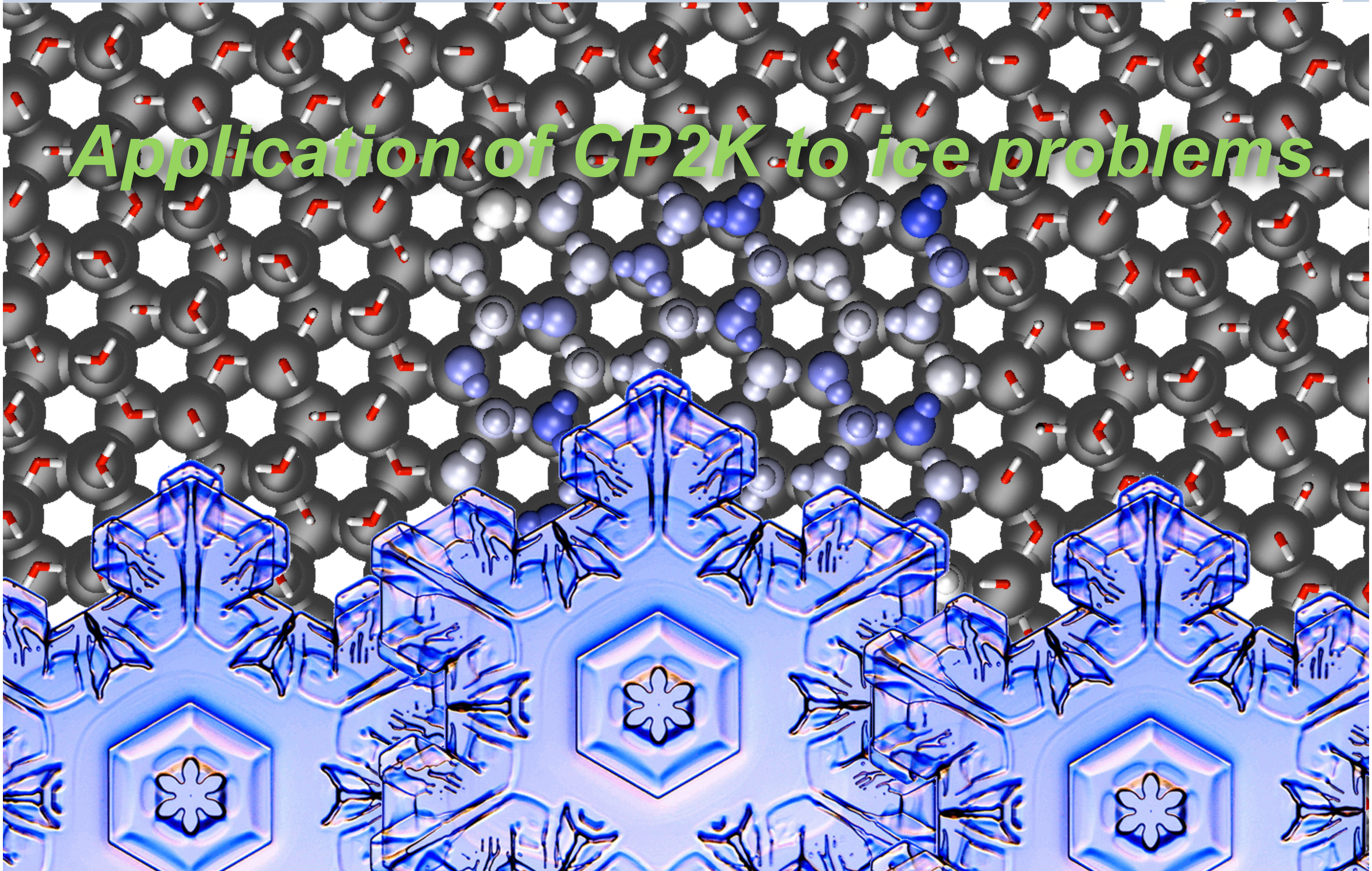
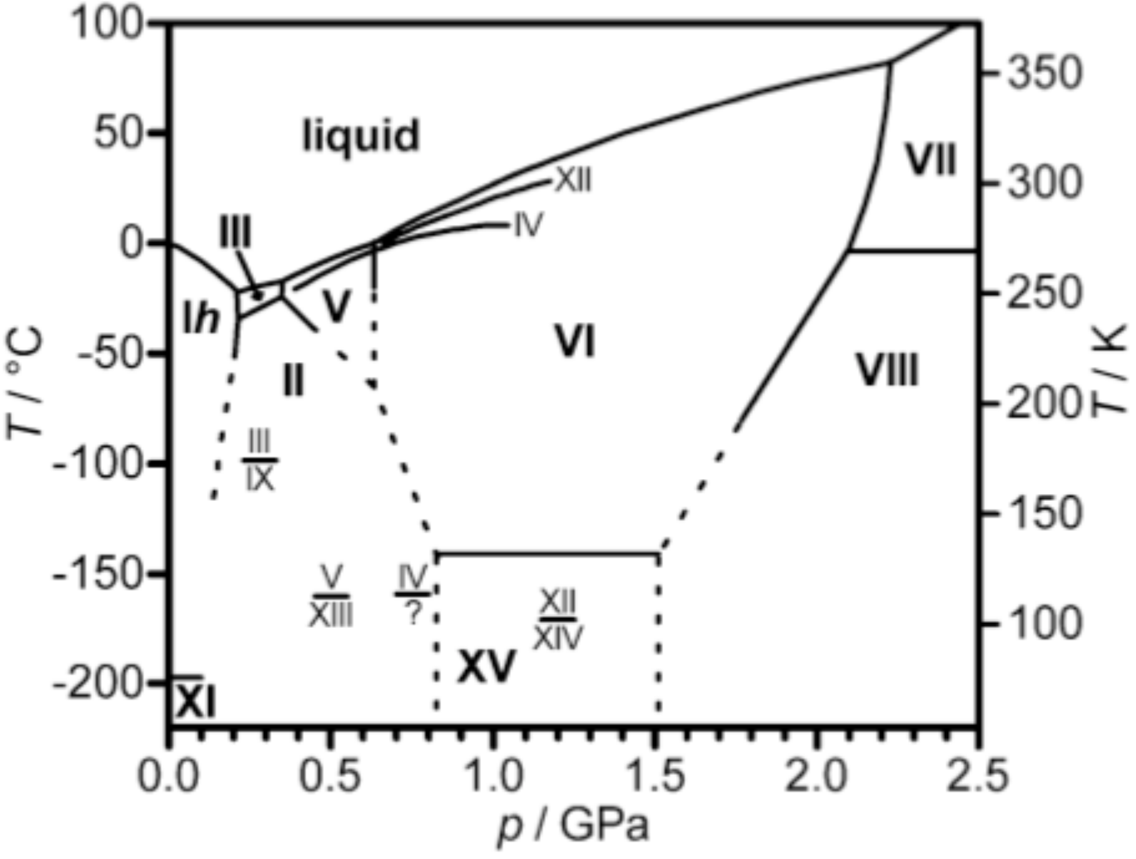
Ben Slater

28/8/14

Application of CP2K to ice problems



Ice phase diagram



15 known crystalline ice phases

Several amorphous forms (e.g. see Martonak et al. JCP 2005)

Many phases are order/disorder pairs e.g. Ih/XI, V/XIII, VII/VIII

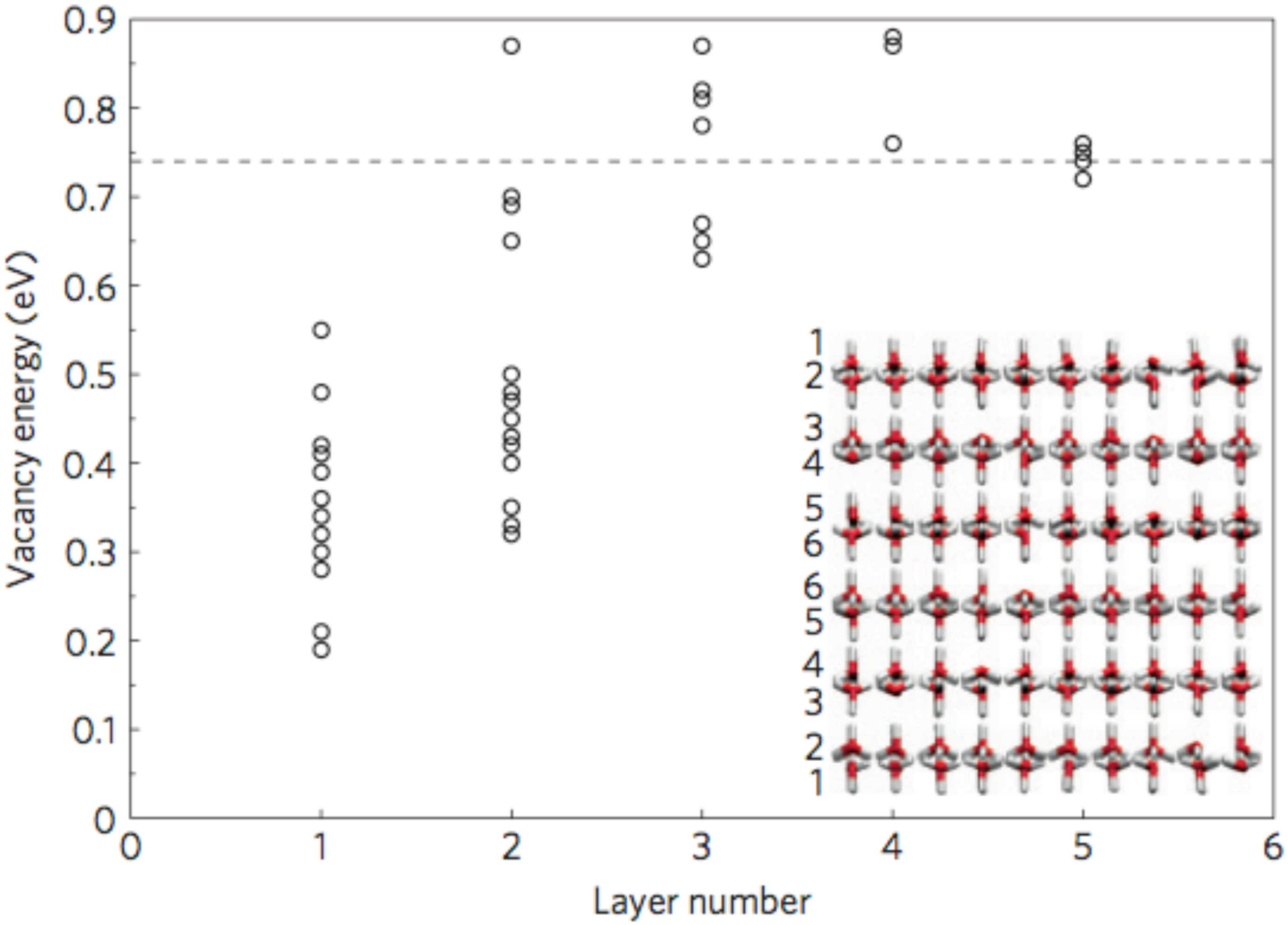
XII found in 1998, 3 further phases reported 2006-2009

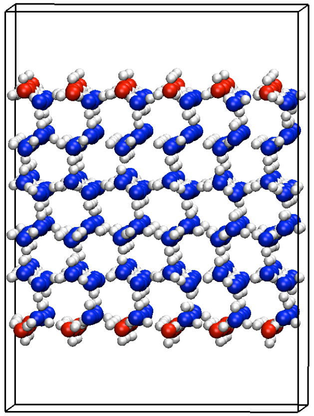
Why ice is like an old mattress

=

M. Watkins, D. Pan, A. Michaelides, J. VandeVondele, B. Slater, *Nature Materials*, **10**, 794 2011

Vacancies in ice

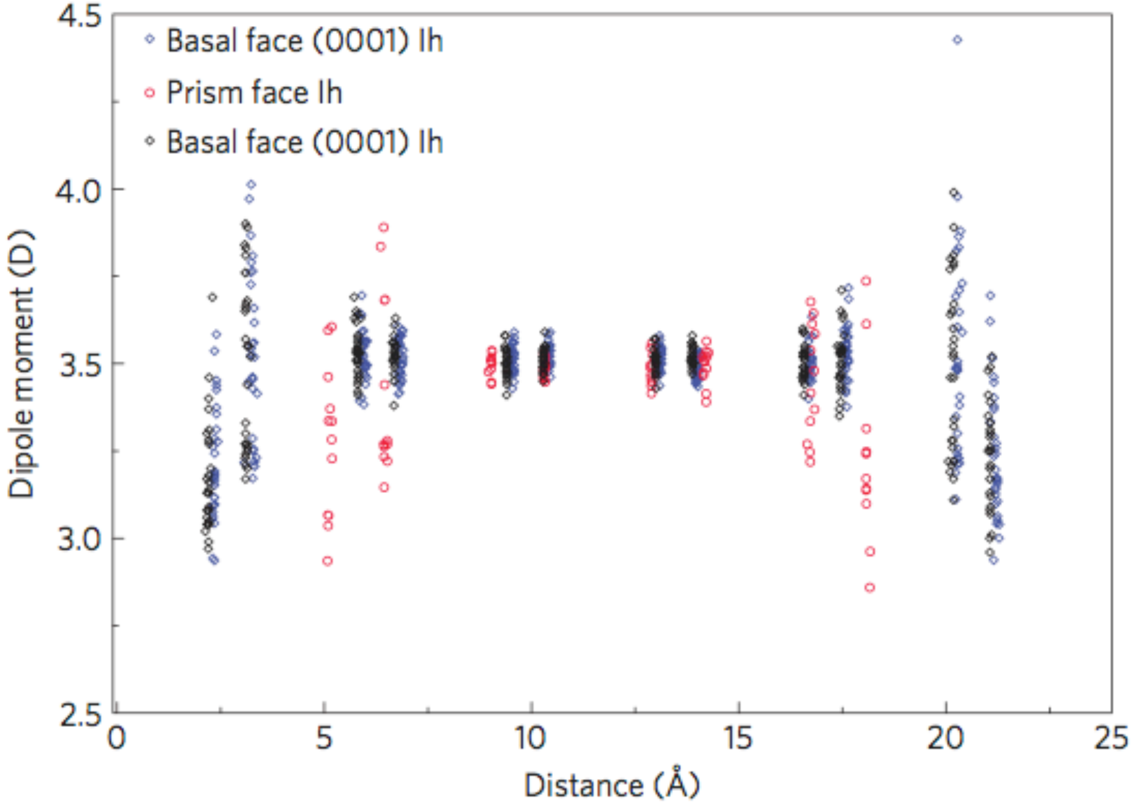


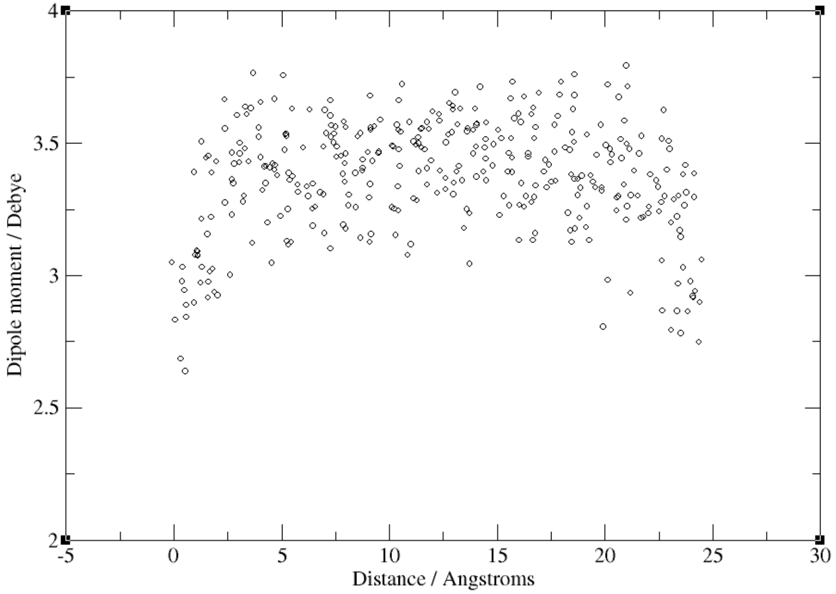


Bulk vacancy energy constant 0.74eV±0.025eV

Surface vacancy energy varies by ~0.8eV and ~0.5eV in outermost layer

Dipoles in perfect ice

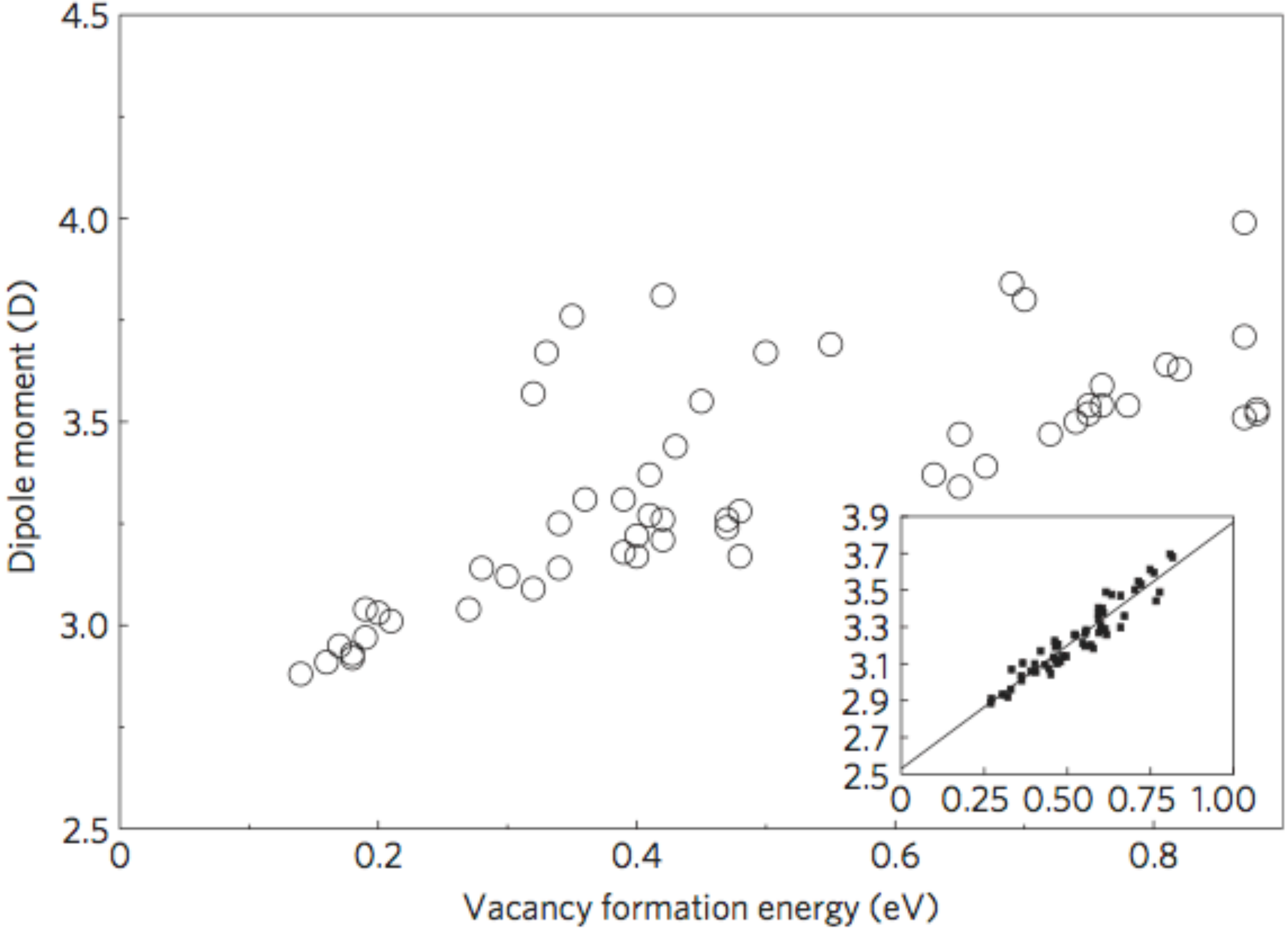




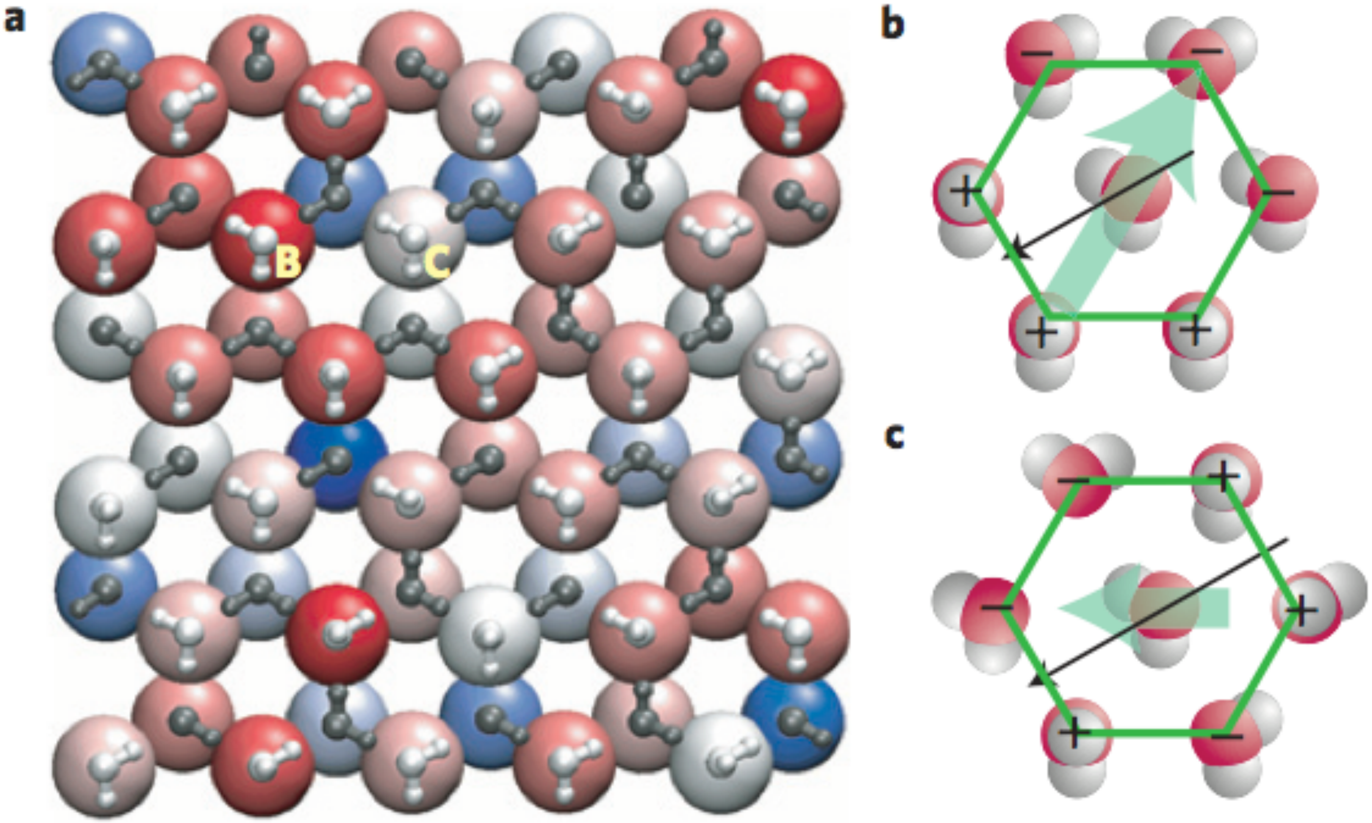
LDA

Dipole variance is an intrinsic property of crystalline ice proton disordered phases

Dipole moment correlated with vacancy energy



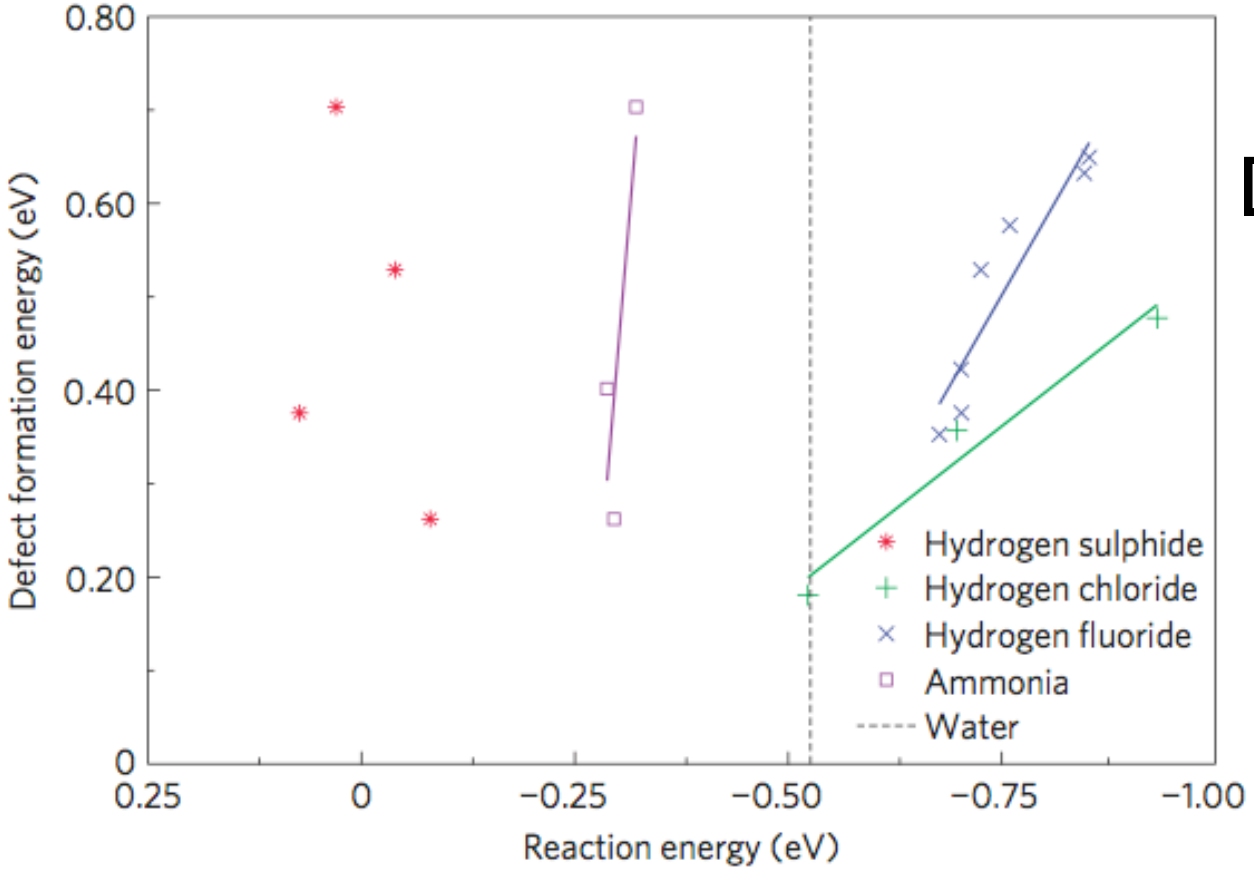
Why does this variance arise?



As part of this study, ADMM was used to compute PBE0 dipole moments on 288 molecule cells with an overhead 100% w.r.t PBE

- Each molecular dipole sits in a frustrated lattice exhibiting orientational disorder
- In the bulk, due to proton disorder and the symmetry of oxygen network, the molecule feels an average field
- At the surface, the symmetry is lowered and local environment has a strong influence on the local ESP
- Generic property - e.g. spin ice, hydrates

Consequences

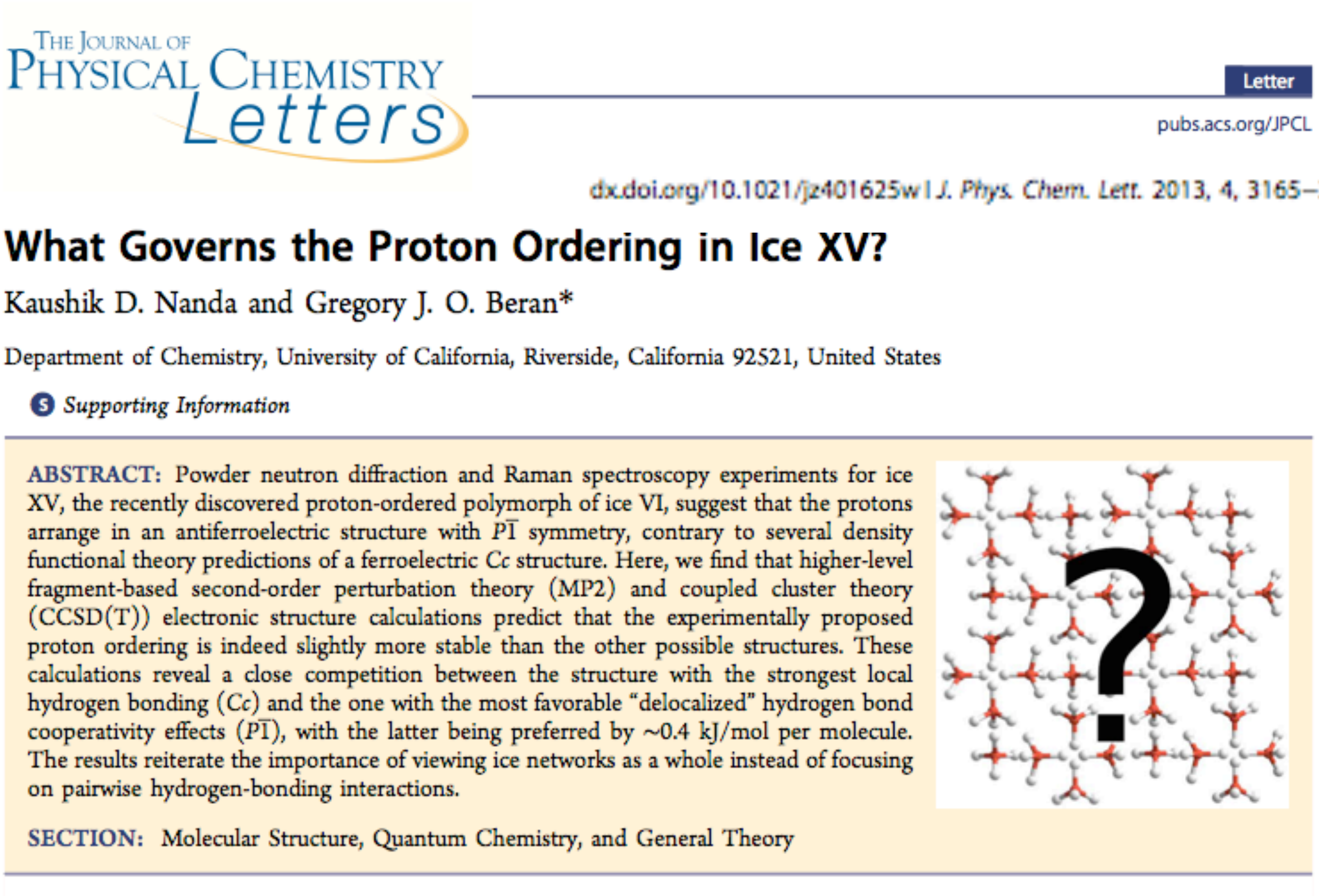


Displacement reaction

- Around 10% of surface sites are comparatively very weakly bound
- At low temperature admolecules formed (proto-QLL)
- All vacancy energies lowered upon vacancy-admolecule formation
- Influence on pre-melting and reaction chemistry

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

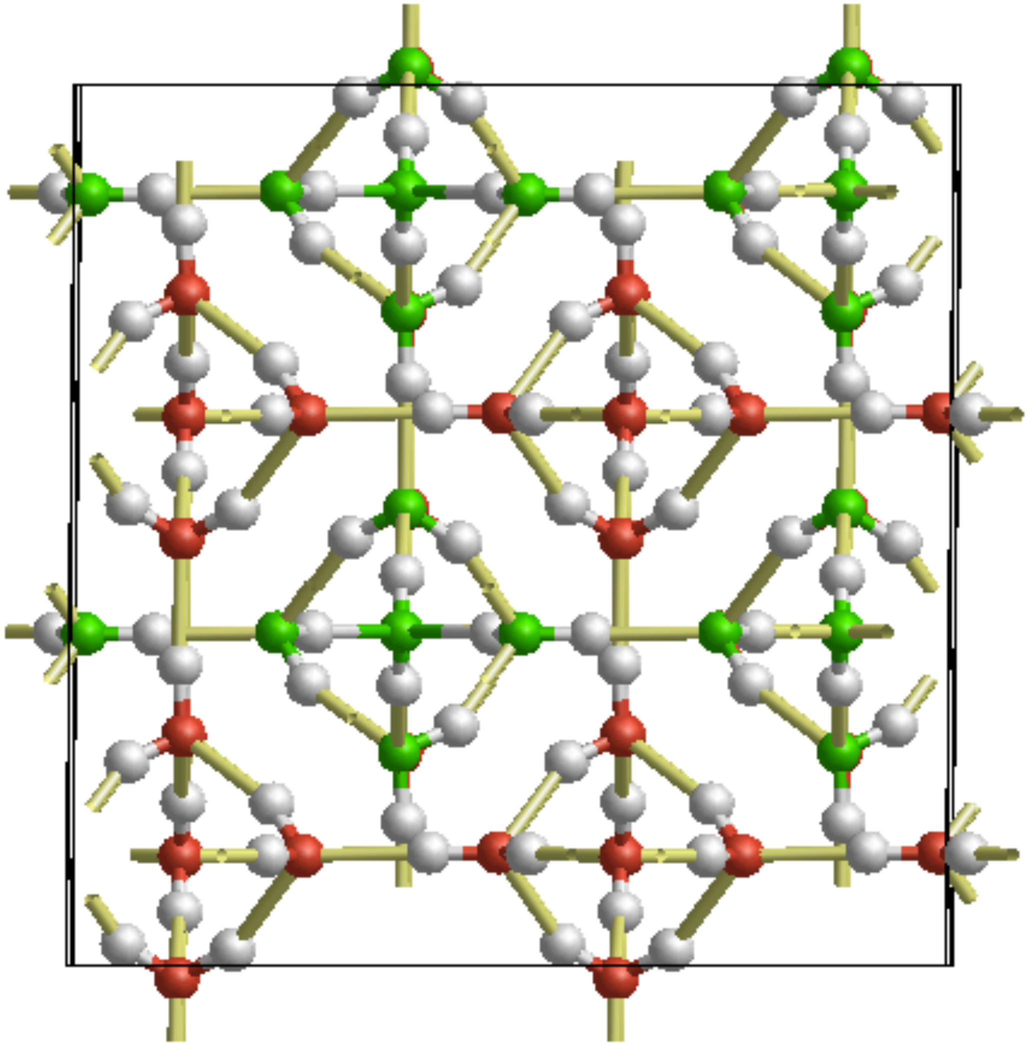
ABSTRACT: Powder neutron diffraction and Raman spectroscopy experiments for ice XV, the recently discovered proton-ordered polymorph of ice VI, suggest that the protons arrange in an antiferroelectric structure with $P\bar{1}$ symmetry, contrary to several density functional theory predictions of a ferroelectric *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

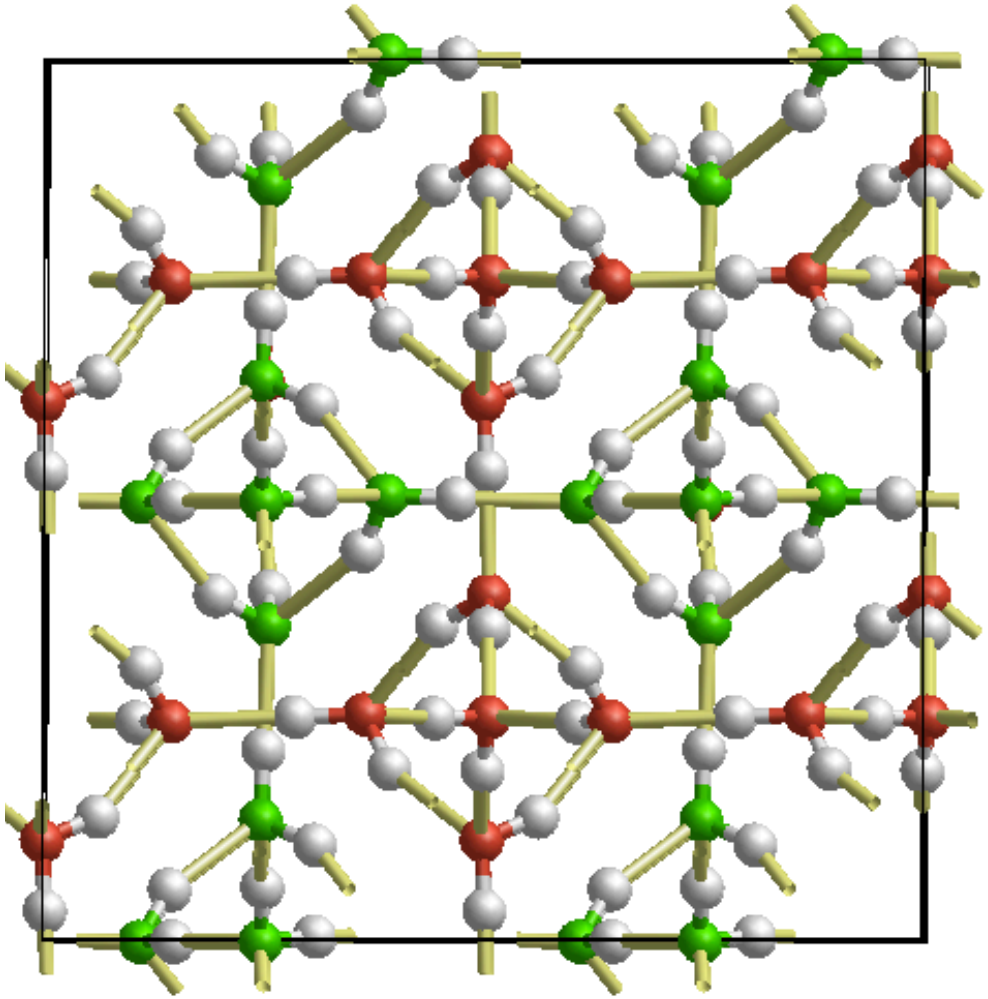
Ice XV/VI
have the
largest
variation in
hydrogen
bond angle
of any phase.

Problem solved?

Key ice XV structures

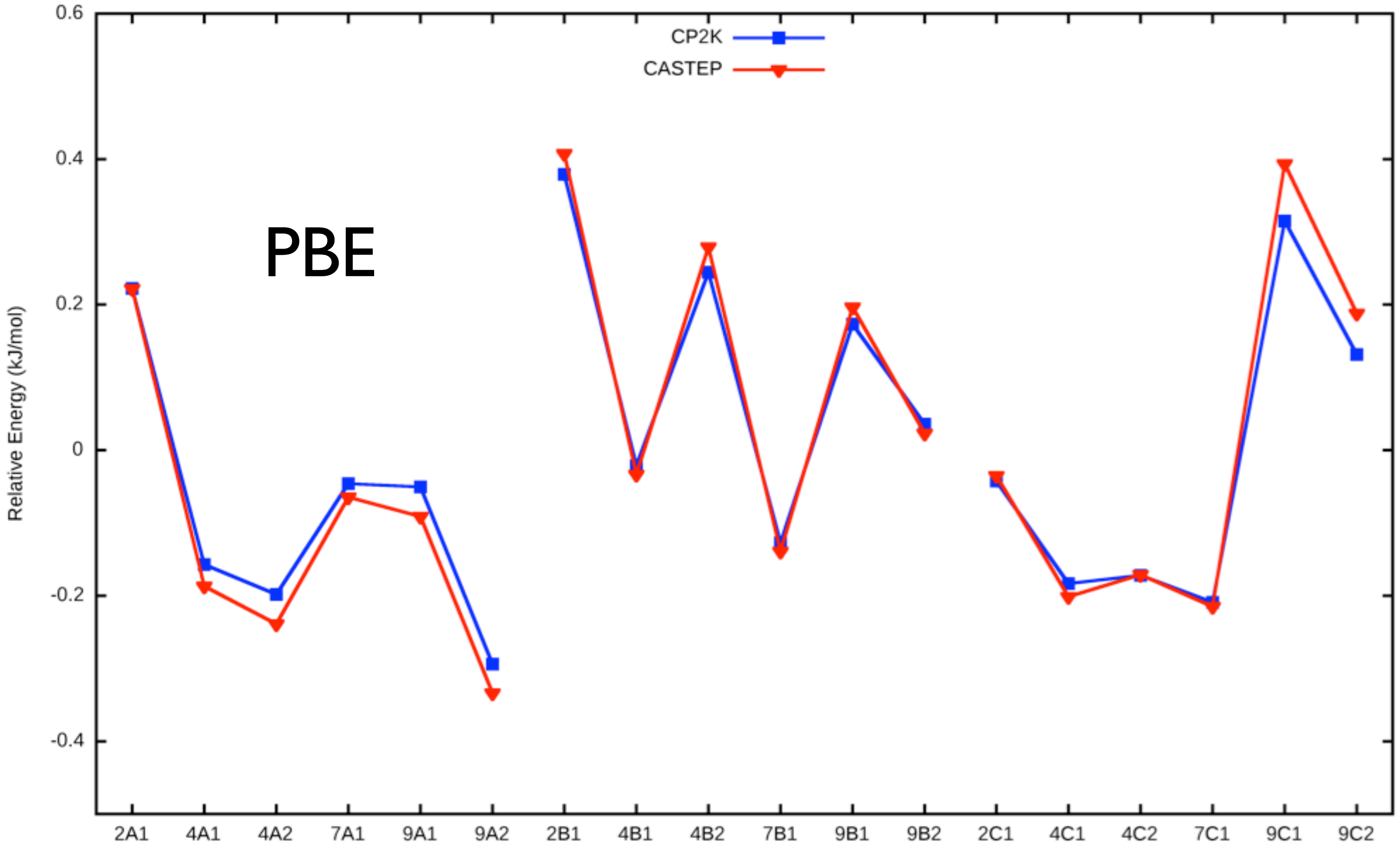


2C1



9A2

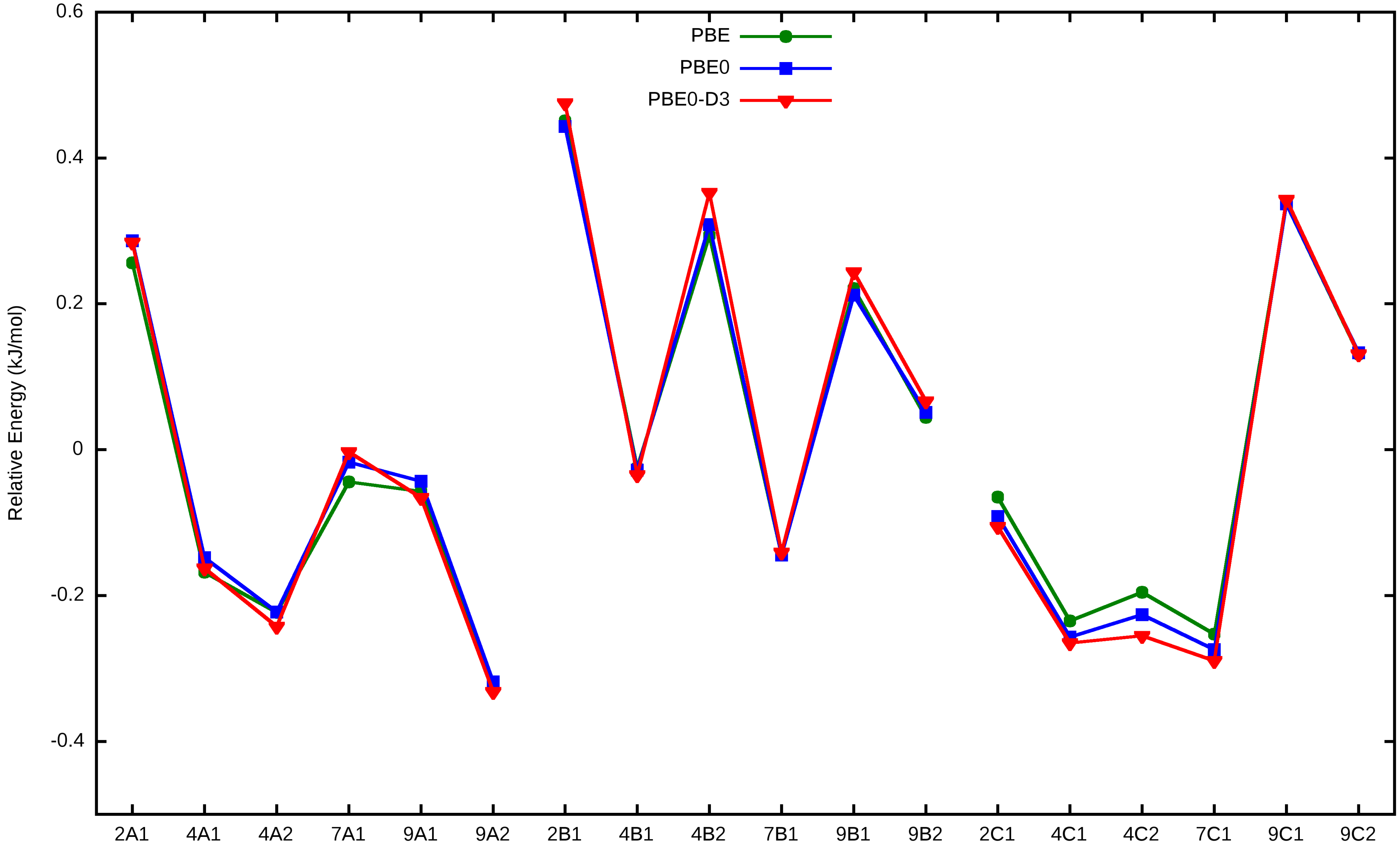
Accuracy of CP2K



Largest discrepancy 0.06 kJ/mol

GPW approach very comparable with full PW

Hybrid and vdW?



Varying HF and vdW does not change the order of stability

RI-MP2

JCTC Journal of Chemical Theory and Computation

Article

Electron Correlation in the Condensed Phase from a Resolution of Identity Approach Based on the Gaussian and Plane Waves Scheme

Mauro Del Ben,*,† Jürg Hutter,*,† and Joost VandeVondele*,‡

```
&XC
 &XC_FUNCTIONAL NONE
 &END XC_FUNCTIONAL
 &HF
  FRACTION  1.0
  &SCREENING
   EPS_SCHWARZ 1.0E-8
   SCREEN_ON_INITIAL_P FALSE
  &END SCREENING
  &INTERACTION_POTENTIAL
   POTENTIAL_TYPE TRUNCATED
   CUTOFF_RADIUS  6.55
   T_C_G_DATA t_c_g.dat
  &END
  &MEMORY
   MAX_MEMORY  1800
  &END
 &END HF
 &WF_CORRELATION
  METHOD  RI_MP2_GPW
  &WFC_GPW
   CUTOFF      300
   REL_CUTOFF  50
   EPS_FILTER  1.0E-12
   EPS_GRID    1.0E-8
  &END
  MEMORY  1800
  NUMBER_PROC  24
 &END
&END XC
```

```
&SUBSYS
 &CELL
  ABC  [angstrom] 4.388266 7.634326 7.182104
  MULTIPLE_UNIT_CELL 3 2 2
 &END CELL
 &TOPOLOGY
  COORD_FILE_NAME  hex.xyz
  COORD_FILE_FORMAT XYZ
  MULTIPLE_UNIT_CELL 3 2 2
 &END TOPOLOGY
 &KIND H
  BASIS_SET          cc-TZ
  RI_AUX_BASIS_SET   RI_TZ
  POTENTIAL GTH-HF-q1
 &END KIND
 &KIND O
  BASIS_SET          cc-TZ
  RI_AUX_BASIS_SET   RI_TZ
  POTENTIAL GTH-HF-q6
 &END KIND
&END SUBSYS
```

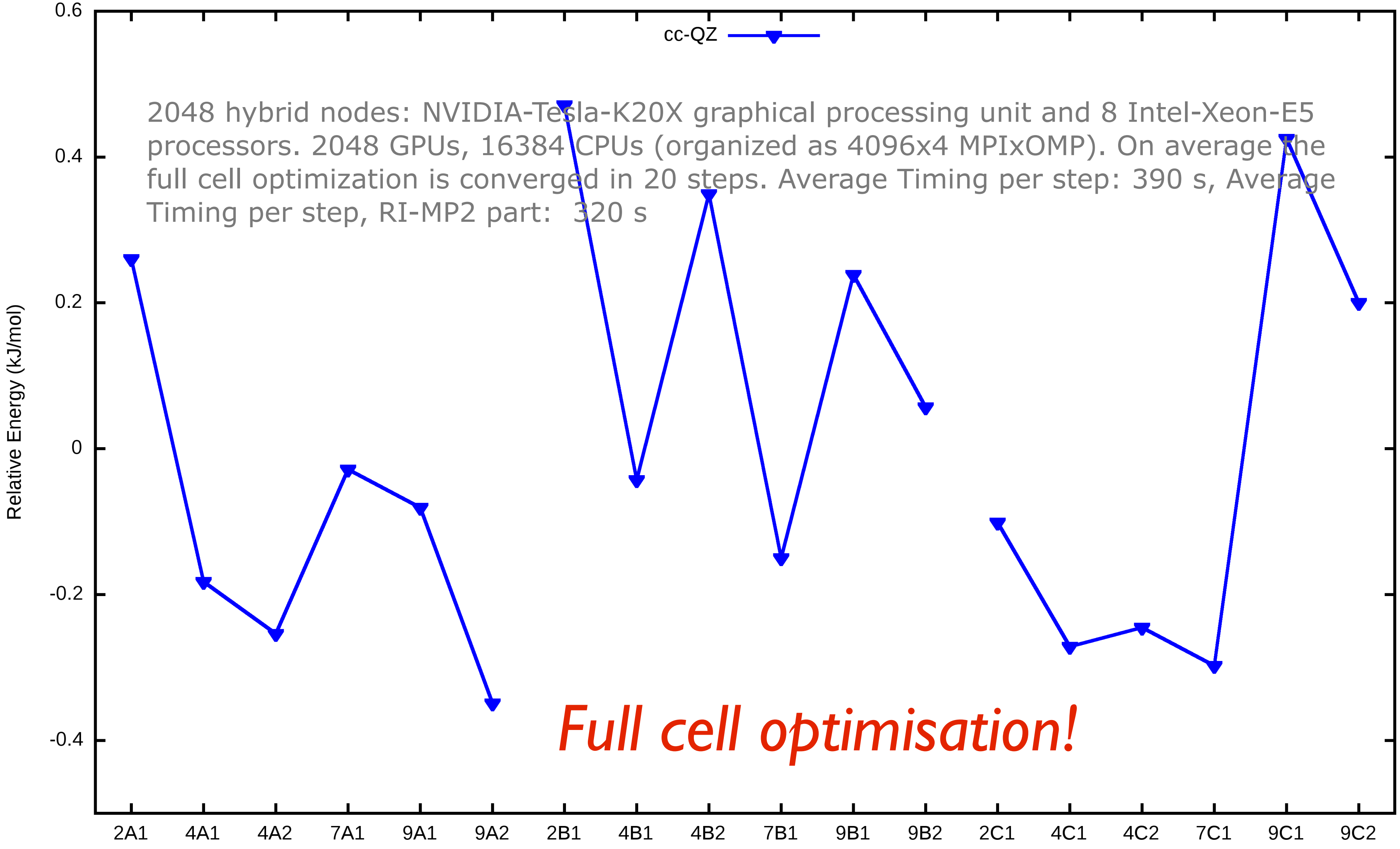
$O(N^5)$

dx.doi.org/10.1021/ct4002202 | *J. Chem. Theory Comput.* 2013, 9, 2654−2671

96 molecules

1078s on 3840 processors (Archer)

RI-MP2 results



2048 hybrid nodes: NVIDIA-Tesla-K20X graphical processing unit and 8 Intel-Xeon-E5 processors. 2048 GPUs, 16384 CPUs (organized as 4096x4 MPIxOMP). On average the full cell optimization is converged in 20 steps. Average Timing per step: 390 s, Average Timing per step, RI-MP2 part: 320 s

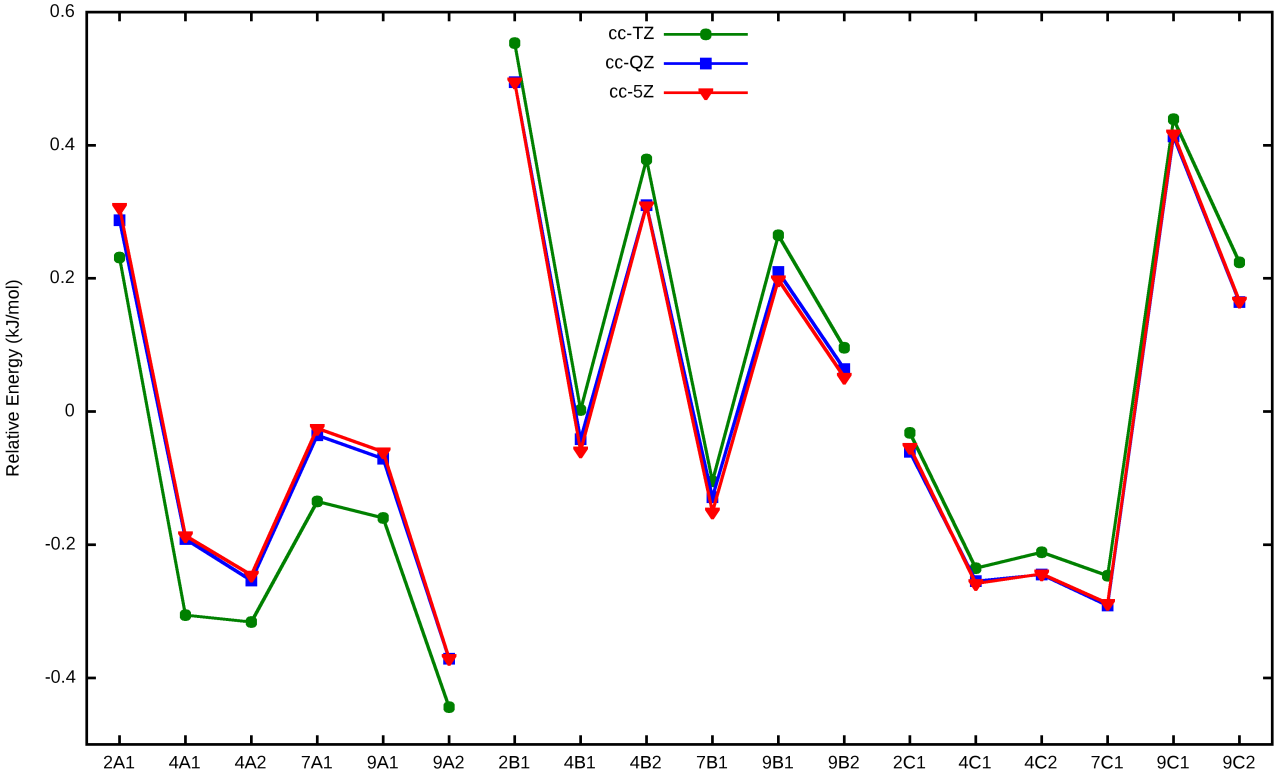
Full cell optimisation!

9A2 = Cc most stable

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

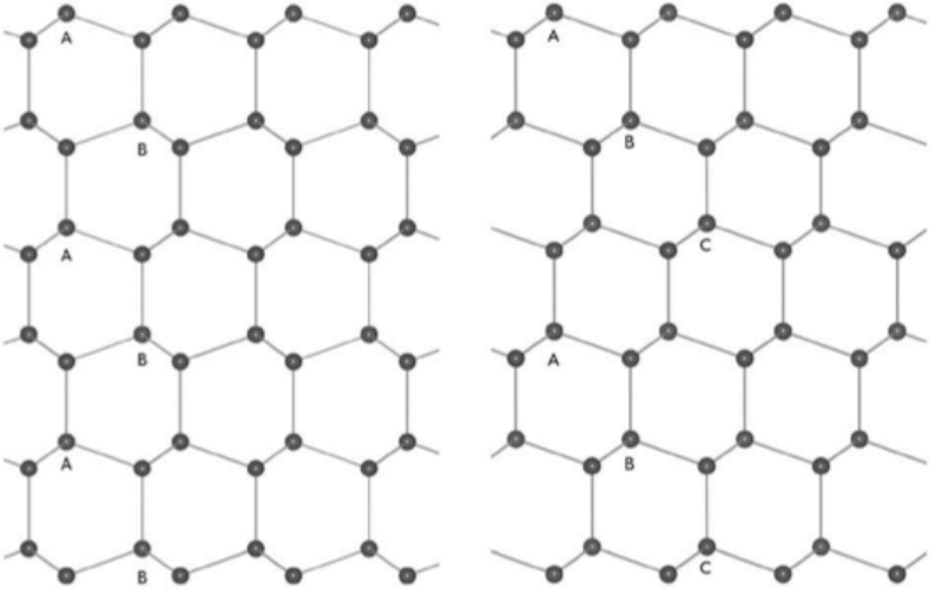
dRPA results

$O(N^4)$



	Basis Functions		Machine	Timing (s)	
	Primary	Auxiliary	Num Hyb Nodes	RI-MP2	RI-dRPA
cc-TZ	4560	10880	1024	279.1	216.9
cc-QZ	9120	19040	2048	523.8	347.6
cc-5Z	16000	29600	4096	-	1165.4

A possible new ice I phase?



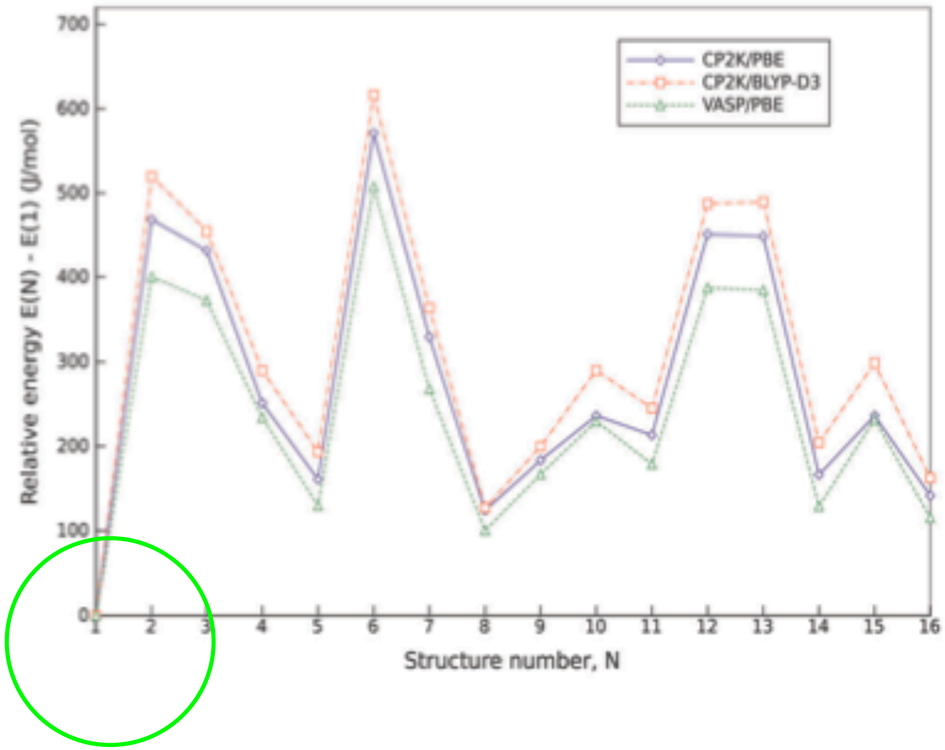
Hexagonal Cubic

•Work esp. by Ben J. Murray et al. (Leeds) (e.g. *Nature*, 2005) has highlighted the potential importance of cubic ice

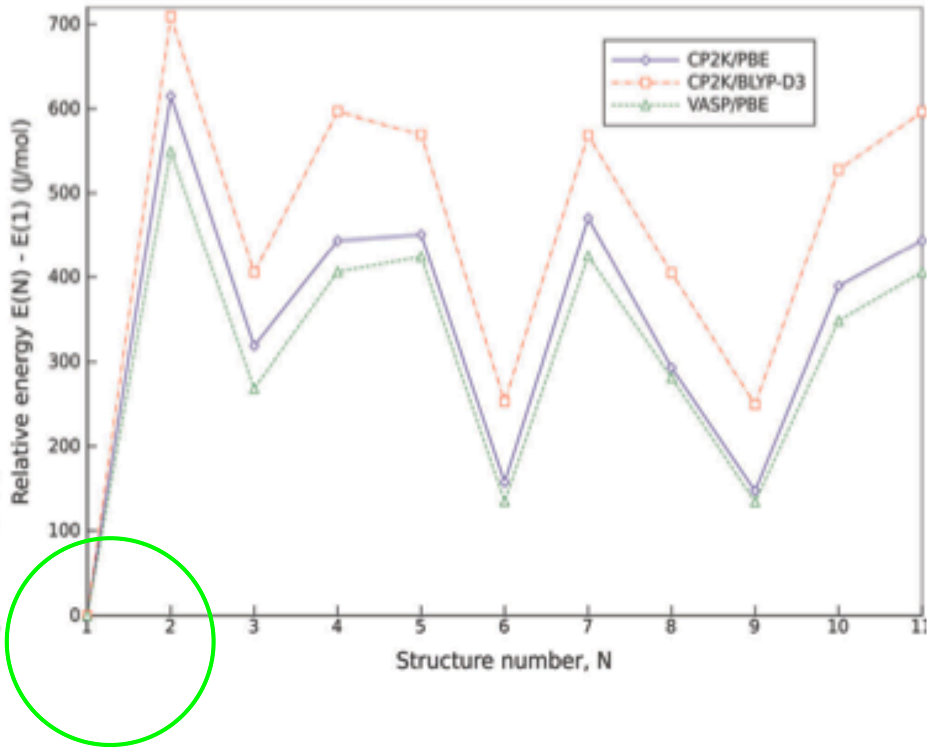
•How trustworthy are potential models for modelling cubic ice and nucleation? (cubic ice typically formed in brute force crystallisation studies despite being metastable w.r.t hexgonal ice)

•Assess proton ordering to establish any intrinsic bias (using DFT as a benchmark)

Comparing Ih and Ic



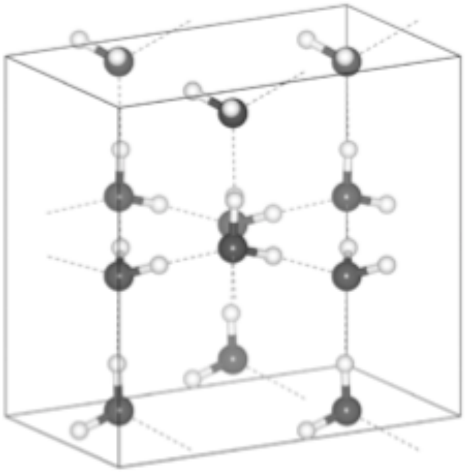
XIh



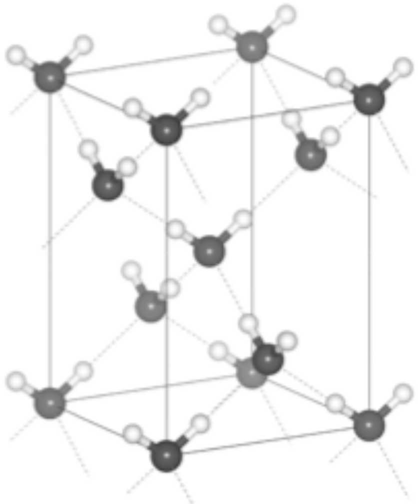
XIc

2 clear favoured configurations

A possible new ice phase?



XIh



XIc

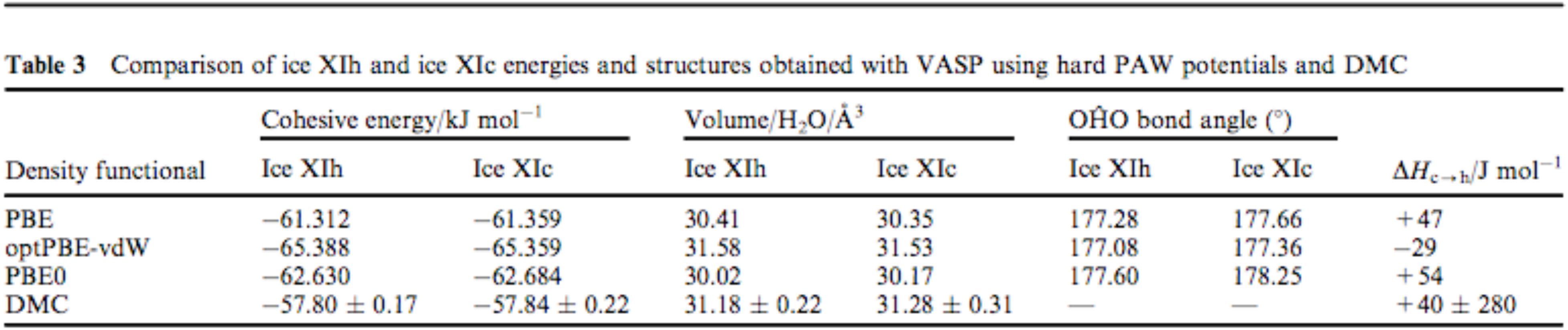


Table 3 Comparison of ice XIh and ice XIc energies and structures obtained with VASP using hard PAW potentials and DMC

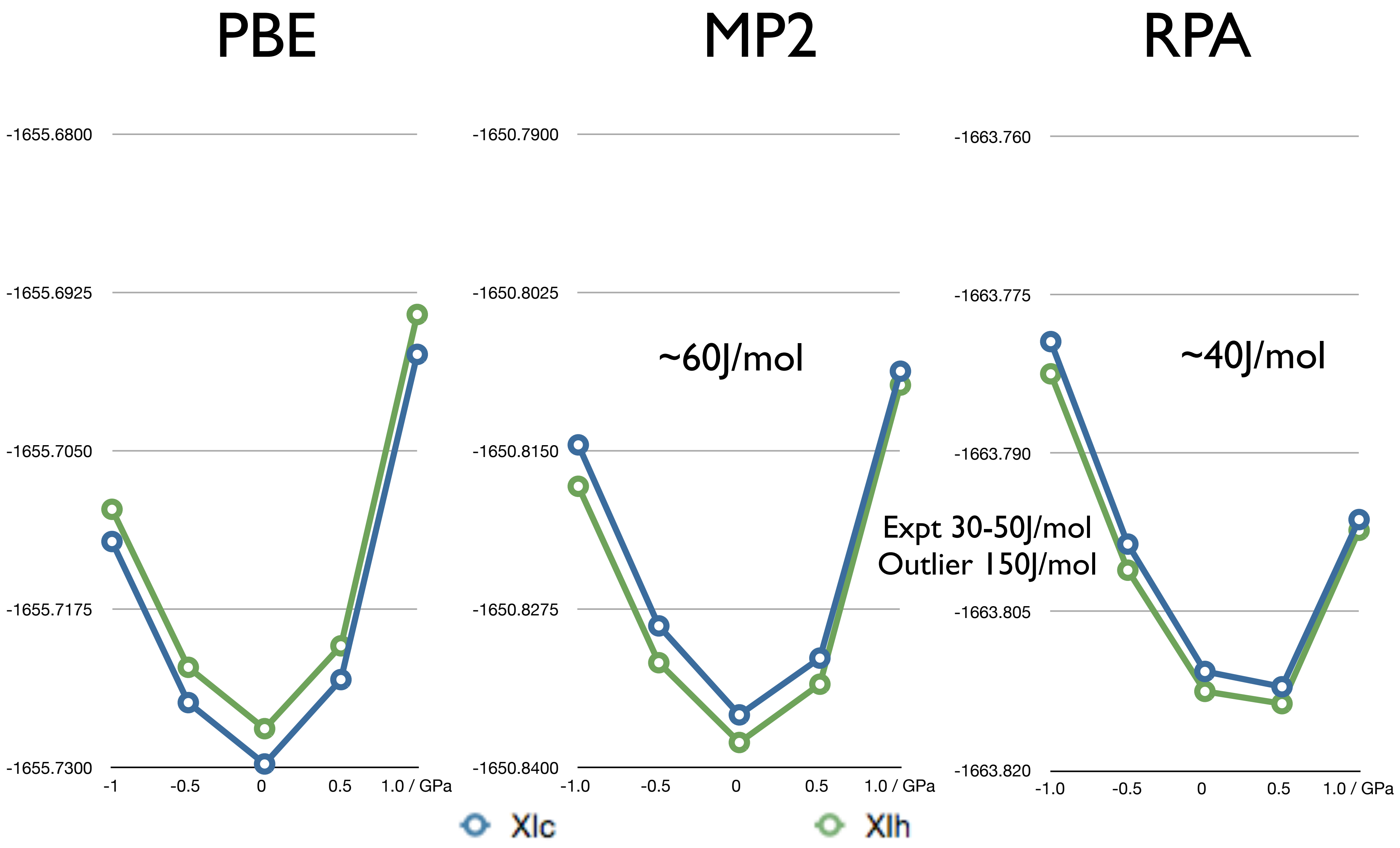
	Cohesive energy/kJ mol^{-1}		Volume/H_2O/Å^3		$O\hat{H}O$ bond angle (°)		
Density functional	Ice XIh	Ice XIc	Ice XIh	Ice XIc	Ice XIh	Ice XIc	$\Delta H_{c\to h}$/J mol^{-1}
PBE	−61.312	−61.359	30.41	30.35	177.28	177.66	+47
optPBE-vdW	−65.388	−65.359	31.58	31.53	177.08	177.36	−29
PBE0	−62.630	−62.684	30.02	30.17	177.60	178.25	+54
DMC	−57.80 ± 0.17	−57.84 ± 0.22	31.18 ± 0.22	31.28 ± 0.31	—	—	+40 ± 280

Structures are isoenergetic

XIc a possible competing phase?

Z Raza et al., PCCP, 2011

Ice XIh/XIc revisited



~60J/mol

~40J/mol

Expt 30-50J/mol
Outlier 150J/mol

XIh has an extra molecule in the second coordination shell - vdW stabilised

Mauro del Ben, Joost VandeVondele, BS, Christoph Salzmann unpublished results

Acknowledgements

Mauro del Ben, U Zurich
Joost VandeVondele, ETH Zurich
Christoph Salzmann, UCL

EPSRC