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Interstitial and Lattice Substituted Models of an Expanded Ice-I_h Lattice

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An ice-I_h lattice (O–O = 0.286 nm) with small molecules placed interstitially and with some placed at lattice positions was investigated by the CNDO/2-MO technique. The interstitial molecules included H_2, N_2, O_2, HF, CO_2, H_2O, NH_3, CH_4 and CH_2O, whereas those involved in lattice substitution included HF, NH_3 and H_2O. From the calculations it is found that all interstitial and lattice substituted systems are stabler than the sum of the components, the enhanced stability depending on the system. Generally, lattice substituted systems are stabler than the corresponding interstitial models. Charges residing on the atomic positions reflect the amount of interaction with the matrix as well as indicating how the change in charge would facilitate other interactions with the solvent.

Key words: Ice-I_h lattice

1. Introduction

Reflecting the opinion of many researchers, Lemberg and Stillinger [1] point out that the physical and chemical properties of liquid water play an essential role in chemical and biological processes. Only recently have theoretical chemists had the necessary technology to investigate molecules and their aggregates, especially water, at the microscopic level. Such investigations use the techniques of molecular dynamics [2] and Monte Carlo computer simulations [3] as well as molecular orbital studies [4, 5]. From these powerful techniques, considerable information related to water has been calculated [6–9] and the results agree with experimental findings. In this presentation, results from a molecular orbital study on the effect of a water lattice structure on interstitial and lattice substituted molecules are reported.

Generally it would be preferable to report findings obtained from an *ab initio* technique, but the time required for large systems considered here, is, at the present time, prohibitive. Despite this drawback, there are several published reports which have successfully investigated large aggregates of water monomers [10–12]. Other studies have employed a semi-empirical MO technique to simulated denser state systems [13–16]. Of these studies, only one [15] has investigated the influence of an environment of water molecules on another molecule situated in a water matrix. For those calculations, an ice-I_c lattice with nearest neighbour oxygen-oxygen distances of 0.276 nm was used to surround oxygen and nitrogen molecules.

Table 1. Geometries of interstitial and lattice substituted molecules[a]

Molecule	Type	Geometry Bond length A–A (nm)	A–B (nm)	A–C (nm)	Bond angle B–A–B	B–A–C
H_2	A_2	0.07415				
N_2	A_2	0.10976				
O_2	A_2	0.1207				
HF	BA		0.0917			
H_2O	B_2A		0.102		109.467	
			0.101		109.467	
NH_3	AB_3		0.102		109.467	
CH_4	AB_4		0.109		109.467	
CO_2	AB_2		0.116		180.0	
H_2CO	B_2AC		0.112	0.121	120.0	120.0

[a] Ref. [24]

The ice-I_h lattice selected to be used in this study is composed of twelve water monomers joined by fifteen hydrogen bonds. This type of structure is the one normally associated with frozen water. It has been estimated that liquid water at low temperatures retains some of this structure [17, 18] although there are undoubtedly deformed lattices and other entities contributing to the water framework. From X-ray data it has been calculated that up to 50% of the structure of water is that of ice-I_h [19]. A Monte Carlo simulation of water [20] computed that the coordination number for water is close to that of ice-I_h.

Since the environment was selected to simulate liquid water, the nearest neighbour oxygen-oxygen distance was set at 0.286 nm. This value was taken from X-ray results for water at 25°C [21]. The oxygen-hydrogen distance was chosen to be 0.102 nm, a distance selected to be different from both solid and gaseous values for water and slightly larger than that ascribed to D_2O [22]. Also it is close to the value obtained from a recent molecular dynamics calculation [1]. The larger dimensions of the lattice will permit the placing of the interstitial molecules without serious steric interactions.

A CNDO/2 technique [23] was used for all calculations.

2. Geometries

2.1. Monomeric Units

The geometries of all molecules to be placed within or in the lattice are listed in Table 1.

2.2. Lattice

The lattice selected to provide the matrix is shown in Fig. 1. This structure has all nearest neighbour oxygen-oxygen distances of 0·286 nm, oxygen-hydrogen distances as either 0.102 nm or 0.184 nm, the latter for hydrogen bonds, tetrahedral coordination about the oxygen centres and linear hydrogen bonds [16]. For one

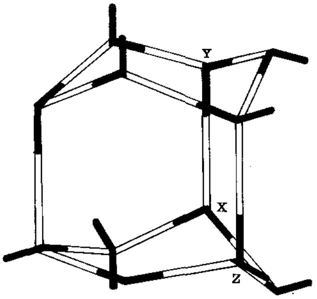

Fig. 1. Ice-I_h lattice used in this study. Black areas denote oxygen-hydrogen bonds

model the nearest neighbour oxygen-oxygen distance was taken as 0.276 nm and the oxygen-hydrogen bond was 0.101 nm.

2.3. *Positioning of Interstitial Molecules*

Illustrated in Fig. 2 are symmetry elements of the ice-I_h matrix; the molecules were positioned within the lattice in the following manner:

1. *Diatomic.* (H_2, O_2, N_2, HF) Each molecule was placed along line K with the two atoms equidistant from Centre C. Two models of HF were considered. One had the fluorine atom closer to line XY and the other had the hydrogen atom closer.

2. *Triatomic.* (H_2O, CO_2) The oxygen atom of water was positioned at point C and the two hydrogens pointed away from line XY in plane R. Plane E bisected the H–O–H angle. This molecule, when placed in the matrix, had similar dimensions to the monomers composing the matrix. Carbon dioxide was positioned along line K with the carbon atom situated at point C.

3. *Tetratomic.* (NH_3, CH_2O) The nitrogen of the ammonia molecule was situated at C and the three hydrogens were directed towards the bottom ring with two of the hydrogens pointing at positions X and Z. Two formaldehyde models were considered. Both had the carbon situated at point C and the carbonyl group along line K. In one model, the hydrogens were in plane E pointing towards line

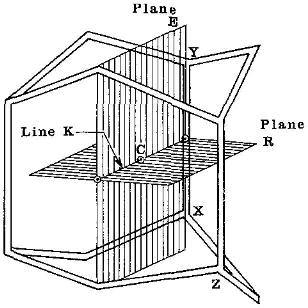

Fig. 2. Symmetry elements of ice-I_h lattice used for positioning interstitial molecules

XY with plane R bisecting the H–C–H angle. The other model had the hydrogens in plane R, pointing away from line XY with plane E bisecting the H–C–H angle.

4. *Pentatomic.* (CH_4) The carbon of methane was placed at C with two of the hydrogens positioned in the same way as the protons of interstitial water. As there is tetrahedral coordination about the carbon, the positions of the other two hydrogens are defined.

2.4. Positions of Molecules at Lattice Sites

Ammonia and HF were placed in the sites labelled X, Y or Z in Fig. 1.

1. HF was substituted at sites Y and Z. When in position Y, the proton pointed towards position X, and when in position Z, the proton participated in a hydrogen bond joining the upper and lower rings of the lattice.
2. NH_3 was substituted in positions X and Y. In both cases, two of the protons completed the lattice structure and the remaining proton pointed out of the ring.

3. Method of Calculating Energies and Charges

3.1. Stabilization Energies

The energy of the lattice system, whether complete or not, was added to the energy of the molecule to be substituted or placed interstitially. This sum was then subtracted from the energy of the total system.

3.2. Net Atomic Charges

The net atomic charge on an atom is equal to $Z_A - P_A$ where Z_A is the core charge on atom A, and P_A is the gross electron population on atom A [23].

4. Results and Discussion

When a molecule enters a lattice, it may or may not interact with it. If it does interact, it may occupy a lattice site by substitution or alter the shape of the lattice. This last possibility is beyond the scope of this work and is not considered further. The degree of interaction can be ascertained by examining the stabilization energy and the charge change on the atoms.

4.1. Stabilization Energies

4.1.1. Interstitial Models

When a model is composed of a lattice and an interstitial molecule, that aggregate is considered stable if the sum of the energies of the constituent parts is less negative than the energy of the interstitial system. In Table 2 are listed the stabilization energies of the systems investigated. All systems were found to be stable: The degree of stability varies from a low of 0.67 kcal to a high of 9.87 kcal.

Table 2. Energy parameters of interstitial systems

Interstitial species	Total energy of System (a.u.)	Energy of molecule in isolation (a.u.)	Stabilization energy of system (kcal)
H_2	240.28313	1.47464	0.593
N_2	261.89068	23.07931	2.40
O_2	275.58049	36.77294	1.43
CH_4	248.92287	10.11273	1.92
HF	267.22885	24.41889	1.51[a]
	267.22865	28.41889	1.38[b]
CO_2	282.42001	43.59784	9.18
H_2O	258.70274	19.890153	3.16
	258.71432[c]	19.889140[c]	4.56[c]
NH_3	252.68883	13.87706	2.65
H_2CO	265.64373	26.83185	2.72[d]
	265.64442	26.83185	3.15[e]

[a] Hydrogen closer to line *XY*.

[b] Fluorine closer to line *XY*.

[c] Lattice used: $r_{O-O}=0.276$ nm and $r_{O-H}=0.101$ nm, the interstitial monomer is identical to monomers comprising the lattice.

[d] Hydrogens closer to line *XY*.

[e] Oxygen closer to line *XY*.

Systems involving HF, NH_3, and formaldehyde would be expected to have stabilization energies comparable to carbon dioxide because of their solubilities in aqueous systems, but such is not the case. Two calculations were carried out on HF with the diatomic molecule in different positions. In both instances the resulting stabilization energy was quite small. The values do not reflect the interactions that must occur between an aqueous environment and the molecule [25]. The stabilization energy calculated for interstitial ammonia is quite large when compared with many of the other interstitial systems. In ice, it is known that HF does not occupy an interstitial position, but does substitute at lattice sites [26]. The positioning of NH_3 is not as well defined, since experimental results are ambiguous, supporting both possibilities [27, 28]. The calculations reported here indicate that the NH_3 is stable in an interstitial position but these results must be compared to the lattice substituted models.

Two different positions of formaldehyde in the lattice were considered. The resulting stabilization energies are quite large with the position of the molecule in the lattice being important. Like carbon dioxide [29], formaldehyde exists as a monomer in aqueous systems [30]. These results show that the gaseous monomer stabilizes the selected water environment.

Interstitial water in water matrices is a subject of considerable interest, both in the solid and liquid phase [31, 32]. For the solid phase of water there is some controversy as to whether interstitial water does indeed occur [31, 33], while in the liquid phase, the degree of occupancy of interstitial sites has been estimated, (e.g. [34]). Two models of interstitial water were investigated. One employed a lattice whose dimensions replicate ice [35] and the other used the lattice predominantly utilized in this study. Both models of interstitial H_2O, have reasonably large stabilization energies, with the smaller system having the greater stability. This may imply that the smaller lattice, as it exists in solid water, would be more

Table 3. Stabilization energies of interstitial systems compared to solubility and enthalpy of the corresponding aqueous systems

Interstitial molecule	Stabilization energy (kcals)	Solubility; S° (cc at S.T.P./10^3 g H_2O; P = 1 At)	Temp (°C)	Heat of solution at 25 °[b] $-\bar{H}^\circ_L - H^*_G$) (cal/g mole)
N_2	2.40	17.7[a]	25.5	2500
H_2	0.59	1.5[a]	25.0	905
O_2	1.43	28.4[a]	25.0	2805
CH_4	1.92	30.1[a]	25.2	3170
CO_2	9.18	774[a]	25.8	
H_2CO	3.14	S[c]		
HF	1.43	S[c]		
NH_3	2.65	S[c]		
H_2O	3.16	S[c]		

[a] Ref. [36]. [b] Ref. [37]. [c] Extremely soluble.

likely to accept interstitial water monomers than larger matrices, such as exist in liquid water. Before drawing specific conclusions from these results, the enhanced stability arising from placing such monomers in vacant lattice sites should be examined. This is done for the model with the larger lattice dimensions in a subsequent section.

The systems involving H_2, N_2, O_2 and CH_4 are considered separately as their low solubilities indicate they do not interact strongly with an aqueous environment. Höjer and Keller [15] found that when oxygen or nitrogen was placed within an unstable ice-I_c lattice of smaller dimensions, the interstitial molecule stabilized the system. The degree of stabilization reported by Höjer *et al.* are larger than those calculated here. This can be partially a result of the lattice type and the dimensions of the lattice. As mentioned in the instance of interstitial water molecules, the model using the smaller lattice was calculated to be 1 kcal more stable than the model with the larger dimensions.

Table 3 lists the solubilities of the gases H_2, O_2, N_2 and CH_4 as well as CO_2. This last gas was included as there is evidence for free CO_2 in aqueous solutions. There is a rough correlation between the stabilization energies of these gases and their solubilities. The same trend is observed when the enthalpies of solvation are compared to the stabilization energies. In both correlations, the model with nitrogen deviates from the trend. Höjer and Keller also calculated the interstitial nitrogen models to be stabler than those containing oxygen in three of the four models of ice-I_c.

4.1.2 Lattice Substituted Models

Before ascertaining the effect of lattice substitution, the role of the monomer at the substitution sites must be considered. The water monomer at site X is a single proton acceptor and a double proton acceptor and a double proton donor. The monomer at site Y is also both a single proton donor and a double proton donor but in this instance one of the protons participates in joining the upper and lower

Table 4. Stabilization energies of lattice substituted systems (O–O = 0.286 nm and n = 1)

Molecule	Substituted lattice site	Stabilization energy (kcals)	Energy of incomplete lattice (a.u.)
HF	*Y*	9.13	218.89077
	Z	11.24	218.89262
NH_3	*X*	13.54	218.89289
	Y	14.78	218.89077
H_2O	*X*	15.32	218.89289
	Y	16.71	218.89077
	Z	15.55	218.89262

six-membered rings while the other contributes to the stable six-membered upper ring [16]. At site *Z*, the monomer is a double proton acceptor and a single proton donor. This proton aids in joining the upper and lower rings.

Listed in Table 4 are the stabilization energies of all the models studied. The lowest stabilization energy is slightly less than that of interstitial CO_2 and the highest is 16.7 kcals, a range of 7.6 kcals. The variation in the stabilization energy depends on which site was initially vacant as well as the molecule placed at the site.

Placing a water molecule at vacant lattice site *Y* results in a greater stabilization energy than placing it at either sites *X* or *Z* when they are vacant. When the monomer is removed from position *Y* to produce the incomplete lattice, the favourable head to tail arrangement of the upper ring is destroyed, with considerable loss of energy. This does not occur with the removal of either monomer at *X* or *Z*. The differences between the stabilization energies for positioning the monomers in vacant lattice sites *X* and *Z* are quite small, only 0.2 kcal. Both of these monomers participate in lattice formation joining the upper and lower rings, one as a proton donor and the other as a proton acceptor.

The HF molecule was positioned at sites *Y* and *Z*. When this molecule is situated at site *Y*, with the proton pointing to site *X*, the system has a lower stabilization energy than when the HF is at site *Z*. In both positions, *Y* and *Z*, the proton joins the upper and lower rings. For the system with HF at *Y*, the favourable head to tail arrangement of the monomers in the upper ring is destroyed. When HF is positioned at *Z*, as a double proton acceptor, the HF fulfils the same function as the water molecule which it replaced.

Positioning the NH_3 molecule at site *Y* results in a stabilization energy greater than that realized by placing the molecule at site *X*. With NH_3 at *Y*, the favourable head to tail arrangement of monomer species in the upper ring is completed. When NH_3 is positioned at either site *X* or *Y*, it fulfils the same function as a water monomer at these positions.

The stabilization energies for the lattice substituted models are greater than those calculated for the corresponding interstitial models. In the solid phase of water it is known that vacant lattice sites are randomly distributed [31]. The number of vacant lattice sites could increase in the liquid phase, and the molecules HF, NH_3 and H_2O easily occupy these sites.

Table 5. Charges residing on atomic centres of molecules in isolation and interstitial position charges

Molecules	Isolation or Interstitial	A	A	B	B	B	B	C
H_2	*IS*	0.000	0.000					
(A_2)	*IN*	−0.008	0.008					
N_2	*IS*	0.000	0.000					
(A_2)	*IN*	−0.010	0.010					
O_2	*IS*	0.000	0.000					
(A_2)	*IN*	−0.003	0.006					
HF	*IS*	−0.232	0.232					
(BA)	*IN*[a]	−0.233	0.233					
	IN[b]	−0.234	0.234					
CO_2	*IS*	0.537		−0.268	−0.268			
(AB_2)	*IN*	0.535		−0.275	−0.245			
H_2O	*IS*	−0.275		0.137	0.137			
(B_2A)	*IN*	−0.297		0.138	0.142			
NH_3	*IS*	−0.242		0.081	0.081	0.081		
(AB_3)	*IN*	−0.246		0.080	0.084	0.084		
CH_4	*IS*	−0.051		0.013	0.013	0.013	0.013	
(AB_4)	*IN*	−0.056		0.019	0.016	0.016	0.012	
CH_2O	*IS*	0.215		−0.015	−0.015			−0.184
(AB_2C)	*IN*[c]	0.216		−0.015	−0.010			−0.183
	IN[d]	0.222		−0.007	−0.008			−0.186

[a] Fluorine closer to line *XY*.
[b] Hydrogen closer to line *XY*.
[c] Hydrogens closer to line *XY*.
[d] Oxygen closer to line *XY*.

4.2. Charges

4.2.1. Interstitial Models

Table 5 lists the charges existing on the atomic centres of the molecules when they are positioned interstitially and when they are in free space. In all cases, the lattice causes a change in charge distribution on the atomic centres of the interstitial molecules. The diatomic molecules when placed interstitially exhibit little change in charge. Interstitial CO_2 and H_2O undergo the largest charge change. The change in charge on the atoms of formaldehyde and to a much lesser extent HF, depend on the positioning of the molecule in the lattice.

Those molecules which interact with the solvent, i.e. formaldehyde, CO_2 and H_2O itself, exhibit the greatest charge change, and the charge density is altered to permit possible future interactions with the solvent. These interactions may include solvation and possibly dimerization. Some of the charge for the models of H_2O and CO_2 is redistributed over the lattice.

4.2.2. Lattice Substituted Models

From Table 6 it can be seen that when HF, NH_3 or H_2O are placed in lattice sites, the charges on the atoms, relative to the isolated molecules change appreciably. As NH_3 and HF interact with water to form ionized species, the change in charge on the atoms would facilitate these processes. In the case of HF, very little

Table 6. Charges residing on atomic centres of molecules placed at lattice sites

Molecule	Isolated or Substituted	Position	Charges A	B	B	B
HF	*IS*		−0.232	0.232		
(BA)	*SU*	*Y*	−0.254	0.251		
	SU	*Z*	−0.249	0.255		
H_2O	*IS*		−0.275	0.137	0.137	
	SU	*X*	−0.321	0.150	0.159	
	SU	*Y*	−0.328	0.160	0.154	
	SU	*Z*	−0.318	0.172	0.142[a]	
NH_3	*IS*		−0.242	0.086	0.086	0.086
	SU	*X*	−0.281	0.108[b]	0.100	0.078[a]
	SU	*Y*	−0.288	0.111	0.105	0.078[a]

[a] Not participating in lattice formation. [b] Joining upper and lower rings.

charge is distributed over the lattice. Considerably more charge is disbursed over the lattice for systems using NH_3 and H_2O.

5. Conclusions

The models investigated were selected to approximate the influence of an environment of water on certain molecules. The results obtained in this limited theoretical study are encouraging as they are in reasonable accord with measured phenomena that occur in aqueous solutions. These may be summarized as follows.

1. All interstitial systems studied are stable, with the degree of stability dependent on the interstitial molecule. This does not imply that each molecule is infinitely soluble, since other competing processes occurring in the aqueous solution may be energetically more favourable.
2. Structures involving HF, NH_3 and H_2O are more stable when these molecules are substituted into lattice sites rather than when they are positioned interstitially. Ice-I_h, at least in the solid phase of water, is disordered and is known to have vacant lattice sites; there are opportunities for these molecules to occupy vacant lattice sites.
3. From the calculations on the models studied, HF should go almost exclusively into lattice sites rather than interstitially, as indeed experimental studies [26] on solid ice-I_h have indicated. Water and ammonia molecules from these calculations preferentially enter lattice rather than interstitial sites. The positioning of these molecules in ice as reported in the experimental literature is inconclusive [31, 33, 27].
4. Interstitial models involving H_2, O_2, N_2 and CH_4 had low stabilization energies and small charge changes on the atomic centres of the interstitial molecules relative to the comparative isolated molecule. This, coupled with the known low solubilities of these compounds, indicate that these gases do not strongly interact with aqueous environments and that they probably retain their integrity as gases in aqueous solutions.

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