Singular Capabilities at ORNL for Evaluating & Characterizing Hydrogen Storage Materials

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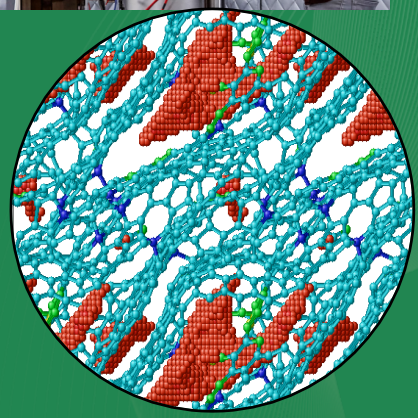
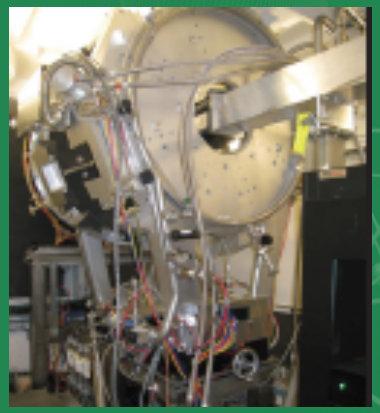
Energy and Transportation Science Division
Sustainable Transportation Program

Hydrogen Storage Lab PI Workshop
NREL, Golden, CO

November 5, 2015





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There are Three Focus Areas at ORNL That Can Provide Unique Information and Insights on the Behavior of Hydrogen Storage Materials

1.) Neutron Scattering at SNS (e.g., VISION Instrument for High throughput Inelastic Neutron Scattering Spectroscopy)

- **Principal Investigator: Timmy Ramirez-Cuesta**

2.) Atomic Resolution Imaging and Spectroscopy (i.e., Electron tomography for 3D nanoscale imaging)

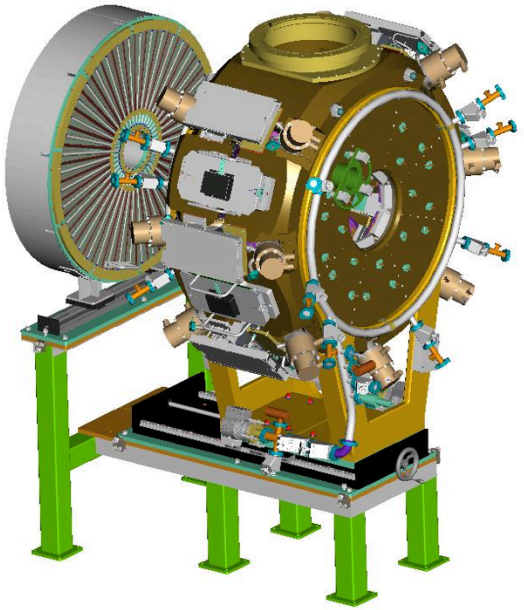
- **Principal Investigator: David A. Cullen**

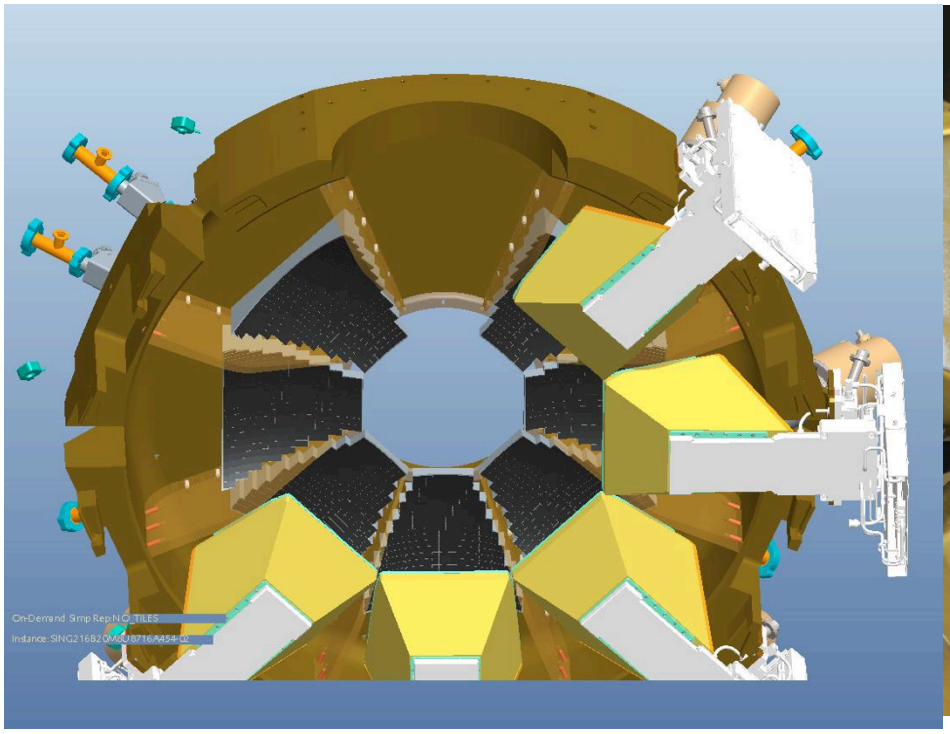
3.) Theory and neutron scattering studies of pore-size dependent gas adsorption (i.e., “Genomics” approach to gas adsorption)

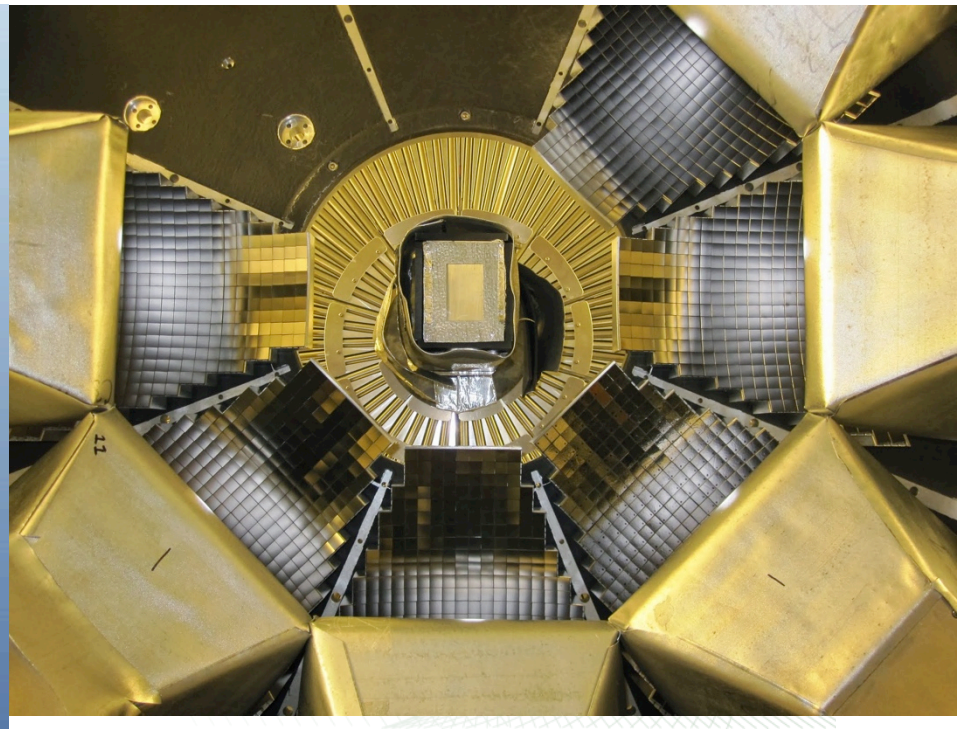
- **Principal investigator: James R. Morris**

VISION INS spectrometer at SNS

Part of SING II project
Has been in the User program since August 2014
This instrument is up to 4000x its predecessor



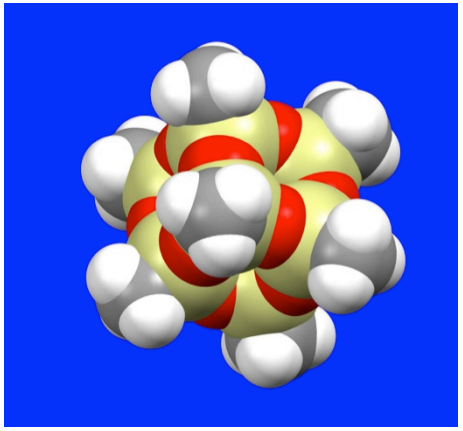


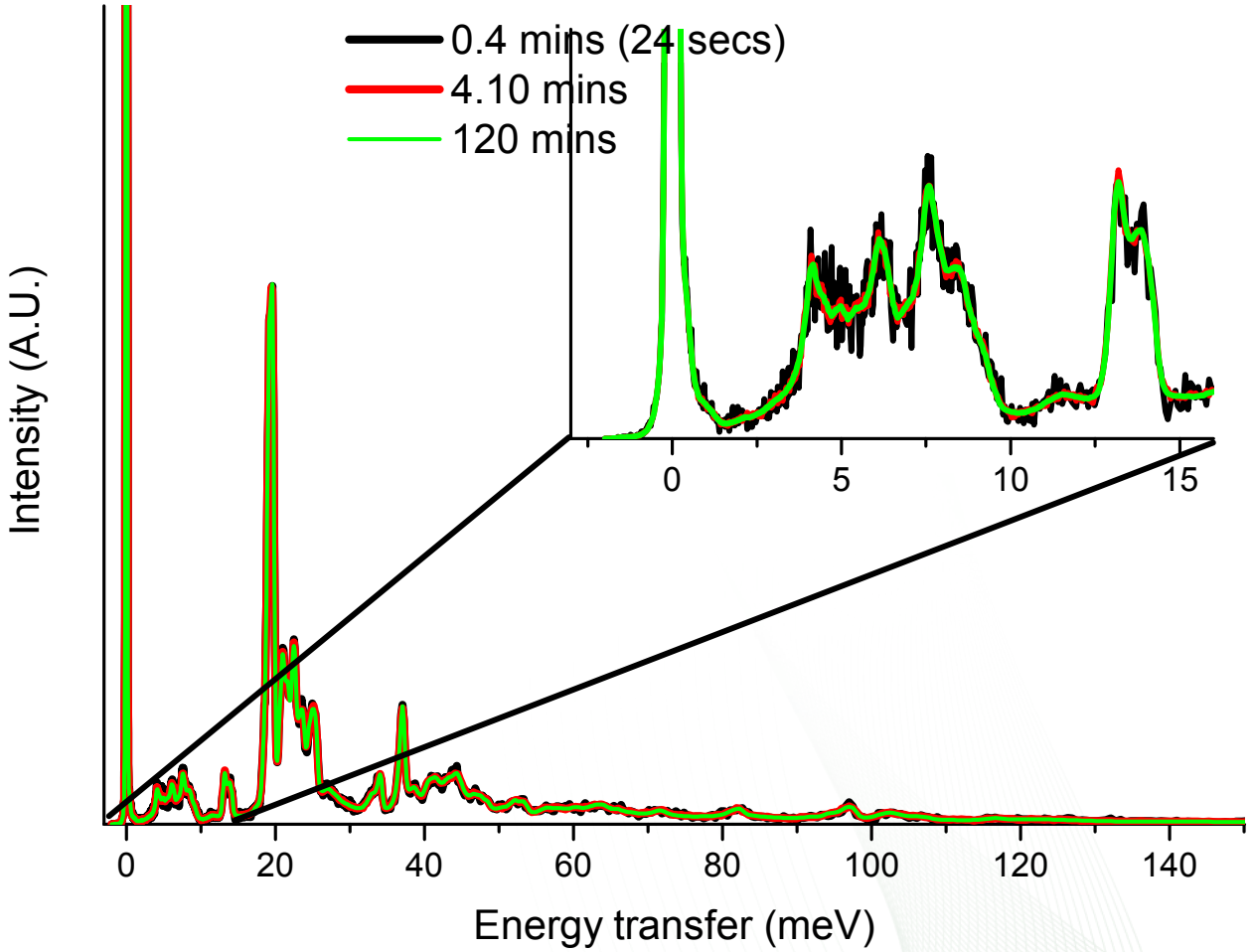


Examples of INS Spectra from the High Throughput VISION Instrument

- VISION

  44 mmol H





High Throughput

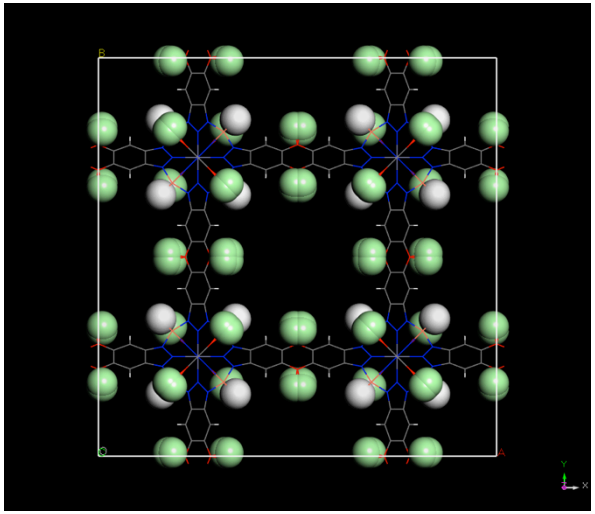
Challenges

- Large volume of Data
- How to handle large number of samples
  - Sample changers
  - Sample environment
  - Gas handling
- How to model and interpret the results

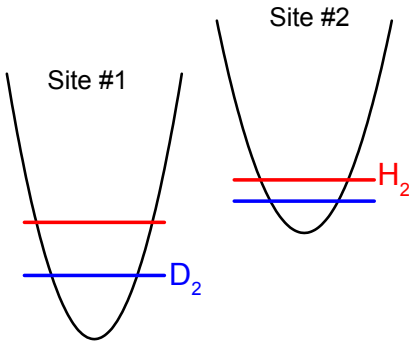
Opportunities

- Databases and Libraries
- Parametric studies
- Kinetic studies
- In-situ studies
- Small signals in large backgrounds
- Modeling

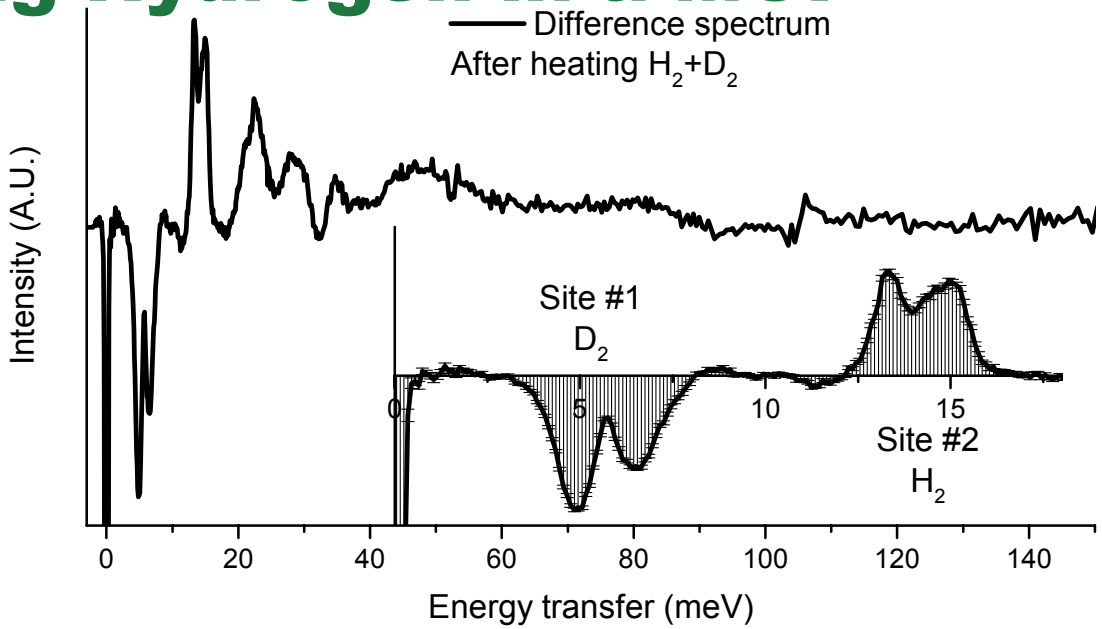
Quantum Sieving Hydrogen in a MOF

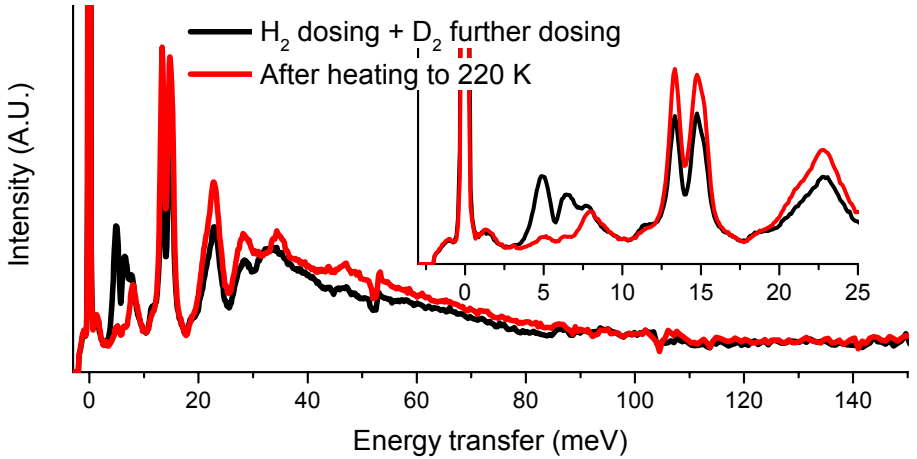


Quantum sieving is a technique for isotope separations; heavier isotopes induce favorable adsorption in nanoscale pores due to the difference in zero point energy of isotopes.



Hydrogen is dosed first, so it mostly takes the lower energy site (Site #1), afterwards deuterium gas is added and has to go to the available site (Site #2)

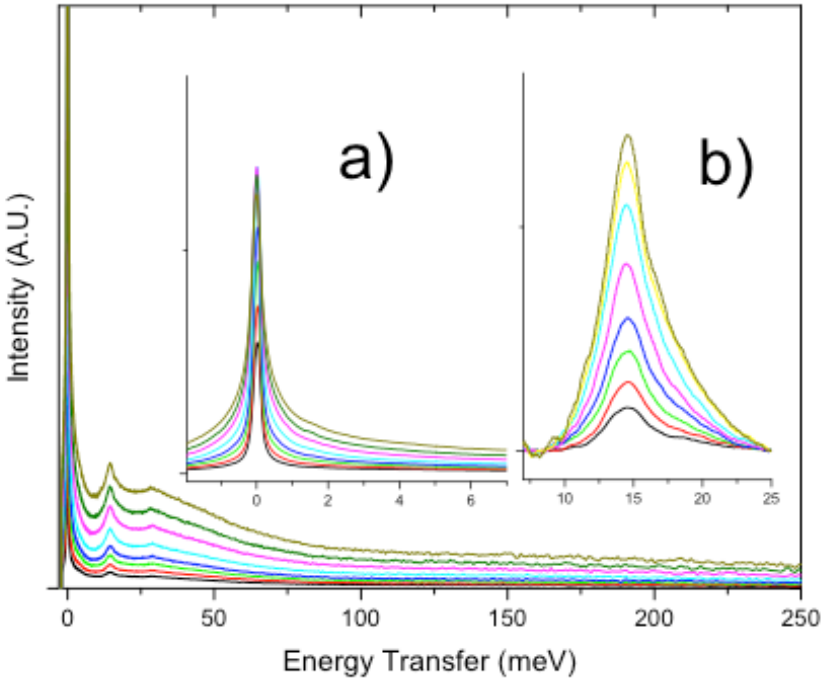




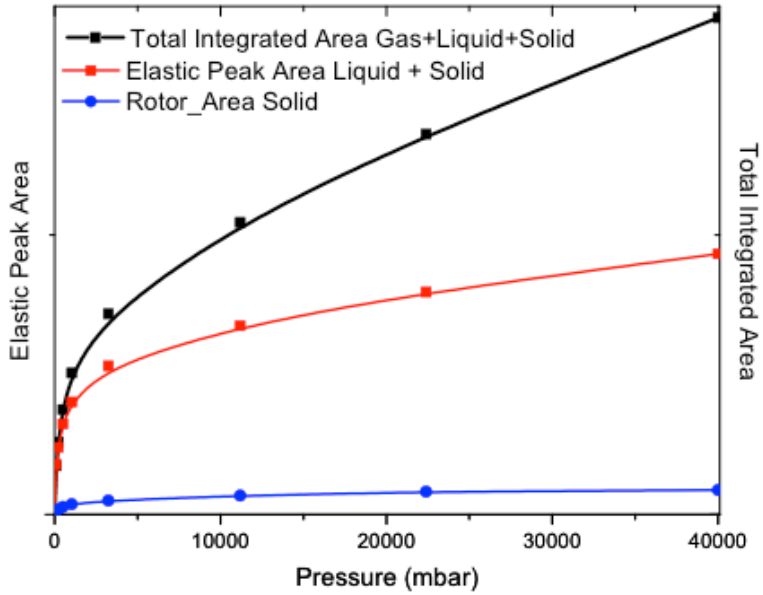
Black trace is hydrogen dosed at 77K and cooled down, further deuterium is added at 77K. Red trace is spectrum after warming sample to 220K and cool down. The hydrogen in site #1 has been displaced to site #2

Collaboration with Ingrid Weinrauch and Michael Hirscher, Max Planck Institute for Intelligent Systems, Germany

Molecular hydrogen in porous carbon



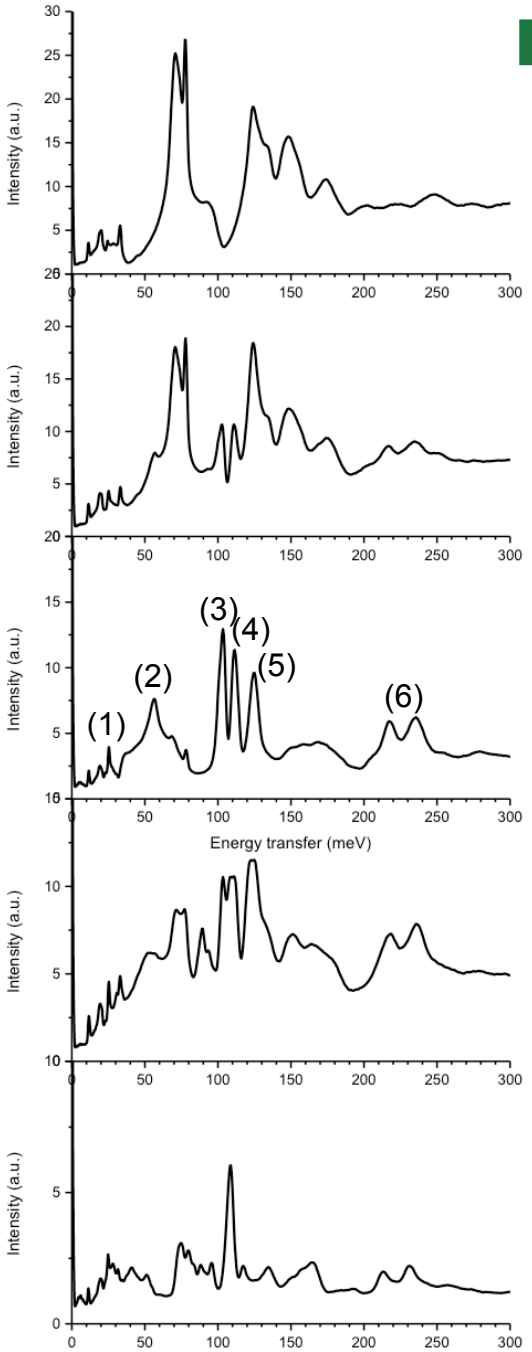
Presence of elastic line at 77K is indication of highly dense molecular hydrogen in the pores.
The broadening of the elastic line is a consequence of the enhanced mobility of the molecules as the amount of hydrogen increases in the system. Larger pores, where hydrogen is less constrained have more mobility. In the gas the signal is extremely broad.

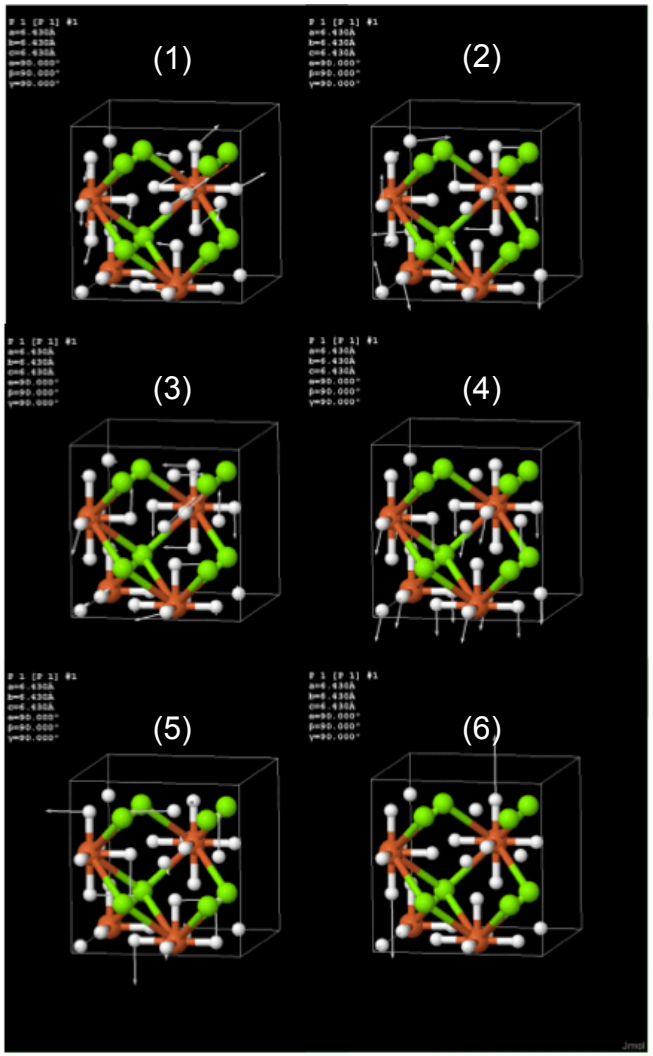


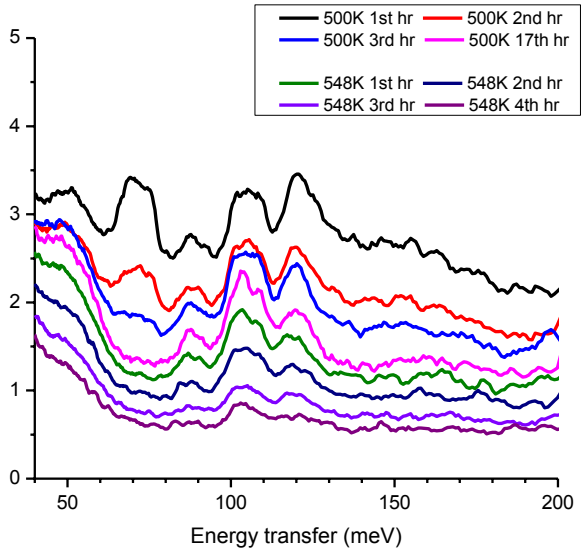
Presence of the rotor line at 77K is indication of completely immobile molecular hydrogen in the pores. In the case of pure para-hydrogen (previous figure) the line disappears when the hydrogen melts. The load keeps increasing even at 40 bar.

1. The total integral of the spectral intensity is proportional to the amount of hydrogen in the system
2. The integrated area under the elastic peak is proportional to the amount of hydrogen that is in a liquid and solid like phase
3. The integrated area under the rotor line is proportional to the amount of hydrogen in solid like phase (right panel)

Hydrogen in metal hydrides







Left) Studying metal hydrides after a series of reaction. The high throughput of VISION couples with a sample changer (in design stage) will allow parametric studies of a series of samples, taking snapshots of reactions etc.

Center) Representation of the modes (DFT calculations)

Top) In-situ decomposition of the hydride in a neutron beam

Collaboration with Jacques Huot, Universite du Quebec a Trois-Rivieres, Canada

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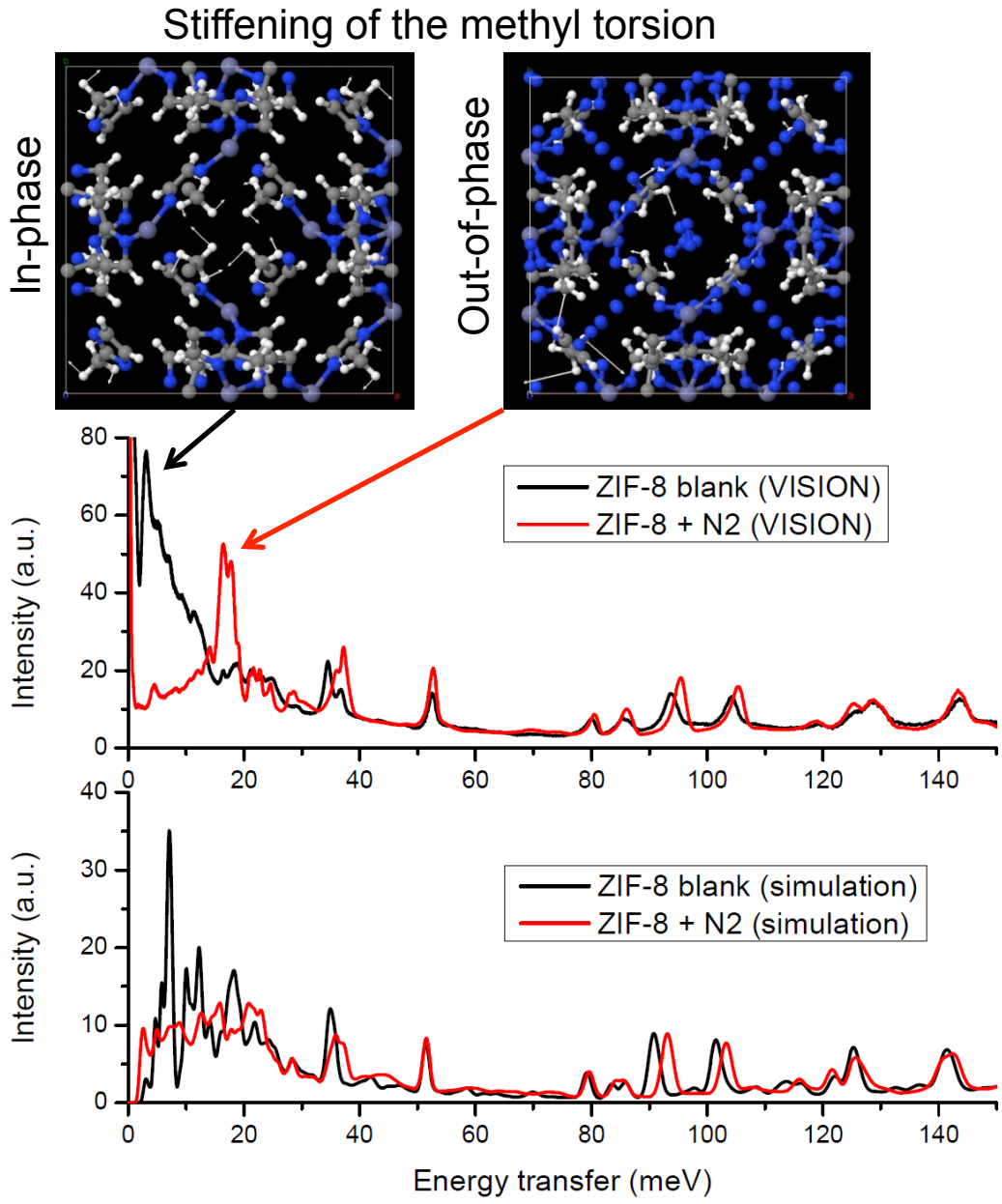
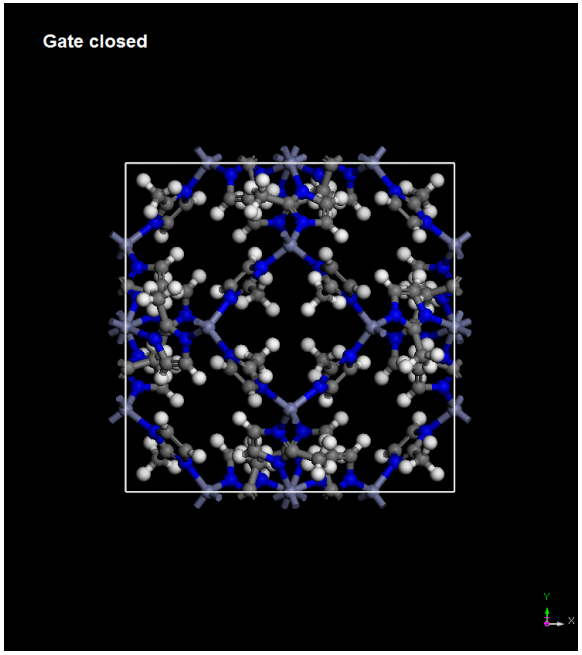
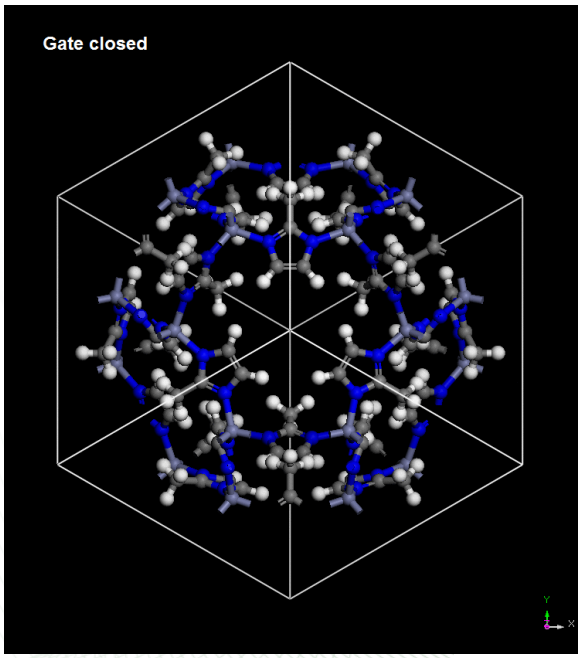
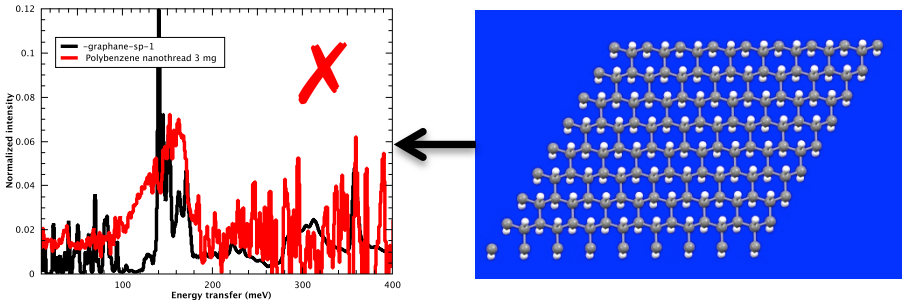
Opening the gate in a porous material: the power of INS + Modeling

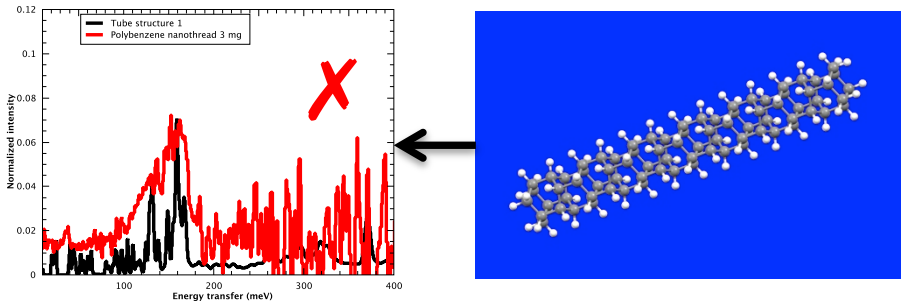


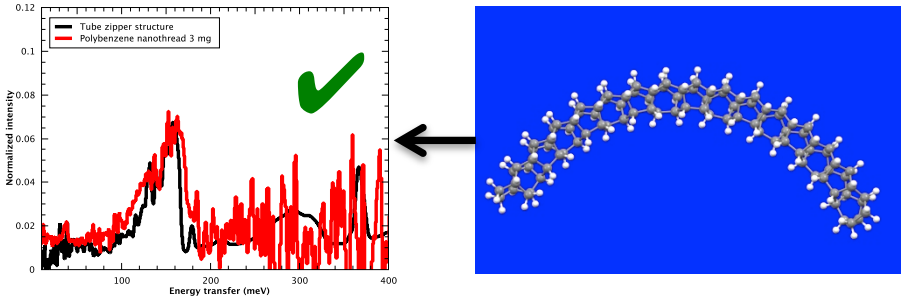




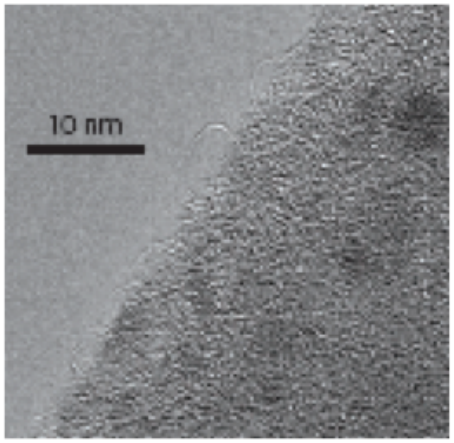
Polybenzene (nanothreads 3mg) formed at high pressure Structural inference through modeling





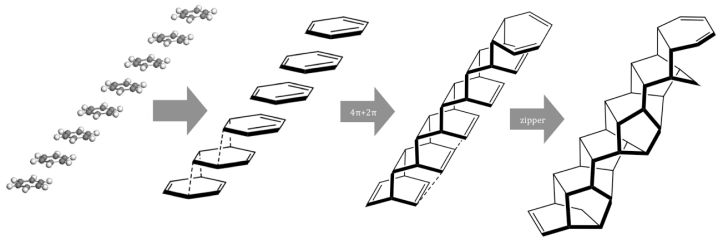


Computer modeling is vital to understand the spectra. The calculations shown here took up to 36 hours using 1024 cores.



Collaboration with Malcolm Guthrie, John Badding, Vin Crespi. Original publication on carbon nanothreads: Nature Materials, **14**, 43 (2015). Data from NOMAD, sample prepared in SNAP
There are 100 structures we filter out the ones that do not conform. Using INS to further inform the structure of the material

Compression-induced polymerized benzene. A 3 mg sample was synthesized on SNAP and measured in VISION.
Comparing the experimental data from VISION and a series of hypothetical structures that can contain sp3 carbon and the correct stoichiometry (H:C ratio 1:1) We can determine which structure correspond to the measured spectra.
We show that the mechanism of formation of the nanothreads (zipper structure) as proposed is compatible with the experimental results.



The tubular structure (highly symmetric, middle figure) does not reproduce the data so well.

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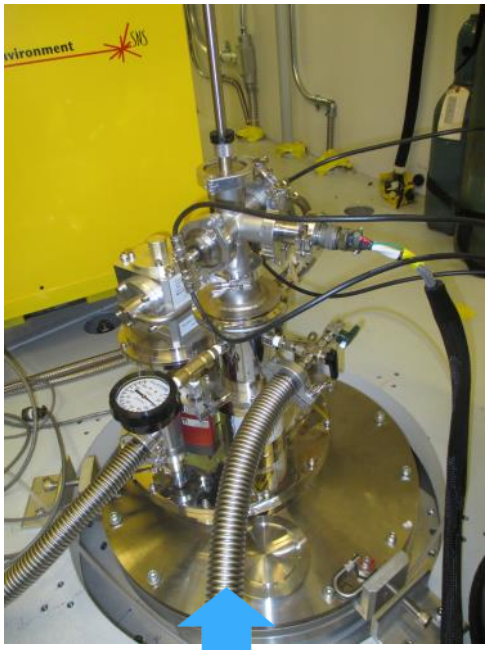
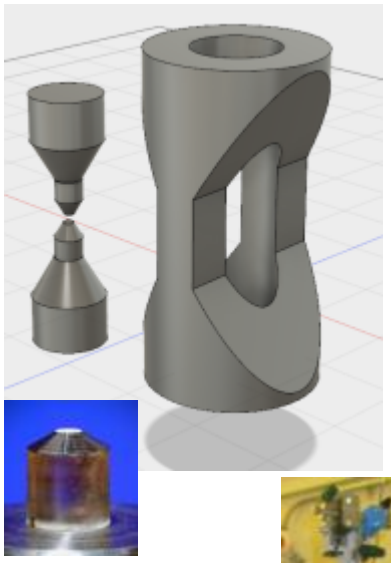
Sample environment

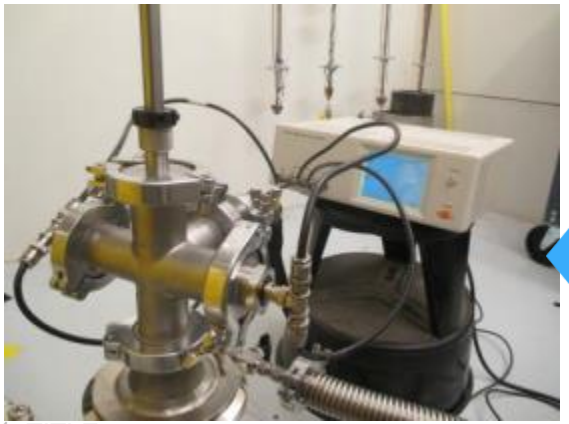


JANIS closed-cycle refrigerator (5-600K)



Pressure cells (piston, gas, diamond anvil).

Gas handling panel for gas dosing, mixing, flow, adsorption (vacuum to 200 bar)



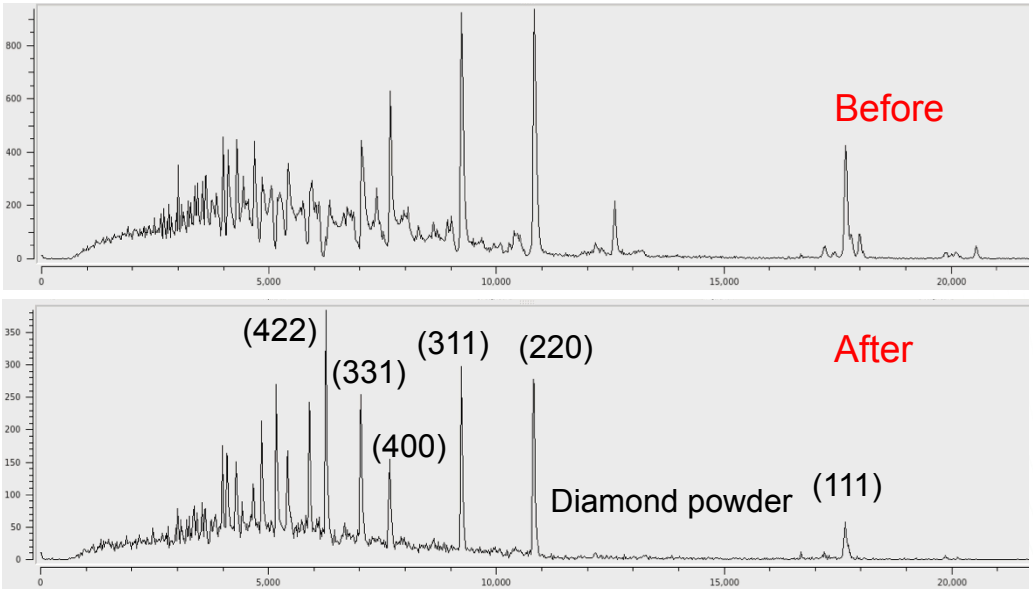
in situ electrochemical impedance spectroscopy (EIS)

ortho/para H_2 converter

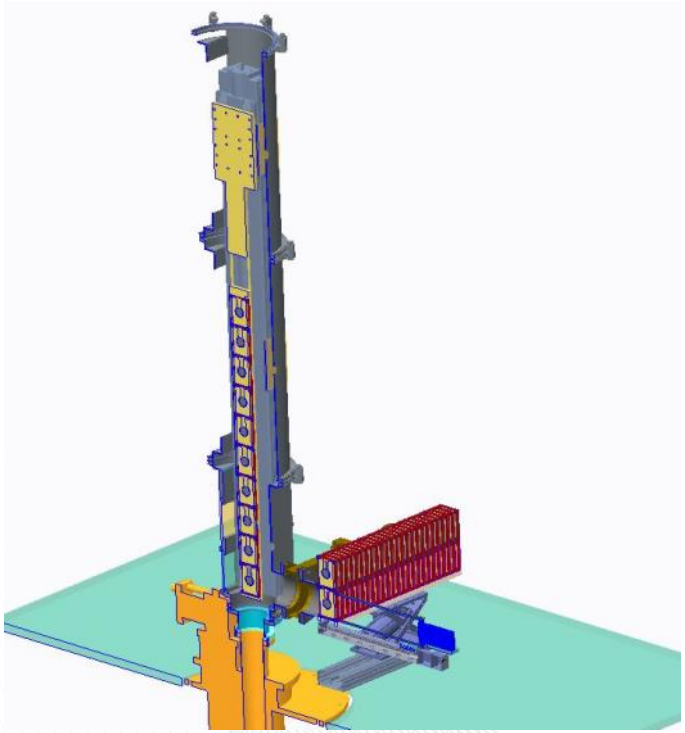
VISION Sample changer and 3D printed collimator

3D printed collimators have been tested for VISION to be used in the backscattering diffraction bank.

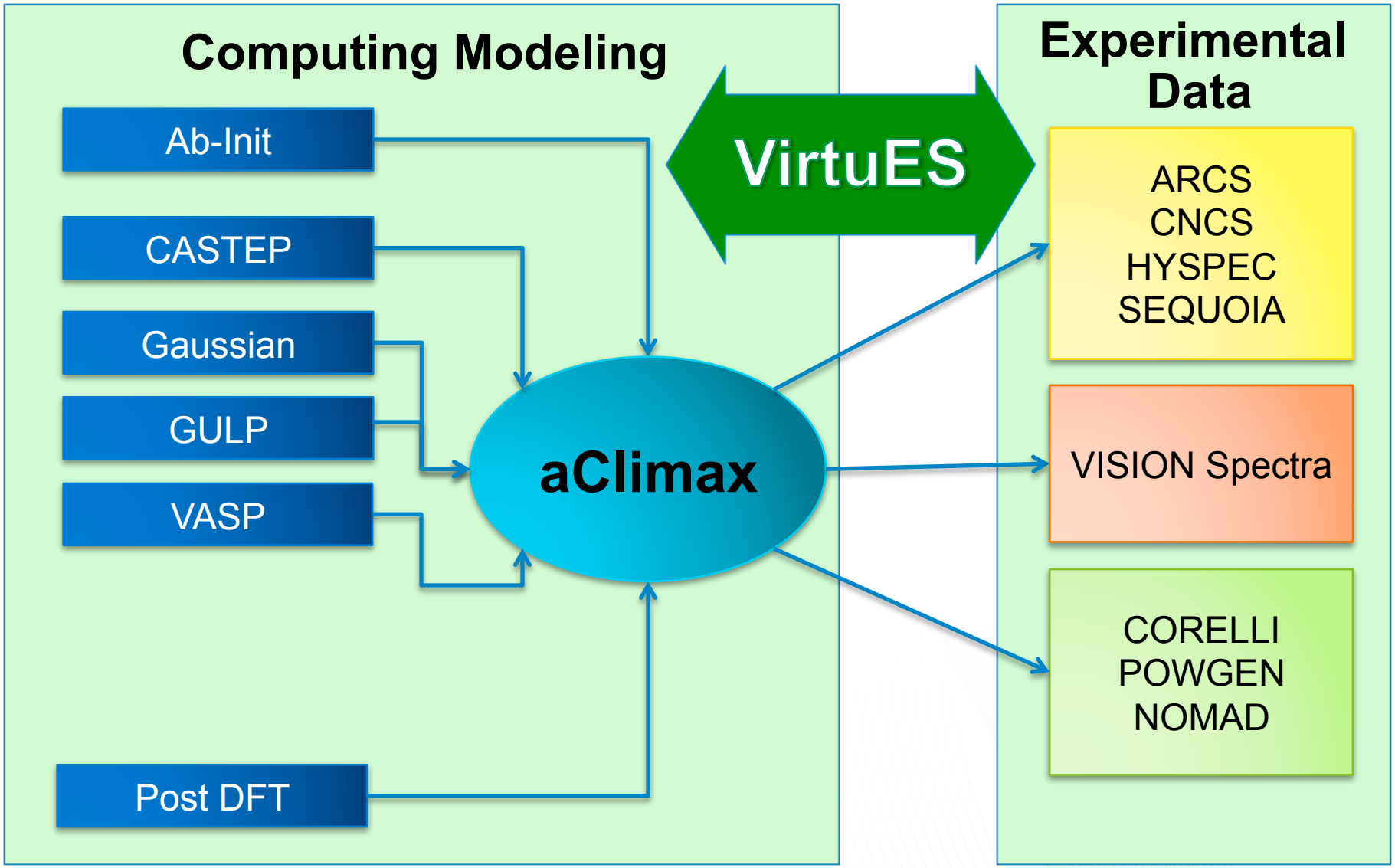
The reduction of the spurious peaks from the sample is very much noticeable.



The high throughput rate of VISION requires very rapid sample changes to make the best use of neutron beamtime and run mail-in program. A sample changer design is being finalized and will be tested December 2015



The FUTURE



INS requires DFT modeling to interpretation

Virtues (Virtual Experiments in Spectroscopy)
Computer modeling is crucial to understand and interpret INS data. The VirtuES cluster provides 2500+ cores and a number of DFT codes for VISION data analysis and interpretation. VISION is the first SNS instrument that has computer modeling as integral part of the data analysis and interpretation of the spectra.

neutrons.ornl.gov/vision

Summary slide

Areas of science

- Catalysis
- Surface chemistry
- Chemistry
- Biology
- Non-hydrogenous
- On the fly computing
- Databases
- Geoscience, hydrous minerals
- Porous materials
  - MOF's
  - Zeolites
  - Gas adsorption
  - Gas separation
  - Molecular hydrogen
- Clathrates
- Fuel cells
- Metal hydrides
- Polymers
- Small molecules
- Nano-materials
- Ionic conductors
- Energy materials
- Hydration

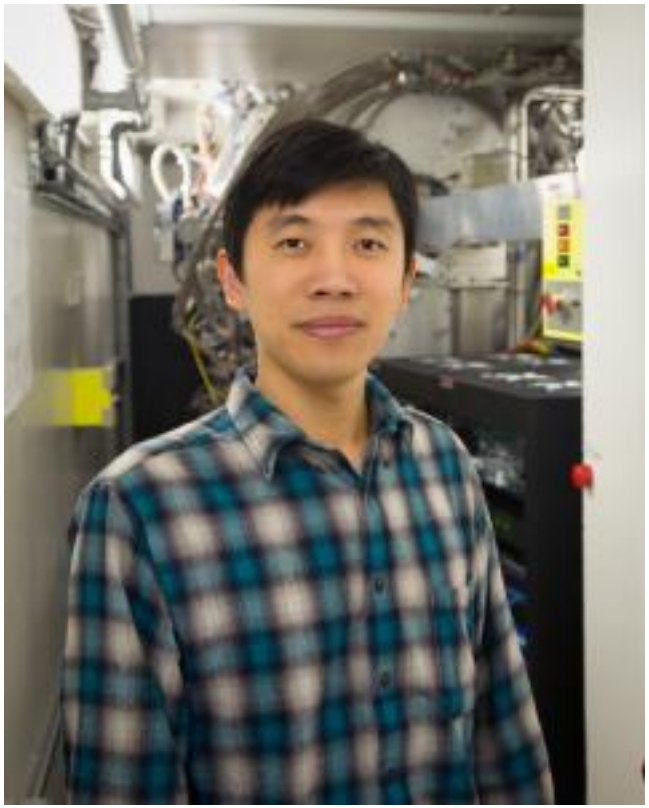
New capabilities

- Impedance spectroscopy
- Raman spectroscopy
- Sample changer
  - High throughput
  - Parametric studies
- Pressure cells
- Gas flow and gas handling
- In situ studies
- Temperature evolution
- Reaction kinetics
- Small samples (DAC)
- On-the fly DFT modeling

User base

- Not necessarily neutron savvy.
- Heavy involvement of the experimental team in the analysis and interpretation of the data

The TEAM



Yongqiang Cheng,
Instrument Scientist

Luke Daemen,
Lead Instrument Scientist

neutrons.ornl.gov/vision

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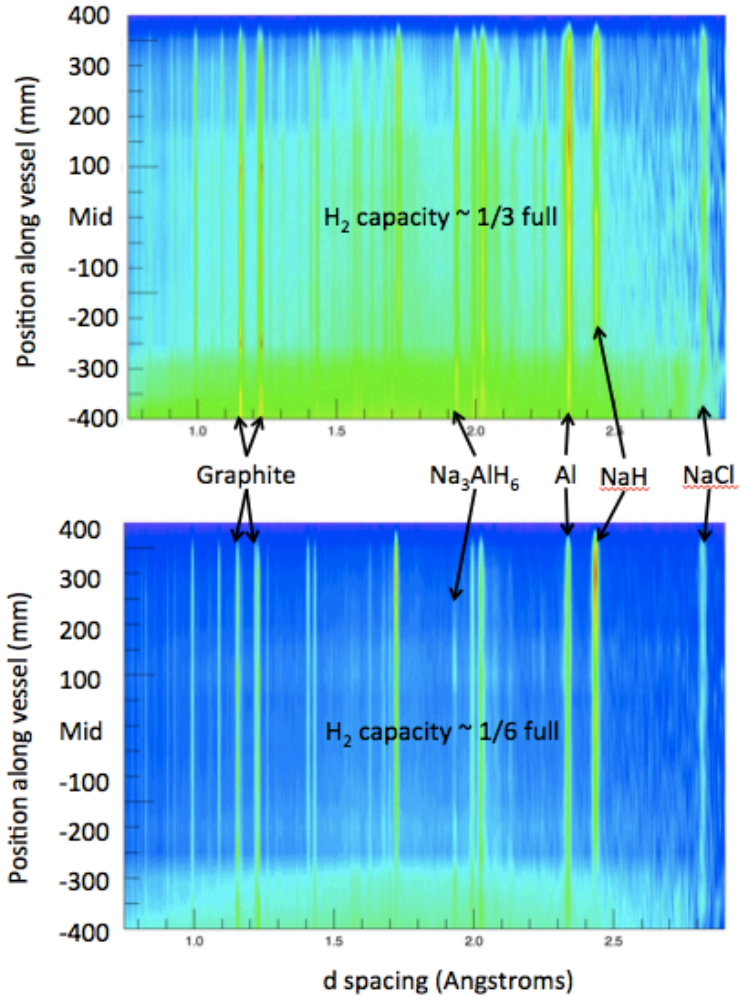
VULCAN instrument for mapping full-scale test articles

Diffraction Basics:

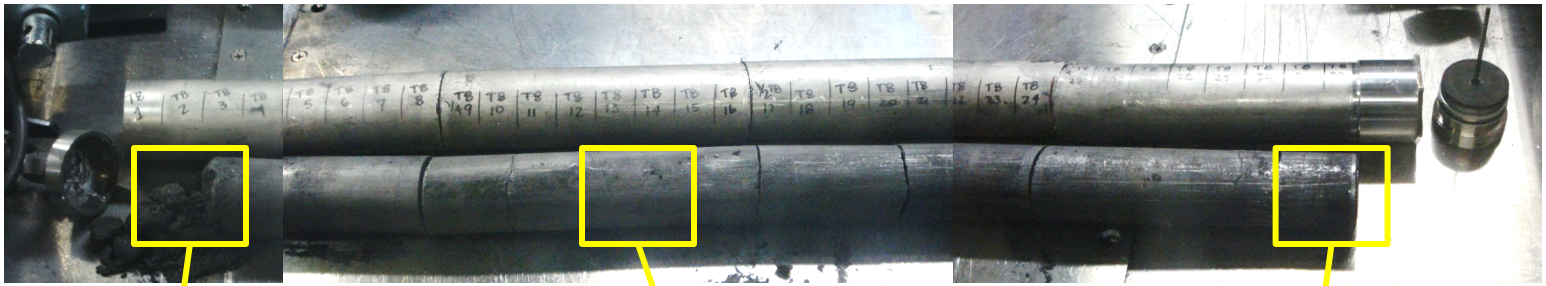
- Neutrons scatter from nuclei
- Polycrystalline materials scatter neutrons at specific angles with different intensities
- Diffraction patterns are known and can be matched to collected data
- Hydrogen is a highly attenuating and incoherent scatterer, so use deuterium
- **Vulcan:**
- High flux, time of flight neutrons
- Slits and detectors allow for range of gauge volumes (e.g., 5 x 5 x 20 mm; 3 x 3 x 20 mm)
- 4-axis stage provides X, Y, and Z travel plus rotation

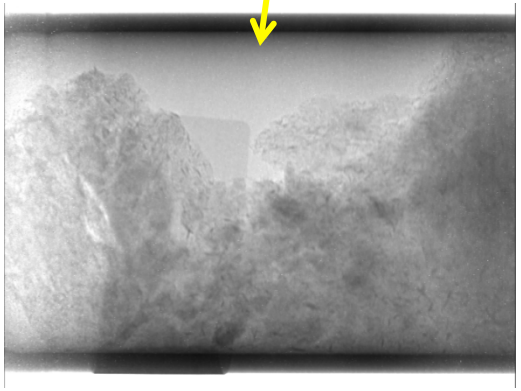
A large variation in background was observed

- Diffraction mapping shows unexpected variation along length of tube
- Possibly residual deuterium?
- Possibly residual hydrogen???

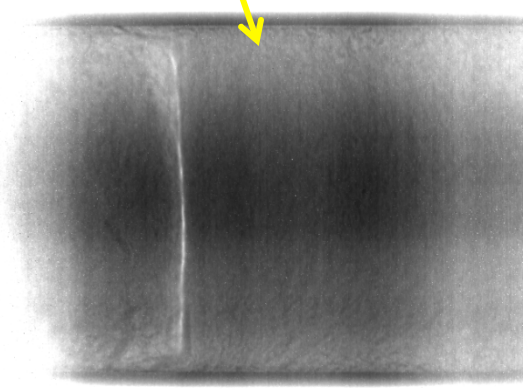


Neutron radiography revealed interesting features

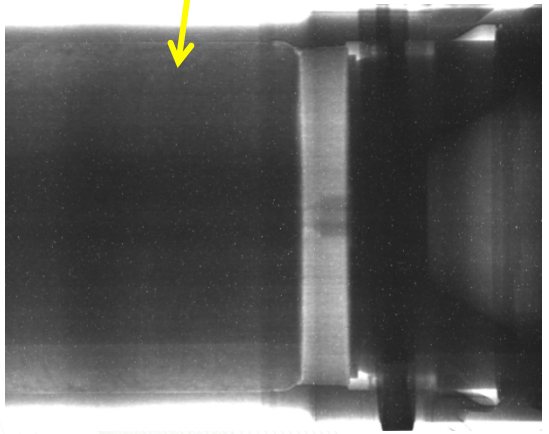




Voids



Large crack



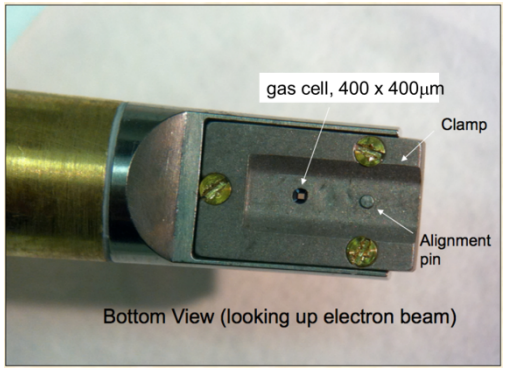
Changing H/D ratio?

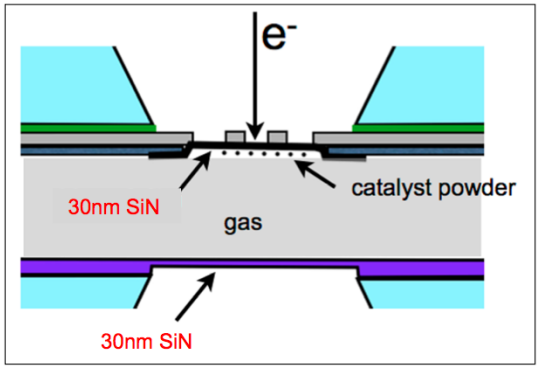
Atomic Resolution STEM Imaging and Spectroscopy

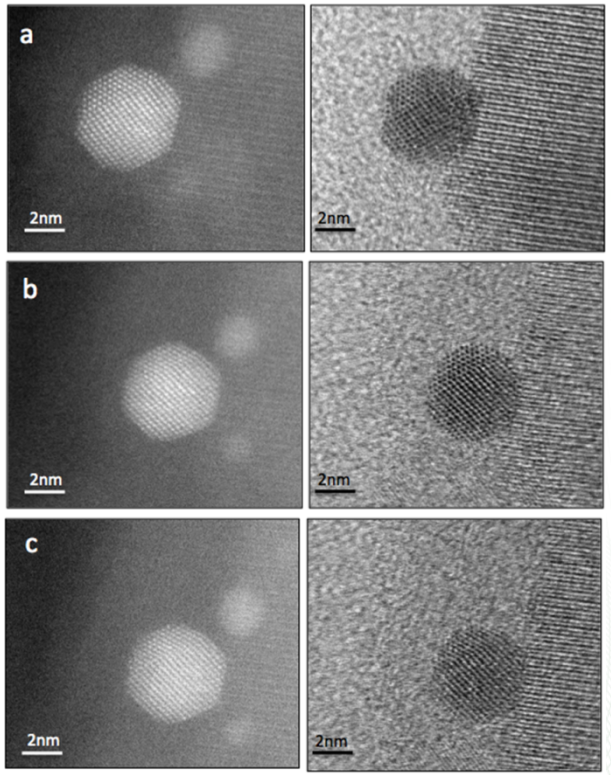
Principal Investigators:
David A. Cullen & Karen More

In Situ TEM Capabilities at ORNL

- Specialized holders allow for in-operando observations of nanomaterials in a gas or liquid environment
- Gas Cell Specifications:
  - Pressure up to 1 atm.
  - Temperature up to 1000°C
  - Atomic resolution
  - Various gases (H_2, O_2, Ar, etc.)







Atomic resolution imaging of Rh nanoparticle on perovskite support.

(a) 350°C, 0.05 Torr H_2/Ar in cell
(b) 350°C, 50 Torr H_2/Ar in cell
(c) 350°C, 730 Torr air in cell

Courtesy Larry Allard

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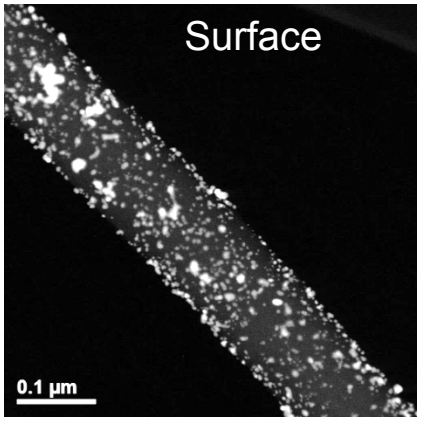
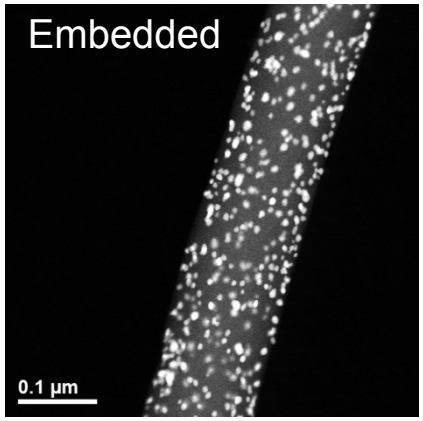
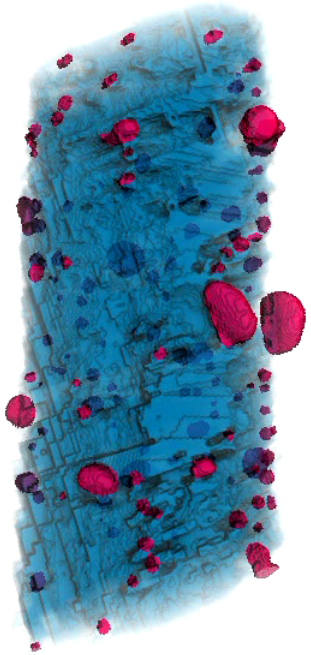
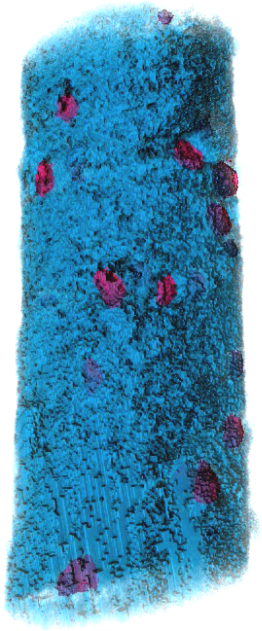
Electron Tomography Capabilities

- Electron tomography is a method for visualizing and quantifying materials in 3D at the nanoscale
- Examples:
  - Visualization of surface vs embedded Pt particles on carbon fibers
  - Nanoporous PtNi nanostructured thin films



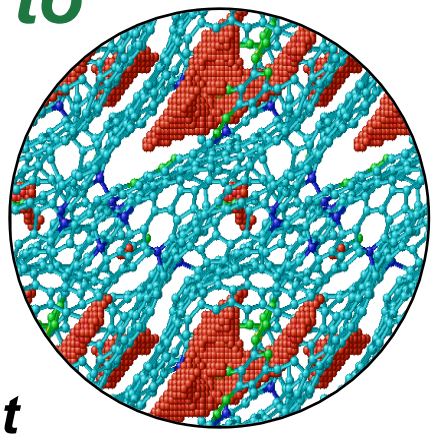






Rational design of adsorption properties

Our goal: develop & validate theory to make this a high-throughput "screening" process!



- *"Genomics" approach to gas adsorption*
- *Not zero temperature limits of ideal systems:* ***predicting microstructure-dependent behavior at finite temperatures and pressures.***
- *Rapid, accurate predictive capability over different systems*
- *Contribute to scientific impact of new neutron scattering capabilities*
- *Close interplay of theory and experiment (beyond "fitting models")*

Framework of prediction scheme:

Givens:
- Adsorbent material
- Adsorbate molecule
- Surface / pore geometry

Map out potential energy surface of molecule on adsorbent
- Not just optimal binding sites, but full map of binding
- Non-empirical methods (electronic structure)
- Capable of handling weak interactions

Given potential energy surface, compute binding at a specific applied pressure and temperature

Outputs:
- Uptake & heats of adsorption
- Position-dependent adsorbate densities
- Optimal pore size / shape / chemistry

Three main pieces to the puzzle:

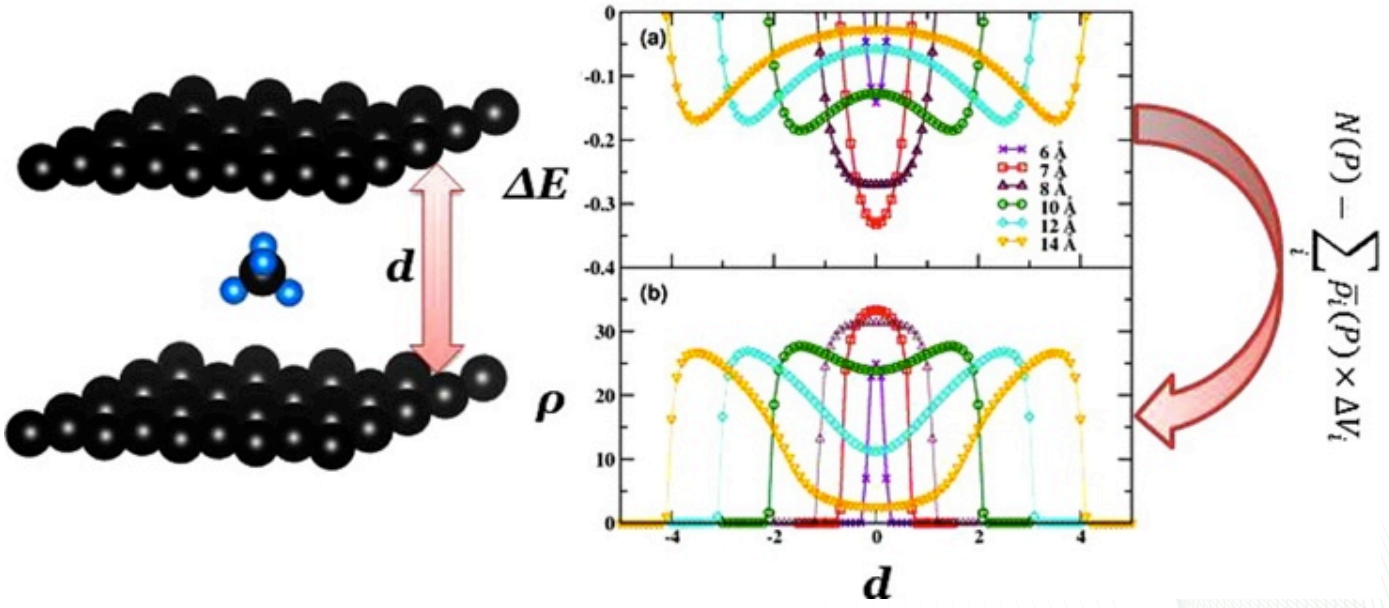
- **Recent improvements to electronic structure methods for accurately treating weak interactions in extended systems (van der Waals density functional theory)**
  - Faster than quantum chemistry with comparable accuracy
- **Continuum methods for rapidly & accurately calculating adsorbate densities from interactions**
  - 100-1000x faster than atomic simulation *without empirical potentials*
- Small angle neutron scattering (SANS) probes of adsorption in small pores (>1-3 nm)
  - New approaches provide capabilities to rapidly characterize nanopores

Initial successes in these separate areas presents a key opportunity for a combined, broader attack.

Detailed comparison with both macroscopic and microscopic experimental probes

- **Macroscopic: Uptake, heats of adsorption**
- **Microscopic: uptake in different pore sizes, at different surfaces / surface preparations**

Example for Gas Adsorption: Accurate Predictions of Methane Uptake in Nanoporous Carbons

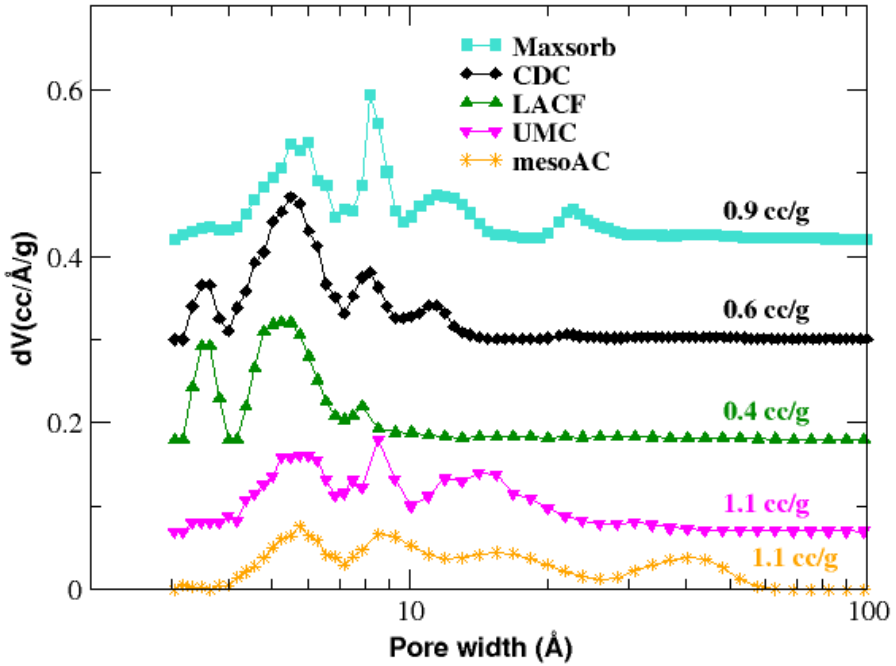


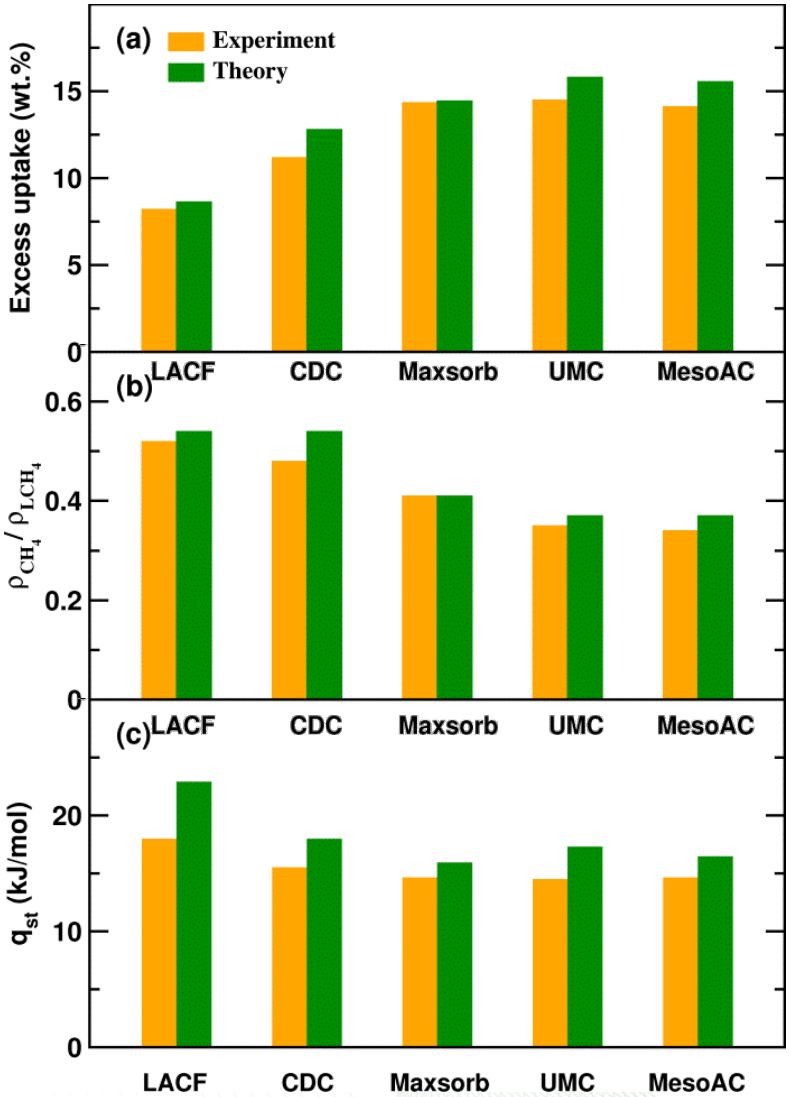
Y. Ihm, et al., J. Chem. Theory Comput. **10** (2014) pp 1–4

Experimentally validated predictions for a variety of porous carbon materials

Ihm et al., *JCTC* (2014)

- Predictions for CH_4 adsorption at T=298 K, 20 bar are consistent with theory
- Pore size distribution must be accounted for directly.
- Higher heat of adsorption *does not result in higher uptake.*
- *No simulation!* Direct calculation of properties





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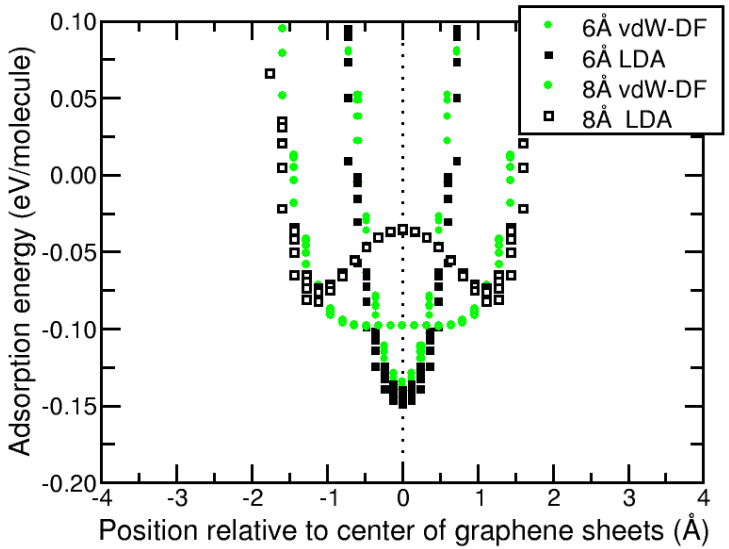
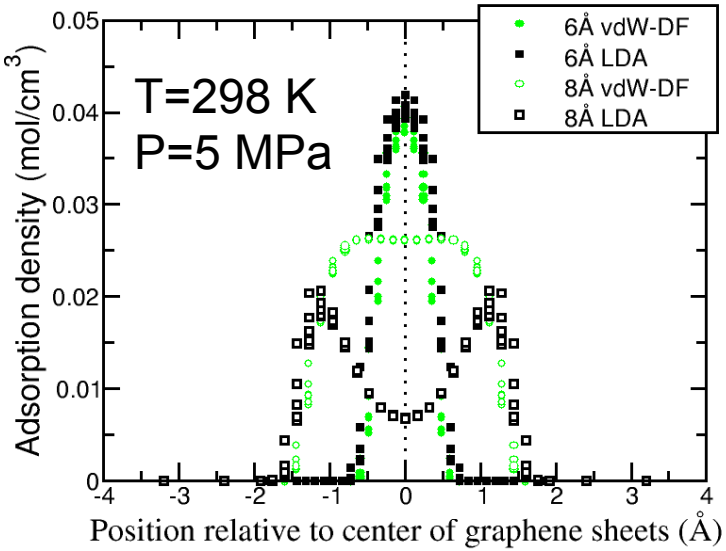
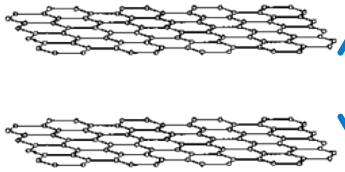
Example: H_2 in carbon nanopores





- Interaction of H_2 in 'slit pore' between graphene sheets
- LDA, vdW-DF calculations similar at 6 **Å, quite different at 8** Å

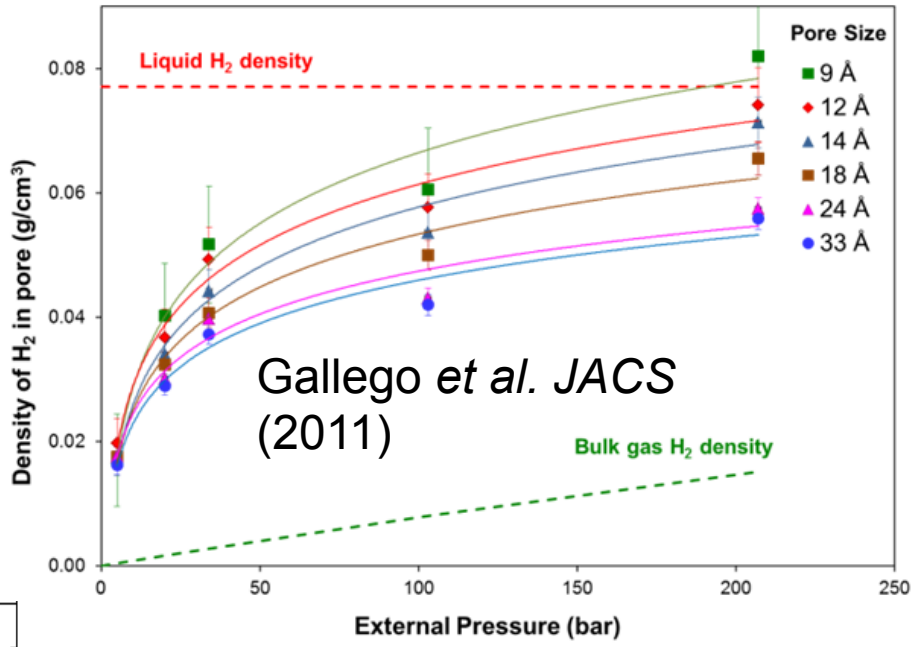


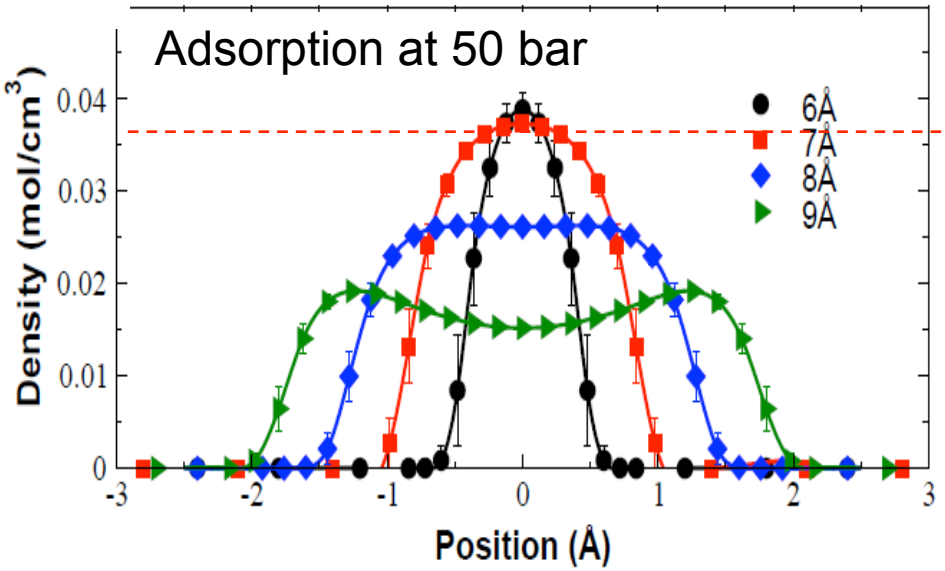
Model pore with controlled "spacing"

- Resultant adsorption at P=5 MPa, T=298 K show significantly increased adsorption for 8 Å separation
- **Used to require significant simulation time to calculate these properties**
- Ihm, et al., *J. Phys. C 24 (2012) 424205*

Experimental validation for H_2 with pore-size dependent adsorption from SANS studies

- ✓ Small angle neutron studies allow us to probe adsorption for different pore sizes.
- ✓ First demonstration of liquid H_2 densities at ambient temperatures.
- ✓ Consistent with our theoretical predictions





Ihm, et al., J. Phys. C 24 (2012) 424205

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Singular Capabilities at ORNL for Evaluating & Characterizing Hydrogen Storage Materials

How can we help?