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QUANTUM MECHANICAL EXAMINATION OF ORIENTATIONAL DEFECTS IN ICE Ih(1)

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ABSTRACT

The techniques of ab initio molecular quantum mechanics are used to examine the energy and geometry of orientational (D and L) defects in ice Ih. Small clusters of water molecules are used to model surface and bulk defect sites. The energy of each point defect is calculated allowing for relaxation of the defect site. The potential surface is examined for the presence of transition states between the normal lattice and the defect configuration.

INTRODUCTION

Water/ice systems are unique in many of their properties. The ability of the water molecule to form hydrogen bonds and serve equally well as a donor or an acceptor of hydrogen in that bond is responsible for much of this uniqueness. Water can also be induced to gain or lose a proton and can be stable as either the OH⁻ or H₂O⁺ ion. This facility to gain or lose protons as well as form hydrogen bonds in several orientations, gives rise to a variety of point defects in the solid phase. Bjerrum(1) postulated that a small fraction of the water molecules in ice are oriented so that the Bernal-Fowler rules are not everywhere obeyed. These orientational defects would either have no hydrogens (L-defect) or two hydrogens (D-defect) along the line joining the oxygen atoms. Such orientational defects, together with ionic defects occurring with the transfer of a proton between the oxygen atoms, form the basis for most theories of electrical properties of ice.

The energy of formation of point defects has been estimated using a variety of models(2-8) ranging from classical electrostatic to molecular orbital. The former studies had the deficiency of using classical models to examine what are fundamentally quantum effects, while the quantum mechanical studies used very small systems (dimers or trimers) or only considered one type of defect. Additionally, the existence of point defects as local minima in the potential energy surface has not been established. Because of the importance of point defects in many of the properties of ice, a systematic study of orientational defects and the subsequent lattice relaxation was begun. These calculations seek to determine whether there exist metastable states whose geometry closely resembles the classic L and D defect states and if so, how their energies differ from a reference Bernal-Fowler state.

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Two classes of orientational defects were examined in this study. In one class the defect site is located along a bond to a surface molecule while in the other the defect is adjacent to a fully bonded "bulk" molecule. Both classes of point defects are modelled using a cluster of water molecules whose hydrogen bond pattern includes the defect to be studied. Previous studies \(^{(6,8)}\) have shown that nearest neighbor (NN) interactions account for more than 90% of the effects observed at a lattice site. Thus, because of the size of the calculation (for the 'bulk' site, 50 electrons and 105 primitive Gaussian functions in the basis) and the expectation that next nearest neighbors (NNN) would have only a small effect on the resulting energy and less on the geometry of the defect state, NNN were not included in these preliminary calculations.

A defect site adjacent to a surface molecule (called a "surface" defect) was modelled by a cluster of four water molecules with the "surface" molecule in the center. As a reference configuration, the cluster geometry was optimized as a function of total energy for a four molecule cluster with no bonding defect. The reference cluster is shown in Fig. 1. In this cluster, the central molecule can have one of two bonding patterns, either acting as a double donor of its hydrogens to form hydrogen bonds or as a double acceptor of hydrogens to interact with its lone pairs of electrons. The arrangement shown in Fig. 1 has the central molecule acting as an AAD (acceptor-acceptor-donor). This configuration was found to be approximately 2 kcal/mole more stable than when the central molecule was DDA.

For modelling a point defect in the bulk, a cluster of five water molecules was used. For the reference cluster, the central molecule has its bonds saturated and hence is AADD. This cluster is shown in Fig. 2. The relationship of the reference clusters to a larger section of ice Ih is indicated in Fig. 3.

It is important to include reference cluster calculations in such model studies because many of the inherent deficiencies such as limited basis sets, constrained geometries and finite extent of the model, significantly cancel when the state of interest, i.e. the defect state, is compared to a defect-free state calculated to the same level of accuracy.

For an L-defect, one of the terminal molecules which is donating a hydrogen to bond with the central molecule is rotated so that its hydrogen lies along a line which is 109.45° from its reference orientation and from its other hydrogen. See Figs. 1 & 2.

For the surface D-defect, the central molecule is rotated so as to place its nonbonded hydrogen along the hydrogen bond to one of its neighbors. See Fig. 1. For the bulk D-defect, a terminal molecule is rotated to place one of its hydrogens along the line which already has a hydrogen from the central molecule. See Fig. 2.
THE CALCULATIONS

All of the water cluster calculations reported involved ab initio molecular orbital calculations performed with the Gaussian-80(9) or GAMESS(10) packages of computer codes. The 3-21G split valence shell basis set(11) was used within the restricted Hartree-Fock formalism. This basis set represents a good compromise between consistency and accuracy of results and number of functions in the set. Smaller basis sets such as STO 3G grossly overestimate the interaction energy between molecules or molecular fragments. Larger basis sets such as 4-31G or 6-31G grossly overestimate the electron redistribution and hence the dipole moments for both the single molecule and the cluster. The 3-21G basis gives better geometries and dipole moments than the larger split valence bases. It also has substantially less basis set superposition error and hence less overestimation of intermolecular interaction energies than STO-3G type bases. Comparison of results(12) for the monomer and dimer with experimental values suggest that the dipole moments will be overestimated by 20% and interaction energies by a lesser amount (~10%).

To simulate the ice Ih lattice, the relative positions of the oxygens were constrained at a tetrahedral angle about the central molecule. For the reference cluster calculations the oxygen-oxygen separations and the hydrogen-oxygen separations were allowed to vary to minimize the total energy. For the defect calculations the oxygen-oxygen and oxygen-hydrogen distances were fixed at the reference values except for the central molecule. After the defect was created, the central molecule was allowed to rotate and change its oxygen-hydrogen distances, internal bond angle and orientation in "relaxing" to minimize the defect energy.

In addition to the reference clusters and the relaxed defect states, an attempt was made to locate a saddlepoint on the potential surface which might correspond to a transition state between the reference cluster and one or more of the defect configurations. The geometry is varied until the matrix of second derivatives of the energy is found to have a single negative eigenvalue (the transition state).

RESULTS AND DISCUSSION

REFERENCE CLUSTERS

All internal and intermolecular parameters were allowed to vary with the exception of the O-O-O angles which were fixed at tetrahedral. This restriction was necessary to keep the reference clusters commensurate with an ice I lattice. Additionally, all O-O distances were constrained to be the same. Hydrogen-oxygen distances for hydrogens not participating in hydrogen bonds were allowed to differ from hydrogen-oxygen distances in which the hydrogen was also hydrogen-bonded to a second water molecule. The geometries at which the energy is minimized are given in Table I for the 4 and 5 molecule clusters. For both cases the O-O distances are remarkably close to that found in ice I (2.757 Å and 2.742 Å).
SURFACE DEFECT

As expected, prior to relaxation, the energy of the cluster containing the D-defect was considerably higher than that of the L-defect cluster (78.1 vs 18.6 kcal/mole less stable than the reference cluster). Neither the structure nor the energy of the L-defect changed significantly upon relaxation. This was expected as the remaining hydrogen bonds were already in the most favorable order (with the central molecule in a DA configuration). However, allowing the D-defect cluster to relax produced a somewhat surprising result. During the course of the relaxation, the central molecule appears to rotate approximately about one of its lone pair axes and in the process, the hydrogen which was along the bond to molecule 4, creating the defect, moves to a final position along the bond to molecule 2, thus replacing the hydrogen which was initially participating in this bond. The displaced hydrogen moves to a location approximately equidistant from molecules 2 and 3 and above the 01-02-03 plane. This final position of the hydrogen is approximately tetrahedral (110.8°) with the hydrogen bonds to the other molecules. This reorientation of the central molecule substantially reduces the energy of the system so that the final energy for 'relaxed' surface D-defect is only 15.6 kcal/mole higher than the reference cluster and is, in fact, lower than the surface 'relaxed' L-defect.

BULK DEFECT

For the bulk point defects, the initial unrelaxed energies were similar to the surface defect states (ca. 18 kcal/mole for the L-defect and ca. 66 kcal/mole for the D-defect.) As for the surface defect, the L-defect state changed very little in geometry or energy on relaxation. For the D-defect, there was a greater difference between the surface and bulk defect. This difference is principally due to the fact that, for the surface defect, rotation of the central molecule could completely remove the defect by orientating the 'offending' hydrogen along a fourth bond direction. This is not possible in the fully bonded 'bulk' defect; the most relaxation can accomplish is to locate the extra hydrogen between the normal bonding orientations in an interstitial position. This configuration will still have substantial hydrogen-hydrogen repulsion and will also introduce strain in the oxygen lattice. Even with relaxation, the energy of the bulk D-defect is 27.2 kcal/mole above the reference cluster.

L-D DEFECT PAIR

For the bulk site, an attempt was made to create a L-D defect pair by rotating the central molecule so as to place two hydrogens along the 01-03 line and thus have no hydrogens between 01 and 02. The attempt to minimize the energy resulted in a rotation of the central molecule so as to move the hydrogen which was originally along the 01-05 bond to a position between 01 and 02, replacing the hydrogen initially in that bond. The hydrogen which initially was part of the D-
defect moved to a position between 01 and 05. The resulting cluster is essentially the same as the reference cluster, both in geometry and in energy.

**L-D TRANSITION STATE**

The starting configuration for the transition state search was the same as the L-D defect pair except that D-defect hydrogen was slightly off the 01-03 bond. In the transition state, the hydrogen initially along the 01-05 bond moves only slightly off the bond, toward 03. The defect hydrogen moves to an interstitial position nearly equidistant between 02, 03, and 04 while increasing the HOH internal angle on the central molecule. The OH bond lengths are different, with the defect bond shorter by .01 Å. The energy of this transition state was quite high, nearly 50 kcal/mole above the reference cluster. The resultant geometry of this transition state resembles the X-L defect suggested by Dunitz.(3).

**CONCLUSIONS**

The calculations reported here represent the first attempt to use ab initio quantum mechanical techniques to examine the potential surface for metastable states corresponding the Bjerrum point defects. States which can be thought of as corresponding to orientational L and D point defects for bulk and surface sites were located, and their energies were compared with the corresponding defect-free site. No evidence was found for a metastable state corresponding to a L-D defect pair on adjacent bonds.

Examination of the results of the geometry optimization for the reference ice-like clusters gives confidence that the basis set chosen gives good geometric parameters when compared with experiment. It is known that this and other split-valence bases overestimate the charge redistribution and hence both the dipole moment for water and the magnitude of the molecular interaction energy. Nevertheless, when comparing stabilization energies for similar systems, the results have been quite satisfactory.(12) Thus while the activation energies obtained from these studies are almost certainly too large in absolute magnitude, the comparison between bulk and surface and between the different types of point defects should be reasonable. The ordering of the activation energies is also valid.

These results should be regarded as an upper limit to the energy of a surface or bulk orientational defect. In addition to the overestimate in stabilization due to the basis set, the constraint imposed on the oxygen lattice would be expected to add from 2 to 10 kcal/mole to the defect states compared to real ice where the NN to the defect site would also experience a small relaxation. The magnitude of this effect was assessed for the bulk L-defect by allowing the 0-0 distance to vary with the reorientation of the central molecule. In this case, the 0-0 distance increased to 2.8 Å with a 2.7 kcal/mole decrease in the energy of the 'relaxed' configuration. The decrease would be expected to be greater with the D-defect, and relaxation of the next neighbors is planned for a future study.

**TABLE I**

<table>
<thead>
<tr>
<th>SURFACE SITE</th>
<th>ΔE(kc/mole)</th>
<th>R(OH)</th>
<th>R(HB)</th>
<th>R(00)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>0.0</td>
<td>0.9672</td>
<td>0.9733</td>
<td>2.7567</td>
</tr>
<tr>
<td>L-Defect 1</td>
<td>18.6</td>
<td>0.9716</td>
<td>0.9748</td>
<td>118.1</td>
</tr>
<tr>
<td>D-Defect 2</td>
<td>15.6</td>
<td>0.9719</td>
<td>0.9748</td>
<td>118.1</td>
</tr>
<tr>
<td>BULK SITE</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reference</td>
<td>0.0</td>
<td>0.9660</td>
<td>0.9776</td>
<td>2.7420</td>
</tr>
<tr>
<td>L-Defect 1</td>
<td>19.5</td>
<td>0.9727</td>
<td>0.9776</td>
<td>118.1</td>
</tr>
<tr>
<td>D-Defect 2</td>
<td>27.2</td>
<td>0.9727</td>
<td>0.9776</td>
<td>56.0</td>
</tr>
</tbody>
</table>

1°OH distance for hydrogen bonded hydrogen
2°Distances given are for central molecule.
3°Rotation of central molecule relative to unrelaxed defect position.
REFERENCES


COMMENTS

J.M. WARMAN

Your results would support the possibility of lattice vacancies being the source of orientational defects in ice if present in sufficiently high concentration. Is this correct?

Answer:

Certainly vacancies would lower the energy required to form the defects and thus would be expected to increase the number of defects in proportion. However I would not expect vacancies to be the sole source of orientational defects.

J.W.GLEN

As an intermediate calculation would it not be most interesting to allow two neighboring water molecules to rotate to see if the defects, perhaps particularly the D-defect, can be essentially spread over more than one bond and molecule.

Answer:

Yes, this is an obvious next step but this requires next nearest neighbors to be included. Then both molecules involved in the defect can "relax" in response to the defect. Not only rotation but also limited translation (change in R(oo)) can be included in the relaxation. Especially for the D-defect I would expect substantial involvement of the 2nd molecule with a corresponding lowering of the defect energy.

W.B. HOLZAPFEL

Could you also calculate the energies of a different kind of defects which would come round to linking the suplattices in ice VIII or position on empty diagonals in ice X.
Answer:

This kind of calculation is certainly possible. It would require ~ twice the number of molecules used in the current calculation. I hope to expand the calculations to be able to study defects in the other ices and the interesting crosslinking you mention could be examined as well.