Perturbation Calculations on the Hydrogen Bond in the Water Dimer for Different Proton Acceptor Orientations

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Using perturbation theory of intermolecular forces (including exchange effects) hydrogen-bond energies are calculated for a simple model representing the water dimer. Several orientations of the proton acceptor with respect to the O⋯O axis are considered and it is found that the optimum orientation depends sensitively on the oxygen lone-pair hybridization assumed. The main orientation-dependent energy term is found to be the classical electrostatic energy between the unperturbed molecules. The relation of the present results to the structures of the ices I and Ic, and to the results of recent SCF studies are discussed briefly.

Die Energien von Wasserstoffbindungen werden für ein einfaches Modell des dimeren Wassers mit Hilfe der Störungstheorie für intermolekulare Kräfte (mit Austauscheffekten) berechnet. Verschiedene Orientierungen des Protonen-Akzeptors bezüglich der O⋯O-Achse werden untersucht; man findet, daß die optimale Orientierung empfindlich von der angenommenen Hybridisierung des einsamen Elektronenpaars des Sauerstoffs abhängt. Der hauptsächliche, von der Orientierung abhängige Energieterm ist die klassische elektrostatische Energie zwischen den beiden ungestörten Molekülen. Die Beziehung der vorliegenden Ergebnisse zu den Strukturen von Eis I und Ic sowie zu den Ergebnissen kürzlicher SCF-Rechnungen wird kurz diskutiert.

1. Introduction

Ordinary ice has a tetrahedral structure, which implies that neighbouring molecules are oriented as shown in Fig. 1. However, it seems likely that this is due to the requirements of a three-dimensional array of four hydrogen bonds around each water molecule rather than to an intrinsic stability of water dimers adopting this orientation. In fact, there is experimental evidence that in linear hydrogen bonds O–H ⋯ O where the proton acceptor is bonded to a *single* donor only, orientations with the donor H atom lying near the acceptor twofold axis are at least as probable as ice-like orientations [1]. Very recently Morokuma and Pedersen (MP) [2], Kollman and Allen (KA) [3] and Diercksen (D) [4] have performed SCF-LCAO-MO calculations which lead to a similar conclusion[1].

Such calculations are beyond the facilities available to us and we therefore investigated whether it is possible to obtain similar information by a direct calculation of the interaction energy using a simple model described previously [6]. In this model the interacting molecules are represented by single-determinant wavefunctions, and the interaction energy is then evaluated including exchange and polarization effects.

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[1] For some recent CNDO/2 calculations on $(H_2O)_2$ which concentrate mainly on rotations of the donor see Ref. [5].

In the present paper we report the H-bond energies that were calculated in this way for water dimers adopting ice-like orientations, and for water dimers with arbitrary acceptor orientations. In all cases the $O-H \cdots O$ group was taken to be linear.

2. Method and Model

Our calculations are based on a perturbation theory of intermolecular forces which includes exchange effects [7]. In this theory the interaction energy is obtained as a sum of first and second-order energies which can be expressed in terms of the occupied and vacant MO's of the interacting molecules [8]. In the present work we employ the orbitals of a model system $O^d-H \cdots O^a$ for this purpose. This model, which is essentially the one of Tsubomura [9] and of Weissmann et al. [10], may be described as follows (see Fig. 1).

The donor O^d-H bond which lies along the z-axis is characterized by a bonding MO $b_1 = N(t_1 + kh)$ and its antibonding counterpart. Here h is a $1s$ orbital on H ($\zeta = 1$), k is an ionicity parameter and t_1 is a hybrid of Slater-type $2s$ and $2p$ AO's ($\zeta = 2.0$), having an s-character of 0.13. In addition to this orbital we assume that O^d carries three equivalent $2s - 2p$ hybrids which are orthogonal to b_1. Two of these are doubly occupied and represent oxygen lone pairs. The third hybrid (t_2) is taken to be singly occupied and simulates an additional O^d-H bond. More precisely, t_2 combines with a $1s$ orbital to form the O^d-H bond orbital b_2, which is doubly occupied. The potential due to the electrons in b_2 can be approximated by putting a single electron in t_2 (i.e. the H atom is assumed not to carry a net charge). Exchange effects involving b_2 are probably rather small and can be approximated by considering exchange with the t_2 part of b_2 only.

Analogously, the acceptor atom O^a carries two equivalent lone-pair hybrid orbitals whose s-character (χ_s) may be varied from 0 (pure p lone pairs) to 0.5 (sp lone pairs). In addition, O^a carries two equivalent hybrids which are orthogonal to the lone pair orbitals. These hybrids are singly occupied and simulate the two O^a-H bonds.

We have written an ALGOL 60 computer program which can be used to calculate the H-bond energy for linear configurations $O^d-H \cdots O^a$ and arbitrary orientations of the acceptor molecule with respect to the $O^d \cdots O^a$ axis. Calculations have been performed at a fixed O^d-H bond length of 2.0 a.u., and for $H \cdots O^a$ distances ($= r_{HO^a}$) from 2.0 to 4.0 a.u. in steps of 0.5 a.u. (1 a.u. = 0.5292 Å). Exact values for the two and three-centre integrals are given as input, along with a list
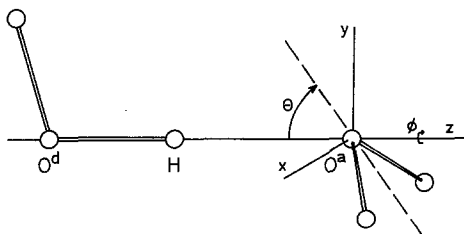

Fig. 1. Orientation of the water molecules in a linear dimer with $\theta = 54.73°$ and $\phi = 0°$

of the remaining parameters in the model, viz. k, χ_s and three Eulerian angles for the acceptor. The program was run on the Electrologica-X8 computer (addition 25 μsec, multiplication 52 μsec) of the Electronisch Rekencentrum of this University. The computations take about 8 min for each choice of the parameters.

The next step was to choose values for the parameters k and χ_s. LCAO-MO calculation on H_2O suggest that we should employ a k-value in the range 0.8–0.9, and that the lone-pair hybridization is intermediate between sp^2 and sp ($\chi_s = 0.33$ to 0.50) [11–13]. However, preliminary calculations showed that in our model little H-bond stability results if we use $k \geq 0.8$ and for this reason we have chosen $k = 0.7$. The choice of χ_s will be discussed below; most calculations were performed for $\chi_s = 0.25$ or $\chi_s = 0.33$.

3. Results

3a. The Water-Dimer Orientations for the Ices *I* and *Ic*

One of the orientations of the acceptor molecule that occur in ice is shown in Fig. 1. Here θ is the angle between the $O^d \cdots O^a$ axis and the two-fold axis of the acceptor and its value is 54.73°. If we take O^a to be sp^3-hybridized ($\chi_s = 0.25$) this implies that one of its lone pairs lies along the z-axis, but this will not be the case for other hybridizations. The other orientations that occur in ice I and Ic result if in Fig. 1 the acceptor is rotated around the z-axis by an angle $\phi = \pm 60°$, $\pm 120°$ or 180°. More precisely, ice I and Ic are composed of puckered layers in which all hydrogen bonds are "staggered" ($\phi = \pm 60°$, 180°). These layers are connected by staggered H bonds in Ic or by "eclipsed" H bonds ($\phi = 0°$, $\pm 120°$) in I. Thus the observed differences between I and Ic (viz. that Ic is metastable with respect to I, and that the eclipsed H bonds in I are about 0.01 Å shorter than the corresponding staggered H bonds in Ic [14]) arise primarily from differences in the interlayer H bonds and we therefore restrict our discussion to these differences.

The energies appropriate to the orientations discussed above and for $\chi_s = 0.25$ are shown in Fig. 2 as a function of the $H \cdots O^a$ distance. The eclipsed orientation $\phi = 0°$ is found to be the most stable at all distances, in agreement with calculations based on a simple dipole-dipole model of the interaction. In addition, this orientation has the shortest equilibrium distance viz. $r_{eq} = 2.10$ Å, whereas the corresponding value for ice is only 1.75 Å. Further evidence that r_{eq} in dimers is much longer than in ice is given at the end of Section 3b. The implication is, of course, that water molecules in a dimer may differ significantly from those in ice, so that our results are not strictly applicable to the situation in ice. The least stable orientation occurs for $\phi = 180°$ and here r_{eq} is about 0.085 Å longer than for $\phi = 0°$. In order to see what these results imply for the difference between the ices I and Ic we have to take an average over the appropriate orientations. If we make the usual assumption that the positions of the H atoms in I and Ic are disordered, then in I all three eclipsed orientations occur with equal weight, and likewise for Ic.

Now it turns out that at a fixed $H \cdots O^a$ distance the H-bond energy varies with ϕ in the following way: $E(\phi) = A - B \cos\phi + C \sin^2\phi$. This implies that at each r_{HO^a} the average energy for the eclipsed orientations exactly equals that of
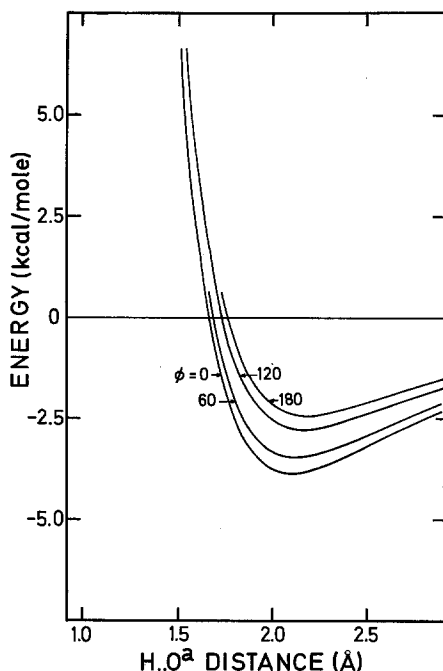
Fig. 2. Calculated H-bond energies as a function of the H $\cdots$ O^a distance for various ice-like orientations ($\theta = 54.73°$ and $\phi = 0, 60°, 120°, 180°$)

the staggered orientations. In fact we should use the average of *equilibrium* H-bond energies (r_{eq} being different for each ϕ), but this again leads to identical H-bond energies for I and Ic, and the average r_{eq} is also found to be the same. Thus, if I and Ic are totally disordered then the present model does not explain the observed differences between these structures.

These results essentially confirm Bjerrum's [15] early calculations which were based on a simple point-charge model (and which were therefore restricted to a single H $\cdots$ O^a distance). We agree with his observation that a small degree of ordering in the H-atom positions is sufficient to stabilize I with respect to Ic. In addition, this would introduce a small difference in interlayer H-bond length in the sense that is actually observed. However, it is difficult to estimate the precise degree of ordering that will take place since this depends on the interactions with the non-nearest neighbours which we have neglected.

3b. Search for the Optimum Acceptor Orientation in the Water Dimer

In our calculations on the optimum acceptor orientation we first considered a rotation of the acceptor around the x-axis, starting from the situation shown in Fig. 1. Using sp^3-hybridization on the acceptor ($\chi_s = 0.25$) we obtained the energies shown in curve DD of Fig. 3, which includes the SCF results of MP, KA and D for comparison. It is seen that there is no agreement in the precise
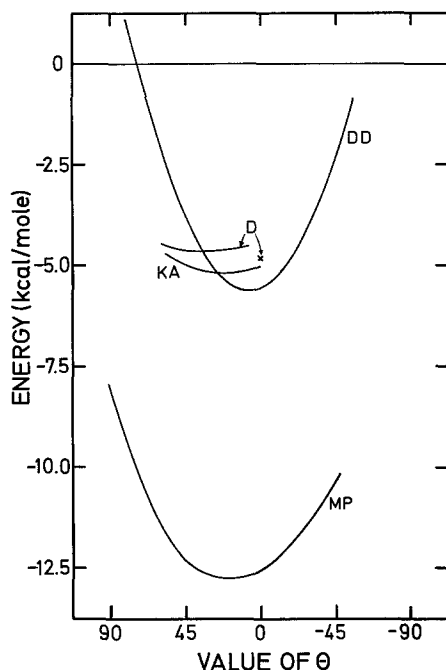
Fig. 3. Collected results for the variation of the H-bond energy with θ. The respective $H \cdots O^a$ distances are as follows: 1.70 Å (MP), 1.85 Å (DD), 2.04 Å (KA and D). In all cases $\phi = 0$, except for D where $\phi = 90°$. Curve DD was obtained with $\chi_s = 0.25$
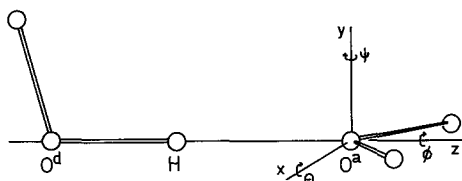

Fig. 4. Orientation of the water molecules for $\theta = \phi = \psi = 0°$

location of the minimum, but in all cases the minimum occurs for positive θ[2]. This is reasonable, since for the donor orientation used in these calculations the dipolar attraction between donor and acceptor has a maximum for $\theta = 33°$.

Next, starting from the orientation with $\theta = 0°$ (cf. Fig. 4) we rotated the acceptor through an angle ϕ about the z-axis. This gives H-bond energies which are slightly less favourable than for $\phi = 0°$, but the difference is not of practical importance (cf. Table 1). Similar results were obtained by MP, KA and D. We finally performed a rotation through an angle ψ around the y-axis, starting from the situation shown in Fig. 4. The results are shown in Table 1 and indicate a sharp decrease in H-bond stability if the acceptor lone pairs are rotated away from the

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[2] θ measures the angle between the z-axis and the acceptor twofold axis in the sense from $+y$ to $+z$ (cf. Fig. 1).

Table 1. *The variation of the H-bond energy with rotations about z and y (cf. Fig. 4)* [a]

r_{HO} [a]		MP	KA	D	Present work [b]
ϕ	ψ	1.70 Å	2.04 Å	2.04 Å	2.12 Å
90°	0°	−12.08	−4.87	−4.82	−5.33
45°	0°	−12.38	—	—	−5.36
0°	0°	−12.59	−5.04	−4.56	−5.39
0°	14°27′	—	—	—	−4.95
0°	31°1′	—	—	—	−3.48

[a] Energies in kcal/mole.
[b] Results for $\chi_s = 0.25$.

donor H atom. As before, these results agree qualitatively with what one expects on the basis of the dipolar-attraction term alone: the rotation about z does not affect this attraction at all and a rotation of 45° about y decreases the dipolar attraction by about 30%.

Thus we conclude that the optimum acceptor orientation for $\chi_s = 0.25$ is near the one shown in Fig. 4. Starting from this orientation the H-bond energy decreases by a rotation around the z or y-axis, the decrease being almost negligible for rotation around z and very large for rotation around y.

Realizing that the optimum acceptor orientation may depend on the parameters in our model we investigated the θ-dependence of the H-bond energy for some additional χ_s-values. The most striking feature in the results was that, going from $\chi_s = 0.25$ to $\chi_s = 0.50$ there is a large change in optimum orientation which is accompanied by a marked destabilization[3] of the H-bond (cf. Fig. 5). Now, according to Bader [12], χ_s ought to be larger than 0.25 and perhaps as large as 0.45–0.50. Likewise, the localized lone-pair orbitals obtained by Ellison and Shull [13] have $\chi_s = 0.46$. However, such values would hardly give any H-bond stability in our model and they yield a θ-dependence which disagrees with the results of KA and D (cf. Fig. 3). Since we do not *a priori* know the χ_s-value that we should use in our model we clearly cannot predict the optimum θ-value. On the other hand, if we assume the θ-dependence obtained by KA and D to be correct then this can be used to determine the χ_s-value which we should employ.

We intend to use the present model for calculating the H-bond energy for a variety of H-bonding systems. This can be done if we choose parameter-values which reproduce the energies of a few systems for which the energy is known with some accuracy. The present calculations on $(H_2O)_2$ were partly undertaken with this object in mind. Guided by the results described above, our final choice for an acceptor H_2O molecule was to use $\chi_s = \frac{1}{3}$. This is a compromise, and in particular the θ-dependence of the energy for this χ_s-value (cf. Fig. 5) is not in good agreement with the SCF results of KA and D (cf. Fig. 3). (The ϕ and ψ-dependence is very similar to that reported in Table 1.)[4]

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[3] Incidentally, these results confirm our previous result that H bonds are destabilized by increasing the acceptor lone-pair s-character [16].

[4] Klessinger [17] recently obtained a lone pair s-character of 0.33 in SCGF calculations on H_2O.
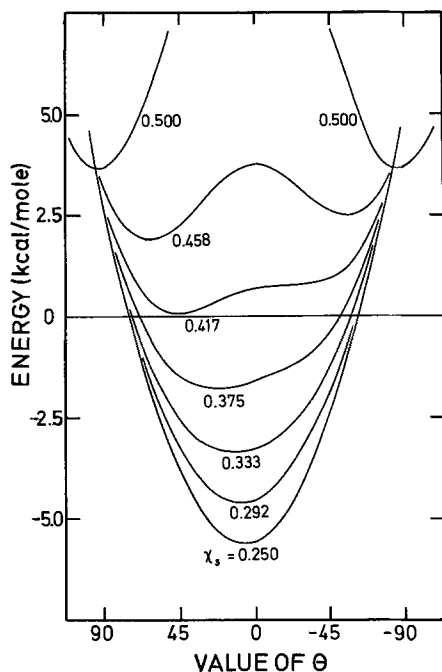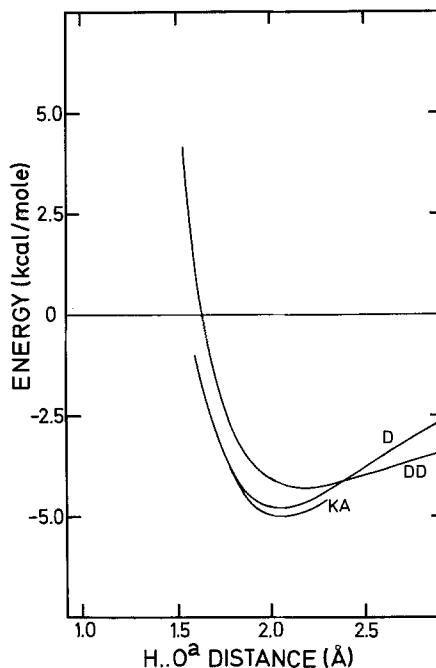
Fig. 5.

Fig. 6.

Fig. 5. The variation of the H-bond energy with θ for different values of the proton-acceptor lone-pair s-character ($r_{\text{HO}}a = 1.85$ Å)

Fig. 6. Collected results for the H-bond energy as a function of r_{HO^a} in water dimers adopting optimum or near-optimum orientations

We finally obtained the H-bond energy for the water dimer as a function of r_{HO^a} for the orientation of minimum energy (i.e. $\theta = 15°$ in Fig. 1) and using $\chi_s = \frac{1}{3}$. The results are shown in Fig. 6 together with those of KA and D. The minimum energy equals 4.3 kcal/mole and occurs for $r_{\text{HO}^a} = 2.16$ Å. Although these values are rather different from those pertaining to the situation in ice, we believe that they represent the situation in the water dimer reasonably well since they agree with the SCF results of KA and D ($r_{\text{OH}^a} = 2.04$ Å, energy = 4.84 [D] and 5.26 [KA] kcal/mole) [5].

4. Final Comments

The contributions to the energy of a H bond between two water molecules were estimated some time ago by Coulson [18] and a few years later by Weissmann et al. [10]. Their results are shown in Table 2, along with the results that were obtained in the present work. The latter values are likely to be more reliable

[5] In fact, almost exact agreement with KA and D can be obtained by taking $k \simeq 0.66$ in our model. However, this corresponds to a very polar OH bond, and a more realistic explanation for the discrepancy between our results and those of KA and D is our neglect of the net negative charge on the acceptor oxygen.

Table 2. *The contributions to the H-bond energy in the water dimer* [a]

r_{HO}[a]	Coulson 1.75 Å	Weissmann 1.80 Å	Present work 1.85 Å	Present work 2.12 Å
electrostatic	−6	−10.6	−12.0	−7.2
exchange repulsion	+8.4	+7.8	+13.1	+5.0
dispersion	−3	—	−1.7	−1.0
delocalization	−8	−9.6	−2.9[b]	−1.1[b]
	−8.6	−12.4	−3.4	−4.3

[a] Energies in kcal/mole. The values in the last two columns are for $\chi_s = \frac{1}{3}$.

[b] in our calculations the delocalization energy is the sum of an induction energy (including a second-order exchange term) and a charge-transfer term.

since we used accurate values for the 3-centre integrals that occur in the problem[6]. They confirm the previous conclusions that the H-bond energy is the sum of some large terms which nearly cancel and a few smaller terms which yield a net attraction.

We have shown that in our model the dipole-dipole contribution to the electrostatic energy is often the main orientation-dependent term. Sometimes, however, the H-bond energy follows the *total* electrostatic energy, rather than its dipole-dipole component. This occurs, for example, in the curves for large lone-pair *s*-character in Fig. 5, the reason for this behaviour being that dipole-quadrupole terms as well as penetration terms [6] give rise to a maximum attraction if an acceptor lone pair points directly to the donor H atom. It should be emphasized, however, that except for the electrostatic energy there are no terms in the H-bond energy that markedly depend on orientation.

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[6] For example, our results in Table 2 for the exchange repulsion are larger than the other values quoted. Of these, Coulson's value is an estimate not based on calculation. Weissmann's value was obtained using approximate 3-center integrals, which causes the repulsion to be underestimated (cf. Ref. [6]).

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