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Molecular Orbital Studies on Ice-Like Structures

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Molecular orbital (MO) calculations were carried out on a series of ice-I_h and ice-I_c type lattices. These lattices were assigned dimensions which approximate conditions in liquid water (O–O = 2.86 Å) and, in addition, the dimensions of the ice-I_h lattices were changed to ascertain the influence of lattice expansion and contraction. Component parts of several lattices were investigated as were lattices lacking one or two individual monomeric units. Results are in accord with current experimental approximations.

As the ice-I_h lattice is expanded, the stabilization energy diminishes. In the liquid model, ice-I_h structures are generally more stable than those of ice-I_c; component rings of the lattice models of ice-I_c determine the stabilities of these models, and a stable ring system can stabilize an unstable system. An ice-I_h lattice model lacking a single monomer is stable. The trend of charges at the oxygen centres closely correlates with the charges on the central oxygen atom of the appropriate trimer.

Key words: Water lattices – Ice-like structures

1. Introduction

Water molecules and their aggregates have been extensively investigated by *ab initio* [1, 2] and semi-empirical [3] MO calculations. Minton [4], employing an iterative extended Hückel MO treatment, investigated water aggregates containing up to eight water monomers. Using a more rigorous technique, Del Bene and Pople [5] ascertained the preferred bonding arrangements of aggregates containing up to six water monomers. Santry [6] used a modified CNDO/2 method to investigate an extensive network of water monomers and Hojer and Keller [7] have investigated ice-like lattices based on ice-I_c.

Most of these investigations determined the influence of one monomer unit on another. The aim of the present investigation is to determine the influence of an environment of water molecules on other simple molecules. Although various forms of ice-like structures, notably ice-*III*, are believed to contribute to the structure of water [8], ice-I_h is a contributing species in many water models and was therefore selected to approximate a dense state. If the chosen MO technique can produce results that agree with known experimental observations, a later study would investigate putting other molecules in and into the lattice.

The nature and geometry of the structure were taken to simulate, to a first approximation, a liquid water environment. The structure is a part of the model suggested by Nemethy and Sheraga [9] and recommended by Narten *et al.*

[10]. As ice-*I* structures are disordered, it was necessary to assign proton positions in this lattice and other ice-*I* environments investigated for comparison. All models were treated by the CNDO/2 technique [11], as it was felt this method could provide the most reliable results with minimum use of computer time.

Comparisons were made between energies of the various models and between the charges residing on the oxygen centres of the lattice structures. This latter comparison is an essential part of the description of the species as they are obtained by minimal manipulation of the data. By contrast, each estimate of a stabilization energy is derived by subtracting a fairly large number from another, to obtain a small value, a method where small errors are often magnified. Figures quoted for stabilization energies are thus less reliable than for charges.

2. Structures and Geometries

2.1. Ice-I_h Models

The ice-I_h lattice selected to provide an aqueous environment for later studies is illustrated in Fig. 1, model II. This structure appeared as part of a larger model suggested by Nemethy and Scheraga [9]. The other two ice-I_h models, I and III, shown in Fig. 1, are slight variations of structure II. Each of the structures has the same arrangement of monomers in the upper ring. For the present purpose, this common feature permits these models to be classified as belonging to the same family of structures. The difference between the three structures occurs in the lower six-membered ring. This difference results from the number of water monomers which provide neither proton to lattice formation. The number of such water monomers in each lattice is designated as n. For the structures investigated, n ranges from zero to two. When only individual component rings are discussed, the number of water monomers providing neither proton for ring formation is represented by m.

All structures utilized linear hydrogen bonds and tetrahedral coordination about the oxygens to permit maximum overlap as found in preliminary studies. As the structures are intended to correspond to the liquid state of water, the oxygen-oxygen distance (d) was taken to be 2.86 Å [12]. To ascertain the effect of

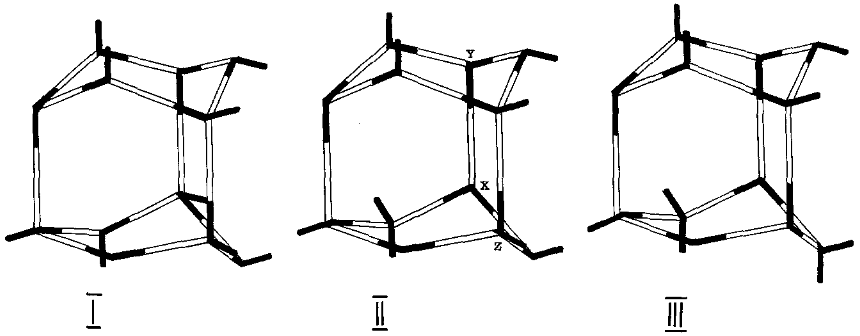

Fig. 1. Ice-I_h tautomers investigated (protons of the participating water monomers are situated at the ends of the solid black lines and the oxygens are at the junctions of the solid black lines)

expansion and contraction of the lattice, oxygen-oxygen distances of 2.76 and 2.96 Å were also employed. When $d = 2.86$ or 2.96 Å, the oxygen-hydrogen bond length was taken to be 1.02 Å. This distance was selected to be larger than either the vapour or the solid state value [13] as there is some evidence that the value for the liquid state is higher than the other two phases [14] and it is near the optimum value calculated for the monomer unit as derived by the CNDO/2 technique. For a nearest neighbour oxygen-oxygen distance of 2.76 Å, as it occurs in the solid [15], an oxygen-hydrogen bond length of 1.01 Å was used.

Selected dimer, trimer and cyclic hexamer components of the lattices were also investigated.

In addition to the investigation of the complete lattice structures of ice-I_h, several incomplete structures were studied. The parent lattice for these structures is shown in Fig. 1, model II, with $d = 2.86$ Å. Monomers were omitted individually from the lattice at points X, Y, or Z and at X and Y.

2.2. *Dimers*

Rotational studies of the linear dimers, as depicted in Fig. 2, were undertaken to establish the contribution of the hydrogen bond energy of particular rotamers of the larger structures. Complete rotational studies were carried out for rotamers having an oxygen-oxygen bond length of 2.86 and 2.96 Å. For an oxygen-oxygen bond length of 2.76 Å, only linear dimeric rotamers contributing to the larger structures were considered. The angle of rotation is counted from one of the eclipsed conformations and increases positively passing through the second eclipsed conformation after a rotation of 120° C.

2.3. *Ice-I_c and Component Models*

The ice-I_c structures investigated are shown in Fig. 3. For those structures, an oxygen-oxygen distance of 2.86 Å was utilized. Structures IV, V, and VI have the same upper ring and hence belong to the same family. They differ in their value of n. Structures VII and VIII belong to a different family and differ in their n values. Structure IX belongs to yet another family and has $n = 4$. The tetramers of the lower structure of models of IV, V and VI of Fig. 3 were investigated individually.

3. Method of Calculating Energies and Charges

3.1. *Energies*

The hydrogen bond energy of the dimer was calculated by subtracting twice the energy of the monomer from the energy of the dimer. To obtain the stabilization energy of the larger aggregates, the following procedure was used. The energies of the appropriate number of monomer units were added to the hydrogen bond energies of all participating dimeric rotamers. Then this total was subtracted from the energy of the aggregate system and was called the crude stabilization energy. This energy could then be divided by the number of water molecules in the system to obtain the stabilization energy per water monomer, or be divided by the number of hydrogen bonds in the system to obtain the stabilization energy per hydrogen bond. If this value is negative, the entity is stable. Only the simple 1–2 (nearest neighbour) interactions were considered.

3.2. Net Atomic Charges

The net atomic charge on any atom is equal to $Z_B - P_B$ where Z_B is the core charge on atom B, and P_B is the gross electron population on atom B [10].

4. Results and Discussion

4.1. Energies

4.1.1. Dimers

The energies of the dimeric rotamers participating in the larger aggregates are listed in Table 1. As the oxygen-oxygen distance increases, the energy of the hydrogen bond diminishes [16]. The smooth curve illustrated in Fig. 2 shows how the energy of the hydrogen bond varies as the rotation proceeds through 360° for $d = 2.86$ Å. A similar curve is obtained for $d = 2.96$ Å. The maxima and minima occur at the same angle of rotation and the energy difference between the maxima remains relatively constant.

4.1.2. Ice-I_h Models

4.1.2.1. Component Rings

The ice-I_h lattices investigated can be depicted as two six-membered rings in pseudo-chair conformations joined together by three hydrogen bonds. The two component rings of structure II in Fig. 1, with $d = 2.86$ Å were investigated individually and their energies are listed in Table 2. The upper ring, which is common to all of the ice-I_h structures and to three of the ice-I_c structures, has an appreciable stabilization energy. The lower ring is unstable.

Table 1. Stabilization energies of rotamers having varying oxygen-oxygen distances

Oxygen-oxygen distance (Å)	Rotamer	Stabilization energy (kcals)
2.76	0°	-5.719
	60°	-5.670
	180°	-5.901
2.86	0°	-4.918
	60°	-4.873
	180°	-5.023
2.96	0°	-3.863
	60°	-3.822
	180°	-3.962

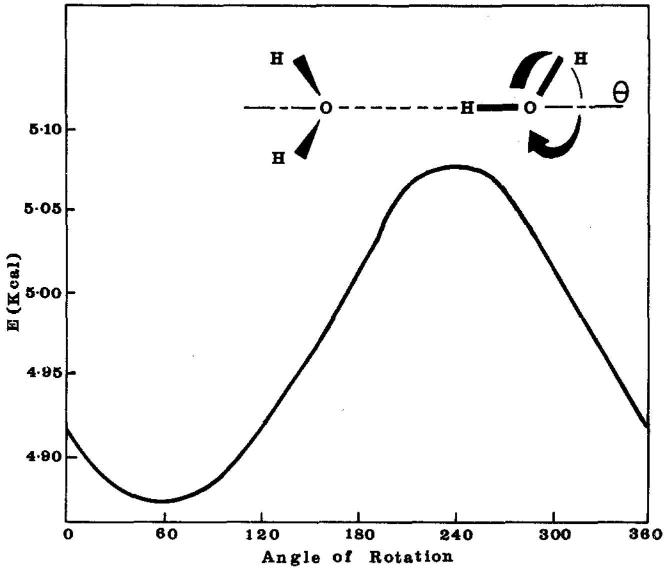

Fig. 2. Rotation of linear dimer (the proton donating monomer is in the plane of the paper and the hydrogens of the proton acceptor monomer are pointing out of the plane of the paper)

Table 2. Energies of component parts of structure II of Fig. 1 ($d = 2.86$ Å)

Structure	m	Total energy (a.u.)	Stabilization energy(kcal/monomer)
Ring on top	0	-119.39326	-0.477
Ring on bottom	2	-119.38745	+0.090
Parent lattice	1(n)	-238.80755	-0.361

In earlier work by Del Bene and Pople [5], it was found that polymers of water are most stable in a head to tail arrangement. Such is the case in the upper ring, where each monomer unit is contributing one proton for ring formation. The lower ring has two monomer units that contribute neither hydrogen for ring formation. It is found to be much less stable than the upper ring. In terms of the nomenclature used in this paper, the upper ring has $m = 0$, and the lower ring, $m = 2$. Included in Table 2 is the stabilization energy of the lattice when both rings are joined through hydrogen bonds. The stabilization energy per water monomer or per hydrogen bond of the ring where $m = 0$, is greater than that of the lattice. The stabilization energy per monomer contributor of the lower ring is, however, appreciably less than that of the lattice. Without interactions between the two rings, when they are joined, the expected stabilization energy would be the average of the two rings. Such is not the case. When the two rings are joined, the resulting stabilization energy is greater than the sum of its parts. Part of the upper ring stabilizes the lower ring, resulting in a stable structure.

Table 3. Energies of ice-I_h structures investigated

Structure as shown in Fig. 1.	d (Å)	n	Total energy (a.u.)	Stabilization energy kcals	Stabilization energy kcal/monomer
I	2.76	0	-238.82033	-7.290	-0.608
I	2.86	0	-238.80927	-5.412	-0.451
II	2.76	1	-238.81794	-5.794	-0.483
II	2.86	1	-238.80755	-4.334	-0.361
II	2.96	1	-238.78020	-3.030	-0.253
III	2.86	2	-238.80588	-3.333	-0.278

Table 4. Lattice expansion energies

n	O-O distance (Å)	Stabilization energy (kcal/monomer)	Lattice expansion energy (kcal/monomer)
0	2.76	-0.608	-0.15
0	2.86	-0.451	
1	2.76	-0.483	-0.12
1	2.86	-0.361	-0.11
1	2.96	-0.263	

4.1.2.2. Lattice Models

Listed in Table 3 are the stabilization energies of all complete ice-I_h structures studied. Two trends are evident: *d* increases for structures of the same *n* value, the stability of the lattices decreases and, as the value of *n* increases for those lattice structures possessing the same *d* value, the stabilization energy diminishes.

a) Constant *n*, variable *d*

The decrease in stabilization energy as the lattice is expanded indicates that energy is needed for the expansion. X-ray analysis of liquid water [8, 12], shows that as the temperature is increased, the nearest neighbour oxygen-oxygen distance also increases. By taking the difference between stabilization energies in kcal per monomer-contributor for structures of the same *n*, a function of the isotropic expansion energy is obtained. The result of this calculation is shown in Table 4. The contribution to the lattice expansion energies as determined by this procedure ranges from −0.15 to −0.11 kcal/mole. Using the equation derived by Kamb [17], an expansion energy of −0.283 kcal/mole is calculated for an expansion of 0.10 Å where the initial oxygen-oxygen distance is 2.76 Å. The MO calculation results are a measure of the extra stability imparted to each monomer unit in the lattice exclusive of primary considerations of monomer and

Table 5. Stabilization energies of ice-I_c structures ($d = 2.86$ Å)

Structure as shown in Fig. 3.	n	Total energy (a.u.)	Stabilization energy (kcal/monomer)
IV	0	-199.00439	-0.460
V	1	-199.00114	-0.285
VI	2	-199.00066	-0.237
VII	0	-199.0010-	-0.266
VIII	1	-198.99519	+0.073

Table 6. Energies of component parts of structures IV, V, and VI of Fig. 3 ($d = 2.86$ Å)

	Energies of components (kcal/participating monomer)		Energy of system(kcal/monomer)	Expected energy of system from component parts (kcal/monomer)
Structure	Upper ring	Bottom tetramer		
IV	-0.477	-0.127	-0.460	-0.337
V	-0.477	-0.096	-0.285	-0.324
VI	-0.477	+0.032	-0.237	-0.319

dimer hydrogen bonding contributions. The agreement between the value derived from the equation [17] and the results of the MO study is reasonable considering the number of approximations involved. However, when expanding lattices containing hydrogen bonds, some consideration should be given to the gain or loss of stability of the lattices themselves.

b) Constant *d*, variable *n*

The decrease in stabilization energy with increasing n, when d remains constant, echoes the observations made on the component rings. An increase in n does not cause as drastic a change as an increase in m.

The calculated lattice binding energy is simply derived by subtracting the energies of twelve monomers, having an interval angle of 104.5° from the energy of the system. For the ice-I_h lattice, where $d = 2.76$ Å, this calculation yields 6.80 and 6.68 kcal/mole, for $n = 0$ and $n = 1$ respectively. This is higher than the value obtained by Santry [6], who used a slightly different method on lattices with smaller nearest neighbour oxygen-oxygen distances.

4.1.3. Ice-I_c Models

Table 5 lists the stabilization energies of the six ice-I_c models studied and Table 6 lists certain energies of selected component species. Except for model IX, all of the ice-I_c structures studied are calculated to be stable.

4.1.3.1. Component Species

Only those lattices containing a six-membered ring similar to the one in the ice-I_h structures are considered. As the ring is common, it is the additional tetramer mostly which alters the energies. These tetramers have considerably less stabilization energy per monomer than the common six-membered ring. This results mainly from the ring structures having the monomeric units in the favourable head to tail arrangement which the tetramers do not. When the energies of the tetramers are combined with that of the six-membered ring, the resulting values indicate that two of the three lattice structures are less stable than their component parts. The two that are less stable are for lattices having n values of 1 and 2. The third lattice, where $n=0$, is more stable than its parts. A similar comparison of the ice-I_h structures showed that for both $n=0$ and 1, the lattice structures were more stable than the sum of the parts.

4.1.3.2. Different Families of Structures

Three different families of ice-I_c structures were investigated. The first three models have the same upper six-membered ring; the next two possess a common upper ring different from the other four lattices; and the last model is unique.

Although structures IV and VII have n values of zero, their stabilization energies differ considerably, by 0.19 kcal per water monomer. Structures V and VIII both have $n=1$. The difference in their stabilization energies is 0.19 kcal per participating monomer as well. When n increases from 0 to 1 for structures of the same family, as occurs when comparing models IV to V and VII to VIII, the stabilization energy changes by 0.17 kcal per monomer. Model VII has m values for its component rings of 1, 1, 2, and 1, while model IX has m values of 2, 2, 2, and 2 for its component rings. The average change in stabilization energy for each monomer contributing to the lattice structure on changing m from 1 to 2 is 0.05 kcal. Changing m from 1 to 2 in model V to simulate model VI of Fig. 3, results in an energy change of 0.048 kcal per participating unit.

From the brief consideration outlined above, the following factors appear to govern the stability of the ice-I_c lattices. First, the more rings present with $m=0$, the greater is the stability of the entity. Second, changing m from 0 to 1 causes a larger loss of energy to the structure than changing from 1 to 2. Third, the effects of changing m values are to a first approximation additive, and the differences in the stabilization energies of the ice-I_c lattices can be correlated by the component ring systems of the lattices. Unlike the ice-I_h structures, which have only two six-membered rings in pseudo-chair conformations, the ice-I_c structures have four such rings. These are more interrelated than in ice-I_h. Structures V and VI have one ring where $m=0$. Structure IV has two rings with m values of 0; this is the most stable model of the ice-I_c structure studied. Structure VII has one component ring where $m=0$ and also $n=0$. Structure V and VII have participating rings whose m values are 0, 1, 1, and 2. The stabilization energies of these two structures only differ by 0.02 kcal per participating monomer. Structure VI has the same sum of m values, 5, as structure VIII. However, structure VI has one ring where $m=0$. The difference in the stabilization

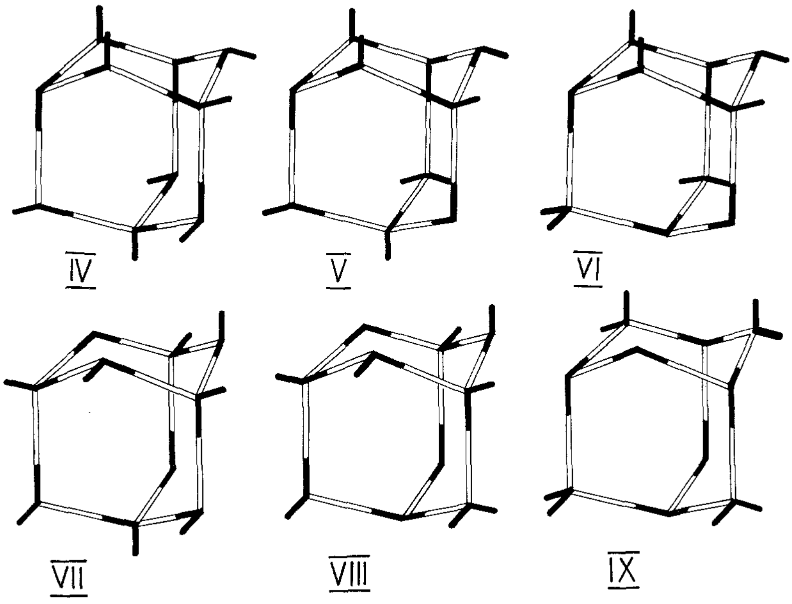

Fig. 3. Ice-I_c tautomers investigated (protons of the participating water monomers are situated at the ends of the solid black lines, away from the junctions of the solid black lines where the oxygens are situated)

energy between these two structures of 0.14 kcal/monomer reflects the contribution to the stabilization of the lattice by a ring whose m value is 0. Structure IX has four rings whose m values are 2. The difference in energy between structures VIII and IX, both of which possess no rings where $m=0$ is 0.168 kcal.

4.1.3.3. Change in n Values

For the first three lattices n changes from 0 to 2 with a decrease in the stabilization energy. The stabilization energies of structures IV and V show a decrease as n alters from 0 to 1. Accordingly, within the same family of structures, as n increases, the stabilization energy decreases. As was noted in the above section, the largest decrease occurs when n changes from 0 to 1 resulting from a change in the m values.

4.1.4. Comparison of Ice-I_h and Ice-I_c Structures

To be effective, the comparison must be between units with specific similarities. The similarities utilized are a common ring contributor and n, with other features remaining the same. Therefore the comparisons will be between the ice-I_h structures (Fig. 1) with $d=2.86$ Å and the first three structures of ice-I_c: IV, V and VI (Fig. 3). The results of the comparison are tabulated in Table 7. Using the units of kcal/participating monomer, the ice-I_c structure is slightly more stable than

Table 7. Comparison of stabilization energies of ice-I_h and ice-I_c structures ($d = 2.86$ Å)

n	Lattice type	Stabilization energy (kcal/monomer)	Stabilization energy (kcal/hydrogen bond)
0	I_h	-0.451	-0.360
0	I_c	-0.461	-0.384
1	I_h	-0.361	-0.288
1	I_c	-0.285	-0.237
2	I_h	-0.278	-0.222
2	I_c	-0.237	-0.197

Table 8. Energies of incomplete ice-I_h lattices based on structure shown in Fig. 1, model II ($d = 2.86$ Å)

Vacant lattice site	Total energy (a.u.)	Stabilization energy (kcal/monomer)
Parent lattice	-238.80755	-0.361
X	-218.89289	-0.355
Y	-218.89077	-0.221
Z	-218.89262	-0.322
X and Y	-198.98457	+0.250

the ice-I_h structure when $n = 0$. When $n = 1$ or 2, the ice-I_h structures possess the greater stability. The comparison is also made in kcal/H bond, this being perhaps more applicable to a continuum model. This comparison shows for $n = 0$, the structure of ice-I_c is now much stabler than that of ice-I_h. The energies of the models, where $n = 1$ or 2, indicate that the ice-I_h structures are still somewhat more stable than those of ice-I_c.

Although the ice-I_c structure is more stable than the corresponding ice-I_h structure for $n = 0$, the ordering of adjacent lattices in multi-lattice models would require lower n values for the ice-I_c than for the ice-I_h lattices. Hence the total ice-I_h system would be expected to be stabler. This agrees with an estimate of 0.04 kcal/M greater stability for ice-I_h relative to ice-I_c [18].

4.1.5. Incomplete Ice-I_h Lattices

Certain incomplete lattices were examined. Each of the incomplete lattices has as its parent lattice structure II of Fig. 1, where $d = 2.86$ Å. The stabilization energies of these lattices are listed in Table 8.

The stabilization energies of these incomplete lattices vary from -0.355 kcal/monomer to $+0.250$ kcal/monomer, lower than the comparable stabilization energy of the complete lattice. Omitting the monomer at site Y results in a

Table 9. Charges residing on the atomic centres of the monomer and selected dimers and trimers

Entity	Rotamer	Charges				
		O_1	O_2	O_3	H	H
Monomer		−0.275			0.137	
Dimer	0°	−0.276	−0.296[a]		0.156[b]	0.126[c]
	60°	−0.276	−0.295[a]		0.156[b]	0.125[c]
	180°	−0.277	−0.297[a]		0.156[b]	0.127[c]
	240°	−0.278	−0.298[a]		0.156[b]	0.128[c]
Trimer						
head to tail	0° + 0°	−0.297[a]	−0.297[a]	−0.278	0.159[b]	0.124[c]
					0.163[b]	0.133[c]
central water acting as double proton acceptor	180° + 180°	−0.280	−0.295[a]	−0.295[a]	0.153[b]	0.128[c]
central water acting as double proton donor	240° + 240°	−0.320[a]	−0.276	−0.276	0.147[b]	0.144[d]
					0.147[b]	

[a] Proton donating oxygen.

[b] Proton participating in hydrogen bond.

[c] Proton of donor not participating in hydrogen bond.

[d] Remaining protons.

stabilization energy of −0.221 kcal/monomer, a value considerably smaller than the values corresponding to lattice lacking monomers at X and at Z. When the monomer at Y is omitted, the chain arrangement of monomers in the upper ring is disturbed. Removing the monomer unit as position X yields a structure having a stabilization energy slightly smaller than that of the parent structure (−0.335 kcal/monomer). The monomer at position Z is a double proton acceptor and a single proton donor, whereas the monomer at site X is a double proton donor and a single proton acceptor next to a double proton acceptor. Removal of the monomer at Z results in a structure with stabilization energy smaller than that of the structure which lacks the monomer at X. Removal of the monomers at positions X and Y yields a structure which is unstable. Here both six-membered pseudo-chair rings are destroyed.

4.2. Net Atomic Charges

Table 9 lists the net charges residing on the monomer and on selected dimers and trimers. Although the geometries of the monomer units are not found in isolated water molecules, the various species described here are the bases of the larger lattice structures. Trends in the charges residing on the atomic centres are similar to those residing on similar structures having a different monomeric geometry. Tables 10 and 11, list the charges residing on the oxygen centres of various rings, and of complete and incomplete lattice structures for $d = 2.86$ Å. The numerical designation of the oxygen centres in Tables 10 and 11 reflect the oxygen sites shown in Fig. 4 which are correlated with the structures shown in

Table 10. Charges at oxygen centres of ice-I_h type structures (O–O = 2.86 Å)

Lattice type	Oxygen centre											
	O_1	O_2	O_3	O_4	O_5	O_6	O_7	O_8	O_9	O_{10}	O_{11}	O_{12}
Structure II Top Ring $m=0$		−0.304	−0.305	−0.305	−0.305	−0.306	−0.305					
Structure II Bottom Ring $m=2$	−0.319							−0.278	−0.296	−0.319	−0.278	−0.296
Structure II $n=1$	−0.321	−0.328	−0.307	−0.327	−0.310	−0.311	−0.298	−0.282	−0.298	−0.318	−0.302	−0.300
Structure I $n=0$	−0.305	−0.323	−0.304	−0.329	−0.310	−0.312	−0.299	−0.302	−0.304	−0.319	−0.302	−0.304
Structure III $n=2$	−0.317	−0.327	−0.307	−0.329	−0.308	−0.309	−0.300	−0.282	−0.296	−0.321	−0.317	−0.280
Structure II Missing Monomers *X* and *Y*			−0.280	−0.325	−0.308	−0.309	−0.299	−0.278	−0.300	−0.320	−0.300	−0.300
Structure II Missing monomer		−0.304	−0.304	−0.327	−0.309	−0.311	−0.301	−0.279	−0.300	−0.319	−0.300	−0.300
Structure II Missing monomer *Y*	−0.319		−0.281	−0.325	−0.308	−0.309	−0.298	−0.280	−0.298	−0.319	−0.302	−0.299
Structure II Missing monomer *Z*	−0.318	−0.327	−0.307	−0.326	−0.307	−0.308	−0.300	−0.283	−0.308	−0.296		−0.279

Table 11. Charges at oxygen centres of ice-I_c type structures (O–O = 2.86 Å)

Lattice type and n	Oxygen centres									
	O_1	O_2	O_3	O_4	O_5	O_6	O_7	O_8	O_9	O_{10}
Structure IV $n=0$	−0.300	−0.326	−0.306	−0.329	−0.311	−0.310	−0.300	−0.304	−0.299	−0.308
Structure V $n=1$	−0.281	−0.322	−0.304	−0.327	−0.308	−0.308	−0.302	−0.319	−0.297	−0.298
Structure VI $n=2$	−0.280	−0.324	−0.306	−0.325	−0.307	−0.306	−0.303	−0.321	−0.280	−0.315
Structure VII $n=0$	−0.319	−0.301	−0.319	−0.303	−0.301	−0.309	−0.301	−0.302	−0.304	−0.305
Structure VIII $n=1$	−0.321	−0.299	−0.319	−0.302	−0.300	−0.303	−0.300	−0.297	−0.282	−0.315
Structure IX $n=4$	−0.323	−0.315	−0.297	−0.315	−0.323	−0.315	−0.279	−0.279	−0.279	−0.315

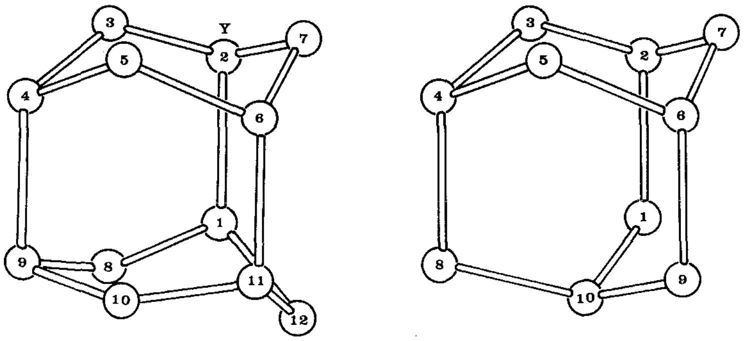

Fig. 4. Designation of the oxygen centres for the ice-I_h and ice-I_c lattices

Figs. 1 and 3. Generally the charges on the oxygen centres of the lattices can be estimated by considering the charge on the central oxygen atom of the appropriate trimer. Also from these tables, it can be seen that the smaller the variance of charges on the oxygen centres, the stabler the structure.

5. Conclusions

The aim of this study was to ascertain if the CNDO/2 MO technique could be successfully used on water aggregate structures. This involved determining if the method of calculating the stabilization energies produces results which are in accord with knowledge of the denser phases of water. The results presented show that the approach is not unreasonable and that certain conclusions can be made and concepts advanced. These are the following:

5.1. Expansion of the Ice-I_h Lattice

As the ice-I_h lattice is expanded, the stabilization energy diminishes. This indicates that energy is required for lattice expansion. X-ray investigations of liquid water report that as the temperature increases, the nearest neighbour oxygen-oxygen distance increases [10, 11]. The isotropic lattice expansion energies, as derived from the MO calculations, are less than a factor of two greater than the results obtained from other calculations [17].

5.2. Stabilization of Ice-I_h Structures Compared to Those of Ice-I_c

Comparison between the ice-I_h and ice-I_c structures showed that the former were more stable when $n = 1$ or 2. In the solid phase of water, ice-I_c is a metastable form of ice-I_h. Of the many theories of liquid water, ice-I_h is often used as at least one of the contributing structures. In the same comparison, it was noted that for $n = 0$, ice-I_c was the stabler entity. Joining other ice-I_c lattices to the original $n = 0$ lattice to make a larger aggregate, necessitates that the other lattices have a much lower value of n. The same is true for ice-I_h. Although there might be single lattices where $n = 0$ in the liquid, adjacent lattices would perforce have higher n values. Therefore, the ice-I_h configuration should be preferred.

5.3. Component Rings of the Lattice Determine the Stability of the Lattice

5.3.1. Ice-I_c

The stabilities of the ice-I_c lattices are correlated with the m values of the component rings. It is possible to judge the comparative stability of an ice-I_c structure by considering the component rings. Greatest stability occurs when there is at least one ring where $m = 0$.

5.3.2. Ice-I_h

The stabilization energies of the component rings of structure II where $d = 2.86$ Å, when compared to the stabilization energy of the lattice, indicate that a stable ring system can stabilize an unstable ring system. The stabilization energy of the lattice is higher than the sum of the parts. This was not found for the comparable ice-I_c structures.

To a first approximation the ice-I_h lattices investigated here can be considered small segments that could exist for a short time in liquid water. As the structure is composed of one stable and one unstable ring (structure II, Fig. 1), the lattice structure could come apart. This would be caused by the upper ring regaining its original high stabilization energy. The lower ring could then either attempt to bond with another six-membered ring, or, undergo an internal tautomerization and then bond with another ring. As each of the rings would be part of other structures, these actions would be occurring simultaneously with other rearrangements. As these rearrangements occur, distortion of bonds could easily take place, resulting in stabler ice-I_h lattices as well as other lattice type structures such as ice-*II* and ice-*III*, which are believed to contribute to the structure of liquid water.

5.4. Stabilization of Incomplete Lattices

The incomplete lattices studied, where only one monomer was omitted, were all stable. In one instance, the stabilization energy of the incomplete lattice was slightly lower than the complete parent lattice. Entry of a different molecule into the vacant site might occur.

5.5. Charges at the Oxygen Centres

Generally, the trend of charges at the oxygen centres can easily be estimated from the charge on the central oxygen atom of appropriate trimer. The difference between the estimated charge and the calculated charge is a measure of the stability of the structure in which the particular centre occurs.

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