Molten Salt Reactor
PROGRAM

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

Heather Felmy, Amanda Lines, Sam Bryan

PNNL

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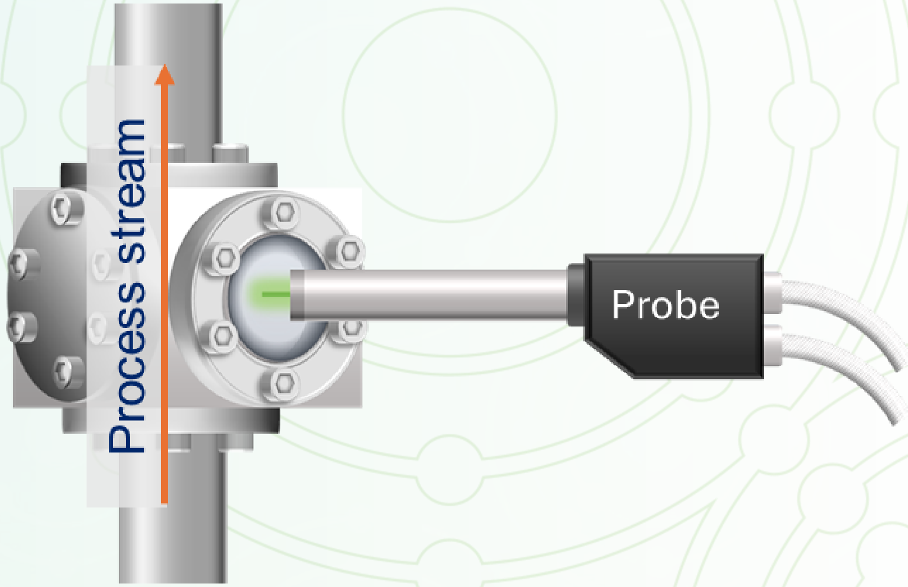
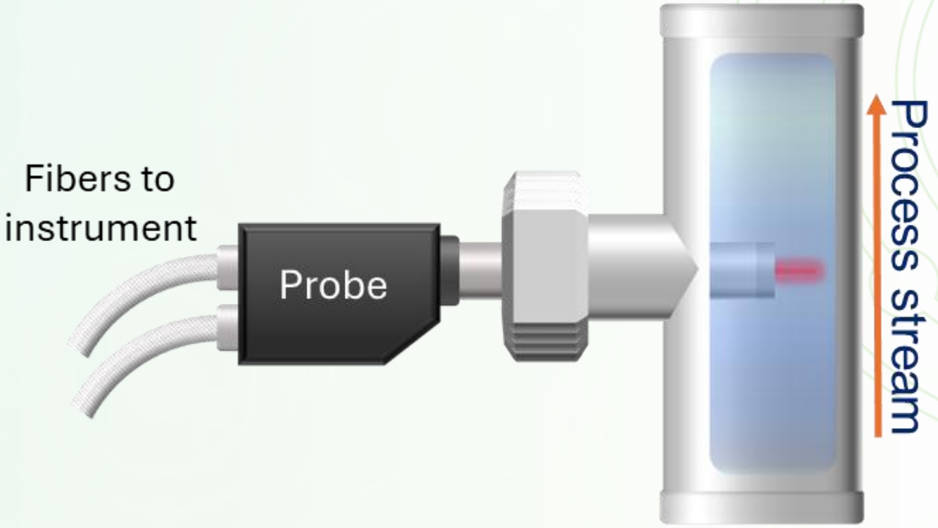
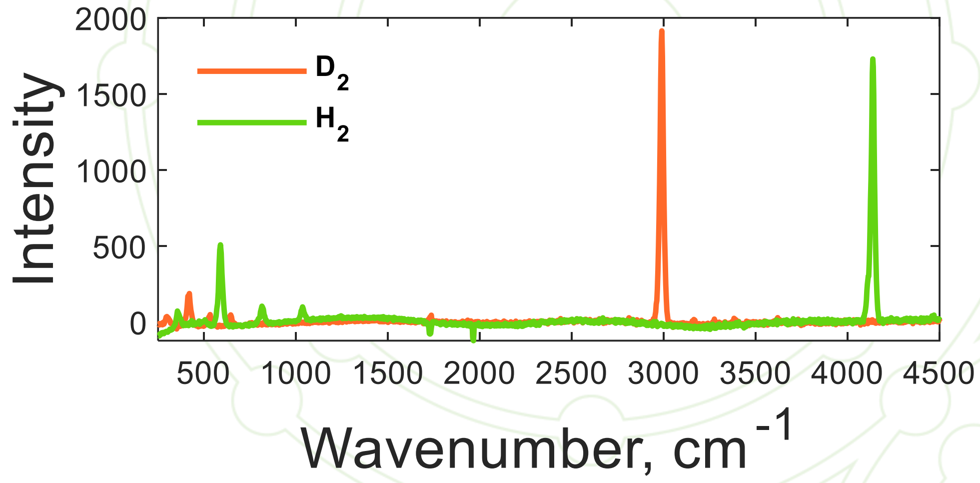
On-line monitoring

- In-line or on-line monitoring can support:
  - Fundamental characterization
  - Efficient process design
  - Scale-up
  - Safe and cost-effective deployment
- Placing sensors on or directly in a process stream
  - In situ and real-time analysis



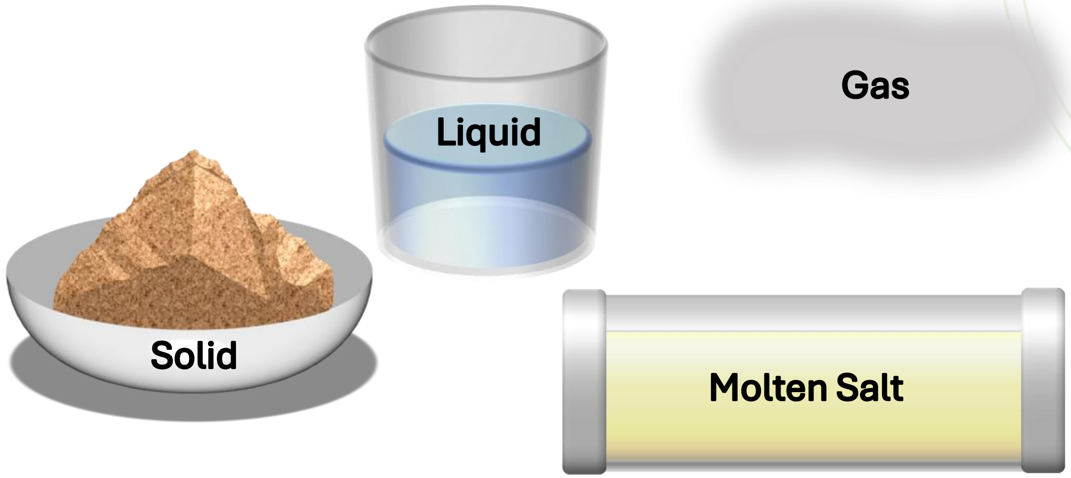


Chemical Characterization: Optical Spectroscopy



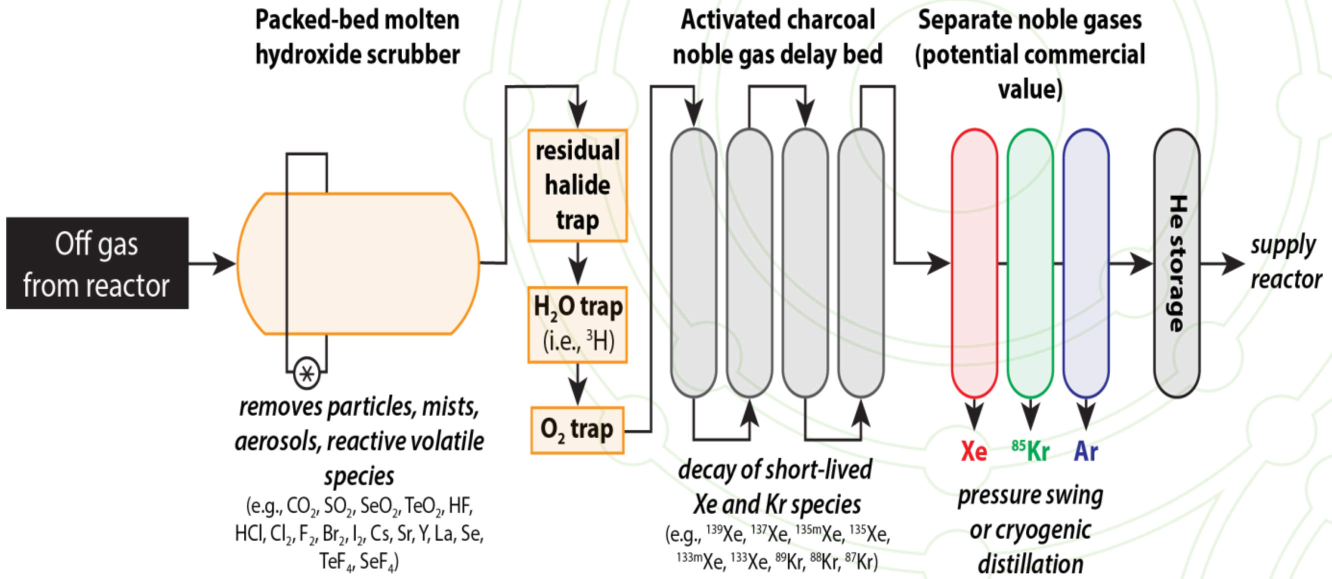
- Provides:
  - Chemical information
  - Identification and quantification
  - Oxidation state information
  - Molecular and elemental speciation
- Highly mature technology
- Simplistic integration
- Robust and versatile

System matrix

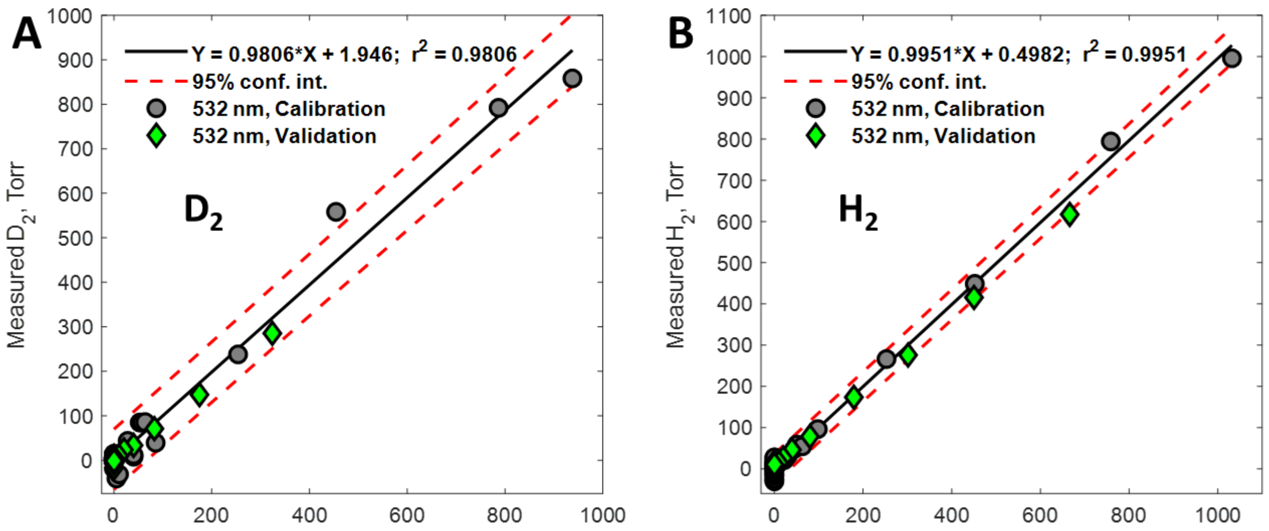


Systems of Focus

- Building tools to support development and demonstration of off-gas treatment systems
  - Aim to monitor and quantify key gas-phase species



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.



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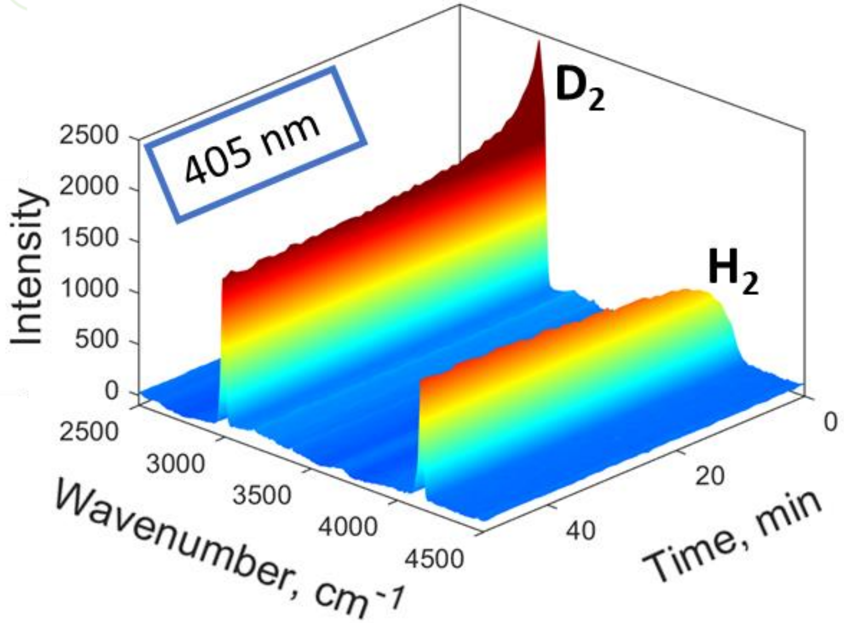
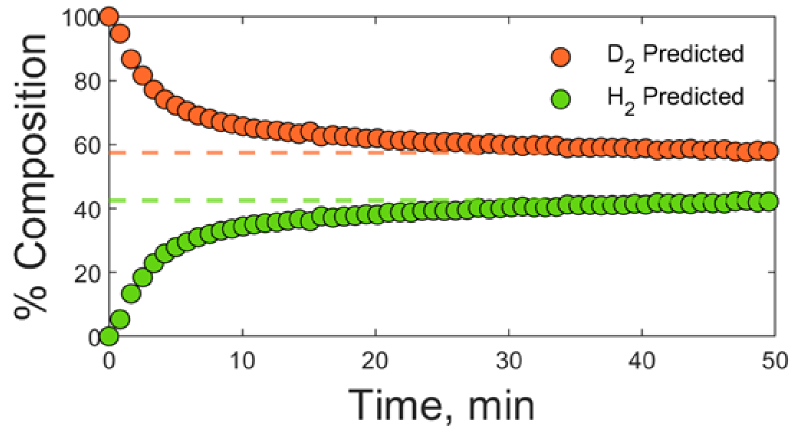
Monitoring of Harsh and Complex Systems

- Two-pronged challenge:
  1. Sensors and instrumentation
     - Improving on COTS (commercial off the shelf) limitations to build sensors compatible with:
       - Highly corrosive systems
       - High temperatures
       - Radiation
     - Improve sensitivity and limit of detection (LOD)
       - Hydrogen isotopes (e.g. H_2, D_2, T_2)
  2. Making smart sensors
     - Building tool kits that can accurately quantify chemical targets using spectral data
       - Apply models to different instrumentation and equipment





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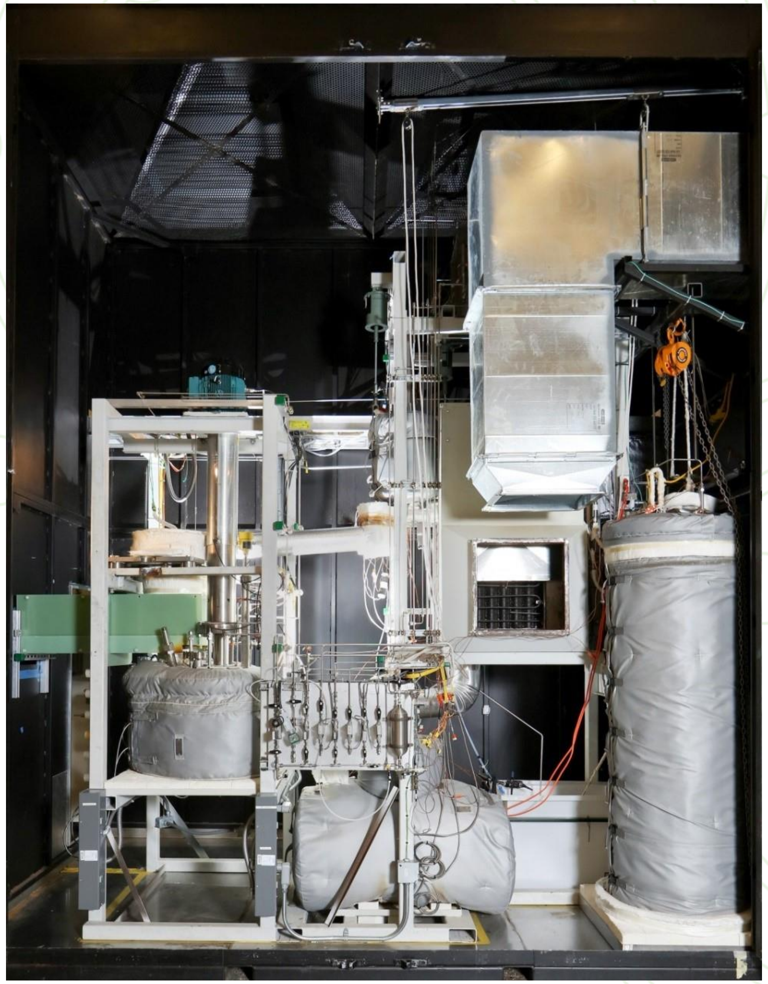
Interlaboratory Collaboration

- Building and demonstrating applications throughout treatment process
- Collaborating with other teams to create comprehensive characterization and control strategies
- Collaboration with ORNL team:
  - Sensor testing
  - Onsite demo on salt loop

ORNL Salt Loop



PNNL Raman Probe

FY25 Project Overview

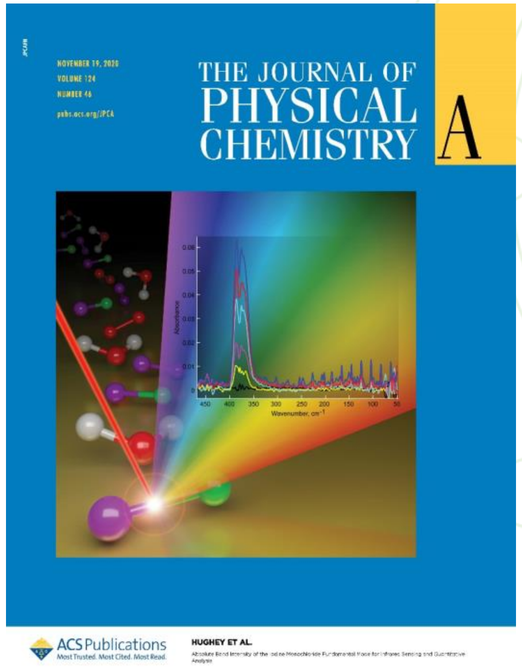
- M3AT-25PN0702061 Complete demonstration of flow cell design on representative gas stream

- Progress to date:
  - Received and currently testing new Raman system for gas phase measurements
  - New gas flow cell on order
  - Preparation for onsite demo at ORNL

Gas-phase Online Monitoring

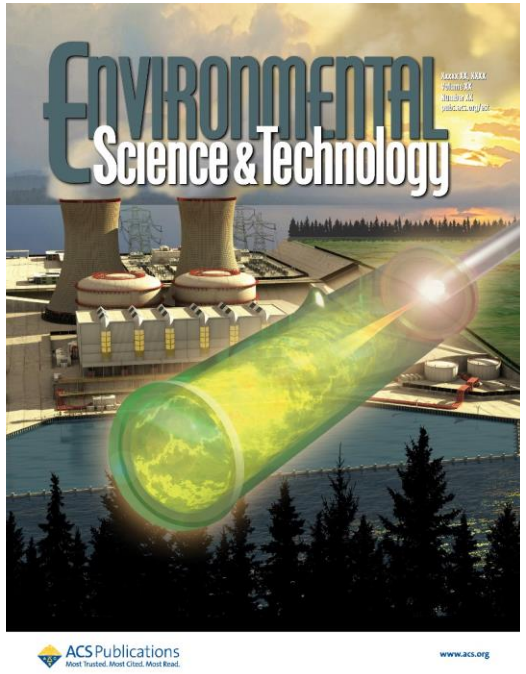
- Ongoing work has studied online monitoring of gas phase species
  - Primarily using Raman spectroscopy but also FTIR
  - Incorporated different sensor and measurement cell designs

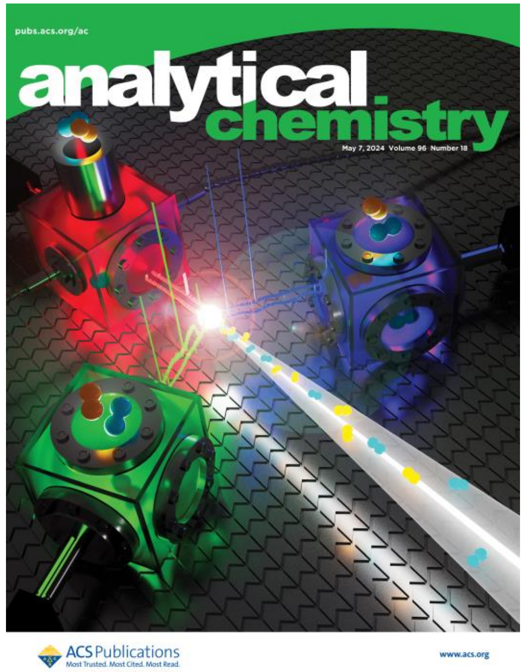
Hughey, K. D.; Bradley, A. M.; Tonkyn, R. G.; Felmy, H. M.; Blake, T. A.; Bryan, S. A.; Johnson, T. J.; Lines, A. M., Absolute Band Intensity of the Iodine Monochloride Fundamental Mode for Infrared Sensing and Quantitative Analysis. *J Phys Chem A 2020, 124* (46), 9578-9588.



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

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.*





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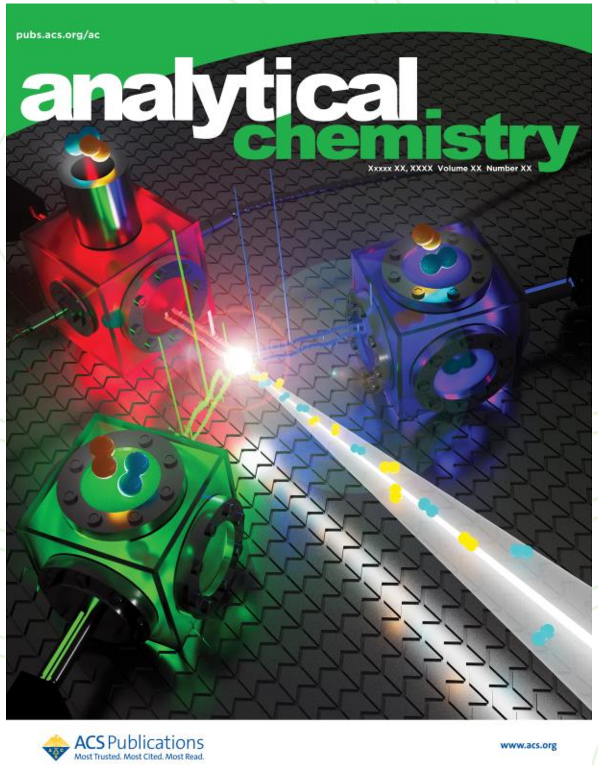
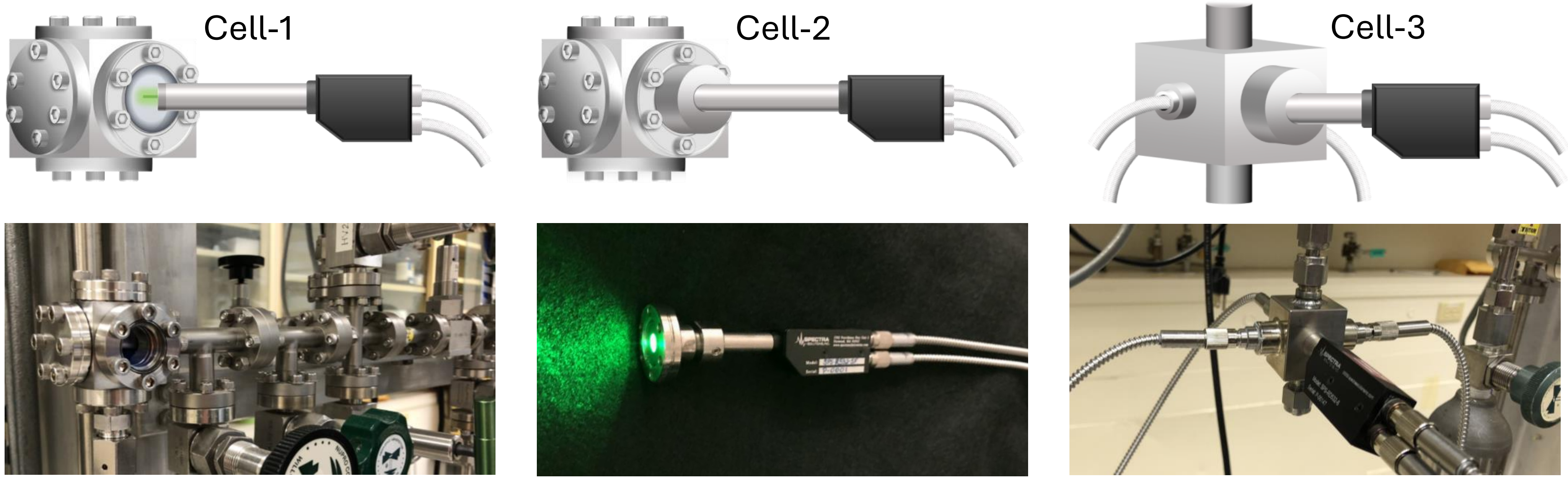
Improving Gas Cell Design

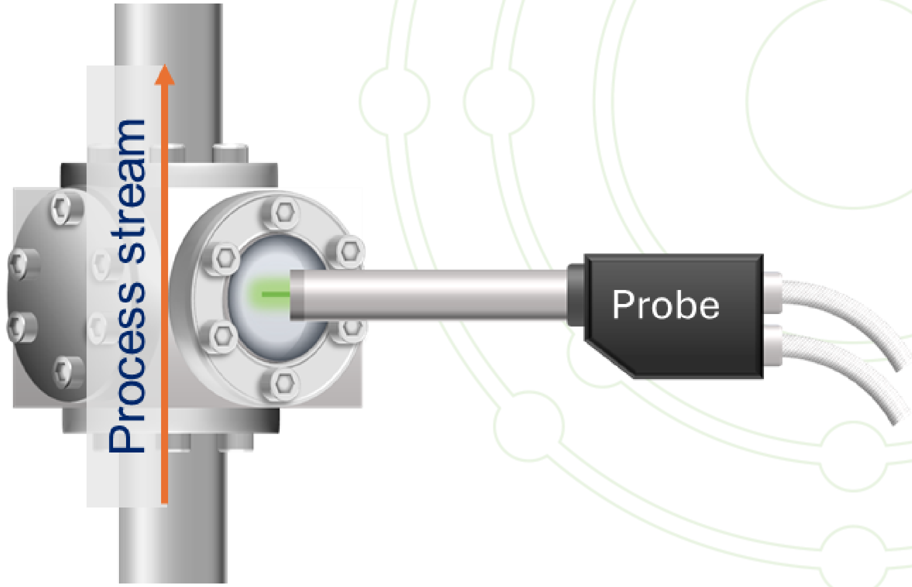
- Tested 3 cell designs and 3 Raman instruments in previous FYs
  - Demonstrated quantification of D_2 and H_2, and transfer of chemometric models between different instruments and gas cells
  - Resulted in 2024 publication:
    - Felmy, H. M.; Cox, R. M.; Espley, A. F.; Campbell, E. L.; Kersten, B. R.; 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**, 96 (18), 7220-7230. DOI: 10.1021/acs.analchem.4c00802.

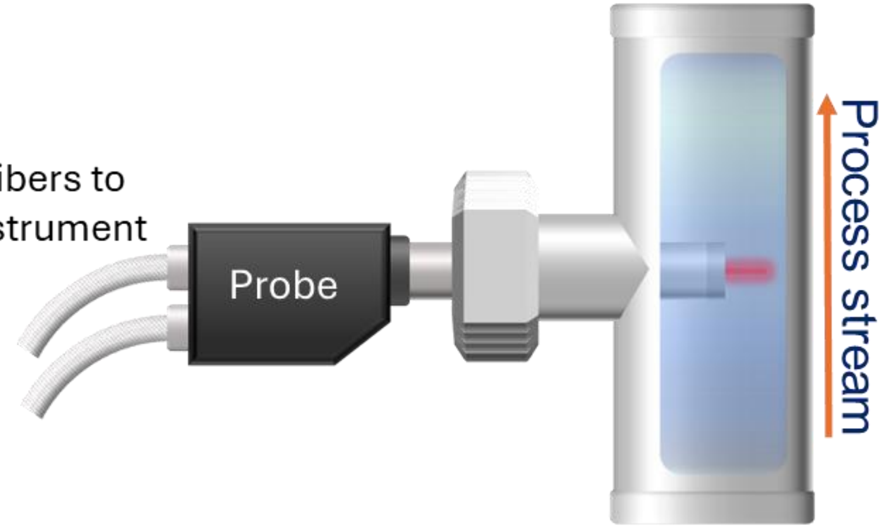


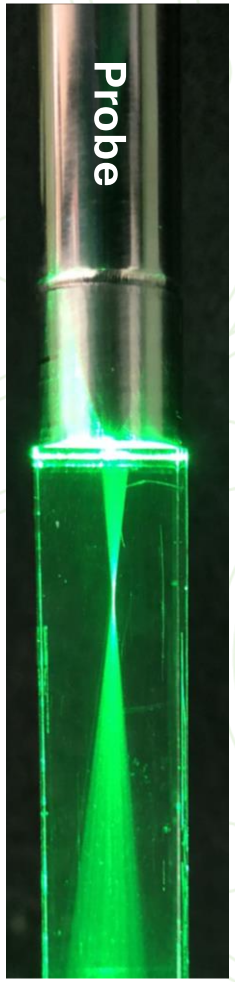


Raman Sensor Details

- Raman probes typically rely on 180° backscattered light
- Measures molecular, polyatomic species including several key gas-phase targets
- Two primary methods to incorporate probe into process stream:
  - Through optical window
  - Immersed directly in stream

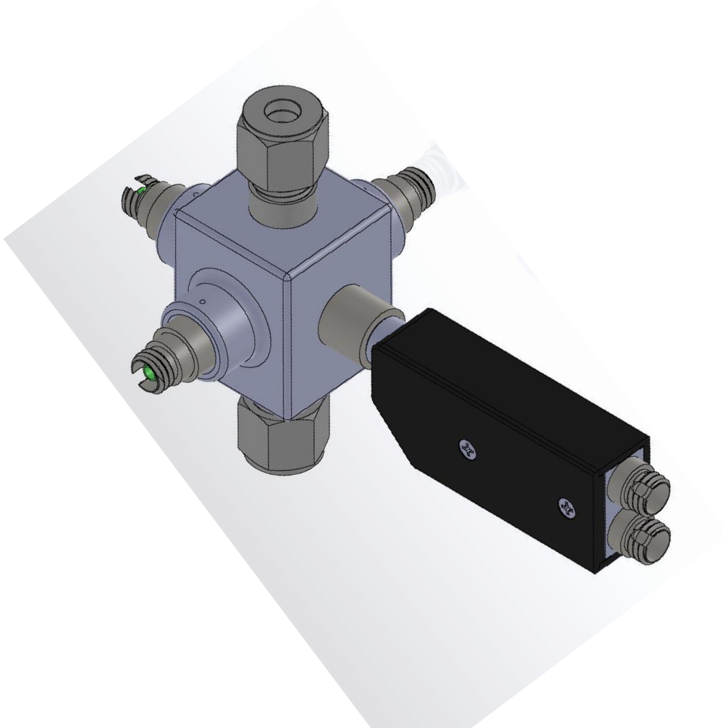


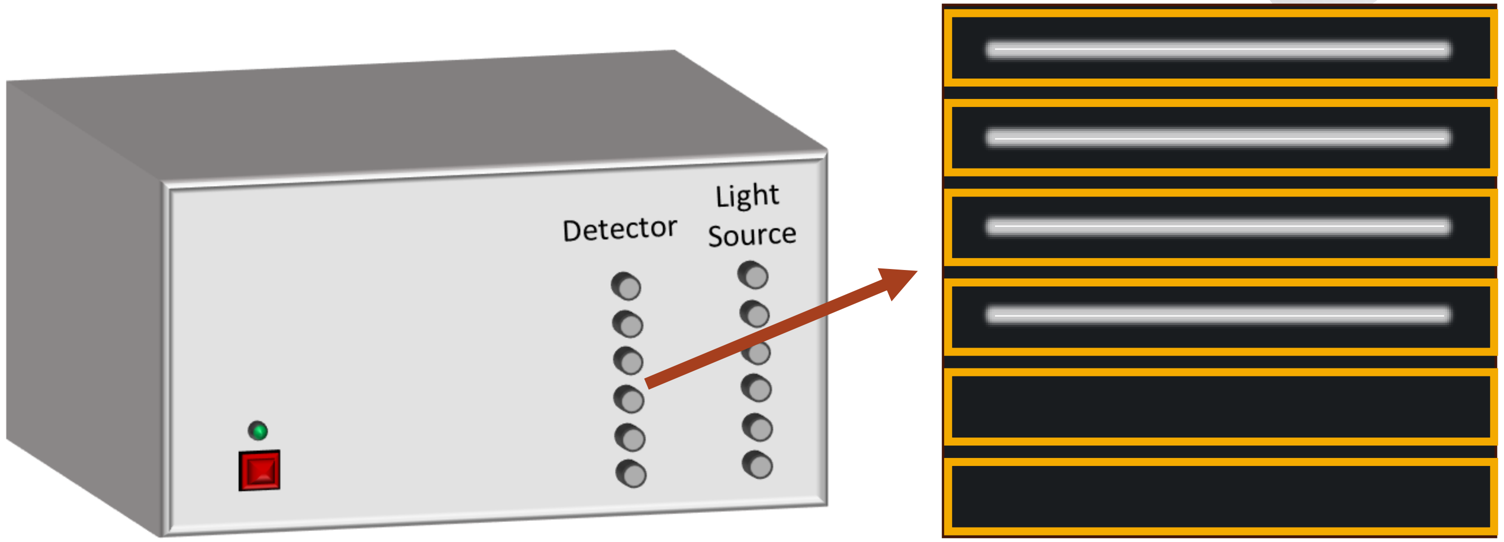


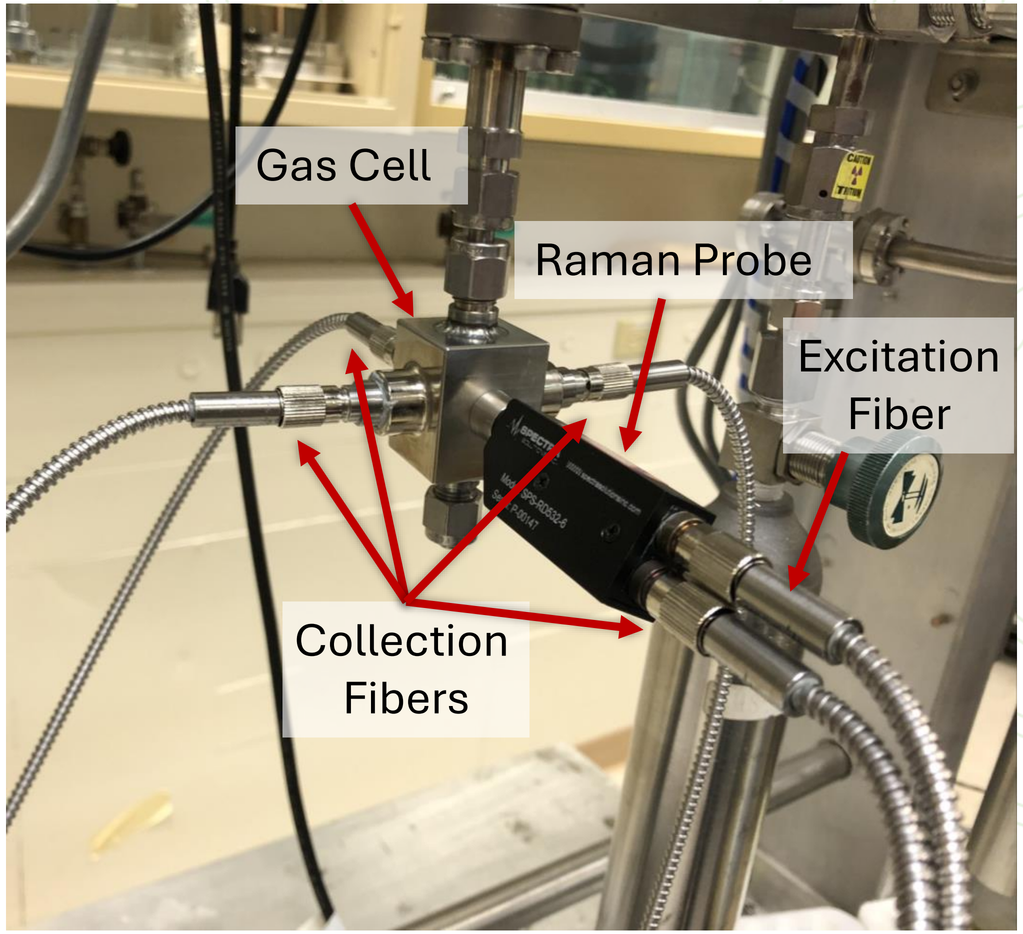


Improving Gas Cell Design

- FY24 cell design
  - 4 collection ports to increase signal
  - Requires multitrack instrument





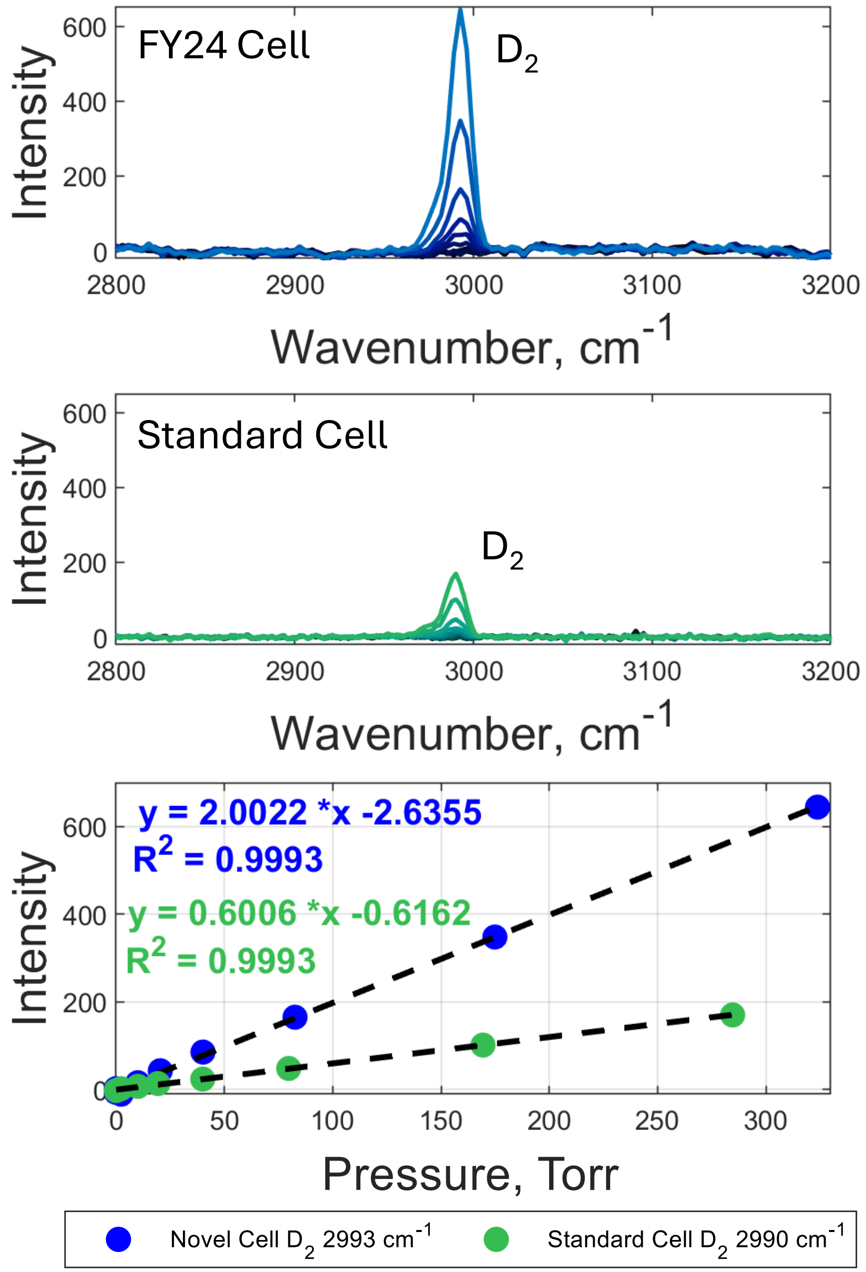


Improving Gas Cell Design

- FY24 cell design
  - 3x higher signal from multiple collection ports
  - Bulky design makes it less convenient to incorporate into gas line
  - Requires multitrack instrument

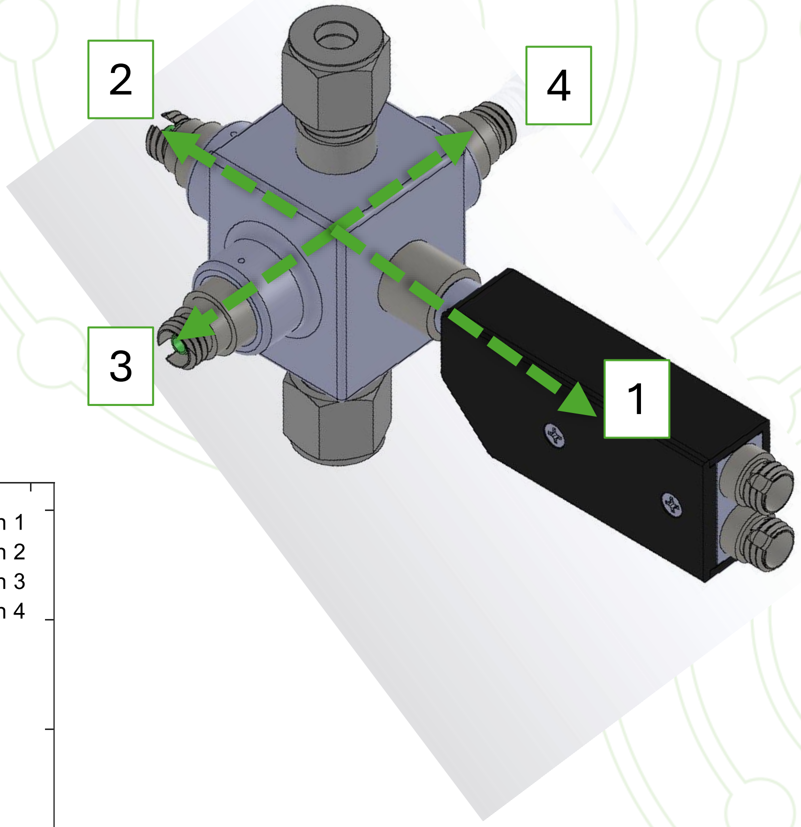
FY24 Cell

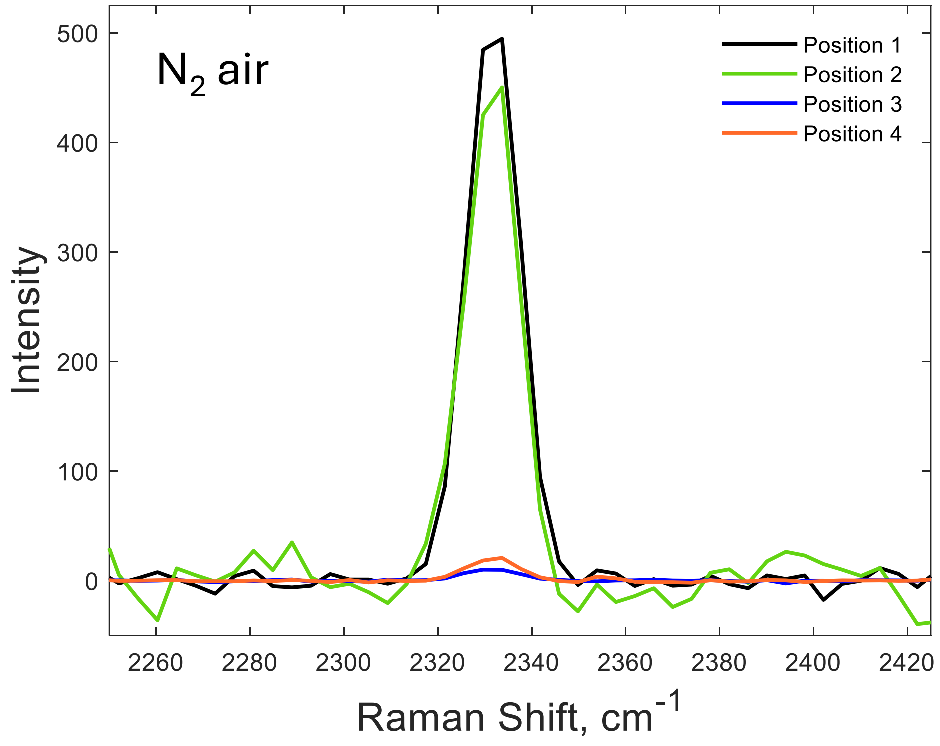
Standard Cell



Improving Gas Cell Design

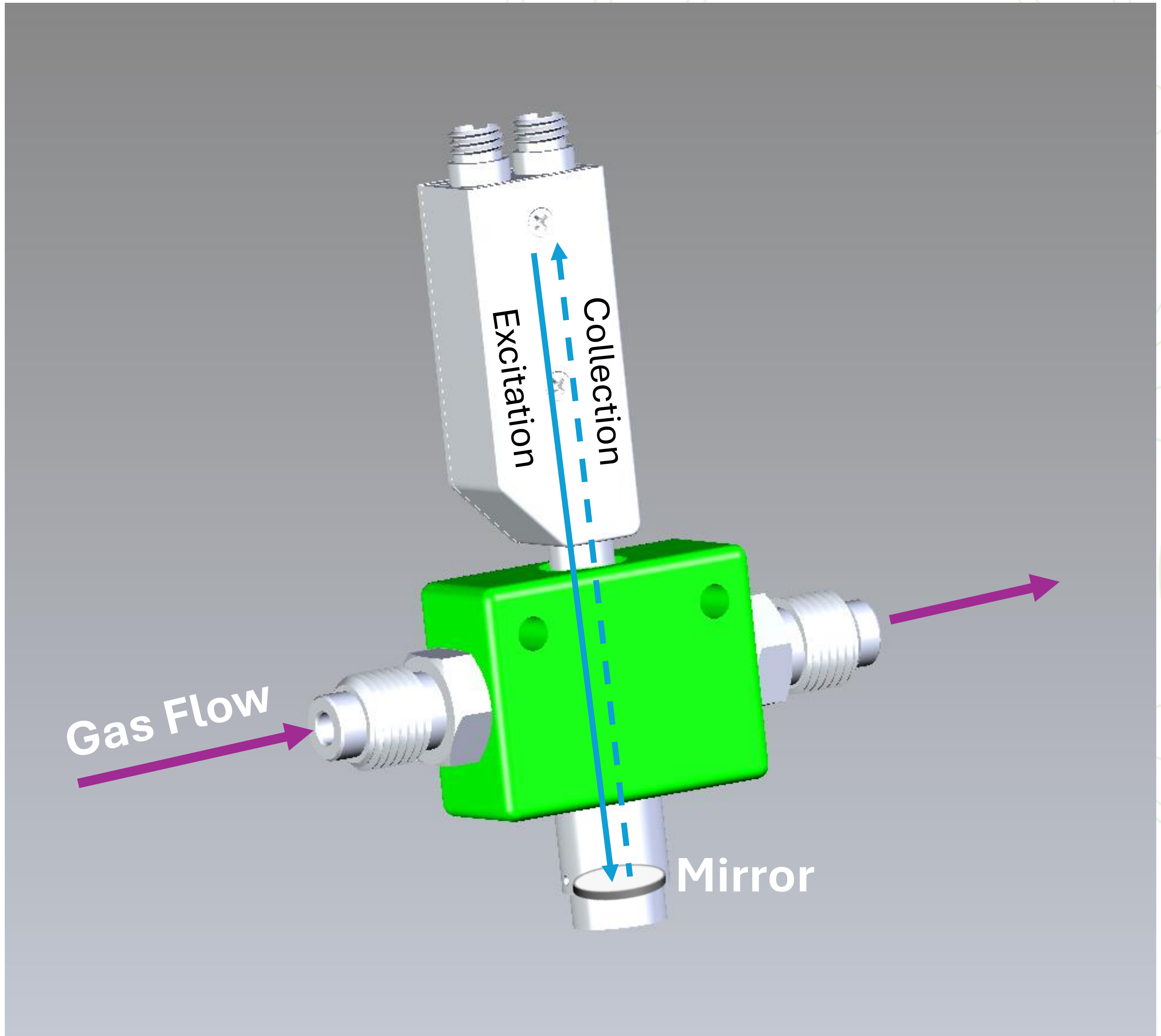
- FY24 cell design
  - Increased signal from additional collection port 180° from probe
  - 90° collection ports did not significantly impact signal





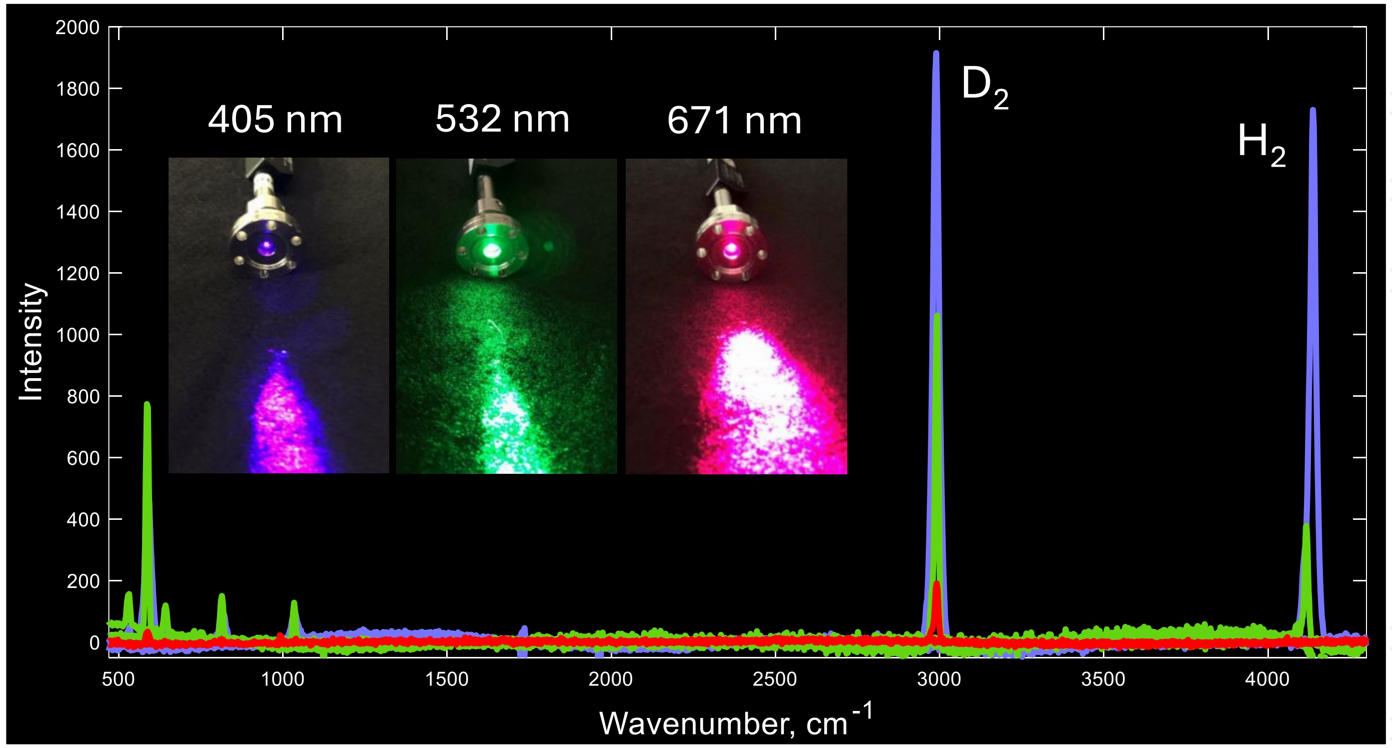
Flow Cell Design

- FY25 flow cell design
  - Simplified design without sacrificing signal
  - Easier incorporation into gas line
  - Requires only 1 collection port
    - Allows for multiple locations to be measured simultaneously with a multitrack instrument
  - Currently on order



Improving Instrumentation

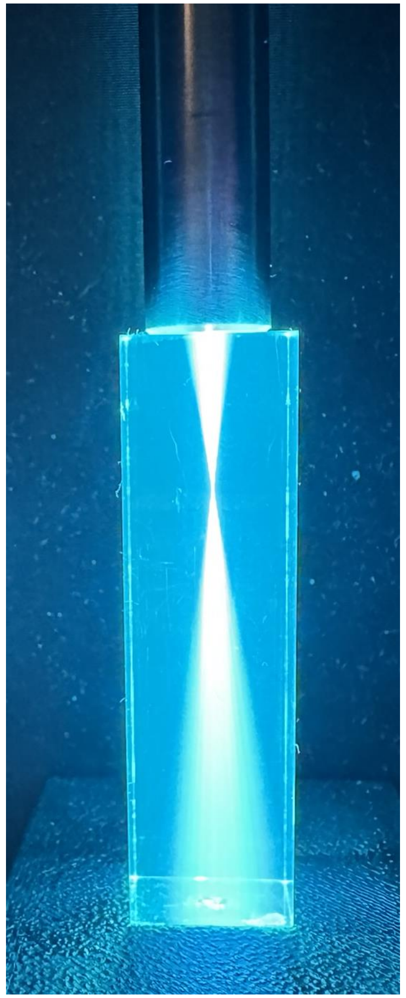
- Procured new Raman instrument with specifications for gas-phase measurements
- Compared to previous work using existing COTS instrumentation:
  - Requires higher sensitivity for low concentration species
  - Previous work determined lower wavelength/higher energy lasers are better for gas-phase work
    - Higher signal without interfering fluorescence
  - Improved detector design
  - Multitrack instrument
    - Allows for measurement of multiple measurement locations simultaneously

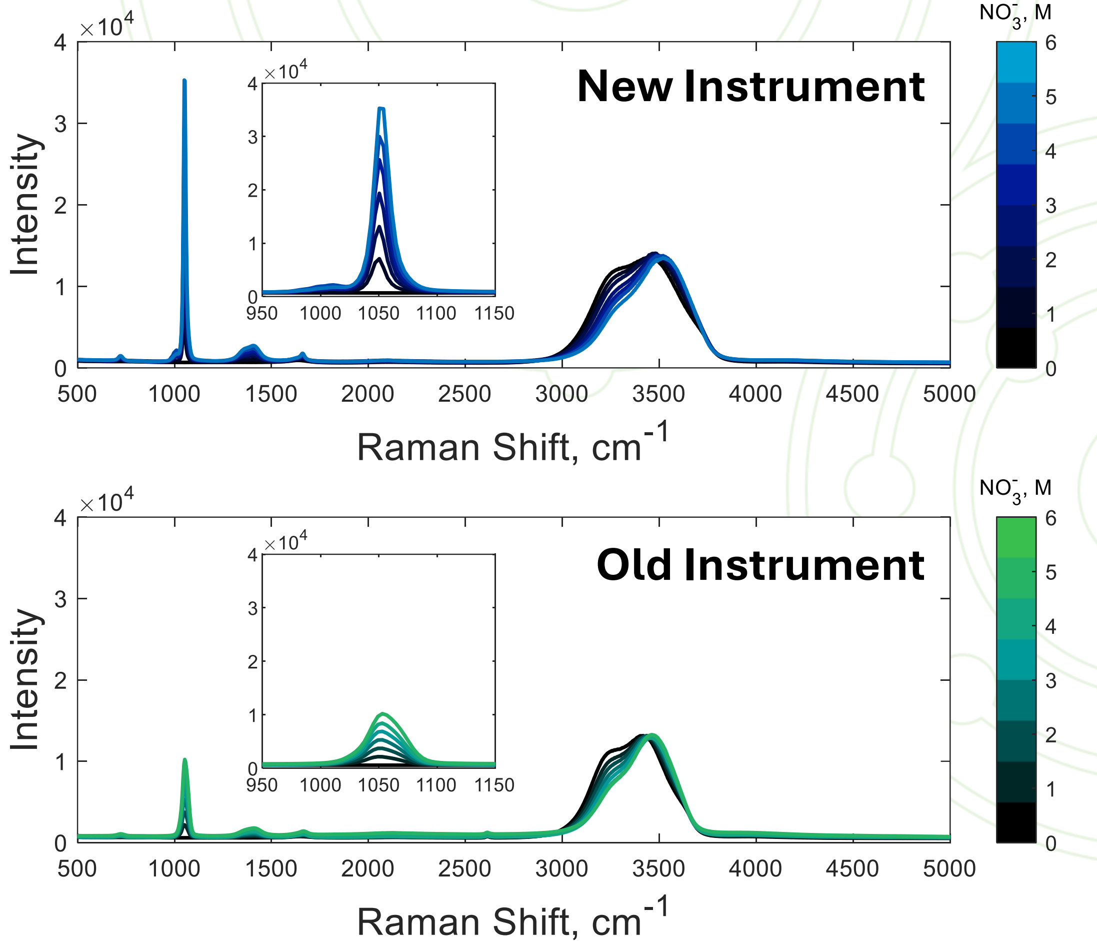


Improving Instrumentation

- Testing new Raman instrument
  - 406 nm (blue) excitation
  - Improved detector design
  - Multitrack
    - Allows for multiple simultaneous measurement locations

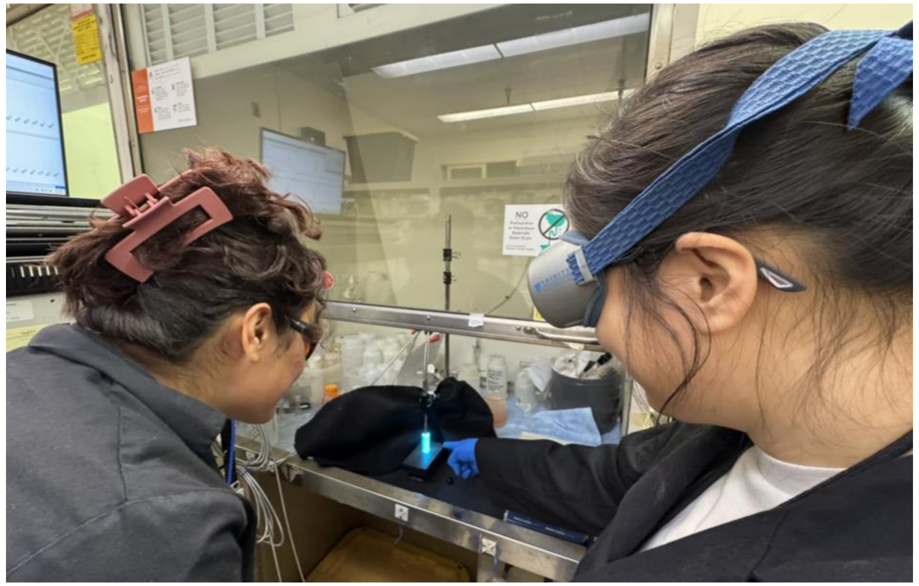
→ Improve sensitivity



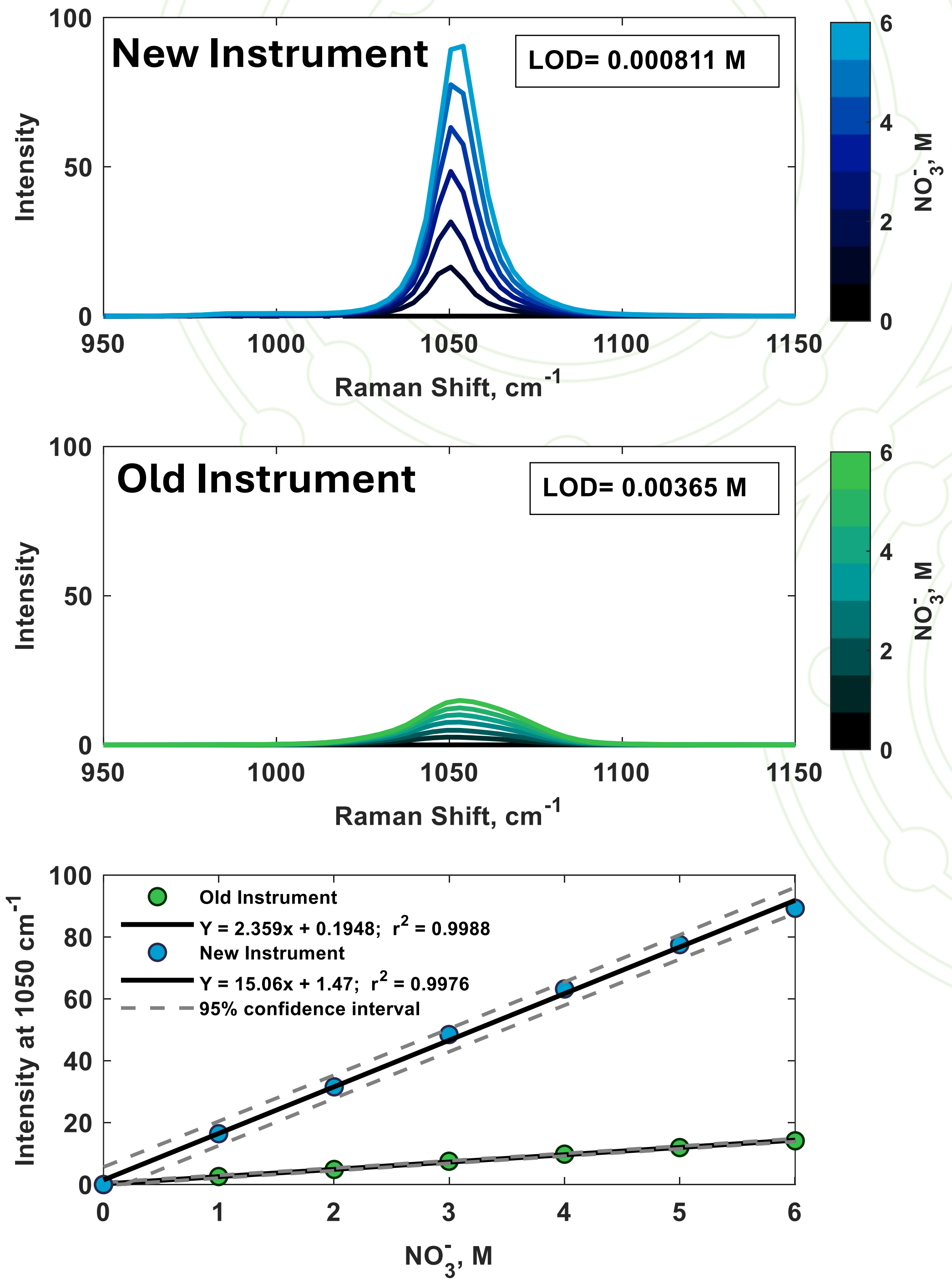


Improving Instrumentation

- Initial solution-phase testing
  - >6x higher peak intensity
  - >4x improvement in limit of detection (LOD)
- Next steps:
  - Move on to gas-phase testing
  - Test with new gas flow cell

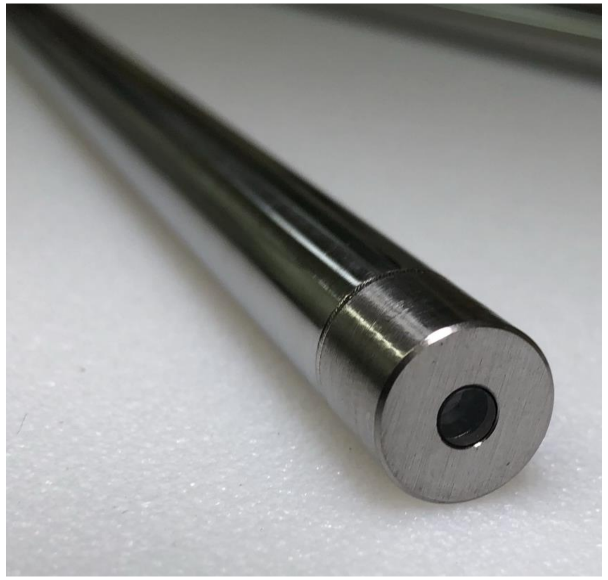


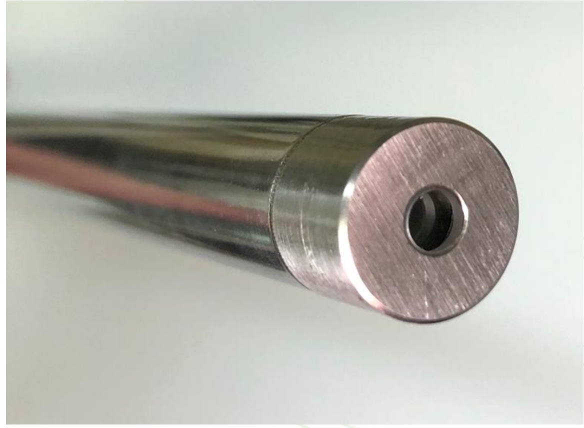
Paulina Guerrero-Almaraz (post doc) and Poki Tse (early career scientist)

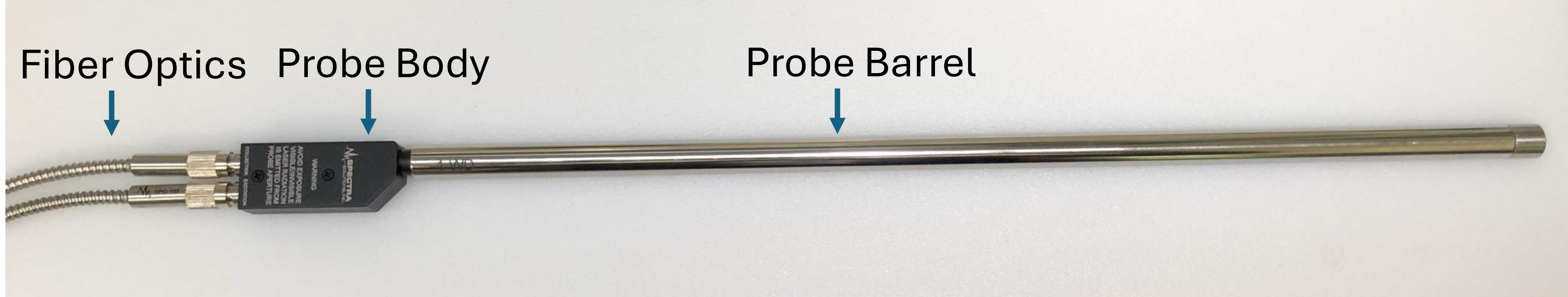


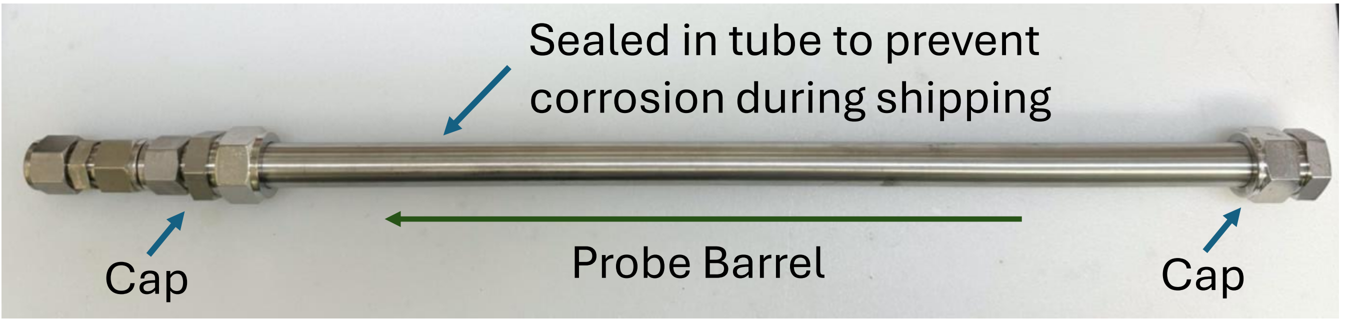
Sensor Testing

- Testing probe materials at ORNL
  - Shipped probe barrels to ORNL for incorporation into various gas phase spaces within salt loops
    - Cascade impactor
    - LSTL storage tank headspace
    - FASTR storage tank
  - Returned to PNNL for characterization









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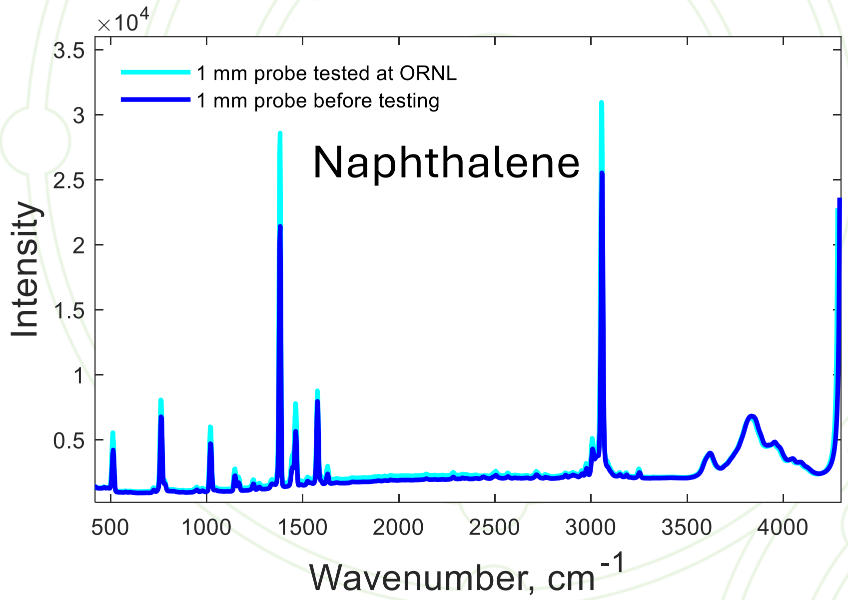
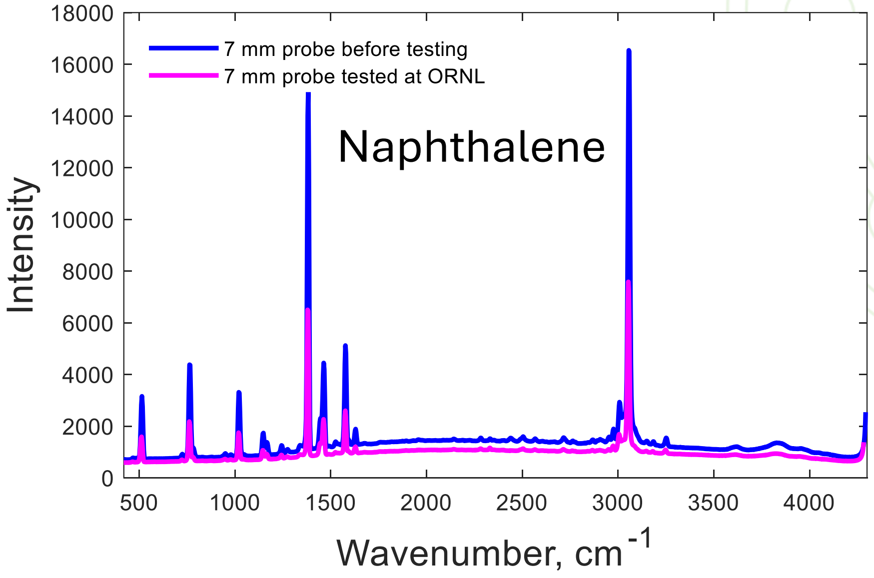
Sensor Testing

- First two probes tested showed little damage from exposure to corrosive and high temperature environments
  - Probe 1: cascade impactor
  - Probe 2: LSTL storage tank
    - Some discoloration
  - Remained functional

Probe 1



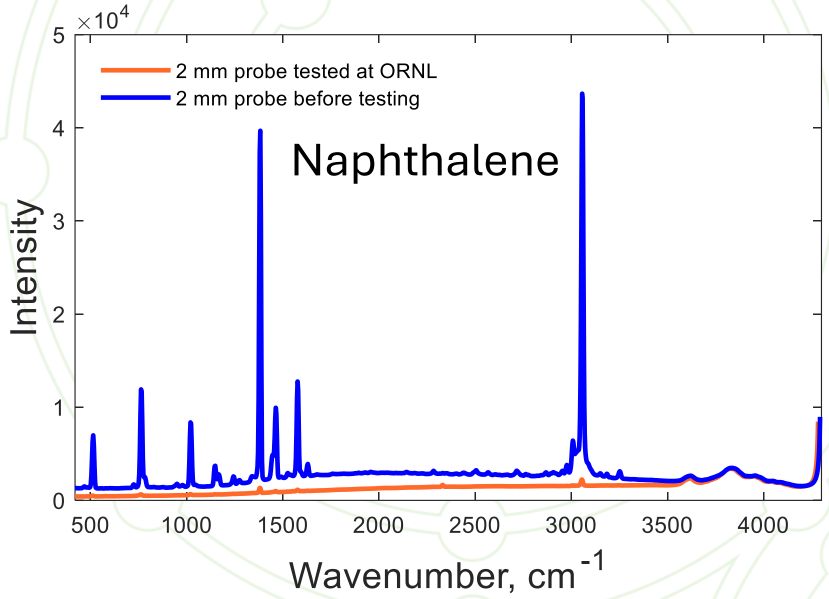
Probe 2



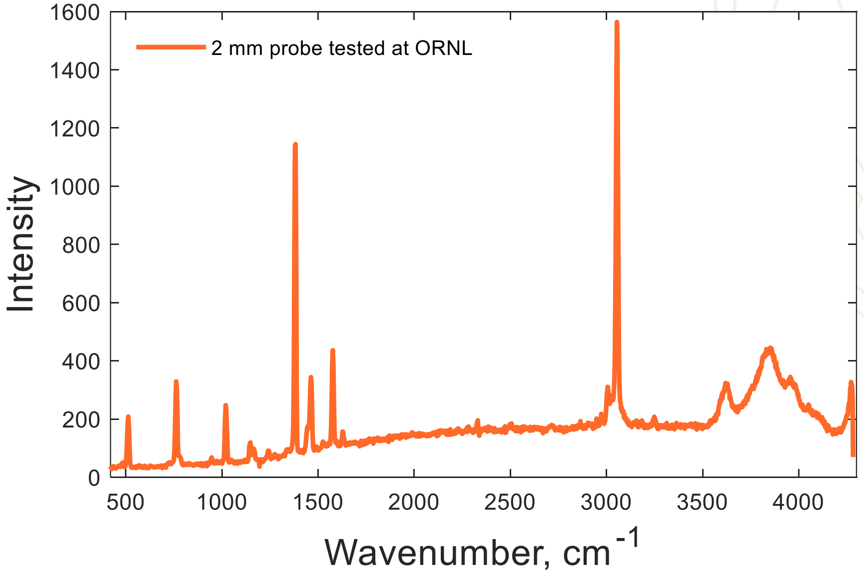
Sensor Testing

- 3rd probe showed more significant damage
  - In headspace of FASTR storage tank
  - Discoloration on lens caused decreased signal
  - Signal processing recovered naphthalene spectrum

Probe 3



Subtraction of blank spectrum



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Planned onsite demo at ORNL

- Demo planned for summer 2025
  - Documentation in place:
    - 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)
- Plan to take new instrument and probes to ORNL

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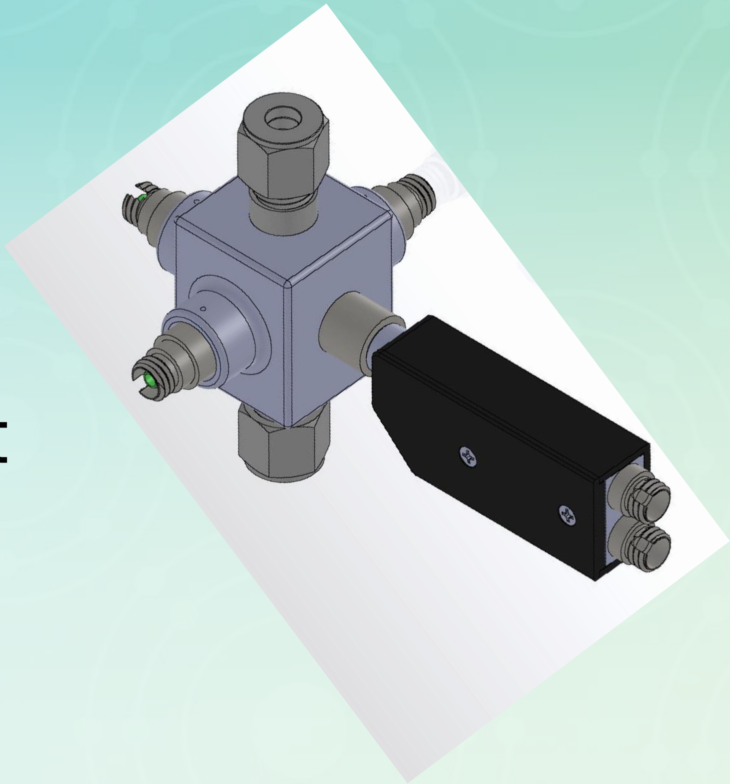
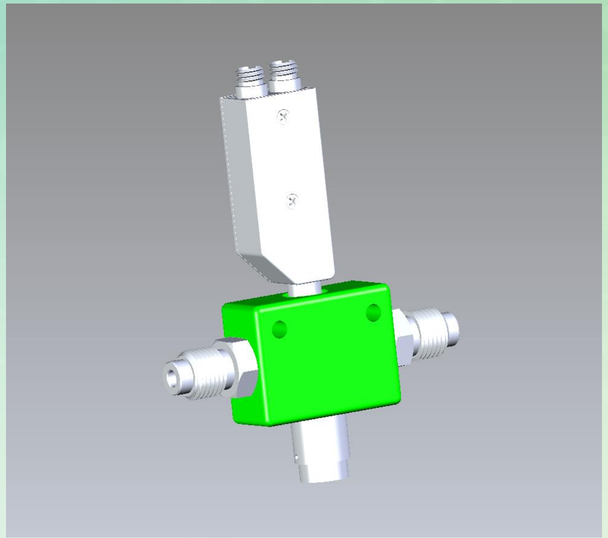
Summary





- Sensor and instrument development
  - Tailored to off-gas targets
  - Improved signal and LOD
    - Gas cell development
    - Improved instrumentation
- Sensor testing at ORNL
  - Probes survived prolonged exposure to gas phase above molten salt
- Continuing planning for onsite demo at ORNL

Conclusions

- Online Monitoring is a powerful tool that can support:
  - More efficient design and testing of chemical processes
    - Off-gas treatment
  - Safer, optimized, and affordable deployment of processes
- Optical sensors can provide complex chemical information
  - Identification and quantification of key analytes of interest
  - Collaborating with other labs to build comprehensive toolkits

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PNNL Team:

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Job Bello (Spectra Solutions Inc.)
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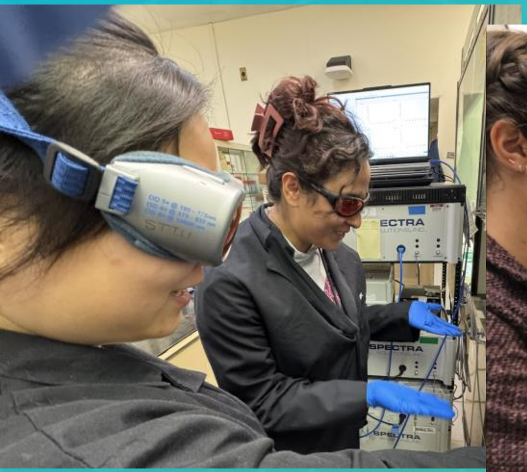
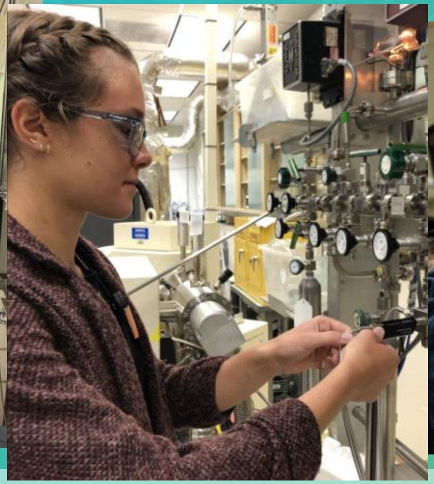
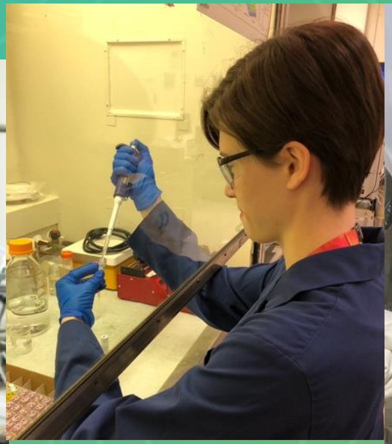
Molly Vitale-Sullivan (SULI)
Andrew Clifford
Bethany Kersten







Thank you

heather.felmy@pnnl.gov

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