

## CALCULATION OF THE EQUILIBRIUM CONFIGURATION AND INTERMOLECULAR FREQUENCIES OF WATER DIMERS AND HEXAGONAL ICE

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Received 19 November 1975

The equilibrium structure and vibrational frequencies of the water dimer and hexagonal ice have been calculated using the Hartree-Fock potential of Clementi and coworkers and the correction for dispersion interactions of Kofos and coworkers. This correction term is proven to improve substantially the calculated results in the solid. The results obtained for the dimer were compared to other semiempirical and ab initio calculations and converging trends of the different studies are pointed out. The point energy effects were analyzed for hexagonal ice. These effects are shown to be important in determining the equilibrium structure of the crystal due to the peculiar behavior of the lattice frequencies as a function of the

### 1. Introduction

Recently there has been increased interest in the study of the interaction between water molecules. Research in this field has been carried out mainly in two directions: semiempirical studies in which an intermolecular potential function is assumed and ab initio calculations which deduce the interaction energy

function in the semiempirical calculations are selected

used in the liquid or solid phase, reproduce the measured values. Among the semiempirical potentials frequently employed are the Ben-Naim-Stillinger potential (BNS) [1], the Shipman-Scheraga potential (SS) [2] and the modification by Stillinger and

analytical representation of these potentials makes

types of calculations [7] which make use of a closed form representation of the potential.

In the field of ab initio calculations several studies have been performed which show general agreement on the equilibrium structure of the water dimer [8-10]. Among these calculations, that of Popkie et al. [9] was carried out near the equilibrium configuration, close to the Hartree-Fock limit. Moreover, Popkie et al.

to fit an analytical representation to this surface. In a

calculations of the dimer and the parameters of the analytical representation of the surface were changed accordingly. Ab initio calculations, however, neglect the correlation energy contribution to the potential surface. To correct

[12,13]. The expression proposed by Kofos and coworkers [12] was calculated by perturbation method

The quality of such ab initio interaction potentials has been examined by using them to compute bulk features such as the cohesive energy of water dimers [11] and orientationally averaged properties such as the virial coefficient of steam [7] and pair correlation functions of liquid water [4]. We feel that a rather

sensitive test of the quality of the potentials regarding their anisotropy, the contribution of electron correlation, the importance of many body forces, etc. could be provided by comparing the calculated results with

scattering). In this paper we report the results of a preliminary study on the binding energies, equilibrium structure and intermolecular frequencies of the water dimer and hexagonal ice (Ih) using the Hartree-Fock interaction potential (HF potential) of Popkie et al. [11] and introducing the correlation corrections

those yielded by various phenomenological potentials and the results for the solid are compared with available experimental data.

## 2. The potentials

The potential  $V_{\alpha,\beta}$  of the Hartree-Fock method of

$$V_{\alpha,\beta}^{(1)} = \sum_{i=1}^4 \sum_{j=1}^4 [a_{ij} a_{ij} / R_{ij} + A_{ij} \exp(-b_{ij} R_{ij})] . \quad (1)$$

and point  $i$  in molecule 2 and  $\alpha = 1, 2, 3, 4$  are

interaction points were located at the oxygen and the hydrogen positions. A fourth interaction point (M) was located in the plane of the HOH molecule in the molecular plane, at a distance of 0.2259 Å from the oxygen [11]. The O-H bond length was taken to be 0.957 Å and the HOH bond angle 105°. It should be stressed that no special meaning was attributed by

the interaction potential or to the position of the in-

teraction centers. The parameters in eq. (1) (in angstroms and kilocalories per mole) are:

$$q_O = 0, q_H = 11.801, q_M = -2q_H ,$$

$$A_{OM} = A_{HM} = A_{MM} = 0 ,$$

$$A_{OO} = 71533 , A_{OH} = 4084.0 , A_{HH} = 779.8 ,$$

$$b_{OO} = 3.969 , b_{OH} = 3.914 , b_{HH} = 3.125 .$$

$$V_{\alpha,\beta}^{(2)} = C_6 / R_{O\dots O}^6 - C_8 / R_{O\dots O}^8 + C_{10} / R_{O\dots O}^{10} , \quad (2)$$

with

$$C_6 = 922.78 , C_8 = 17283.5 \text{ and } C_{10} = 24119.7 .$$

The potentials  $V_{\alpha,\beta}^{(1)}$  and  $V_{\alpha,\beta}^{(1)} + V_{\alpha,\beta}^{(2)}$  are used here to

## 3. The water dimer

Six degrees of freedom are necessary to describe the conformation of the system composed of two rigid monomers. A configuration of minimum energy has to be found in this six-dimensional space. For our

Cartesian coordinates of the  $N = 8$  points which represent the two monomers [14]. Since the ab initio intermolecular potential was calculated assuming a rigid geometry for the individual monomers we chose

the correct bond lengths and bond angles for the

between inter- and intramolecular frequencies. This approximation should not appreciably affect the calculated intermolecular modes due to the large separation between inter- and intramolecular frequencies.

Starting from an arbitrary initial configuration we reach a configuration of minimum energy using steepest

The final results were shown to be independent of the

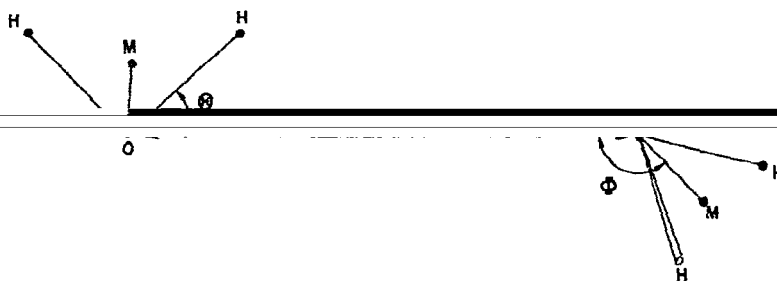


Fig. 1. Intermolecular coordinates for the water dimer.

Table 1  
Calculated conformation and stabilization energy of the water dimer

	Potential				
	CP <sup>a)</sup>	HF	HFK	SS <sup>b)</sup>	ST2 <sup>c)</sup>
$R$ (Å)	2.974	2.98	2.73	2.85	2.852
$\theta$ (°)	4.6	3.6	14	5.8	-1.0
$\phi$ (°)	119.0	124.8	103	100.2	128.2
Stabilization energy (kcal/mole)	5.6	4.89	6.48	5.76	6.839

a) From ref. [10]. Calculations carried out with the 6-31G\* basis set.

b) From ref. [16]. c) From ref. [15].

initial configuration in the calculations we carried out

one minimum in either energy surface although several saddle point configurations (which exhibit imaginary frequencies in the dynamic calculations) have been found in both surfaces.

Our results with both potentials agree with other ab initio [10] and semiempirical [15,16] calculations which show that the minimum energy configuration is the one for which one water molecule and the bisector of the HOH angle of the second molecule lie in one

system. The configuration of the dimer can thus be

given in fig. 1. In table 1 we present the configurations

ab initio methods by Curtiss and Pople (CP) [10] using the 6-31G\* basis set and the results obtained with the semiempirical potentials SS [16] and ST2 [15]. It can be seen that all potentials predict, within 15°, a linear hydrogen bond ( $\theta = 0$ ). It should be mentioned

that the stable dimer structure predicted by both the

initial HF and HFK potentials differs markedly from the structure which would be stable for dipole and quadrupole interactions [15]. Thus, nonclassical short range polarization effects seem to contribute to determining the equilibrium conformation.

The O...O distance, which seems to be the most important conformational parameter, is longer for the HF potential ( $R_{O...O} \approx 2.98$  Å) than for the semiempirical potentials ( $R_{O...O} \approx 2.85$  Å) but is sub-

stantially shorter for the HFK potential ( $R_{O...O} = 2.73$  Å).

Our interest is focused by comparing the results

obtained with the CP, HF, HFK, SS and ST2 potentials. The oxygen atoms. This shortens the  $O_1...O_2$  distance, permitting better electrostatic interaction between the H(2) of the donor molecule and the M center of the acceptor molecule. This in turn allows a reduction in the  $\phi$  angle from 124° to 103°, resulting in close re-

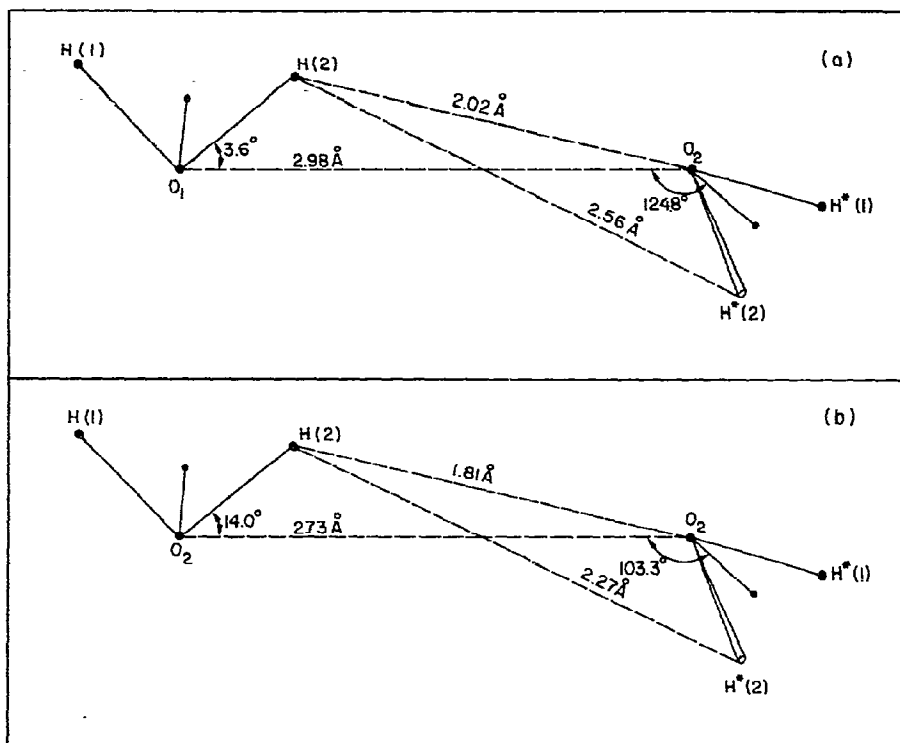


Fig. 2. Interatomic distances at the equilibrium conformation of the water dimer calculated with (a) the HF potential; (b) the HFK

Table 2

dimer is the creation of closer interatomic distances

A'	452	343.8	427.9	451
	204	174.6	238.1	183
	185	126.8	79.4	106
A''	536	552.5	635.6	681
	118	141.6	121.7	113

for all potentials the equilibrium geometry of the dimer has a  $C_s$  symmetry, the frequencies can be divided in every case into three planar modes of symmetry,  $A'$ , and 3 out-of-plane modes of symmetry,  $A''$ . The analysis of the symmetries of our calculations shows that the

a) From ref. [10]. Calculations carried out with the 4-31G

b) From ref. [16].

pulsive contacts between  $H(2)\cdots O_2$ ,  $H(1)^*\cdots H(2)$  and  $H(2)^*\cdots H(2)$  which are relieved by widening the  $\theta$  angle from about  $4^\circ$  to  $14^\circ$ . Thus the overall effect of the correction term on the equilibrium geometry of the

upper  $A'$  mode has, basically, the character of an hydrogen bond bend whereas the two lower  $A'$  modes are hydrogen bond stretch mixed with plane bend

The upper  $A''$  mode is clearly a hydrogen bond out-of-plane bend, a motion in which the  $H\cdots O$  distance changes substantially. The second  $A''$  mode is a torsion of the two monomers around the hydrogen bond, and the third mode is a mixture of bending and the torsional kind of displacement.

(a) The calculation by Curtiss and Ropie [10] with the 4-31G basis set consistently yields  $A'$  and

they recalculated the diagonal force field with the more extended 6-31G\* basis set, they obtained smaller diagonal  $A'$  force constants. In an approximate calculation (using only diagonal terms) they carried out with these force constants, the hydrogen bond stretch frequency of  $204 \text{ cm}^{-1}$  (column 2, table 2) was reduced to  $170 \text{ cm}^{-1}$ . This compares very well with the  $174 \text{ cm}^{-1}$  value obtained in the HF calculation.

(b) When comparing the frequencies calculated with the HF potential to those obtained with the HEK

cies increase, whereas the three low frequencies decrease. The character of the normal modes and their relative order remain unchanged by introducing the dispersion forces. The frequencies are rather sensitive to the inclusion of the correlation contribution.

(Changes of up to 50% are seen.) The measurement

tive correction to the HF surface.

(c) The SS potential yields frequencies which are relatively close to the HF results, in most cases much closer than to the pure restricted HF calculations. This is the behavior one would expect from an empirical potential which implicitly includes the effect of the dispersion forces.

#### 4. Hexagonal ice

Our aim is to calculate the lattice frequencies

method [17], in which one parametrizes the force constants to obtain agreement between calculated and experimental normal modes [18,19] or on phenomenological approaches which deduce the elements

[20,21]. In this section we report the uniaxial and biaxial force constants of hexagonal ice which result from

the ab initio interaction potentials. The calculations

molecules. This assures that the calculated frequencies are consistent with the employed potentials [22,23]

by locating 4 oxygen atoms of a primitive unit cell in special positions  $\pm(1/3, 2/3, z; 2/3, 1/3, 1/2 + z)$  of the  $P63/mmc$  ( $D_{6h}^4$ ) hexagonal space group [24]. According to the experimental results  $z = 1/16$  and the unit cell dimensions  $a$  and  $c$  are such that all the  $O \cdots O$  distances are equal and the sublattice formed by the oxygen atoms is tetrahedral [25]. The hydrogen atoms were located  $0.957 \text{ \AA}$  from the oxygens and allowed to depart from the  $O \cdots O$  line so as to form an HOH angle of  $105^\circ$ . (If the hydrogens would be on the  $O \cdots O$  line they would also form a tetrahedral

is given by

$$V_{u,\text{cell}} = \frac{1}{2} \sum_{\alpha=1}^4 \sum_{\beta=\alpha}^M V_{\alpha,\beta} \quad (3)$$

Here  $V_{\alpha,\beta}$  is the interaction energy between monomer  $\alpha$  in the basic unit cell and monomer  $\beta$  located anywhere

potential (eq. (1)) or as the sum of eqs. (1) and (2) (HEK potential).  $M$  is the number of monomers in

action with the 124 unit cells surrounding the basic unit cell and hence  $M = 496$ . The energy per molecule, which is the quantity to be related to the sublimation energy of ice, is one-fourth of  $V_{u,\text{cell}}$ . For hexagonal ice we carried out two parallel studies. In a first approximation we neglected zero point energy effects and looked for a crystal configuration which minimizes the static energy given by eq. (3). The energy was minimized with respect to the rotations and translations of

the unit cell parameters  $a, b, c, \alpha, \beta$  and  $\gamma$ . No constraints were imposed on the minimization path except to assume that the crystal is built by translating the basic unit cell [26]. In other words, the four monomers in

unit cells lengths and angles were allowed to change independently without imposing the hexagonal con-

ization was carried out in the 3N cartesian coordinates

Table 3  
Conformation of ice Ih at which the lattice energy is a minimum

	Potential	
	HF	HFK
$a$ (Å)	4.857	4.530
$b$ (Å)	4.812	4.541
$c$ (Å)	7.852	7.403
$\alpha$	89.5	89.7
$\beta$	88.9	90.2
$\gamma$	117.9	119.9
HO...O (°)	2-6	3-5
Lattice energy (cal/mole)	8.62	8.71
Frequencies (cm <sup>-1</sup> ):		
Acoustical	692	789
Optical	660	762
	653	679
	569	635
	544	556
	465	445
	423	410
	341	281
	339	274
Translations	234	271
	217	269
	38	37
	31	28

space of the  $N = 16$  centers of interaction of the four monomers in the unit cell. Results for the calculated unit cell parameters, lattice energy and  $k = 0$  lattice frequencies for the configuration which minimizes the static energy are given in table 3. It can be seen that with

the unit cell parameters are substantially shortened when the correlation energy term is included in the calculation.

Since the monomers are allowed to behave as inde-

pendent units no single value of the calculated O...O bond length, or HO...O hydrogen bond angle can be given, but the differences in the O...O length and the angle of the hydrogen bond formed by the different monomers are definitely small. From table 3 it can be seen that the HFK potential predicts O...O distances 0.2 Å smaller than the HF calculations and that in both cases the bond is almost linear.

It is difficult to describe the exact character of the normal modes, since symmetry rules are not operative here. But even though the eigenvectors show that there are translational and rotational contributions to each

group: higher frequencies, at which the molecules mainly librate and lower frequencies where the motions are basically translational. The effect of increasing some of the frequencies and lowering others, caused by the correlation potential in the dimer can be noticed clearly here in the librational modes. The higher librational frequencies calculated with the HFK potential are about 100 cm<sup>-1</sup> higher than the high frequencies yielded by the HF potential. On the other hand the lower librational modes are about 60 cm<sup>-1</sup> lower with the HFK potential.

equilibrium configuration of the crystal, by repeating our calculations at a series of preestablished molar volumes. In every case the starting conformation of the crystal was taken as the tetrahedral arrangement of the

to the same unit cell volume. As before, the geometry of this case the unit cell axes were kept at fixed values which satisfy the relation  $c/a = 1.628$  with angles  $\alpha = \beta = 90^\circ$ ,  $\gamma = 120^\circ$ . We omitted a complete calculation of the density of states to evaluate the zero point energy and assumed in this preliminary study that the average of each one of the optical modes over the whole Brillouin zone equals its  $k = 0$  value, and that the three acoustical modes can be estimated by a Debye model

mentioned that such an approximation was shown to be very good in the case of N<sub>2</sub> crystals [22,23]. The results at the crystal configuration which minimizes the

Table 4  
Conformation of ice Ih which minimizes the total energy of the crystal. Frequencies calculated at this conformation

	Potential	
	HF	HFK
$a = b$ (Å)	4.854	4.602
$c$ (Å)	7.927	7.516
Energy per molec (kcal/mole)	6.20	8.53
Librations	753	835
	715	778
	704	762
	616	701
	592	624
	549	570
	444	452
	375	306
	344	283
	339	267
Translations	237	260
	220	259
	202	253
	201	246
	190	228

Comparing tables 3 and 4 it can be seen that the

volume in such a way that their average is a function which depends only weakly on the volume. Another interesting effect we noticed is that the gap between translational and librational modes (defined as the difference between the higher translational frequency and the higher translational frequency) is proportional to the volume at which the calculations are carried out. The gap is 19  $\text{Å}^3/\text{molec}$  for the HF potential and 38  $\text{Å}^3/\text{molec}$

Table 5  
Comparison between calculated and experimental data for ice Ih

	Calculated		Experimental
	HF	HFK	
$a$ (Å)	4.854	4.602	4.4968 a)
$c$ (Å)	7.927	7.516	7.3198 a)
Sublimation energy (kcal/mole)	7.39 b)	9.72 b)	11.31 c)
( $\text{cm}^{-1}$ )			
Lower libration ( $\text{cm}^{-1}$ )	339	267	$\sim 525$ d)
Librational bandwidth ( $\text{cm}^{-1}$ )	414	568	$\sim 500$ d)
Higher translation ( $\text{cm}^{-1}$ )	237	260	
Translational bandwidth ( $\text{cm}^{-1}$ )	203	232	

a) From the low temperature results of ref. [27].

b) These values were obtained by adding to the results in table 4, +1.19 kcal/mole (ref. [28]) to account for the intramolecular zero point energy.

the HF and HFK potentials with available experimental data. It can be seen from the table that the dispersion forces contribute to making the unit cell smaller and the sublimation energy larger. These dispersion forces

potential. But, still, the HFK potential yields unit cell dimensions larger and sublimation energy smaller than the experimental values. This could be due to the fact that these and more body terms are not included in the potential and account for about 10% of the stabilization energy of water trimers and tetramers [11]. A sublimation energy within 5% of the experimental value

In table 5 we compare some values calculated with

mental results.

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