Canadian Journal of Chemistry
Revue canadienne de chimie

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Journal:	<i>Canadian Journal of Chemistry</i>
Manuscript ID	cjc-2017-0201.R1
Manuscript Type:	Article
Date Submitted by the Author:	27-Apr-2017
Complete List of Authors:	Yong, Xue; University of Saskatchewan, Physics and Engineering Physics Tse, John; University of Saskatchewan, Physics English, Niall; University College Dublin,
Is the invited manuscript for consideration in a Special Issue?:	TK Sham
Keyword:	ab initio molecular dynamics, pressure effect, ice, density functionals

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**optPBE-vdW Density Functional Theory Study of Liquid Water and Pressure-
Induced Structural Evolution in Ice Ih**

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ABSTRACT

The accuracy of several local and non-local van der Waals-corrected exchange correlation functionals on the description of the effect of pressure on ice has been investigated. In a preliminary survey, the non-local van der Waals-correction used in conjunction with the optPBE functional was shown to provide the best overall agreement on the structural parameters of ice *Ih* with experiments. More importantly, this combination reproduced correctly the recently observed crystal $\rightarrow$ crystal transformation in ice-*Ih* at 80 K *prior* to amorphisation. The predicted transition pressure of 1.9 GPa is somewhat higher, showing the current generation of *vdW*-functionals are still not sufficiently accurate for the ice system. The existence of an intermediate crystalline state with a shear-hexagonal structure confirms the earlier prediction that the collapse of crystalline structure under compression originates from the softening of phonon modes in ice *Ih*'s basal plane.

Key words: pressure, DFT, *vdw*

26

27 **Introduction**

28 Under different temperature and pressure conditions, water can exist in as many as 16
29 crystalline forms^{1,2} and several amorphous states^{3–6}. The discovery of pressure-induced
30 transformation from crystalline ice *Ih* to a high-density amorphous (HDA) phase at 77 K and 1
31 GPa in 1984³ was a major milestone in the study of the physics and chemistry of ice. HDA was
32 believed originally to be related to thermodynamic melting³, but it was later suggested that at low
33 temperatures (< 160 K), the formation of HDA is the result of a mechanical instability in the
34 water lattice where one of Born's stability conditions (Born's stability criteria require that all
35 elastic energy are positive definite)⁷ was violated⁸. It was conjectured that this putative violation
36 led to the collapse of the crystalline structure and resulted in the formation of the metastable
37 HDA form⁸. However, recently, experimental X-ray diffraction measurements⁹ under quasi-
38 hydrostatic conditions have led to discovery of a crystal→ crystal transition at ~1.1 GPa *prior* to
39 HDA formation. This observation has been reproduced by constant-pressure molecular-dynamics
40 (MD) calculations using the TIP4P/ice¹⁰ water potential by small pressure increment steps. This
41 experimental finding and MD analysis have provided significant and new information on the
42 modifications of the hexagonal lattice of crystalline ice leading to amorphisation, and detailed
43 characterisation of the resultant amorphous structure.

44 The accuracy of computed water properties depends critically on the methodology as well as on
45 the quality of the intermolecular potential. MD employing empirical force-fields has succeeded
46 reasonably well in reproducing many experimental properties of ice and liquid water under a
47 variety of thermodynamic conditions. Examples of properties include site-site radial distribution
48 functions, X-ray and neutron structure factors, the heat of vaporisation, and the maximum
49 density of liquid water^{11,12}. Naturally, the use of empirical force fields requires substantially less

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computational resources than first-principles-based methods, and can be applied to large systems. Recently, and perhaps more desirably for future studies, Density Functional Theory (DFT)-based *ab initio*-MD (AIMD) methods have also been used to model the structure and properties of water and ice in a wide range of environments^{13,14}.

The currently available generation of exchange-correlation functionals within the framework of the Generalised Gradient Approximation (GGA) is known to suffer from several known deficiencies when applied to the study of water, such as self-interaction error and lack of nuclear quantum effects. Another important reason for the failure of GGA functionals in the prediction of the structure of liquid water lies in the neglect of van der Waals (*vdW*) dispersion interactions. Indeed, based on such an approach, the polarisability of the water molecule is overestimated, leading to the cooperative enhancement of hydrogen bonding and “over-structuring”^{15–18}. Thus, there is a very low diffusion rate at room temperature with such a “pure” GGA approach, due to substantial underestimation of the fraction of broken hydrogen bonds. GGA functionals also produce inaccurate pressure-volume relationships^{15–17}. For example, an ambient-pressure and temperature equilibrium density of 0.80 g/cm³ was obtained by simulations performed within the isobaric-isothermal (*NPT*) ensemble using the PBE functional¹⁹. Recently, the application of DFT to water has been reviewed and the crucial role of dispersion interaction is explained^{13,14}. Uses of *vdW*-correction have led to better description on the structures of gas-phase clusters and liquid water. However, a similar understanding regarding the properties of ice remains elusive, although English had discussed the structures and system-size effects on liquid water and ice *Ih* with the Dion’s non-local dispersion approach²⁰. Santra *et al.* evaluated the *vdW* effects from the contribution of *vdW* interaction to the lattice energy and density on several ice phases at ambient and at high pressures²¹. In the present study, we compare the performance of several *vdW* exchange-correlation functionals implemented in the periodic electronic structure code, Vienna

ab initio simulation package (VASP)^{22–25} on ice *Ih*. The best functional will be used to investigate the pressure-induced structural evolution of ice *Ih* by AIMD simulations.

Computational methodology

The objective of this study is to determine the best-performing *vdW*-GGA functional suitable for simulation of water in the condensed phase. For this purpose, we test the fidelity of several *vdW* functionls in reproducing the experimental structural parameters on a proton-disordered hexagonal ice *Ih* configuration²¹ consisting of 12 water molecules (labelled as ‘Ice-*Ih*-12’, see Figure 1a) We have studied the Grimme’s empirical DFT-D2²⁶ and DFT-D3²⁷ (the latter with and without Becke-Johnson damping^{27,28}), and non-local *vdW*-DF proposed by Dion *et al*²⁹. in conjunction with the optPBE-*vdW* and rPW86-*vdW* functionals^{30,31}. Electron orbitals were expanded by PW basis sets with an energy cut-off of 1000 eV. Γ -point Brillouin-zone sampling was used. A time step of 1.0 fs was used for all MD calculations, using Born-Oppenheimer propagation. The SCF energy convergence threshold was set to 10^{-5} eV. As will be shown below (*vide infra*), the optPBE-*vdW* functional was found to be most suitable for our purposes.

To investigate the structural evolution of ice *Ih* under mechanical pressure, an orthorhombic proton-disordered ice model with 96 molecules (taken from ref. ³² and labelled ‘Ice-*Ih*-96’), Figure 1b was used. The system was first equilibrated at 80 K and 0.0 GPa with AIMD in the canonical (*NVT*) ensemble. This was followed by a series of AIMD calculations in the *NPT* ensemble with Langevin thermostat; these were performed from 0.0 GPa to 0.9 GPa with in step of 0.2 GPa. Each simulation was run for at least 10 ps. Near the anticipated phase transition between 1.0 GPa to 2.0 GPa, a smaller pressure increment of 0.1 GPa was used. Each simulation was run for 30 ps. Additional calculations were performed at 2.2 GPa, 2.4 GPa and 3.0 GPa after collapse of the ice structure. Each simulation was run for 10 ps. In addition, for completeness,

the DFT-D2 and optPBE-*vdW* functional was also used to simulate liquid water via AIMD, on a model system consisted of 96 molecules at a density of 1.0 g/cm³. After initial relaxation, MD simulations at 300 and 330 K were performed in the *NVT* ensemble for at least 10 ps.

Results and Discussion

Comparison of *vdW*-corrected functionals on the prediction of the cell constants of ice *Ih*

Table 1 compares the experimental³³ and fully optimised internal coordinates and lattice constants from a variety of *vdW*-corrected functionals on the Ice-*Ih*-12 model. Within this group of functionals, results obtained with the non-local rPW96-*vdW* and optPBE-*vdW* functionals are in better agreement with experimental data than the empirical Grimme's *vdW* empirical D2 and D3 functionals. The rPW96-*vdW*-predicted *a* and *b* cell constants are 0.12 Å longer, and the *c* axis is 0.30 Å shorter. In comparison, the optPBE-*vdW*-predicted *a*- and *b*- axis lengths of 7.72 Å are in reasonable agreement with experiment, whilst that of the *c*-axis is also underestimated, by 0.47 Å. The overall volume predicted by optPBE-*vdW* functional is in slightly better agreement with the experimental value and, although this functional is not perfect, it was chosen for ensuing ice *Ih* AIMD calculations

Pressure-induced structural transformations in ice *Ih*

It is known from experiment that if ice is compressed at 80 K, it transforms to a high-density amorphous form³. The underlying transformation mechanism is debated. Recently, from experiment under quasi-hydrostatic condition, we found that ice *Ih* transformed to a new crystalline structure *prior* to amorphisation⁹. This observation was reproduced by carefully compressed *NPT* MD calculations with the TIP4P/ice water potential. Indeed, reproducing this result would constitute a challenging problem for AIMD, and we pursue this goal further here. In so doing, we performed *NPT* AIMD using the optPBE-*vdW* functional. The evolution of the

computed density with pressure at 80 K is shown in Figure 2. Up to 1.8 GPa, density increased monotonically until 1.9 GPa, where a sudden jump was observed. Examination of the resulting structure indicated it was not amorphous and remained crystalline. Therefore, a crystal $\rightarrow$ crystal transformation has occurred. Further compression led to complete amorphisation at 2.3 GPa. Snapshots of the temporal changes in the structure taken from the AIMD trajectory at different pressures are shown in Figure 3. A clearly distorted oxygen lattice was observed. The static structure factor $S(q)$ calculated from the MD trajectory for this intermediate crystalline phase shows splitting of the Bragg reflections, and is in reasonable agreement with the observed x-ray diffraction pattern, as shown in Figure 4. The occurrence of a novel crystal $\rightarrow$ crystal structural transformation was correctly reproduced by the present AIMD as well as classical MD calculations using the TIP4P/ice model; naturally, pressures were adjusted carefully in small increments near the phase transition. The AIMD crystalline transition pressure of ~ 1.9 GPa is higher than the experiment pressure and that predicted by TIP4P/ice-based MD calculations of 1.1 – 1.3 GPa. A higher calculated transition pressure of *ca.* 0.8 GPa is not unreasonable, as *vdW* corrected density functional calculations also overestimate the transition pressures between several high- pressure crystalline forms of ice¹³. This seems to be a deficiency of the current generation of *vdW*-functionals.

To examine structural changes in compressed ice, we have computed the O-O-O angle (θ , see Figure 5a) distribution function, $P(\theta)$ (cf. Figure 5b). The results depicted in Figure 5b show three types of distributions. Before the transition, the O-O-O angle is distributed between 90° and 120° , with the maximum at 109° , the expected tetrahedral angle in ice *Ih*. For the intermediate crystalline phase, $P(\theta)$ becomes broadened, spanning between 80 and 140° , with the mean angle shifted to $\sim 100^\circ$. In the amorphous state at 2.4 GPa, $P(\theta)$ is very broad with a plateau

region spread between 70° and 120° . The analysis shows that the main structural change in the transition to the sheared form is the distortion of the O-O-O angle from the ideal tetrahedral arrangement.

We now focus on how the local environment of individual water molecules were affected by pressure and how these changes are related to the phase transitions. Figure 6a depicts the local chemical environment of a water molecule (labeled as 0) in ice, where the four hydrogen-bonded molecules (1–4) to 0 formed the 1st-nearest neighbour shell of 0. The 2nd-nearest neighbour shell of 0 is shown as molecule 5, which can be both hydrogen-bonded and non-hydrogen bonded to 0. Figure 6a shows the oxygen-oxygen radial distribution functions, $g_{OO}(r)$ for ice at different pressures: ice *Ih* at 1.6 GPa, shared-crystalline ice at 2.0 GPa, and HDA at 2.4 GPa and 3.0 GPa, and ice XV at 0.9 GPa. From Figure 6b, it is clearly visible that the positions of the first peak (first coordination shell) in $g_{OO}(r)$ for all of the ice forms are similar at different pressures. However, profound differences in the profiles and interatomic O-O distances of the second peak are found. In ice-*Ih*, the first and second peaks are clearly separated with a gap of ~ 1.0 Å. In comparison, in the intermediate crystalline phase, the width of the second peak (*i.e.*, the oxygen distribution in the second coordination shell) is broader, and its onset moves closer to the first peak, and is only separated from the first peak by ~ 0.4 Å. In HDA, the second peak is even broader, and moves gradually towards the first peak. The absence of a clear separation between the first and second O-O peaks indicates that the oxygen atoms in the second shell are now compressed closer to the first coordination shell. Incidentally, the mean position of the second peak in the $g_{OO}(r)$ of HDA at 3.0 GPa is similar to that of crystalline ice XV.

To better identify the structures of the first and second coordination shells, the oxygen-oxygen radial distributions of the fourth ($g_{OO4}(r)$) and fifth ($g_{OO5}(r)$) neighbours (cf. Figure 6a) of the ice

systems were computed, and the results are shown in Figure 7. The calculated $g_{\text{OO}}(r)$ of the ices are quite similar, except the width is clearly much broader in the HDA case. In comparison, the peak in the $g_{\text{OO}}(r)$ distribution shifts progressively from 4 Å in lower-density ice *Ih* to 3.0 Å in HDA and approaches the peak position of $g_{\text{OO}}(r)$, which corresponds well with that of crystalline ice XV. Moreover, the peak width also becomes broader with increasing pressure. The observation leads again to the same conclusion that water molecules in the second coordination shell are compressed into the first coordination shell, a fact known already from a previous study⁸. It is important to identify the origin of the water molecule forced into the empty space, as it can be either linked to the central water through a hydrogen bond (*e.g.*, 4th water) or not linked directly (non-hydrogen bond, *i.e.*, 5th water). To distinguish the two possibilities, the probabilities of hydrogen-bonded ($p_{\text{hb}}(r)$) and non-hydrogen bonded ($p_{\text{nhb}}(r)$) of the fourth and fifth water in ice *Ih*, the intermediate crystalline phase, and HDA were computed and are compared in Figure 6c. In ice *Ih*, water molecules situated in the first and second coordination shells are linked to water molecule's oxygen atom *via* continuous hydrogen-bond networks, and, therefore, $p_{\text{nhb}}(r)$ is zero. Upon compression, in HDA, $p_{\text{nhb}}(r)$ increases significantly, and, at 3.0 GPa, the mean positions of $p_{\text{hb}}(r)$ and $p_{\text{nhb}}(r)$ of HDA-3.0 GPa almost overlaps with that of ice XV at 3 Å. This indicates that in the second shell, the fourth and fifth water molecules are actually located in the first coordination shell. The comparable $p_{\text{nhb}}(r)$ of HDA with ice XV bears the hallmark of incipient formation of an independent and inter-penetrating network, a feature of high-density ice XV and VIII. Therefore, HDA ice may simply be regarded as an intermediate structure between the continuous hydrogen-bonding network of lower-pressure ices (ice *Ih*, II and IX) and the independent inter-penetrating hydrogen-bonded network structure in high-density ices. In fact, when HDA ice is compressed beyond 4.5 GPa, a structure with $g_{\text{OO}}(r)$ reminiscent of ice VIII has been predicted and was observed experimentally³⁴. It is expected that

substantial energy will be required to surpass the energy barrier for such a large-magnitude displacement required to re-arrange the hydrogen atoms in order to convert a continuous hydrogen-bonded network (*e.g.*, as in ice *Ih*) into independent and inter-penetrating hydrogen-bonded networks (a quintessential signature of ices XV and VIII). The required energy is likely to be inaccessible at low temperatures, and, therefore, compression of ice *Ih* at below 150 K led to the formation of a frustrated, disordered dense ice (HDA) structure.

Structure of liquid water with *vdW*-corrected functionals

Even though the structure and properties of liquid water computed from AIMD has been thoroughly reviewed recently¹³, we compare for completeness the performance of the empirically-corrected (D2) and optPBE-*vdW* functionals on the simulation of liquid water. The DFT-D2 calculated oxygen-oxygen ($g_{OO}(r)$), oxygen-hydrogen ($g_{OH}(r)$), and hydrogen-hydrogen ($g_{HH}(r)$) radial distribution functions ($g(r)$) at 300 K and 330 K are shown in Figure 9. Compared to PBE results, significant improvements are observed - in essential agreement with experiment for the peak positions and heights for ($g_{OO}(r)$), ($g_{OH}(r)$), and ($g_{HH}(r)$). However, the optPBE-*vdW* calculations provide even better radial distribution functions for liquid water when compared to experiment. Compared to DFT-D2 and PBE, the first peak of ($g_{OO}(r)$) of 2.78 Å obtained from optPBE-*vdW* shifted by 0.02 Å to a longer distance (Figure 9a). Moreover, the height of the first peak is reduced significantly. Hence, the optPBE-*vdW* produced a “softer” structure and is in better agreement with experiment. These results are consistent with previous investigations^{19,20}, where a similar systematic improvement vis-à-vis PBE in $g_{OH}(r)$ and $g_{HH}(r)$ was observed from the inclusion of non-local *vdW* effects (cf. Figure 9b-c).

We further examined the effects of *vdW*-treatment on hydrogen bonding. A hydrogen bond is defined based on the geometry constraint related to the hydrogen-bond acceptor (A) and donor (D) atoms. Two H₂O molecules are considered to be hydrogen bonded when the O-O distance is

216 less than 3.5 Å and the $H_D-O_D-O_A$ angle (β) is less than 30°^{11,16} (cf. Figure 10a). We computed
 217 the average number of intact hydrogen bonds on one water molecule, and decomposed them into
 218 hydrogen-bond-accepting-(A) and donating-(D) types. The results suggest that the DFT-D2,
 219 *vdW*-DF (specifically, optPBE-*vdW*), and PBE functionals all produce liquid water with most
 220 molecules (~80%) adopting the A2D2 type of hydrogen bond – featuring two acceptors and two
 221 donors, *i.e.*, the commonly-accepted tetrahedral environment (cf. Figure 10b). This is the
 222 traditional condensed-phase picture of a water molecule, which accepts and donates two
 223 hydrogen bonds. However, some water molecules have partially broken hydrogen bonds, and
 224 therefore adopt A1D1, A1D2, A2D1 and A3D2 motifs, but at much lower probabilities. The
 225 main difference in the results obtained from DFT-D2, *vdW*-DF, and PBE functionals lies in the
 226 relative ratios between A1D1:A1D2:A2D1:A3D2. DFT-D2 and PBE produced similar results.
 227 For non-local *vdW*-DF functional calculations, the number of A2D2 hydrogen bonds decreases
 228 slightly, whilst there is a concomitant increase in the number of A1D1, A2D1 and A1D2 species.
 229 These results indicate once again that the non-local *vdW* effect is to ‘soften’ the water structure,
 230 leading to a greater prevalence of broken hydrogen bonds. This is in agreement with the broader
 231 peaks in the RDF of liquid water obtained from the *vdW*-DF functional. It is significant to point
 232 out the A1D1:A1D2:A2D1:A3D2 ratios obtained from the present *vdW*-DF calculations are
 233 almost identical to previous work where a more elaborate functional including exact exchange
 234 and non-local *vdW* correction was used¹⁹. The calculated diffusion coefficient
 235 ($D = \frac{1}{6} \frac{d}{dt} \langle |\mathbf{r}(t) - \mathbf{r}(t_0)|^2 \rangle$) from optPBE-*vdW* is $1.5 \times 10^{-9} \text{ m}^2/\text{s}$ at 330 K and $1.4 \times 10^{-9} \text{ m}^2/\text{s}$ at 300
 236 K. In comparison to the experimental values of $2.3 - 2.4 \times 10^{-9} \text{ m}^2/\text{s}$ ³⁵⁻³⁷ at 300K, the theoretical
 237 values are somewhat lower but not unreasonable. In addition, the current results are very similar

to a more elaborate DFT study of liquid water¹⁹ which included exact-exchange and dispersion effects.

Conclusions

Compared to local *vdW*-corrected DFT-D2/3 and PBE functionals, it is found that the non-local *vdw*-corrected optPBE-*vdW* functional gave the best lattice parameters of crystalline ice *Ih* in comparison with experiment. Significantly, the recently observed crystal→ crystal transition *prior* to amorphisation at 80 K was also correctly reproduced with AIMD calculations using this functional. The results confirm the transformation from the ice *Ih* to the intermediate sheared lattice is due to a sheared instability predicted in an earlier study⁸. The presented results suggest that, at 80 K, pressure-induced amorphisation of ice *Ih* is not a one-step process, as conjectured previously, but takes place rather *via* an intermediate crystalline structure. The major structural change accompanying pressurisation lies in the collapse of the second coordination shell into the first, gradually *forming an independent inter-penetrating hydrogen-bonding network* similar to that underlying crystalline ice XV which is the thermodynamically stable polymorph in the same pressure range. It is also shown the optPBE-*vdW* functional reproduces a softer liquid water structure with the calculated radial distribution functions and hydrogen-bonding network in better agreement with experiment.

Acknowledgements

XY acknowledges the financial support from the China Scholarship Council. All authors thank the Irish Centre for High-End Computing and Compute Canada for provision of computational facilities.

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315 Figure 1. Structure of (a) Ice-Ih-12 and (b) Ice-Ih- 96.

316 Figure 2. Density changes (ρ/ρ_0) with pressure relative to 0.5 GPa for the Ice-Ih-96 from *NPT*
317 AIMD calculations at different pressures.

318 Figure 3. Structure of the Ice-Ih-96 at 0 GPa, the intermediate phase at 1.9 GPa, and amorphised
319 ice at 2.2 GPa.

320 Figure 4. X-ray diffraction patterns for the intermediate phase from AIMD calculations (red) at
321 2.0 GPa and experimental X-ray diffraction patterns (black) at 1.13 GPa corresponding to that of
322 the sheared structure⁹.

323 Figure 5. (a) Schematic representation of the O-O-O angle, (θ), in ice. (b) The θ -angle
324 distribution function, $P(\theta)$ in ice Ih, the intermediate crystalline phase, and HDA.

325 Figure 6 (a) Schematic representation of the local environment of a water molecule (labeled as 0)
326 in ice, where the four hydrogen bonded molecules (1–4) to 0 form the 1st nearest neighbour shell
327 of 0. The 2nd nearest neighbour of 0 is shown as molecule 5, which can be both hydrogen-bonded
328 and non-hydrogen bonded to 0. (b) Oxygen-oxygen radial distribution functions, $g_{OO}(r)$ for ice-
329 Ih (1.6 GPa), intermediate crystalline phase (2.0 GPa), HDA at 2.4 and 3.0 GPa and ice XV (0.9
330 GPa). (c) The probability of hydrogen bonded ($p_{hb}(r)$) and non-hydrogen bonded ($p_{nhb}(r)$) 2nd
331 nearest neighbour for ice Ih, sheared phase, and HDA at 2.4 GPa.

332 Figure 7. Comparison of the distribution of the (a) fourth and (b) fifth nearest neighbour water in
333 ice Ih, intermediate crystalline phase, the HDA at 2.4 and 3.0 GPa with ice XV.

334 Figure 8. (a) Calculated oxygen-oxygen radial distribution functions ($g_{OO}(r)$) for ice XV
335 (labelled as ice XV) and HDA at 3.0 GPa (labelled as HDA-3.0GPa). (b) The probability of

hydrogen-bonded ($p_{\text{hb}}(r)$) and non-hydrogen-bonded ($p_{\text{nhb}}(r)$) 2nd nearest neighbour for ice XV and HDA at 3.0 GPa.

Figure 9. The (a) oxygen-oxygen ($g_{\text{OO}}(r)$), (b) oxygen-hydrogen ($g_{\text{OH}}(r)$) and (c) hydrogen - hydrogen ($g_{\text{HH}}(r)$) radial distribution function obtained from NVT-MD simulations at 300 and 330 K and 0.0 GPa using different exchange-correlation functionals compared with the experimental data³⁸; the vdW-DF used is optPBE-vdW.

Figure 10. (a) Depiction of the geometric position for the definition of a hydrogen bonding in ice, where O_{D} and O_{A} are the hydrogen-bonding donor and acceptor. The $\text{H}_{\text{D}}\text{-O}_{\text{D}}\text{-O}_{\text{A}}$ angle is labelled as β . Two oxygen atoms are considered as hydrogen bonded if their distance is within 3.5 Å and the related angle β is less than 30°. (b) Percentage-wise decomposition into hydrogen-bond-accepting-(A), and donating-(D) types of the intact hydrogen bonds per water molecules in liquid water from NPT AIMD simulations at 300 K; the vdW-DF used is optPBE-vdW.

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Table 1. Comparison of calculated and experimental lattice constants and volume for ice Ih-12

Functional	a (Å)	b (Å)	c (Å)	Volume (Å ³ /H ₂ O)
PBE	7.64	7.64	7.19	30.32
DFT-D2	7.52	7.52	7.08	28.90
DFT-D3	7.55	7.55	7.09	29.18
DFT-BJ	7.55	7.55	7.09	29.15
optPBE- <i>vdW</i>	7.72	7.72	7.26	31.27
rPW86- <i>vdW</i>	7.90	7.90	7.43	33.45
Exp ^a	7.78	7.78	7.73	32.05

^a Experimental results taken from ref. 33

Fig. 1 Structure of (a) Ice-Ih-12 and (b) Ice-Ih- 96.

80x29mm (192 x 192 DPI)

Density changes (ρ/ρ_0) with pressure relative to 0.5 GPa for the Ice-Ih-96 from NPT AIMD calculations at different pressures.

338x190mm (96 x 96 DPI)

Structure of the Ice-Ih-96 at 0 GPa, the intermediate phase at 1.9 GPa, and amorphised ice at 2.2 GPa.

338x190mm (96 x 96 DPI)

X-ray diffraction patterns for the intermediate phase from AIMD calculations (red) at 2.0 GPa and experimental X-ray diffraction patterns (black) at 1.13 GPa corresponding to that of the sheared structure⁹.

238x165mm (96 x 96 DPI)

Figure 5. (a) Schematic representation of the O-O-O angle, (θ), in ice. (b) The θ -angle distribution function, $P(\theta)$ in ice Ih, the intermediate crystalline phase, and HDA.

207x105mm (96 x 96 DPI)

(a) Schematic representation of the local environment of a water molecule (labeled as 0) in ice, where the four hydrogen bonded molecules (1–4) to 0 form the 1st nearest neighbour shell of 0. The 2nd nearest neighbour of 0 is shown as molecule 5, which can be both hydrogen-bonded and non-hydrogen bonded to 0. (b) Oxygen-oxygen radial distribution functions, $g_{OO}(r)$ for ice-Ih (1.6 GPa), intermediate crystalline phase (2.0 GPa), HDA at 2.4 and 3.0 GPa and ice XV (0.9 GPa). (c) The probability of hydrogen bonded (phb(r)) and non-hydrogen bonded (pnhb(r)) 2nd nearest neighbour for ice Ih, sheared phase, and HDA at 2.4 GPa.

217x144mm (192 x 192 DPI)

Comparison of the distribution of the (a) fourth and (b) fifth nearest neighbour water in ice Ih, intermediate crystalline phase, the HDA at 2.4 and 3.0 GPa with ice XV.

332x122mm (96 x 96 DPI)

(a) Calculated oxygen-oxygen radial distribution functions ($g_{OO}(r)$) for ice XV (labelled as ice XV) and HDA at 3.0 GPa (labelled as HDA-3.0GPa). (b) The probability of hydrogen-

174x212mm (96 x 96 DPI)

229x144mm (192 x 192 DPI)