



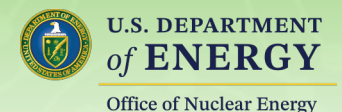
On-line Monitoring for MSR Off-Gas Treatment: Molecular Approach

Heather Felmy, Amanda Lines, Sam Bryan

PNNL

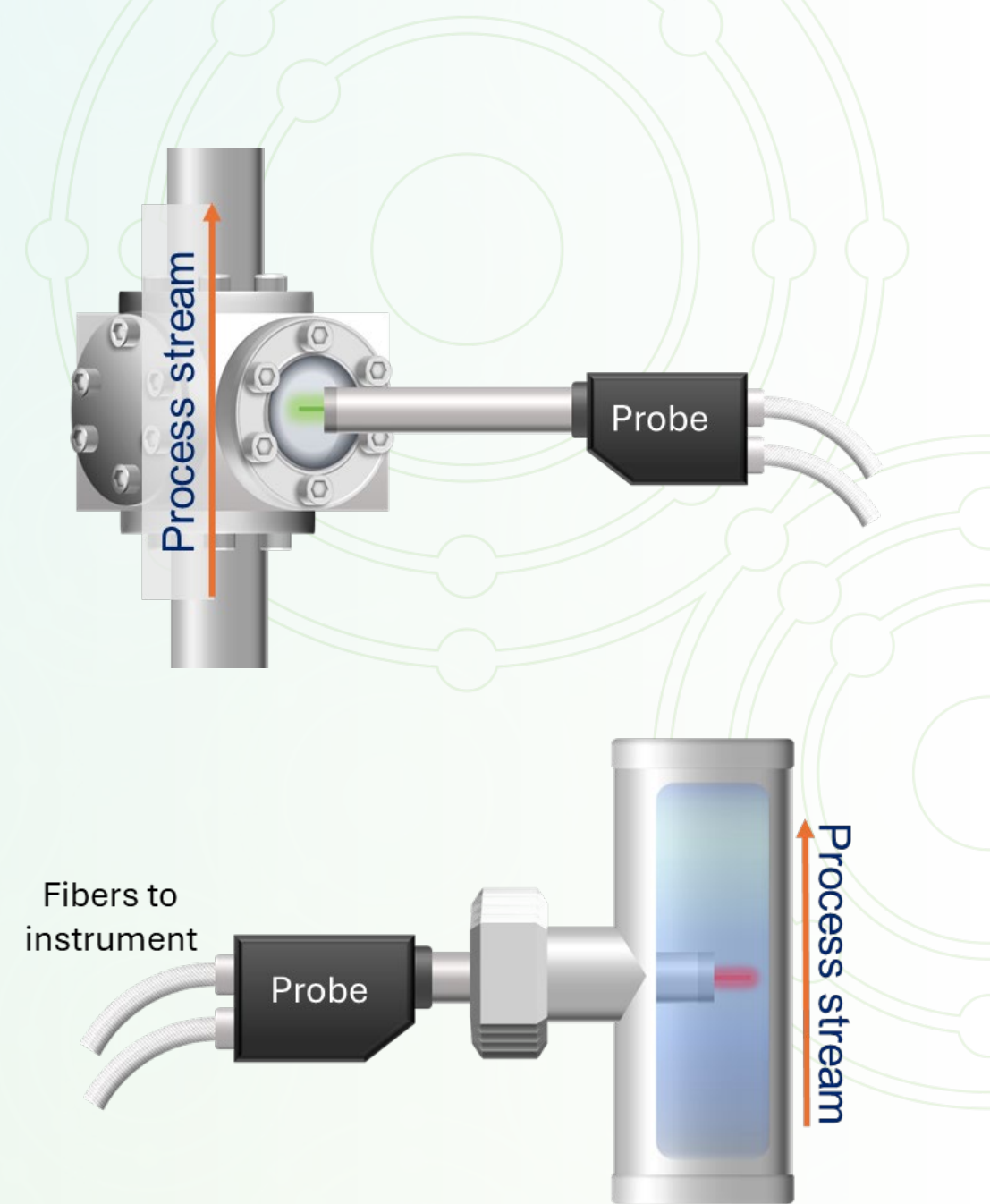
Annual MSR Campaign Review Meeting April 21-24, 2026

PNNL-SA-222063



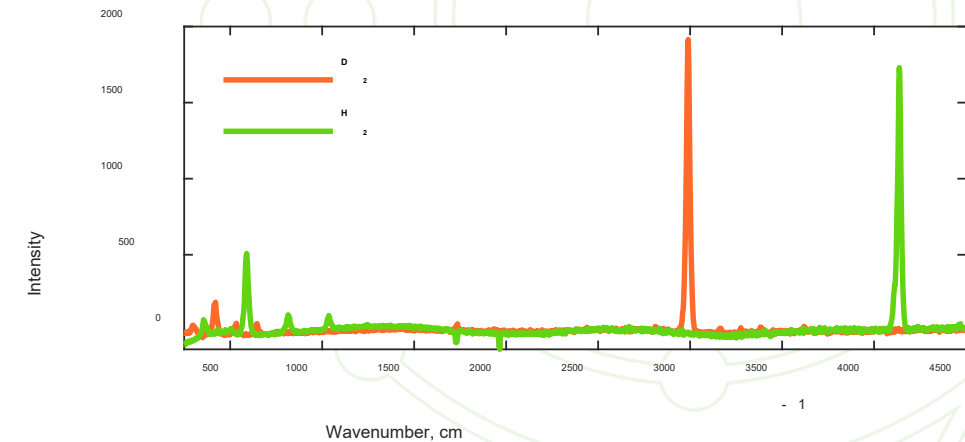
On-line monitoring

- 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

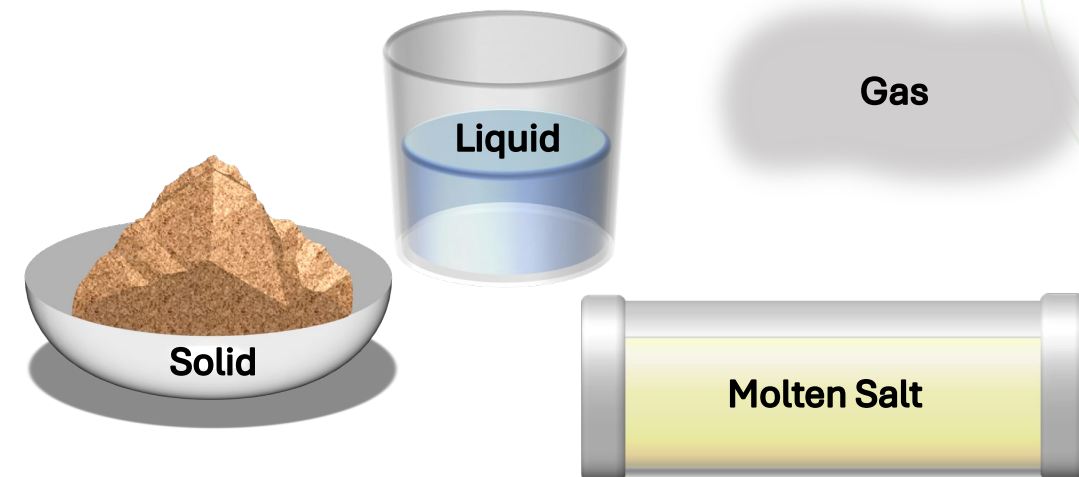


Chemical Characterization: Optical Spectroscopy

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

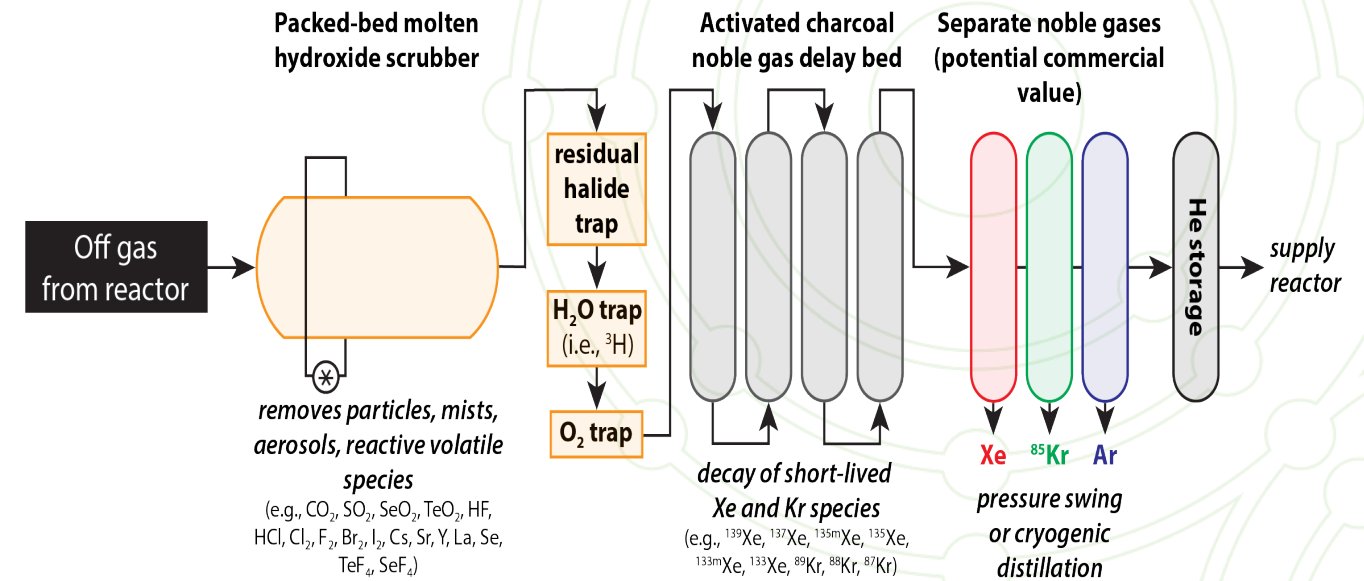


System matrix

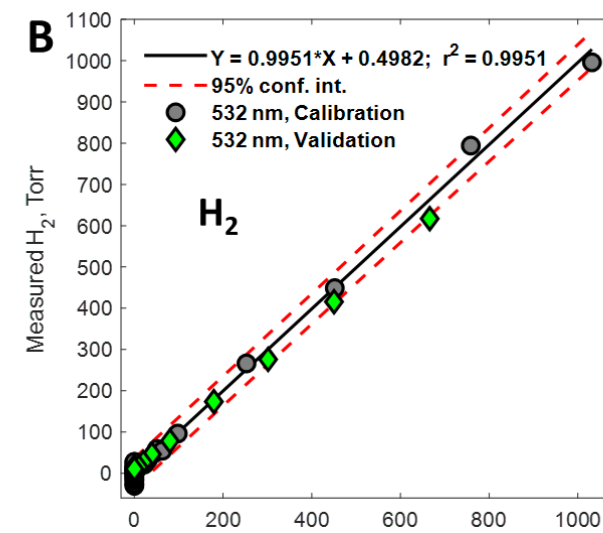
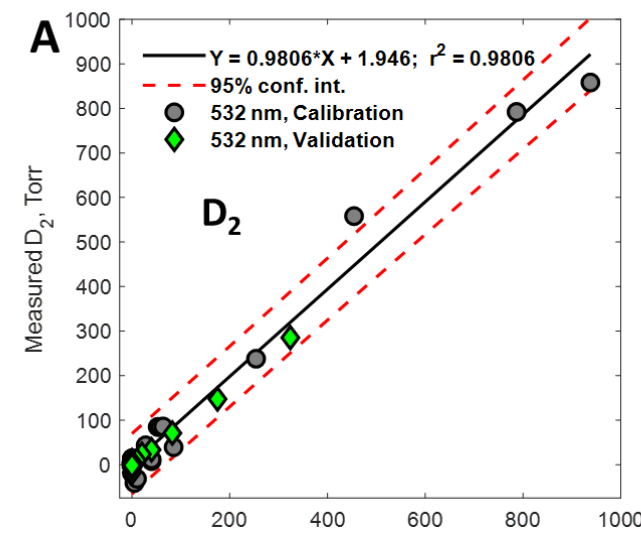


Systems of Focus

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



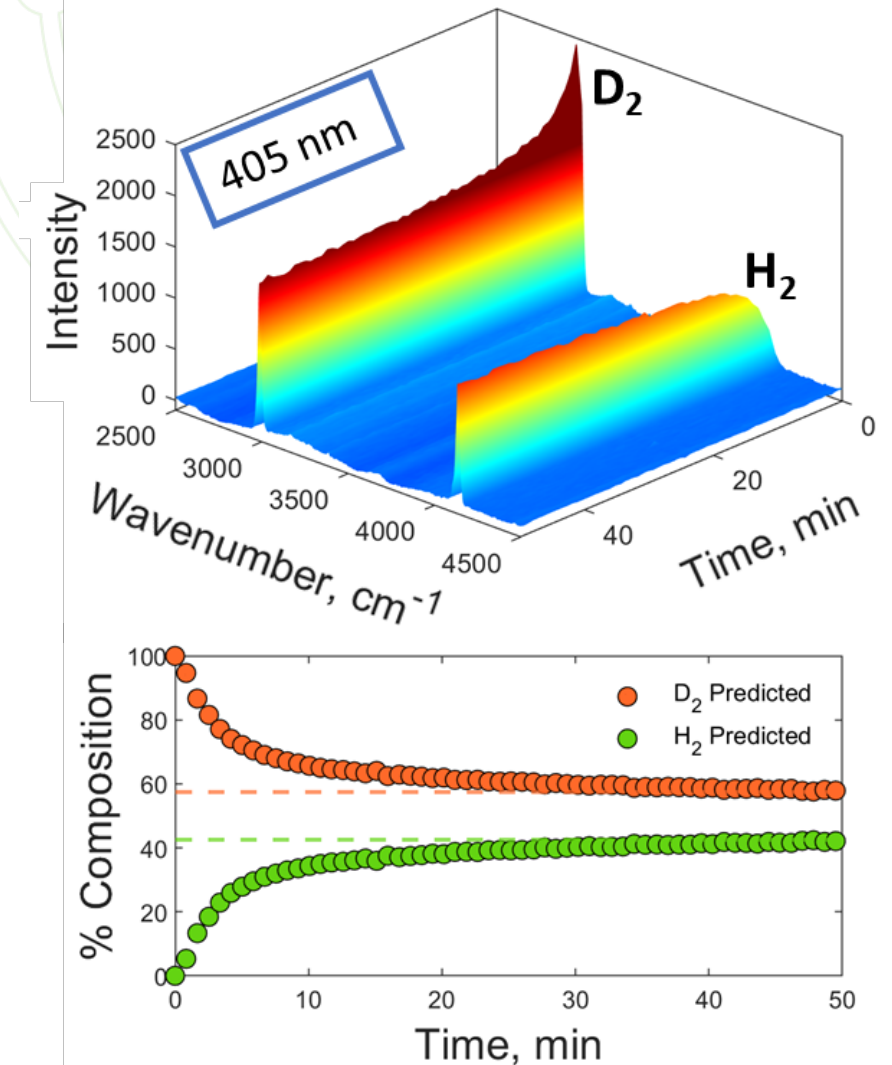
Mcfarlane, J.; Ezell, N.; Del Cul, G.; Holcomb, D. E.; Myhre, K.; Chapel, A.; Lines, A.; Bryan, S.; Felmy, H. M.; Riley, B. Fission Product Volatility and Off-Gas Systems for Molten Salt Reactors; Oak Ridge National Lab.(ORNL), Oak Ridge, TN (United States): 2019.



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.

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



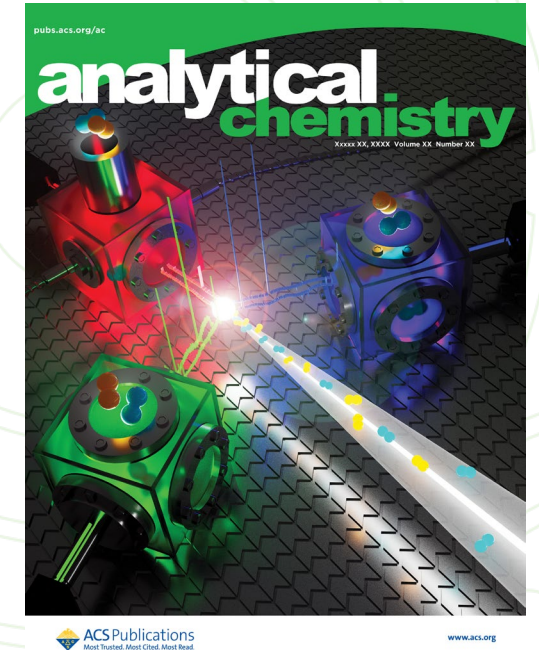
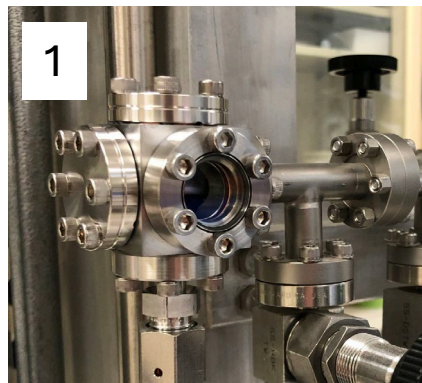
FY26 Project Overview

- Progress to date:
 - Completed bulk of the data collection on single component and mixed gases
 - Building quantification models
 - Joint PNNL-ORNL paper draft

Milestone	Deliverable Description	Due Date	Status
M3AT-26PN0702051	Complete development of models for the simultaneous quantification of multiple gas-phase species	9/30/26	On Time

Improving Gas Cell Design

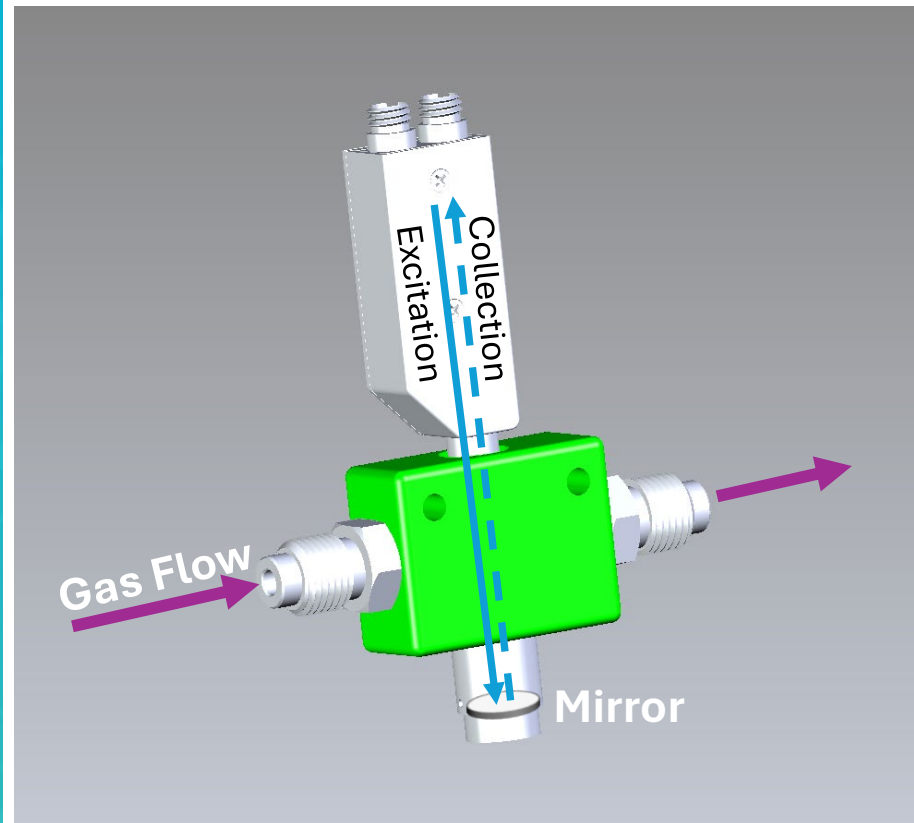
- 4 generations of gas cells have been designed and tested
- Goal of improving sensitivity and versatility
- FY25 probe designed to enhance signal while maintaining a small profile



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.

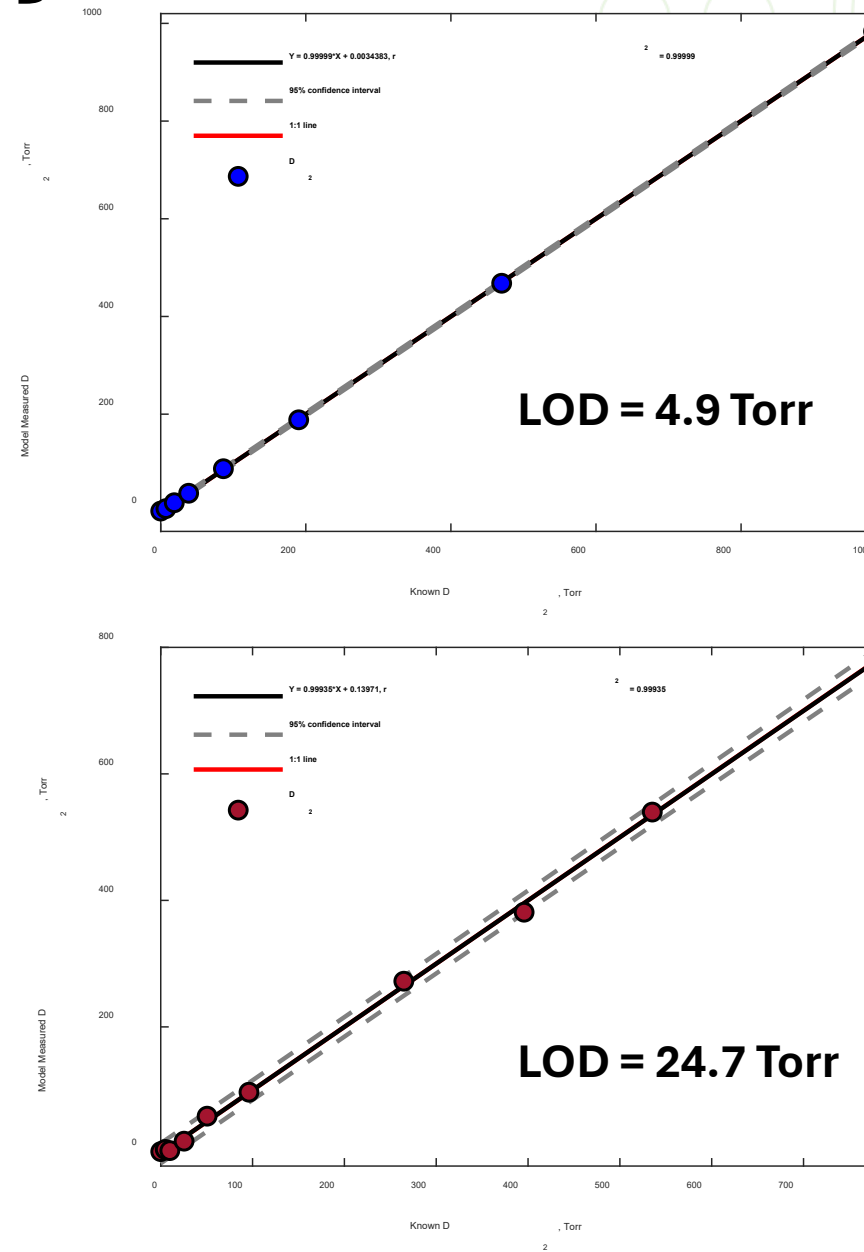
Improving Gas Cell Design

FY25 Design



Improving Sensitivity

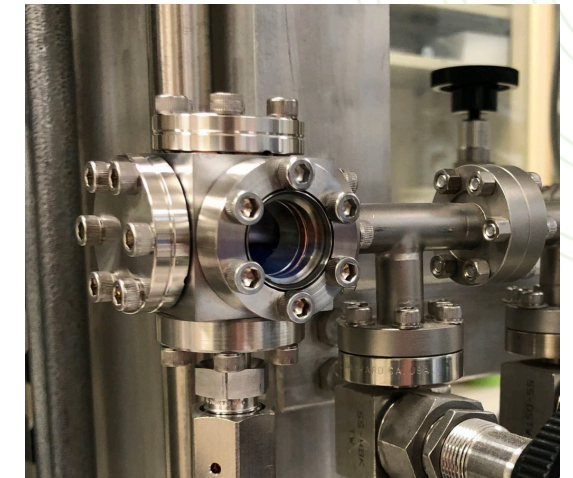
- FY25 gas cell with new instrument produced a 5x improvement in LOD for D₂
- Measured under the same conditions (integration time, averaging, laser power, etc.)



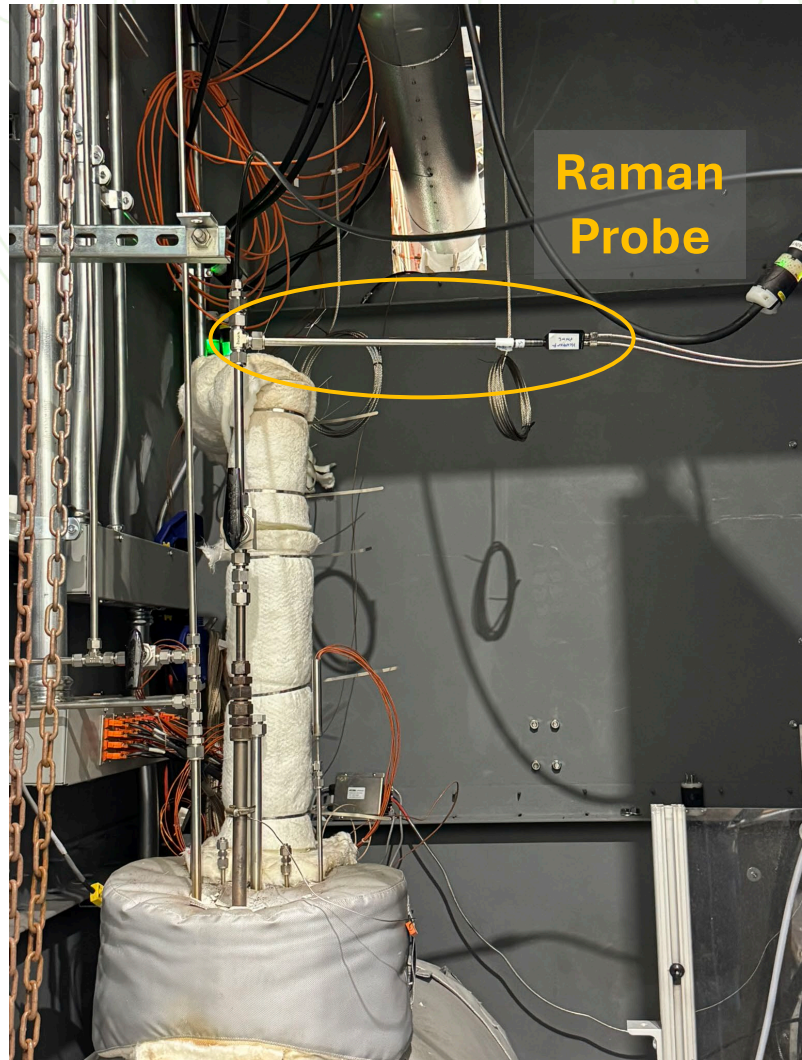
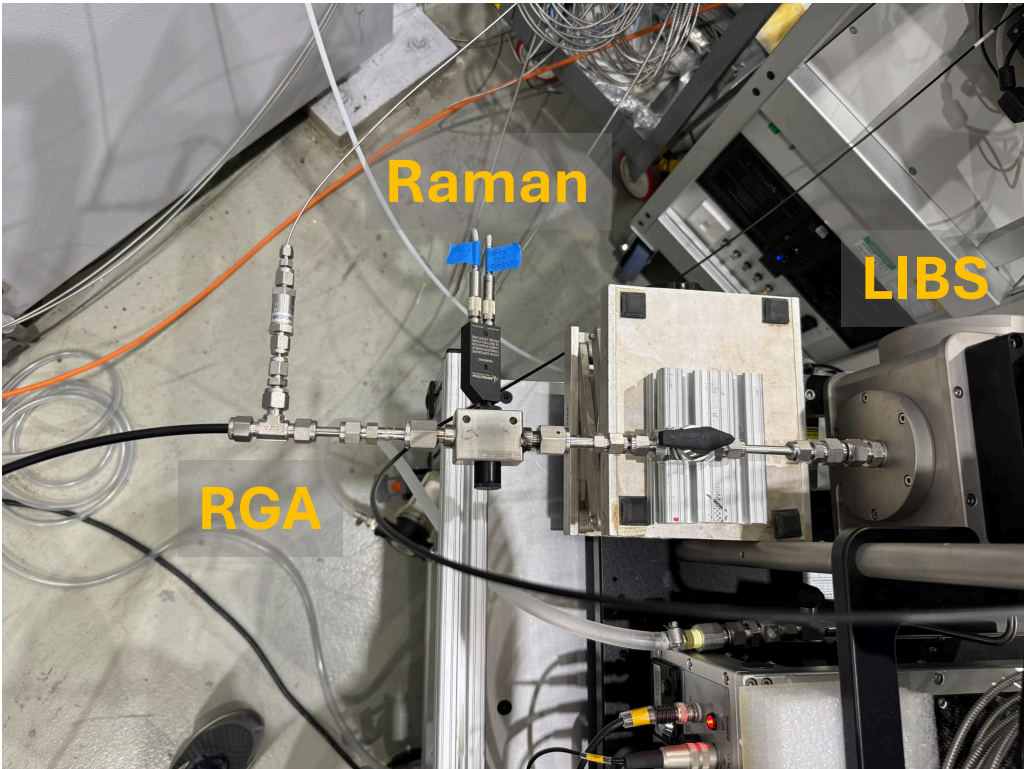
New instrument
New gas cell



Old instrument
Old gas cell

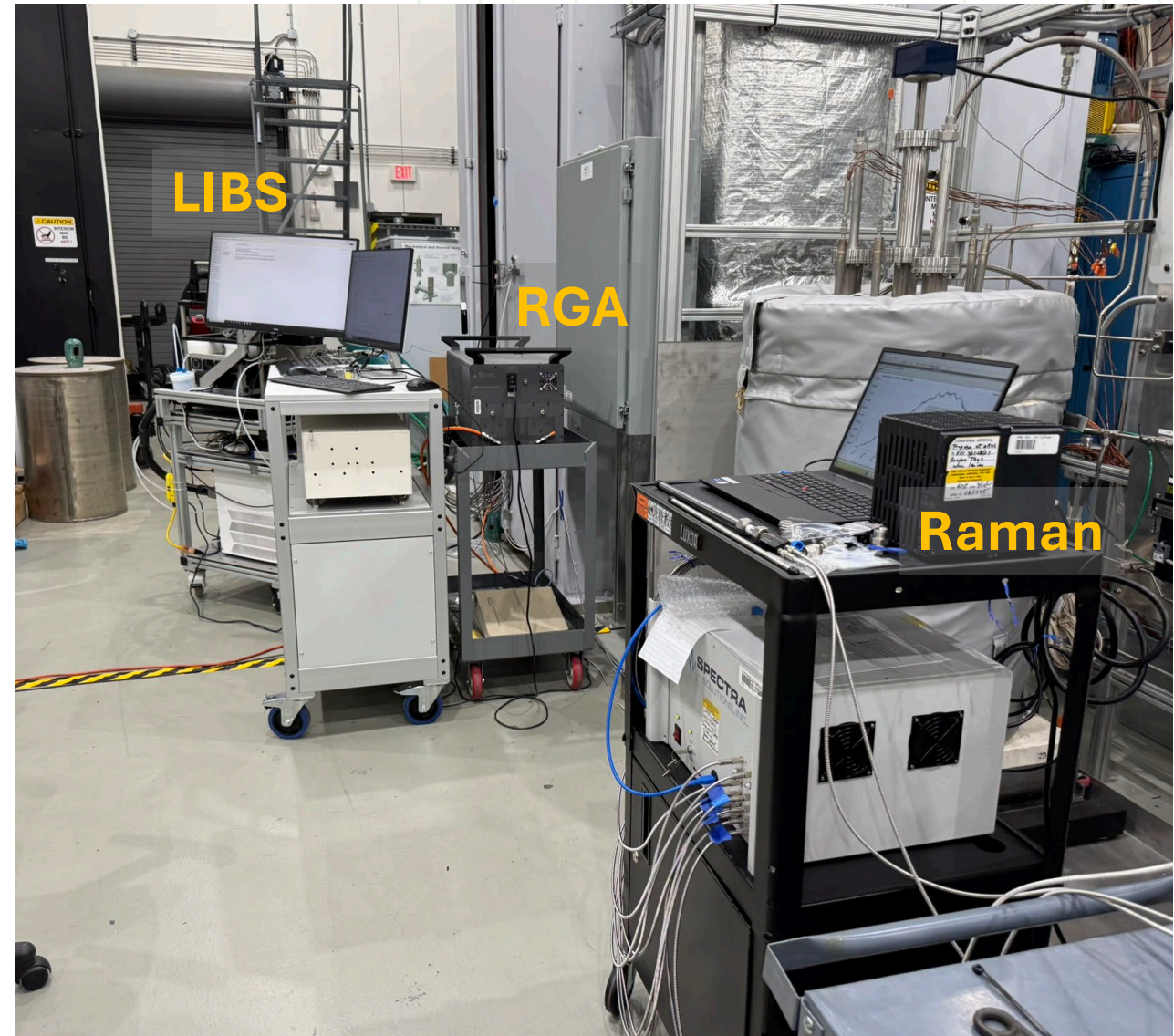


PNNL-ORNL Demo



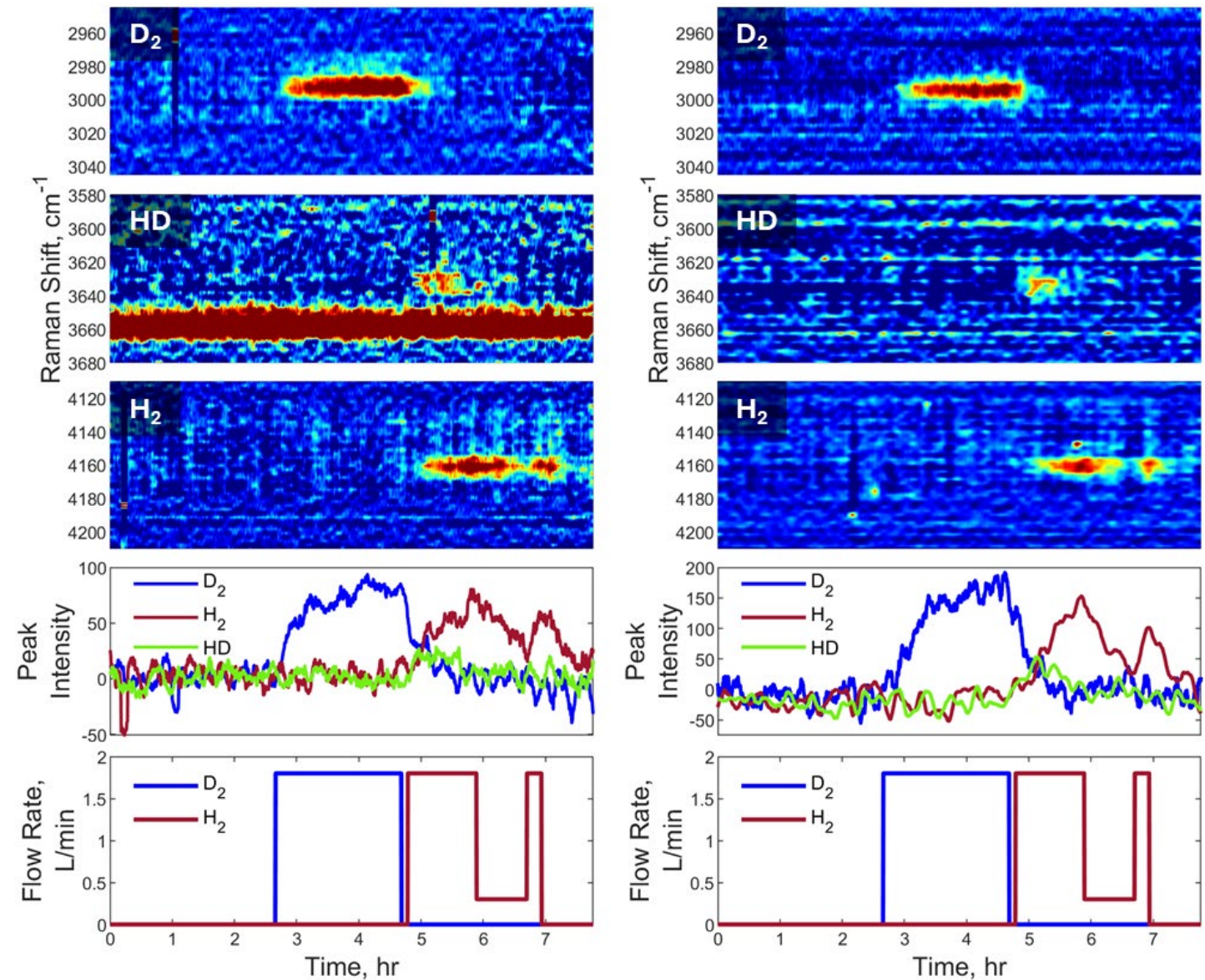
PNNL-ORNL Demo

- Tandem measurement of Raman, LIBS, and RGA
- Measuring gas phase above salt in storage tank
- Bubbled in H₂ and D₂ above salt in storage tank



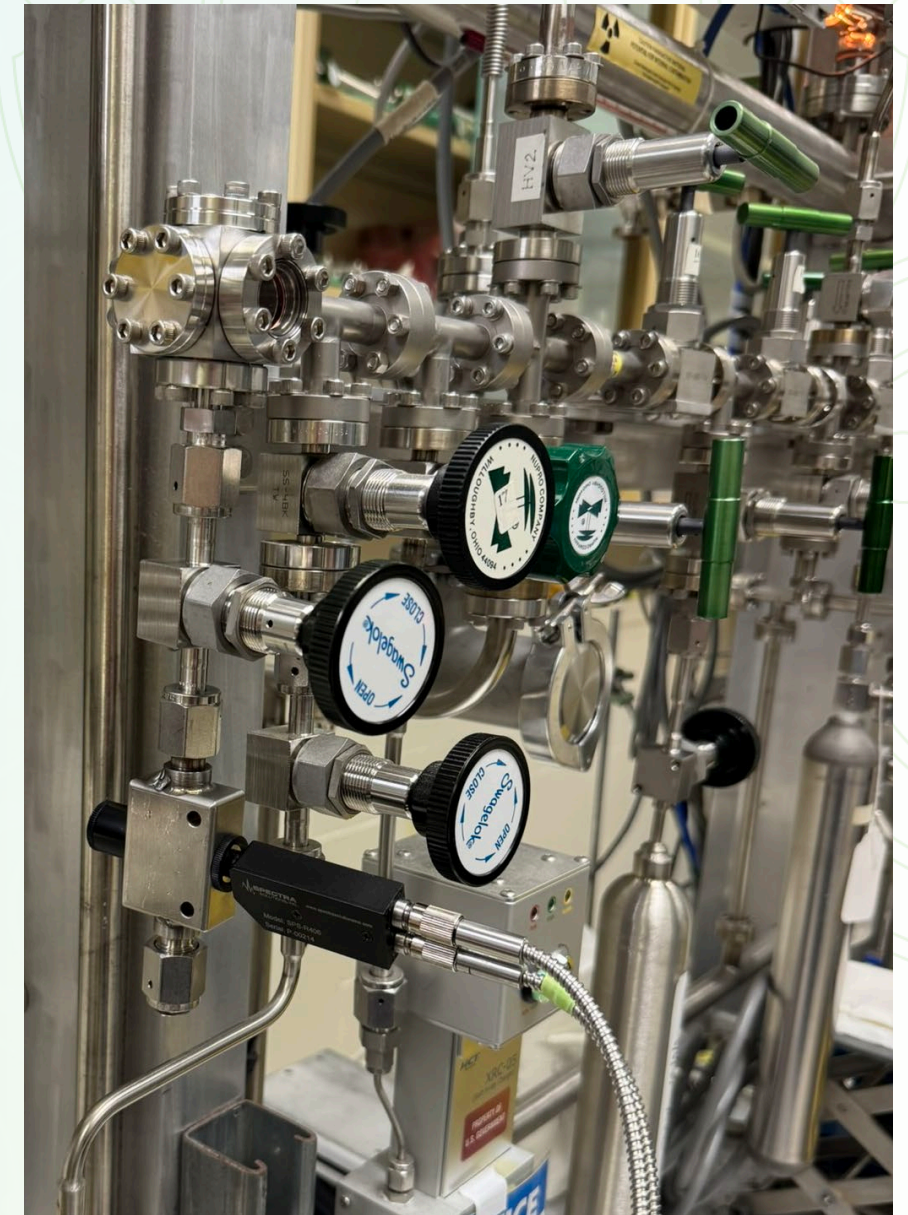
PNNL-ORNL Demo

- Two Raman sensors successfully measured D_2 and H_2 changes over time
- Detected possible formation of HD
- Currently collaborating with ORNL on a publication



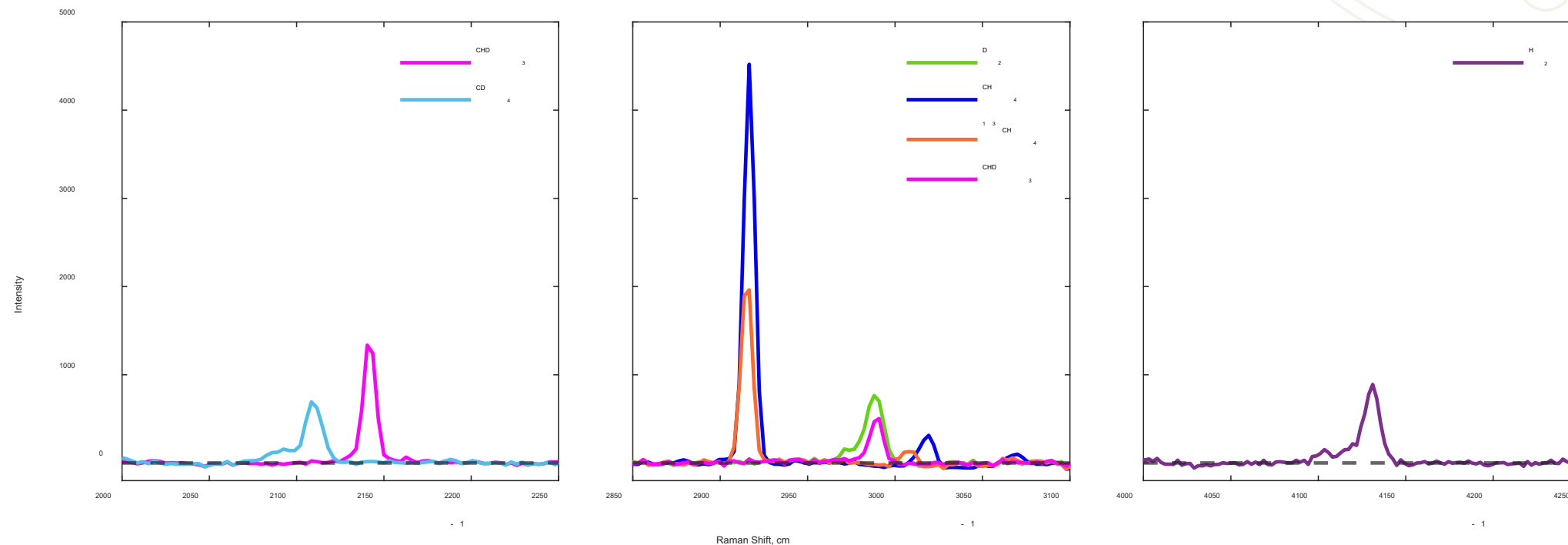
Gas Mixture Studies

- Tandem Raman-Mass Spectrometry studies
- Pure gases and mixtures
 - Methane and hydrogen isotopologues
 - Gas mixing studies
- Methane demonstration
 - CH_4 , CHD_3 , CH_2D_2 , CD_4
 - Challenging for mass spec
 - Distinct Raman fingerprints with minor band overlap
 - Goal to develop models that quantify gas species in mixtures



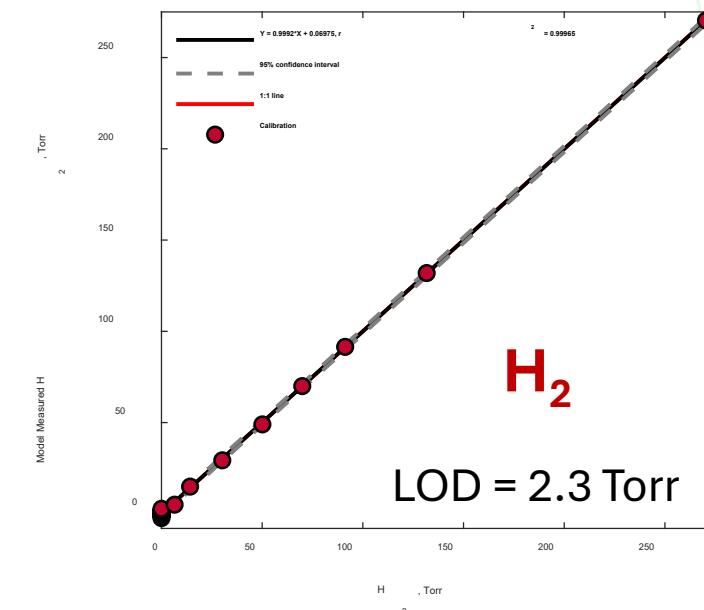
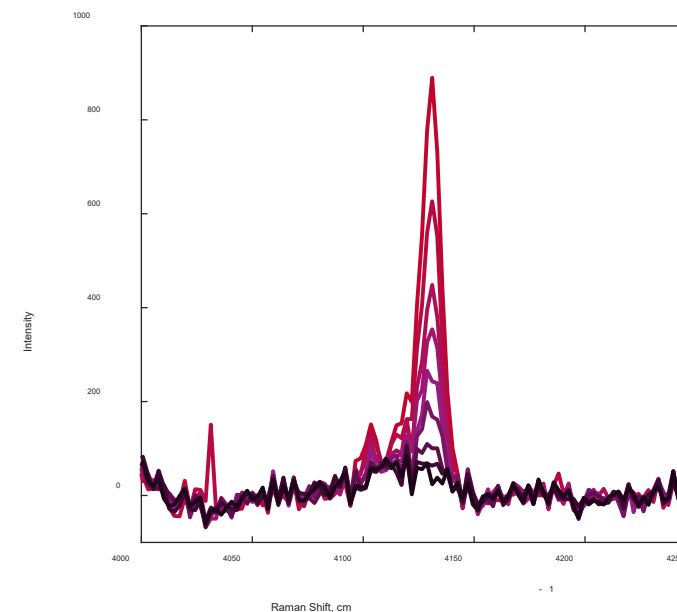
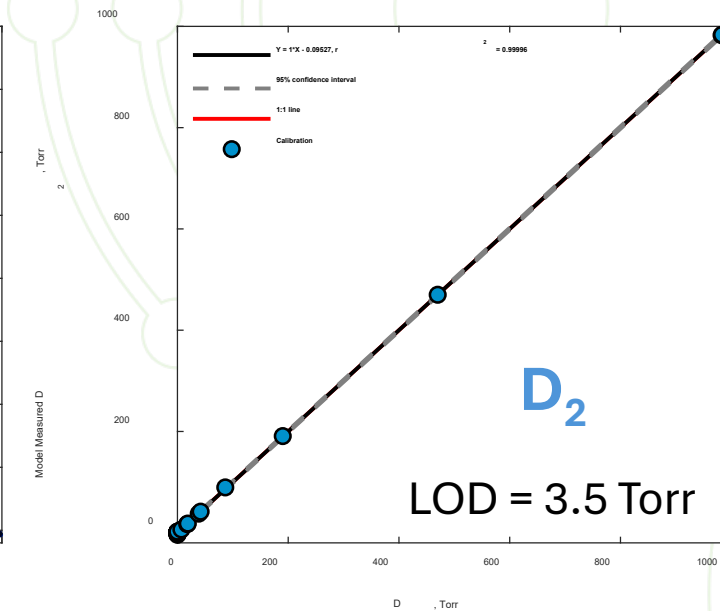
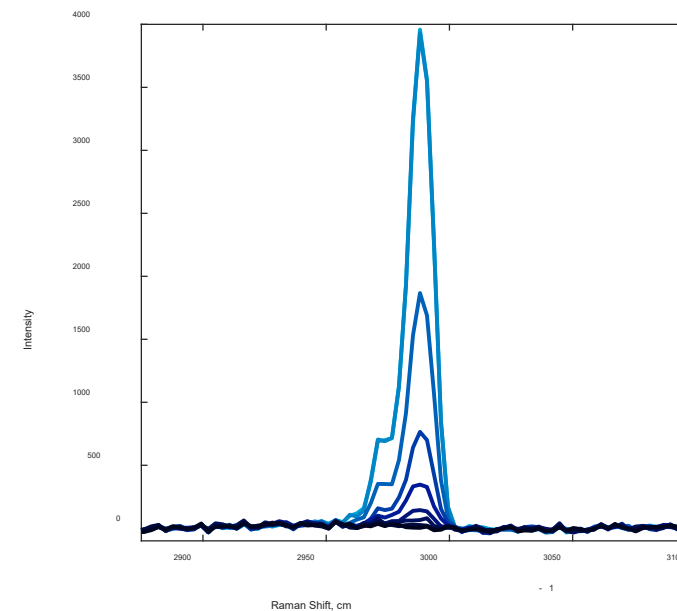
Initial pure component measurements

- Measured Raman and mass spec
 - CH_4 , $^{13}\text{CH}_4$, CHD_3 , CD_4 , H_2 , D_2



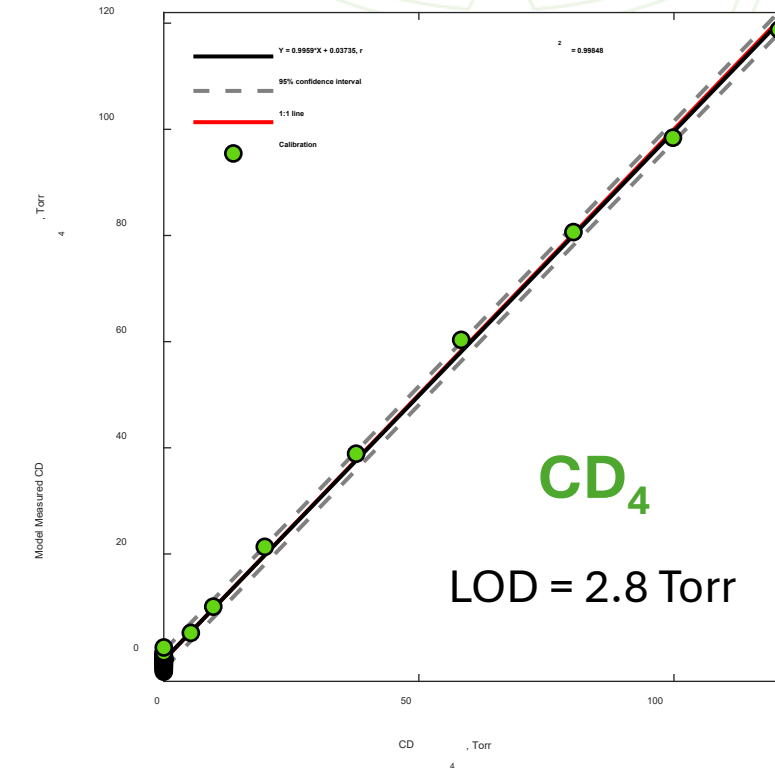
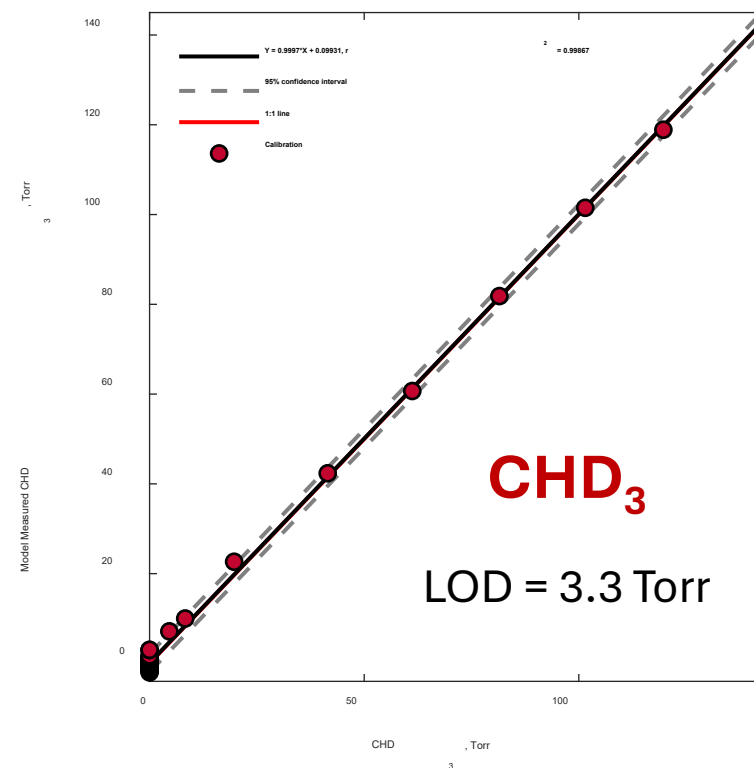
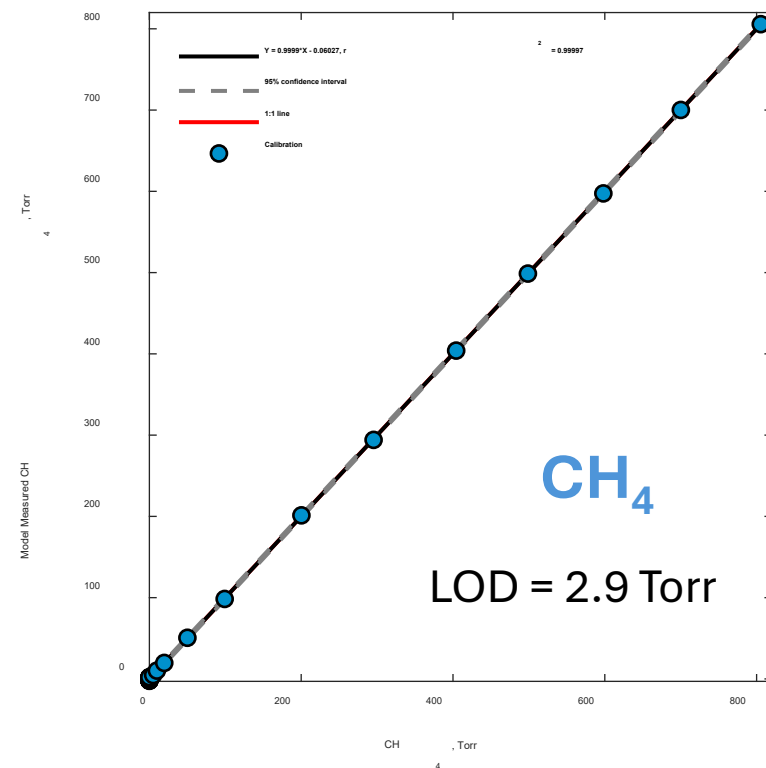
Initial pure component measurements

- Measured H₂ and D₂ on new instrument and gas cell
- Lower LODs compared to previous instrumentation and cell designs



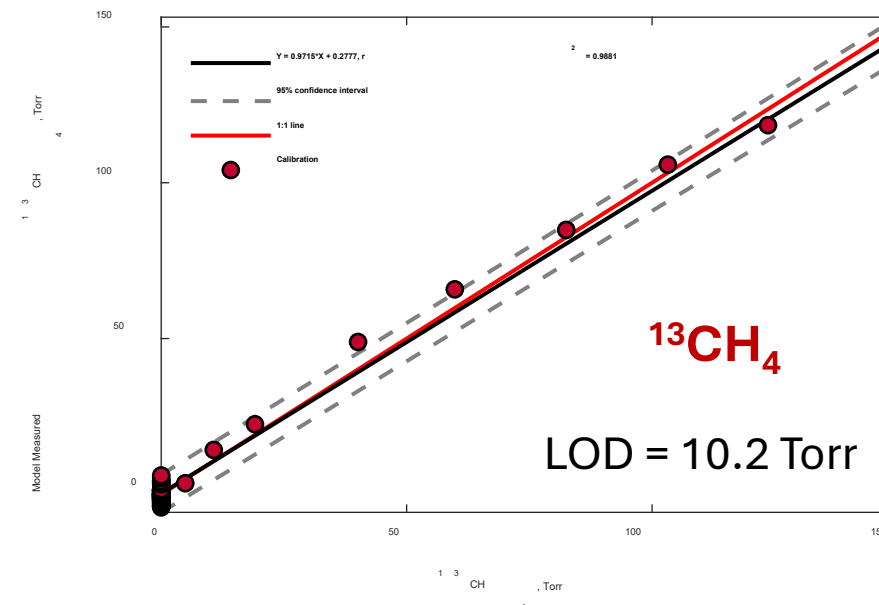
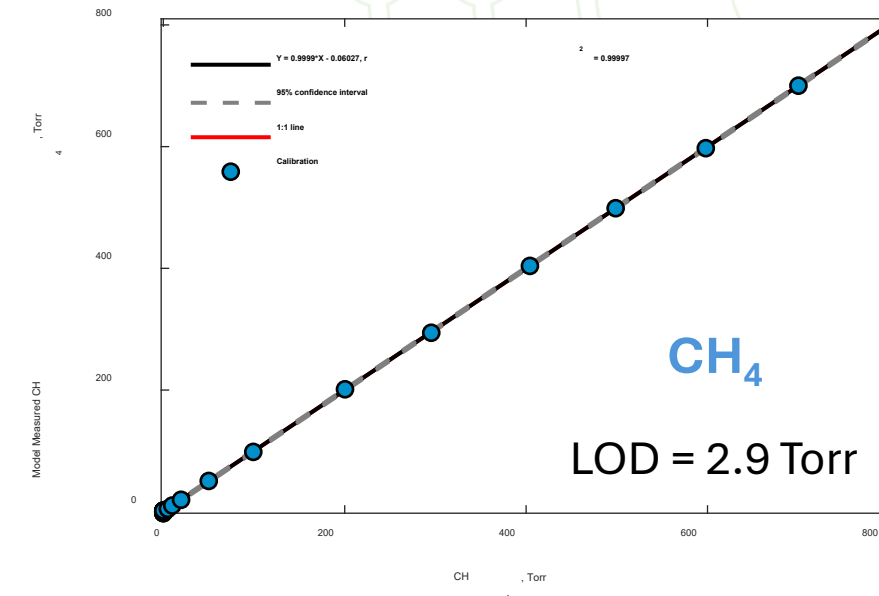
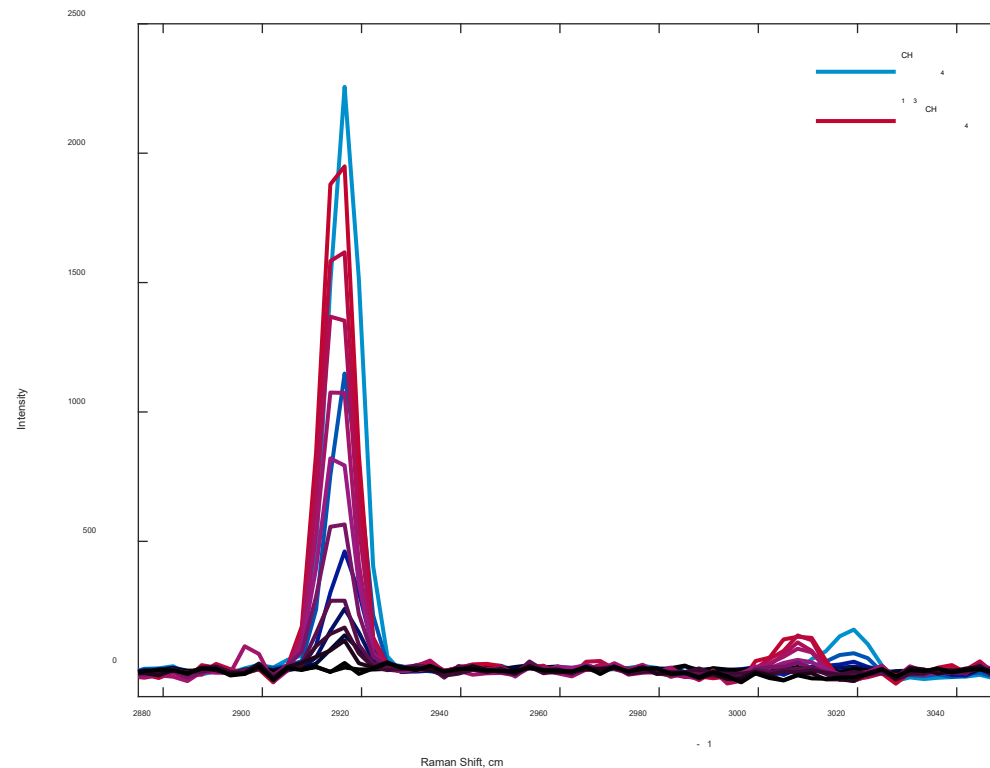
Initial pure component measurements

- Measured Raman and mass spec
 - CH_4 , $^{13}\text{CH}_4$, CHD_3 , CD_4
- Developing models for each methane species



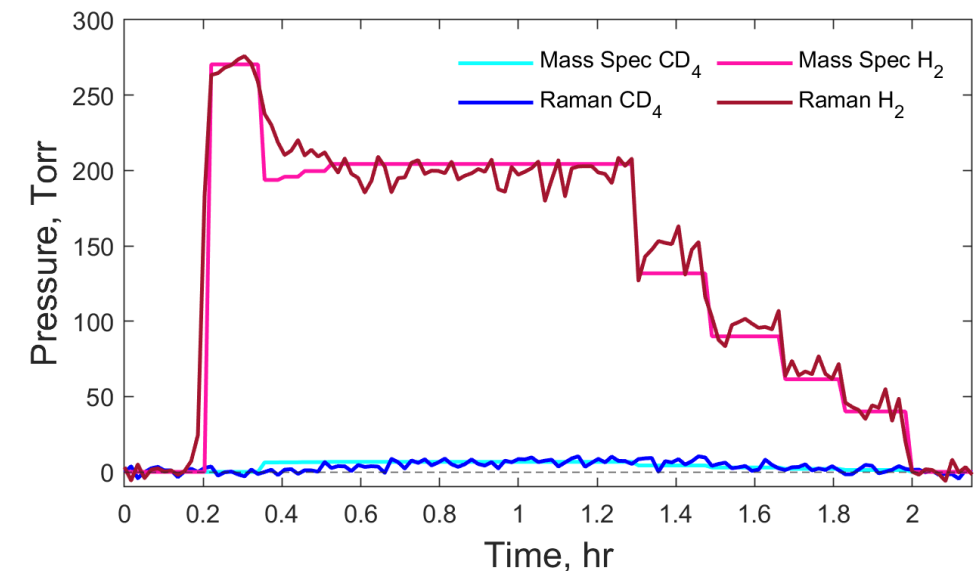
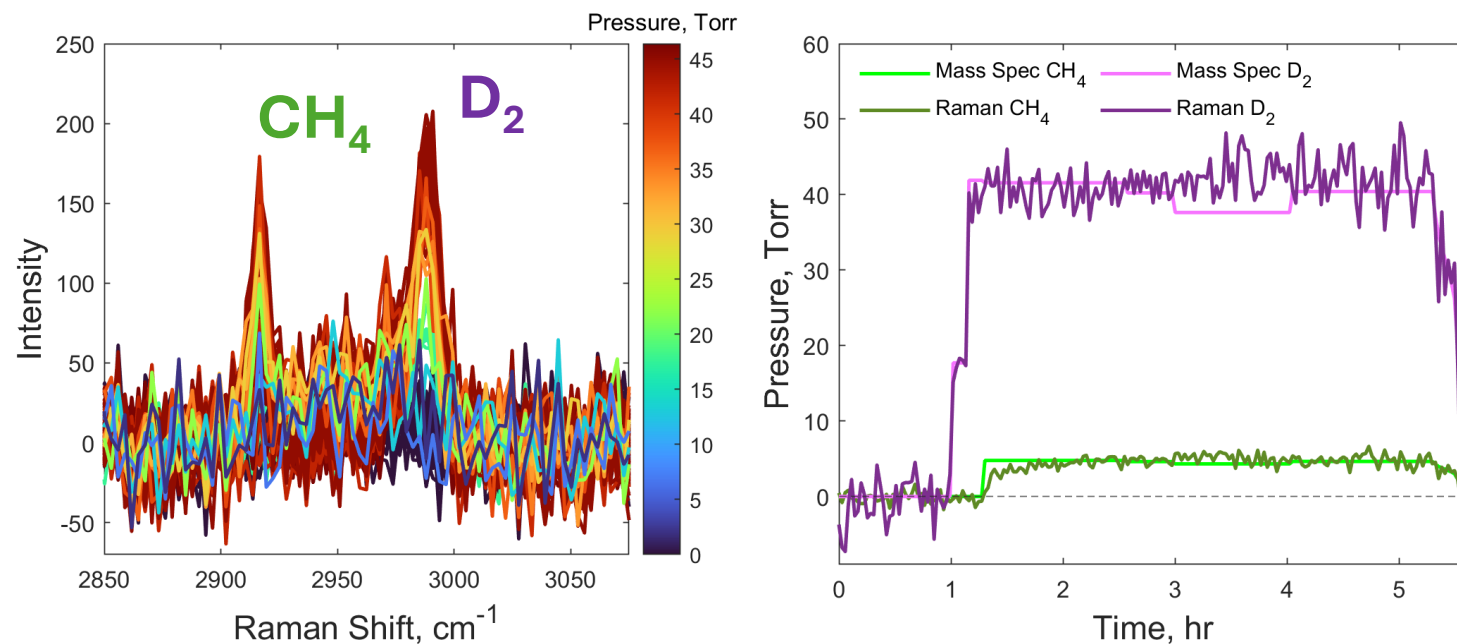
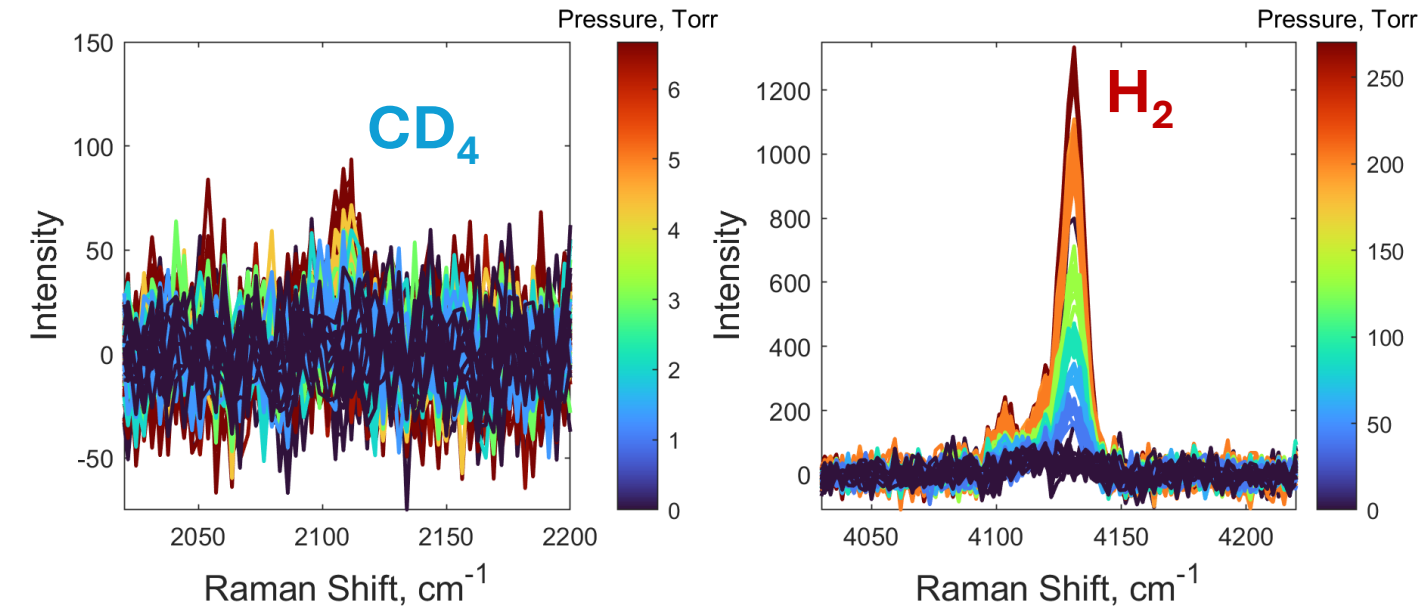
Initial pure component measurements

- Overlapping spectral fingerprints
 - Challenging for models but still able to distinguish between analytes



Mixing studies

- Able to track gas composition in mixtures at relatively low pressures
- Raman in good agreement with mass spec results
 - Mass spec estimated composition from grab samples



Conclusions and Next Steps

- Raman spectroscopy is an important tool that can aid in the identification and quantification of molecular species
 - Can easily distinguish between isotopologues of gas species which can be challenging for other techniques
- Next steps:
 - Finish collecting Raman and mass spec data for remaining pure component gases and additional mixtures
 - Pair Raman and mass spec results for further analysis
 - Draft journal manuscript

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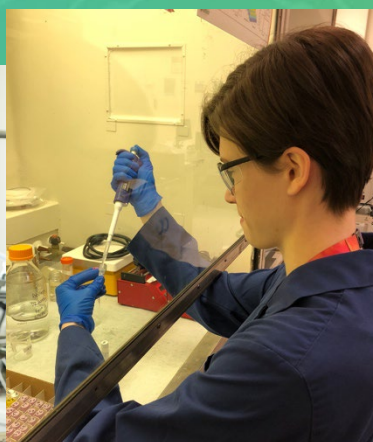
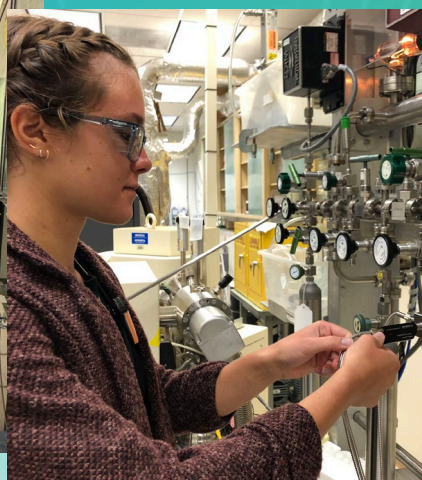
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Kevin Robb
Daniel Orea

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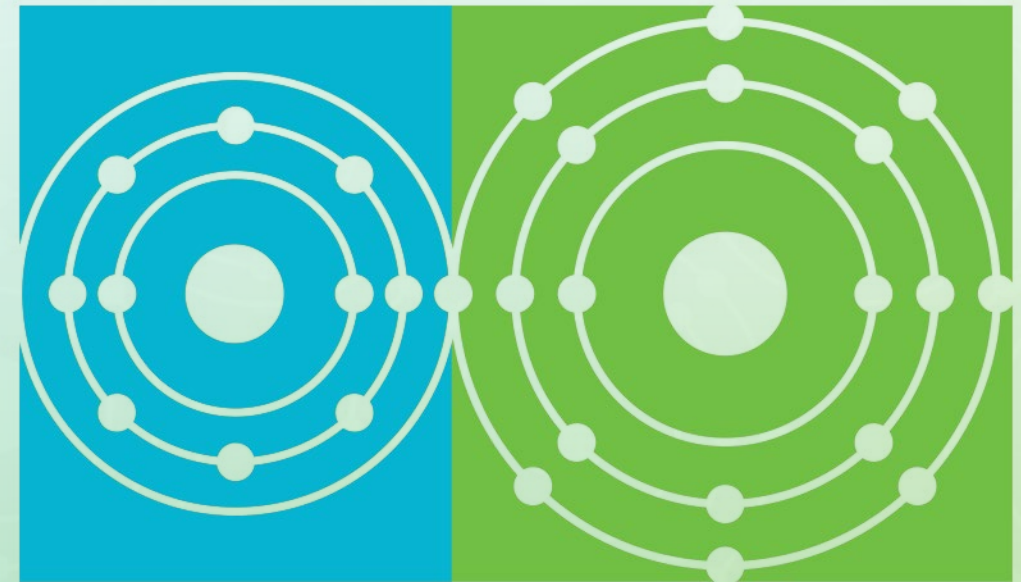
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Job Bello (Spectra Solutions Inc.) Andrew Clifford
Alyssa Espley Bethany Kersten
Nikolas Boily



Thank You

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Molten Salt Reactor

P R O G R A M