HYDROGEN-BOND ENERGY NONADDITIVITY IN WATER *

D. HANKINS, J. W. MOSKOWITZ
Chemistry Department, New York University
Washington Square College, New York, New York 10003, USA

and

F. H. STILLINGER
Bell Telephone Laboratories Incorporated, Murray Hill, New Jersey 07974, USA

Extended double zeta Gaussian basis SCF LCAO MO calculations have been performed on various configurations of the linearly hydrogen-bonded water dimer and two of the triplet clusters which occur in both cubic and hexagonal ices. A hydrogen bond energy of −4.72 kcal/mole was found for the dimer in the most favorable configuration. We find that triplets with sequential hydrogen bonds significantly stabilize condensed phases which incorporate them, and they exert a strong compressive effect to reduce nearest-neighbor distances.

Chemists have long been interested in understanding the nature and consequences of hydrogen bond formation in the various physical states of water. The value of accurate quantum-mechanical computation of electron cloud deformations in molecular clusters, and of at least two and three molecule potential energy surfaces, has long been recognized despite the difficulty and expense of implementation. Since these computations have not been feasible in the past, approximate calculations based on point-charge and multipole-expansion models have been carried out to examine the electrostatic effects of successive shells of neighbors upon a central molecule, and to evaluate the component energies which contribute to the total hydrogen-bond stabilization. The early wave-mechanical calculations adopted valence bond and SCF molecular orbital approaches and were applied only to incomplete fragments of the hydrogen-bonded system. A summary of these efforts can be found in the review by Eisenberg and Kauzmann [1].

Perhaps the most interesting of the current questions, and still a very difficult one to answer completely, concerns the origin and magnitude of possible pairwise nonadditivity of cluster stabilization energy and its dependence upon distances and orientations. If $E(1,2)$ and $E(1,2,3)$ are the

total energies respectively of a pair (dimer) and a triplet cluster (trimer), and if $E(1)$ is the energy of an isolated molecule, then the two-molecule and three-molecule stabilization energies are given by:

$$S(1,2) = E(1,2) - 2E(1),$$
$$S(1,2,3) = E(1,2,3) - 3E(1).$$

We may now define the triplet cluster pairwise nonadditivity $P(1,2,3)$ as follows:

$$P(1,2,3) = S(1,2,3) - S(1,2) - S(1,3) - S(2,3).$$

In several of the theories of liquid water [2] it is conjectured that formation of hydrogen bonds can be enhanced by this pairwise nonadditivity, a phenomenon often referred to as a "cooperative effect". Weissmann et al. [3] have examined this question for the four possible ice-lattice orientations of a neighboring hydrogen bond relative to a given one. Their calculation used wave functions which included only the four electrons directly involved in the hydrogen-bonded system, and it corresponds to a first-order perturbation on the stabilization of the one bond due to the other. As such it does not account for any mutual deformation that would result from their interaction; in fact, no significant net cooperative effect was found, although useful information was obtained about the relative magnitudes of the effect for the four configurations studied. The present program was undertaken primarily to investi-
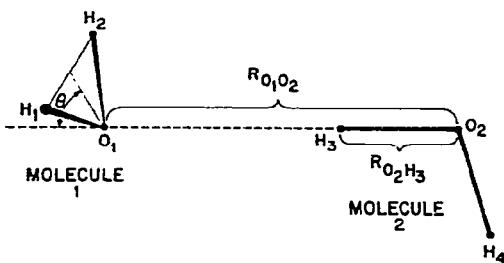
Fig. 1. Linear water dimer. Nuclei O_1, H_3, O_2, and H_4 lie within the symmetry plane of the configuration. In this and the following figures the individual monomer geometries were fixed at their calculated minimum, ∢ HOH = 106°, R_{OH} = 0.945 Å.

gate these effects in greater depth.

The first ab initio molecular orbital studies of hydrogen bond formation, in which all electrons were included and all integrals evaluated exactly, were performed by Morokuma and Pederson [4]. Utilizing a limited Gaussian basis they investigated the interaction energy of two nomomers in several configurations, and they found the most stable structure involved a linear hydrogen bond with energy $S(1,2) = -12.6$ kcal/mole. More recently the dimer computation has been repeated by Kollman and Allen [5] in a larger Gaussian basis ($S(1,2) = -5.3$ kcal/mole), by Morokuma and Winick [6] in a minimal Slater basis ($S(1,2) = -6.55$ kcal/mole), and by Del Bene and Pople [7] ($S(1,2) = -6.09$ kcal/mole).

In this note we report the results of far more accurate SCF calculations on several configurations of dimers and trimers in a basis of contracted Gaussian functions. A modified version of the large contracted water basis of Neumann and Moskowitz [8], a basis of 30 functions derived from 45 primitives, was employed for each monomer in the clusters; i.e., 60 functions for the dimer and 90 functions for the trimer. The basis included d-functions on the oxygens, and p-functions on the hydrogens in order to allow for adequate polarization of the molecular charge distribution.

Fig. 1 shows the energetically preferred dimer configuration, with essentially linear approach and a plane of symmetry [4-7]. We have carried out an extensive search on this configuration to determine the minimum energy geometry and to obtain salient features of the potential surface near this minimum. The parameters varied were θ, $R_{O_1O_2}$, and $R_{O_2H_3}$, and a minimum was found at $\theta = 40°$ and $R_{O_1O_2} = 3.00$ Å, corresponding to

Table 1
Stabilization energies of water dimer for geometries considered [a]

θ [b]	$R_{O_1O_2}$ [b]	$R_{O_2H_3}$ [b]	$S(1,2)$ [c]
25°	3.00	0.945	-4.63
40°	3.00	0.945	-4.72
48°	3.00	0.945	-4.70
40°	2.88	0.945	-4.60
40°	2.94	0.945	-4.69
40°	3.00	0.952	-4.70
40°	3.00	0.960	-4.62

a) The monomer geometries were fixed at the calculated minimum (R_{OH} = 0.945 Å, ∢ HOH = 106°). All distances are in Å, and all energies in kcal/mole.
b) See fig. 1.
c) See text for definitions.

a stabilization energy $S(1,2) = -4.72$ kcal/mole. This energy was computed relative to the value for the monomer at the calculated minimum geometry of ∢ HOH = 106° and R_{OH} = 0.945 Å (experimentally, ∢ HOH = 104.5°, R_{OH} = 0.958 Å [1]). No stretch of the O_2H_3 distance was found although the potential curve for this variation was considerably flattened. Some of the results of this investigation are reported in table 1.

Following this introductory exercise, we initiated a much more difficult series of calculations on some of the triplet configurations which occur in the hexagonal and cubic ice lattices. In view of the strong persistence of tetrahedral coordination in water upon melting [9], we felt that these triplets were relevant to liquid-phase studies as well. Five geometries of the first triplet (configuration I, fig. 2) and three geometries of the second (configuration II, fig. 3) have been examined thus far. The results are given in table 2. Again the energies are computed relative to the value for the monomer at its minimum-energy geometry.

The last column of table 2 indicates a definite "cooperative effect" and shows that $P(1,2,3)$ varies strongly with triplet geometry. So far as distance variation is concerned, triplet I experiences a mild three-body expansion effect near 2.76 Å. However the sequential hydrogen-bond triplet II exhibits a stronger three-body compression. Table 1 indicates that nearest-neighbor forces by themselves would give an O-O spacing in hexagonal or cubic ice around 3.00 Å; the aggregate effect of the $P(1,2,3)$ energies for these crystals ought to be dominated by the strong compressions of the four-times-more common sequential triplets (non-nearest-neighbor interactions should enhance that compression
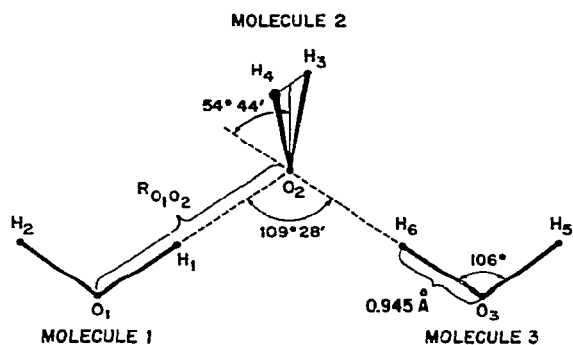
Fig. 2. Trimer configuration I. Molecules 1 and 3 lie within the same plane, which also includes O_2. Molecule 2 is perpendicular to that plane. Nuclei H_1 and H_6 approach O_2 along ideal tetrahedral directions, and distances $R_{O_1O_2}$ and $R_{O_2O_3}$ are kept equal as both vary.
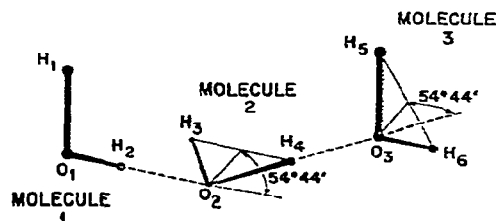
Fig. 3. Trimer configuration II. This configuration consists precisely of two dimers in sequence (each with $\theta = -54°44'$, see fig. 1). Molecules 1 and 3 lie in parallel planes, and molecule 2 is perpendicular to those planes. Distances $R_{O_1O_2}$ and $R_{O_2O_3}$ are varied together.

Table 2
Total stabilization energies and pair-wise nonadditivities of trimer for geometries considered[a]

Configuration I[b]	$R_{O_1O_2} = R_{O_2O_3}$	$S(1,2,3)$[c]	$S(1,2) = S(2,3)$[c]	$S(1,3)$[c]	$P(1,2,3)$[c]
	2.76	-3.14	-2.40	1.31	0.346
	2.90	-5.30	-3.24	1.08	0.109
	3.00	-5.96	-3.43	0.95	-0.049
	3.15	-6.12	-3.36	0.79	-0.184
	3.39	-5.46	-2.87	0.61	-0.317
Configuration II[d]					
	2.76	-6.77	-2.40	-0.61	-1.363
	3.00	-8.29	-3.43	-0.43	-0.994
	3.15	-7.96	-3.36	-0.36	-0.863

a) The monomer geometries were fixed at the calculated minimum ($R_{OH} = 0.945$ Å, $\sphericalangle$ HOH $= 106°$). All distances are in Å, and all energies in kcal/mole.
b) See fig. 2.
c) See text for definitions.
d) See fig. 3.

slightly). Consequently we conclude that the observed ice distance (2.76 Å) is significantly smaller than the most favorable distance that obtains for two real water molecules, if this latter could actually be observed in the vapor phase. Recent work by Bolander et al. [10] seems consistent with this conclusion.

Specification of the interaction energy for various sets of water molecules constitutes vital input for the fundamental statistical mechanics of liquid water and aqueous solutions. In particular, reasonably accurate calculations of the type reported here can be used to assess proposed water pair potentials such as Stockmayer's [11], and Rowlinson's [12]. At a more sophisticated level, nonadditivity effects (i.e. $P(1,2,3)$ and its four,

five, ... molecule analogs) may be incorporated into the theory via a variationally defined "effective pair potential" [13], and the result used for reliable Monte Carlo or molecular dynamics simulations of local liquid structure.

A more detailed and extensive report on this program will be offered at its completion. At that time we will estimate the effects of neglected electron correlation, make comparisons with the findings of less accurate computations, and provide a more penetrating account of the chemical and statistical-mechanical implications of the results.

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