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THEORETICAL STUDY OF PROTON-TRANSFER ENERGY SURFACES IN SMALL WATER CLUSTERS AND CUBIC ICE

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Abstract: The energetics of proton transfer in water clusters of size from two to six molecules and in cubic ice was analyzed in detail using both Hartree Fock and gradient-corrected density functional theory. Since the energy of ion-pair structure created by proton transfer is always higher than that of neutral water structure grid calculations and constrained geometry optimization are needed. In the case of cubic ice various arrangements of the hydrogen atoms on a fixed oxygen lattice were investigated. In this system the proton transfer leads to the creation of ionic point defects which are saddle points on the potential energy surface.

1. Introduction

Water — water interactions are important in many fields of science and thus have been the subject of many experimental [1, 2], and theoretical [3, 4, 5, 6, 7] studies. One of the aspects of such interaction is creation of the H_3O^+ OH^- ions on water dissociation and further transport.

Most of the theoretical it *ab initio* calculations have been limited to small systems, typically to water dimer or clusters with a few molecules, due to the computationally intensive nature of the calculations. The experimental results, however, pertain to ice and liquid water. Ice is a specially good model for studying proton transfer because of fixed oxygen lattice. The problem is that water forms more solid phases than any known substance. Only three out of ten ice structures discovered so far are proton ordered, as indicated by neutron diffraction results, measurements of dielectric properties, and the measured entropy change going from proton-disordered to proton-ordered structures.

The common form of ice, ice Ih, is proton disordered, i.e., each hydrogen-atom site in the crystallographic unit cell is on average (in the crystallographic sense) only 50% occupied. The interpretation of this disorder is far from straightforward. Proton mobility is anomalously high and normal ionic diffusion plays only a secondary role.

Protons simply jump from one oxygen atom to the next one across hydrogen bond. In proton conduction it is the hydrogen bond arrangement that migrates not the particles themselves. Thus, no particular hydrogen bond arrangement can be observed, but only the average position of hydrogens.

The "ordinary" ice Ih has a crystal structure, as far as the positions of oxygen atoms are concerned, which can be considered as two inter-penetrating hexagonal closely packed structures. This is the structure taken by the form of ZnS called wurtzite. There is a cubic analogue of this structure (Ic) consisting of two inter-penetrating face-centered cubic lattices based on the points (0, 0, 0) and $\left(\frac{1}{4},\frac{1}{4},\frac{1}{4}\right)$, which is a diamond-type structure. Such a form was found by Koning in thin films of ice deposited from the vapour in an electron diffraction apparatus below about -100°C. The nature of the phase has been well confirmed (see Ref. [8] for a review): the lattice parameter is 6.350 ± 0.008 at −130°C, which gives essentially the same volume per molecule as in the hexagonal phase. In fact, the nearest-neighbor environment in both cases is identical, the differences instructure only affecting second or more distant neighbors. The infrared spectra of ice Ih and Ic over the range of 350–4000 cm^{-1} are essentially identical [9] and both show broadening features in the case of H_2O–D_2O mixtures, which can be interpreted as the effect of proton disorder. Electron diffraction can also give direct evidence for the position of the protons in the ice structure and this was used for ice Ic in [10, 11], where the authors found unambiguous half-hydrogen distribution with the O–H distance of 0.97 Å. Ice Ic has the same configurational entropy as ice Ih and is in every respect simply its cubic analogue.

Because of the considerable interest in ice and hydrogen-bonded structures in general, it is not surprising that a large number of theoretical calculations on ice have been reported in the literature. These calculations have essentially been of two types: (i) rigid- or flexible-molecule calculations based on analytical intermolecular pair potentials, sometimes combined with explicit potential functions to describe non-additive contributions to the intermolecular energy, and (ii) molecular-orbital calculations of isolated $(H_2O)_n$ four-rings, ice-like six-rings and tetrahedral pentamer clusters. *Ab initio* calculations for ice crystals, not just water clusters are quite recent. From periodic *ab initio* calculations, one can obtain information regarding properties connected with long-range intermolecular interactions in the crystal, as well as local properties of an individual water molecule. The density functional approach has many advantages for such calculation. The origin of the popularity of density functional theory in solid-state physics is its convenience and efficiency in dealing with many-atom systems.

The challenge of applying DFT methods to problems of chemical interest demands greater accuracy of the calculated energies. There is continuous effort to improve the functionals by extending local density approximation (LDA) to nonlocal terms of the form of a gradient correction (GC). Recently, the search for efficient GCs has met with some success. The majority of GC schemes currently in use treat exchange and correlation (C) separately. Perdew proposed a parameter-free GC functional (P) for the correlation effect, which he derived from a consistent truncation of the gradient expansion of the correlation energy E_C [12]. The reference state of this expansion is the exact local C functional of the homogeneous electron gas. The Perdew (P) functional can be combined with the Becke (B) X-only GC. The resulting functional is usually indicated by BP, and it is the GC functional which is used in the calculations presented in this work. In a recent publication, it has been shown that the gradient-corrected (GC) density functionals give excellent description of the water dimer [13], small water clusters [7] and of high-pressure ice [6].

In this work the proton-disordered cubic ice Ic has been studied using gradient-corrected density functional theory with periodic boundary conditions using the CETEP program. This density functional theory approach is currently the most accurate method available for such calculations. First, the results for small water clusters from both density functional theory, Hartree-Fock and Hartree-Fock with electron correlation at the MP2 level are compared with each other and with experimental data. Next, the properties of ice Ic, various arrangements of the hydrogen atoms on a fixed oxygen lattice and point defects in ice Ic crystal are discussed. Most of the DFT calculations have been done on a massive parallel computer — the Cray T3D. This is the only way to fulfil the requirements for fast processing speed and extremely large amount of memory.

2. Methods

2.1 Hartree-Fock calculations

Ab initio molecular orbital single point calculations, geometry optimization, and normal coordinate analyses were performed using the GAMESS US program [14]. Most of the computations were initially carried out at the restricted Hartree-Fock (RHF) level. In some cases corrections to energy due to dynamical electron correlation were calculated at the Moeller-Plesset second-order perturbational (MP2) level of theory. The 6-31++G basis set was used for calculations of water clusters. This basic set was chosen because it is computationally efficient and suitable for ionic systems which appear during the investigation of the proton-transfer phenomenon. Anions such as OH usually require diffuse basis functions to properly represent their spatial electron distribution.

Molecular geometries were optimized using a quasi-Newton gradient method implemented in GAMESS, taking internal coordinates as variables. Initial orbitals were guessed using the Huckel Hamiltonian. In MP2 calculations non-gradient optimization of geometry was used in HINT internal coordinates (Hilderbrandt style internals [15]). All grid calculations were done using built in SURFACE option or more flexibly written program for data-input generation for single point energy or energy and gradient calculations. Analytic Hessian was used for normal coordinate analyses of stationary points found on the potential energy surface. Grid calculations were used to guess the geometries of the saddle points and then structures were refined by the mode following method. The eigenvalues of the energy Hessians were computed at saddle points, in order to check that the Hessians have the desired characteristics.

For validated saddle points, the Intrinsic Reaction Coordinate (IRC) defined as the minimum energy path connecting the reactants to products via the saddle point was calculated. This was accomplished by numericalintegration of the IRC equations by the Gonzalez-Schlegel 2nd order method.

2.2 Density Functional Theory

Geometry optimization, grid calculations at the Density Functional Theory (DFT) level were performed using the CETEP (parallel code) and CASTEP (serial code) programs. The Kohn-Sham equations were solved by expanding the electronic orbitals in plane waves and using Bloch's theorem to express the wavefunction of the infinite crystal in terms of the wavefunction at reciprocal space vectors of a Bravais lattice. Only valence electrons were considered. Core electrons were implicitly taken into account by atomic pseudopotential. The wave number cutoff in the basis set was specified by the corresponding eigenvalue K_c of electron kinetic energy, equal to 70 R_y. The examination of proton transfer in the water dimer and all ice Ic calculations was performed using the gradient-corrected density functional because it can be correctly described only with including correlation in the DFT equation. For geometry and wave function optimizations, a preconditioned conjugate gradient method was used.

2.3 Setting up the initial configurations of hydrogen atoms

As mentioned in the Introduction, ice Ic has a hydrogen-disordered structure. For the examination of various possible arrangements of the hydrogen atoms on a fixed oxygen lattice an auxiliary program was written. It reads fractional positions of oxygen atoms in the periodic box and then calculates all possible proton position for a given oxygen lattice (excluding point defects). It uses the Ewald energies and symmetry elements to distinguish and reduce the number of possible configurations. At the end it generates output in a format suitable for CETEP and also for the MOLDEN program that is used to visualize the geometries.

3. Results and Discussion

3.1 Water dimer $(H_2O)_2$

Water dimer is the simplest system with hydrogen bonds between water molecules. The structure (see table 1) agrees with experimentally observed Cs structure. The significant variation of θ (defined in table 1), especially for MP2 optimized structure can be explained as result of ineffective non-gradient minimization used during calculations. The DFT/GGA results are also worse than those obtained in [7].

The dimer of water molecules was optimized in a 12×6×6 Å tetragonal periodic box which could be too small, results from [7] are from otherwise identical calculations with a 10×10×10 Å cubic cell.

Table 1. *Structural properties of water dimer. q is defined as the angle between the C_2 axis of proton acceptor and the O-O line.*

Method/Basis set	$E_b ind$ [kJ/mol]	d_{OO} [Å]	∠OHO [deg]	θ [deg]
HF/6-31++G	33.47	2.826	178.6	112.0
MP2/6-31++G	36.66	2.822	179.9	90.0
DFT/GGA	24.43	2.858	162.0	171.0
experiment	22.2 ± 0.8	2.98 ± 0.01	174 ± 10	123 ± 10

The water dimer was used to investigate proton-transfer potential energy profiles (PTP), that correspond to the transition between an uncharged water-dimer structure to the $H_3O^+ \ldots OH^-$ ionic pair. These PTPs were obtained by fixing the nuclear intermolecular distance d_{OO} and calculating the total-energy variations for the acidic-proton migration from one H_2O molecule to another. For larger intermolecular distances the profiles show a double-well shaped potential. The minimum at short d_{OH} distances corresponds to a neutral hydrogen-bonded complex, whereas the second shallow minimum at longer d_{OH} distance corresponds to the ion pair structure. For short intermolecular distances a second minimum does not exist and ion pair structure is not stable. The PTPs calculated using HF/6-31++G, MP2/6-32++G and DFT/GGA level of theory for different intermolecular distances are visualized in figure 2 as colour contour maps. The HF, and MP2 maps consist of 660 grid points (44×15), while the DFT map consist of only 154 points (irregular grid), and is therefore not so smooth.

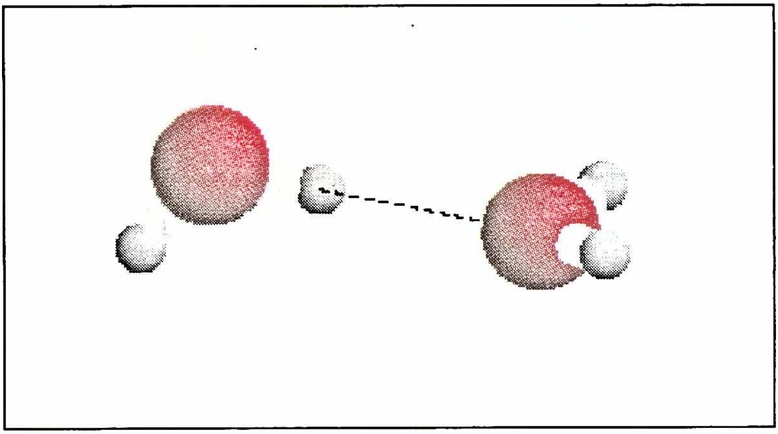

Figure 1. The low energy structure of water dimer.

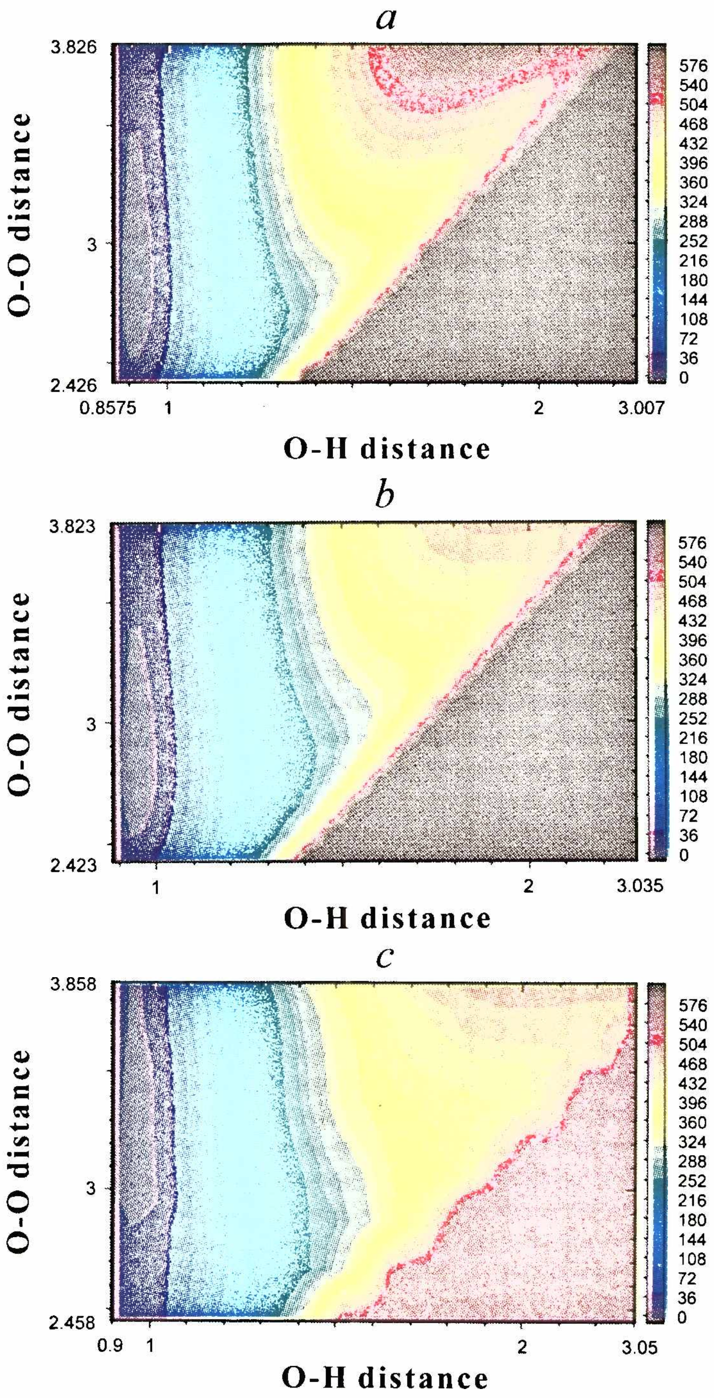

Figure 2. *Proton-transfer potential energy profiles of the* H_2O*...* H_2O *system for various O-O distances visualized as color contour maps, the energy is expressed in kJ/mol, the distances in Å.*
(a) HF/6-31++G, (b) MP2/6-31++G, (c) DFT/GGA

3. Concerted proton transfer in $(H_2O)_3$ and $(H_2O)_4$

The potential energy profiles corresponding to the concerted transfer of two or three protons were calculatedfor both $(H_2O)_3$ and $(H_2O)_4$ water cluster at frozen configuration such as those found in cubic ice. In $(H_2O)_3$ the cluster ionic configuration H_2O^+... H_2O... HO^- is not stable. In $(H_2O)_4$ cluster similar ionic configuration H_2O^+... H_2O...H_2O... HO^- is metastable under geometry minimization with oxygen atoms frozen and is shown on Figure 3.

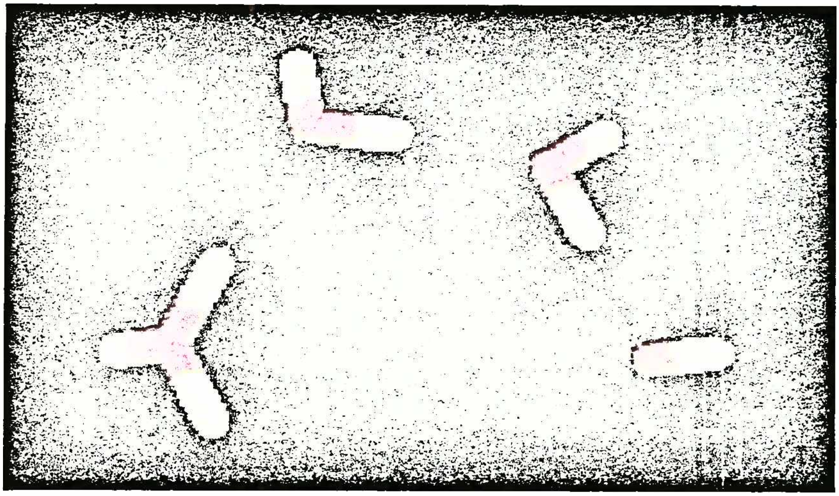

Figure 3. The metastable configuration of $(H_2O)_4$ (with frozen oxygen atom positions) after proton transfer from upper to lower water molecule.

The only reason is greater distance between negative and positive charges as there are two water molecules between them in the hydrogen-bonded network. Grid calculations of correlated proton transfer at HF level using 6-31++G base set also indicate no minimum in $(H_2O)_3$ and shallow one for $(H_2O)_4$ — see Figure 4.

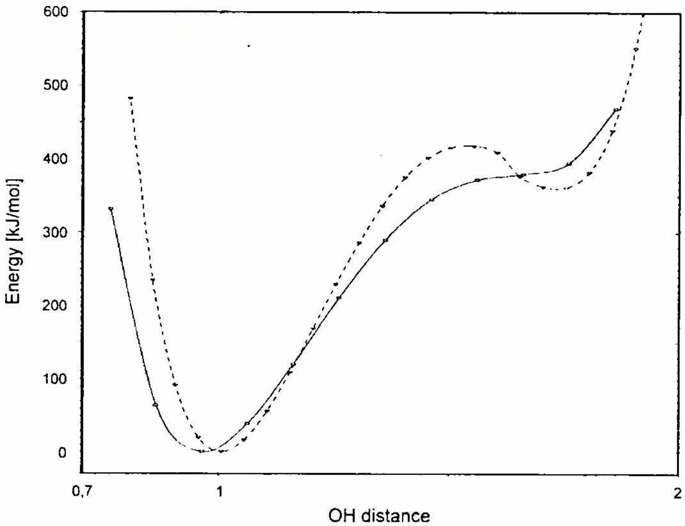

Figure 4. Potential-energy profiles of the concerted transfer of two (squares, solid line) and three (triangles, dashed line) protons calculated at HF/6-31++G level

3. 3 Water hexamer $(H_20)_6$

For water hexamers several equilibrium geometries exist which are all similar in energy [7]. These hexamer structures are found in cubic ice. The lowest-energy one is a slightly chair-like ring (R6) with binding energy 47.02 kJ/bond (HF/6-31++G). Reference [7] gives a DFT/GGA binding energy of 31.74 kJ. There are many low-energy isomers, for instance: a book-like structure (B6) found by Kim at al [4], two-ring structure characterized by a flat four-molecule ring with a "handle" of two molecules. The R6 structures with different proton arrangements are shown in Figure 5.

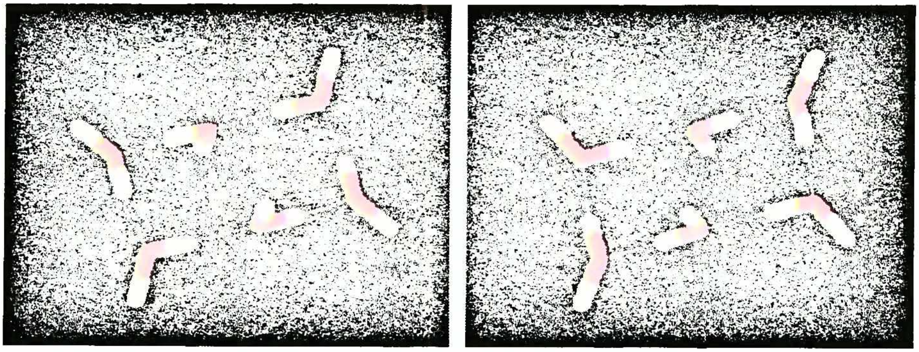

Figure 5. *Water hexamers $(H_20)_6$ in chair-like ring (R6) conformation with two different hydrogen arrangements*

The proton-transfer pathway, that leads to the transition between the two structures was investigated by several methods using HF/6-31++G level of theory. First for the frozen geometry of oxygen atoms in configuration such as those found in cubic ice the energy profile was calculated under the assumption that the proton transfers occur in a concerted manner. The same was done for relaxed geometryof water hexamer. In the second case it was also possible to find a saddle point between the two hexamers differing by hydrogen arrangements by gradient minimization. The saddle point was validated by Hessian calculation and its geometry is shown in Figure 6. Starting from this transition state intrinsic reaction coordinate (IRC) was calculated. The results of grid and IRC calculations are shown in Figure 7.

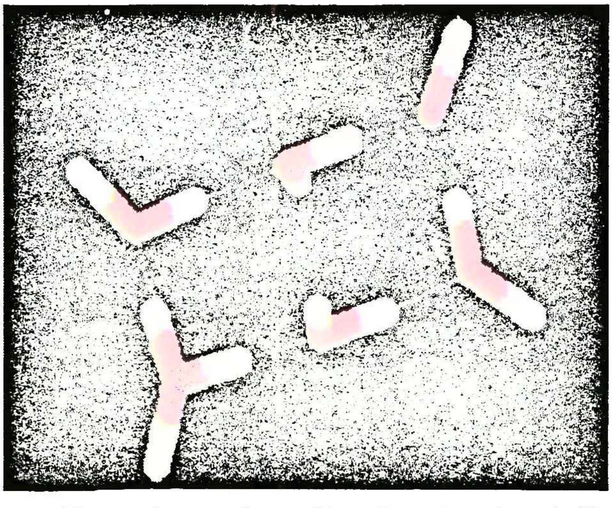

Figure 6. *Saddle point between the two R6 configurations shown in Figure 5*

The saddle point is not the configuration with all six protons in the middle between oxygens in six membered rings. It is an ionic configuration with OH and H_3O^+ in opposite corners of the ring and it is created by the movement of three protons only. The remaining three protons move next and as a result the hydrogen atoms are rearranged. Even in the second stage the protons are not shifted in a concerted manner. The IRC pathway shows the "breathing" of the whole ring during the courseof proton transfer: first distances between oxygen atoms decrease, protons are transferred, and then distances between oxygen atoms increase to former value.

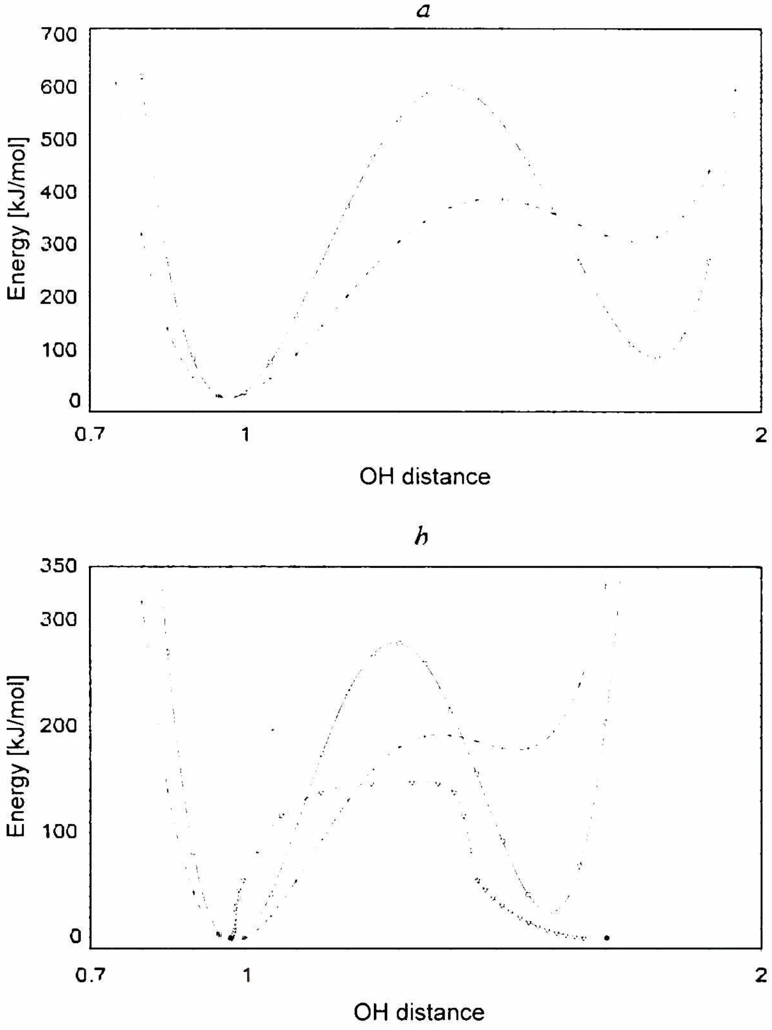

***Figure** 7. Concerted six (squares and solid line) and three proton (crosses anddashed line) transfer potential profiles calculated by grid at HF/6-31++G level and IRC pathway (triangles and dashed line). (a) frozen oxygen atoms geometry in configuration such as thosefound in cubic ice, (b) relaxed geometry.*

Finally, grid calculations of concerted three-proton transfer were performed on both frozen and reflexed geometries to investigate difference in potential-energy profiles of correlated grid and IRC pathway.

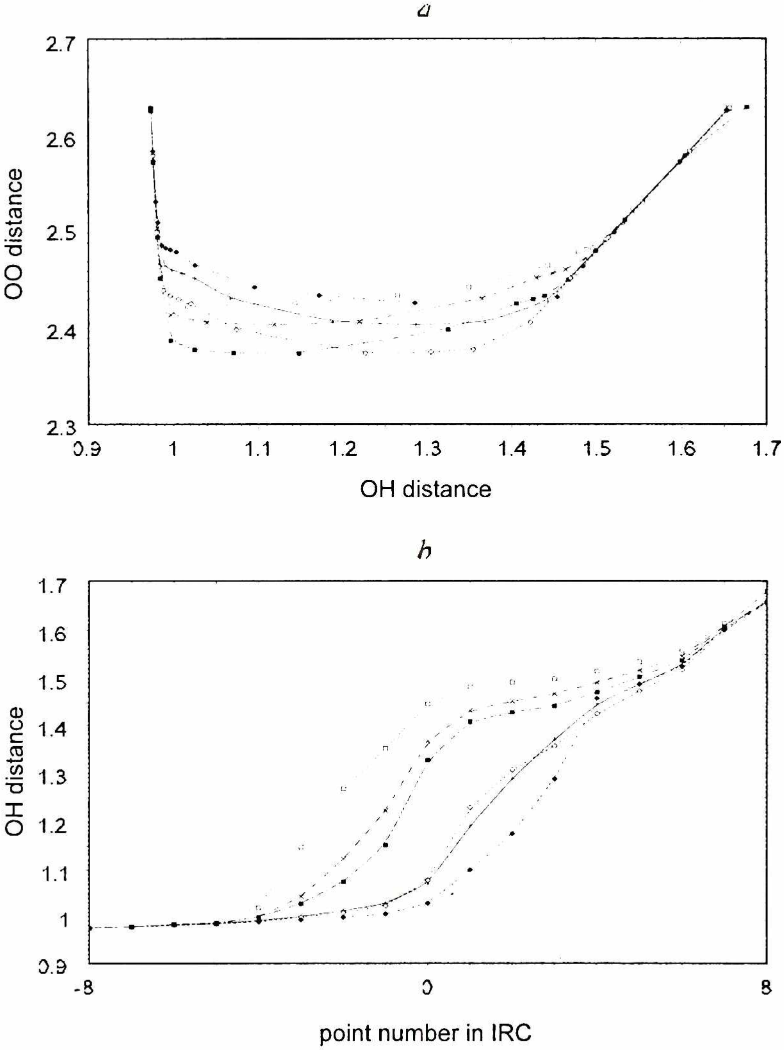

Figure 8. Distance between (a) oxygen atoms and between (b) oxygen and hydrogen atoms on the IRC pathway for proton transfer in six membered ring of water molecules, 0 indicates saddle point.

3.4 Ice Ic

Cubic ice Ic is proton disordered, i.e., each hydrogen-atom site in the crystallographic unit cell is on the average (in the crystallographic sense) only 50% occupied.

The number of possible hydrogen atom configurations on a fixed oxygen-atom lattice in cubic box with eight water molecules and periodic boundary conditions was evaluated. With eight water molecules — sixteen hydrogen atoms and with periodic boundary conditions there is also sixteen oxygen atom pairs in distance 2.735 Å. For each such pair hydrogen can be near one or other oxygen. This gives 2^{16} possibilities, but most of them are ionic point defects — if we are interested only in realistic configurations we should apply the following rule: there are only two hydrogens close to each oxygen. This gives 90 configurations, but by symmetries of cubic ice crystal it is possible to reduce this number to four different configurations. These configurations are shown in Figure 9.

The geometry of all four configurations was optimized at DFT/GGA level of theory using one special k-point in the Brillouin zone. Total energies, Ewald energies dipole moments and number of symmetry elements of four configurations are listed in Table 2.

Table 2. *Cubic proton dissorderd ice properties*

No	Energy [*kJ/mol*]	Ewald energy [*kJ/mol*]	total dipole moment	number of sym. elem.	number of those in set
1	-362787.09085	-144055.57716	8	8	6
2	-362785.76563	-144079.76049	$4\sqrt{2}$	4	24
3	-362785.01459	-144079.22435	4	4	48
4	-362784.35762	-144095.34637	0	8	12

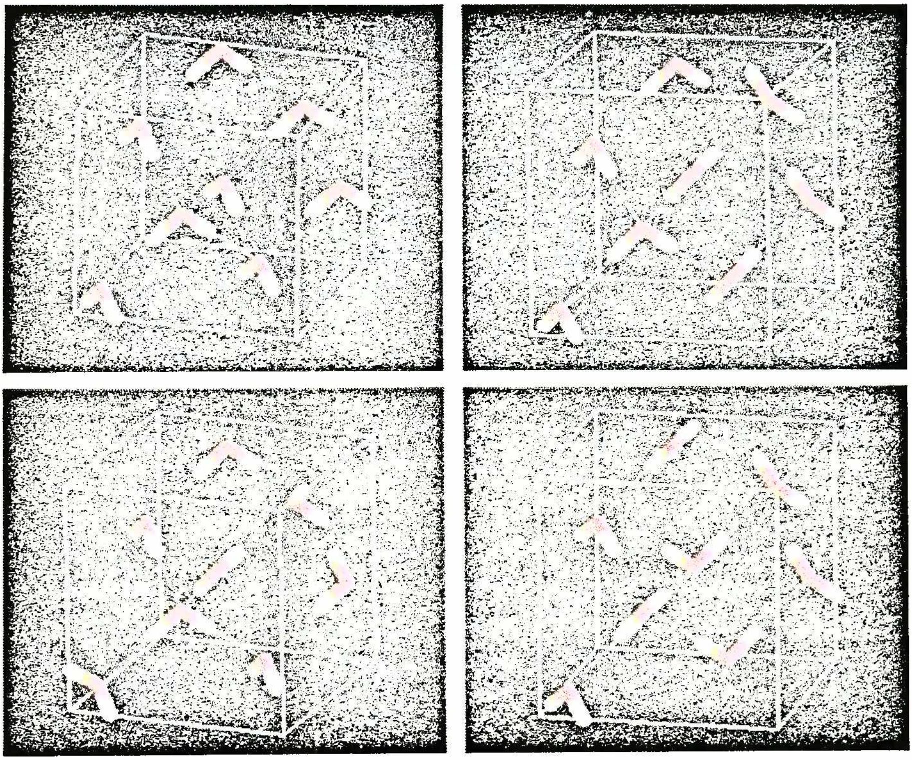

Figure 9. *Configuration No 1, 2, 3 and 4*

Each oxygen atom in each configuration has the same distances to corresponding neighbors. Each hydrogen atom also has the same distances to all the corresponding oxygen atoms in each configurations. The only difference is in case of some hydrogen neighbors of each hydrogen. Configurations No 1 and 4 have eight elements of symmetry and each hydrogen atom is equivalent. Configurations No 1 and 4 have only four elements of symmetry and two different types of hydrogens can be found. But always distances to neighbors up to 3 Å are the same. Another difference between configurations as indicatedin Table 2 is the overall dipole moment of box. Directions of dipole moment.ofeach water molecule in the box are shown in Figure 10.

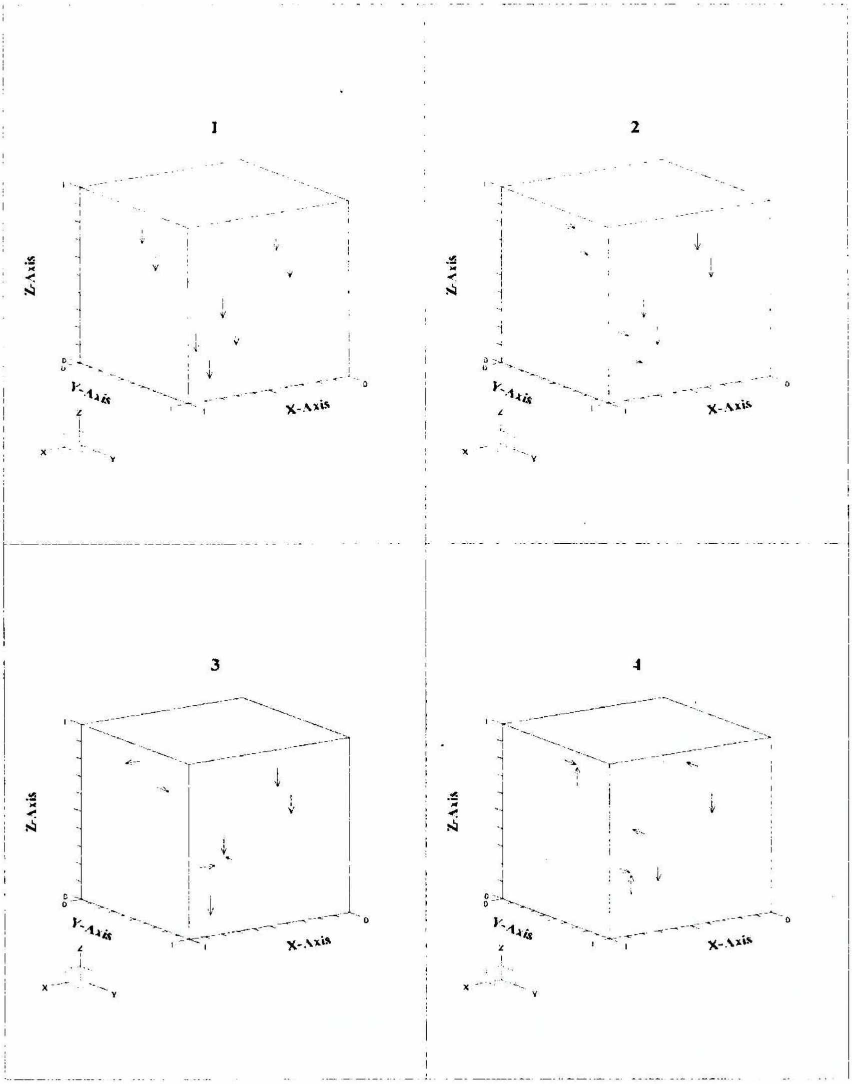

__Figure 10.__ Dipole moments vectors for configurations 1-4.

It is easy to find qualitative and quantitative correlation between the overall dipole moment, Ewald energy and the total energy. Ewald energy of configurations with nonzero cell dipole moment depends on the shape of thecell. Only the configuration 4, which has zero cell dipole moment, can represent ideal cubic ice.

In configuration No 3 there are six membered rings of water molecules with hydrogen arrangements the same as those investigated in the previous section. It is easy to find them if instead of a cubic box with 8 water molecules we use a box extended with one direction by translation as shown in Figure 11.

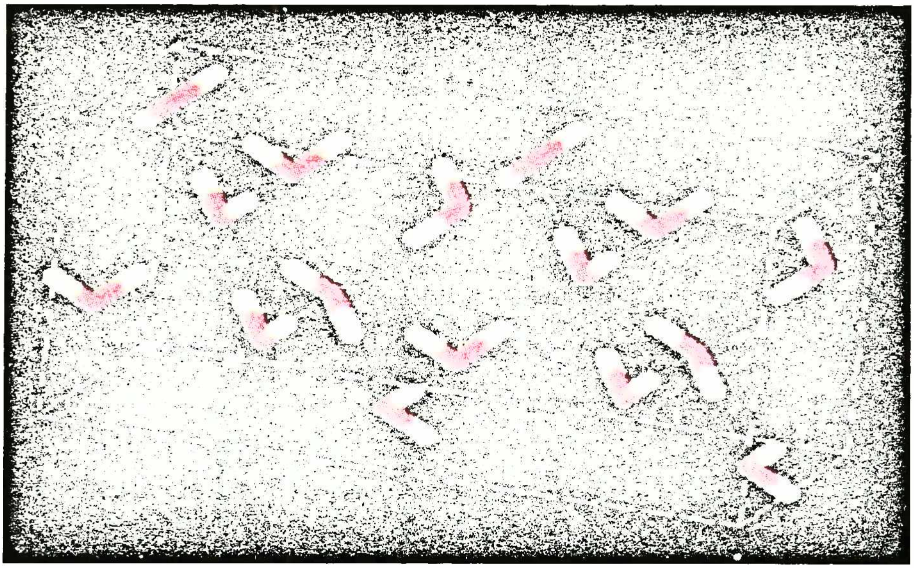

Figure 11. *Box used for proton transfer calculations in six membered ring.*

Proton transfer in such ring was investigated at DFT/GGA level of theory using grid method for correlated transfer of both three and six protons. Results are shown in Figure 12, where proton potential profile for normal transfer between two water molecules in cubic ice is also drawn. In case of ice a saddle point is simply ionic point defect, as with the water hexamer. Using only grid calculations it is not possible to find that whether configuration is a saddle point or a minimum. Analogy to relaxed geometry water cluster results suggests the ionic point defect is a saddle point.

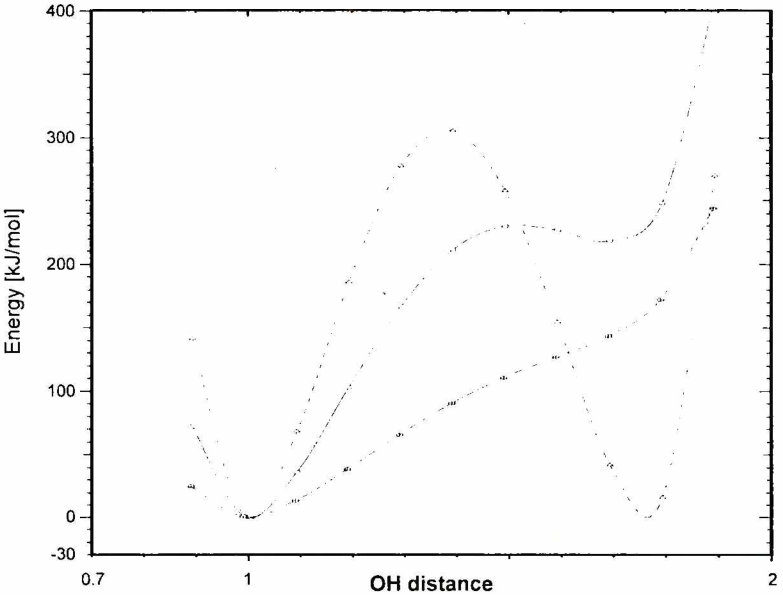

Figure 12. Correlated six (triangles and dashed line) and three (squares andsolid line) protons transfer potential profiles in six membered ring calculated by grid at DFT/GGA level in cubic ice, normal protons transfer potential profile in cubic ice (crossed circles and dashed lines)

Another type of point defects - orientational defects were also investigated at DFT/GGA level of theory. These defects are produced, formally, by rotation of a single molecule through $\frac{2\pi}{3}$ about one of its bond directions, leading to one doubly occupied bond (D-defect) and one unoccupied bond (L-defect). The molecular rotations involved can be pictured quite equivalently as involving an oblique jump of a single proton from one bond to another on the same molecule, the jump distance involved being about 1.65 Å. Whilst the model of an L-defect as a bond direction with no proton on it is fairly satisfactory, it is apparent that it is an oversimplification to consider a D-defect as an undistorted colinear structure with two protons lying on the bond. In such structure protons would be separated by only 0.74 Å. One would expect the defect to distort the surrounding structure by increase of the d_{OO} distance along the bond and by small rotation so that O-H... H-O configuration is no longer collinear. Several geometry optimizations from various starting configurations of orientational point defect were performed. It seems that this orientational point defect is not a stationary point on potential energy surface of cubic ice, however further investigations are necessary.

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