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A Theory of Anomalous Water

A cyclic, symmetrically bonded form of water and related species have a stability comparable to their liquids.

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In this article we attempt to provide an independent and reasonably quantitative theoretical reference point for assaying the likelihood that the new form of water originally reported by Deryagin *et al.* (*1, 2*) exists, with the properties suggested by Deryagin and by the recent spectroscopic measurements of Lippincott *et al.* (*3*). The stability, bonding, geometry, spectroscopy, formation, viscosity, and high- and low-temperature behavior of this substance are discussed on the basis of many-electron quantum mechanical calculations.

Computational Methods

We have made quantum mechanical calculations using a combination of *ab initio* and semiempirical, many-electron, molecular orbital methods to obtain electronic wave functions and predict properties for various models of anomalous water.

During the last half dozen years a great deal of progress has been made in developing practical techniques for constructing *ab initio* polyatomic wave functions (*4*) and in further elucidating the theory (*5*). When the finite basis set (the Roothaan) scheme is used to expand the molecular orbitals and when an adequate basis set is used (as was done in the studies discussed here), it proves possible to obtain molecular geometries accurate to within about 2 percent and expectation values such as dipole moments, quadrupole coupling constants, and ionization potentials accurate to within 5 to 25 percent, and to give a very good account of the charge distribution. On the other hand, the well-known instantaneous electron-electron correlation error, inherent in the doubly occupied Hartree-Fock approximation, in general leads to a poor estimate of the absolute binding energy, and this remains an uncertainty in our anomalous-water wave functions. However, there is considerable evidence that relative stabilities among closed-shell species are reasonably well represented by highly accurate molecular orbital calculations (*6–8*) (see Tables 1 and 2).

A development paralleling that of the *ab initio* approach has taken place for semiempirical molecular orbital methods. Two classes may be distinguished: the one-electron schemes (for example, the Extended Hückel Theory), and schemes including two-electron terms [for example, the CNDO and INDO schemes of Pople *et al.* (*9*)]. The Extended Hückel Theory has been tested by us (*10*) and by others (*11*) on hydrogen-bonded systems and related bonding problems and has been found to be totally inadequate for ascertaining stabilities and bond distances, thus useless for our present purposes. In the semiempirical schemes containing two-electron terms, zero differential overlap is assumed; this results in omission of most of the difficult-to-evaluate, many-center integrals and causes an unbalance between one- and two-electron terms (*12*). The schemes containing two-electron terms are generally more accurate than the one-electron techniques, but, by themselves, they have not yet evolved to a state which permits a priori quantitative predictions (in contrast to qualitative rationalizations). Although in principle these methods can be regarded as approximations to the *ab initio* approach, most of the applications reported in the literature have not been coordinated with corresponding *ab initio* calculations. In the calculations reported here, *ab initio* wave functions provide our fundamental reference and give us increased confidence in the significance of our results. The specific method chosen was CNDO/2 with Pople's original parameterization. In addition to the approximations noted above, this method (i) equates the energy of *s* and *p* orbitals in many integrals, thereby causing great overestimation of binding energies for wave functions containing ionic contributions (positive or negative); (ii) results in underestimation (from 0 to 10 percent) of internuclear separations (this is a well-known deviation due largely to the use of single-term exponential atomic orbitals); (iii) builds in experimental data from atomic spectra; and (iv) has been found to possess (*13*) a considerably greater ability to discriminate between different structures made from the same atoms than between structures containing different types of atoms (*14*).

Although it should be apparent from our discussion that contemporary semiempirical methods have many limitations, the nature of our present problem is such that CNDO/2 is remarkably well suited for elucidating the electronic structure. Many theoretical features required for the description of ordinary hydrogen bonding

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have parallels in anomalous water, and the comparisons of Table 2 for hydrogen-bonded dimers show CNDO/2 capable of yielding quantitatively significant results. CNDO/2-generated potential energy surfaces for cyclic tetramers of water and of hydrogen fluoride with symmetrically placed hydrogen atoms are also qualitatively similar to preliminary *ab initio* valence bond calculations recently carried out in this laboratory. We may conclude that, for systems involving various associations of water molecules, CNDO/2 is acting as a successful interpolation and extrapolation scheme.

On the other hand, CNDO/2-predicted binding energies for negative and positive ions are very much too large, as may be seen from the values of Table 1, the error being so large and variable that the numbers generated are not useful. As discussed in the next section, the possibility that negative ions are present in anomalous water is eliminated on physical grounds. Likewise, CNDO/2 computations on positive ions have not been used in determining the properties of anomalous water or of related species.

Stability and Bonding

Before describing details, we will summarize the results of our calculations. The principal structural unit of anomalous water is a symmetrical O-H-O bond with a "strength" very close to that of the hydrogen bond in liquid water (~ 5 kcal) and O···O separation of 2.3 to 2.40 angstroms. These structural units are combined into sheets of hexagons, and the sheets in turn are interconnected by O-H-O bonds of slightly less strength and 15 percent greater length to form a neutral three-dimensional lattice. All the oxygens are four-coordinate. Three types of three-dimensional lattice arrays are suggested, all of which possess essentially the same internal energy (Fig. 1). In the parallel-stacked, type A lattice the primitive-unit-cell dimension coincides with the alternate-layer repeat distance of 5.2 to 5.4 angstroms. Figure 2 is a photograph of a 30-water-molecule model of the type A lattice, the large balls representing oxygen atoms and the small ones hydrogens. The staggered sheets of the type B lattice repeat every fourth layer (7.5 to 7.8 angstroms) and have a minimum repeat distance (primitive unit cell) of 3.3 to 3.6 angstroms. Type C lattices are double sheets of 2.6- to 2.7-angstrom separation weakly bonded to other double sheets 2.6 to 2.8 angstroms distant—an arrangement that gives a repeat distance on the order of 5.2 to 5.6 angstroms. The viscosity, density, peculiarities of formation, and high- and low-temperature behavior, as well as the available nuclear magnetic resonance, infrared, Raman, and optical excitation spectra, are all compatible with the electronic wave functions we have computed.

Calculations for a wide variety of molecular conformations show that, when hydrogen atoms are symmetrically located between oxygen atoms, a hexagonal placement of the oxygen atoms is the most stable arrangement. The properties and consequences of this conformation are treated here. Detailed analysis of other possible geometries is given in the next section. In Tables 3A to 3F are presented data on a cyclic hexamer in which the O···O separation, the external O-H distance, and the internal-to-external H-O-H angle θ have all been varied. If we choose θ to be 120 degrees (sp^2 around O) (see Table 3A), the atomic arrangement can be infinitely repeated and, for this case, we obtain the moderate stabilization energy, per O-H-O bond, of 8.46 kcal/mole (*15*). On the other hand, we see that a greater bond energy is obtained for $\theta = 109.8$ degrees. This angular result, along with the possibility of an asymmetric hydrogen bond, is a very significant matter, and it is dealt with below in the section on formation. For both cases the O···O separation is predicted to be 2.32 angstroms, and the external O-H distance, 1.03 angstroms. This latter distance is almost identical to the equilibrium bond length computed by the CNDO/2 method for an isolated H_2O molecule. For two rings (naphthalene-like) the O···O separation again shows a minimum energy for 2.32 angstroms, but the bond energy is reduced to 5.61 kcal/mole as a result of the additional electron repulsion introduced by the shared bond of the two naphthalene rings—an effect present for all systems larger than one hexagon. The addition of more rings can follow either of two patterns: (i) a linear series of rings in a row, or (ii) clusters of rings, where the number of internal bonds is at a maximum. Extrapolation from

Table 1. Dissociation energies (in kilocalories) from experimental data and *ab initio* and CNDO/2 calculations.*

Process	Experimental	*Ab initio*	CNDO/2
$H + F \rightarrow HF$	141	71	407
$2H + O \rightarrow H_2O$	232	116	751
$3H + N \rightarrow NH_3$	298	162	1102
$2H_2O \rightarrow (H_2O)_2$	6 ± 3	5.3	5.9 (8.4)†
$2NH_3 \rightarrow (NH_3)_2$	Not known	2.83	3.7
$2HF \rightarrow (HF)_2$	6.7, 7.9	4.4	6.6 (9.0)†
$HF + F^- \rightarrow FHF^-$	58.5	73	102.7
$6HF \rightarrow (HF)_6$	40.2		100.0
$H^+ + H_2O \rightarrow H_3O^+$	184 ± 7	181	248.4
$H_2O + H_3O^+ \rightarrow H_5O_2^+$	21.9	37	52

* Experimental and CNDO values for $H + F \rightarrow HF$, $2H + O \rightarrow H_2O$, and $3H + N \rightarrow NH_3$, from Sichel and Whitehead (*45*); *ab initio* dissociation energies of HF, H_2O, and NH_3, from Fink (*46*); *ab initio* results on dimer, from Kollman and Allen (*6*); CNDO dimer results, from Kollman and Allen (*13*); $(HF)_2$ and $(HF)_6$ experimental data, from Frank and Meyer (*47*); experimental bond lengths in $(H_2O)_2$ and $(HF)_2$ estimated from crystal values in Pimentel and McClellan (*48*); $H_5O_2^+$ distance estimated from other symmetric O···O hydrogen bonds; $(H_2O)_2$ experimental data, from Gebbie *et al.* (*49*); FHF^- experimental and theoretical results, from Erdahl (*50*); and H_3O^+ and $H_5O_2^+$ formation energies, from De Pas *et al.* (*51*). † The first value is obtained by means of experimental monomer geometries; the value in parentheses is obtained by means of CNDO calculated monomer geometries. The relative stability at the two geometries is preserved.

Table 2. Bond lengths (in angstroms) in hydrogen bond formation, from experienced data and *ab initio* and CNDO/2 calculations.*

System	Experiment	*Ab initio*	CNDO/2
$(H_2O)_2$ O···O distance	2.8–2.9	3.0	2.53
$(HF)_2$ F···F distance	2.6–2.7	2.88	2.45
FHF^- F···F distance	2.25	2.30	2.26
$(HF)_6$ F···F distance	2.53		2.25
$H_5O_2^+$ O···O distance	2.4–2.5	2.387	2.41

* *Ab initio* results on dimer, from Kollman and Allen (*6*); CNDO dimer results, fom Kollman and Allen (*13*); $(HF)_6$ experimental data, from Jansen and Bartell (*38*); experimental bond lengths in $(H_2O)_2$ and $(HF)_2$ estimated from crystal values in Pimentel and McClellan (*48*); $H_5O_2^+$ distance estimated from other symmetric O···O hydrogen bonds [see Hamilton and Ibers (*48*)].

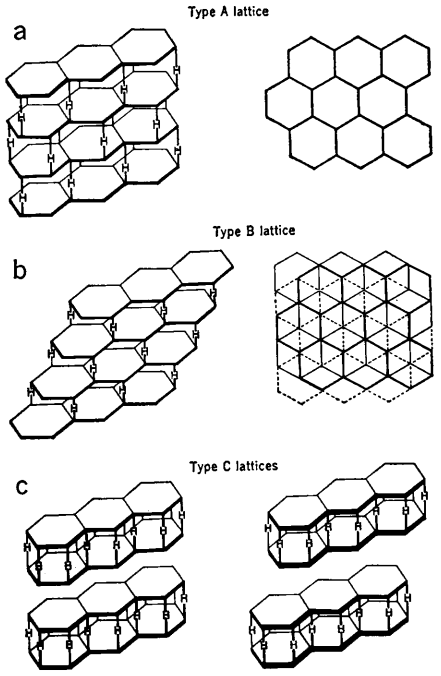

Fig. 1. The three types of anomalous water lattices. (a) Type A lattice; (b) type B lattice; (c) type C lattice.

the results for two to five rings in a row (Table 3B) gives an infinite sequence stability of about 4 kcal/mole per bond. A sheet of clustered rings (Table 3C) leads to a very small stabilization. External and internal bonds have not been distinguished in these two calculations, but separate optimization for the two-bond environments (Tables 3C and 3D) shows very little increase in stability. In all these calculations a neutral structure has been maintained by placing one hydrogen per ring (for all systems larger than a single ring) above or below the plane. The relatively small per-bond stabilization energy is due to the two-dimensional nature of the sheets, and, in fact, when the full three-dimensional lattice is realized, formation of a cube of material is more likely than formation of a lattice one ring thick. (The low stability of the cluster relative to the linear array is due to the repulsion between the positive charge on the short perpendicular O-H bond and the positive charge on the symmetric hydrogens in the plane. There are more symmetric hydrogens close to a perpendicular O-H bond for the ring clusters than for rings joined in series.) Optimization of the bond length for the internal perpendicular O-H bond leads to the expected small lengthening of the bond and to a very small increase in stabilization.

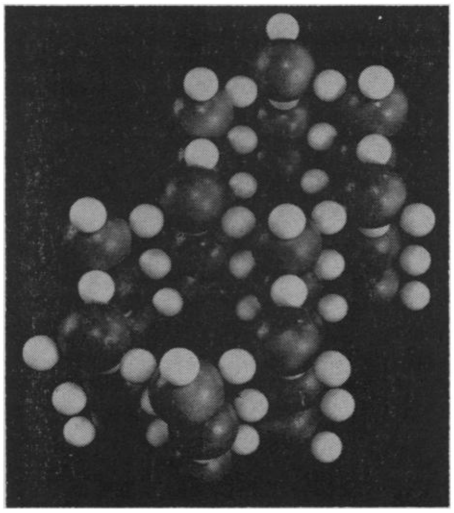

Fig. 2. Styrofoam model of anomalous water.

Interconnection between the two-dimensional arrays can be made in the three ways displayed in Fig. 3. Table 4 shows that the energy lowering for each of these arrangements is striking. The calculations also illustrate (Table 4, D and E) that a lattice built from clusters of hexagons has essentially the same energy as one built from rows of hexagons. Several factors account for the relatively high stability of the three-dimensional lattice: (i) new bonds are created; (ii) the repulsion of the perpendicular O-H bonds is partly relieved; (iii) there is a redistribution of charge throughout the lattice that enables the oxygen to achieve its favorable four-coordinate environment and makes possible a three-dimensional network of the especially stable symmetric rings; (iv) the large charge separation between oxygen and hydrogen which is characteristic of the symmetric hydrogen bond (see the section on spectral assignments below, and Table 5) contributes an important Madelung stabilization term. This term favors a three-dimensional block of material more than is revealed by the limited size of systems accessible to direct computation.

The average bond energy for the three schematic lattice models (Fig. 3) varies from 7 to 9 kcal/mole. This value is influenced to some extent by an edge effect arising from the position assumed for the perpendicular O-H bond in the naphthalene-like reference plate (Tables 3B and 4F), and our best overall estimate is that all of the interconnection schemes will result in almost the same total energy, with an average per-bond energy relative to separated H_2O molecules of about 9 kcal/mole (*16*). In addition to these three modes of interconnection, two sets of the rings of Fig. 3a can interact weakly, and this interaction is evaluated by the four-ring calculation of Table 4G for the case in which perpendicular O-H bonds are pointed away from one another. The resulting very small attraction amounts to about 0.05 kcal per bond and is not unlike a very weak conventional hydrogen bond. Ring-to-ring separation distances for this situation and the three interconnection schemes of Fig. 3 are also a result of the calculations and are listed in Table 4. The lattice precursors modeled in Fig. 3 and listed in Table 4 lead directly to the three three-dimensional layer structures of Fig. 1. The structures of Figs. 3b and 3c become the infinite type A and type B lattices, respectively, while the structure of Fig. 3a leads to any of the several repeat patterns available to the double layers of the type C lattices. As noted above, the CNDO/2 method frequent-

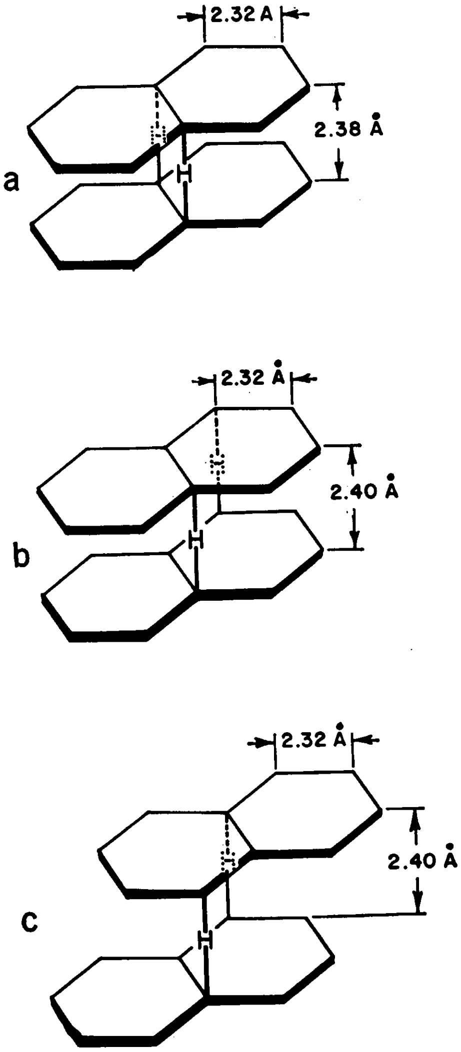

Fig. 3. Three modes of connection between layers.

ly leads to underestimation of internuclear separations by as much as 10 percent—particularly for longer bond distances (see the first two entries of Table 2). Thus, for the alternate-layer elementary repeat distance of the type A lattice we predict a value of 5.2 to 5.4 angstroms. Predicted spacings for the type B infinite lattice are a layer repeat length (three intersheet distances) of 7.5 to 7.8 angstroms with a primitive-unit-cell dimension of 3.5 $\cong [(2.3)^2 + (2.6)^2]^{1/2}$. Type C lattices should have a repeat distance of 5.2 to 5.6 angstroms. Another important consequence of the computed $O \cdots O$ internuclear separation and layer spacings for the three lattice types is a computed density of approximately 1.6 g/cm^3. As discussed below, we believe that anomalous water is randomly oriented microcrystallites of one of the three-dimensional lattices, and this hypothesis is compatible with the measured density value of 1.4 g/cm^3.

Determination of relative and absolute binding energies for the O-H-O unit is obviously a central question, and to answer it we must consider a liquid-water reference. In view of recent studies (*17*, *18*), it appears that the simplest and most logical reference structure is the tetrahedrally bonded, four-coordinate geometry of the well-known ice I structure. The energy for a pentamer with this structure is 8.32 kcal/mole ($O \cdots O$ distance, 2.53 angstroms). However, edge effects limit our ability to estimate the infinite-structure energy from the energy of the pentamer, and we have therefore obtained energies for two other model structures. One of these is the linear chain of tetrahedrally hybridized hydrogen-bonded waters for which it is easy to find the infinite-length energy limit (10.4 kcal/mole), and the other is a cyclic hexamer with asymmetric hydrogen bonds (10.8 kcal/mole). Both of these models correspond to unusually favorable configurations in the normal liquid and thus provide an upper limit to its internal energy. The three model calculations considered together lead us to a CNDO/2 normal liquid reference energy of 8 to 11 kcal/H-bond. Comparison of this range of values with the value 9 kcal obtained for the anomalous water bonds leads us to a conclusion unanticipated by other investigators and constitutes the single most important result of our calculations: the internal energy of anomalous water is very close to that of liquid water. The appropriate experimental value for the liquid relative to our model is approximately 5 kcal/mole (*18*), and thus in CNDO/2 calculations the binding energy is overestimated by 3 to 6 kcal. Examination of the HF and H_2O dimer binding energies in Table 1 (using CNDO-calculated monomer geometries) shows that this error fits in with the deviations found for these systems, and the anomalous water O-H-O bond is therefore expected to be 3 to 6 kcal/mole (*19*). Separate values for in-plane and between-plane O-H-O bond energies would be quite useful, but obtaining these proves more difficult than might initially appear to be the case, since there is a redistribution of charge throughout all four rings when two pairs of rings are connected. However, calculations discussed below show that considerably more energy is lost when in-plane rings are broken open than when planes are pulled apart, and we may definitely conclude that the between-planes bond is less strong than the in-plane bond. Our computations also show between-plane bonds to be about 15 percent longer than in-plane bonds.

Table 3A. Rings of planar anomalous water. Hexagon [symmetric internal hydrogens, external hydrogens ($r = 1.03$ Å) may be in or out of plane].*

R ($O \cdots O$) (Å)	r(O-H ext) (Å)	$\theta(H_{int}\text{-}O\text{-}H_{ext})$ (deg)	E (a.u.)
2.225	1.0	120	−119.3814
2.225	1.2	120	−119.1332
2.225	1.3	120	−118.8529
2.1	1.05	120	−119.2005
2.3	1.15	120	−119.2818
2.5	1.25	120	−118.9311
2.15	1.075	120	−119.2769
2.20	1.10	120	−119.3125
2.25	1.125	120	−119.3125
2.225	1.1125	120	−119.3165
2.225	1.05	120	−119.3841
2.225	.95	120	−119.3108
2.225	1.025	120	−119.3901
2.2	1.03	120	−119.3668
2.3	1.03	120	−119.4253
2.4	1.03	120	−119.4057
2.2	1.03	105	−119.3638
2.3	1.03	105	−119.4340
2.4	1.03	105	−119.4240
2.2	1.03	112	−119.3736
2.3	1.03	112	−119.4383
2.4	1.03	112	−119.4238

* Minimum energy at $R = 2.32$ Å, $\theta = 109.8°$, alternating (staggered) external hydrogens, $E = 10.0$ kcal/mole; at $\theta = 120°$, $E = 8.46$ kcal/mole. All stabilizations calculated relative to isolated H_2O molecule, minimum energy = −19.8911, r(O-H) = 1.03 Å, θ(H-O-H) = 105°.

There are two other issues germane to stability and bonding.

1) Electrical neutrality of the anomalous water structural units has been emphasized above, and we believe that a polyelectrolyte hypothesis such as

Table 3B. Rings of planar anomalous water. Planar hexagons in a line.

No. of rings	E (a.u.)	Total stabilization (a.u.)	Stabilization per H bond over isolated H_2O (kcal)
2	−199.0097	0.0987	5.63
3	−278.7013	.1259	4.93
4	−358.1912	.1514	4.52
5	−437.7814	.1772	4.27

Table 3C. Rings of planar anomalous water. Hexagons with maximum internal bonds.

No. of rings	E (a.u.)	Total stabilization (a.u.)
3	−258.6754	0.0911
4	−318.3331	.0755
5	−377.9779	.0470

Table 3D. Rings of planar anomalous water. Two rings, optimized central bond [naphthalene-like (see Fig. 4a) external $O \cdots O$ separation fixed at 2.32 angstroms].*

R (Å)	E. (a.u)
2.28	−199.0077
2.32	−199.0100
2.36	−199.0104

* Minimum energy at $R = 2.33$ Å, $E = -199.0105$ a.u., average bond energy = 5.64 kcal/mole.

Table 3E. Rings of planar anomalous water. Three rings, optimized central bonds (three internal bonds, external $O \cdots O$ separation fixed at 2.32 angstroms).*

R (Å)	E (a.u.)
2.24	−258.6525
2.32	−258.6729
2.40	−258.2422

* Minimum energy at $R = 2.30$ Å, $E = -258.676$ a.u., average bond energy = 3.83 kcal/mole.

Table 3F. Rings of planar anomalous water. Three rings, optimized perpendicular central O-H bond (three internal bonds, external $O \cdots O$ separation fixed at 2.32 angstroms, other perpendicular bond fixed at 1.03 angstroms).*

r(O-H) (Å)	E (a.u.)
1.03	−258.6729
1.10	−258.6703
1.15	−258.6582

* Minimum energy at $r = 1.05$ Å, $E = -258.6740$ a.u.

that advanced by Lippincott *et al.* (*3*) is untenable. From the standpoint of electronic structure, the large negative charges would tend to inhibit the buildup of sheets and the large sheet charges implied might also make the structure unstable in the presence of small positional changes in the counterions. From the standpoint of empirical observations, the coexistence of normal and anomalous water under certain conditions and the two-phase behavior at low temperatures argue against a polyelectrolyte. Charged sheets and hydronium ions would interact strongly with normal water, and coexistence is unlikely. It seems reasonable to believe, also, that the bonding in anomalous water should retain a kinship with that in normal water, rather than show the gross disparity represented by a polyelectrolyte.

2) The bonding scheme we have used to describe neutral blocks of anomalous water represents a new form of bonding, and the special position of the hydrogen atoms immediately suggests the need to test for a potential *p*-orbital contribution on these centers. *Ab initio* calculations on planar, sp^2 hybridized $H_5O_2^+$ with and without *p*-orbitals placed on the symmetric H center provide a stringent test, and this test results in a lowering of energy of only 0.18 kcal (other data on $H_5O_2^+$ are given in Table 2). This shows that the doubly occupied atomic *p*-orbitals of oxygen have no tendency to delocalize their charge.

Table 4. Anomalous water, three-dimensional layer structure. O···O separations = 2.32 angstroms; external hydrogen O-H distance = 1.025 angstroms.

R (between plates) (Å)	*E* (a.u)	Total stabilization (a.u)	Additional stabilization from intersheet connections (a.u)
	*A. Two plates, four rings (Fig. 3a)**		
2.20	−398.0410		
2.316	−398.0886		
2.40	−398.0961		
	B. Two plates, four rings (Fig. 3b)†		
2.20	−397.9538		
2.32	−398.0034		
2.40	−398.0123		
	C. Two plates, four rings (Fig. 3c)‡		
2.3	−398.0324		
2.4	−398.0406		
2.5	−398.0271		
	D. Two plates [each plate is three rings in a row (total No. of H_2O, 28)]§		
2.40	−557.3393	0.3885	0.1367
	E. Two plates [each plate is three rings with maximum internal bonds (total No. of H_2O, 26)]§		
2.40	−517.5275	0.3589	0.1767
	F. One plate, two rings (extra hydrogen above oxygen adjacent to internal bond. Serves as a reference for staggered plates, B and C above)		
	−198.8891		
	G. Two plates, four rings (modified Fig. 3a) with two extra hydrogens pointing away from each other. Serves as a model for interaction between layers made of double plates ||		
2.8	−398.0254		
2.6	−398.0268		
2.316	−398.0229		

* Minimum energy at *R* = 2.386 Å, *E* = 398.0964 a.u., average bond energy = 7.2 kcal/mole.
† Minimum energy at *R* = 2.40 Å, *E* = −398.0123 a.u., average bond energy = 8.2 kcal/mole.
‡ Minimum energy at *R* = 2.37 Å, *E* = 398.0415 a.u., average bond energy = 9.0 kcal/mole.
§ Stability per H bond relative to isolated H_2O = 7.03 kcal.
|| Minimum energy at *R* = 2.62 Å, *E* = 398.0269 a.u.; indicates a shallow attractive minimum of about 1.25 kcal between double layers.

Geometry Search

In addition to planar sheets of hexagons there are a number of other arrangements of symmetrical O-H-O bonds worth considering; these are illustrated in Fig. 4. As discussed above, CNDO/2 has been found successful in discriminating among possible geometries, and we can therefore have confidence in the energy optimizations presented in Fig. 4. (To preserve neutrality, Fig. 4b should have an additional hydrogen below one of the middle oxygens, and in Fig. 4c a hydrogen should be removed from each end.) It is at once apparent that all other symmetrical hydrogen-bonded configurations are of higher energy than planar hexagons. A particularly striking feature is a pronounced preference for cyclic structures [hexagon, puckered hexagon, and square (Fig. 4, a, b, and d) over chains sp^2, sp^3, and *sp* (Fig. 4, e, f, and g)]. All the chains are unstable relative to isolated water molecules.

Planar sheets of squares have been proposed by Bellamy *et al.* (*20*), and it is interesting to find that this is a favorable geometry (although less so than the hexagon) when the H_{int}-O-H_{ext} angle is 105 degrees. For a continued sheet, however, this angle must be 90 degrees, and at this angle the energy is considerably raised.

The diborane-like, tetrahedrally hybridized, linear polymer of Fig. 4c is one of the more novel geometries, and analysis of our wave functions shows that it is the electron repulsion between the oxygen atoms that makes the diborane-like structure so unfavorable.

Table 5. Force constants, in dynes per 10^5 centimeters and (values in parentheses) vibrational frequencies, in waves per centimeter, from experimental data and *ab initio* and CNDO/2 calculations.

Vibrational mode	Experimental	*Ab initio*	CNDO/2
H_2O stretch	7.76* (3756)	10.4†	33.8 (reference)
H stretch in H-bonded H_2O dimer	7.52‡	10.0†	17.1
Anomalous H_2O in plane stretch	1.4 § (1595)		18.0 (2740)
H_2O bend	.69* (1595)	.48†	0.79 (reference)
Anomalous H_2O in plane bend	.61|| (1410)		.87 (1675)
Anomalous H_2O out of plane bend	.59|| (1360)		.61 (1400)
FHF^- symmetric, F···F stretch	4.0 ¶ (595)	4.8¶	13.0 (reference)
Anomalous H_2O O···O stretch	4.2** (630)		17.2 (685)

* See Barrow (*52*).
† See Kollman and Allen (*6*).
‡ See M. Van Thiel, E. D. Becker, G. G. Pimentel, *J. Chem. Phys.* **27**, 486 (1957). The force constant was obtained by averaging the monomer symmetric and asymmetric stretch and comparing this value with the average for the corresponding dimer bands.
§ Force constant estimated from the frequency of the known water-vapor stretch and that reported for anomalous water by Lippincott *et al.* (*3*).
|| Value estimated from water-vapor bend frequency and the frequency given by Lippincott *et al.* (*3*).
¶ See *50*.
** Value estimated from known FHF^- stretch frequency and the Raman bend given by Lippincott *et al.* (*3*).

Table 6. Optical excitation (in electron volts), from experimental data and *ab initio* and CNDO calculations.

System	Excitation	Experimental	*Ab initio*	CNDO
H_2O vapor	$^1B_1$	7.4*	13.9†	25.55
H_2O vapor	$^1A_1$	9.5*	19.3†	26.68
Anomalous H_2O (planar hexamer)	$^1E_1$	2.4‡		19.4
Anomalous H_2O (planar hexamer)	$^1A_2$			23.5

* From Carrington (*53*). † From Horsley and Fink (*54*). ‡ From Lippincott (*26*).

This structure is electron-rich rather than electron-deficient as in diborane, and the additional repulsion outweighs the additional attraction. The staggered ring geometry of Fig. 4h has much in common with the diborane-like structure, and it also may be expected to have a high energy. Finally, a tetrahedrally coordinated pentamer with symmetrical hydrogens (for all O • • • O separations) is less stable than five isolated water molecules.

The results discussed so far verify the geometrical hypothesis qualitatively put forth by Lippincott *et al.* (*3*)—that is, that the basic unit in anomalous water is symmetrical hydrogen bonds located between hexagons of sp^2 oxygens at an O • • • O internuclear distance of 2.3 to 2.4 angstroms.

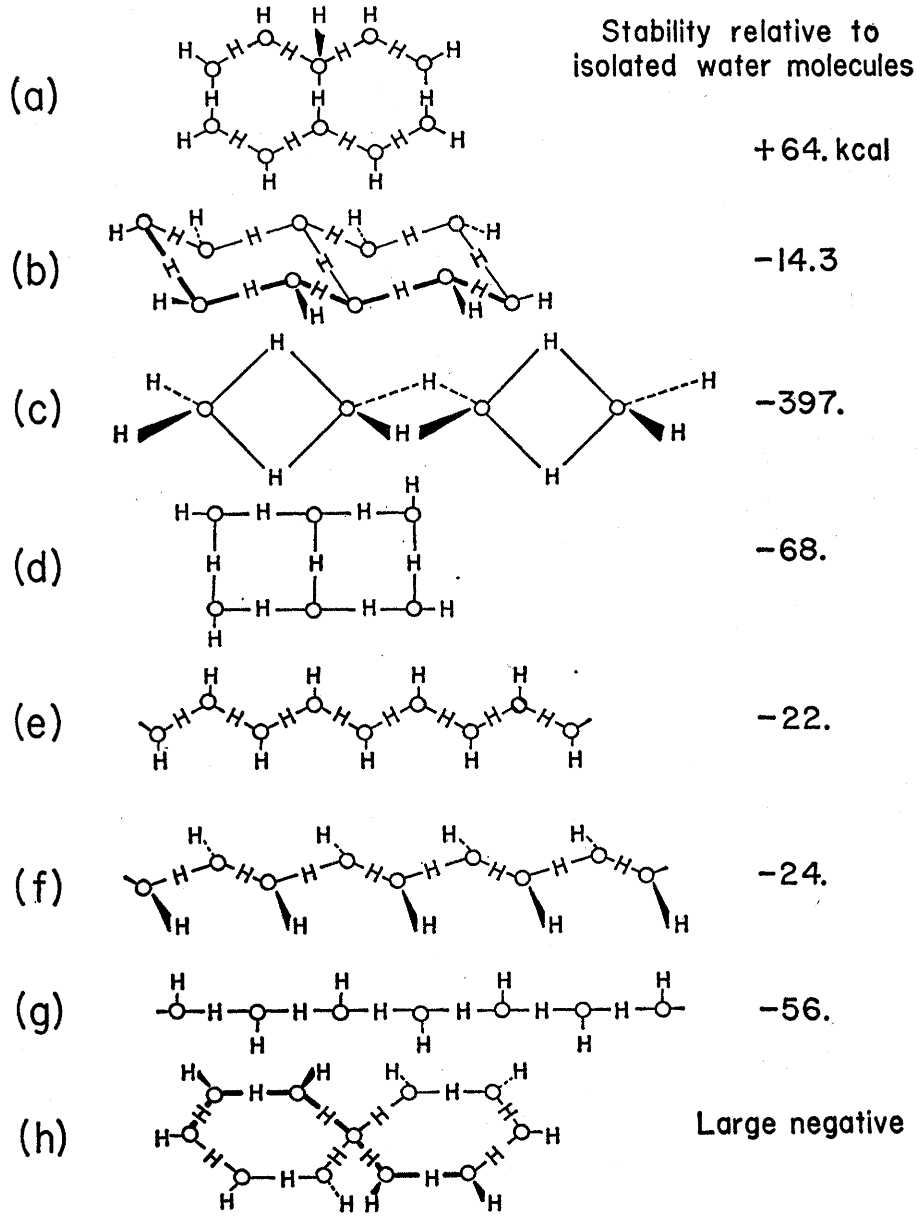

Fig 4. Possible geometries explored in this study.

Two other structures have been postulated. The tetrahedral cluster $(H_2O)_4$ proposed by Bolander *et al.* (*21*) is not substantiated by the recent mass spectrometry measurements of Willis *et al.* (*22*), which yield a vapor molecular weight for anomalous water of 18 instead of 72. A rhombohedral structure similar to ice II (just as normal water is similar to ice I) has been proposed by Erlander (*23*), but this model does not involve an unusual protonic environment such as is obtained by the nuclear magnetic resonance studies (*24, 25*), nor would it give rise to the observed Raman spectrum (*3*).

Spectral Assignments

There now exist a number of infrared, Raman, nuclear magnetic resonance, and optical excitation measurements, and we have used CNDO/2 calculations (again with *ab initio* results as references) to analyze and interpret these data. Our quantum mechanical results are in many cases not as direct or as accurate for establishing spectral properties as they are for determining stability and geometry, but the trends and ratios obtained successfully discriminate against alternatives and characterize the spectra-related properties of anomalous water.

Infrared and Raman spectra. Computed and experimental force constants and the corresponding frequencies for water vapor and anomalous water are reported in Table 5, and we see that the *ab initio* results are in reasonably good accord with the pattern of experimental data for the reference systems. The CNDO/2 calculations greatly accentuate the *ab initio* errors, but trends are maintained. The hydrogen stretch, both in the conventional hydrogen-bonded dimer and in anomalous water, are in poorest agreement with observation, and this is in line with the relative crudeness of potential surfaces we have constructed for this motion. It is worth noting that the magnitude of the numerical value of the stretching frequency for end atoms in a three-atom system cannot be related in any obvious way to the hydrogen bond energy, but there is a very rough relation for the O-H stretch, and we see that this indicates an anomalous water bond weaker than an ordinary covalent one.

Optical excitation. The relatively primitive nature of the CNDO/2 scheme generally makes it inappropriate to use anything more elaborate than the unoccupied, virtual orbitals for investigating excited states. It is known that this approximation leads to great overestimation of excitation energies, but energy differences have more meaning. In Table 6 are given *ab initio* and CNDO/2 virtual orbital excitation energies (only the ground-state basis set was used) for the two lowest-lying singlet excitations in the H_2O vapor reference system. Trends are reproduced by CNDO/2 and yield a 6.1-electron-volt lowering of the lowest excited singlet of anomalous water, as compared to a 5-electron-volt lowering observed by Lippincott (*26*). This excitation is compatible with the slightly yellow cast often observed for samples of anomalous water. On the basis of our calculations we expect the excitation of the second singlet to be 4 to 7 electron volts higher than that of the lowest one.

Nuclear magnetic resonance. Nuclear magnetic resonance frequency shifts are controlled by both the polarizability and the magnitude of the electronic charge around the nucleus under consideration, but it has proved possible to understand most differential chemical effects on the basis of charge-magnitude considerations alone, and these in turn are adequately represented by the Mulliken population analysis scheme. Similarly, charge redistribution upon bond formation computed *ab initio* and by CNDO/2 have been shown to be practically the same for conventional hydrogen-bonded systems (*13*). As shown in Table 7, the significant charge-distribution feature of anomalous water is the dramatic shift of electrons from the symmetrical hydrogens to the oxygens—a shift in the same direction but of considerably larger magnitude than that accompanying ordinary hydrogen bonding (*27*). The 5-parts-per-million downfield proton shift observed by Petsko (*24*), and by Page *et al.* (*25*) is entirely compatible with the hydrogen charge we have computed. Between-sheet hydrogens are shifted a little less, and this may be one factor in the broadening of approximately 1.7 parts per million observed for the nuclear magnetic resonance line. The more highly ordered structure (therefore the shorter relaxation time) that characterizes the anomalous water microcrystallites is the major factor in the broadening. Willis *et al.* (*22*), in the one nuclear magnetic resonance investigation so far reported in the literature, found only the normal water resonance line, but it seems likely that their experiments did not include a frequency search extensive enough to pick up the large downfield shift.

Table 7. Nuclear magnetic resonance. Electronic charge (number of electrons) from population analysis.

System	Charge
H_2O vapor	
O	8.272
H	0.864
H-bonded H_2O dimer	
O	8.306
H in H-bond	0.836
H outside H-bond	.880
Asymmetric cyclic hexamers	
O in planar hexamer	8.39
H in ring of hexamer	0.75
H outside ring of hexamer	.86
Anomalous H_2O (cyclic hexamers)	
O in planar hexamer	8.471
H in ring of hexamer	0.658
H outside ring of hexamer	.871
H between planes in double plate	.710

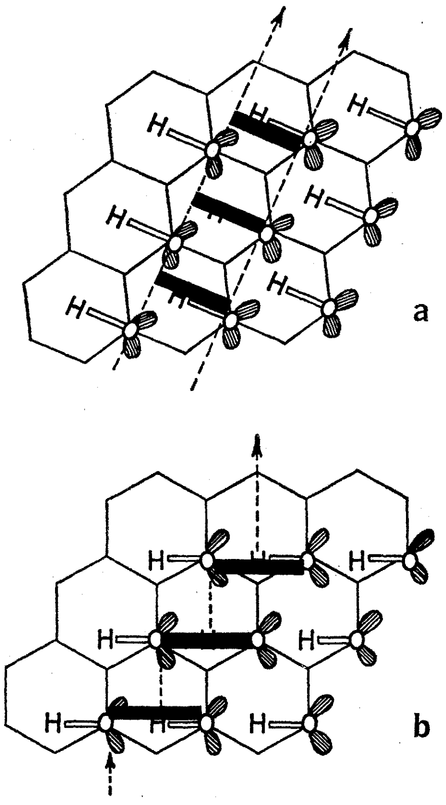

Fig. 5. (a) Layer formation for type A lattice. (b) Layer formation for type B lattice.

Formation

As discussed above, anomalous water has an internal energy close to that of normal water; because of this fact plus the greater entropy of normal relative to anomalous water, formation of the latter requires a highly specific surface catalysis mechanism.

Silica surfaces have been studied extensively, and the results of these studies are well summarized in a book by Hair (*28*) and in an article by Peri and Hensley (*29*). Assuming that the general features of silica gel surfaces apply to quartz and Pyrex (borosilicate) surfaces, one can say that pairs of hydroxyl groups attached to surface silicon atoms constitute the principal active sites associated with water absorption processes. In recent work, Hair (*30*) has made quantitative water absorption measurements on carefully prepared surfaces with a pressure range around that found necessary to form anomalous water. He finds that, on silica surfaces containing only H-bonded hydroxyl group pairs, the number of water molecules absorbed per hydroxyl is between four and seven (*31*).

This information, in combination with the knowledge about structure presented above and the results of some further calculations, enables us to build up a detailed picture of the formation process. The unwet surface of a quartz capillary freshly drawn in air will possess H-bonded surface hydroxyl pairs. Individual water molecules are attracted to these hydroxyl pairs by ordinary hydrogen bonding, and the pair hydroxyl geometry, along with the computational results of Table 8, A–D, shows that cyclic hexamers held together by conventional (asymmetric) hydrogen bonds are most likely to be formed initially (*32*). Figure 5 shows schematically a top view of the two possible orientations for H-bonded surface hydroxyls. Oxygen atoms are located directly above silicon sites, the shaded lobes indicating their lone pairs. Three representative rings are indicated edge-on by the solid black bars (the dashed lines are meant to bring out the symmetry relationship between the rings), and these are in an appropriate position to allow interconnection between rings. A perpendicular interconnection is more favorable both geometrically and energetically (bent hydrogen bonds have a slightly higher energy). The energy to be gained by interconnection is great, and only a few cyclic hexamers will form before interconnection occurs. As soon as interconnections are achieved, the hexamers move from asymmetric to symmetric hydrogen bonds. The computational results that demonstrate this are the 0.0767 atomic unit (a.u.) (48 kcal) gain obtained for two interplate symmetrically bonded ring pairs as compared with the 0.0221 atomic unit (14 kcal) gain obtained by interconnecting corresponding asymmetric ring pairs. Because of the necessarily small size of our model systems, only two out of 20 oxygen atoms are interconnected, but for infinite lattices there is one interconnection per two oxygens, and this will make the symmetric lattices more stable than any asymmetric arrangement will (*33*). We now see the answer to the puzzling "surface wetting" phenomena repeatedly observed empirically: because the free energy of anomalous water is less than that of normal water, there is not much chance of catalyzing the formation of anomalous water if the surface has been wet with ordinary water. Water molecules approaching an already wet surface will simply find themselves in a normal water environment and will continue the formation of normal water.

Table 8. Computational results for symmetric and asymmetric water.

R (O···O) (Å)	θ (deg)	E (a.u.)	Stabilization: Total	Stabilization: Per H bond (kcal)	Stabilization: Additional, from intersheet connections (a.u.)
*A. $(H_2O)_6$ cyclic symmetric H's**					
2.2	105	−119.3638			
2.3	105	−119.4340			
2.4	105	−119.4240			
2.2	112	−119.3736			
2.3	112	−119.4383			
2.4	112	−119.4238			
2.2	120	−119.3668			
2.3	120	−119.4253			
2.4	120	−119.4057			
A. $(H_2O)_6$ cyclic asymmetric†					
2.4	105	−119.4464			
2.5	105	−119.4487			
2.6	105	−119.4390			
2.4	112	−119.4463			
2.5	112	−119.4454			
2.6	112	−119.4334			
2.4	120	−119.4275			
2.5	120	−119.4227			
2.6	120	−119.4079			
B. $(H_2O)_{10}$ naphthalene-like (symmetric H's $\theta = 109.5°$)‡					
2.25		−198.9704			
2.316		−199.0195			
2.40		−198.9970			
B. $(H_2O)_{10}$ naphthalene-like (asymmetric H's, $\theta = 109.5°$)§					
2.40		−199.0521			
2.50		−199.0588			
2.60		−198.9769			
C. Asymmetric normal H-bonded structure (planar rings, extra H perpendicular to plane): 2 rings					
		−199.0498	0.1388	7.91	
C. Asymmetric normal H-bonded structure: 3 rings (maximum internal connections)					
		−258.7647	0.1804	7.54	
D. $(H_2O)_4$ square [θ (H_{int}-O-H_{ext}) = 105°] H's symmetric [r(O-H_{ext} = 1.03 Å)]					
2.2		−79.5354			
2.3		−79.5924			
2.4		−79.5936			
D. $(H_2O)_4$ square [θ(H_{int}-O-H_{ext}) = 105°], internal H's asymmetric [all r(O-H) = 1.03 Å]					
2.4		−79.6122			
2.5		−79.6198			
2.6		−79.6175			
E. Double plate, four rings, asymmetric [all r(O-H) = 1.03 Å] ǁ					
2.40		−398.1217	0.2997		0.0221

* All the external hydrogens (those pointing away from the ring) were kept at their minimum distance of 1.03 Å; this is the same minimum O-H distance found in the water monomer. θ is the H_{int}-O-H_{ext} angle. Through least square analysis, the minimum is found at $R = 2.33$ Å, $\theta = 109°$, with an energy of —119,4430 and average H-bond energy = 10.0 kcal/mole. † H_{ext} was kept at R (O-H) = 1.03 Å, as in the symmetric case; a minimum was found at $R = 2.44$ Å, $\theta = 107.5°$, with an energy of —119.4502 and average H-bond energy = 10.8 kcal/mole. ‡ Minimum energy at $R = 2.34$ Å, $E =$ —199.0238 a.u., bond energy = 6.41 kcal/mole. § Minimum energy at $R = 2.45$ Å, $E =$ —199.0668 a.u. bond energy = 8.86 kcal/mole. ǁ Stability per H bond =7.83 kcal/mole.

The charge redistribution accompanying the mechanism described above is a smooth and continuous one, as may be observed by the sequence of hydrogen and oxygen atomic shifts for the species—isolated water, hydrogen-bonded dimer, asymmetric cyclic hexamer, anomalous water—displayed in Table 7. It is also apparent that very little bond strain and no elaborate atomic rearrangements are involved. Anomalous water produced on Pyrex surfaces has a lower and broader molecular weight distribution than that produced on quartz (*3*). This is due to the fact that, on Pyrex surfaces, up to a third of the silicon atoms are replaced by boron atoms (*28*), and this causes discontinuities in the otherwise smooth process.

The formation mechanism presented above is believed to occur under equilibrium or quasi-equilibrium conditions. Bonds to the surface of the tube wall lower the free energy of the anomalous material which is forming to a value below that for the normal liquid. Calculations based on the CNDO/2 model indicate that the effect of the wall extends outward from the surface for only a short distance (10 to 15 angstroms), and that a microcrystallite, after forming within this range, creeps or agglomerates away from the wall. The motion away from the wall is aided by the increase in entropy produced by random orientation of successively accumulating microcrystallites and by their surface tension, which seeks to minimize the surface area. The surface tension of anomalous water will be high—as much as 25 percent greater than the surface tension of the normal liquid. The basic reason for this lies in the large charge separation (and therefore the large bond dipole) between the hydrogens and the oxygens. The magnitude of this charge separation is comparable to that in hydrazine and hydrogen peroxide (*34*) or in sodium hydroxide, all of which compounds have notably higher surface tension than ordinary liquid water has. As anomalous material moves from the surface, new material will take advantage of the strong surface bonds, and, even though the material away from the surface is in a higher energy state than that directly adjacent to the tube walls, the formation process will continue until the average free energy of the material in the tube is equal to that of the normal liquid. Removal of the anomalous material from the tube surface requires energy, but, once separated, the anomalous material is less stable than the normal liquid. It is not to be expected that new anomalous material will readily form on existing material, because of the high kinetic barrier against bond breaking and bond making.

Viscosity

The viscosity of anomalous water is somewhere between that of heavy motor oil and molasses. Unfortunately, it is very difficult to quantitatively compute viscosity from first principles, and we cannot assign specific values to our three lattice types. It is obvious, however, that a type C lattice would sheer like graphite. For types A and B lattices the observed viscosity would probably arise from the tumbling of microcrystallites. Besides its large value, the other interesting observation concerning the viscosity is the decrease that occurs when anomalous water is moved up and down a capillary. The reason for this decrease is straightforward. Some of the oxygen or hydrogen atoms of a microcrystallite will become attached to surface silicon atoms or to another microcrystallite, and this will cause breaks in the between-sheet links or in the sheets themselves, or in both. Viscosity lowering attributable to mechanical stresses of movement is known for pseudocrystalline organic polymers, and this may be the explanation in the case of anomalous water.

High- and Low-Temperature Behavior

Perhaps the most unusual property of anomalous water is its apparent failure to decompose until it reaches very high temperatures. This seems even more surprising in view of our calculations showing that its internal energy is comparable to that of ordinary water. The origin of this high-temperature behavior lies in its geometry. The energy required to free one molecule from our liquid-water model is 2×8 to $2 \times 11 = 16$ to 22 kcal/mole, as calculated by CNDO/2. The corresponding process in anomalous water is cyclic hexamer → linear pentamer + H_2O, yielding a CNDO/2 energy of 75 kcal/mole (*35*). These values give the essential information necessary to understand observations made to date; to go further will require more refined experiments. Various investigators have reported that anomalous water is "stable" or "does not decompose" at temperatures up to 800°C, but it is well known in the field of high-temperature polymers (*36*) that the only way to establish the stability of a material like anomalous water relative to known substances is to measure the weight loss for a given time at a given temperature in some standardized temperature reference system, such as the temperature required for 50 percent weight loss in 35 minutes.

One may ask for a deeper understanding of the 75 kcal/mole energy of vaporization, and this is to be found in the characteristics inherent in the ring as opposed to the chain (essentially the same value of 75 kcal/mole may be read directly from Fig. 4, as the difference in the stability of the cyclic and the chain hexamers). We know from the elementary example of the one-dimensional particle on a ring as compared to the one-dimensional particle in a box that restriction of the coordinate range in the box problem leads to a higher energy in the box than in the ring. The end effects in the chain are another important aspect. End molecules are in a higher potential energy environment than interior molecules are, and, in addition, the chain does not permit the charge delocalization rearrangement that is available to the ring.

Extensive low-temperature studies have been carried out by the Russian investigators (*1*). They find a thermal expansion $\Delta L/L$ for pure anomalous water to be a simple linear contraction as the temperature is lowered from above room temperature to about -35°C, followed by no change as the temperature is lowered still further. This is exactly the behavior one would expect for our three-dimensional lattices. The sharp knee suggests type C lattice double layers coming together, but it may also be the maximum density packing of randomly oriented microcrystallites of types A and B lattices.

In the temperature range $-12°$ to -20°C, pure anomalous water has been observed to separate into two phases whose densities differ by about 10 percent, but above and below these temperatures it is monophasic. It is probable that this behavior results from differences in the packing of the microcrystallites rather than from a change of lattice structure. We may hypothesize that at -12°C the entropy term in the free energy has become sufficiently small to allow the setting up of a better defined geometrical relationship between the microcrystallites, and that from -12°C to -20°C two different, loose, conventional hydrogen-bonded arrangements compete with each other or with symmetric bonds. At -20°C and lower temperatures the probability that loose, conventional hydrogen bonds of relatively high entropy exist becomes very small.

It is also known that, at about room temperature, the anomalous material is hydroscopic, and this is logical because conventional hydrogen bonds can attach themselves at numerous places on a small block of anomalous water. However, the interaction between the normal liquid and anomalous water will not be great because of the very different geometries and potential energy surfaces, thus it is not surprising that anomalous water can coexist with normal water. There is no danger that the presence of a block of anomalous water will cause normal water to assume the anomalous form because each liquid-water molecule is already "wet"—that is, has a more favorable entropy and potential energy environment than it would have as anomalous water.

Analogous Systems

One of the principal methods by which newly observed phenomena become understood is the method of reasoning by analogy and extrapolating from the properties of known systems. The hydrogen fluoride hexamer, the diamond-graphite system, and certain polymeric systems are examples of this approach.

If H_2O finds a way to organize itself into cyclic hexamers with symmetrical hydrogen bonds, we would expect that hydrogen fluoride should do so with even greater ease, because of the larger per-bond binding energies and the smaller entropy effects to be expected. CNDO/2 calculations (*13*) predict that a cyclic hexamer will be found to be the most stable grouping of molecules in the gas phase. A planar conformation has a lower energy than a puckered one. Table 9 shows that symmetric placement of the hydrogen

Table 9. Computational results for other anomalous compounds.

Compound	Minimum separation* (Å)	Stabilization† (kcal)
HF		
Cyclic planar asymmetric [$F \cdots F$ optimized, R(F-H) = 1.00 Å]	2.28	14.7
Cyclic planar symmetric ($F \cdots F$ optimized, H symmetric)	2.25	16.7
Linear hexamer [H symmetric, except at end for which R(F-H) = 1.0 Å; $F \cdots F$ optimized]	2.25	1.3
NH_3		
Puckered ring (sp^3) [internal hydrogens symmetric; external hydrogens, R(N-H) = 1.06 Å]	2.47	− 9.2
Puckered ring (sp^2) [internal hydrogens symmetric; external hydrogens, R(N-H) = 1.06 Å]	2.49	−12.9
Linear hexamer [all external hydrogens, R(N-H) = 1.06 Å]	2.45	− 8.8
Methanol		
Cyclic hexamer asymmetric	2.44	7.7
Cyclic hexamer symmetric	2.31	7.3
Formic acid		
Cyclic hexamer asymmetric	2.45	10.0
Cyclic hexamer symmetric	2.31	10.2
Linear tetramer, sp^3 around O	2.35	− 5.4
Linear tetramer, sp^2 around O	2.35	− 5.2

* For HF, $F \cdots F$; for NH_3, $N \cdots N$; for methanol and formic acid, $O \cdots O$. † Stabilization per HF, NH_3, CH_3OH, and (HCOOH), respectively, for the four compounds listed.

atoms, with an $F \cdots F$ separation of 2.28 angstroms, is favored over an asymmetric placement by an energy stability ratio of about 10/9 (*37*). A very recent electron diffraction study by Jansen and Bartell (*38*) supports the major aspects of these predictions. Monomers, dimers, and hexamers are the main ingredients of vapor-phase hydrogen fluoride, and Jansen and Bartell find a cyclic hexamer with an $F \cdots F$ separation of 2.52 angstroms. Although the best fit to their diffraction peaks is obtained for an FFF angle of 106 degrees, they emphasize that thermal bending of the extremely flexible structure does not permit assignment to a well-defined puckered ring. Of greatest interest is their finding that a large fraction of the hydrogens in the ring (55 percent at room temperature) may be symmetrical. Because only one hydrogen is attached to the fluorine it is not possible for hydrogen fluoride to form repeated-ring sheets, and for the same reason the relatively smaller entropy contribution to the free energy allows ring formation without surface catalysis.

A second analogy may be found in the diamond-graphite system (*39*, pp. 694 and 708), with diamond likened to ice Ic and graphite likened to our anomalous water lattices. The existence of a tetrahedral carbon lattice (sp^3) and of several parallel sheet lattices (sp^2) with slightly different stacking patterns provides a compelling analog. Likewise, the free energy of diamond is known to be very similar to that of graphite. That some carbon compounds should be related to certain oxygen compounds is not at all unexpected, since the ground configuration of carbon, $(1s)^2$ $(2s)^2$ $(2p)^2$, is greater by two electrons than a closed shell, whereas the ground configuration of oxygen, $(1s)^2$ $(2s)^2$, $(2p)^4$ is two electrons less than a closed shell (*40*).

Both acetaldehyde (*39*, p. 701) and carbon disulfide (*41*) can exist either as a liquid or as a polymer, and some of their properties resemble those of anomalous water. Black carbon disulfide is a polymer, prepared under special conditions of temperature and pressure, which can coexist with the ordinary liquid, has no tendency toward interconversion or further polymerization, and does not decompose until it reaches high temperatures.

Other Anomalous Species

Cyclic hexamers of ammonia with symmetrical N-H-N bonds (Table 9) are considerably less stable than six isolated ammonia molecules—in sharp contrast to $(HF)_6$ and $(H_2O)_6$. Also, unlike the case for anomalous water, the puckered-ring (sp^3) conformation is relatively more stable than the planar (sp^2) form. This latter result is not unexpected since, both in the single ring and in sheets of rings, the extra hydrogen (relative to H_2O) introduces nonbonded repulsions which are most easily lowered by the cyclohexane form. The inversion barrier in ammonia is also known to be greater by several kilocalories than the barrier in H_3O^+. A linear, tetrahedrally hybridized chain of symmetrically bonded ammonia is of higher energy than the isolated monomers, and thus the existence of anomalous ammonia is unlikely.

On the other hand, calculations on formic acid as a representative acid and on methanol as a representative alcohol (Table 9) show a good likelihood of their existence as stable cyclic hexamers (*42*). Formic acid parallels hydrogen fluoride in that the symmetric structure ($O \cdots O$ separation, 2.31 angstroms) is more stable than the asymmetric ($O \cdots O$ separation, 2.45 angstroms), whereas methanol parallels water in that the asymmetric structure is more stable than the symmetric. Both the acid and the alcohol are very stable relative to six monomers. Linear, symmetrically bonded chains of formic acid, like those of water, are much less stable than the monomers. A similar result will certainly be found true for methanol, and thus it appears that cyclic hexamers are a central feature of all symmetrically bonded anomalous species (*43*). Dimer formation must be considered for both the alcohols and the acids. In particular, the cyclic formic acid dimer is quite stable. Murthy *et al.* (*44*) find, through CNDO calculation, a binding energy of 8.4 kcal/mole, using the experimentally determined geometry, but we know (*13*) that this energy is rather sensitive to the assumed geometry, and we therefore conclude that it is possible that three cyclic dimers have a binding energy comparable to that of a cyclic, symmetrically bonded hexamer. In the vapor, the entropy term would greatly favor dimer over hexamer formation. But again, as in anomalous water, a surface catalysis mechanism can serve to produce cyclic, symmetric rings (but not sheets) of acids and alcohols.

It is perhaps useful here to consider an appropriate nomenclature for materials of the type described. "Anomalous" or "super" are not mnemonics for the characteristic feature of these species, and "polywater" is misleading because the water lattices are not more polymer-like than the ice I lattices. We propose "cyclimetric" water. This term is a contraction of *cyclic* and *symmetric*, and it represents a combination of two geometrical forms, just as "methanol" represents a combination of two functional groups.

Summary

A very large number of reputable scientists have grave doubts as to the probable existence—let alone detailed properties—of a new, well-defined form of water. We have presented arguments, supported by quantum mechanical calculations, which we believe establish its existence and characterize its properties. The development of suitable computational methods involved critical analysis of existing semiempirical schemes and use of *ab initio* wave functions as a reference.

Anomalous water consists of microcrystallites of a neutral, three-dimensional lattice structure of formula $(H_2O)_n$, whose layers are composed of hexagonally arranged, four-coordinate oxygen atoms ($O \cdots O$ separation, 2.3 angstroms) with hydrogen atoms symmetrically placed between them. Several layer separation distances (for example, 5.2 to 5.4 angstroms for a type A lattice) and stacking patterns are possibilities, and each gives rise to a density greater than that of normal water. The structure of anomalous water is related to that of ice Ic as graphite is related to diamond. It is the relative motion of the microcrystallites which causes the observed viscosity, and their strong interaction produces a high surface tension.

An especially important conclusion, which follows directly from our calculations, is that the internal energy of anomalous water is comparable to that of the normal liquid. Failure to observe the anomalous form more widely in nature is an immediate consequence. The high kinetic barrier computed for ring opening explains the apparent stability at high temperatures.

In-plane and out-of-plane hydrogen-bonding frequencies and the H and $O \cdots O$ stretching frequencies observed by infrared and Raman spectroscopy, the optical excitation of 20,000 waves per centimeter, and the downfield nuclear magnetic resonance shift of 5 parts per million with a broadened line are all consistent with, and collaborated by, our computed electronic wave functions. The electronic structure manifest in this new material is the first example of multiple bonds from a normally monovalent atom to electron-rich atoms; and to stabilize this arrangement it is necessary to position the atoms symmetrically in rings. The large effective charges on the atoms also play a role in the stabilization. This type of bonding can occur equally well in other species, such as alcohols and acids. For example, one expects to find that formic acid and methanol are stable as cyclic symmetric hexamers as well as in their usual monomeric form. We believe that the term "cyclimetric" is more descriptive of the nature of this newly investigated form of matter than other names previously proposed.

Formation of cyclimetric water is catalyzed in a highly specific fashion on hydrogen-bonded hydroxyl pairs present at capillary surfaces. There is a smooth transition from an initial conventional hydrogen bonding, through asymmetric cyclic hexamers, to the final three-dimensional lattice. The inability to form cyclimetric water on a "wet" surface and the observed modification of its weight distribution when it is formed on Pyrex instead of on quartz follow directly from the formation mechanism and the surface properties.

Wall binding energy provides the additional energy lowering required for the formation of anomalous water. Optimum utilization of the surface is provided by the entropy of the microcrystallites and their high surface tension. Condensation of fresh water molecules on anomalous material off the wall is unlikely because of the high kinetic barrier to bond breaking and bond making.

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15. Anomalous water and conventional hydrogen bonds both involve a lowering of energy of the total system when isolated water molecules are associated, thus the binding energy of anomalous water or of conventional hydrogen bonds is measured relative to free water molecules. It is the energy required to infinitely separate an oxygen and a hydrogen atom in a region of association and to leave isolated water molecules with ordinary covalent bonds.
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32. Even though the asymmetric cyclic hexamer has a per-bond binding energy comparable to, or slightly greater than, tetrahedral coordination, its geometry is not favorable for formation of the normal liquid because of its very low entropy relative to the tetrahedral arrangements.
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55. We thank Michael Hair for several informative conversations on surface properties, and for preprints; Gregory Petsko for a preprint and for numerous talks about his various spectral and x-ray studies; Ellis Lippincott for general discussion of his research program; and Walter Kauzmann for vigorous and extended discussion on all aspects of anomalous water. The services of the Princeton University Computer Center (supported by NSF grants GU-34 and GU-3157) are acknowledged, and we appreciate the financial support of the Directorate of Chemical Sciences of the Air Force Office of Scientific Research, through grant AF49(638)-1625. This article is condensed from a manuscript originally submitted to *Science* on 30 September 1969.

Underwater Vision

The physical and psychological bases of the visual distortions that occur underwater are discussed.

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It is often said nowadays that man, after millennia of merely scratching the ocean's surface, stands on the threshold of returning to the sea. Many believe that the conquest of "inner space," as it is sometimes called, will prove to be far more important than the conquest of outer space. The oceans obviously contain incalculable treasures of food and minerals. A presidential commission has recently urged a vigorous and systematic investment in efforts to understand, exploit, and preserve the oceans (*1*). Nevertheless, the return is still more of a challenge than a temptation. Countless difficulties await man in the cold, bleak, and dangerous depths. Among them is simply seeing. In this article we review part of the research that we have recently been doing at the Naval Submarine Medical Center in Groton, Connecticut, on some of the problems of seeing underwater.

Alterations of the Physical Stimuli

Every aspect of vision appears to be altered underwater. These modifications in the appearance of the scene have a physical basis, for radiant energy is profoundly changed when it travels through water rather than air. First, water transmits far less total energy than air does. The fundamental equation describing the transmission of energy is the same for air and water:

$$P = P_0 e^{-\alpha d}$$

where P is the radiant power reaching a distance without loss, P_0 is the radiant power at the initial point, e is the base of the natural logarithmic system, α is the extinction or attenuation coefficient, and d is the distance (*2*, *3*). The numerical value of α, however, is generally larger by a factor of 1000 or more for water than for air. The relatively large size of α means a rapid attenuation of light with increasing depth. If 90 percent of the incident energy is transmitted through 1 meter of water, 81 percent will be transmitted through 2 meters and only 37 percent through 10 meters.

The magnitude of α depends on the size of two components, (i) loss due to scattering of the energy by minute particles suspended in the water, and (ii) absorption of the energy by the water. Each of these has important visual consequences.

Scattering causes a loss of energy from the line of sight between the object and the eye, blurring of the outline of the object, and a decrease in the natural contrast between the object and its environment (*3*). As a rough rule of thumb, we can say that the luminance contrast between an object and its background must be at least 2 percent in order for the object to be visible (*4*). While rarely a problem in air (except in fog or smog), the loss of contrast does become significant in water, because of this scattering.

The interesting aspect of the loss of energy due to absorption is that it varies with wavelength and with the particular type of water involved. Figure 1 shows transmission curves measured through a distance of 1 meter of water for some of the different bodies of water in which

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