



## Predicting the hydrogen bond ordered structures of ice Ih, II, III, VI and ice VII: DFT methods with localized based set

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### ABSTRACT

We analyzed the transferability of the density functional methods in “predicting” the proton ordered structures of ice Ih, II, III, VI and ice VII and found that the subtle energetic associated with proton ordering only depends on the electrostatic components of the total energy. Four commonly used exchange–correlation functionals (BLYP, PBE, PW91 and RPBE) were tested and all of them yielded consistent results, provided sufficiently high order multipolar expansion (up to hexadecapole) of the electron density is included. The proton ordered structures of the above-mentioned phases predicted by first principle methods agree well with the experimental findings.

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### 1. Introduction

Recently, the proton-ordering transition in crystalline ice has received renewed attention [1–5]. Two new proton ordered phases of ice related to ice V and ice XII were found experimentally in ice samples doped with HCl [1]. It is suggested by the experimentalists that subtle difference in relative stability governs the proton-ordering transitions [3,6,7]. This means it is important to predict the exact relative energies of different configurations of an ice phase for both current empirical models of water and modern quantum chemical methods. While it was shown that many of the commonly used empirical models failed to yield correct proton ordered form of ice Ih even after adjusting their parameters deliberately [2], the first principle methods have demonstrated their capabilities in the analysis of proton-ordering transitions and orientational disorder patterns in ice Ih and ice VII [2,5,9]. Inspired by recent success of the first principle methods, we will systematically study the transferability of first principle methods in “predicting” proton ordered forms of crystalline phases.

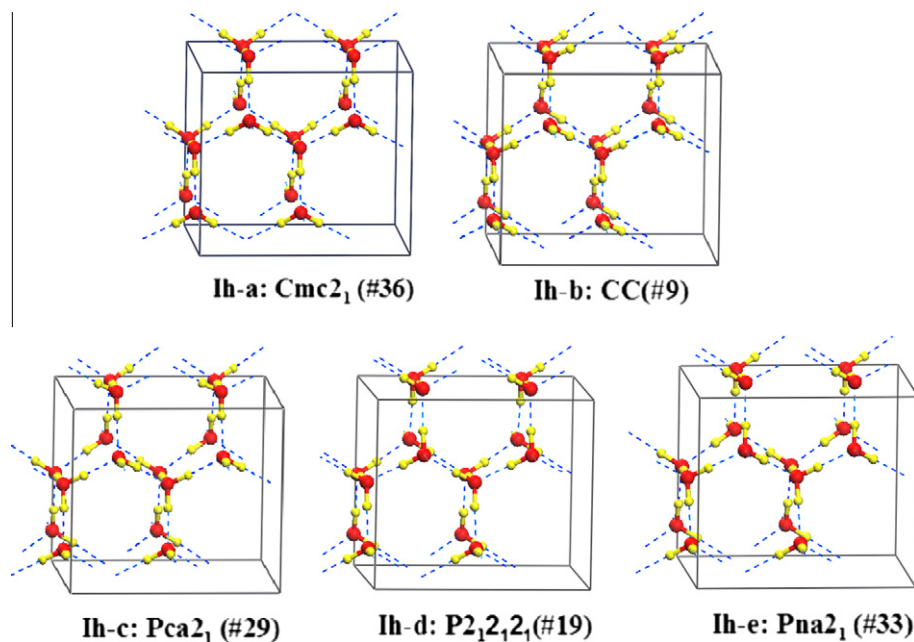
So far proton-ordering transitions have been observed experimentally in some “crystalline” phases of ice adjacent to liquid phase (ice Ih, III, V, VI and ice VII), but not all transitions have been calibrated with the same level of confidence by experiments [3,4]. The most experimentally well-calibrated order/disorder transition is between ice VII and ice VIII [5]. In 1980s, it is found that proton-ordering transition from disordered ice Ih to proton ordered ice XI

can only be found on ice sample doped with KOH [6,7]. The same dopant, however, does not seem to promote proton ordering in ice V and ice VI [8]. Recently, it is found that HCl is a more effective dopant and a new proton ordered phase related to ice V and ice XII is identified [1]. Different proton ordering schemes in ice VI were proposed in the literature [9,10], but the proton ordered counterpart of ice VI has not been identified by direct neutron diffraction experiment. It should be noted here that the transition between ice III and ice IX is quite different from other cases. Normally, the space group symmetry is reduced in the proton-ordering transitions (ice Ih, ice V and ice VII), but both ice III and ice IX have the same symmetry  $P4_12_12$ . This space group does not require the proton positions on the bonds to be equivalent, therefore all possibilities between full order and full disordered are allowed. So far, thermodynamic evidences concerning the degree of ordering in ice III and ice IX is not consistent [4,11,12].

On the theoretical side, it is interesting to note that the inconsistency in the prediction of proton ordering schemes by first principle methods in the above-mentioned phases seem to closely follow their experimental uncertainties [5,13]. As far as we know, the structure of ice VIII (proton ordered form of ice VII) is the only case that is free from ambiguity, while the most studied case would be ice Ih and ice XI. Also, there has been a long debate on whether ice XI is ferroelectric (Ice Ih(a) in Fig. 1) or anti-ferroelectric (Ice Ih(b) in Fig. 1). Even until recent years, conflicting results regarding the relative stability between these two structures were reported [10,14]. In the cases of ice IX (proton ordered form of ice III) and ice VI' (tentative name for the proton ordered form of ice VI), different candidates were proposed in the literature [10,14].

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**Fig. 1.** Five ice Ih configurations: Ih-a is a ferroelectric structure with  $Cmc2_1$  (#36) symmetry group and was identified as the structure of ice XI [7], Ih-b is the structure with largest net dipole moment and it has  $CC$  (#9) symmetry group, Ih-c is a ferroelectric structure with  $Pca2_1$  (#29) symmetry group, Ih-d is an anti-ferroelectric structure with  $P2_12_1$  (#19) symmetry group, and Ih-e is an anti-ferroelectric structure with  $Pna2_1$  (#9) symmetry. The lattice constants are fixed at  $a = 4.4923$  Å,  $b = 7.7808$  Å and  $c = 7.3358$  Å [32].

First principle methods are certainly not free from approximations: various forms of the exchange and correlation functionals and different choices of basis functions were used in previous theoretical studies. As a result, a direct comparison between two calculations might not be very conclusive. In addition, a few issues regarding the effects of the small unit cell size, and the convergence of a basis set were mentioned in the previous studies. We consider that it is important to carry out a systematic study to verify the predictive power of first principle methods. In this work, we will focus on examining the proton ordered form of ice Ih, ice III, ice VI and ice VII. In addition, we have also added ice II, a truly proton ordered phase that is stable to relative high temperature, into our testing set to serve as an independent check.

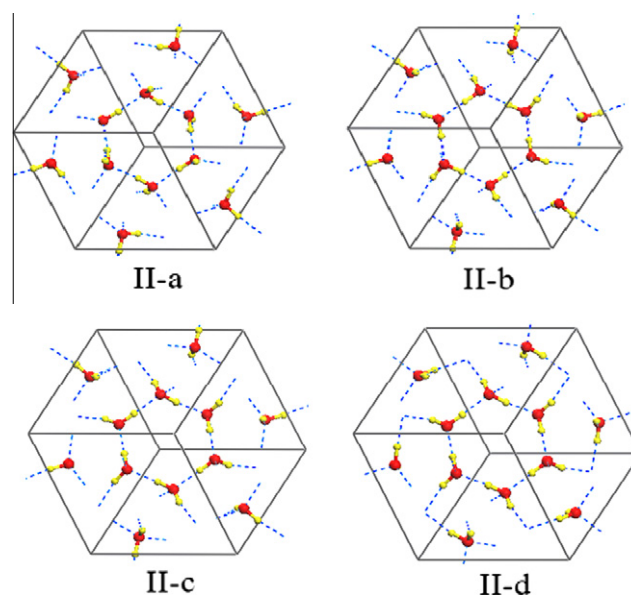
## 2. Methodology

### 2.1. Selection of the ice structures

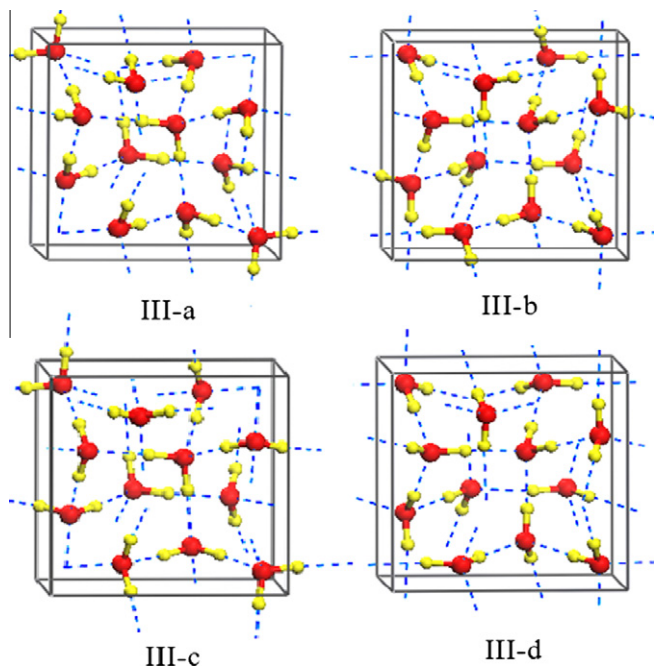
Our main objective in this work is to check whether DFT methods can faithfully capture the relative stability of different proton arrangements, therefore it is important to include a reasonable number of ice configurations that is within the limit of our computational power (an ice configuration is a proton arrangement that satisfies the ice-rules [15]) in our testing set. The enumeration of all the symmetrically distinct ice configurations reported here for a given unit cell can be efficiently done by an algorithm based on graph and group theory [16]. On average, we have chosen about 4–5 ice configurations for each of the above-mentioned phases which are predicted to be low energy states. In the following, we will describe our criteria for selecting the ice configurations for DFT calculations.

The proton distribution in Ice II is ordered throughout its entire thermal stability range but, to our knowledge, enumeration of ice configurations under the constraint of ice-rules has not been reported in the literature. The primary unit cell of ice II is rhombohedral cell with 12 water molecules. We found that there are 546 possible ice configurations satisfying the ice-rules and only four

symmetrically distinct ice configurations (shown in Fig. 2) are found to have the same symmetry as the experimental findings (that is R-3). The selection of ice configuration in ice III is similar to that of ice II. Enumeration of ice structures in the primary unit cell of ice III has been reported in our previous work [10]. Here, we included only four symmetrical distinct ice configurations that have the same symmetry as ice III and ice IX ( $P4_12_12$ ). These structures in their tetragonal cell with 12 water molecules are shown in Fig. 3. For ice Ih, VI and ice VII, we picked up several configurations



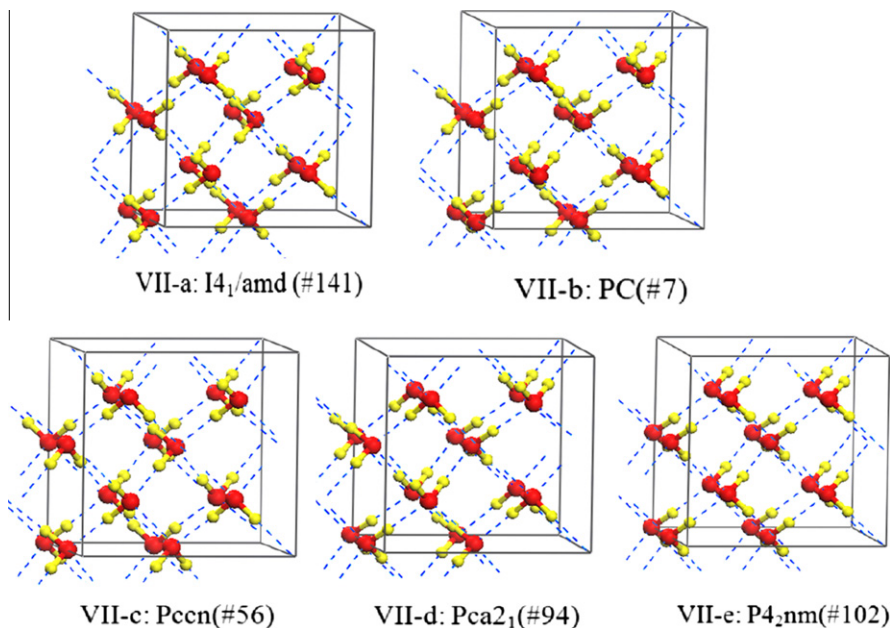
**Fig. 2.** Four possible ice configurations with  $R-3$  symmetry in ice II's primary unit cell. During geometry optimization, lattice constants of the rhombohedral unit cell with 12 water molecules are fixed at  $a = b = c = 7.708$  Å and the  $\alpha = \beta = \gamma = 113.12^\circ$  [33]. II-a is the structure identified by neutron diffraction experiments. All these four structures have no net dipole moment.



**Fig. 3.** Four possible ice configurations with  $P4_12_1$  symmetry in ice III's primary unit cell. Lattice constants of the tetragonal unit cell with 12 water molecules are fixed at  $a = 6.6662 \text{ \AA}$  and  $c = 6.9358 \text{ \AA}$  [12]. III-a is the structure suggested by neutron diffraction experiments [12] and III-d is found to be more stable by a DFT calculation [10]. Under  $P4_12_1$  symmetry, all the four structures have zero net dipole moment.

which were displayed in Figs. 1, 5 and 4, respectively, from the previous studies [13,18,17].

In general, we made sure that the most, the 2nd most and the least stable forms are included. Furthermore, the notion that electrostatic interaction may play an important part in determining the subtle energy difference also suggested that we need to include structures with different dipole moment.



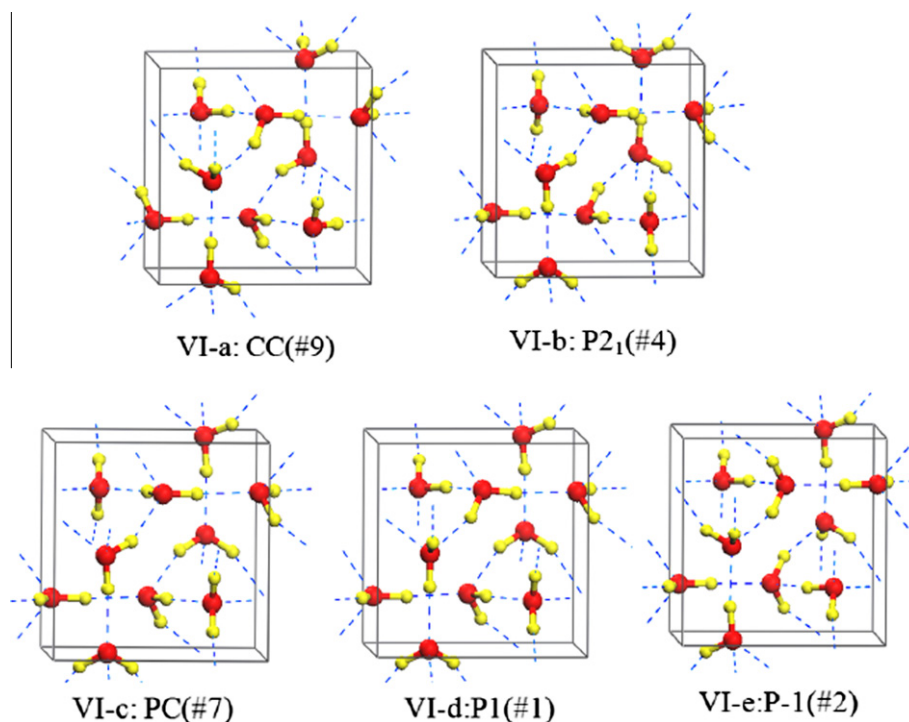
**Fig. 4.** Five ice VII configurations: VII-a is an anti-ferroelectric with  $I4_1/amd$  (#141) symmetry group and is identified as the structure of ice VII by neutron diffraction [5], VII-b is the 2nd most stable structure found in previous study [17] with symmetry  $PC$  (#7), VII-c has  $Pccn$  (#56) symmetry with zero net dipole moment, VII-d has  $Pca2_1$  (#94) symmetry with zero net dipole moment, and VII-e is a ferroelectric structure with symmetry  $P4_2nm$  (#102). The lattice constant of ice VII is fixed at  $3.337 \text{ \AA}$  [5] for all the configurations.

## 2.2. Quantum chemical methods

All DFT calculations reported in this work were carried out using *DMol3* [18,19] in Material Studio [20]. All atomic positions were fully relaxed with fixed lattice constants. It is well known that the lattice relaxation is important, but in this case we fixed lattice parameters for the following reasons. Firstly, the lattice constants in the calculation are from the experimental data which includes the effects of pressure and temperature. Secondly, different proton arrangements result in small change of oxygen lattice and it has been found that the small changes in lattice constant do not play a significant role for the relative energies between different proton configurations in previous studies [10,21]. Both energies and forces were evaluated with DNP basis functions [18], and a Monkhorst–Pack grid [22] with largest  $k$ -point spacing less than  $0.04 \text{ \AA}^{-1}$  was used to sample the Brillouin zone. Multipolar expansion of the electron density was truncated at the octupole. To ensure that all structures are fully relaxed, strict convergence criteria were used; that is the energy difference and every displacements between two optimization steps has to be less than  $10^{-5}$  hartree and  $0.005 \text{ \AA}$  and the root-mean-square of the gradient being smaller than  $0.002 \text{ hartree/\AA}$ .

To examine sensitivity of relative energies of the above mentioned ice configurations to the choice of exchange and correlation functional, lattice energies of the above mentioned ice configurations were studied by a range of generalized-gradient approximations (GGA) [Perdew–Burke–Ernzerhof (PBE) [23], Perdew–Wang generalized-gradient approximation (PW91) [24], Becke exchange plus Lee–Yang–Parr correlation (BLYP) [25], and Revised PBE functional (RPBE) [26]]. Here, local density approximation is not considered since it cannot give an appropriate description of water molecule geometry [18,27].

The effect of lattice vibration on the relative stability of different proton arrangement is possible, especially for different conformations of water clusters and for the interaction between ice layer and water molecules on metal surface [28]. However, calculating phonon spectra for all possible hydrogen bond topologies with



**Fig. 5.** Five ice VI configurations: VI-a has  $CC$  (#9) symmetry with zero net dipole moment, VI-b has  $P2_1$  (#4) symmetry, VI-c has  $PC$  (#7) symmetry, VI-d has  $P1$  (#1) symmetry, and VI-e has  $P-1$  (#2) symmetry and with zero net dipole moment. The lattice constant of ice VI is fixed at  $a = 6.27$  Å and  $c = 5.79$  Å [5].

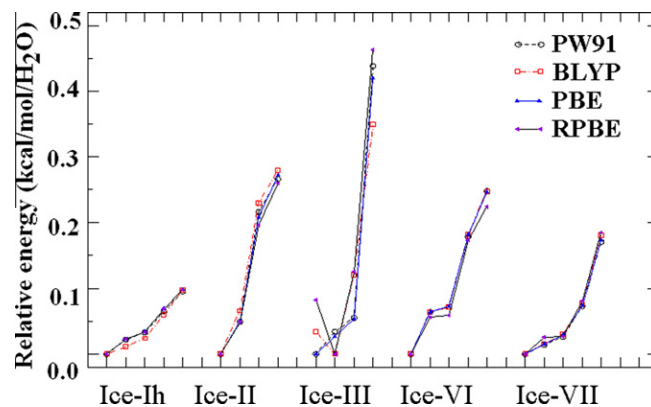
the same accuracy as the binding energy is a daunting task. In the present work, we do not anticipate the results would be affected by the negligence of zero point vibration. With statistic average in large supercell, the dispersion of vibration model is not significant, considering the mean vibration frequency is very similar [29]. When the zero-point energy is estimated, the weak dispersion of intermolecular vibration bands means the high-frequency vibrational modes (HFVMs) are just sensitive to the localized intermolecular interaction. Thus, the contribution of HFVMs to zero-point energy almost is equivalent for the different proton-ordered configurations with same phase. The long-range low-frequency vibrational modes (LFVMs) are possible to be weakly sensitive to the different proton-ordering. The approximate equivalency of oxygen lattice means the difference of LFVMs is very small for different proton-ordered configurations. In additional, the energy of LFVM is low. Thus, the difference of ZVP energy due to the contribution of LFVMs can be ignored for different proton-ordered configurations.

### 3. Results and discussions

In this work, we will report only the relative stability among ice configurations in each crystalline phase and zero of the energy scale is chosen as the lattice energy of the first structures shown in the above figures (that is Ice Ih(a), Ice II(a), Ice III(a), ice VI(a) and Ice VII(a)). We should point out that these structures, (except ice VI(a)), predicted by DFT as the lowest energy structures, are the proton ordered forms identified by experiments. This consistency between experimental results and DFT calculation is independent of the simulation parameters and exchange–correlation functional recipes which shows the transferability of DFT methods and gives us the confidence in the further “prediction” work on ice VI.

We have included four exchange and correlation functionals (BLYP, PBE, PW91, and RPBE) that are commonly used to study

water in condensed phases to check whether the relative stability of different ice configurations is sensitive to choice of the functional recipe. For consistency and easy comparison across different phases, the unit of the relative energy is reported in kcal/mol/ $H_2O$ , unless it is explicitly stated. The results from our calculations are summarized in Fig. 6. It is very exciting to find that all these four functionals yield very consistent relative stability in ice Ih, ice II, ice VI and ice VII. This may suggest the exchange–correlation recipe is not mainly responsible for the observed energy difference. By inspection of the DFT total energy expression, one could infer that the differences in total energy are expected to be due to the electrostatic interactions.



**Fig. 6.** Relative energy by different exchange and correlation functionals with octupole expansions of the electron density. All four functionals yield very consistent relative stability in ice Ih, ice II, ice VI and ice VII. There is noticeable inconsistency in ice III, BLYP and RPBE suggest a different proton ordered structure from that reported in neutron diffraction experiments.



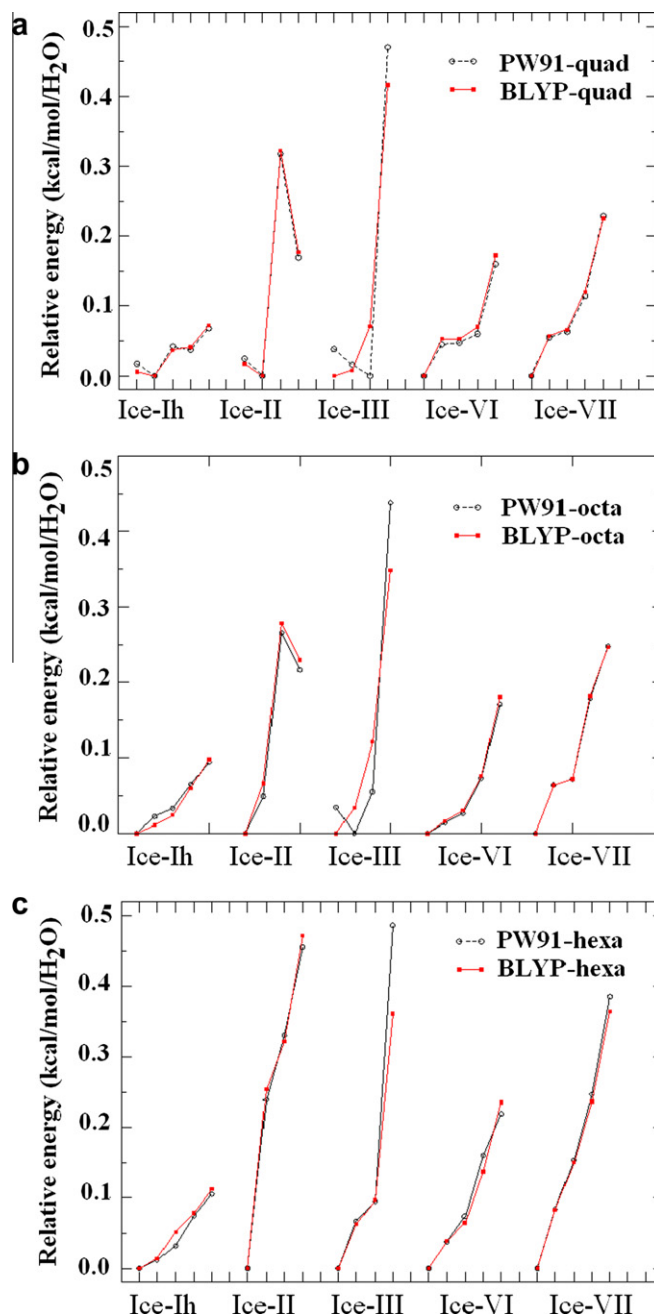
However, significant differences noted in ice III and the four functionals seem to fall into two categories. While PW91 and PBE yield the same structure as reported by neutron diffraction [12], BLYP and RPBE suggest a different proton ordered structure. In the following, we will prove that the discrepancy in ice III is due to deficiency in describing high order multipolar component of the electron density in our default recipe.

We notice that the electron density is fitted to a set of auxiliary functions in DMol [3] and it is necessary to specify the maximum angular momentum ( $L_{max}$ ) in the fitting function. In previous calculation, the multipolar expansion of electron density is truncated at octupole (that corresponds to setting  $L_{max} = 3$ ). In the following, we will test whether the relative stability is sensitive to the multipolar expansion of the electron density, similar issue was also noted by Batista et al. [30] and Tribello et al. [31]. Quadrupole and hexadecapole are used to stand for truncating the multipolar expansion at  $L_{max} = 2$  and at  $L_{max} = 4$ , respectively. Since we have found that different DFT functionals yield inconsistent relative stability in ice III, we have carried out our testing with both BLYP and PW91.

The results are summarized in Fig. 7 and it is interesting to see that BLYP and PW91 yield consistent results for ice Ih, ice II, ice VI and ice VII regardless of the multipolar expansion used. By comparing with experimental proton ordered structures, however, it is clear from Fig. 7a that quadrupole expansion of the electron density is not sufficient as it yields incorrect proton ordered form of ice II and ice Ih. This implies that current empirical potential models may not be able to reproduce the position of the proton ordered ice phases in phase diagram without extension to describe high order electrostatic. From Fig. 7c, we can see that the discrepancy among different exchange and correlation functionals disappears if up to hexadecapole expansion of the electron density is included. In this case, we can see BLYP and PW91 agreeing with each other quite well and in addition the correct proton ordered structures were identified unambiguously in all the five phases we have tested.

We can therefore conclude that the possible factor in determining the proton ordering energetics in ice phases can thus be understood as a purely electrostatic issue arising from variance in the electrostatic interactions among different hydrogen bonding networks in a given oxygen sublattice. Therefore, it is not surprising that empirical potentials, which are often fitted to gas phase dipole and polarizability, are failed to describe the proton ordering energetics in ice adequately. These results from first-principles methods provide the essential information that successful ice potential must describe sufficient details of electron density at least up to quadrupoles and octupoles.

Van der Waals (vdW) interaction has been ignored largely in the present four exchange–correlation functionals and the lack of vdW leads to an incomplete description of hydrogen bonds among water molecules or in ice phases. Here, we will argue that the above results based on the difference of relative energy of different proton-ordered configurations are still effective. Firstly, the vdW effect is expected to be similar for the figures with different ordering of protons in each ice phase, since the equivalence of cell sizes of different configurations reveals equivalent of the distance between water molecules with statistic average to some extent. Secondly, vdW interaction is explicitly included in most empirical potential functions, but these empirical potential models cannot predict effectively the low-energy proton-ordered configuration. Therefore, the effective estimate of electrostatic interactions is considered to be more important in analyzing the difference of energy of proton-ordered configurations in one ice phase. Furthermore, the predicted proton-ordered configurations with DFT calculations are compared with the structures from experiments.



**Fig. 7.** Relative energies by different multipolar expansions of the electron density: (a) up to quadrupole, (b) up to octupole, and (c) up to hexadecapole. It is clear from Fig. 7a that quadrupole truncation of the electron density is not sufficient and results in incorrect proton ordered form of ice Ih and ice II. When octupole components are included (Fig. 7b), the agreement between BLYP and PW91 is improved and the inconsistency is restricted to ice III only. From Fig. 7c, it is clear that the inclusion of high order multipolar components of the electron density improves transferability of the DFT functionals.

The energy gap between the most stable and the second most stable ice configurations in each of these five phases are summarized in Fig. 8. Ice II has a very large energy gap and this is consistent with the fact that ice II is proton ordered throughout its entire thermodynamically stable range. The high phase transition temperature between ice VII and ice VIII is inline with our calculations that the energy gap in ice VII is larger than the other phases. Along this line, we would expect the transition temperature for proton ordering in ice VI, if it can be observed, to be lower than that of between ice III and ice IX.

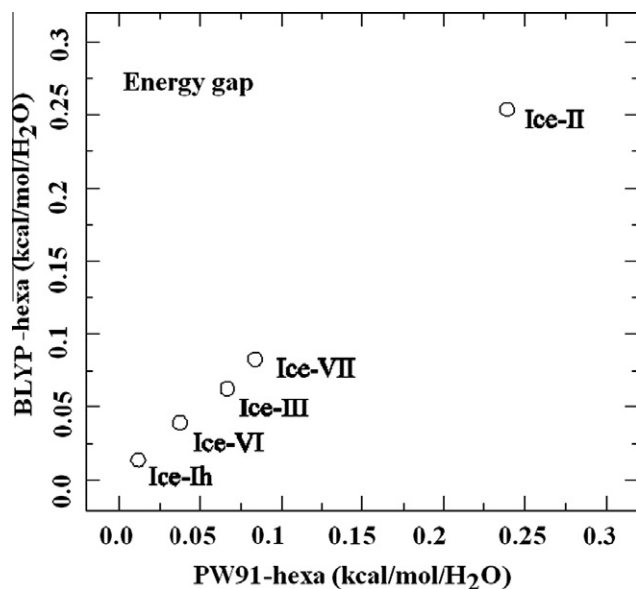


Fig. 8. The energy difference (or energy gap) between the most and the second most stable ice configurations in each phases. The magnitude of the energy gaps agrees quantitatively with the experimental phase transition temperatures.

#### 4. Conclusions

Motivated by recent successes of DFT methods in describing the proton-ordering transitions in ice Ih and ice VII, we have analyzed the transferability of density functional methods in “predicting” the proton ordered structures of ice Ih, II, III, VI and ice VII. We have tested four exchange–correlation functionals (BLYP, PBE, PW91 and RPBE) and the energy difference of configurations for an ice phase is found to be insensitive to the exchange–correlation functionals. With the analysis of the calculation results, it is found that the subtle energetics of proton ordering in ice phases is mainly depended on the electrostatic components of the total energy and high order multipolar expansion of the electron density is important to predict the real proton ordered state. This may be the reason that the empirical potentials are failed to describe the proton ordering energetics in some ice phases.

With sufficiently high order multipolar expansion of the electron density (hexadecapole), all the four functionals yielded consistent results. It is found that the proton ordered structures of the ice phases (ice Ih, II, III and ice VII) predicted by first principle methods are agreed well with the experimental findings. Thus, we deduce that the proton ordered structure predicted from our calculations

is possible to be the real ground state of ice VI. The magnitude of the energy gap between the most stable and the second most stable proton arrangements qualitatively followed the expectation based on their experimental phase transition temperature, too.

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