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A Blind Structure Prediction of Ice XIV

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Many of the known ice phases exhibit a proton ordering transition, for example the transition from proton disordered hexagonal ice (I*h*) to proton ordered ice XI.[1] Most recently, two new proton ordered ice phases (XIII and XIV) have been reported[2] relating to ice V and XII, respectively. Preparation of several ice phases is not straightforward, which explains why until recently, only one new ice phase had been discovered in the last 20 years.[3] In particular, ordered forms of ice can be difficult to isolate within the laboratory because of kinetic barriers to molecular rotation that are important at low temperatures. Computer simulation offers an adjunct methodology in which the effects of pressure, temperature, and configuration can notionally be controlled quite precisely, to permit systematic mapping of the phase diagram. However, the verity of any simulation method hinges upon its ability to reproduce disparate state points on the phase diagram. As a challenge to theory, we recently undertook a blind test to predict the proton ordered form of ice XII termed ice XIV.

Although each ice oxygen atom must have tetrahedral coordination (in a perfect lattice), the hydrogen atoms may be disordered. The arrangements of protons within an ice structure are determined by the Bernal−Fowler ice rules[4] which stipulate that (1) there must be two hydrogen atoms adjacent to each oxygen and (2) there must be only one hydrogen per hydrogen bond. Pauling[5] showed that for any ice phase there are approximately $({}^{3}/_{2})^{N}$ ways in which the hydrogen atoms can be arranged and suggested that all possible structures of a given phase are degenerate. However, the existence of proton ordered phases invalidates this postulate. The proton ordered phases have distinct properties from their disordered parent phases; for example, ice VII can transform to proton ordered ice VIII with an associated change in the lattice parameters and density.

To predict the lowest enthalpy structure of a given ice phase, one must be able to establish the structure/energy relationship with extremely high accuracy. The energy changes associated with permuting proton positions are typically much less than one kcal mol^{-1}, which can only be reliably extracted from ab initio approaches. In recent years, Singer et al.[6−8] have studied proton ordering transitions from ice I*h* to ice XI, and ice VII to ice VIII using graph theory to enumerate distinct bonding topologies. Graph theory yields topological invariants, which can be fitted to the density functional theory (DFT) energy and then used to explore hypothetical proton networks. Their method showed that the relative energy of any given proton topology is a function of the hydrogen-bonding arrangements of all pairs of neighboring water molecules within the cell. This observation is compatible with our recent finding[9] that the relative energies of ice phases depend strongly on short-ranged terms of $1/r^4$ and higher in the electrostatic multipole expansion, which are negligible beyond the first coordination sphere of an ice water molecule. Because ordering is short ranged, the proton ordered form would be expected to have maximal symmetry for a given phase, as is found, in proton ordered ice VIII, IX, and XI. Thus a simple computational recipe for rapidly locating the lowest energy proton ordered state entails generating all possible structures within the ice XII unit cell (applying the Bernal−Fowler rules) and then calculating the symmetry of the cell. Since the proton ordered form will have maximal symmetry, only the structures with the highest symmetry need be considered using DFT.

Table 1. Optimized Energies of Proton Ordered $P2_12_12_1$ Ice XII Structures

configuration number	energy per molecule/kcal mol^{-1}
1	−10865.948
2	−10865.987
3	−10866.094
4	−10866.137

Application of this methodology leads to enumeration of 692 possible hydrogen-bonding networks for an ice XII unit cell containing 12 water molecules. Structures exhibiting four space groups were found: $P2_12_12_1$, $P2_1$, $P2$, and $P1$ (using the FINDSYM software[10]). Following earlier assertions, the expected structure of the ordered form will be $P2_12_12_1$ of which there are 16 structures, only 4 of which are distinct. The relative energies of each topology were calculated using the plane-wave code CASTEP[11] using the PW91[12] functional, a Monkhorst−Pack 2 × 2 × 4 grid of *k* points, and an electronic cutoff of 500 eV. Each structure was relaxed in *P*1 symmetry at constant zero pressure, and the relative energies are given in Table 1.

From the calculated relative energies, structure 4 was proposed as the observed proton ordered structure and passed to one of us (C.G.S.) for independent verification, prior to the publication of the structure. We (G.A.T. and B.S.) also suggested the possibility that a second phase might be observable because of the extremely small energy difference between configurations 3 and 4. In the reported structure solution, strain was noted in the fit, which was minimized by assigning fractional occupancies to four distinct hydrogen positions. Best fit to the neutron data[2] was obtained with occupancies ∼0.4:0.6 to H4:H5 and ∼0.6:0.4 to H12:H13 in the reported structure (we adopt the labeling convention of Salzmann et al., substituting H for D). It was proposed from previous work[2] that strain prevented the structure from adopting a single-phase proton ordered state (reminiscent of the ice I*h* to XI transition) and that the true structure would display fully occupied positions at either H5:H12 *or* H4:H13, with the former expected to be preferred owing to the larger measured occupancy. It transpired that the predicted lowest energy state (configuration 4) equates to full occupancy at H5:H12, (i.e. the binary string 0110 in the sequence H4:H5:H12:H13), while model 3 equates to full occupancy at H4:H13 (i.e. 1001). These two structures are shown in Figure 1.

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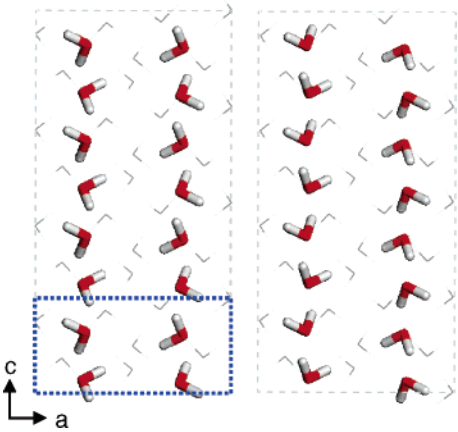

Figure 1. Supercell structures of configuration 4 (left) and configuration 3 (right) expanded along in *c*, and viewed down [010]. The water molecules, shown with a red oxygen center, highlight the contrasting structure. Hydrogen atoms are shown in gray and other oxygen atoms shown in dark gray. The unit cell is shown in blue.

Structures 3 and 4 feature subtly different hydrogen-bond networks along [001]. In the lowest energy state the interatomic O−H distance parallel to [001] is 1.750 Å, while the separation alternates between ∼1.713 and ∼1.726 Å in the higher energy structure. The larger hydrogen-bond network in model 4 is lower in energy because of the reduced suprafacial intermolecular proton repulsion in comparison to configuration 3. The anti-ferroelectric water dipole ordering is also distinct being aligned along [001] in configuration 3 but perpendicular to [001] in model 4. Intriguingly, one can hypothesize two structures with the binary populations 1010 and 0101. Permutation of the 1D chains in this manner does not violate the ice rules but does reduce the symmetry to $P2_1$. These two structures were relaxed and found to be degenerate with energies of −10866.101 kcal mol^{-1}, intermediate between the phases 3 and 4. From the energetic information, we therefore propose that the data measured by neutron diffraction may be due to a composite of at least two and, more probably, three structures. The lattice parameters of configurations 3, 4, and the mixed 3:4 phase show a sizable variance of ∼1% (see Supporting Information), where *a* ranges from 8.116 to 8.195 Å and *b* from 8.258 to 8.318 Å. The disparity in lattice parameters suggests a possible source of the strain observed within a polycrystalline sample,[2] arising from two or more closely related but inequivalent phases.

Since the cooling of ice XII was carried out on a laboratory time scale, the rate of cooling could influence the proportions of phases 3, 4, and 3:4. Reversibly slow cooling of ice XII is expected to give rise to a single phase of configuration 4, while cooling at a finite rate will produce 3, 4, and 3:4. The mixed 3:4 structures can account entirely for the populations at H4:H13, raising the question of whether structure 3 is present. However, the energy difference between models 3 and 3:4 is so small, that one expects comparable populations of 3 and 3:4. Given the thermodynamic preference for structure 4, the populations of H5:H12 would be expected to be larger than H4:H13, as was observed experimentally. The relative energies of the three phases suggest that all structures would be expected to be observable within a temperature range of ∼20 K, and hence extremely delicate cooling would be required to form a single pure phase of structure 4. Annealing may enhance the proportion of the lowest energy structure, which may explain the experimental observation that the lattice parameters were found to deviate from their original values upon heating and re-cooling.

In summary, we suggest that two or more metastable, proton ordered forms of ice XIV are formed under kinetically controlled conditions. The two additional phases, which could be termed ice XIV′ and XIV″, have distinct crystallographic lattices from the most stable ice hydrogen ordered form of XII. To our knowledge, such behavior has not been observed in any ice phase and while the phenomenon could be unique to ice XIV, it would seem plausible that other proton ordered forms of ice could display metastable phases. It is possible that the identity and concentration of dopants may influence the accessibility of these phases, by altering their stability relative to the most thermodynamically stable phase. Interestingly, pressured calculations at 1.2 GPa show an increase in the stability of configuration 4 relative to 3, indicating that pressure enhances the formation of the lowest energy hydrogen ordered state and also favors the transition from the disordered to the ordered state. Equivalently, the cooling of ice XII at lower pressures would be expected to yield higher proportions of the satellite phases.

Finally, we comment that ice XI and perhaps other hydrogen ordered ice phases may merit reinvestigation, as the computed relative energies[8] of several hypothetical XI hydrogen-bond networks are similar to those found in ice XIV.

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Supporting Information Available: The structures of configurations 4, 3, and 3:4 are given in CIF format. A separate document with comment upon zero point energies and total energies obtained using other functionals is supplied. This material is available free of charge via the Internet at http://pubs.acs.org.

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