# IV.I.1  Novel Theoretical and Experimental Approaches for Understanding and Optimizing Hydrogen Interactions in Metal Organic Framework Materials

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## Program Scope

In order to improve the gravimetric and volumetric capacities of metal organic framework (MOF) materials at room temperature beyond the 5 wt% and 40 g $H_2$/L, it is important to increase the $H_2$ binding energy above **20 KJ/mole**. This research aims to establish the scientific basis for such improvements by **i)** quantifying the interaction of $H_2$ molecules with MOF materials at room temperature to guide the synthesis of better storage MOF materials, **ii)** exploring $H_2$ loading kinetics and competitive impurity adsorption in practical environments over the 10 K-300 K temperature range, and **iii)** characterizing the effect of metal catalysts and associated spill over processes. To determine the $H_2$ binding energy, we have combined ***high pressure infrared (IR) absorption, adsorption isotherms and isosteric heat of adsorption measurements*** with a new first principles calculation method, the van der Waals density functional (vdW-DF), [1-3] to study a number of different MOF materials.

## Recent Progress

### 1. Theoretical and Experimental Developments

During this past year, several issues were resolved to perform calculations on MOF structures:

1.  By adopting the new computational algorithm of  Roman-Perez and Soler [arXiv:0812.0244], we have achieved a many-fold efficiency enhancement allowing large van der Waals vdW-DF calculations to be done  for large MOF systems at essentially the same rate as ordinary LDA or GGA calculations. This will be enabling greatly increased productivity, and has also enabled first principles structural relaxations with multiple dihydrogens within a MOF.

2.  The exchange functional used with the vdW-DF has a history of giving spacings between $H_2$ and its surroundings that were a slightly too large.  We have developed an improved method for exchange that better agrees with exact Hartree-Fock calculations, which is expected to fix this problem.

3.  We are now able to treat not only the translational modes of $H_2$'s in a MOF, but also the rotational modes.  For example, we can predict from first principles the spectra obtained from neutron scattering for the para-ortho transition at different $H_2$ loadings, including rather large and irregular triplet splittings and translational sidebands.

Experimental problems for IR absorption measurements have been identified and addressed as follows:

1.  To avoid water contamination in the MOFs (affecting the IR spectra and competing with $H_2$ for available space), purification of $H_2$ gas was achieved by filters/hot $H_2$ gas cleaning of pipes.

2.  Perturbation of MOF matrix by high pressure gas (due to modification of combination bands of the MOF in the $H_2$ stretch spectral region) was identified using He gas.  A new procedure was established to acquire good quality data using $D_2$ as reference for $H_2$ measurements.

3.  Both solvent and thermal activation of the MOFs *prior* to pressing them on KBr pellets was found to greatly improve $H_2$ loading.  Alternative activation methods are being investigated as well.

### 2. Role of Organic Linkers and Structures in the Uptake and Binding Energy of $H_2$ in Microporous MOFs:

An initial effort was placed on **$M_2(BDC)_2(TED)$**, where M = Zn(**1**), Cu(**2**), Co(**3**) and Ni(**4**), BDC = benzenedicarboxylate, and TED = triethylene-diamine. These MOFs crystallize in the tetragonal crystal system, space group P4/ncc. The crystal structure is a 3D microporous framework composed of paddle-wheel $M_2(COO)_4(TED)_2$ secondary building units (SBUs), each linked by four BDC linkers and two TED pillars. The high resolution Ar and $H_2$ gas adsorption-desorption measurements were performed at various temperatures and pressures.  The Ar sorption isotherms were collected in a relative pressure range from $10^{-6}$ to 1 atmosphere at 87K, and hydrogen sorption isotherms were collected in a pressure range from $10^{-4}$ to 1 atmosphere (low pressure) at 77 K and 87 K (e.g. Figure 1 for **1** and **2**), and from  $10^{-4}$ to 40 bar (high pressures, not shown
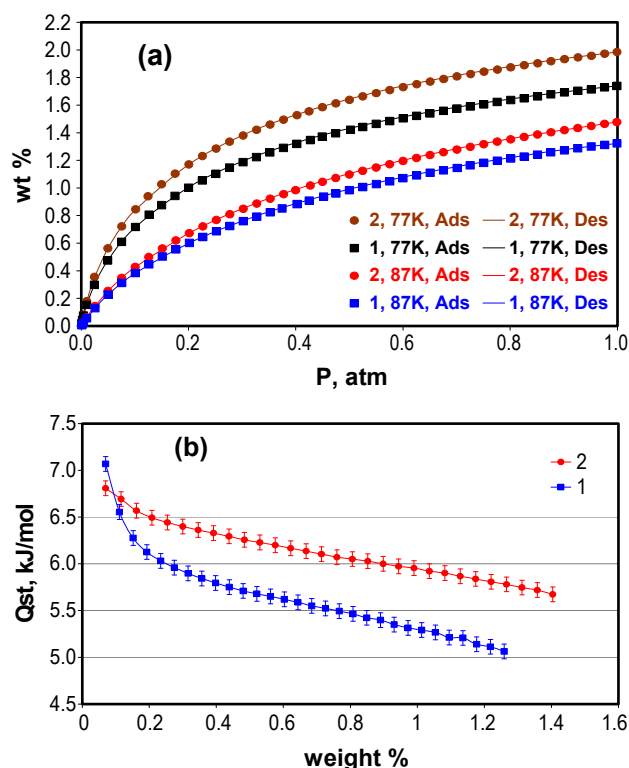
FIGURE 1.  (a) $H_2$ adsorption isotherms for **1** and **2** at 77 and 87 K. (b) Calculated isosteric heat of adsorption, $Q_{st}$, for both structures.
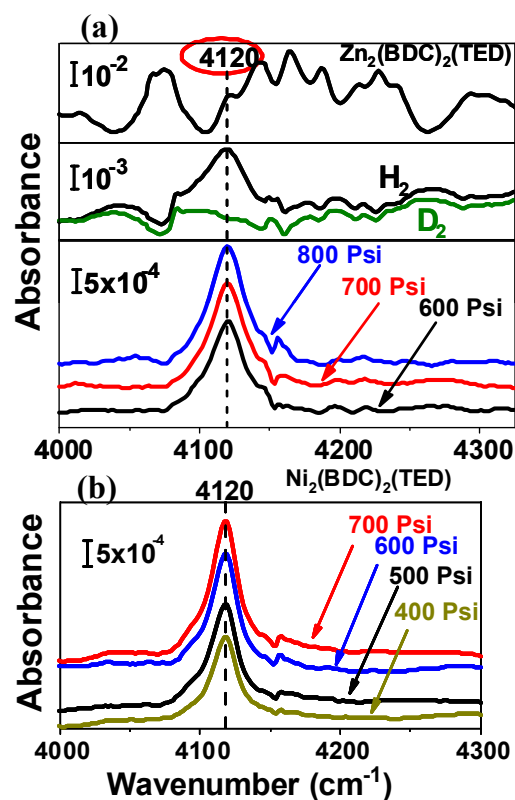


FIGURE 2.  (a) IR absorbance of $Zn_2(BDC)_2(TED)$ at RT. ***Top panel***: plain MOF at ambient pressure; ***Middle Panel***: MOF at 800 psi $H_2$ (upper curve) and $D_2$ (lower curve); ***Bottom panel***: Difference between $H_2$ and $D_2$ at several pressures for (a) $Zn_2(BDC)_2(TED)$ and (b) $Ni_2(BDC)_2(TED)$.

here).  At 77 K and 1atm, the hydrogen uptakes are 2.1, 1.8, 2.13 and 2.08 wt% for **1-4**.  The uptake values are 4.1 and 3.5 wt% for **1** and **3** at 77 K and 40 bar, respectively.  More details are summarized in Table 1.

TABLE 1.  Pore Volume, Surface Area, $H_2$ Uptake and $Q_{st}$ for Zn(**1**), Cu(**2**), Co(**3**), Ni(**4**)

| M | Pore Vol (DA, cc/g) | Sur Area (BET, m²/g) | $H_2$, wt% (77 K, 1 atm) | $Q_{st}$ (kJ/mol) |
|---|---|---|---|---|
| Ni(**4**) | 0.74 | 1,783 | 2.08 | 5.0-6.0 |
| Co(**3**) | 0.83 | 1,881 | 2.13 | 5.0-5.7 |
| Cu(**2**) | 0.63 | 1,497 | 1.80 | 4.9-6.1 |
| Zn(**1**) | 0.84 | 1,888 | 2.10 | 5.0-5.3 |

The IR absorption of $H_2$ in $Zn_2(BDC)_2(TED)$, was measured by using $D_2$ as reference.  Figure 2a (top panel) shows that the spectral region contains several components from overtone and combination MOF modes, which are affected by high pressure gas (see middle panel with $D_2$).  By subtracting the spectrum obtained with $D_2$ at similar pressures, the $H_2$ stretch spectrum is reliably measured (Figure 2a bottom panel).  There is a single mode centered at 4,120 cm$^{-1}$ (composed of ¾ ortho- and ¼ para–hydrogen), i.e. located -35 cm$^{-1}$ lower than the unperturbed ortho $H_2$ frequency (4,155 cm$^{-1}$).  The intensity of this mode is linear

with pressure (Figure 3), as expected since the room temperature loading is still low ($\sim$10% of maximum $H_2$ loading achieved at low temperatures).

The position of the $H_2$ mode in $Zn_2(BDC)_2(TED)$ and $Ni_2(BDC)_2(TED)$ is identical (Figure 2b), indicating that the corner metal atoms in these MOF do not play a role in $H_2$ loading.  A similar $H_2$ vibrational frequency (4,120 cm$^{-1}$) was obtained upon loading ZIF-8, $[Zn_3(MeIm)_6]$, where (MeIm = methylimidazolate), a zeolite-like MOF, having different cage size and pore characteristics.  Calculations are needed to understand this intriguing result.

The $H_2$ binding energy in $Zn_2(bdc)_2(ted)$ was mapped as a function of position.  The deepest binding regions lie within channels of two types, A and B, whose position within the unit cell are indicated by the blue and brown lines respectively, where dashed circles indicate where the channels enter the respective adjoining cell, as shown in Figure 4.

The contour maps of these channels are shown in Figure 5 for channel A (left) and channel B (right).  The fact that each of the strongest  binding sites all have approximately the same binding energy of $\sim$10 kJ/mole is consistent with the experimental fact that the loading
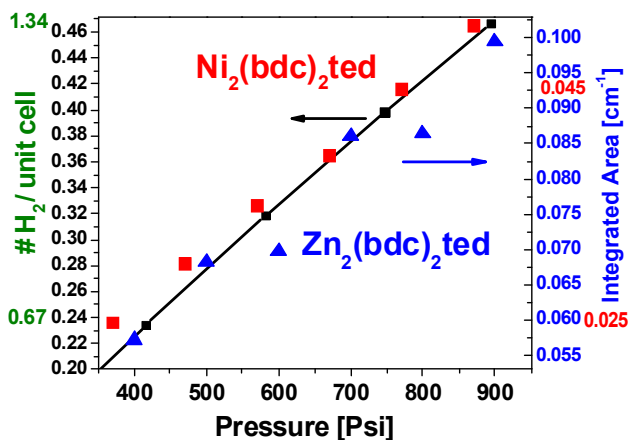
**FIGURE 3.** IR integrated area of H$_2$ stretch for both MOFs and H$_2$ loading inferred from H$_2$ adsorption isotherms at RT



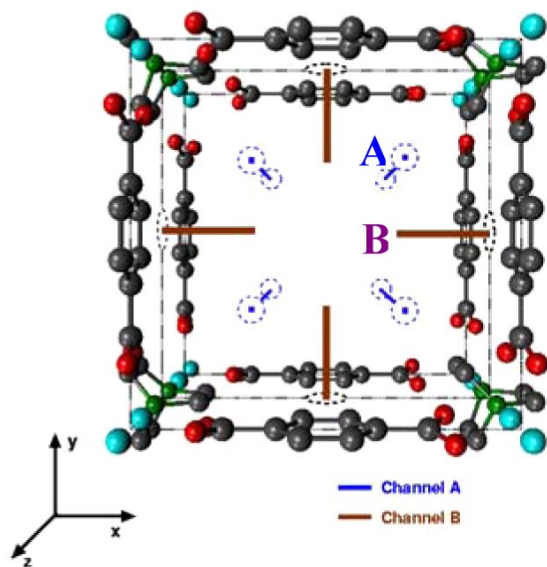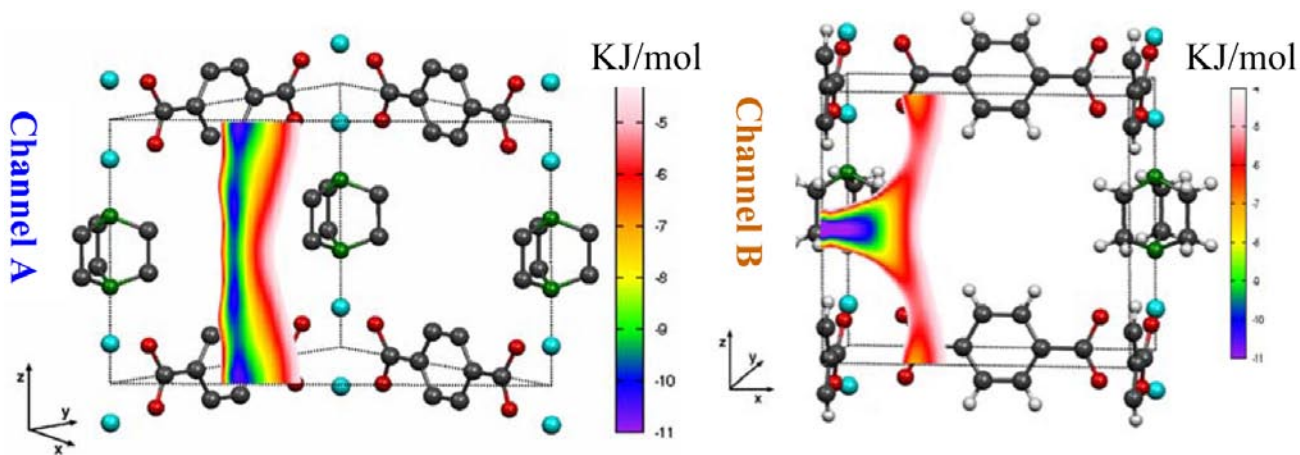**FIGURE 4.** Unit cell

vs. pressure isotherms can be fitted precisely to a single Langmuir isotherm rather than a sum of two or more. Also, preliminary calculations indicate that little is changed for M=Cu or M=Co.

Furthermore, we find that the MOF can be loaded with up to ~12 H$_2$ before H$_2$ repulsions begin to make each other addition more costly, in agreement with the isotherm-derived experimental number of ~13. Our well-bottom values for the binding energy are reduced by zero point energies and thermal effects, which bring the net into reasonable agreement with the experimental isosteric heat of sorption. Finally we have calculated the shifts in the H$_2$ stretch frequency: at the strongest binding sites in each channel it is ~-30 cm$^{-1}$, which is in reasonable agreement with the measured ~-35 cm$^{-1}$. We are in the process of applying our recently developed hindered rotation analysis to this MOF. This is expected to bring the experimental and theoretical heats of sorption into nearly perfect agreement.

***These results show that H$_2$ adsorption in M$_2$(BDC)$_2$(TED) is due to the organic linkers and the channels are located away from high binding energy sites of each individual linker.***

## 3. Frustrated Translational Motion in Smaller Restricted Channels in MOF

We have studied the [M$_3$(HCOO)$_6$]·DMF compounds, with M = Co(**5**), Mn(**6**), Ni(**7**) that have very different ligands. The asymmetric unit contains four crystallographically independent M(II) and six formate anions. This structure form one-dimensional zig-zag channels where the H$_2$ molecule can enter after removal of the DMF guest. The aperture of the channels is ~5-6Å roughly (excluded van der Waals radius), and the connection between channels exhibits a restriction.

The surface area was calculated to be 354 m$^2$ g$^{-1}$ (Langmuir) and 304 m$^2$ g$^{-1}$ (BET), respectively, in the



**FIGURE 5.** Channels A and B

pressure range of $7.94 \times 10^{-4} < P/P° < 1.4 \times 10^{-2}$.  The DA (Dubinin-Astakhov) micropore volume of the sample was 0.14 $cm^3$ $g^{-1}$ based on the $N_2$ sorption data collected at 77 K.  The main pore size was determined to be ~5.0 Å from H-K pore size distribution with a good agreement with crystallographic data.  Hydrogen uptakes were 0.75 and 0.65 wt% of at 77 K and 87 K and 1 atm, respectively.  The isosteric heats of hydrogen adsorption ($Q_{st}$) were calculated to be in the range of 8.3-6.5 kJ mol-1 at low coverage region (0.06-0.26 wt%).

Figure 6 shows the IR absorption data.  Interestingly, the $H_2$ stretch vibration (4,126 $cm^{-1}$) exhibits a smaller shift (lesser perturbation) than for the previous class of MOFs (29 vs 35 $cm^{-1}$), stressing again the role of the ligand.  Furthermore, the spectra exhibit a distinct side band, centered at ~4,040 $cm^{-1}$, which is assigned to the frustrated translation mode of the $H_2$ molecule.  The sideband is detectable in this case, because of the constraint exerted by the restriction for $H_2$ molecules trapped in the channels.

## 4. A Path Towards Higher Binding Energies

The $Zn_2(BPDC)_2(BPEE)$, where *bpdc=4,4'-biphenyldicarboxylate and  bpee=1,2-bipyridylethene*, is interesting because its structure is made of layers of two-fold interpenetrating Zn(BPDC) nets interconnected by BPEE that lead to the formation of unusual, high-binding energy sites.  The Ar adsorption-desorption isotherms showed a typical Type I behavior.  The surface area was estimated to be 328 $m^2/g$ (BET) and 483 $m^2/g$ (Langmuir), respectively.  The total pore volume was calculated to be 0.165 cc/g.  The IR absorption is characterized by a very sharp $H_2$ stretch at 4,117 $cm^{-1}$, i.e. with a higher binding energy than that of all previous MOF studied so far (Figure 7).
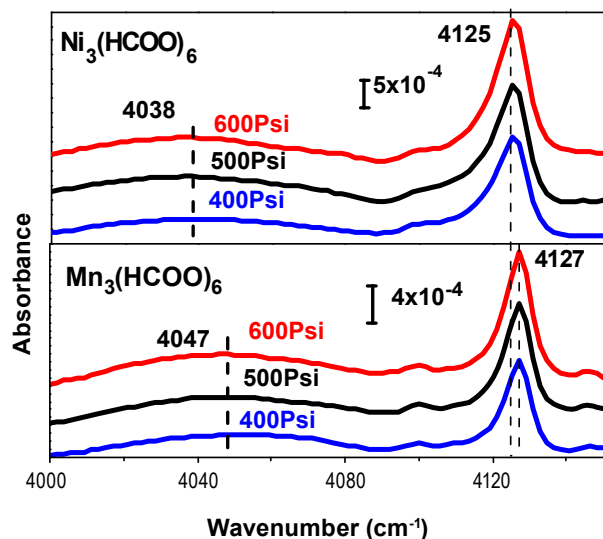
Theoretically, the $H_2$ binding energy contours were mapped as a function of position in this MOF.  These are shown in the primitive unit cell to the right.  The binding is substantial at four sites shown (~15 kJ/mol), with four more equivalent sites in the upper pore of the cell.  The strongest binding points are at the tips of each football shaped objects, and similarly in the other three large pores, yielding a total of 8 $H_2$ per primitive cell.  This loading coincides with the loading where the experimental isotherms sharply break their slope and no longer increase sharply with pressure.

The calculations of the translational and hindered rotational zero point energies are not yet complete, but in analogy with previous MOFs we expect a net heat of sorption to be ~11 kJ/mol, in rough agreement with the measurements.  We have calculated the shift in the $H_2$ stretch frequency, which is ~-40 cm-1 at the strongest binding sites, and ~-30 cm-1 in the green regions in Figure 8.
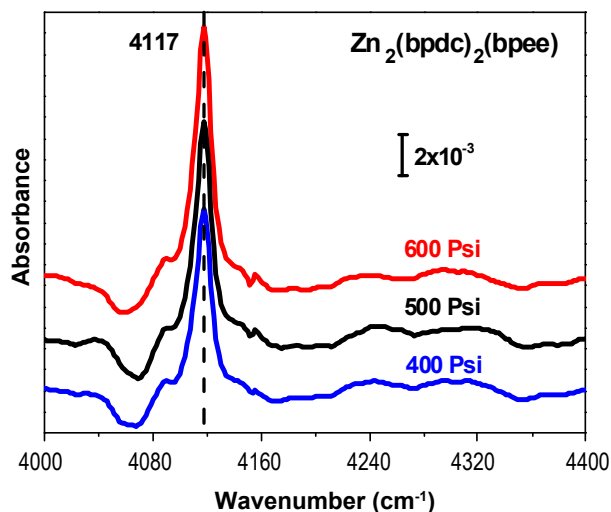


FIGURE 7.  IR absorption spectra of $H_2$ in $Zn_2(BPDC)_2(BPEE)$



FIGURE 6.  IR absorption spectra of $H_2$ in $Ni_3(HCOO)_6$ and $Mn_3(HCOO)_6$
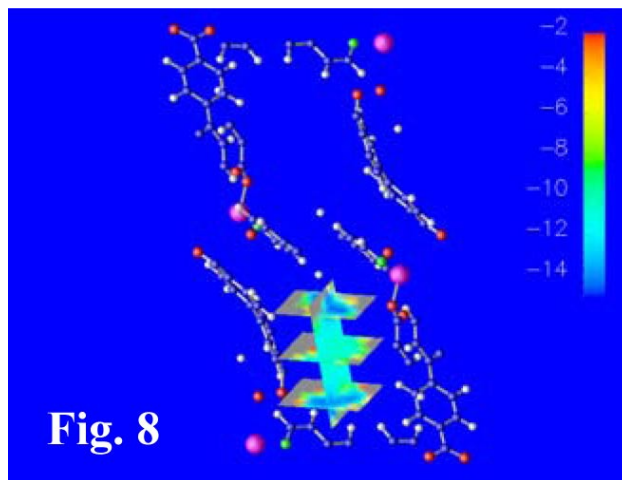


Fig. 8

*What have we learned about increasing $H_2$ binding in MOFs?  Not including typical zero point and thermal reductions of up to ~5 kJ/mol, we can say the following:* The binding of $H_2$ to a single pi-aromatic structure (e.g. a benzene like ring) is ~5 kJ/mol.  In $Zn_2(BDC)_2(TED)$ the binding is double this, as the strong binding sites in both channel A and channel B are near the strong binding points of two such pi structures, and the binding has increased to ~10 kJ/mol.  However, for $Zn_2(BPDC)_2(BPEE)$, there are no less than four pi-aromatic complexes near each of the strong binding sites.  Here the binding is ~15 kJ/mol, and probably would be more if the complexes were more ideally situated.  *These findings suggest that we are close to the ultimate limit, i.e. energies in the 20 kJ/mol range could be achieved, so that MOF materials may prove suitable for practical storage devices.*

## Current and Future Plans

Our spectroscopy effort will focus on i) low T measurements (10 K) to obtain a better comparison with theory at both low and high $H_2$ loading, and ii) addressing the spill over processes using a variety of model systems (MOF on catalytically active metal surfaces, small catalytic active nanoparticles deposited on MOFs, incorporation of catalytically active centers within MOFs.

Theoretically, we are considering the MOF-74, a material [4] that was recently [5] studied by inelastic neutron scattering at 4 K to sharpen our low temperature theoretical techniques for application to new MOFs created within our collaboration.  The vdW-DF predictions were remarkably close to the experimentally measured positions of the 24 dihydrogens per cell.  The most tightly bound one is found to have a binding energy of 12.5 kJ/mol, and with the translational and hindered rotational (see below) zero point energies this is reduced to 8.5 kJ/mol, in almost perfect agreement with the experimental values of 8.5 and 8.8 kJ/mol [5,6].  This contrasts with LDA and GGA values of 22 kJ/mol and 4.4 kJ/mol, respectively.  The most exciting part of the story is the analysis of the **para-to-ortho transition**, where the experiment measured energy loss by scattering from different loadings of 100% para-$H_2$.  The result is a series of loss peaks representing singlet to triplet transitions from the two most tightly bound types of $H_2$ sites, with the triplets split by the local potential energy contours.  Using our *ab initio* energy contours, we solved the Schrödinger equation for the $H_2$ rotations for both types of site for various loadings, finding results agreeing with the experiment astonishingly well.  As far as we know, **this is the first successful ab initio analysis of the hindered rotational spectrum of $H_2$ as function of $H_2$ loading** in a MOF, or possibly in any other material.  The immediate impact on the H-storage problem is a well tested method for including the non-negligible rotational zero point and excitation energies on heats of sorption.

**Synthesis and high pressure hydrogen isotherms:** Based on the above findings, it is clear that structure components (e.g. ligands), crystal structures, pore size and shape play important roles in the amount of adsorbed hydrogen and binding energy.  In general, smaller pore size, structure component with stronger hydrogen interactions, and larger number of binding sites will lead to higher isosteric heats of adsorption.  The larger pore volume and internal surface area give rise to higher hydrogen uptake.  Future synthesis will focus on optimized structures taking into consideration of these factors and incorporation of catalytical centers into the MOF structures via several mechanisms (e.g. spillover and metalloligands) to enhance MOF-hydrogen binding power.  High pressure hydrogen isotherm measurements will be carried out on all newly synthesized MOFs at variable temperatures (up to 100 bar).  The cryogenic (77 and 87 K) temperatures will be achieved using liquid nitrogen and liquid argon as coolant.  A temperature controller unit will be used for temperatures ranging from 245 K to 425 K.

## References

**1.** Dion, H. Rydberg, E. Schroder, et al., Physical Review Letters **92**, 246401 (2004).

**2.** T. Thonhauser et al., Phys. Rev. B 76, 125112 (2007).

**3.** D.C. Langreth et al., J. Phys.: Condens. Matter **21**, 084203 (2009).

**4.** J.L.C. Rowsell and O.M. Yaghi, J. Am. Phys. Soc. 128, 1304 (2006).

**5.** Y. Liu, C.M. Brown, D.A. Neumann, and C.C. Ahn, Langmuir 24, 4772 (2008).

**6.** W. Zhou, H. Wu, and T. Yildirim, J. Am. Chem. Soc. 130, 15268 (2008).

## 1. Updated List of Awards

**1. Chabal**:  2009 Davisson-Germer prize (American Physical Society, March 2009).

## 2. Publications (acknowledging DOE support)

Hot papers:

**1.** "A luminescent Microporous Metal-Organic Framework for the Fast and Reversible Detection of High Explosives", Lan, A.J.; Li, K.H.; Wu, H.H.; Olson, D.H.; Emge, T.J.; Ki, W.; Hong, M.C.; Li, *J. Angew. Chem. Int. Ed.* **2009**, ASAP.  http://www3.interscience.wiley.com/journal/26737/home/2002_hotpaper.html

Others:

**1.** "Theoretical and experimental analysis of $H_2$ binding in a prototypical metal-organic framework material", Lingzhu Kong, Valentino R. Cooper, Nour Nijem, Kunhao Li, Jing Li, Yves J. Chabal, and David C. Langreth, Phys. Rev. B **79**, 081407(R) (2009).

**2.** "A Density Functional for Sparse Matter", D.C. Langreth, B.I. Lundqvist, S.D. Chakarova-Käck, V.R. Cooper, M.Dion, P. Hyldgaard, A. Kelkkanen, J. Kleis, Lingzhu Kong, Shen Li, P.G.Moses, E. Murray, A. Puzder, H. Rydberg, E. Schröder, T. Thonhuaser, J. Phys.: Condens. Matter 21,084203 (2009).

**3.** "Unique Gas and Hydrocarbon Adsorption in A Highly Porous Metal-Organic Framework Made of Extended Aliphatic Ligands", Li, K.H.; Lee, J.Y.; Olson, D.H.; Bi, W.H.; Eibling, M.J.; Emge, T.J.; Li, J. Chem. Comm. **2008**, 6123.

**4.** "A Luminescent Microporous Metal Organic Framework for the Fast and Reversible Detection of High Explosives", Lan, A.J.; Li, K.H.; Wu, H.H.; Olson, D.H.; Emge, T.J.; Ki, W.; Hong, M.C.; Li, J. Angew. Chem. Int. Ed. **2009**, ASAP.

**5.** "Microporous Metal Organic Frameworks as Functional Materials for Gas Storage and Separation", Pan, L.; Li, K.H.; Lee, J.Y.; Olson, D.H.; Li, J. in <u>Design and Construction of Coordination Polymers</u>, John Wiley & Sons, Inc., in press.

**6.** "RPM3: A Multifunctional Microporous MOF with Recyclable Framework and High $H_2$ Binding Energy", Lan, A.J.; Li, K.H.; Wu, H.H.; Kong, L.Z.; Nijem, N.; Olson, D.H.; Emge, T.J.; Ki, W.; Chabal, Y.J.; Langreth, D.C.; Hong, M.C.; Li, J. Inorg. Chem. 2009, to be submitted.

## 3. Invited Talks at conferences (+ 17 at Universities not listed)

**1.** "Hydrogen storage in nanoporous materials", Y.J. Chabal, American Physical Society, Pittsburgh, PA March 16-20, 2009.

**2.** D.C. Langreth, "International workshop: New achievement in density functional theory and quantum simulation of large systems", Institute of Mathematics and its Applications, University of Minnesota, Minneapolis, August 2007.

**3.** D.C. Langreth, "International DOE workshop on Long range interactions in nanoscale science", Annapolis, October 2007.

**4.** D.C. Langreth, Materials Research Society (MRS) meeting, San Francisco, March 2008.

**5.** D.C. Langreth, International workshop on Mathematical and Algorithmic Challenges in Electronic Structure, Institute of Mathematics and its Applications, University of Minnesota, Minneapolis, September 2008.

**6.** D.C. Langreth, DOE Workshop of the Computational Materials Science Network (CMSN) on Predictive modeling of the growth and properties of energy relevant thin film and nanostructures, Gatlinburg, October 2008.

**7.** D.C. Langreth, American Physical Society meeting, Pittsburgh, March 2009.

**8.** D.C. Langreth, Second International Symposium and Workshop on Correlated Electrons in Matter (ONRL & LLNL), Gatlinburg, April 2008.

**9.** D.C. Langreth, Kavli Institute of Theoretical Physics (KITP) program on Excitations in Condensed Matter: From Basic Concepts to Real Materials, Key participant, UCSB, Santa Barbara, November 2009.

**10.** V. Cooper, American Physical Society meeting, New Orleans, March 2008 V. Cooper, American Chemical Society National Meeting, New Orleans, April 2008.

**11.** V. Cooper, ES08, International workshop on Recent developments in electronic structure, Urbana-Champaign, June 2008 (Cooper).

**12.** V. Cooper, Gordon Research Conference on Computational Chemistry, Mount Holyoke, July 2008 (Cooper).

**13.** "Microporous Metal Organic Frameworks as Functional Materials for Gas Storage and Separation", Jing Li, JeongYong Lee, Kunhao Li, Long Pan, David H. Olson, 5th National Symposium on Structural Chemistry, Fuzhou, P.R. China, October 27, 2007.

**14.** "Microporous Metal Organic Frameworks: Porosity and Multifunctionality", Jeongyong Lee, Kunhao Li, Long Pan, David H. Olson, and Jing Li, 325th ACS National Meeting, New Orleans, LA, April 6–10, 2008.

**15.** "Microporosity and Functionality: An Update on MMOF Research", J. Li, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, China, July 11, 2008.

**16.** "Microporous Metal Organic frameworks: New Sorbent Materials for Hydrogen Storage", J. Li, 4th Conference on Hydrogen Storage Materials, Guangzhou, P.R. China, April 11, 2009.

## 4. 14 Contributed Talks

## 5. List of people working on the project

In Chabal's group, the work has been initiated by a research associate, **Jean-Francois Veyan**, who has worked on the project from the beginning with full funding. A student, **Nour Nijem**, has been training during the spring semester 2008 and is now being funded 100% by the grant, along with a new graduate student, **Kui Tan**, who has begun in Sept. 2008 and works on MOF synthesis. Chabal participates at the level of 2 months/year without support for summer salary.

In Langreth's group, a postdoc (**Valentino Cooper**) started the theoretical effort. He was funded from an NSF account prior to arrival of DOE funds and for leveraging (budget too low to cover a full postdoc for three years). As of April 1, 2008, a new postdoc (**Lingzhu Kong**) has started and is being funded 100% by this DOE grant. Valentino Cooper stayed at 10-20% level until September 2008 to help with

the transition.  David Langreth participates at the level of 2 months/year without support for summer salary.

In Li's group, Dr. **Kunhao Li** (postdoc) has been engaged in this research full time since the start of the program (August 2007).  Two graduate students, **JeongYong Lee** and **Sanhita Pramanik**, have also been involved and partially supported by this program (1/2 time).  Jing Li has been participating at the level of 1.5 months (academic year) and 0.5 month last summer without summer salary.