-30

- **Publications**
  - 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
  - Manuscript on H isotope analysis in progress

- **Team expansion**
  - Integrating new students

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 based sensors can provide complex chemical information**
  - PNNL is collaborating with other labs to build comprehensive tool kits

Future Opportunities

- **Full demo of Raman monitoring within ORNL salt loop**
- **Application of redesigned gas cell to targets of interest**
  - E.g. tritium with opportunities to collaborate with INL
- **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
Adan Schafer Medina
Richard Cox
Bethany Kersten
Brian Riley

ORNL Team:

Joanna Mcfarlane
Hunter Andrews
Kevin Robb

Students/visiting faculty/guests:

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

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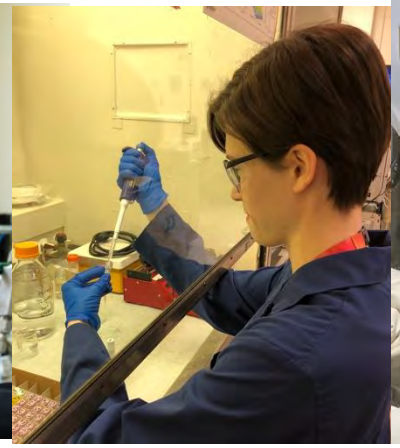

Thank you

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