Sample Environment Development for Neutron Scattering

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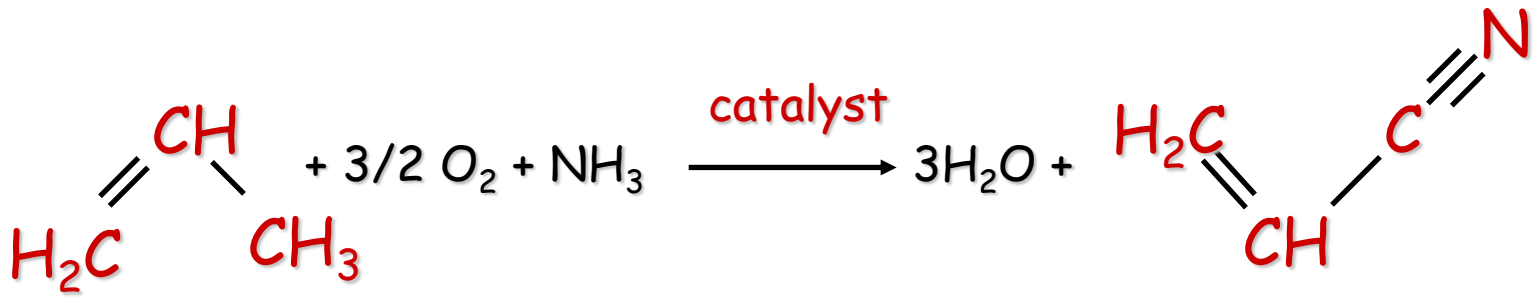
POWDER DIFFRACTION (GPPD and POWGEN)

- Catalysis: Gas Handling
- Hydrogen Storage
- SOFC: Gas Handling
- Battery: Electrochemistry
- Low Temperature Sample Changer

The SOHIO Process

Acrylonitrile is an important industrial chemical which is used extensively in the manufacture of synthetic (acrylic) fibers, resins, plastics, rubber for consumer goods and in fumigants.



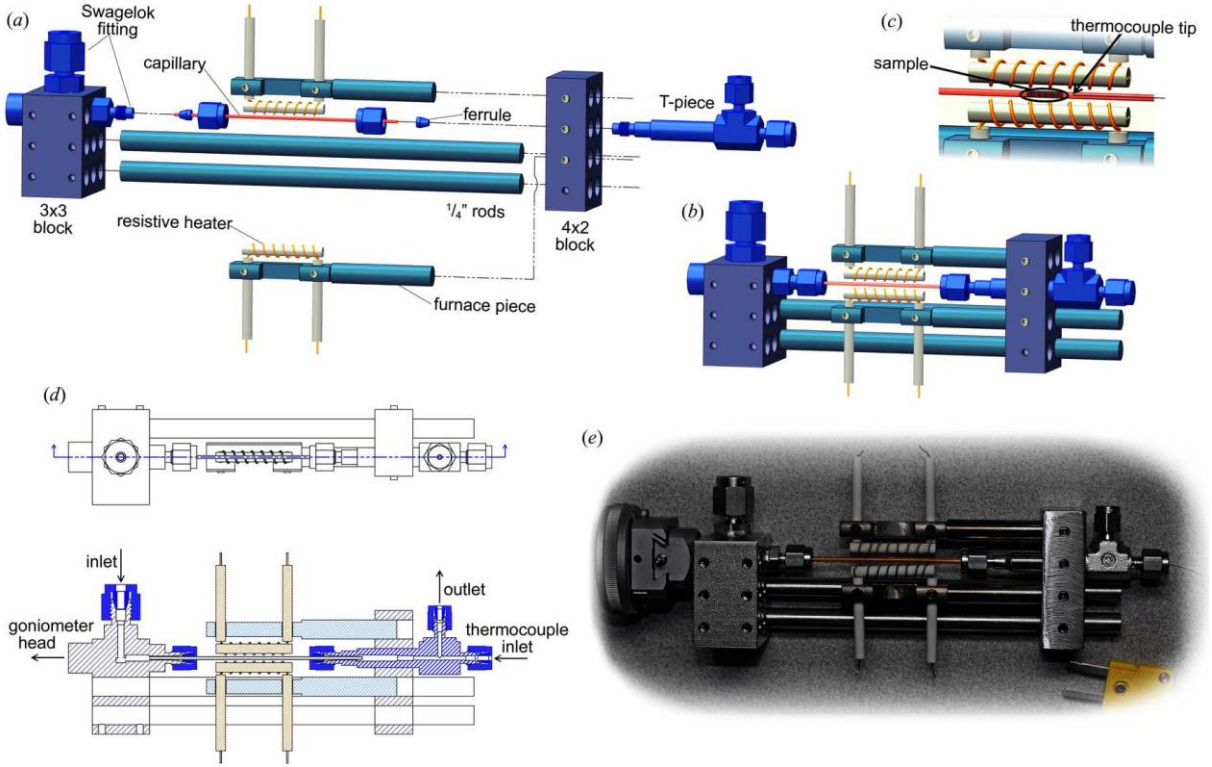
propylene

Acrylonitrile (ACN)

- Catalyst system: $M^{+2}/M^{+3}/Mo/Bi/O$
- Model catalyst phases: Bi_2MoO_6-$Fe_2Mo_3O_{12}$-$CoMoO_4$

My first SE development project (IPNS 2003-2005)

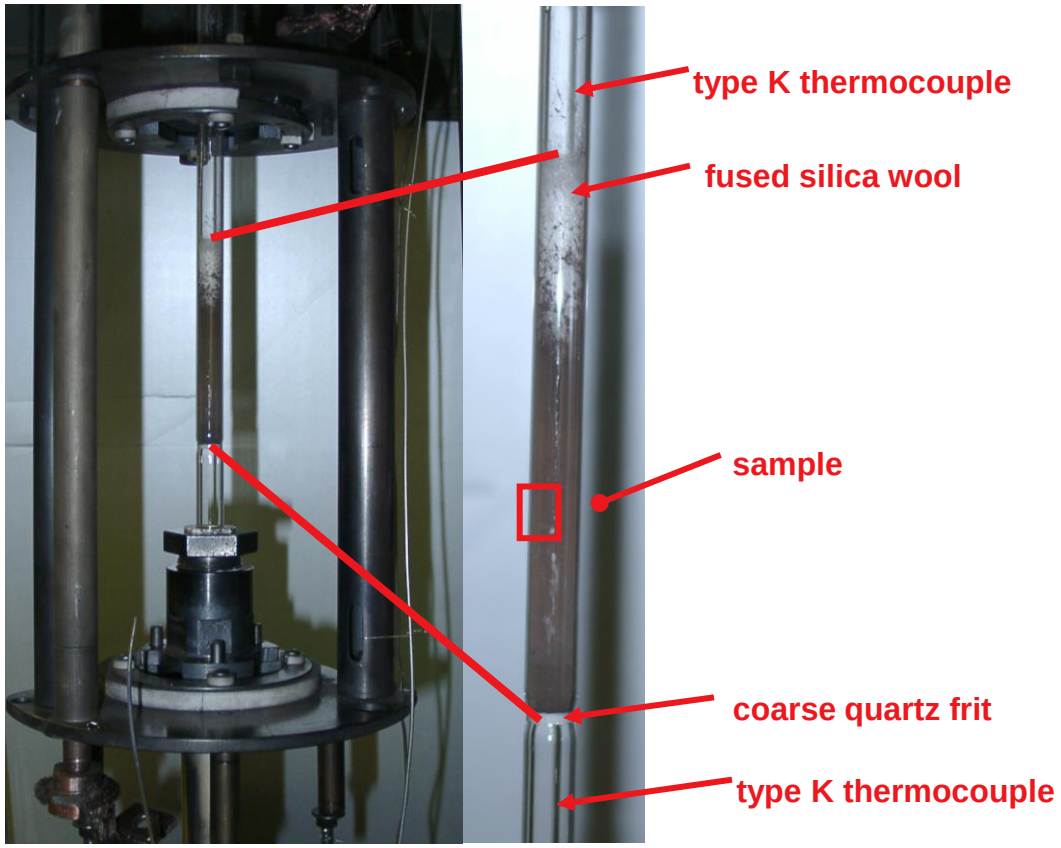
- Corrosive Ammonia Gas
- High Temperature (< 500C)
- Oxidizing
- Humid
- Sample reacts with Alumina



Inspiration from X-ray world

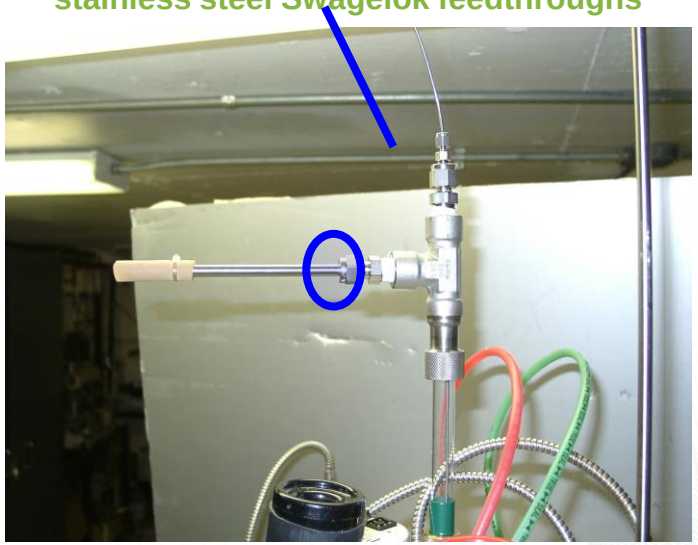
Adapt Existing Vacuum Furnace with Quartz insert

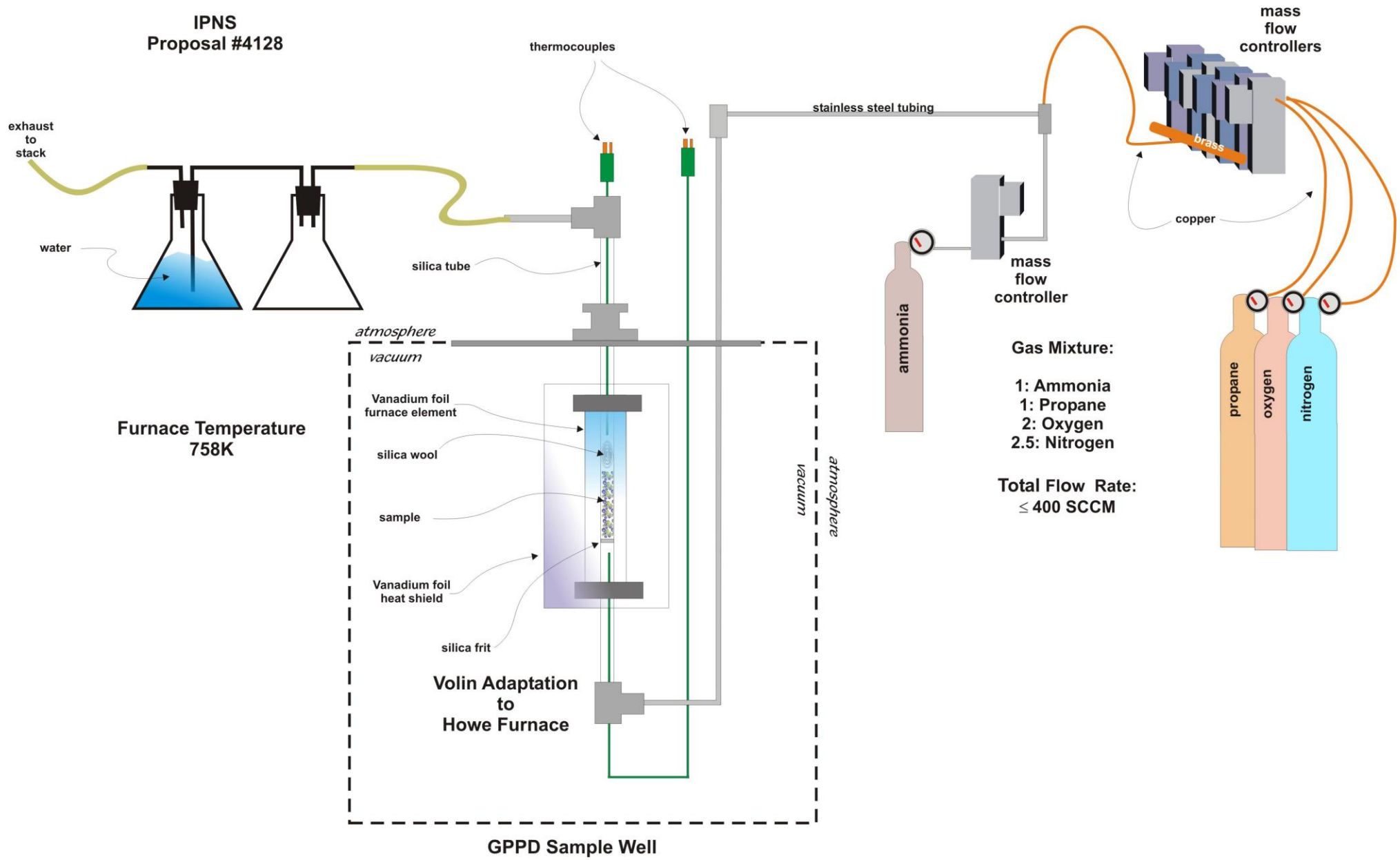
To accommodate a user requiring a flow of reactive gas through the sample, the Howe furnace was modified with a fused silica tube outfitted with a coarse quartz frit to hold the powder sample. The gas, along with sheathed thermometry, are attached to the fused silica tube with stainless Swagelok fittings.



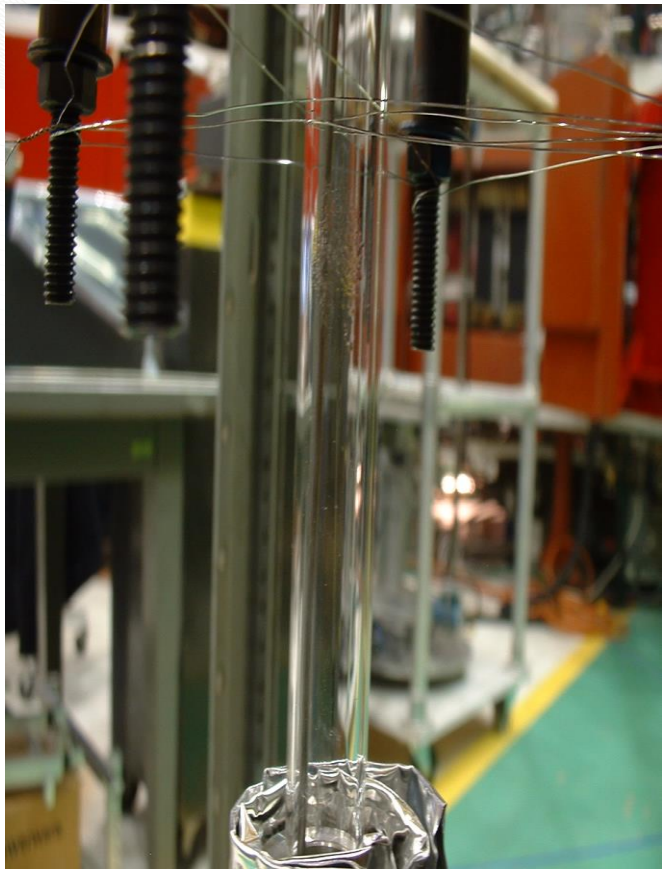
A professional scientific glassblower installed the quartz frit into the fused silica tubes while the rest of the modifications were done by IPNS staff.

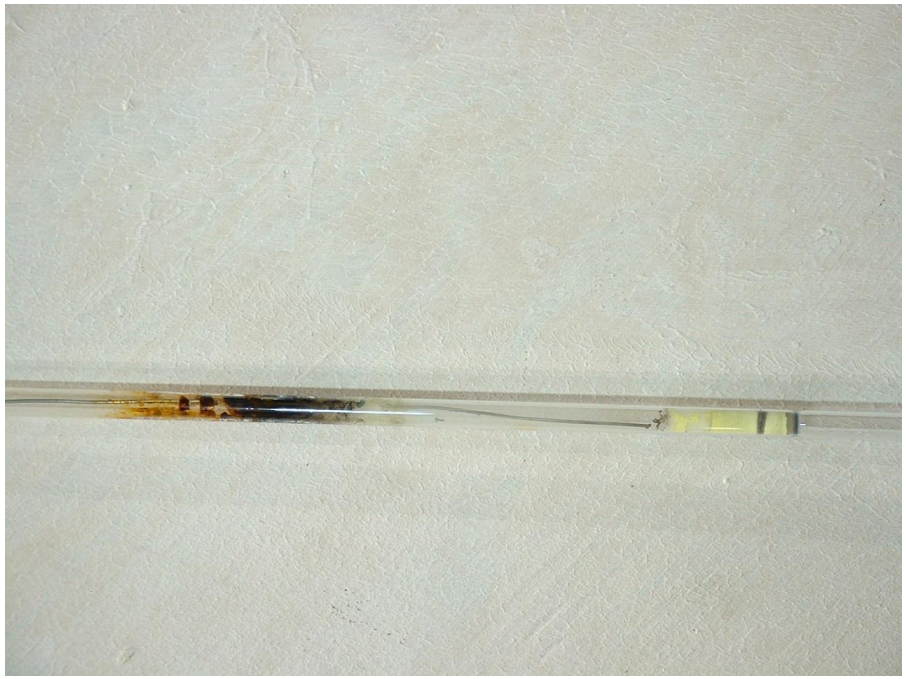
stainless steel Swagelok feedthroughs




IPNS
Proposal #4128
thermocouples
stainless steel tubing
mass
flow
controllers
brass
copper
exhaust
to
stack
water
silica tube
atmosphere
vacuum
Vanadium foil
furnace element
silica wool
sample
Vanadium foil
heat shield
silica frit
Furnace Temperature
758K
Volin Adaptation
to
Howe Furnace
vacuum
atmosphere
GPPD Sample Well
ammonia
mass
flow
controller
Gas Mixture:
1: Ammonia
1: Propane
2: Oxygen
2.5: Nitrogen
Total Flow Rate:
≤ 400 SCCM
propane
oxygen
nitrogen

Sample after *in situ* measurement



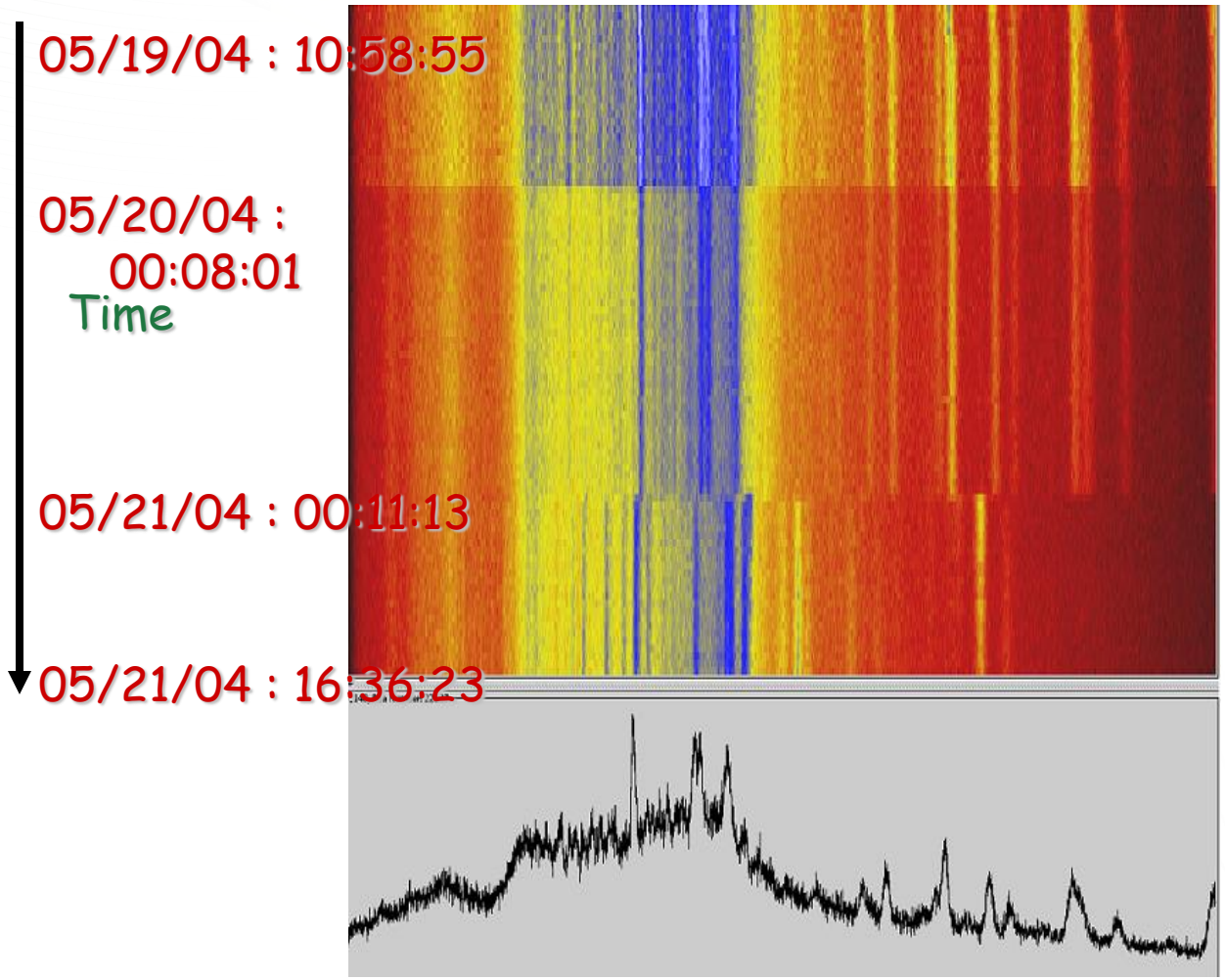


Picture of the quartz tube after experiment. Polymeric acrylonitrile products can be observed on the walls downstream of the catalyst charge.

GPPD data (Sample : $Fe_2Mo_3O_{12}$ 60 degree bank)

Flow rates (9.8:2.2:1:1)

$N_2:O_2:C_3H_6:NH_3$



GHSV=2100hr^{-1}

α $Fe_2Mo_3O_{12}$ — Fe(3+)

β $Fe_2Mo_3O_{12}$ — Mo(6+)

GHSV=2700 hr^{-1}

β $Fe_2Mo_3O_{12}$ + amorphous MoO_3, Fe_2O_3

GHSV=3300 hr^{-1}

β $Fe_2Mo_3O_{12}$ + amorphous MoO_3, Fe_2O_3

$Fe_2Mo_3O_8$, β $FeMoO_4$, MoO_2, Fe_3O_4 — Fe(2+), Mo(6+), Mo(4+)

T=445°C

Safety

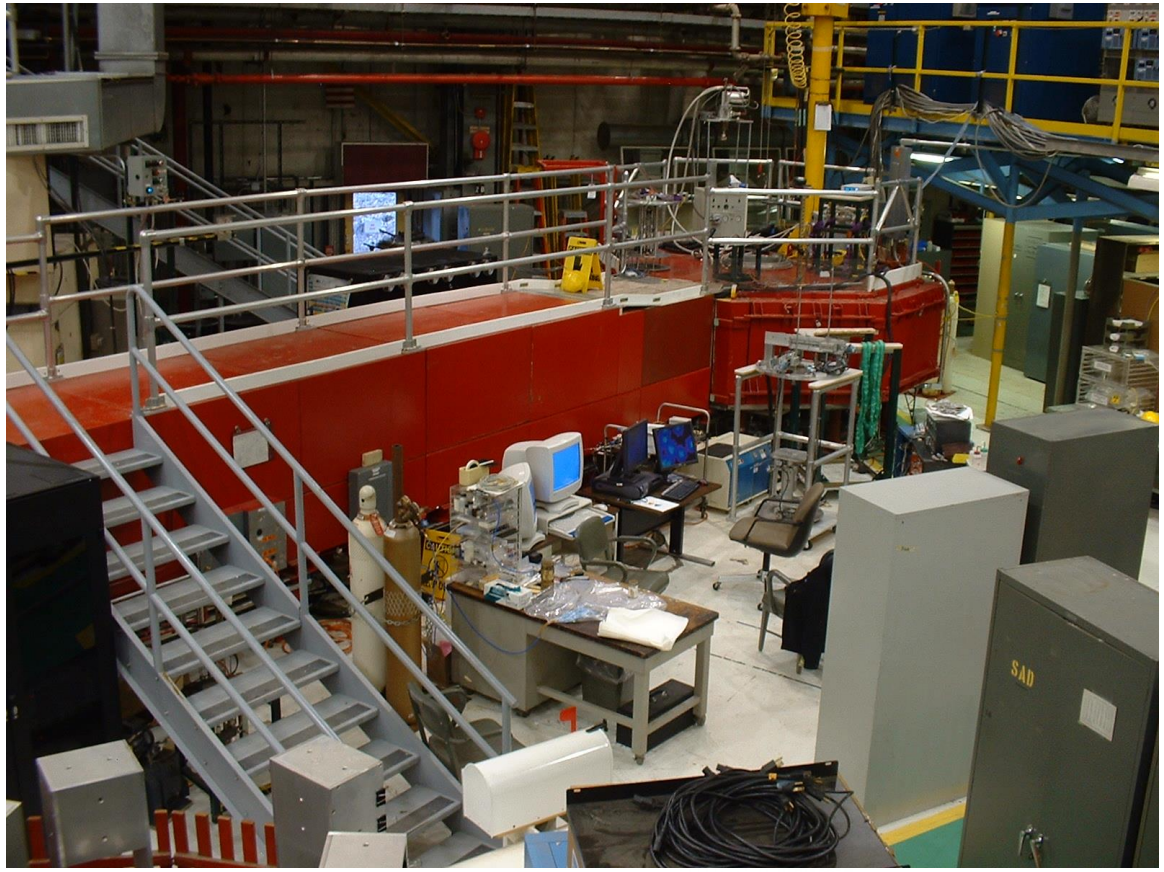
The following action steps or conditions will be satisfied before this experiment is performed:

1.The portion of the experiment using the propane/ammonia/oxygen/nitrogen gas mixture will be performed during the day shift (approximately 7 a.m. to 7 p.m.). There are no restrictions on other portions of the experiment.

2.Instrument personnel (who will be identified) will provide constant monitoring at the instrument during the portion of the experiment using the propane/ammonia/oxygen/ nitrogen gas mixture.

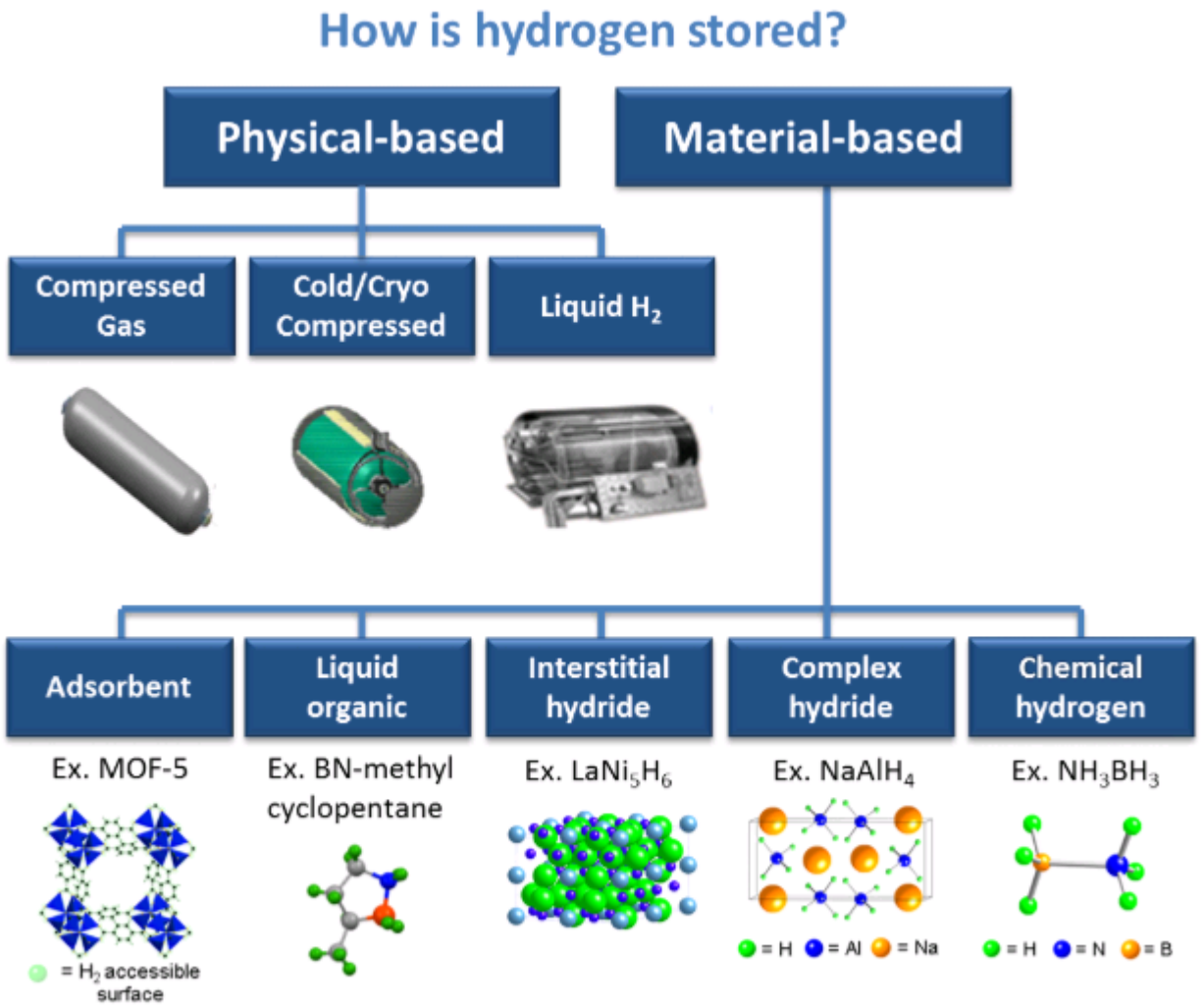
3.E. Maxey will prepare a procedure detailing emergency response steps.

4.E. Maxey will train the people who will be monitoring the experiment on the emergency procedures and document this training.



From this area personnel will watch gas flows and furnace temperatures and look listen and smell for any signs that the experiment is not going as planned.

Hydrogen Storage



Science Motivation

- Physisorption:
  - MOFs: ~7wt% generally at 77K and 70-80 bar
  - Carbon Materials: ~8wt% at 83K and 120bar(SWNT)
  - Zeolites: ~ 2wt% at 83K 0-15bar
  - Prussian Blue: ~1.6wt% at 77K
- Metal Hydrides: (interstitial hydrides)
  - $PdH_{0.6}$, $REH_{2\ or\ 3}$ or MgH_2 etc
  - $LaNi_5H_{6.5}$ or Mg_2NiH_4 : max ~4wt% 1 bar 300C
- Complex Hydrides
  - Imide/Amides:
  - Alanates & Boro hydride: ~8-13wt% at 150C-580C and 60-150bar
  - Ammonia Borane: 7wt% ~100C (irreversible)

Design Criteria:

- ~100bar of H_2/D_2 pressure
- Up to 500C

- Neutron friendly (limit diffraction peaks from container)
- User friendly (robust and easy to use)
- Separate Heating and Pressure

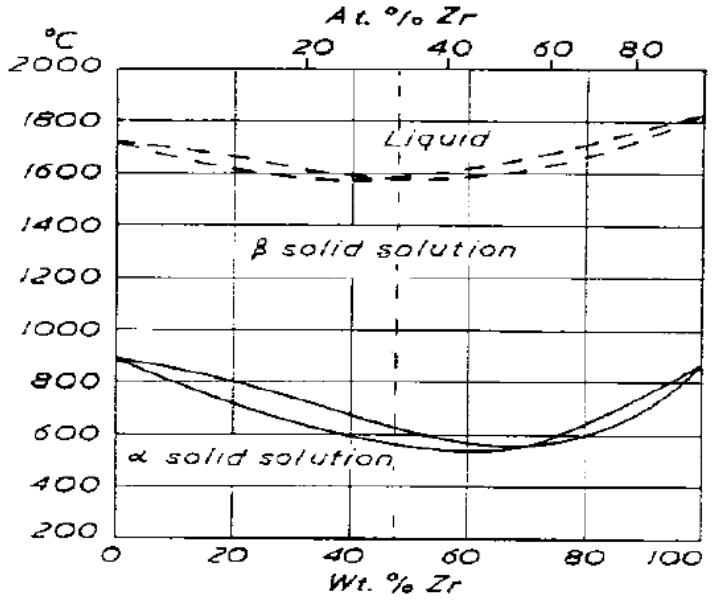


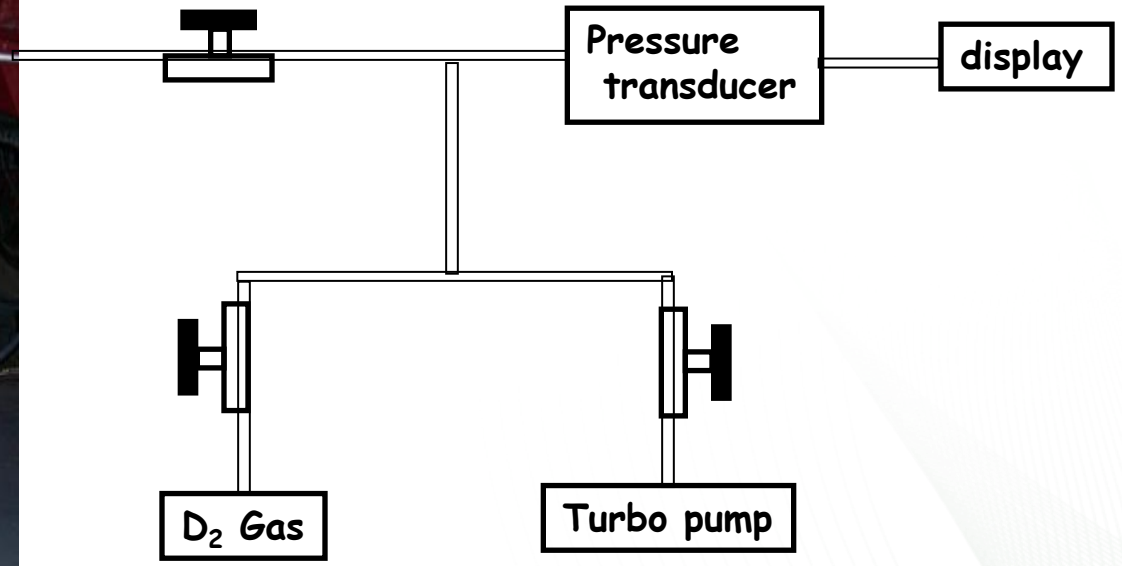
FIGURE 1 Phase diagram of Ti–Zr alloy.

Material Choice:

- Null Matrix (Ti(66%)-Zr(34%): 200C and 10bar reacts with H_2. In a few hours alloy is reduced to powder. (Same with V)
- Above 200C even 316 stainless is undesirable due to hydrogen diffusion to produce measurable leak.
- All consideration => Best choice Inconel 718. Good resistance to H2 embrittlement in the desired pressure and temperature range.

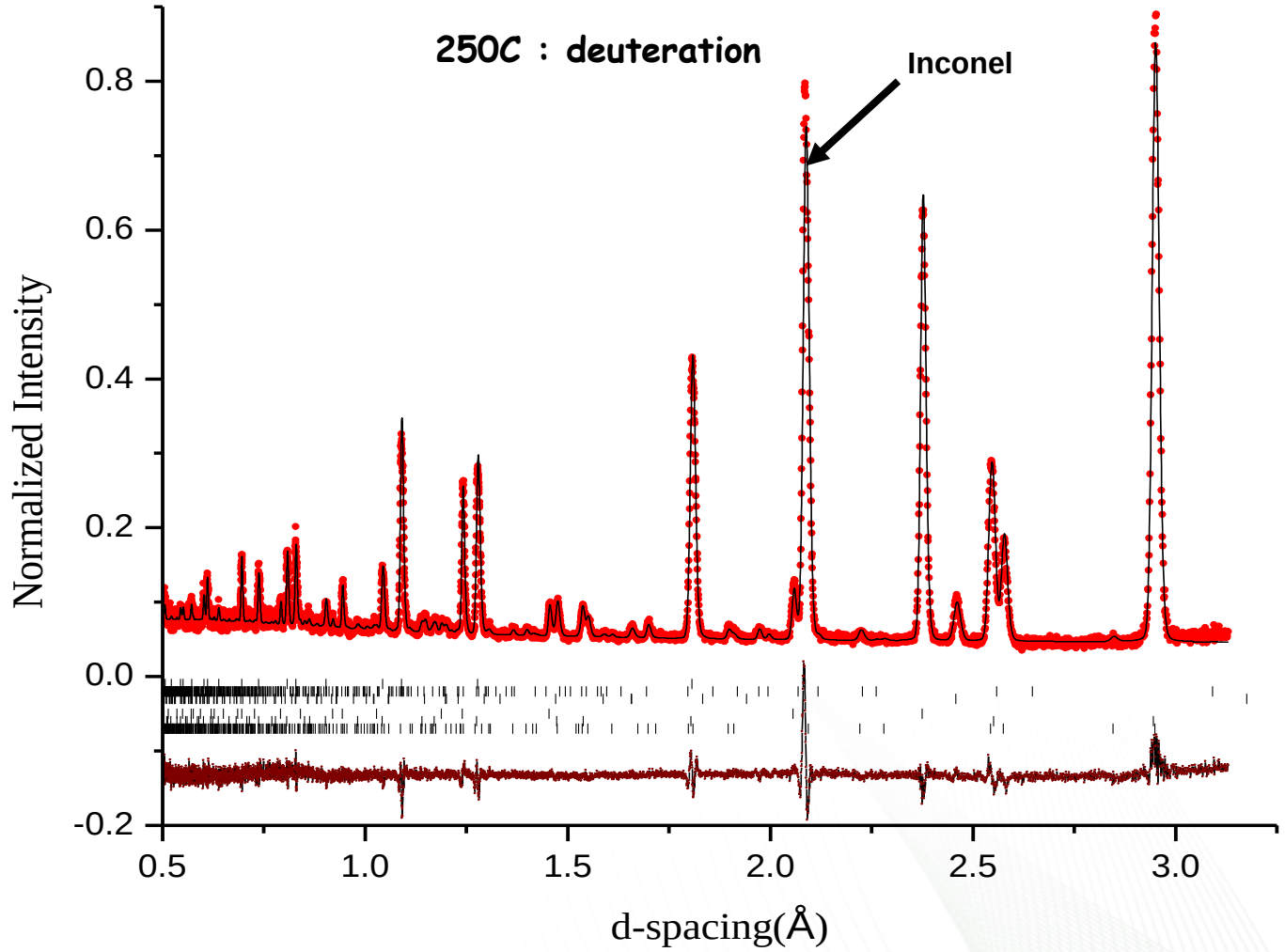
Bailey et. al. , High Pressure Research, 24, 309 (2004)

Experimental Setup for in-situ measurements (2004-2007)



Inconel cell: 100 bar and 500C

Synthesize sample with Li^7: significant improvement in signal from sample. Allows us to refine Li and D occupancies.

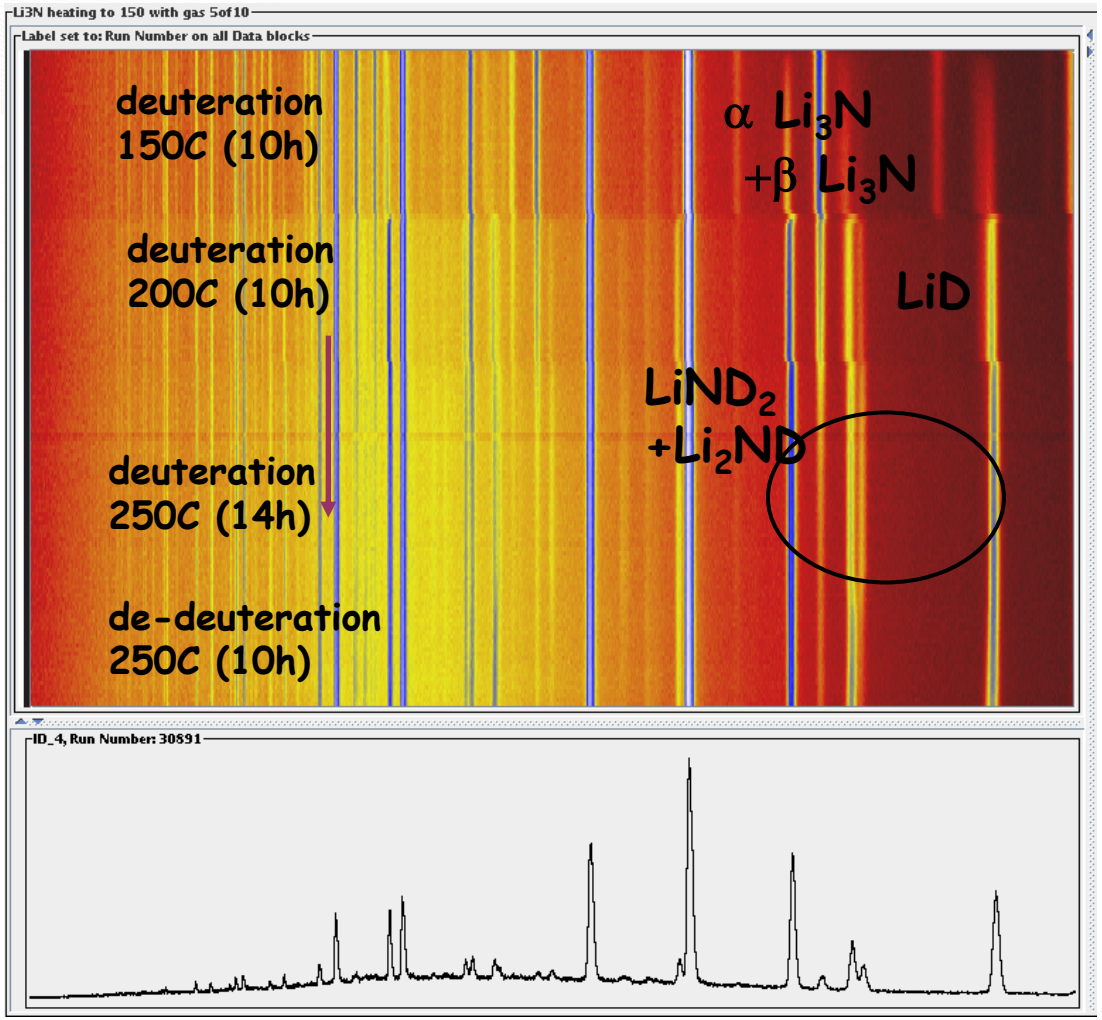


15 minute scan of ~4g of starting Li_3N (GPPD, IPNS).

In situ Deuteration & De-deuteration: Frenkel defect pair model

Time
(2 days)

34h: deuteration
10h: pumping



d spacing

- Dehydrogenation: Movement of Li cation to adjacent, vacant tetrahedral or octahedral site.

I. $LiNH_2+LiNH_2 \longleftrightarrow [LiLiNH_2]^+ + [\square NH_2]^-$

II. $[LiLiNH_2]^+ \longrightarrow LiNH_2+Li^+$

III. $[LiLiNH_2]^+ \longrightarrow Li_2NH+H^+$

IV. $[\square NH_2]^-+H^+ \longrightarrow NH_3$

- Li^+ mobility driven hydrogenation

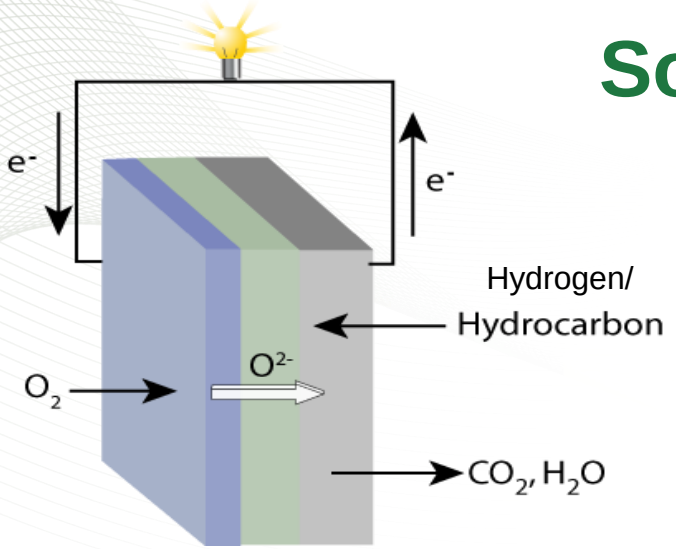
I. $Li_2NH \longrightarrow [\square LiNH]^-+Li^+$

II. $Li^+ + H_2 \longrightarrow LiH + H^+$

III. $H^+ + [\square LiNH]^- \longrightarrow [\square LiNH_2]$

David et. al., JACS 129,1594,2006

Solid Oxide Fuel Cell (SOFC)



Electrolyte/electrodes: Solid ceramic inorganic oxide

Fuel: Mixture of H_2 and CO (synthesis gas).

Operation temp: 800-1000 °C

- **Cathode: Oxygen from air is reduced.**

$$O_2 + 4e^- \rightarrow 2O^{2-}$$

- **Anode: Oxidation of fuel. Current cells have a reformer to generate CO/H_2 fuels from hydrocarbons.**

$$H_2 + O^{2-} \rightarrow H_2O + 2e^-$$

$$CO + O^{2-} \rightarrow CO_2 + 2e^-$$

Ideally we can utilize hydrocarbons directly.

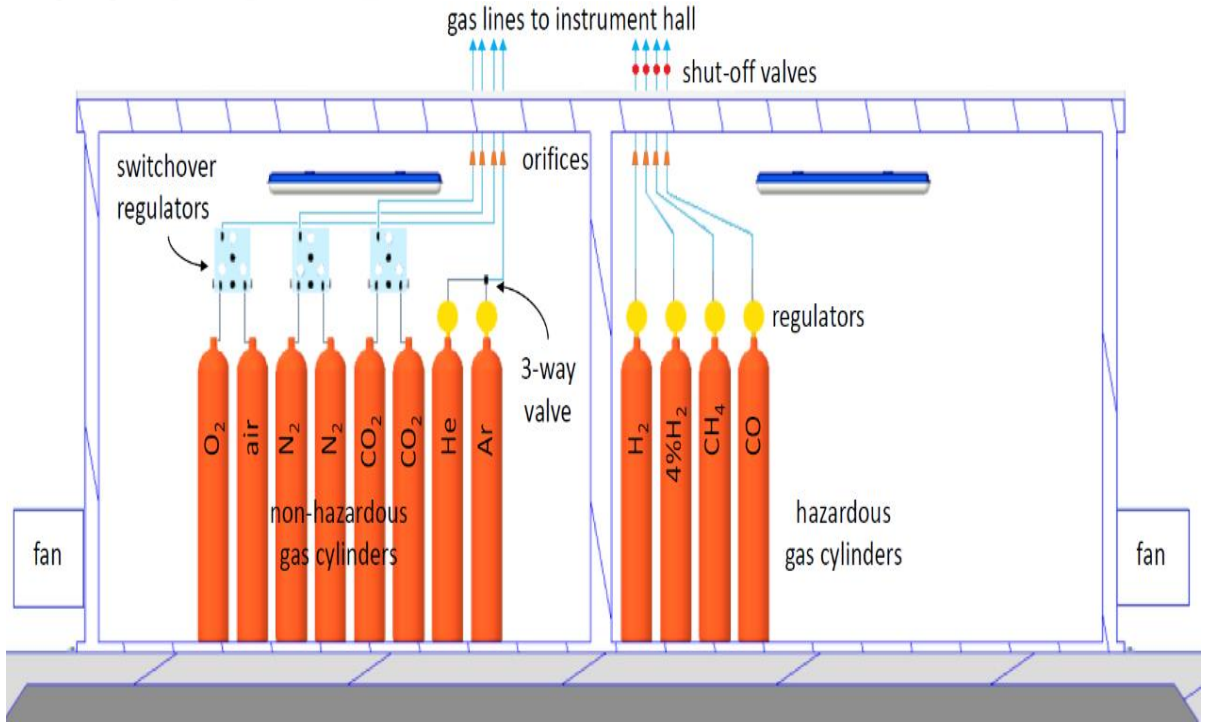
$$CH_4 + 4O^{2-} \rightarrow CO_2 + 2H_2O + 8e^-$$

Main Specifications for Materials Palette

	Anode	Electrolyte	Cathode	Interconnect
Material requirements	Chemical stability under reducing atm. (pO_2 ~ 10^{-18} Atm)	Chemical stability under high pO_2 gradient (10^{-18} to 1 Atm)	Chemical stability under oxidizing atm. (pO_2 ~ 1 Atm)	Chemical stability and corrosion resistance.
Density	Porous (20-40%). Preferably with gradient.	Dense (>95%)	Porous (20-40%). Preferably with gradient.	Dense (>95%)
Ionic conductivity	Delocalize the electrochemical reaction.	Highest (YSZ: 10^{-1} S/cm at 1000°C 10^{-2} S/cm at 750 °C)	Delocalize the electrochemical reaction.	
Electronic conductivity	Highest (Ni-Cermet 10^3 S/cm at 800-900°C).	Negligible compared to ionic conductivity.	Highest (LSM ~ 10^2 S/cm at 800-900°C).	Highest (including protective coating and oxide layer).

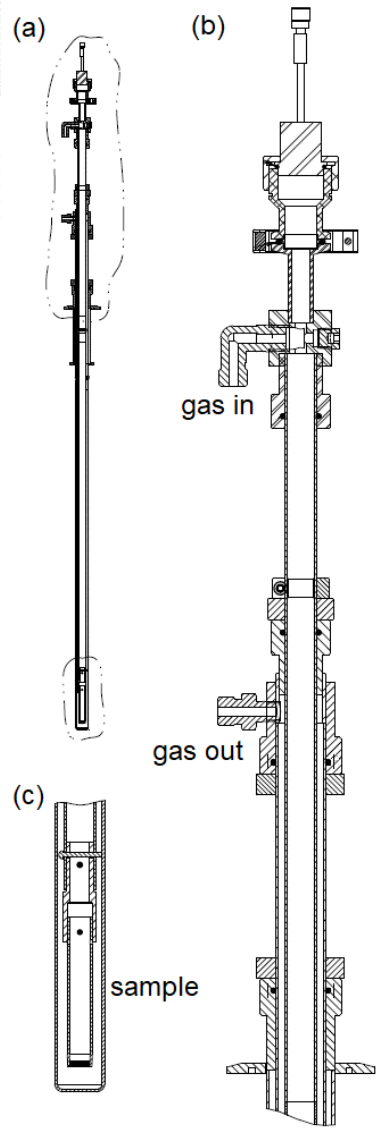
Sometimes regulations and safety dictates design

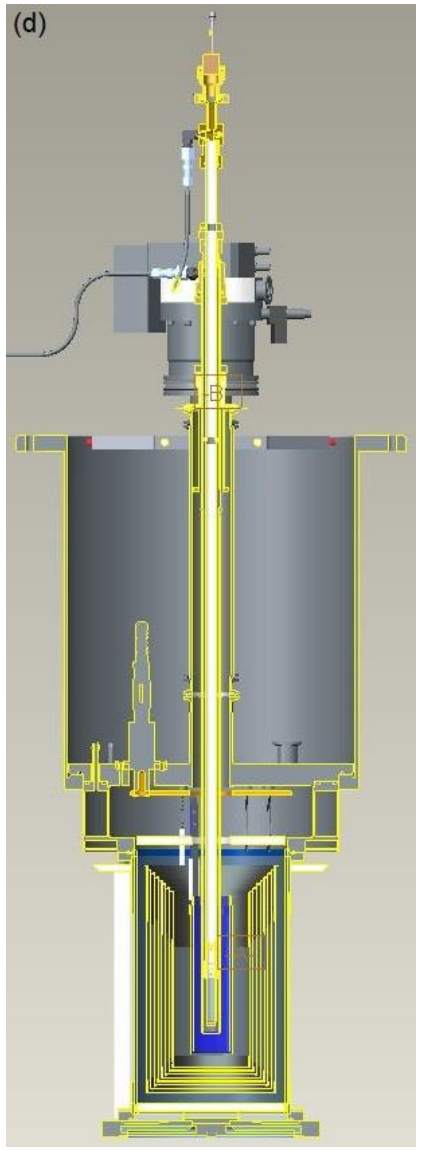
SNS target has 14 Tons of Hg which restricts amount of Hydrogen in the Target Building. Gas tanks have to be stored outside.



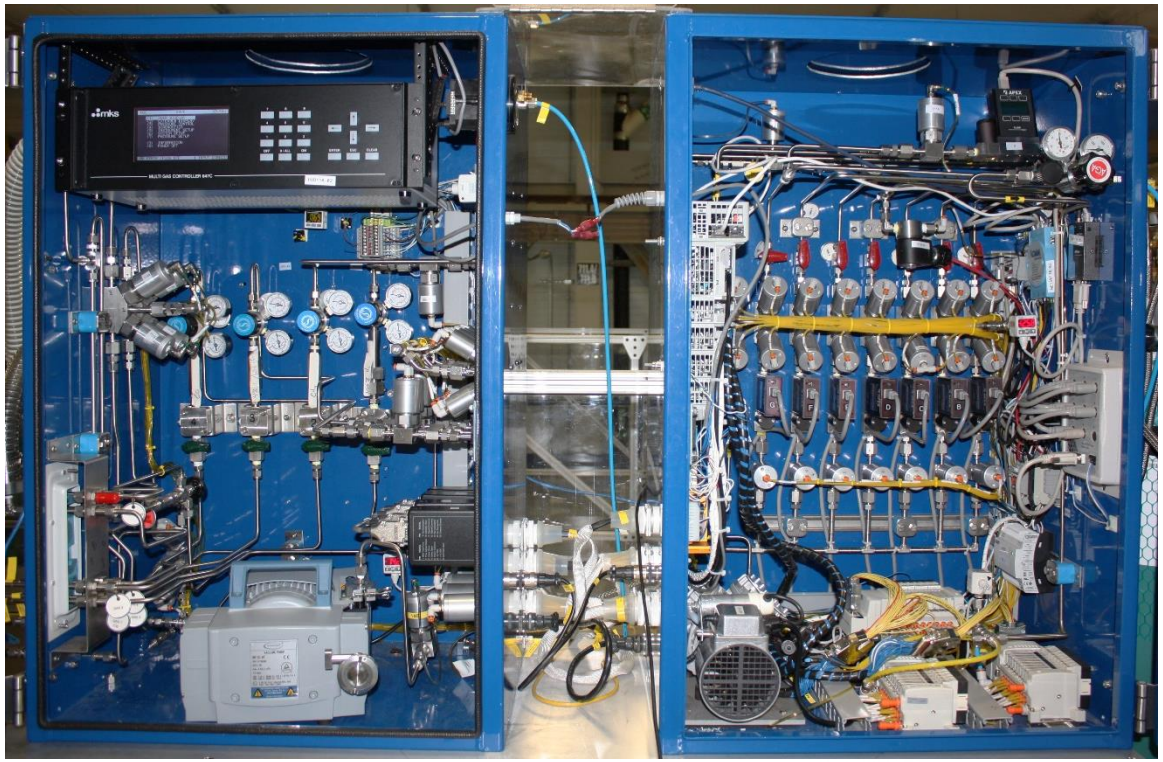
Gas Type	Category	Max Flow Rate (sccm)
Hydrogen H_2/D_2	hazardous	500
Methane CH_4	hazardous	500
Carbon Monoxide CO	hazardous	100
Nitrogen N_2	inert	500
Carbon Dioxide CO_2	inert	100
Helium He	inert	100
Argon Ar	inert	100
Mix 4% H_2 in He	inert[a]	500
Oxygen O_2	oxidizer	500
Air‡ 21% O_2 in N_2	oxidizer	500
[a]This mix of 4% H_2 is below the LEL.		

Similar Gas Inserts for furnace as before

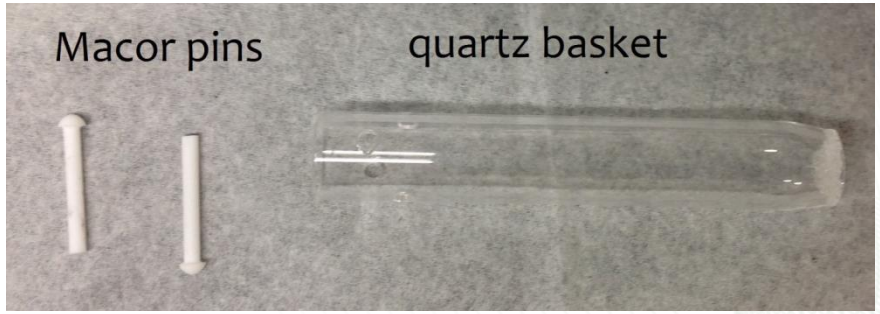




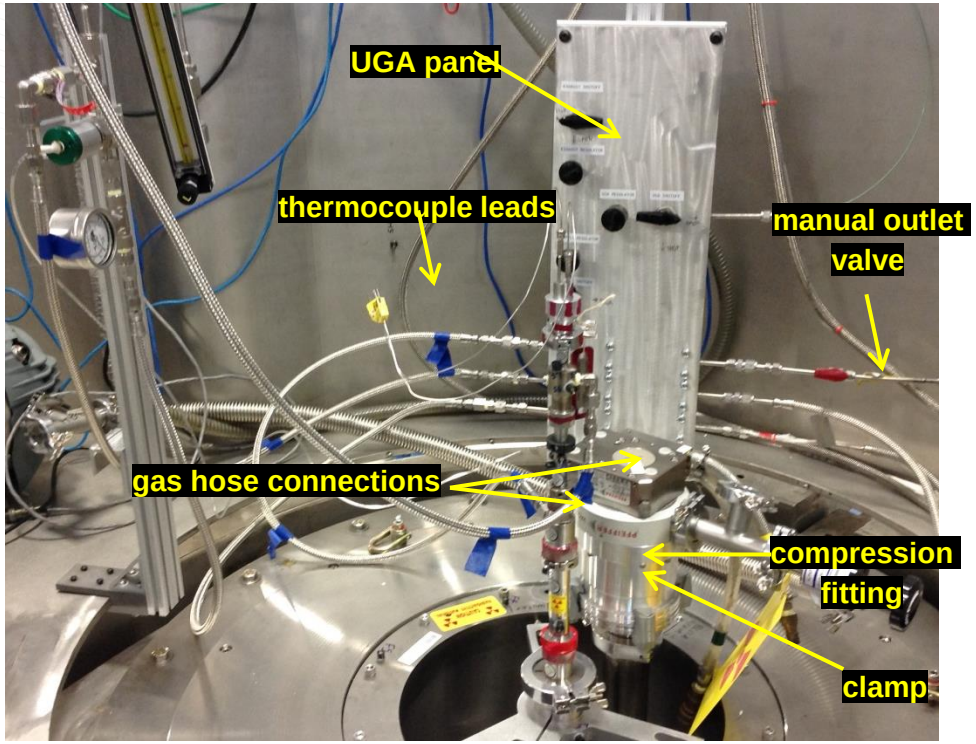
Quartz Inserts for ILL Type Furnace

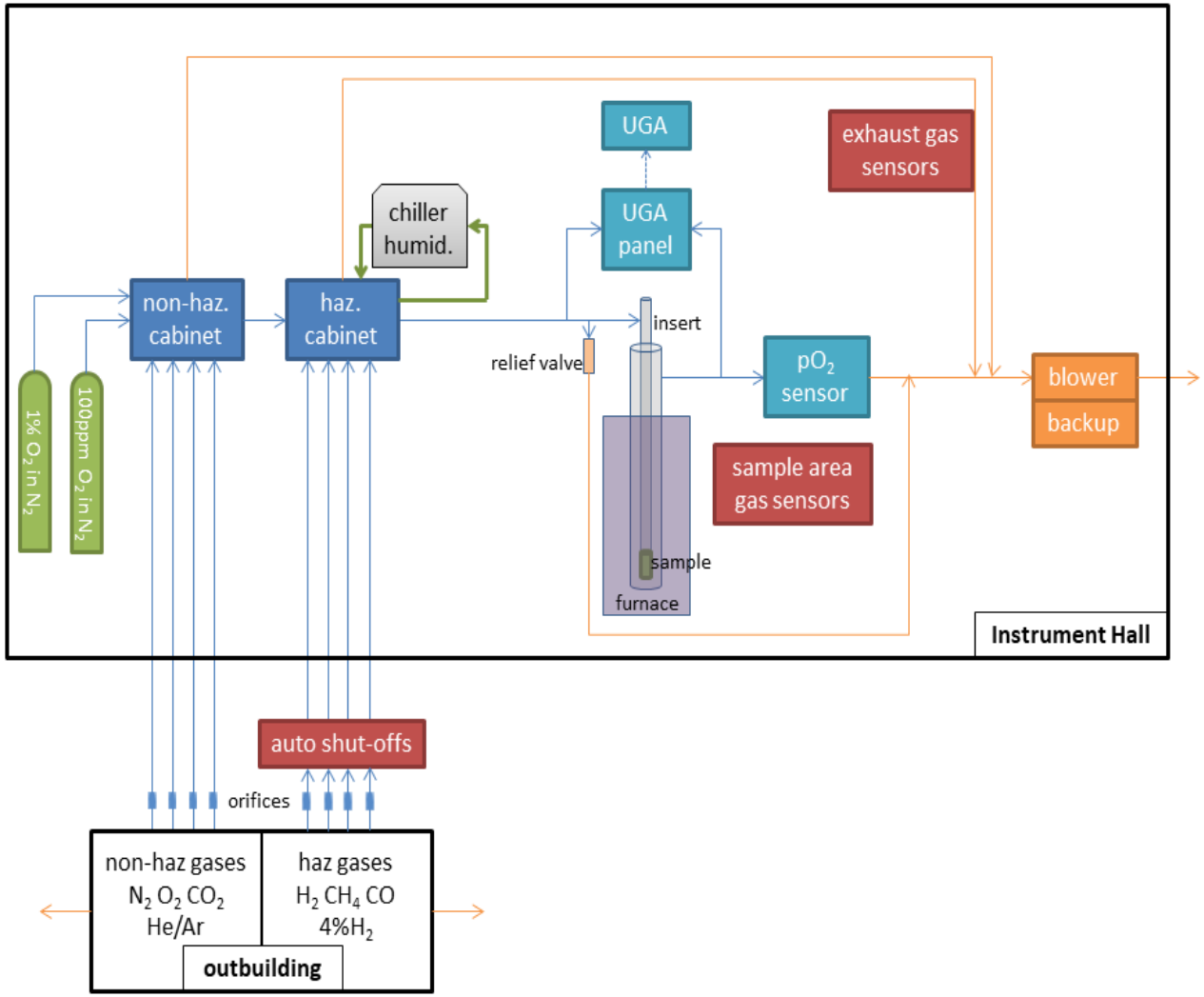


GAS Cabinets

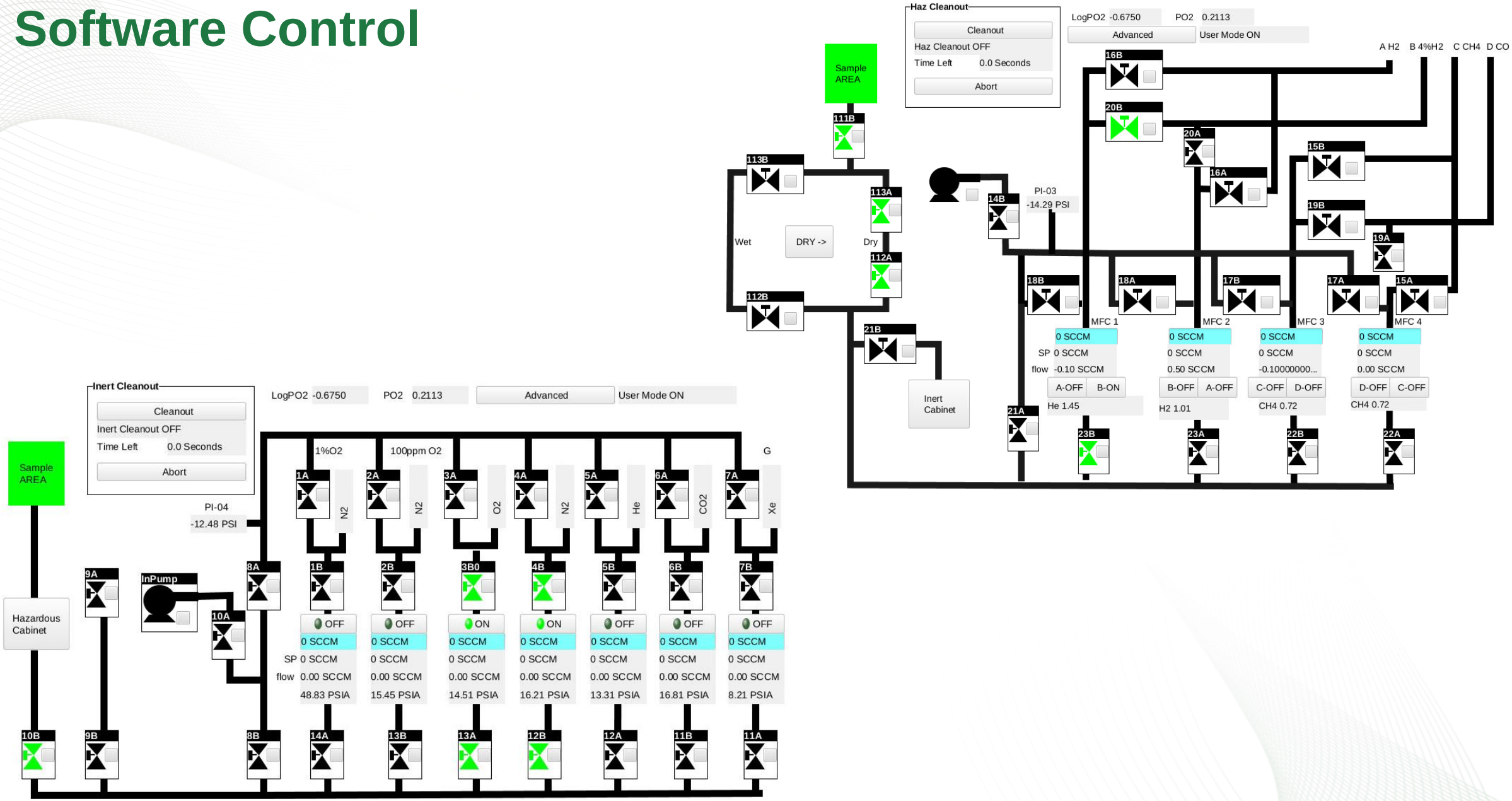


POWGEN Automated Gas Handling System (AGES)

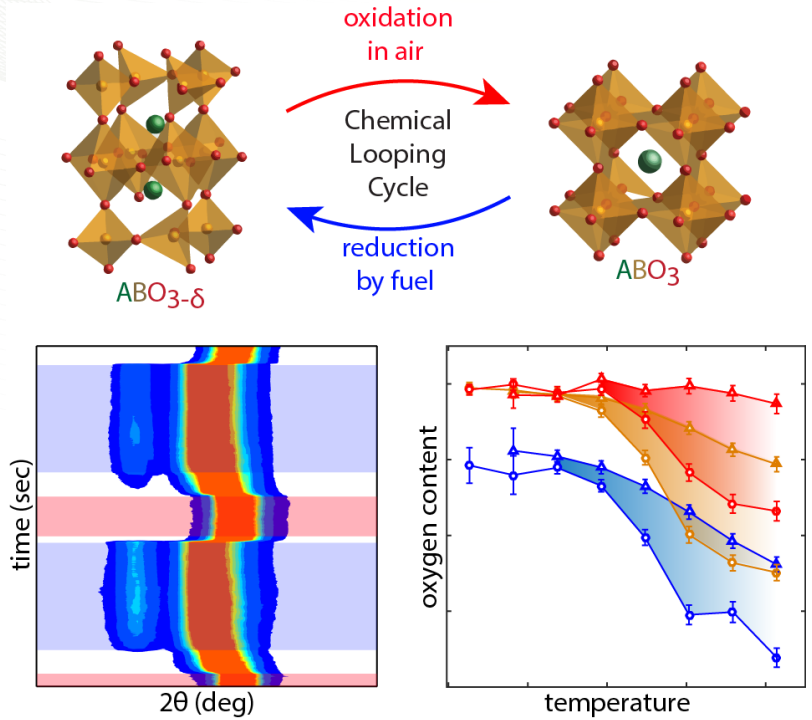




Software Control



In situ diffraction study of oxygen storage materials for the chemical-looping oxidation of methane



Schematic representation of the chemical-looping process (top). Here, a perovskite is alternatingly exposed to air and a fuel (e.g. methane) in order to cycle the material. The oxidation and reduction of the sample can be tracked with in situ X-ray diffraction (bottom left) and the oxygen storage capacity can be refined from in situ neutron diffraction (bottom right)

Work was performed at the ORNL Spallation Neutron Source's POWGEN instrument (neutrons) and the Advanced Photon Source's (APS) 17BM (X-ray) beam lines.

Scientific Achievement

In situ neutron and synchrotron X-ray diffraction were used to study the oxygen storage properties of the series $La_{1-x}Sr_xFeO_{3-\delta}$. This system has shown promise for use in the chemical-looping generation of syngas from methane. Neutrons were critical in determining the availability of lattice oxygen for the oxidation of methane.

Significance and Impact

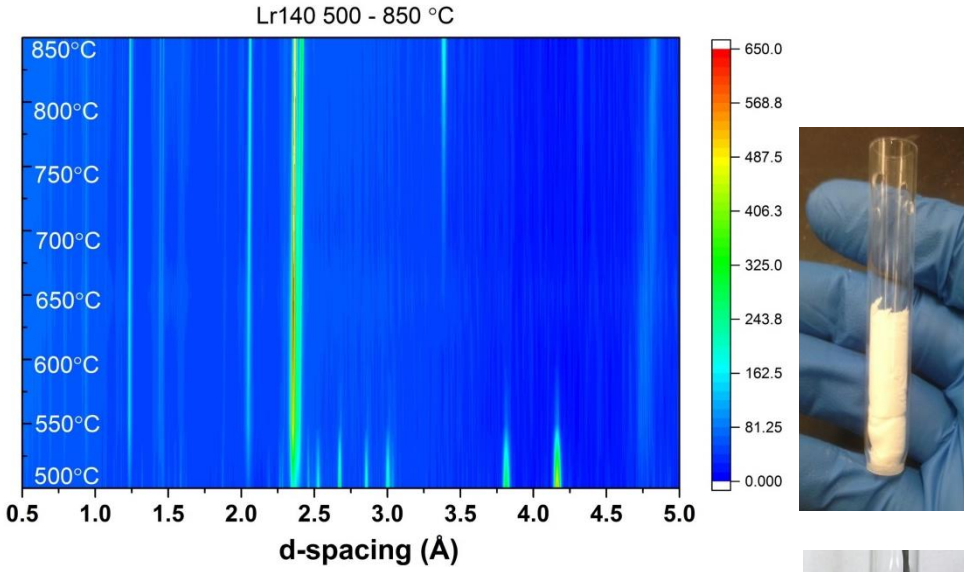
By gaining insight into the role of structure and composition in determining the performance of oxygen storage materials, we will be better able to design these materials in the future.

Research Details

- Neutron diffraction with Rietveld refinement provided the oxygen storage capacity as a function of temperature for each sample
- Synchrotron X-ray diffraction provided kinetic information for the reaction of each sample with methane
- $La_{2/3}Sr_{1/3}FeO_{3-\delta}$ was determined to be the optimal oxygen storage material for chemical-looping with methane

(1) Taylor, D. D.; Schreiber, N. J.; Levitas, B. D.; Xu, W.; Whitfield, P. S.; Rodriguez, E. E. Oxygen Storage Properties of $La_{1-x}Sr_xFeO_{3-\delta}$ for Chemical-Looping Reactions—An In Situ Neutron and Synchrotron X-Ray Study. Chem. Mater. 2016, 28, 3951–3960.

Key challenge is reaction compatible sample environments & some proposed solutions

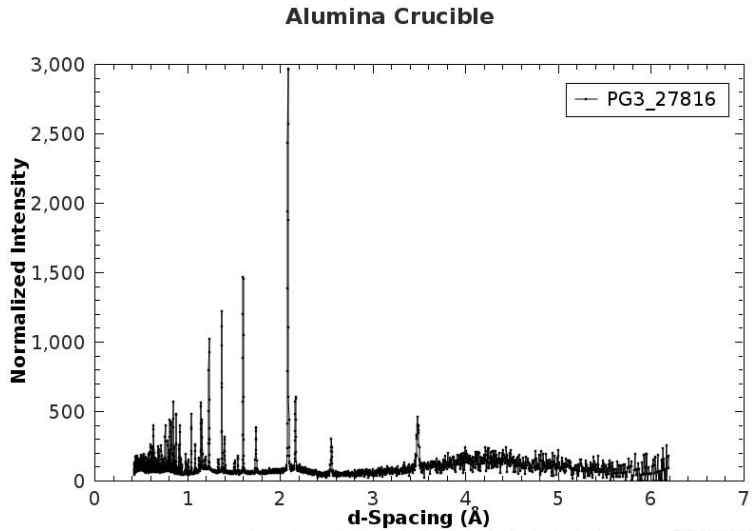


Crucibles made of ceramic and other noble metals have large number of Bragg peaks.

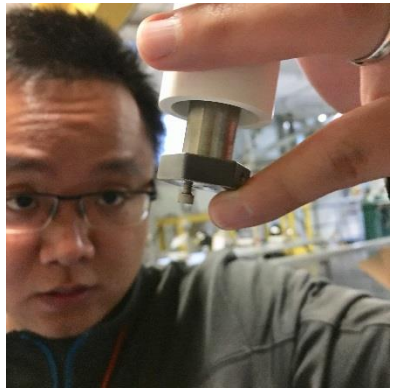
- Eliminate Bragg peaks from container by using custom built radial collimator.

Quartz crystallizes in the presence of Li, eventually causing the tube to break.

- Need other amorphous holder materials that do not react with compounds of interest.



In operando neutron powder diffraction during cycling

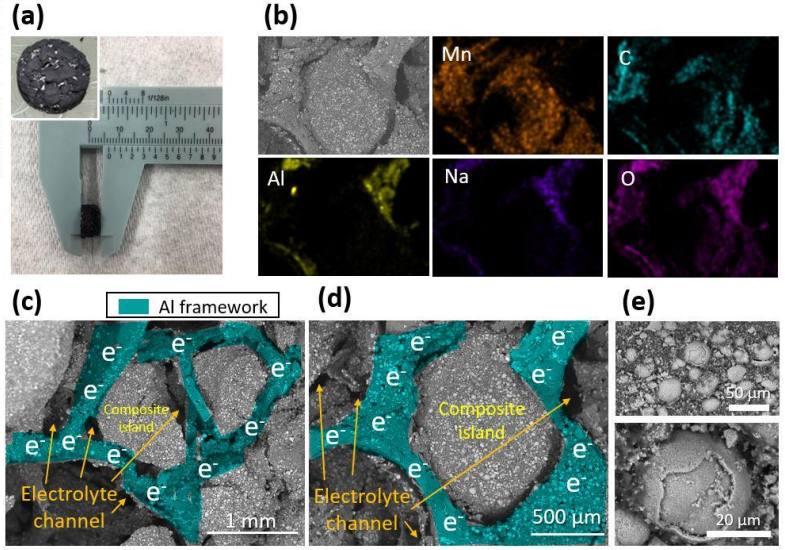


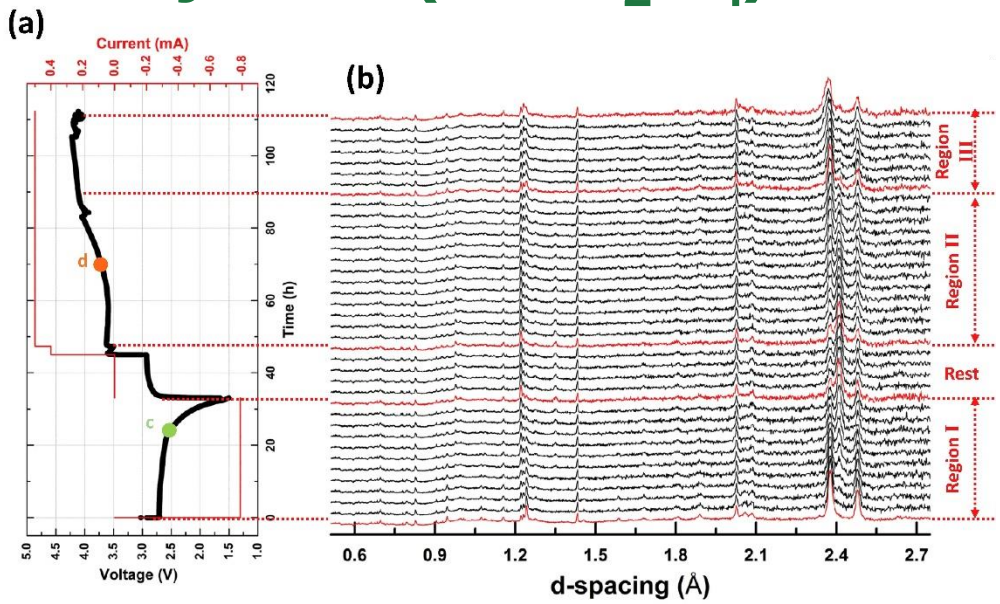
Two main challenges

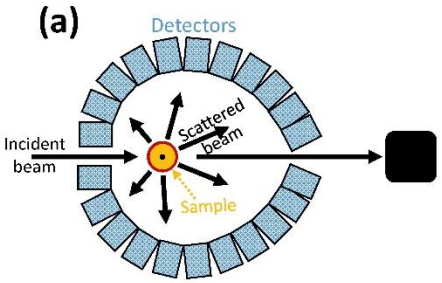
1. **preparation of a thick electrode**
   - Active material > 0.3 g (for high-quality neutron data to be collected)
   - Thickness > 5 mm
   - High porosity to shorten diffusing length of Li^+ ions
   - Tiny amount or no binder to minimize H coherent and incoherent scattering

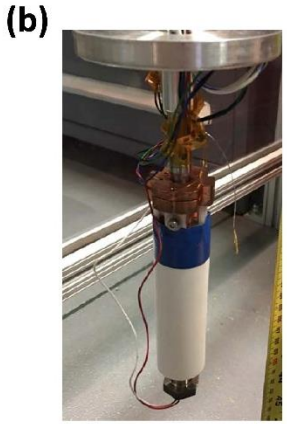
2. **Design and assembly of *in-situ* liquid electrochemical cell**
   - Loading a thick electrode
   - Air and moisture tight design
   - Deuterated electrolyte used
   - Reduce contact resistance among various components
   - Neutron-friendly components to reduce background signal such as using Ti_2Zr alloy

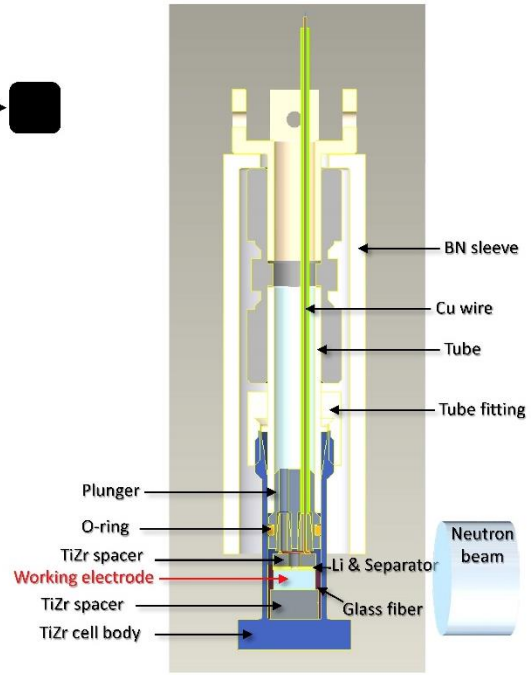
Thick cathode and Neutron Friendly Cell ($LiMn_2O_4$)

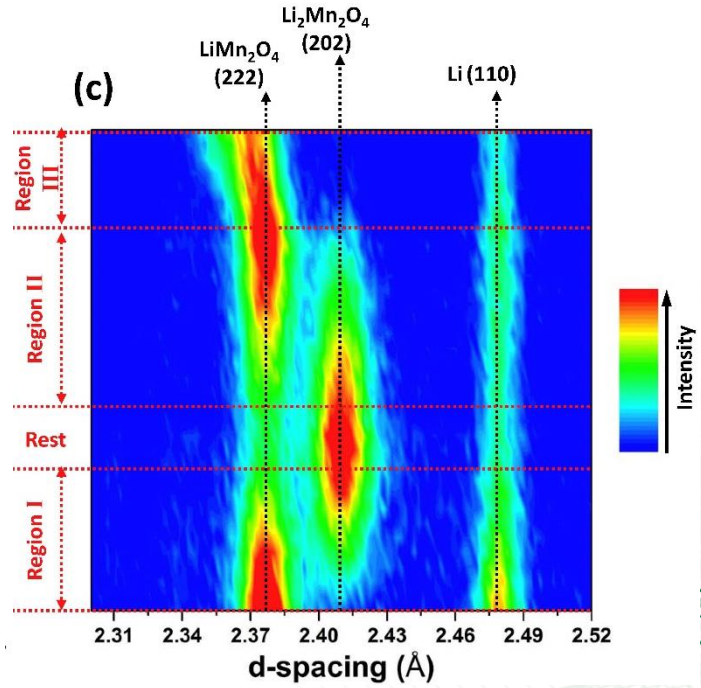








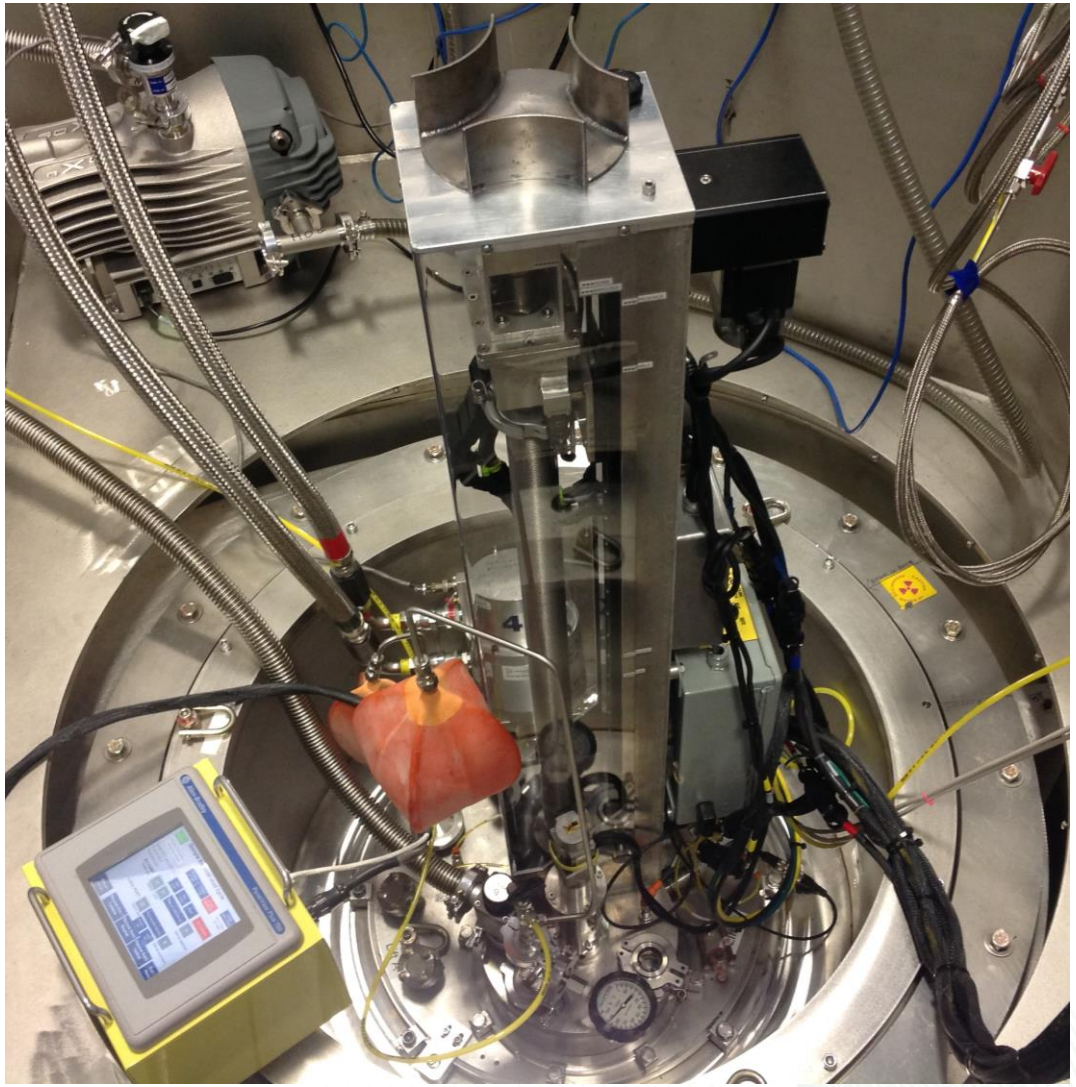




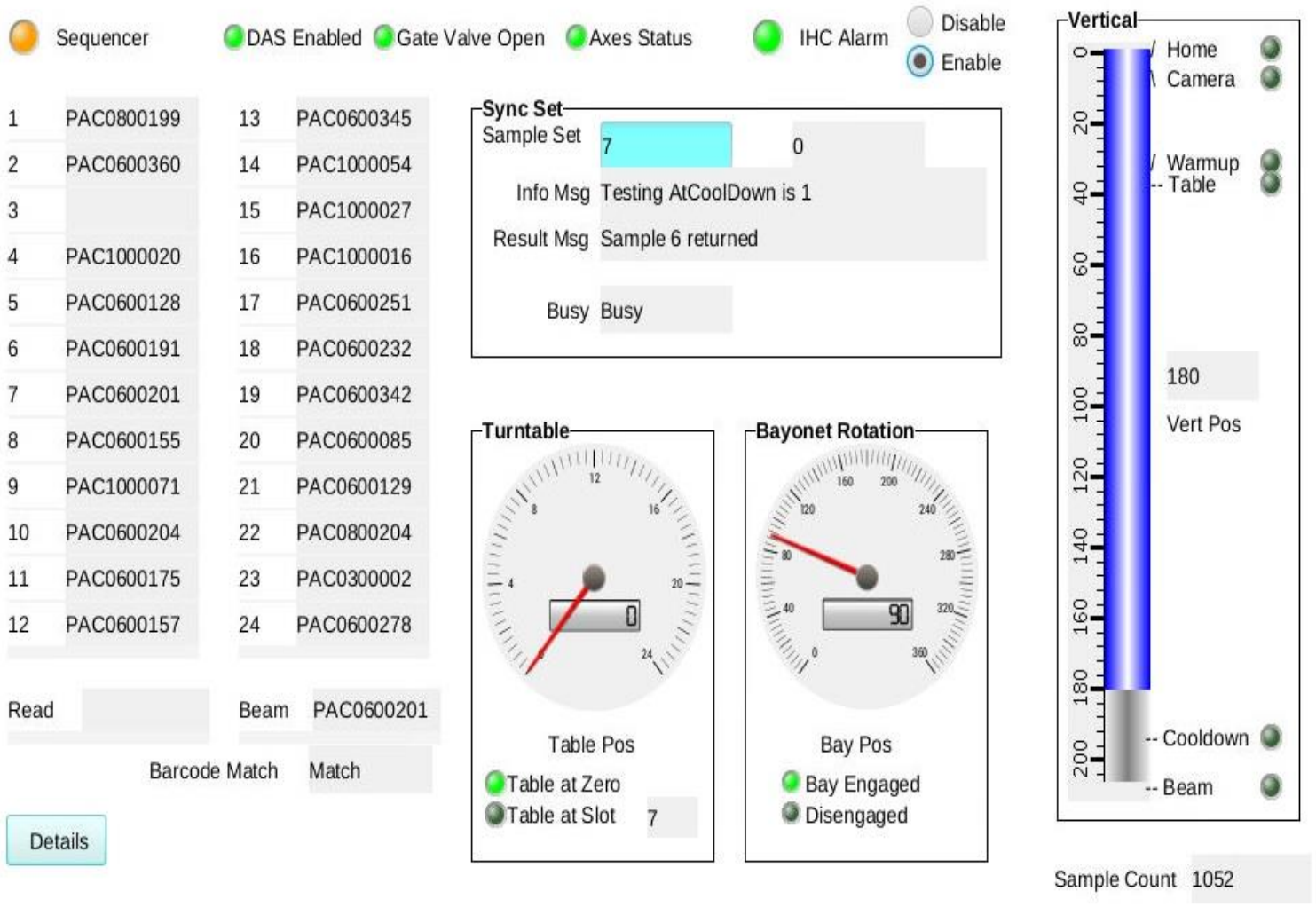
HIGH FLUX ISOTOPE REACTOR | SPALLATION NEUTRON SOURCE

Powgen Auto-Changer (PAC)

- Automatic sample changes
- Turntable holds 24 samples
- CCR for temperatures of 10-300K
- Sample changes at any temperature including base temperature of 10K



PAC Controls



- PAC may be monitored and controlled remotely via EPICS interface.
- Sample changes and temperatures may be scripted
- Alarms sent if system faults

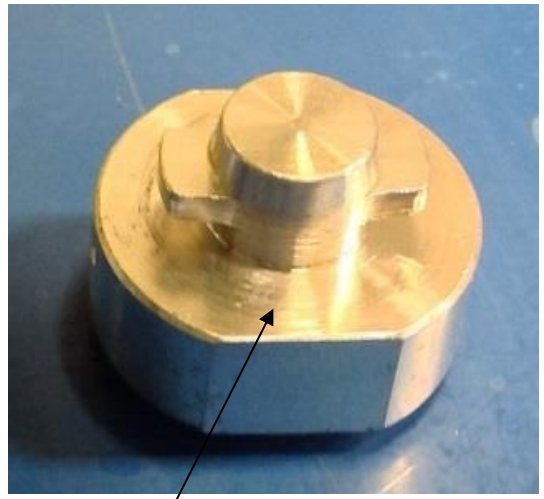
Auto Sample Change Sequence

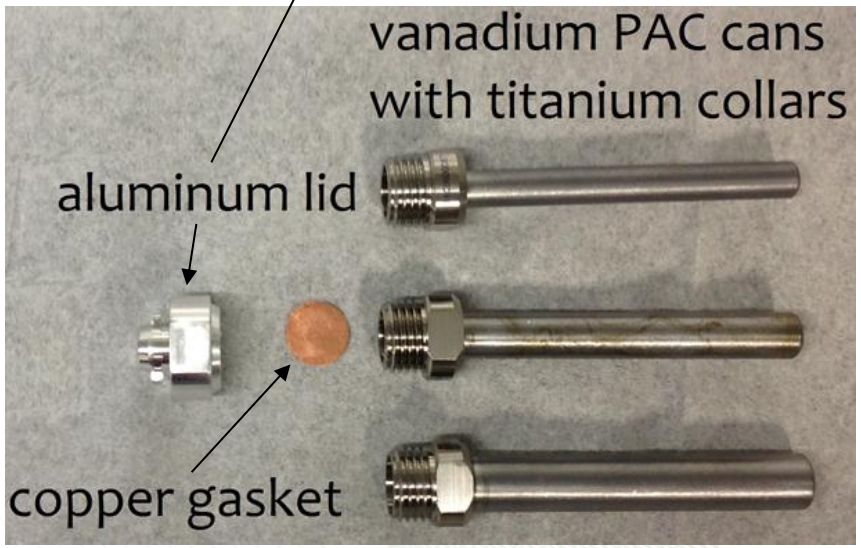
To Remove Sample from Beam:

1. Vertical to beam position
2. Bayonet to engaged
3. Vertical to warmup
4. Vertical to camera
5. Presence detect – PASS
6. Vertical to home
7. Table to slot number
8. Extend table locking pin
9. Vertical to table
10. Bayonet to disengaged
11. Vertical to camera
12. Presence detect – FAIL
13. Vertical to home
14. Table to through-hole

To Place Sample into Beam:

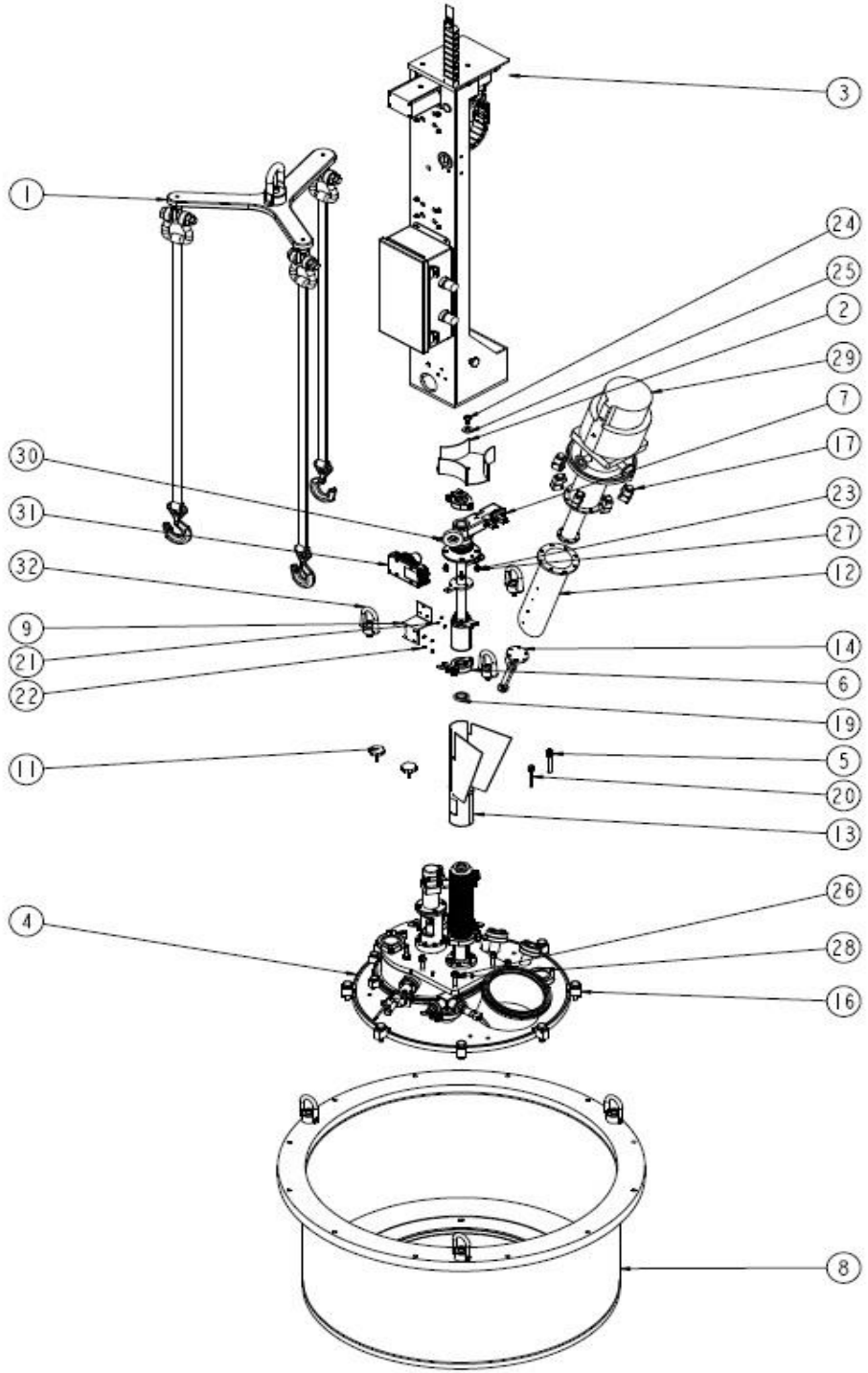
1. Table to slot number
2. Extend table locking pin
3. Vertical to table
4. Bayonet to engaged
5. Vertical to camera
6. Presence detect – PASS
7. Barcode check
8. Bayonet to engaged
9. Vertical to home
10. Table to through-hole
11. Vertical to cool down
12. Vertical to beam position
13. Bayonet to disengaged
14. Vertical to camera
15. Presence detect – FAIL
16. Vertical to home





Place Sample Logic Sequence
Is Bayonet at Home
Is Bayonet Disengaged
Rotate Table to Sample #
Is it Rotated To Table Sample#
Move Bayonet to Carrousel
Is Bayonet at Carrousel
Engage Bayonet
Is Bayonet Engaged
Move to Camera
Is it at Camera
Start Bar Code Check
Is Bar Code Complete
Is Bar Code Check Pass
Move Bayonet to Home
Is Bayonet at Home
Move Carrousel Thru Hole
Is Carrosuel at Thru Hole
Move to Cool Down
Is it at Cool Down
Wait Cool Down Time
Move to Beam
Is it at Beam
Disengage Bayonet
Is Bayonet Disengaged
Move to Camera
Is it at Camera
Start Presence Check
Is Presence Check Fail
Disengage Bayonet
Is Bayonet Disengaged
Move Bayonet to Home
Is Bayonet at Home
Idle

Get Sample Logic Sequence
Is Bayonet at Home
Is Bayonet Disengaged
Is Carrosuel at Thru Hole
Move to Beam
Is it at Beam
Engage Bayonet
Is Bayonet Engaged
Move to Warmup Defog
Is it atWarmup Defog
Warmup_sample
Move to Camera
Is it at Camera
Start Presence Check
Is Presence Check Pass
Engage Bayonet
Is Bayonet Engaged
Move Bayonet to Home
Is Bayonet at Home
Rotate Table to Sample #
Is it Rotated to Table
Move Bayonet to Carrousel
Is Bayonet at Carrousel
Disengage Bayonet
Is Bayonet Disengaged
Move to Camera
Is it at Camera
Start Presence Check
Is Presence Check Fail
Disengage Bayonet
Is Bayonet Disengaged
Move Bayonet to Home
Is Bayonet at Home
Move Carrousel Thru Hole
Is Carrosuel at Thru Hole
Idle



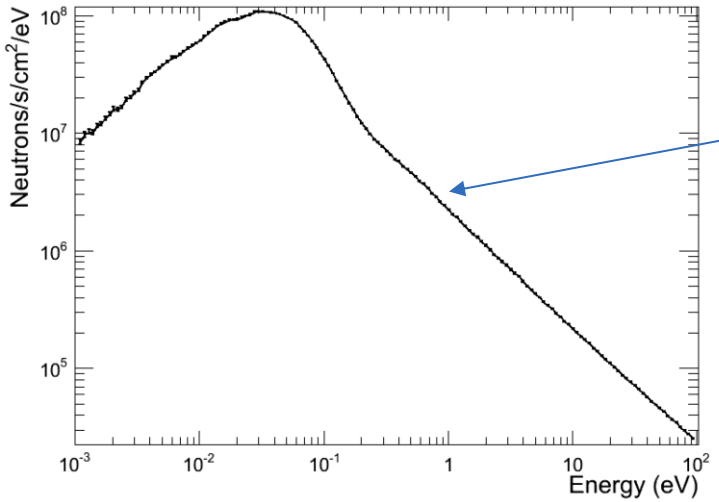
Chemical Spectroscopy (VISION)

- INS + Raman
- Hydrogen and Pressure
- Sample Changer

Simultaneous INS/Raman scattering

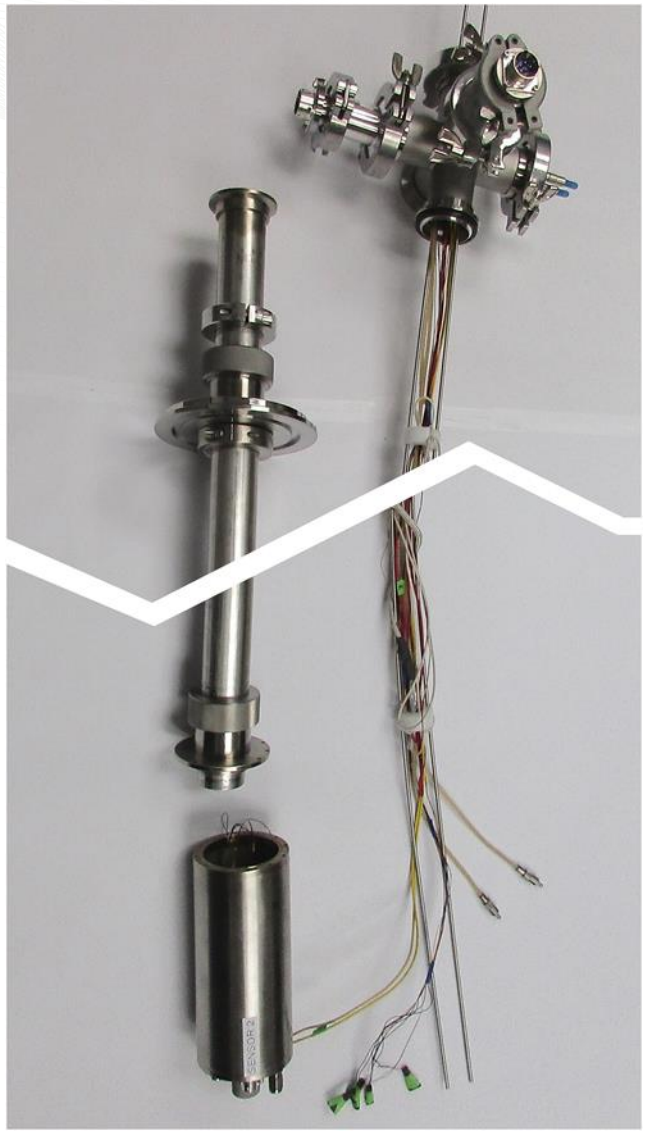
- At high energy transfer (> 2500 cm-1), the VISION flux on sample is low and energy resolution is relatively poor. This range typically corresponds to bond stretches that are easily observable with Raman or FTIR.

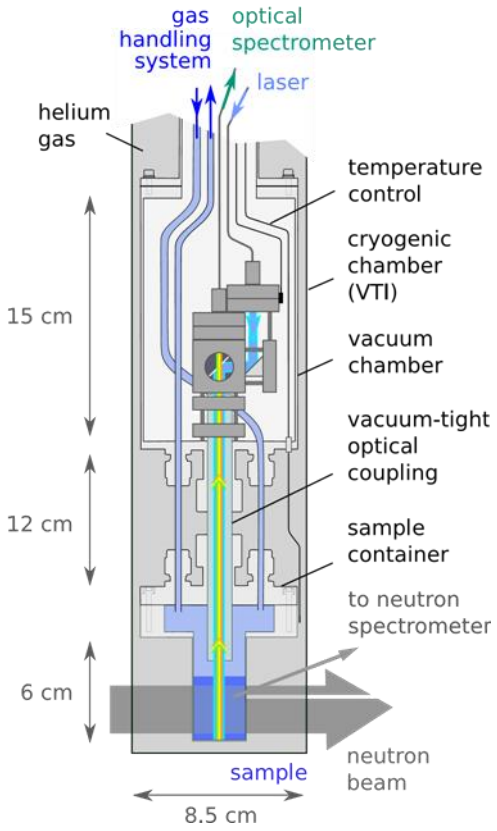
- An in situ Raman probe on VISION (usable at low temperature and allowing for gas injection into the sample) would be helpful to complement INS data.

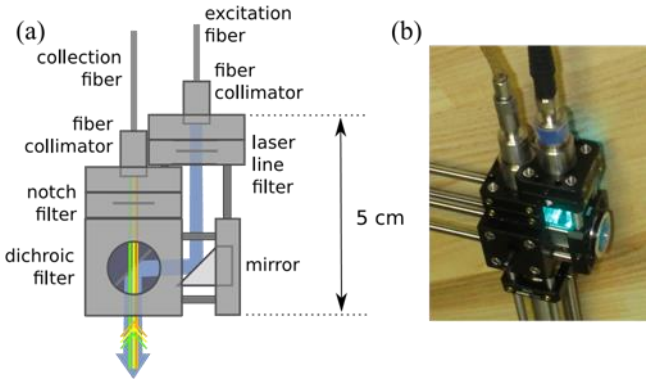


Neutron flux at higher energies is lower by more than 10x compared thermal energy range.

Simultaneous INS/Raman scattering





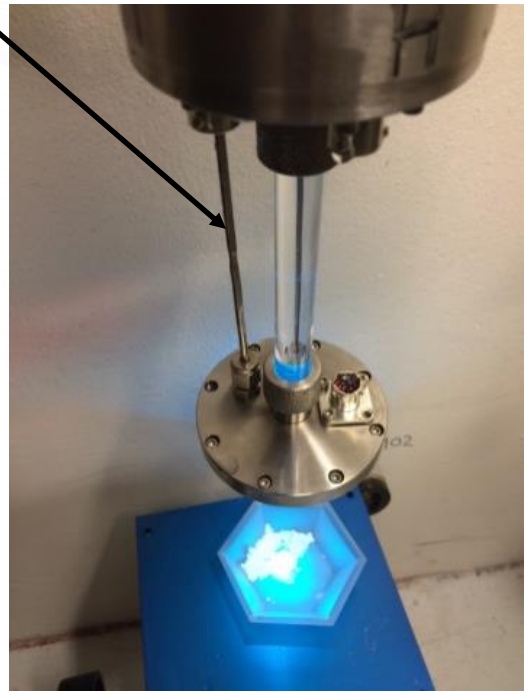


(a) The optical assembly, showing the path of the excitation and collected light. (b) A photograph of the optical assembly before it was incorporated into the center stick. The steel rods emerging at bottom and left were used during alignment and were removed before incorporating the assembly into the center stick.

Laser excitation at 488 nm, 50 mW; Ocean Optics HR2000 spectrometer used in Raman mode

Simultaneous INS/Raman scattering

Capillary for gas injection in situ



Optical coupling to the sample is through a 1 cm diam. Quartz rod. The top flange of the sample holder is shown.

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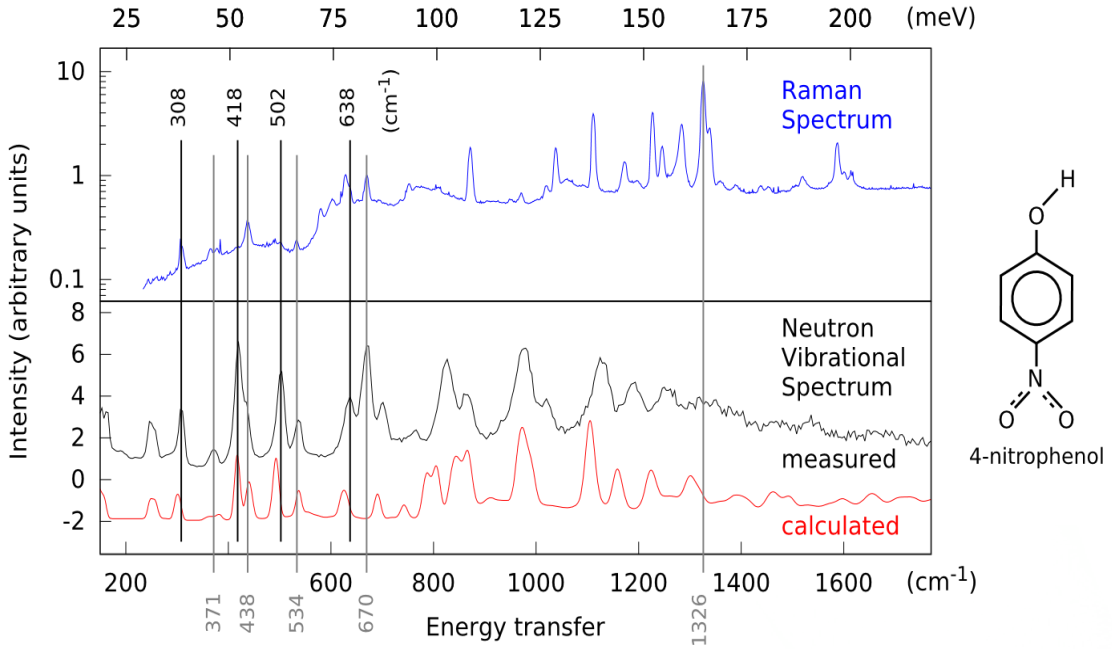
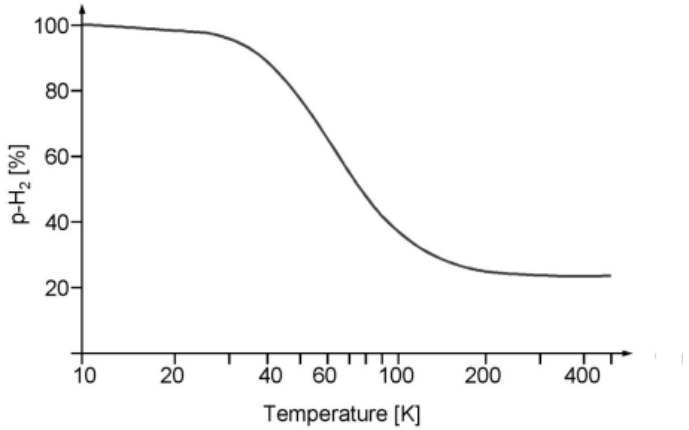
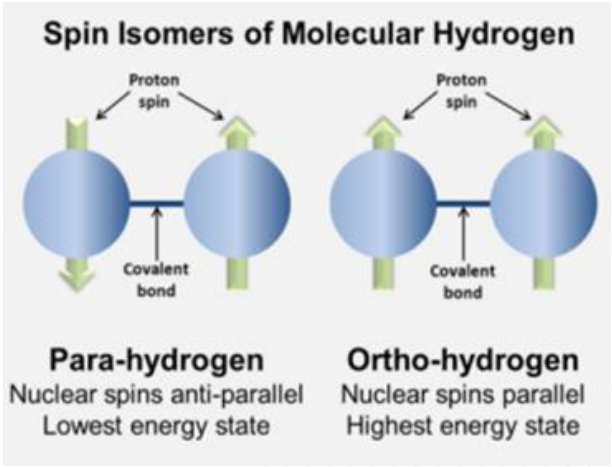


Simultaneous Raman and neutron vibrational spectrum of 4-nitrophenol at 20 K. The neutron data are from the backscattering inelastic detectors of VISION, which are positioned at a scattering angle of 135°.

Quantum dynamics of confined molecular hydrogen

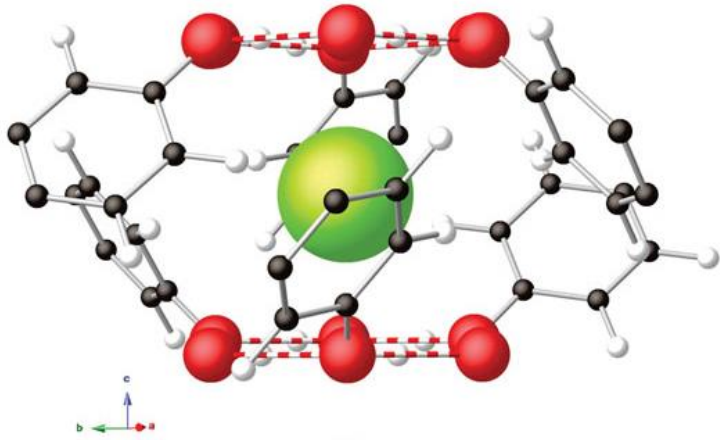
- A particle in a box and a rigid rotor are fundamental physical concepts that represent simple, but significant applications of Schroedinger's equation.
- In H_2, the protons are indistinguishable fermions. The antisymmetry requirement for the wavefunction leads to two spin isomers: parahydrogen and orthohydrogen.
- H_2 quantum dynamics are influenced by interaction potentials (e.g., 3D confinement).
- Confinement of H_2 in hydroquinone clathrates with well-defined interaction potentials provides an opportunity to probe the coupled translational-rotational states of H_2 in a simple model system.





Quantum dynamics of confined molecular hydrogen

H_2@β-hydroquinone (HQ) was synthesized by pressurizing α-HQ with H_2 at ~200 MPa, then samples were quenched to low temperature and the pressure was released. INS measurements were then performed on VISION at 5K.



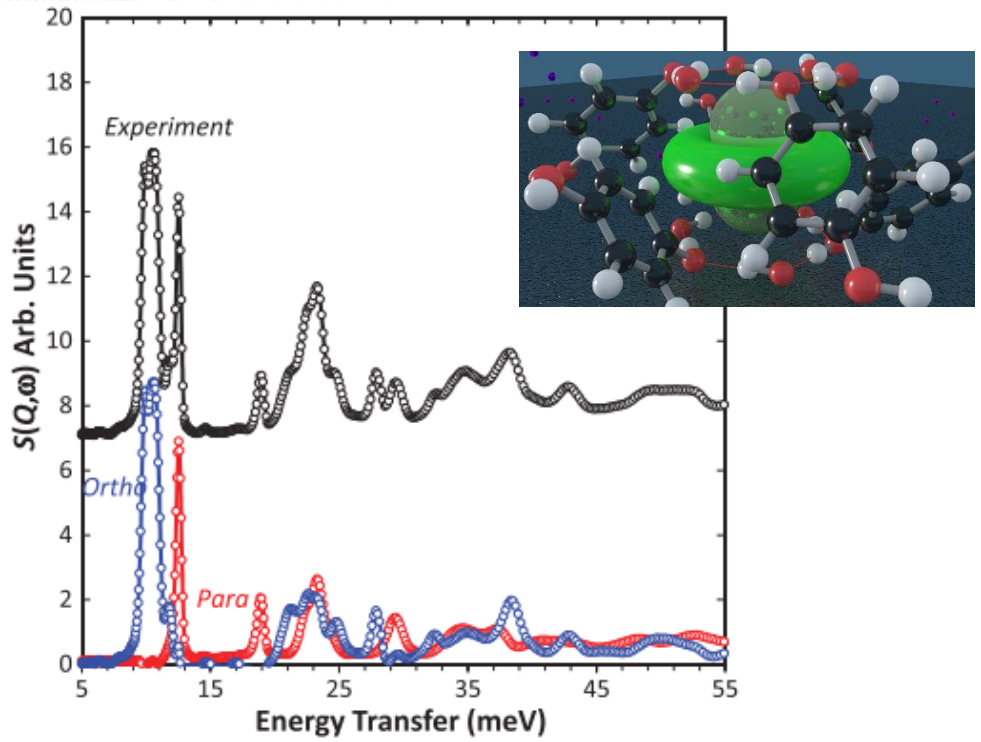
This experiment (sample synthesis in situ) was enabled by the fabrication of a CuBe pressure cell for use with H2 at high pressure (up to 7 kbar). A standard Bridgman seal was used and sealed well at 5K. Cell volume is 1 cm^3.

CuBe pressure cell

Bridgman seal

Pressure pumping system for H_2 work

Quantum dynamics of confined molecular hydrogen



INS spectrum of trapped hydrogen (with the ortho and para contributions). Inset: the probability distribution of a rotating hydrogen molecule trapped inside an organic clathrate cage. Credit: Tim Strobel.

Scientific Achievement

Inelastic neutron scattering (INS) experiments allow direct measurements of the quantum behavior of isolated molecular hydrogen trapped in molecular clathrate cages. The results indicate relatively strong attractive interaction between guest and host with a strikingly large splitting of rotational energy levels compared with similar guest-host systems.

Significance and Impact

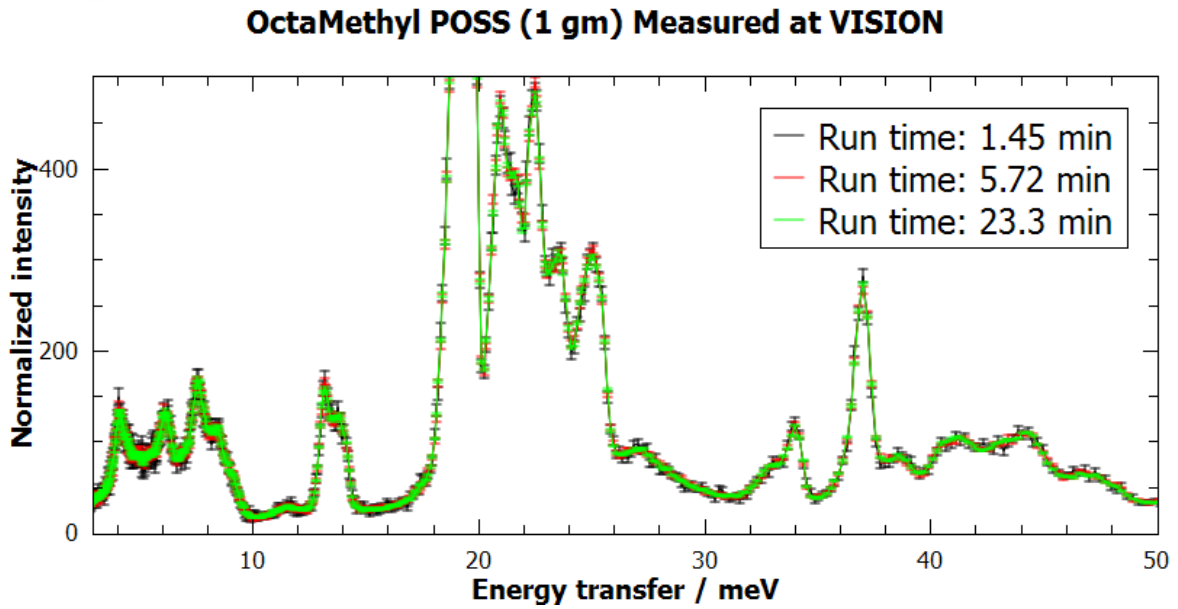
Hydrogen trapped within cage-like, guest-host materials has been of recent interest due to the ideal nature of these systems to understand quantum dynamics and for the possibility of these materials to store hydrogen for energy applications. Clathrate cages provide ideal nanoscale confining potentials for small molecules, and thus provide the rare opportunity to probe the coupled translational-rotational states under model-like conditions. This work demonstrates the first two-dimensional rotation of H_2 in a molecular clathrate.

High-resolution inelastic neutron scattering experiment was performed at the VISION spectrometer of ORNL's Spallation Neutron Source, which is a DOE Office of Science user facility.

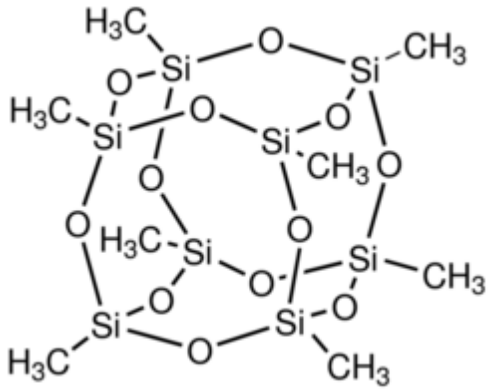
Timothy A. Strobel et al. Quantum Dynamics of H_2 Trapped within Organic Clathrate Cages, Physical Review Letters (2018). DOI: 10.1103/PhysRevLett.120.120402

VISION Sample Changer

- VISION is a high flux, high throughput instrument (1 TB data/day).
- Hydrogenous samples in gram quantities produce spectra in minutes.
- Sample change (= mounting sample on stick, stick exchange, cooling, DAQ programming) can take more time than data collection alone!

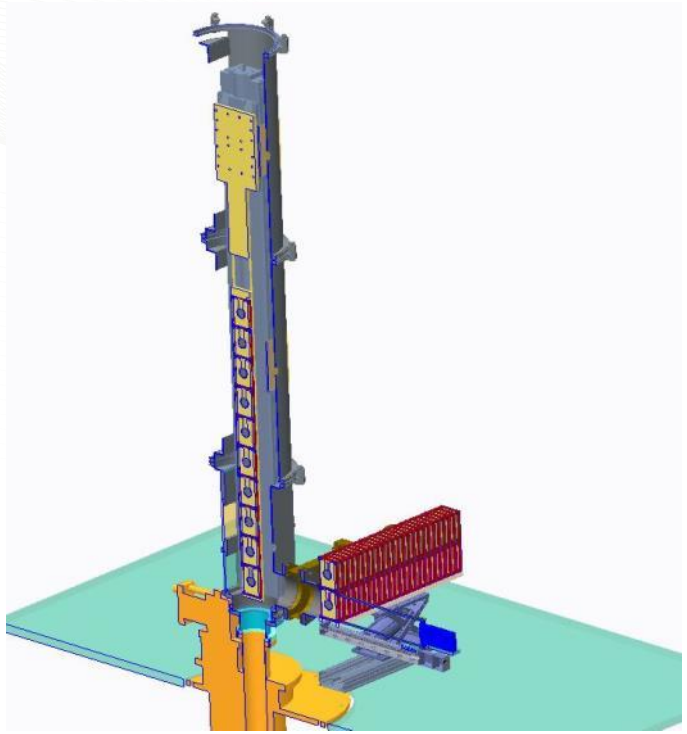


With 14 inelastic banks and 16 diffraction banks, VISION has the highest data rate (up to millions of events per second) among all neutron beamlines in the world.



After a few minutes, the spectral features for 1 gram of octamethyl POSS no longer change !

Sample changer

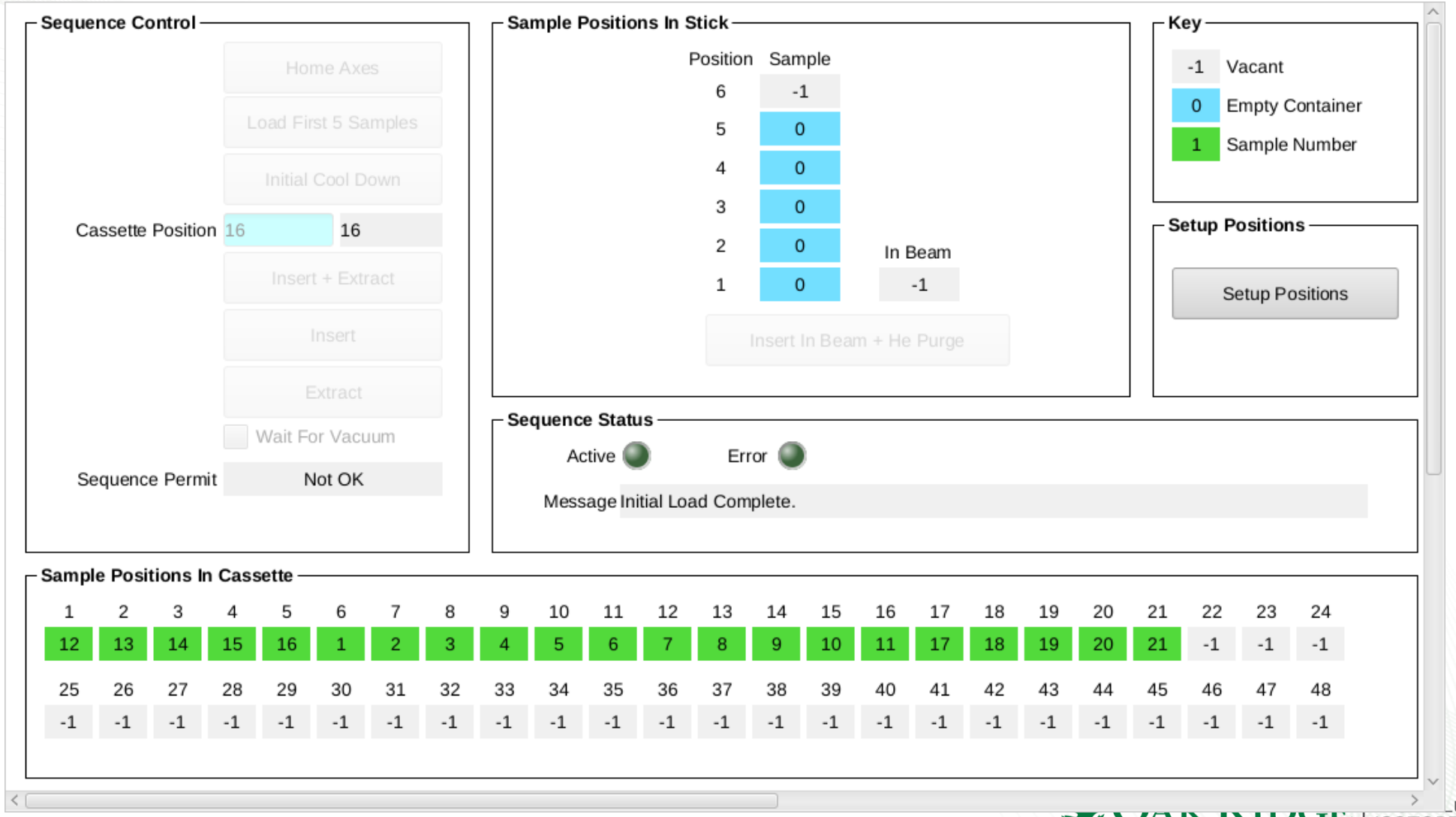


A sample change takes 15 minutes, compared to > 1.5 hr for a manual sample change.

Design and fabrication of an automatic sample changer started in 2017. It has a capacity of 54 samples and allows for sample pre-cooling and sample exchange at 5 K. This capability is operational as of June 2018. A mail-in program is in place as a result of the recent tests (June 2018).

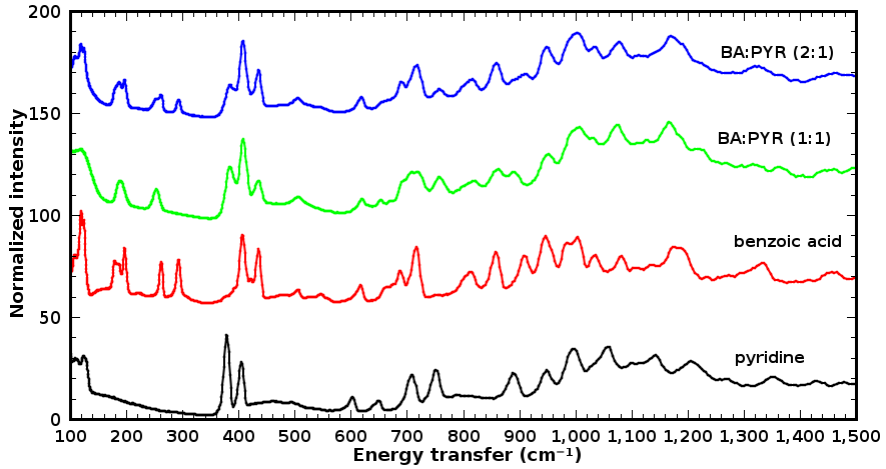
Sample changer

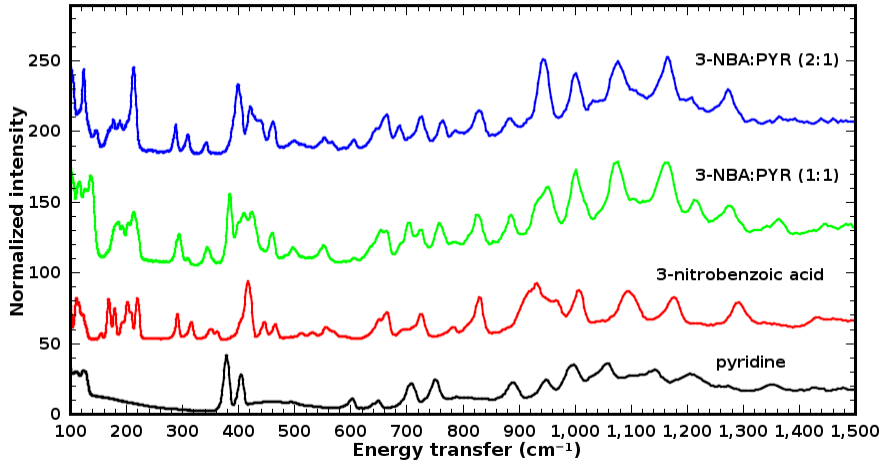
Sample changer control is fully integrated into CSS (Control System Studio)



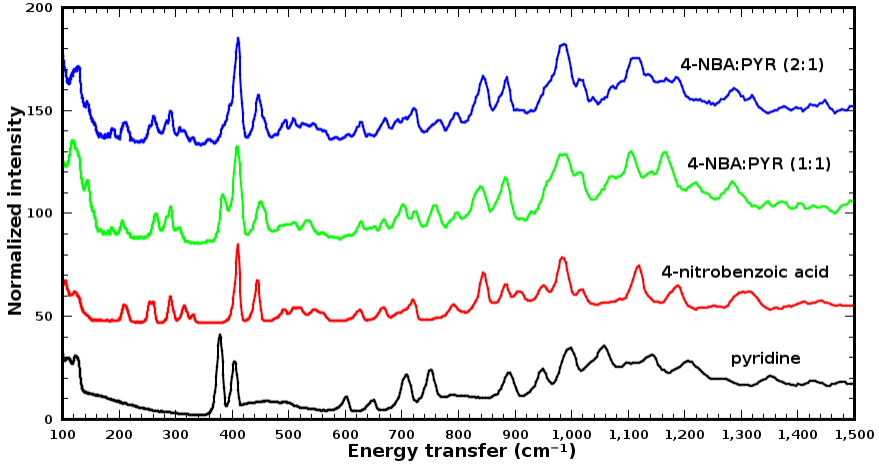
Sample changer

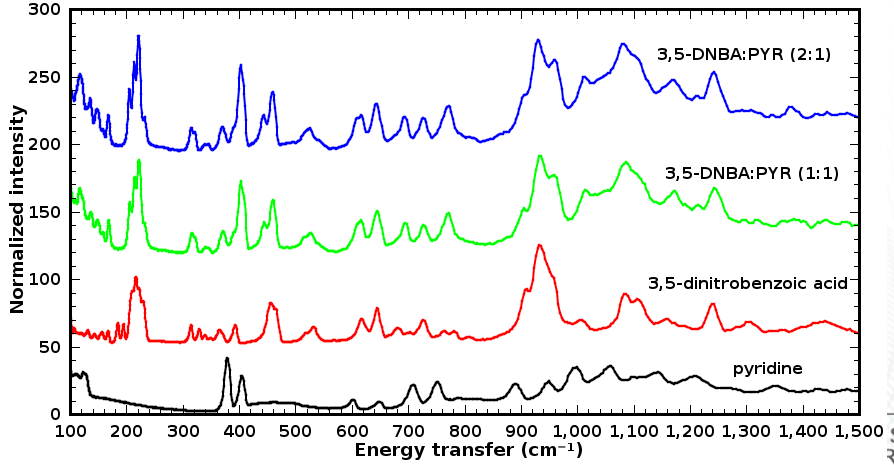
Data collected June 25, 2018. Molecular complexes of pyridine with nitro derivatives of benzoic acid. These complexes for short hydrogen bonds. Bond strength varies with the position of the nitro group on the ring.





13 spectra collected continuously in 12 hours with pre-cooling and cold sample change





Acknowledgements

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- Gas Handling System: Jason Hodges, Melanie Kirkham, Luke Heroux, Mariano Ruiz-Rodriguez, Bruce Hill, Randy Summers, Lorelei Jacobs and Donald Montierth
- All spectroscopy work done by VISION Team: Luke Daemen, Yongqiang Cheng, Timmy Ramirez

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