Miami University/NREL DoD/DLA Project

High throughput combinatorial screening of biomimetic metal-organic materials for military hydrogen-storage applications

Philip Parilla - *NREL*

Joe Zhou, Dan Zhao - *Miami U, Ohio*

Jeff Blackburn, Kevin O'Neill, Lin Simpson, Mike Heben - *NREL*

Outline

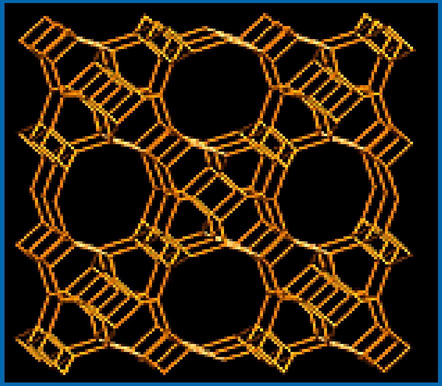
- Miami/NREL Project
  - Synthesis (Miami)
  - High Throughput Characterization (NREL)
  - Other Characterization
- Other High Throughput Activities (NREL)
  - Parallel Sieverts
  - Parallel Gravimetric
- Final Comments

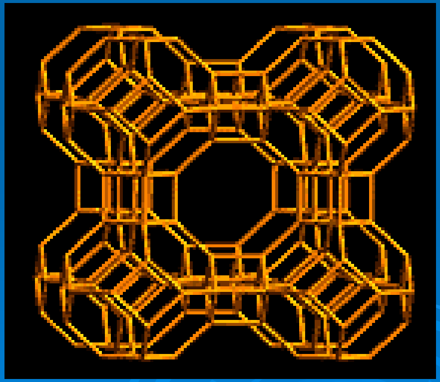
Overview of Miami/NREL Project

- Goals
  - Development of H_2 storage materials based on MOFs, targeting 15 kJ/mole binding energy and high density of H_2 sites
  - Development of optical-based detection of adsorbed H_2 allowing rapid screening of samples
- Approach
  - Combinatorial MOFs synthesis involving 8 transition-metal-based secondary building units (SBUs) and 18 carboxylate linkers

Metal-Organic Frameworks (MOFs)

- Crystalline inorganic-organic hybrids
- Zeolite-like networks
- Desirable characteristics:
  - porosity
  - chirality
  - gas sorption / storage
  - selective adsorption / ion exchange
  - fluorescence
  - magnetic susceptibility
  - optical properties
- Great variety of topologies and network types possible

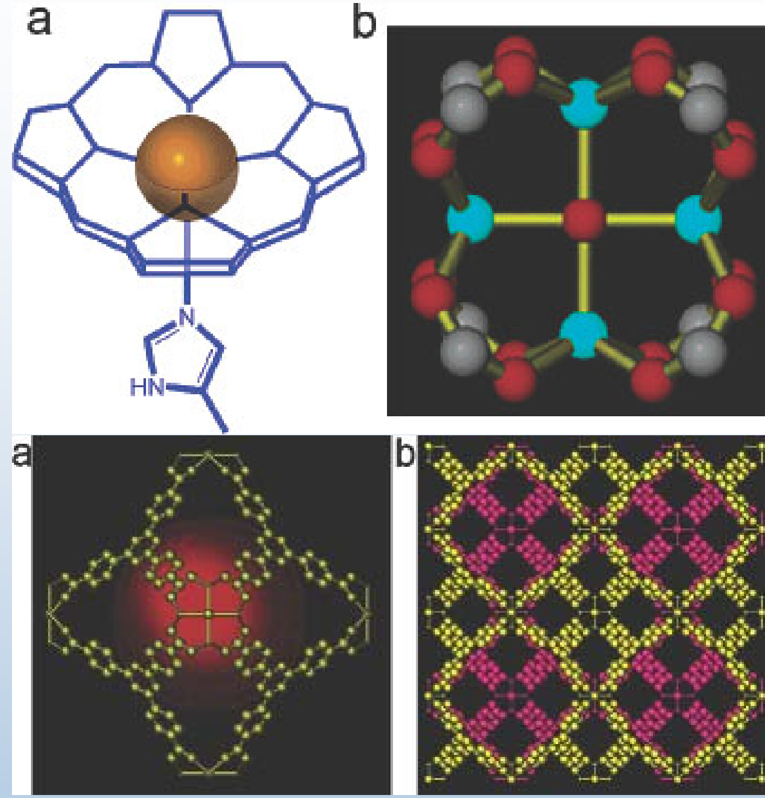


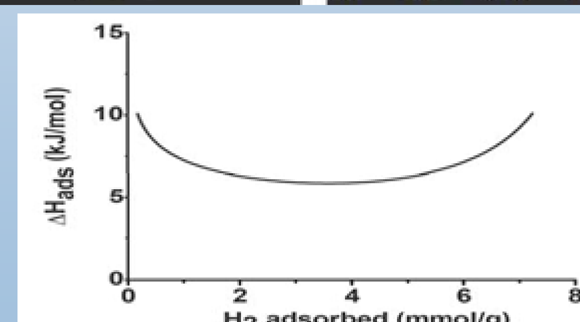


Zhou *et al, Eur. J. Chem.* **2006**; Zhou *et al*, *Chem. Commun*. **2005.**

Metal Coordination & H_2 Binding

- Goal is to put metal into an *entatic* state which could enhance H_2 binding
- Entatic states often found in biological systems, eg., hemoglobin
- PCN-9 system shows high (ΔH~10 kJ/mole) H_2 binding (77 K)





S. Ma and H.-C. Zhou, JACS **128**, 11734 (2006)

A Practical Approach for High Throughput/Combinatorial Screening of Hydrogen-storage MOFs

- Reagents:

  18 ligands + 8 metals + a number of solvents + a series of reaction temperatures

- Reactions:

  3*8 reaction rack to run solvothermal reactions

- Screening:

  Optical method to screen the products for hydrogen storage

MOFs Compositional Space

V^{3+}

Cr^{3+}

Mn^{2+}

Fe^{2+}

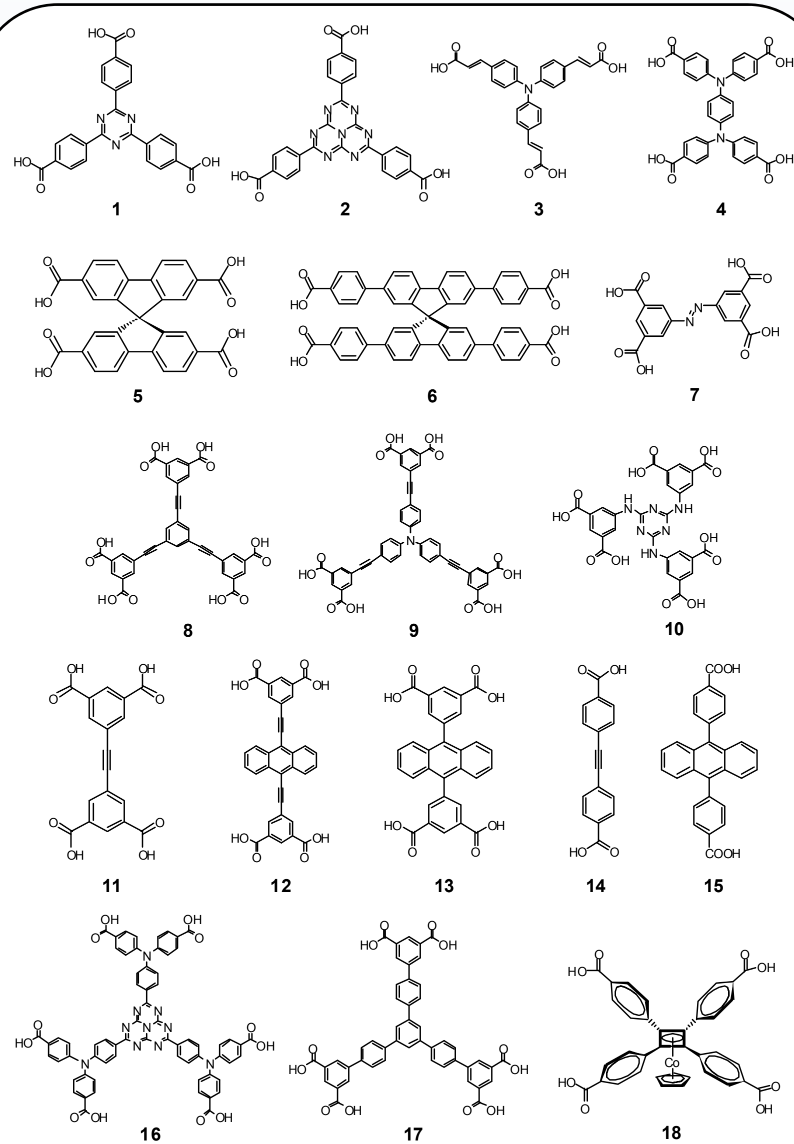
Co^{2+}

Ni^{2+}

Cu^{2+}

SBU metal ions

×



Carboxylate linkers

×

□

Ni

Pd

Pt

bare metal

Vibrational Spectroscopy of Hydrogen

Raman

•H_2 in gas phase is Raman active due to large polarizability

•Vibration-rotation spectrum:

- •Q branch: $\Delta\nu = +1, \Delta J = 0$
- •S branch: $\Delta\nu = +1, \Delta J = 2$

•Spin information:

- •Ortho H_2 – spins parallel, $J = 1$ $(Q(J) = Q(1))$
- •Para H_2 – spins paired, $J = 0$ $(Q(J) = Q(0))$

•Strength of adsorption inferred from shifts relative to gas-phase H_2

- •Because of overlap with gas-phase peak, deconvolution often needed

Infrared

•Homo-nuclear diatomic molecules, e.g. gas-phase H_2 are IR-inactive

•IR absorption induced by inter-molecular interactions

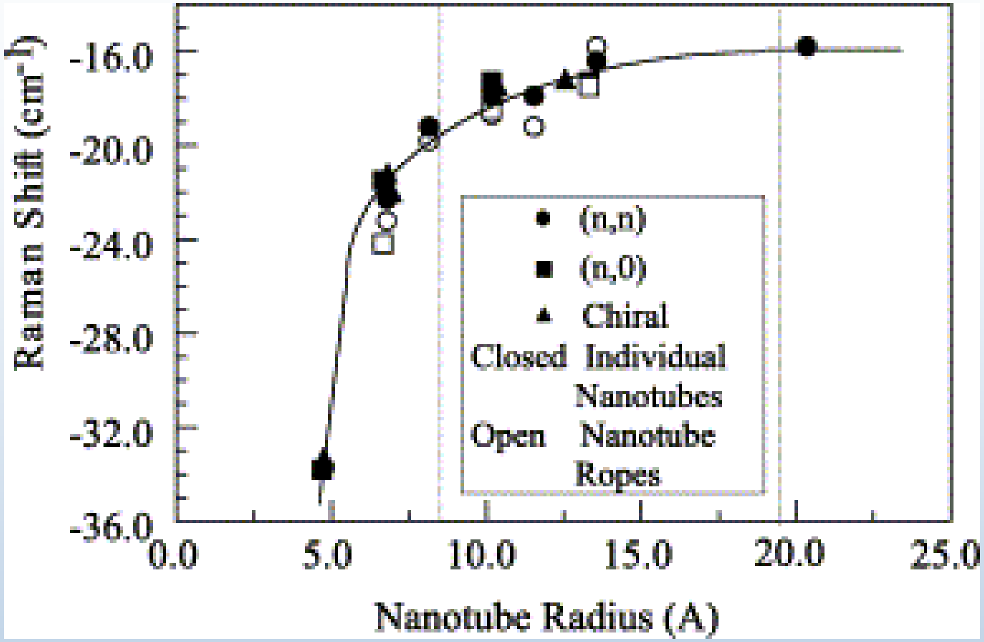
- •Collision-induced (high P or near T_c)
- •Adsorbent interactions create a bond dipole

•ΔE_{ad} from shifts relative to H_2 gas

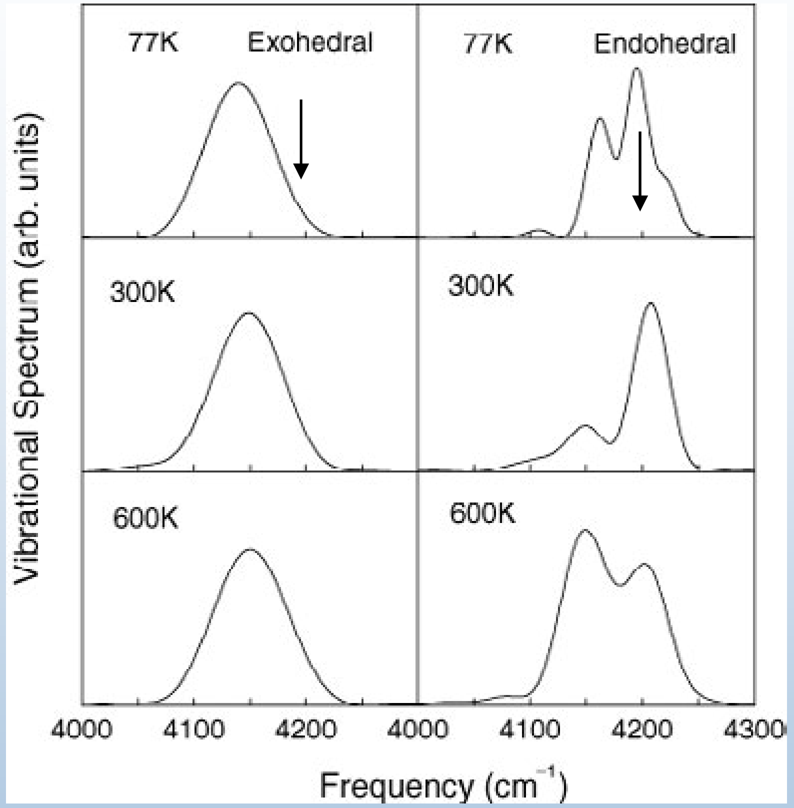
- •Because no gas peak, no deconvolution necessary
- •Metal sites, carbon sites, Lewis sites, etc. give well-separated shifts

Theoretical Raman Shifts for H_2 on SWNTs

endohedral



= predicted gas-phase shift



Chem. Phys. Lett. **334**, 18 (2001)

New Jour. Phys. **5**, 124 (2003)

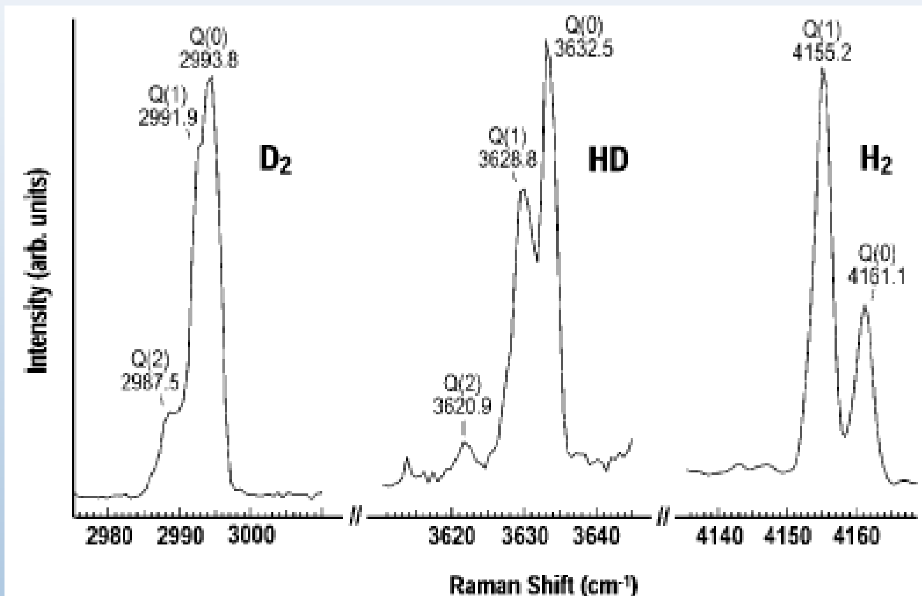
- Predict fairly large (16 – 50 cm^{-1}) red-shifts upon adsorption
- Can be complex, depending on exact adsorption environment
- Partial charge transfer weakens H-H bond, ⇒ red-shift
- Are such strong interactions seen experimentally?

VOLUME 88, NUMBER 16 PHYSICAL REVIEW LETTERS 22 APRIL 2002

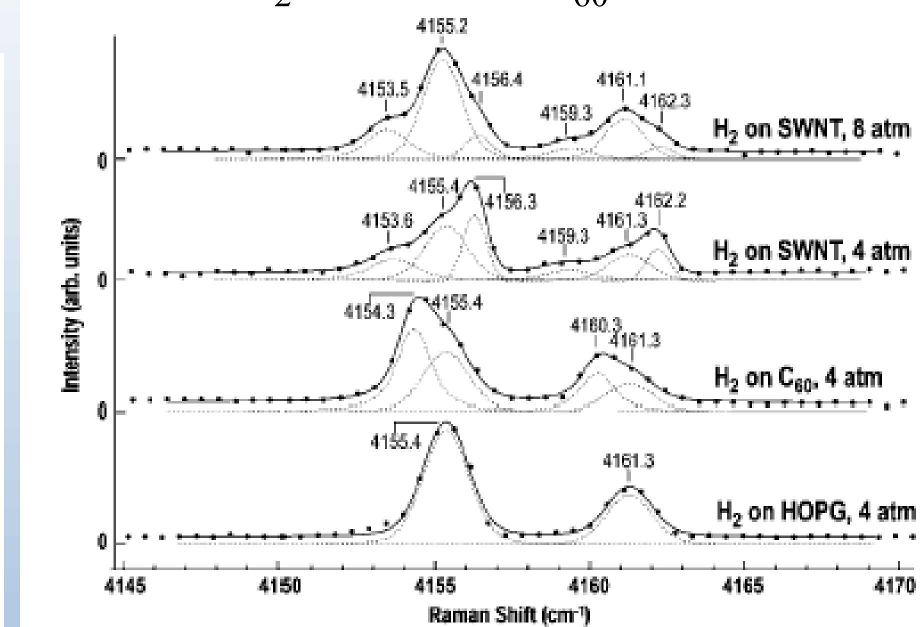
Raman Spectroscopic Investigation of H_2, HD, and D_2 Physisorption on Ropes of Single-Walled, Carbon Nanotubes

Keith A. Williams,* Bhabendra K. Pradhan, Peter C. Eklund,† Milen K. Kostov, and Milton W. Cole

Gas-phase hydrogen



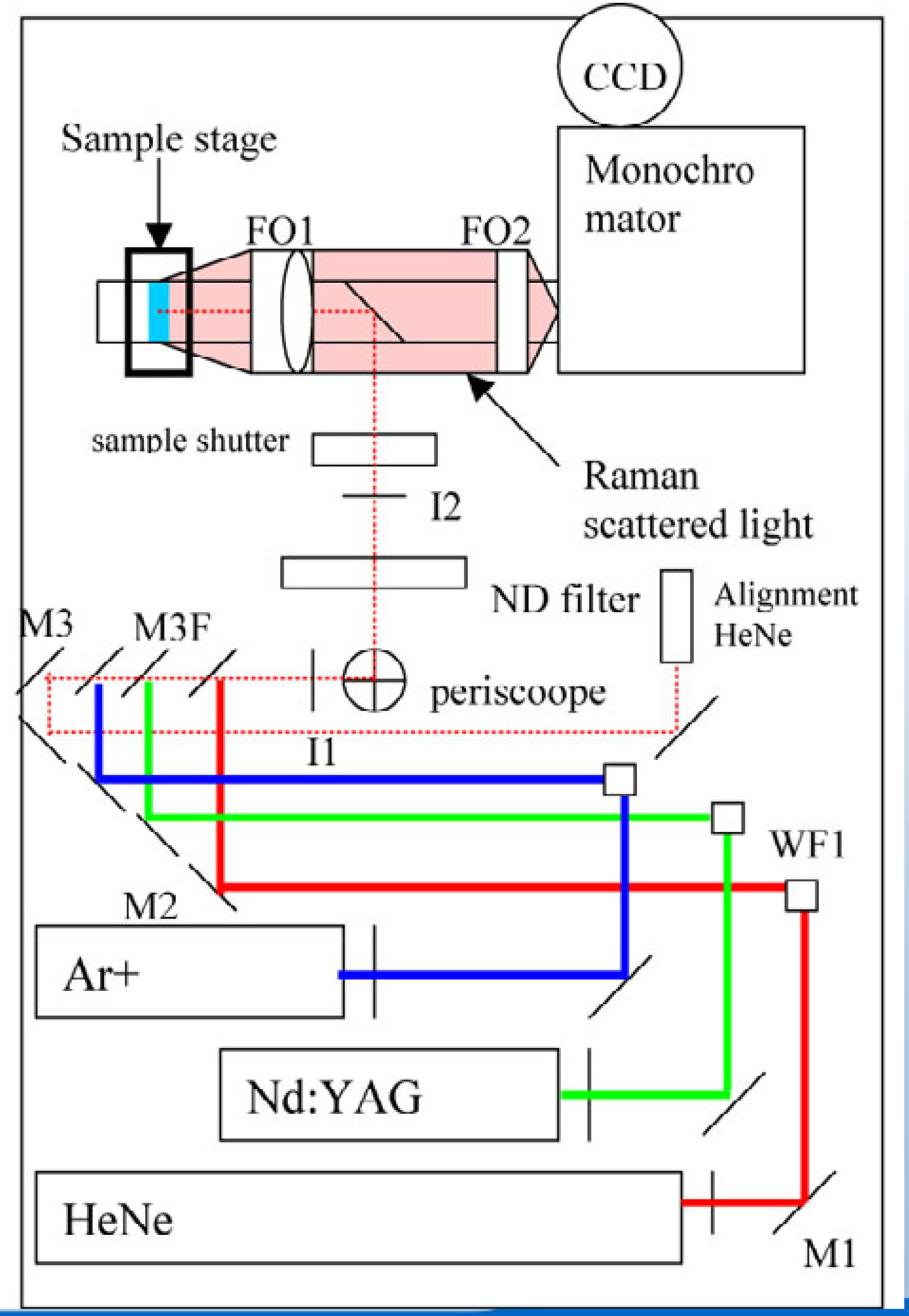
H_2 on SWNT/C_{60}/HOPG



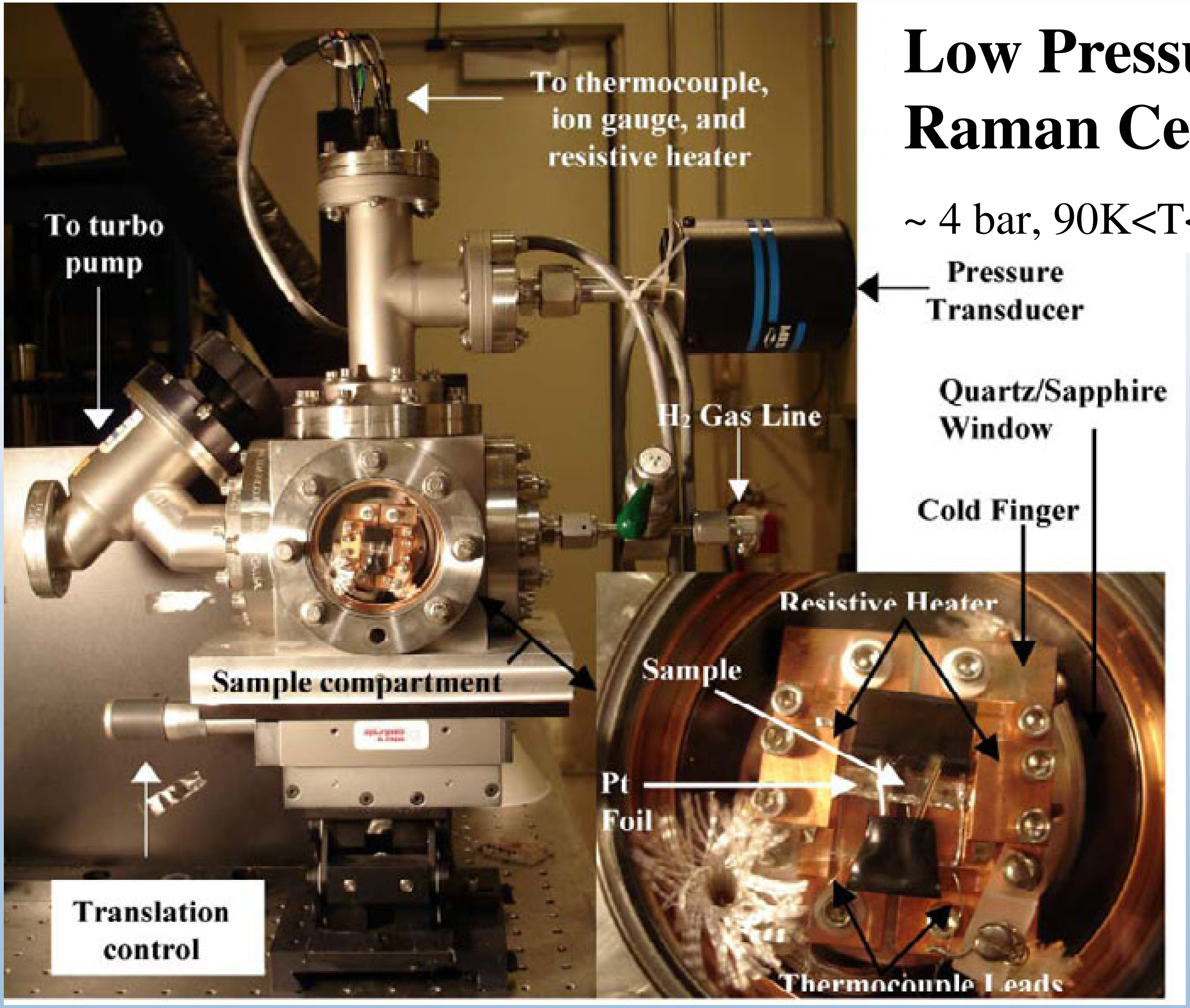
- 8 atm H_2 on SWNTs $\Rightarrow$ small (~2 cm^{-1}) red and blue-shifts
- Small shifts consistent with physi-sorption, require deconvolution
- Two sites: flat outer or inner surfaces, groove sites

Raman Bench

- 3 excitation wavelengths:
  - 488 nm (Ar ion)
  - 532 nm (Nd:YAG)
  - 632 nm (HeNe)
- Non-fundamental lines removed by 90º grating filters (WF1)
- Fundamental removed before monochromator with notch filter
- Energy resolution: 2 – 8 cm^{-1}
- Lower limit of detection: ~50 cm^{-1}



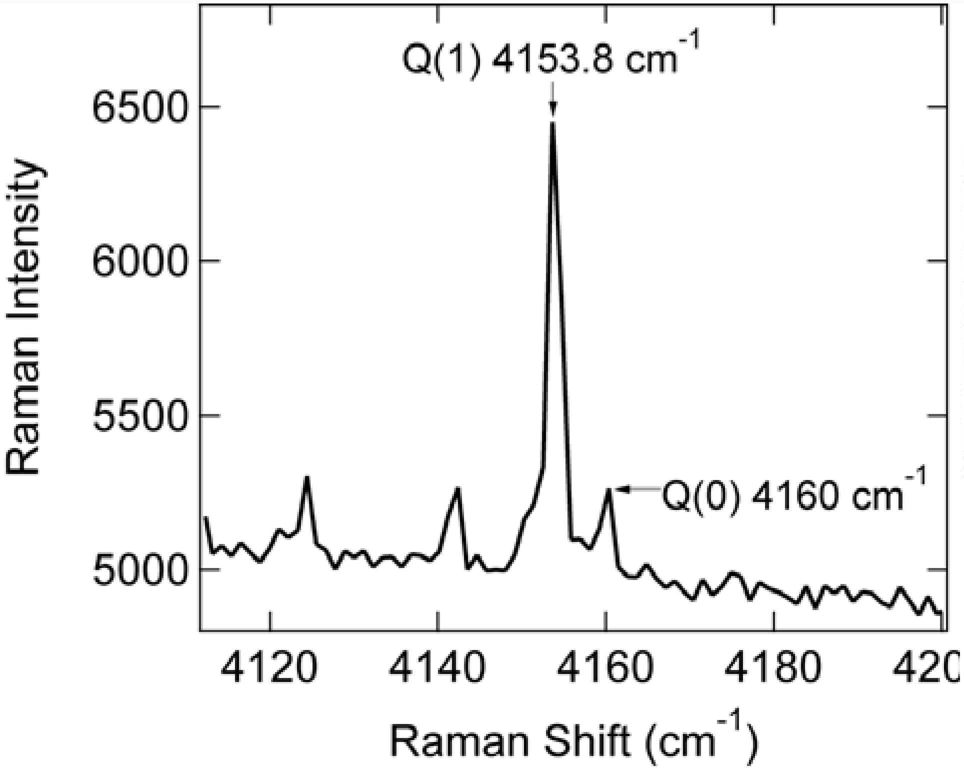
Pressurizable in-situ Raman cell

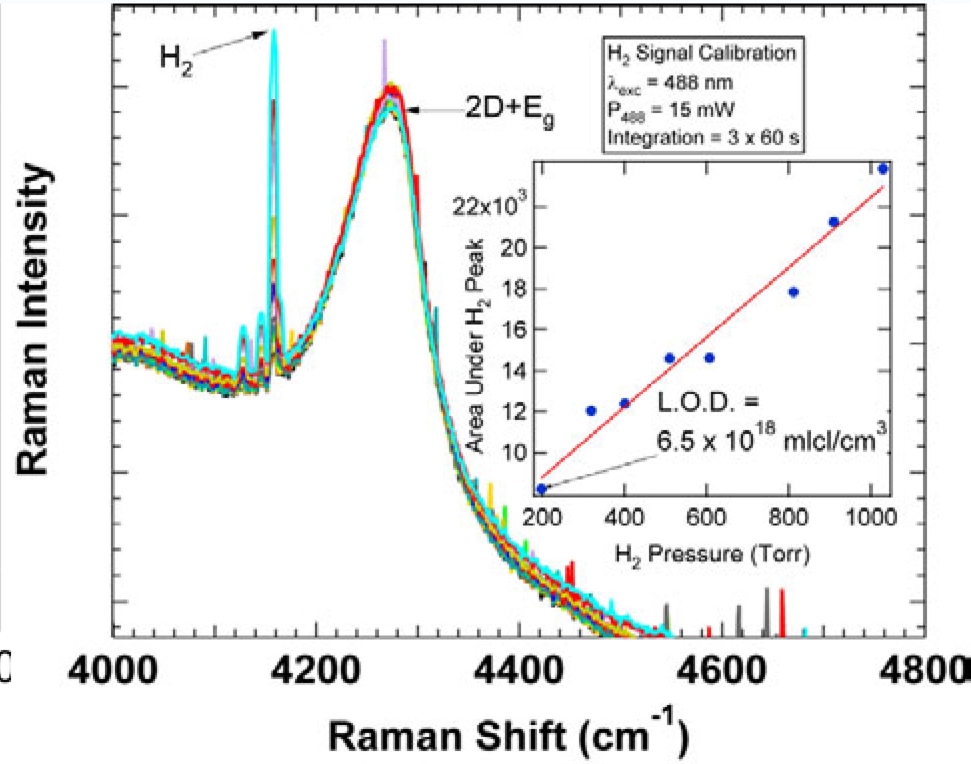


Low Pressure Raman Cell

~ 4 bar, 90K<T<500K

Gas-phase H_2 and SWNTs





a) Raman spectrum of H_2 gas in the Q branch region at room temperature.

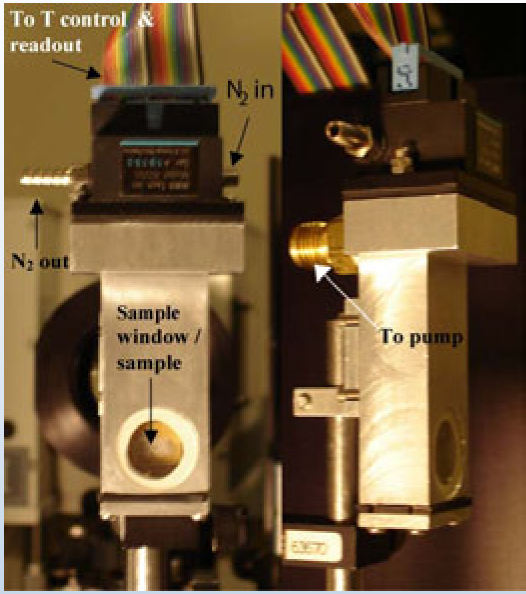
b) Raman spectra of hydrogen gas over a SWNT sample with increasing hydrogen gas pressure; inset – Area under H2 Q(1) peak as a function of hydrogen gas pressure.

L.O.D. determined by calibrated volume

Other Characterization

- FTIR measurements also possible to look for IR modes
- Sieverts measurement to verify optical capacity measurements
- Structural studies using single crystal diffraction (Miami)
  - May be possible to find trends and screen with combinatorial powder XRD (NREL)
- Standard methods also available

  (TPD, TGA, DTA, BET,…)

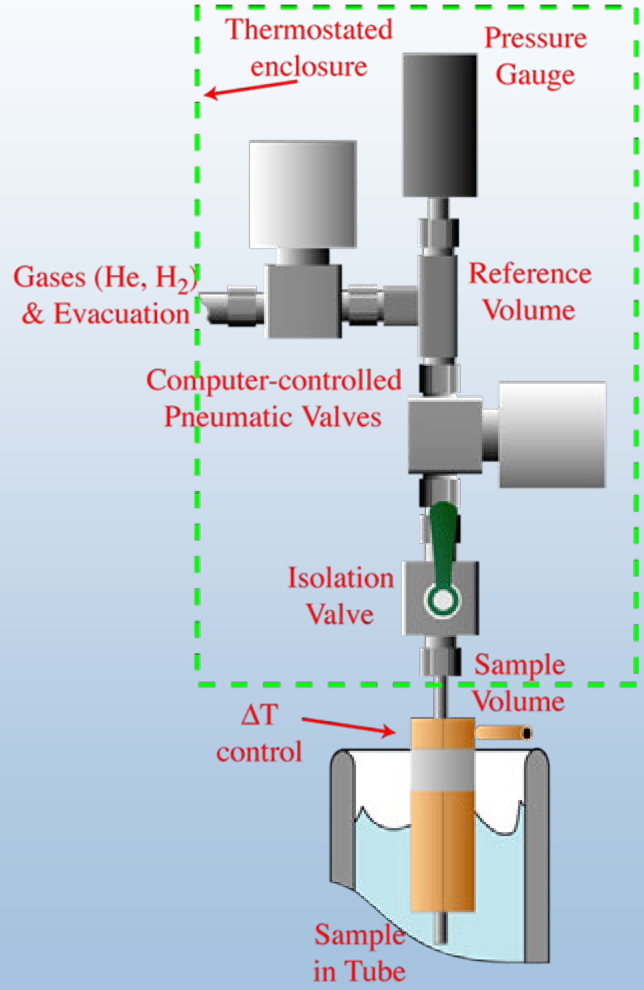


NREL High Through-Put Activities

- Motivation
  - Many samples; many types of materials
  - Need fast medium-to-high pressure screening technique for small samples
- Possible Approaches
  - Manometric (aka Sieverts, volumetric)
    - Reduced steps for isotherm
    - Several inexpensive systems in parallel
  - Gravimetric
    - Parallel quartz microbalance
    - True combinatorial capability

Parallel Manometric

- Manometric approach must have isolated volumes
  - Most useful if each system independent
  - Cannot share sensors or volumes
- Small Inexpensive Systems Run in Parallel
  - Small volumes for high sensitivity
  - Shared common resources such as gases, gas purifiers, vacuum, manifolds, thermostat system, DAQ, computer
  - Sensitivity vs. sample size still a challenge



Parallel Gravimetric

Quartz Crystal Microbalance

- Advantages
  - Common chamber
  - QCMs technology well developed & understood
- Uncertainties
  - Performance at high P
  - Sample mounting (for adsorbents)
  - Temperature performance

Final Comments

- High throughput methods require significant commitments to enact (equipment, labor, $)
- Best implemented first in “bottleneck” applications
- Full implementation requires significant data storage, handling and software development