Neutron Characterization of Carbon-Based Materials

carried out in the

DOE Center of Excellence on Carbon-based Hydrogen Storage Materials

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May 23th 2005

This presentation does not contain any proprietary or confidential information

STP33

Overview

Timeline

- Project start date: FY05
- Project end date: FY09
- New Start

Budget

- Total project funding
  - 100 % DOE
- FY05 $ 130k

Barriers

- Barriers addressed
  - Towards the Understanding of Hydrogen Physisorption and Chemisorption.

Partners

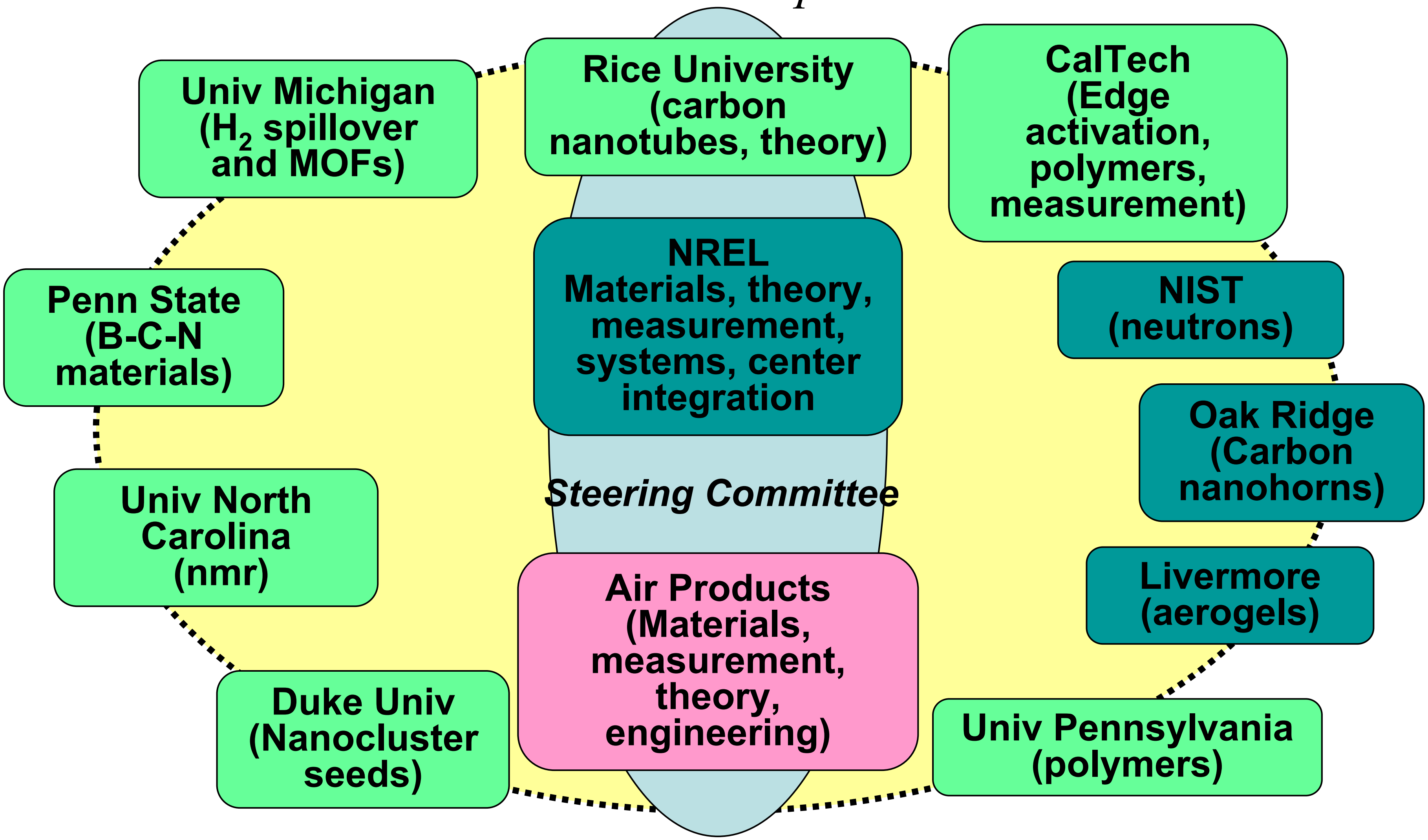
- -Carbon center

Objectives

- To achieve the required level of hydrogen storage in a timely manner, it is imperative that trial-and-error testing of materials be avoided. Thus the focus must be upon the rational design of new systems. From a thorough understanding of the physics and chemistry that governs the hydrogen-substrate interactions, we will be able to make a more concerted effort to push the frontiers of new materials.

CbHS Center of Excellence Partners

9 university projects (at 7 universities), 4 government labs, 1 industrial partner



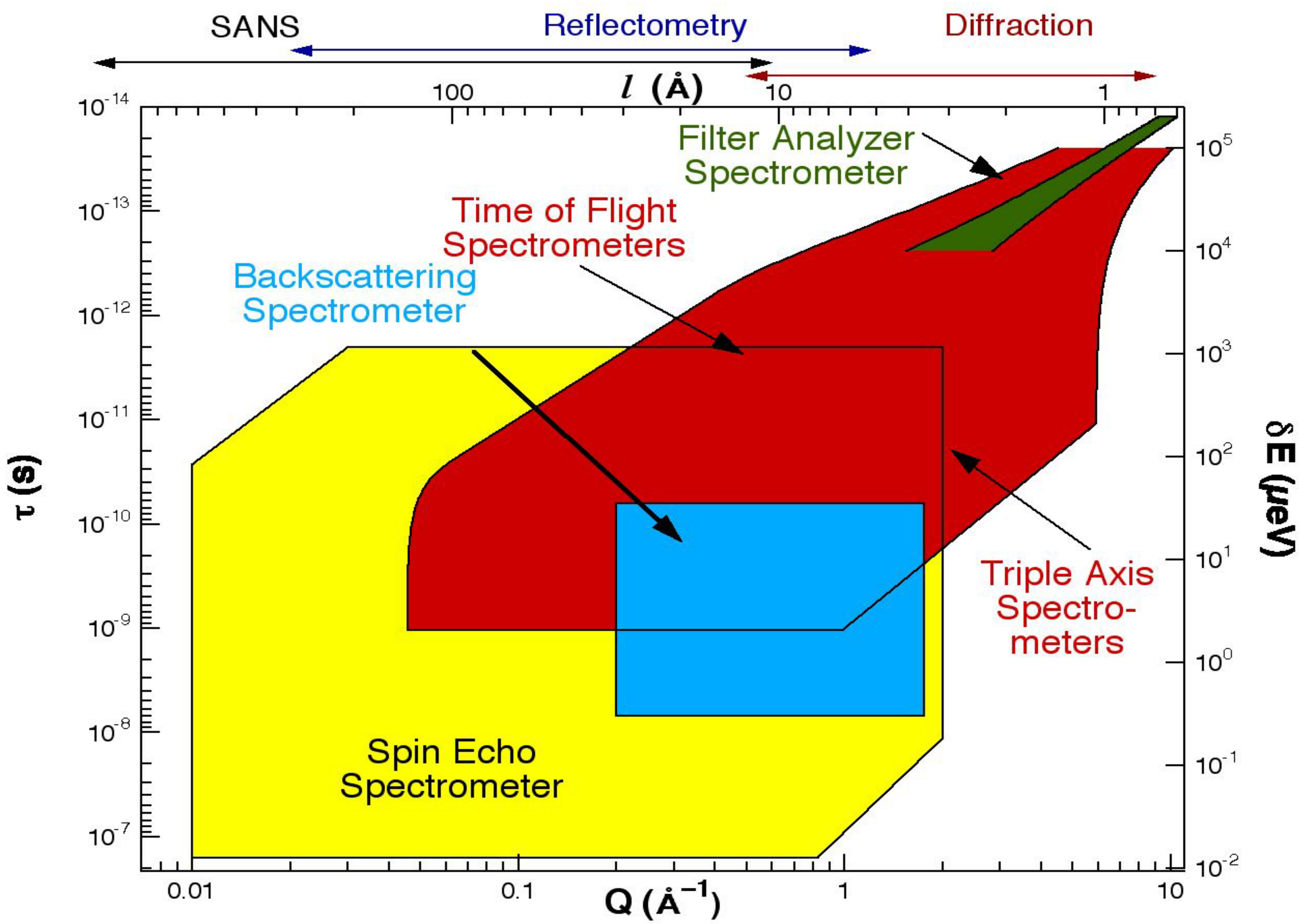
Objectives

- We will perform measurements on the wide variety of samples produced by other members of the center and will initiate comparisons of the adsorption mechanisms and interaction strengths of hydrogen in various carbon materials leading to a more detailed atomic and nanoscale understanding of the adsorption mechanisms.

Approach

- neutron scattering will be used to address the following questions:
- **Where is the hydrogen?**
- **Is the hydrogen atomic or molecularly adsorbed?**
- **Can we identify adsorption sites and activation barriers?**
- **What are the diffusion mechanisms?**
- **How is the substrate influenced upon adsorption?**
- **Do sorption processes change as the system lengthscale decreases to the nanoscale?**
- **Does manipulating the host electronic structure change these processes?**

Approach

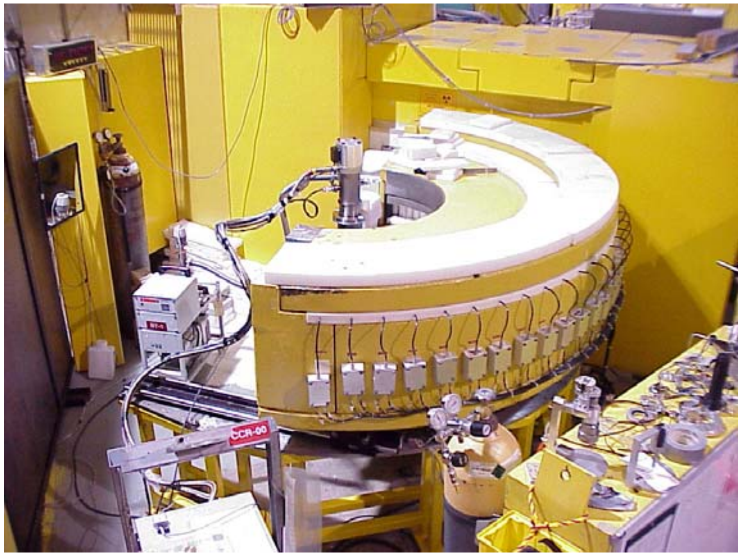


SANS
Reflectometry
Diffraction
l (Å)
100
10
1
10^{-14}
10^{-13}
10^{-12}
10^{-11}
10^{-10}
10^{-9}
10^{-8}
10^{-7}
τ (s)
10^{5}
10^{4}
10^{3}
10^{2}
10^{1}
10^{0}
10^{-1}
10^{-2}
δE (μeV)
0.01
0.1
1
10
Q (Å^{-1})
Filter Analyzer Spectrometer
Time of Flight Spectrometers
Backscattering Spectrometer
Triple Axis Spectro- meters
Spin Echo Spectrometer

Approach

Where is the hydrogen?

Neutron Powder Diffraction



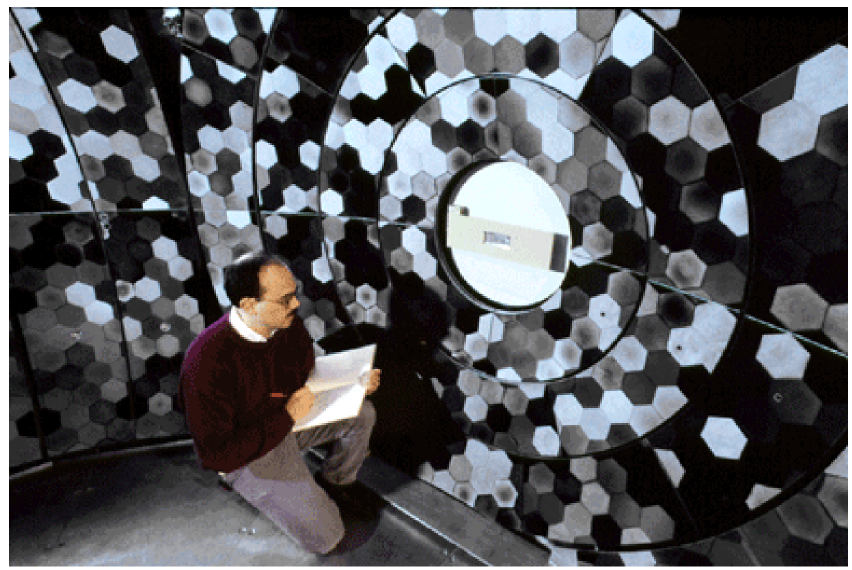
Small Angle Neutron Scattering

Approach

- Is the hydrogen atomic or molecularly adsorbed?
- Can we identify adsorption sites and activation barriers?
- What are the diffusion mechanisms?

Neutron Vibrational Spectroscopy

Time-of-Flight Spectroscopy

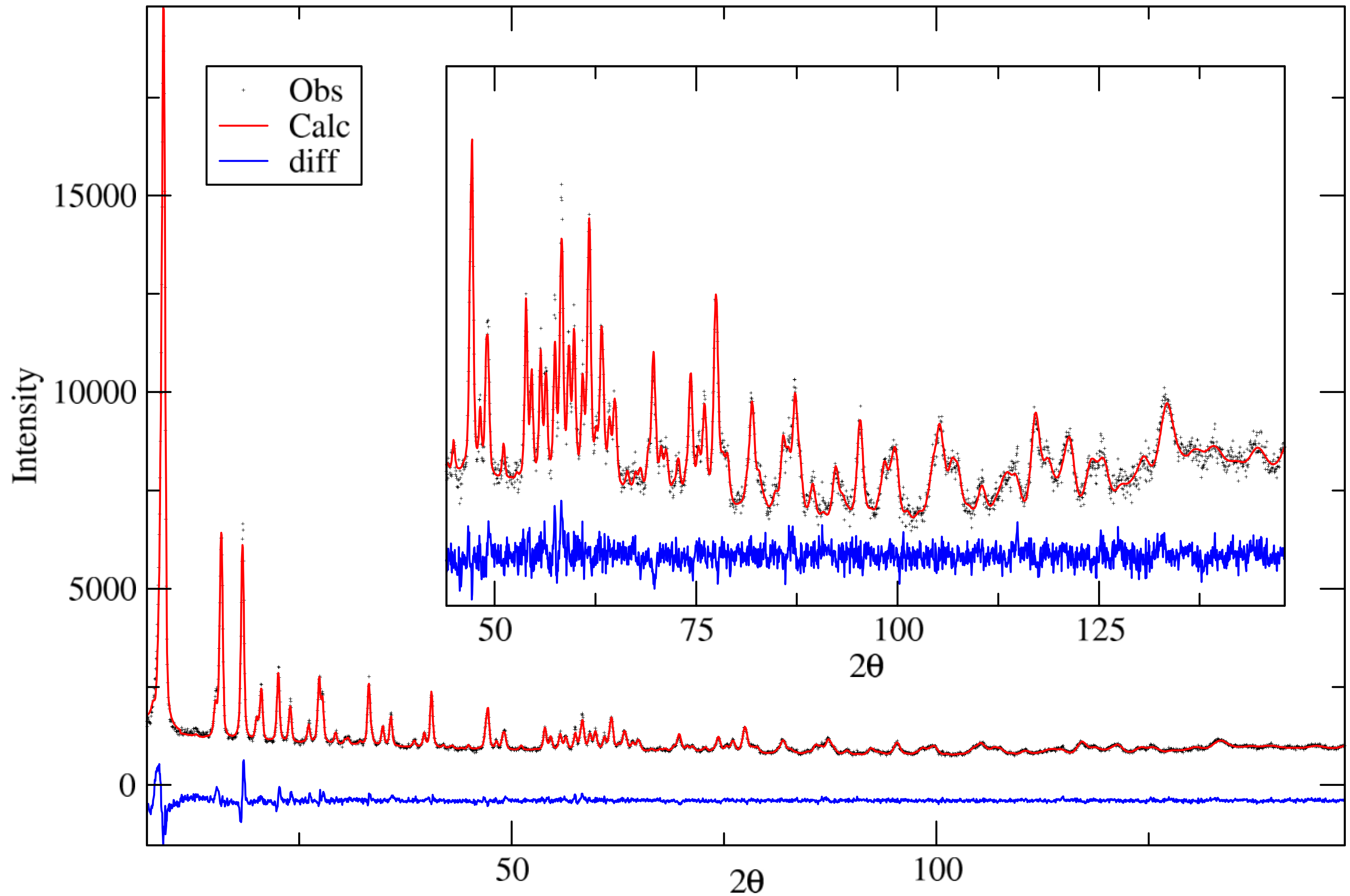


Neutron Backscattering Spectroscopy

Technical Accomplishments/ Progress/Results

- Synthesis and structural characterization of the metal-organic MOF-5.
- Simple, high-yield synthesis
- On route to quantifying adsorbed hydrogen amounts, location and binding strengths
  - using crystallography, isotherms and spectroscopy

MOF-5 DEUTERATED



Refinement Results

Neutron wavelength = 2.0787 Å

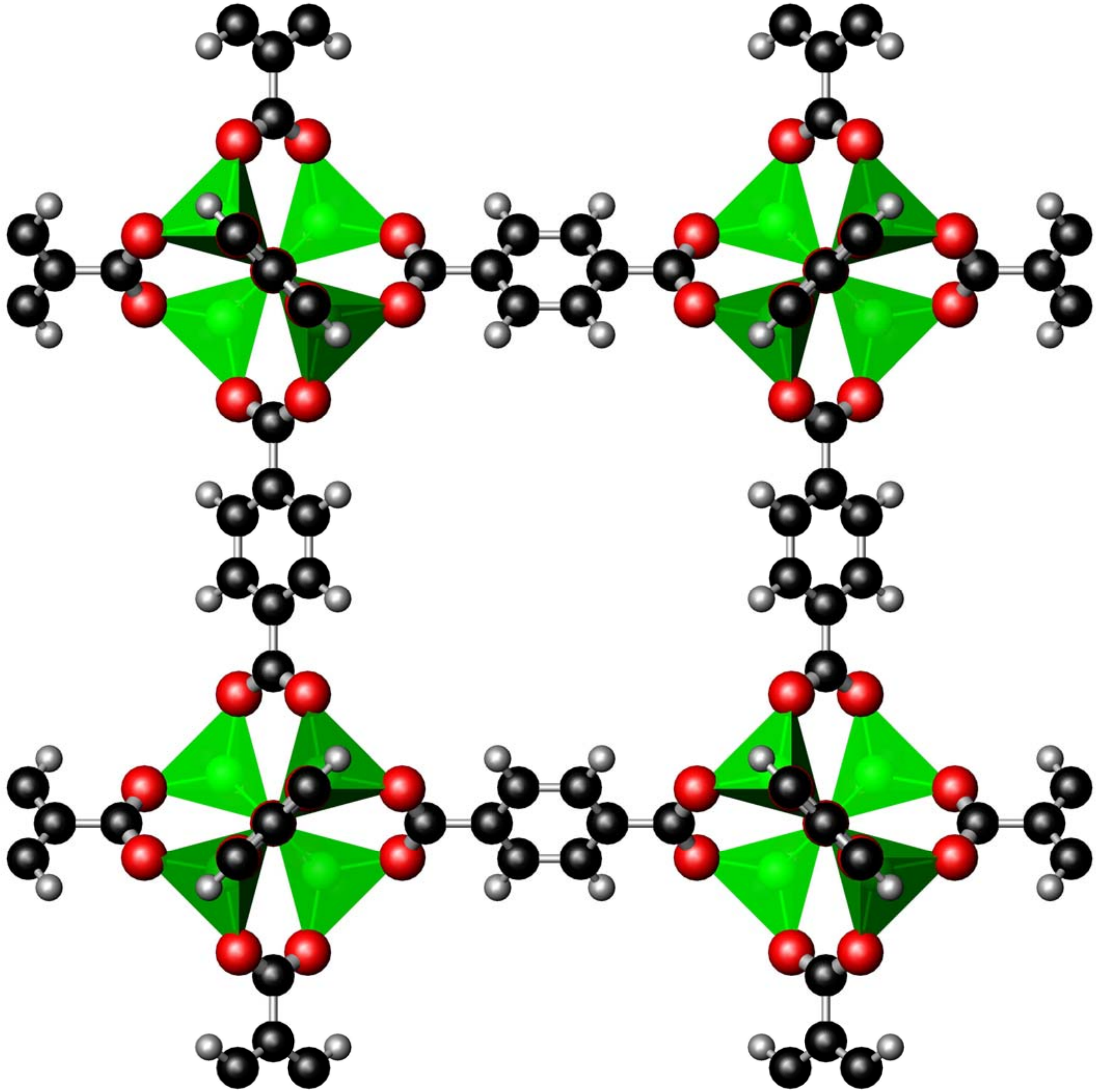
a=25.8847(7) Å

Cell volume=17343.2(15)

Symmetry Fm-3m

R_f = 0.0351

Atom	x	y	z	Uiso
Zn	0.29382 (29)	0.20618 (29)	0.20618 (29)	0.015 (5)
O	0.25	0.25	0.25	0.015 (7)
O	0.28108 (19)	0.21892 (19)	0.13336 (25)	0.0090 (20)
O	0.25	0.25	0.1124 (4)	0.0098 (26)
C	0.25	0.25	0.05246 (33)	0.0049 (25)
C	0.28221 (18)	0.21779 (18)	0.02812 (26)	0.0114 (16)
D	0.30828 (20)	0.19172 (20)	0.04708 (30)	0.0175 (21)



Future Work

- Remainder FY05
  - The characterization of hydrogen-substrate interactions in metal-organic framework compounds using inelastic neutron scattering and powder diffraction. Correlate rotational hindering potentials to useful hydrogen storage characteristics and supply theorists with physical data that can be used to validate models of the various interactions of hydrogen and metal/organic linkers.
  - Measurements of hydrogen diffusion using quasielastic neutron scattering.

Future Work

- FY06
  - Characterization of the adsorption site interaction potential that the hydrogen experiences on the best candidate materials from MOF’s, nanohorns (closed, opened and doped), aerogels and well-characterized nanotubes from the relevant synthesis groups.
  - Perform neutron inelastic scattering experiments to identify molecular hydrogen (from tunneling spectra) and/or atomic hydrogen (from vibrational spectra). Samples include graphitic nanofibers, candidates for spillover studies and the wide variety of doped samples that will be produced by members of the center.

Hydrogen Safety

The most significant hydrogen hazard associated with this project is:

Total release of hydrogen from a gas cylinder while in the reactor confinement building. Not only is the space confined (asphyxiation), but also stratification of hydrogen at the ceiling could push its concentration beyond the flammability point. The ignition energy of a hydrogen/air mixture can be as low as 20 micro-joules making this extremely dangerous in an area of multiple sources of electronic ignition.

Hydrogen Safety

Our approach to deal with this hazard is to limit the total volume of hydrogen in the confinement building and monitor for hydrogen concentration. Specifically:

1) Gas cylinders are not allowed into the confinement building.

-Use small portable gas loading systems or hydrogen generators.

2) The total releasable hydrogen cannot exceed 100 liters (STP, ~ 4.1 moles) or around 10% of the flammability limit.

-for the practical purposes of hydrogen storage experiments on gram quantities of samples, this is not a hindrance. Future experiments on operating fuel cells will need to be redesigned to accommodate this requirement with hydrogen gas sensors at the ceiling and possible external exhaust systems.

3) Reduce the risk of actual leaks following OSHA 1910.03 guidelines.

-Piping, tubing, and fittings for hydrogen delivery shall be suitable for hydrogen service and for the pressures and temperatures involved. Valves, gauges, regulators, and other accessories shall be suitable for hydrogen service.

4) Monitoring of hydrogen concentration in the confinement building is mandatory.

5) Hydrogen venting/release should take place outside of the confinement building