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Structure and Dynamics of Hydrogen-Bonded Systems

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On the accuracy of density-functional theory exchange-correlation functionals for hydrogen bonds in water

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On the accuracy of density-functional theory exchange-correlation functionals for hydrogen bonds in water

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[2]London Centre for Nanotechnology,
and Department of Chemistry, University College London, London, UK

Structure and Dynamics of Hydrogen-Bonded Systems

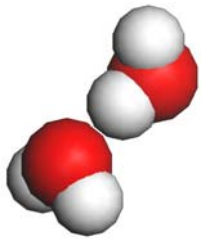
MONET
Molecular Networks at Phase Boundaries

Outline

Part I

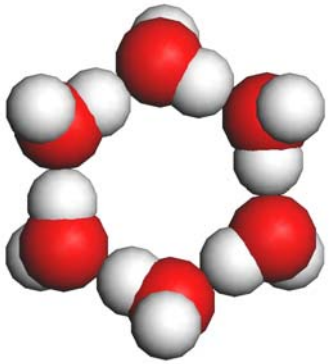
- Accuracy of DFT exchange-correlation functionals:
  (i) Equilibrium gas phase water clusters (dimer - pentamer).

  (ii) Water dimers representing DFT liquid water.

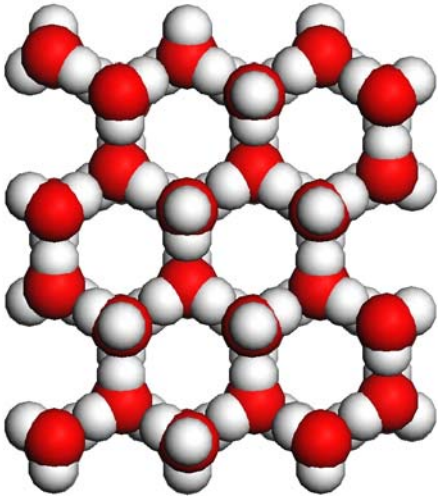


Part II

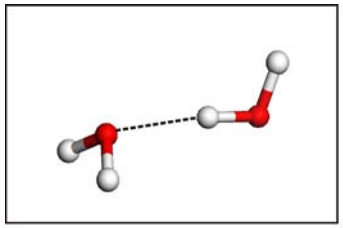
- The importance of van der Waals interactions:
  (i) Gas phase water hexamers.



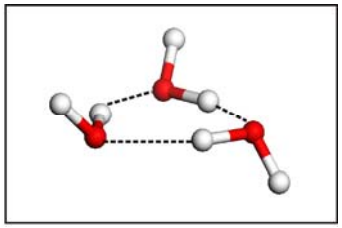
(ii) Crystalline ice.



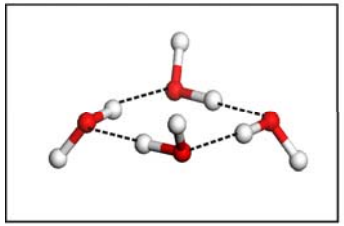
Equilibrium gas phase water clusters



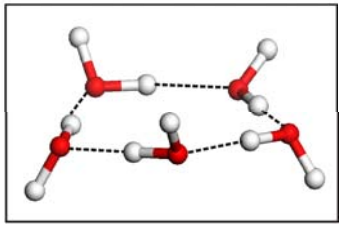
Dimer



Trimer



Tetramer



Pentamer

Few technical details for benchmark:

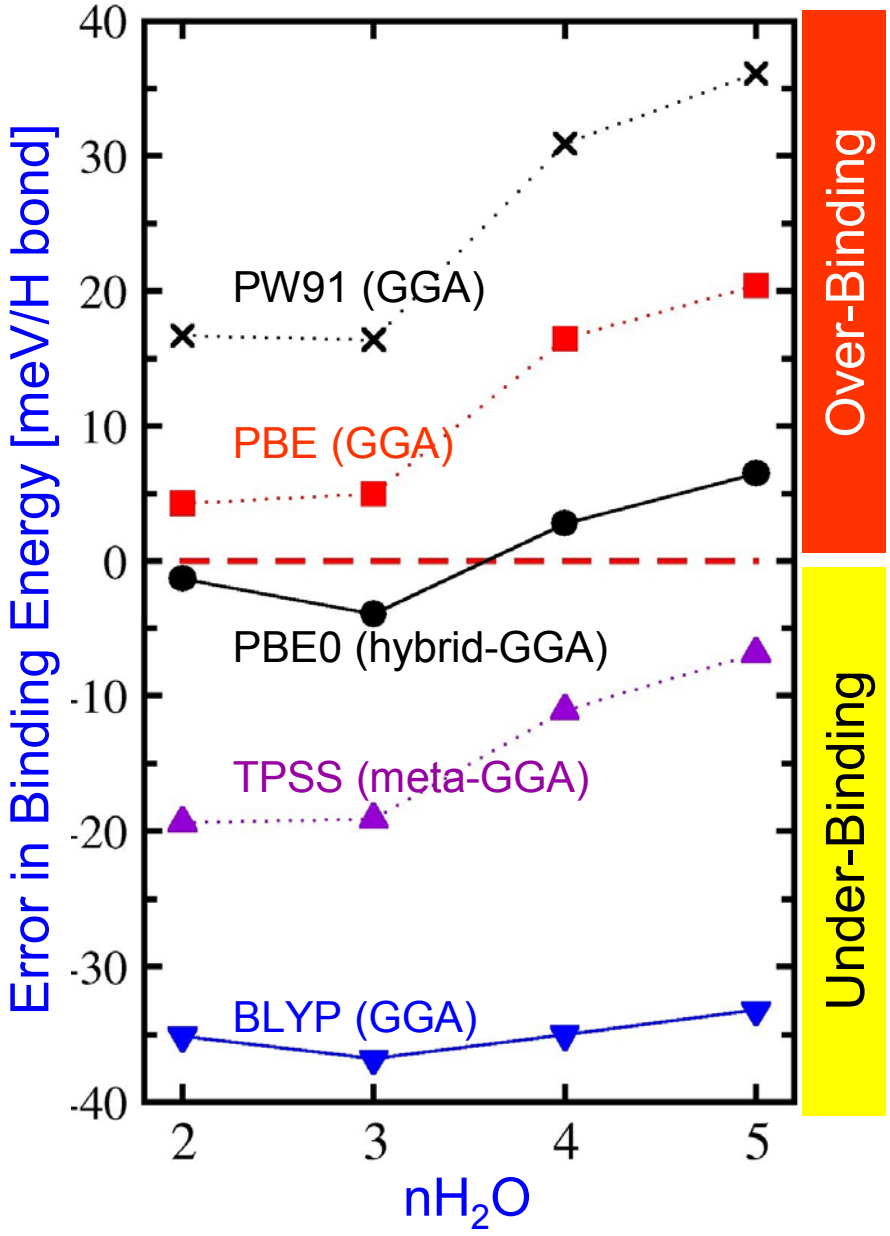
- Large localized Gaussian basis sets.
- Accurate reference: MP2 @ the complete basis set limit.
- All electron DFT calculations with aug-cc-pV5Z basis set.
- Code used: G03[5] and NWChem5.0[6].

- Water dimer binding energy (meV)

MP2	215.8 ± 2.0
CCSD(T)[1]	217.6 ± 2.0
DMC[2]	218.0 ± 3.0
Experiment[3,4]	217 ± 30

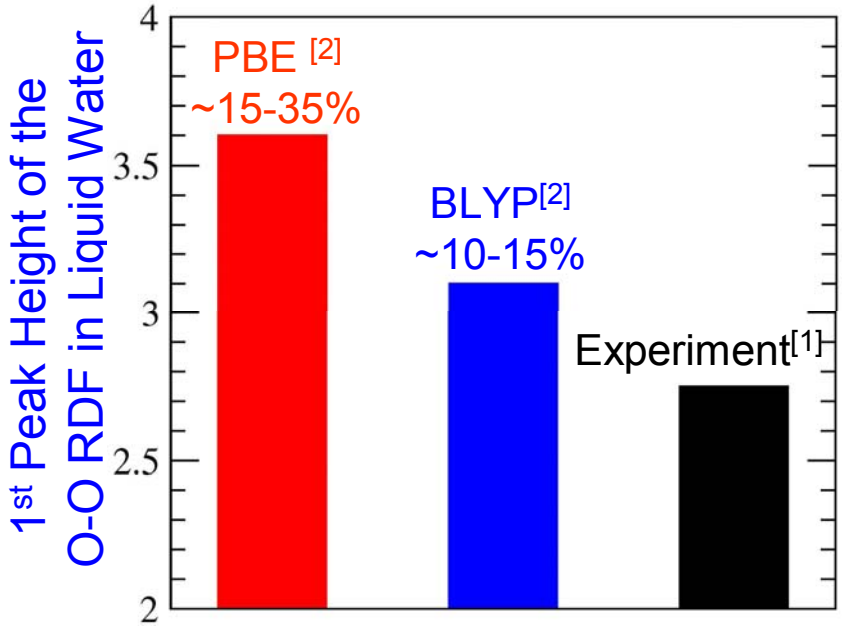
[1] W. Klopper *et al*., Phys. Chem. Chem. Phys. **2**, 2227 (2000). [2] I. G. Gurtubay and R. J. Needs, J. Chem. Phys. 127, 124306 (2007). [3] E. M. Mas *et al*., J. Chem. Phys. **113**, 6687 (2000). [4] L. A. Curtiss, D. J. Frurip, and M. Blander, J. Chem. Phys. **71**, 2703 (1979). [5] M. J. Frisch *et al.,* GAUSSIAN 03, C.02 (2004).[6] E. J. Bylaska *et al.*, NWChem, Version 5.0 (2006).

Equilibrium gas phase water clusters



A debate on the structure of DFT liquid water

- PBE and BLYP produce over-structured Liquid water

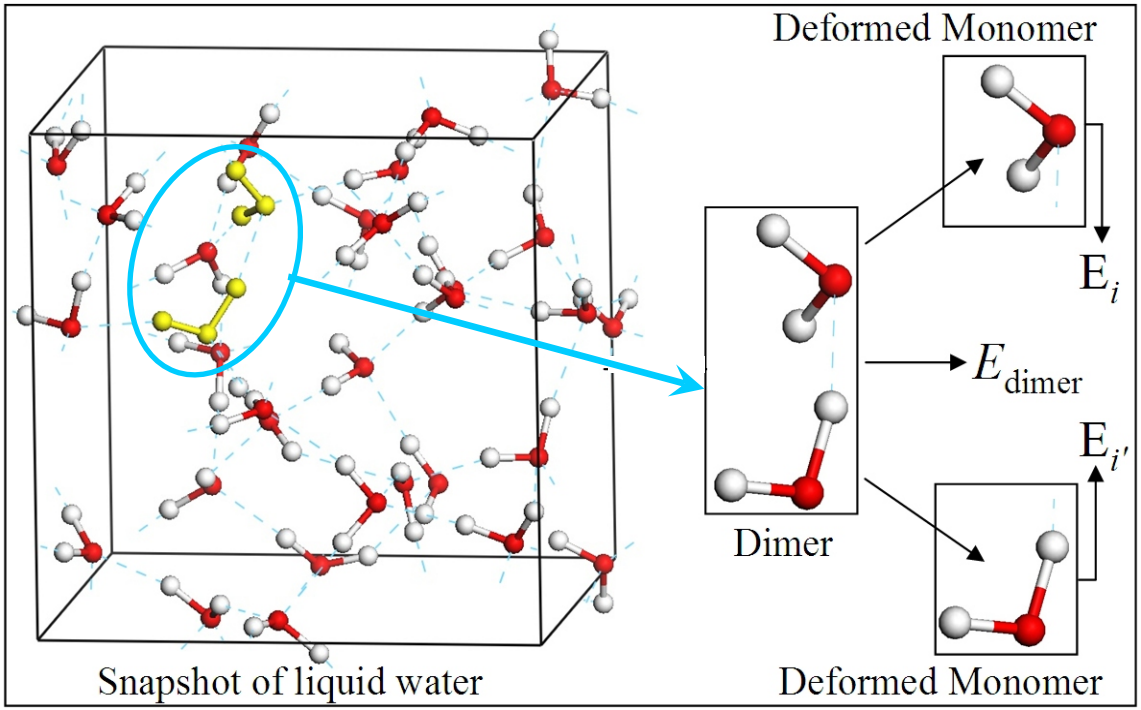


[1] A. K. Soper, Chem. Phys. 258, 121 (2000).
[2] Morrone *et al.*, PRL (2008); Kühne *et al.*, JCTC (2009); Lee *et al.*, JCP (2006, 2007); Schmidt et. al., JPCB (2009); Guidon *et al.*, JCP (2008); Todorova *et al.*, JPCB (2006); VandeVondele *et al.*, JCP (2005); Grossman *et al.*, JCP (2004); Fernández-Serra *et al.*, JCP (2004); and more …

Benchmarks on Dimers Representing Liquid

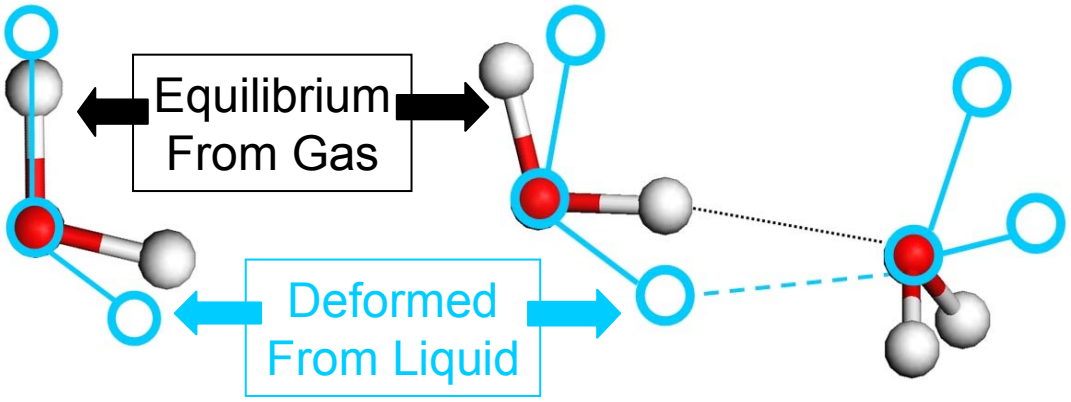
Step 1. MD simulation:

- BOMD
- 32 D_2O
- XC: PBE
- GTH PP, 125 Ry
- NVT, @ T=330K
- 30 ps
- Code: CPMD[1]



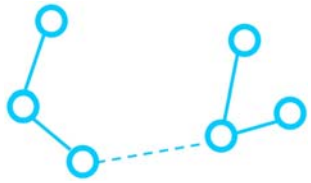
Step 2. Cluster calculations:

- Accurate reference: CCSD(T) @ CBS
- DFT: PBE, BLYP, PBE0
- 66 dimers extracted
- Code: NWChem5.0[2]

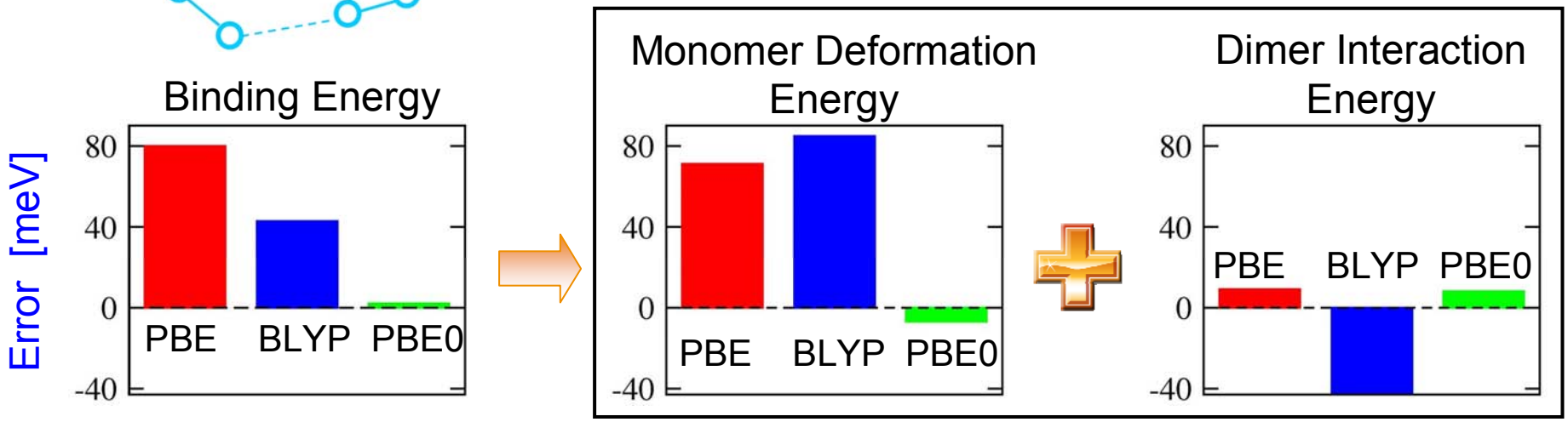


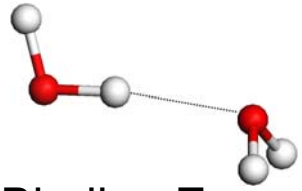
[1] J. Hutter *et al.*, CPMD, version 3.11; 1990-2006. [2] E. J. Bylaska *et al.*, NWChem, Version 5.0 (2006).

Benchmarks on Dimers Representing Liquid

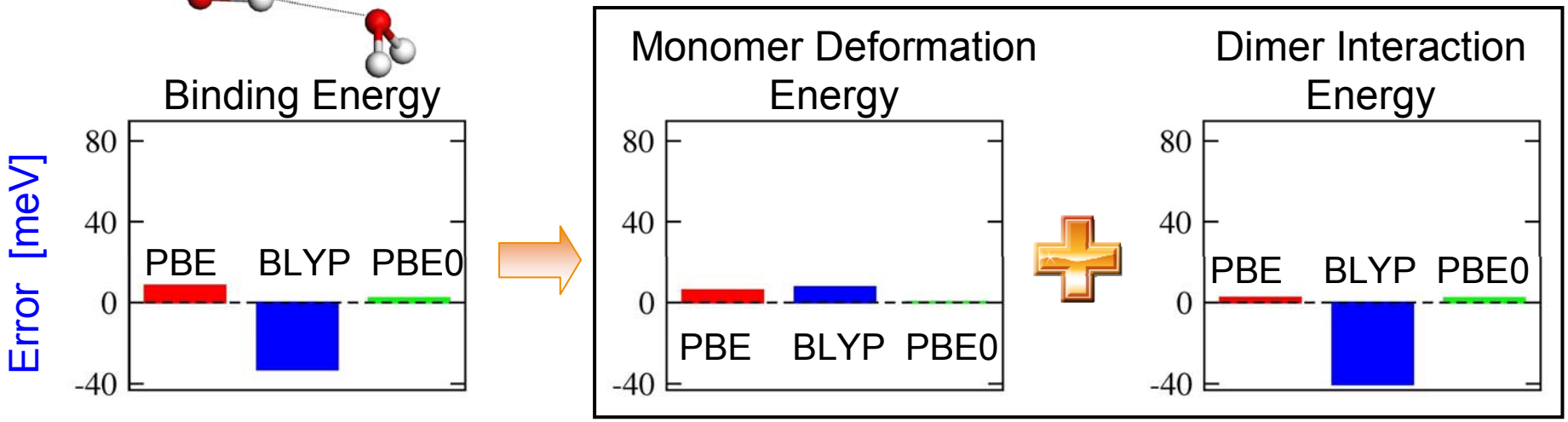


Deformed Dimers from Liquid Phase



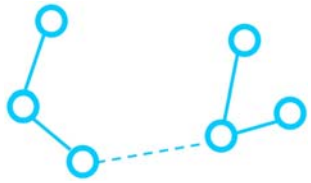


Equilibrium Dimer from Gas Phase

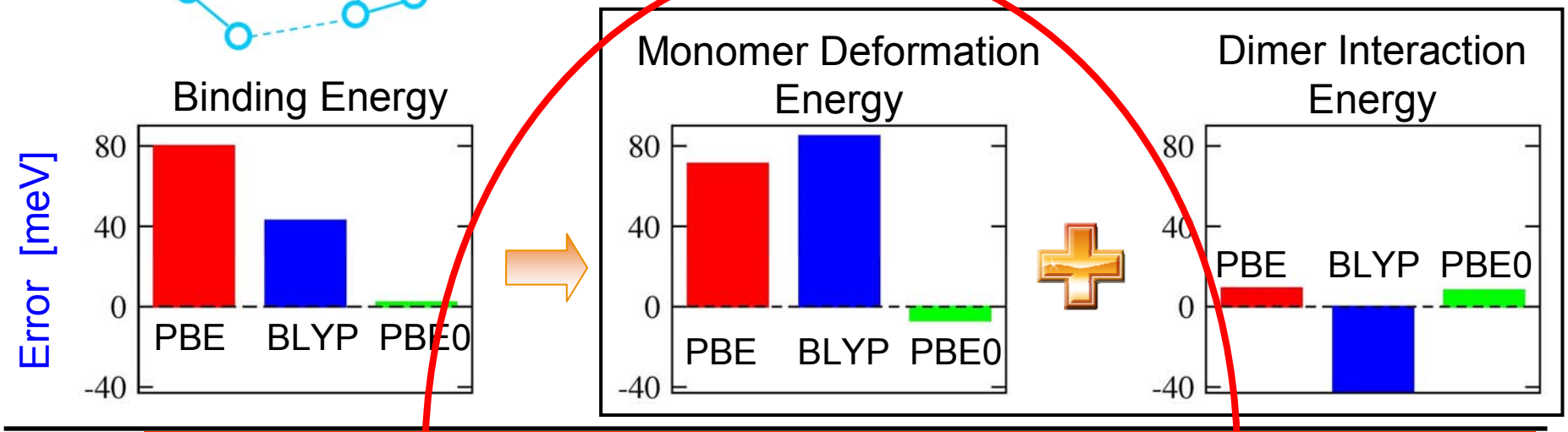


B. Santra, A. Michaelides, M. Scheffler, J. Chem. Phys. **129**, 124509 (2009).

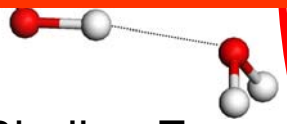
Benchmarks on Dimers Representing Liquid



Deformed Dimers from Liquid Phase



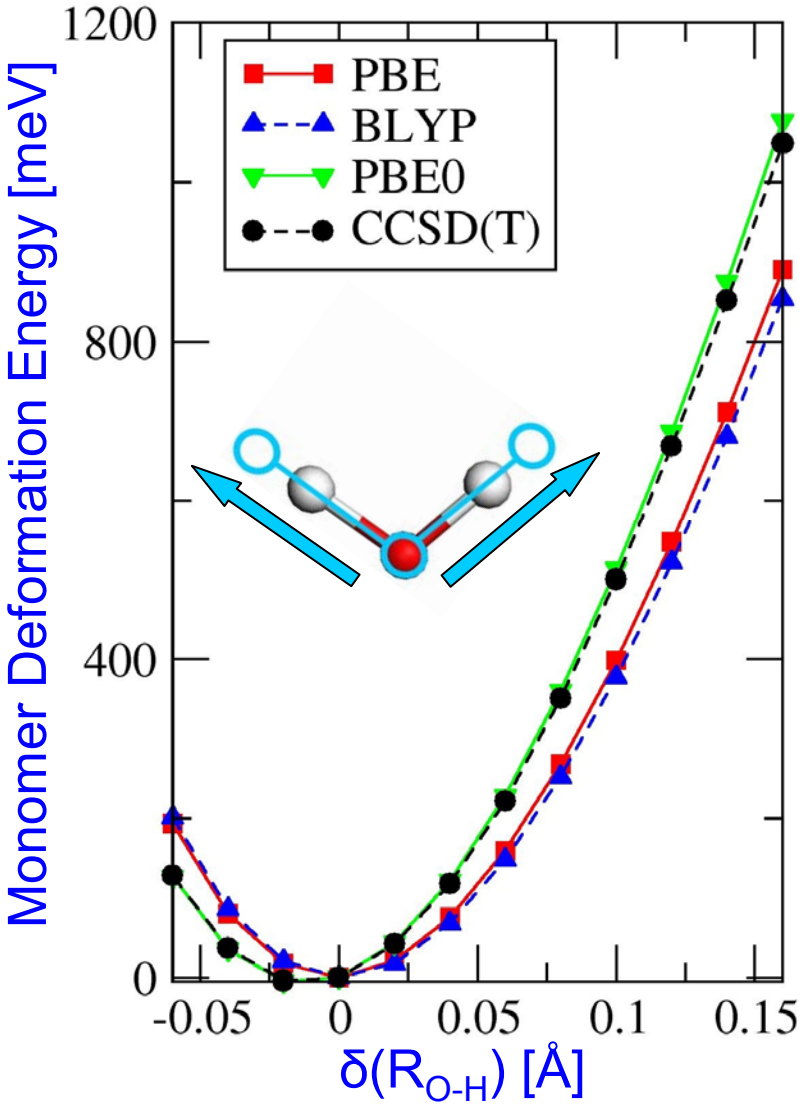
Too large error in monomer deformation with pure GGAs

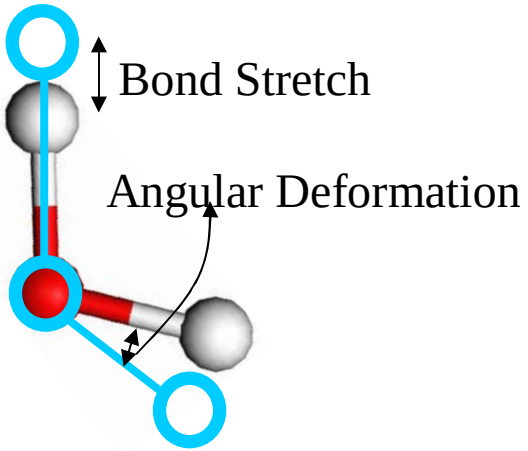


B. Santra, A. Michaelides, M. Scheffler, J. Chem. Phys. **129**, 124509 (2009).

Monomer Deformation

Too easy covalent O-H bond stretching with pure GGAs





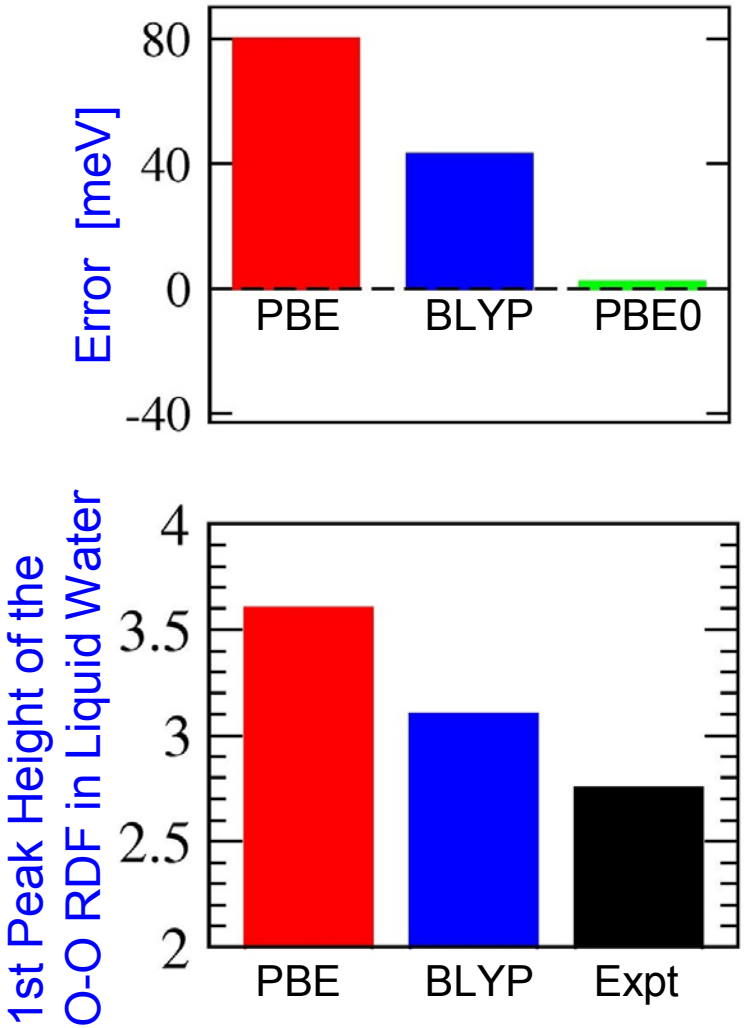
- Harmonic vibrational frequencies (cm^{-1})

	Asymmetric Stretch	Symmetric Stretch	Bending
CCSD(T)	3921	3812	1648
PBE	3800	3696	1593
BLYP	3756	3655	1596
PBE0	3962	3856	1633

B. Santra, A. Michaelides, M. Scheffler, J. Chem. Phys. **129**, 124509 (2009).

Benchmarks on Dimers Representing Liquid

Correspondence between the performance of pure GGAs for the dimers extracted from liquid and the 1st peak height of liquid water O-O RDF



B. Santra, A. Michaelides, M. Scheffler, J. Chem. Phys. **129**, 124509 (2009).

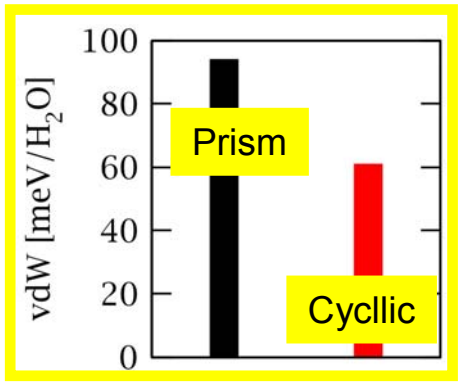
Part II

Importance of van der Waals interaction

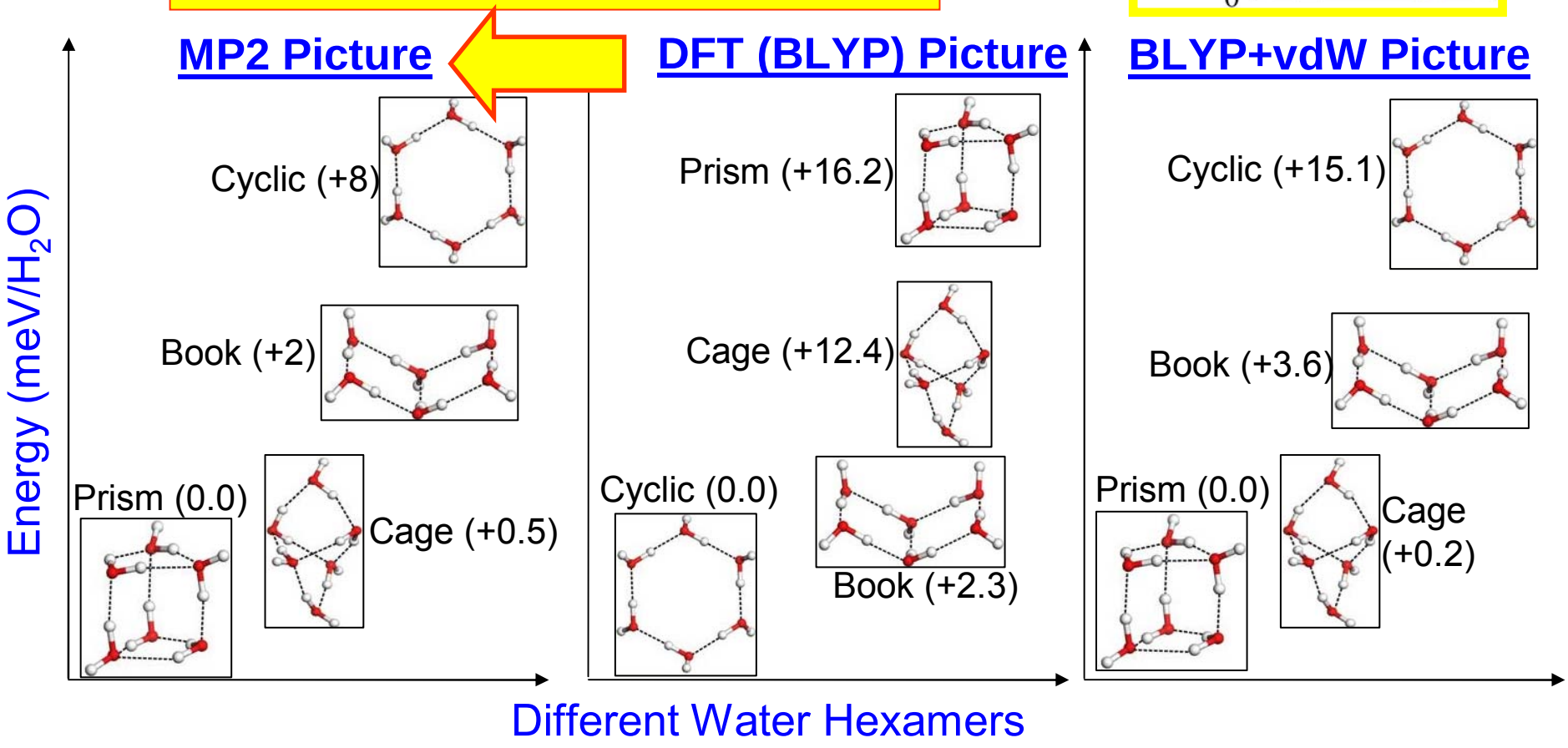
Water Hexamer

(In collaboration with Alexandre Tkatchenko, Martin Fuchs,

- Transition from 2-D to 3-D cluster.

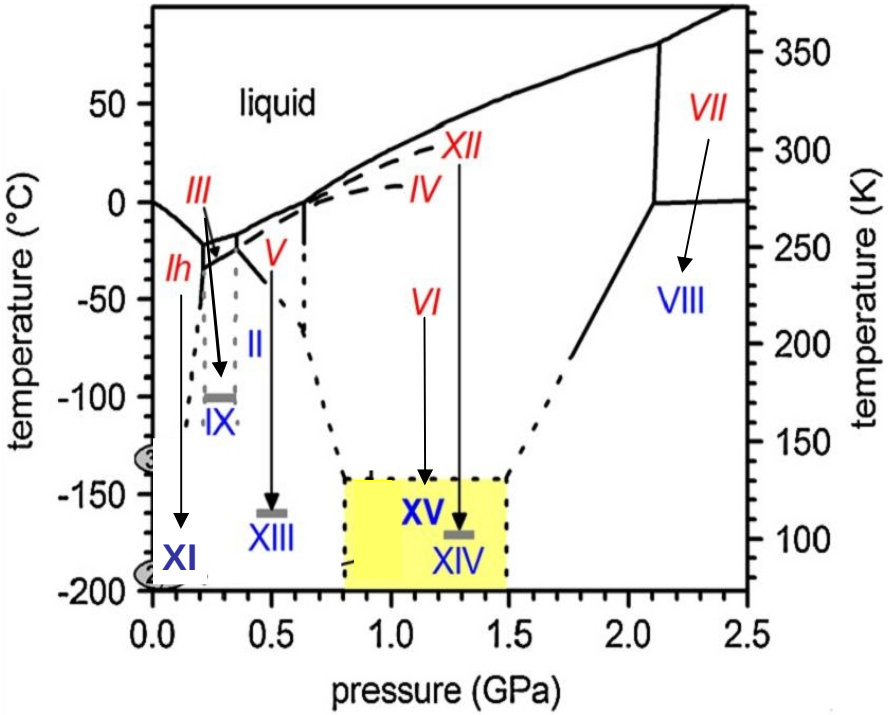


van der Waals interactions



B. Santra *et al.*, J. Chem. Phys. **129**, 194111 (2008); A. K. Kelkkanen *et al.*, J. Chem. Phys. **131**, 046102 (2009); P. L. Silvestrelli, Chem Phys. Lett. **475**, 285 (2009).

vdW Interactions in Crystalline Ice



C. G. Salzmann et al., PRL **103**, 105701 (2009)

$$E_{Total} = E_{DFT} + E_{vdW}$$

$$E_{vdW}^{[2]} = -\sum_{j>i} f_{damp}(R_{ij}, R_{ij}^0)\frac{C_{6ij}}{R_{ij}^6}$$

$$f_{damp}(R_{ij}, R_{ij}^0) = \frac{1}{1+\exp[-d(\frac{R_{ij}}{S_R R_{ij}^0}-1)]}$$

Can be obtained from *ab intio* calculations using scheme of Tkachenko *et al.*
[A. Tkachenko and M. Scheffler, PRL **102**, 073005 (2009).]

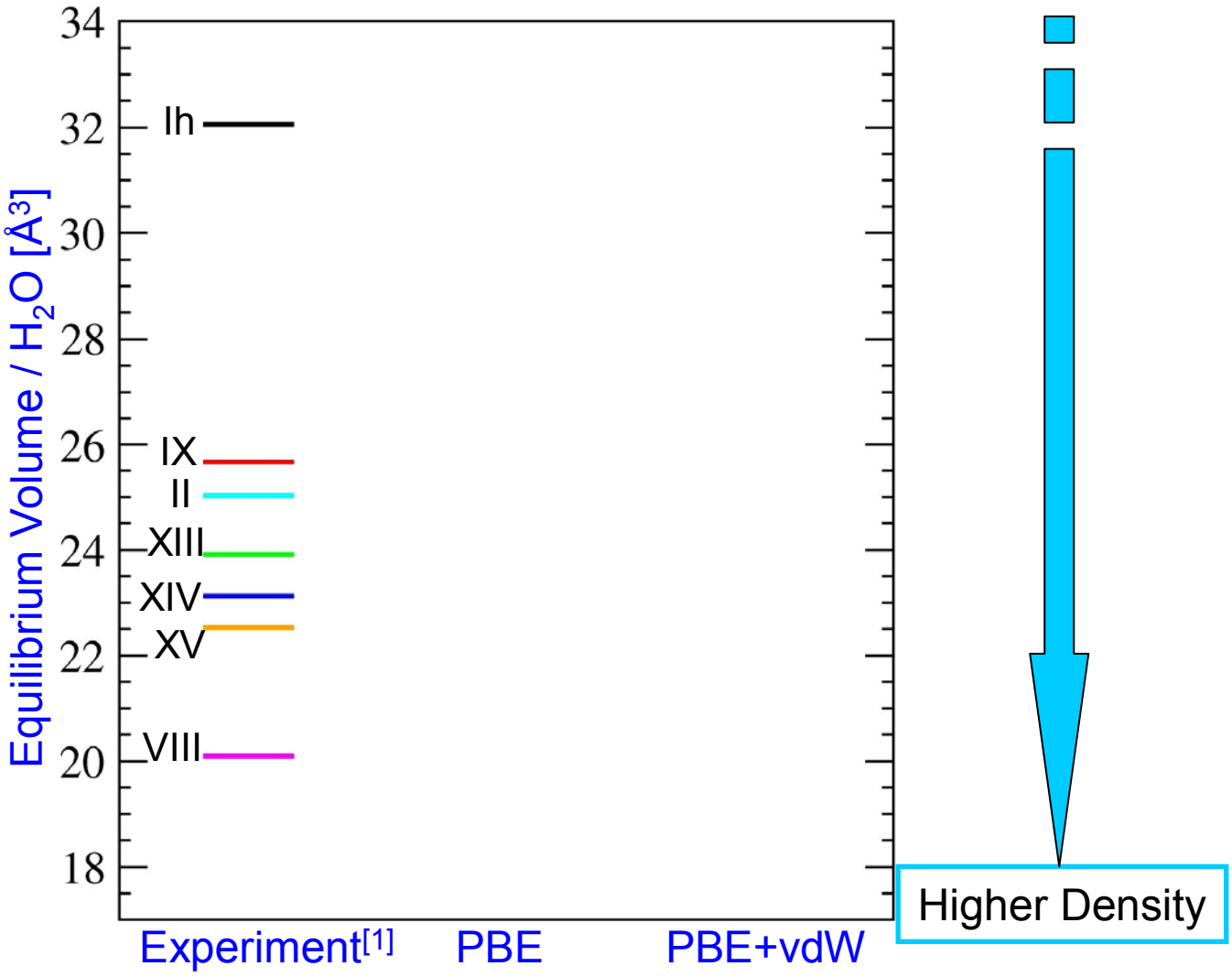
Need to be fitted for each DFT xc funtional

- All proton ordered phases and natural ice Ih
- Numerical atom centered basis, all electron
- Code: FHI-AIMS[1]
- DFT xc: PBE, BLYP, PBE+vdW, BLYP+vdW
- Equilibrium volumes and cohesive energies obtained using Murnaghan equation of state.

[1] V. Blum *et al.,* Comput. Phys. Com. **180**, 2175 (2009).

[2] R. Ahlrichs, R. Penco, and G. Scoles, Chem. Phys. **19**, 119 (1977); Q. Wu and W. Yang, J. Chem. Phys. **116**, 515 (2002); S. Grimme, J. Comput. Chem. **25**, 1463 (2004).

Ice: Equilibrium volume



[1] V. R. Bill and A. Tippe, Acta. Cryst. 23, 343 (1967); E. Whalley, J. Chem. Phys. **81**, 4087 (1984); C. G. Salzmann et al., Science **311**, 1758 (2006); W. F. Kuhs et al., J. Chem. Phys. **81**, 3612 (1984); C. G. Salzmann et al., PRL, **103**, 105701 (2009).

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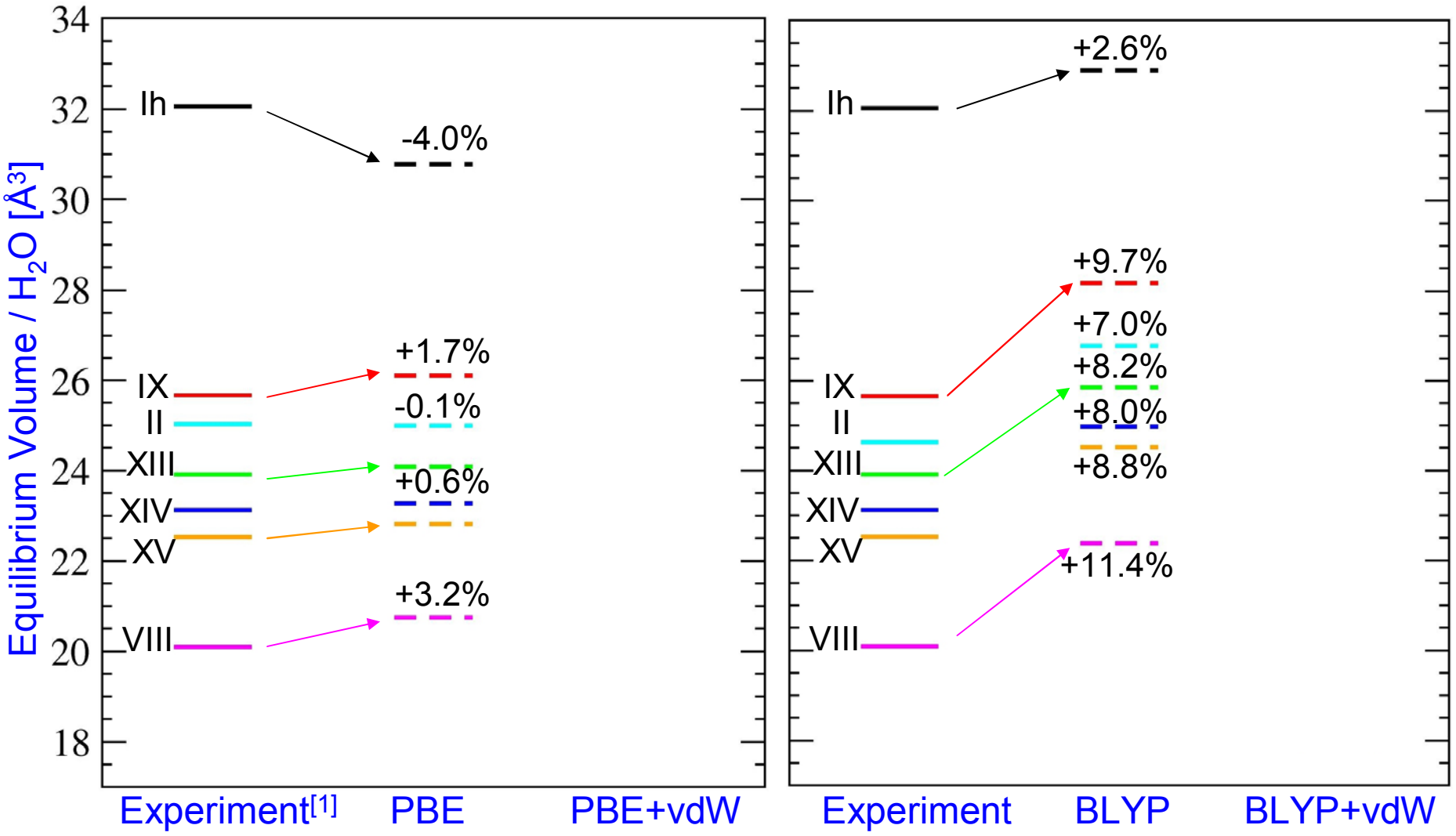

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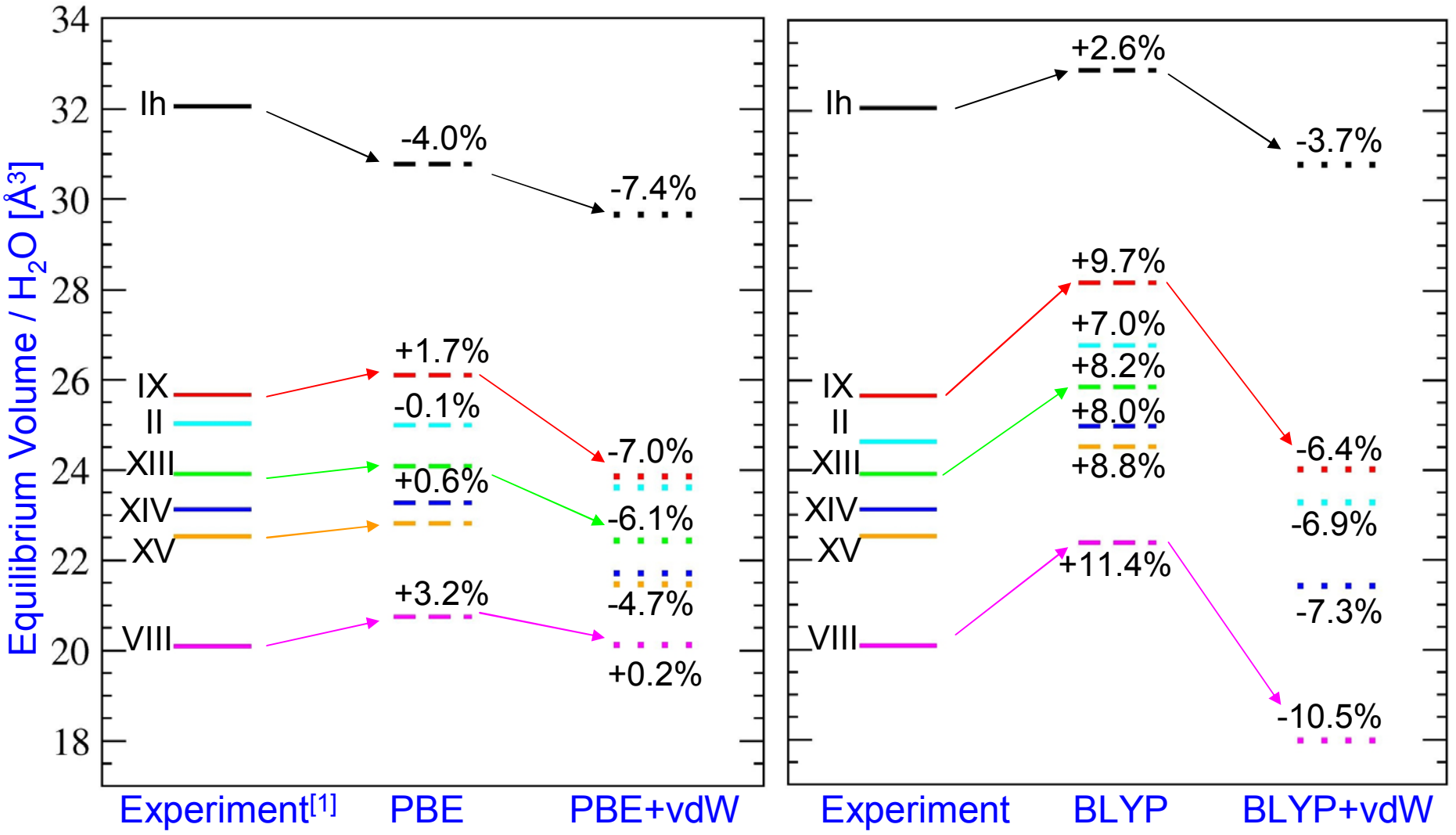

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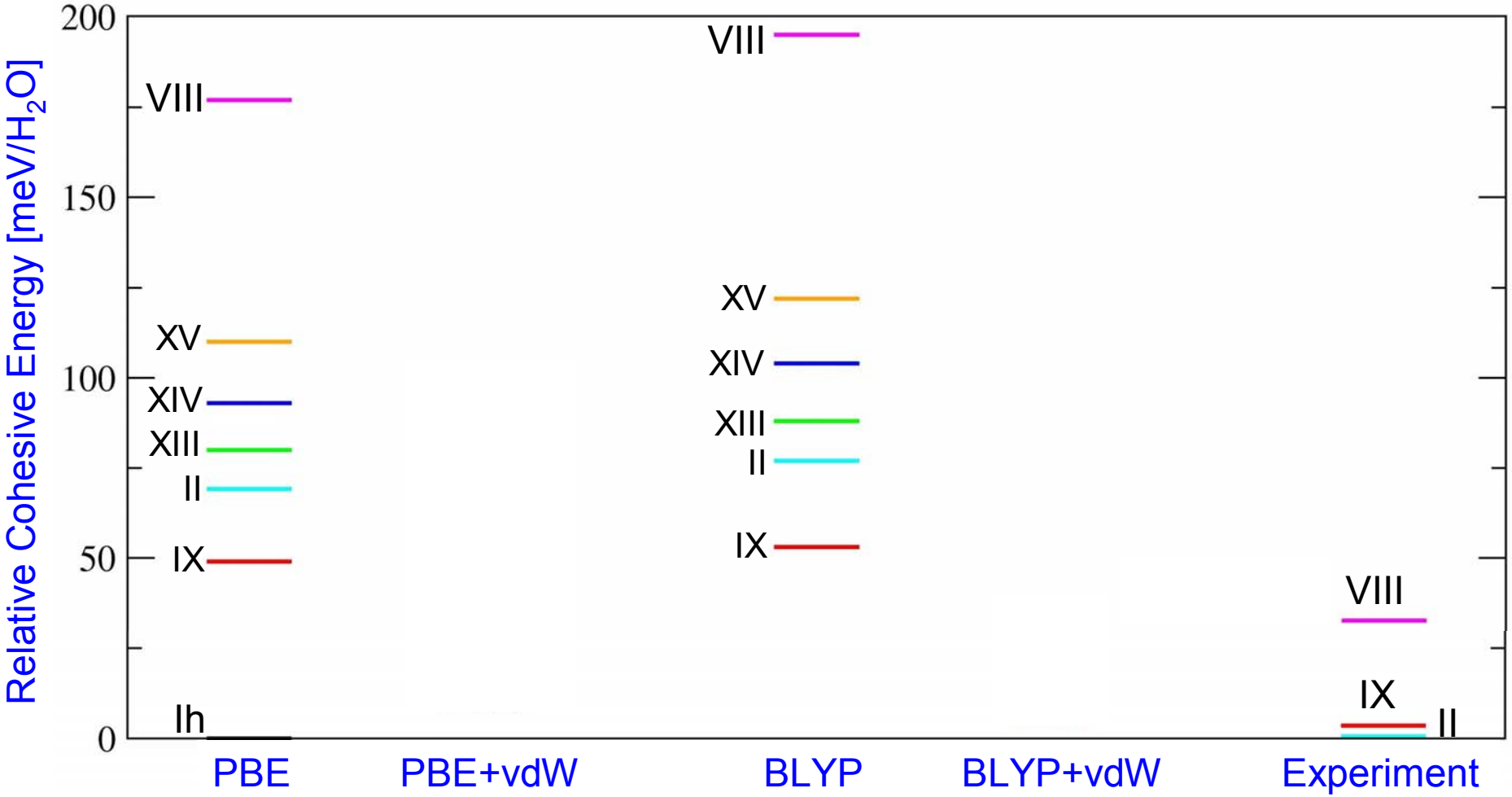
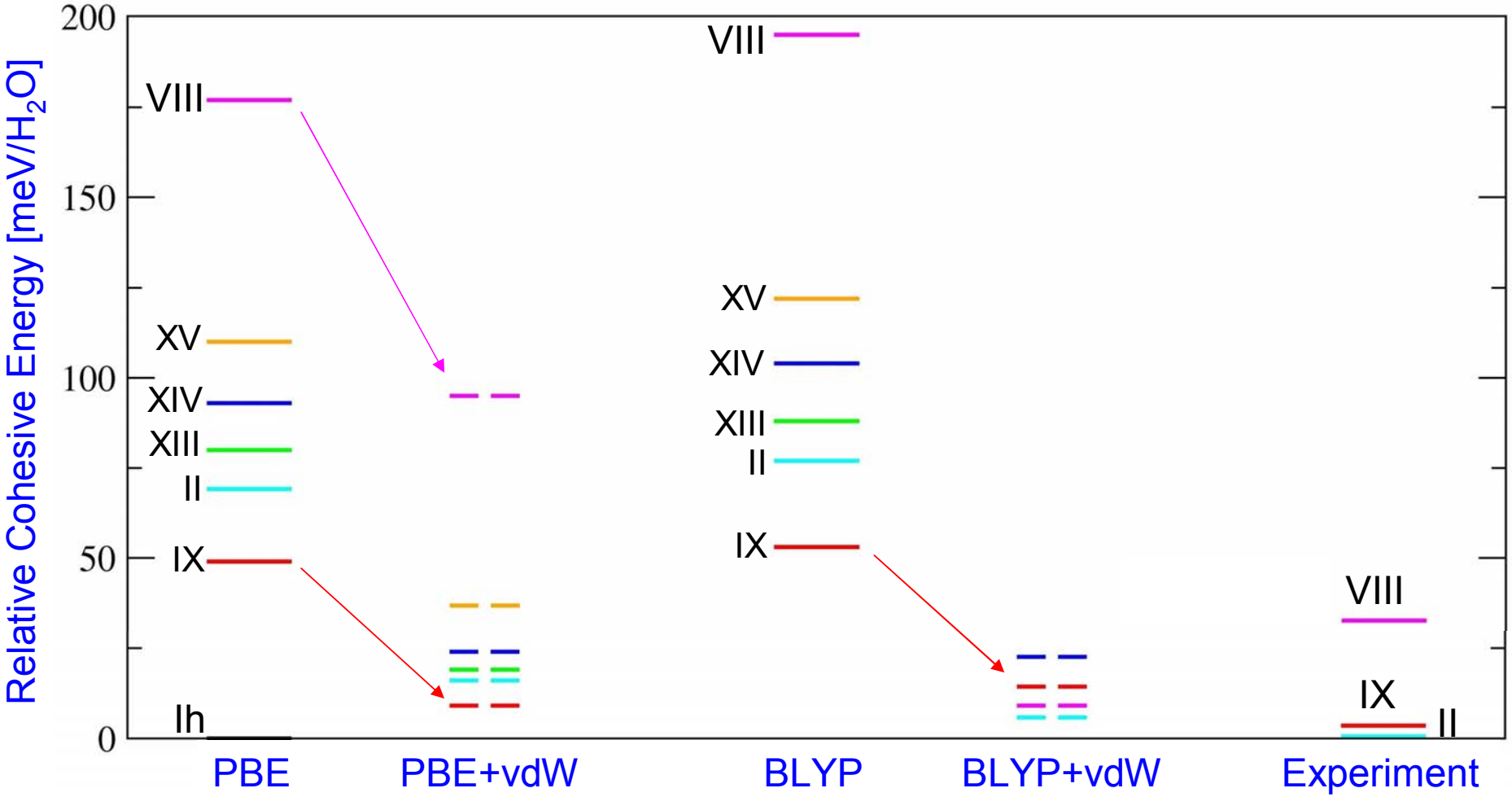
Ice: Cohesive energy



Experiment[1]	PBE	PBE+vdW	BLYP	BLYP+vdW
610	636	714	526	666

[1] E. Whalley, J. Chem. Phys. **81**, 4087 (1984)

Ice: Cohesive energy



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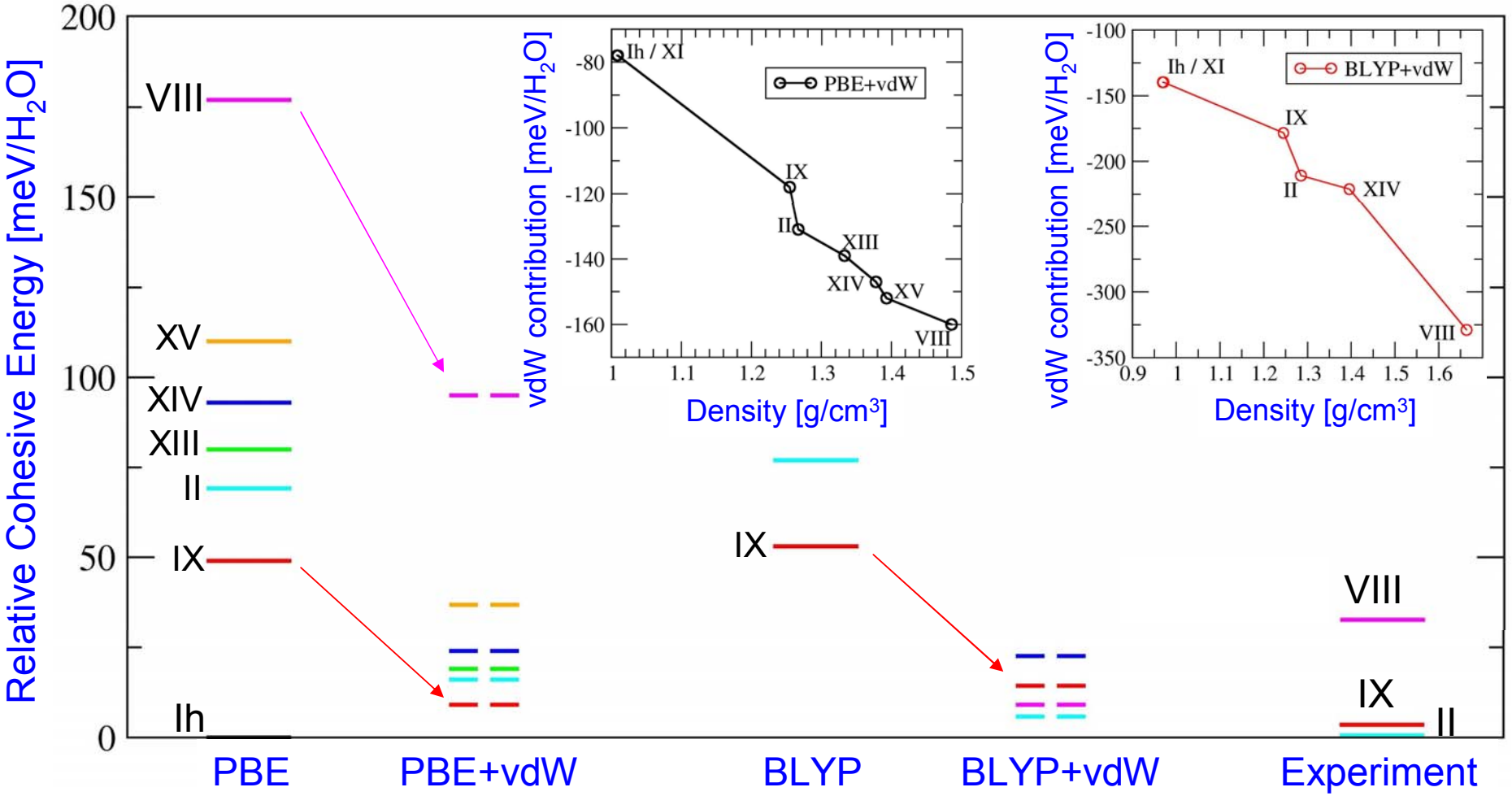


Cohesive Energy of Ice Ih (meV/H_2O)

Experiment[1]	PBE	PBE+vdW	BLYP	BLYP+vdW
610	636	714	526	666

[1] E. Whalley, J. Chem. Phys. **81**, 4087 (1984)

Summary

• It is too easy to stretch covalent O-H bonds with pure GGAs, which effectively produce too large binding for the water dimers extracted from liquid.

• vdW interactions are important for the stabilization of water hexamers.

• Addition of vdW interactions on top of DFT xc functionals increases the density of the ice phases.

• Relative stabilities of the high density ice phases increase when vdW interactions are included.

Acknowledgements

- Martin Fuchs
- Alexandre Tkatchenko

- ICE Group Members
http://www.chem.ucl.ac.uk/ice/

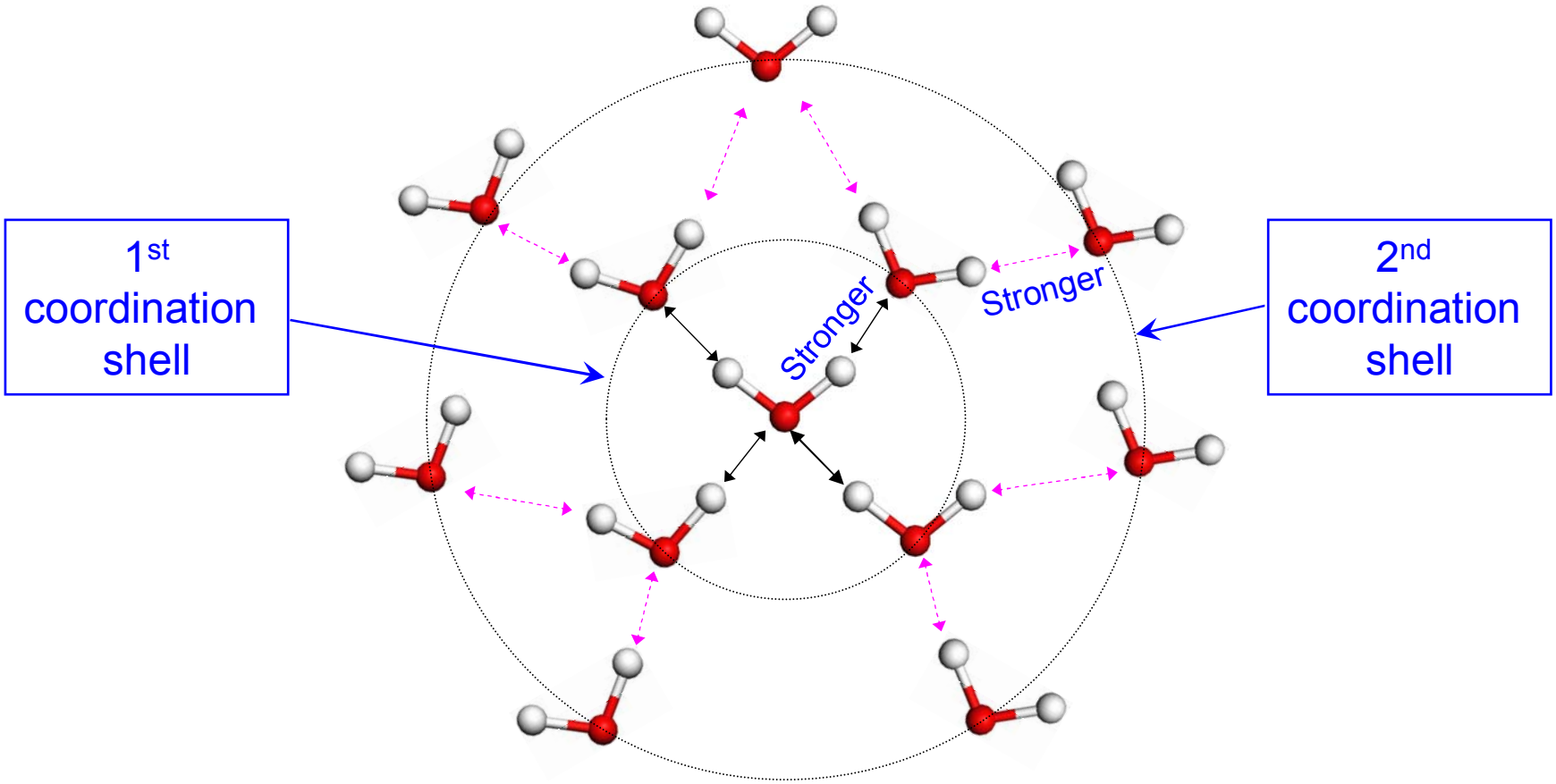
- FHI Colleagues
http://www.fhi-berlin.mpg.de/th/

- MONET (For Funds)
http://www.sljus.lu.se/monet/

THANK YOU

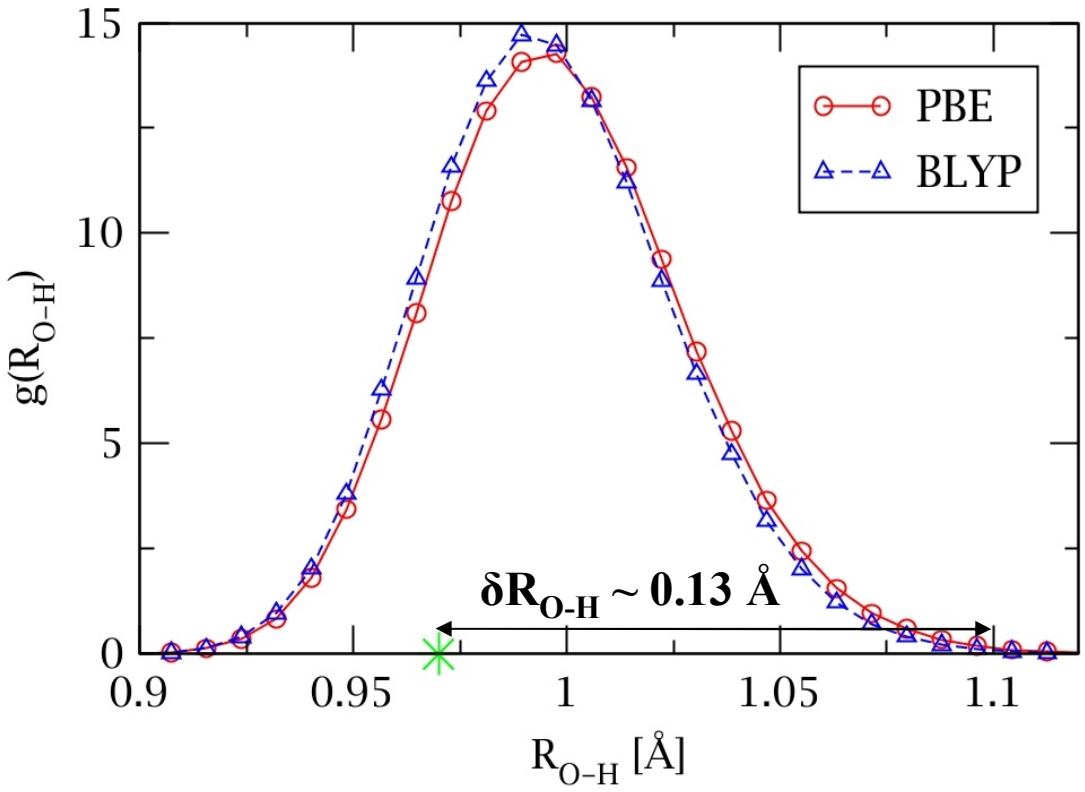
Ice: Expand or Shrink?

Adding vdW, will it ‘expand’ or ‘shrink’?



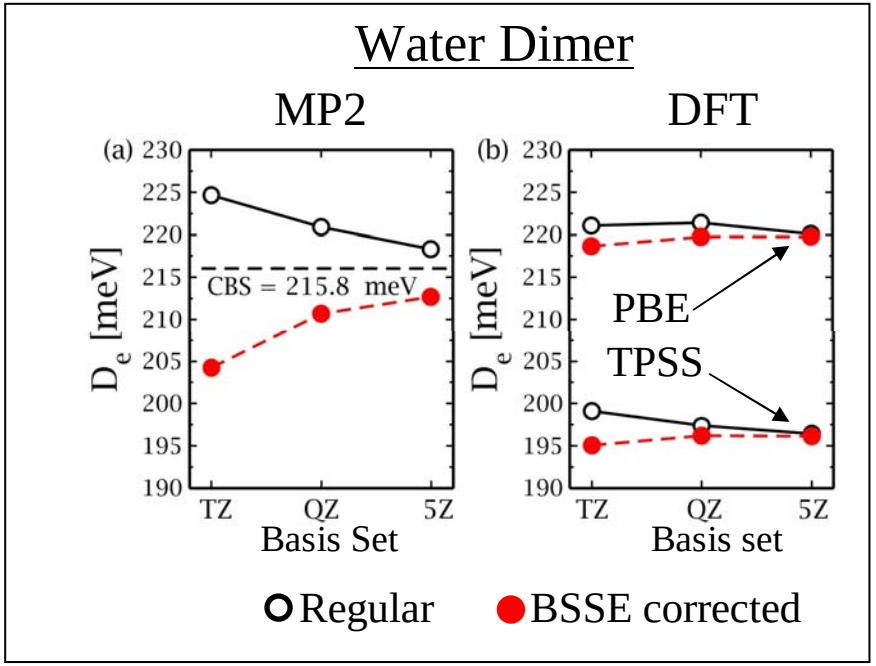
A schematic diagram to show vdW effect on structure of ice

Distribution of monomer O-H bonds in DFT liquid water



Strategy for the benchmark

- MP2 and DMC are chosen for reference.
- All electron (frozen core) calculations with Gaussian-type localized basis functions, Dunning's correlation consistent basis sets i.e., aug-cc-pVnZ; n = T, Q, and 5.
- Extrapolated to Complete Basis Set (CBS) limit by the well established heuristic methods.
- Codes used: G03, NWChem, CPMD, and CHAMP.



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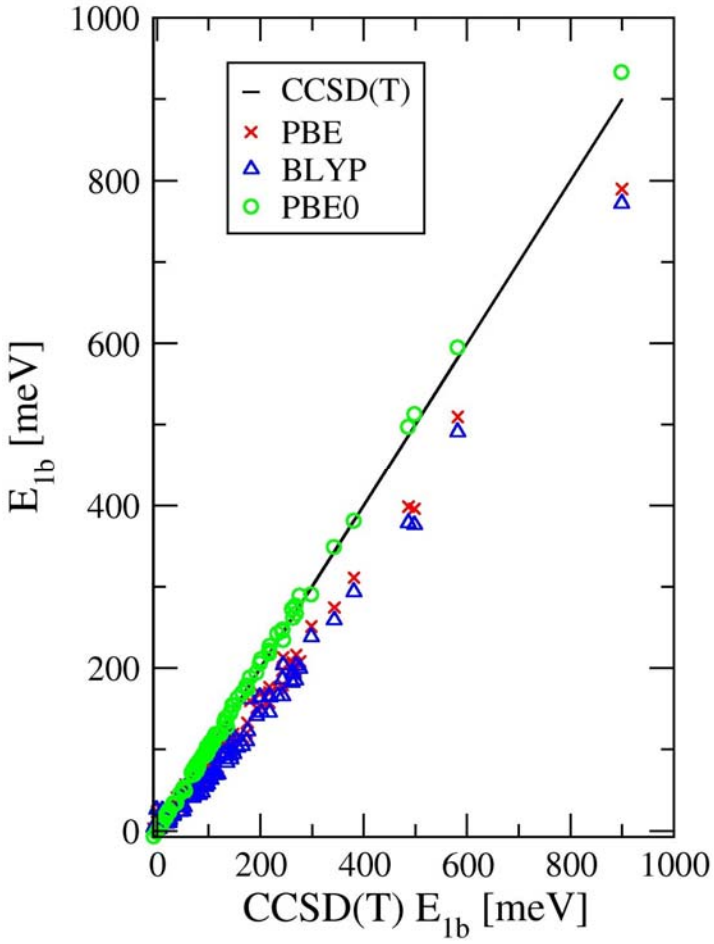
[2] E. M. Mas *et al.*, J. Chem. Phys. **113**, 6687 (2000).
[3] L. A. Curtiss, D. J. Frurip, and M. Blander, J. Chem. Phys. **71**, 2703 (1979).

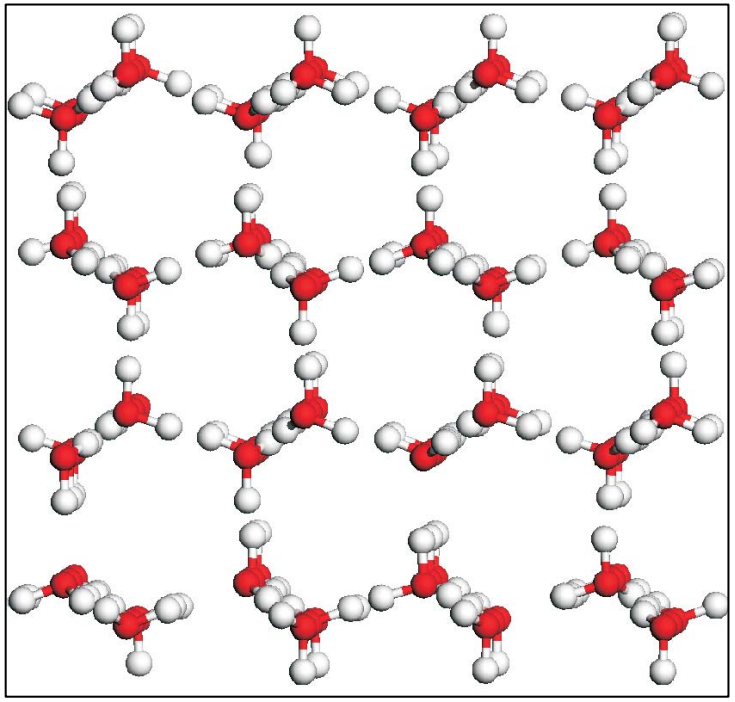
Benchmarks on Dimers Representing Liquid

Too easy to deform monomer in liquid with pure GGAs

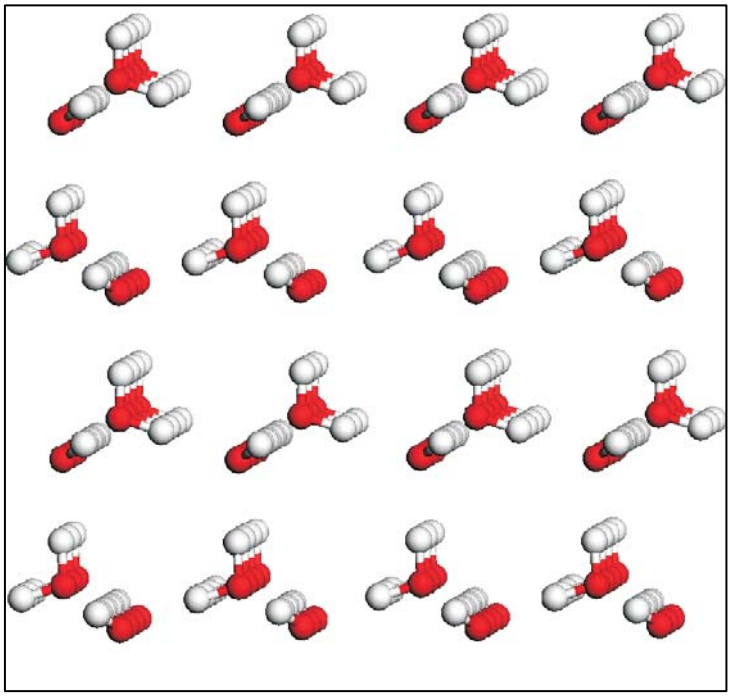


Ice: Proton disorder vs order

Proton disordered Ice Ih



Proton ordered Ice XI



C. G. Salzmann et al., PRL **103**, 105701 (2009)
D. Pan et al., PRL **101**, 155703 (2008)

Equilibrium volumes

Equilibrium volume/water (Å^3) for different phases. Values in the parenthesis for the DFT columns are percentage errors with respect to the experimental volumes. Values in parenthesis in the experimental column is the extrapolated volumes at zero pressure.

	PBE	PBE+ vdw	BLYP	BLYP+ vdw	Expt	MP2/C CSD(T)
Ih	30.78 (-4.0)	29.67 (-7.4)	32.89 (+2.6)	31.10 (-3.0)	32.05[1] (32.03[2])	32.12[5]
XI	30.75	29.64	32.83	30.99	31.98	
IX	26.11(+4.1)	23.86 (-4.7)	28.17 (+12.4)		25.06 (25.67[3])	
XIII	24.08 (+0.7)	22.44 (-6.1)	25.86 (+8.1)		23.91	
XIV	23.27 (+0.6)	21.71 (-6.1)	24.97 (+8.0)		23.12	
VIII	20.74 (+13)	20.13 (+9.6)	22.38 (+22)	16.94 (-7.7)	18.36 (20.09[4])	

1. ~13 K, atm pressure, V. R. Bill and A. Tippe, Acta. Cryst. 23, 343 (1967)
2. ~77 K and zero pressure; 3. ~110K and zero pressure; 4. ~108 K and zero pressure
5. PRL 101, 183005 (2008)

Cohesive energies

Cohesive energies (meV/H_2O) at the equilibrium volume for different phases. Values in the parenthesis are relative energies with respect to the ice Ih.

	PBE	PBE+ vdw	BLYP	BLYP+ vdw	Expt	MP2/CCSD(T)
Ih	-636	-714	-526	-721	-610[1]	-577[2]
XI	-639	717	-529	-723		
IX	-587 (+49)	-705 (+9)	-473 (+53)			
XIII	-556 (+80)	-695 (+19)	-438 (+88)			
XIV	-543 (+93)	-690 (+24)	-422 (+104)	-715(+6)		
VIII	-459 (+177)	-619 (+95)	-331 (+195)	-751 (-30)		

1.
2. PRL 101, 183005 (2008)

Lattice parameters

Ice XI (Number of water molecules: 8):
Spacegroup: $Cmc2_1$, Lattice constants are: a=4.465, b=7.858, c=7.292 Å

Ice XIV (Number of water molecules: 12):
Spacegroup: $P2_12_12_1$, Lattice constants are: a=8.3499, b=8.1391, c=4.0825 Å

Ice XIII (Number of water molecules: 28):
Spacegroup: $P2_1/a$, Lattice constants are: a=9.2417, b=7.4724, c=10.297 Å, β=109.6873º

Ice VIII (Number of water molecules: 8):
Spacegroup: $I4_1/amd$, Lattice constants are: a=4.656, b=4.656, c=6.775 Å,

ICE IX (Number of water molecules: 12):
Spacegroup: $P4_14_12$, Lattice constants are: a=6.6925, b=6.6925, c=6.7152 Å,