An Illustrated and Illustrative Tour of Recent Work with CP2K

Ben Slater

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Elias Garcia Martinez (1930)

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Summary

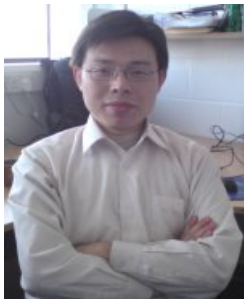
UCL

Selected examples of work on porous materials and ice

Zeolites: Hybrid Functionals/ADMM
Ice: SS-NEB
MOFs: REPEAT scheme
SCAN functional
Ice: RPA/MP2

Elucidating framework aluminium distribution in catalytic zeolites

Rachel Fletcher

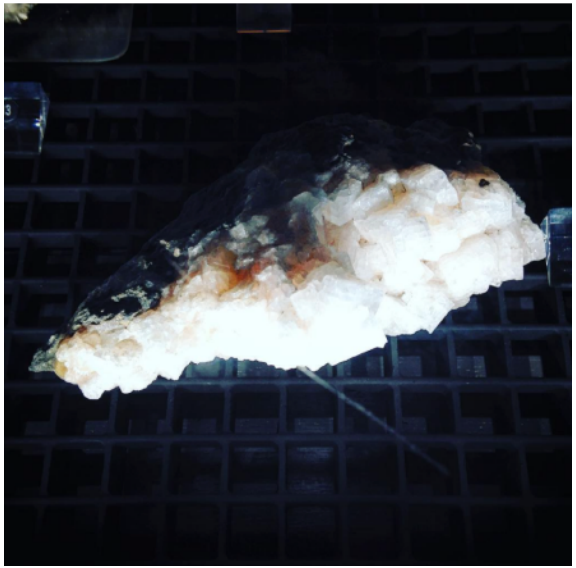


Dr. Sanliang Ling

R.E. Fletcher, S. Ling, B. Slater, 'Violations of Löwenstein's rule in zeolites' (2016)
arXiv:1612.04162 [cond-mat.mtrl-sci]

Zeolites

- Microporous, crystalline aluminosilicate solids
- Petrochemical processing
  - Cracking, isomerisation and alkylation
- Increasing concern for the environment has motivated development of sustainable and environmentally benign alternatives to traditional petrochemical methods
- The use of traditional zeolite catalysts in atypical processes
  - Pollution control
  - Hydrocarbon production



Chabazite (CHA)

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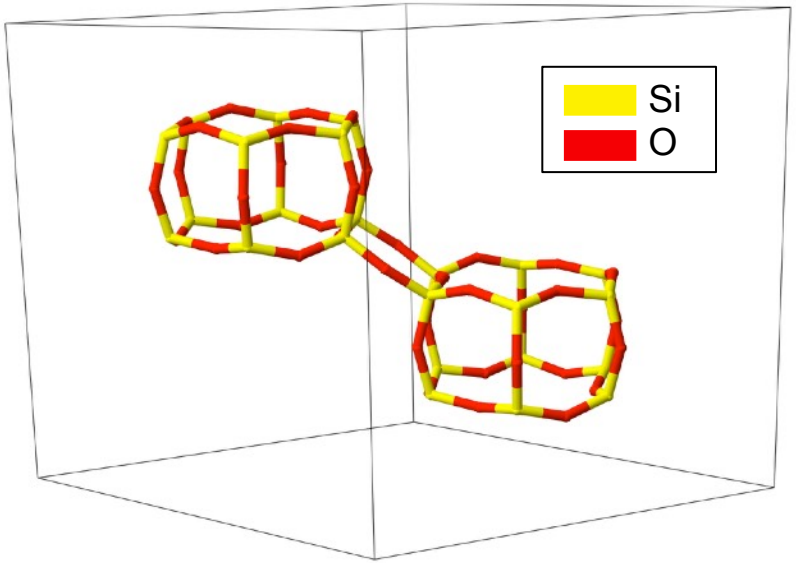

SSZ-13 (CHA)

Zeolites

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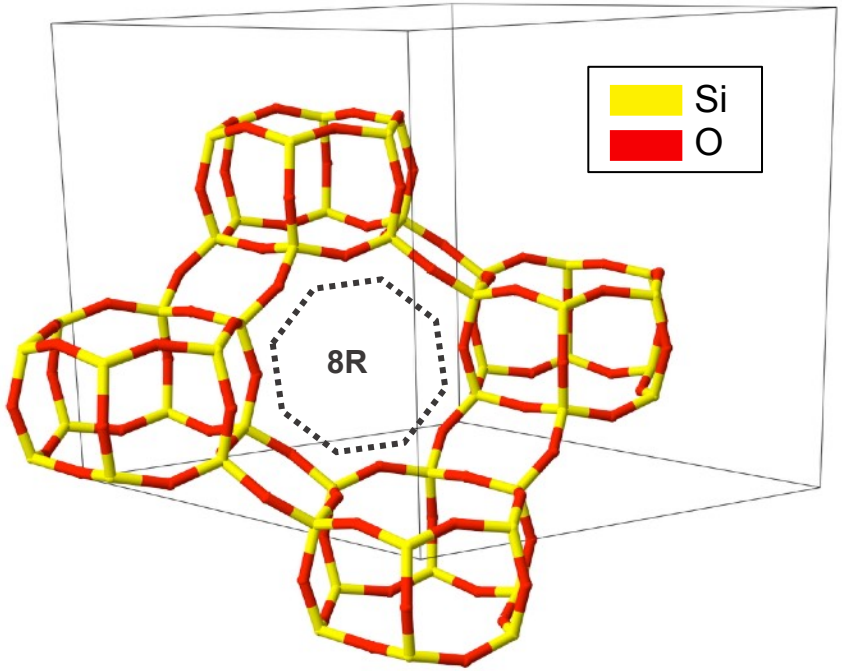
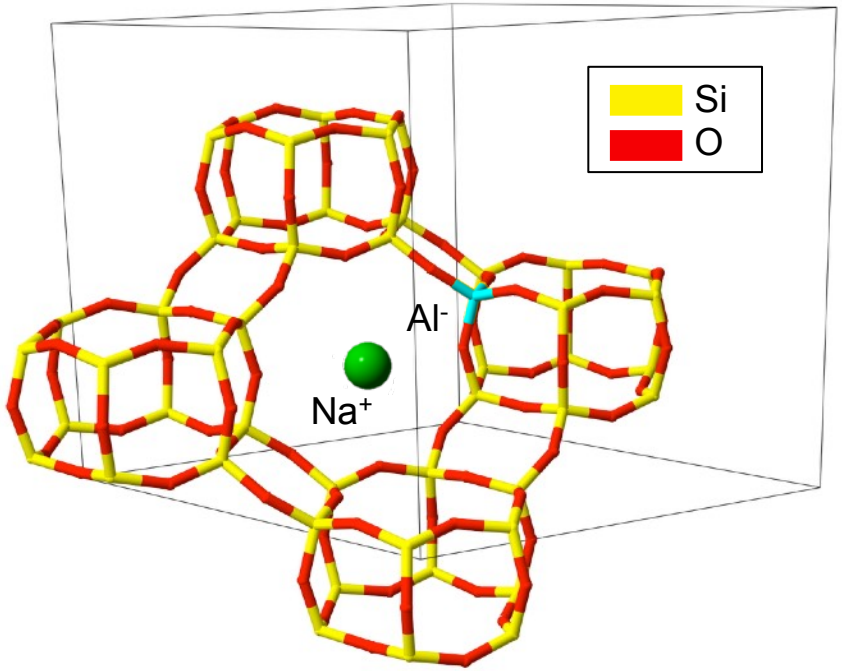


SSZ-13 (CHA)

Catalysis and Si/Al distribution

- Substituting tetravalent silica with trivalent alumina introduces a negative charge to the zeolite framework
- Charge-balancing counter cations (K^+, Na^+, Cu^{2+} H^+)
- Generally accepted that Al and associated cations play a crucial role in catalysis, particularly protonated zeolites, in which a Brønsted acidic site is formed.
- Before we can begin to investigate catalytic mechanisms, and design new zeolite catalysts, we first need a full understanding of Al's framework location.

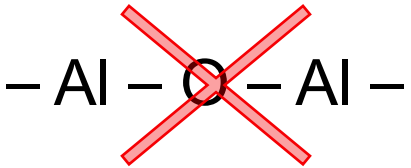


SSZ-13 (CHA)

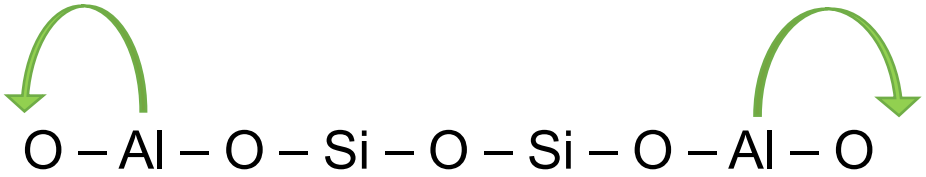
Where is Al?

Löwenstein's Rule – 1954

> "There is a disinclination for T-O-T linkages of adjacent tetrahedral units to possess more than one aluminium atom, forbidding the formation of Al-O-Al bonds within the zeolite framework."



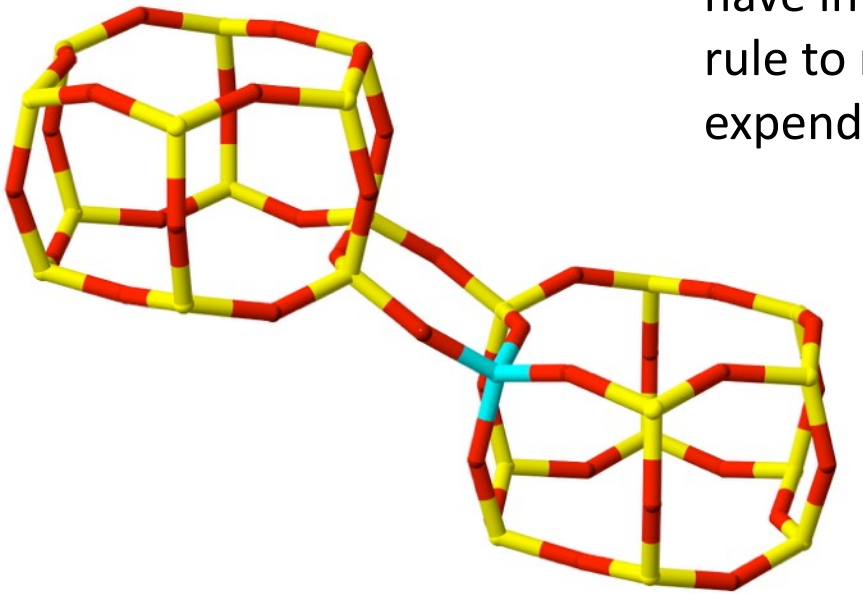
Dempsey's Rule – 1969



> "On the basis of electrostatic arguments, framework Aluminium ions assume the furthest distance from one another."

W. Löwenstein, American Mineralogist 39, (1954)
E. Dempsey et al., J. Phys. Chem. 73, no. 2 (1969)

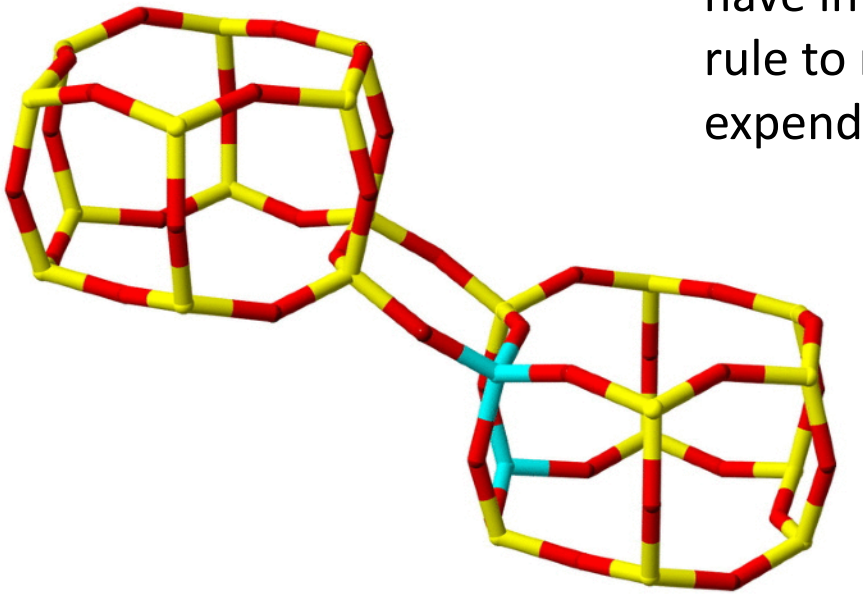
Investigating Al distribution in SSZ-13



Previous investigations have invoked Lowenstein's rule to reduce computational expenditure.

2 Al per unit cell (Si/Al = 17)

Investigating Al distribution in SSZ-13



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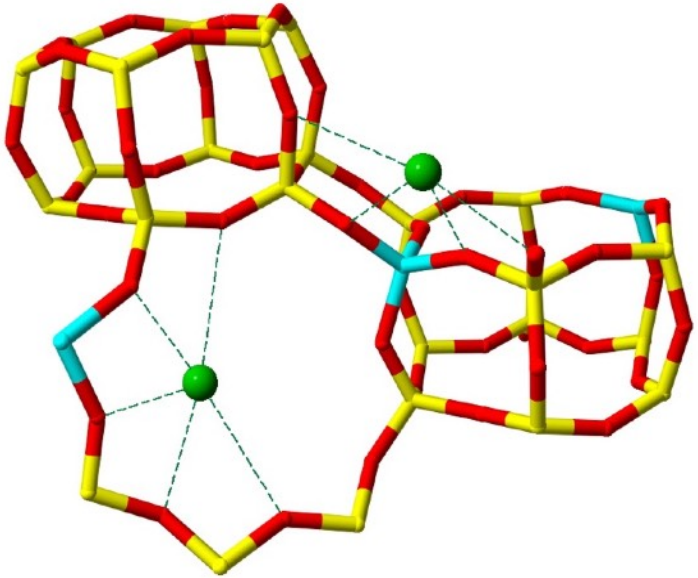
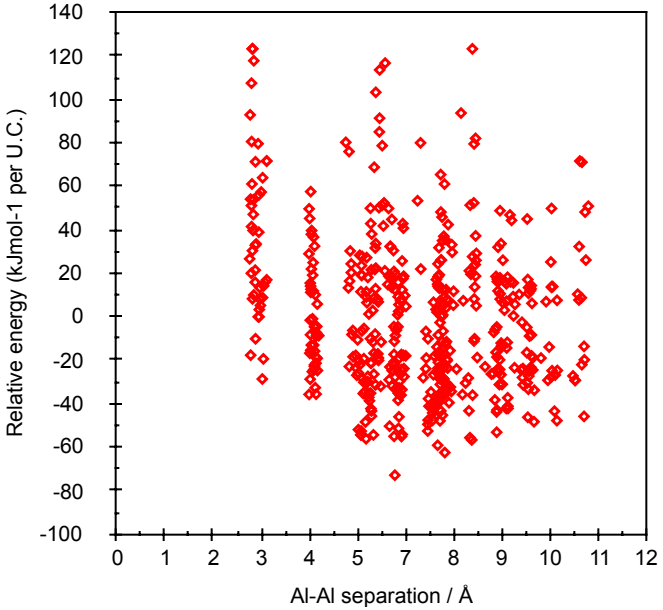
DFT data Na-SSZ-13 Si/Al = 17

‘Löwensteinian’ global minimum structure



CP2K, GGA – PBE functional, TZV2P basis



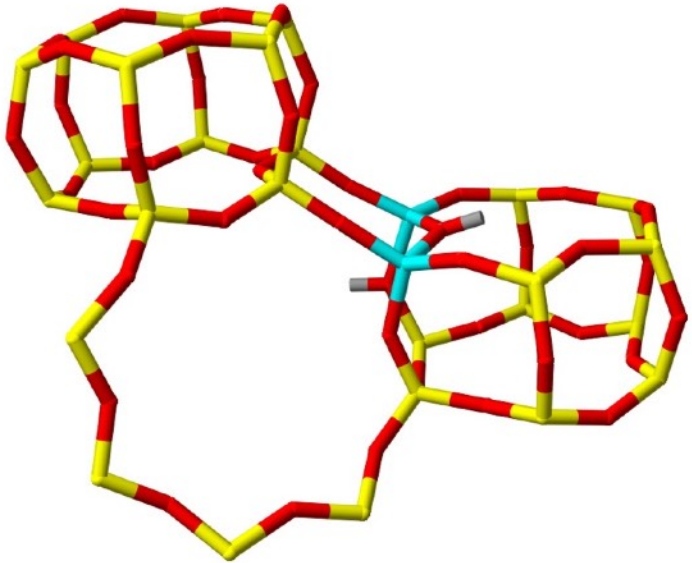
2 Al per unit cell (Si/Al = 17)

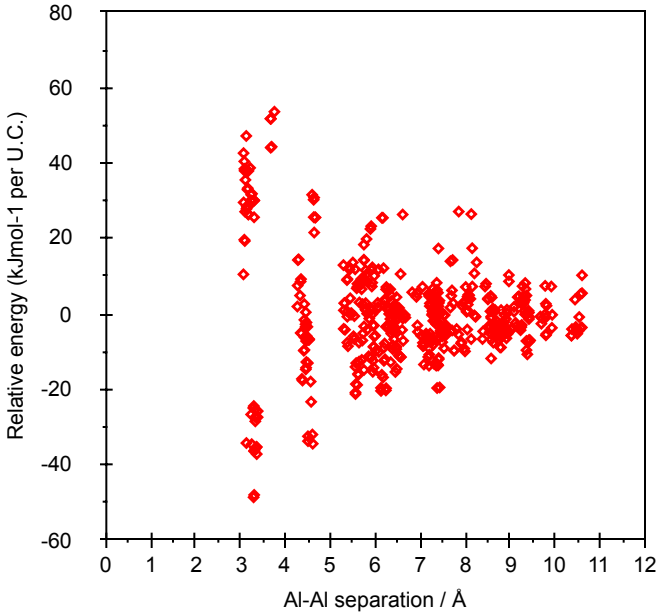
$\Delta E(NL_{\text{global minimum}} - L_{\text{global minimum}})$ = **+44 kJ mol^{-1} per U.C.**

DFT data H-SSZ-13 Si/Al = 17

‘non-Löwensteinian’ global minimum structure

CP2K, GGA – PBE functional, TZV2P basis





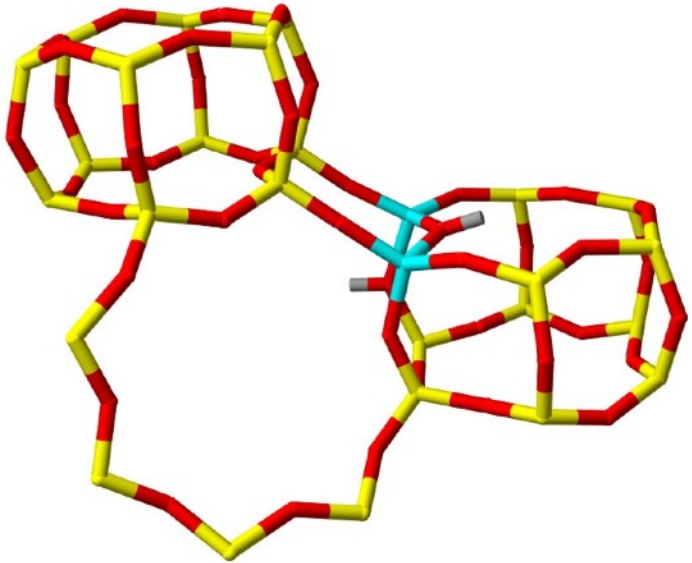
2 Al per unit cell (Si/Al = 17)

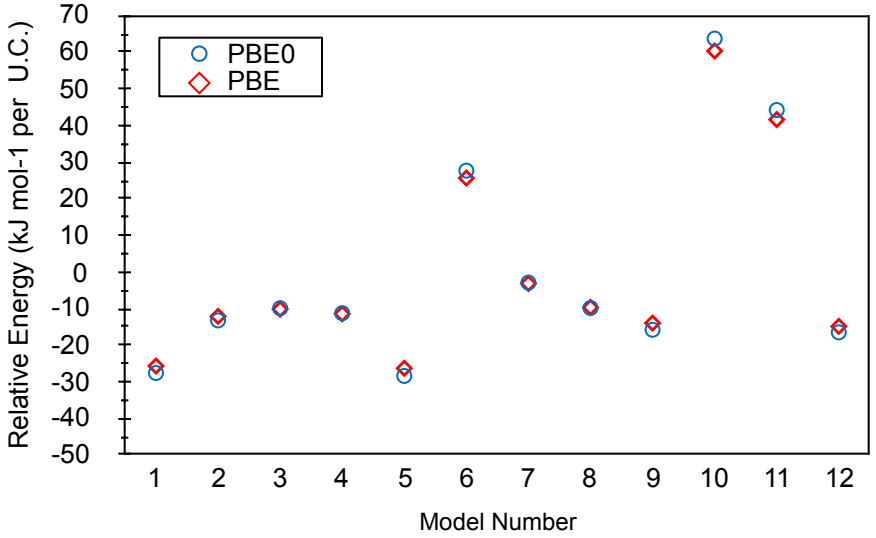
$\Delta E(NL_{global\ minimum} - L_{global\ minimum})$ = **-14 kJ mol^{-1} per U.C.**

DFT data H-SSZ-13 Si/Al = 17

‘non-Löwensteinian’ global minimum structure

CP2K, GGA – PBE functional, TZV2P basis

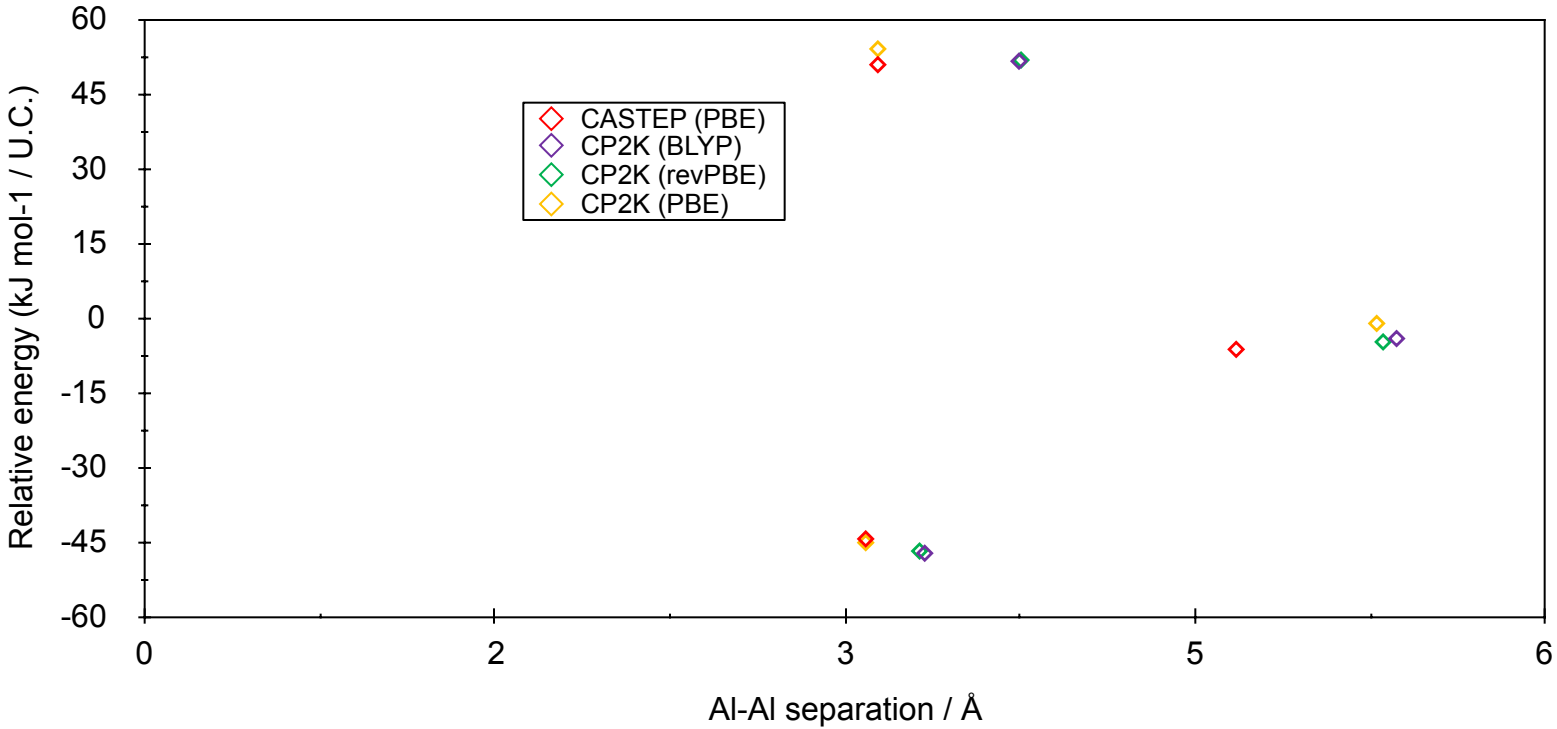




2 Al per unit cell (Si/Al = 17)

$\Delta E(NL_{global\ minimum} - L_{global\ minimum})$ = **-14 kJ mol^{-1} per U.C.**

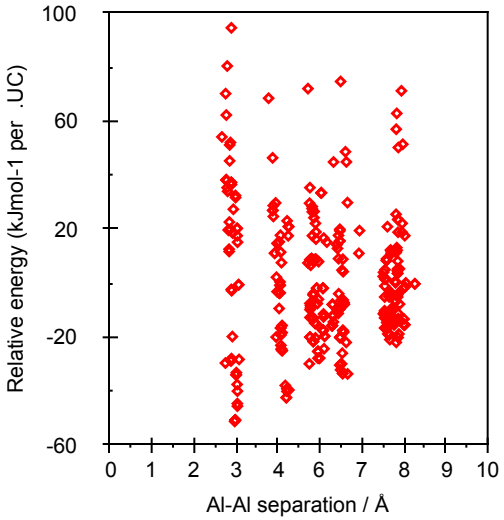
Other functionals/codes



Other zeolites

$\Delta E(NL_{\text{global minimum}} - L_{\text{global minimum}})$

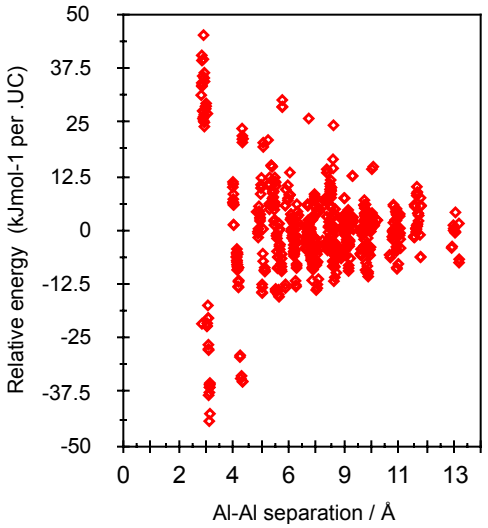
-8.3 kJ mol^{-1} per U.C.



LTA

Density = 14· 2 Tnm^{-1}
(CHA = 15·1 Tnm^{-1})

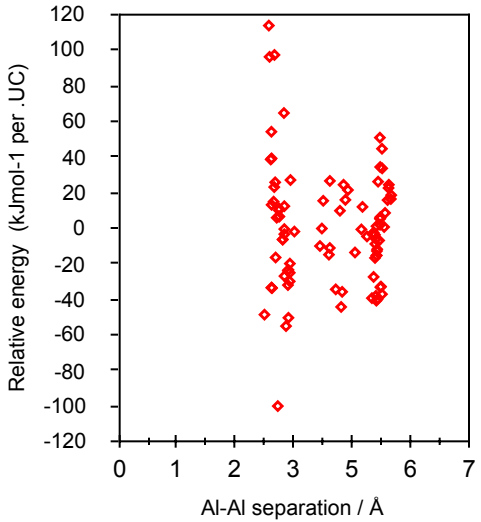
-9·2 kJ mol^{-1} per U.C.



RHO

14· 5 Tnm^{-1}

-55·7 kJ mol^{-1} per U.C.

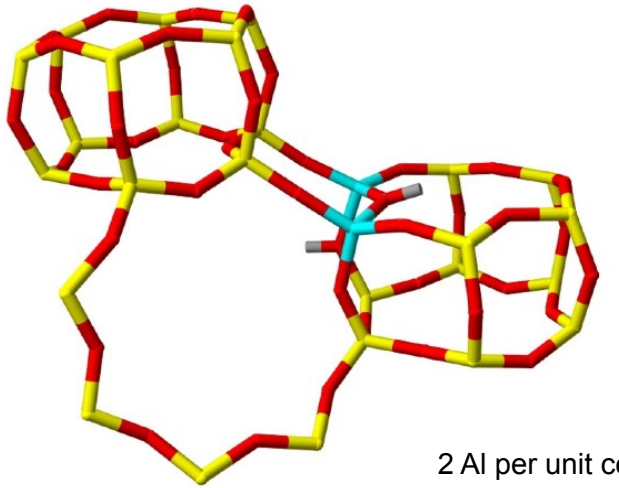


ABW

16· 1 Tnm^{-1}

But why?

‘non-Löwensteinian’ global minimum structure



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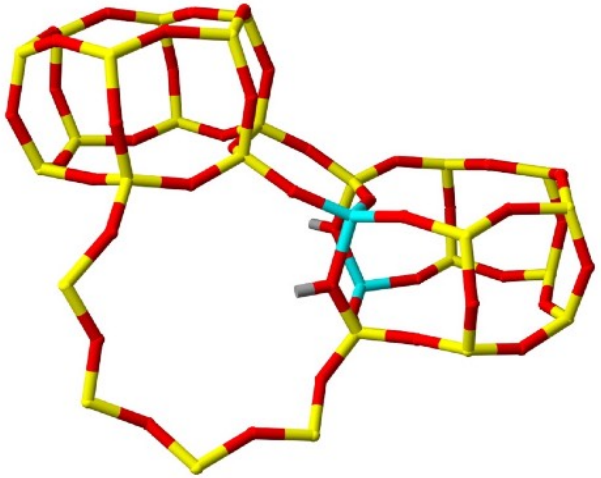

2 Al per unit cell (Si/Al = 17) H-S

+14 kJ mol^{-1}

But why?

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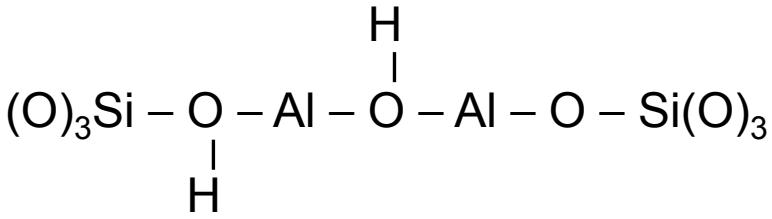

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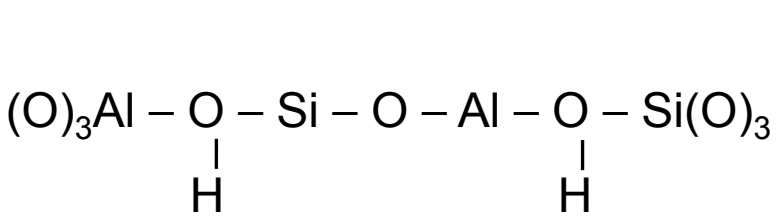

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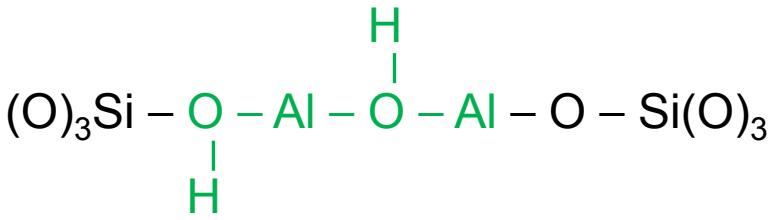
But why?

‘non-Löwensteinian’ global minimum structure

3 Al-O(H) linkages



‘Löwensteinian’ global minimum structure

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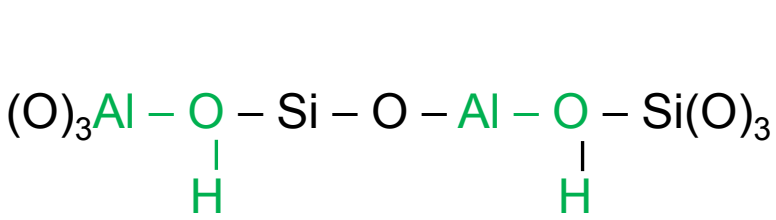
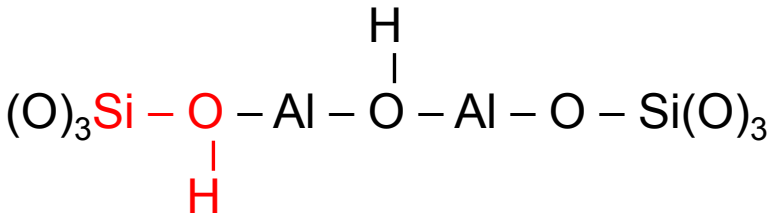


+14 kJ mol^{-1}

But why?

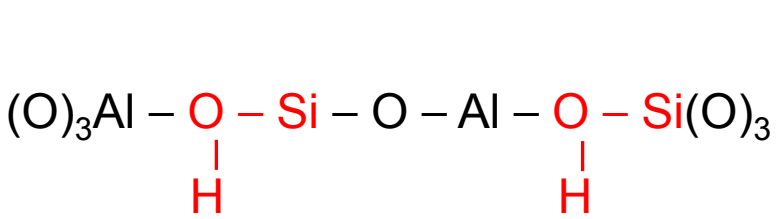
‘non-Löwensteinian’ global minimum structure

3 Al-O(H) linkages
1 Si-O(H) linkage



‘Löwensteinian’ global minimum structure

2 Al-O(H) linkages
2 Si-O(H) linkages



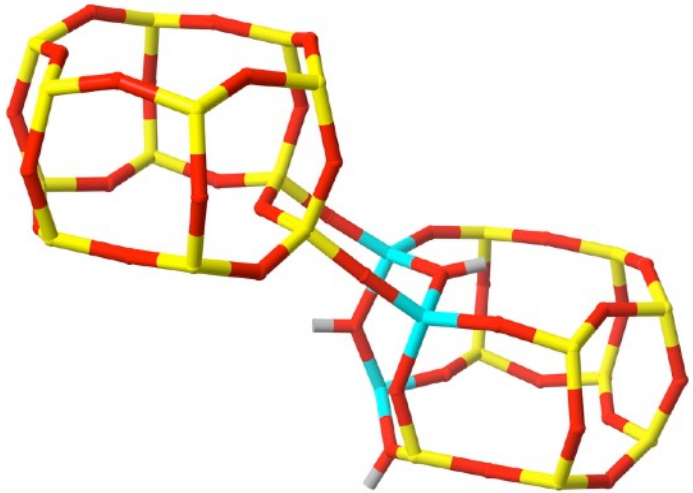
+14 kJ mol^{-1}

kT approx 5kJ/mol

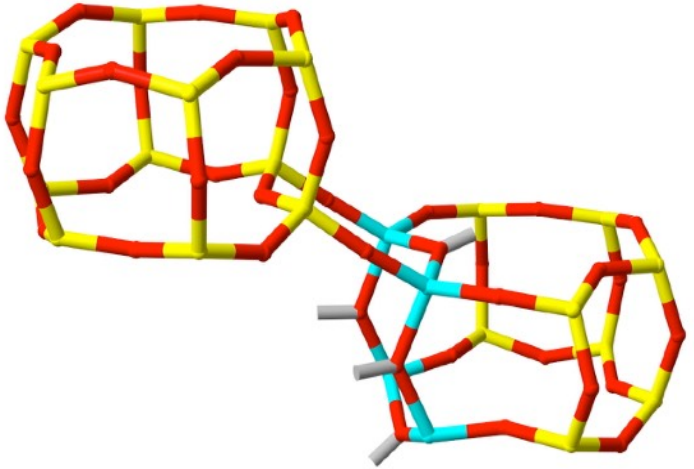
Free energy difference is comparable to internal energy difference

Na-SSZ-13 $\Delta E(NL_{global\ minimum} - L_{global\ minimum})$ = **+44 kJ mol^{-1} per U.C**.

DFT data SSZ-13 Si/Al > 17



3 Al per unit cell (Si/Al = 11)



4 Al per unit cell (Si/Al = 8)

What does this mean?

- Potentially invaluable for understanding existing zeolite catalytic mechanisms and Brønsted acidity, to the development of new zeolite catalysts, and the synthesis of hierarchical materials.

But….

- How can we make these structures?

  Reverse dealumination

- What signatures could be used to unambiguously identify these -Al-O-Al-?

  ^{17}O SS MAS NMR

Summary

- Evidence for non-Löwensteinian ordering in protonated zeolite frameworks
- Preference for the formation of discrete aluminium clusters in low silica frameworks.
- Not the case for sodium-containing zeolites, where the global minimum structures are Löwensteinian ordered frameworks.
- Demonstrates the the influence of counter-cation identity on framework aluminium location.
- We hope this work stimulates experimental investigation into the direct or post-synthesis of non-Löwensteinian ordered zeolites and further characterisation of existing materials

R.E. Fletcher, S. Ling, B. Slater, 'Violations of Löwenstein's rule in zeolites' (2016)
arXiv:1612.04162 [cond-mat.mtrl-sci]

MOF/ADMM example

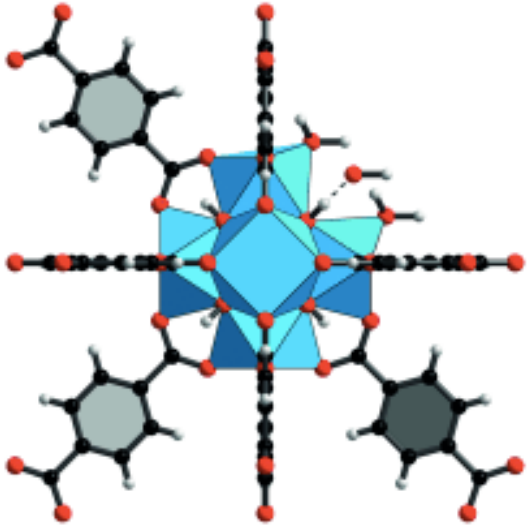
UCL

Metal-Organic Frameworks

International Edition: DOI: 10.1002/anie.201505461
German Edition: DOI: 10.1002/ange.201505461

Definitive Molecular Level Characterization of Defects in UiO-66 Crystals

*Christopher A. Trickett, Kevin J. Gagnon, Seungkyu Lee, Felipe Gándara, Hans-Beat Bürgi, and Omar M. Yaghi**



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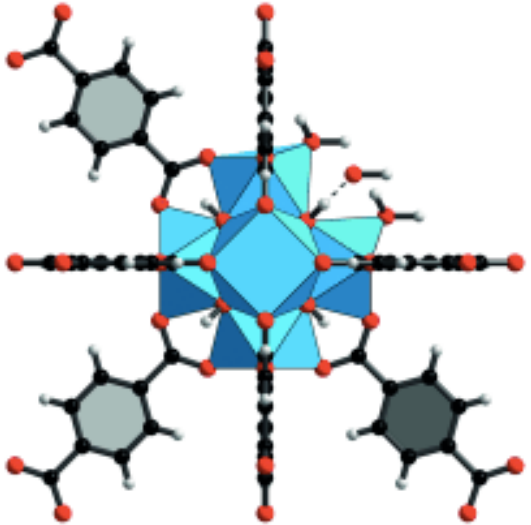
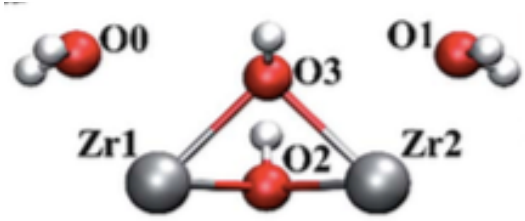
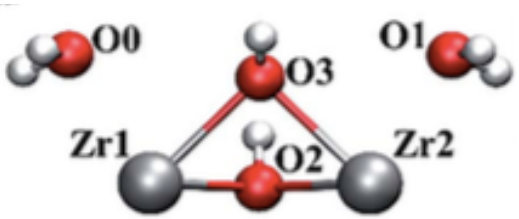


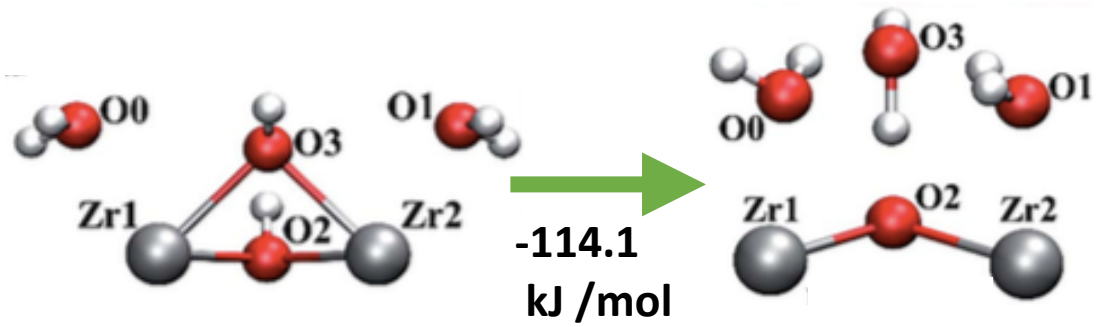


True defect structure?



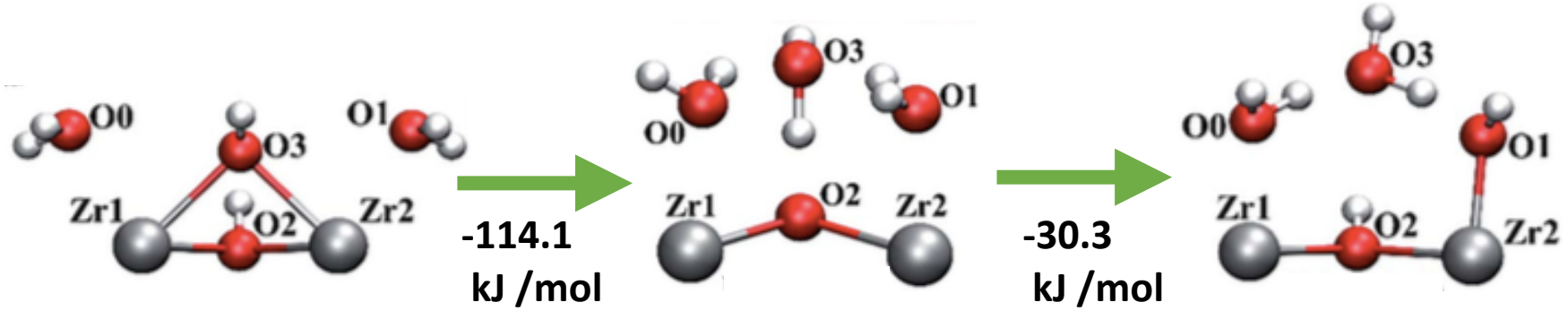
S. Ling, B. Slater, *Chem. Sci*, **7**, 4706, 2016

Proton *abstraction* favourable



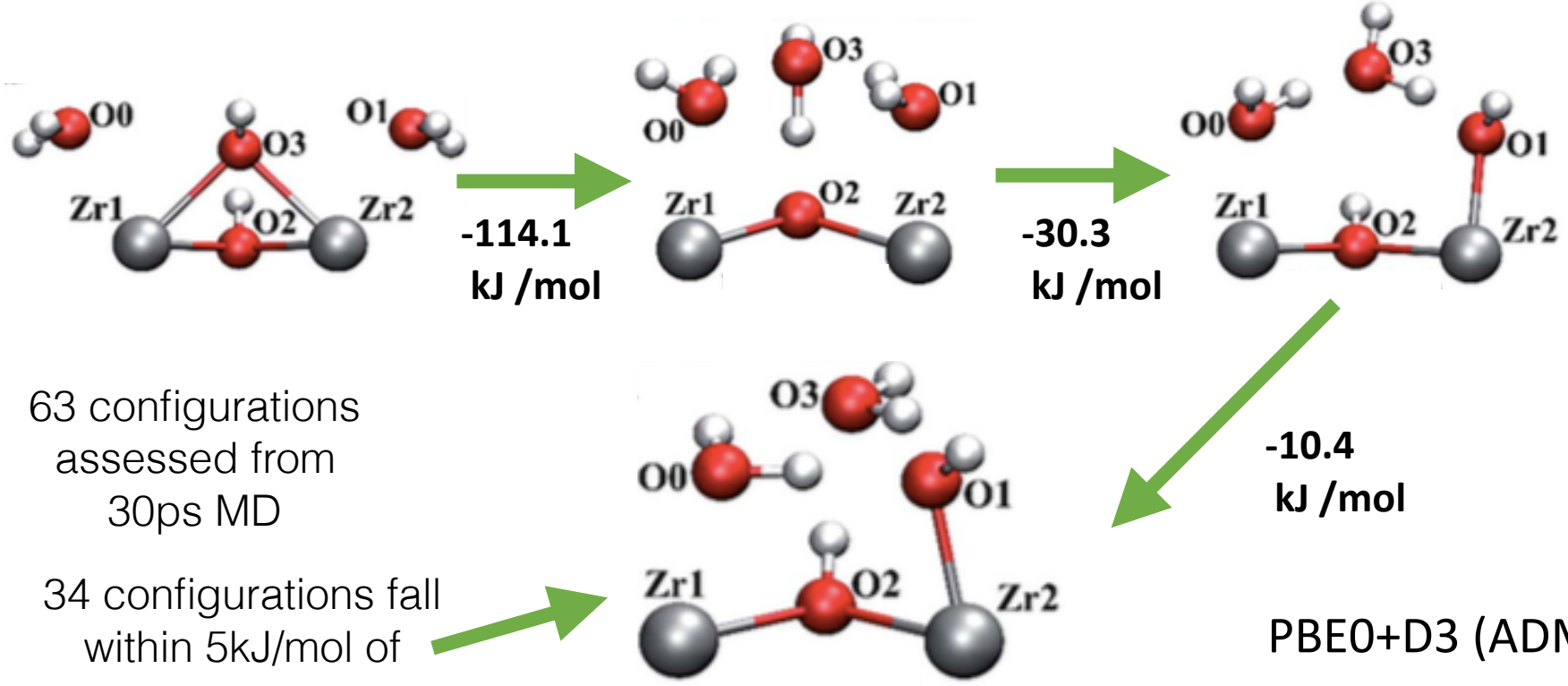
S. Ling, B. Slater, *Chem. Sci*, **7**, 4706, 2016

Proton *migration* favourable



S. Ling, B. Slater, *Chem. Sci*, **7**, 4706, 2016

Definitive defect structure?



63 configurations assessed from 30ps MD

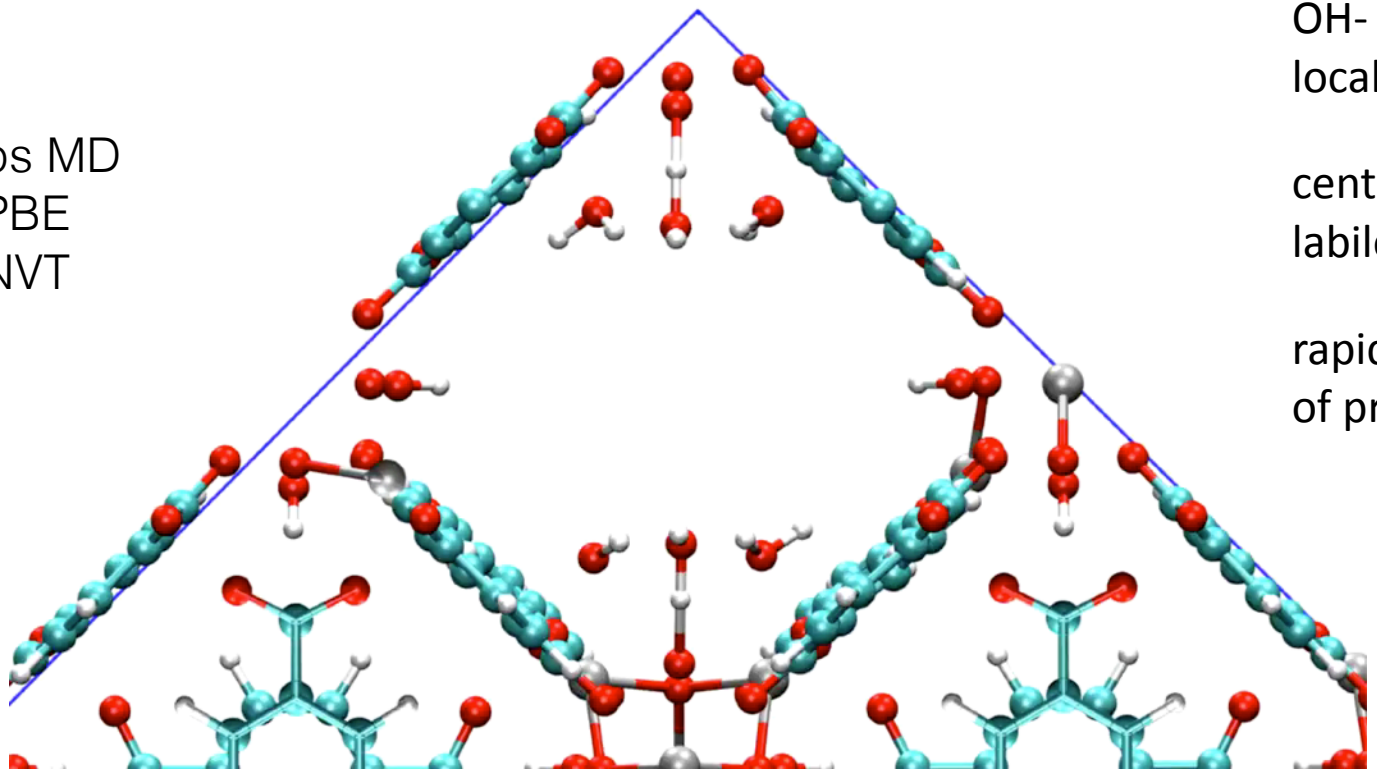
34 configurations fall within 5kJ/mol of

PBE0+D3 (ADMM)

S. Ling, B. Slater, *Chem. Sci*, **7**, 4706, 2016

Defect structure is *fluxional*

30ps MD
PBE
NVT



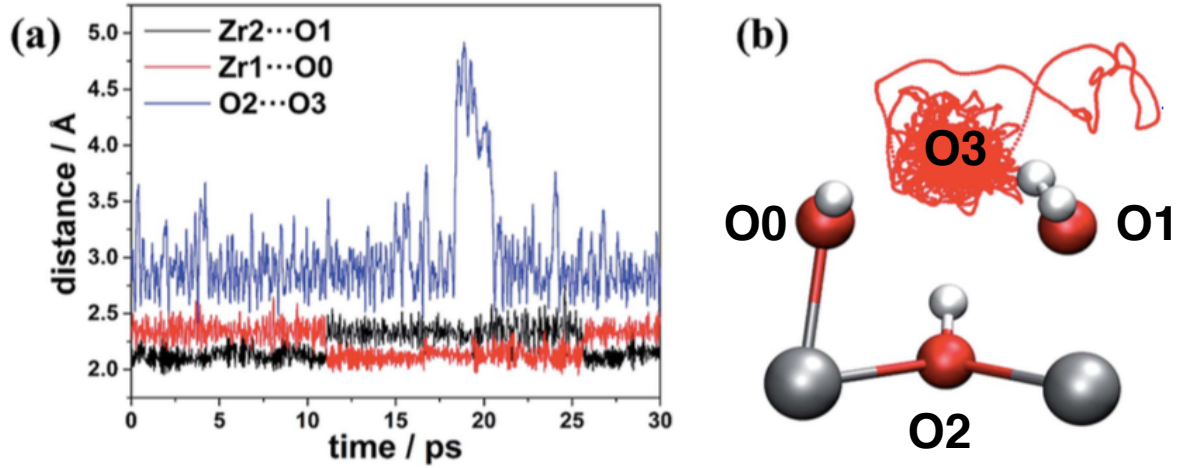
OH- proton localised

central water is labile

rapid interchange of protons

S. Ling, B. Slater, *Chem. Sci*, **7**, 4706, 2016

Where is the hydroxide?

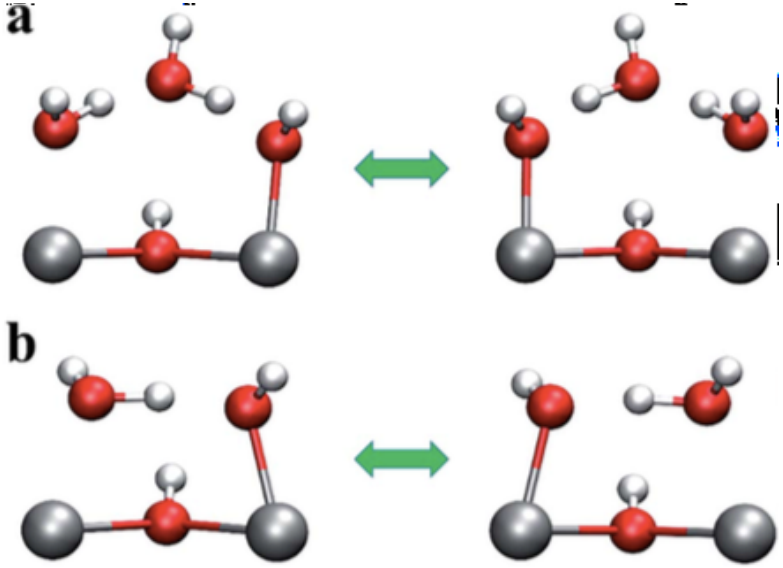


Rapid exchange of protons

Static picture from XRD misses dynamic exchange

S. Ling, B. Slater, *Chem. Sci*, **7**, 4706, 2016

Proton migration barrier height?



Ea = 27.5 kJ/mol

PBE0+D3 (ADMM)

Ea = 6.5 kJ/mol

Source of proton tunnelling/intrinsic proton conduction

Possible frustrated Lewis acid site at high T (dehydrated)

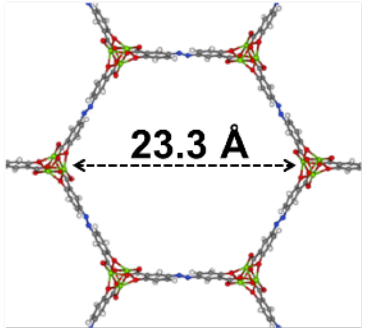
S. Ling, B. Slater, *Chem. Sci*, **7**, 4706, 2016

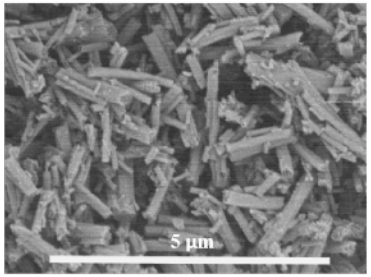
High throughput screening of MOFs

PubChem Compound Database (~60,000,000 structures)

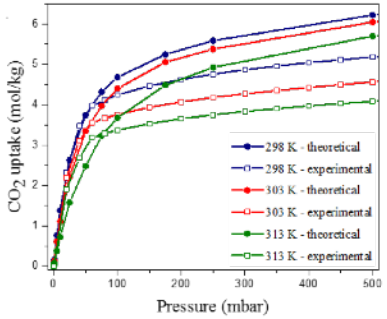
***In Silico* Screening**

A total of 61 MOF-74 Analogs





Experimental Synthesis



CO_2 Adsorption Isotherms

In collaboration with Dr Maciej Haranczyk (LBNL) and Prof Berend Smit (University of California, Berkeley and EPFL)

Witman, Ling, et al., *Chem. Sci.*, **7**, 6263 (2016)

REPEAT charge partitioning

Table S1. Summary of partial atomic charges derived from VASP (previous work) and CP2K (this work). The naming convention of atom types can be found in the previous work.[1]

Atom type	VASP/REPEAT	CP2K/REPEAT
Mg	1.56	1.66
Oa	-0.90	-0.92
Ob	-0.75	-0.76
Oc	-0.90	-0.97
Ca	0.90	0.88
Cb	-0.31	-0.32
Cc	0.46	0.48
Cd	-0.23	-0.26
H	0.19	0.21

Variance in the ESP is fitted

Witman, Ling, et al., *Chem. Sci.*, **7**, 6263 (2016)

Properties validation

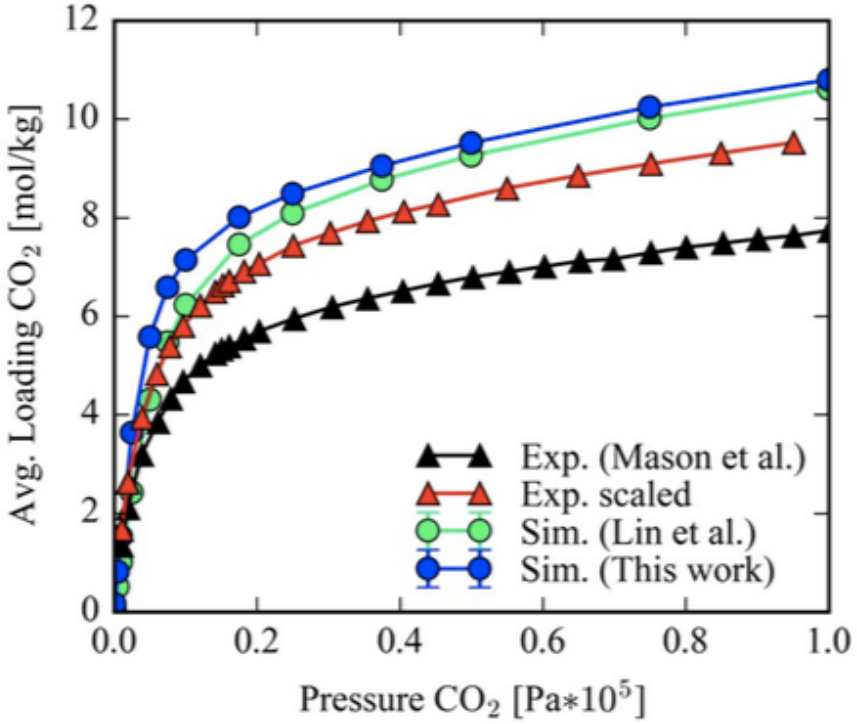
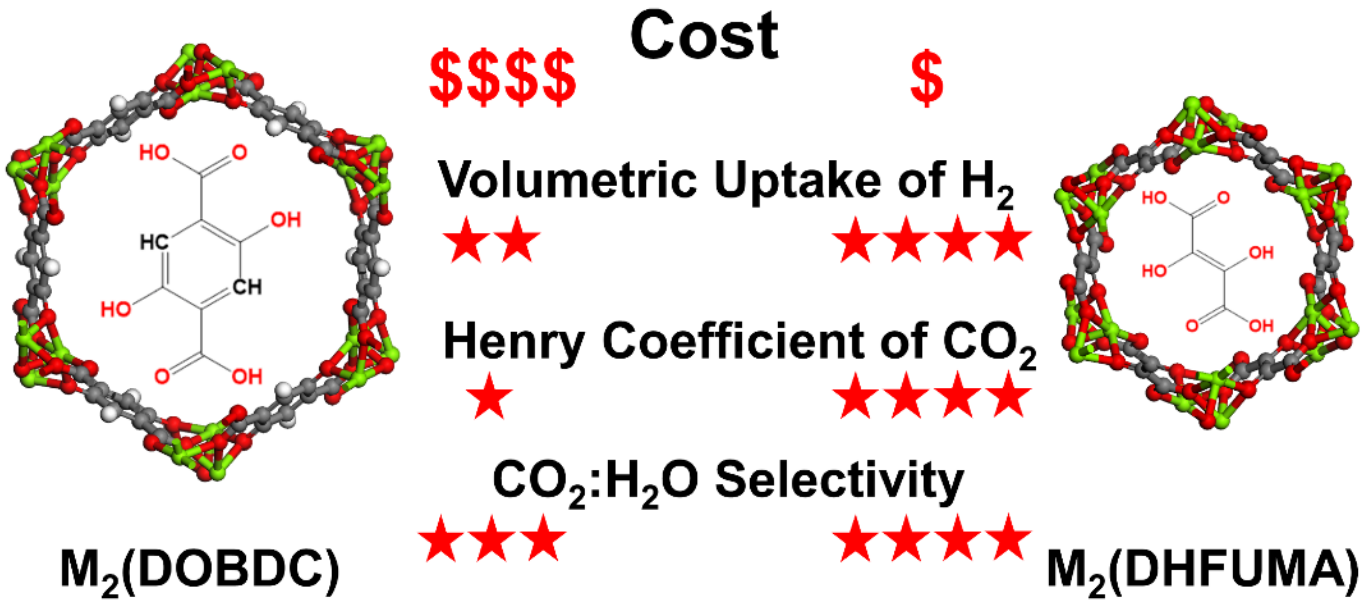


Figure S1. The CP2K relaxed structure and REPEAT derived atomic partial charges were validated by comparison of the CO_2 adsorption isotherm in the original MOF-74 structure with the previously published results of Lin et al. The experimental isotherm of Mason et al.[2] is scaled due to 80% accessibility of the material.

Rational design of low-cost, high-performance MOFs for hydrogen storage and carbon capture



Witman*, Ling*, et al., *J. Phys. Chem. C*, 2017; DOI: 10.1021/acs.jpcc.6b10363 (*Equal contribution)

The SCAN functional

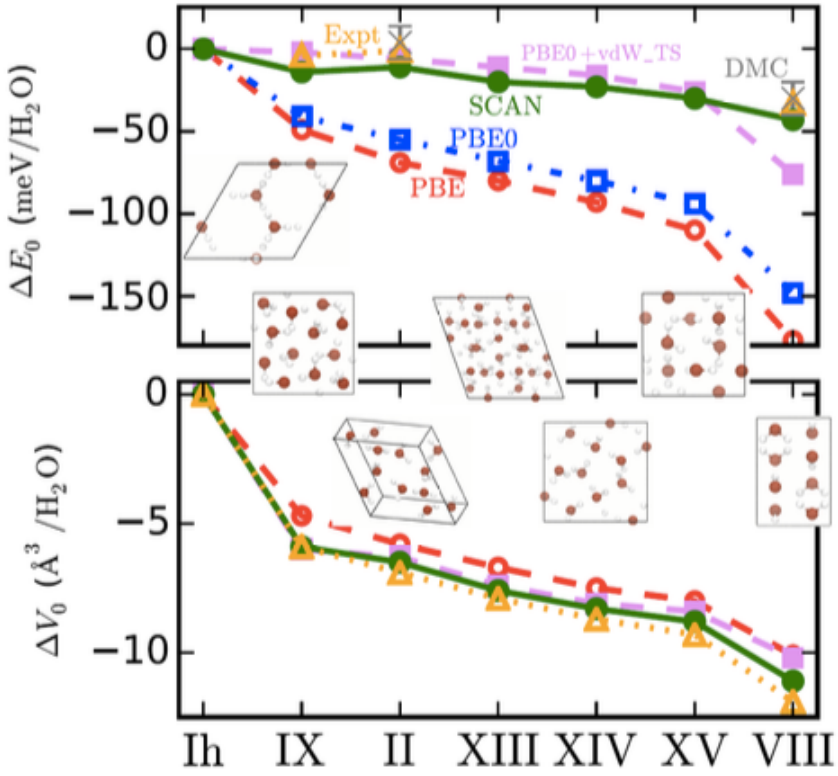
Accurate first-principles structures and energies of diversely bonded systems from an efficient density functional

Jianwei Sun[1]*, Richard C. Remsing[2,3], Yubo Zhang[1], Zhaoru Sun[1], Adrienn Ruzsinszky[1], Haowei Peng[1], Zenghui Yang[1], Arpita Paul[4], Umesh Waghmare[4], Xifan Wu[1], Michael L. Klein[1,2,3] and John P. Perdew[1,2]

One atom or molecule binds to another through various types of bond, the strengths of which range from several meV to several eV. Although some computational methods can provide accurate descriptions of all bond types, those methods are not efficient enough for many studies (for example, large systems, *ab initio* molecular dynamics and high-throughput searches for functional materials). Here, we show that the recently developed non-empirical strongly constrained and appropriately normed (SCAN) meta-generalized gradient approximation (meta-GGA) within the density functional theory framework predicts accurate geometries and energies of diversely bonded molecules and materials (including covalent, metallic, ionic, hydrogen and van der Waals bonds). This represents a significant improvement at comparable efficiency over its predecessors, the GGAs that currently dominate materials computation. Often, SCAN matches or improves on the accuracy of a computationally expensive hybrid functional, at almost-GGA cost. SCAN is therefore expected to have a broad impact on chemistry and materials science.

Sun et al. Nature Chemistry, **8**, 831, 2016

The SCAN functional: the good



The SCAN functional: the good

Method	ΔE (kJ/mol/Zn)			
	ZIF-1	**ZIF-4**	**ZIF-zni**	**MAD**
PBE	0.27	-0.46	0.00	8.05
PBE+D3+C9	16.80	16.97	0.00	8.93
rVV10	20.76	20.42	0.00	12.63
M06L	22.04	21.20	0.00	13.66
M06L+D3	25.70	24.79	0.00	17.29
SCAN	10.11	9.44	0.00	**1.82**
Expt	**6.88**	**9.03**	**0.00**	

The SCAN functional: the bad

Method	ΔE (kJ/mol/Si) quartz	ΔE (kJ/mol/Si) MFI	ΔE (kJ/mol/Si) FAU	MAD
PBE	0	0.4	2.0	9.67
PBE+D3	0	9.4	13.9	**0.73**
PBE+D3+C9	0	8.5	12.6	**0.64**
PBEsol+D3	0	7.1	10.9	**1.91**
HSE06+D3+C9	0	6.6	11.1	**2.05**
vdW-DF	0	9.8	14.8	**1.37**
vdW-DF2	0	8.9	14.1	**0.62**
optB88	0	12.6	17.9	4.35
optPBE	0	12.0	17.3	3.73
rVV10	0	10.8	15.6	**2.31**
C09X-vdW	0	13.5	18.1	4.90
SCAN (expt)	0	6.7	8.7	3.19
Expt	**0**	**8.2**	**13.6**	

The SCAN functional: the bad

Method	ΔE (kJ/mol/Si) quartz	ΔE (kJ/mol/Si) MFI	ΔE (kJ/mol/Si) FAU	MAD
PBE	0	0.4	2.0	9.67
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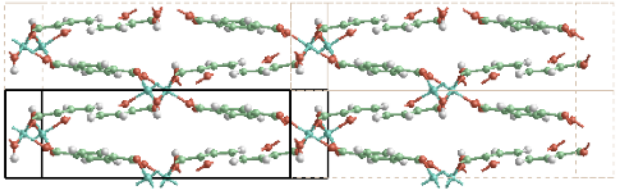
PBE+D3+C9	0	8.5		**0.64**
PBEsol+D3	0	7.1		**1.91**
HSE06+D3+C9	0	6.6		**2.05**
vdW-DF	0	9.8		**1.37**
vdW-DF2	0	8.9		**0.62**
optB88	0	12.6		4.35
optPBE	0	12.0		3.73
rVV10	0	10.8		**2.31**
C09X-vdW	0	13.5		4.90
SCAN (expt)	0	6.7	8.7	3.19
Expt	**0**	**8.2**	**13.6**	

Unexpected properties of breathing MOFs

Al-MIL-53 (Ferey *et al.*)

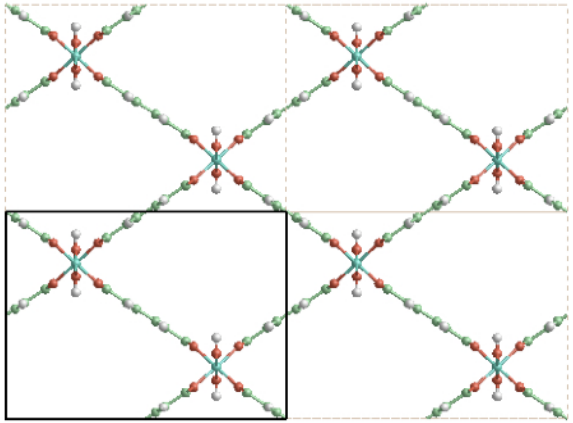


864Å^3

325-375K

⇌

125-150K



1419Å^3

- In the presence of a guest (e.g. *p*CO2), the cell volume ~doubles
- In 2008, Brown et al., *JACS*, showed cell hysteresis in the absence of a guest.
- DFT+D and vdwDF approaches showed the dense phase is stabilised by dispersion. (~8-14 kJ / mol per Al) (Exp. 7.5 kJ / mol/ Al - calorimetry)
- Vibrational entropy drives the expansion (low frequency modes)

A.M.Walker et al., *Angew. Chemie Int. Ed.*, ***49***, *7501*, 2010

Most GGA/Hybrids: good/bad

MIL-53-Al

Method	*np*-MIL-53-Al					
	A	B	C	beta	volume	$\Delta E^{(np-lp)}$
PBE	-	-	-	-	-	-
PBE+D3	20.99	6.57	6.65	65.96	837.6	-8.66
PBEsol+D3	21.03	6.28	6.61	64.93	791.4	-10.54
PBE+D3+C9	20.95	6.73	6.66	66.25	858.8	-3.85
HSE06+D3+C9	20.78	6.75	6.61	66.35	848.8	-3.1
vdW-DF	20.92	6.71	6.69	67.51	867.6	-10.88
C09x-vdW	21.05	5.95	6.6	65	749.7	-27.99
optB88	21.07	6.08	6.62	65.02	768.7	-25.82
optPBE	20.96	6.28	6.66	66.87	807.3	-21
vdW-DF2	20.8	6.46	6.73	69.32	845.1	-7.36
rVV10	20.93	6.34	6.67	67.62	818	-14.43
Expt[b]	**20.82**	**6.87**	**6.61**	**66.05**	**863.9**	-7.5

The SCAN functional: the ugly

MIL-53-Al

Fixed_expt_lattice		kJ/mol per Al center
lp_ortho_symm-np	SCAN	-4.38
lp_ortho_symm-np	M06-L	17.16
lp_ortho_symm-np	PBE+D3+C9	5.79
Fixed_PBE+D3+C9_lattice		**kJ/mol per Al center**
lp_ortho_symm-np	SCAN	-4.91
lp_ortho_symm-np	PBE+D3+C9	4.72

The ice XV problem

see The polymorphism of ice: five unresolved questions, Salzmann et al., PCCP, 2011

THE JOURNAL OF PHYSICAL CHEMISTRY Letters

Letter

pubs.acs.org/JPCL

dx.doi.org/10.1021/jz401625w | J. Phys. Chem. Lett. 2013, 4, 3165−3169

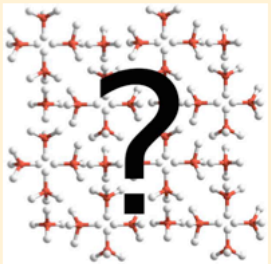
What Governs the Proton Ordering in Ice XV?

Kaushik D. Nanda and Gregory J. O. Beran*

Department of Chemistry, University of California, Riverside, California 92521, United States

Supporting Information

ABSTRACT: Powder neutron diffraction and Raman spectroscopy experiments for ice XV, the recently discovered proton-ordered polymorph of ice VI, suggest that the protons arrange in an antiferroelectric structure with $P\bar{1}$ symmetry, contrary to several density functional theory predictions of a ferroelectric *Cc* structure. Here, we find that higher-level fragment-based second-order perturbation theory (MP2) and coupled cluster theory (CCSD(T)) electronic structure calculations predict that the experimentally proposed proton ordering is indeed slightly more stable than the other possible structures. These calculations reveal a close competition between the structure with the strongest local hydrogen bonding (*Cc*) and the one with the most favorable "delocalized" hydrogen bond cooperativity effects ($P\bar{1}$), with the latter being preferred by ~0.4 kJ/mol per molecule. The results reiterate the importance of viewing ice networks as a whole instead of focusing on pairwise hydrogen-bonding interactions.

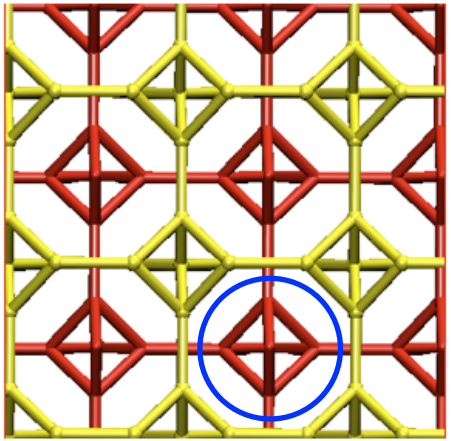


SECTION: Molecular Structure, Quantum Chemistry, and General Theory

Ice XV/VI have the largest variation in hydrogen bond angle of any phase.

Problem solved?

Ice VI/XV*

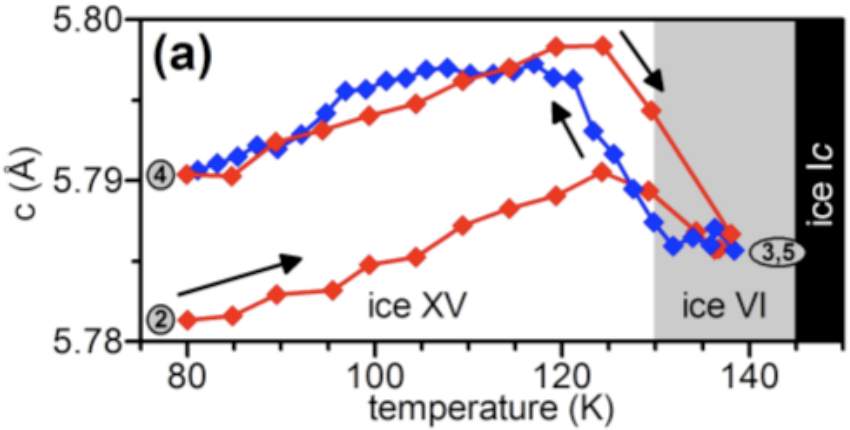


VI - SG 137

↓

XV - SG 2

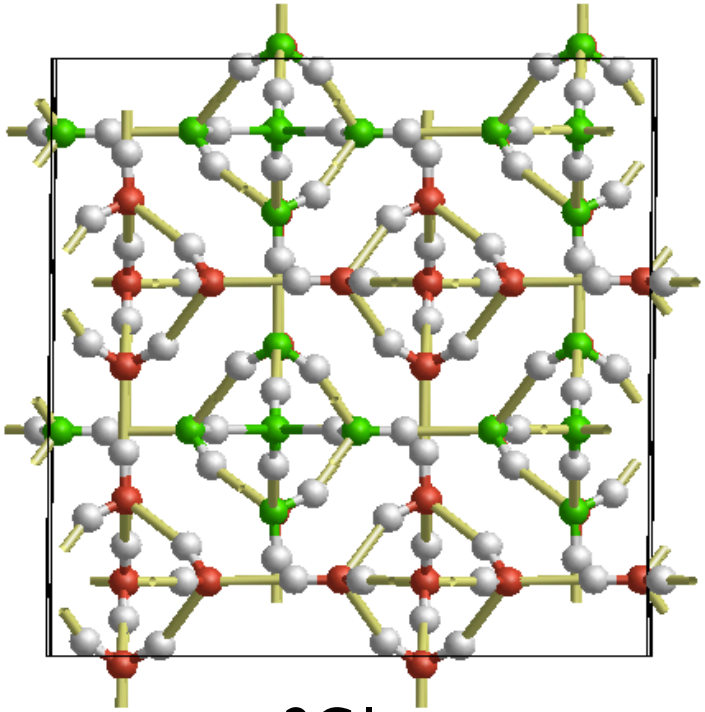
Interpenetrating lattices formed from hexameric chains



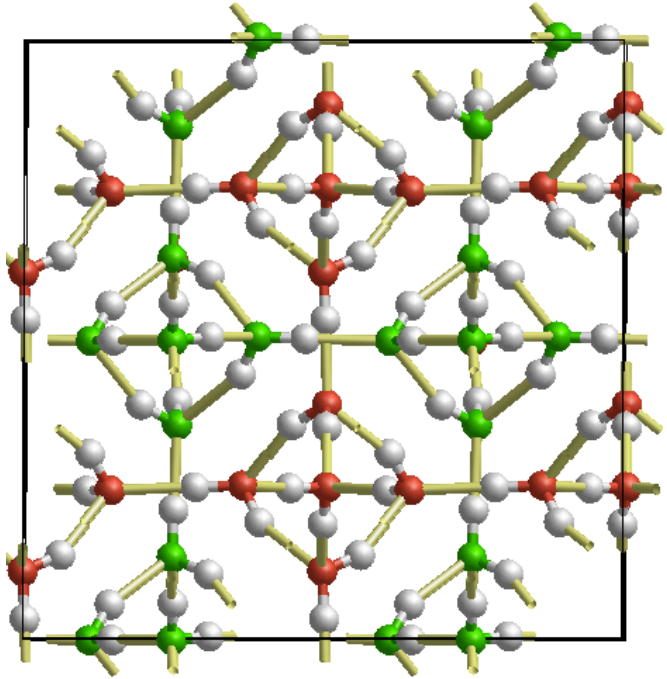
XRD data taken from Salzmann et al. PRL 2009

Key ice XV structures

Dense structure (~1GPa)

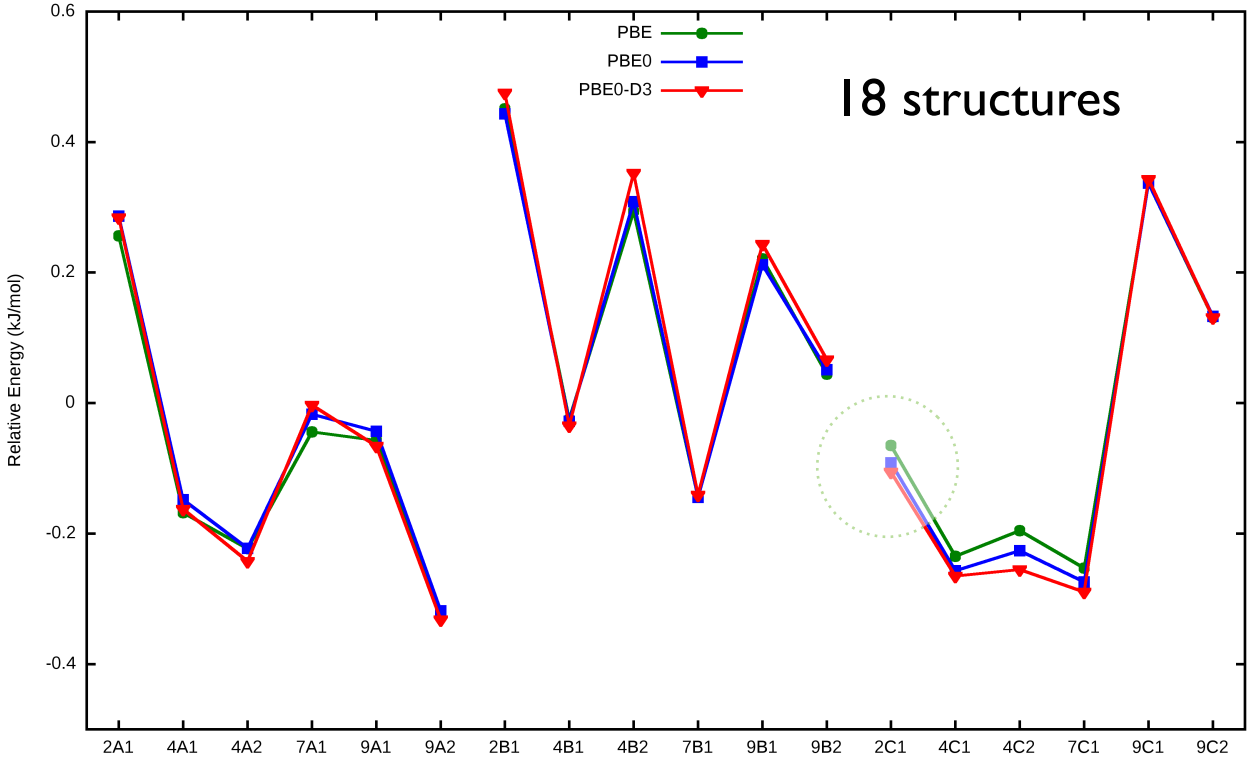


2C1



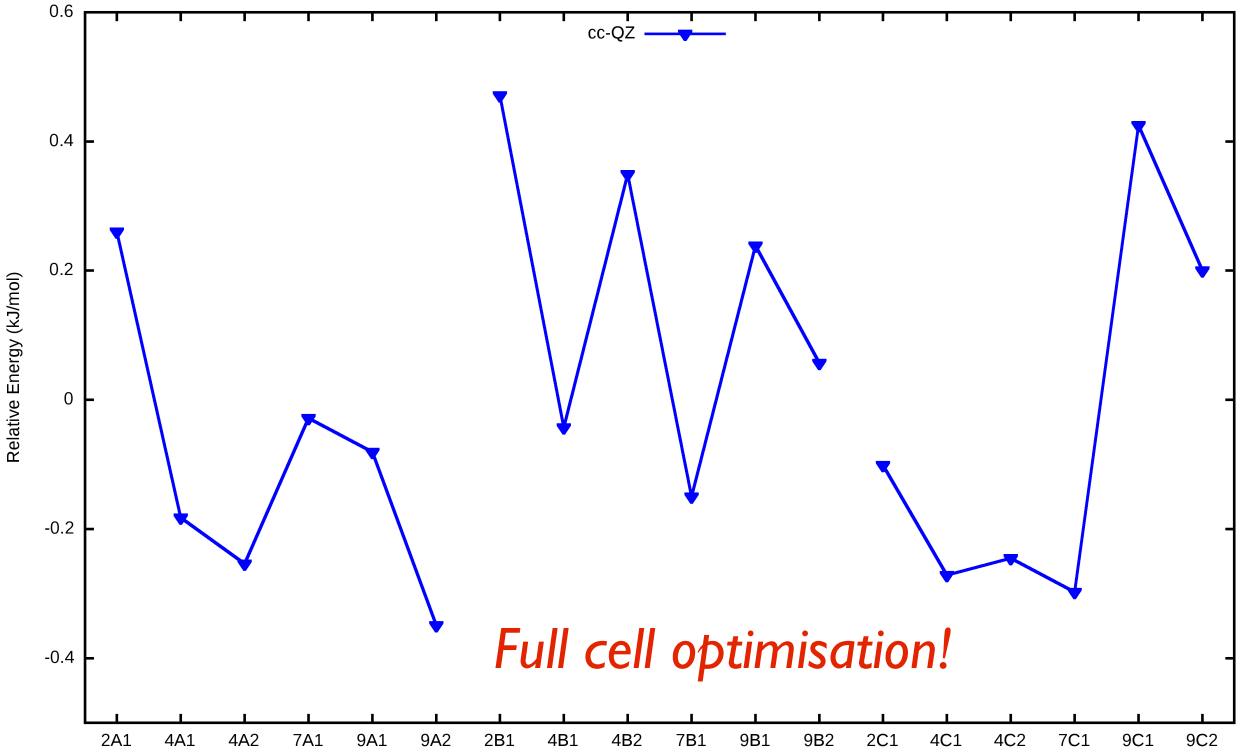
9A2

Hybrid and vdW?



Varying HF and vdW does not change the order of stability

RI-MP2 results

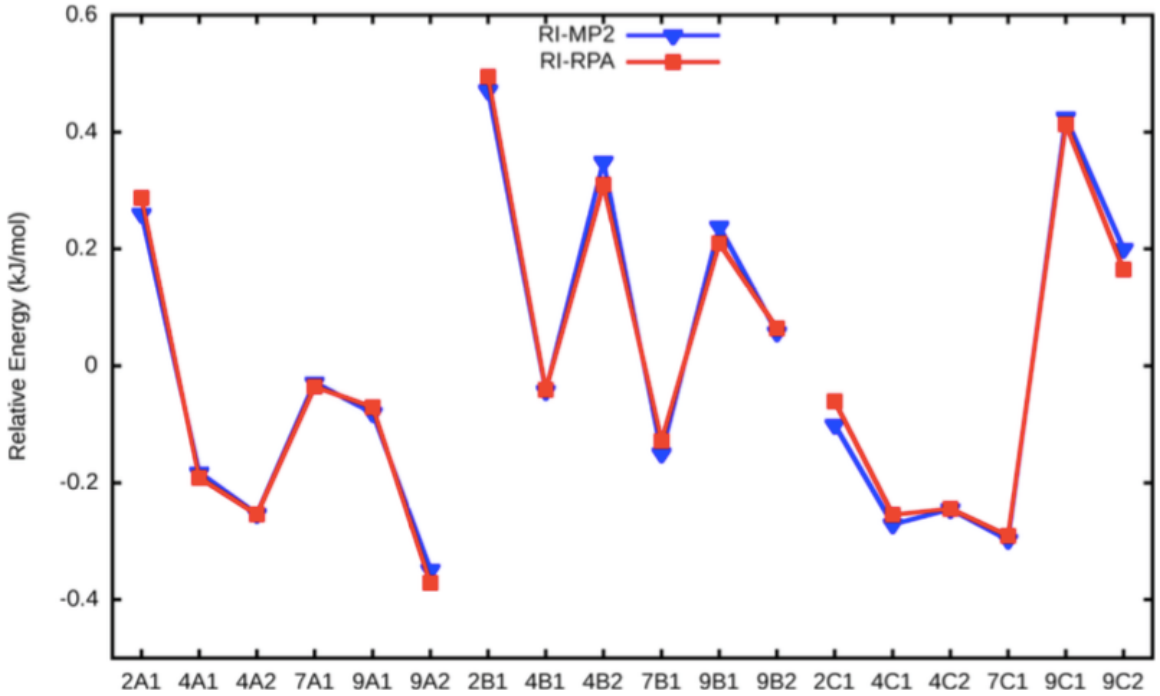


Full cell optimisation!

9A2 = Cc most stable 1078s on 3840 processors (Archer)

Theory still predicts exptl (2C1) structure to be metastable

RI-MP2 vs RPA results



9A2 = Cc most stable 1078s on 3840 processors (Archer)

Theory still predicts exptl (2C1) structure to be metastable

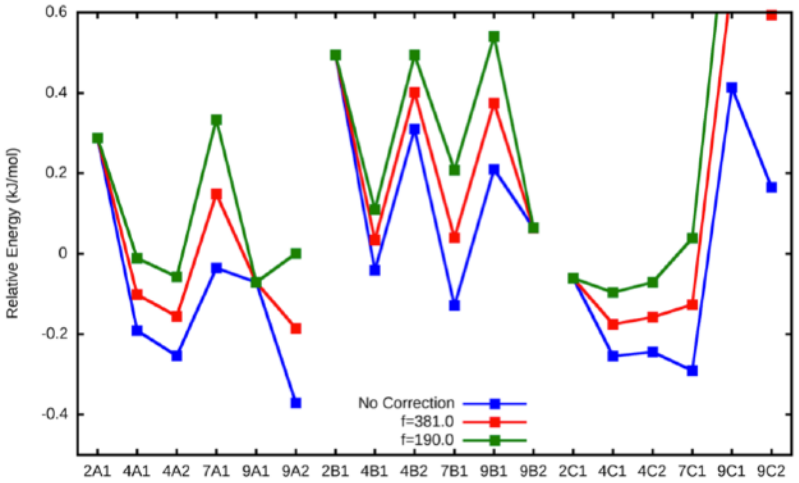
Experiment and theory still in conflict

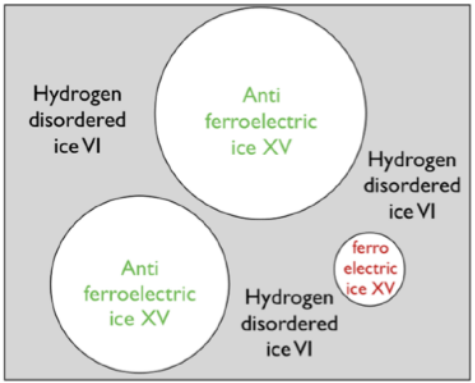
Theory still predicts wrong ground state

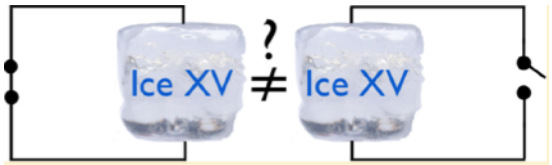
Experimentally, only about 70% of ice VI->XV

Grains of ice XV in a matrix of VI

$$U_{\text{corr}} = \frac{2\pi}{Vf} M^2$$

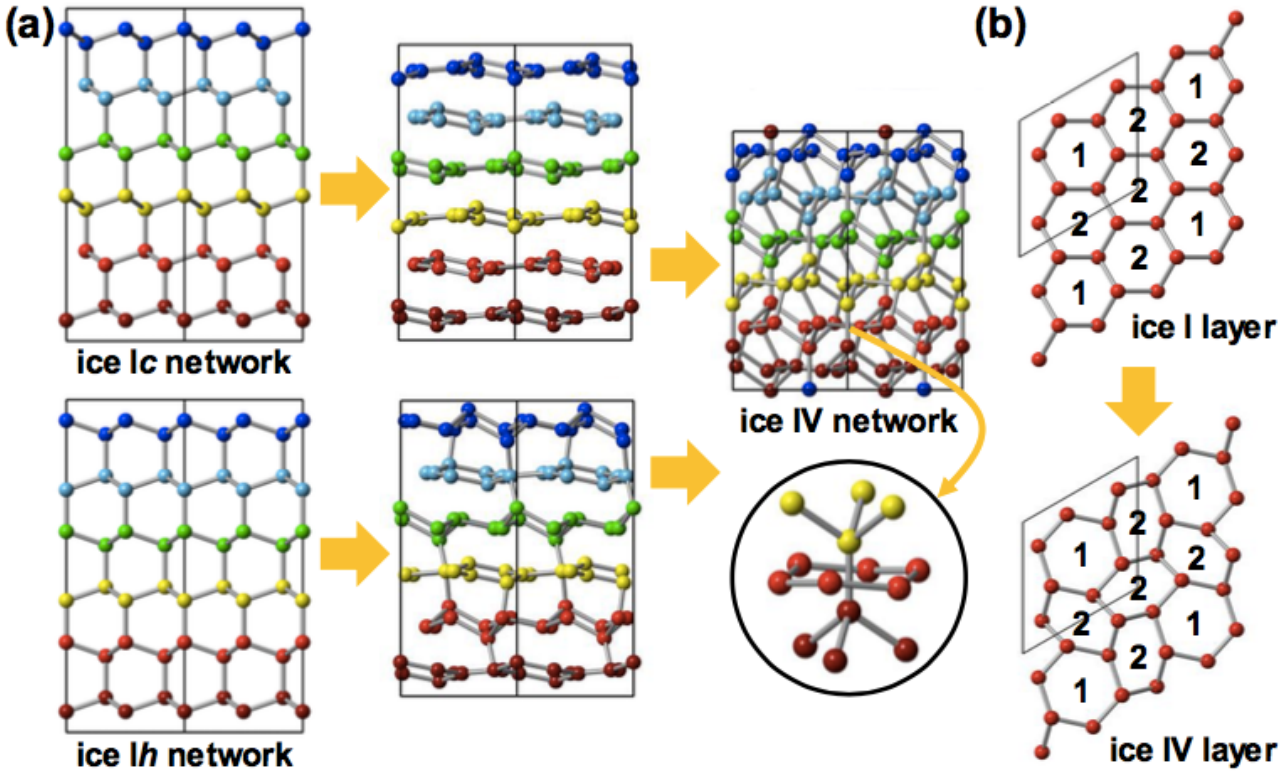






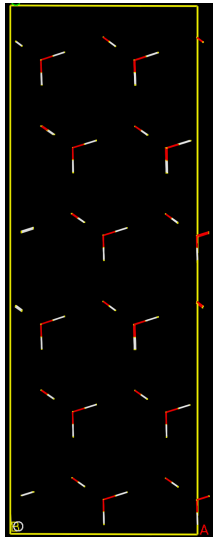
dx.doi.org/10.1021/jz501985w | J. Phys. Chem. Lett. 2014, 5, 4122−4128

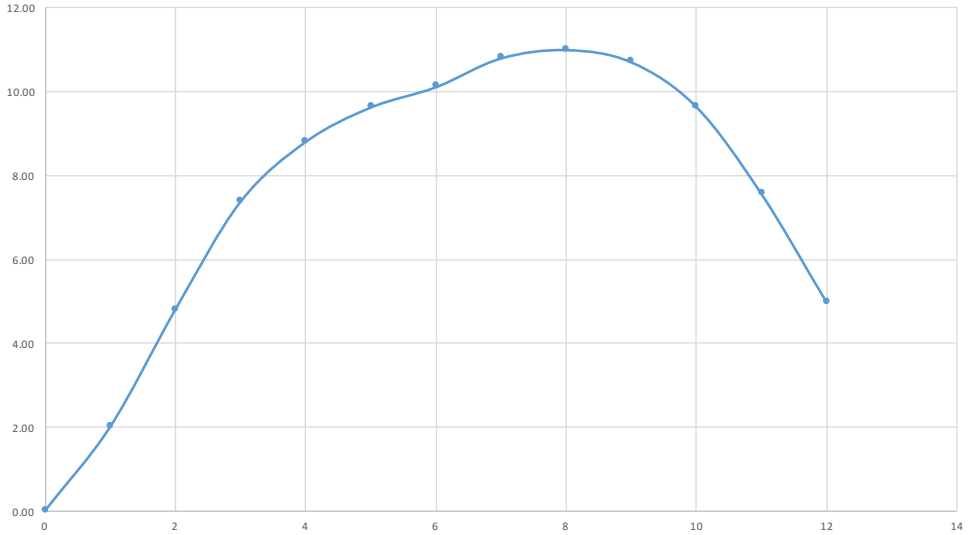
Solid state NEB - ice XIc-IV

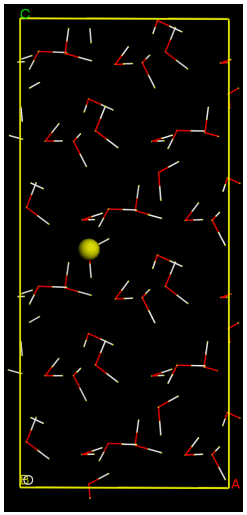


Solid state NEB - ice XIc-IV

D. Sheppard, P. Xiao, W. Chemelewski, D. D. Johnson, and G. Henkelman, A generalized solid-state nudged elastic band method, *J. Chem. Phys.* **136**, 074103 (2012).







XIc (0.93) to IV (1.27 g/cm$^{3)}$

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MOF-74

Matthew Whitman (Berkeley)
Liangheng Tong (formerly KCL)
Dr Maciej Haranczyk (LBNL)
Prof Berend Smit (University of California, Berkeley and EPFL)

Ice XV - MP2/RPA

Mauro del Ben (LBNL)
Joost VandeVondele (Formerly ETH, now ?)

Unpublished work - SS-NEB

Jacob Shephard (Edinburgh)
Christoph Salzmann (UCL)

EPSRC
Engineering and Physical Sciences Research Council

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