From fundamental understanding to predicting new nanomaterials for high capacity hydrogen storage

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2006 DOE Hydrogen Annual Review BES Activities…

Add-on project to DE-FG02-98ER45701 (Duration:03/01/06 – 06/30/07)

We thank DOE (in particular Dr. Harriet Kung and Dr. Sunita Satyapal) for supporting this add-on project to get us working on this important field immediately…

Program Scope

We will focus on achieving fundamental understanding of the chemical and structural interactions governing the storage and release of hydrogen in a wide spectrum of candidate materials.

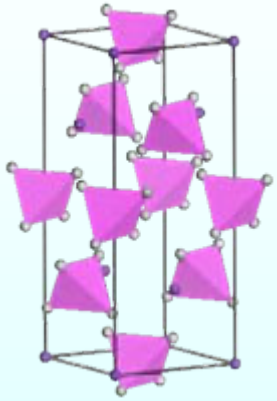
The goals are:

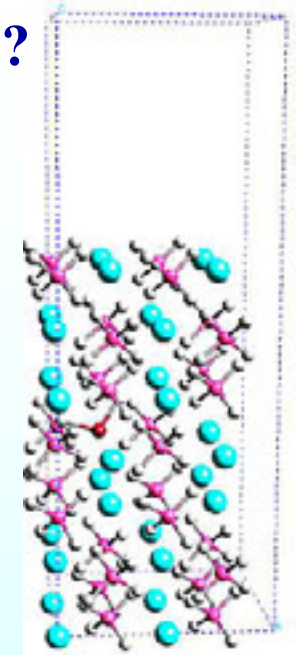
•To provide fundamental underatanding of how the most of the candidate materials (MOF's, alanates, destabilized chemical hydrides, etc) interact with H_2 chemically, structurally and energetically; and
•To provide timely feedback and guidance from theory to *de novo* materials design and targeted syntheses throughout the DOE programs.

We expect that this new modeling initiative will have a major impact on the extensive experimental work at NIST, where senior staffs are coupled to essentially all of the EERE Centers of Excellence.

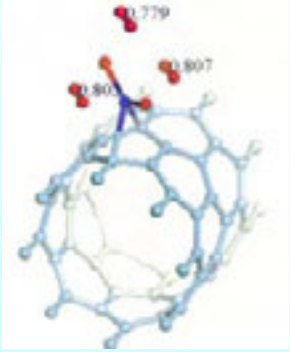
Outline

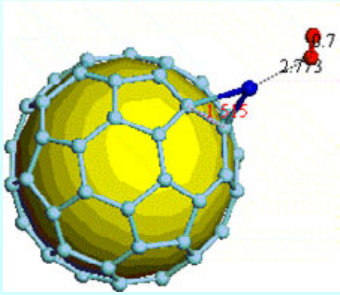
- **Sievert Measurements in (P-T) plane – What EOS to use?**
- **H_2 and CH_4 in MOF5**
- **MAGIC ROLE OF Ti in HYDROGEN STORAGE MATERIALS:**





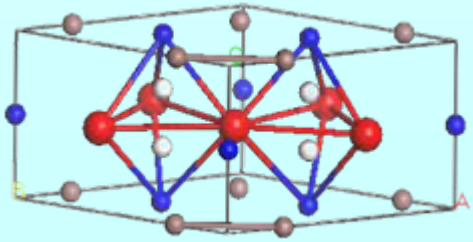
♦ **Ti-doped Alanates**
(see see *cond-mat/0604472 (April, 2006).*
Appl. Phys. Lett. **86**, 103109 (2005)
Phys. Rev. B ***70****, 060101 (R) (2004))*





♦ **Dynamics in Ti-SWNT and Ti-C_{60}**
Phys. Rev. Lett. 94,175501 (2005)
Phys. Rev. B **72**, 153403 (2005)

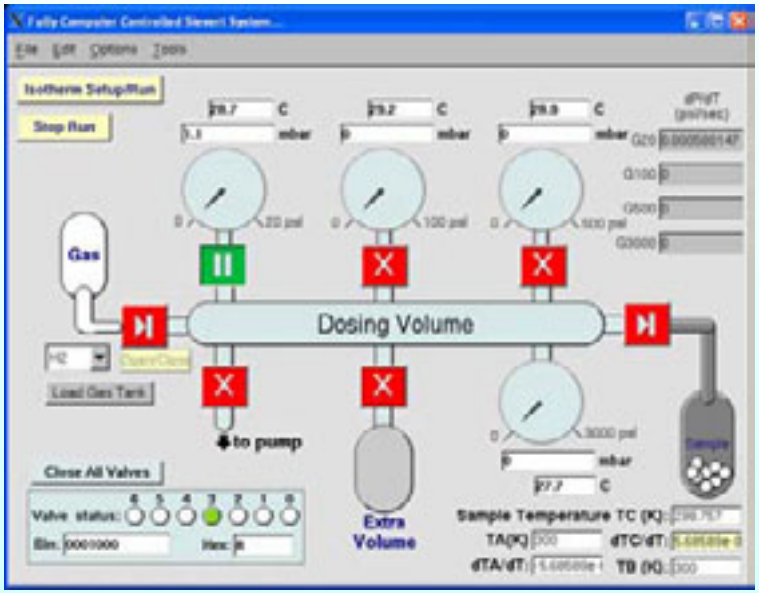
- **RE $NiInH_x$ (x=1.333 and 0.666)**

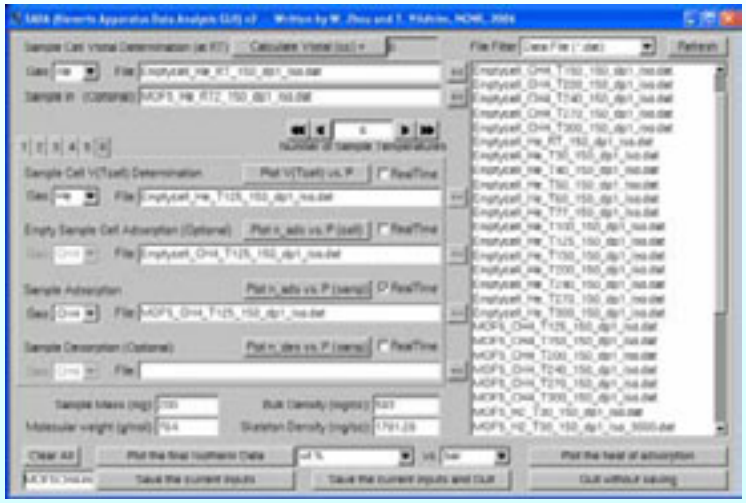


Details can be found at
http://www.ncnr.nist.gov/staff/taner/h2

II. Hydrogen Adsorption Isotherms

In order to determine the hydrogen adsorption isotherms, we developed a fully computer-controlled Sieverts apparatus which works for a large range of pressures (P: 0-100 atm) and temperatures (T: 4 –1500 K).





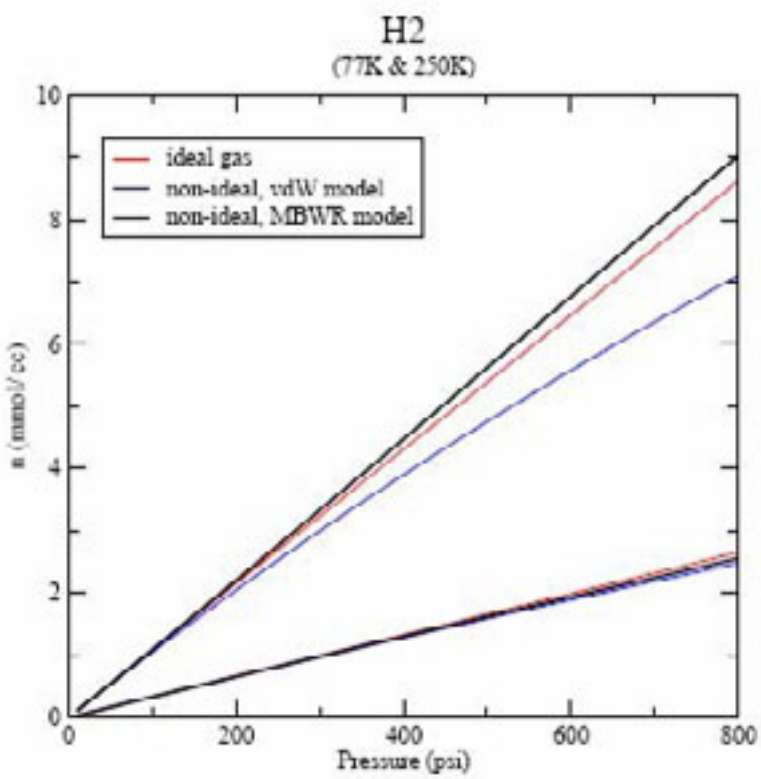
We found that in a volumetric method, the widely used vdW equation of state (EOS) is not accurate enough. To obtain reliable isotherms, the NIST-MBWR EOS should be used in the data reduction.

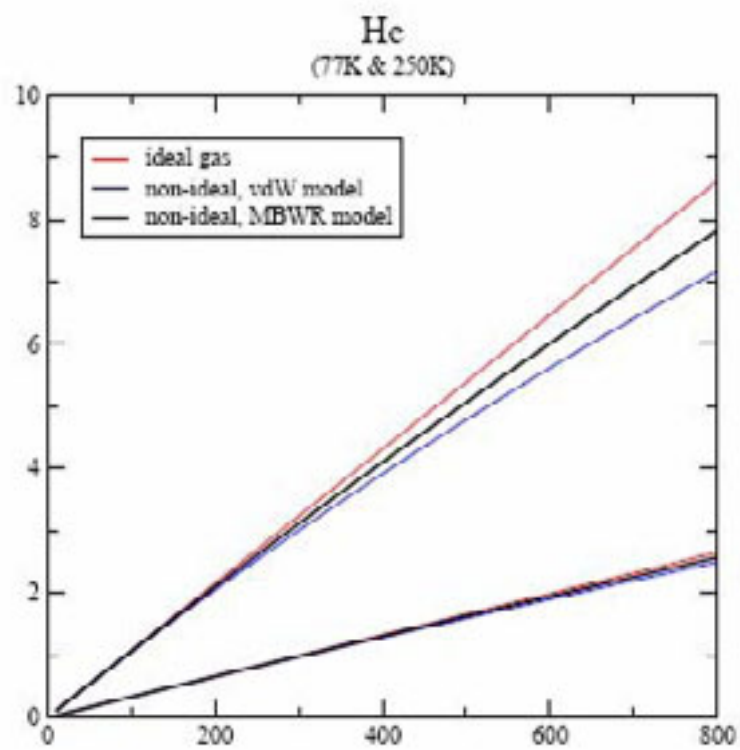
High pressure sorption/Sieverts expts: EOS matters

$$P = \frac{nRT}{V}$$ (ideal gas)

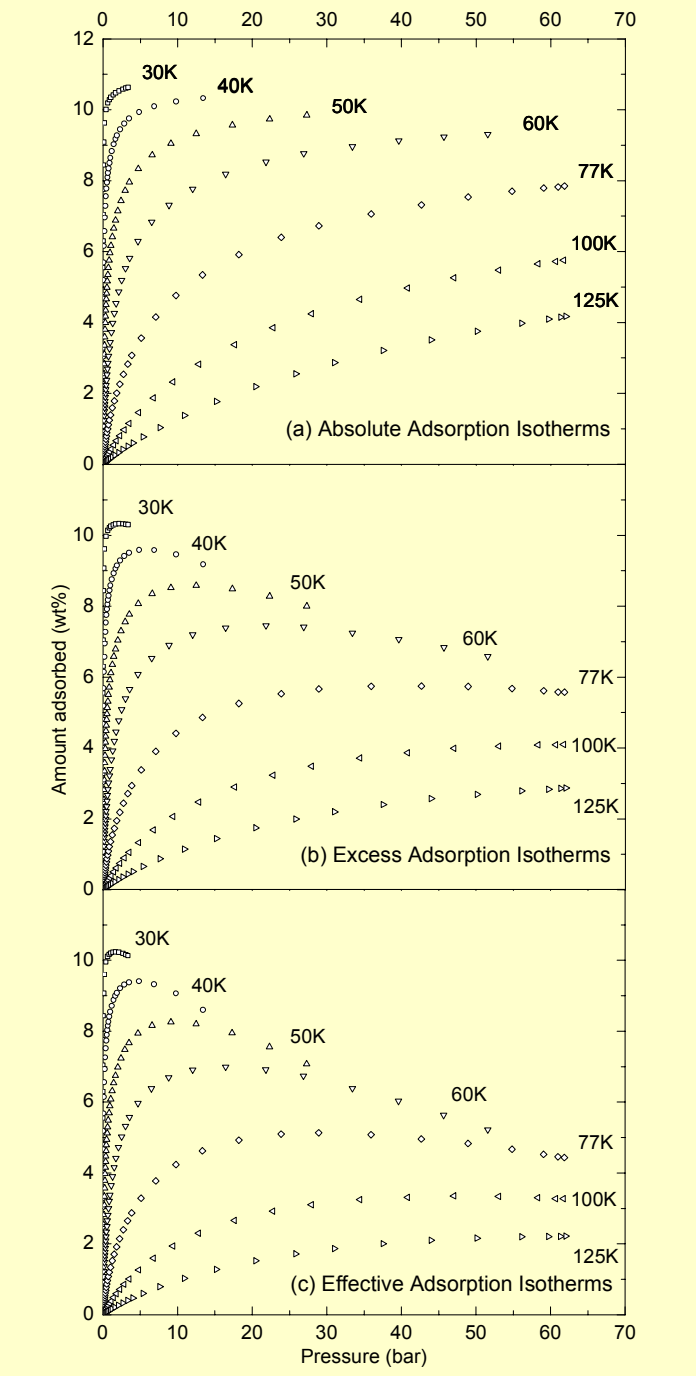
$$P = \frac{nRT}{V - nb} - \frac{n^2}{V^2} a$$ (vdW EOS)

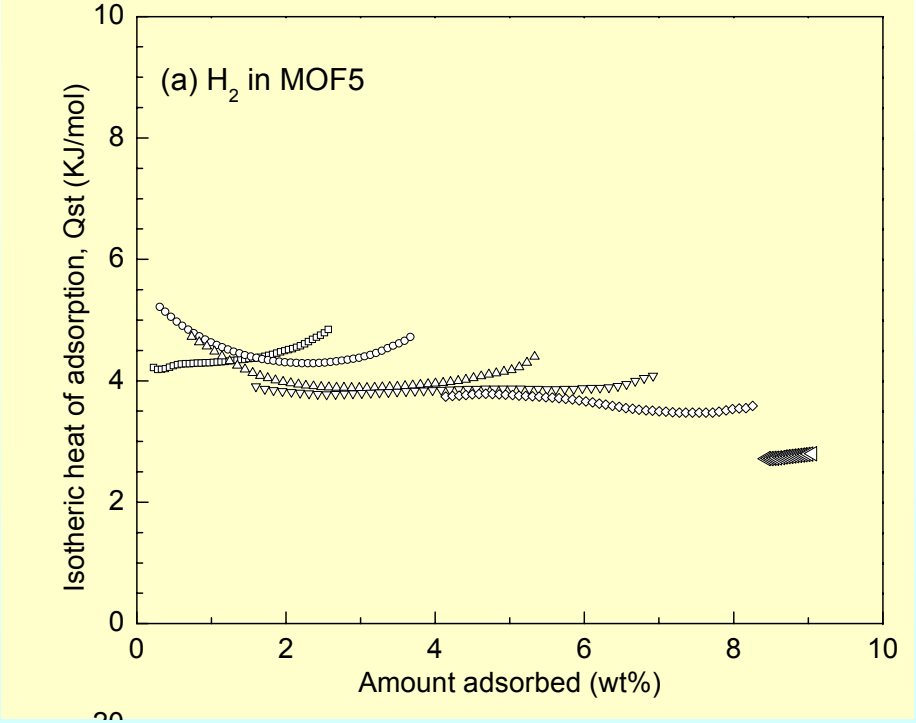
$$P = \sum_{n=1}^{9} a_n/V^n + \exp(-V_c^2/V^2) \sum_{n=10}^{15} a_n/V^{2n-17}$$ **(NIST MBWR EOS)**



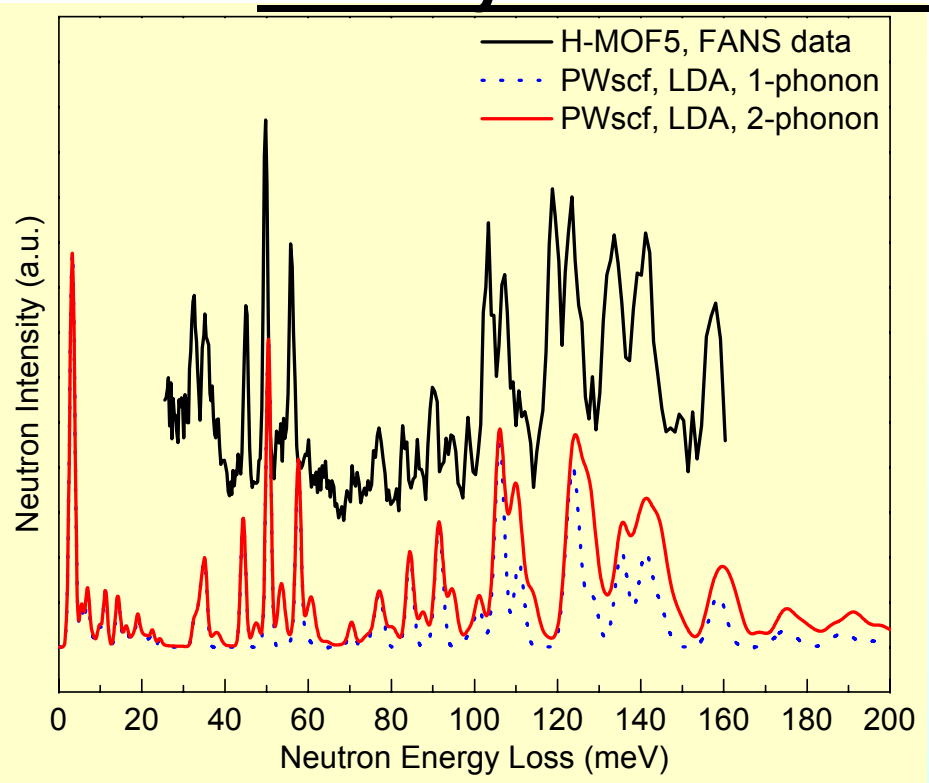


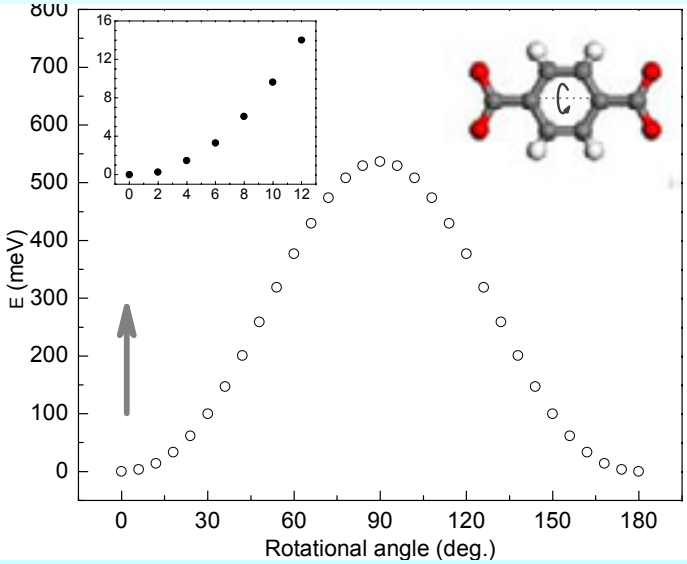
High pressure H2 isotherms in MOF5:

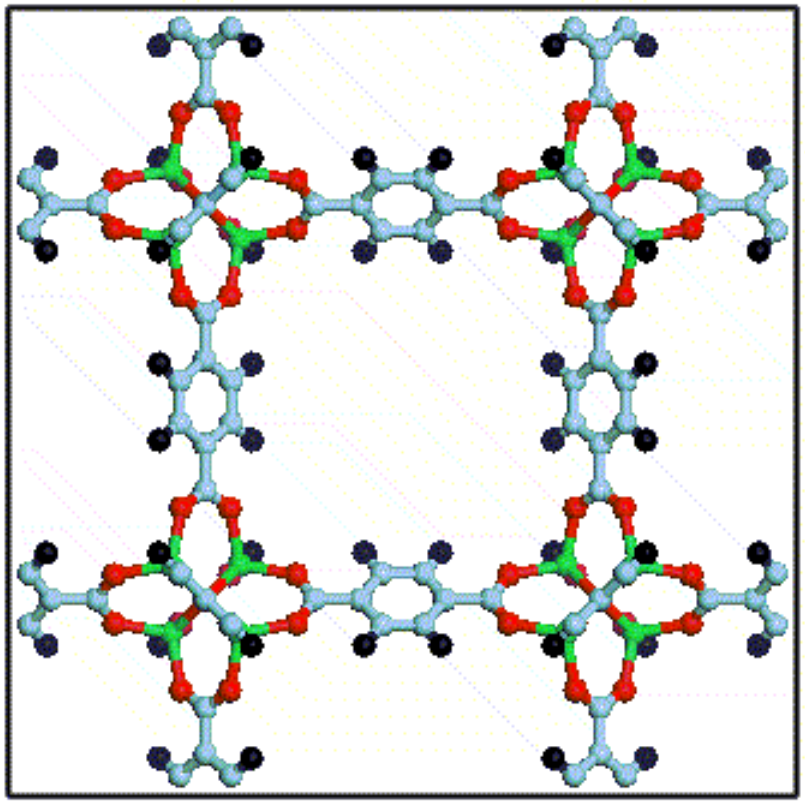




Stability and Lattice Dynamics of bare MOF5?





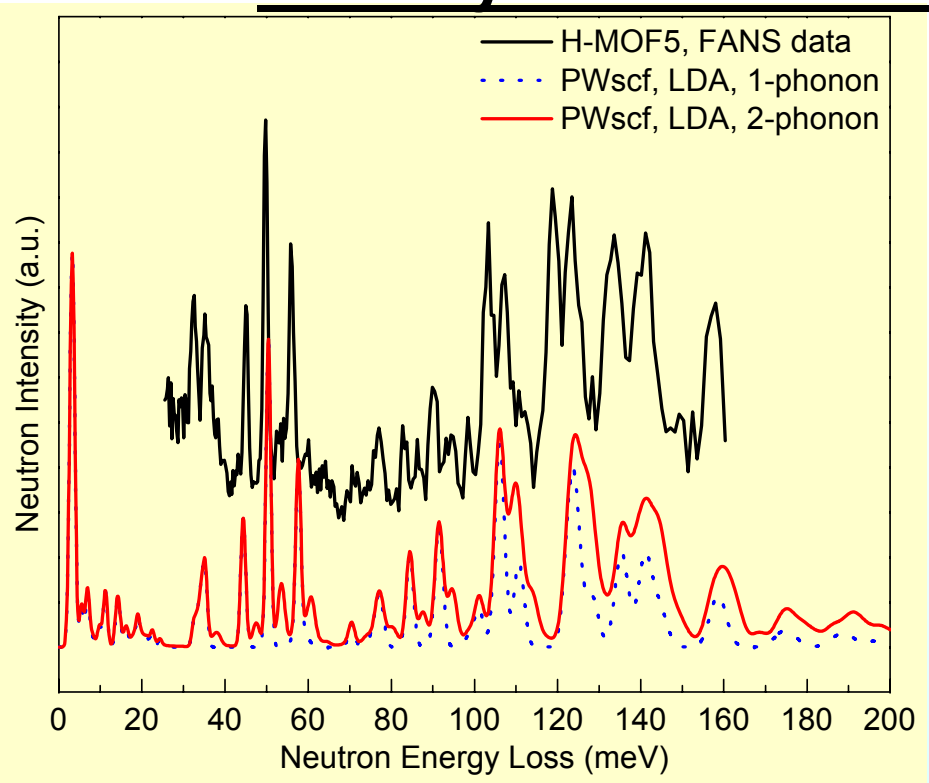


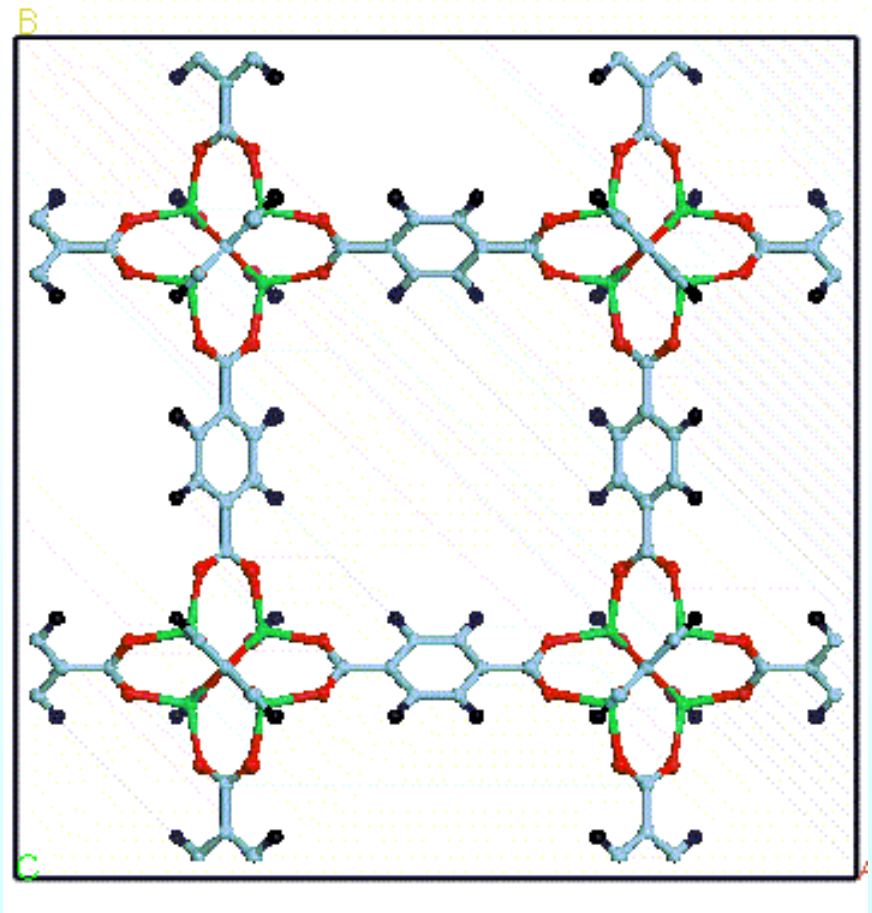
The lowest energy mode:

ω=2.66 meV

Description: All C_4H_4-linker twist around crystal axis a, b, and c. It's single degenerate.

Stability and Lattice Dynamics of bare MOF5?



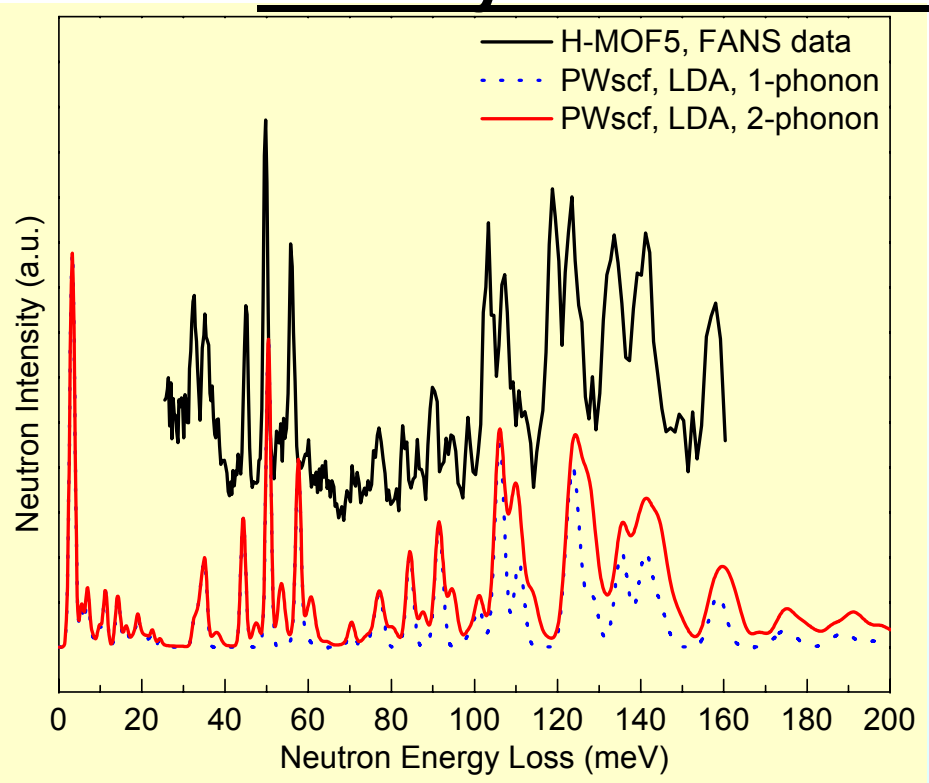


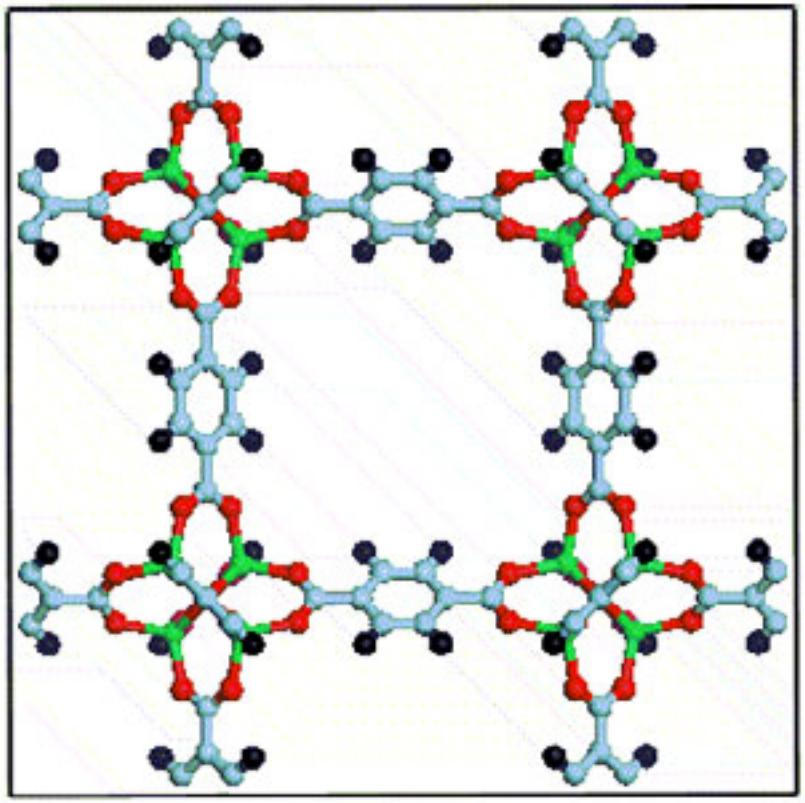
The 2nd lowest energy mode:

ω=3.21 meV

Description: Two of three C_4H_4-linker twist around two crystal axes. It's 3-fold degenerate.

Stability and Lattice Dynamics of bare MOF5?



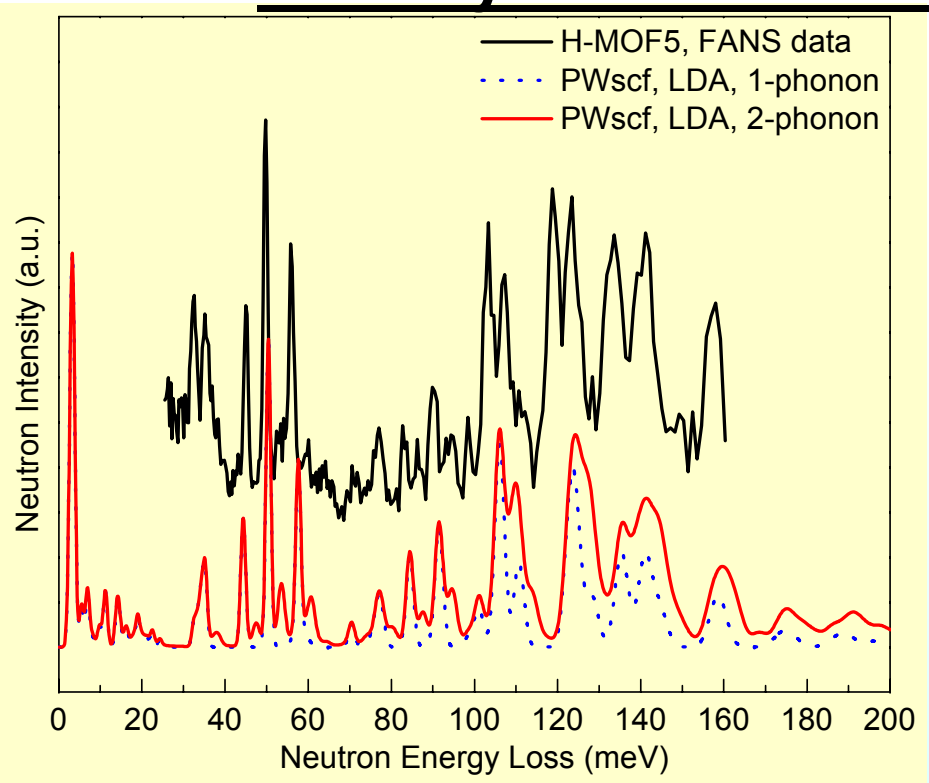


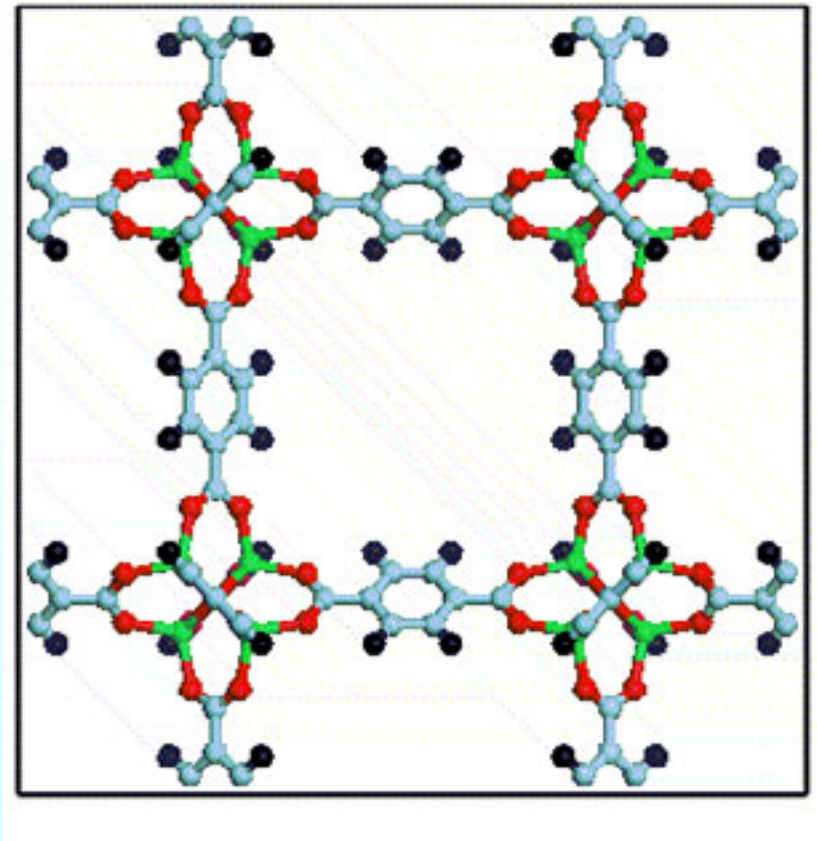
The 3rd lowest energy mode:

ω=3.77 meV

Description: All C_4H_4-linker translate along crystal axis a, b, and c. It's 3-fold degenerate.

Stability and Lattice Dynamics of bare MOF5?

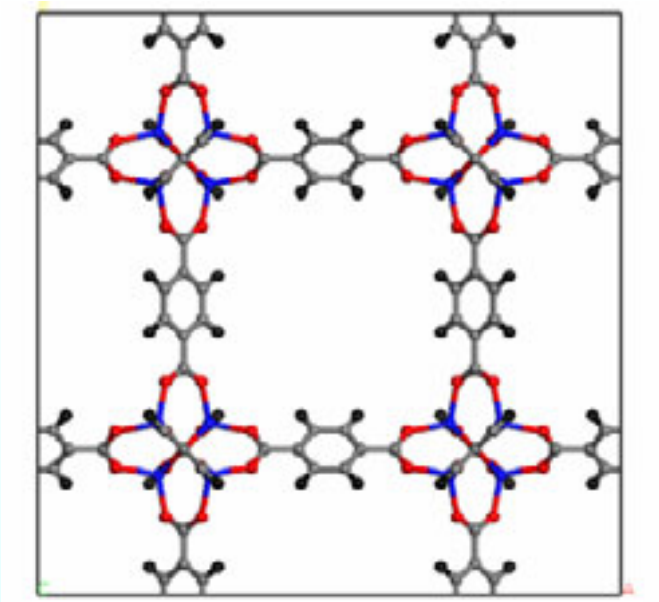


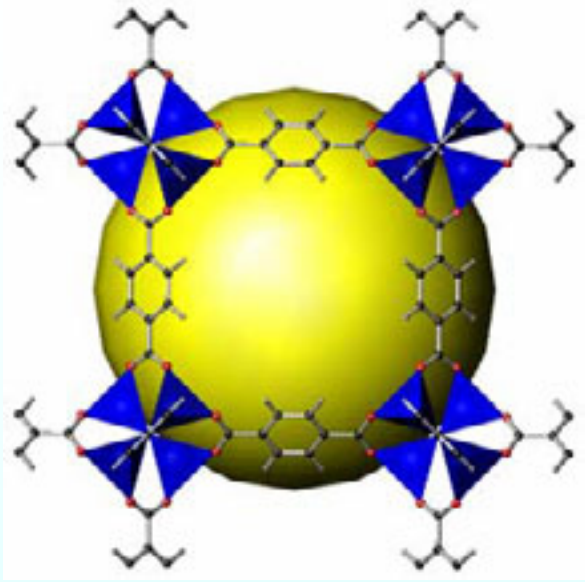


The breathing mode of ZnO_4-cluster:

ω=29 meV

Where does Hydrogen go in MOF5?





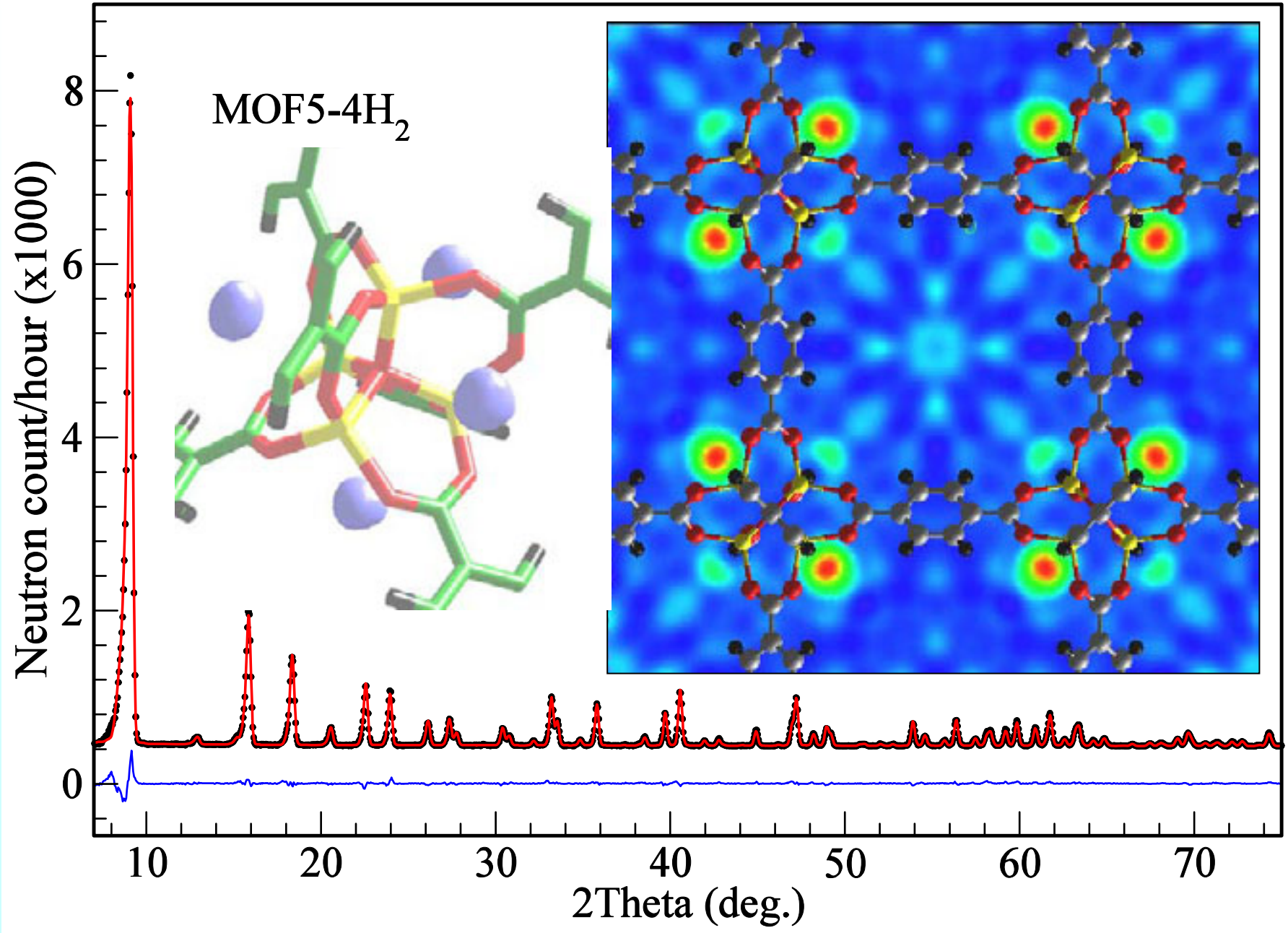
Please note that 1 H_2/4Zn → 0.255 wt%

1 wt% → 6 kg H_2/m^3 (Liquid H_2 at 20.3 K has 70 kg H_2/m^3)

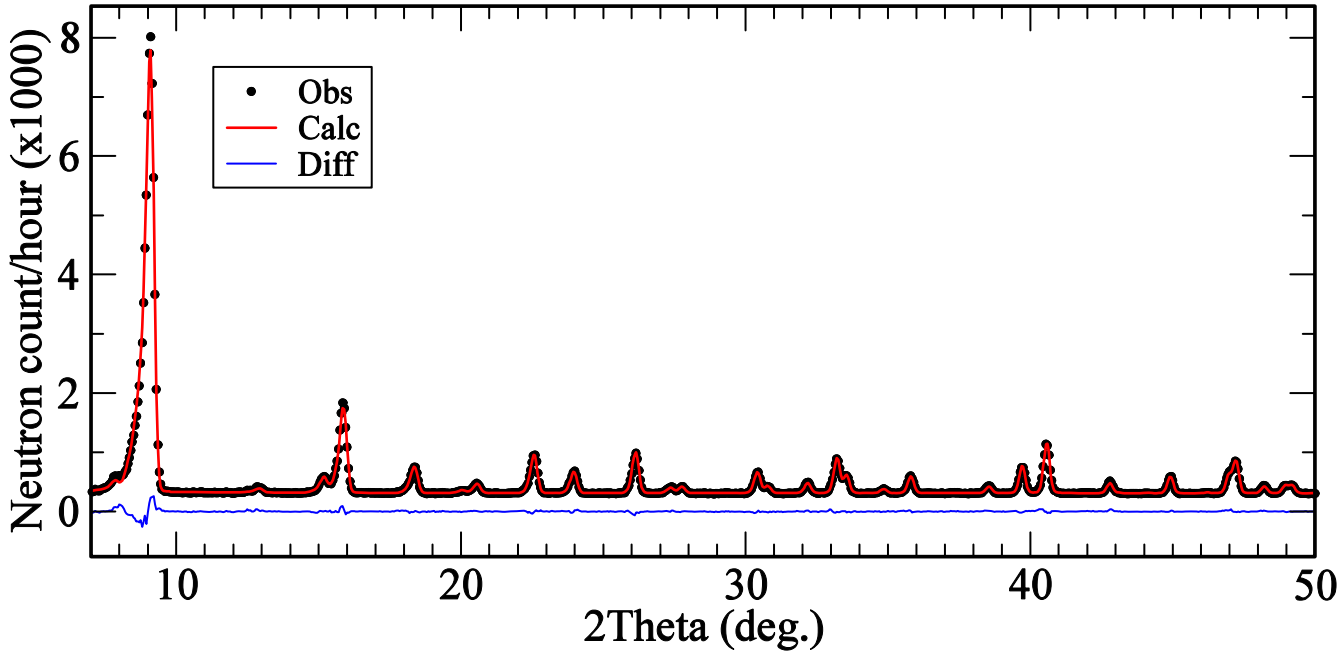
The difference Fourier Analysis of Neutron Powder Diffraction is an ideal way to locate the absorbed molecules in host lattice:

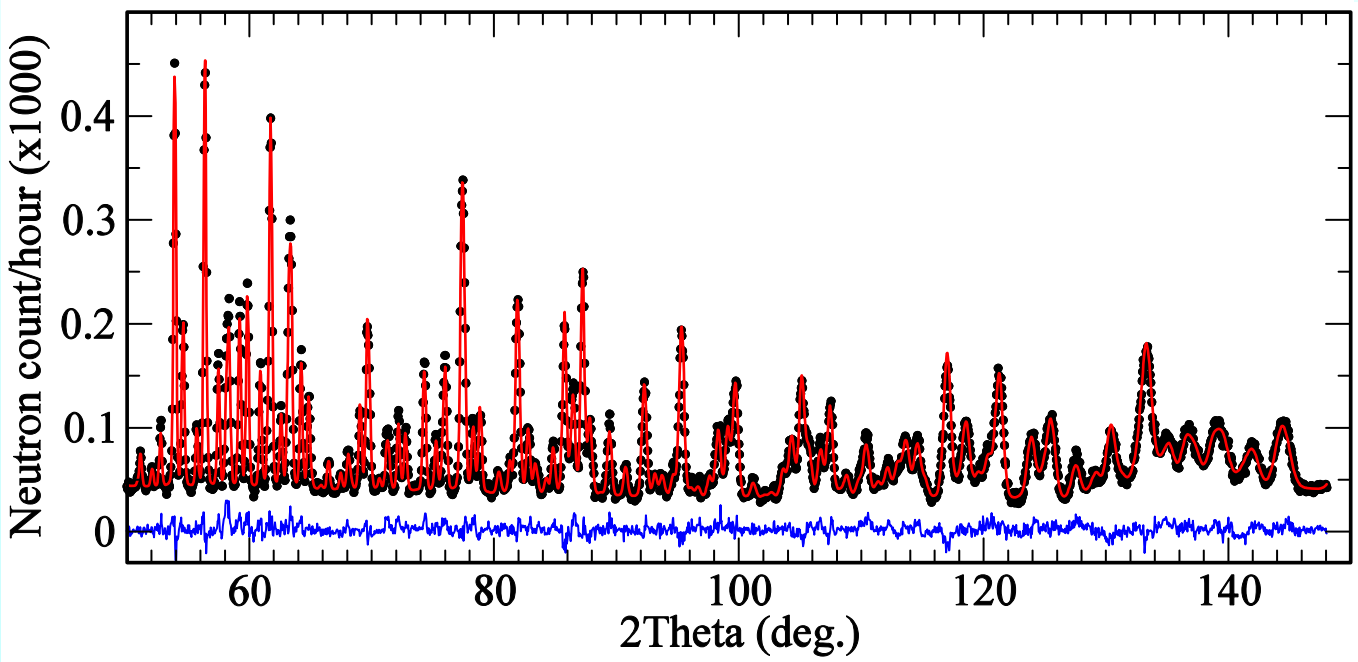
ρ (absorbed molecule) = ρ (host+molecule) – ρ (host)

Rietveld Refinement of $4H_2$/4Zn in MOF5

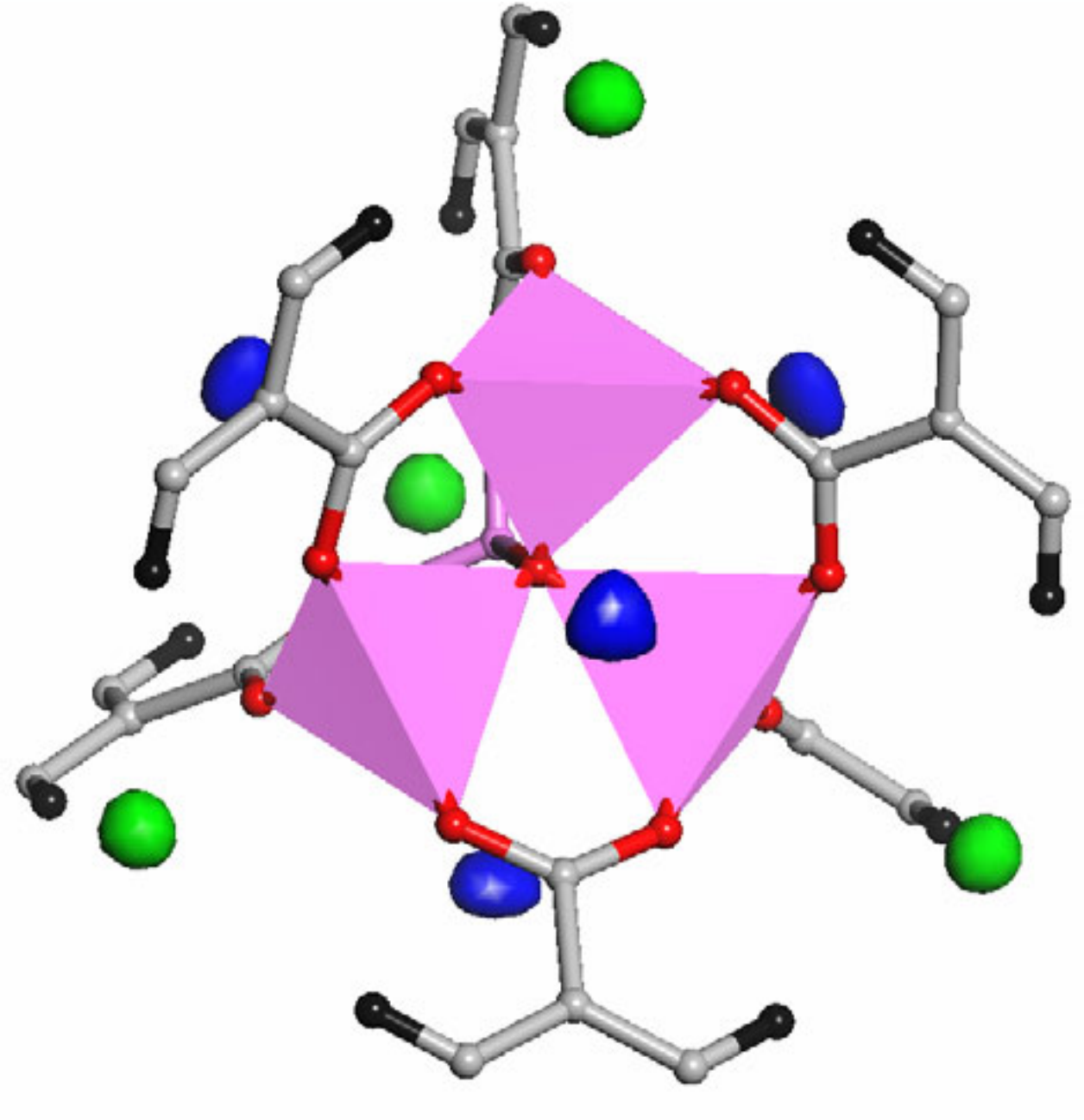


Rietveld Refinement of the 8H2-4Zn MOF5 at 3.5 K





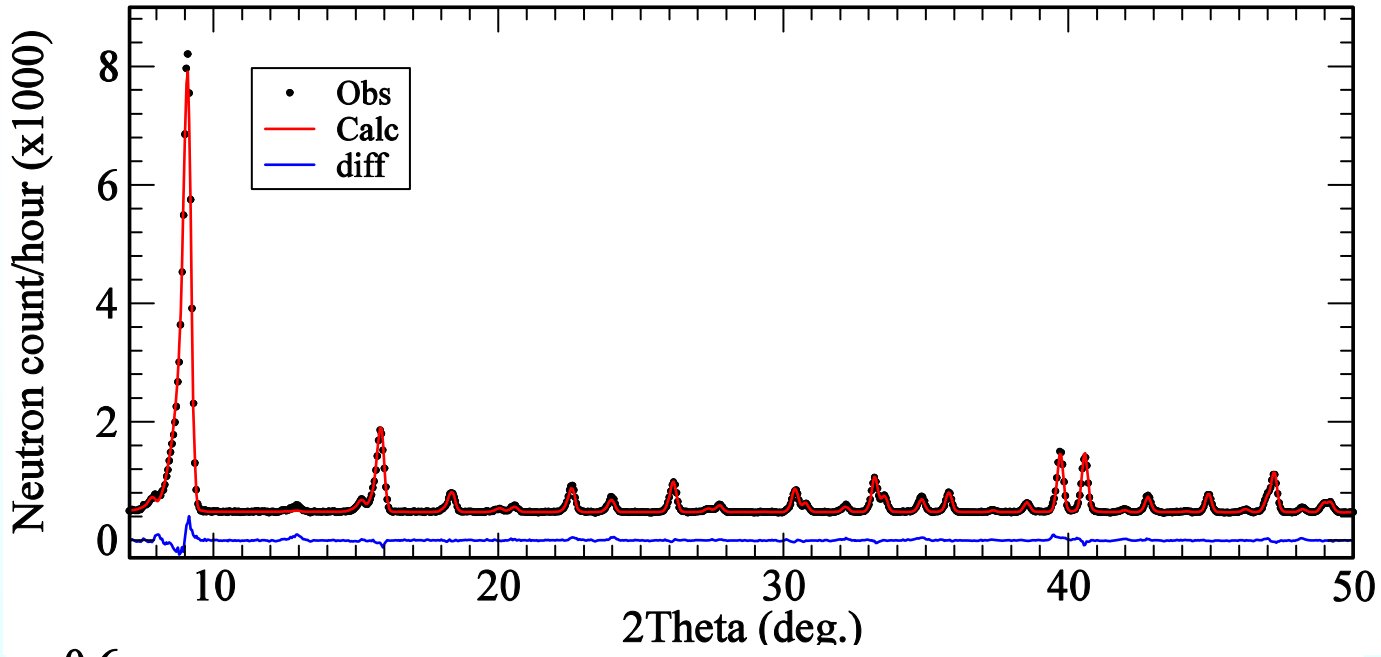
First Two Absorption Sites in MOF5 at 3.5 K

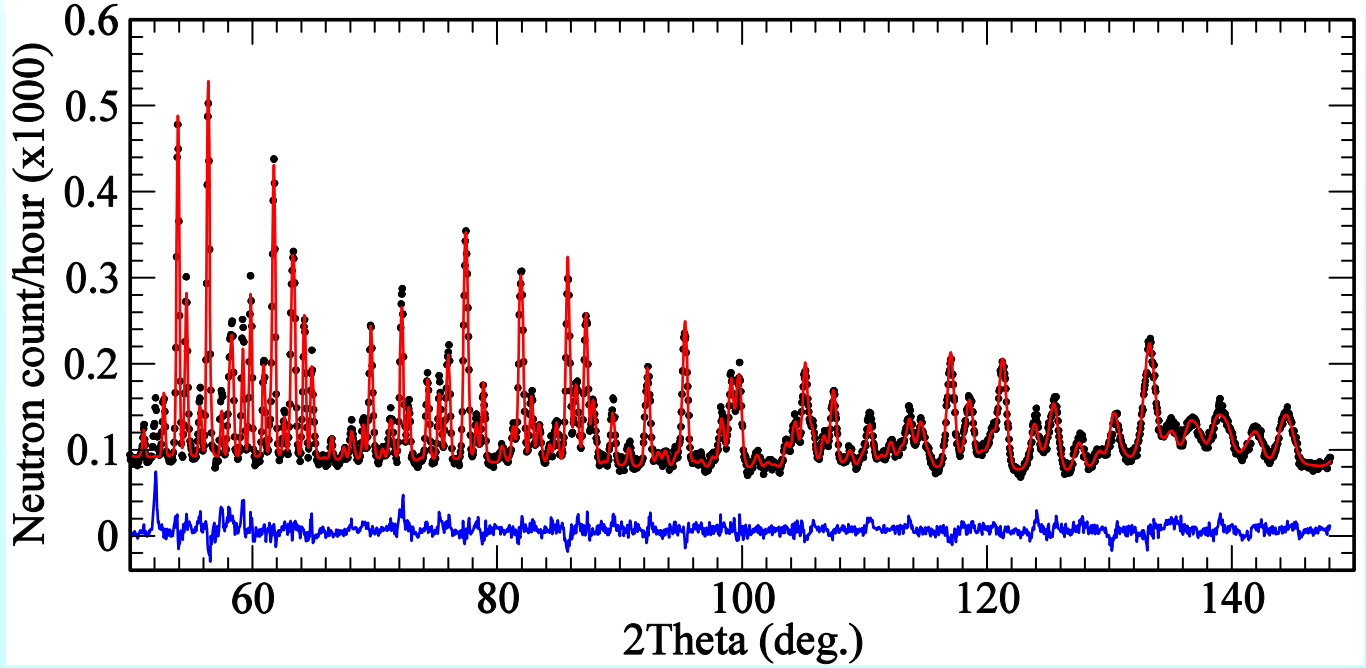


Cup-site:
(x,x,x)
x=0.1657

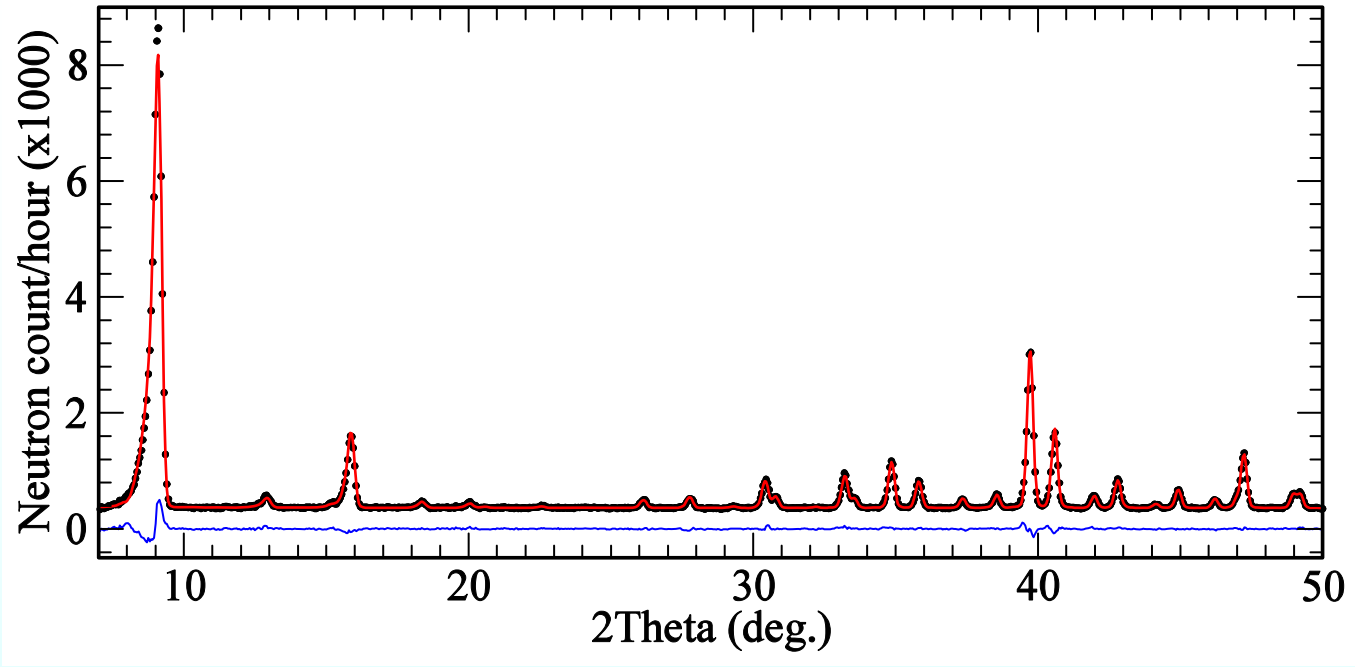
ZnO_3-site:
(x,y,y)
x=0.3730
y=0.1270

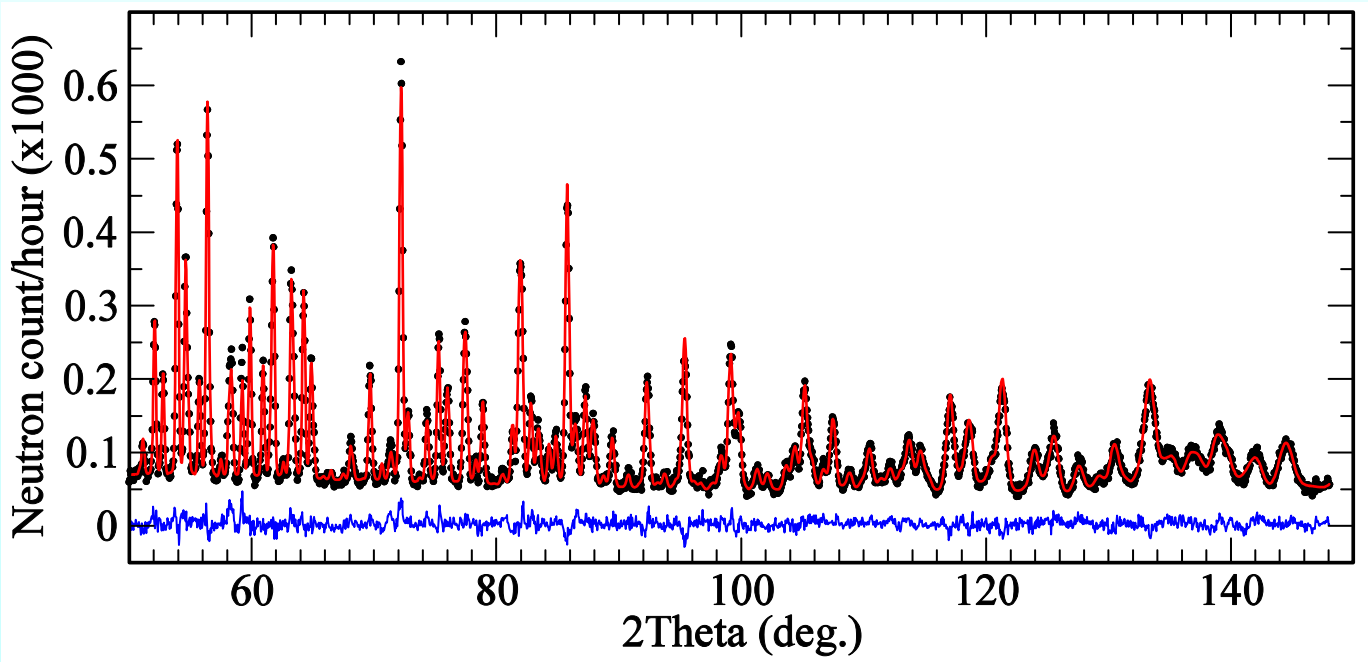
Rietveld Refinement of the 14H2-4Zn MOF5 at 3.5 K



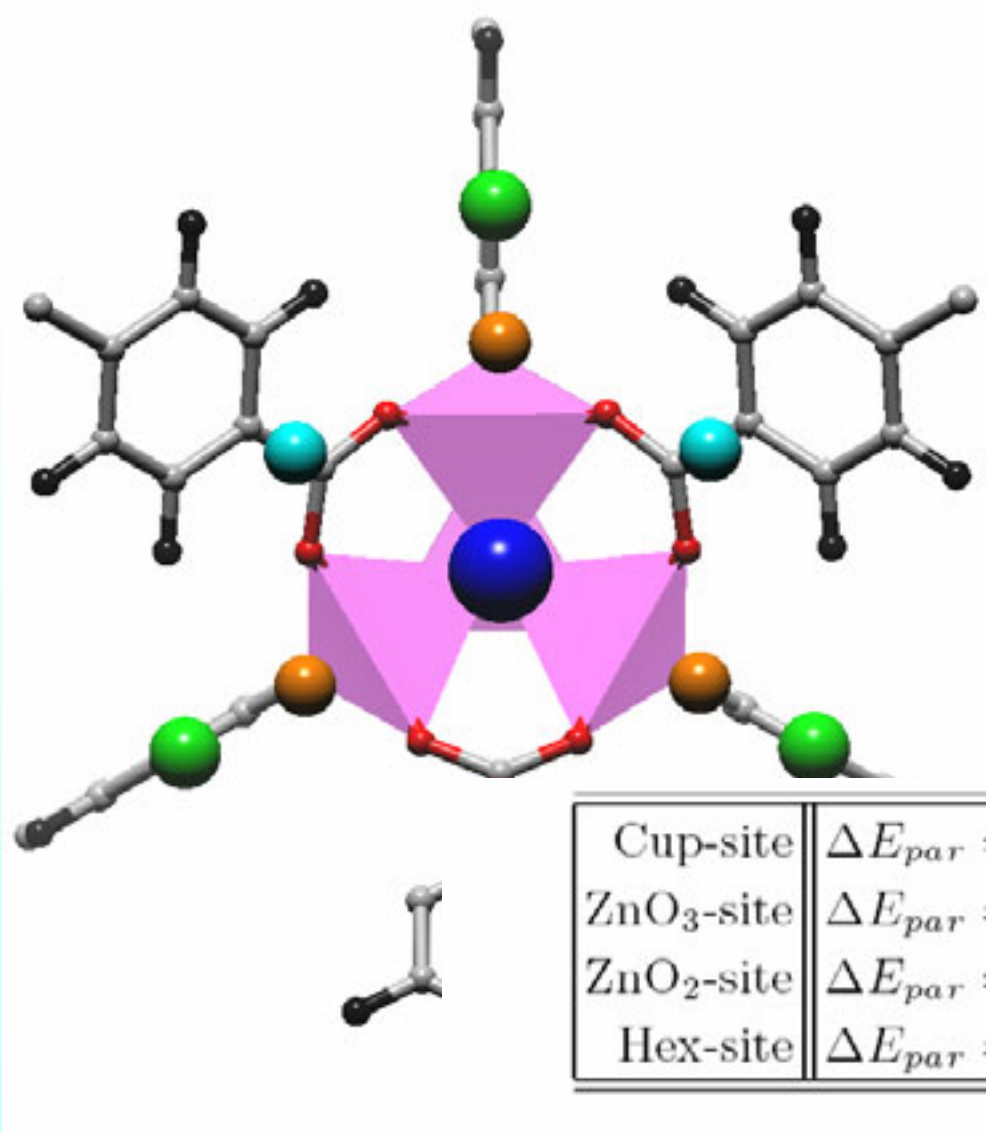


Rietveld Refinement of the 26H2-4Zn MOF5 at 3.5 K





Four Different Absorption Sites in MOF5 at 3.5 K



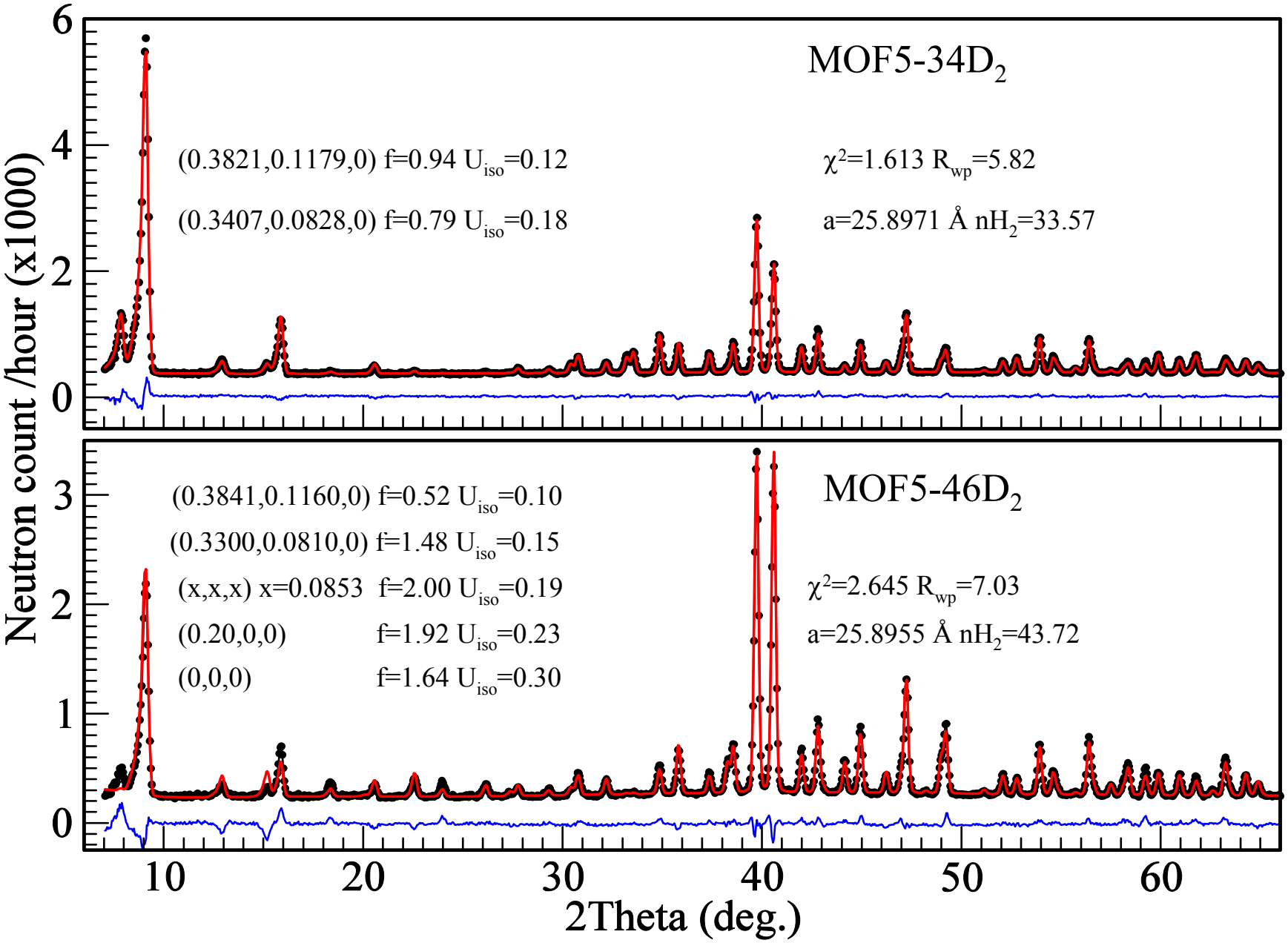
ZnO_2-site:
(x,y,y)
x=0.2496
y=0.0953

Hex-site:
(x,x,0)
x=0.1621

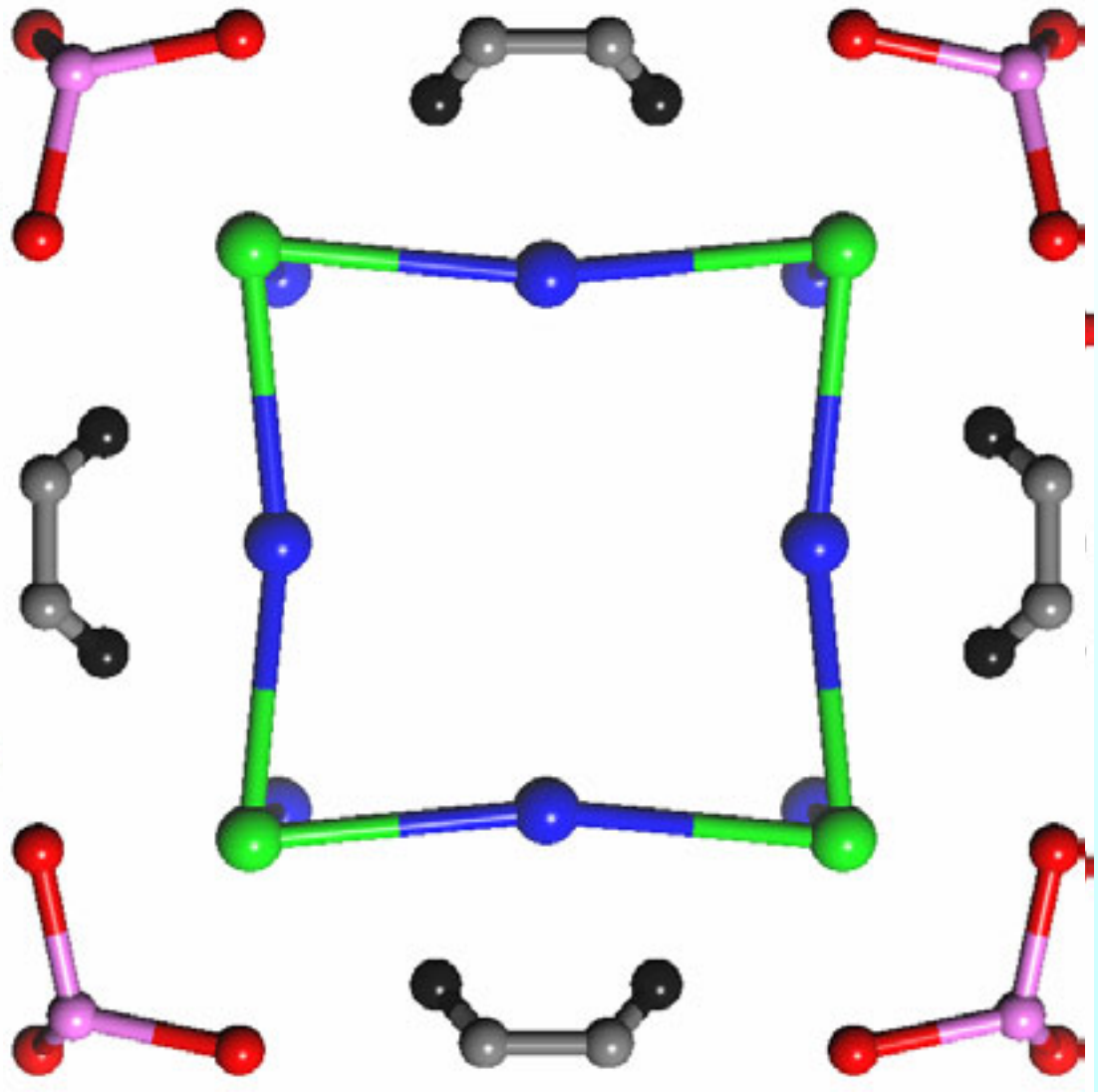
Cup-site	$\Delta E_{par} = 0.133$ eV	$\Delta E_{perp} = 0.160$ eV
ZnO_3-site	$\Delta E_{par} = 0.086$ eV	$\Delta E_{perp} = 0.115$ eV
ZnO_2-site	$\Delta E_{par} = 0.056$ eV	$\Delta E_{perp} = 0.108$ eV
Hex-site	$\Delta E_{par} = 0.092$ eV	$\Delta E_{perp} = 0.106$ eV

TABLE I: The calculated binding energies for four-adsorption sites when H_2 molecule is parallel and perpendicular to the 3-fold axis near the adsorption sites.

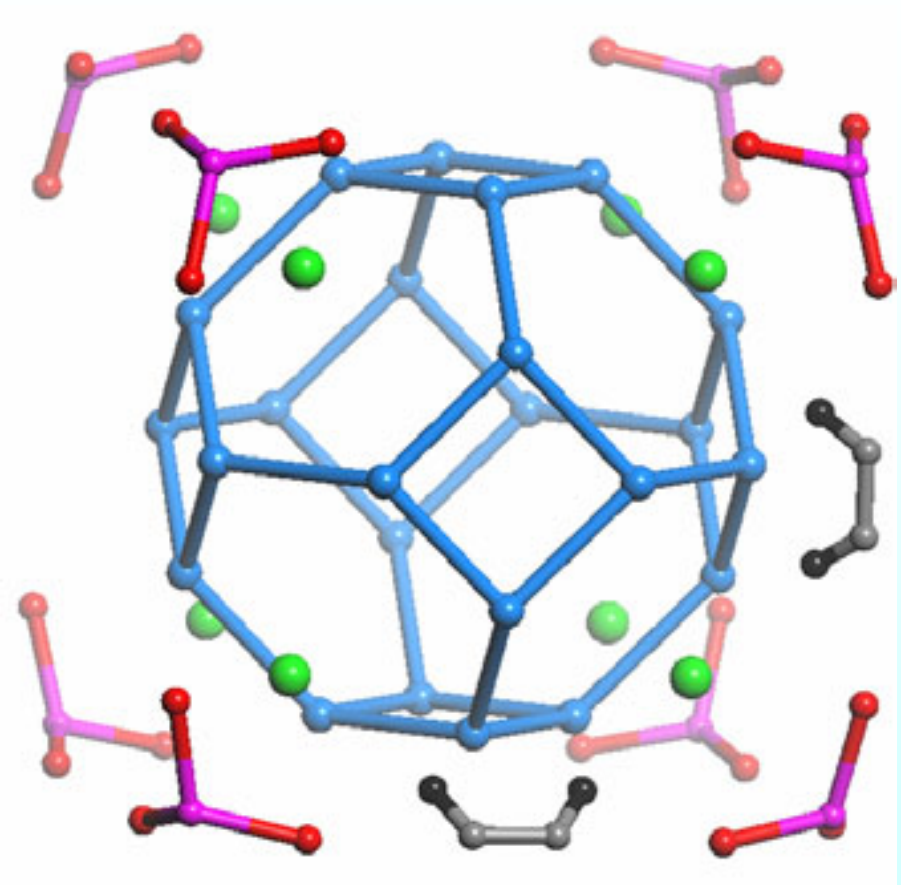
Hydrogen Nanocage Formation at high-loading 34 and 46D2-4Zn

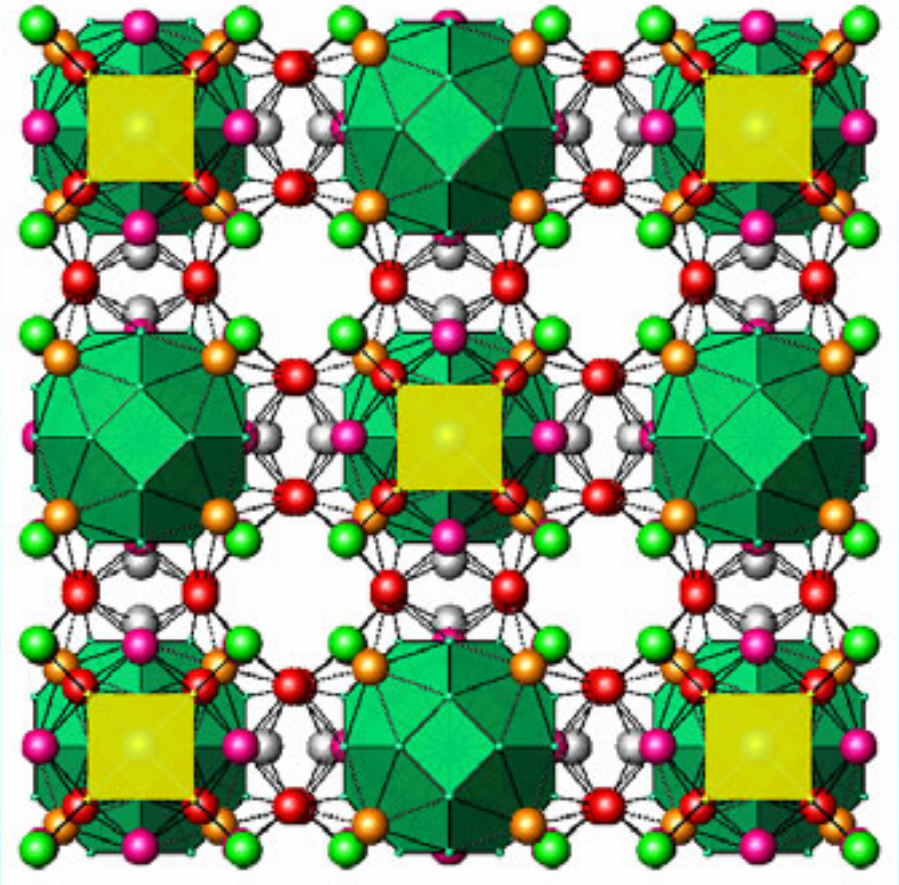


Hydrogen Nanocage Formation at high-loading 34 D2-4Zn



Rietveld Refinement of the 46H2-4Zn MOF5 at 3.5 K

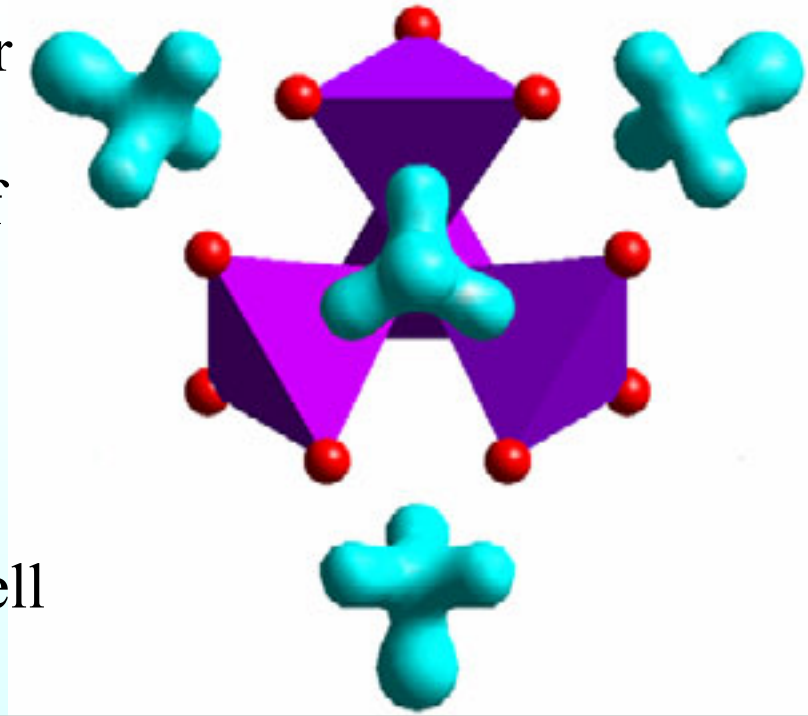




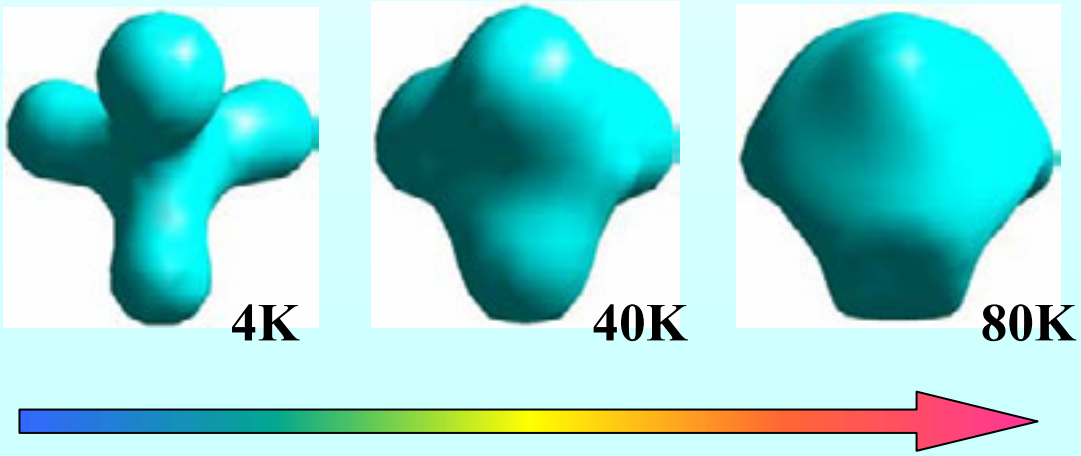
At high-concentration hydrogen loading, we observed 3D interlinked high-symmetry hydrogen nanocages with short intermolecular distances of 3.0 Ang.

III. CH_4 Adsorption Sites in MOF5

The isosurface of the difference-Fourier (DF) neutron scattering-length density superimposed with the ZnO_4 clusters of the MOF5 host structure, indicating the location of the first methane adsorption sites. This is a "direct measurement" (like taking a picture) of the methane molecules packed in the solid with a well defined orientation.

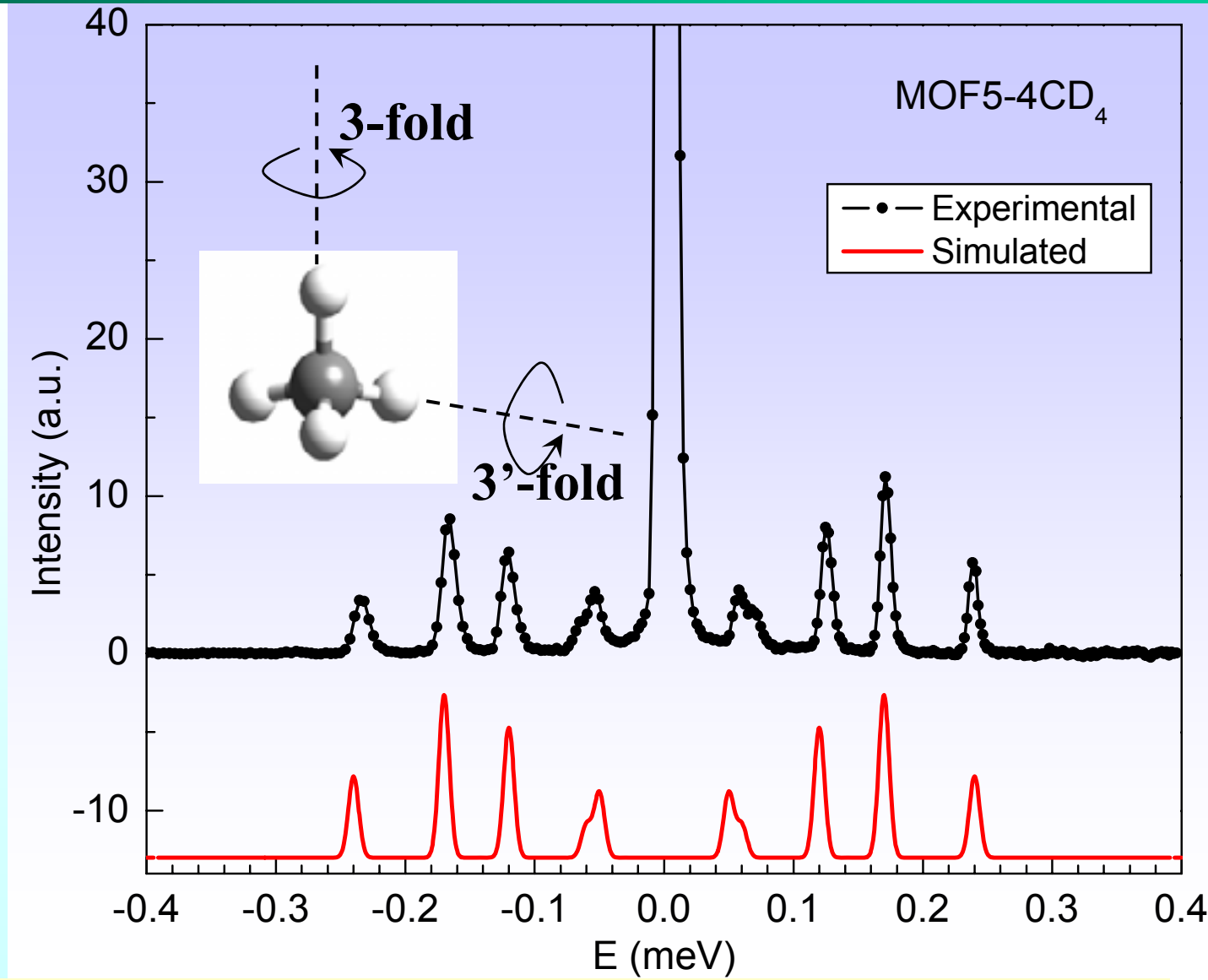


"Temperatue-dependent DF-neutron scattering" is further used to visualize the methane orientational dynamics with increasing temperature as shown on the right:



IV. Quantum Rotational Tunnel Splitting of CH_4

The rotational tunneling spectrum of CH_4-MOF5 taken at DCS. The spectrum can be interpreted using a simple theory based on a tunneling around two 3-fold axes…



The rotational barriers about the **3**- and **3'**-fold axes were found to be ~41 and ~22 meV respectively, as shown in the inset.

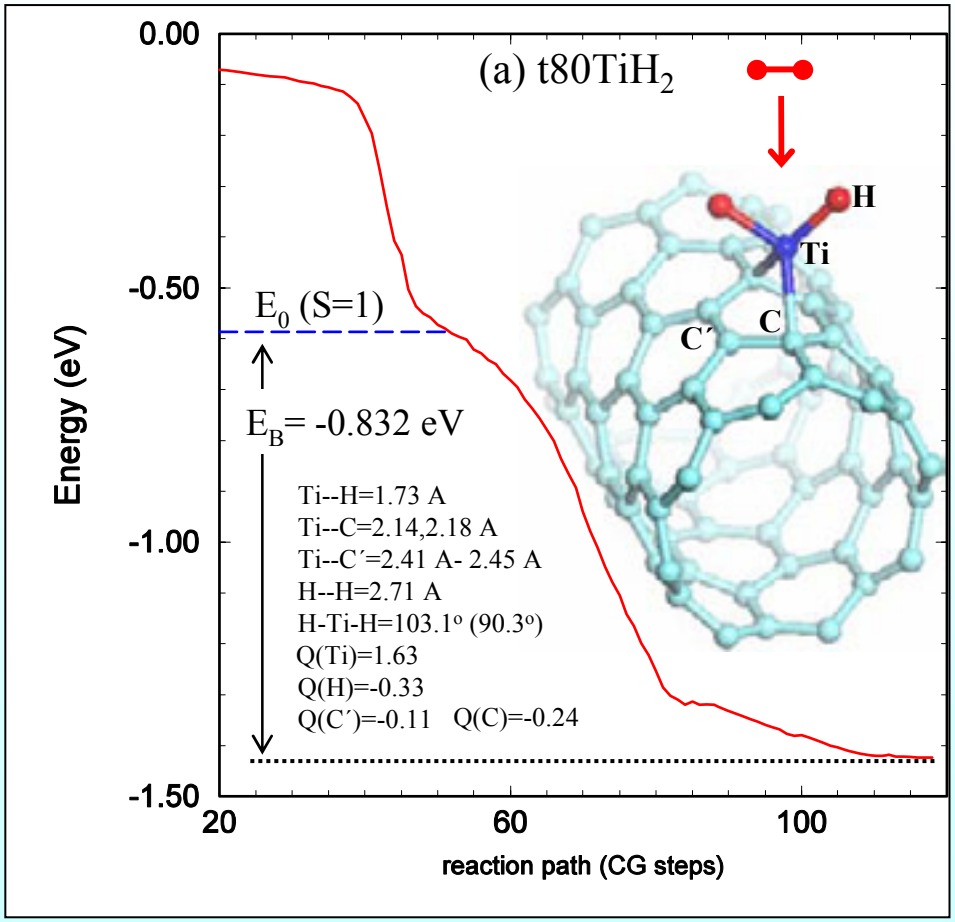
Magic Role of Ti in Hydrogen Storage Materials

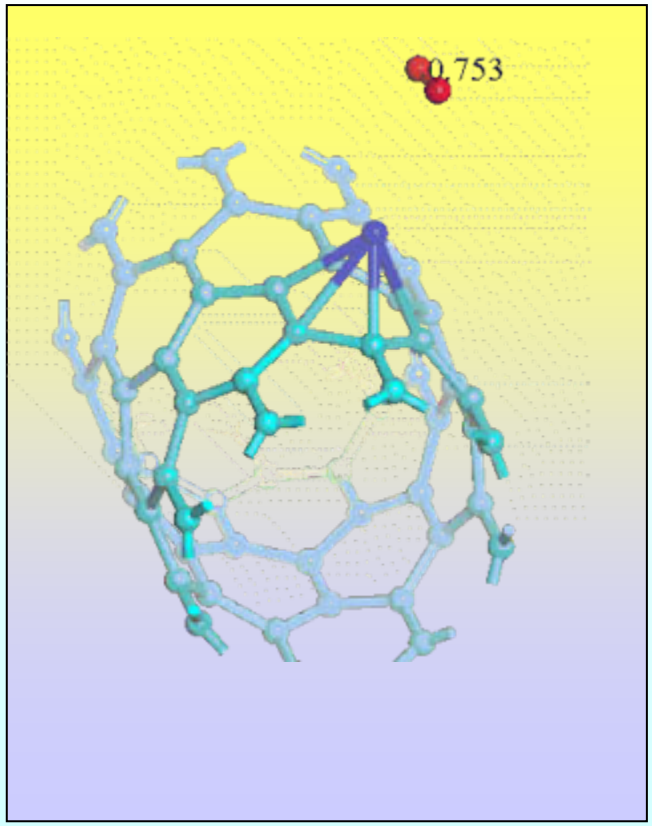
Most research on hydrogen storage attempts to achieve practical goals based on classic interactions of **physisorption** (on high surface area materials) or **chemisorption** (complex metal hydrides).

Our concept is much simpler and more versatile. We propose to decorate light transition metals (TM) onto different molecules/nanostructures through Dewar coordination (hybridization of nanostructure LUMO orbitals with TM d-orbitals), which will then bind multiple molecular hydrogens *via* Kubas interactions (hybridization between H_2-σ^* antibonding and TM d-orbitals).

$t80TiH_2$

Dissociative Adsorption of a single H_2 over Ti-SWNT

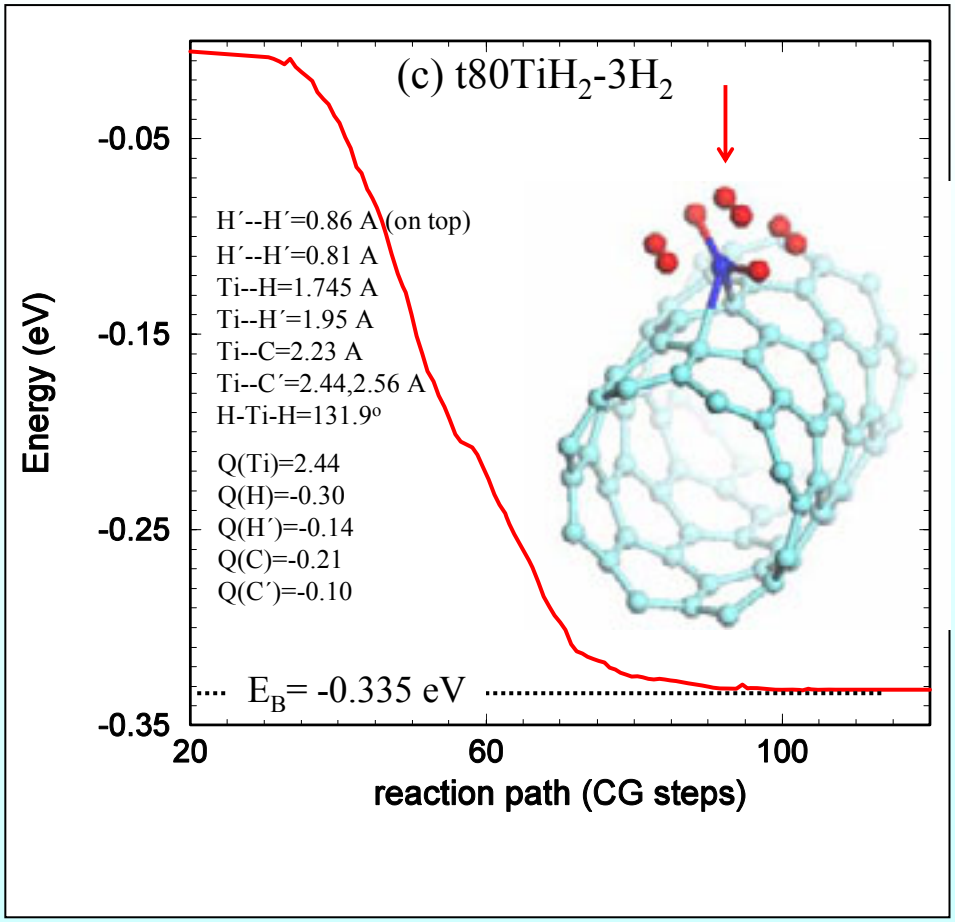


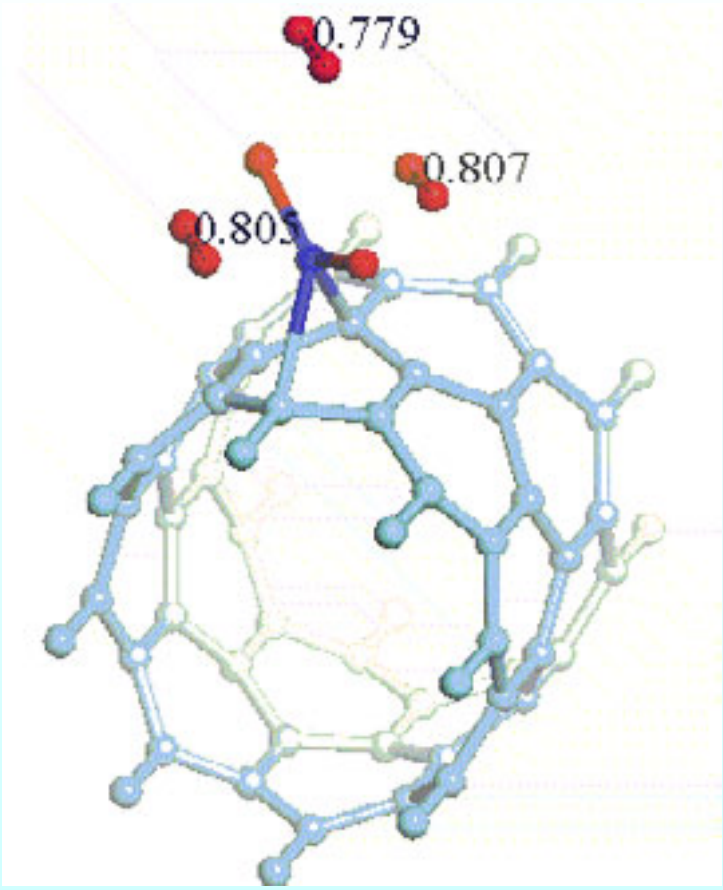


LEFT: Energy versus the reaction path for the dissociative desorption of H_2. H_2 first approaches to Ti, then it dissociates and then TiH_2 group rotates so that H comes over C atoms! See the animation. The binding energy is –0.832 eV per H_2.

$t80TiH_2$-$3H_2$

Strong adsorption of fourth H_2 over $t80TiH_2$!

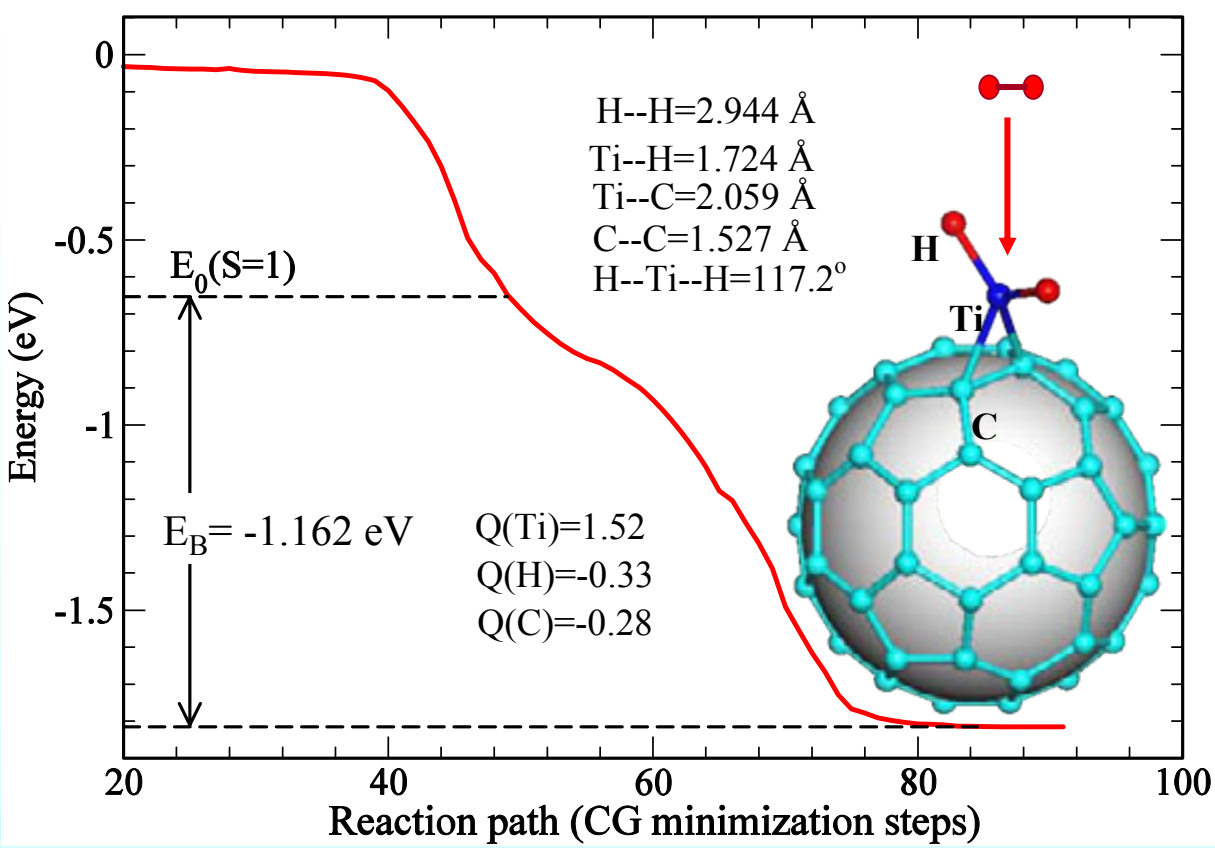


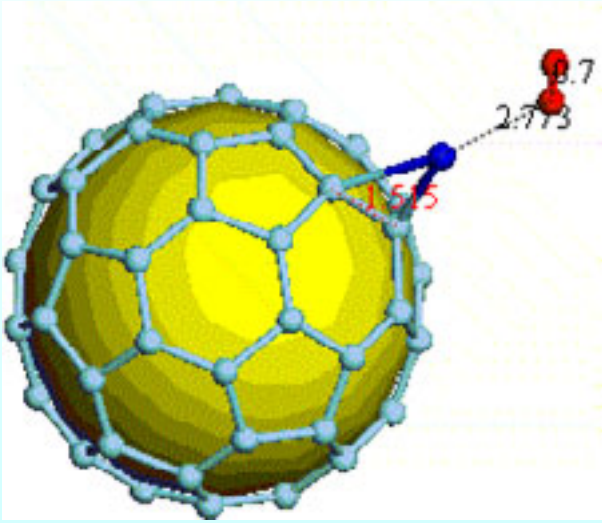


LEFT: Energy curve as the fourth H_2 molecules approaches from top to TiH2 group (red arrow). The binding energy for the 4th H_2 is –0.335 eV, slightly different than the binding energy of the side H_2 molecules (which was 0.445 eV).

$C_{60}Ti(D)H_2$

Dissociative Adsorption of a single H_2 over $C_{60}Ti(D)$

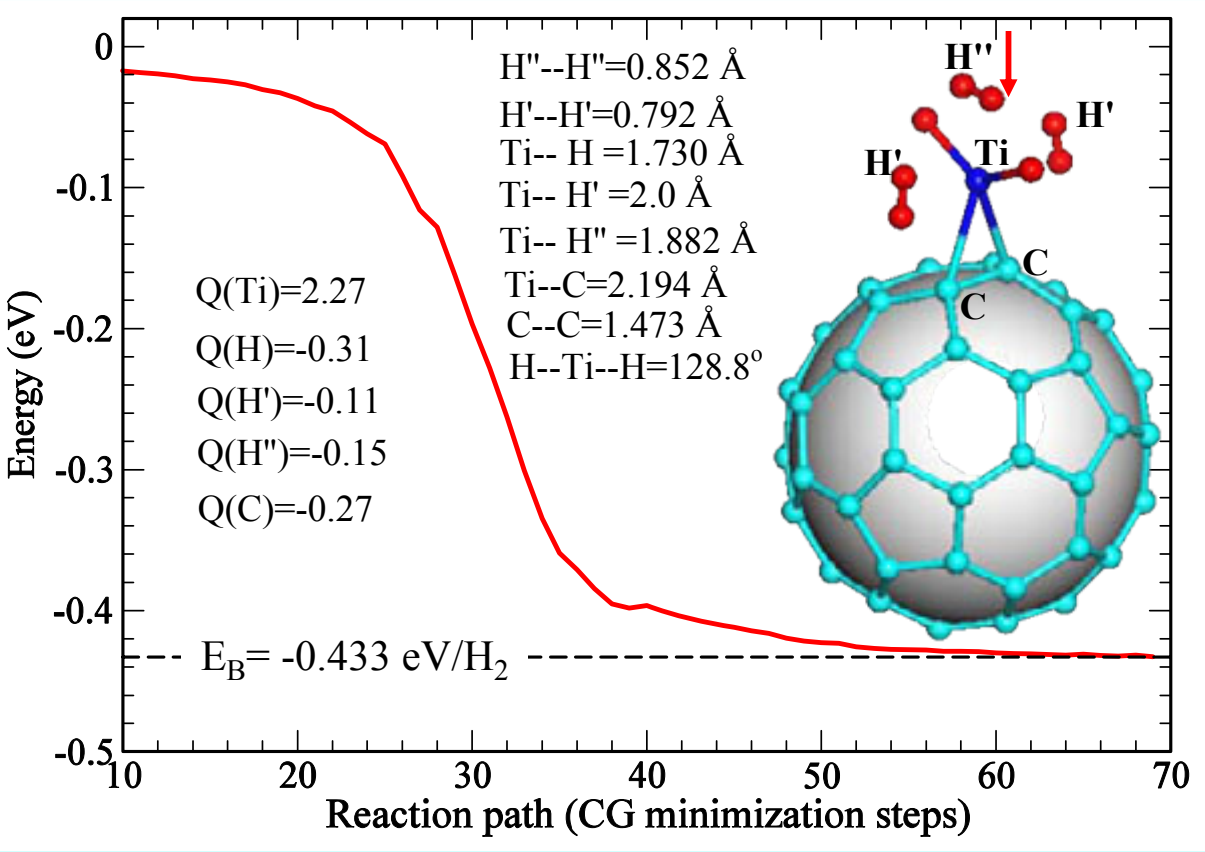


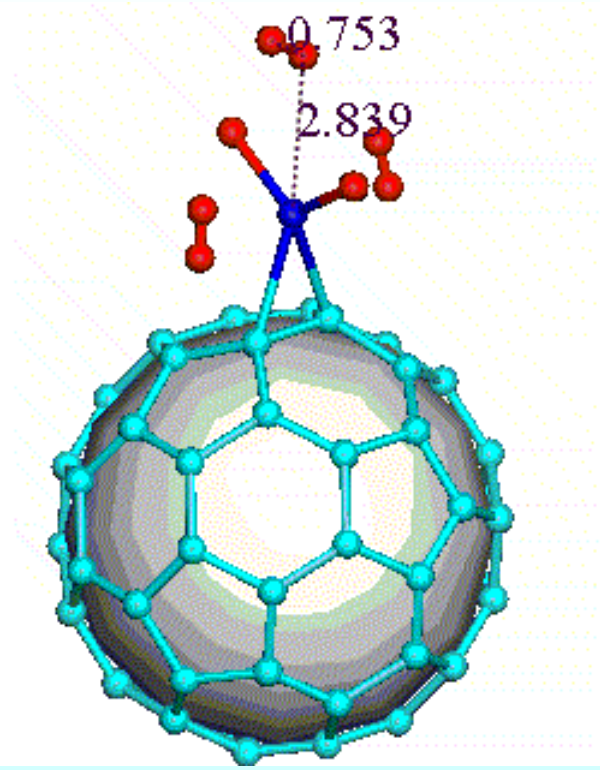


Energy versus the reaction path for the dissociative desorption of H_2. H_2 first approaches Ti while H-H bond distance increases to 0.9 A (near CG step 44), then Ti-H rapidly decrease to 1.75 A (near CG step 50) at which H2 starts to dissociate to form TiH_2 group (H-Ti-H angle increases from 35 to 117 between CG steps 50-80)! See the animation. The binding energy is –1.162 eV per H_2.

$C_{60}Ti(D)H_2 - 3H_2$

Molecular Adsorption of 3rd H_2 over $C_{60}Ti(D)H_2$-$2H_2$





Energy versus the reaction path for the molecular absorption of a third H_2 molecules on C60Ti(D)H2-2H2. The energy continuously drops as the H2 approaches Ti atom, with increasing bond length which is 0.852 A at the minimum configuration where Ti-H is 1.88 A. The binding energy for the third H2 molecule is –0.433 eV.

Ti-Cluster Formation!
(Pure Jena *et al JACS 127, 14583, 2005*)

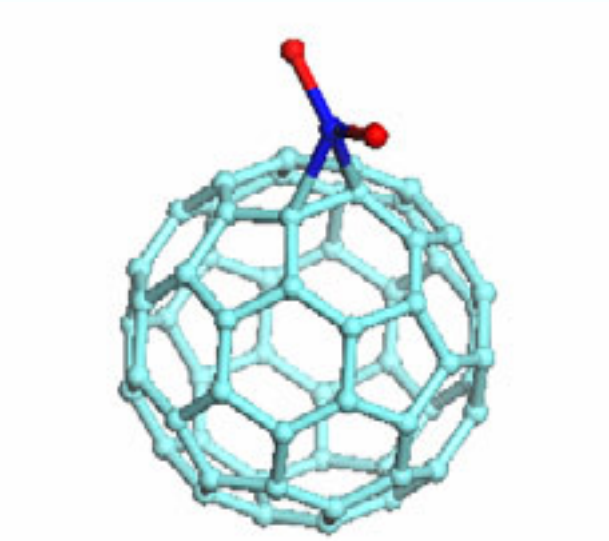
The authors compared the total energies of different structures and then jump to conclusion that the one with higher energy is not stable and tends to transform to the lowest energy structure!!!!

With the same logic, one then concludes that the expensive diamond that we got for our wifes should eventually transform to cheap graphite that we find in pencil because graphite has lower energy than diamond!!!!

CONCLUSION

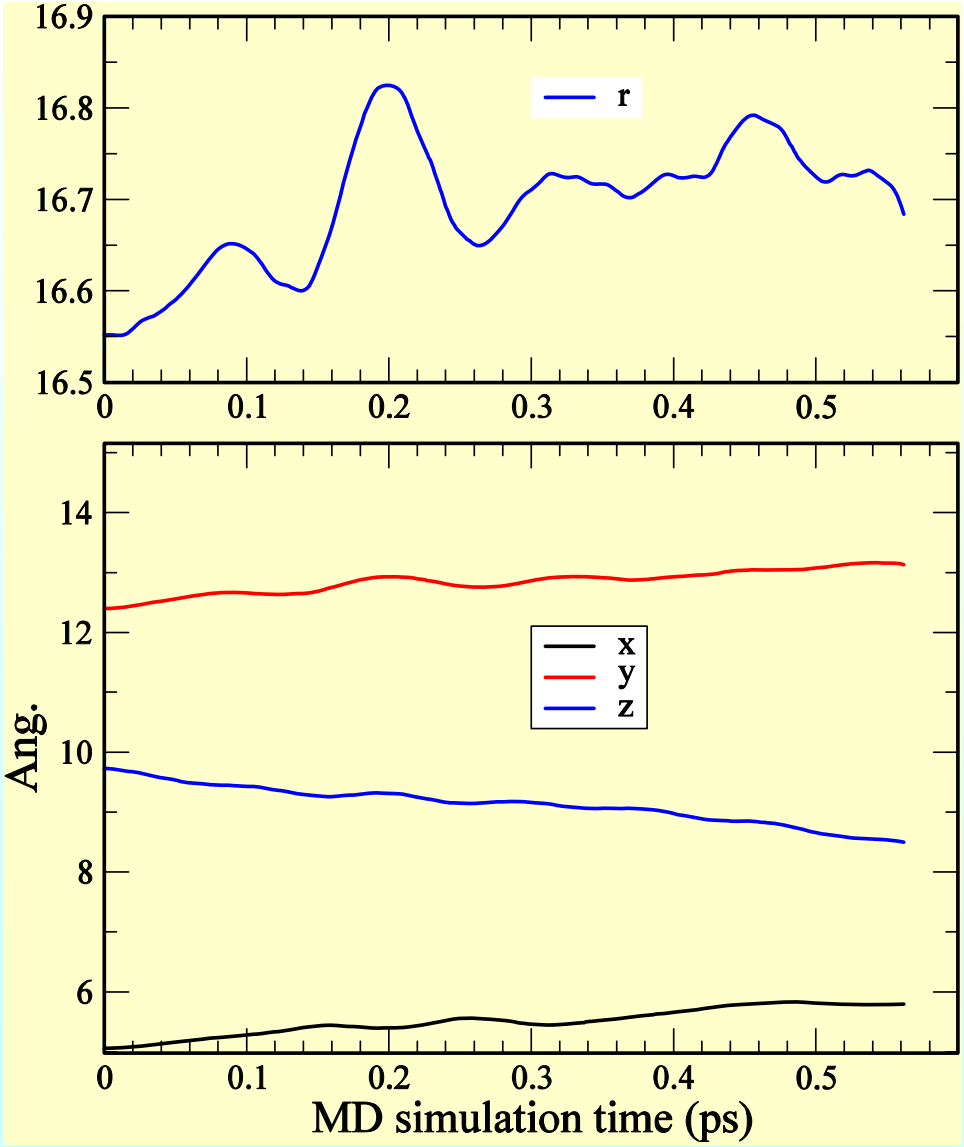
We can not simply compared the energies of two phases to decide if one of the phase is not stable. Sometime thermodynamically favored (i.e. energetically most stable) phase is not observed because a phase with higher energy is kinetically favored…

Ti-Cluster Formation!

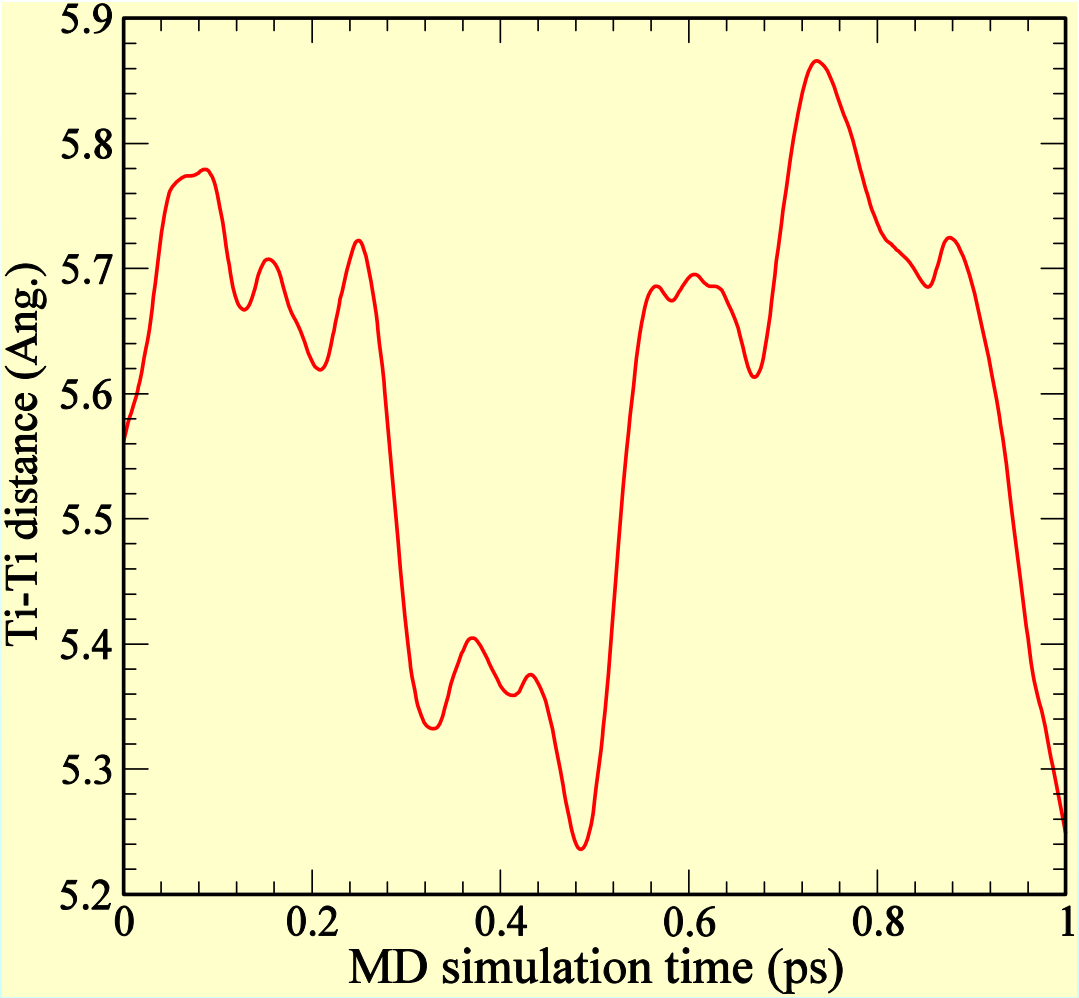


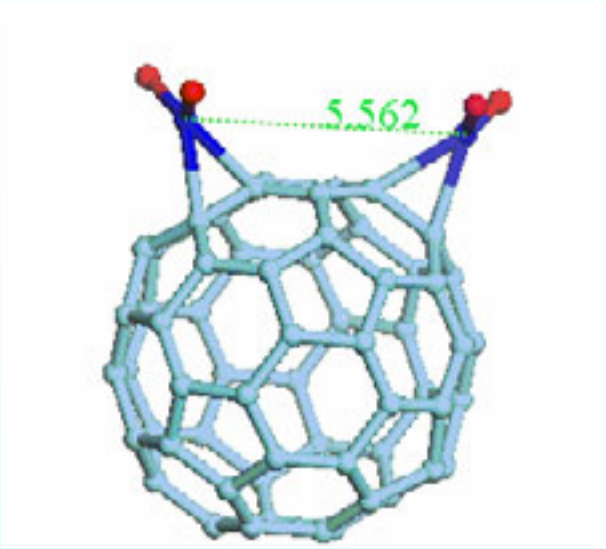
It's probably better to treat "TiH_2" on C_{60} rather than Ti-alone!

TiH_2 on C_{60} does not jump to other minima, indicating very low segregation of TiH_2 on C_{60}!



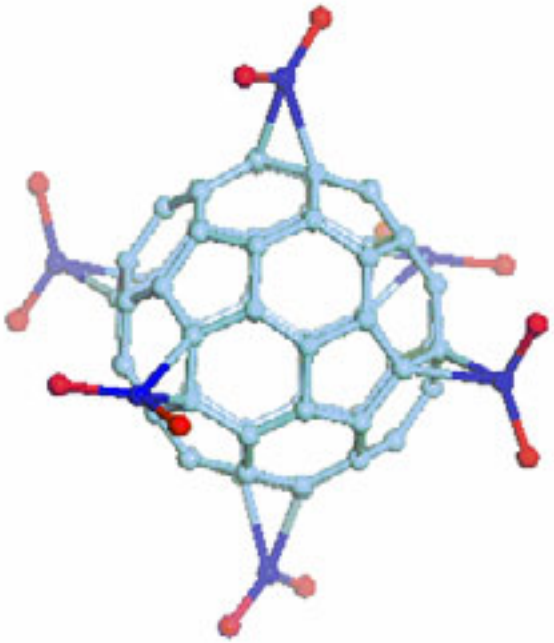
Ti-Cluster Formation!

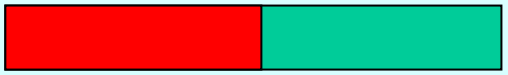




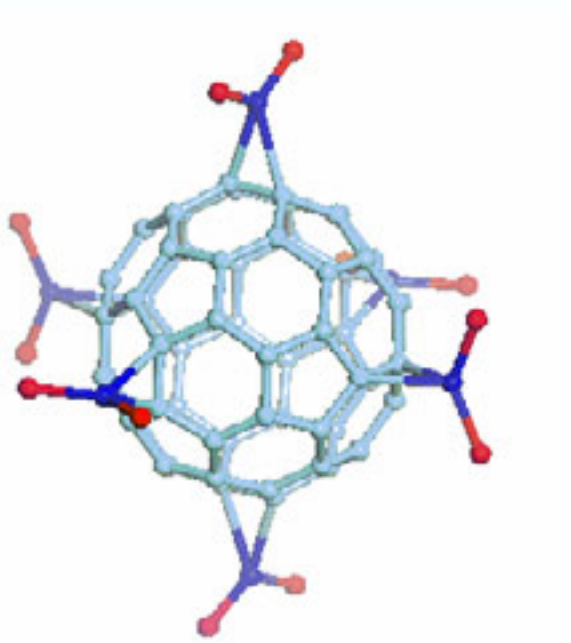
No evidence of Ti-dimer formation from two nearest-neighbor TiH_2 groups on C_{60}

No clustering for $C_{60}(TiH_2)_6$ at high T!

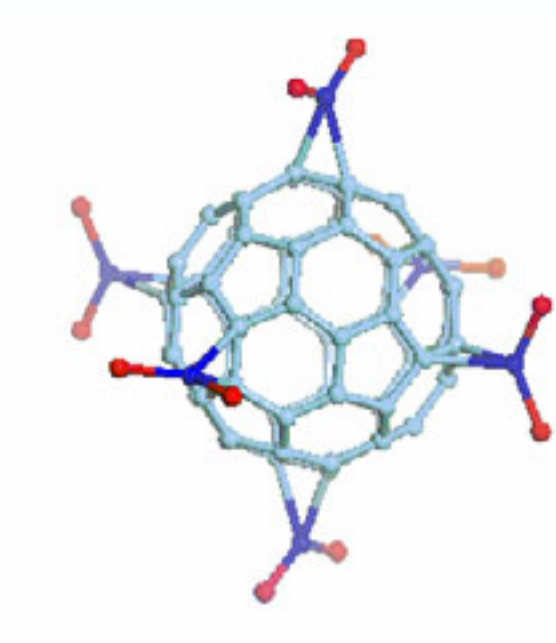




300 K

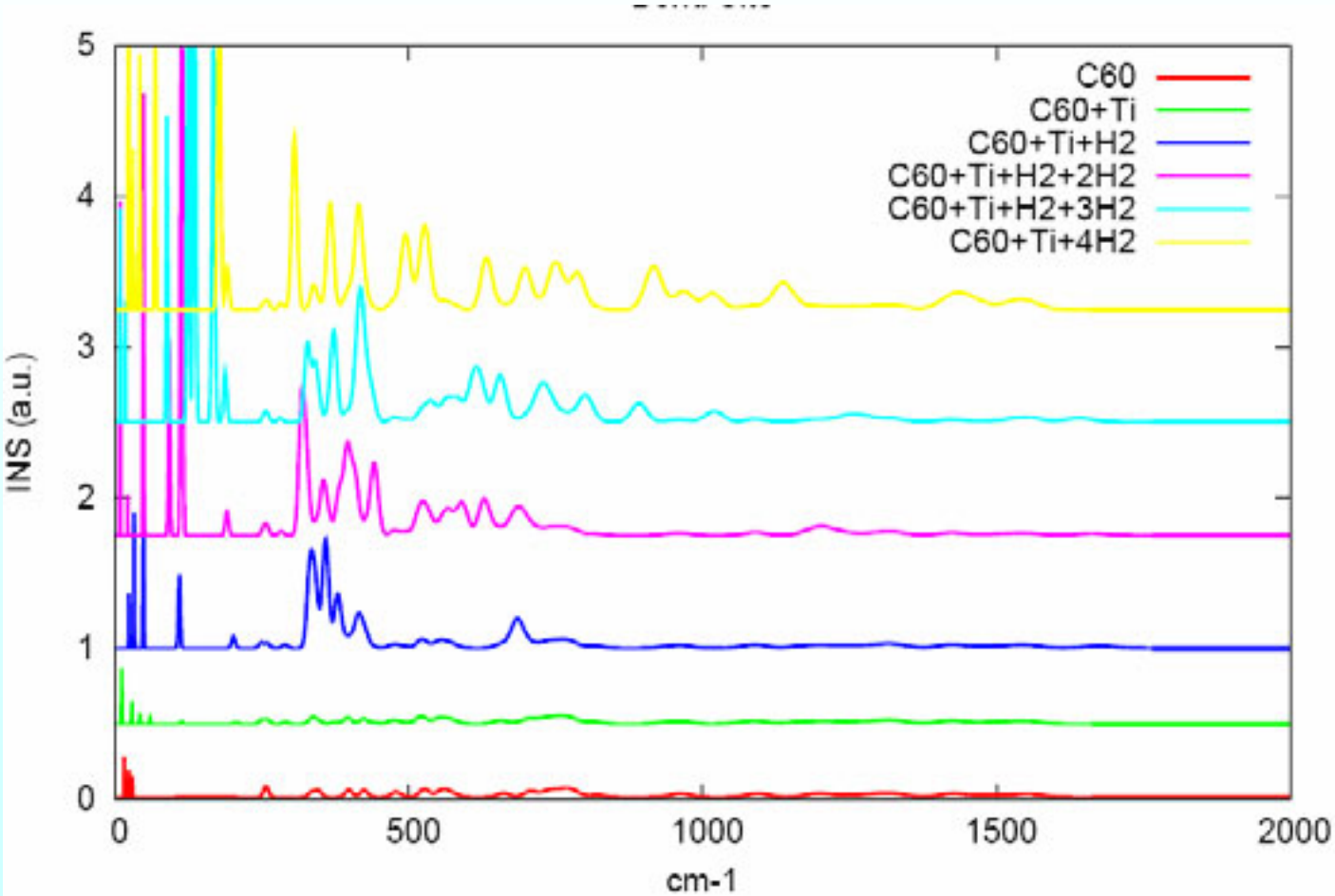


600 K



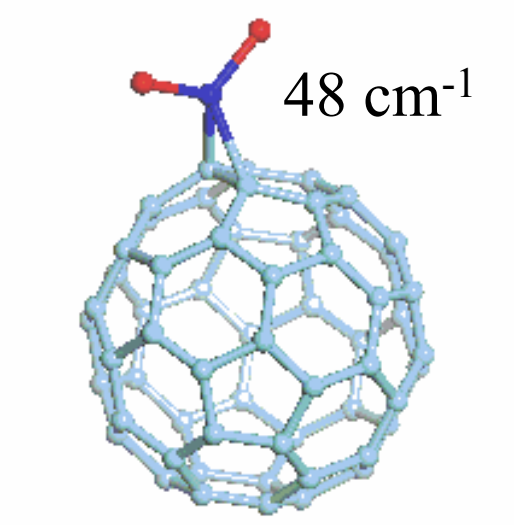
800 K

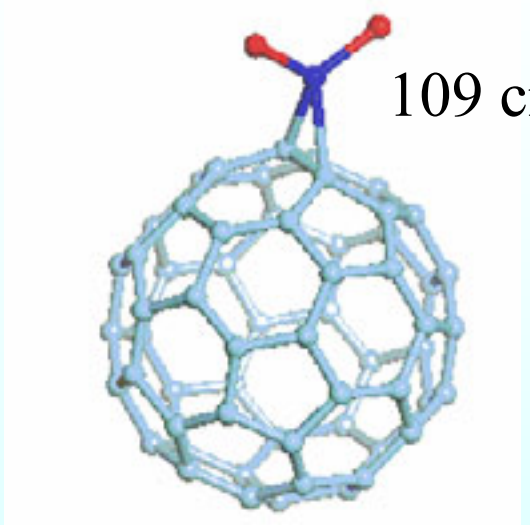
NORMAL MODE ANALYSIS OF C60TiHx!

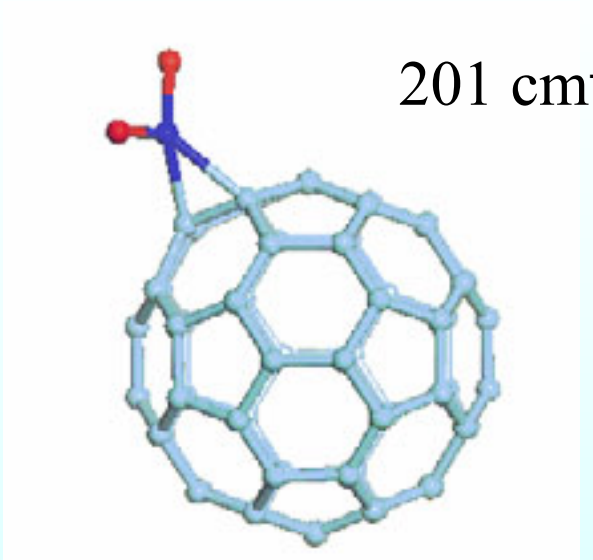


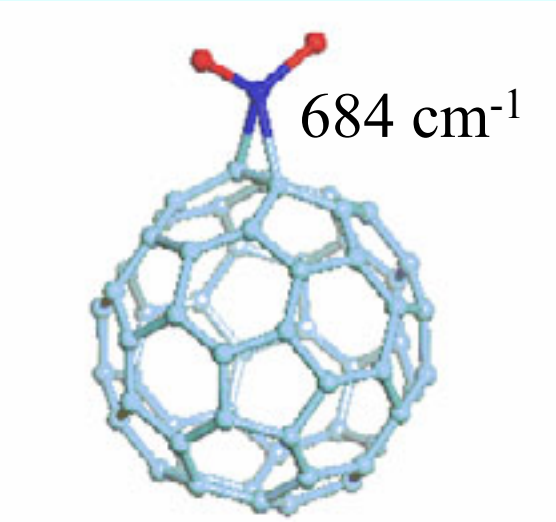
Vibrational spectra (neutron, Raman or IR) for different isomers of TiHx on C60 are different enough to characterize the samples which may have the proposed TiHx-bonding!!!

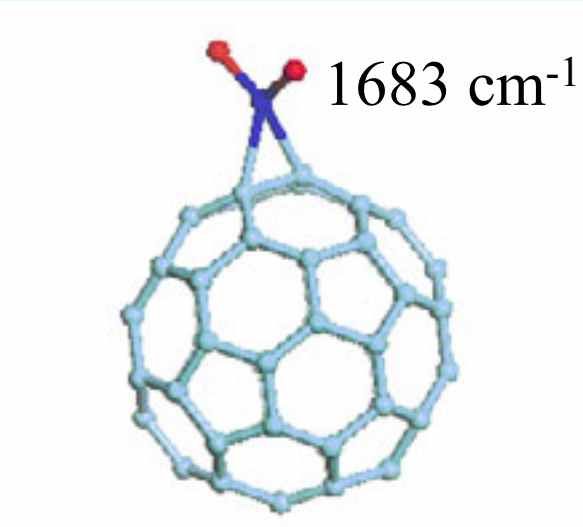
NORMAL MODE ANALYSIS OF C60TiH2!

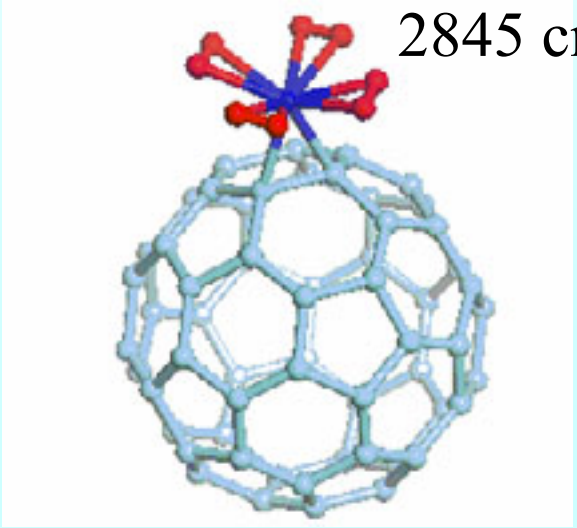










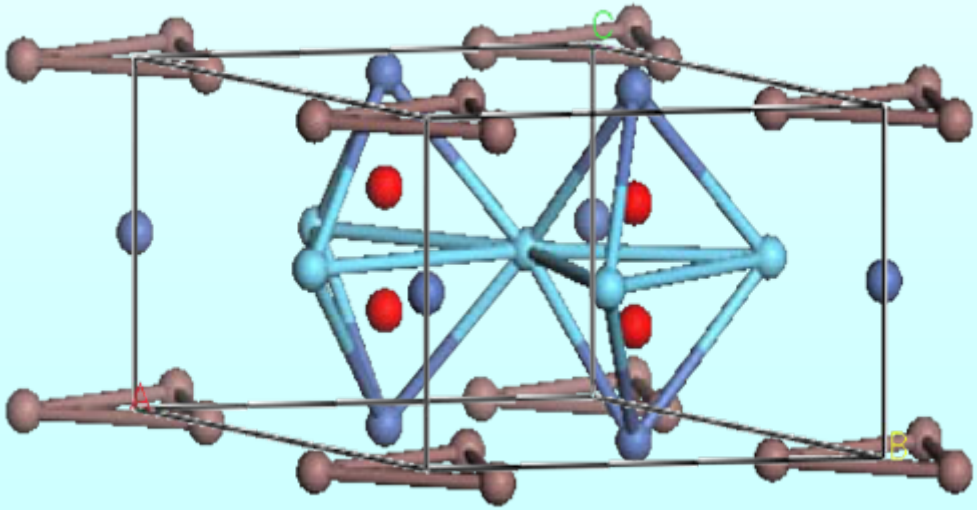


Unusually Short Hydrogen-Hydrogen distance in $LaNiInH_x$

a combined first-principles and neutron vibrational spectroscopy study

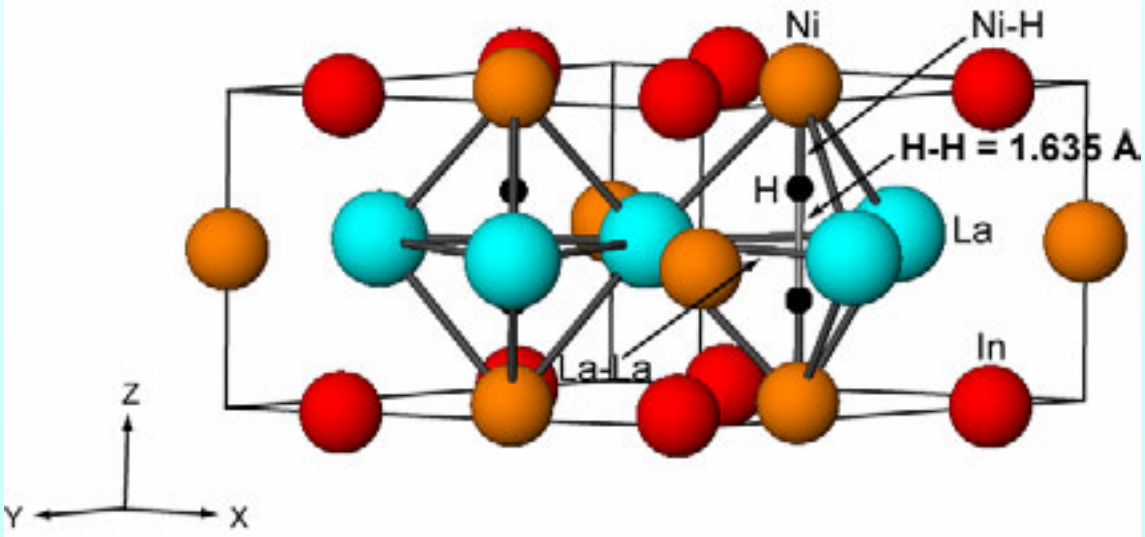
T. Yildirim, J. Iniguez, T. J. Udovic, V. A. Yartys,

PRB rapid comm. (in prep.)



$LaNiInH_x$ *MOTIVATION*

•A recent neutron powder diffraction study of the *R*NiIn-D_2 systems (*R* = La, Ce, Nd) [J. Alloys Comp. 330-332 (2002) 132] showed an unusual double H occupancy in the trigonal bipyramidal R_3Ni_2 sites leading to the formation of hydrogen pairs with the shortest documented interatomic H···H separation (1.56-1.63 Å) for intermetallic hydrides, ***raising several important fundamental questions and possible practical applications related to hydrogen storage.***

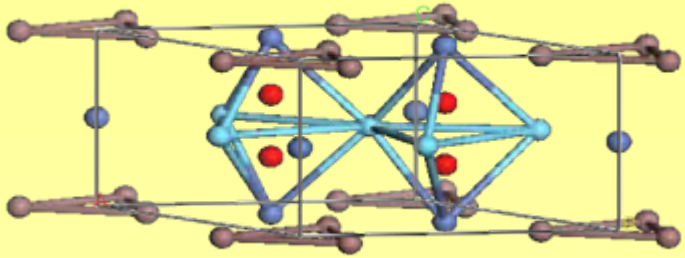


$LaNiInH_x$ APPROACH

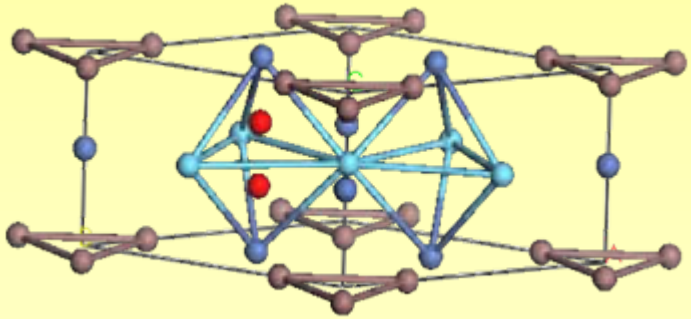
In order to understand the nature of bonding, structure and dynamics in these interesting intermatallic hydrides, RNiIn-H_x, we have performed

- Inelastic neutron scattering measurement for x=1.333 and 0.666.
- Performed first-principles structure and dynamics calculations for the following three systems:

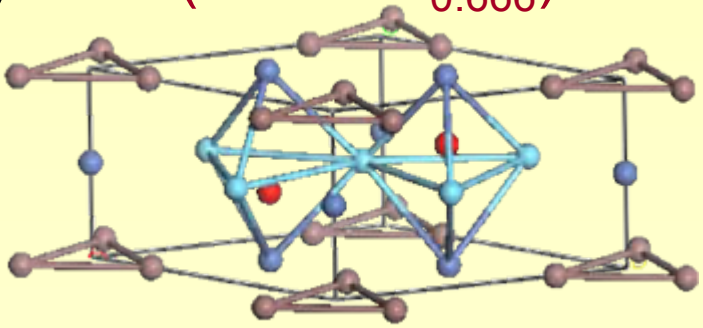
(1) H2-H2 ($LaNiInH_{1.333}$)



(2) H2-0 ($LaNiInH_{0.666}$)

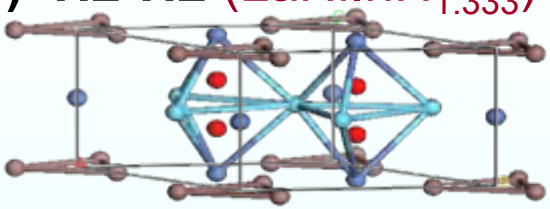


(3) H-H ($LaNiInH_{0.666}$)

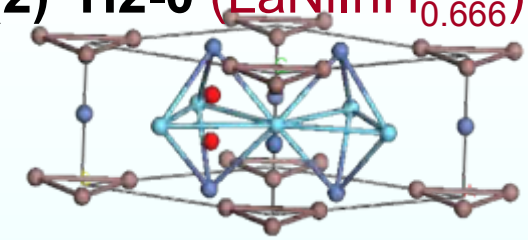


$LaNiInH_x$ STRUCTURE

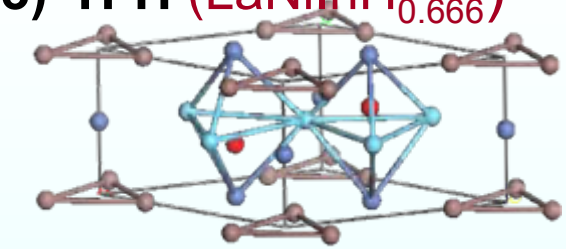
(1) H2-H2 ($LaNiInH_{1.333}$)



(2) H2-0 ($LaNiInH_{0.666}$)



(3) H-H ($LaNiInH_{0.666}$)



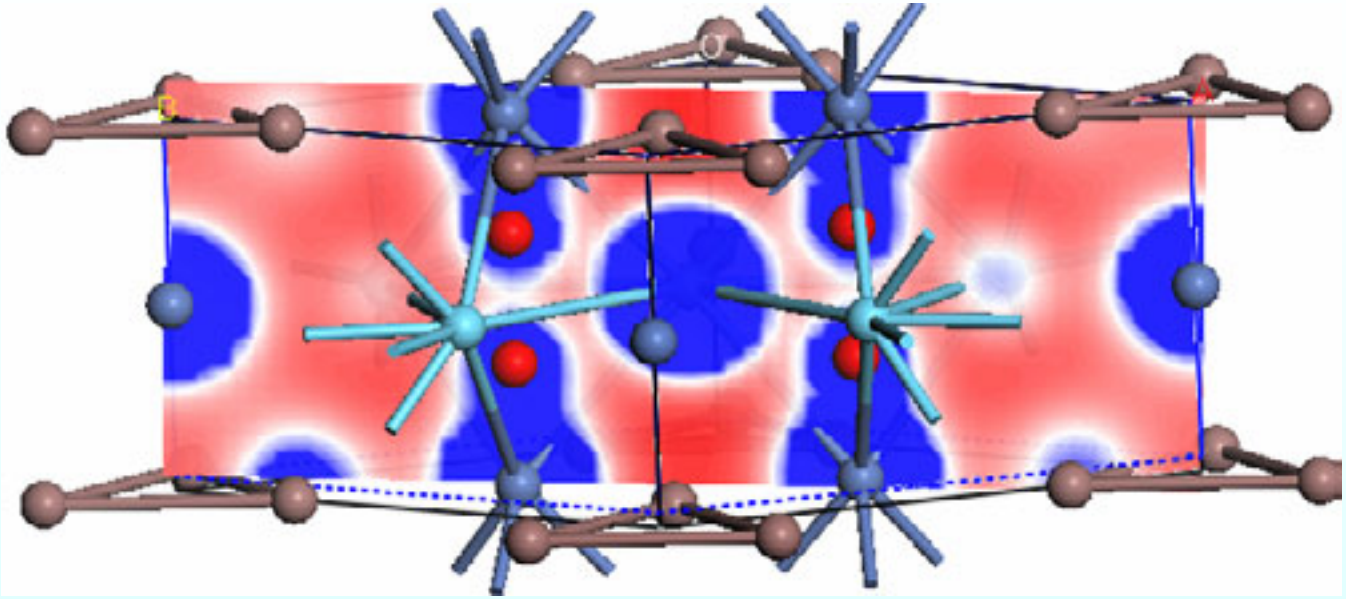
	H2-H2	H2-0	H-H
a=b (Å)	7.425 (7.381)	7.451	7.472
c (Å)	4.689 (4.649)	4.515	4.472
V (Å^3)	223.87	217.03	216.57
Energy(eV)	xxx	-11401.50	-11401.75

ΔE=0.25 eV

The calculated atomic positions are also in perfect agreement with experimental values:

H= (2/3,1/3,0.3243 (0.3241)
In=(0,0.2438 (0.2437),0)
La=(0,0.6034 (0.6035), 0)

$LaNiInH_x$ NATURE OF BONDING



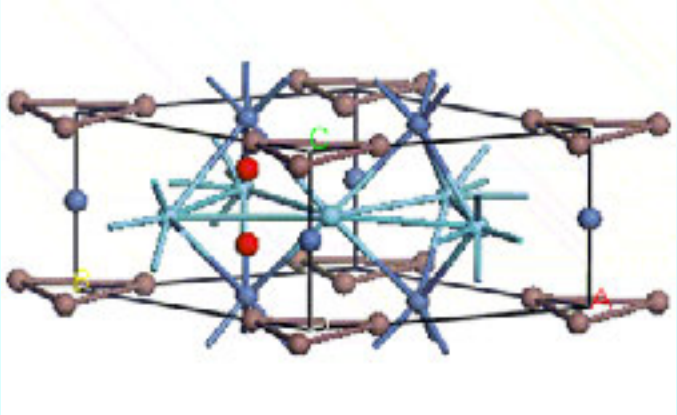
Calculated charge density plot (left) and Mulliken analysis indicate that H atoms are bonded to Ni strongly and there is no H-H bond (covalent or ionic).

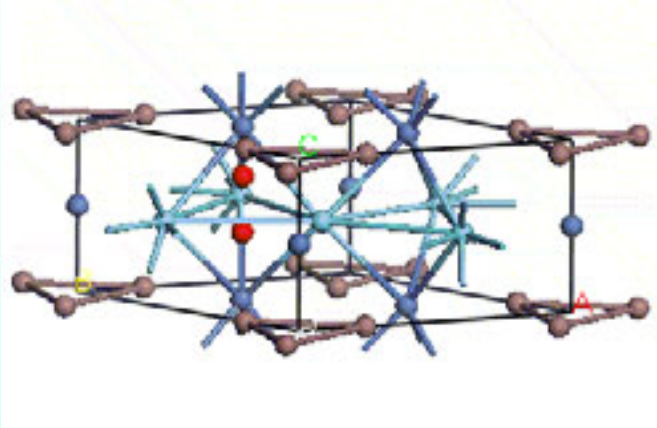
	H2-H2	H2-0	H-H
Q(La)	1.35 e	1.19 e	1.25 e
Q(In)	-0.48 e	-0.49 e	-0.52 e
Q(Ni1)	-0.53 e	-0.54 e	-0.55 e
Q(Ni2)	-0.35 e	-0.36 e	-0.46 e
Q(H)	-0.34 e	-0.32 e	-0.35 e
d(Ni—H)	1.521 (bp=0.38)	1.510 (bp=0.4)	1.621 (bp=0.53)
d(H—H)	1.647 (bp=0)	1.495 (bp=0)	-----

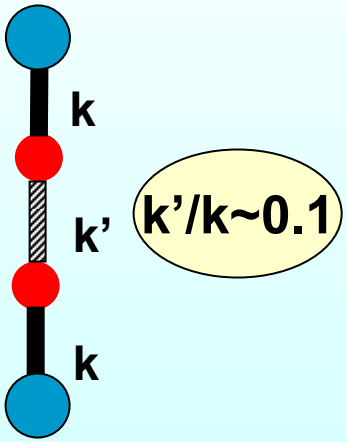
Hence, the system should NOT be considered as H-H pairs but rather as NiH-pairs. This explains the puzzle of very unusual H-H distance!

Lattice Dynamics from First-Principles

(2) H2-0 ($LaNiInH_{0.666}$)







ω=1903 cm^{-1}

ω =1719 cm^{-1}

$LaNiInH_x$ CONCLUSIONS

- **We have carried out neutron scattering measurements on $LaNiInH_{1.333}$ and $LaNiInH_{0.666}$**
- **Both INS spectrum and calculations suggest that in $LaNiInH_{0.666}$, H atoms are on different sites.**
- **Charge and bond-population analysis indicate that the bonding in these interesting system is a combination of ionic and covalent. There is a little H—H chemical bonding (if any)!**
- **Vibrational spectrum shows only the modes where H vibrates in the ab-plane.** ***Somehow the high-energy vibrations along the c-axis are missing (probably due to anharmonic behavior which results in large rms displacement, and therefore large temperature-factor)!***
- **Comparison between experiement and calculations indicate that the force constant between H—H is about 10% of the Ni-H force constant..**

Future Work

- **Major emphasis will be placed on fundamental issues, such as understanding the mechanism of hydrogen interaction in different candidate materials, by employing a powerful combination of first-principles modeling and closely coordinated neutron scattering experiments to develop and test intermolecular potential surfaces, etc.**
- **A major focus will be on nanoscale materials and the practicality of exploiting metastable states, in contrast to traditional theory which goes to great lengths to avoid local minima in atomic configuration energies. This approach is much more consistent with the manner in which many of these materials are synthesized, e.g. ball-milling to realize Ti-doped alanates, in which high energy nonequilibrium methods are a prerequisite to obtain the targeted phase.**
- **Theory and experiment will be done under the same roof...**

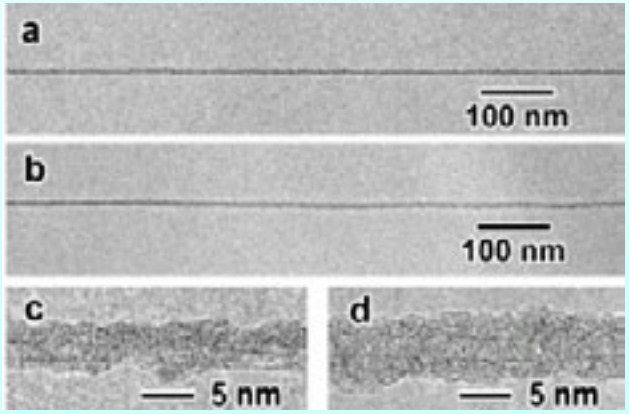
Acknowledgement

The work described here were done in collaboration with

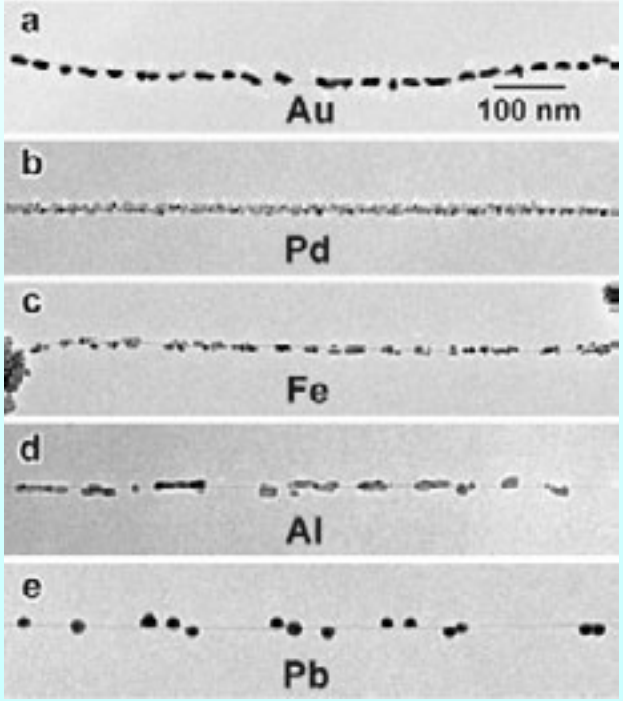
T. J. Udovic (NIST), C. M. Jensen and M. Sulic (Hawaii) (Alanate INS)
J. Iniguez (former postdoc, Spain– Alanates, Ti-SWNT,Ti-C_{60})
Prof. S. Ciraci's group at Bilkent, Ankara, Turkey (Ti-SWNT,Ti-C_{60})
M. Hartman (for H_2-MOF study)
W. Zhou (High-pressure sievert, MOF, CDC, etc)
V. A. Yartys (*Inst. for Energy Technology, Norway)* for $LaNiInH_x$

METAL COATING OF CARBON NANOTUBES

- Stable metal nanowires are very important for nano-electronics and other nano-device applications.
- It has been shown that such nanowires can be produced by depositing metal atoms on SWNT templates (Y. Zhang *et al.* Phys.Lett. **77**,3015 (2000), Chem. Phys. Lett. **331**, 351 (2000)).

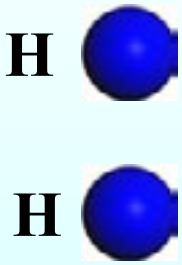


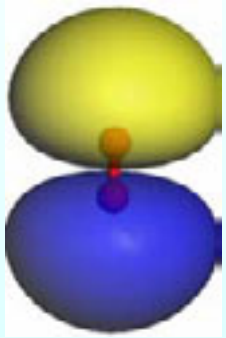
TEM image of Ti-coated SWNT

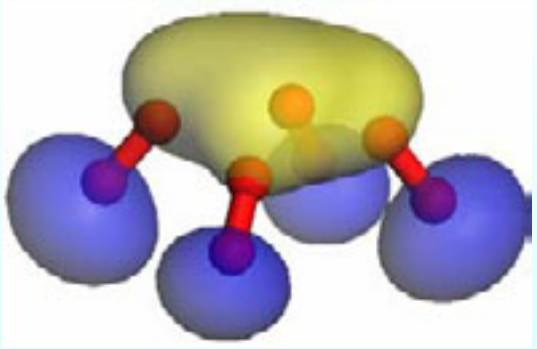


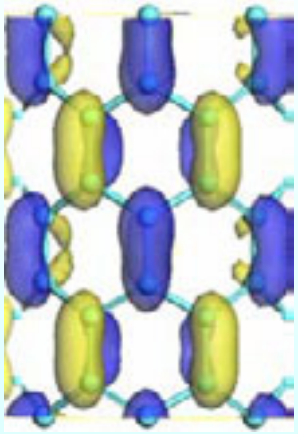
WHAT IS THE BONDING MECHANISM!

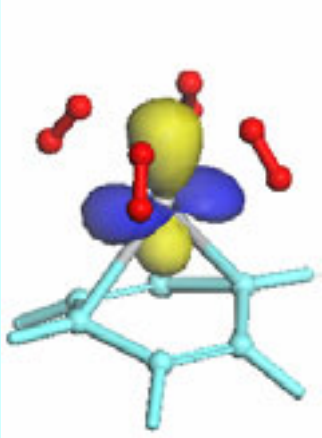
The mechanism is very similar to Dewar, Chatt, and Duncanson model, where the interaction is viewed as a donation of charge from the highest occupied orbital of the ligand to the metal empty states and a subsequent back donation from filled d-orbitals into the lowest unoccupied orbital of the ligand.



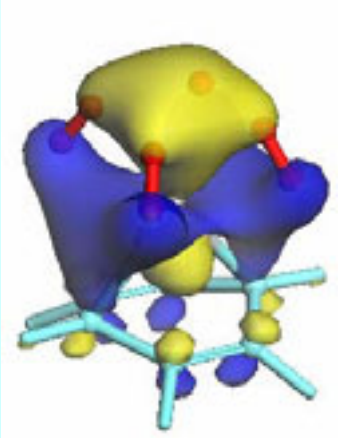




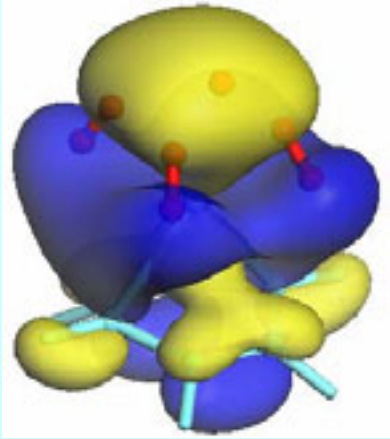




ψ=0.08



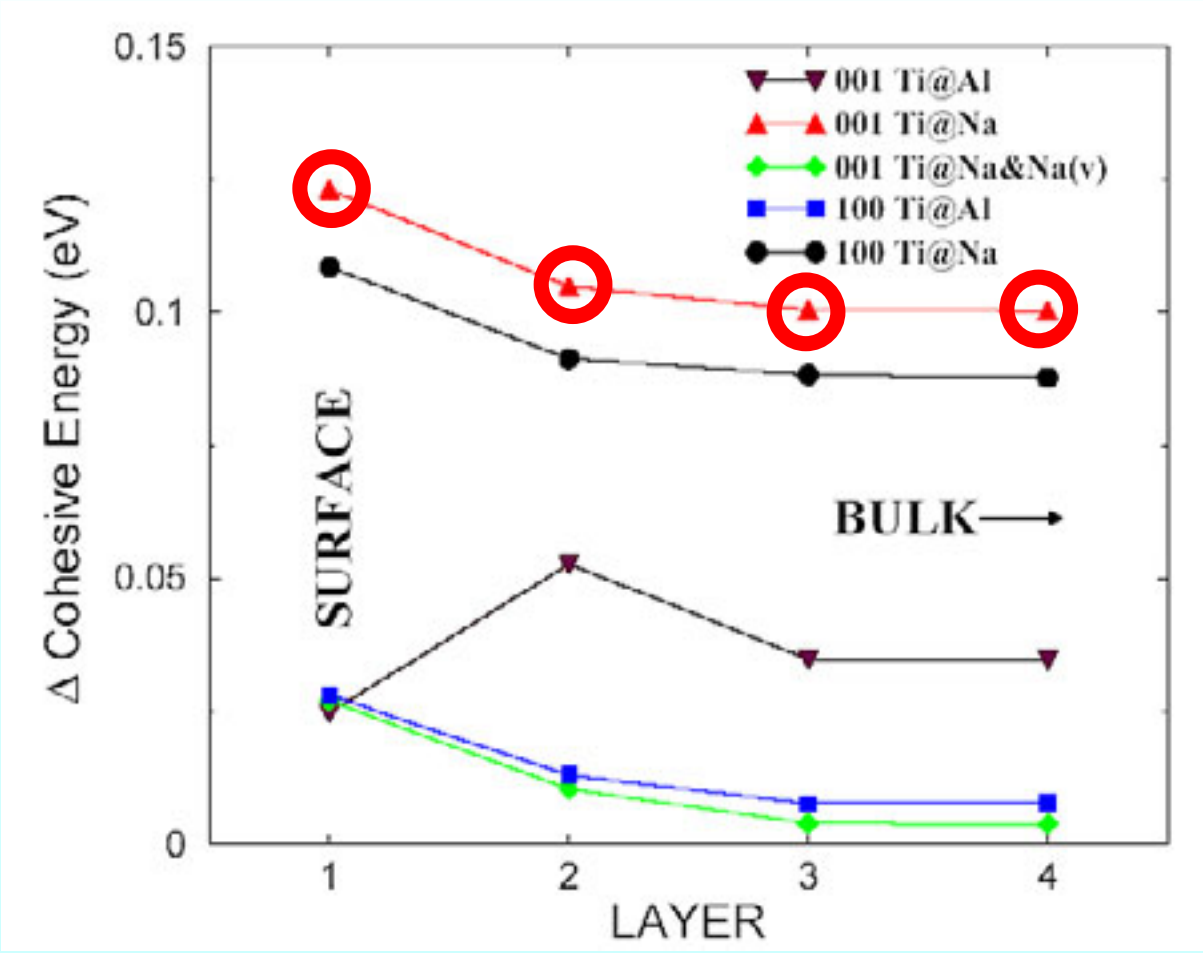
ψ =0.04

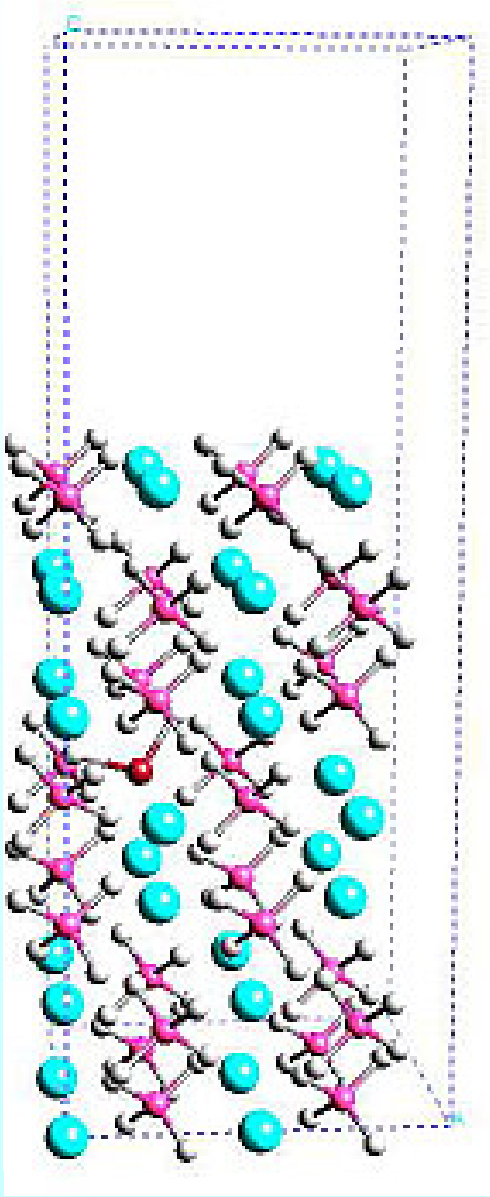


ψ =0.02

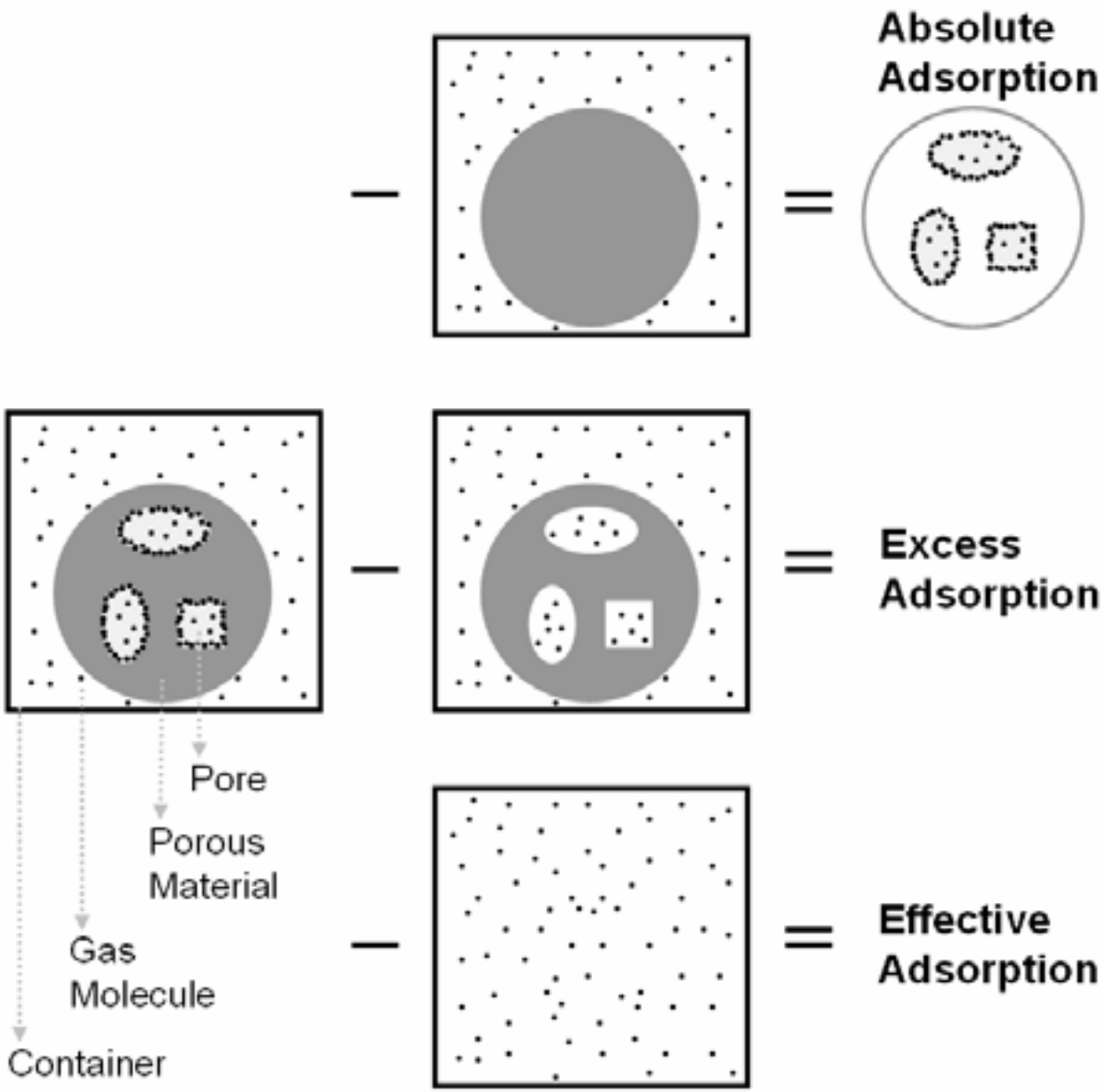
Question 2: Where does the Ti go?

→ Calculate E_{coh} as a function of Ti position





Schematic showing the three definitions of adsorption: Absolute, Excess and Effective adsorption.

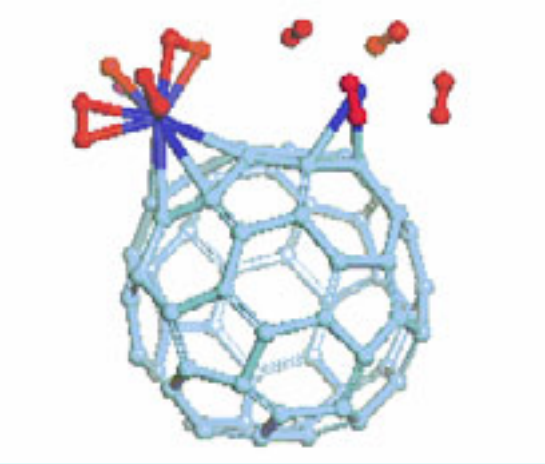


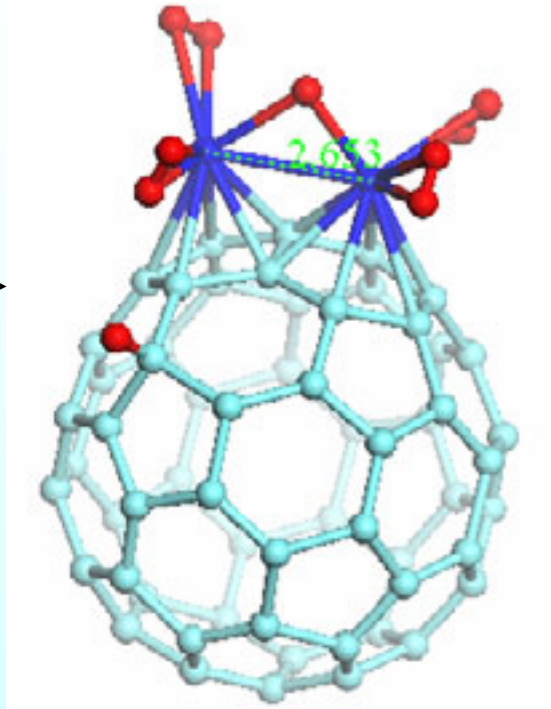
The absolute adsorption is the total amount of gas introduced to the sample cell minus the amount outside the sample in the gas phase, thus it accounts for the total amount of adsorbate molecules residing in pores.

The excess adsorption is the absolute amount of gas contained in the sample pores less the amount of gas that would be present in the pores in the absence of gas-solid intermolecular forces.

Effective adsorption is the net gain of the amount of gas stored in a container by using an adsorbent material.

Hydrogen spill-over at high T and H-loading!





1. It's premature to discuss the technical problems such as dimerization!
2. The predicted Ti-H interaction is so unique, it alone deserves more attention regardless it is useful or not for hydrogen storage.
3. Main focus should be to realize an experimental system which demonstrates such a unique Ti-H bonding that we predict!!!