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Validation of a Nonbonded Force Field for Metal-Organic Frameworks

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Acknowledgements

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Motivation: A force field for MOF-5

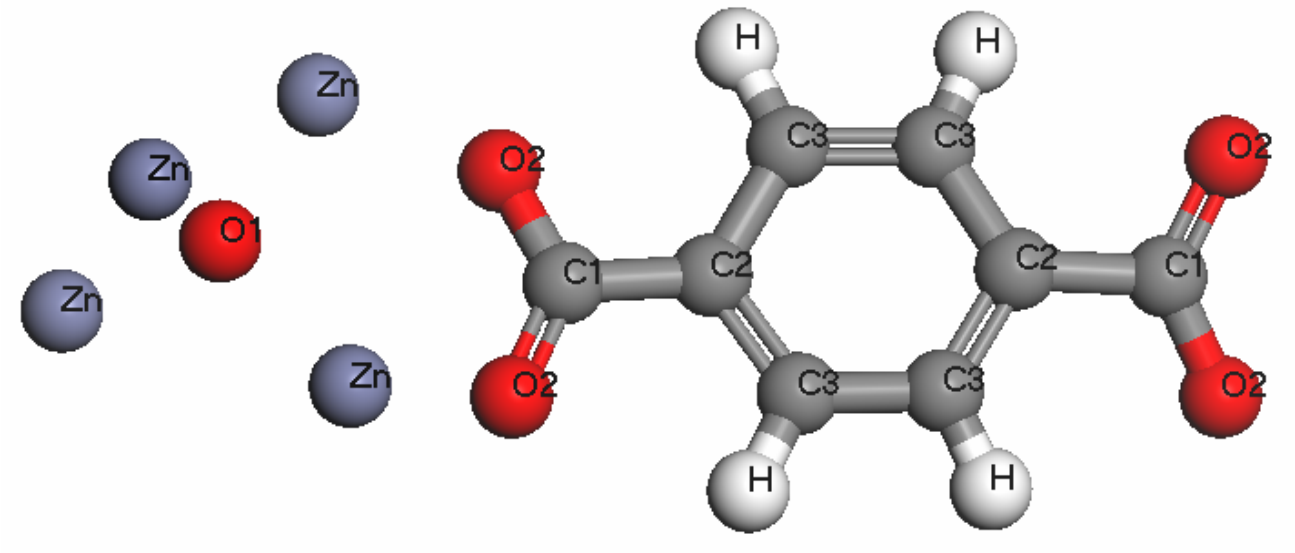
- A number of MD and MC calculations:
  - Sagara et al. 2004 (UFF), Düren and Snurr 2004 (DREIDING), Gargeroglio et al. 2005 (UFF and DREIDING force fields), Skoulidas and Sholl 2005 (UFF and DREIDING force fields), Yang and Zhong 2005 (OPLS-AA), Huang et al 2007 (quantum-based flexible FF)
  - Charges estimated from ab initio methods (e.g. DFT, MP2, or CC) performed on molecular clusters
- Problem: Standard FFs do not reproduce geometry
  ➔ lattice was kept rigid at experimental geometry
- Target of our project:
  - FF parameterized to reproduce geometry and lattice deformation
  - A non-bonded FF to model formation and breaking of framework

Bochum-group: a flexible MM3-type FF (*Angew. Chemie*. **2006**)

Sandia-group: a flexible non-bonded FF (*J. Am. Chem. Soc.***2006**)

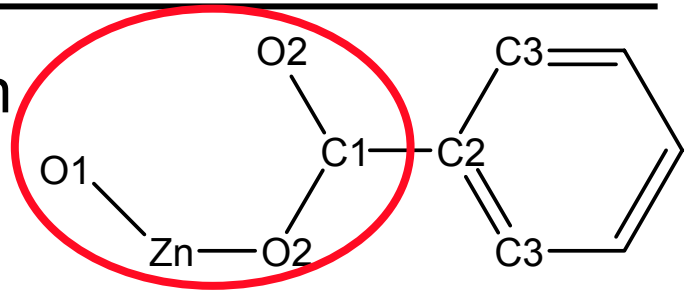
A non-bonded MOF force field permits assessment of structural effects of sorption and chemical reaction

- Zn_4O (electrostatic and VDW only) parameters based on zincite structure (ZnO)
- CVFF parameters for dicarboxylate (bonded) including intramolecular terms
- VDW parameters for Zn-O interactions adjusted to fit MOF5 crystal structure



Atomic Charges: Crucial for a non-bonded FF

- Point charges from DFT calculation
  (Charges on C1, C2, and O2 changed slightly from their CVFF values)



			O1	Zn	O2	C1
1)	ZnO	Periodic DFT/6-31G*	-1.2	1.2		
2)	MOF-5	Cluster DFT/6-31+G, CHELPG	-1.44	1.26	-0.67	0.68
3)	MOF-5	Cluster DFT/6-31G**, CHELPG	-1.79	1.31	-0.63	0.62
4)	MOF-5	**This work**	-1.2	1.2	−0.6	0.6

1) D.M. Teter, unpublished results. 2) Sagara et al, *JCP* **2004**, *121*, 12543
3) R. Schmid (Bochum), unpublished results

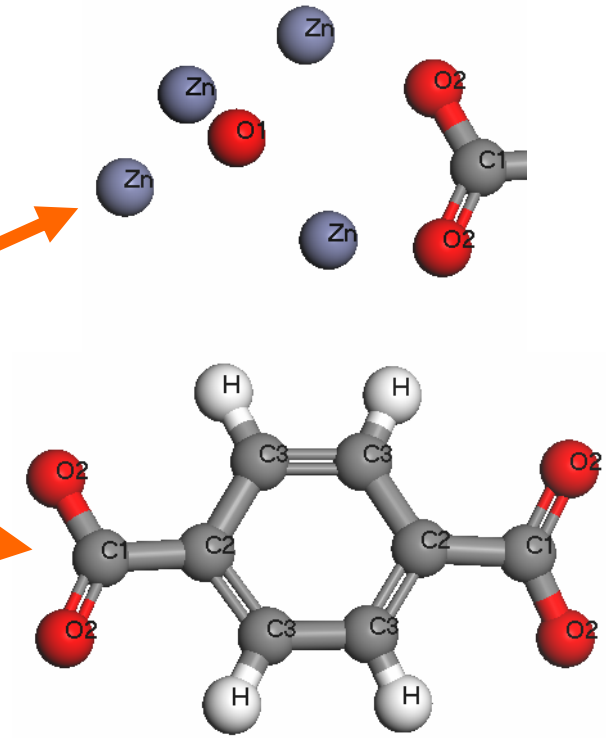
Molecular dynamics simulations

LAMMPS code

- 2 x 2 x 2 unit cell repeats (3400 atoms)
- Adsorbate molecules inserted into MOF-5 cavities
- Constant pressure (NPT) ensemble to calculate volume and lattice parameters
- Potential energy expression:

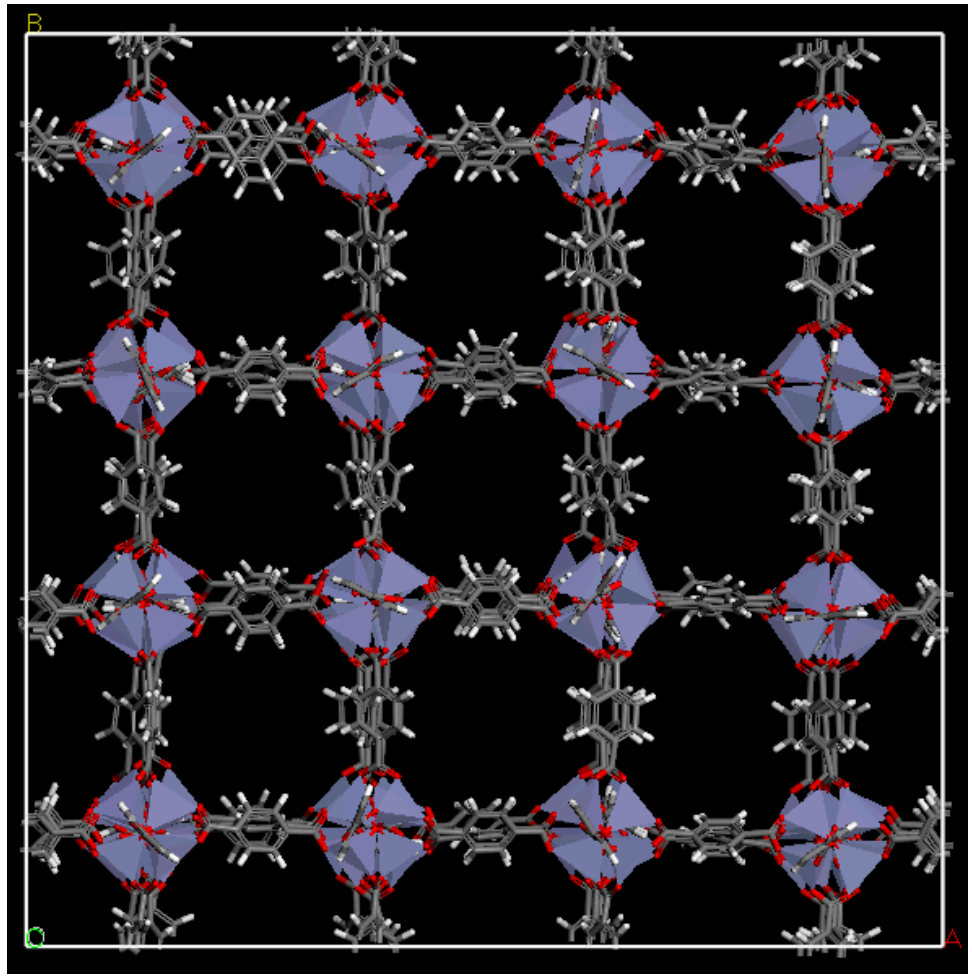
  All atoms: VDW and electrostatic

  BDC and guests: CVFF parameters (bond, angle, dihedral, out-of-plane)

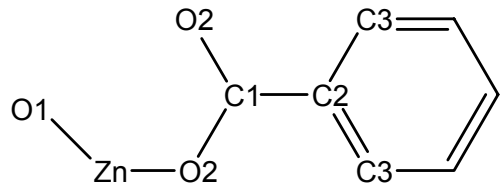


Pure MOF-5

- Short-range forces evaluated every 0.5 fs, long-range electrostatics (PPPM) every 1.0 fs
- NPT production runs 1.0 ns in length
- NVT runs (1.0 ns) for PV plots
- NVT runs (40 fs) for power spectra



Pure MOF5 Structure Comparison



Bond lengths (Å)

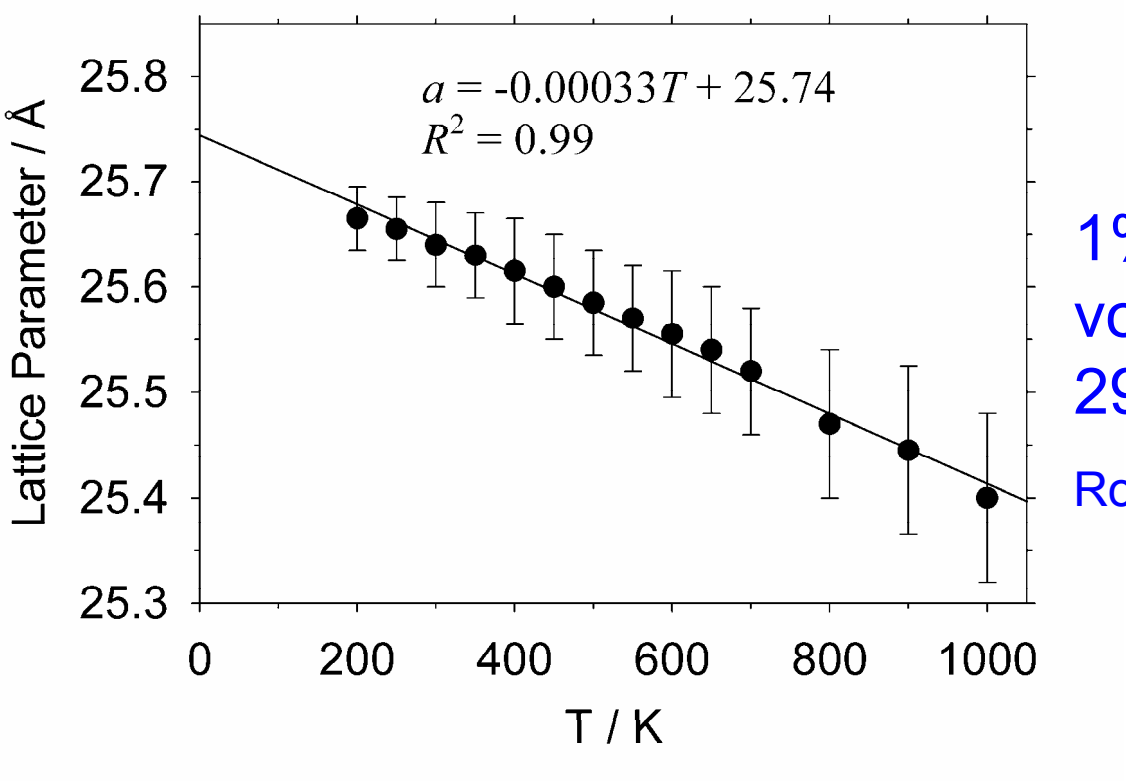
	C3-H	C2-C3	C1-C2	C1-O2	Zn-O1	Zn-O2
Simulation	**1.08**	**1.40**	**1.50**	**1.26**	**1.93**	**1.93**
DFT/B3LYP	**1.10**	**1.34**	**1.37**	**1.26**	**1.95**	**1.95**
GGA (periodic)	**1.08**	**1.40**	**1.48**	**1.28**	**1.96**	**1.94**
Experiment*		**1.39**	**1.49**	**1.30**	**1.94**	**1.92**

Angles (°)

	O2-C1-C2	O2-C1-O2	Zn-O2-C1	O2-Zn-O2	O2-Zn-O1	Zn-O1-Zn
Simulation	**117 ± 3**	**126 ± 2**	**127 ± 9**	**110 ± 7**	**108 ± 6**	**109 ± 4**
DFT/B3LYP	**118.3**	**123.3**	**132.8**	**108.1**	**110.8**	**109.5**
Experiment*	**116.8**	**126.4**	**129.5**	**106.2**	**112.5**	**109.5**

*Yaghi et al, 2002

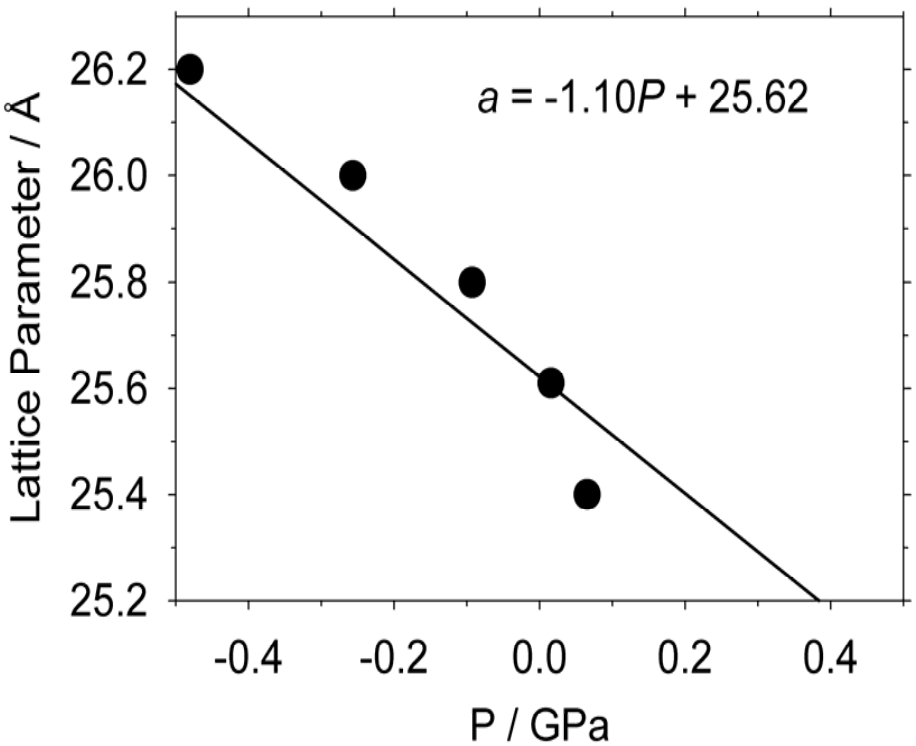
MOF5 Thermal Expansion – 1.0 ns NPT Simulations



1% increase in cell volume upon cooling from 293 K to 30 K.

Rowsell et al, *Science* **2005**

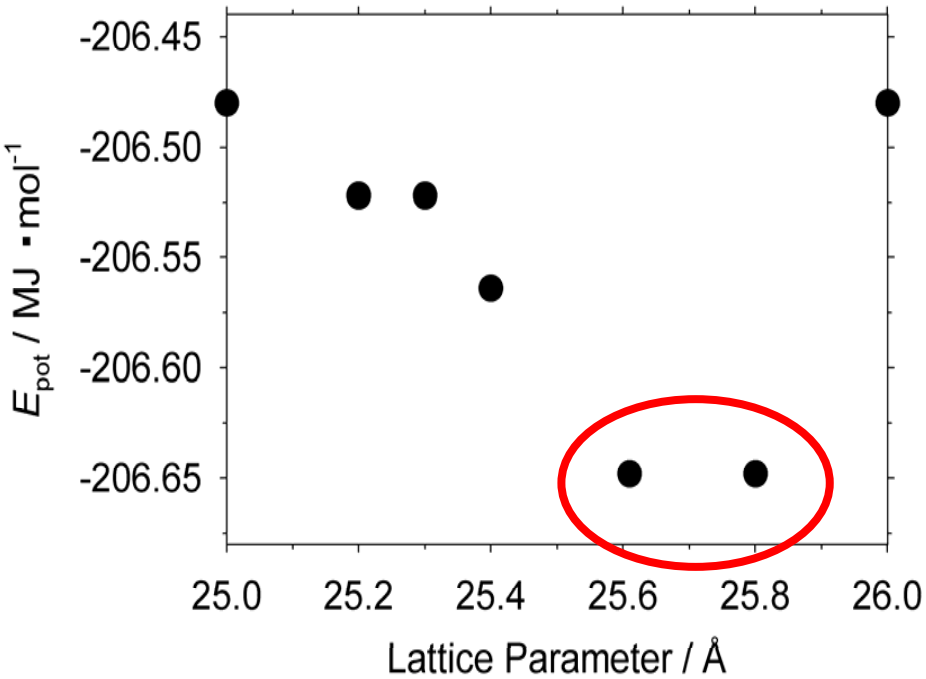
Pressure Dependence – 1.0 ns NVT Simulations



DFT slope = –0.46 Å·GPa^{-1}

Zhou and Yildirim, *Phys. Rev. B* **2006**

Energy Minimum at 25.6-25.8 Å

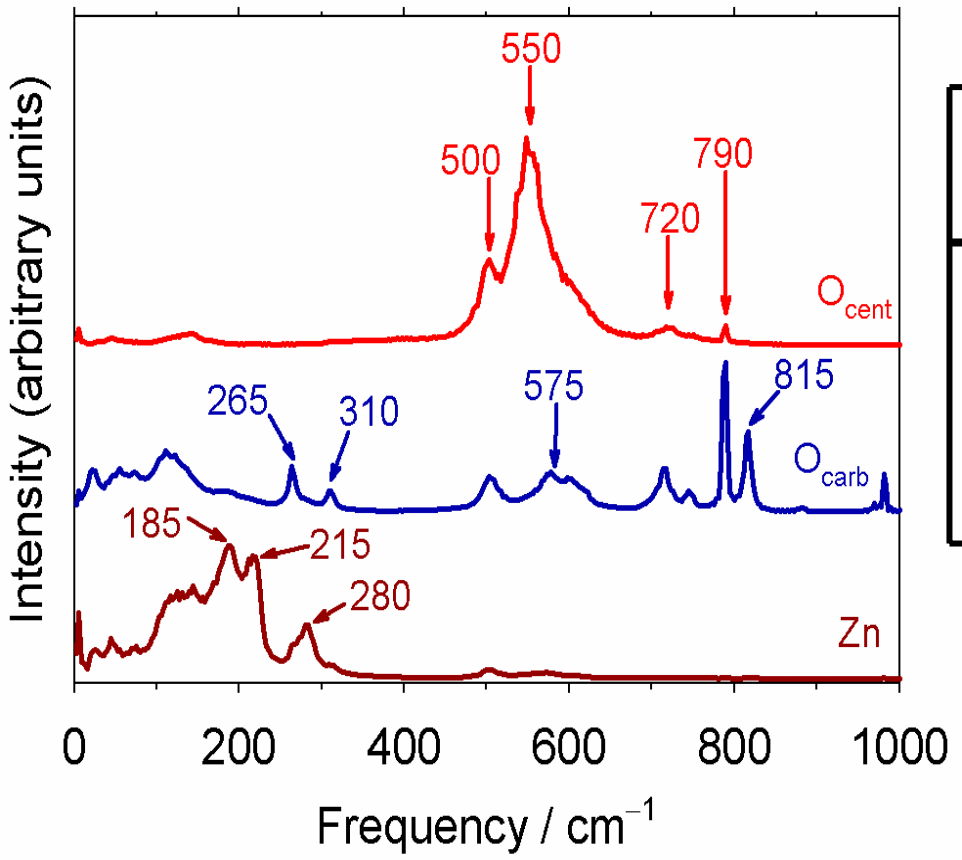


DFT minimum at 25.6 Å

Zhou and Yildirim, *Phys. Rev. B* **2006**

Vibrational Spectra

- Obtained from velocity autocorrelation functions (VACF)
- Rigorous test of the nonbonded force field parameters



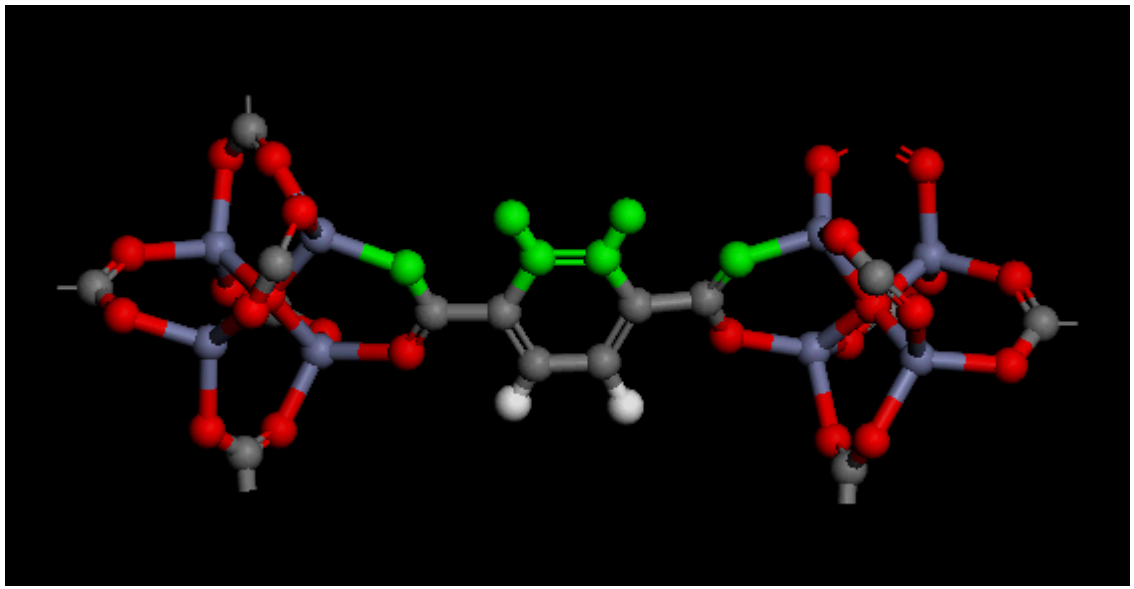
Key Frequencies (cm^{-1})

Mode	This Work	Bonded FF*
Zn-O	185-310 500-575	200-260 473-576
Carboxylate	720-815	
Phenyl	40	60-80

* Tafiposky et al, *J. Comp. Chem.* **2007**

Phenyl rotation about C_2 axis, 40 cm^{-1}

MOF-5, 400 K



- Rotation involves phenyl atoms only, Zn-O_{carb} bonds not broken
- More common at 400 K than 300 K*
- DFT energy barrier calculated to be 15 kcal·mol^{-1}**

*Gonzalez et al, *Micropor. Mesopor. Mater.* **2005**

** Zhou and Yildirim, *Phys. Rev. B* **2006**

Free Volume

Adsorption Results

guest	guest/ unit cell	guest mass %	lattice parameter (Å)	Free volume ($cm^3 g^{-1}$)[a]	guest volume %[b]
None			25.64		
CH_3CH_2OH	95	41.5	25.56	0.90	55.2
CH_2Cl_2	88	54.8	25.70	0.91	55.1
$CHCl_3$	71	57.9	25.69	0.93	56.0
CCl_4	59	59.6	25.70	0.92	55.7
C_6H_{12}	51	41.1	25.77	0.90	53.5

[a] Calculated as the volume of guest (assuming bulk liquid density) divided by the unit cell mass of pure MOF-5

[b] Calculated as the ratio of guest volume to total volume.

Free Volume

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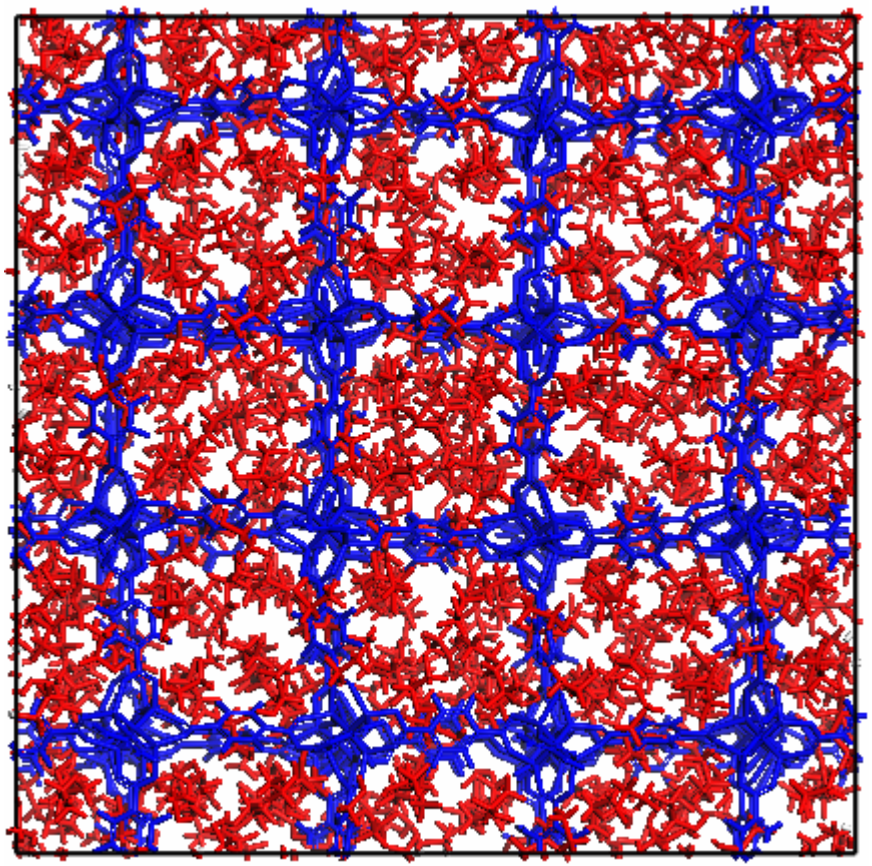
55-60% free pore volume from sorption and XRD studies.

Eddaoudi et al, *J. Am. Chem. Soc.* **2000**

[a] Calculated as the volume of guest (assuming bulk liquid density) divided by the unit cell mass of pure MOF-5

[b] Calculated as the ratio of guest volume to total volume.

Free Volume - Ethanol

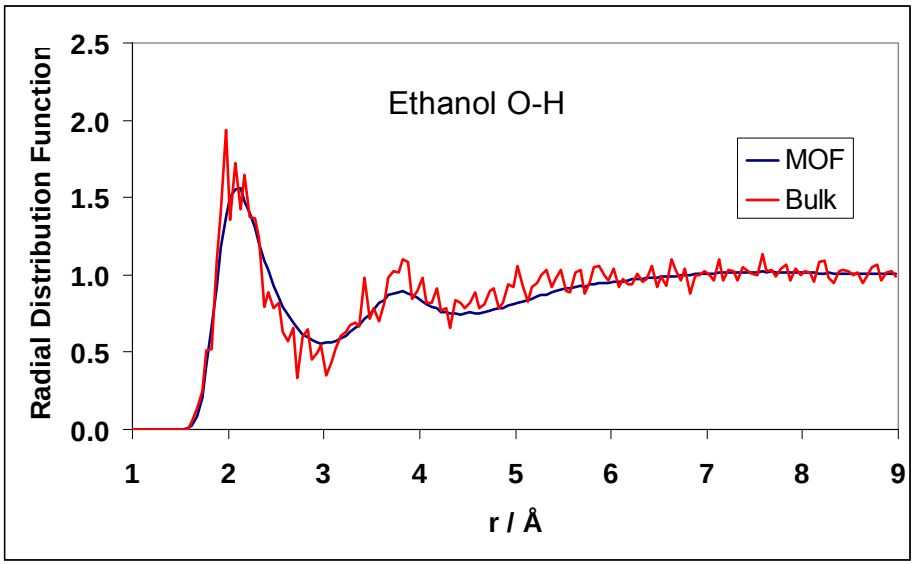


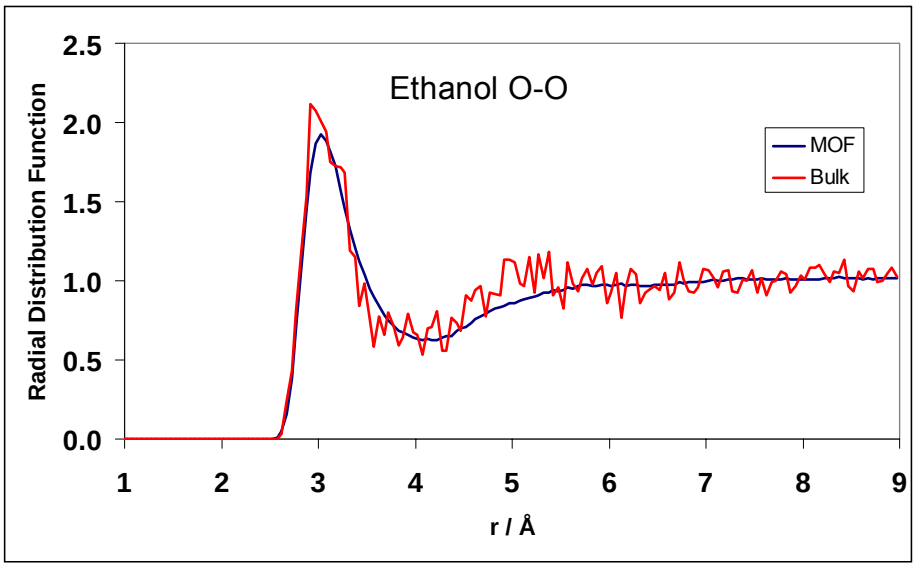
Blue = MOF-5

Red = ethanol

- 95 ethanol molecules / unit cell (41.5 % by mass ethanol)
- Ethanol preferentially binds near the Zn_4O corners, leaving empty space in the pores

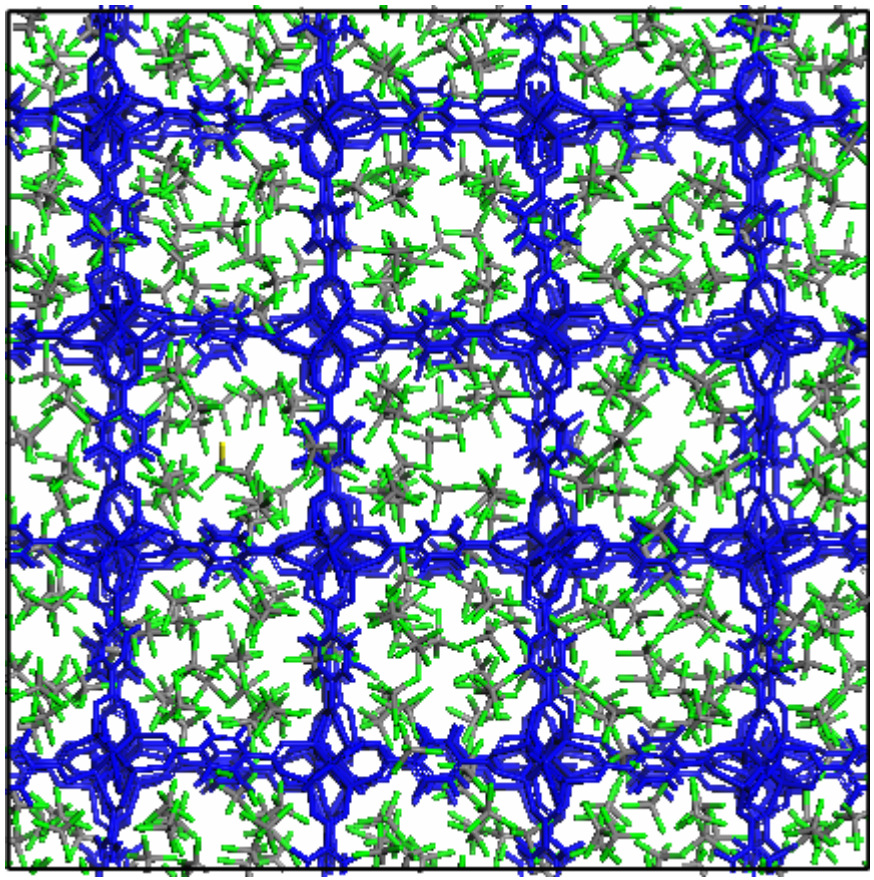
Free Volume - Ethanol





- Bulk data from NVT simulations of ethanol at liquid density (0.79 g·mL^{-1})
- Similarity between ethanol RDFs in MOF pore and ethanol RDFs in bulk liquid.

Free Volume – CCl_4

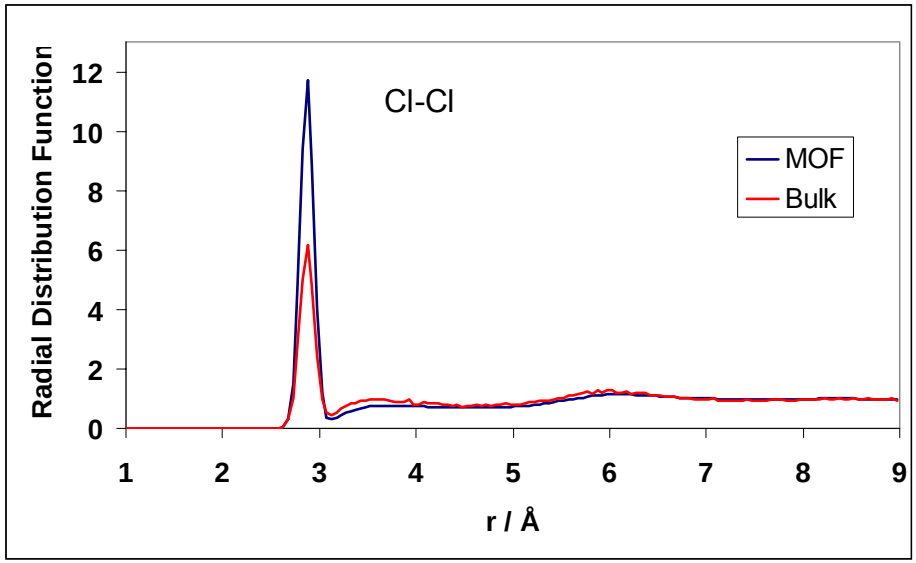


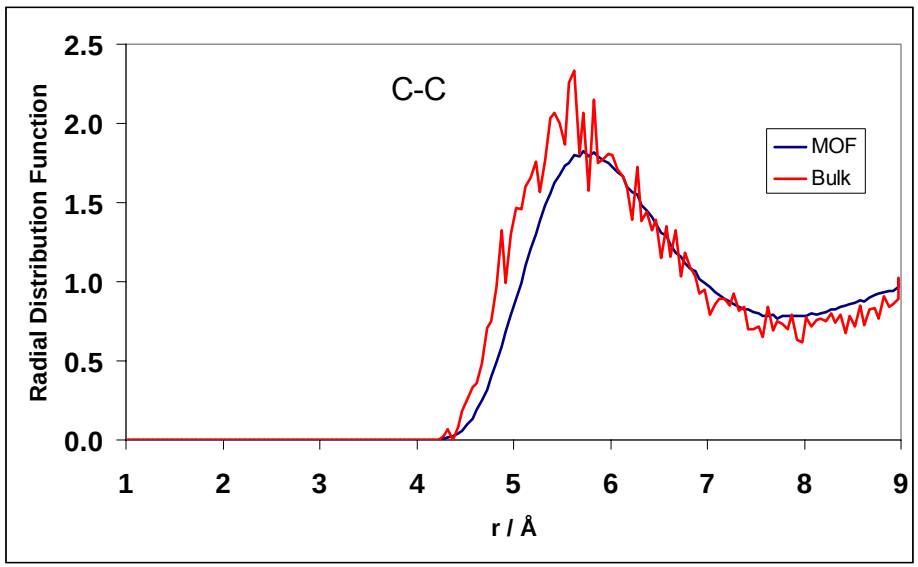
Blue = MOF-5

Green = chlorine

- 59 CCl_4 molecules / unit cell (59.6 % by mass CCl_4 ethanol)
- Zn_4O sites are not preferred, corners, but still empty space in the pores

Free Volume – CCl_4





- Bulk data from NVT simulations of CCl_4 at liquid density (1.59 $g \cdot mL^{-1}$).
- Shorter C-C distance in bulk than in MOF-5 pore.

New Directions

- Adsorption isotherm simulations (Monte Carlo simulations) for MOF-5 are needed as a further validation of the nonbonded force field.
- Transferable to other Zn-based MOFs – new ligands.
- Water stability issue – new ligands or MOFs from other metals
- MOFs that undergo large volume changes upon adsorption of guests