Novel theoretical and experimental approaches for understanding and optimizing hydrogen-sorbent interactions in metal organic framework materials

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Presenter: Timo Thonhauser
University of Texas – Dallas
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WAKE FOREST UNIVERSITY

Project ID: BES003

Our Research Team

Y. Chabal

Characterization

UTD

J. Li

Synthesis

THE STATE UNIVERSITY OF NEW JERSEY
RUTGERS

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Theory

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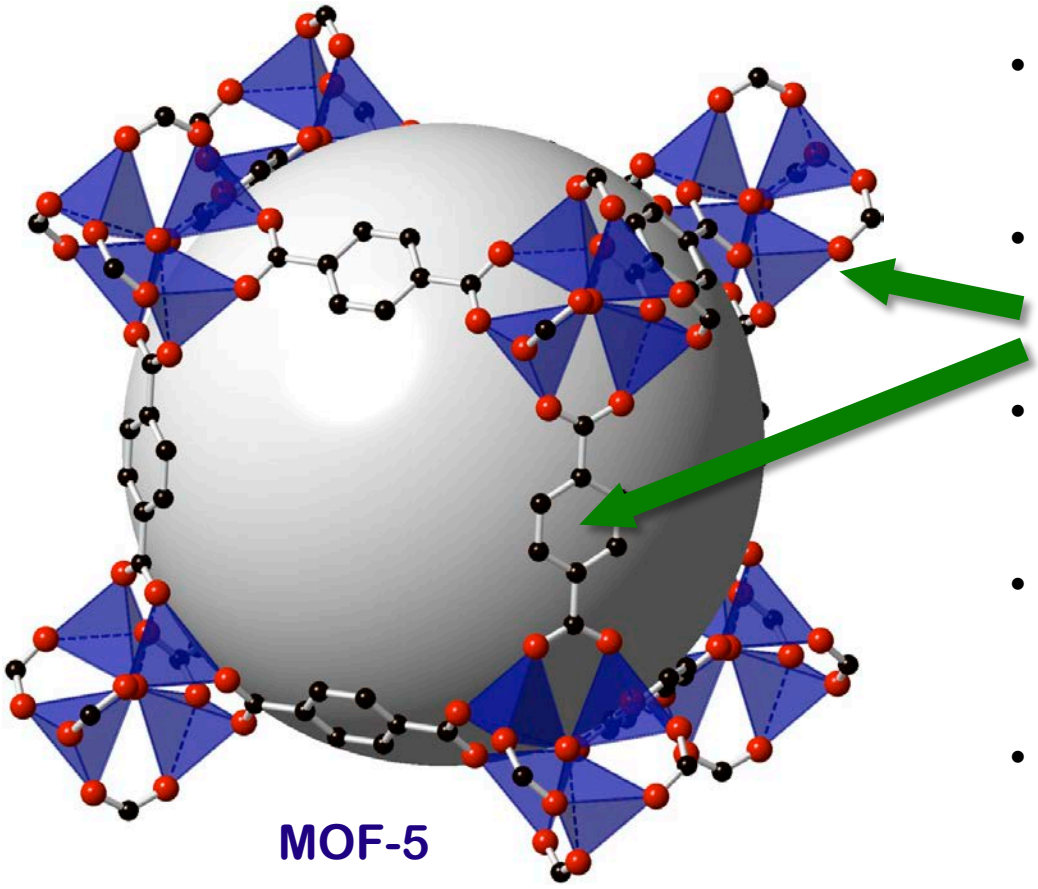
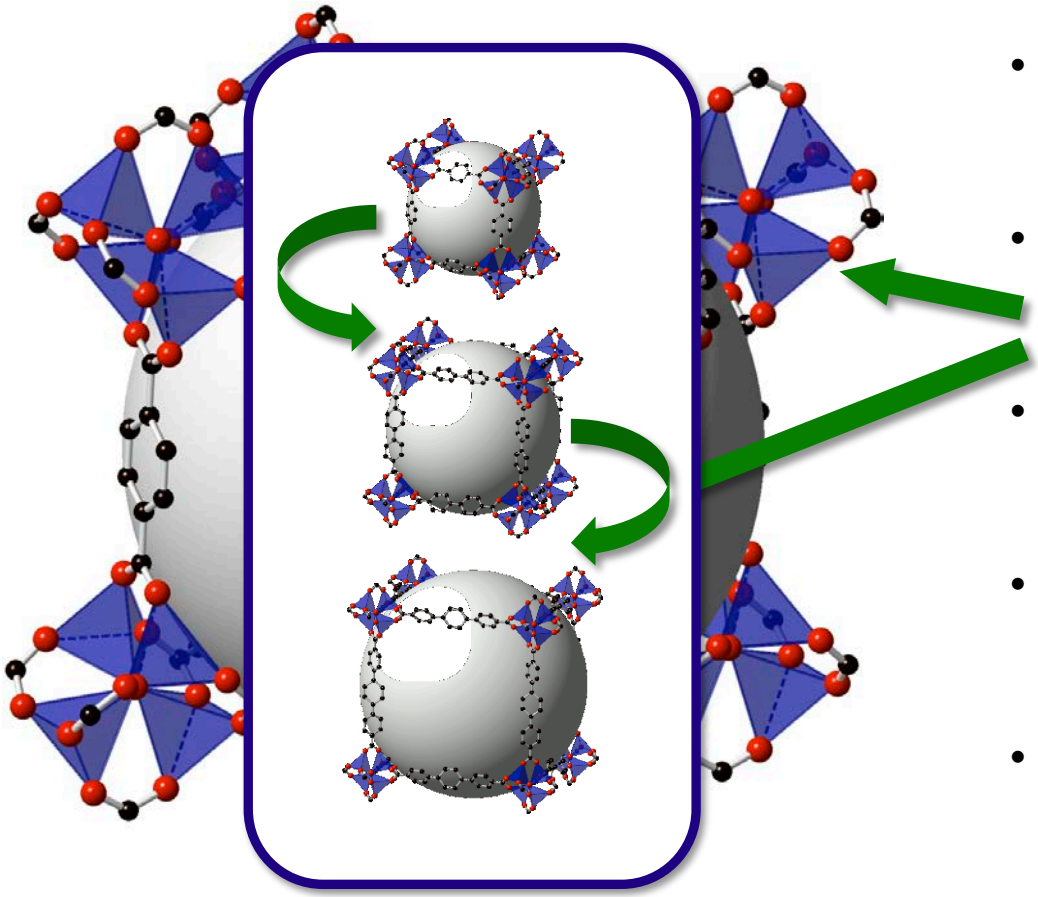
Metal Organic Framework Materials



MOF-5

- MOFs have porous crystalline structures that can be tailored
- $Zn_4O(CO_2)_6$ corners connected by phenylene linkers
- High surface areas, e.g. MOF-210 BET SA 6240 m^2/g
- Fast adsorption/desorption kinetics through channels
- Building blocks can be changed

Metal Organic Framework Materials



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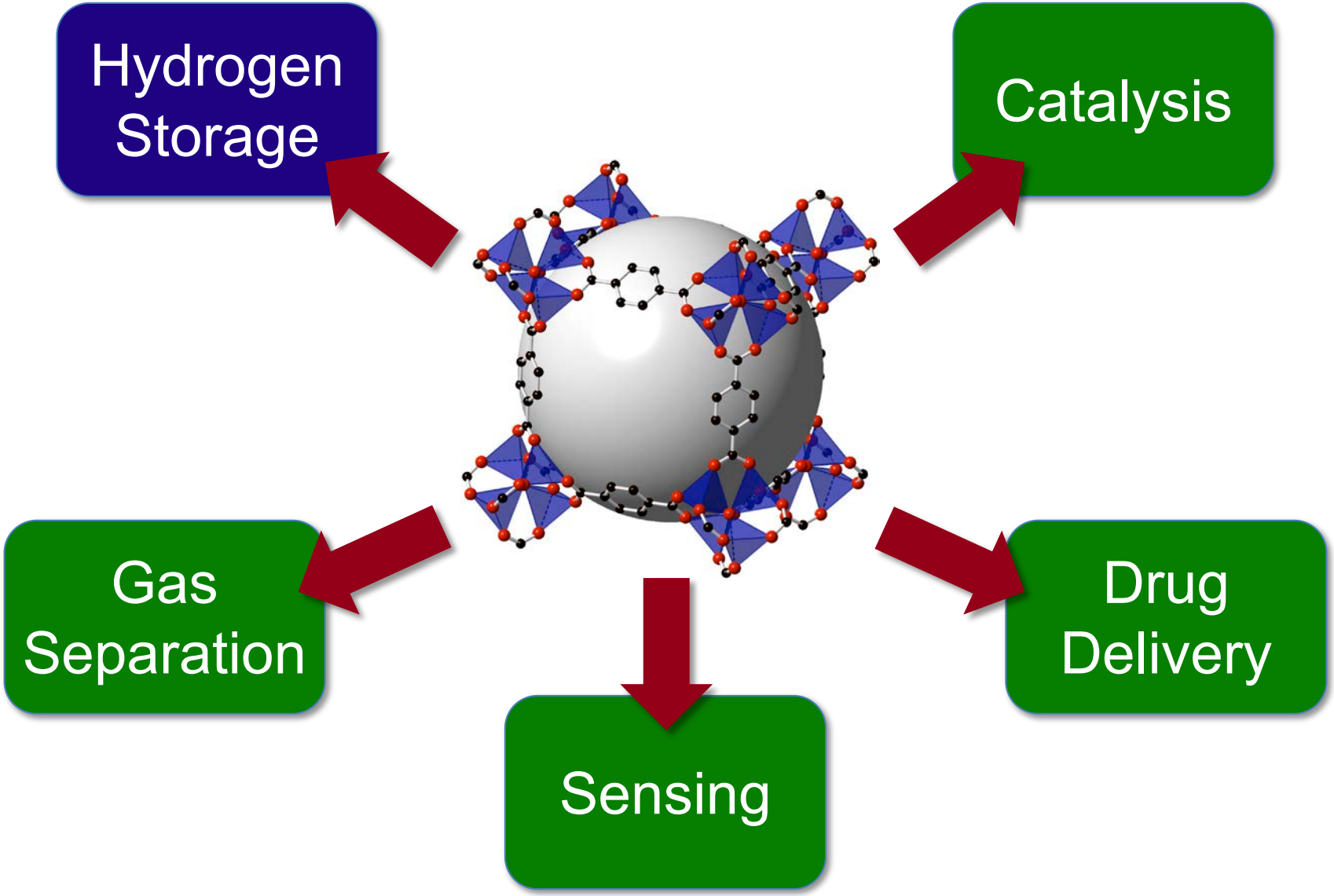
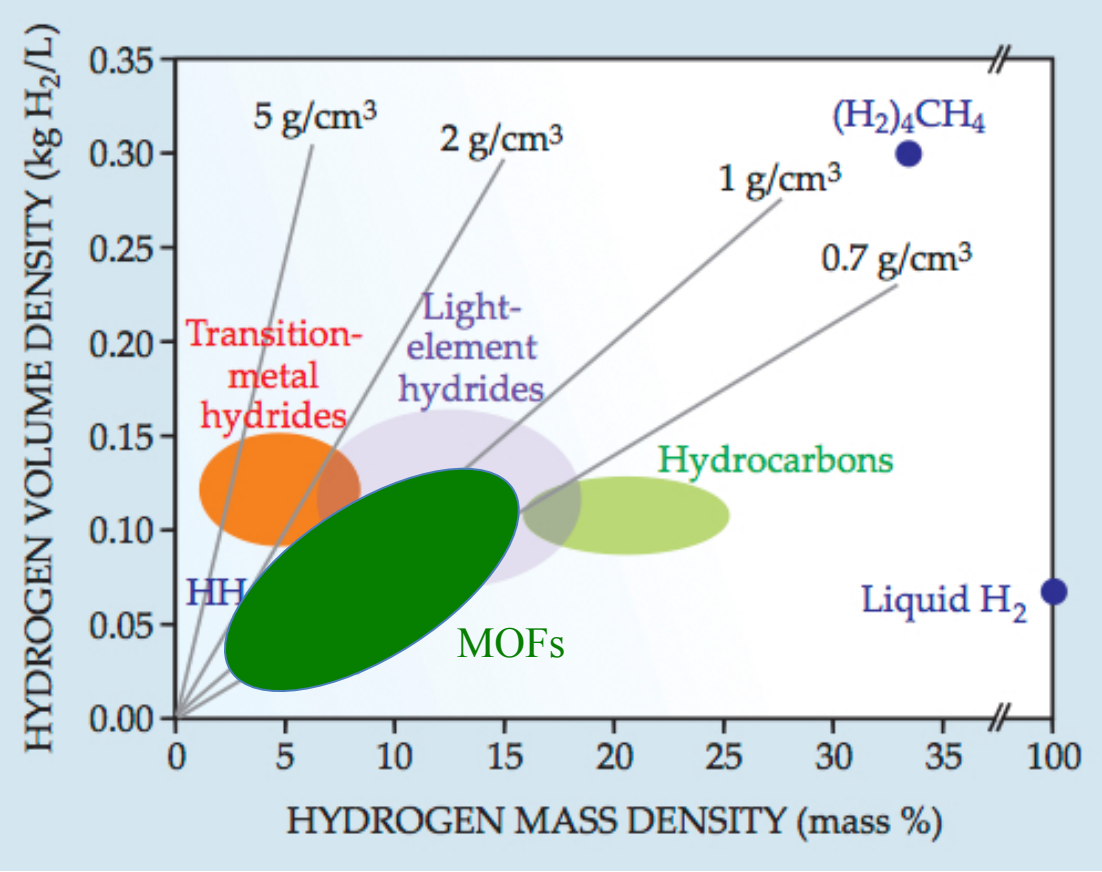
MOF Applications



Hydrogen Storage in MOFs



W. L. Mao et al., Phys. Today **60**, 42 (2007)

Hydrogen Storage in MOFs

Advantages

Physisorption (little heat)

Stores molecular hydrogen

(Fairly) easy to synthesize

Inexpensive

Uses only industrial metals

Fast adsorption/desorption

Can be easily tailored

Disadvantages

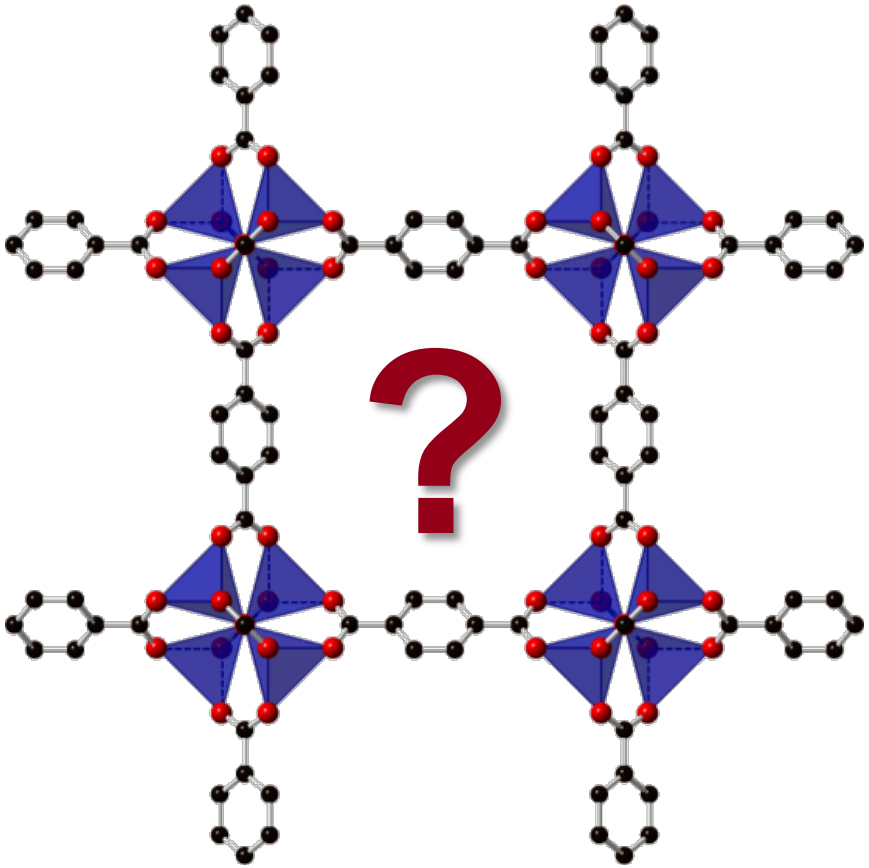
Physisorption (low temp.)

Low binding energy

MOF-210: Gravimetric adsorption of H_2 176 mg/g at 77K

W. L. Mao et al., Phys. Today **60**, 42 (2007)

Approach

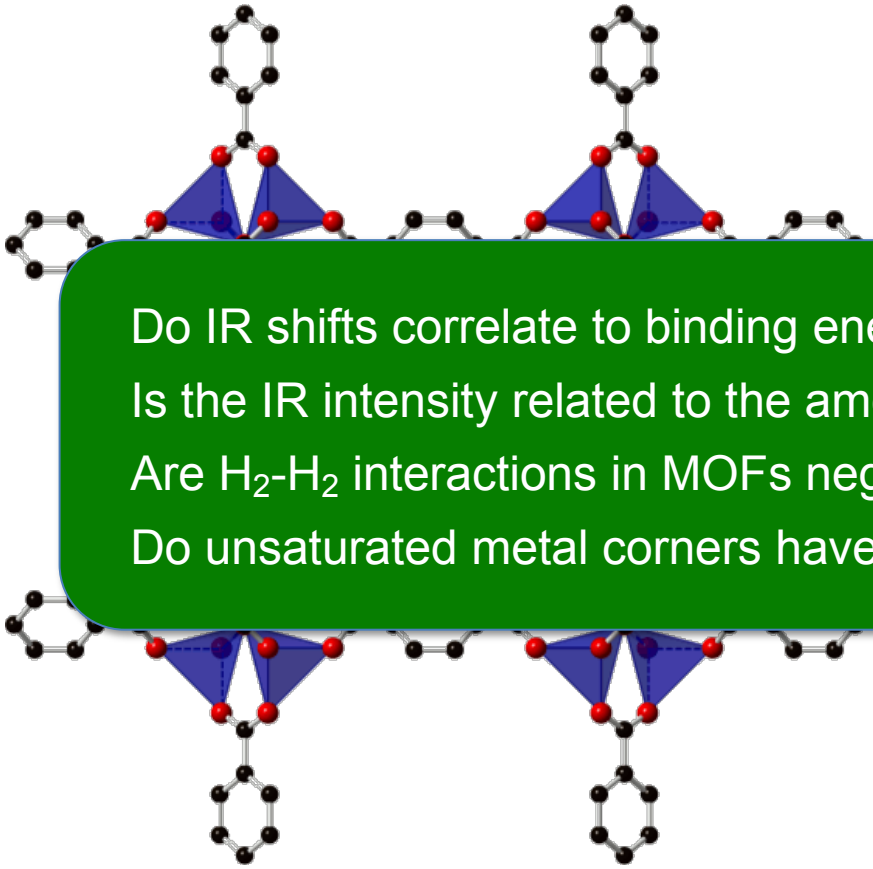


To design new MOFs, we need to understand the **H_2 / MOF interaction**

- Where does it bind?
- How strong does it bind?
- How much can bind?
- What are the barriers?

- High-pressure and low-temp IR
- Raman
- Adsorption isotherms
- Isosteric heat
- First-principles DFT (vdW-DF)

Approach



To design new MOFs, we need to understand the **H_2 / MOF interaction**

Do IR shifts correlate to binding energies of adsorbed H_2 ?

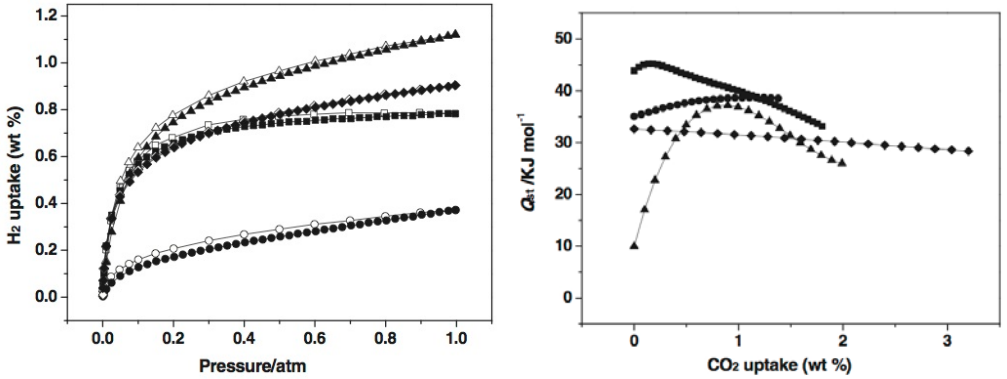
Is the IR intensity related to the amount of adsorbed H_2 ?

Are H_2-H_2 interactions in MOFs negligible?

Do unsaturated metal corners have benefits over saturated ones?

- …p IR
- Raman
- Adsorption isotherms
- Isosteric heat
- First-principles DFT (vdW-DF)

Experiments

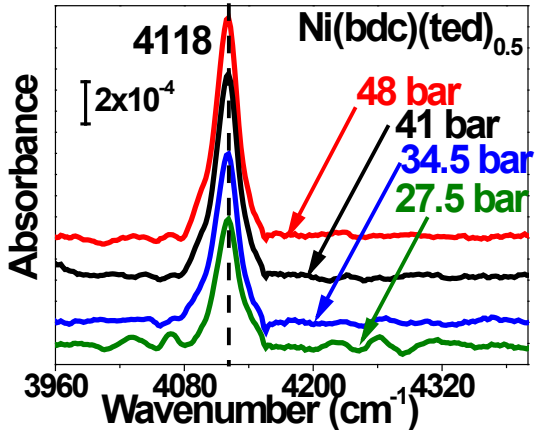


H. Liu et al., Adv. Funct. Mater. **21**, 4754 (2011)

Isotherm measurements: information about H_2 uptake

Average effects: no specific guest-host interaction

Need to understand effects at the molecular level: Spectroscopy



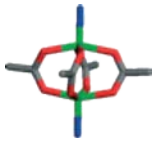
Nijem et al., JACS **132**, 1654 (2010)

Induced IR activity because of an interaction induced-dipole moment between H_2 and the framework atoms

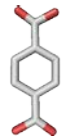
Shift of H_2 vibrational modes from the free H_2 (para at 4161cm^{-1} and ortho at 4155 cm^{-1}) upon adsorption

Synthesis of New Functionalized Ligands

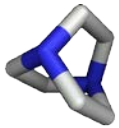
$Zn(bdc)(ted)_{0.5}$



$Zn_2(COO)_4(ted)_2$ Paddle-Wheel (SBU)



1,4-benzene-dicarboxylic acid (BDC)



triethylenediamine (TED)

Y. G. Zhao et al., Chem. Eur. J. **17**, 5101 (2011)

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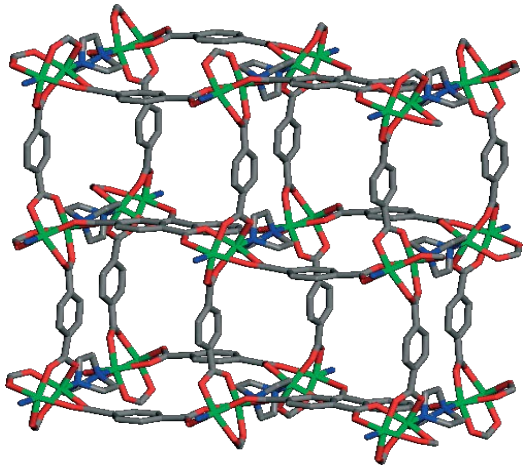

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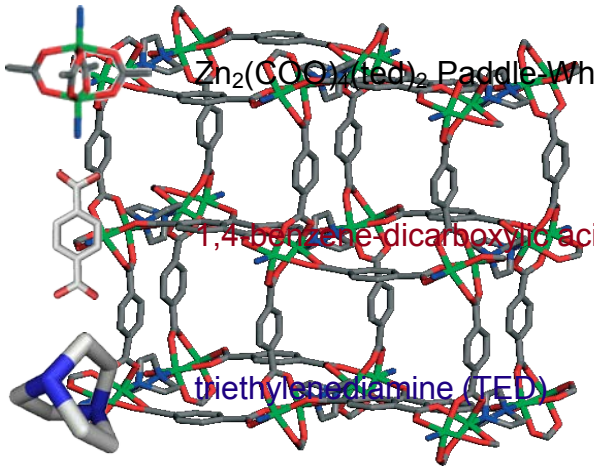

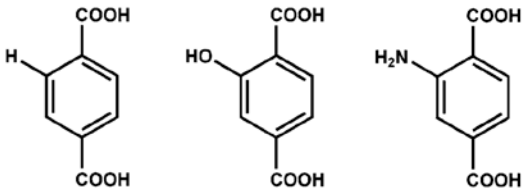

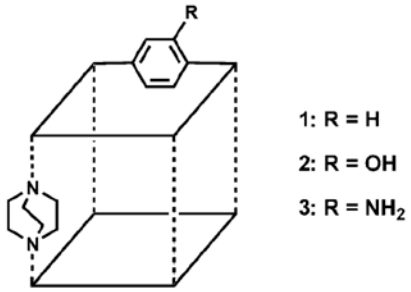

1: R = H

2: R = OH

3: R = NH_2

Y. G. Zhao et al., Chem. Eur. J. **17**, 5101 (2011)

Synthesis of New Functionalized Ligands

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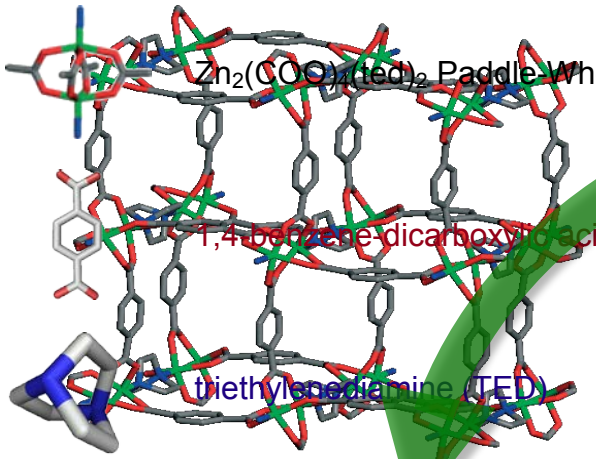

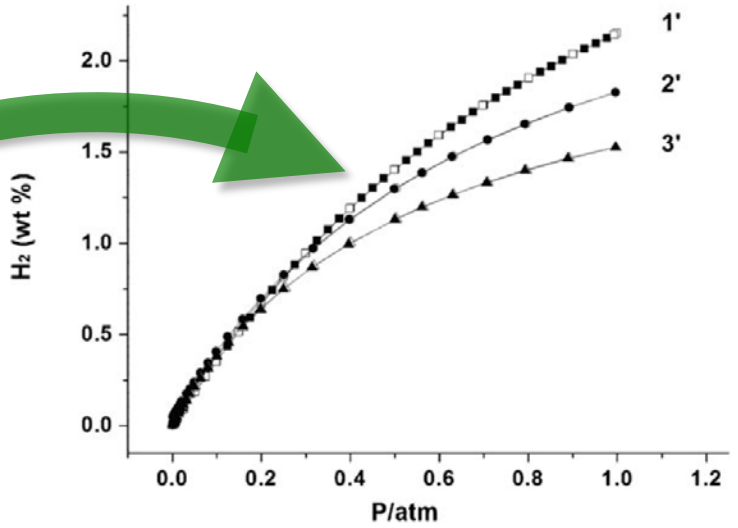

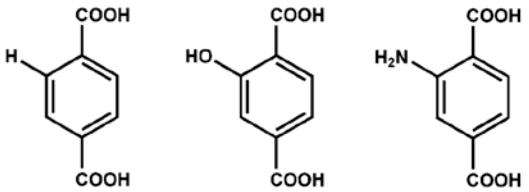

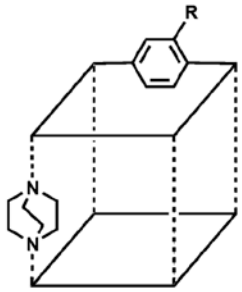

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Y. G. Zhao et al., Chem. Eur. J. **17**, 5101 (2011)

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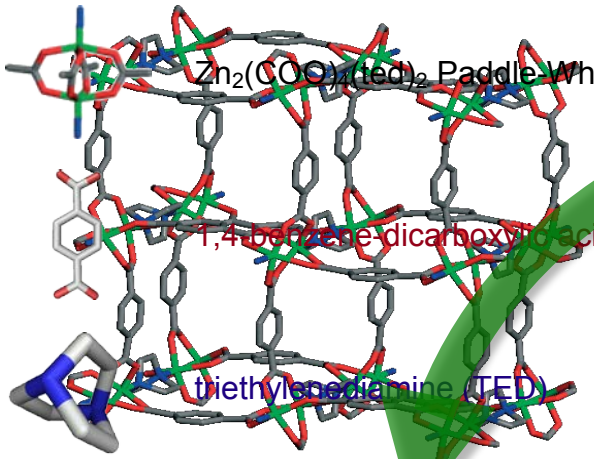

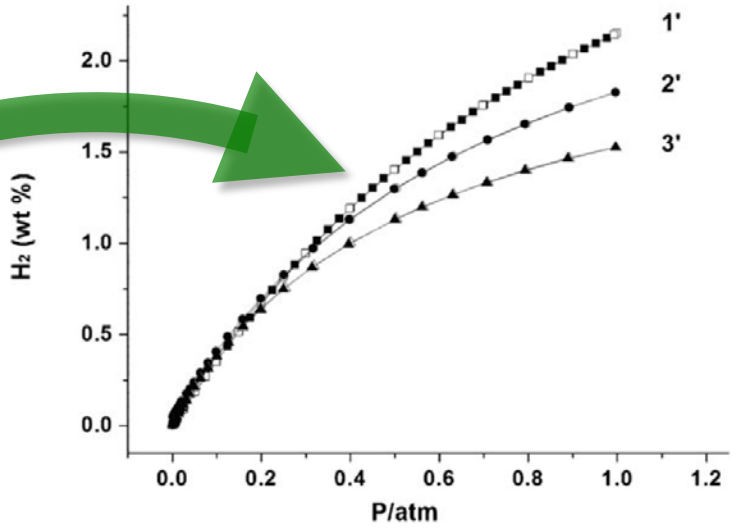

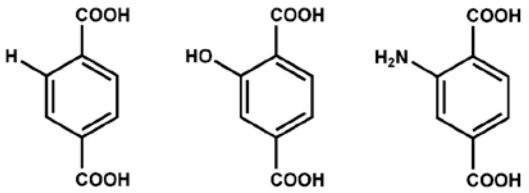

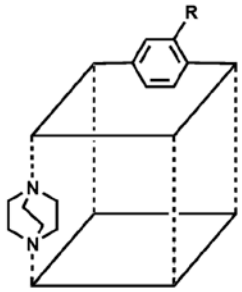

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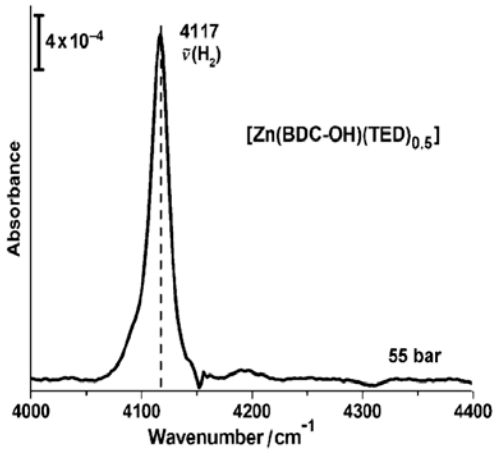
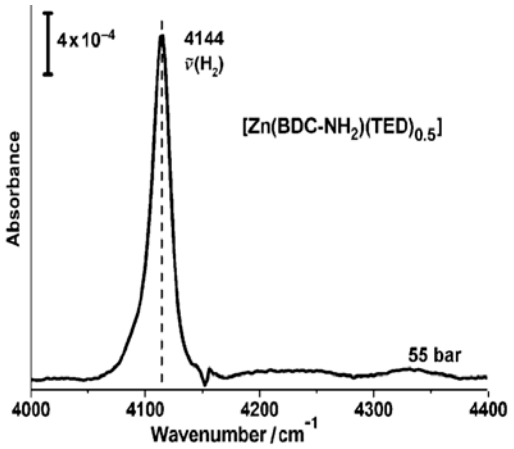
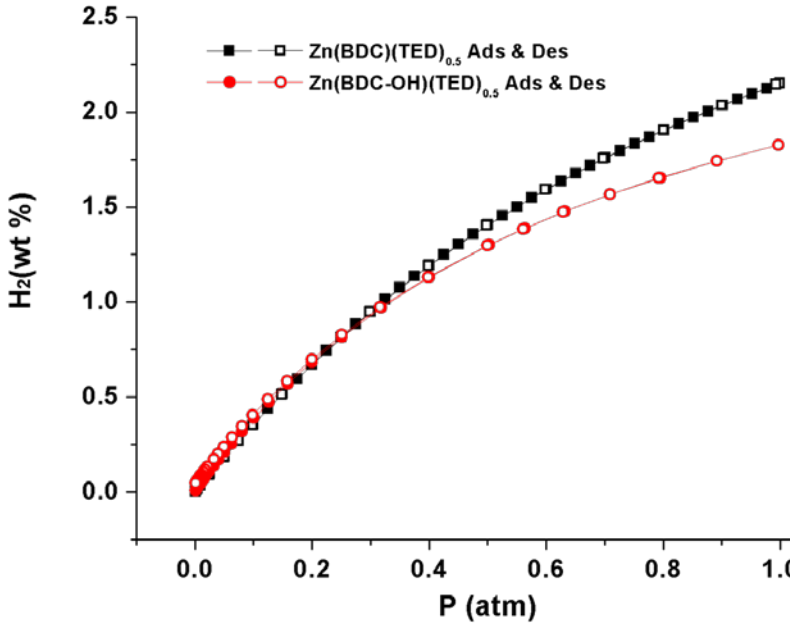
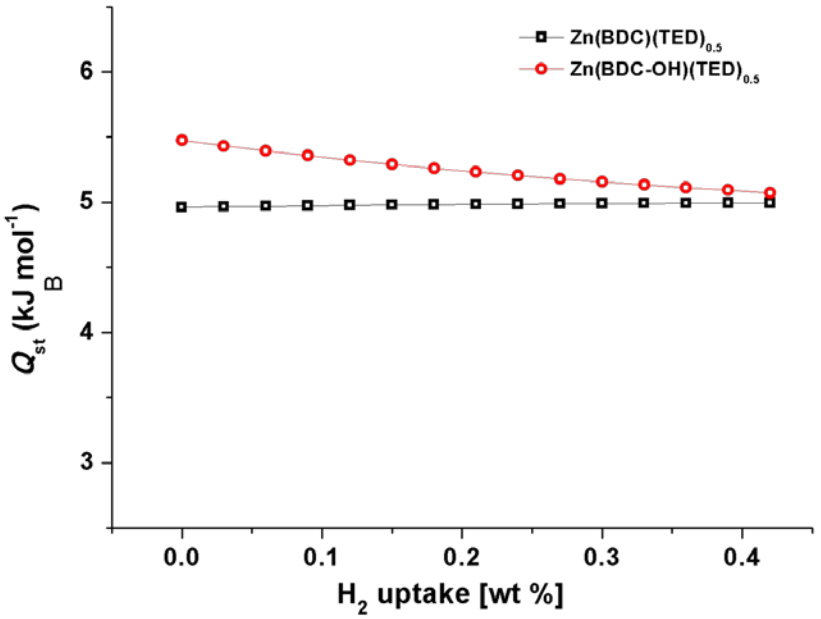




Y. G. Zhao et al., Chem. Eur. J. **17**, 5101 (2011)

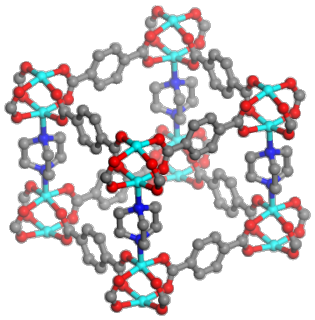
H_2 Uptake at 77K and Qst





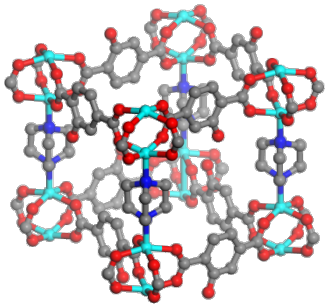
	$Zn(bdc)(ted)_{0.5}$	$Zn(bdc\text{-}OH)(ted)_{0.5}$
Pore Size, Å	7.5	5
Langmuir (BET), m^2/g	2057 (1937)	1111 (1023)
Pore Volume, cc/g [1]	0.75	0.56
H_2 Uptake, wt% [2]	2.1	1.8
Qst (H_2), kJ/Mol	4.9 - 5.0	4.9 - 5.5

[1] N_2 data; [2] 77K, 1 atm



$Zn(bdc)(ted)_{0.5}$

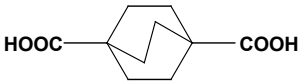
J. Y. Lee, J. Li, et. al. manuscript in preparation.

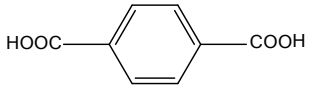


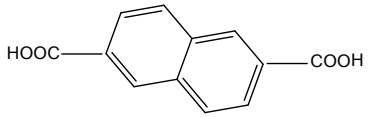
$Zn(bdc\text{-}OH)(ted)_{0.5}$

H_2 Uptake at High Pressure

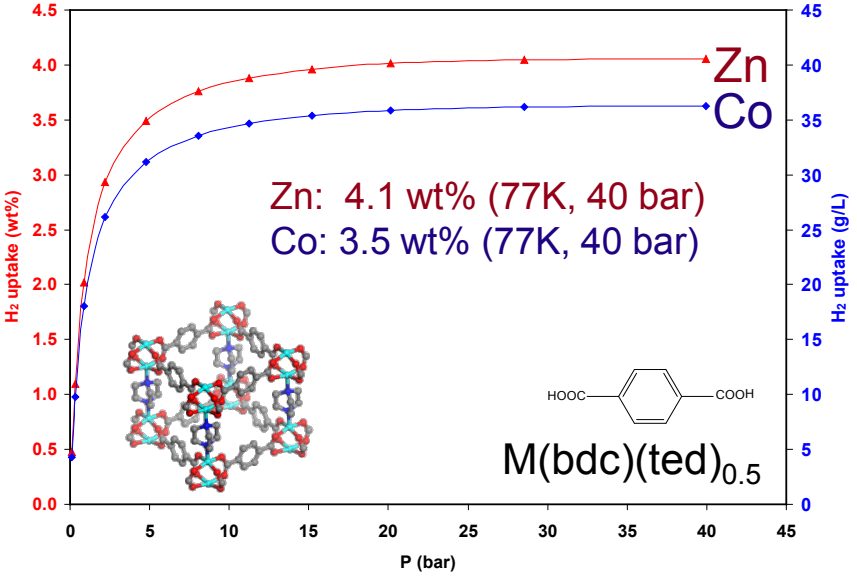
Zn(L)(TED)0.5

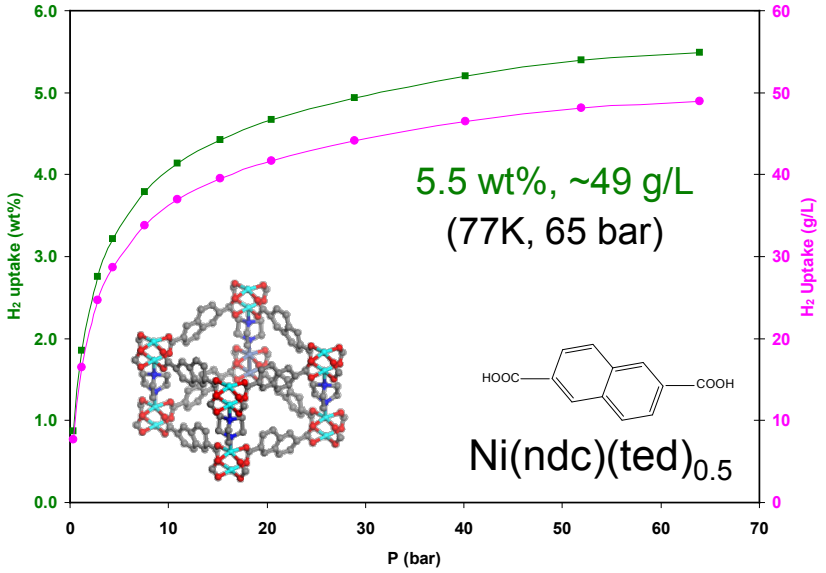






Solvent Accessible Volume (%)	57	61	67
H-K Pore Distribution (Å)	5.0	7.5	9.2
Pore Volume (cc/g, P/P^0 = 0.99)	0.47	0.73	1.05
Surf Area (BET/Langmuir, m^2/g)	958/1244	1888/2174	2090/2919
H2 Uptake (wt%, 77K, 40 bar)	2.7	4.1	5.2

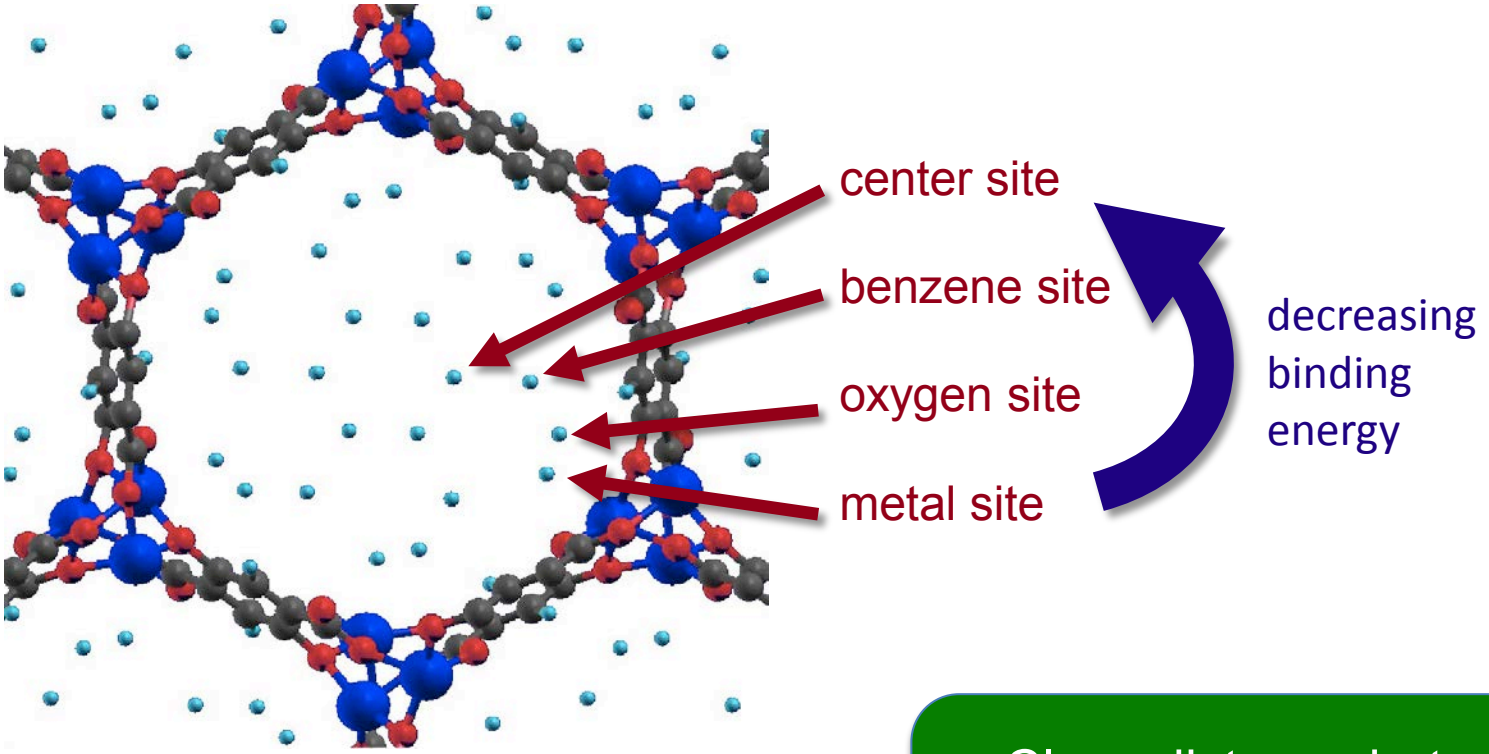




J. Y. Lee, J. Li, et. al. manuscript in preparation.

H_2 Adsorption in MOF-74-Mg

8-13 kJ/mol H_2 binding energy; ~10 Å 1D channels; aromatic ligand;
M-H_2 range (~2.1-2.8 Å) depending on the metal (M=Zn, Mg, Ni)



Neutron diffraction at 4K (D_2)

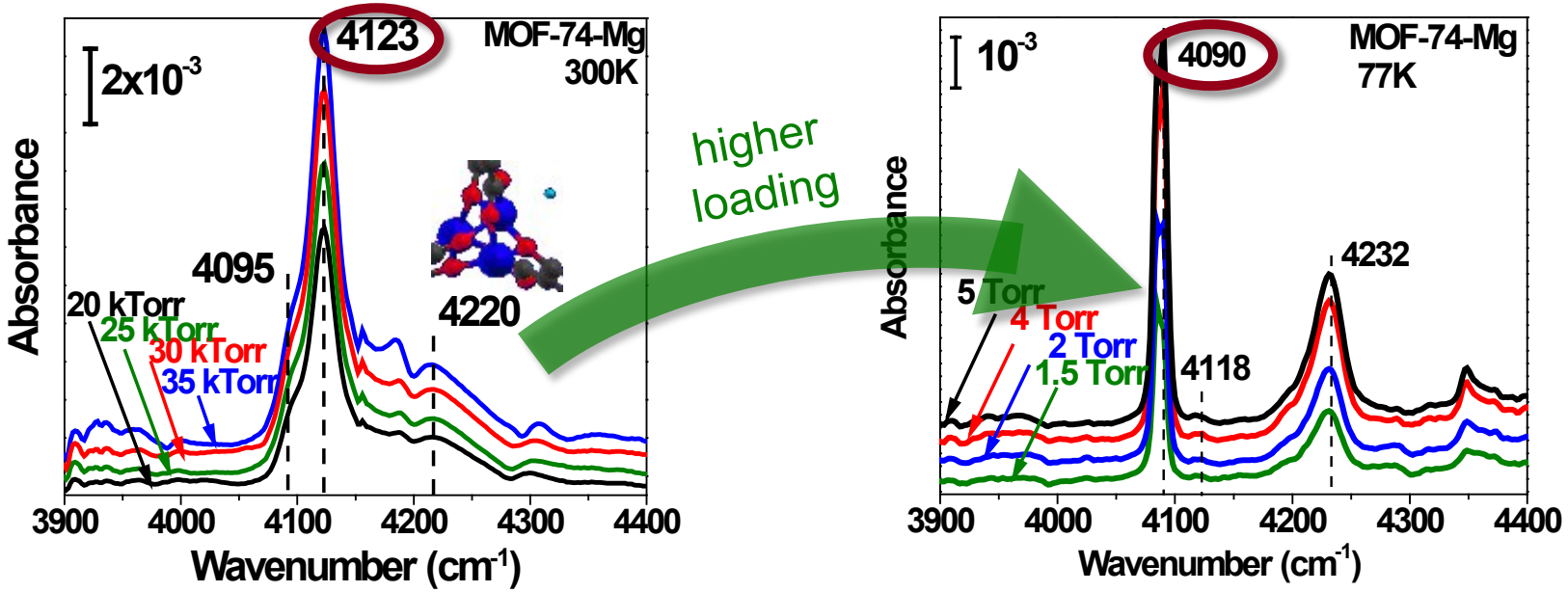
Y. Liu et al., Langmuir **24**, 4772 (2008)

Close distance between metal and oxygen site ~2.9 Å: H_2-H_2 interactions possible!

H_2 Adsorption in MOF-74-Mg

RT: $\Delta\nu(H_2)$ = -32 cm^{-1}

77K: $\Delta\nu(H_2)$ = -71 cm^{-1}



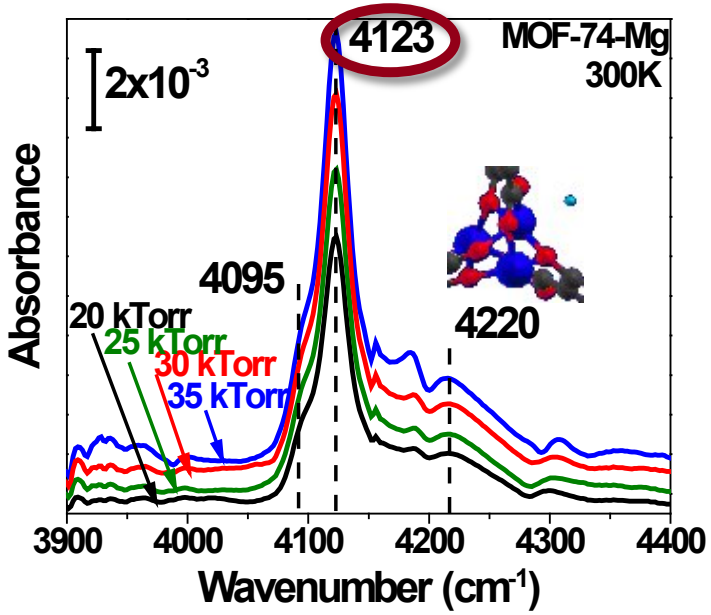
Uptake ~1 wt%
Isolated H_2 at the metal site
Lower H_2 shifts than $Zn(bdc)(ted)_{0.5}$

Higher H_2 loading → larger IR shift
change in $\Delta\nu$ = -39 cm^{-1}

Nijem et al., JACS **132**, 14834 (2010)

H_2 Adsorption in MOF-74-Mg

RT: $\Delta\nu(H_2)$ = -32 cm^{-1}

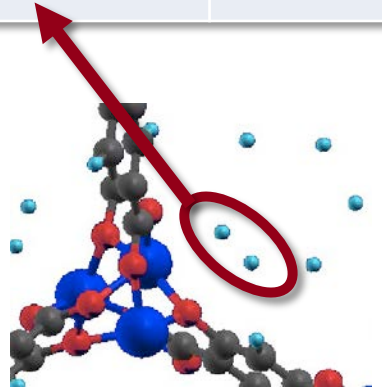


Nijem et al., JACS **132**, 14834 (2010)

vdW-DF IR shifts for different loadings for MOF-74-Mg (in cm^{-1})

	$\Delta\nu(H_2)$ Mg	$\Delta\nu(H_2)$ O
$1H_2$/unit cell	-51	NA
$12H_2$/unit cell	-67	-41

H_2 "pairing" interaction

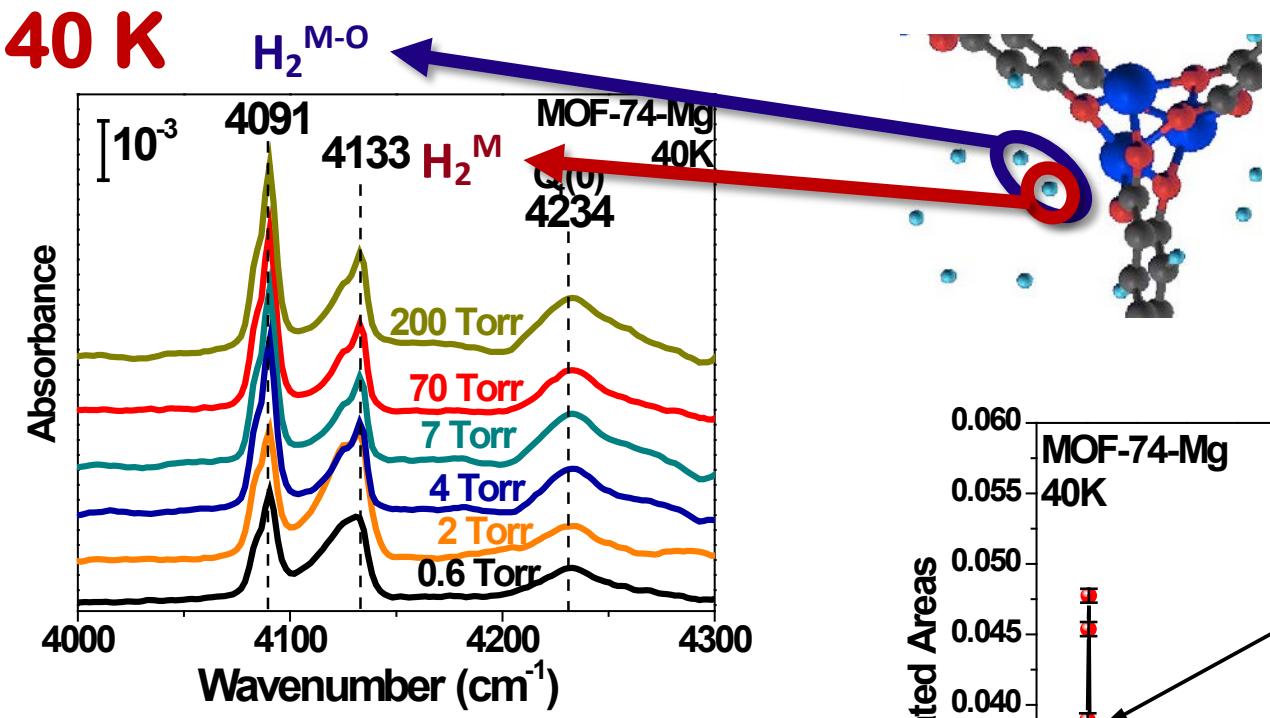


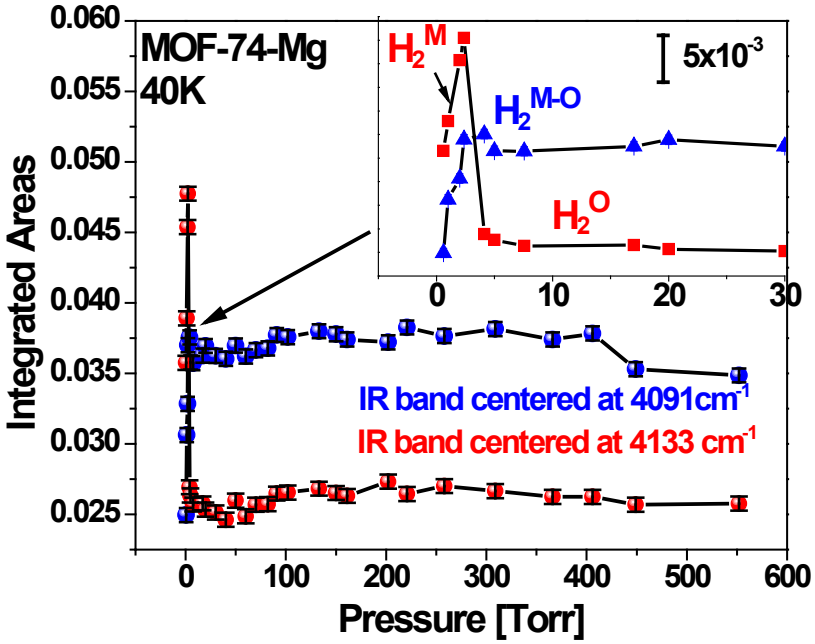
vdW-DF dipole moment of H_2

	Mg	O
$1H_2$/unit cell	4.1	NA
$12H_2$/unit cell	3	4.8

Decrease in dipole moment H_2^M due to H_2-H_2 interactions + activation energy to form the H_2-H_2 dimer

H_2-H_2 Interactions in MOF-74-Mg

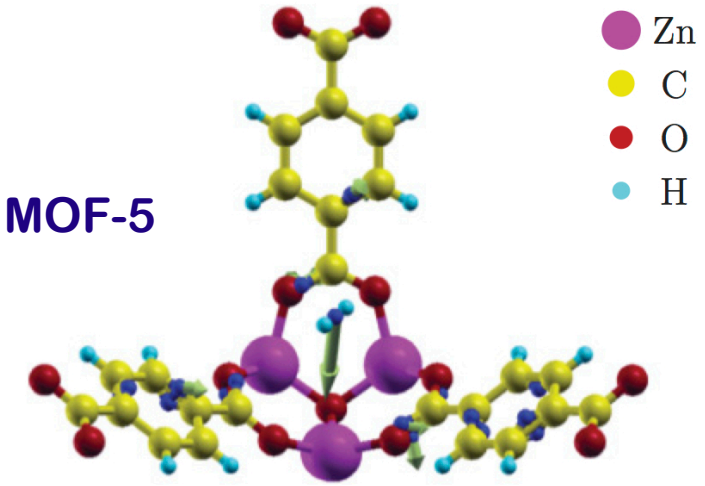


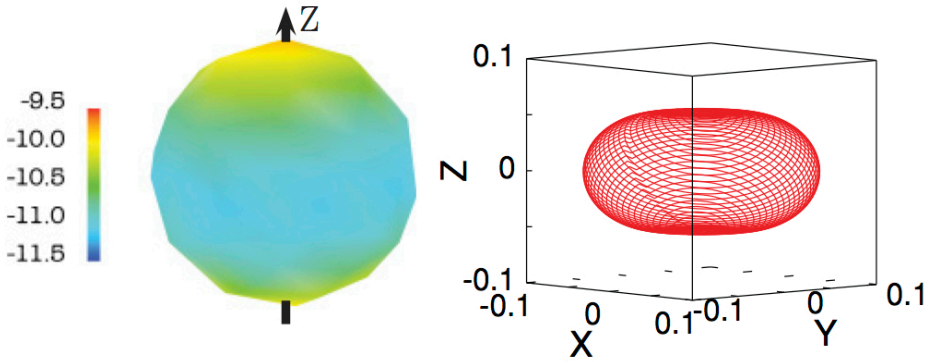


Slower kinetics
Contribution from both bands
Decrease in dipole moment of H_2^M due to H_2-H_2 interactions

Nijem et al., JACS **132**, 14834 (2010)

Accurately Calculating IR Intensities





Stretch frequency shift of adsorbed H_2

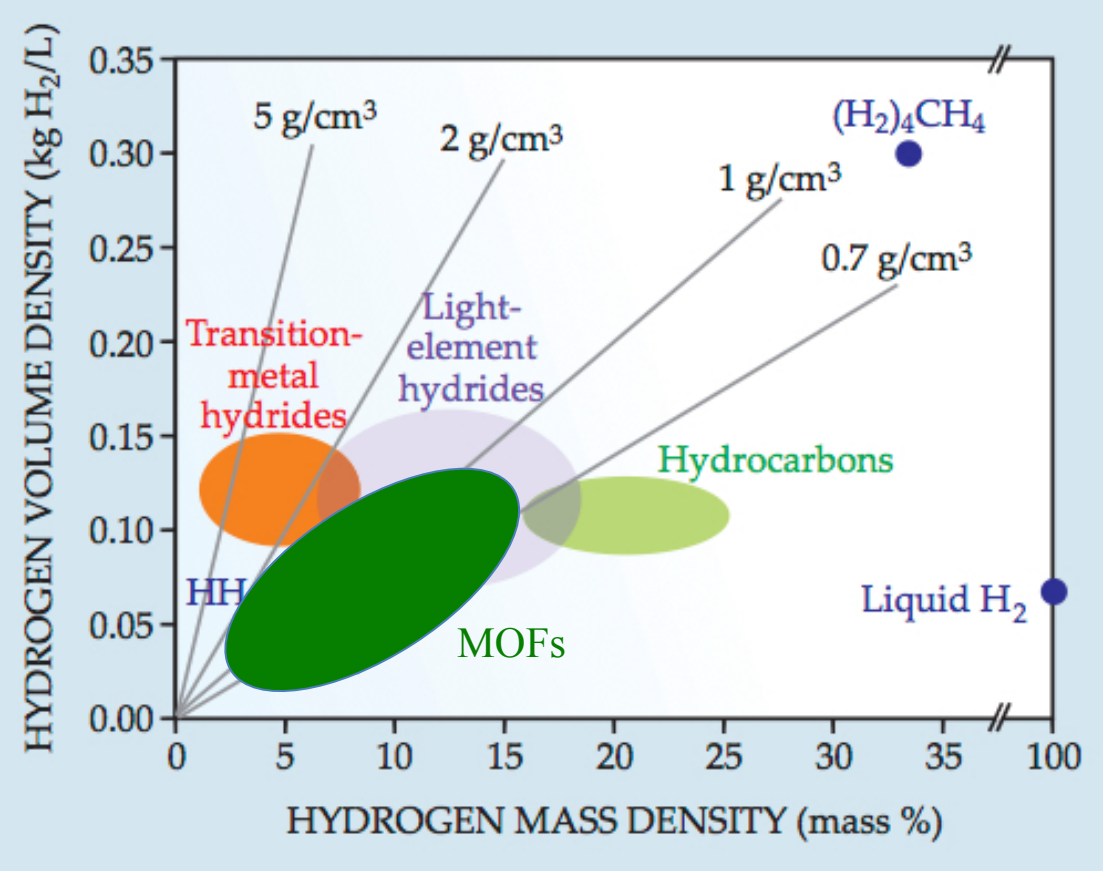
Site	Theory (cm^{-1})	Expt. (cm^{-1})	Calculated E_B (kJ/mol)
cup	−23	−27.5	−11.1
O2	−22	−19.0	−7.9
O3	−13	−17	−7.8
benzene	−15	—	−5.4

Theory vs experiment for RV transitions

	m_i	m_f	Theory Δv	Theory Int.	Experiment Δv	Experiment Int.
$Q(0)$	0	0	−23	2		abs
$Q(1)$	±1	±1	−23	97	−27.5	str
	0	0				
$Q^*(1)$	±1	0	22	9	39	wk
$S(0)$	0	±2	−44	58	−49.3	str
		±1	−12	5	−6.8	wk
		0	−1	2		abs
$S(1)$	±1	±3	−34	100	−36.8	str
		±2	−9	6	−0.8	wk
		±1	6	9	21.6	wk
		0	11	3		abs
	0	±3	−78	0		abs
		±2	−53	3	−61	wk
		±1	−50	~0		abs
		0	−33	~0		abs

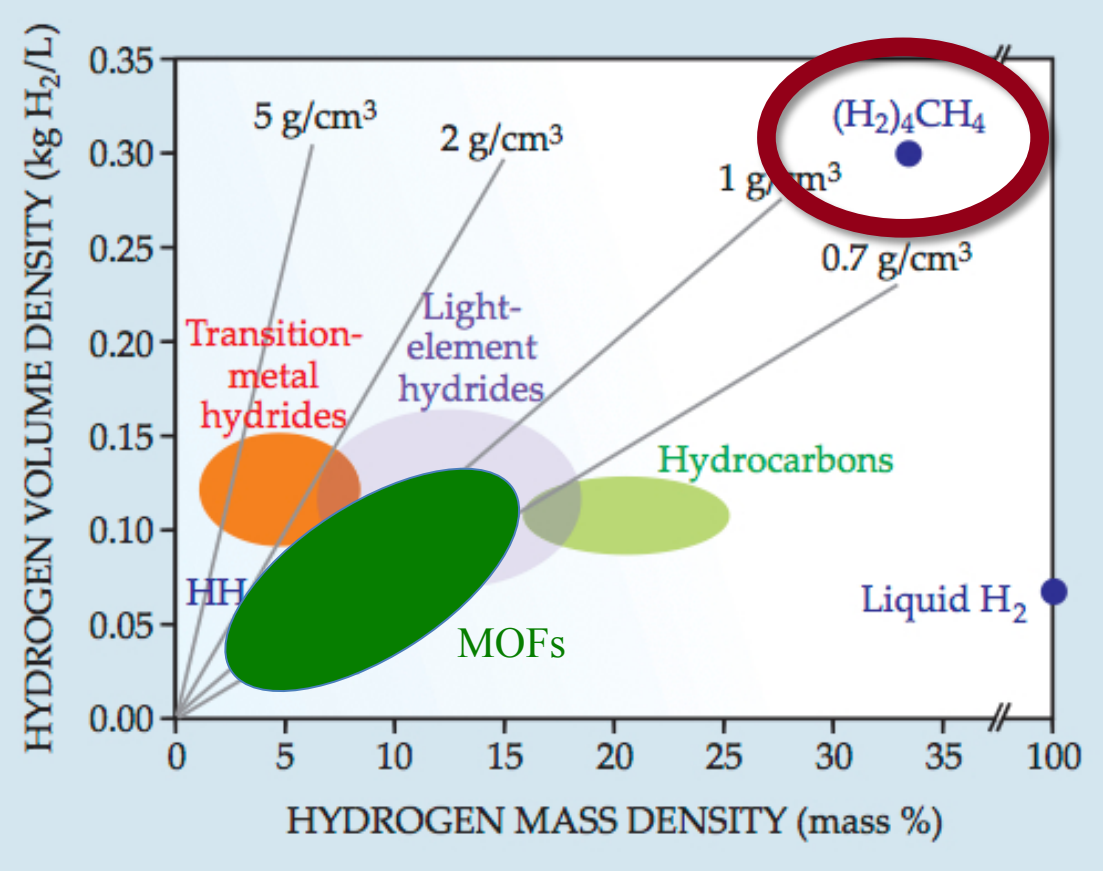
L. Kong, Y. J. Chabal, and D. C. Langreth, Phys. Rev. B **83**, 121402 (2011)

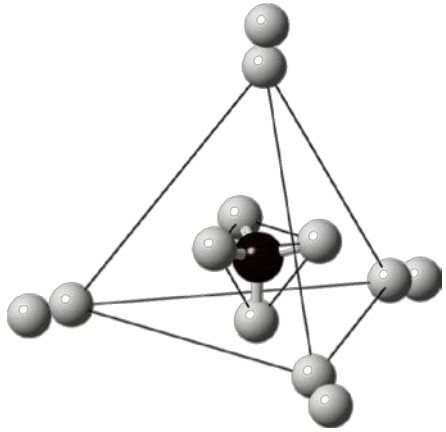
$(H_2)_4CH_4$ in MOFs and CNT



W. L. Mao et al., Physics Today **60**, 42 (2007)

$(H_2)_4CH_4$ in MOFs and CNT

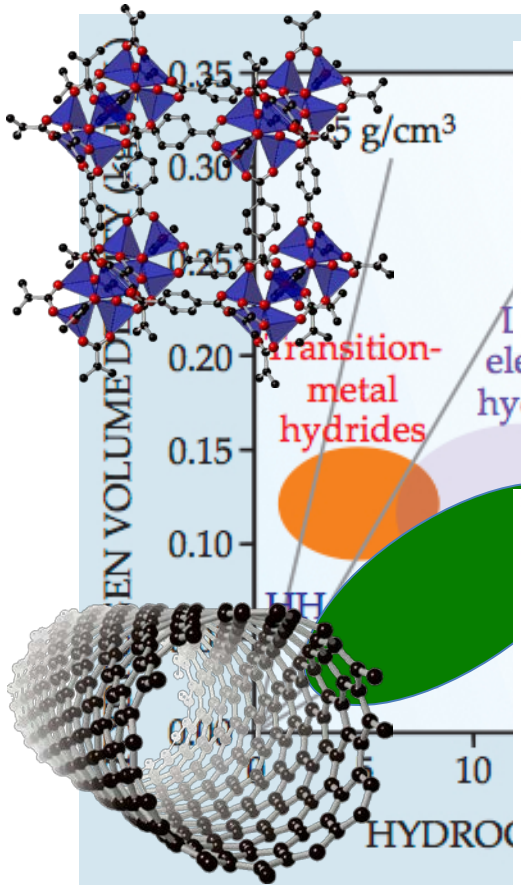




Requires 5 - 6 GPa at RT

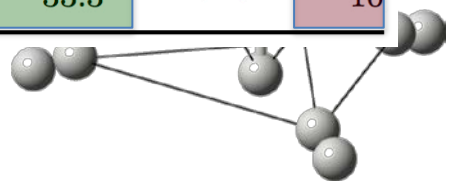
W. L. Mao et al., Physics Today **60**, 42 (2007)

$(H_2)_4CH_4$ in MOFs and CNT



W. L. Mao et al

System	Free	Fixed	Filling	ρ^{w}_{mass}	$\rho^{w/o}_{mass}$	Max. P	T
MOF-5	11.2	18.6	$2 \times 2 \times 2$	10.0	6.7	3.9	224
irMOF-10	15.4	24.5	$3 \times 3 \times 3$	19.5	13.0	2.3	172
irMOF-16	19.1	28.8	$3 \times 3 \times 3$	15.3	10.2	1.5	126
Pure H4M	—	—	—	50.2	33.3	—	10

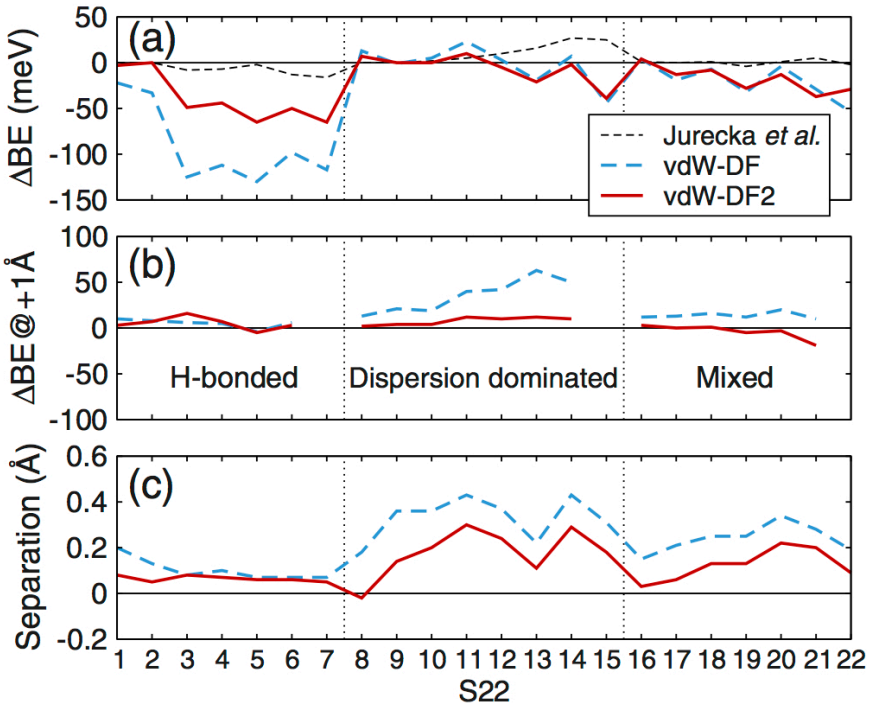


System	Radius	Filling	ρ^{w}_{mass}	$\rho^{w/o}_{mass}$	ρ_{vol}	E_r	ε
(10,0)	3.95	$1 \times 1 \times 1$	2.4	1.6	0.028	870	0.7
(16,0)	6.30	$2 \times 2 \times 1$	5.6	3.7	0.055	555	1.0
(24,0)	9.43	$3 \times 3 \times 1$	7.9	5.3	0.065	373	1.6
(32,0)	12.56	$4 \times 4 \times 1$	10.0	6.7	0.070	280	2.1
(40,0)	15.69	$5 \times 5 \times 1 + 8$	14.6	9.7	0.097	224	2.6
(48,0)	18.82	$6 \times 6 \times 1 + 12$	16.7	11.1	0.102	187	3.1
(56,0)	21.96	$7 \times 7 \times 1 + 16$	18.4	12.2	0.103	160	3.6
(64,0)	25.08	$8 \times 8 \times 1 + 24$	20.4	13.6	0.110	140	4.1
H4M	—	—	50.2	33.3	0.160	—	—

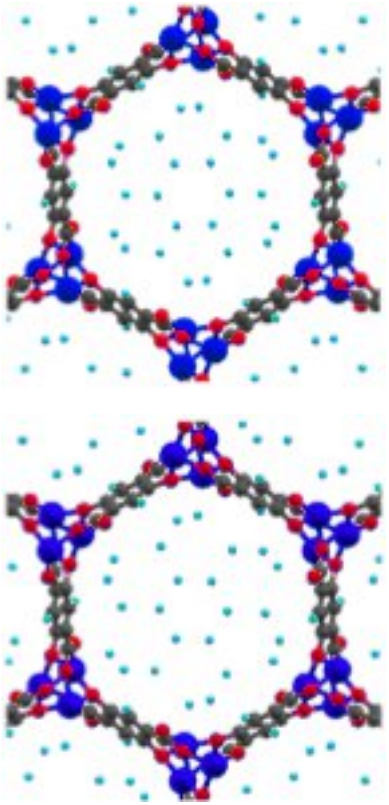
Q. Li and T. Thonhauser, J. Phys.: Condens. Matter, in press (2012)

Computational Improvements

Improved description of van der Waals interactions within DFT through a better exchange-correlation functional:
vdW-DF → vdW-DF2



K. Lee et al., Phys. Rev. B **82,** 081101R (2010)



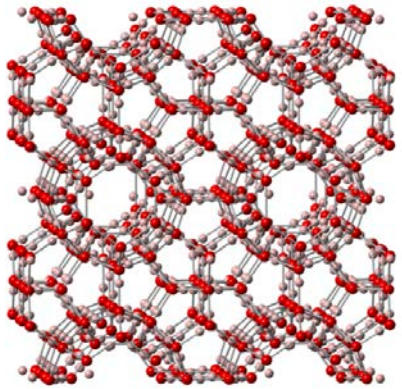
vdW-DF2

neutron diffraction

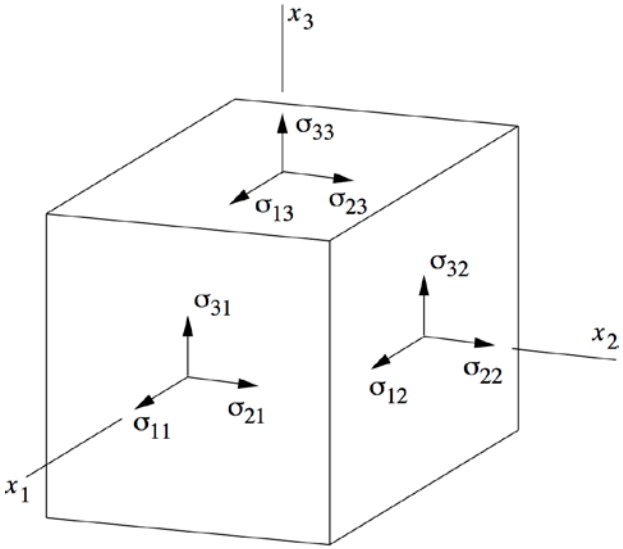
MOF74-Zn

Computational Improvements

We implemented vdW-DF and vdW-DF2 in the computer code PWscf (part of the open-source QUANTUM-ESPRESSO package), which shows a speed up of approximately a factor of 2 – 3, compared to our original implementation in ABINIT.



H_2 in SII clathrate:
408 atoms/unit cell



We have also derived a formalism that allows us to calculate the vdW-DF stress tensor, allowing for a much more efficient structural optimization.

Future Directions

Spin-polarized calculations are not yet possible and interesting cases such as MOF containing Fe, Co, Ni are excluded. Future: spin-polarized vdW-DF.

Dynamical and temperature effects are excluded at the moment. Future: implement vdW-DF in molecular dynamics code.

Framework is in place for adsorption of a variety of small molecules (CO, CO_2, N_2, H_2O, CH_4, …). Future: apply Framework to study co-adsorption and gas separation.

Conclusions

A combination of vdW-DF calculations and spectroscopic data gives a mechanistic understanding of molecular adsorption in MOFs.

Knowledge of this interaction is important to design and test MOF structures with desired functionality.

Tools and methodology are in place to address more complex systems, such as co-adsorption of several gases and gas separation.

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