

HYDROGEN-BOND TOPOLOGY AND PROTON ORDERING IN ICE AND WATER CLUSTERS

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I. INTRODUCTION: HYDROGEN-BOND CONNECTIVITY AND PHYSICAL PROPERTIES

Water is a unique substance. Most small molecules (nitrogen, oxygen, carbon dioxide, methane, e.g.,) exist only as gases under ambient conditions. In contrast, water is commonly found as a vapor, liquid, or solid. The uniqueness of water arises because of the strong hydrogen bonds (H-bonds) between water molecules. Not only are H-bonds unusually strong intermolecular bonds, they are directional. A water molecule prefers to accept two H-bonds and donate two other H-bonds in tetrahedral directions (Fig. 1). Understanding the properties of ice and the structure of many water clusters is an exercise in working out the ramifications of building water H-bonds according to this pattern. A good illustration is H-bond order-disorder phenomena in ice, which will be the major concern in this chapter. In the known phases of ice at pressures less than 10 GPa, water molecules donate and accept two H-bonds with four neighbors, as shown in Fig. 1. The previous statements express what is known as the Bernal–Fowler “ice rules” [1].

While the oxygen atoms form a periodic lattice, the hydrogen atoms are disordered in ices Ih, III, V, VI, VII, and XII, which undergo a phase transition to ices XI, IX, XIII, XV, VIII, and XIV, respectively, as temperature is lowered. The origin of the disorder is easily seen in Fig. 1, where the central water molecule is shown donating to the two upper neighbors. In the disordered ice phases, the water molecules may donate to any two among its four neighbors. Hence, a water molecule constrained to orient hydrogen atoms in two of four possible tetrahedral directions may be found in $4 \cdot 3/2 = 6$ different configurations. Several possible unit cells of ice Ih are shown in Fig. 2. Of course, the orientation of the neighboring molecules are partially constrained if the central molecule is fixed, so the number of available H-bond configurations is considerably less than 6^N , where N is the number of water molecules. In 1935, Linus Pauling [2] estimated that there are $(\frac{3}{2})^N$ different ways to arrange the H-bonds of N water molecules subject to the ice rules

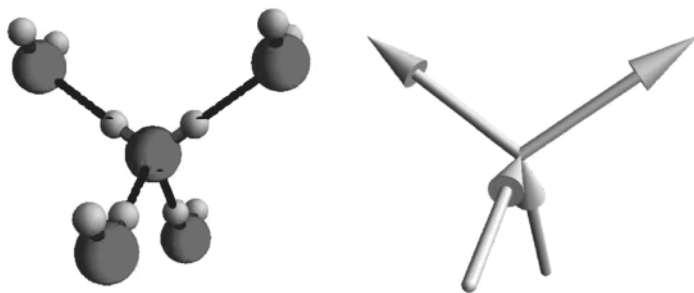


Figure 1. The central water donates a H-bond to the two upper molecules, and accepts a H-bond from the lower molecules. The directionality of the H-bonds is indicated by the arrows on the right.

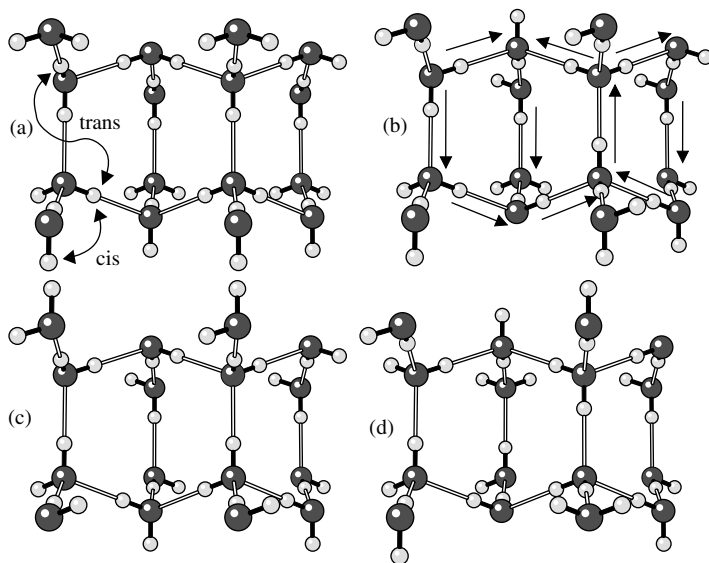


Figure 2. Four possible arrangements of H-bonds within a 16-water-molecule orthorhombic unit cell of ice Ih. Here, cis and trans bonds are defined as whether protons lie on the same or opposite side of the H-bond, respectively, as indicated for structure (a). The H-bond isomers are summarized mathematically by directed graphs in which directional bonds point from H-bond donor to H-bond acceptor, as illustrated for the isomer (b).

in the lattice of ice Ih, the phase of ice formed when water freezes under ambient pressures. The contribution to the entropy would be $R \ln \frac{3}{2} = 0.806 \text{ cal K}^{-1} \text{ mol}^{-1}$. Pauling's estimate would prove to be remarkably accurate compared with more powerful solutions of the counting problem [3, 4]. Earlier in 1932, based on the measurements of others, Giauque and Ashley [5] had calculated the residual entropy of ice Ih near 0 K to be in the range of $0.87\text{--}0.96 \text{ cal K}^{-1} \text{ mol}^{-1}$, and attributed the entropy at 0 K to "the persistence of rotation of water in ice below 10°K ". In 1936, Giauque and Stout [6] measured the heat capacity of ice. Combining their results with known thermodynamic properties of the liquid and vapor and a spectroscopic estimate of the absolute entropy of water vapor, they estimated the residual entropy of ice to be $0.82 \text{ cal K}^{-1} \text{ mol}^{-1}$, which is $R \ln \frac{3}{2}$ within their experimental error of $0.05 \text{ cal K}^{-1} \text{ mol}^{-1}$. The experiment confirmed that the H-bonds in ice are in a nearly random arrangement, (i.e., the H-bonds are disordered). Thus, somewhere between the freezing temperature of water and 0 K, ice falls out of equilibrium.

While the origin of the residual entropy of ice seemed settled, it was recognized that an ordered phase of ice Ih could exist if a suitable experimental means was available to allow equilibration [7]. Little progress was made concerning a possible

low-temperature form of ice until the 1980s, when calorimetry experiments on samples doped with impurities, particularly potassium hydroxide (KOH), exhibited a clear signature of a proton-ordering transition at 72 K [8–10]. The transition temperature was independent of the KOH concentration, indicating that KOH acts like a catalyst. This proton-ordered structure suggested by subsequent diffraction experiments [10–15] is called ice XI. It is structure (a) of space group symmetry $Cmc2_1$ in Fig. 2, where ice XI can be seen to be ferroelectric on account of the ordered c -axis bonds. The mechanism by which KOH induces the proton-ordering transition in ice Ih is unclear. Furthermore, the ferroelectric structure of ice XI is unexpected. There has been continued debate and research as to whether the H-bond arrangements in the high-temperature phase of ice are actually random or partially ordered [16, 17], whether a phase transition to a fully H-bond ordered structure exists [15, 18–20], and if so, its identity. Hydrogen-bond order–disorder transitions in other parts of the ice phase diagram have been long known [21], and new examples continue to emerge [22–24].

Like the phases of ice, water clusters can be grouped into families among which the oxygen atoms occupy nearly the same position, and that differ in the direction of the H-bonds between those oxygens. Unlike ice structures, where the energy difference per water between different H-bond structures is on the order of $0.1 \text{ kcal mol}^{-1}$, the energy difference between H-bond isomers in water clusters can amount to several kilocalories per mole per water. As a result, the H-bond disordered ice phases tend toward nearly complete disorder while only the lowest energy isomer or isomers of water clusters are typically observed in cluster beam experiments. The properties of the cubic water clusters (Fig. 3) illustrate this

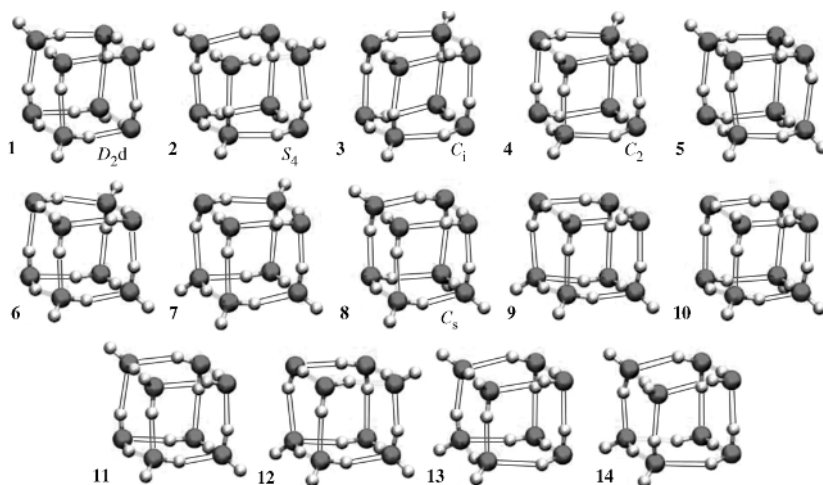


Figure 3. The 14 symmetry-distinct H-bond arrangements possible when the oxygen atoms of eight waters form a cubic structure. The point group symmetry is indicated when it is higher than C_1 .

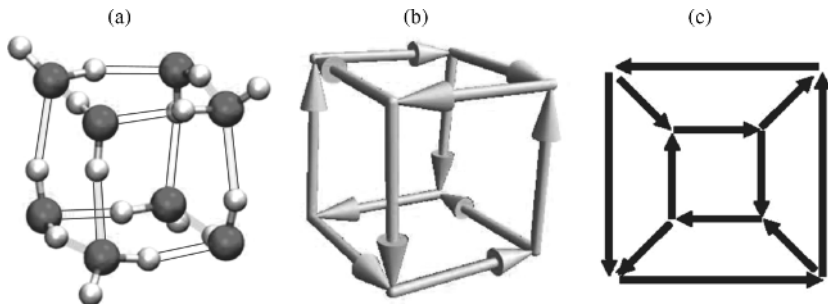


Figure 4. The full molecular geometry of a cubic water cluster with D_{2d} symmetry is shown in (a). In (b) and (c) are two representations of the H-bond topology in terms of directed graphs. In (b) representation, the depiction of the vertices are faithful to the molecular geometry. The same H-bond topology is captured by the graph in (c).

behavior. There are 14 symmetry-distinct ways to connect waters in a cubic arrangement [25]. Among those, the D_{2d} and S_4 clusters (structures **1** and **2** of Fig. 3) are the lowest energy isomers [26], and the only ones observed experimentally [27].

While the molecular coordinates completely specify the unit cells of Fig. 2 or clusters of Fig. 3, it is natural to distill the H-bond topology from the molecular geometry and ask to what extent physical properties can be predicted on the basis of the H-bond topology alone, as first conceived by Radhakrishnan and Herndon [28]. The abstraction from full atomic coordinates to the H-bond topology can be described in several ways. The topology can be summarized using directed graphs [29, 30], either for ice crystals (Fig. 2b) or finite clusters (Fig. 4), in which each vertex corresponds to a water oxygen and an arrow connecting two vertices indicates the presence of a H-bond and the direction from H-bond donor to H-bond acceptor. The ice rules require that all vertices in defect-free ice have two incoming and two outgoing bonds. Another language to describe the mapping of deep local minima of the potential surface to patterns of H-bond connectivity abstraction is to describe a mapping to a spin-lattice model [31, 32]. In fact, there exist magnetic compounds, known as spin ices, in which the electronic spins obey ice rules [33–35].

Is there *utility* in abstracting from the atomic coordinates to the H-bond connectivity? Of course, order parameters for order–disorder transitions like ice Ih/XI can be cast in the language of topological properties. However, can we make physical predictions based on the correspondence between deep minima on the potential energy surface of water molecules and directed graphs or spin configurations? In this chapter, we will hopefully build a convincing case that the answer to these questions is affirmative. As a preview, consider the fact that, to date, there is no empirical potential function for water that describes the small energy differences among H-bond isomers in various phases of ice [36]. While it may be feasible to perform electronic structure calculations on several H-bond isomers for a small

unit cell (10–100 waters), it would certainly be impractical to perform the same level of calculation on the numerous H-bond isomers of a unit cell large enough to approximate the thermodynamic limit. The problem of statistical sampling of H-bond configurations can potentially be solved by linking the energy of a configuration to the orientation of the H-bonds, the arrows in Fig. 2. Group theoretical tools can be used to construct analytic expressions, as functions of the H-bond orientations, which exploit the symmetry of the ice lattice [37, 38]. These functions, that we call graph invariants, provide the link between H-bond topology and scalar physical properties of the system, such as energy. In one very important application, graph invariants provide a means to bootstrap from expensive electronic density functional theory (DFT) calculations for small unit cells to statistical mechanics simulations using much larger simulation cells. A logical extension to higher tensorial quantities is possible. For example, combinations of bond variables that transform as vectors are the proper way to link local site displacements in ice to H-bond topology [39].

This chapter aims to provide an introduction to H-bond order–disorder phenomena in water ice and water clusters. It also provides an introduction to theoretical methods that can be used to describe the energetics and statistical mechanics of these systems. Readers seeking a review of the phenomena without delving deeply into the theory may skip Section II.C. These readers will find a summary of experimental work at the beginning of the part of Sections III, V, and VI. It will be apparent when attention is turned to the theory in these sections. Other readers may use Sections II.C.1 and II.C.3 as an introduction to the theory without the technical material in Section II.C.2.

II. HYDROGEN-BOND ORDER–DISORDER TRANSITIONS IN ICE

At present, there are 15 crystalline phases of ice whose structures have been characterized and reported in the literature. In total, there are six equilibrium or metastable phases of disordered ice (Ih, III, V, VI, VII, and XII as highlighted in Figs. 5 and 6) which when cooled under appropriate conditions transform to a proton ordered version (XI, IX, XIII, XV, VIII, and XIV, respectively). The VII/VIII system is the best characterized of all the proton order–disorder transitions in ice, as it proceeds over a wide pressure range without taking special measures, such as the introduction of dopants, to activate the transition. The transition from ice III to metastable ice IX also occurs spontaneously upon cooling, provided that ice III is cooled faster than $\sim 1 \text{ K min}^{-1}$. Otherwise, ice III transforms into the thermodynamically stable phase under these conditions, ice II.

The other known transitions between H-bond ordered–disordered phases require doping with either acid or base to catalyze the transition. This finding is not surprising because reorientation of water molecules in ice by breaking and

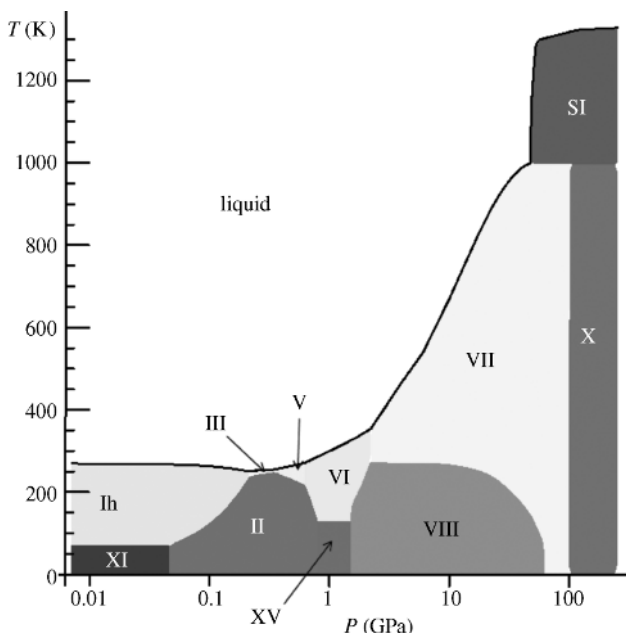


Figure 5. Liquid- and solid-phase boundaries of water. Some ice phases appear in pairs (Ih/XI, VI/XV, VII/VIII) in which the oxygen atoms have nearly the same lattice positions. Hydrogen-bonds are disordered in the high-temperature member of the pair, and are locked into an ordered arrangement in the low-temperature member. Only equilibrium phases are shown here. Some metastable phases are depicted in Fig. 6. Several phase boundaries are estimated. The superionic phase [40, 41] is labeled “SI”. (See insert for color representation of the figure.)

re-forming H-bonds would require passage over very large barriers. Presumably the introduction of defects provides lower-energy activation pathways for H-bond rearrangements. Ice XI has been observed to form upon doping of ice Ih with hydroxide. Doping with acid promotes the formation of ice XIII, XV, and XIV from ice V, VI, and XII, respectively [22, 24, 42]. The mechanism by which H-bond order–disorder transitions are catalyzed by excess protons or hydroxide is poorly understood. Recent experiments indicate that ionic defects are immobilized on an accessible experimental time scale somewhere between 100–200 K [43, 44]. If there are no ionic defects actively diffusing at 72 K, then it is unclear how hydroxide ions catalyze the ice Ih/XI transition. It is also not clear why excess protons are effective for the ice VI/XV and XII/XIV transitions, while excess hydroxide catalyzes the ice Ih/XI transition.

The disordered phases of ice discussed above are often regarded as fully disordered phases. However, studies on ices III [45, 46] and V [46], however, have shown that these phases are only partially disordered (i.e., some H-bond arrangements

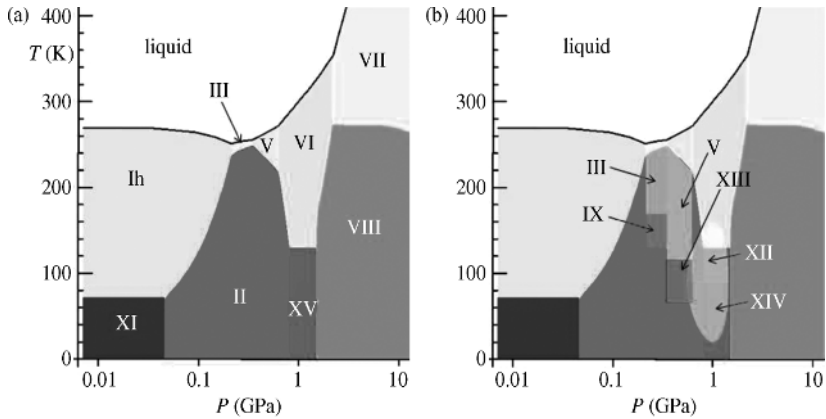


Figure 6. Low pressure expanded view of the liquid- and solid-phase boundaries of water. Only equilibrium phases are shown in (a), while some of the metastable phases are also indicated in (b). Pairs of equilibrium ice phases distinguished by H-bond order-disorder while oxygen atoms have nearly the same lattice positions include Ih/XI, VI/XV, and VII/VIII. Pairs of this type in which the low-temperature member is metastable include III/IX and V/XIII. The pair XII/XIV involves two metastable phases. Several phase boundaries are estimated, and the full range of the metastable phases is not known. To avoid obscuring other phases, the full region where ice XII is known to be metastable is not shown. (See insert for color representation of the figure.)

are preferred over others). The degree of partial order in the high-temperature phase, and partial disorder in the low-temperature phase can be measured using diffraction techniques. Hydrogen-bonds that are completely disordered appear to have half a hydrogen atom covalently bonded to each of the oxygens linked by the H-bond. In certain families of H-bonds that are unconstrained by the point group symmetry, the fractional occupancy of the two possible H-atom sites observed in diffraction experiments can depart from $\frac{1}{2}$. The degree of partial ordering is generally quantified by an order parameter varying between 0 and 1, and equal to the fractional occupancy of one of the hydrogen atom sites. Experiments on several H-bond disordered phases, ice Ih [16, 17], ice III [45, 46], and ice V [46], have measured departures from fully random H-bond statistics. The degree of partial order above the transition and partial disorder below the transition can also be estimated from the transition entropy, as measured by the latent heat. In the limit where the high-temperature phase is almost completely disordered and low-temperature completely ordered, the transition entropy should be close to the full Pauling entropy of $R \ln \frac{3}{2}$ per mole. A transition entropy less than this value is a signature of either partial order above the transition or partial disorder below the transition, or both.

Disordered phases of ice are locally inhomogeneous, the result of the pattern of H-bonds that changes from site to site in the lattice. As a result, bond lengths, bond angles, and displacements of atoms from perfect lattice sites vary according to the

local H-bond topology. Experimental data is available that can be used to interpret the local site displacements in disordered ice VII [47, 48]. It is worthwhile to note that defects in ice diffuse through a lattice that is not locally periodic, but reflects the local H-bond disorder.

A. The Statistical Mechanics of Hydrogen-Bond Order–Disorder Transitions in Ice

The Born–Oppenheimer potential energy surface for all but the very highest pressure ice phases consists of a number of deep minima, each corresponding to a different H-bond topology. Several of the deep minima for ice Ih are represented in Fig. 2. Each of these minima corresponds to an oriented graph of the type shown in Fig. 4. Configuration space for N water molecules can be partitioned into basins of attraction on the electronic potential energy surface [49–57]. If the system rarely samples boundaries between these basins of attraction, an excellent approximation here, the canonical partition function is well approximated by a sum over the M H-bond topologies available to a system of N water molecules.

$$Q = \sum_{i=1}^M f_i e^{-\beta E_i} Q_{\text{vib},i} = \sum_{i=1}^M f_i e^{-\beta(E_i + A_{\text{vib},i})} \quad (1)$$

In the following, we use a boldface $\mathbf{N}$ to stand for $(N_{\text{O}}, N_{\text{H}})$, the number of hydrogen and oxygen atoms. Let $V(\mathbf{r}^{\mathbf{N}})$ be the Born–Oppenheimer ground-state potential energy surface for N oxygen atoms and $2N$ hydrogen atoms, where $\mathbf{r}^{\mathbf{N}}$ is an abbreviation for all atomic coordinates. E_i is the Born–Oppenheimer electronic ground-state energy evaluated at $\mathbf{r}_i^{\mathbf{N}}$, the minimum of the i th potential energy basin.

$$E_i = V(\mathbf{r}_i^{\mathbf{N}}) \quad (2)$$

$Q_{\text{vib},i}$ is a vibrational partition function for motion on the potential energy surface $V(\mathbf{r}^{\mathbf{N}}) - V(\mathbf{r}_i^{\mathbf{N}})$ in the i th basin of attraction. It can be evaluated quantum mechanically, or in the classical limit.

$$Q_{\text{vib},i} = e^{-\beta A_{\text{vib},i}} = \frac{1}{\mathbf{N}!} \frac{1}{\Lambda^{3\mathbf{N}}} \int_{\mathcal{D}_i} d\mathbf{r}^{\mathbf{N}} e^{-\beta[V(\mathbf{r}^{\mathbf{N}}) - V(\mathbf{r}_i^{\mathbf{N}})]} \quad (3)$$

$\Lambda^{3\mathbf{N}\mathbf{N}!}$ stands for $(\Lambda_{\text{O}}^{3N_{\text{O}}} \Lambda_{\text{H}}^{3N_{\text{H}}} N_{\text{O}}! N_{\text{H}}!)$, where Λ_k is the thermal deBroglie wavelength of atom k , $\Lambda_k = \sqrt{\beta \hbar^2 / 2\pi m_k}$, and m_k is the mass of atom k , and $\mathcal{D}_i$ is a domain about the i th minimum of the potential energy surface. The sum over i in Eq. (1) can be restricted to symmetry-distinct configurations, in which case f_i is a degeneracy factor.

Several questions immediately arise as to the practical evaluation of the partition function and the prediction of phase transitions. Will classical statistical

mechanics suffice? Is the statistical mechanics controlled by relative stabilities E_i of the different H-bond isomers, or by the vibrational free energies $A_{\text{vib},i}$? The answers to these questions will determine the best practical methods for calculating or simulating order–disorder transitions in ice. Presently, these questions cannot be answered definitively for all ice phases, although cases studied to date indicate that classical statistical mechanics is adequate as long as the region of H-bond symmetrization at very high pressure is excluded, and that despite the small differences in E_i between H-bond configurations, the differences in $A_{\text{vib},i}$ are even smaller. We briefly review the justification for these statements.

To date, there is no evidence that nuclear quantum effects affect order–disorder transitions in ice. According to classical statistical mechanics, nuclear mass has no effect on the location of phase boundaries, aside from the very small mass effects on the Born–Oppenheimer potential energy surface. The very small difference in freezing temperature of H_2O and D_2O at ambient pressures, (0.0 vs 3.8°C) is evidence that quantum effects, although present, are still minor. Similarly, the ice Ih/XI order–disorder transition has been measured [8, 9, 58–60] to take place at 72 K in H_2O and 76 K in D_2O . This is one of the ice order–disorder transitions that occurs at the lowest temperature, yet isotope effects are minor. With the exception of tunneling that occurs as the H-bonds tend toward symmetric in ice X, to date it appears that classical statistical mechanics can safely be used to study order–disorder transitions in ice. As more detailed calculations and experiments emerge, we may learn of cases where quantum effects must be treated.

An immediate practical question arises as to the relative importance of the E_i or $A_{\text{vib},i}$ in the evaluation of the partition function. Differences in E_i are known to be small. The transition enthalpy $T\Delta\bar{S}$ can be estimated using the Pauling entropy $\Delta\bar{S} \approx R \ln \frac{3}{2}$, which should be an upper bound to the transition entropy (see discussion above), giving $\Delta\bar{H} \approx \Delta\bar{E}$ in the range of several hundred joules per mole J mol^{-1} for the known order–disorder transitions in ice. This number is far smaller than, say, the zero-point energy for a water stretching vibration. Therefore, it may seem like vibrational effects might be dominant. However, the statistical mechanics of H-bond arrangements is controlled by *differences* in the vibrational free energy for the H-bond isomers. Here, the evidence indicates that the vibrational free energy of the various H-bond isomers is so similar, that the effect of vibrations is secondary. First, the absence of large isotope effects suggests that large zero-point energies are nearly canceling. Second, the H-bond arrangement calculated to have the lowest E_i has turned out to be the observed low-temperature phase for ice XI, VIII, IX, XIII, and XIV. The lone exception is ice XV, the low-temperature form of ice VI, where calculations disagree with experiment (discussed below in Section III.2.E).

The third piece of evidence that tells us that differences in vibrational free energy $A_{\text{vib},i}$ of various H-bond isomers are smaller than the differences of their equilibrium energy E_i is recent calculations performed by Beck and Singer for

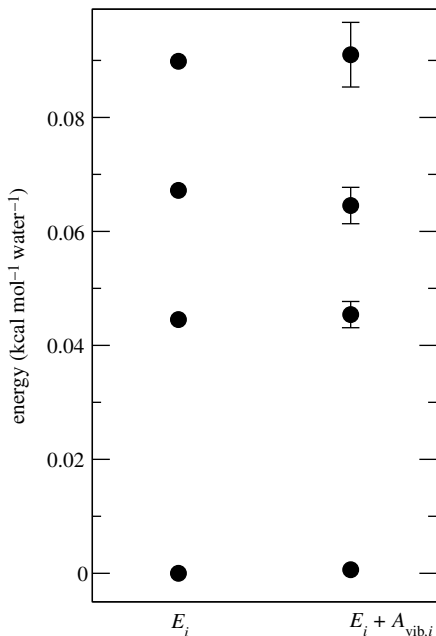


Figure 7. Comparison of E_i , the energy of H-bond arrangements at local minima of the potential energy surface, with $E_i + A_{\text{vib},i}$, the total free energy including vibrational contribution, for the four H-bond isomers of an 8-water unit cell of ice Ic [61].

cubic ice Ic [61] and Umemoto et al. [62]. In Fig. 7, E_i alone is compared with $E_i + A_{\text{vib},i}$ for the four symmetry-distinct H-bond arrangements possible in a 8-water unit cell of ice Ic. The vibrational free energies were calculated using a modification of the Bennett acceptance ratio method [61, 63]. The zero of energy is assigned to one of the isomers in Fig. 7. The differences between $E_i + A_{\text{vib},i}$, and E_i is within the error bars in the calculation of $E_i + A_{\text{vib},i}$. The calculations presented in Fig. 7 are classical, and deserve to be rechecked with quantum mechanics, for example, in a harmonic approximation through second-order expansion of $V(\mathbf{r}^N) - V(\mathbf{r}_i^N)$. However, as mentioned above, the absence of known isotope effects suggests that quantum effects are not significant.

Umemoto et al. have incorporated vibrational free energies in a harmonic approximation for ice VII and calculated the ice VII/VIII phase boundary [62]. They demonstrated that vibrational effects, particularly zero-point energy, have a significant effect on the pressure–volume equation of state of the solid. However, the error in predicting the VII/VIII phase boundary incurred by approximating A_{vib} as constant for all H-bond isomers is relatively minor up to extremely high pressures where the effect of H-bond symmetrization is beginning to take hold. Below 40 GPa, incorporation of vibrational free energy affects the transition temperature by 20 K or less. Errors inherent in the electronic DFT method and failure to extrapolate properly to the thermodynamic limit are more important sources of error. The calculation of Umemoto et al. is significant because it shows that the dependence

of the E_i on unit cell volume in Eqs. (1) and (2) can describe the evolution of the ice VII/VIII phase boundary with increasing system density. Neglect of vibrations causes a 10% error in the density–pressure relationship at zero pressure, but that error decreases with increasing pressure [62].

Oxygen atoms are nearly stationary in proton-ordering transitions. For example, the transformation of ice Ih to ice XI results in a compression along the a - and c -axes of only -0.75 and -0.36% , respectively, and an elongation of the b -axis of 0.84% [14]. Similar changes are observed in the proton-ordering transformation of ice VII in which the a - and c -axes differ by -1.0 and 2.0% , respectively. The lattice constants change by $+0.4$ and -3.3% for a and c , respectively, when ice III is cooled from 250 to 165 K to form ice IX [45]. The distortion of the unit cell in the low-temperature phase has been neglected in theoretical work to date.

B. Energetics of H-Bond Arrangements in Ice

The options for describing the delicate energy differences among H-bond isomers in ice are empirical potentials and *ab initio* methods. Common empirical potentials have been notably unsuccessful in describing H-bond order–disorder phenomena in ice [36, 64–66], although there is no reason to be pessimistic that future improvements in water models will lead to more successful prediction, as discussed below in Section II.B.3. Initial results have shown that even modest levels of electronic density functional theory can correctly predict the H-bond topology of the low-temperature structures of ice and provide a qualitative estimate of the transition temperatures.

1. Empirical Potentials

Enormous effort has been devoted to devising analytic potential models (i.e., “empirical potentials”) capable of describing the structural and dynamic properties of water, and substantial improvements have been made since the first computer simulations of liquid water [67, 68]. Initial tests of the predictions of various available water models at the time by Morse, Rice [69, 70] Townsend et al. [71] found varying quality of structure predictions. The ϵ_{inter} variant of the MCY potential [72] gave reasonable ice structures, while the ST2 potential [73] revealed serious flaws. More recently, Sanz et al. [74] calculated the entire phase diagram of the TIP4P [75] and SPC/E [76] water models (with the exception of ice X, which these models are incapable of describing). Although the phase boundaries are shifted to lower temperature by roughly 40 K, the TIP4P model gave a particularly good account of the phase diagram and, although not nearly as successful, the phase diagram of the SPC/E model bore some resemblance to experiment.

While current empirical potentials show some hope of reproducing the melting lines of the various ice phases and transitions between ice phases with different oxygen atom positions, these potentials do not capture the energetics of the H-bond

rearrangements, or predict the location of H-bond order–disorder transitions in the ices and the identity of the low-temperature phases. Buch et al. [36] calculated the energies of H-bond isomers of ice Ih using the SPC [77], TIP52 [75], TIP4P [75], RWK2 [78, 79], and several others, including one optimized by those authors in hopes of obtaining the $Cmc2_1$ ferroelectric ice XI structure as the ground state. The energy difference between the least and most stable isomers varied by an order of magnitude among the potential models. None of the models, including the one designed by Buch et al. [36] predicted the ferroelectric ice XI structure to be the ground state. Tribello and Slater [80] report that the AMOEBA water potential predicts the antiferroelectric $Pna2_1$ structure of ice Ih as lower than the $Cmc2_1$ structure.

A transition between disordered ice VII and ordered ice VIII was obtained by Sanz et al. [74] in their phase diagram of the TIP4P model, but the coexistence line has qualitatively the wrong shape. The calculated ice VII/VIII boundary exhibits a strong variation with pressure, while the experimental ice VII/VIII boundary is almost pressure-independent over a wide range of pressure between 2 and 10 GPa. Vega et al. [66] found that the SPC/E [76], TIP4P [75], and TIP5P [81] models transform at low temperature from ice Ih into the antiferroelectric structure of $Pna2_1$ space group symmetry first proposed for H-bond ordered ice by Davidson and Morokuma [82], not the experimental ice XI structure. Rick examined proton ordering in the SPC/E [76], TIP4P [75], TIP4P-FC, TIP5P-E [81], and a model specifically designed by Nada and van der Eerden for ice Ih near the melting point [83] which, following Rick [65] and Vega et al. [66], we designate as the NvdE model. The NvdE model was the only one for which the $Cmc2_1$ ferroelectric structure was the lowest energy H-bond isomer. However, the NvdE model evidently allows significant fluctuations away from the $Cmc2_1$ structure at low temperature. At 25 K the H-bond order parameters Rick obtained from Monte Carlo simulations of the NvdE model bore little resemblance to those expected for the $Cmc2_1$ structure, and actually were close to those of a fully disordered lattice [65].

2. *Ab Initio Methods*

At present, DFT with gradient-corrected functionals is the most practical option for *ab initio* description of the energetics of H-bond rearrangements in ice. Given the expected accuracy of this modest level of electronic structure theory, it may at first seem rather hopeless to expect DFT to be useful in this situation. However, description of H-bond fluctuations requires energy differences between configurations that are quite similar. Evidence to date indicates there is a cancellation of contributions on which common electronic DFT methods either do a poor job or fail, such as dispersion interactions. The energy differences between H-bond configurations seem to be most sensitive to properties for which electronic DFT can be trusted (with some caution, see Section II.B.3).

The evidence that electronic DFT can produce meaningful energetics for H-bond fluctuations comes from the fact that, unlike empirical potentials, trends are not sensitive to choice of electronic density functional, the energy differences among H-bond isomers can be rationalized by the dominance of electrostatic interactions [80], which even modest electronic DFT can capture. Furthermore, as will be reviewed in Section III, the predicted low-temperature H-bond arrangement and transition temperatures are in general agreement with experiment.

Hirsch and Ojamäe [84] first brought to light the remarkable insensitivity of the energetics of H-bond arrangements to choice of density functional [84–86]. (Pioneering calculations by Casassa et al. [85, 86] did not have enough precision and did not study a sufficient number of H-bond configurations to elucidate the trends found in later work.) They compared the energies of the 16 H-bond isomers of an 8-water orthorhombic unit cell of ice Ih using two different density functionals and basis sets. A comparison of energies of H-bond isomers for two units cells of ice Ih after a third method was added by Singer and co-worker [87, 88] is shown in Fig. 8. All methods predict that the ferroelectric $Cmc2_1$ structure is most stable. The relative energies of the various isomers are hardly sensitive to the electronic structure method before and after optimization of the energy with respect to the atomic coordinates. One of the methods (using CASTEP [93]) also includes optimization of the energy with respect to unit cell parameters. While it cannot be

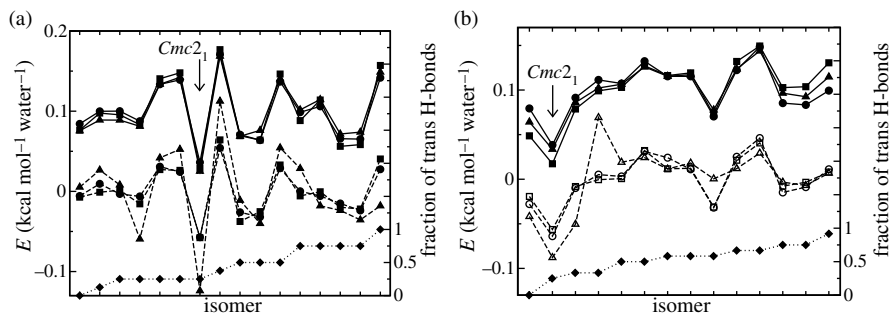


Figure 8. Relative energy of H-bond isomers calculated by periodic electronic DFT methods for (a) 16 isomers of an 8-water orthorhombic unit cell, and (b) 14 isomers of a 12-water hexagonal unit cell, listed in order of increasing fraction of trans H-bonds. (See the caption of Fig. 2 for a definition of cis and trans H-bonds.) The lowest graph (dotted lines) gives the fraction of trans H-bonds associated with each isomer. The energy of the H-bond isomers were calculated with the programs (●, ○) CPMD [89] using the BLYP density functional [90, 91] and a plane wave basis, (■, □) DMol [92] using the BLYP density functional and numerical basis functions, and (▲, △) CASTEP [93] using the PW91 density functional [94–96] and a plane wave basis. Solid lines: energy of H-bond isomers before geometry optimization. Dashed lines: energies after optimization of the molecular coordinates, and for the CASTEP results cell dimensions as well. The 6 energy data sets in each panel, optimized and unoptimized, are plotted with their average taken as the zero of energy to facilitate comparison of the relative energies of the isomers. For clarity, the $Cmc2_1$ isomer is noted and the optimized data sets are shifted by $0.06 \text{ kcal/mol}^{-1}$.

directly compared to the other data sets, cell optimization actually makes only a minor correction to the energies.

Tribello and Slater [80] confirmed the previous findings of Hirsch and Ojamäe [84], and found that the insensitivity to density functional extended to more methods, even including simple LDA (local density approximation). They traced the insensitivity with respect to the electronic density functional to the fact that the exchange and correlation contributions to the total energy varied little between the H-bond isomers, and that the dominant contribution to the energy differences arose from electrostatic interactions [80]. Significantly, Tribello and Slater [80] found that the electrostatic interactions between water molecules, when expressed as a multipole expansion, required rather high-order multipole moments to achieve convergence. Moments up to hexadecapole were required for ice Ih, and up to octopole for ice VII.

3. Outlook

Even though we could not find any satisfactory results from currently available empirical potentials, there are some reasons to be optimistic that an empirical potential capable of describing H-bond energetics in ice may be developed in the future. Several findings point to long range electrostatic interactions as key properties. Buch et al. [36] found that shifting the polarizability center of the KW potential [97] from the oxygen toward the hydrogens lowered the energy of the $Cmc2_1$ structure relative to the average energy of disordered ice Ih. Rick established that interactions out to seventh nearest neighbors are significant in determining the relative stability of the $Cmc2_1$ and $Pna2_1$ structures. Most significantly, Tribello and Slater [80] demonstrated that electrostatic interactions are the dominant contribution to the energy differences among H-bond isomers calculated using electronic density functional theory. While it may be computationally expensive to incorporate the effect of high-order electric multipoles in an empirical potential, there is some hope that the result will be a model with greater applicability to H-bond order-disorder phenomena in ice.

While even modest electronic DFT shows promising results, there may be cases where it fails, as in the ice VI/XV transition described in Section III.E. While we have discussed several factors that give us some confidence in electronic DFT methods in Section II.B.2, comparison with more accurate and more “convergeable” Schrödinger equation based electronic structure methods is essential in future work.

C. Tensorial Combinations of Hydrogen-Bond Variables: Graph Invariants and Higher-Order Functions

Calculating the E_i and $A_{\text{vib},i}$ for the billions of H-bond topologies found in a “simulation cell”, a unit cell large enough to approximate the thermodynamic limit, is not feasible using first-principles methods. Yet given the lack of empirical

potentials with sufficient accuracy to describe the energetics of H-bond rearrangements in ice, it is what would be needed to, predict proton-ordering phase transitions in ice. A link between H-bond topology and the energy, if such a correlation did exist, would provide an inexpensive route to the energies needed to predict H-bond order-disorder phenomena in ice. Even if a suitable empirical potential was available (and we are optimistic that one will be developed), a description in terms of H-bond topology would provide a concise language for analyzing and understanding H-bond fluctuations in ice. In this section, we review a method to link physical quantities with H-bond topology. The cases considered in Sections III and V will provide evidence that physical quantities can be described conveniently and concisely in terms of the H-bond topology.

The key idea is that since energy is a scalar, invariant to symmetry operations, it must depend on combinations of H-bonds that are likewise invariant to symmetry operations. Hence, we write the energy in terms of such combinations, which we have called *graph invariants*. Alternatively, local site displacements transform as vectors. Hence, the site displacements that arise from local variations of H-bond topology must depend on combinations of H-bond variables that transform as a first-rank tensor. While there is an exceedingly large number of H-bond configurations available in even a small simulation cell, the number of invariant combinations of H-bonds needed to describe the energy or the number of vectorial combinations of H-bonds needed to describe site displacements will turn out to be quite small. Furthermore, they can be parametrized by first-principles calculations (Section II.B.2) on small unit cells.

The idea of linking the H-bond topology to energetics in ice has been around since the work of Bjerrum [98] and Pitzer and Polissar [99], who postulated that trans H-bonds, those where the nonbonded hydrogens lie on opposite sides of the bond, are lower energy than cis H-bonds [100]. (See Fig. 2 for an illustration of cis and trans H-bonds.) However, such past attempts were rather *ad hoc* in nature and not sufficiently general to provide accurate predictions. Consider how the scheme would work for the energy if one accepted Bjerrum's conjecture about cis and trans H-bonds: The energy difference between a cis and a trans H-bond in ice-Ih could be established by *ab initio* calculations on small unit cells, for which this type of detailed calculation is feasible. Such *ab initio* calculations are not possible for the many H-bond arrangements in large simulation cells, but it is certainly possible to either enumerate all the H-bond topologies (Section IV) or perform a Monte Carlo simulation for large cells and assign an energy to each configuration based on the number of cis and trans H-bonds. The energies E_i needed in Eq. (3) for the billions of topologies possible for large unit cells would be given, relative to an all-trans configuration, by counting the number of cis bonds in each topology and multiplying by the cis-trans energy difference. This illustrates the two ingredients needed in our scheme. First, parameters are derived from detailed calculations (like *ab initio*) on small unit cells. Second, it also illustrates that an invariant for small

unit cells, in this case the number of cis and trans H-bonds, is also an invariant for large cells and that the energetic parameter obtained for small cells is applicable to a large cell. The vibrational free energies $A_{\text{vib},i}$ in Eq. (3) can also be linked to H-bond topology, although to date approximating the vibrational free energy as nearly the same for all the H-bond isomers appears to be acceptable.

Of course, using a single parameter, the relative number of cis and trans H-bonds, is not likely to furnish an accurate description of H-bond energetics in ice. In this section, we give a generalization of this idea, showing how a hierarchy of parameters, the graph invariants, can be generated to describe scalar physical properties, and how graph invariants of increasing complexity can be added until convergence is attained. Even when using the appropriate graph invariants, the two essential ingredients remain detailed calculations for small unit cells, and the ability to immediately generate the appropriate energy expression for the enormous number of configurations available to a larger unit cell that are sampled either by direct enumeration of H-bond topologies or by Monte Carlo methods.

1. *Informal Introduction to Oriented Graphs and Graph Invariants*

Each H-bond in ice or water clusters consists of a hydrogen covalently bonded to one oxygen, the donor, and H-bonded to a second oxygen, the acceptor. Hence, H-bonds are directional, and are conventionally taken to point from donor to acceptor. Proton arrangements in ice are summarized by oriented graphs, a set of vertices linked by directed edges [29, 101, 102]. The symbol b_r stands for the orientation of the r th H-bond with respect to a canonical orientation, $b_r = +1$ if the H-bond points in the same direction as the canonical orientation, $b_r = -1$ if the direction is opposite.

To illustrate the theory, let us take a simple example, “square ice”, which, like ordinary ice, consists of four-coordinate water molecules. (Applications to the real ice lattices are presented below in Section III.) Part of the square ice lattice and the direction of bonds, all in an arbitrarily chosen canonical bond orientation, are shown in Fig. 9. Six possible graphs within the 2×2 unit cell of square ice, shown in Fig. 10, when periodically replicated realize an H-bond topology in agreement with the Bernal–Fowler ice rules. The eight bonds of the 2×2 unit cell are given an arbitrary index ranging from 1 to 8, as indicated in graph (a) of Fig. 10. The value of the bond variables $b_1, b_2, \dots, b_8$ for the graphs in Fig. 10 are given in Table I.

Some of the graphs shown in Fig. 10 are related to each other by a symmetry operation. Graph (d) is obtained from graph (a) by either a C_4 rotation or reflection operation. Therefore, the energy and other scalar properties of the two configurations should be identical. The same is true for graphs (b) and (e), and graphs (c) and (f). If the energy depends on the topological features of the H-bond network, then it must depend on functions of the bond variables b_r that are identical for configurations related by a symmetry operation.

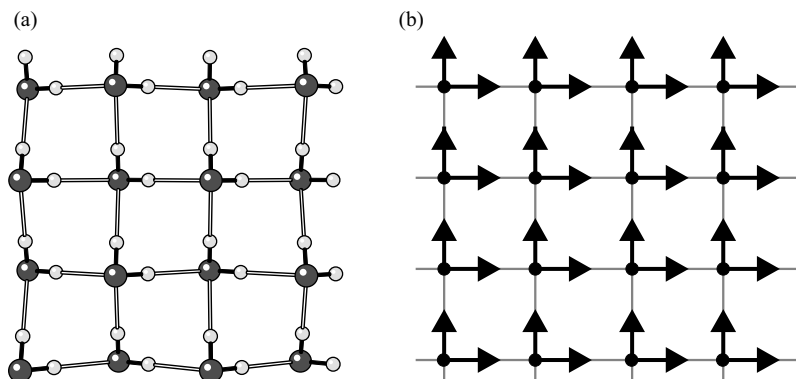


Figure 9. A square ice lattice used to illustrate graph invariants. The molecular configuration, shown in (a), is summarized by the directed graph appearing in (b). The H-bond arrangement shown here is adopted as the canonical bond orientation. Other periodic H-bond arrangements are possible, as illustrated in Fig. 10.

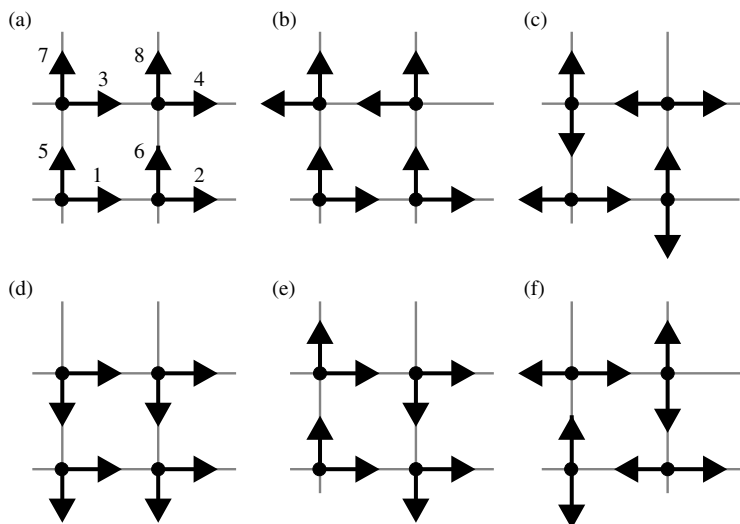


Figure 10. Graphs that lead to periodic H-bond patterns satisfying the Bernal–Fowler ice rules in the square ice lattice depicted in Fig. 9. In graph (a), the bonds are arranged in their canonical orientation, the same one shown in Fig. 9. The eight bonds associated with the 2×2 unit cell are numbered according to the scheme indicated on graph (a). In some graphs, the bonds associated with unit cells neighboring the primary unit cell are shown to make it more apparent how the orientation of complete water molecules are indicated by the graphs. For example, in graph (b) the periodic image of bond 4 is actually drawn to the left of bond 3. In graph (b) bond variables b_1, b_2, b_5, b_6, b_7 , and b_8 all have value $+1$, while bonds b_3 and b_4 have value -1 , all defined relative to the canonical orientations of graph (a).

TABLE I

Value of the Bond Variables and Graph Invariants Associated with Each of the Graphs Depicted in Fig. 10

Graph	a	b	c	d	e	f
b_1	1	1	1	1	1	-1
b_2	1	1	-1	1	1	1
b_3	1	-1	-1	1	1	1
b_4	1	-1	1	1	1	-1
b_5	1	1	-1	-1	1	1
b_6	1	1	1	-1	-1	-1
b_7	1	1	1	-1	1	-1
b_8	1	1	-1	-1	-1	1
$I_{13}^{2 \times 2}$	1	0	-1	1	0	-1
$I_{23}^{2 \times 2}$	1	0	1	1	0	1
$I_{12}^{2 \times 2}$	1	1	-1	1	1	-1
$I_{15}^{2 \times 2}$	0	0	-1	0	0	-1
$I_{11}^{2 \times 2}$	1	1	1	1	1	1

Consider the combination of bond variables,

$$I_{13}^{2 \times 2} = \frac{1}{4} (b_1 b_3 + b_2 b_4 + b_5 b_6 + b_7 b_8) \quad (4)$$

which is an example of a *graph invariant*. (The notation $I_{13}^{2 \times 2}$ indicates that this invariant is obtained by application of the group theoretical projection operator for the totally symmetric representation on the bond product $b_1 b_3$ of a 2×2 unit cell.) Notice in Table I that $I_{13}^{2 \times 2}$, has exactly the same value among the three pairs of graphs related by symmetry operations. Here, $I_{13}^{2 \times 2}$ also has a clear physical interpretation. It is a sum of dot products of four pairs of parallel bonds. $I_{13}^{2 \times 2}$ effectively counts the number of cis H-bonded pairs in which nonparticipating hydrogens lie on the same side of the H-bond [100]. Bjerrum postulated that this type of bond is higher energy than those in which the nonbonded hydrogens are more distant [96, 97]. In Fig. 10, all four bonds of graphs (a) and (d) are cis. In graphs (b) and (e), one-half of the bonds are cis, and the other one-half are trans. None of the bonds are cis in graphs (c) and (f).

Clearly, $n_{\text{cis}} = 2(I_{13}^{2 \times 2} + 1)$ as follows from the dot product nature of Eq. (4) and can be verified from Fig. 10. Hence, if Bjerrum's conjecture turns out to be correct then the graph invariant $I_{13}^{2 \times 2}$ will be the appropriate link between a scalar physical property, the energy in the case of Bjerrum's conjecture, and the topology of the H-bond network. If the conjecture is valid, we would be able to approximate the dependence of energy on the H-bond topology by a relation of the form,

$$E \approx E_0 + \alpha_{13} I_{13}^{2 \times 2} \quad (5)$$

The validity of Bjerrum’s notion of strong and weak H-bonds has been debated for many years in the literature [36, 99, 103, 104]. While certainly appropriate for the water dimer [105], it is not clear that H-bonds in ice-Ih fall into strong and weak groups according to their cis–trans nature. The reliable way to identify which topological features of the H-bond lattice are most relevant to its stability is to systematically identify *all* symmetry-invariant features of the H-bond topology upon which scalar physical properties may depend. For the 2×2 unit cell of our square ice example, there are four other graph invariants that depend on pairs of bond variables.

$$I_{23}^{2 \times 2} = \frac{1}{4} (b_2 b_3 + b_1 b_4 + b_6 b_7 + b_5 b_8) \quad (6)$$

$$I_{12}^{2 \times 2} = \frac{1}{4} (b_1 b_2 + b_3 b_4 + b_5 b_7 + b_6 b_8) \quad (7)$$

$$I_{15}^{2 \times 2} = \frac{1}{16} (b_1 b_5 - b_2 b_5 - b_3 b_5 + b_4 b_5 + b_1 b_6 + b_2 b_6 + b_3 b_6 - b_4 b_6 \\ + b_1 b_7 + b_2 b_7 + b_3 b_7 - b_4 b_7 + b_1 b_8 - b_2 b_8 - b_3 b_8 + b_4 b_8) \quad (8)$$

$$I_{11}^{2 \times 2} = \frac{1}{8} (b_1^2 + b_2^2 + b_3^2 + b_4^2 + b_5^2 + b_6^2 + b_7^2 + b_8^2) \quad (9)$$

An improvement over Eq. (5) would be given by using all the invariants that depend on bond variables.

$$E \approx E_0 + \alpha_{13} I_{13}^{2 \times 2} + \alpha_{23} I_{23}^{2 \times 2} + \alpha_{12} I_{12}^{2 \times 2} + \alpha_{15} I_{15}^{2 \times 2} + \alpha_{11} I_{11}^{2 \times 2} \quad (10)$$

While Eqs. (5) and (10) are written for the energy, we emphasize that the dependence of any scalar physical quantity on H-bond topology can be parametrized in that fashion.

For the ice lattice, both real ice-Ih and our illustrative example square ice, all invariant linear combinations of single-bond variables (first-order invariants) are identically zero. The graph invariants in Eqs. (4)–(9) are a complete set of invariant bond combinations for the 2×2 unit cell of square ice that can be constructed from products of two bond variables. We call such combinations of pairs of bond variables *second-order invariants*. Procedures for generating graph invariants are described in Section II.C. More complicated invariants, made from products of three or more bond variables (third- and higher-order graph invariants) are possible as well, although one may hope for convergence with respect to the description of physical properties as more complicated invariants are included. We have been able to document that second-order invariants adequately describe the dependence of energy and other scalar properties on H-bond topology in clusters [37].

The four additional invariants presented in Eqs. (6)–(9) can be assigned physical interpretations, just as we discussed for $I_{13}^{2 \times 2}$ with relation to Bjerrum’s conjecture regarding cis and trans H-bonds. For example, $I_{12}^{2 \times 2}$ measures the degree to which chains of H-bonds along the x or y directions align in the same direction. Because

of the constraints of the ice rules, this also measures the number of water molecules whose OH bonds are both parallel to the x or y directions. (Only graphs (c) and (f) contain such waters. All other graphs contain waters with one bond pointing along x and one pointing along y .) Here, $I_{15}^{2 \times 2}$ can be seen to measure this same property. In fact, with regard to the graphs shown in Fig. 10, $I_{12}^{2 \times 2}$ and $I_{15}^{2 \times 2}$ are linearly dependent on each other: $I_{12}^{2 \times 2} = 2I_{15}^{2 \times 2} + 1$. It often happens that, when evaluated for graphs that satisfy constraints like the ice rules, invariants are linearly dependent on each other. Relaxing the ice rules, for example, by allowing hydronium or hydroxide to appear in the lattice, will break the linear dependence of the invariants. The invariant $I_{11}^{2 \times 2}$ is rather trivial for the graphs shown in Fig. 10, merely giving the fraction of filled H-bonds in a unit cell.

Let us return to Bjerrum's conjecture that the energy of different H-bond topologies can be linked to the number of cis or trans H-bonds present in the lattice. The beauty of Bjerrum's simple conjecture is that it can be applied to both regular, periodic patterns of H-bonds, as well as disordered arrangements. Put another way, the number of cis and trans H-bonds is a topological invariant for periodically replicated lattice of arbitrary size, for both small unit cells, cells large enough for numerical simulations, or cells whose size tends toward infinity in the true thermodynamic limit. We have demonstrated [38] that this property of cis and trans H-bonds is shared by all the invariants we generate: Invariants like the ones we presented in Eqs. (4)–(9) for the 2×2 unit cell of the square ice lattice are also invariants of larger unit cells.

Larger unit cells will also generate new invariants that have no counterpart in small unit cells. However, these new invariants involve bond combinations more distant from each other than in a small unit cell. As a result, one may expect that at a certain point these new, long-range invariants will not be important in capturing physical properties of the system. This sets up a strategy for describing the properties of large unit cells, those large enough for statistical simulations in terms of properties derived from small unit cells. Even though the large unit cells admit millions or billions of H-bond topologies, the energy, free energy, or other scalar physical properties of each of these topologies, if the calculations reviewed in Section III and V are any guide, depends on the value of a handful of invariants.

Assuming the simplest linear dependence including the fact that high-order invariants could be regarded as complementing a more complicated functional form [104], the energy of an H-bond isomer as a function of the bond variables is written as:

$$E(b_1, b_2, \dots) = E_0 + \sum_r \alpha_r I_r + \sum_{rs} \alpha_{rs} I_{rs} + \sum_{rst} \alpha_{rst} I_{rst} + \dots \quad (11)$$

With enough high-order terms in the expansion, the above expression will eventually parametrize the dependence of any scalar function of H-bond topology. In our experience, applying this expression to water clusters and ice, truncating the

expression at second order and only using second-order invariants for which bonds rs are either neighbors or next nearest neighbors has been sufficient to provide acceptable accuracy. This provides a very compact expression linking the energy to the H-bond topology. It is important to emphasize that Eq. (11), although written for the energy, is applicable to any scalar physical quantity. Expansions for vectorial and higher-order quantities follow analogously.

The linear expansion of Eq. (11) is not the most general relation between scalar properties and H-bond topology, and in certain situations we may expect nonlinear dependence of physical properties on the invariants. To give an example, in a simple model where the total dipole moment arises from bond dipoles μ_r , the total dipole moment could be expressed in terms of our bond variables as:

$$\mu = \sum_r b_r \mu_r \quad (12)$$

and we expect the squared magnitude of the total dipole moment to be well described by a linear expansion in second-order graph invariants, $|\mu_r|^2 \approx \sum_{rs} \alpha_{rs} I_{rs}$, and indeed find this to hold nicely for H-bond topologies of the $(\text{H}_2\text{O})_6$ cage cluster [37]. The parameter $|\mu_r|$ itself is also a scalar physical quantity. Equation (12) implies that a linear expansion of $|\mu_r|$ through second-order invariants would not be as successful, unless a series expansion of the square root of $|\mu_r|^2$ converged rapidly. Instead, the nonlinear function $\sqrt{\sum_{rs} \alpha_{rs} I_{rs}}$ would be the expansion of choice for $|\mu_r|$. (For nonlinear functions, the classification of invariants into first, second, and higher orders loses its significance.) Of course, since products of invariants are also invariants, a linear expansion for $|\mu_r|$ in the form of Eq. (11) would eventually converge but might require higher-order terms.

2. Graph Invariants via Space Group Projection Operators

Graph invariants, functions of bond variables that are unchanged under any symmetry operations, can be constructed using standard group theoretical projection operators. The application of a projection operator to a single-bond variable, b_r , takes the form,

$$I_r = C_r \sum_{\alpha} g_{\alpha}(b_r) \quad (13)$$

where C_r is a normalization constant chosen for convenience, g_{α} is a member of the symmetry group of the system, and the sum runs over the entire symmetry group. The characters of the totally symmetric representation are identical for all symmetry operations. Therefore, to construct a linear combination that transforms according to the totally symmetric representation of the group, the terms $g_{\alpha}(b_r)$ are combined in Eq. (13) with equal coefficients. The appropriate group for a crystal lattice is the space group. We assume that the crystal is large and periodic,

so the translation subgroup is of order $N_x N_y N_z$ [or obviously $N_x N_y$ for a two-dimensional lattice like square ice]. We use x, y, z to designate the crystal axes, but nothing in our formalism requires that these axes be orthogonal.

Other invariants can be constructed similarly:

$$I_{rs} = C_{rs} \sum_{\alpha} g_{\alpha}(b_r b_s) \quad (14)$$

$$I_{rst} = C_{rst} \sum_{\alpha} g_{\alpha}(b_r b_s b_t) \quad (15)$$

$\vdots$

We take the normalization constant to be the inverse of the order of the group, making the invariants intensive quantities.

$$C_{rs\dots} = \frac{1}{\#(G)} \quad (16)$$

We refer to I_r as a first-order invariant, I_{rs} as a second-order invariant, and so on. From the definition of invariants, it is obvious to see that $I_{rs} = I_{sr}$. More generally, invariants with permuted subscripts are equivalent. When all bonds are filled, all bond variables $b_r = \pm 1$. Therefore, we have $I_{rr} = \text{constant}$, as well as $I_{rrstu\dots} = I_{stu\dots}$. We have previously shown that if a symmetry operation can bring a single bond b_r into $-b_r$, the first-order invariant of b_r is identically zero [37]. More generally, if $g_{\alpha}(b_r) = \pm b_s$, I_r and I_s are equivalent. Local constraints, for example, ice rules, can cause further degeneracy.

Symmetry properties are manifested by a group of permutation operations mapping the set of vertices onto themselves. The space group of a crystal can be treated as a finite group by invoking periodic boundary conditions. Consider a lattice with possibly nonorthogonal unit cell vectors $\{a_x, a_y, a_z\}$. Even though we label the cell vectors with “ x, y, z ”, our expressions apply equally well to nonorthogonal basis vectors. The full space group is designated as G . Γ , the crystallographic translational group, is generated by the elementary translation operators $\{\tau_x \tau_y \tau_z\}$, where $\tau_x^u \tau_y^v \tau_z^w(\mathbf{R}) = \mathbf{R} + u\mathbf{a}_x + v\mathbf{a}_y + w\mathbf{a}_z$. That is,

$$\Gamma = \{ \tau_x^u \tau_y^v \tau_z^w | u = 0, 1, \dots, N_x - 1, v = 0, 1, \dots, N_y - 1, w = 0, 1, \dots, N_z - 1 \} \quad (17)$$

We will always assume a large but finite crystal with periodic boundary conditions.

$$\tau_x^{u+N_x} = \tau_x^u, \tau_y^{v+N_y} = \tau_y^v \quad \text{and} \quad \tau_z^{w+N_z} = \tau_z^w \quad (18)$$

Hence, Γ becomes a finite group and $\#(\Gamma)$, the order of Γ , is $N_x N_y N_z$.

As is well known in the theory of space groups [106], G can be decomposed into a sum of cosets of Γ :

$$G = \Gamma p_1 \cup \Gamma p_2 \cup \Gamma p_3 \cup \dots \quad (19)$$

where the p_β are coset representatives and $\cup$ stands for a summation of two sets, which is the set of all objects that are contained in at least one of the sets. The set of cosets form the factor group G/Γ . Conventionally, the coset representative p_β is chosen to be a pure point group operation if possible, or a space group operation involving a minimal translation if a screw or glide operation.

The projection operation for the totally symmetric representation of G , denoted here as $\hat{G}$, is generated by applying all operations of the group with coefficients proportional to the characters of the totally symmetric representation, that is, with equal coefficients. The projection operator for the totally symmetric representation of the pure translation group, denoted here as $\hat{\Gamma}$ is simply

$$\hat{\Gamma} = \sum_{u=0}^{N_x-1} \sum_{v=0}^{N_y-1} \sum_{w=0}^{N_z-1} (\tau_x)^u (\tau_y)^v (\tau_z)^w \quad (20)$$

and for the full space group the projection operator is

$$\hat{G} \equiv \sum_{\alpha \in G} g_\alpha = \sum_{\beta \in G/\Gamma} \hat{\Gamma} p_\beta \quad (21)$$

The first sum is over all elements in G , while the second sum is over the coset representatives. Our previous Eq. (13) and (14) for graph invariants can be rewritten in terms of projection operators:

$$I_r = C_r \hat{G}(b_r) \quad (22)$$

$$I_{rs} = C_{rs} \hat{G}(b_r b_s) \quad (23)$$

$$I_{rst} = C_{rst} \hat{G}(b_r b_s b_t) \quad (24)$$

and so on for higher-order invariants.

In an H-bond disordered phase of ice, the periodicity reported in, say, an X-ray or neutron diffraction experiment is broken by the local H-bond disorder. In practical calculations, even for a 0 K (but H-bond disordered) structure, we cannot use the primitive unit cell because that refers to an average over local H-bond disorder. In practical calculations, we use a sequence of nonprimitive cells (“nonprimitive” from the crystallographer’s point of view) of increasing size until the thermodynamic limit is attained. Periodic boundary conditions are enforced for a $n_x \times n_y \times n_z$ nonprimitive cell, but within that enlarged cell H-bond disorder breaks the periodicity of the averaged X-ray or neutron diffraction structure. Practical calculations envisioned for enlarged unit cells may be *ab initio* studies

on smaller unit cells, or a statistical simulation on a larger “simulation cell”. To obtain explicit expressions required to generate invariants for enlarged unit cells, we transform expressions like Eqs. (22)–(24) into a form that explicitly incorporates the choice of a nonprimitive unit cell. The graph invariants of Eqs. (4)–(9), which arose in the simple example of square ice, were generated using projection operators designed for nonprimitive unit cells.

For an $n_x \times n_y \times n_z$ unit cell with basis $\{n_x \mathbf{a}_x, n_y \mathbf{a}_y, n_z \mathbf{a}_z\}$, the translation group, denoted as $\Gamma_{n_x \times n_y \times n_z}$, can be written as:

$$\Gamma_{n_x \times n_y \times n_z} = \left\{ (\tau_x^{n_x})^u (\tau_y^{n_y})^v (\tau_z^{n_z})^w \mid u = 0, 1, \dots, \frac{N_x}{n_x} - 1 \right. \\ \left. v = 0, 1, \dots, \frac{N_y}{n_y} - 1, w = 0, 1, \dots, \frac{N_z}{n_z} - 1 \right\} \quad (25)$$

(Recall that we label our cell vectors with the familiar Cartesian directions “x, y, z” even though our expressions apply equally well to nonorthogonal systems.) It is elementary to see that Γ is equivalent to $\Gamma_{1 \times 1 \times 1}$ and $\Gamma_{n_x \times n_y \times n_z} \subset \Gamma_{1 \times 1 \times 1} = \Gamma$. For any $\Gamma_{n_x \times n_y \times n_z}$, we have

$$\#(\Gamma_{n_x \times n_y \times n_z}) = \#(\Gamma)/n_x n_y n_z = N_x N_y N_z / n_x n_y n_z \quad (26)$$

For graphs satisfying the periodic boundary condition of an $n_x \times n_y \times n_z$ unit cell, the value of a bond variable at a position translated by one of the members of $\Gamma_{n_x \times n_y \times n_z}$ is equal to the bond variable at the original position:

$$\forall \tau_i \in \Gamma_{n_x \times n_y \times n_z} \quad \text{value of } \tau_i b_r = \text{value of } b_r \quad (27)$$

It is crucial to realize that bond $\tau_i b_r$ is distinct from bond b_r , even though their *values* are the same on account of periodic boundary conditions. Equation (27) provides fewer constraints on the H-bonds than for the smaller $1 \times 1 \times 1$ unit cell. As the periodic cell is enlarged, a greater variety of H-bonding patterns is permitted until, as the cell size approaches the thermodynamic limit, it is capable of describing all manner of disorder in ice.

The full space group can be decomposed into cosets of the translation subgroup $\Gamma_{n_x \times n_y \times n_z}$. While the pure translation group for the crystal with $n_x \times n_y \times n_z$ unit cell is smaller than for the $1 \times 1 \times 1$ cell, the set of coset representatives is correspondingly enlarged by a factor of $n_x n_y n_z$. The set of coset representatives $p_\beta^{n_x \times n_y \times n_z}$ for the larger cell is given by

$$\left\{ \tau_x^u \tau_y^v \tau_z^w p_\beta \mid \beta \in G/\Gamma, u = 0, 1, \dots, n_x - 1, v = 0, 1, \dots, n_y - 1, w = 0, 1, \dots, n_z - 1 \right\} \quad (28)$$

The space group G may be decomposed into cosets appropriate for either the $n_x \times n_y \times n_z$ or $1 \times 1 \times 1$ cells.

$$\begin{aligned} G &= \Gamma p_1 \cup \Gamma p_2 \cup \Gamma p_3 \cup \dots \\ &= \Gamma^{n_x \times n_y \times n_z} p_1^{n_x \times n_y \times n_z} \cup \Gamma^{n_x \times n_y \times n_z} p_2^{n_x \times n_y \times n_z} \cup \Gamma^{n_x \times n_y \times n_z} p_3^{n_x \times n_y \times n_z} \cup \dots \end{aligned} \quad (29)$$

In Eq. (29), we have decomposed G into right cosets. For the full translation subgroup, the choice between left and right cosets is irrelevant because Γ is a normal subgroup of G , for which left and right cosets are identical. However, $\Gamma^{n_x \times n_y \times n_z}$ might not be a normal subgroup of G , and the left and right cosets may be distinct. In this case, decomposition into right cosets is the most convenient choice because, according to Eq. (27), following the action of a coset representative with any member of $\Gamma^{n_x \times n_y \times n_z}$ leaves the *value* of the bond expression unchanged, as explained in the discussion accompanying Eq. (27).

The application of $\hat{G}$ on a product of bond variables can be written using the coset representatives of the enlarged $n_x \times n_y \times n_z$ cell.

$$I_{rs\dots}^{n_x \times n_y \times n_z} = \frac{1}{\#(G/\Gamma)^{n_x n_y n_z}} \sum_{u=0}^{n_x-1} \sum_{v=0}^{n_y-1} \sum_{w=0}^{n_z-1} \tau_x^u \tau_y^v \tau_z^w \left[\sum_{\beta \in G/\Gamma} p_\beta(b_r b_s \dots) \right] \quad (30)$$

The sum over coset representatives now includes translations that would be symmetry operations for the averaged X-ray crystallographic cell. In the enlarged cell, these translations bring bond variables b_r into another one that may not have an identical value because of H-bond disorder. Equation (30) is our main result for non-primitive cells. It can be used to prove that any invariant for a smaller unit cell is also an invariant for a larger unit cell [38]. This property enables us to parametrize an expansion for the energy [Eq. (11)] of a large simulation cell using, say, *ab initio* calculations for smaller cells. Equation (30) also states that any new invariants introduced as the unit cell is enlarged involve products of bonds separated by the size of the enlarged cell. These interactions are more distant, and of less importance. This provides a natural hierarchy of approximations for decomposing the dependence of tensorial physical properties on H-bond topology. The most local and dominant effects would be captured by fitting to invariants at the level of the small cell. If these effects are completely dominant, then physical properties for a larger $n_x \times n_y \times n_z$ cell would be accurately predicted in terms of invariants that are from the smaller cell, summed over all portions of the $n_x \times n_y \times n_z$ cell. Deviations from this picture are used to parametrize physical properties in terms of the invariants of still larger cells. This improved characterization could, in principle, be tested at even larger levels until convergence is achieved.

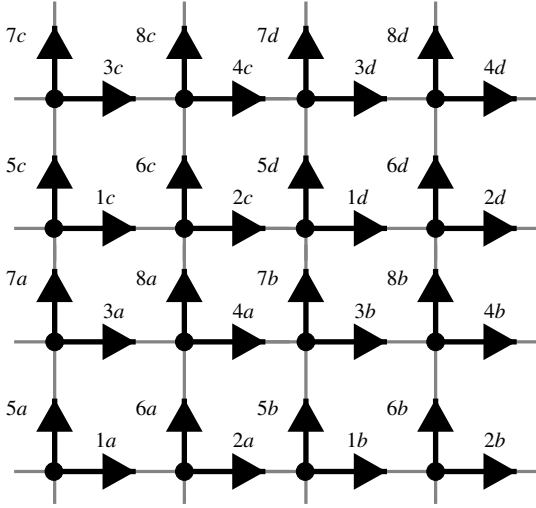


Figure 11. Labeling scheme for bonds in the 4×4 unit cell of “square ice”.

3. An Illustration for Square Ice

In Section II.C.1, we exhibited the five second-order graph invariants $I_{rs}^{2 \times 2}$ associated with the 2×2 unit cell of our “square-ice” example. The formalism of Section II.C.2 explained how those graph invariants were generated with projection operators, and exposed relations between graph invariants for unit cells of arbitrary size. The very practical consequence of these relations is that calculations feasible for only small unit cells, such as *ab initio* energetic calculations, can be applied to larger unit cells appropriate for statistical simulations. Since the formalism of Section II.C.2 may be forbidding at first glance, we illustrate the relationship between graph invariants for unit cells of different size for square ice. We discuss the connections with the graph invariants of the smaller 2×2 unit cell.

We begin by examining the result of projecting onto bonds $1a$ and $3a$ of the 4×4 unit cell (Fig. 11).

$$\begin{aligned}
 I_{1a,3a}^{4 \times 4} = \frac{1}{32} \{ & b_{1a}b_{3a} + b_{2a}b_{4a} + b_{5a}b_{6a} + b_{7a}b_{8a} \\
 & + b_{1b}b_{3b} + b_{2b}b_{4b} + b_{5b}b_{6b} + b_{7b}b_{8b} \\
 & + b_{1c}b_{3c} + b_{2c}b_{4c} + b_{5c}b_{6c} + b_{7c}b_{8c} \\
 & + b_{1d}b_{3d} + b_{2d}b_{4d} + b_{5d}b_{6d} + b_{7d}b_{8d} \\
 & + b_{1c}b_{3a} + b_{2c}b_{4a} + b_{5c}b_{6a} + b_{7c}b_{8a} \\
 & + b_{1a}b_{3c} + b_{2a}b_{4c} + b_{5a}b_{6b} + b_{7a}b_{8b} \\
 & + b_{1b}b_{3d} + b_{2b}b_{4d} + b_{5c}b_{6d} + b_{7c}b_{8d} \\
 & + b_{1d}b_{3b} + b_{2d}b_{4b} + b_{5d}b_{6c} + b_{7d}b_{8c} \}
 \end{aligned} \tag{31}$$

Bond variables $b_{j\alpha}$ ($j = 1 - 4$, $\alpha = a, b, c, d$) in Eq. (31) are labelled in Fig. 11. The $b_{j\alpha}$ with the same value of α refer to bonds within the same 2×2 subunits of the 4×4 cell. Each of the first four lines of Eq. (31) are clearly recognizable as $I_{13}^{2 \times 2}$ of Eq. (4) evaluated for each 2×2 sector of the 4×4 unit cell. Each of the terms represent the product of bond variables for bonds that are parallel and separated by one lattice unit in either the x or y direction, an interaction that could be estimated by a calculation for the smaller 2×2 cell. Terms like $b_{1a}b_{3c}$ may seem to violate this condition, since bonds $1a$ and $3c$ lie three lattice units from each other in the y direction. However, the term $b_{1a}b_{3c}$ actually represents the interaction of the bond $1a$ with another bond below it that lies in a neighboring unit cell. Because of lattice periodicity, that bond has the same *value* as its periodic image bond $3c$. Hence, in the term $b_{1a}b_{3c}$, the variable b_{3c} represents the *value* of another bond that is its periodic image in the lattice. This example illustrates the distinction, made immediately after Eq. (27), between bond variables and their value. In expressions like Eq. (31), it is most convenient to replace actual bond variables, which might be bond variables outside a primary unit cell, with other variables within the primary cell that have the same value. Returning to Eq. (31), we could have just as well said that the term $b_{1a}b_{3c}$ represents the interaction of a bond $3c$ with another bond one lattice unit above it whose value is the same as its periodic image, bond $1a$.

Expression (31) is an illustration of the general formula, Eqs. (30). The terms in the last four lines would be identical in value to those of the first four lines if the lattice still had 2×2 periodicity. Put another way, if the letters were removed from the subscripts in the last four lines, thereby enforcing 2×2 periodicity, the last four lines would duplicate the first four lines. These terms are indeed part of $I_{13}^{2 \times 2}$, but they do not appear explicitly in Eq. (4) because their *value* is identical to terms already present in that expression. In the 4×4 setting, these terms must be included as distinct contributions. Provided the additional invariants introduced at the 4×4 level do not make significant contribution, the contribution of an invariant like $I_{1a,3a}^{4 \times 4}$ to a scalar physical property like the energy could be estimated from *ab initio* calculations for the 2×2 unit cell.

As discussed in Section II.C.1, invariants like $I_{1a,3a}^{4 \times 4}$ of Eq. (31) has the physical interpretation of counting the number of cis and trans H-bonds of square ice. Therefore, if Bjerrum's conjecture was correct and the energetic difference between a cis and trans H-bond was established for a 2×2 unit cell and the parameter α_{13} of Eq. (5) established, then for the 4×4 unit cell the energy would be given by

$$E \approx E_0 + \alpha_{13} I_{13}^{4 \times 4} \quad (32)$$

where α_{13} is the same number as in Eq. (5) and has been established by detailed calculations on the smaller unit cell. Of course, an expression like Eq. (32) would only be appropriate if Bjerrum's conjecture about cis and trans H-bonds was valid. Therefore, an expression using additional invariants, like Eq. (10) for the 2×2

cell, would be more accurate. In the following paragraph, we illustrate that each of the invariants appearing in Eq. (10) also appears as an invariant of the 4×4 cell [as predicted in general by Eq. (30)], and so the α 's of Eq. (10) determined for the smaller cell provide information about the 4×4 cell.

Just like $I_{1a,3a}^{4 \times 4}$ in Eq. (31), each of the graph invariants given below in Eqs. (33)–(36) has a counterpart in among those of the 2×2 unit cell, specifically in Eqs. (6)–(9).

$$I_{2a,3a}^{4 \times 4} = \frac{1}{64} \sum_{\alpha, \beta=a,b,c,d} (b_{2\alpha}b_{3\beta} + b_{1\alpha}b_{4\beta} + b_{6\alpha}b_{7\beta} + b_{5\alpha}b_{8\beta}) \quad (33)$$

$$I_{1a,2a}^{4 \times 4} = \frac{1}{32} \left\{ \sum_{\alpha=a,b,c,d} (b_{1\alpha}b_{2\alpha} + b_{3\alpha}b_{4\alpha} + b_{5\alpha}b_{7\alpha} + b_{6\alpha}b_{8\alpha}) \right. \\ + \sum_{(\alpha,\beta)=(a,b),(c,d)} (b_{1\alpha}b_{2\beta} + b_{2\alpha}b_{1\beta} + b_{3\alpha}b_{4\beta} + b_{4\alpha}b_{3\beta}) \\ \left. + \sum_{(\alpha,\beta)=(a,c),(b,d)} (b_{5\alpha}b_{7\beta} + b_{7\alpha}b_{5\beta} + b_{6\alpha}b_{8\beta} + b_{8\alpha}b_{6\beta}) \right\} \quad (34)$$

$$I_{1a,5a}^{4 \times 4} = \frac{1}{64} \left\{ \sum_{\alpha=a,b,c,d} (b_{1\alpha}b_{5\alpha} - b_{3\alpha}b_{5\alpha} - b_{1\alpha}b_{6\alpha} + b_{2\alpha}b_{6\alpha} \right. \\ + b_{3\alpha}b_{6\alpha} - b_{4\alpha}b_{6\alpha} + b_{3\alpha}b_{7\alpha} - b_{3\alpha}b_{8\alpha} + b_{4\alpha}b_{8\alpha}) \\ + \sum_{(\alpha,\beta)=(a,c),(b,d)} (b_{1\alpha}b_{8\beta} + b_{8\alpha}b_{1\beta} - b_{2\alpha}b_{8\beta} - b_{8\alpha}b_{2\beta} - b_{7\alpha}b_{1\beta} - b_{1\alpha}b_{7\beta}) \\ + \sum_{(\alpha,\beta)=(a,b),(c,d)} (b_{5\alpha}b_{4\beta} + b_{4\alpha}b_{5\beta} - b_{2\alpha}b_{5\beta} - b_{5\alpha}b_{2\beta} - b_{4\alpha}b_{7\beta} - b_{7\alpha}b_{4\beta}) \\ \left. + \sum_{(\alpha,\beta)=(a,d),(c,b)} (b_{2\alpha}b_{7\beta} + b_{7\alpha}b_{2\beta}) \right\} \quad (35)$$

$$I_{1a,1a}^{4 \times 4} = \frac{1}{32} \sum_{\alpha=a,b,c,d} (b_{1\alpha}^2 + b_{2\alpha}^2 + b_{3\alpha}^2 + b_{4\alpha}^2 + b_{5\alpha}^2 + b_{6\alpha}^2 + b_{7\alpha}^2 + b_{8\alpha}^2) \quad (36)$$

Each of the invariants listed so far for the 4×4 unit cell involves products of bonds that lie sufficiently close to each other so that they also generate an invariant for the smaller 2×2 cell, and their contribution to scalar physical properties can be estimated from calculations for the smaller 2×2 cell. In other words, if the α 's in Eq. (10) were determined for the 2×2 cell, then an estimate for the properties of the larger number of H-bond isomers of the 4×4 cell would be available.

If the energy or free energy of the 2×2 unit cell was parametrized according to the value of $I_{13}^{2 \times 2}$, $I_{23}^{2 \times 2}$, $I_{12}^{2 \times 2}$, $I_{15}^{2 \times 2}$, and $I_{11}^{2 \times 2}$, then a first guess for the energy of configurations of the 4×4 cell would be in terms of the invariants in Eqs. (31)–(36). At this level of approximation, the parameters needed to describe the many H-bond isomers of the 4×4 cell, the α 's of Eq. (11), would be known from calculations for the smaller 2×2 cell, and only direct enumeration or Monte Carlo sampling of topologies required for the 4×4 cell. Perhaps comparison with more expensive, detailed calculations for the 4×4 cell would indicate reasonable convergence of the energy. If not, use of invariants involving bond pairs further separated from each other would be an option to improve the description. This would involve invariants for the 4×4 cell which have no counterpart in the 2×2 cell.

III. ANALYSIS OF THE HYDROGEN-BOND ORDER-DISORDER IN ICE

A. Ice Ih/XI

As reviewed in Section I, our fundamental notions of H-bond disorder in ice Ih have been shaped by Linus Pauling's prediction of the residual entropy of ice [2] and its experimental confirmation by Giauque and Stout [6]. Close to the melting point of ice, the H-bonds are fully disordered subject to the ice rules. The motion of protons within the ice lattice occur via Bjerrum (orientational) or ionic (protonic) defects [98]. As ice is cooled to low temperatures, H-bond rearrangements come to a halt, and a glassy transition has been observed to occur near 110 K [107] prohibiting the transition to a proton-ordered phase.

As tabulated in [108], numerous dielectric studies on powder and single-crystal samples have been performed over the years. Kawada and Niinuma [109] and Kawada [110] reported results on dielectric studies on single crystals with a Curie–Weiss temperature of 46 and 55 K for H_2O and D_2O [58], respectively, with the electric field parallel to the c -axis. Studies by Johari and Whalley [108] on powdered samples of H_2O indicate a Curie–Weiss temperature significantly lower, 6.2 K. However, in samples doped with impurities, particularly KOH, a clear calorimetric signature of a first-order phase transition is observed at 72 K with weak dependence on the concentration of the KOH impurity [8, 58]. In experiments with samples of D_2O , the transition temperature is shifted by 4° and occurs at 76 K. Antarctic ice samples have been examined with neutron diffraction and Raman spectroscopy. It is believed that these samples, kept at a constant low temperature for thousands of years, have equilibrated to a proton-ordered arrangement [111]. Those studies indicate that a second-order phase transition to an H-bond ordered phase of ice occurs at 237 K, which is significantly larger than the observed transition temperature in KOH doped ice samples. Neutron diffraction spectra of Greenland ice samples, prepared under similar conditions, showed no distinct

differences when compared to the spectra of ice Ih, thus casting doubt onto the earlier Antarctic studies [112]. Additional diffraction studies on Antarctic ice samples concur that it is unlikely to observe a proton-ordered arrangement under such conditions [113]. In addition to the numerous experimental reports, there have also been theoretical investigations of this proton-ordering transition. In 1981, Minagawa [114] calculated a Curie–Weiss transition at 69 K to a ferroelectric structure based on an electrostatic model that reproduced the experimental dipole and quadrupole of water molecules, and included only nearest neighbor interactions.

The unit cell of ice Ih is hexagonal with space group $P6_3/mmc$. The symmetry of the low-temperature proton-ordered configuration, ice XI, shown in Fig. 2a, is orthorhombic, space group $Cmc2_1$, as indicated by neutron scattering [10, 11, 14, 115] and thermal depolarization experiments [13, 116] on KOH doped ice Ih. Bonds that are oriented parallel to the c -axis all point in the same direction. The ab layers, composed of bonds oriented perpendicular to the c -axis are polarized parallel to the b -axis with alternating layers oppositely aligned. Thus, the structure is overall antiferroelectric in the a and b directions and ferroelectric in the c direction. This antiferroelectric arrangement of the ab layers gives rise to a slight displacement of the oxygen lattice parallel to the b -axis in the direction of the polarization.

This view has been contested: Iedema et al. [18] referred to more recent claims as “UFI citings (underidentified ferroelectric ices) in the literature”. Even if the $Cmc2_1$ structure proves to be correct, there is some justification for characterizing the current state of knowledge of low-temperature ice Ih/XI as “underidentified”. While a mechanism has been proposed for incomplete conversion of ice Ih to ice XI [117], several features of the presumed ice Ih/XI transition are not understood: While the calorimetric signature of the Ih/XI transition is remarkably insensitive to KOH concentration, the amount of conversion, as measured by the total heat of transformation, is strongly concentration dependent. If KOH truly acts as a catalyst and samples have adequate time to equilibrate, there should be no concentration dependence. The KOH seems to be playing another role, perhaps related to the crystal strain discussed by Johari [117]. Furthermore, there are reports that protons in ice become immobile below a certain temperature due to being trapped by the defects present in ice [118]. Wooldridge and Devlin [43] performed Fourier transform infrared (FTIR) experiments that indicated that proton motion comes to a halt below 100 K. More recently, “soft-landing” experiments by Cowin et al. [44] indicate that hydronium ions are in fact immobile at all temperatures below 190 K. If hydroxide is as immobile as excess protons at low temperature, then the basis for the catalytic role of hydroxide would be thrown in doubt. Recent dielectric and calorimetric experiments [119] indicate that the alkali hydroxide dopants polarize nearby water molecules to promote orientational ordering at low temperatures that may explain the observed weak concentration dependence on the amount of transformation achieved.

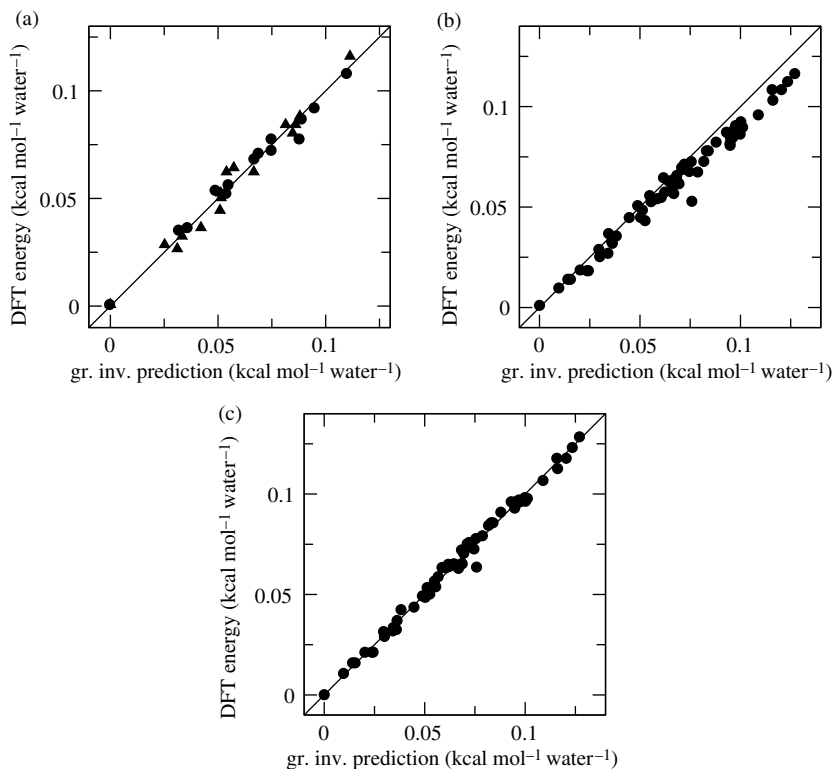


Figure 12. (a) Graph invariant (gr. inv.) fit to the energies of the 14 H-bond isomers of a 12-water hexagonal(●) unit cell and the 16 H-bond isomers of an 8-water orthorhombic(▲) unit cell of ice Ih. (b) Calculated DFT energy of H-bond isomers of a 48-water hexagonal ice Ih unit cell plotted against energies predicted from graph invariant parameters derived from the small unit cells. (c) Graph invariant fit to the energies of the 63 “semirandomly” chosen H-bond isomers of a 48-water hexagonal unit cell of ice Ih. A line of slope unity is shown to indicate where points would lie for perfect agreement.

Electronic DFT calculations for ice Ih using three different combinations of density functionals and basis sets for two smaller unit cells of ice Ih are reported in Fig. 8. The results of these calculations were used to fit the coefficients (the α 's) in Eq. (11). Three graph invariant functions plus an overall constant (the overall constant can be regarded as a fourth invariant) were used to fit the energy of the H-bond isomers, indicating the economy of this description.. The quality of that fit is shown in Fig. 12a. According to the theory of Section II.C, the parameters obtained from calculations on the smaller 8-water orthorhombic (half of Fig. 2) and 12-water hexagonal (Fig. 13a) unit cells, can be used to predict the energies of larger unit cells. The quality of the prediction for the larger 48-water cell shown

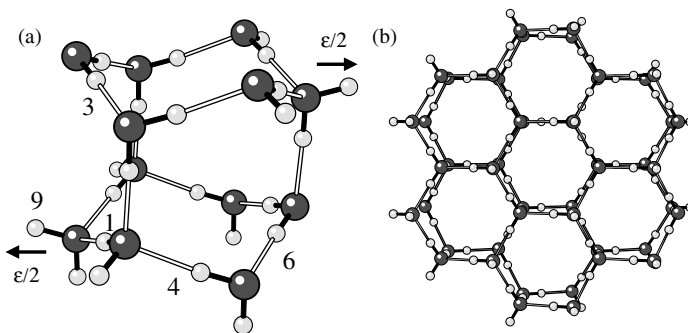


Figure 13. (a) An H-bond isomer of a 12-water primitive unit cell of ice Ih. Bonds representative of the three second-order graph invariants used to fit the DFT energies are shown. All bonds used to generate second-order invariants, used to describe energy differences for H-bond fluctuations in a large simulation cell, lie perpendicular to the c -axis and are referred to as ab bonds. (b) An H-bond isomer of a 48-water unit cell of ice Ih measuring $2 \times 2 \times 1$ primitive cells on each side. Both H-bond isomers shown are the lowest energy isomer for each unit cell in agreement with the experimentally proposed ferroelectric, space group $Cmc2_1$, ice XI structure. Arrows indicate direction of the relative displacement, $\epsilon/2$, of the ab layers that are oppositely polarized.

in Fig. 13 is assessed in Fig. 12b. There is only a slight deviation between the prediction obtained from smaller cells and electronic DFT calculations performed on the larger cell. As we determined later, the convergence at the small cell level is even better than indicated in Fig. 12. The small deviation in Fig. 12b is due to the fact that only the Γ point was used in the electronic DFT calculations on the small cell. When k -point sampling is employed for the small cells, the predictions for the larger cells are improved [120]. By refitting the invariant coefficients to the large cell energies (Fig. 12c), we are able to, with Eq. (11), calculate the energy differences arising from the various H-bond configurations in Metropolis Monte Carlo simulations of a large ice Ih system.

Using the fit to the H-bond energetics of Fig. 12c, Monte Carlo simulations of ice Ih were performed using an orthorhombic cell measuring $7 \times 4 \times 4$ primitive cells on each side containing 896 water molecules. Average energy as a function of temperature (Fig. 14a) indicate that a first-order transition to the low-temperature proton-ordered structure occurs near 98 K. The structure of the low-temperature phase is that of the experimentally proposed ferroelectric $Cmc2_1$ structure, shown in Fig. 2a. Entropy as a function of temperature, shown in Fig. 14b, indicates that as ice Ih is cooled, the system loses 11% of its configurational entropy before the transition, in agreement with pretransitional effects seen calorimetrically [8] and in diffraction studies [14]. Only 1% of the configurational entropy for an ideal ice phase is lost below the transition resulting in 88% of the ideal entropy lost at the transition.

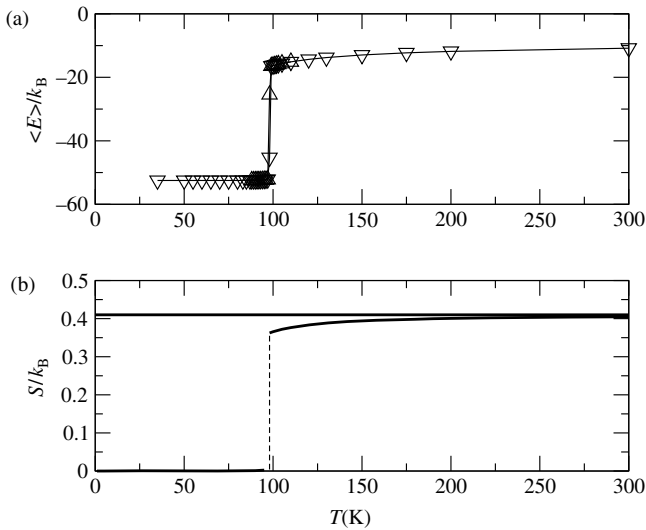


Figure 14. (a) Average energy plotted as a function of temperature from Metropolis Monte Carlo simulations of a large simulation cell of ice Ih. Data is presented for series of Metropolis Monte Carlo runs ascending (Δ) and descending (∇) in temperature. (b) Entropy plotted as a function of temperature. The horizontal line is the Pauling entropy, $k_B \ln \frac{3}{2}$, for a fully disordered ice lattice.

As discussed above, the ab puckered sheets of the $Cmc2_1$ structure have a net polarization. The polarization alternates from sheet to sheet making the ice XI structure antiferroelectric in the ab direction. Thus, the puckered sheets are slightly displaced in the direction of the polarization, as shown in Fig. 13, by a magnitude of $\epsilon/2$, where ϵ is the relative displacement of two adjacent layers. Using the optimized geometry of the 12-water $Cmc2_1$ structure, obtained using the Car-Parrinello [121, 122] molecular dynamics (CPMD) program [89], as described above, we calculated the distance between the center of mass for each of the ab layers. The calculated value, $\epsilon = 0.11 \text{ \AA}$, is in agreement with the experimentally determined value, $\epsilon = 0.12 \text{ \AA}$ [10].

B. Ice VII/VIII

In contrast to the controversy surrounding the ice Ih/XI proton-ordering phase transition, the ice VII/VIII transition has been well characterized. Ice VII was first identified by Bridgman [123] in 1937. Ice VII has one of the simplest structures out of all the high-pressure phases of ice; two interpenetrating, but not interconnected ice Ic lattices. The unit cell of the ice VII crystal is cubic, space group $Pn3m$, containing two water molecules (Fig. 15). X-ray [124, 125] and neutron [47] diffraction studies indicate that the H-bonds in ice VII, the structure of which

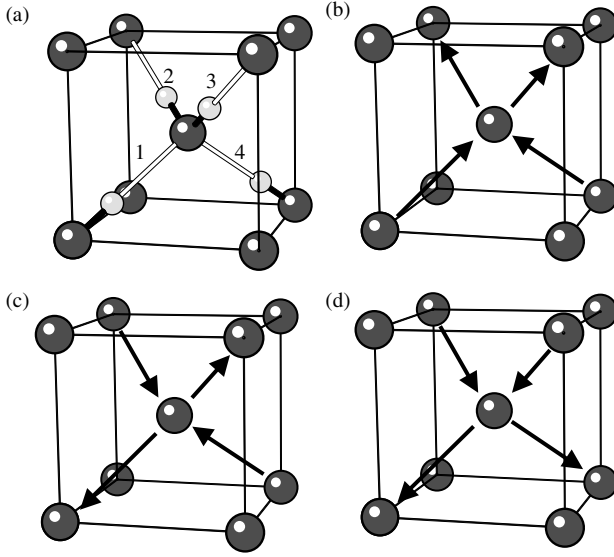


Figure 15. (a) An isomer of a 2-water primitive unit cell of ice VII, obeying the Bernal-Fowler ice rules, is shown. The thin black lines outline the unit cell and neighboring oxygen atoms are included for clarity. The orientation of H-bonds in this isomer are assigned to be the canonical arrangement of H-bonds. The H-bonds are labeled from 1 to 4 to provide a means to associate a bond variable, b_r , with each H-bond labeled r . (b) The H-bond configuration in (a) is summarized by a directed graph. The H-bonds are taken to point from oxygen donor to acceptor as discussed in the text. (c and d) Additional directed graphs corresponding to other H-bond isomers of ice VII that satisfy the Bernal-Fowler ice rules and periodicity constraints. As an example, if all the bond variables, b_r , for configuration (b) were assigned the value $+1$, then all the b_r values for configuration (d) would take the value -1 since all H-bonds are reversed.

is shown in Fig. 16, are fully disordered subject to the ice rules. Ice VIII is the corresponding low-temperature proton-ordered structure. The ice VIII unit cell is tetragonal, space group $I4_1/amd$, containing eight water molecules. Both sublattices are ferroelectrically aligned parallel to the c -axis, but the sublattices are oriented opposite to one another resulting in an overall antiferroelectric structure. The relative oxygen positions remain essentially unchanged from that of ice VII structure except for a small distortion, $\sim 0.2 \text{ \AA}$ [126–128], arising from the non-bonded oxygen–oxygen interactions between the sublattices.

1. Ice VII/VIII Transition

The ice VII/VIII proton-ordering transition was first observed when dielectric experiments indicated that the Debye relaxation disappeared below 0°C [129]. Over a range of pressures from 2.1 to 12 GPa, proton ordering, via rearrangement

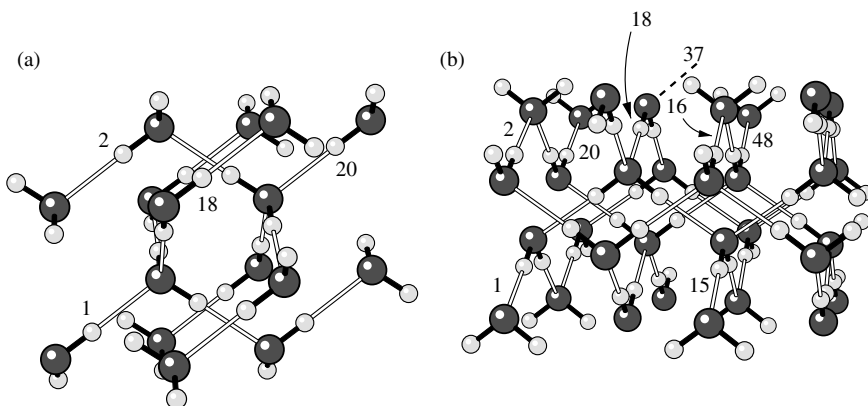


Figure 16. (a) An H-bond isomer of a 16-water unit cell of ice VII measuring two primitive unit cells on each side. Bonds representative of the three second-order graph invariants used to fit the DFT energies are shown. (b) The ground-state H-bond isomer of a 32-water unit cell of ice VII measuring $2\sqrt{2} \times 2\sqrt{2} \times 2$ primitive cells on each side corresponding to the experimentally determined ice VIII structure. Bond pairs representative of the second-order graph invariants, including bond pairs not possible in the smaller 16-water unit cell, used to fit the DFT energies are shown. Bond 37 connects to a water molecule in an adjoining cell.

of H-bonds, occurs at nearly constant temperature. All experiments are in general agreement on the ice VII/VIII transition temperature, 263–273 K [47, 130], although hysteresis [131] effects make the precise determination difficult. The effects of D_2O on the transformation are negligible at these temperatures, shifting on the order of a degree [132], indicating quantum effects are minimal. In the ice Ih/XI transition, the transition temperature shifts from 72 K for H_2O to 76 K for D_2O . With still higher pressure, the ice VII/VIII transition temperature abruptly decreases as the mechanism of the transition shifts to proton tunneling across the shortened H-bonds. Our calculations are pertinent to the temperature-independent region.

The smallest unit cell we examined was a cubic 16-water unit cell of ice VII, 2 primitive unit cells on each side, as shown in Fig. 16. All first-order invariants for the $2 \times 2 \times 2$ cell were identically zero for reasons described in Section II.C. There are eight second-order graph invariants for this cell that were evaluated for the 52, symmetry-distinct H-bond isomers possible in this unit cell. The electronic DFT energies are plotted against a linear fit to the 52 energies using three invariants plus an overall constant. In Fig. 17, perfect agreement is indicated when points lie on the diagonal line.

Next, calculations were performed on a larger ice VII unit cell, measuring $2\sqrt{2} \times 2\sqrt{2} \times 2$ primitive cells on each side. As discussed in Section II.C, all invariants from the smaller cell were also found in the larger unit cell. The DFT

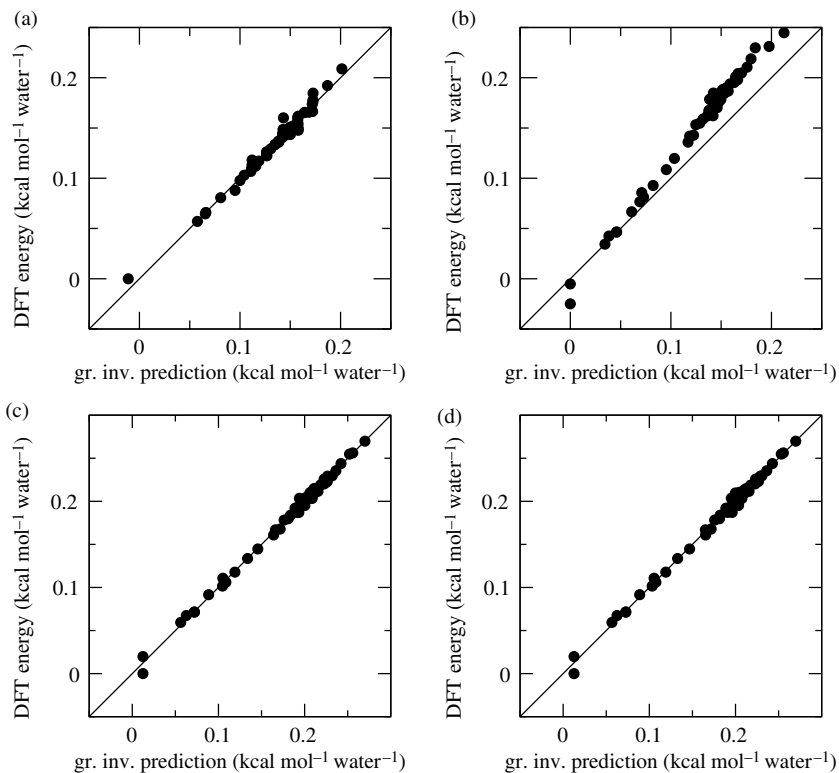


Figure 17. (a) Graph invariant (gr. inv.) fit to the energies of the 52 H-bond isomers of a 16-water unit cell of ice VII. (b) Calculated DFT energy of H-bond isomers of a 32-water ice VII cell plotted against energies predicted from graph invariant parameters derived from the 16-water cell. (c) Graph invariant fit, using second-order invariants whose generating bond pairs are farther apart than possible in the smaller 16-water unit cell, to the energies of the H-bond configurations for the 32-water unit cell. (d) Same as plot c except only invariants whose generating bond pairs exist in the smaller 16-water unit cell were fit to the energies. A line of slope unity is shown to indicate where points would lie for perfect agreement.

calculations were performed on 50 H-bond isomers chosen “semirandomly” from the 35806 symmetry distinct H-bond configurations possible in this unit cell [25, 37, 128] in the following manner. From a prediction based on the graph invariant parameters fit to the $2 \times 2 \times 2$ cell, we selected isomers that would cover the entire energy range, plus other isomers that would test whether the new invariants that appear for the larger $2\sqrt{2} \times 2\sqrt{2} \times 2$ cell are actually needed to fit the energy of the isomers for the larger cell. The energies of the 32-water unit cells are well predicted using invariants parameters obtained from calculations on the 16-water cell,

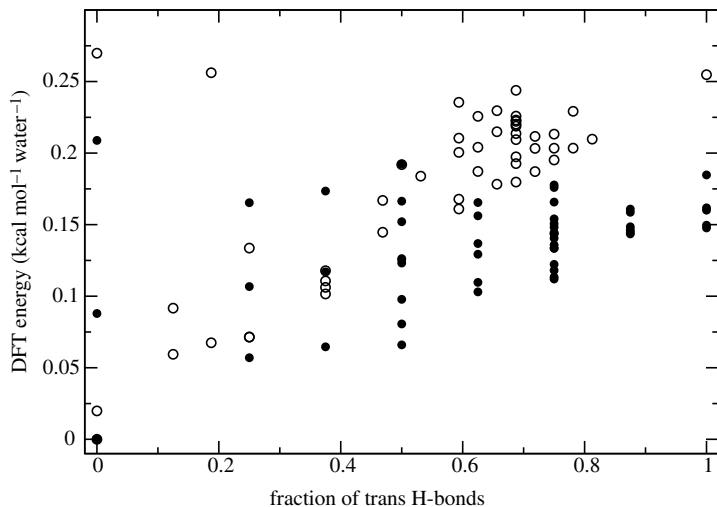


Figure 18. Relative DFT energy of H-bond isomers of a 16-water (●) and 32-water (○) unit cell of ice VII plotted against fraction of trans bonds for each isomer. The lowest and highest energy isomers for both unit cells contain no H-bonds in the trans configuration thus indicating that features of the H-bond topologies other than cis–trans H-bonds are important if physical properties are to be correctly described.

shown in Fig. 17b. However, there is a small systematic discrepancy in which the invariant prediction overestimates the energy differences in the 32-water cell. This discrepancy is actually not a consequence of requiring more invariant parameters for the larger cell, but instead arises because of the lack of k -point sampling in the electronic structure calculations for the smaller cell.

A fit of the DFT energies incorporating invariants whose generating bond pairs were farther apart than possible in the smaller 16-water unit cell (Fig. 17c) yielded a fit just as good in quality as that obtained from only using invariants whose generating bond pairs existed in the smaller cell (Fig. 17d). We conclude that the energy of the H-bond isomers is accurately described by invariants whose generating bond pair contain vertices that are nearest neighbors. Energy plotted as a function of the percent of trans H-bonds is shown in Fig. 18. For both unit cells, the ground-state and highest energy configurations contain no bonds that are trans. If the relative number of trans bonds was the only feature of the H-bond topology used to describe the energetics, those configurations would then be degenerate. Clearly, it is evident that additional features of the H-bond topology, exhibited by the graph invariants, are necessary to accurately describe the relative energetics of H-bond isomers of ice.

Using the improved invariant parameters and Eq. (11), we have a Hamiltonian describing the energy differences due to fluctuating H-bonds in a large simulation

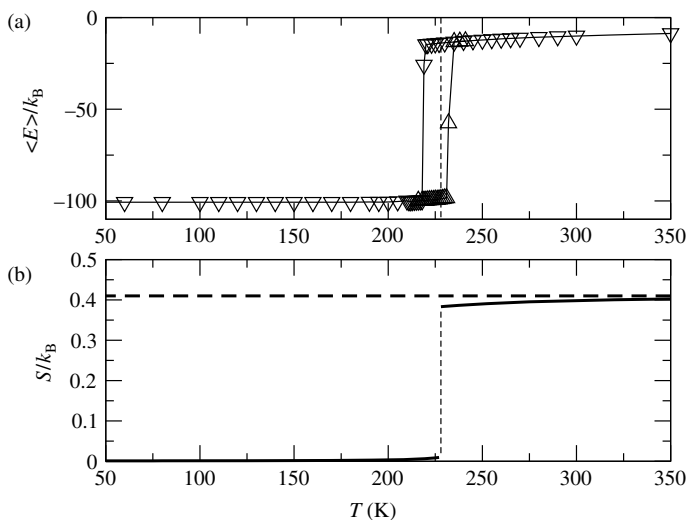


Figure 19. (a) Average energy plotted as a function of temperature from Metropolis Monte Carlo simulations for large simulation cell of ice VII/VIII. Data is presented for series of Metropolis Monte Carlo runs ascending (Δ) and descending (∇) in temperature. The vertical line is located at the calculated transition temperature near 228 K. (b) Entropy plotted as a function of temperature. The horizontal line is the Pauling entropy for a fully disordered ice lattice subject to the ice rules.

cell. Metropolis Monte Carlo simulations were performed on a simulation cell measuring eight primitive cells on each side containing 1024 water molecules. The Monte Carlo simulations yield a prediction of a first-order phase transition near 228 K with significant hysteresis, as shown in Fig. 19a. The transition temperature is calculated as the point of equal free energy ($\Delta A = 0$) between the two phases as determined by thermodynamic integration of the low-temperature proton-ordered phase from 0 K and the high-temperature proton-disordered phase from infinite temperature. Since we neglect the effect of what is known to be a small change in the lattice constant with temperature, we do not include a pressure-volume term in the free energy. Entropy as a function of temperature is plotted in Fig. 19b. With decreasing temperature, 7% of the ideal entropy for a fully disorder ice phase is lost before the transition. The calculated entropy at the transition, 228 K, is 91% of the ideal configurational entropy associated with H-bond disordering compared with experimentally reported values of 83% for H_2O and 91% for D_2O [130].

Umemoto et al. [62] recently calculated the ice VII/VIII phase boundary as a function of increasing density or pressure. To our knowledge, this is the first calculation of this sort with variable cell size. They obtained the isomer energies E_i from electronic DFT, and A_{vib} in the harmonic approximation for the 52 symmetry-distinct isomers of a 16-water unit cell. They estimated the VII/VIII

transition point from the 16-water cell without extrapolation to the thermodynamic limit. As discussed in Section II.A, the density dependence of the transition is carried by the E_i , and the A_{vib} have minor effect. Significantly, Umemoto et al. [62] demonstrated that this is sufficient to describe the decrease in VII/VIII transition temperature with increasing density. This finding is quite remarkable because H-bonds are beginning to show effects of symmetrization in this range. The vibrational free energy does have an important contribution to the pressure–density relationship at very low pressure, although the effect diminishes at higher pressures.

Despite the challenge posed by small energy variation among H-bond isomers, our results qualitatively match the observed features of the ice VII/VIII phase transition in several respects: (1) the calculated ground state is the known ice VIII antiferroelectric structure [128], (2) the transition temperature, 228 K, is similar to the experimental transition point measured in the range 263–274 K [47, 130], and (3) the detectable partial ordering above the transition and partial disordering below the transition, as measured by the entropy at the transition, is in agreement with experiment.

2. Site Disorder in Ice VII

The proton-ordering phase transition of ice VII to antiferroelectric proton-ordered ice VIII is, in many respects, considered to be well characterized. What is not well understood, however, is the apparent site disorder of the oxygen atoms suggested by recent neutron diffraction studies [47, 48, 133]. Studying ice VII in its region of stability, Kuhs et al. [47] achieved a good fit to neutron diffraction data treating the thermal motion of the oxygens anharmonically. This model led to a surprisingly short O–D distance of 0.89 Å that lengthened by 0.13 Å when this distance was allowed to vary freely after another refinement with a rigid water geometry. From this analysis, it appeared that there was significant motion along the set of $\langle 100 \rangle$ axes suggesting disorder of the oxygen atoms about their perfect lattice sites. Here, the symbol $\langle 100 \rangle$ stands for all axes related by symmetry to the $[100]$ axis, for example: $[100]$, $[\bar{1}00]$, $[010]$, $[0\bar{1}0]$, $[001]$, and $[00\bar{1}]$. Jorgensen and Worlton [132] investigated the structure of ice VII using a time-of-flight neutron diffraction technique. They also found it difficult to separate the static and thermal displacements of the oxygen atoms. Introducing a multisite model for the hydrogens did elongate the O–D distance somewhat, but it suggested D–O–D angles that did not seem probable. Thus, they also concluded that some displacement of the oxygen along the $\langle 100 \rangle$ directions, away from the covalently bonded deuteriums, would allow for the lengthening of the O–D distance.

More recently, an investigation by Nelmes et al. [48] refined neutron diffraction data using various combinations of multisite models for both the oxygen and hydrogens treating the thermal motion harmonically. A good fit of their models was measured by the closeness of the water molecule geometry to that found in

ice VIII, the proton-ordered phase, with an O–D distance and D–O–D angle of 0.970 Å and 107.3°, respectively [48]. They found the best fit was achieved when oxygen atoms were displaced along the set of $\langle 111 \rangle$ axes and the hydrogens shifted along threefold sites surrounding the $\langle 111 \rangle$ axes. This gave an O–D distance and D–O–D angle of 0.977 Å and 107.1°, respectively. The best fit that could be achieved using the $\langle 100 \rangle$ axes for oxygen, with threefold sites for hydrogens, resulted in a water geometry of 1.01 Å and 107°, consistent with the earlier work of Kuhs et al. [47]. Regardless of model, all fits yielded site displacement magnitudes of 0.135 Å. The $\langle 100 \rangle$ model for oxygen displacement yielded H-bonded oxygen–oxygen distances of 2.833 and 2.839 Å, both in close agreement with their data from ice VIII under similar conditions. However, the $\langle 111 \rangle$ model that gave the best water geometry overall also predicted two sets of H-bonded oxygen–oxygen distances that were ~ 0.1 Å longer and shorter than the H-bond distances in ice VIII. As the authors indicate, this is a feature not yet observed in spectroscopic studies.

Site displacements arise in part from the variations in H-bond topology from location to location in the lattice, and in part from vibrational fluctuations. We can describe the former by linking site displacements, a vectorial quantity, with combinations of bond variables that transform as vectors. An option is to use projection operators to obtain combinations of bond variables that transform as components of a first-rank tensor. Since this is the only instance where we have ventured from scalars to higher-rank tensors, we eschewed more formal machinery and explored the simplest possibility, which gave a good account of site displacements in ice VII [39]. In particular, we used linear combinations of bond variables $b_r = \pm 1$ that transform as vectors. In a bond dipole approximation, a unit vector $\hat{\mu}_i$ in the direction of the dipole vector of a water molecule near lattice site i is a sum of vectors for each incident H-bond r , $\mathbf{v}_{ir}$, that point along the bonds of the lattice.

$$\hat{\mu}_i = \sum_{r \text{ incident on } i} \mathbf{v}_{ir} b_r \quad (37)$$

The signs of the vector coefficients $\mathbf{v}_{ir}$ are defined in an obvious way given the canonical orientations chosen for the H-bonds.

The site displacements obtained from electronic density functional theory calculations on 50 H-bond isomers of a 32-water unit cell of ice VII were fit to the following linear form [39],

$$\mathbf{d}_0 = \mathbf{c}_0 \hat{\mu}_0 + \sum_{i=1}^2 \mathbf{c}_i \hat{\mu}_i + \sum_{i=3}^4 \mathbf{c}_i \hat{\mu}_i + \sum_{i=5}^{14} \mathbf{c}_i \hat{\mu}_i + \cdots \quad (38)$$

where the $\mathbf{c}_i$ are 3×3 coefficient matrices. The indices are defined in Fig. 20. The dipole vectors are used to describe the local H-bond topology, and an electrostatic

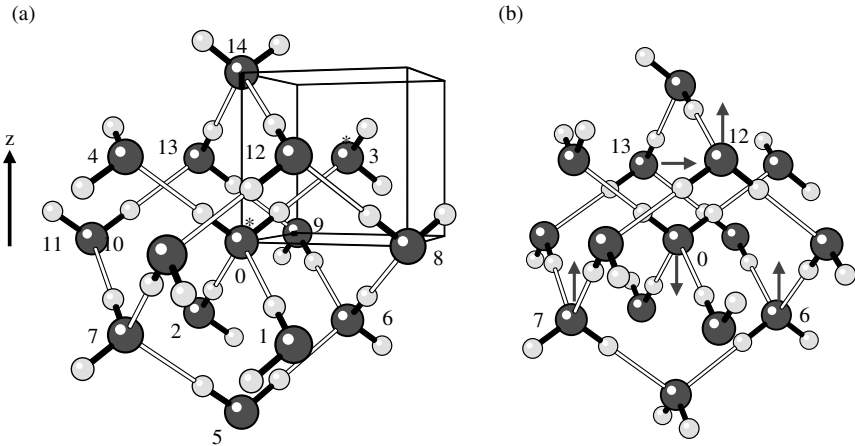


Figure 20. (a) Nearest H-bonded neighbors (1–4), nearest non-H-bonded neighbors (5–14) surrounding a central water labeled “0” in the figure. We refer to the orientation of the central water, dipole pointing in the + z -direction and H-bonds along the $\langle 111 \rangle$ axes, as the “canonical” orientation. Water molecules labeled with asterisks are those that make up the primitive unit cell of ice VII, which the thin black lines outline. (b) Arrows on the central water and its four nearest-nonbonded neighbors indicating the direction of the site displacements as discussed in the text. The water labeled “13” has its dipole vector in the xy -plane while the other labeled waters (0,6,7,12) have their dipoles pointing along the z -axis.

model is not implied here. The leading term in the expression is a multiple of the dipole vector of the water whose site displacement is being described. It is found that the water is displaced in a direction opposite to the direction of the dipole, bringing the center of mass of the molecule closer to the perfect lattice site. Keeping only this leading term in the expression results in a model identical to the $\langle 100 \rangle$ model used to fit experimental data.

$$\mathbf{d}_0^{(100)} = c_0 \hat{\mu}_0 \quad (39)$$

The next two terms in Eq. (38) arise from nearest neighbors on the same sublattice that donate and accept H-bonds, respectively. Each of these four waters can only take three of the six allowed orientations, due to the ice rules, resulting in 81 possible displacements from the set of $\langle 100 \rangle$ axes. The next term in the expression comes from the 10 closest neighbors found on the other sublattice that was divided into 5 groups of waters depending on their height with respect to the z -axis. We found no significant improvement in fitting the oxygen site displacement when additional waters were included in the linear model. Despite its simplicity, this scheme gives a model for oxygen site displacements that is richer than either of the simple $\langle 100 \rangle$ or $\langle 111 \rangle$ models previously used to analyze diffraction data. Earlier, Kuo and Klein [126] reported average bond distances and angles and root-mean-square deviations based on periodic density functional theory calculations

for unit cells of ice VII consisting of 16 water molecules. They did not construct a model linking the direction and magnitude of site displacements to the local H-bond topology, as we have, and could not extrapolate their site displacements to the bulk limit. Kuo and Klein also calculated sublattice shifts in ice VIII, and our calculations agree with these earlier results.

There are two ways to measure the degree to which the model of Eq. (38) links site displacements to H-bond topology: (1) prediction of the displacements in their original crystal lattice orientation from perfect lattice positions and (2) rotation of each water into the canonical orientation defined in Fig. 20a and then measuring the displacement from the perfect lattice position. In the former case, the displacements range from -0.1 to $+0.1$ Å. The displacements of waters in their original crystal lattice orientation take place with equal magnitude in six directions from the perfect lattice sites. In the latter case, because the waters are now oriented in the same way and the displacement largely occurs in a direction opposite to the water dipole, the displacements now range from -0.1 to 0 Å in the z -direction, the direction of the dipole in the canonical orientation, and are much smaller in the x - and y -directions. The ability of the site displacement model to fit displacements from periodic DFT calculations is demonstrated in Fig. 21 for water molecules

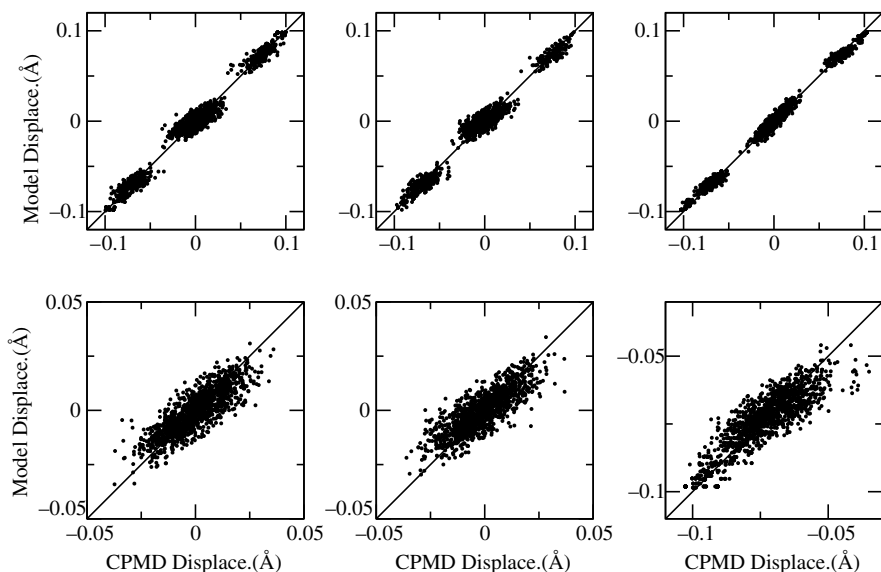


Figure 21. Fit of the oxygen-displacement model to the oxygen displacements of waters in the 50 optimized H-bond configurations. The top row shows the data for waters in their original orientation in the crystal lattice where the dipoles can point in any one of six directions. The bottom row shows data for all waters in the canonical orientation where their dipole now points towards positive z . The columns, left to right, show the agreement along the x -, y -, and z -axes, respectively. All points would lie on the straight line if there was perfect agreement.

in their original crystal lattice orientation (top three panels) and the canonical orientation (bottom three panels). The largest disagreement between the model displacements and the optimized structures is $0.03 \text{ \AA}$ with only 3% of oxygens having deviations larger than $0.02 \text{ \AA}$. The bottom three panels of Fig. 21 compare oxygen displacements after the coordinate system is rotated to the same orientation with respect to the perfect lattice orientation. The deviations now lie within a narrow range and are plotted on a magnified scale in the panels, so the scatter of data points appears magnified as well. The root-mean-square (rms) deviation of our site displacement model from *ab initio* data was $3.75 \times 10^{-3} \text{ \AA}$. When a simple $\langle 100 \rangle$ model was used to fit the *ab initio* structures, the rms deviation increased threefold to $1.17 \times 10^{-2} \text{ \AA}$. The largest disagreement obtained using predictions from the simple $\mathbf{d}_0^{(100)}$ model was $0.04 \text{ \AA}$ with 38 and 5% of oxygens having deviations larger than 0.02 and $0.03 \text{ \AA}$, respectively.

The theory described in Section II.B.1 predicts the energetics of H-bond arrangements in ice VII and VIII [87, 88], and provides Boltzmann-weighted distributions of H-bond arrangements in ice VII. Using the site displacement model of Eq. (38), we can now generate thermally averaged site displacements via Monte Carlo sampling [39]. Data obtained at 300 K for ice VII showed only minor effects of partial H-bond ordering, in line with the fact that only 7% of the configurational entropy is lost before the ice VIII ordering transition in our simulations [87, 88]. The three-dimensional probability distribution of the atomic center of oxygen displaced from its perfect lattice site, obtained from Monte Carlo simulations at 300 K, is shown in Fig. 22a. The probability distribution is spread across six sites that are located on the $\langle 100 \rangle$ axes, as discussed above. The oxygen site distribution in Fig. 22 has a complex shape. The simple $\langle 100 \rangle$ model would replace the complex distribution of Fig. 22a with six delta-function peaks. Any model that confines the oxygens to a small number of points along a few lattice directions will not achieve quantitative agreement with diffraction data, and will confuse static displacements arising from local variations in H-bond topology with thermal vibrational motion. The site displacement model described here naturally reverts to the geometry of antiferroelectric ice VIII, including the relative displacement of the two sublattices, when the H-bonds are placed in the ice VIII arrangement. We hope this work will stimulate detailed comparison with neutron diffraction data.

C. Ice III/IX

The stability region of ice III occupies a small portion of the phase diagram, in comparison to the other stable phases, extending from 240–260 K and 0.2–0.4 GPa. Ice III, first identified by Tammann in 1900 [135], is described by a tetragonal arrangement of oxygen atoms, space group $P4_12_12$, as determined by X-ray [136–138] and neutron [45, 46, 139] diffraction experiments. Proton order was suggested by IR spectra [140] near 100 K, and later confirmed when dielectric experiments

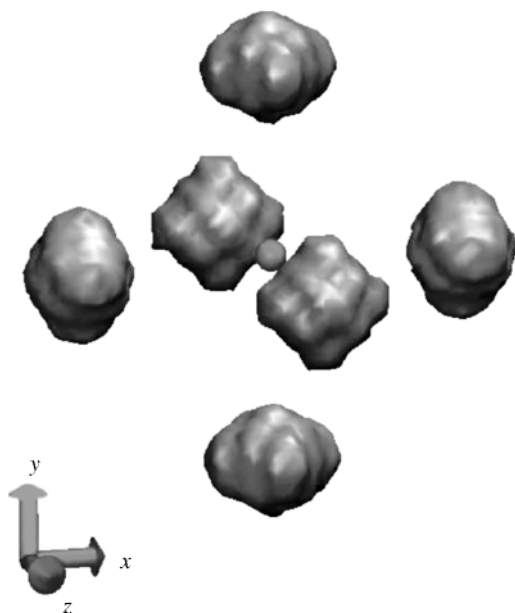


Figure 22. Third-dimensional probability distribution of the position of the oxygen centers relative to the perfect lattice site, small sphere, obtained from Monte Carlo simulations at 300 K. The center of each lobe is located on one of the $\langle 100 \rangle$ axes.

[141] indicated that a progressive ordering takes place as the temperature is lowered from 210 to 165 K. Ice III, when cooled at about 1 K min^{-1} or faster, transforms to a metastable H-bond ordered version known as ice IX, that has the same symmetry as its proton-disordered counterpart [45, 134, 138, 141, 142]. Subsequent warming of ice IX back across the transition results in the formation of ice II, the stable phase in this region of the phase diagram. The space group $P4_12_12$ allows for the possibility that the H-bonds may be partially ordered or disordered in ice III and IX, respectively. La Placa et al. [134] identified one of four possible H-bond arrangements possessing the appropriate symmetry, configuration (d) in Fig. 23, to be the structure of ice IX, in agreement with earlier suggestions [138, 141]. The error in their refinement was acceptable only after deuterons were allowed to fractionally occupy sites other than those of the dominant H-bond arrangement. They proposed that this disagreement with dielectric experiments [141], which suggested a fully ordered structure, may have resulted either from the rate of cooling or as a feature of the ice IX structure. Calculations reported by Handa et al. [143] also suggested that ice IX was fully ordered, but their calculated heat of transition was almost twice that measured by Nishibata and Whalley [142]. This discrepancy has yet to be resolved.

Using a differential calorimetric technique, Nishibata and Whalley [142] measured the heat of transition, -56 cal mol^{-1} , for the ice III–IX phase transition. The measured change in entropy, $-0.32 \text{ cal K}^{-1} \text{ mol}^{-1}$, is nearly 40% of the expected

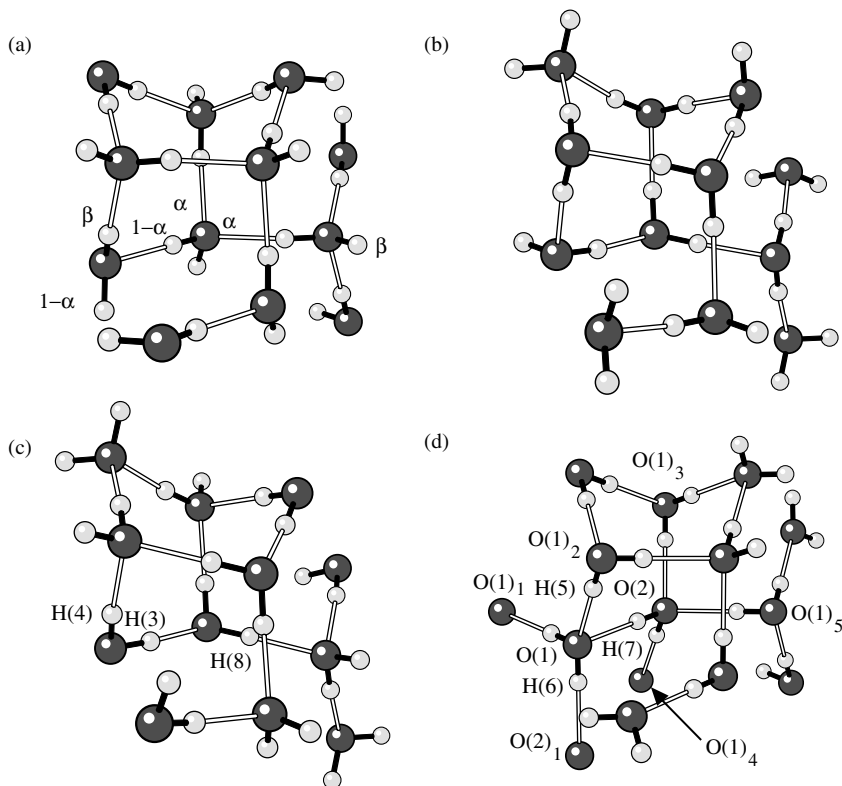


Figure 23. Examples of H-bond configurations of the primitive unit cell of ice III that have $P4_12_12$ symmetry and obey periodic boundary conditions. After the cell is periodically replicated, each water molecule is hydrogen bonded to four others. The space group $P4_12_12$ allows for two occupational probabilities, α and β , to describe the H-bond topology. If one site of an H-bond has a probability of being occupied of α , then the other site, within the same H-bond, has a probability of $(1 - \alpha)$. All proton sites related by symmetry have the same occupational probability. The configurations are labeled (a,b,c,d) corresponding to those configurations considered in [134], with configuration (d) representing the fully ordered ice IX structure where α and β equal zero. Configurations (c) and (d) differ in that all H-bonds are reversed. Oxygen atoms found in adjacent unit cells are also shown for clarity. O(1)_{*i*} and O(2)_{*i*} identify two families of symmetry-related oxygen atoms in the unit cell of ice III. Oxygen atom O(1)₄ is H-bonded to H(7)-O(2) as indicated by the arrow.

value if ice III was fully disordered and ice IX is fully ordered. This suggests that to some degree, ice IX is partially disordered and ice III is partially ordered. Neutron diffraction experiments are able to determine occupational probabilities for deuteron sites. The symmetry of the ice III/IX structures permits the probabilities of protons residing in one of two possible sites along a given H-bond to be

summarized by two occupancy probabilities, α or β , as shown in Fig 23. For the ice IX structure, Londono *et al.* [45] determined that α and β were 2.9 and 5.6%, respectively, in agreement with earlier reported values of $\alpha = 3.4\%$ and $\beta = 5.1\%$ [134]. For partially ordered ice III, Londono *et al.* [45] determined that α and β were 33 and 41%, respectively. With samples of higher quality and a more flexible refinement, Lobban *et al.* [46] determined that $\alpha = 35\%$ and $\beta = 50\%$. Mean-field statistical mechanical models have been developed to approximate the configurational entropy of partially ordered structures using these occupational probabilities as input [114, 144–146]. The most recent of which is able to account for multiple occupational parameters which is necessary in ices III and V [147]. Lobban *et al.* [46] discussed how their diffraction data used in conjunction with these models imply changes in entropy at the ice III/IX transition significantly different than that reported by Nishibata and Whalley [142]. Results from statistical simulations [120], as discussed in this section, may provide insight into this discrepancy.

The bonds in the unit cell of ice III belong to one of three sets (orbits) of symmetry-related bonds. The projection operator for the totally symmetric representation, Eq. (30), when applied to the bonds in Fig. 23, $\hat{G}(b_r)$, yielded three unique, linearly independent first-order invariants. The second-order invariants obtained by applying the projection operator onto bond pairs could be sorted into groups based on geometrical features of the generating bond pairs, such as the distance between the two bonds of the generating pair. Energy as a function of the H-bond topology could be fit with acceptable accuracy using only invariants generated by bonds in close proximity [120], a total of nine first- and second-order invariants. Metropolis Monte Carlo simulations were performed on a simulation cell measuring five primitive unit cells on each side containing 1500 waters [120]. The simulations predict a first-order phase transition near 126 K (Fig. 24) to the antiferroelectric ice IX ground-state identified from calculations on the 12- and 48-water unit cells with $2 \times 2 \times 2$ and Γ -point sampling, respectively.

Entropy as a function of temperature is shown in Fig. 24b. With decreasing temperature, 29.7% of the entropy is lost before the transition while 2.6% is lost after the transition. The calculated entropy at the transition is 67.7% of the ideal Pauling entropy for a fully disordered ice phase that is larger than the experimentally observed change in entropy, 40% [142]. The lattice distortion that accompanies the phase transition may further lower the transition entropy [120]. Also plotted in Fig. 24b is predicted entropy as a function of temperature calculated using various mean-field theories with the occupational probabilities, α and β , obtained from our simulations as input. Our value for α , 38%, at the transition is close to the experimental values, 33% [45] and 35% [46]. Our β , 38%, is close to the value extracted from one diffraction experiment, 41% [45], but rather low compared to a more recent report, 50% [46].

The data in Fig. 24 suggests a resolution of an apparent discrepancy between diffraction [45, 46, 134] and calorimetric [142] experiments. Thermodynamic data

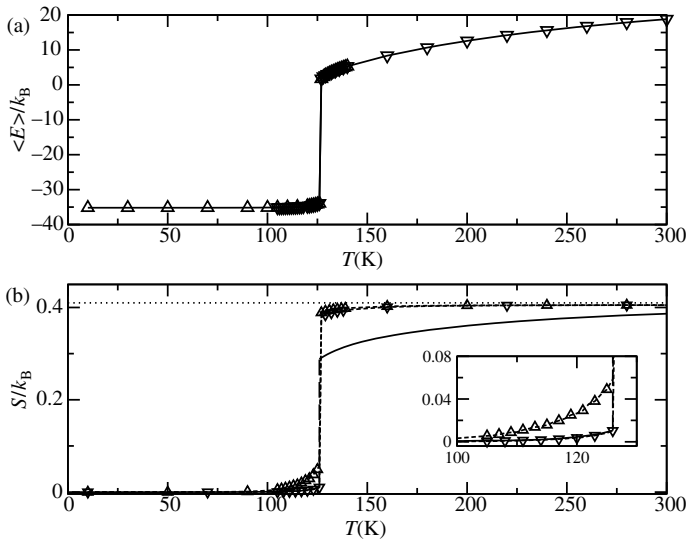


Figure 24. (a) Average energy plotted as a function of temperature from Metropolis Monte Carlo simulations for a simulation cell of ice III containing 1500 waters. Energies are presented for a series of Metropolis Monte Carlo runs ascending (Δ) and descending (∇) in temperature. (b) Entropy from the present work (thick solid line) plotted as a function of temperature where the horizontal line is the Pauling entropy for a fully disordered ice lattice. With decreasing temperature, 29.7% is lost before the transition, 67.7% at the transition, and 2.6% as the fully ordered ice IX structure is formed. In addition, entropy as a function of temperature calculated using the occupational probabilities, α and β obtained from our simulations, is plotted using the one parameter expressions of Nagle(Δ) [145] and Howe and Whitworth(∇) [146].

may be obtained directly from calorimetry, or inferred from diffraction data using mean-field theories [114, 144–147] that relate the system entropy to hydrogen site occupations α and β . Because we have a full statistical mechanical model of ice III and ice IX, we can calculate the exact entropy and exact site occupations. We can compare the exact entropy with the entropy that would be predicted on the basis of mean-field theories. We find that all existing mean-field theories significantly overestimate the entropy of the disordered ice III phase. When used to interpret diffraction data [45, 46], they imply a value for the transition entropy that is too large.

In our simulations, the value of β never significantly differed from α , so we could effectively model the system with a one parameter theory for partially disordered ice systems. Using the average of α and β as the single occupational probability for each temperature, predicted entropy is plotted as a function of temperature obtained from the expressions by Nagle(Δ) [145] and Howe and Whitworth(∇) [146] in Fig. 24. Application of the two parameter expression by MacDowell et al. [147],

with α and β from our simulations as input, yielded entropy as a function of temperature that was quantitatively the same as that obtained using the one parameter expression of Howe and Whitworth [146], because our model predicts that α and β are very close to each other. Howe and Whitworth's expression was used by Lobban et al. [46] to determine the thermodynamic implications of their diffraction data. As seen from the inset, the entropy of the low temperature ice IX phase calculated from our simulations is in very good agreement with the entropy predicted from Howe and Whitworth's expression. Nagle's expression overestimates the entropy for partially disordered ice IX in agreement with previous analysis [146]. Both models, however, when asked to estimate the entropy of partially ordered ice III based on occupational probabilities α and β , significantly overestimate the configurational entropy. This test of the mean-field theories does not depend on the quality of our effective Hamiltonian, unless our model is somehow grossly atypical of the true Hamiltonian for this system (and we would argue, based on its agreement with experiment, it is at least qualitatively accurate). The mean-field theories are given the exact occupational probabilities for the model and should return a value close to the exact simulations, if accurate.

We can also run the comparison in the opposite direction. Using the entropy calculated from our simulations, we use the Howe and Whitworth's expression to determine the occupational probability as a function of temperature. The parameter α would have to be 25%, significantly lower than the results of our simulations, $\alpha = 38\%$, and experiment [45, 46] to yield the true entropy. The transition entropy obtained from our calculation is in better agreement with the value reported from the calorimetric experiments of Nishibata and Whalley [142].

D. Ice V/XIII

In 2006, the proton-ordered version of ice V, ice XIII, was first reported by Salzmann et al. [22] Unlike the ice Ih/XI transformation [8, 9, 58–60], where doping with hydroxide enables formation of ice XI near 72 (76)K for H₂O (D₂O), ice V reversibly transforms to ordered ice XIII in the presence of excess protons in the form of HCl dopant [22–24]. In both cases, dopants presumably facilitate H-bond rearrangements enabling a phase transition that otherwise has prohibitive activation barriers. No ordering of ice V was observed when pure ice or samples doped with hydroxide were cooled. Using Raman spectroscopy and monitoring the change in lattice parameters, the ordering transition was found to be reversible [22–24]. When cooling samples of ice V, the beginning of the ordering transition occurred near 117 K and upon heating ice XIII, it started near 108 K [24]. The unit cell of ice V, containing 28 water molecules, is a monoclinic, space group $A2/a$, as determined by X-ray and neutron diffraction techniques [46, 148, 149]. The unit cell of ice XIII, also containing 28 water molecules, is monoclinic with space group $P2_1/a$, a reduction in symmetry from the ice V space group.

The region of stability for proton disordered ice V is 210–270 K and 3.4–6.3 kbar [46]. Similar to ice III [45, 46, 142], there exists some degree of partial ordering of the protons in ice V. Results from IR [140] and dielectric [150] studies were only able to indicate that ice V was proton disordered, not the degree of the disorder. A neutron diffraction study on single crystals of ice V, recovered to ambient pressure, indicated some proton sites had larger probabilities of being occupied than others at 110 K [149]. Recently, neutron diffraction experiments on ice V conducted in its region of stability has shed light onto the degree of partial order [46]. Lobban et al. [46] measured lattice constants and occupation probabilities from 100–254 K at 5 kbar. They found no evidence of a transition to an ordered structure with $P2_1/a$ symmetry that was first proposed by Kamb and LaPlaca [151] and later was supported with calorimetric evidence by Handa et al. [152]. (The ordered phase eventually characterized by Salzmann et al. [22] does indeed possess $P2_1/a$ symmetry.) In their work, Lobban et al. [46] only observed a gradual ordering of the protons, not a change in the space group that is necessary for a transition to an ordered H-bond configuration. Johari and Whalley [153] discussed these results in the context of dielectric studies on ice V and agreed that partial antiferroelectric ordering occurs as temperature is lowered in ice V.

In electronic DFT calculations using the BLYP functional [90, 91], a plane wave cutoff of at least 90 Ry is required to converge the ice XIII structure as the ground state H-bond isomer. The ordering of some of the isomers lying close in energy above the ground-state shift as the cutoff is increased to 120 Ry, and then again at 150 Ry. In preliminary tests with the PBE [154] and revPBE [155] density functionals, the group of energetically low-lying isomers remained intact, although the ordering within the group, including the ground state, was sensitive to the functional. All density functional calculations mentioned here agree on the same group of low-lying structures. They lie so close together in energy, on the order of $0.002 \text{ kcal mol}^{-1} \text{ water}^{-1}$, that their ordering is likely beyond the limits of electronic DFT. In the remainder of this section, we report results using the (Becke–Lee–Yang–Pen) (BLYP) functional.

Due to the size and symmetry of the ice V unit cell (Fig. 25), there are a large number of possible H-bond configurations. There are 69380 symmetry-distinct H-bond configurations possible for the 28-water unit cell [156]. There are even 35 symmetry-distinct possibilities possessing the same space group as the experimental ground state. There are eight sets (orbits) of bonds related by symmetry in the unit cell of ice V. Because of the complexity of the ice V crystal structure, a large number of linearly independent first- and second-order graph invariants are possible. We found that an overall good fit to the energy was achievable using approximately 10 invariants. However, the predicted ordering of the low-energy isomers was a difficult property to converge without using more invariants. Eventually, we employed two sets of invariants to test how sensitive results were to the invariant parametrization [156]. Both models included three first-order graph

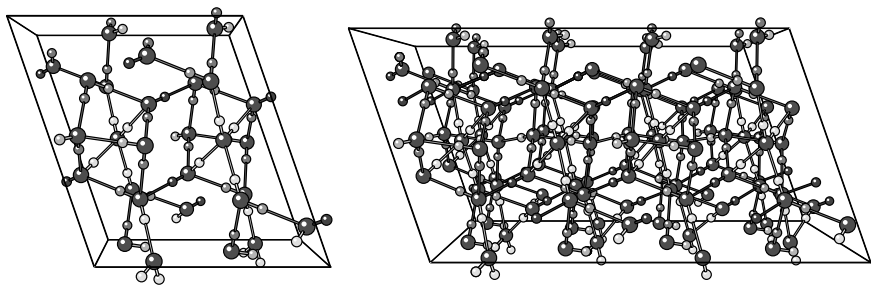


Figure 25. Hydrogen-bond configurations of two unit cells, as viewed down the b -axis, used in periodic electronic DFT calculations containing 28 and 112 waters, respectively. Hydrogens related by symmetry and thus contributing to the same order parameter are similarly colored: α (yellow), β (green), δ (blue), γ (violet), and ϵ (turquoise). The configuration shown here is the ground state at a plane wave cutoff of 90 Ry or higher that corresponds to the experimentally determined proton ordered ice XIII. (See insert for color representation of the figure.)

invariants. They differed in the number of second-order invariants, either 11 or 16. Both models predicted a transition to the ice XIII structure near 70 K [156], although the details of the transition are different in the two models. In the following, we focus on the results above 100 K, which are insensitive to the invariant parametrization.

The space group symmetry of the ice V structure permits the use of five occupation probabilities, or order parameters, that describe the probability of protons being on one or the other side of a particular H-bond (Fig. 25). The order parameters have traditionally been designated by the first five Greek letters, α , β , γ , δ , and ϵ , and range from 0 to 1 in an obvious way where $\frac{1}{2}$ indicates equal probability of the H-bond pointing in two possible directions. As might be expected, the occupation probabilities are strongly related to some of the graph invariants. Due to the symmetry of the ice V phase, the H-bonds described by the ϵ parameter must be fully disordered (i.e., $\epsilon = \frac{1}{2}$).

In Fig. 26, occupation probabilities as a function of temperature are compared with data obtained from the neutron diffraction studies of Lobban et al. [46]. From the simulations, we can calculate occupation probabilities for each model. At temperatures above 100 K, the order parameters from the two graph invariant schemes used to fit the energy are nearly superimposable. At high temperatures, all order parameters take the value $\frac{1}{2}$, corresponding to a fully disordered structure. The ϵ bonds, similar to experiment, remain fully disordered until the system approaches the transition temperature below 100 K. The ground-state configuration, fully ordered ice XIII, is described by the following occupation parameters: $\delta = 1$, $\alpha = \gamma = \frac{1}{2}$, and $\beta = 0$. There are two symmetry-related configurations corresponding to the ground state in which $\epsilon = 0$ or 1.

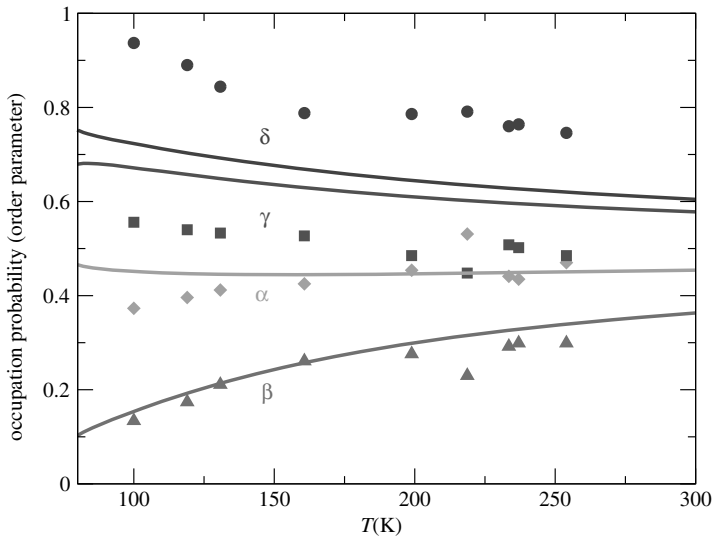


Figure 26. Occupation probabilities plotted as a function of temperature. The solid lines are data obtained from statistical mechanical calculations and symbols are data taken from the neutron diffraction data of Lobban et al. [46]. The occupation probabilities from top to bottom are δ ($\bullet$), γ ($\blacksquare$), α ($\blacklozenge$), and β ($\blacktriangle$). Data from both models are nearly superimposable at temperatures above 100 K, thus only the data from model 2 is shown for clarity. The ϵ type bonds, also not shown, are fully disordered ($\epsilon = 0.5$) above 100 K, identical to experiment. (See insert for color representation of the figure.)

Perhaps the most gratifying comparison between theory and experiment for ice V is contained in Fig. 26, where predicted- and measured-order parameters are in qualitative agreement for γ and δ , and near quantitative agreement for α and β . The energy, entropy, and order parameters (Fig. 26) in the ice V phase were largely insensitive to the parametrization of the invariant coefficients in Eq. (11). However, the closely lying low-energy H-bond isomers in this system presents special challenges to the electronic DFT used to estimate their energy. The ice XIII phase should be revisited when more accurate electronic structure methods become available.

E. Ice VI/XV

In 1965, Kamb noticed an X-ray reflection at 77 K that was incompatible with the $P4_2/nmc$ space group of ice VI and could have signaled the formation of a H-bond ordered version of ice VI [157]. Later, he reported neutron diffraction data taken at 100 K on a sample previously equilibrated at high pressure and 77 K that indicated antiferroelectric ordering [144]. In 1976, Johari and Whalley [158] predicted an ordering transition at 47 K to a ferroelectrically ordered state in ice VI

based on observed Curie–Weiss behavior of the low-frequency dielectric constant. Later they concluded that the high-frequency permittivity of ice VI at 0.9 GPa indicated a very slow phase transition occurs in the temperature range 123–128 K, but these experiments did not reveal the structure of the low-temperature phase. Kuhs et al. [47] obtained neutron diffraction data on ice VI under temperature and pressure conditions where ice VI is stable, unlike earlier diffraction experiments where the diffraction experiments were performed at ambient pressure on samples recovered from high-pressure cells. They took data at 225, 125, and 8 K, but data was not sufficient to fully determine the structure. They found no evidence of the transformation observed by Johari and Whalley [159].

The ordered form of ice VI, ice XV, was discovered in 2009 by Salzmann et al. [42]. They first pressurized D₂O doped with 0.01 M DCl to 0.9 GPa to form ice VI, and then cooled to 80 K. The sample was analyzed at ambient pressure, where a reversible phase transition near 130 K was observed by neutron diffraction. The phase transition from ice VI to ice XV is marked by a 0.2% increase in the *c* lattice constant. Rietveld refinement indicates an antiferroelectric $P\bar{1}$ structure.

In contrast to the antiferroelectric $P\bar{1}$ structure reported by Salzmann et al. [42] electronic DFT calculations predict that the lowest energy H-bond isomer is the ferroelectric *Cc* structure shown in Fig. 27b [160, 161]. The energies of the 45 symmetry-distinct H-bond isomers allowed in the 10-water primitive unit cell of ice

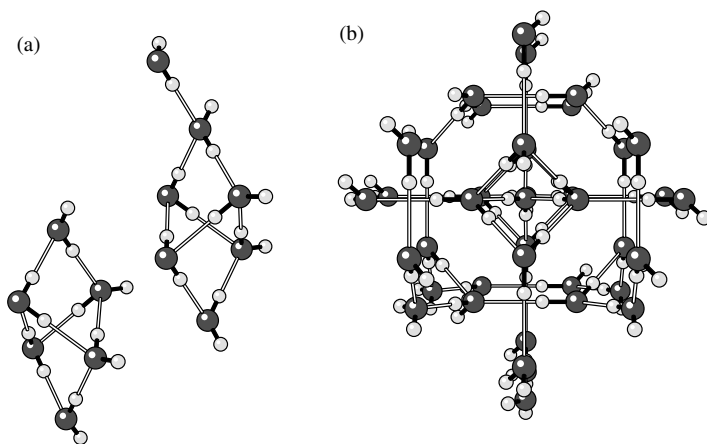


Figure 27. (a) A fragment of ice VI, as viewed perpendicular to the *c*-axis, depicting the 10-water primitive unit cell of ice-VI, and some additional waters that help clarify the bonding pattern. (b) A larger unit cell, measuring $\sqrt{2} \times \sqrt{2} \times 2$ primitive cells on each side, containing 40 water molecules as viewed down the *c*-axis. It consists of two interpenetrating, but not interconnected lattices. The lowest energy isomer found using electronic DFT is shown. Bonds that appear horizontal in the figure all point to the left, while bonds that are vertical all point downward.

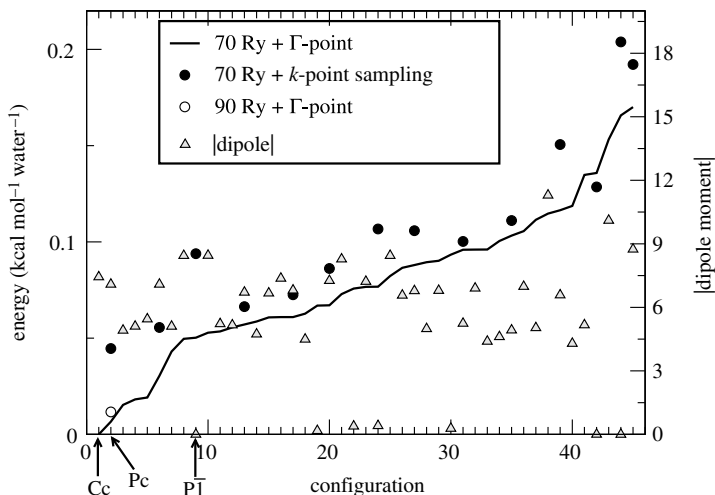


Figure 28. Energies E_i [see Eq. (1)] relative to the lowest energy isomer, and unit cell dipole moments of the 45 symmetry-distinct H-bond isomers of a 10-water primitive unit cell of ice VI. The ground state according to electronic DFT is the Cc ferroelectric structure. The position of the experimentally observed PI structure is indicated.

VI [160] are displayed in Fig. 28. The lattice constants used in the calculations were $a = 6.181 \text{ \AA}$ and $c = 5.698 \text{ \AA}$ as determined by diffraction experiments [47] in the region of stability of ice VI, at 1.1 GPa and 225 K. Energies calculated using the BLYP density functional with a 70-Ry plane wave cutoff at the Γ -point (solid line) are compared with calculations performed either with k -point sampling or a larger plane wave cutoff in Fig. 28. In all cases, the Cc ferroelectric structure remains the ground state. Kuo and Kuhs [162] found that changing the lattice constant to values typical of metastable ice VI at ambient pressures where diffraction experiments have been performed [42] did not affect the identity of ground state.

At present, the origin of the discrepancy between electronic DFT and experiment in this case is not clear. Among the 45 H-bond isomers possible for the 10-water primitive unit cell, 7 have zero electric polarization, as indicated in Fig. 28. According to electronic DFT, the experimental PI structure is the lowest energy of the electrically unpolarized structures. Knight and Singer [156] also identified an anti-ferroelectric structure of $P2_12_12_1$ symmetry (Fig. 29b) that was only 4 K per water molecule higher in energy, as determined from DFT calculations on the 40-water unit cell. The two structures actually have many H-bonds oriented in the same way. Those bonds that must be reversed to go from the ferroelectric to antiferroelectric structures are circled in Fig. 29. The antiferroelectric structure of Fig. 29b does not agree with the diffraction data of Salzmann et al. [42].

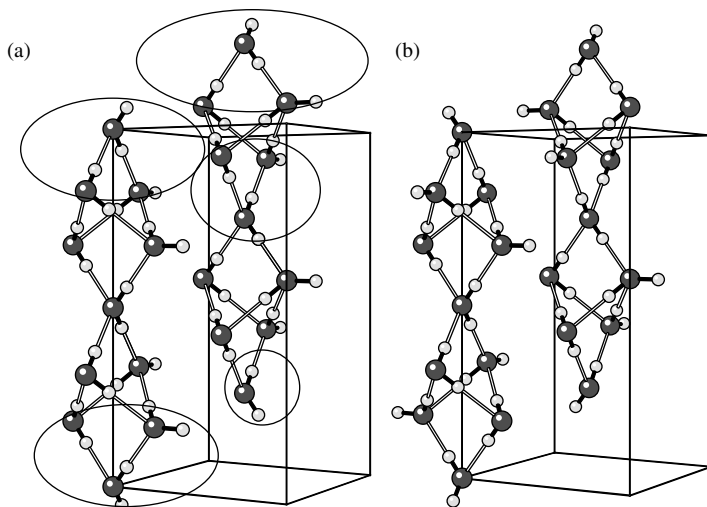


Figure 29. The smallest repeating unit for each of the independent lattices that generate (a) the lowest energy and (b) second lowest energy isomer, as determined from DFT calculations on a 40-water unit cell of ice VI [160], viewed perpendicular to the c -axis. Structure (b) is antiferroelectric. This arrangement of H-bonds has tetragonal symmetry and is assigned the space group $P2_12_12_1$ [163]. The H-bonds parallel to the a - and b -axes point in a counterclockwise fashion as one looks down the c -axis. The bonds that must be reversed to interconvert the two structures are circled in (a).

The energies, as predicted by electronic DFT (Fig. 28), can be fit using graph invariants and a first-order transition to the Cc structure is found at 108 K [120]. Despite the near-degeneracy of the ferroelectric and antiferroelectric structures of Fig. 29, fluctuations to antiferroelectric configurations do not persist to lower temperatures. Simulations initialized with the H-bond configuration of Fig 29b rapidly transformed to the ferroelectric ground state, Fig. 29a, indicating that factors beside energetics (i.e., entropic factors) seem to also favor the ferroelectric state. Significant proton ordering is observed in these calculations above the transition over a wide temperature range. If the high-temperature predictions are valid, and, of course, there is some doubt in this case, which stems from the discrepancy with the experimental ground state, this should be observable in calorimetric experiments provided that H-bond arrangements can equilibrate on an experimental time scale.

F. Ice XII/XIV

A little more than a decade ago, the twelfth phase of ice was proposed based on the results of neutron diffraction experiments. This new phase of ice was found within the stability region of ice V by quickly cooling liquid water to 270 K at 0.55 GPa

followed by additional cooling to 260 K at a rate of 2.5 K hr^{-1} [164]. The unit cell of ice XII is tetragonal with space group $I\bar{4}2d$ and contains 12 water molecules. The H-bond topology in this phase is unlike the other phases of ice in that it only forms seven- and eight-membered rings [165]. Ice XII is proton disordered as indicated by the space group (the symmetry of which does not permit any degree of hydrogen ordering) and confirmed by Raman spectroscopy [166].

Shortly after the initial identification of ice XII, it was realized that the crystal impurities observed in the formation of high-density amorphous (HDA) ice obtained by compressing ice Ih to pressures above 1 GPa at temperatures below 150 K were actually ice XII [167, 168]. The relative amount of HDA and ice XII is sensitive to the rate of compression. It was shown that during this compression, ice XII is only formed via HDA ice and only after a sudden pressure drop [169]. Kohl et al. [169] suggested that ice XII was not metastable at the low temperatures at which it was formed by compression of HDA ice [167, 168], but rather it formed at warmer temperatures attained when pressure was released in the sample causing shock waves.

The metastability of ice XII with respect to ice V was determined using differential scanning calorimetry and X-ray diffraction techniques [170]. At higher pressures, ice XII is also metastable with respect to ice VI [171]. In this portion of the phase diagram, Loerting *et al.* [172] identified the region of metastability for ice XII to be 158–212 K and 0.7–1.5 GPa when HDA was heated isobarically.

The proton-ordered version of ice XII, ice XIV, was identified in 2006 [22]. The proton-ordering transition to ice XIV has only been achieved in the presence of a small amount of dopant, HCl, presumably introducing point defects. The unit cell of ice XIV is orthorhombic with space group $P2_12_12_1$ and also contains 12-water molecules. Ice XIV was formed by cooling ice XII from 180 to 80 K at 0.8 K min^{-1} [22]. The transition to ice XIV was observed by monitoring the change from tetragonal-to-orthorhombic unit cell parameters. Using Raman spectroscopy, Salzmann et al. [173] demonstrated the reversibility of the proton-ordering transition by heating ice XIV at ambient pressure from 77 to 110 K and subsequently cooling.

Electronic DFT calculations using the BLYP functional [90, 91] with a plane wave cutoff of 90 Ry and a $2 \times 2 \times 4$ k -point grid using the Monkhorst–Pack scheme [175] gave the configuration of Fig. 30a, the experimental ice XII structure as the ground state. Lower-level calculations, for example, a 70-Ry cutoff using only the Γ -point, were inadequate and predicted the structure of Fig. 30b to be the ground state. There are 25 second-order graph invariants possible in this unit cell, but only 7 of them were necessary to achieve a good fit to the energies, as shown in Fig. 31. The energies reported in Fig. 31 were calculated with the more stringent plane wave cutoff and k -point sampling. These DFT calculations yield energetic differences for the four symmetry-distinct configurations shown in Fig. 30 in agreement with previous calculations by Tribello et al. [174] with another functional.

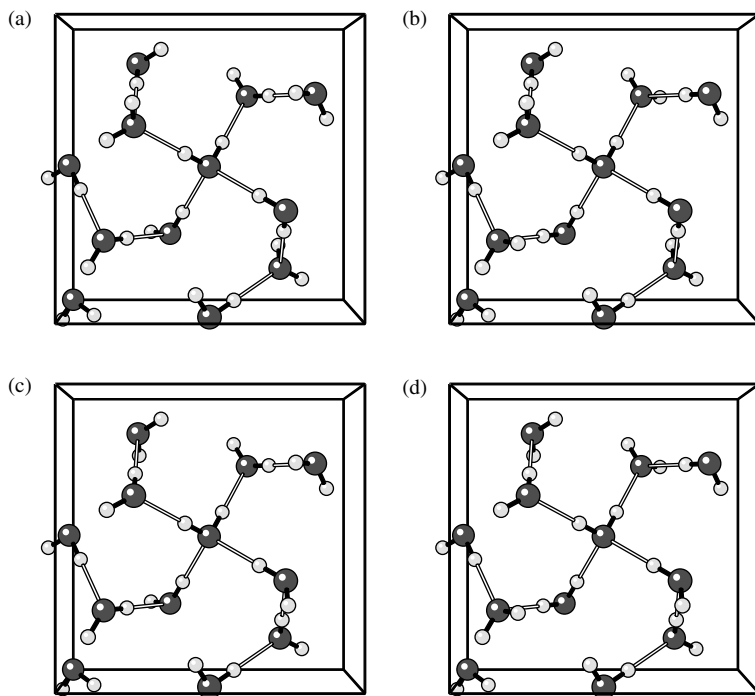


Figure 30. The four symmetry-distinct H-bond configurations of the primitive unit cell of ice XII that have $P2_12_12_1$ symmetry ordered from lowest-to-highest energy. Configuration (a) corresponds to proton-ordered ice XIV. The thin black lines outline the unit cell.

G. Hydrogen-Bond Order–Disorder at the Surface of Ice

There has been a continued interest in trying to understand the structure of the surface of ice, the chemistry on the ice surface, and the nature and implications of H-bond disorder at the surface of ice [176–181]. The surface of ice plays an important catalytic role in atmospheric processes [178]. The reaction between hydrogen chloride (HCl) and chlorine nitrate (ClONO₂) to form chlorine gas (Cl₂), which plays an important part in the depletion of ozone ([176, 179] and references cited therein), is a prominent example. In this case, the surface of ice particles provides a platform on which small reactant molecules can adsorb, and into which they can possibly dissolve. The availability of ice particles provides a larger target compared to reactions in the gas phase, leading to a larger collisional probability and thus an increased reaction rate.

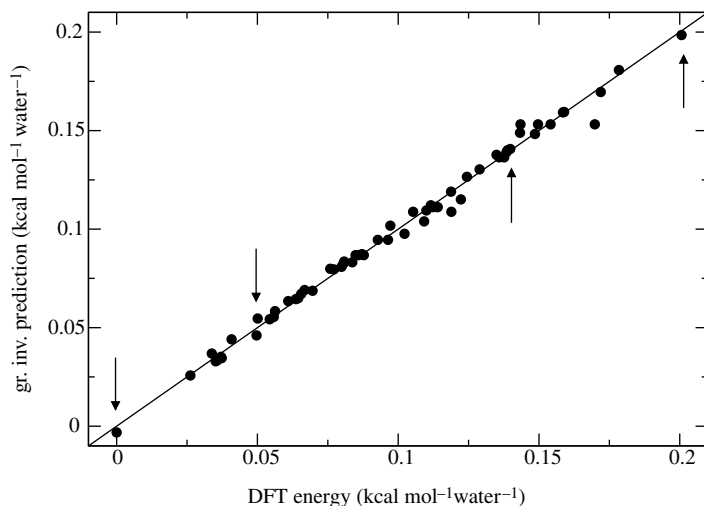


Figure 31. Test of the ability of the graph invariant expansion to fit the energies of the 62 symmetry-distinct H-bond isomers of a 12-water unit cell of ice XII. The arrows indicate those symmetry-distinct configurations possessing $P2_12_12_1$ symmetry, the ordering of which is identical to that previously reported [174].

At higher temperatures, but still below the melting point of ice, water molecules on the surface of ice are more mobile than those in the bulk due to their lower H-bond coordination. This topmost liquid-like (quasiliquid) layer has been the topic of scientific discussion for more than a century [182]. In one recent study, the surface of some ice samples were investigated by examining the elastic scattering of low-energy helium atoms [183]. The angular distribution of the scattered He atoms from the ice surface is sensitive to the degree of order on the ice surface. In this study, an ordered surface corresponds to a crystalline surface, not necessarily an ordered arrangement of H-bonds. It was observed that the intensity of the angular distribution decreases linearly as the temperature is raised from 150–180 K after which the intensity rapidly decreases. This rapid decrease was interpreted by the authors in terms of strongly anharmonic surface vibrations and a first sign of increased mobility of water molecules on the ice surface.

At temperatures below this premelting transition, where there is a solid-like ice surface, one would expect distinguishable H-bond arrangements to exist at the surface in conjunction with proton disorder in the bulk. One topological feature of the ice surface is the distribution of dangling oxygen and hydrogen atoms (free OH bonds). Surface sensitive techniques, such as sum-frequency generation spectroscopy, can detect these free OH bonds. In one recent study on the ice–vapor interface, the maximum tilt angle and orientational-order parameters for the free

OH bonds were measured [184, 185]. Their results indicated the transition from a solid- to a liquid-like surface occurs starting at 200 K and the degree of disorder increasing with temperature.

More than a decade ago, Fletcher [186], using a simple electrostatic model, proposed that the lowest energy configuration for the surface H-bonds consisted of alternating rows of dangling oxygen and hydrogen atoms. This arrangement of surface H-bonds has been reported in recent molecular simulation studies to indeed be a candidate for the lowest energy configuration [180, 181]. Molecular simulations of ice surfaces were reported by Buch et al. [180] where they examined three different types of patterns for the surface H-bonds: striped, honeycomb, and disordered surfaces. For each H-bond pattern, energy minimizations were performed for ~ 200 H-bond configurations. It was found that the mean energy for the striped (Fletcher type) surfaces was the lowest. The disordered configurations tended to have the highest energies. Using these energy distributions, they estimated an ice surface order–disorder transition temperature to be roughly 100 K above the melting temperature for ice. They determined the transition temperature from the striped phase to the honeycomb phase to be 290 K.

In another study, the surface energy for an ice Ih slab was calculated using *ab initio* methods for several different H-bond configurations, including proton-ordered ice XI [181]. It was determined that the variation in the surface energy was 100 meV per water in the topmost part of each slab. This is ~ 20 times larger than the range of values observed for the bulk cohesive energy. They constructed an order parameter to quantify the average distance between free OH bonds on the surface. When the surface energy was plotted against this order parameter, a linear relationship was observed that indicated increasing surface energy with increasing inhomogeneity of the distribution of dangling OH groups. Those slabs with few free OH bonds on the surface were relatively unfavorable. They performed Monte Carlo simulations with an empirical potential and found that thermal energy alone was insufficient to introduce significant additional disorder at the surface.

Although there is evidence for which types of ice surface topologies are most stable, it is not yet known which of the numerous surface H-bond configurations is the lowest energy. Enumerating all of the different surface topologies and identifying the ground-state configuration is a problem that can be readily tackled by the graph invariant approach described in this chapter.

Much remains to be learned about H-bond order–disorder at the ice surface. In the two studies discussed, the striped phase was identified as a candidate for the most stable H-bond configuration. What happens to the relative ordering of the surface configurations in the presence of adsorbates (including water itself)? Is the striped phase still the most stable? Theirfelder et al. [187] used *ab initio* methods to determine the binding energy of water molecules to the surface of ice. Their absorption energies are relatively insensitive to H-bond rearrangements below the surface, but highly sensitive to local H-bond orientation near the absorption site.

They report adsorption energies for five different geometries that take values in the range 0.548–0.576 eV and are approximately 80% of the bulk cohesive energy. The binding of water molecules to the ice surface is thus a favorable process and leads to surface roughness.

IV. ENUMERATION OF HYDROGEN-BOND CONFIGURATIONS

When system size is not prohibitively large, it is useful to have an enumeration of all symmetry-distinct H-bond isomers for a given unit cell of ice, or water cluster. For example, nothing is gained by performing computationally expensive electronic structure calculations on structures that are related by a symmetry operation. Throughout Section III, we have made reference to the number of symmetry-distinct H-bond structures for given unit cells of the ices. For systems beyond the reach of *ab initio* calculations, it is desirable to either have an alternative to, or check Monte Carlo sampling of H-bond structures.

The cost of enumerating symmetry-distinct H-bond structures nominally grows rapidly as the square of the number of structures considered. Among N H-bond topologies generated before eliminating symmetry-redundant ones, $N(N - 1)/2$ symmetry comparisons are required. The cost of the task grows even more rapidly with system size for periodic systems, because each symmetry comparison between two structures involves applying all the symmetry operations to one structure and detecting whether that other structure is produced. When considering nonprimitive crystalline unit cells, the symmetry group is proportional to the cell size. Using the language of Section II.C.2, the number of coset representatives of an $n_x \times n_y \times n_z$ non-primitive cell is $n_x n_y n_z$ times bigger than that of the primitive cell.

The N^2 or N^3 (depending on whether the symmetry group increases with N) scaling, can be brought down to an effectively $N \ln N$ dependence on system size using graph invariants [37]. Consider precalculating m invariants for N graphs before symmetry comparisons. The value of all invariants of two symmetry related graphs must be identical. If any one of the m invariants differs between two configurations, they cannot be symmetry-related, and hence expensive comparisons applying all operations of the symmetry group can be avoided. The calculation of m invariants for N configurations scales as N^2 because the number of terms in expression like Eqs. (13)–(15) (e.g., number of nearest-neighbor bond pairs) is proportional to system size. However, the calculation of invariants involves very few arithmetic operations and, in our experience, has never been a significant fraction of the total cost of an enumeration (even for a 46-water unit cell of a type I clathrate [61]).

Once m invariants for N configurations are calculated, the elimination of symmetry-redundant graphs scales as $N \ln N$. First, consider using the first of the m invariants to divide N graphs into P groups, each one with a different value

of that first invariant. If we would stop at this stage, symmetry comparisons need only be done within each of the P groups. Assuming roughly even distribution of graphs into the P groups, each group contains on the order of N/P graphs. The work of symmetry comparisons now scales like $(N/P)^2$ within each group. After separation into P groups, the work of symmetry comparison scales like $P(N/P)^2 = N^2/P$, an improvement by a factor P in efficiency.

Instead of using just one invariant to sort the graphs into smaller subsets, imagine using m different invariants to sort the graphs m times. For simplicity, we will assume that the graphs are sorted into P equal piles according to each new invariant. After employing the first invariant, the graphs are divided into P groups. Then, the next invariant divides each of those groups into P subgroups, making a total of P^2 groups. Finally, after m such sorts, the graphs are partitioned into P^m groups of size

$$n = \frac{N}{P^m} \quad (40)$$

The goal is to reduce the groups to a target size n , which is small enough to employ a conventional symmetry comparison method. From Eq. (40), the number of sorts required to reach a target size n is

$$m = \frac{\ln(N/n)}{\ln P} \quad (41)$$

Each time the graphs are sorted, each of the graphs is either labeled or moved to another location in memory or on disk. Hence, the cost of sorting is proportional to mN .

$$mN = N \frac{\ln(N/n)}{\ln P} \quad (42)$$

Associating a coefficient A with the computational cost of sorting the graphs into groups of target size n , and another coefficient B associated with $\mathcal{O}(n^2)$ conventional symmetry comparisons within each of N/n groups, the total work of eliminating symmetry related graphs scales like

$$AN \frac{\ln(N/n)}{\ln P} + B \frac{N}{n} n^2 = \frac{A}{\ln P} N \ln N + \left(Bn - A \frac{\ln n}{\ln P} \right) N \quad (43)$$

The total work contains components that scale as $N \ln N$ and as N , far more efficient than conventional symmetry comparison.

We arrived at $N \ln N$ scaling by assuming that each sort breaks the graphs into P groups of equal size. Actual computations are more complicated. The number of groups into which the graphs are sorted is the number of different values an invariant takes over the set of graphs. This varies from invariant to invariant. Moreover, the graphs are, in general, broken into groups of unequal size. Therefore, the parameter

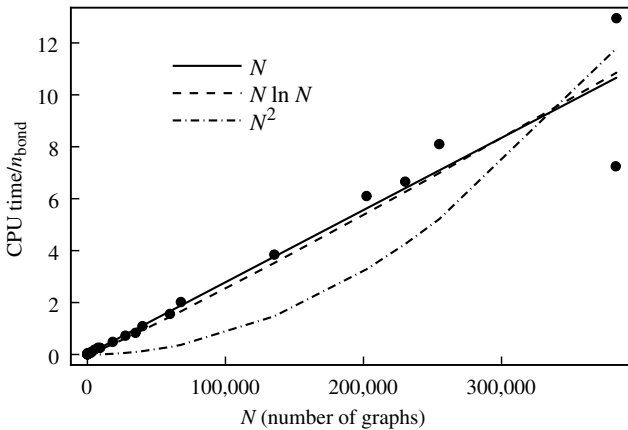


Figure 32. The CPU time for enumeration of all symmetry-distinct H-bond topologies for a $(\text{H}_2\text{O})_{20}$ dodecahedral water cluster is plotted against the number of graphs from which symmetry-redundant configurations are eliminated [37]. Data is generated for a sequence of structures containing a subset of the bonds, and then finally the full cluster. Total CPU time, including calculation of invariants and sorting is plotted. Least-square fits clearly show that the computational cost scales as either N or $N \ln N$.

P used in Eqs. (40)–(43) must be taken as an average or effective number of groups. The basic idea is confirmed, and evidence presented in Fig. 32 showing $N \ln N$ scaling in a realistic calculation.

V. WATER CLUSTERS

In common with the disordered phases of ice, there are families of water clusters $(\text{H}_2\text{O})_n$ for which the oxygen atom positions are similar, and that differ in the connectivity of the H-bonds. The 14 isomers of cubic $(\text{H}_2\text{O})_8$ shown in Fig. 3 are a good example [25, 26]. There are 27, 96, 10, 70, and 194 H-bond topologies possible for the $(\text{H}_2\text{O})_6$ cage, book, prism, chair, and boat clusters, respectively [188]. All of the possible cage and prism topologies appear to correlate with actual local minima on the potential energy surface of $(\text{H}_2\text{O})_6$, while in other cases the fraction of topologies that correspond to actual minima decreases with the openness (i.e., H-bond per water molecule) of the cluster. The beautiful $(\text{H}_2\text{O})_{20}$ dodecahedron (Fig. 33) has received significant attention [189–196], despite the possibility that it may nowhere exist as an isolated cluster. McDonald et al. [25] were the first to determine that the $(\text{H}_2\text{O})_{20}$ dodecahedron possesses 30026 symmetry-distinct H-bond isomers, and to elucidate their properties [37].

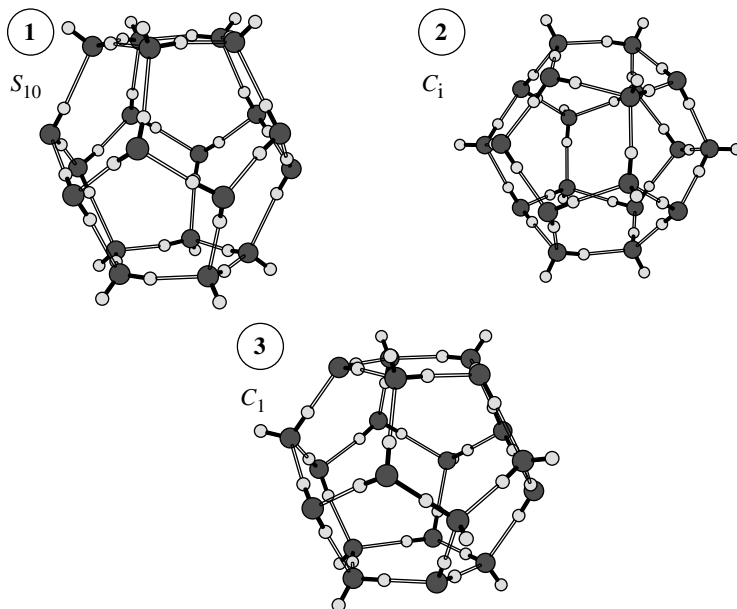


Figure 33. Three of the 30026 H-bond isomers of the $(\text{H}_2\text{O})_{20}$ dodecahedron [25]. Structure (1) is a high-symmetry (S_{10}), and also high-energy structure. Structure (2) is of C_i symmetry, and structure (3), a very stable structure, has no symmetry (C_1).

Graph invariants, constructed using the point group operations of a finite cluster, provide a precise way to link scalar physical properties of clusters to their H-bond topology.

$$I_r = C_r \sum_{\alpha} g_{\alpha}(b_r) \quad (44)$$

$$I_{rs} = C_{rs} \sum_{\alpha} g_{\alpha}(b_r b_s) \quad (45)$$

$$I_{rst} = C_{rst} \sum_{\alpha} g_{\alpha}(b_r b_s b_t) \quad (46)$$

...

In the above equations, the sums are over all elements g_{α} of the cluster point group, and Eqs. (44)–(46) generate first-, second-, and third-order invariants, respectively, for finite water clusters. In line with our experience for ice, we have never found the need to go further than second-order invariants to describe water clusters.

The $(\text{H}_2\text{O})_{20}$ dodecahedron provides an example of the ability of graph invariants to organize and describe scalar physical properties among H-bond isomers.

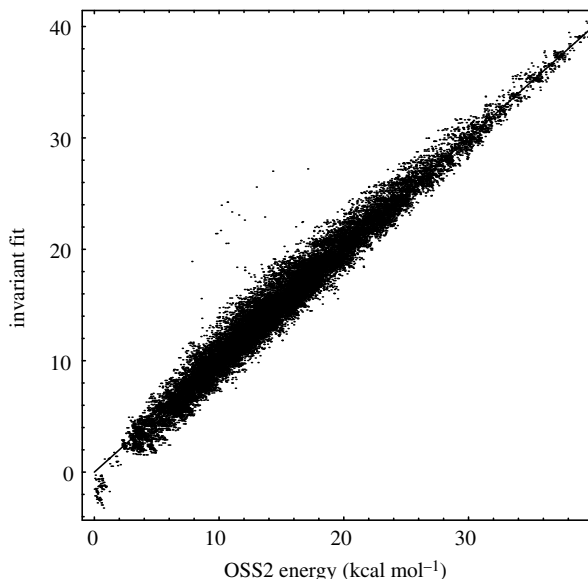


Figure 34. Energies of local potential energy minima of the $(\text{H}_2\text{O})_{20}$ dodecamer compared with a graph invariant prediction to the energies based on 20 randomly selected isomers.

The plot in Fig. 34 is actually not a least-squares fit of $(\text{H}_2\text{O})_{20}$ dodecamer energies to invariant functions, as was provided for ice structures in Section III. Rather, the energies of only 20 of the 30026 $(\text{H}_2\text{O})_{20}$ isomers, calculated using the OSS2 empirical potential [197, 198], were used to fit seven invariants. [One of those invariants was a constant, analogous to the E_0 term in Eq. (11), so more precisely an irrelevant overall constant and the six invariant functions were used to describe the energy of 30,026 isomers in Fig. 34.] The plot in Fig. 34 compares the prediction from the invariant fit to the energies of only 20 isomers, to the actual energy calculated using the same model for all 30,026 isomers. The energies were organized in this way to show that graph invariants furnish a powerful method to quickly sift through data, and to search for the ground state. With just 20 data points, candidates for the ground state are identified, and the energy of most structures is fit to within a small fraction of the total energy range. The small number of points that lie far from the line in Fig. 34 are quite interesting cases. They are structures that optimize to a different, sometimes zwitterionic, topology from the starting configuration [199].

Graph invariants and their higher tensorial extensions provide a complete and unambiguous method for correlating physical properties with H-bond topology. Normal H-bonding of neutral molecules constrain the directed graphs describing H-bond topology to have at most two incoming and two outgoing bonds at each vertex. Under these constraints, many of the possible invariant combinations are linearly dependent on others. The minimal number of linearly independent invariants at any given order can be established, but of course the selection of linearly

independent representatives from among a large set of basis functions is not unique. This has led to confusion in the literature, and meaningless claims of new methods. The $(\text{H}_2\text{O})_{20}$ dodecahedron serves as a good example.

In 1998, McDonald et al. [25] examined the energy of the 30,026 isomers of the $(\text{H}_2\text{O})_{20}$ dodecahedron with an empirical potential (Fig. 34) and found that the number of a certain type of H-bond was the most important factor determining the energy of those clusters. They linked the energy of the dodecahedral $(\text{H}_2\text{O})_{20}$ isomers to $n_{(2A \rightarrow 2A)}$, the number of $2A \rightarrow 2A$ bonds, bonds in which both waters are double-acceptors (2A). In terms of directed graphs, 2A waters on the dodecahedron are vertices with two incoming bonds. Since all water of the dodecahedron is three-coordinate, this implies that both water molecules of a $2A \rightarrow 2A$ bond have a dangling hydrogen atom. The maximum number of $2A \rightarrow 2A$ bonds possible in the $(\text{H}_2\text{O})_{20}$ dodecahedron is 10, an example of which can easily be discerned in structure (1) of Fig. 33 where the top and bottom pentagons each contain five bonds with nearest-neighbor dangling hydrogen. These are the least stable dodecahedral water clusters. The minimum number of $2A \rightarrow 2A$ bonds is 3. These are the most stable water clusters, an example of which is structure (3) of Fig. 33.

A decade later Kirov et al. [200] proposed a “new discrete model” for the $(\text{H}_2\text{O})_{20}$ dodecahedron as an improvement over previous work. Their model “has only one preferred H-bond, the one of (t1d)-type”. The designation “t1d” refers to a trans bond (Fig. 2) with one dangling bond on the donor water molecule. The number of t1d bonds is easily shown to be given in terms of the number 2A bonds by the following relation:

$$n_{\text{t1d}} = 10 - n_{(2A \rightarrow 2A)} \quad (47)$$

(Let n_{2A} be the total number of double-acceptor waters, $n_{2A \rightarrow 2A}$ be the number of bonds in which a 2A donates to another 2A, and $n_{2A \rightarrow 2D}$ be the number of bonds in which 2A donates to a 2D (double-donor water). Since each double acceptor is a single donor, each 2A is in 1:1 correspondence with a bond that point from a 2A to either another 2A or a 2D: $n_{2A} = n_{2A \rightarrow 2A} + n_{2A \rightarrow 2D}$. Therefore, $n_{2A \rightarrow 2A} = n_{2A} - n_{2A \rightarrow 2D}$. An H-bond from a 2A to a 2D is what Kirov et al. [200] call a t1d bond. For polyhedral water clusters with three-coordinate waters, $n_{2A} = \frac{1}{2}(\text{number of vertices})$, which is 10 for the case of the $(\text{H}_2\text{O})_{20}$ dodecahedron. Hence, we arrive at the conclusion that $n_{\text{t1d}} = 10 - n_{2A \rightarrow 2A}$.)

McDonald et al. [25] found that $n_{(2A \rightarrow 2A)}$ ranged from 3 to 10 with lowest energy correlated with lowest $n_{(2A \rightarrow 2A)}$. Kirov et al. found in their “new” model that n_{t1d} ranged from 0 to 7 (Table 3 of [198]) with lowest energy correlated with highest n_{t1d} , as must occur according to Eq. (47). Clearly, the model of [199] is merely a linear transformation of the parametrization used by McDonald et al. [25].

In dodecahedral $(\text{H}_2\text{O})_{20}$, $n_{(2A \rightarrow 2A)}$, and obviously by Eq. (47) n_{t1d} as well, is a second-order graph invariant. They are parameters on the lowest level (second-order graph invariants), of a hierarchy of topological parameters of increasing

complexity (third-order invariants, fourth-order invariants, . . .). The invariant formalism determines the full set of independent parameters and exposes connections among them. Since certain topological parameters are related to others in ways that are not altogether obvious, picking topological parameters in an *ad hoc* fashion, as the $(\text{H}_2\text{O})_{20}$ example shows, is fraught with dangers.

Anick [201, 202] has criticized the graph invariant approach to clusters with some legitimacy on two counts. First, Anick points out that it is not clear how to transfer invariant parameters from system to system [201]. When dealing with *ad hoc* parameters, like $n_{(2A \rightarrow 2A)}$ or n_{t1d} mentioned earlier in connection with dodecahedral $(\text{H}_2\text{O})_{20}$, it is easier to imagine transferring the parametrization to another polyhedral cluster. Actually, transference of parametrization using invariants is quite powerful in another context, going from smaller to larger unit cells in ice, as explained in detail in Section II.C. While one can similarly envision transferring parameters from smaller to larger clusters within a family of polyhedral water clusters, transferring between different phases of ice or between very different water clusters remains to be explored. Another objection is the fact that as the symmetry of a cluster decreases, the number of independent invariant functions increases, sometimes to an unwieldy number [202]. In clusters with high symmetry, and the dodecahedron is a prime example, the invariant formalism is most powerful. At present we do not have a method to collapse invariant functions that are not exactly the same but nearly the same to curtail the growth of independent parameters as the symmetry is lowered.

VI. DEFECTS

Up to this point, in the ice phases we only examined the case where each water molecule accepts and donates two H-bonds, thus no defects or impurities were present in the ice lattices. In clusters, we only considered perfect, polyhedral structures. However, there is considerable motivation to examine defects, and the interaction of defects with the surrounding H-bond disordered medium.

There are several disordered phases of ice (Ih, V, VI, and XII) for which the ordering transitions only occurs when a small amount of dopant (either excess acid or base) is present. The mechanism by which the introduced defects facilitate H-bond ordering transitions is not completely understood. Remember that the H-bond disorder sets up a random medium for these defects to diffuse with some local H-bond arrangements potentially forming traps for the defects. With an appropriate description of defects in ice, the mobility of defects throughout the disordered ice lattice, and hence the mechanism of H-bond order and disorder in ice could be investigated. In clusters, there are equally strong motivations for studying impurities that furnish model systems that mimic the behavior of adsorbates on the surface of ice.

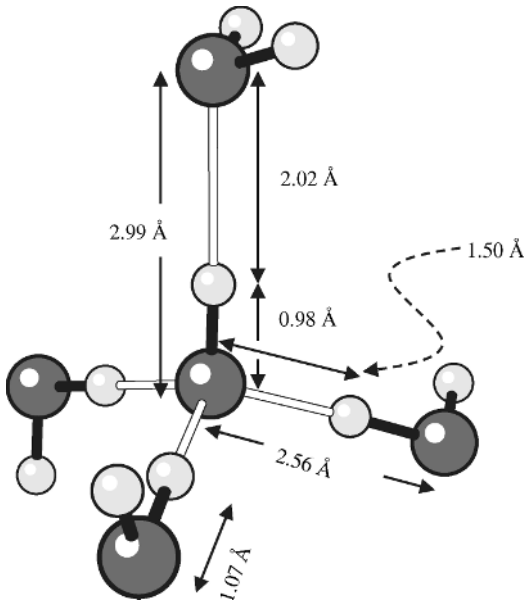


Figure 35. Structure of an “in-lattice” hydroxide defect in ice.

The oriented graph formalism can be extended to describe defects or impurities by defining new types of bonds that link water molecules to defects. One may picture the new bonds as having a different color. This extension was applied to treat a hydroxyl radical defect in a cubic water cluster [203]. It is also possible to use the same techniques to describe the interactions of an “in-lattice” hydroxide ion in an ice Ih lattice [204]. The in-lattice hydroxide corresponds to a graphical vertex with three incoming and one outgoing directed bond (Fig. 35). To make a periodic system, it must be compensated by another vertex, like an L-defect. (Notably, Buch and co-workers [205, 206] show that an “out-of-lattice” configuration in which the hydroxide hydrogen points into an interstitial space is more stable than an in-lattice hydroxide. Hence, the out-of-lattice configuration represents a trap for the hydroxide, and in-lattice a possible intermediate for diffusive motion.) Using graph invariants to search for low-energy configurations, the lowest energy H-bond configuration surrounding an “in-lattice” hydroxide ion is found to be the ice XI structure [204].

VII. CONCLUSION

Our objectives in this work have been twofold. First, to provide a review of H-bond order–disorder phenomena in water ice and in water clusters. Second, we have summarized how these phenomena can be described usefully and compactly by exploiting a link between H-bond topology and physical properties. In

the solid state, deep minima of the potential surface of water are in 1:1 correspondence with the oriented graphs that describe the H-bond topology. Phenomena like the several known H-bond order–disorder transitions between ice phases can be understood as discontinuous changes in the H-bond topologies sampled by the system, while the oxygen lattice changes minimally.

The statistical mechanical description of H-bond order–disorder requires the relative energies of a large number of H-bond arrangements, growing exponentially with system size, and therefore present special challenges without appropriate tools. Since in this case the property of interest is a scalar, it can be related to topological properties that are invariant to all symmetry operations. In this manner, the energetic properties of H-bond arrangements can be captured by a handful of relevant parameters. Physical properties that transform as higher-order tensors, such as lattice site displacements and dipole moment, can also be treated in an analogous fashion.

With better techniques and more experience in the synthesis of new phases, the number of known phases of ice has increased dramatically. Four new phases of ice have been discovered just since 1998. This will provide a fertile source of new challenges and opportunities in the theory of H-bond order–disorder in the ices.

Acknowledgments

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