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The Structure of Ordinary Water

New data and interpretations are yielding new insights into this fascinating substance.

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In view of the great importance of ordinary water (*1*) in a wide spectrum of contexts, from the most practical to the most theoretical, it is not surprising that there should be a great deal of interest in its structure (*2*, *3*). Most research workers know, sometimes from painful experience, that there are many questions, both about water itself and about aqueous solutions, to which satisfactory answers cannot yet be given. What is perhaps not so widely realized is that the acquisition of new kinds of data is beginning to make it practicable to draw upon several fields at once, with information in one area used to help close a logical gap left by information in another. This will permit us, at least in principle, to draw firmer conclusions than formerly, so that after many years of speculating about what water *might* be like in order that it display certain properties, we can now begin to ask what water *must* be like if certain pieces of data are, simultaneously, to be accepted as reliable (*4*).

The structure of water must be discussed in these circumstantial terms because the liquid molecules, the details of their mutual relationship and interaction, and the nature of the kinetic and transport processes in which they are involved are all inaccessible to direct observation or measurement. Moreover, there is not, in the present state of things, any early prospect that theoretical calculations, independently, will be able to give us useful information about any liquid as complex as water. We are therefore thrown back on the consideration of hypothetical models and on the hope that, as we try to account for the results of various experiments, the success or failure of different imagined alternatives will permit us to make firm choices from among them. Unfortunately, until rather recently the kinds of data that could be obtained from experiments on water have usually not been such as to enable investigators to give unequivocal answers to the questions which physicists and chemists were able to ask. Sometimes, also the answer to a particular question has seemed to oscillate from "yes" to "no" and back again as successive items of new information have become available. In this article an attempt will be made to assess some aspects of the situation on the "water front," and to illustrate in two instances the advantage to be gained from drawing upon the resources of several fields at once.

General Background: Forces between Water Molecules

The individual water molecule is by now well characterized (*3*, chapter 1), and many of its properties can be computed by quantum-mechanical calculation with the results in good agreement with experiment (*3*, pp. 23–35). The O–H bond length is 0.957 angstrom and the H–O–H angle is 104°31′. The electrons may be represented by a charge cloud which has, in addition to the appropriate density along the bonds, lobes comprising the so-called lone pairs, which extend above and below the H–O–H plane and are directed somewhat backward away from the hydrogens so that the whole structure can be represented by a somewhat distorted tetrahedron, the protons directed toward two of the vertices and the lone pairs toward the other two. The dipole moment is 1.83 debye units and the quadrupole moment is -5.6×10^{-26} electrostatic unit.

The fact that the melting point, boiling point, and critical temperature of H_2O are so high relative to those of the isoelectronic species Ne and CH_4 results from the H_2O dipoles (and higher multipoles) and from the fact that H_2O molecules can form hydrogen bonds with each other. The hydrogen bond, about which more will be said below, is a short-range interaction involving a proton of one molecule and a lone pair of another; the presence on each H_2O of two protons and two lone pairs in approximately tetrahedral geometry makes possible the fitting together of a space-filling network of hydrogen bonds in the four-coordinated structure of ice (*3*, pp. 71–77; *5*) shown in Fig. 1. In this structure the O–O distances are almost exactly equal (*c* axis and basal plane) at 2.76 angstroms, the O–O–O angles are almost exactly tetrahedral, and the protons lie almost exactly in the O–O lines (*6*), each being about 1.0 angstrom from the oxygen to which it, for the time being, "belongs."

In the dilute vapor the mutual relationship among water molecules is also comparatively easy to describe, and good numerical success has been attained (*7*) in calculating the second virial coefficient from reasonable assumptions regarding the various attractive and repulsive forces to be expected in a pairwise encounter. As stated above, the qualitative difference between what happens here and what happens in a pairwise encounter between two Ne atoms or two CH_4 molecules can be ascribed, to the first order, to the permanent dipole carried by an H_2O

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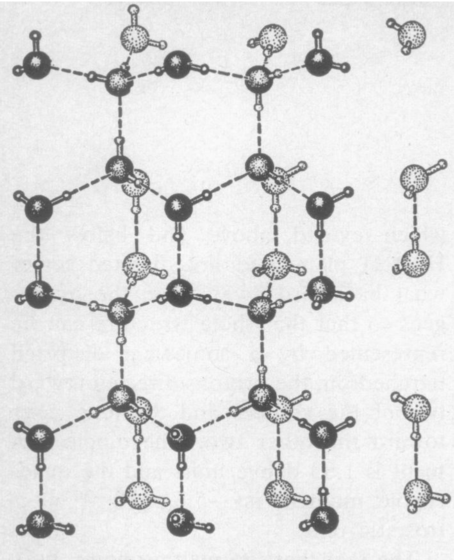

Fig. 1. The structure of ordinary ice.

molecule. This permanent dipole attracts (on the average) the permanent dipole of another H_2O and, in addition, acts on the polarizability of the other molecule to produce an induced dipole which it also attracts. These effects, however, are known not to be simply additive since values of the third virial coefficient, which describes the interaction of triplets, computed on the basis of such additivity, differ grossly from those derived from experimental data (*3*, p. 56). The situation becomes even more complicated as the vapor becomes denser and more and more molecules enter into simultaneous mutual interaction; and it is almost impossible to say anything about the details of what a molecule "sees" at the critical point (374.15°C; 218.3 atmospheres; 59.1 cubic centimeters per mole) or at high densities and supercritical temperatures. A few qualitative statements seem to be justified, however. One is that the "advantage" in having equal numbers of protons and of lone pairs has not been lost at the critical point, for both HF and NH_3 have considerably lower critical temperatures (230°C and 132°C, respectively), although both also have permanent dipoles (1.91 and 1.47 debye units, respectively) and both can form hydrogen bonds—HF forms stronger ones than H_2O (*8*). It also seems likely that at the critical temperature and volume the molecule must be in some sort of rotational state (*9*). In such a case, the cohesive energy can perhaps be thought of as arising largely from mutual polarization in which the dipole of one H_2O polarizes both the electronic and the rotational motions of its neighbors, so that, although the relative orientations of neighboring molecules must be essentially random, a proton on any given molecule will, on the average, be "looking at" an induced negative charge.

In contrast to these interactions, that referred to by the name "hydrogen bond" is geometrically well defined in the sense that it involves a single proton of one molecule and a single lone pair of another. The physical nature of this involvement has been much discussed in the past (*10*), but it appears that at least some of the earlier ideas will require reconsideration in light of the results of *ab initio* calculations that are now being made (*11*, *12*), in which advantage is taken of advances in quantum-mechanical techniques and in computer capabilities. In these treatments exact solutions are obtained for the electronic wave functions (linear combination of atomic orbitals–self-consistent field) of systems comprised of two or more H_2O molecules (the 20, 30, 40, . . . electrons in the fields of the appropriate nuclei in various configurations) in terms of basis sets chosen in order to combine a useful approach to "realism" with a practical degree of tractability. Because the basis sets have been chosen differently in different treatments, the results naturally differ somewhat in detail, but the relative stabilities of different configurations are similar in all of them, and all of the treatments agree, insofar as their results overlap, in the answers they give to certain important questions.

It appears, for instance, that the most stable arrangement of atoms in a system of two H_2O molecules is very close to that of the *trans* configuration of two neighboring molecules in ice (Fig. 1), and that other configurations, including the *cis* configuration in ice, the parallel lining up of the dipole moments, and the closed-ring or "double" hydrogen bond, that at one time have been thought to be favorable (*10*, p. 100) are considerably less stable. Another expectation, however—that the formation of a hydrogen bond should be accompanied by a transfer of charge (*10*, p. 235)—is borne out in the finding that the Lewis base molecule, or electron donor, does indeed part with about 1/20 of an electron. The presumed existence of such a charge separation had earlier led Frank and Wen to suggest (*13*) that hydrogen bonds in series should reinforce each other, and this is also confirmed. A chain trimer in the most favorable "chair" configuration is held together by an energy 2.4 times that of one hydrogen bond (*12*). As *n* increases in a favorably oriented chain *n* monomer units long, the mutual stabilization

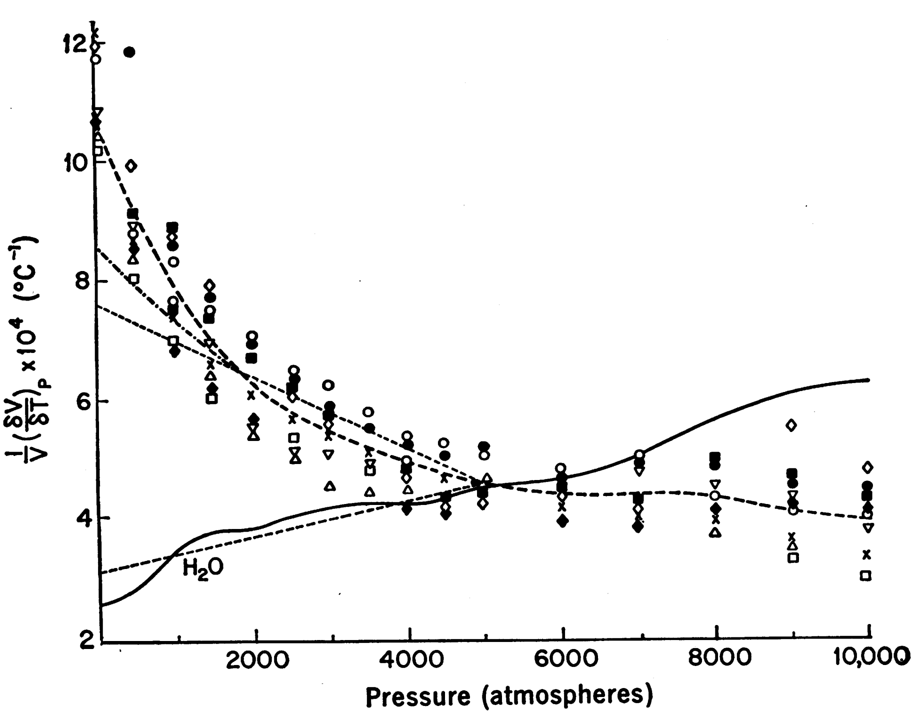

Fig. 2. The coefficients of thermal expansion of several liquids at 25°C, as these are affected by increase in pressure. The low expansibility of water at 1 atmosphere and its negative expansibility below 4°C are the result of the same influence (*63*). X, PCl_3; ○, CH_3OH; ◇, CS_2; ●, C_2H_5Cl; ■, C_2H_5I; △, C_2H_5OH; ▽, C_3H_7OH; ♦, isobutyl alcohol; □, $C_5H_{11}OH$.

grows more pronounced, at least to $n = 5$ (*12*); but the mutual stabilization is very sensitive to configuration, and, when two bonds "buck" each other, destabilization occurs—for example, the average bond strength in a trimer, in which the central H_2O donates either protons or electrons to both end molecules, is less than that of an independent bond (*12*).

Closed rings of bonds are always more stable than the most stable open chains of the same polymer number, the extra energy of the additional bond outweighing, even in the ring trimer, the unfavorable effects of ring strain which, in small rings, pulls the hydrogen out of the O---O line (*12*).

When Ice Melts

The four-coordination which characterizes the structure of ordinary ice (Fig. 1) is a very inefficient way of filling space. The ice structure of Fig. 1 contains void spaces, and the fact that the water formed when ice melts is denser than ice is to be accounted for in terms of a liquid structure in which such voids either (i) no longer exist, or (ii) have been partially filled, or (iii) have been reduced in relative size by bond-bending or reorganization. These three alternatives have all been proposed (although not in the chronological order given here) as bases for structural models of liquid water.

In the explanations offered in such models for the shrinkage which occurs when ice melts, there must also be a way to account for a group of additional, and related, peculiarities, such as the phenomenon of maximum density (*14*), the increase of thermal expansibility when pressure is applied (Fig. 2), and the effect of increased pressure in *lowering* the viscosity of cold water (*15*). These experimental properties of water make it look for all the world as though the structural change, whatever it is, that takes place when ice melts stops short of completion at 0°C and 1 atmosphere pressure but can be driven farther forward by warming or by squeezing. This is, in effect, the explanation put forward by Roentgen in 1892 (*16–18*) in what seems to be the first published paper devoted primarily to explaining these peculiarities of water. This explanation, with appropriate modifications, is also a feature of such later models as those of Eucken (*19*), Hall (*20*), Grjötheim and Krogh-Moe (*21*), Wada (*22*), Nemethy and Scheraga (*23*), and Davis and Litovitz (*24*). On the basis of the assumption that there are two distinguishable species in equilibrium in liquid water, a bulky low-energy one and a dense high-energy one, and the straightforward application of the Le Chatelier principle, one can, by means of such a model, in principle, account not only for the peculiarities already named, but also for the remarkably high heat capacity of liquid water (*17*).

An entirely different proposal about what happens when ice melts was put forward in 1933 by Bernal and Fowler (*25*). These authors postulated, from its assumed electrostatic character as a simple coulombic interaction between rigid charge distributions, that the hydrogen bond could be bent but not broken, and so they interpreted the melting of ice as a collapse into a "broken-down" lattice, still fully bonded and characterized by a statistical average degree of bond-bending which changes in temperature and pressure could alter. A statistical-mechanical discussion of a bond-bending model was given by Pople in 1951 (*26*), and this has been the model usually taken as a starting point by present-day adherents of the "uniformist" representation. A very recent elaboration of the "uniformist" view has been the introduction of the idea of randomness in senses not restricted to broken-down structures deriving from Ice I. Examples are the concept discussed by Bernal (*27*) of intrinsic disorder as characteristic of the liquid state, the discussion by Ben-Naim and Stillinger (*28*) of a random network, and the suggestion by Del Bene and Pople (*12*) that the small ring polymers of H_2O which they find to be stable may occur with appropriate relative frequencies either as separate species or as faces of transitory irregular polyhedra of which water might be imagined to be composed.

A third method by which the density could be increased when ice melts seems first to have been proposed by Samoilov (*29*), and then independently by Forslind (*30*) and by Danford and Levy (*31*). According to this theory, the ice framework undergoes relatively minor alteration, but interstitial molecules enter the void spaces which the framework encloses. A variation upon this theme is that of Pauling (*32*), who imagined the framework to be that of one of the clathrate hydrates (*33*) rather than that of ice. It is easy to show (*34*) that within the framework of an interstitial model one can, in principle, account for the maximum of density and its related phenomena if one allows the interstitial sites to be filled to a fractional degree, the fraction adjusting itself with changes in temperature and pressure. The extensive body of Russian work on water is largely based on Samoilov's ideas (*35*), and the x-ray crystallographers at Oak Ridge National Laboratory have adapted the ice-interstitial model to a computer analysis in which their x-ray scattering data are used to determine the parameters of the structure (*36*). In the version of Narten *et al.* the model contains one interstitial site for each two framework molecules and about half the interstitial sites are occupied at room temperature so that about 20 percent of the molecules are interstitial.

Is Water a Mixture?

The idea that water should be regarded as a mixture has over the years been attractive to chemists and, since 1933, repugnant to physicists. This generalization is, of course, too sweeping, but it contains several elements of truth. Among other things the mixture idea has been extremely useful in the interpretation of the properties of aqueous solutions (*13, 37*), and this success has recommended it to those who have had to deal with solution phenomena. On the other hand, it has been difficult, since the appearance of the paper by Bernal and Fowler, for chemical physicists to see how one molecule in liquid water could avoid being subject to the same strong forces as acted on every other molecule. This has made the concept of an "unbonded" molecule unpalatable to most chemical physicists and has inclined them toward what have been referred to as "uniformist" models, in which all molecules must be regarded as equivalent.

Case History: Do "Unbonded" Molecules Exist?

In 1965 Wall and Hornig (*38*) published the results of a Raman-scattering study of the valence-stretching motions of the HDO molecule and presented their findings as a strong, straightforward argument that liquid water cannot be a mixture in the generally understood sense. Study of the HDO molecule in dilute solutions in either H_2O or D_2O

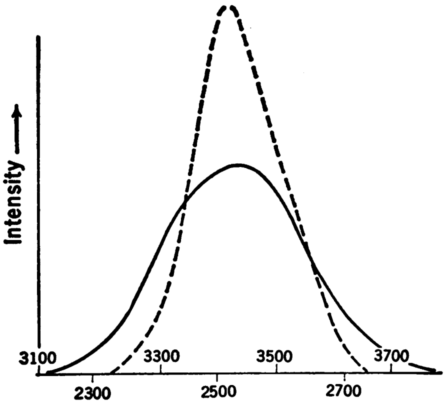

Fig. 3. Raman spectra of the HDO molecule in a D$_2$O medium (uncoupled O–H stretch, solid curve) and in an H$_2$O medium (uncoupled O–D stretch, dashed curve), respectively (*38*). [Courtesy of the American Institute of Physics]

(obtained by dissolving a little D$_2$O in H$_2$O or a little H$_2$O in D$_2$O) is an ingenious device for bypassing some of the technical complications involved in the interpretation of the valence-stretching regions in the Raman and infrared spectra of H$_2$O and D$_2$O themselves. In the dilute vapor the HDO molecule shows an O–H stretching frequency at 3707 reciprocal centimeters and an O–D stretch at 2727 cm^{-1}. These frequencies are shifted downward in condensed phases (to about 3250 cm^{-1} and 2420 cm^{-1}, respectively, in ice), and an operational rule in infrared spectroscopy relates the magnitude of the downward frequency shift, $\Delta\bar{\nu}$, which accompanies hydrogen bond formation, to the strength of the bond which is formed (*10*, pp. 83–85). The results of Wall and Hornig are shown in Fig. 3. They place $\bar{\nu}_{OH}$ at 3450 cm^{-1} and $\bar{\nu}_{OD}$ at 2520 cm^{-1}, and these values are interpreted as an indication that the O–H and O–D groups in liquid water form hydrogen bonds, but weaker ones than in ice. The more important conclusion drawn by Wall and Hornig, however, is that the simple shape of the curves rules out the possibility that there are two categories of O–H or of O–D stretching motions. They will admit 2000 "species" of O–H or of O–D, each corresponding to one of 2000 intervals into which the frequency range under the band can be divided, each of these intervals, in turn, representing a $\Delta\bar{\nu}$ which corresponds to the strength of the hydrogen bond which accompanies the particular O–O distance in the configuration responsible for scattering in that particular interval. Indeed, by using a standard correlation curve connecting $\Delta\bar{\nu}$ and O–O distances in hydrogen-bonded crystals (*10*, pp. 87–89), Wall and Hornig transcribe the O–H band of Fig. 3 into a distribution curve of the expected shape for O–O distances in water. The results of an infrared absorption study of these same systems by Falk and Ford (*39*) are in full agreement with those of Wall and Hornig and were similarly interpreted. Both sets of authors emphasized that, even though both liquid bands (O–H, or O–D) were broad enough to include finite intensities at the frequencies characteristic of the dilute vapor (3707 cm^{-1} and 2727 cm^{-1}), these intensities were so small as to preclude the existence of any significant fraction of unbonded molecules in the liquid phase.

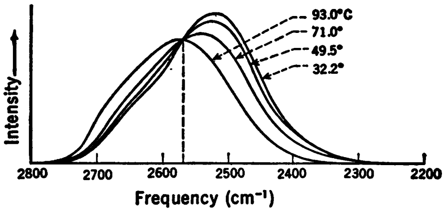

Fig. 4. Raman spectrum of the O–D stretching motion of HDO in an H$_2$O medium, taken at several temperatures. The common intersection of the curves is called an isosbestic point (*42*). [Courtesy of the American Institute of Physics]

There is no reason, however, to expect that an "unbonded" molecule should vibrate at the same frequency in the dense aqueous fluid as in the dilute vapor. Indeed, it must be expected not to do so if the reasoning to be presented below is valid (*40*). Moreover, an apparently featureless band like those in Fig. 3 is not necessarily simple in origin (*41*) but could equally well be the sum of subbands, broad enough and close enough together in central frequency to be unresolved. That the Raman band for the O–D stretch in Fig. 3 may in fact be the sum of two such subbands is suggested by Walrafen's finding (*42*) that superposition of a series of such bands measured at different temperatures (Fig. 4) reveals the existence of an isosbestic point. This is just what would be found if there were an equilibrium between two kinds of O–D groups which vibrate in different environments, each characterized by a broad band, one centered near 2520 cm^{-1} and the other near 2650 cm^{-1}, for increase in temperature would be expected to cause a change in the relative populations of the two "species," thus raising the intensity of the high-frequency band and lowering the intensity of the other. (In this case, each of the subbands could owe its breadth to the sort of distribution of binding strengths invoked by Wall and Hornig.) An isosbestic point was also found by Senior and Verrall (*43*) to occur in infrared absorption data, and although, by itself, the existence of an isosbestic point does not prove the existence of such an equilibrium as just described, it becomes a very strong argument when accompanied by other indications of band complexity, such as those that have been found both by Walrafen and by Senior and Verrall. Walrafen used laser excitation to remeasure the Raman band in question (*42*) and he found an overt shoulder on the high-frequency side (Fig. 5). Evidence of a corresponding shoulder in the infrared was found by Senior and Verrall (*43*) who plotted the numerically computed derivative of their band envelope, where an overt hump is now likewise evident. Bernstein (*44*) has also used laser excitation to measure the O–D stretch band in dilute HDO in H$_2$O. He obtained the same results and drew the same inferences as Walrafen.

However, this conclusion that these humps show that the O–D stretching motions that give rise to these spectra fall into two categories is not yet universally accepted. This seems (*3*, pp. 239–241) to be so largely because of the pervasiveness of the conviction that all interactions between water molecules involve only one kind of physical mechanism, with the result that there exists a one-to-one correspondence between

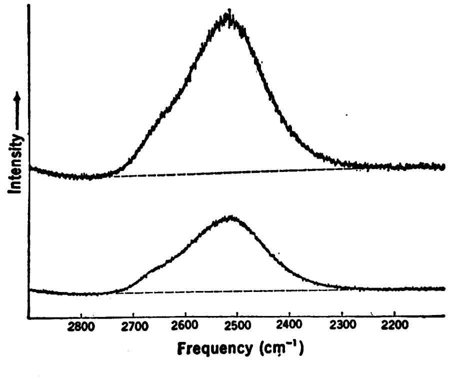

Fig. 5. Raman spectrum of the O–D stretching motion of HDO in an H$_2$O medium, taken with laser excitation. The two curves are duplicate runs taken with different gain settings (*42*). [Courtesy of the American Institute of Physics]

$\Delta\bar{\nu}$, the shift of the O–D frequency from that in the dilute vapor, and a single parameter, the "strength of the hydrogen bond." If this were true, it would, of course, follow that the strange shapes of the curves of Fig. 5 could only result from peculiarities in the distribution of hydrogen bond strengths, as alleged by Eisenberg and Kauzmann (*3*, pp. 239–241). This last-named hypothesis seems at best to be far-fetched, however, and loses greatly in credibility when it is realized that the requirement of a single parameter to determine $\Delta\bar{\nu}$ may be not only unnecessary, but even improbable, on the basis of the physical considerations presented earlier in the discussion of forces between water molecules.

These considerations make it appear that the interaction between water molecules in the dense high-temperature vapor or supercritical fluid, although physically quite different from what is properly called a hydrogen bond (*45*), should also produce a lowering in the O–H or O–D stretching frequency. In that case an observed $\Delta\bar{\nu}$ would no longer have a unique interpretation as a necessary result of hydrogen-bonding. It is therefore of prime importance that experimental evidence for just such an effect, from a new area of work, can now be adduced. This evidence is found in the results of spectroscopic studies, made by E. U. Franck and his students, of water at temperatures up to 500°C and pressures up to 5000 bars. Above the critical temperature, temperature and density are "uncoupled" so that, for instance, it was possible for Franck and Roth (*46*) to examine the infrared absorption band of the O–D stretch in H_2O at 400°C as a function of density, over a continuous range from 0.016 to 0.9 gram per cubic centimeter. Especially interesting is their curve for the frequency of maximum absorption of this band as a function of temperature at a constant high density (Fig. 6). At low temperatures these results agree with those of Falk and Ford (*39*) and of Senior and Verrall (*43*). As the temperature increases without limit, however, $\Delta\bar{\nu}_{\max}$ for $\rho = 0.9$ gram per cubic centimeter approaches an asymptotic limit of some 2620 cm^{-1}; the important point is that this value is as far below the frequency in the dilute vapor, namely, 2720 cm^{-1}, as it is above the lower frequency in water at room temperature, namely, 2520 cm^{-1}. The high-temperature limit corresponds, by definition, to complete randomness of mutual orientation of the water molecules, and this fact suggests strongly that here $\Delta\bar{\nu}$ is produced by the "rotational" interaction described earlier. This explanation receives additional support from the Raman study of Franck and Lindner (*47*), in whose results (Fig. 7) the frequency of the isolated molecule, the "rotational interaction frequency," and the broad spread corresponding to high density are clearly displayed, each under the expected conditions. It is, of course, important to the argument here being put forward that the "rotational interaction frequency" at high temperatures is the same, within a few reciprocal centimeters, as the frequency of maximum absorption which has been inferred by Walrafen (*42*) and by Senior and Verrall (*43*) for the "unbonded" subbands revealed in their analyses. When all of the data are taken into account, therefore, the balance of probability seems to have swung to the side of the two-species concept.

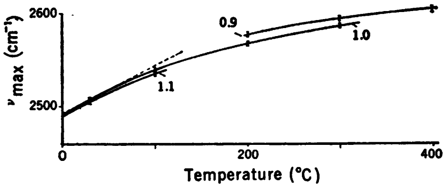

Fig. 6. Effect of temperature changes on the frequency of maximum absorption of the infrared spectrum of the O–D stretching motion of HDO in an H_2O medium. The solid lines correspond to measurements made at the constant densities (in grams per cubic centimeter) shown (*46*). The dotted line represents the data of Falk and Ford (*39*) taken on the liquid at the lower temperatures. [Courtesy of Aberdeen Univ. Press, Ltd., Aberdeen, Scotland]

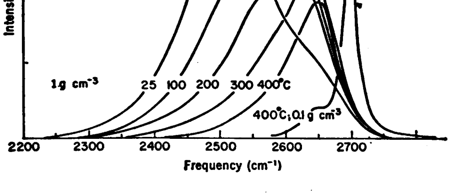

Fig. 7. Raman spectrum of the O–D stretching motion of HDO in an H_2O medium (6.2 mole percent D_2O dissolved in H_2O), taken under widely differing conditions of temperature and density, as indicated (*47*). Slit width, 18 cm^{-1}; argon laser, 4880 angstroms.

Small Angle X-Ray Scattering

Another interesting inference about water, recently drawn by Narten and Levy (*48*), lends support to, and, in turn, receives strong support from, the conclusion just drawn. The new experimental evidence cited is the angle-dependence of the intensity of scattering of x-rays from water at very small angles. The intensity $I(\theta)$ (at an angle 2θ from the direction of the incident x-ray beam) is related to the amount and kind of fluctuation in density in the liquid, and the shape of the curve of Levelut and Guinier, in which they plotted $I(\theta)$ as a function of θ (*49*) [their data were confirmed at Oak Ridge by R. W. Hendricks (*50*)] is interpreted by Narten and Levy as reducing almost to zero the likelihood that there are, in regions larger than a few molecular diameters, patches of water among which the density differs to more than a trivial extent.

The significance of this inference resides in the fact that the explanation given in typical mixture models for the density maximum and for the extra, or "relaxational," compressibility (*24*) of water implies the existence of sizable density differences (several tenths of a gram per cubic centimeter) between patches of dense and of bulky species which are big enough for the bulk of the bulky species to have established itself in them. It would appear, therefore, that if the interpretation of Narten and Levy is right, such models can be ruled out, thus leaving only the bent-bond and interstitial classes of models as possibilities. The bent-bond model, however, has always been proposed as a part of a denial that the liquid could contain two clear-cut types of bonding. By contrast, not only are there two types of bonding required in an interstitial model, but such a model also satisfies the other requirement, that of providing a believable type of surroundings in which a nonhydrogen-bonded molecule could exist for some suitable residence time. The inferences drawn from the spectroscopic and from the x-ray data thus seem to be nicely compatible with each other.

It does not necessarily follow, however, that the interstitial model favored by these interpretations must be exactly icelike in the details of its framework (*51*). An alternative that seems perhaps more likely is that the framework may be characterized by some such randomness as Bernal (*27*) or Ben-Naim and Stillinger (*28*) have discussed.

Before we go too far in rejecting an ordered framework, however, evidence from another type of experiment must be considered. The coupled molecular motions in ice give rise to "intermolecular" Raman scattering (*52*), with one band, centered near 220 cm^{-1} (ν_T), being ascribed to "hindered translation," that is, to stretching and compression of the O–H---O distances, and an especially broad band, between 350 and 900 cm^{-1} (ν_L) being ascribed to libration, or bond-bending. These bands have well-studied (*53*) counterparts in cold water which gradually disappear as the water is heated. This raises the question, which cannot now be answered but which must be kept in mind, of how much randomness can be accepted in the framework of cold water before it becomes impossible to account for the intermolecular Raman spectrum.

If a certain amount of randomness is assumed for the framework, there arises the logical question of whether the "interstitial" molecules should be expected to be completely unbonded, and thus interstitial in the customary sense, or only "semi-interstitial" by reason of having been left for the moment, by the local accidents of the game of "musical chairs" imposed on the bonding by the vagaries of thermal fluctuation, with one or more protons or lone pairs "dangling" unengaged (*54*). Here again, it does not seem clear a priori that a semi-interstitial structure would be sufficiently successful in producing the negative "structural compressibility," which is needed to account for the maximum of density and which must decrease in absolute magnitude with increasing pressure in order that one account for the data of Fig. 2. It will therefore be interesting to learn the effect of pressure on such a laser Raman band as that presented in Fig. 5.

Other Properties

It has been possible in the foregoing to refer to only a small fraction of what is known or has been written about water. Perhaps the most notable gap is in the area of molecular motions and transport processes. Information in these fields has come from studies of self-diffusion (*55*), dielectric relaxation (*56*), nuclear resonance relaxation (*57*), acoustic absorption (*58*), and cold neutron scattering (*59*). The very recent development of the laser is also making available hyper-Raman (*60*), and stimulated Raman emission (*61*), spectra which seem likely to be in support of some, and in conflict with others, of the older inferences about water. Finally, because of the influence which water structure has on the properties of aqueous solutions, our understanding of the nature of water can be expected to receive further contributions from the further study of solutions (*62*).

Conclusion

The train of thought pursued in this article has led to the conclusion that the structure of cold water seems likely to consist, for the most part, of hydrogen-bonded, four-coordinated, framework regions, with interstitial monomers occupying some fraction of the cavities the framework encloses. The precise geometry of the framework has not been specified, but some evidence suggests that it is rather regular at low temperatures and becomes more random as the water gets warmer. These conclusions, meager as they are in comparison with what we shall eventually need to know about water, are still "subject to change without notice." Such a change would, for instance, be made necessary by the discrediting either of the data or of the interpretations on which the model is based. The discovery of new facts, or of new meanings in old facts, which were clearly in conflict with the model, would also make it necessary to modify, if not to abandon, it. Even this would be progress, however, for it would be another product of the method of drawing upon data from diverse sources and would be a further step toward the progressively more comprehensive model to which this method will lead and the progressively greater confidence we will be able to place in our conclusions.

References and Notes

1. The word "ordinary" is used here to distinguish the subject of this article from the "anomalous" water [for example, B. V. Derjaguin, *Discuss. Faraday Soc.* **42**, 109 (1966)], sometimes now called "polywater" [E. R. Lippincott, R. R. Stromberg, W. H. Grant, G. L. Cessac, *Science* **164**, 1482 (1969)] which has aroused so much recent attention. Whatever else may be said about this material, it seems clear that it is a very different substance from ordinary water. No more mention of it will be made in this article.
2. Among other evidences of this, reference may be made to the continuing appearance of books and review articles (see also *3*) devoted to water, for example, J. L. Kavanau, *Water and Solute-Water Interactions* (Holden-Day, San Francisco, 1964); E. Wicke, *Angew. Chem. Int. Ed. Engl.* **5**, 106 (1966); N. E. Dorsey, Ed., *Properties of Ordinary Water-Substance in All Its Phases* (Hafner, New York, 1968).
3. D. Eisenberg and W. Kauzmann, *The Structure and Properties of Water* (Oxford Univ. Press, New York, 1969). The Dorsey reprint (*2*) and the Eisenberg and Kauzmann monograph are of particular value as sources of data; the Eisenberg and Kauzmann monograph also gives critical discussions of many of the ideas and methods of chemical physics that are used in the study of water.
4. Asking and answering such questions is one of the techniques recommended by Platt in his stimulating discussion of "Strong Inference" [J. R. Platt, *Science* **146**, 347 (1964)]. The use of these methods calls for enterprise and ingenuity on the part of the researcher, as Platt points out, but it requires also certain minimally favorable circumstances in the area chosen for study, which seem heretofore not to have existed in the case of water.
5. Strictly speaking, this should now be called Ice Ih, to distinguish it from the cubic material (Ice Ic) which can be formed at low temperatures and from Ices II through VIII which exist in various temperature-pressure ranges. Information about the various ices is well summarized in reference (*3*), pp. 79–92.
6. S. W. Peterson and H. A. Levy, *Acta Crystallogr.* **10**, 70 (1957).
7. W. H. Stockmayer, *J. Chem. Phys.* **9**, 398 (1941).
8. L. Pauling, *The Nature of the Chemical Bond* (Cornell Univ. Press, Ithaca, ed. 3, 1960), p. 461; *ibid.*, p. 468.
9. The classical statistical-mechanical treatment that leads to the Stockmayer potential (*7*) can be transcribed into the language of quantum mechanics in certain cases, for example, for a model of the HCl molecule [J. O. Hirschfelder, C. F. Curtiss, R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954), pp. 997–1004]. Although such a calculation is much more difficult in the complicated case of the asymmetric top rotor which would represent the H_2O molecule, the quantization of the motions of the water molecule can hardly be ignored, as there are only 15 rotational term values listed [R. T. Hall and J. M. Dowling, *J. Chem. Phys.* **47**, 2454 (1967)] for which the equivalent temperature ($\theta = \hbar c\bar{\nu}/k$, where $\hbar$ is Planck's constant, c is the velocity of light, and k is the Boltzmann constant) is less than 400°K, so that the situation, even at the critical point, can hardly be amenable to accurate discussion in purely classical terms; that is, even in the dense vapor, where the individual molecule does not have good rotational quantum numbers, its orientation seems very likely to have something of the uncertainty prescribed in quantum mechanics for the isolated molecule.
10. See, for example, G. C. Pimentel and A. L. McClellan, *The Hydrogen Bond* (Freeman, San Francisco, 1960), chap. 8.
11. K. Morokuma and L. Pedersen, *J. Chem. Phys.* **48**, 3275 (1968); P. Kollman and L. C. Allen, *ibid.* **51**, 3286 (1969); D. Hankins, J. W. Moskowitz, F. H. Stillinger, *Chem. Phys. Lett.* **4**, 527 (1970); K. Morokuma and J. Winick, *J. Chem. Phys.* **52**, 1301 (1970).
12. J. Del Bene and J. A. Pople, *Chem. Phys. Lett.* **4**, 426 (1969); *J. Chem. Phys.* **52**, 4858 (1970).
13. H. S. Frank and W. Y. Wen, *Discuss. Faraday Soc.* **24**, 133 (1957).
14. Apparently the first published observation of this remarkable property of water was made in the experiments of the Florentine Academy about 1658. These are described in the *Saggi di Naturali Esperienze* of the academy. English translations are to be found in *Phil. Trans.* **5**, 2020 (1670) and in *Essayes of Natural Experiments*, translated by R. Waller, 1684 (Johnson Reprint Corporation, New York, 1964).
15. P. W. Bridgman, *Proc. Amer. Acad. Arts Sci.* **61**, 57 (1926).
16. W. K. Roentgen, *Ann. Phys.* **45**, 91 (1892). Earlier statements of essentially this idea were made by Rowland (see *17*) and by Whiting (see *18*), but in each of these cases the observation was incidental to a discussion that was not primarily concerned with water. Roentgen referred to the idea he

was setting forth as "by no means new," and it would not be surprising if additional early references to it should someday come to light.

17. H. A. Rowland, *Proc. Amer. Acad. Arts Sci.* **15**, 75 (1880).
18. H. Whiting, thesis, Harvard University (1884).
19. A. Eucken, *Nachr. Ges. Wiss. Göttingen* **1946**, 38 (1946).
20. L. Hall, *Phys. Rev.* **73**, 775 (1948).
21. K. Grjötheim and J. Krogh-Moe, *Acta Chem. Scand.* **8**, 1193 (1954).
22. G. Wada, *Bull. Chem. Soc. Jap.* **34**, 604 (1961).
23. G. Nemethy and H. A. Scheraga, *J. Chem. Phys.* **36**, 3382 (1962).
24. C. M. Davis, Jr., and T. A. Litovitz, *ibid.* **42**, 2563 (1965).
25. J. D. Bernal and R. H. Fowler, *ibid.* **1**, 515 (1933).
26. J. A. Pople, *Proc. Roy. Soc. London Ser. A Math. Phys. Sci.* **205**, 163 (1951).
27. J. D. Bernal, *ibid.* **280**, 299 (1964).
28. Referred to in a chapter by A. Ben-Naim and F. H. Stillinger, in *Structure and Transport Processing in Water and Aqueous Solutions*, R. A. Horne, Ed. (Wiley, New York, in press).
29. O. Ya. Samoilov, *Zh. Fiz. Khim.* **20**, 12 (1946).
30. E. Forslind, *Acta Polytech. Scand.* **115**, 9 (1952).
31. M. D. Danford and H. A. Levy, *J. Amer. Chem. Soc.* **84**, 3965 (1962).
32. L. Pauling, in *Hydrogen Bonding*, D. Hadži, Ed. (Pergamon, New York, 1959), p. 1.
33. M. von Stakelberg and H. R. Müller, *Z. Elektrochem.* **88**, 25 (1954).
34. H. S. Frank and A. S. Quist, *J. Chem. Phys.* **34**, 604 (1961).
35. Samoilov's 1957 monograph is available in English translation with a 1964 author's preface [O. Ya. Samoilov, *Structure of Aqueous Electrolyte Solutions and the Hydration of Ions*, translated by D. J. G. Ives (Consultants Bureau, New York, 1965)]. *Zhurnal Strukturnoi Khimii*, also available in English translation as *Journal of Structural Chemistry*, is a principal medium of publication for a vigorous and productive school of Russian workers in this field.
36. A. H. Narten, M. D. Danford, H. A. Levy, *Discuss. Faraday Soc.* **43**, 97 (1967).
37. F. Franks and D. J. G. Ives, *Quart. Rev. London* **20**, 1 (1966).
38. T. T. Wall and D. F. Hornig, *J. Chem. Phys.* **43**, 2079 (1965).
39. M. Falk and T. A. Ford, *Can. J. Chem.* **44**, 1699 (1966).
40. There is an extensive literature on solvent, or medium, effects in infrared spectroscopy [see, for example, A. D. Buckingham, *Proc. Roy. Soc. London Ser. A Math. Phys. Sci.* **248**, 169 (1958)]. The kind of influence discussed in the following paragraphs in the text may be regarded as a special case of the general reaction field effect.
41. H. S. Frank, *Discuss. Faraday Soc.* **43**, 137 (1967).
42. G. E. Walrafen, *J. Chem. Phys.* **48**, 244 (1968).
43. W. A. Senior and R. E. Verrall, *J. Phys. Chem.* **73**, 4242 (1969).
44. H. J. Bernstein, *Raman Newsletter No. 1* (November 1968).
45. The idea that there are at work between water molecules forces of two qualitatively disparate sorts receives independent support [H. S. Frank, in *Desalination Research Conference Proceedings* (Nat. Acad. Sci.–Nat. Res. Counc., Publ. No. 942, 1963), p. 141] from the fact that the vapor pressure curves of H_2O and D_2O cross between room temperature, where H_2O is the more volatile by some 10 percent, and the critical temperature which is some 3°C lower for D_2O [I. Kirshenbaum, *Physical Properties and Analysis of Heavy Water* (McGraw-Hill, New York, 1951), p. 25]. The fact that the net isotope effects are of opposite sign in the two states suggests that the physical interactions which preponderate are of different character.
46. E. U. Franck and K. Roth, *Discuss. Faraday Soc.* **43**, 108 (1967).
47. E. U. Franck and H. Lindner, *Ber. Bunsenges. Phys. Chem.*, in press.
48. A. H. Narten and H. A. Levy, *Science* **165**, 447 (1969).
49. A. M. Levelut and A. Guinier, *Bull. Soc. Franc. Mineral. Cristallogr.* **40**, 445 (1967).
50. Cited in reference (*48*) as a personal communication.
51. A very recent exchange in *Science* [B. Kamb, *Science* **167**, 1520 (1970); A. H. Narten and H. A. Levy, *ibid.*, p. 1521] has brought out that the details of the model described in references (*31*) and (*36*), having been evaluated by a least-squares procedure involving a considerable number of adjustable parameters, bear a rather tenuous relation to the actual nature of the water sample, since, in such a case, the computer is forced to use whatever means are available to it in attempting to take account of whatever features the data may display, whatever their physical origin. Thus large "temperature factors" are used to represent the absence of long-range order; this modification permits local ice-like (by definition) cells in different parts of the liquid to face in different directions. It would seem that by the same means one might also be able to take account of altered (within limits) geometries of local cells.
52. N. Ockman, *Advan. Phys.* **7**, 144 (1958).
53. G. E. Walrafen, *J. Chem. Phys.* **44**, 1546 (1966).
54. That these vagaries should be able to produce completely unbonded molecules in a certain fraction of cases seems likely not only on intrinsic topological grounds but on energetic ones as well if some such dependence of hydrogen bond strength on length and configuration of bond chains as that reported in reference (*12*) is to be accepted. According to the numbers given there, not only is a ring pentamer plus an unattached monomer more stable than two ring trimers, but for a group of 16 water molecules three ring pentamers plus a monomer are more stable than four ring tetramers. In three dimensions, therefore, it is by no means inconceivable that a local situation might arise in which the closing of a polyhedral figure with favorable bond angles, with a monomer left enclosed, would be energetically preferable to the incorporation of the monomer into the bonded structure. If the monomer were left, unbonded, this transaction need not, in fact, yield an actual profit in bond energy; small losses in energy should also be acceptable, by reason of the entropy advantage presumably entailed.
55. J. H. Wang, C. V. Robinson, I. S. Edelman, *J. Amer. Chem. Soc.* **75**, 466 (1953).
56. C. H. Collie, J. B. Hasted, D. M. Ritson, *Proc. Phys. Soc. London* **60**, 145 (1948).
57. For example, H. G. Hertz, *Ber. Bunsenges. Phys. Chem.* **71**, 979 (1967); *ibid.*, p. 999.
58. W. M. Slie, A. R. Donfor, T. A. Litovitz, *J. Chem. Phys.* **44**, 3712 (1966).
59. G. J. Safford, P. S. Leung, A. W. Naumann, P. C. Schaffer, *ibid.* **50**, 4444 (1969).
60. R. W. Terhune, P. D. Maker, C. M. Savage, *Phys. Rev. Lett.* **14**, 681 (1965).
61. M. J. Colles, G. E. Walrafen, K. W. Wecht, *Chem. Phys. Lett.* **4**, 621 (1970).
62. A very large literature exists, for example, references (*13*) and (*37*); R. L. Kay and D. F. Evans, *J. Phys. Chem.* **70**, 2328 (1966); *ibid.*, p. 2336; E. M. Arnett, in *Physico-Chemical Processes in Mixed Aqueous Solvents*, F. Franks, Ed. (Heinemann, London, 1967), pp. 105–127.
63. Computed from the data of P. W. Bridgman as quoted in *International Critical Tables*, vol. 3, pp. 40–42.

64. Supported in part under a grant made by the Office of Saline Water, U.S. Department of the Interior.

A Multiple Origin for Plastids and Mitochondria

Many independent symbiotic events may have been involved in the origin of these cellular organelles.

Peter H. Raven

In view of much accumulating evidence, it now seems almost certain that the plastids and mitochondria in eucaryotic cells originated as free-living procaryotes which found shelter within primitive eucaryotic cells and eventually were stabilized as permanent symbiotic elements within them (*1*). This evidence, however, has been largely ignored in the construction of phylogenetic classifications of living organisms, such as the excellent one recently presented by Whittaker (*2*). What implications for the phylogenetic relationships between groups of organisms does a symbiotic origin of plastids and mitochondria have?

Evidence for Symbiotic Origin

The evidence for a symbiotic origin of mitochondria and plastids will be presented in two parts. First, we shall review the properties of these cellular organelles themselves, and then we shall consider the nature and occur-

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