Chemical Physics 13 (1976) 433–440
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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 Kołos 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. Zero point energy effects were analyzed in hexagonal ice. These effects are shown to have little influence on determining the equilibrium structure of the crystal due to the peculiar behavior of the lattice frequencies as a function of the molar volume.

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 from first principles. The parameters of the energy function in the semiempirical calculations are selected so that the calculated values of some observable quantities 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 Rahman (ST2) [3] of the BNS potential. The explicit analytical representation of these potentials makes them particularly applicable to studies in molecular dynamics [3], Monte-Carlo methods [4–6] or other 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. used their extensive study of the Hartree–Fock surface to fit an analytical representation to this surface. In a more recent work by these authors [11] the ab initio calculations were extended to less constrained configurations 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 this, several analytical expressions have been suggested [12,13]. The expression proposed by Kolos and coworkers [13] was calculated by perturbation method. The fact that the analytical representation of the intermolecular forces of Popkie et al. and the correction term of Kolos and coworkers were derived by very accurate quantum mechanical calculations makes them of particular interest.

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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 furnished by comparing the calculated stable crystal structure, unit cell parameters and various lattice dynamic properties with the existing experimental data on the solid phase (e.g. crystallographic structure, infrared and Raman spectra and inelastic neutron 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 (HFK potential) as given by Kolos and coworkers [13]. The results obtained for the dimer are compared with those yielded by various phenomenological potentials and the results for the solid are compared with available experimental data.

2. The potentials

The analytical fit to the Hartree–Fock surface of the two monomers is given by a point–point interaction potential

$$V^{(1)}_{\alpha,\beta} = \sum_{i=1}^{4} \sum_{j=1}^{4} [q_i q_j / R_{ij} + A_{ij} \exp(-b_{ij} R_{ij})] \ . \qquad (1)$$

Here R_{ij} is the distance between point i in molecule α and point j in molecule β and q_i, q_j, A_{ij}, b_{ij} are parameters.

Interaction points were located at the oxygen and the hydrogen positions. A fourth interaction point (M) was placed on the bisector of the HOH angle 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 Popkie et al. [9,11] to either the analytical form of the interaction potential or to the position of the interaction centers. The parameters in eq. (1) (in angstroms and kilocalories per mole) are:

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

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

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

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

The direct perturbation calculation on the water dimer by Kolos and coworkers [13] was fitted to an analytical form which depends only on the oxygen–oxygen distance $R_{O...O}$ [4].

$$V^{(2)}_{\alpha,\beta} = C_6/R^6_{O...O} - C_8/R^8_{O...O} + C_{10}/R^{10}_{O...O} \ , \qquad (2)$$

with

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

The potentials $V^{(1)}_{\alpha,\beta}$ and $V^{(1)}_{\alpha,\beta} + V^{(2)}_{\alpha,\beta}$ are used here to compute various structural and dynamic properties of the water dimer and hexagonal ice.

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 convenience we carried out the energy minimization in the $3N$ dimensional space composed of the three 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 an artificially stiff intramolecular potential to yield the correct bond lengths and bond angles for the monomers. We thus explicitly neglected the coupling between inter- and intramolecular frequencies. This approximation should not appreciable 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 descent and Newton–Raphson minimization techniques. The final results were shown to be independent of the

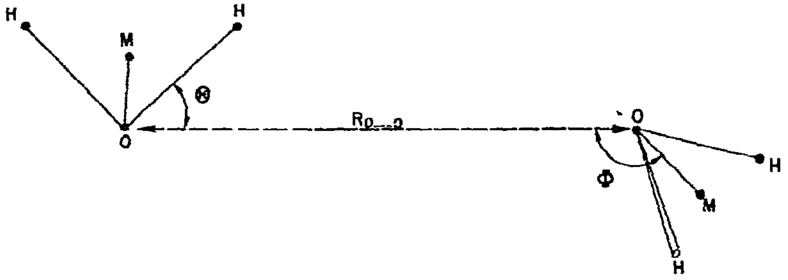

Fig. 1. Intermolecular coordinates for the water dimer.

Table 1
Calculated conformation and stabilization energy of the water dimer

	Potential				
	CP[a)]	HF	HFK	SS[b)]	ST2[c)]
R (Å)	2.974	2.98	2.73	2.85	2.852
θ (°)	4.6	3.6	14	5.8	−1.0
ϕ (°)	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 with both potentials. That is, there seems to be only 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 plane, and that this is a plane of symmetry of the system. The configuration of the dimer can thus be described in terms of the three coordinates R, θ and ϕ given in fig. 1. In table 1 we present the configurations of minimum energy for both potentials, and compare them with the results of the study carried out with 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 phenomenological SS and ST2 potentials and the ab initio 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 ($R_{O\cdots O} \approx 2.98$ Å) than for the semiempirical potentials ($R_{O\cdots O} \approx 2.85$ Å), but is substantially shorter when calculated with the HFK potential ($R_{O\cdots O} = 2.73$ Å).

The influence of the correlation correction on the HF surface is best seen by comparing the results presented in figs. 2a and 2b. Basically, the correction term provides an extra attractive force between the oxygen atoms. This shortens the $O_1\cdots O_2$ 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 ϕ angle from 124° to 103°, resulting in close re-

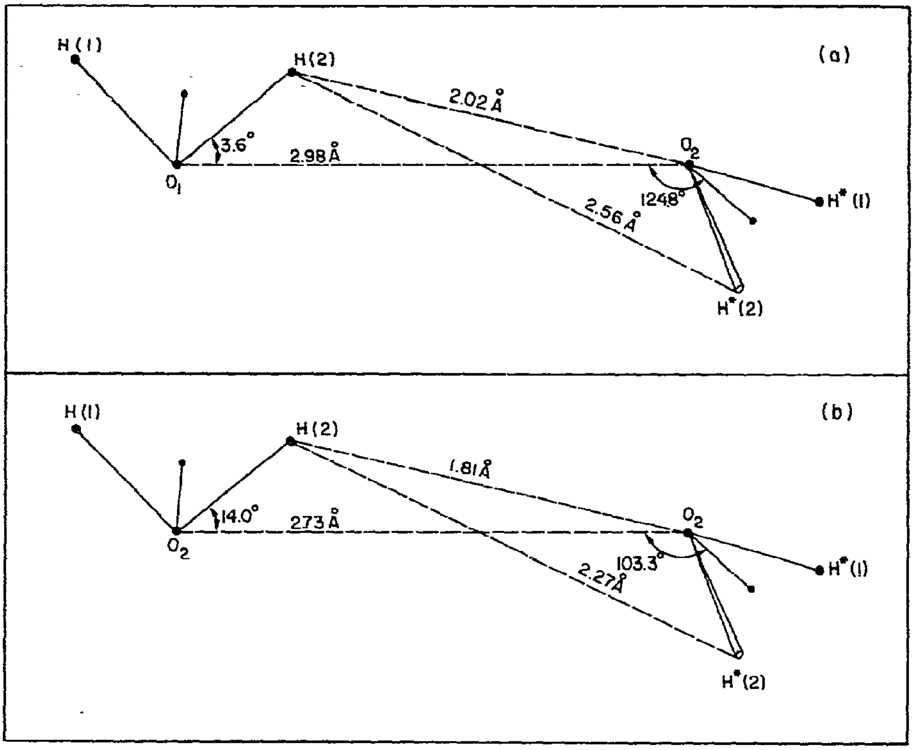

Fig. 2. Interatomic distances at the equilibrium conformation of the water dimer calculated with (a) the HF potential; (b) the HFK potential.

Table 2
Intermolecular frequencies of the water dimer

Frequencies (cm^{-1})	Potential CP[a]	HF	HFK	SS[b]
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
	81	110.9	44.7	63

[a] From ref. [10]. Calculations carried out with the 4-31G basis set.
[b] From ref. [16].

pulsive contacts between H(2)···O_2, H(1)*···H(2) and H(2)*···H(2) which are relieved by widening the θ angle from about 4° to 14°. Thus the overall effect of the correction term on the equilibrium geometry of the dimer is the creation of closer interatomic distances nad a less linear hydrogen bond.

Table 2 presents the six intermolecular frequencies of the dimer as calculated by Curtiss and Pople (CP) by Shipman et al. (SS) and by us (HF and HFK). Since for all potentials the equilibrium geometry of the dimer has a C_s symmetry, the frequencies can be dividied in every case into three planar modes of symmetry, A', and 3 out-of-plane modes of symmetry, A". The analysis of the eigenvectors of our calculations shows that 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 planar bend. The upper A" mode is clearly a hydrogen bond out-of-plane bend, a motion in which the H···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.

From a comparison of the results in table 2 several trends can be observed:

(a) The calculation by Curtiss and Pople [10] with the 4-31G basis set gives consistently higher A′ and lower A″ frequencies than the HF calculation. When 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 cm^{-1} (column 2, table 2) was reduced to 170 cm^{-1}. This compares very well with the 174 cm^{-1} value obtained in the HF calculation.

(b) When comparing the frequencies calculated with the HF potential to those obtained with the HFK potential it is observed that although the interatomic distances are shortened, only the three high frequencies 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 of the dimer intermolecular frequencies could thus serve as a sensitive test of the quality of the perturbative correction to the HF surface.

(c) The SS potential yields frequencies which are relatively close to the HFK 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

Previous attempts to calculate the lattice frequencies of hexagonal ice have been based either on the FG 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 of the dynamical matrix from various elastic constants [20,21]. In this section we report the infrared and Raman frequencies of hexagonal ice which result from the *direct* calculation of the dynamical matrix from the ab initio interaction potentials. The calculations were carried out for configurations of the crystal in which there are no forces or torques acting on the molecules. This assures that the calculated frequencies are consistent with the employed potentials [22,23].

An initial configuration of the crystal was generated 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 $P63/_{\mathrm{mmc}}$ (D^4_{6h}) 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···O distances are equal and the sublattice formed by the oxygen atoms is tetrahedral [25]. The hydrogen atoms were located 0.957 Å from the oxygens and allowed to depart from the O···O line so as to form an HOH angle of 105°. (If the hydrogens would be on the O···O line they would also form a tetrahedral structure and the HOH angle would be of 109.27°.)

The energy of the 4 molecules in a basic unit cell is given by

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

Here $V_{\alpha,\beta}$ is the interaction energy between monomer α in the basic unit cell and monomer β located anywhere in the crystal. $V_{\alpha,\beta}$ was taken either as the pure HF potential (eq. (1)) or as the sum of eqs. (1) and (2) (HFK potential); M is the number of monomers included in the lattice. In our study we included the interaction with the 124 unit cells surrounding the basic unit cell and hence $M = 496$. The energy per molecule, which is the quentity to be related to the sublimation energy of ice, is one-fourth of $V_{\mathrm{u.cell}}$. 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 four monomers and, in this first approximation, to the unit cell parameters a, b, c, α, β and γ. 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 the unit cell were treated as independent units, and unit cells lengths and angles were allowed to change independently without imposing the hexagonal geometry. Again, as in the case of the dimer, the minimization was carried out in the $3N$ cartesian coordinates

Table 3
Conformation of ice Ih at which the lattice energy is a mimimum. Frequencies ($k = 0$ modes) calculated at this conformation

	Potential	
	HF	HFK
a (Å)	4.857	4.530
b (Å)	4.812	4.541
c (Å)	7.852	7.403
α	89.5	89.7
β	88.9	90.2
γ	117.9	119.9
O···O (Å)	2.94 – 3.00	2.74 – 2.81
HO···O (°)	2 – 6	3 – 5
Lattice energy per molec (kcal/mole)	8.95	11.85
Frequencies (cm^{-1}):		
Librations	736	832
	692	789
	660	762
	653	679
	569	635
	544	556
	465	445
	423	410
	382	325
	375	320
	341	281
	339	274
Translations	234	271
	217	269
	200	250
	198	244
	182	223
	153	186
	130	165
	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 either potential, the departure from hexagonal symmetry ($a = b, \alpha = \beta = 90°, \gamma = 120°$) is small and that 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 independent 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 normal mode, they can definitely be divided into two groups: 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^{-1} higher than the high frequencies yielded by the HF potential. On the other hand the lower librational modes are about 60 cm^{-1} lower with the HFK potential.

In the second part of our study we estimated the influence of the zero point energy in determining the 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 oxygen sublattice, with O···O distances corresponding to the given unit cell volume. As before, the energy of the crystal was minimized with respect to the rotations and translations of the molecules in the unit cell but in this case the unit cell axes were kept at fixed values which satisfy the relation $c/a = 1.628$ with angles $\alpha = \beta = 90°, \gamma = 120°$. 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 with a characteristic frequency equal to the lower optical mode at the given molar volume. It should be mentioned that such an approximation was shown to be very good in the case of N_2 crystals [22,23]. The results at the crystal configuration which minimizes the total energy are given in table 4.

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
Frequencies (cm^{-1}):		
Librations	753	835
	715	778
	704	762
	616	701
	592	624
	549	570
	444	452
	431	407
	386	314
	375	306
	344	283
	339	267
Translations	237	260
	220	259
	202	253
	201	246
	180	228
	157	188
	135	162
	39	34
	34	28

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)
Higher libration (cm^{-1})	743	835	1000 d)
Lower libration (cm^{-1})	339	267	~525 d)
Librational bandwidth (cm^{-1})	414	568	~500 d)
Higher translation (cm^{-1})	237	260	
Lower translation (cm^{-1})	34	28	
Translational bandwidth (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.
c) From ref. [29].
d) Given in ref. [28].

Comparing tables 3 and 4 it can be seen that the inclusion of the zero point energy has relatively little influence on the determination of the equilibrium unit cell parameters. This is due to the fact that even though individual normal modes are appreciably volume-dependent, some of them go up and some go down with 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 lower librational frequency and the higher translational frequency) is proportional to the volume at which the calculations are carried out. This goes down to zero at a molar volume of 39 $Å^3$/molec for the HF potential and 38 $Å^3$/molec for the HFK potential. This prediction could be tested by infrared and Raman pressure-dependent experiments.

In table 5 we compare some values calculated with 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. They also generally give better agreement between the different spectroscopic predictions and experimental values. One exception is that the lower librational frequency is predicted too low by the HF potential and even lower by the HFK 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 three and more body terms are not included in the employed potentials. These terms have been shown to be attractive and account for about 10% of the stabilization energy of water trimers and tetramers [11]. A similar contribution in ice would bring the calculated sublimation energy within 5% of the experimental value and would cause a shortening of the unit cell parameters, thus bringing them to closer agreement with the experimental results.

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