

Quantum Mechanical Studies of the Energetics of Ionic Defects in Icelike Systems

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Received: October 11, 1996[®]

Previous research in this series^{1,2} used model clusters to examine the energy required to produce configurational defects in ice I_h and the subsequent relaxation of the lattice. The current studies use similar cluster models to investigate the energy requirements and lattice distortions associated with the production and migration of ionic defects. Two model clusters, each containing eight water molecules, are used to study the energy required to form and stabilize an ion pair. These initial calculations suggest that the ion pair can be stabilized if relaxation and annihilation would require a simultaneous shift of three or more protons. At least in these model clusters, barrierless paths exist for the shift of two protons, leading to the recombination of the ions. The energies required for the formation, with subsequent separation and stabilization, is of the order of 1–2 eV.

Introduction

The properties of ice, especially its electrical properties, have been topics of intensive interest for many decades. The experimental problems associated with separating the effects of intrinsic and impurity defects, surface vs volume conduction, and the effects of the presence of grain boundaries and other mechanical defects have all served to obscure even the identity of the charge carriers in various environments. In pure ice, much has been illuminated in the last decade, and there is general agreement that conductivity is determined by proton motion.³

The motion of protons, whether along hydrogen bonds via tunneling or as a result of molecular reorientation, is credited with a major role in many ice properties. Some of these properties such as the photoplastic deformation of ice and its unusually large static dielectric permittivity near 0 °C apparently depend on proton disorder and the ease of reorientation of hydrogen bonds. However this ease of rotational motion of the molecule about its lattice site depends on the presence of point defects. These defects are of four types: the Bjerrum or configurational defects occurring when the line joining two adjacent oxygen atoms has either no hydrogen (L-defect) or two hydrogens (D-defect) and ion defects where either H_3O^+ or OH^- replaces a neutral water molecule at its site in the ice lattice. The ion defects move by the displacement of a proton from one end of a hydrogen bond to the other while the Bjerrum defects move by rotation of the molecule. These same displacements or rotations are also responsible for the formation of the point defects. Thus we can simultaneously examine the energies of formation and motion of ionic defects. Knowledge of the energy to both create a defect and to move it to a location where it cannot instantaneously recombine is critical to understanding many of the properties of ice.

In this report, ab initio quantum mechanical calculations are employed to examine the energy associated with the formation of ion defects and their subsequent stabilization in a model water system. In a future report, the motion of the ion will be followed using molecular dynamics simulations of the model system.

Description of the Model

For this study two eight-molecule clusters of water were selected to serve as surrogates for the ice lattice system. In

contrast to the clusters used in the previous study of configurational defects, these clusters have no dangling (singly bonded) molecules—all molecules participate in two or three hydrogen bonds. One structure has essentially D_{2d} symmetry (Figure 1) and is reported to have the lowest energy for eight molecules of water.^{4,5} Hence this cubic cluster is apparently the global minimum for the octamer. This cluster, which has all molecules participating in three hydrogen bonds, can serve as a model for ices having O—O—O angles less than 100 degrees or 4-fold rotational axes such as ice III and ice IX. The total number of hydrogen bonds for this cluster is 12, and the orientation of the hydrogen bonds is sequential around each face of the cube.

The second structure chosen for this study was initially proposed by Stillinger and David⁶ and found by them to be the global minimum for their polarization potential. This structure (Figure 1b) can be described as the aqueous analog of the saturated hydrocarbon bicyclo[2,2,2]octane and consists of three rings, each composed of six water molecules. Two molecules, at the bridgeheads, participate in three hydrogen bonds while the remainder participate in two, each acting as a proton donor and a proton acceptor in the bonds. This structure has a total of nine hydrogen bonds, three less than the cubic cluster, and three hydrogen bond chains of three molecules each. As noted by Stillinger, one of the hydrogen bond chains is polarized in a direction opposite to the other two, with the nonbonded hydrogens adjacent to the bridgehead molecules oriented in opposite directions. This cluster is a fragment of ice I_h and can serve as a model for this system.

Description of the Calculations

Electronic structure calculations were carried out for the model water clusters. Because of the size of the clusters, 138 internal degrees of freedom, the Hartree–Fock level was used for energy minimization with all geometric parameters unconstrained. The basis set employed was the standard 6-31G(d) which has been shown to give reasonable descriptions of hydrogen-bonded systems. To gain information about the importance of correlation effects on these systems, second-order Møller–Plesset⁷ MP2 energies and unconstrained geometries were calculated for the starting model clusters.

Gaussian 94⁸ installed on a SGI Power Challenge was used for these calculations. After convergence on the cluster energy, the Hessian matrix was examined to identify the nature of the

[®] Abstract published in *Advance ACS Abstracts*, June 15, 1997.

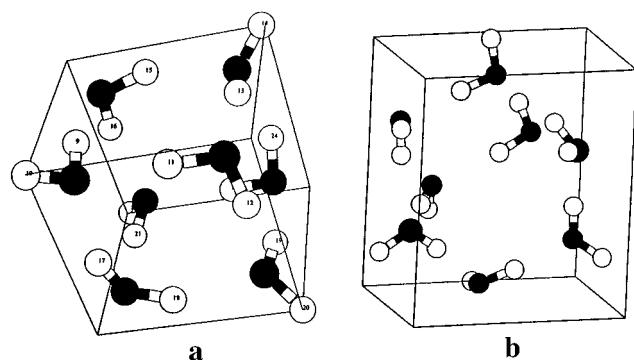


Figure 1. Structures of the neutral octamer water clusters. The oxygen atoms are dark, and hydrogens are white. The boundary box is simply a guide to the eye. The hydrogens are numbered on the cubic D_{2d} -like cluster (on the left, 1a) for ease of comparison with the S_4 -like cluster shown in Figure 3. The cage-like octamer is on the right, 1b).

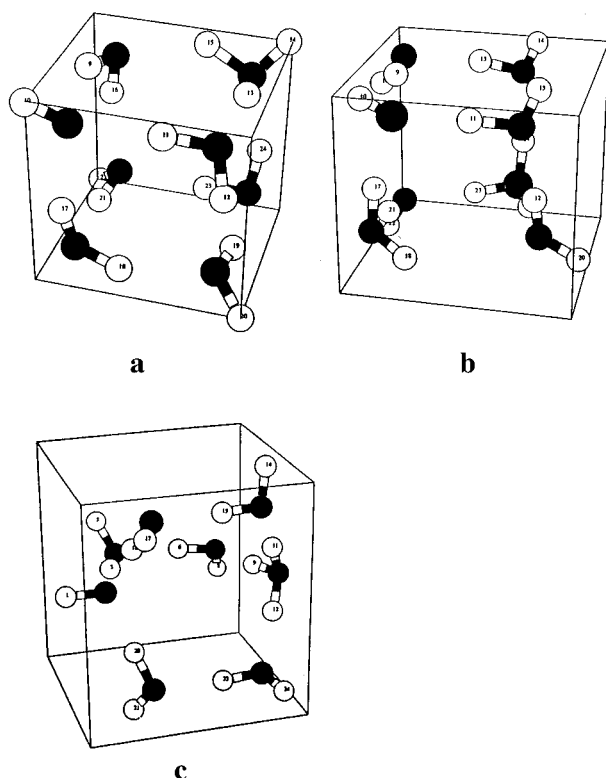


Figure 2. Initial ion pair structure of the cubic cluster. The ions are located on opposite corners of the top face (2a). This structure relaxes to the neutral S_4 -like cluster shown in Figure 3. Figure 2b is the stable cubic zwitterion structure. The ions are located on opposite ends of the body diagonal. The stable zwitterion structure for the cage octamer is shown in Figure 2c.

stationary points obtained. After locating a minimum on the potential surface corresponding to each of the model clusters, a proton was translated along a bond to produce an ion defect. In order that the system did not immediately relax to the initial structure, an additional proton was shifted so that at least one neutral molecule was located between the ion pair (Figure 2a,b,c). The geometries of the model clusters containing the ion pairs were then fully optimized.

Results and Discussion

The total energy and range of geometric parameters obtained for the optimized clusters are given in Table 1. The resulting structure of the cage-like cluster closely resembles the structure resulting from the polarization potential calculations. The

TABLE 1: Structure Parameters and Energies (6-31G(d))^{a,b}

	cubic	cage
R(OH) ^c	0.948–0.965 0.970–1.003	0.948–0.963 0.969–1.001
∠HOH	105.2–106.7 103.6–105.8	103.1–106.3 101.0–106.3
R(O···O)	2.771–2.917 2.683–2.824	2.770–2.978 2.681–2.875
∠O···HO	157.2–169.8 158.7–171.0	151.3–178.7 146.3–179.1
dipole moment	0.0004 0.0001	4.2158 4.5190
number of H-bonds	12	9
energy per bond	7.82	8.73
zero-point energy	137.224	134.786
total energy	–608.209 447 –609.743 567	–608.194 144 –609.719 196

^a The values given in boldface are MP2 results. ^b Distances are given in angstroms, angles in degrees, dipole moments in Debyes, total energies in au, and bond and zero-point energies in kcal/m. ^c The clusters exhibit a range of values for each geometric parameter and are presented as providing more insight than an average with standard deviation.

TABLE 2: Zwitterion Structure Parameters and Energies (6-31G(d))^a

	cubic	cage
R(OH) ^b	0.947–0.999	0.947–0.999
∠HOH ^c	104.9–107.3	105.5–106.5
R(O···O) ^d	2.575–2.642	2.571–2.662
∠O···HO	168.8–170.3	175.2–177.3
dipole moment	6.5194	2.3916
number of H-bonds	10	9
energy per bond	3.07	3.61
zero-point energy	135.95	135.16
total energy	–608.134 914	–608.137 772

^a The clusters exhibit a range of values for each geometric parameter and are presented as providing more insight than an average with standard deviation. ^b Distances are given in angstroms, angles in degrees, dipole moments in Debyes, total energies in au, and bond and zero-point energies in kcal/m. ^c Angle in H_3O^+ opened up to ca. 110° for the cage zwitterion and to ca. 108° for the cubic zwitterion. ^d Two or three of the hydrogen bonds have lengthened to nearly 2.5 \AA (an O···O distance of $>3.4 \text{ \AA}$) and so are considerably weakened if not broken. Thus the contribution the stability of the cluster is estimated at 10 hydrogen bonds.

geometric parameters for the cubic and the cage-like clusters were also obtained at the MP2(FC) level of theory. The stability of the cubic cluster was more highly dependent on correlation effects, and its stabilization relative to the more open cage-like cluster was underestimated at the Hartree–Fock level of theory.

For the ice fragment cage-like structure, the ion pair was created by a concerted shift of three protons along one of the chains. This has the effect of introducing a negative OH ion at one bridgehead molecule while creating a positive H_3O^+ at the other bridgehead molecule, a zwitterion. This shift also serves to orient the hydrogens so that the polarization is now the same in each of the three chains which make up the structure. Upon optimization with all geometric parameters unconstrained, this zwitterion was determined to be a local minimum on the potential surface. See Table 2. When this structure (the zwitterion) was examined using the polarization model,⁶ it was found to be metastable and not a local minimum. However, in the calculations with the polarization model, the oxygen atoms were not allowed to alter their positions. This calculation exhibited a very high barrier, 141 kcal/mol, between the neutral cluster and the zwitterion. In the attempt to relax the cluster, this barrier apparently disappeared and Stillinger and David concluded that the zwitterion was not locally stable. This is in

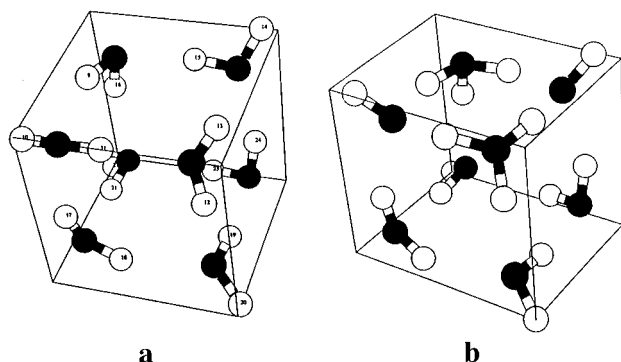


Figure 3. The cubic structure (3a) resulting from the relaxation of the face diagonal ion pair structure has approximate S_4 symmetry, and the protons on the upper face have been shifted clockwise from their bonding positions in the D_{2d} cluster. The transition state cluster which lies between the S_4 and the D_{2d} structures is shown on the right (3b). Note that this cluster contains two ion pairs with ions of opposite charge located on adjacent lattice positions.

TABLE 3: Cluster Energy Summary (kcal/mol) (HF/6-31G(d))

	relative energy	stability ^a	E/bond	E/molecule	E/ion pair ^b
D_{2d}	0	77.46	6.45	9.68	
S_4	0.12	77.34	6.44	9.67	
cage	9.60	67.86	7.54	8.48	
transition state	43.93	33.54	2.79	4.19	21.97 (0.95)
cage with ion pair	44.98	32.49	3.61	4.06	35.38 (1.53)
cubic with ion pair ^c	46.77	30.69	3.07	3.84	33.87 (1.47)

^a Stability is relative to eight water molecules, uncorrected for zero-point vibrational energies. ^b Energy in parentheses is in eV per ion pair. ^c Energy for the ion pair system relative to the neutral cluster has been reduced by the energy of two hydrogen bonds.

contrast to the Hartree–Fock (HF) results for this ion-containing cluster where frequency analysis produces all positive frequencies. On the other hand, the energy difference between the neutral cluster and the zwitterion was essentially very similar in both calculations, ca. 36 (HF calculation) vs 41 kcal/mol (polarization potential) higher energy for the zwitterion.

Repeated attempts to locate a transition state between the neutral cage and the corresponding zwitterion failed. This inability to identify a transition state suggests that the structure of such a state differs substantially from either the zwitterion or the neutral cluster and/or it has a very high energy. The added flexibility of the two bonded molecules, not present in a larger fragment of the ice lattice, may be adding to the difficulty in locating a minimum energy path between the two structures.

For the cubic cluster, the initial location of the ion pair was on opposite corners of the diagonal of one of the faces. The structure was created by the simultaneous shift of two protons along the edges of the cube. Here a single neutral molecule separated the ions in each of two directions. The attempt to minimize the energy starting with this structure resulted in the elimination of the ion pair and a continued shift of the protons to produce a new neutral cluster. This resultant cluster has reduced symmetry (ca. S_4 rather than D_{2d}) but differs only slightly in energy from the original cubic cluster. See Figure 3a and Table 3.

A transition state was located between the two neutral cubic clusters. The structure of this transition state was quite surprising. See Figure 3b. For the cubic clusters, instead of obtaining a stable zwitterion, a cluster containing two ion pairs

was located and identified as a transition state or saddle point between two stable structures of differing symmetries.

As a second attempt to produce an ion pair which could be stabilized in the cubic cluster, protons were shifted so as to place the members of the ion pair on opposite corners of the body diagonal. This configuration separates the ions by two neutral molecules in contrast to a single neutral molecule in the preceding example. Optimization of the structure of this zwitterion resulted in a stationary point on the potential surface. Examination of the Hessian matrix identified this stationary point as a local minimum. However the bonding structure of the initial cubic cluster was significantly altered by the inclusion of the ion pair.

As a separate look at the stabilization of an ion pair, several smaller clusters were examined. The smallest cluster which has all molecules participating in two hydrogen bonds is the cyclic water trimer.⁹ When each molecule serves as both a donor and an acceptor of a proton in the hydrogen bonds, this structure is reported to be the global minimum for the water trimer. Even though in this system an ion pair cannot be separated, it was of interest to determine if the zwitterion was a saddle point between two conformers of the cyclic trimer. For this system, attempts to locate such a stationary point of order 1 were not successful.

Previous studies in this series^{10,11} have shown that the cyclic pentamer is a stable cluster structure over a wide temperature range, and in contrast to the cyclic trimer, the ion pair can be separated by a neutral molecule. Initially all of the molecules in the cluster participate in two bonds, and each acts as a donor and an acceptor of hydrogen to the hydrogen bond. Migration of two protons introduced an ion pair into the ring pentamer. A number of attempts to locate a stable cyclic pentamer containing such an ion pair failed. In all cases the structure containing the ion pair relaxed, without intercepting a potential barrier, to the neutral cyclic cluster. Whether the bonding direction reversed in the process of relaxation appeared to depend on whether the hydrogens on molecules adjacent to the cation in the starting structure were initially on the same side or on opposite sides of the ring. The latter conformation results in the same type of migration of protons as was observed in the cubic cluster, producing a different sequential bonding pattern than was present in the initial cluster.

Conclusions

The potential surface for water systems is exceedingly complex. Even for the smallest aggregates of water, many structures of local stability are present. The model octamer clusters chosen for this study have been predicted to be stable (at least a local minimum if not a global minimum on the potential surface) by a variety of empirical potentials, by different parameter sets in semiempirical quantum mechanical calculations, by a variety of basis sets, and at several levels of theory in *ab initio* quantum mechanical calculations. The agreement concerning stability of such a wide range of theoretical approaches plus the ability of the chosen clusters to exhibit the types of hydrogen-bonding patterns found in several of the ices make the cubic and cage clusters reasonable models for the energetics of ion pair formation in water aggregates or in an ice lattice.

The precise magnitude of the predicted formation energies as well as the relative energy differences in the different clusters may well be both basis set and level of theory dependent. However, since the same general trends^{5,4,12,13} have been found for the neutral clusters independent of choice of interaction potential or inclusion of correlation, the results obtained in this

study should be sufficiently realistic to provide valuable insights into the energetics of ionic defect production.

While not exhaustively tested, these studies indicate that for a stable ion pair to exist the water cluster needs at least one molecule which participates in three or more hydrogen bonds. Thus ring structures and clusters containing fewer than seven to eight molecules are unlikely to support ion pair formation which can be stabilized. This result is suggestive as to the relaxation of ionic defects in or near the ice surface. In addition, for both of the "stable" zwitterions described in this study, the separation of the ions was on the order of 4.3 Å. To achieve this separation, the initial structures had to contract in the direction of the line joining the ion pair by about 13%. This suggests that ion pairs separated by shorter distances, such as on the face diagonal of the cubic cluster, cannot be stabilized. At shorter distances, the ions either recombine to return to the original structure or shift the hydrogen-bonding pattern in the process of recombination at different sites.

It is interesting to examine the local charges associated with the ion pairs. The results of Mullikan population analysis¹⁴ for both of the zwitterions has +0.76 e associated with the H_3O^+ moiety and -0.69 e with the OH^- moiety. It appears that the negative charge is slightly shared with the nearest neighbors to the OH^- ion. This value might be compared with Maeno et al.¹⁵ who estimate of the ratio of effective charge of H_3O^+ to a proton of 0.626 e. For the transition state with its two ion pairs, the charge on each of the H_3O^+ sites is +0.655 e while on the OH^- sites the charge is -0.649 e, much more nearly the same.

In the transition state, the structure attains a metastability with ions on adjacent molecules. Thus in this case, no energy is required to separate the ions after formation. It will be most informative to employ molecular dynamics to examine the relaxation of this transition state to the D_{2d} or the S_4 neutral cluster. These studies are planned. It is also possible that the dynamics may locate a lower energy pathway which results in the production of an ionic defect in the system. Cooperative motion of several atoms was shown to lower energy barriers¹¹ for structural changes and bonding interconversions in earlier simulations in smaller water clusters.

For both of the model clusters, the production and stabilization of an ion pair required that the ions be separated by at least two neutral water molecules. The energy associated with the resulting zwitterion was about 1.5 eV greater than the neutral cluster in each case. (See Table 3.) It is unclear whether this energy should be directly compared with the experimental estimate of 1 eV³ to produce an ion pair. In these calculations, the added energy associated with the zwitterion includes not only the production of the ion pair but also the relaxation and weakening of some of the hydrogen bonds to accommodate the ions. Future studies will be undertaken to see if the introduction

of an ion pair in a larger cluster can be accommodated at a lower energy cost. Since the coordination for surface molecules is 2 or 3, the same as that for the clusters used in these studies, the energy required to produce and separate the ion pair in these model clusters might be better compared to the activation energy for surface conduction. Maeno and Nishimura¹⁶ estimated the temperature independent activation energy for surface conduction as 1.43 eV. The 1.47 eV and 1.53 eV per ion pair for the stable zwitterions identified in this study are suggestively similar. These values are also in reasonable agreement with the values of 0.96 eV as the lowest limit and 1.4 eV as the "available" upper limit¹⁷ for bulk hexagonal ice.

In summary, study of the energy associated with the formation ion pairs in model clusters has provided valuable insights into ionic defect formation and the conditions under which the ion can be stabilized. The ability of these clusters to distort to an extent greater than that of the lattice will certainly affect the magnitude of the effects predicted in these studies. Nevertheless, it is hoped that these results have shown that such calculations can provide reasonable models for many of the processes in the macroscopic system and also provide the impetus for quantum mechanical calculations on larger systems.

Acknowledgment. The author expresses appreciation to the Computer Center, University of Missouri-Columbia, the *SHIVA* support staff, and the Special Projects Group for the computer time needed for these studies and for support of the software systems used in the analysis.

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