A First Principles Study on the Structure of Ice-VI: Static Distortion, Molecular Geometry, and Proton Ordering

Jer-Lai Kuo* and Werner F. Kuhs*†

School of Physical and Mathematical Sciences, Nanyang Technological University, 1 Nanyang Walk, Singapore 637616, Singapore, and GZG Crystallography, Universität Göttingen, Goldschmidtstrasse 1, 37077 Göttingen, Germany

Received: September 16, 2005; In Final Form: January 12, 2006

We have studied the structure of ice-VI by examining all ice-rule-allowed structures in its primary unit cell of 10 water molecules with first principles methods. A significant amount of static distortions in the oxygen positions away from their crystallographic positions are found, which is in good agreements with significant higher-order terms in the atomic displacement parameters obtained from X-ray and neutron diffraction data. Structural anomalies (such as exceptionally short OH bonds and small H-O-H angles) noted in conventional crystal structure refinements were not seen in our ab initio calculations, and it is evident that these structural anomalies arose from oversimplified models in which static distortions are not properly accounted for. Our results also show that the molecular geometry of water in ice-VI is similar to but richer than those in ice-Ih and ice-VII. Larger distortions in bond lengths/angles and correlation between the molecular geometry and the neighboring environments were found. Different proton-ordering schemes proposed in the literature were examined, and our calculations provide evidence in favor of a ferroelectric phase of the proton-ordered counterpart of ice-VI at about 80 K.

I. Introduction

Ice-VI plays a key role in connecting our understanding of the structures of various phases of ice that compose the rich and complicated phase diagram of water.1,2 Similar to other high-pressure phases (ice-VII, ice-VIII, and ice-X), there are two interpenetrating but independent hydrogen-bonded (H-bonded) sublattices in ice-VI. However, the molecular geometry of water molecules in ice-VI is closely related to other intermediate pressure phases (ice-II, ice-III, ice-IV, ice-V, and ice-IX), which are characterized by considerable distortions in bond angles and distances. In fact, ice-VI shows the largest H-bond bending of all known phases of ice, twice as large as those in ices II and III and 50% larger than that in ice-V. Neutron diffraction data suggested that the H-O-H angles in ice-VI vary between 98.0° and 115.5° in contrast to that in ice-VII where the distribution centers at 105.6° with a small variation.3

Ice-VI occupies a unique position in the phase diagram of H2O; for example, ice-VI has four triple points (of which three are experimentally well established), and there could potentially be two more triple points if the existence of a low-temperature proton-ordered counterpart of ice-VI is confirmed. In comparison to ice-V and all lower-pressure forms of ice, the denser packing of ice-VI (1.373 g/cm³ at 225 K and 1 GPa) is achieved by interpenetration of two independent H-bonded networks. The density is comparable to that of high-density amorphous (HDA) ice as well as the recently discovered very-high-density amorphous (VHDA) ice at correspondingly higher pressures.4–7 In fact, the formation conditions for both HDA and VHDA are experimentally well established, and there could potentially be two more triple points if the existence of a low-temperature proton-ordered counterpart of ice-VI is confirmed. In comparison to ice-V and all lower-pressure forms of ice, the denser packing of ice-VI (1.373 g/cm³ at 225 K and 1 GPa) is achieved by interpenetration of two independent H-bonded networks. The density is comparable to that of high-density amorphous (HDA) ice as well as the recently discovered very-high-density amorphous (VHDA) ice at correspondingly higher pressures.4–7

Partly overlapping with the stability field of ice-VI is also the field of existence of metastable ice-XII,8 which consists of noninterpenetrating seven- and eight-membered rings producing similar molecular densities as ice-VI. While it was suggested earlier that HDA and VHDA may contain self-interpenetrating H-bonded networks,9 recent work indicates that such networks are not present; neutron spectroscopy6 does not find evidence for features related to interpenetrating lattices and molecular dynamics simulations10 suggest that the density increase compared to the low-density amorphous (LDA) form is achieved by building ring structures larger than six-membered and shifting the predominant size with increasing pressure.11 Therefore, it seems that the interpenetrating networks of ice-VI, the thermodynamically stable form of condensed water in the pressure range from 0.6 to 2 GPa, presents a rather unique structure not easily reproduced locally in low-temperature preparations of the amorphous forms in this pressure range.

The crystal structure of ice-VI was first determined by Kamb12 in 1965 on samples recovered to ambient pressure at 98 K. The space group of P43/mmc and a tetragonal unit cell consisting of 10 water molecules were assigned. The first direct measurement of the structure of ice-VI under pressure was carried out by Kuhs et al.13 in 1984 using powder neutron diffraction. More accurate X-ray and neutron diffraction measurements were subsequently carried out by Kuhs and co-workers.13–16 Significant higher-order terms in the structural analysis were found, and the authors attributed the origin of the high-order terms to the existence of static displacement of oxygen atoms from their high-symmetry crystallographic positions.17

Static distortions away from the high-symmetry sites are common in various “crystalline” phases of ice as the orientations of water molecules are random, and therefore individual molecules can deviate from their lattice sites and change their
molecular angles and bond lengths in response to different arrangements of the neighboring molecules. In contrast to phases of higher symmetry (for example, ice-Ih\textsuperscript{18} and ice-VII\textsuperscript{3}) on which various elaborate disorder models were tested for crystal structure refinement, the more difficult detailed crystallographic analysis for the oxygen displacements from positions of lower symmetry have not yet been performed. Hence, one of our objectives in this work is to use first principles calculations to assess the amount of static distortions as well as to study how water molecules adjust their molecular geometries to different environments.

The H-bond orientation in ice-VI is found to be random,\textsuperscript{12} and two possible schemes for a low-temperature proton-ordered phases were proposed by Kamb\textsuperscript{19} (recovered samples, antiferroelectric ordering) and Johari and Whalley (under-pressure, ferroelectric ordering).\textsuperscript{20,21} However, neither scheme has support from neutron in situ diffraction measurements.\textsuperscript{3} It is important to keep in mind that a significant difference in lattice constants was found in recovered and under-pressure samples. Thus, to test the possible ordering scheme of either type, we also need to take into account the possible effects of the lattice constants; proton-ordering and lattice constants were found to be interrelated in the case of ice-III/IX.\textsuperscript{22} Although the energy difference between the order and the disorder configurations is small (so is the low phase transition temperature), the applicability of our methodology has been validated by its success in describing the correct ground-state (proton-ordered) structures for ice-VII\textsuperscript{23,24} and ice-Ih.\textsuperscript{24,25} It is worth mentioning that the most reputable empirical force fields failed to reproduce the latter.\textsuperscript{26}

The remainder of this paper is structured as follows. In section 2, we will summarize the structure of ice-VI and briefly cover the enumeration of all ice-rule-allowed configurations in its primary unit cell as well as the procedure to generate their initial geometries. We will also provide a detailed description of our geometry optimization procedure and issues regarding k-point sampling and the lattice constants. In section 3, we will present the relative energetics and structural data of all 45 ice configurations predicted by ab initio calculations and compare them with experimental results. We shall conclude with a short summary.

2. Methodologies

Generation of Ice-Rule-Allowed Configurations. The symmetry group of ice-VI is \textit{P4}\textit{\textsubscript{2}2\textit{\textsubscript{1}}2\textit{\textsubscript{1}}}, which requires a proton-disordered structure. The primary unit of ice-VI (shown in Figure 1) is a tetragonal cell with 10 water molecules, and among them there are two kinds of crystallographically distinct oxygen atoms with multiplicities of 2 and 8. From the convention used in previous neutron diffraction studies,\textsuperscript{3,13,16} the former is denoted as O\textsubscript{1} and the latter O\textsubscript{2} (their positions are shown with different colors in Figure 1A). Similar to other high-pressure phases of ice, ice-VI has two interpenetrating and independent sublattices, and we highlighted the two sublattices with different colors in the two lower figures (Figure 1B). Focusing on the red sublattice in the lower-right figure, it is easy to see that each of the sublattices can be regarded as a network of water hexamer cages (as shown in Figures 2 and 3).

The orientation of the water molecules in ice-VI is found to be random and assumed to be subjected only to the constraints of the ice rules.\textsuperscript{27,28} As a first step to understand the effects of H-bond orientation on the structure of ice-VI, we enumerated all the possible configurations in the primary unit cell. We found 576 possible arrangements of the H-bond network satisfying ice rules, and most of these configurations are chemically identical, meaning that they are related by some symmetry operations. For all “chemically identical” structures, only one
parameters from neutron diffraction data. For simplicity, the initial positions of the hydrogen atoms are assigned to locate along the straight line between two oxygen atoms, and the initial oxygen–hydrogen bond length is assumed to be one-third of the oxygen–oxygen distance.

Special attention was paid to test the influence of lattice constants on the structure and the relative energies of different ice configurations. It is important to note in this context that (1) experimental measurements on under-pressure and recovered samples showed significant difference in the lattice constants and (2) different proton-ordering schemes were proposed by Kamb (recovered samples, antiferroelectric) and Johari and Whalley (under-pressure, ferroelectric). In total, three sets of lattice constants were used (1) \( a = 6.27 \text{ Å}, c = 5.79 \text{ Å} \) (recovered samples), (2) \( a = 6.166 \text{ Å}, c = 5.689 \text{ Å} \) (1.1 GPa and 8 K), and (3) \( a = 6.181 \text{ Å}, c = 5.698 \text{ Å} \) (1.1 GPa and 225 K).

**Geometry Optimization.** In the geometry optimization all degrees of freedom are allowed to relax, except the lattice constants. All ab initio calculations are carried out using the Car–Parrinello molecular dynamics methods (CPMD) based on the Becke–Lee–Yang–Parr (BLYP) functional, using norm-conserving pseudo-potentials (Troullier and Martins form) with a plane-wave cutoff of 70 Ry, and considering only the \( \Gamma \) point of the Brillouin zone. These are the standard conditions employed in numerous investigations of liquid water and crystalline phases of ice.

There are some concerns in the literature about the k-point sampling (that is sufficient k-point sampling is required to achieve convergence of the total energy). In our previous study on ice-VII and ice-VIII, we found that while the total energy converges slowly with respect to the k-point used, the molecular geometry is not sensitive to the increase in k-point mesh. Hence all geometry optimizations were carried out with the \( \Gamma \) point only, and total energy from single-point calculations with a \( 2 \times 2 \times 2 \) mesh (Monkhorst–Pack scheme) were used to calculate the relative stability.

### 3. Results and Discussions

**Static Distortion of the Oxygen Lattice.** In principle the amount of static distortion can be extracted either from the temperature dependency of atomic displacement parameters, from their higher-order terms, or from introducing suitable split position models. This has been done on various phases of ice with high symmetry. The relatively low local symmetry of the oxygen positions in ice-VI leads to a large number of degrees of freedom for split models, and it is very difficult to obtain reliable structural refinements with so many free parameters. However, single-crystal data have permitted determination of atomic displacement parameters up to fourth order, often indicative of static displacements, but more difficult to evaluate quantitatively. Theoretical calculations, however, can offer detailed structural insights and give a quantitative description on the amount of static distortion.

There are two major categories of static distortions. First, we consider the amount of deviation for an oxygen atom from its averaged crystallographic position (denoted as \( \delta \)). This kind of distortion is very common in most phases of crystalline ice, and the tetragonal symmetry of ice-VI gives two distinct directions; therefore the amount of \( \delta \) in O1 can be separated in (100) \( \langle \delta \rangle_{ab} \) and (001) \( \langle \delta \rangle_{c} \). Another kind of distortion arises from the fact that ice-VI has two independent sublattices. We use \( \epsilon \) to represent the amount of relative deviation of the two sublattices compared to the experimental averaged structure.

**Geometric Parameters.** The amount of static distortion can be quantified as the differences in lattice parameters and oxygen–oxygen distances. Table 1 shows the comparison of static distortion in ice-VI, ice-VII, and ice-Ih from first principles calculations.

<table>
<thead>
<tr>
<th></th>
<th>ice-VI</th>
<th>ice-VII</th>
<th>ice-Ih</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \langle \epsilon \rangle )</td>
<td>0.045</td>
<td>0.043</td>
<td>N/A</td>
</tr>
<tr>
<td>( \langle \epsilon_{ab} \rangle )</td>
<td>0.037, 0.026</td>
<td>0.037, 0.014</td>
<td>0.027, 0.033</td>
</tr>
<tr>
<td>( \langle \delta \rangle_{ab} )</td>
<td>0.040</td>
<td>0.043</td>
<td>0.047</td>
</tr>
<tr>
<td>( \langle \delta \rangle_{c} )</td>
<td>-</td>
<td>0.037</td>
<td>0.047</td>
</tr>
</tbody>
</table>

* The units are in angstroms, and the tetragonal symmetry of ice-VI gives two distinct directions: \( \langle \delta \rangle_{ab} \) stands for the \( \langle \delta \rangle \) in (100) and \( \langle \delta \rangle_{c} \) for (001).

Similarly, the amount of \( \epsilon \) in (100) and (001) are represented by \( \epsilon_{ab} \) and \( \epsilon_{c} \), respectively.

Our theoretical estimate on the different sources of static distortion is summarized in Table 1. The isotropic averages are \( \langle \delta \rangle_{ab} = 0.040 \text{ Å}, \langle \delta \rangle_{c} = 0.043 \text{ Å} \), and \( \langle \epsilon \rangle = 0.045 \text{ Å} \); these numbers are comparable with their counterparts in ice-VII and ice-Ih. The correlation between the energetics with either \( \epsilon \) or \( \delta \) is found in ice-VI. A systematic study of connecting the energetics of an ice configuration with its H-bond topology patterns can be done by employing graph invariant methods and shall be addressed in a future publication.

**Molecular Geometry of H2O and H-Bonding.** The fact that each of the sublattices in ice-VI can be viewed as a network of cage water hexamers (there are 27 symmetrically distinct isomers), different ab initio methods can be applied to assess the accuracy of density functional theory (DFT)/generalized gradient approximation (GGA) used herein. Second, by comparing the water structure in hexamers and in ice-VI, we can also separate the influence due to local constraints from the effects due to periodic boundary conditions.

The four crystallographically distinct hydrogen positions in ice-VI are shown in Figure 2. In other words, there are four kinds of H-bonds, and in this work we adapted the notations used in previous neutron diffraction experiments. H2 atoms are the only species that is covalently bonded to O2, and H1 atoms are the complementary half-hydrogen positions of H2 along the same H-bond. H3 are those sitting on the H-bonds that connect the water hexamers in the \( a \) and \( b \) directions. H4 are hydrogen positions on the puckered four-membered H-bonded rings (oriented perpendicular to the \( c \)-axis) of the hexamer units.

The averaged structural data of the different H-bonds from our ab initio calculations are summarized in Table 2. For comparison, we also listed the results from previous neutron diffraction experiments. In general, the ab initio calculations agree well with the experimental data except for the \( R(\text{OH}) \) length. The surprisingly short \( R(\text{OH}) \) length (<0.94 Å) resulting from a standard crystallographic analysis of the neutron diffraction data is likely due to the neglect of static distortions in the oxygen lattice; we will elaborate on this below. It is well-
known that DFT/GGA methods tends to overestimate the $R(\text{OH})$ length. In our previous studies we found that the amount of elongation in $R(\text{OH})$ length is about 0.01 Å in both ice-Ih\textsuperscript{25} and ice-VII.\textsuperscript{23} Assuming the elongation of the $R(\text{OH})$ length is similar here, the averaged $R(\text{OH})$ in ice-VI is about 0.98 Å. This estimate agrees with the experimental estimate based on the empirical relation between the OH distance and stretching frequency,\textsuperscript{42} and it is also similar to the $R(\text{OH})$ length in the water hexamers.\textsuperscript{40}

The six symmetrically distinct orientations of water are shown in Figure 3. For water molecules centered at $O_1$, there are two distinct orientations (shown in Figures 3A and 3B). Orientation A is part of a four-membered ring, and in orientation B the shortest loop consists of eight water molecules on several hexamer units. Similarly, the four symmetrically distinct orientations for $H_2O$ centered at $O_2$ can be organized as the following: Orientations C and D are part of the four-membered ring, and D and E belong to an eight-membered ring. In short,

\[
\begin{array}{cccccc}
\text{multiplicity} & R_{\text{OO}} & \angle\text{OHO} & R_{\text{OH}} & R_{\text{OO}} & \angle\text{OHO} & R_{\text{OH}} \\
O_2-H_1...O_1 & 8 & 2.788(24) & 161.81(5.19) & 0.937(55) & 2.8141(189) & 161.18(2.49) & 0.9912(12) \\
O_2-H_1...O_2 & 8 & 2.788(24) & 161.58(4.41) & 0.986(48) & 2.8056(262) & 161.40(1.36) & 0.9921(10) \\
O_2-H_2...O_2 & 8 & 2.726(38) & 175.22(4.33) & 0.976(51) & 2.8148(104) & 176.51(2.04) & 0.9884(07) \\
O_2-H_2...O_2 & 16 & 2.778(28) & 156.64(3.09) & 0.938(32) & 2.8001(226) & 158.16(2.10) & 0.9909(13) \\
\end{array}
\]

\(a\) Neutron diffraction (italic text), DFT calculations in ice-VI (bold text), and DFT calculations in (H\textsubscript{2}O\textsubscript{6}) cages (bold italic text). Bond lengths are in angstroms, and bond angles are in degrees. The standard deviations are given in brackets.
the shortest H-bond loops in ice-VI are either four- or eight-membered (as opposed to a homogeneous size of six in ice-Ih and ice-VII), and it is worth mentioning that these loop sizes are among the smallest and largest found in the crystalline phases of ice.

While the variation in \( R(\text{OH}) \) is small in ice-VI, the molecular angle of water \( (\angle \text{HOH}) \) appears to be more sensitive to the molecular orientations (summarized in Table 2). It is not surprising that the \( \angle \text{HOH} \) would be strongly affected by the \( \angle \text{OOO} \) to accommodate a reasonable H-bonding angle. Nevertheless it is clearly indicated in Table 2 that even under extreme cases (where \( \angle \text{OOO} \) is less than 90°) the molecular angle remains much closer to its gas-phase value than previous interpretations based on neutron diffraction data. ³ Our ab initio calculations indicate the small \( \angle \text{HOH} \) angles (i.e., parts A, C, and D in Figure 3) in ice-VI range from 101.71° to 103.51°. It is intriguing to note that while the \( \angle \text{OOO} \) angles in ice-VI are larger than their counterparts in water hexamers, the \( \angle \text{HOH} \) angles show the opposite trend. We think the reduction in \( \angle \text{HOH} \) is mostly likely due to the repulsive force between water molecules in the independent sublattices, and our conjecture is supported by the observation that the molecular angle in ice-VII²³ is 105.38(26)° as compared to the molecule angle of 106.34(36)° in ice-Ih.²⁵

It is fairly clear from the above discussions that the molecular geometry of water in ice-VI remains normal as compared to its gas-phase value and structural anomalies (such as very short \( R(\text{OH}) \) and improbable \( \angle \text{HOH} \) ) indicated in conventional structural refinements³ can be attributed to the fact that an oversimplified model (that cannot appropriately consider all sorts of static distortions caused by the randomness of the H-bond orientation) were used for structure refinement.

Proton Ordering. Possible Low-Temperature Proton-Ordered Phase and the Effect of Lattice Constants. There are indirect evidences for proton ordering in ice-VI, but the low-temperature proton-ordered form has not been identified by direct neutron diffraction experiments. In fact, two possible proton-ordering schemes were proposed by Kamb (recovered samples, antiferroelectric)⁹ and Johari and Whalley (under-pressure sample, ferroelectric). ²¹ Furthermore, Kuhs et al. ¹² pointed out the significant difference in lattice constants between under-pressure³ and samples recovered to ambient pressure. ¹² This raises concerns on the possible interrelation of the lattice constants with the actual proton ordering.

The energies of all 45 symmetrically distinct ice configurations of ice-VI are shown in Figure 4, where the zero of the energy scale is set to the averaged energy. In light of the possible effects of different lattice constants in recovered and under-pressure samples, we have reoptimized all 45 ice configurations under several sets of lattice constants under different experimental conditions (details see the caption of Figure 4). It is evident from Figure 4 that lattice constants play a very minor role in the relative stabilities, and under all three sets of lattice constants we considered, a ferroelectric structure shown in Figure 5 is found to be the ground state.

![Figure 5](image-url)  
**Figure 4.** Effects of lattice constants on the relative energetics. The x-axis is the energy difference (in mhartree) of all 45 symmetrically distinct ice configurations with lattice constants under 1.1 GPa at 8 K  
\( (a = 6.166 \text{ Å}, c = 5.689 \text{ Å}) \). The energies with lattice constants under 1.1 GPa and 225 K \( (a = 6.181 \text{ Å}, c = 5.698 \text{ Å}) \) are shown as solid circles, and the energies with lattice constants from the recovered sample \( (a = 6.27 \text{ Å}, c = 5.79 \text{ Å}) \) are shown as open diamonds. The nonsignificant role of the lattice constants on the relative energetics is evident by the fact that most of the points do not deviate much from the diagonal line. Under all three sets of lattice constants we considered, a ferroelectric structure shown in Figure 5 is found to be the ground state.

![Figure 5](image-url)  
**Figure 5.** A candidate for the low-temperature proton-ordered form of ice-VI—the most stable structure as determined by DFT calculation on all 45 symmetrically distinct ice configurations permitted in the primary unit cell of ice-VI. Our ab initio calculations also confirm that its preferred stability is valid regardless the lattice constants used (see caption of Figure 4).

The temperature dependence of the heat capacity (⁵⁰) and the average energy \( (\langle E \rangle) \), derived from the partition function, are shown in Figures 6a and 6b, respectively. Our calculations indicate a “phase transition temperature” at around 80 K, but we should note that this temperature is a very rough estimate because the “ensemble” used here is limited to those configurations in the primary unit cell. A more extensive sampling of the phase space (including ice configurations with more disordered H-bond networks in larger unit cells) is required and will be addressed in a forthcoming paper.

Local Ordering of \( \text{O}_1 \). Beside the long-range proton ordering as discussed above, it is also possible that the ordering is partial...
and short-ranged as suggested by dielectric data. The latter
would not be reflected in the Bragg diffraction data and only
be visible in diffuse scattering contributions, which are very
difficult to measure at high pressure. In the following, we shall
discuss one possible local ordering scheme that is unique in
ice-VI, and we should also note that other local ordering
schemes on a short-range scale are possible.

In a fully disordered structure every water molecule has six
possible orientations. In the ice-VI structure a peculiarity arises
in that for O1 all neighboring H atoms belong to only one
crystallographically distinct species, H2 (Figures 2 and 3). Still,
as a consequence of the tetragonal symmetry of the O1 site,
two crystallographically distinct water arrangements exist shown
as parts A and B in Figure 3. In the time—space-averaged picture
that is sampled by Bragg diffraction, no distinction can be made
between a situation where all six configurations occur with equal
probability of 1/6 and the other extreme, in which the four
configurations of type B occur with a probability of 1/4 each
and the two configurations of type A do not occur at all; all
transitions between these two extremes can occur. This fact
allows for a systematic partial water molecule ordering around
the O1 site without changing the space group symmetry of the
crystal structure. In contrast, a systematic partial ordering on the
O2 site preferring one of the configurations cannot be achieved
without a change of space group symmetry.

Theoretical calculations can fill the void, due to experimental
limits explained above. In our theoretical framework, the
temperature dependence on local ordering of O1 can be derived from
the approximated partition function (QN). For example,
the probability for water molecules centered on O1 to take orienta-
tion B (denoted as P(B;T)) can be calculated by

$$P(B;T) = \sum_{i} B(O_1) f_i \exp(-\beta E_i)/Q_N$$

where

$$B(O_1) = \begin{cases} 1 & O_1 = B \\ 0 & O_1 = A \end{cases}$$

It is obvious that the probability for water molecules at O1
to take orientation A (denoted as P(A;T)) is equal to 1 − P(B;T);
thus only the temperature dependence of P(B;T) is shown in
Figure 6c. It is clear from Figure 6c that at low temperatures
orientation B is preferred, which is in line with the fact that the
ground-state structure (shown in Figure 5) has 100% orientation
B. As the temperature increases, P(B;T) drops rapidly at “phase
transition” temperature, and in the high-temperature limit P(B;T)
approaches 2/3, indicating a true disorder case.

4. Conclusions

We have examined the structure of ice-VI by density
functional methods, and the intrinsic disorder is investigated by
studying all ice-rule-allowed ice configurations in its primary
unit cell. We found a significant amount of static distortions,
by averaging through 45 symmetrically distinct configurations
that represent a total of 576 possible arrangements, and the
isotropic average of the static distortions from first principles
calculations is consistent with previous indirect experimental
estimates.

The covalent bond R(OH) in ice-VI is found to be about 0.98
Å, which is consistent with previous experimental estimates.
Together with previous studies on ice-Ih and ice-VII, we
conclude that the R(OH) is not sensitive to the change of the
neighboring H-bond arrangements. The molecular angle of water
(\(\angle \HOH\)), however, shows strong dependence on the molecular
orientation. While the \(\angle \HOH\) follow the trends of the \(\angle \OOO\)
to accommodate a reasonable H-bonding angle, we found the
deviation of \(\angle \HOH\) in ice-VI from its gas-phase value is
smaller than previously assumed. It is also interesting to note
that the \(\angle \HOH\) in ice-VI is smaller than that of the isolated
cage water hexamers; we think this reduction of \(\angle \HOH\) in
crystalline phases is likely due to the repulsive interaction
between the water molecules in the two sublattices.

Different proton-ordering schemes in the literature were
examined, and the possible roles of the different lattice constants
in under-pressure and recovered sample were also investigated.
In total we have considered three sets of lattice constants,
and a ferroelectric structure (shown in Figure 5) is found to be the
ground-state regardless of the change in lattice constants. Our
estimated phase transition temperature is about 80 K; under such
low temperature it is difficult for proton ordering to occur.
Attempts have been made by Mineva-Sukarova et al. and
Handa et al. using KOH-doped ice samples, but no convincing
evidence has been seen so far. It may, however, be possible to
promote the ordering by adding other dopants.

Acknowledgment. Computational resources provided by
BIRC at Nanyang Technological University (NTU) and
financial support from NTU (J.L.K.) and DFG grant Ku920/9
(W.F.K.) are gratefully acknowledged.

References and Notes

(2) Petrenko, V. F.; Whitworth, R. W. *Physics of Ice*; Oxford University
1984, 81, 3612.
2005, 94, 025506.
2005, 94, 122506.
Lett. 2004, 397, 335.
(9) Klotz, S.; Hamel, G.; Lovelady, J. S.; Nelmes, R. J.; Guthrie, M.;
First Principles Study on Ice-VI


3703


(12) Kamb, B. Science 1965, 150, 205.


