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WATER STRUCTURE MODELS

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CONTENTS

A. INTRODUCTION

Water being the most important chemical compound in nature, the structure of liquid water is of interest to many investigators in various scientific fields. One expression of this interest has been the several reviews on diverse aspects of the properties and structure of liquid water which have been published[1–18].

The present selective review does not aim at a comprehensive description of all the properties of liquid water. It is intended, rather, to give a detailed account of the current models of liquid water structure, to discuss their merits and to single out the experimental data which contribute most to the understanding of the structure of water.

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The description of the models of water structure is preceded by a short introductory description of the properties of water. As this review is model-oriented, experimental evidence on the structure of water is discussed after the models are presented. The experimental data are discussed mainly insofar as they supply criteria for evaluating the models. In addition, some space has been devoted to the discovery of what seems to be a new form of water ("anomalous water" or "polywater") by Deryagin et al. and the follow-up research of this species by other investigators. Some attention has also been given to interfacial effects on the structure and measured properties of water. The literature survey extends through 1969.

The reader interested in a comprehensive review on the properties and structure of water in the vapor, solid and liquid phases, is referred to the excellent book by Eisenberg and Kauzmann[1]. An exhaustive compilation of data on water is to be found in Dorsey's book[2].

B. THE STRUCTURE OF THE WATER MOLECULE IN THE VAPOR PHASE AND IN ORDINARY ICE

The structure of the water molecules (Fig. 1) determines their intermolecular interactions, and hence the properties of water and ice.

In the isolated water molecule in the gaseous state, three nuclei form an isosceles triangle, the OH distance being 0.958 Å and the HOH angle 104° (Ref. 86*a*). The symmetry group of the molecule is C_{2v}. Of the ten electrons surrounding the three nuclei of the water molecule, the two 1*s* electrons of the oxygen atom are confined to the vicinity of their nucleus. The other eight electrons belong to four orbitals which point to the vertices of a somewhat distorted tetrahedron, the center of which corresponds approximately to the oxygen nucleus[19–21]. Two of the four orbitals are directed along the OH bonds and their electrons are unequally shared between the O and H atoms. The electrons of the other two orbitals, the so-called "lone-pair electrons", do not participate in bonds, in the gaseous (isolated) state. However, water molecules can form intermolecular hydrogen bonds involving a hydrogen atom of one molecule and an atom possessing lone-pair electrons and belonging to another molecule. This type of intermolecular bonding can be found in ordinary ice–ice I, see Fig. 2. (For reviews on the structure of various forms of ice, see Refs. 1, 3, 22–27.) The ice I structure will be discussed in some detail, as in some models the liquid water structure is assumed to be a broken-up ice I structure.

Ordinary ice has a tridymite-like structure. (Tridymite is one of the crystalline forms of silica, SiO_2.) The oxygen atoms lie in layers of puckered hexagonal rings. Each oxygen atom is surrounded tetrahedrally by four other atoms at a distance of 2.76 Å. The positions of the oxygen atoms were obtained by X-ray diffraction studies[28–30], but the positions of the hydrogen atoms could not be found by this method because of the low scattering power of hydrogen atoms for X-rays. Electrostatic energy considerations indicated that the most favorable position of the hydrogen atom is on the O—O line of centers[30,31].

The magnitudes of the changes of properties from water vapor to ice are not large enough to allow for an ionic structure of ice[32] (although such a possibility was suggested by Barnes[30] who held that water molecules in ice are fully ionized to $2H^+ + O^{2-}$ and that

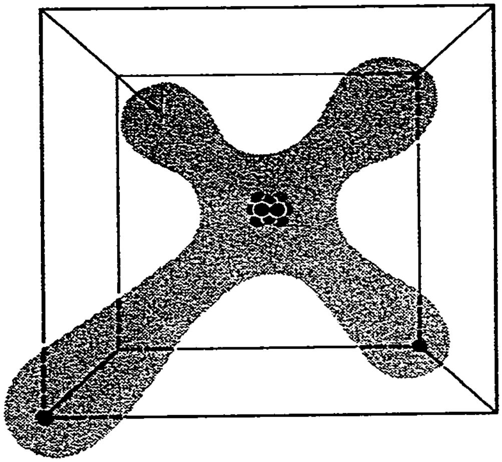

Fig. 1. Molecule of water[22].

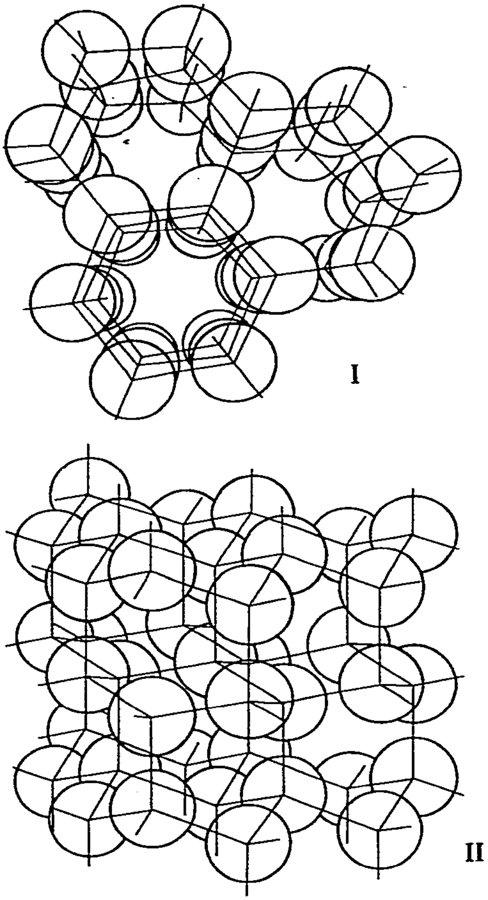

Fig. 2. Water molecules in ice crystal[22].

one proton is located in the middle of each O---O line of centers). For example, the small differences in the stretching vibrations of the OH bonds, observed for water vapor and ice, have been interpreted[33] as corresponding to a value of 0.99 Å for the length of the OH bond in ice. Thus, ice consists of discrete molecules, intermolecularly hydrogen bonded.

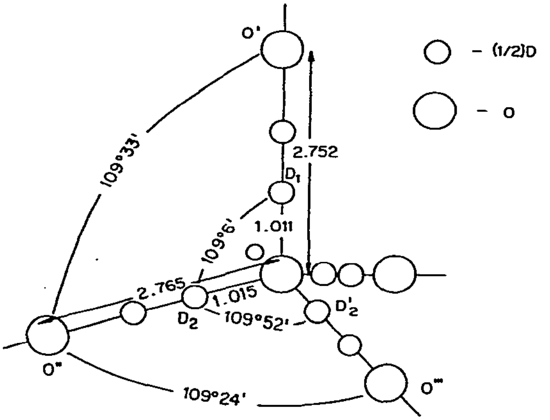

Fig. 3. Structural relationships in one tetrahedron of the ice structure. The distances and angles are[35] those at −50°C.

The hydrogen atom bonded to two oxygen atoms O′ and O″ can occupy two positions, H′ and H″, between those atoms (Fig. 3). Position H′ corresponds to an intramolecular bonding of H and O′, and position H″ corresponds to an intramolecular bonding of H and O″. Although both positions cannot be simultaneously occupied, the discovery of residual entropy in ice at 0°K[34] led Pauling to the conclusion that over a sufficiently long time interval, each of the two positions H′ and H″ is occupied for half the time. (Pauling[32] suggested that the change of positions occurs either by rotation of molecules, or by movement of the hydrogen atoms between the two possible positions along the O---O lines, or by both those processes.)

In their neutron-diffraction studies of D_2O-ice I[35], Peterson and Levy obtained a Bragg pattern agreeing with an assignment of "half-a-deuteron" to each of the two available positions between oxygen atoms O′ and O″. This is just the Bragg pattern which would have been predicted on a basis of a Pauling disorder such as described above. Other important conclusions drawn from the data[35] are that there are two non-equivalent sets of tetrahedra in the ice I structure, that the deuterons are almost collinear with the O---O center lines and that the OD distance is 1.01 Å (see Fig. 3). However, as pointed out[35], this model of ice I is not unique in being capable to account for the diffraction data. Thus, Chidambaram[36] proposed a model of ice I in which the D-O-D angle has the vapor phase value of 104.5° (instead of 109° as maintained by Peterson and Levy) and correspondingly the hydrogen bonds are bent. Chidambaram[36] showed that his model cannot be ruled out on the basis of neutron-diffraction data[35]. Each interstice of ice I is bounded by six water molecules at a distance of 2.9 Å from its center. Samoilov[5] and

Forslind[37] considered that these interstices can accommodate a non-associated water molecule without greatly disturbing the structural order of the lattice.

C. MODELS OF THE STRUCTURE OF WATER

(i) *The unique properties of water and their early explanations*

The physical properties of liquid water (high m.p. and b.p., high dielectric constant, IR, Raman and NMR spectra, ionizing ability, etc.) all point to strong hydrogen bonding in liquid water. Water is distinguished from most other liquids by its numerous anomalous properties[1,2,5]. Examples of "anomalies" of liquid water are:

(1) the density maximum at 4°C;

(2) the C_v increase upon melting and the heat of fusion are anomalously large;

(3) the coefficient of thermal expansion increases with pressure between 0–45°C (i.e. in this temperature range the compressibility decreases on raising the temperature), while in normal liquids a pressure increase is accompanied by a decrease in the coefficient of thermal expansion;

(4) the viscosity decreases as the pressure increases (in the temperature range 0–20°C), has a minimum near 1000 kg/cm^2 and then increases in a normal fashion;

(5) the pressure dependence of the static dielectric constant, the self-diffusion coefficient, and other thermodynamic and transport properties of water are anomalous.

The earliest theories[2,6] attempted to explain the anomalous properties of water, by postulating water to be an equilibrium mixture of different water polymers. This approach was abandoned after the publication of X-ray diffraction studies[38–41] of water, which disclosed that water is characterized by short range order. The approach was unable to account for this, as well as for other observed properties of water, and so was superseded in most later models by an emphasis on extensive hydrogen bonding, and the formation of spatial networks. This change in point of view was initiated in 1933 by Bernal and Fowler[31]. Even before the publication of the X-ray diffraction data, the validity of the "polymer" theories was questioned[42], because no polymers could be separated or detected in liquid water.

(ii) *The concept of "water-structure"*

The fundamental difference between the earlier "polymer" theories and subsequent theories, was that the former tried to explain the properties of water in terms of the properties of a single molecule and an equilibrium between different types of molecules, while the latter tried to explain the properties of water in terms of "water-structure", i.e. in terms of the relative positions and motions of the molecules, and of intermolecular interactions.

The models of water structure which will be described in this review start from the premise that certain "structures" or angular correlations of molecules exist in liquid water. The question of what may be the life-time and the spatial dimensions of "structures" in water, is fundamental to the appraisal of the various models. There are certain experimental data pertinent to this question. They will be cited here, as they constitute a framework to which any proposed model of "water-structure" must conform:

(1) according to graphs of radial distribution functions of water (section E, i), a given water molecule induces a certain order to a distance of 8 Å (at 0 °) from its center. Above this distance, the distribution of molecules around a given molecule is completely random. This datum limits the assumed dimensions of "networks" and other structures of water;

(2) IR and Raman spectra of water (section E, ii) disclose that water molecules oscillate about temporary equilibrium positions, the average period of time for an oscillation being 2×10^{-13} sec;

(3) the self-diffusion, viscosity, dielectric relaxation and NMR relaxation of water[1], show that the equilibrium positions and orientations of liquid water molecules experience frequent changes. The dielectric relaxation time of water indicates that a molecule (near 0°C) experiences a displacement roughly every 10^{-11} sec;

(4) water has only one sharp PMR absorption peak. This shows that within the observation time of the NMR technique, water seems to be a homogeneous structureless liquid. The NMR technique supplies information on the average structure of the examined material, in periods of times not shorter than 10^{-4} sec. It follows then, that any structures which possibly exist in water, have life-times shorter than 10^{-4} sec;

(5) there is only one structural technique which is currently applied to liquid water and which has a shorter observation time than NMR. This is vibrational spectroscopy for which the observation time is 10^{-12}–10^{-14} sec. The interpretation of the vibrational spectrum of water is a controversial subject (section E, ii). Some investigators hold that this spectrum indicates that distinct "species" of water molecules (i.e. water molecules in different states of energy, arrangement and bonding) exist in water. Others hold that the vibrational spectrum shows that water is a homogeneous structureless liquid within the observation time of this technique. A more detailed account is given in section E, ii.

(iii) The Bernal–Fowler model

Bernal and Fowler[31] postulated the existence of three structural forms of water:

(1) water I: tridymite-ice-like, present to a certain degree at low temperatures below 4°;

(2) water II: quartz-like, predominating at ordinary temperatures;

(3) water III: close-packed, ideal liquid, predominating at high temperatures for some distance below the critical point at 374°;

At any temperature, the liquid is taken to be homogeneous, its average structure resembling water I, II and III to a greater or lesser degree. The increase in the density of water on melting may thus be ascribed to a transition from the ice I tridymite-like structure to the denser quartz-like structure.

The crystalline character of this model was apparently suggested by X-ray diffraction curves which disclosed the short range order characteristic of liquid water[38–41].

The Bernal–Fowler model has been criticized because of its rigidity and the undue bending strain exerted on the hydrogen bonds in the quartz-like structure[43–46] (the OHO angle in the quartz-like structure being 135°[47,48], i.e. a deviation of 45° from bond-linearity). Nevertheless, the principal features of this model, i.e. the existence of extensively hydrogen bonded regions, and the gradual breakdown of hydrogen bonding with rising temperature have been incorporated into most of the later models. They are firmly supported by the results of X-ray scattering experiments and IR, Raman and NMR spectroscopy.

(*iv*) *"Network" models*

The crystalline ideal liquid model of Bernal and Fowler does not account for the fluidity of water. The models proposed by Samoilov[5,49] and Forslind[37] overcame this deficiency. They consider water as an ice-like crystalline system. The liquid differs from the solid mainly in its higher bulk density, due to the appearance of non-associated interstitial molecules, and in the increased number of interstitial molecules coupled with vacant lattice sites.

The open channelled structure and the non-associated state of interstitial molecules allow molecular translatory motion. The translatory motion consists of a series of activated jumps[5,49] between equilibrium positions in the "network" (relative energy minima are situated in interstitial positions). The "hydrophobization" idea[50,51] furnishes an explanation of the non-associated state of interstitial molecules. According to it, the field acting on the molecules may have a considerable degree of rotational and translational freedom owing to the averaging-out of directional interactions.

This model is a two-state model, i.e. according to it, liquid water is a mixture of molecules in two different states. State I: framework, hydrogen bonded molecules and state II: "monomeric" interstitial molecules. This "network" model can supply a qualitative account of the density, specific heat, thermal expansion, compressibility and viscosity anomalies of water[5].

(*v*) *"Gas-hydrate" models*

Water forms crystalline hydrates with xenon, chlorine, methane and many other non-polar substances with sufficiently small molecular size[52,26,61]. X-ray diffraction experiments[53–55] have confirmed the suggestions[54,57] that the distances and angles between the water molecules in those hydrates differ but little from their corresponding values in ordinary ice (ice I). The water molecules in these hydrates are found at the corners of various polyhedra the faces of which are pentagons and hexagons. These polyhedra constitute cages which enclose cavities with diameters varying from 5.2 to 6.9 Å, all or most of the cavities containing a non-polar molecule. The interactions between non-polar molecules entrapped in the interstices and framework molecules are assumed to be mostly transient dipole-induced dipole and permanent dipole-induced dipole[58]. These compounds, typified by the entrapment of certain molecules by a lattice formed by other molecules, belong to the well-known clathrates group.

The entrapped non-polar molecules interfere very little with the dynamics of the "host" lattice and, consequently, can rotate freely[59,60]. Pauling[46,26] suggested that water has a range of labile structures similar to those of its gas and salt hydrates. The cages in the water-clathrate structures may be empty or occupied by water molecules which are non-hydrogen bonded and free to rotate, owing to the high field symmetry in the interstices.

Pauling[46] takes a pentagonal dodecahedral complex (Fig. 4) as an example for such a labile structure, which has the advantage (over an ice-like aggregate of similar size) of higher stability as represented by the number of hydrogen bonds that are formed. It also has the advantage of mobility while keeping hydrogen bonds formed with surrounding complexes.

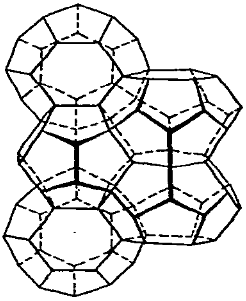

Fig. 4. A dodecahedral complex is shown in the center of the drawing. The polyhedra that surround it are tetrakaidecahedra each having two hexagonal faces and 12 pentagonal faces[46].

(*vi*) *"Flickering-cluster" models*

Frank and Wen[62,63] considered that there is a sizeable covalent contribution to the energy of the hydrogen bond. It follows that there should be sharp energy minima at small bending angles of the hydrogen bond. Thus, Frank and Wen kept the term hydrogen bond only for approximately linear hydrogen bonds and considered molecules associated by "bent" hydrogen bonds as "non-associated" molecules. Moreover, Frank and Wen considered that hydrogen bonded molecules are mutually polarized, the resulting charge separation being such that the free ends of the associated molecules have a higher affinity for further hydrogen bonding than the ends of non-hydrogen bonded molecules (i.e. the non-hydrogen bonded oxygen of an associated molecule is more basic and the non-hydrogen bonded hydrogen atom more acidic than the corresponding atoms of a non-associated water molecule). Consequently, hydrogen bonding in water was postulated to be mainly a cooperative phenomenon, so that formation of one hydrogen bond will lead to formation of a "cluster" of hydrogen bonded molecules and the breaking of one hydrogen bond will be followed by the "dissolution" of a whole cluster. Thus, water was described as a mixture of clusters and a surrounding liquid of monomer molecules.

The main distinction between clusters and monomers is that the former have a covalent contribution to their intermolecular interaction energies. However, it must be kept in mind that the "monomers" or "non-associated" molecules in the sense of Frank and Wen, still have strong electrostatic interactions with their surroundings and have no considerable degree of random arrangement or rotational freedom. (No mechanism of molecular motion was described by which the non-random, rotationally restricted monomer liquid can reproduce the fluid properties of water.)

It was believed that melting of clusters into monomers and formation of clusters from monomers were involved with small enough free energies, so as to be controlled by local energy fluctuations. It was also estimated that if the clusters should have meaningful existence, their half-life must be 10^{-10} or 10^{-11} sec which is 10^2 or 10^3 times a molecular vibration period. The monomers were assumed[62,63] to be denser than the clusters and than ice, which explains the density maximum of liquid water. No particular semi-crystalline structure was postulated for the clusters and no structural requirement was imposed on the clusters besides that of hydrogen bond linearity. Néméthy and Schéraga[4] added to this the requirement that the clusters should contain a maximum of hydrogen bonds and be compact, i.e. most of the molecules in a cluster should be four-coordinated (these two requirements can be fulfilled by many crystalline arrangements, e.g. ice I, the pentagonal dodecahedral complex of Pauling, etc.). The requirement of Néméthy and Schéraga was questioned by Vand and Senior[64] who concluded that there should be many non-quadruply bonded molecules in a cluster. It should be stressed, however, that the only structural feature of the clusters which is essential to explain their formation is hydrogen bond linearity in the clusters so that both the picture of the clusters formed by Néméthy–Schéraga and the one by Vand–Senior are consistent with the original "flickering-cluster" model.

(*vii*) *The "bent-bond" model*

Pople and Lennard-Jones[19,20] stated that a considerable percentage of broken hydrogen bonds in liquid water is inadmissible on thermodynamic grounds. The latent heat of fusion and the value of RT at 0°C are 1.4 and 0.5 kcal/mole, respectively, while Pauling's[26] estimate of the energy of the hydrogen bond between two water molecules is 4.5 kcal/mole. Assuming also that there are two hydrogen bonds per water molecule in ice, and that bending of bonds will require much of the latent heat of fusion, the aforementioned conclusion is reached. Moreover, Pople[44] asserted that hydrogen bonds in liquid water are flexible and can bend continuously. In a very approximate calculation of the average value of cos θ (θ being the bending angle of the hydrogen bond), he equated:

$$(\cos\theta)_{\text{average}} = \coth(g/kT) - (kT/g)$$

where $g = (d^2F/d\theta^2)_{\theta=0}$, T is the temperature, k the Boltzmann constant and F the energy of the hydrogen bond. A calculation of the radial distribution function of water, gave the best fit with experiment when the value of $g/kT = 10$ was used. From this, $\cos^{-1}(\cos\theta)_{\text{average}}$ was calculated to be 26° and 30° at 0°C and 100°C respectively. Molecular motion in water was depicted as involving continual breaking and reformation of bonds in such a manner that at any given time almost all of the molecules form their full complement of bonds, even though they may be bent. It was contended that the main difference between ice and water is that the four hydrogen bonds formed by each liquid water molecule can bend independently, while in ice, those distortions can be performed only in such a way that the lattice order is maintained. Due to this structural flexibility, periodic molecular arrangement in liquid water does not extend beyond few molecular diameters. The increased freedom of individual bonds permits movement of some of the molecules into formerly unoccupied regions of the ice I lattice. Consequently, volume diminution on melting will be observed.

The theoretical assumptions leading to this model can be seriously criticized. The energy of 4.5 kcal/mole (as estimated by Pauling[26]) is the energy required to separate two water molecules to an infinite distance. A separation of two water molecules to a distance of a few Angströms which will cause a hydrogen bond to break, may require considerably less energy. Thus, the conclusion stemming from Pauling's estimate, namely, that almost all of the hydrogen bonds in water remain intact, is not entirely convincing. Moreover, the value of g, the hydrogen bond bending force constant, which also led to this conclusion, was estimated in a crude semi-empirical manner. Thus, the fundamental idea of the "bent-bond" model, i.e. that the distortion angles of bonds in water will be quite large, has no firm theoretical foundation.

(*viii*) *The Davis–Litovitz model*

From the Raman spectrum of water it was estimated[33] semi-quantitatively that water appears on the average to be slightly more than two-coordinated in the temperature range 25–90°C. From the area under the first peak in the radial distribution curves calculated from X-ray diffraction data, it was estimated[65] that the number of nearest neighbors of a water molecule is 4.4.

Davis and Litovitz[66] suggested that the difference in the number of nearest neighbors obtained from the Raman spectrum and from X-ray diffraction is evidence for the existence of different types of neighbors in water, only some of which are hydrogen bonded. Hydrogen-bonded molecules were defined as molecules which occupy sites corresponding to those in ice. A "broken" hydrogen bond was defined as a bond having no covalent contribution to its energy. This is an acceptance of Frank and Wen's views on the covalent, cooperative and directional nature of the hydrogen bond. Davis and Litovitz also accepted Pauling's[26] view (see section C, vii) that a large number of broken hydrogen bonds is incompatible with the small latent heat of fusion of ice. They consequently proposed a two-state model of water which consists of puckered hexagonal rings in water, similar to those in ice. The formation of such rings is assumed to be favoured by the highly directional cooperative nature of the hydrogen bond. In water these rings are postulated to occur in an equilibrium distribution of two structures: an open ice-like structure optimal for forming hydrogen bonds between rings, and a close-packed nearly complete body-centered cubic structure. The open structure is assumed to be identical to ordinary ice structure, i.e. a molecule in this structure has four hydrogen bonded nearest neighbors. In the close-packed structure, a molecule is assumed to have two hydrogen-bonded nearest neighbors. It was shown that this requires only 18% of the hydrogen bonds to be broken at melting, so that it conforms with Pauling's preclusion of a large percentage of broken hydrogen bonds in water at 0°C.

(*ix*) *Discussion of the models*

Clearly, all the models considered hitherto are intuitive and heuristic, none having a firm theoretical and physical foundation. This does not prevent them, of course, from reproducing successfully many properties of liquid water, or from being conceptually adequate. Some of the models start from a similarity between the properties of water and ice (for a similarity of the spectroscopic properties, see E), and assume that liquid water is a broken-up ice I structure (e.g. the Bernal–Fowler and the "network" models). Other models (e.g. the "bent-bond" and the "gas-hydrate" models) propose structures of water embodying a requirement for a maximum hydrogen bonding, which is by no means shown to be justified (see section C, vii). Still other models are based on the ideas of Frank and Wen[62,63] about the covalent, directional and cooperative nature of the hydrogen bond (e.g. the "flickering-cluster" and the Davis–Litovitz models). Frank and Wen's ideas about the cooperative nature of the hydrogen bond in water, seem very plausible. However, it should be pointed out that the validity of the "flickering-cluster" model is highly dependent on the relative magnitude of the contribution of the cooperative element to the energy of the hydrogen bond. For, if such a cooperative contribution, though existent, is weak in comparison to other contributions to the hydrogen bond, it will not lead to a simultaneous "freezing" of many molecules into a cluster, and to a simultaneous "melting" of the molecules contained in such a cluster. Thus, even if it is granted that the hydrogen bond in water is cooperative, this does not necessarily lead to a "flickering-cluster" structure for water. The experimental evidence invoked by Davis and Litovitz in support of their suggestion of two states of water molecules in the liquid (see section C, viii) is based on data inadequate for this purpose. The calculation of Cross et al.[33] is admittedly semi-quantitative. Also the calculation of the number of nearest neighbors from the area under the first peak in the radial distribution curves of Morgan and Warren[65] is ambiguous as the right-hand side of the peak is not fully resolved.

In general, the current models of water structure can be divided into two groups: "mixture" models (such as the "network", the "gas-hydrate" and the "flickering-cluster") and "continuum" models (such as the "bent-bond"). According to "mixture" models, water molecules in the liquid may be said to belong at least to two species, i.e. they may be found in at least two different states. The species (states) of water molecules differ in the number of their hydrogen bonds. They are assumed to be short-lived and to interchange roles. The strength, and the bending angles of the hydrogen bonds are considered as discrete quantities with values characteristic of each state. The non-hydrogen-bonded species in these models are taken to be much more mobile than the hydrogen bonded species which are situated in rather rigid structures. In order to account for the fluidity of water, these models have to assume a considerable percentage of mobile non-hydrogen-bonded molecules.

In the "continuum" models the energy of the hydrogen bond is assumed to be a continuous and a smooth function of the bending angle, so that every bending angle corresponds to a possible temporary equilibrium state of a molecule. There is a continuous distribution of molecular environment and energies. It is also assumed that a high percentage of the hydrogen bonds in water are bent. In a "continuum" model, even the more-hydrogen-bonded molecules are located in rather flexible structures, so that even if the less-hydrogen-bonded molecules are postulated to exist in a minute amount, the fluidity of water can be accounted for.

Any model which assumes that there exist in liquid water molecules which differ a great deal in their environment, that is, in the degree of hydrogen bonding and energies, can account qualitatively for most of the properties of water. Both the current "mixture" and the "continuum" models of water fulfill this requirement. The existence of mobile, less-hydrogen-bonded molecules accounts for the fluidity of water, while the existence of more-hydrogen-bonded molecules accounts for the high m.p., b.p., dielectric coefficient and other unusual properties of water. The appearance of anomalous temperature dependence for certain properties of water may be explained by such models as follows. Let us consider a property A of water which is a function $f(T)$ of the temperature, T, and has an extremum in a certain temperature range (while no such extremum appears for normal liquids in any temperature range). Let it be assumed that water consists of groups of molecules: $i_1, i_2 \ldots, i_n$ ($n = 2,3 \ldots$). For each group, property A takes a characteristic functional form: $f_1(T), f_2(T) \ldots f_n(T)$ respectively. Let it also be assumed that the relative amounts of molecules in the different groups form the set of functions: $g_1(T), g_2(T) \ldots g_{n-1}(T)$. Even if the functions $f_1(T) \ldots f_n(T)$ are expected to have no extremum in the given temperature range, $f(T)$, which is a functional of the set of functions $f_1(T), \ldots f_n(T), g_1(T) \ldots, g_{n-1}(T)$, may have an extremum in this temperature range.

The conclusion of this discussion is that, considering the qualitative account of the properties of water given by the models described in this review, the Bernal-Fowler, the "gas-hydrate" and the Davis-Litovitz models are inferior to the other current models because of their rigidity. Of the three other models (the "flickering-cluster", the "bent-bond" and the "network" models) none can be preferred over the other.

The models of water structure have naturally been built with the known properties of water in mind, so as to account for them. Thus, all the models described hitherto explain qualitatively most of the known properties of water, but their inadequacy shows up clearly in their inability to predict quantitatively or qualitatively unknown properties of water.

The reader who is interested in examples which further illustrate some of the preceding observations is referred to Holtzer and Emerson's discussion[67] on the usefulness of the concept of water structure in the rationalization and prediction of some physical properties of H_2O and D_2O and the influence of solutes on the properties of water. Their analysis points out the ambiguities and the failures of many predictions inherent in and derived from current theories of water structure.

D. QUANTITATIVE TREATMENTS OF THE MODELS

(*i*) *Introduction*

Quantitative treatments of various models of water will be described in this chapter. "Quantitative treatment" in the present context means the translation of the features of a model into mathematical terms and the subsequent calculations of various properties. At present, the price for obtaining mathematically tractable treatments of models of water structure is an oversimplification of the models. Most of the calculations of the properties of water are concerned with its thermodynamic properties, static dielectric constant, and X-ray scattering properties. The results of calculations of these properties will be compared with experiment in this and the next section (E). The usefulness of such comparison as a criterion for the validity of the models will also be discussed. As the current models of water were developed intuitively rather than rigorously, it is obvious that the agreement of properties calculated according to a certain model with experimental data, is not real proof of the validity of the examined model. A conceptually wrong model may reproduce successfully certain properties, while a conceptually correct model may fail to do so. Nevertheless, a good fit often indicates that a model reflects some aspects of the actual structure of water. Before describing the quantitative treatments of various models of water, it should be mentioned that the ability of the current models to reproduce the dielectric, thermodynamic and X-ray scattering properties of water, seems of smaller importance compared with the compatibility of the models with spectroscopic and other data (this view is supported by the conclusions of the discussions in sections D, iv and E, i).

(*ii*) *Thermodynamic properties*

A treatment[50] of a "gas-hydrate" type model, yielded good *P–V–T* correlations for liquid water over limited ranges of pressure and temperature, but failed to reproduce the C_v of water.

A treatment of the "flickering-cluster" model by Néméthy and Schéraga[4] postulated that liquid water contains five distinguishable species of water molecules. The proposed species were of molecules having none, one, two, three or four hydrogen bonds. The model was used to calculate the free energy, the enthalpy and the entropy of liquid water in the temperature range 0–70°C. The results agree with experiment to within 3%. However, the temperature dependence of C_v is too large. Only two adjustable parameters were used.

A "network"-type model[68] was used to calculate the Helmholtz free energy, the entropy, the volume, and the pressure of water, in the temperature range 0–200°C. The results are in good agreement with experiment except for the volumes and the quantities depending on the second derivative of the partition function (e.g. C_v). Eucken[43] used a model containing aggregates of two, four and eight molecules in the liquid (much in the spirit of the earlier "polymer" theories). The octamer was postulated with a structure such that it has a larger volume per molecule than the monomer or the smaller aggregates. The mole fractions of the aggregates were adjusted so that very good agreement with compressibility and thermal expansion data was obtained.

Studies of the IR spectrum of liquid water near 8000 cm^{-1} (see section E, ii) led Buijs and Choppin to conclude[69,70] that liquid water consists of three types of molecules: (*a*) molecules with both O–H groups participating in hydrogen bonds; (*b*) molecules with one O–H group in a hydrogen bond and (*c*) molecules with two free O–H groups. Vand and Senior[64] considered the results of Buijs and Choppin and concluded that their data cannot be reconciled with a model for water based on three sharp levels of energy. It was suggested[64] that each species of water should be associated with an energy band rather than with a sharp energy level. The model incorporates features of both "mixture" (as it assumes the existence of distinct species) and "continuum" (as it assumes a continuous distribution of energy for each species). Thus, Vand and Senior developed a partition function based on the above postulates. Their calculation assumed that the molecules are spread in Gaussian energy bands around the mean energy for each of the species. They obtained values of the Helmholtz free energy, internal energy, and C_v in the temperature range 0–100°C, deviating from experiment by less than 1%. However, they concluded that their model is not unique in being able to account for the thermodynamic properties of water. This conclusion was based on a recalculation of the above values using a simple model consisting of only one species of water with one energy band. This model also yielded satisfactory numerical values for the thermodynamic properties of water.

The Davis-Litovitz model was used[66] to calculate the expansion coefficient of water (in the range of 0–100°C). All the values obtained, except for one case, agree with experiment within 4%.

A model of liquid water as a mixture of two species of "solid-like" clusters of molecules in equilibrium, proposed by Mu Shik Jhon et al.[71], was used to calculate the molar volume and vapor pressure (at the melting point and boiling point), the Helmholtz free energy (in the range 0–200°C) and entropy of vaporization (range 0–140°C). In all these cases, good agreement with experiment was obtained.

An admittedly heuristic model for a quantitative treatment of water, proposed by Orentlicher[72], is a simple cell model, consisting of a tetrahedral single structure for water, the molecules having zero to four hydrogen bonds each. The calculations involved three adjustable parameters, and reproduced successfully the volume, entropy and C_v of water in the range 0–100°C.

(*iii*) *Dielectric properties*

The static dielectric constant, ϵ, of water has been calculated using various models of water. The numerical results are presented in Tables 1 and 2.

Oster and Kirkwood[73] assumed water to be approximately tetrahedrally coordinated in accordance with the Bernal-Fowler model. A directed hydrogen bond about which there is free rotation but no bending is assumed to exist between neighboring molecules. The Kirkwood theory of dielectric polarization of polar liquids was applied to this model. Kirkwood's theory was also applied by Haggis, Hasted and Buchanan[74], but they assumed water molecules from zero to four-coordinated. The distribution of the molecules

TABLE 1

Comparison of ϵ of water based on application of Kirkwood's theory to different models of water

t(°C)	Experimental[75]	Calculated		
		Oster and Kirkwood[73]	Pople[20]	Haggis et al.[74]
0	87.7	84.2	71.9	89.0
25	78.3	78.2	63.8	78.3
60	66.3			65.8
62	66.2	72.5	53.0	
83	60.1	67.5	47.8	
100	55.7			53.7

between different species was calculated by a probability method. Finally, Pople[20] applied Kirkwood's theory to his model of "bent-bond" water.

While Table 1 compares several models to which the same theory is applied, Table 2 presents a comparison of the results of the application of different theories of dielectric polarization to the calculation of ϵ, all of them using the same model: the "bent-bond" model. The Tables show that two theoretical treatments[74,76] gave both the correct magnitude and temperature variation of ϵ. Two others[20,77] reproduced only the correct temperature variation of ϵ. The comparisons do not lead to any clear preference for either a single model or a single theory.

TABLE 2

Comparison of values of ϵ of water calculated by different theoretical methods using the Pople model

t(°C)	Experimental[75]	Equations used			
		Kirkwood[20]	Fröhlich[76]	Harris and Alder[76]	Harris[77]
0	87.74	71.9	73.0	90.7	83.7
25	78.30	63.8	64.0	79.9	74.0
62	66.17	53.0	53.0	65.7	60.2
83	60.14	47.8	48.0	59.6	54.8

(*iv*) *Discussion*

Observation of the results of the quantitative treatments reviewed shows that in many instances, calculations applied to very different structural models of water yield results in agreement with experiment and/or with each other. On the other hand, different quantitative treatments of the same model yield very different results (e.g. calculations of ϵ using the Pople-"bent-bond" model).

The above indicates that the values obtained for the properties of water are, of course, sensitive to the structural features of the qualitative models used, but are even more so to the methods of calculation. Regrettably, a "generous" use of adjustable parameters is often made. For example, Eucken's model[43] has been criticized as having little physical foundation[4,5,45,78], and its success in *P-V-T* correlations has been ascribed to adjustment of mole fractions of the polymers postulated in the model. Thus, Eucken's polymers can be regarded as convenient computational parameters, which have no real "existence" in liquid water[45].

It would seem then, that the results of the quantitative treatments reviewed are inadequate as criteria for the validity of the examined models. The quantitative treatments seem unable to establish a preference among the various models of water.

E. ANALYSIS OF WATER STRUCTURE BY SPECTROSCOPIC METHODS

(i) X-ray scattering

(a) The interpretation of experimental results

The most accurate X-ray scattering measurements of water to date are those of Narten et al.[79]. Their results show that a considerable degree of short range order and the low coordination characteristic of the tetrahedrally bonded structure of ice, persist in liquid water. Thus, they indicate, that in contrast to simple, close-packed liquids (such as neon and argon), the structure of water is a very open one (the X-ray diffraction pattern of a disordered close-packed arrangement of molecules is very different from the observed diffraction pattern of water). The graph of the radial distribution function g(R) which Narten et al. calculated from their X-ray diffraction patterns is shown in Fig. 5.

The main features of this curve are:

(1) g(R) vanishes for all values of R less then 2.5 Å. It follows that water molecules do not approach within 2.5 Å of the central molecule;

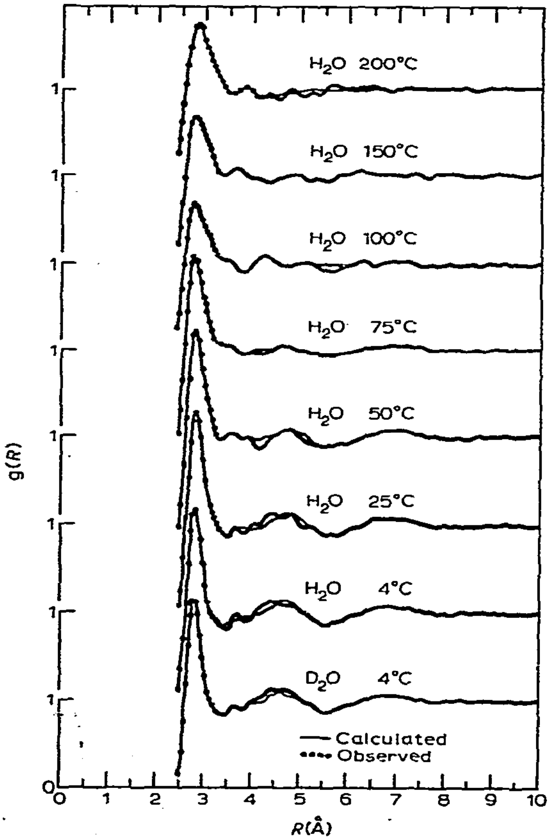

Fig. 5. Observed and model radial distribution functions of water[79].

(2) at 4°C, g(*R*) is nearly equal to unity for all *R* greater than 8 Å, i.e. the average density of neighboring molecules at these distances is equal to the bulk density. This shows that the order induced by a central molecule on the average positions of its neighbors does not extend beyond 8 Å. At 200°C short-order range does not extend beyond 6 Å;

(3) a well-resolved peak appears near 2.9 Å. This is due to the nearest neighbors of the central molecule. The average number of nearest neighbors, estimated from the area under the first peak of the radial distribution curves, is about 4.4 at temperatures from 4° to 200°C. The number of nearest neighbors of neon and argon is 8.6 and 10.5, respectively[80]. Additional evidence for the persistence of tetrahedral arrangement in liquid water comes from the sequence of position of peaks and troughs in the radial distribution function. In ice I where almost exact tetrahedral coordination exists, there is a high density[1] at distances of 2.76 Å, 4.5–5.3 Å, and 6.4–7.8 Å. The peaks[79] of g(*R*) for water roughly coincide with those of ice I. There also appears a trough[1] between 5.3–6.4 Å both in water and in ice I, so that most features of the g(*R*) of water are consistent with tetrahedral coordination (however, there does appear a peak near 3.5 Å, which is inconsistent with tetrahedral coordination[79]).

There are other X-ray diffraction studies which are in good agreement with the work of Narten et al.[65,81,82]. However, Van Eck et al.[83,84], and Heemskerk[85] obtained X-ray diffraction curves which are distinctly different. Following their results, they postulated octahedral arrangement and a six-fold coordination to exist in liquid water. According to Narten et al.[79] the differences between their results and those of the former investigators result mainly from neglect of data for large scattering angles in the previous work.

(*b*) *Theoretical calculations*

Theoretical calculations of the radial distribution functions of water have been made on the basis of the Bernal–Fowler[31], the "bent-bond"[20], the "flickering-cluster"[4], the "gas-hydrate"[82], the "network"[82] and the Davis–Litovitz[66] models. In all cases, except Danford and Levy's calculation[82] the authors reported their calculations to be in good agreement with experiment. However, an analysis of these calculations[79] led to the conclusion that most models are either incompatible with the observed X-ray scattering, or insufficiently defined (on the molecular level), for adequate testing. The analysis specifies the details which should be given so that it will be possible to test the validity of the models with X-ray scattering data. If this is not done, the diffraction data cannot be invoked as evidence for or against the correctness of the model. Any model that claims agreement with the observed diffraction patterns of liquid water should reproduce not only the first peak, but all the other significant features of the radial distribution functions, as well. These conditions provide a powerful criterion for the validity of proposed water models. The following specific remarks on the theoretical calculations mentioned are worth mentioning:

(1) Pople's "bent-bond" model calculations[20] involve the unjustifiable assumption that the distribution of neighbors about any atom is independent of the distribution about the neighboring atoms. The model is not sufficiently detailed;

(2) calculations based on Bernal-Fowler and "flickering-cluster" models yield curves which are incompatible with experimental data;

(3) the "gas-hydrate" model is also incompatible with experimental data[79,82]. Calculations performed on a modified type of this model did not improve agreement. The large cavities appear to be the unsatisfactory feature of the model;

(4) the Davis–Litovitz model is again insufficiently detailed and the calculated radial distribution curves are incompatible with experiment;

(5) the "network" model is sufficiently detailed to permit calculation of $g(R)$, and such calculations by Danford et al.[82] and Narten et al.[79] seem to agree with experiment.

The above analysis leads to the conclusion that to date only one of the tested models (a "network" model) is both detailed enough to permit calculations of radial distribution curves and has been shown to give agreement with both large and small angle X-ray scattering. However, it is also obvious from the above that the "flickering-cluster", the "bent-bond" and the Davis–Litovitz models cannot be ruled out on the basis of X-ray diffraction data. These models have not yet been adequately tested, and have not been shown as conceptually incompatible with X-ray diffraction data. Also, a different mathematical treatment of them may yield agreement with experiment, despite the failure of former treatments to do so. Nevertheless, at present, X-ray scattering data seem to favor "network" models over other models.

(ii) Vibrational spectroscopy

(a) Interpretation of the vibrational spectrum of water

The vibrational spectrum is sensitive to the local environment of molecules. It follows that vibrational spectroscopic techniques (such as IR, Raman and cold neutron scattering spectroscopy) are expected to supply valuable information on the "structure" of water (in the time range 10^{-11}–10^{-14} sec which is the observation time of these techniques). Unfortunately, the vibrational spectrum of water is uniquely complex, and its interpretation is still controversial. The main controversy is whether the vibrational spectra are better interpreted by "continuum" or by "mixture" models.

The interpretation of the spectra of water in the liquid phase is based on the analysis of the IR and Raman spectra of water vapor. The isolated water molecule in the vapor phase has three normal modes of vibration: ν_1- and ν_3-stretching of the OH bond, and ν_2-bending of the bond[86b]. The overtones and combination bands of the fundamentals are also detected in the vapor spectrum. The IR and Raman bands of water vapor in the frequency range below 13,000 cm^{-1} are listed in Table 3.

The formation of hydrogen bonds on condensation of water causes distinct changes in the vibrational spectrum of water. The effect of H bonding on the IR and Raman bands is to shift their frequency, to broaden their widths and to enhance their intensity. Moreover, in liquid water new bands appear which do not occur in the gas. The broadening, the appearance of new broad bands and the resulting coupling of vibrations and overlapping of bands, considerably complicate the vibrational spectrum of water. Another typical feature of the vibrational spectrum of a hydrogen bonded system which occurs also in liquid water is the strong temperature dependence of the shapes of the bands. The main features of the vibrational spectrum of liquid water contrasted with the spectrum of water vapor are listed in Table 4. The Raman spectra and the IR spectra of liquid H_2O and HDO and D_2O are shown in Figs. 6, 7, 8. The reader interested in further details of

TABLE 3

IR and Raman bands of H_2O vapor[86]

ν_{vacuum} (cm^{-1})	1	2	3
1595.0	0	1	0
3151.4	0	2	0
3651.7	1	0	0
3755.8	0	0	1
5332.0	0	1	1
6874	0	2	1
7251.6	1	0	1
8807.05	1	1	1
10613.12	2	0	1
11032.36	0	0	3
12151.22	2	1	1
12565.01	0	1	3

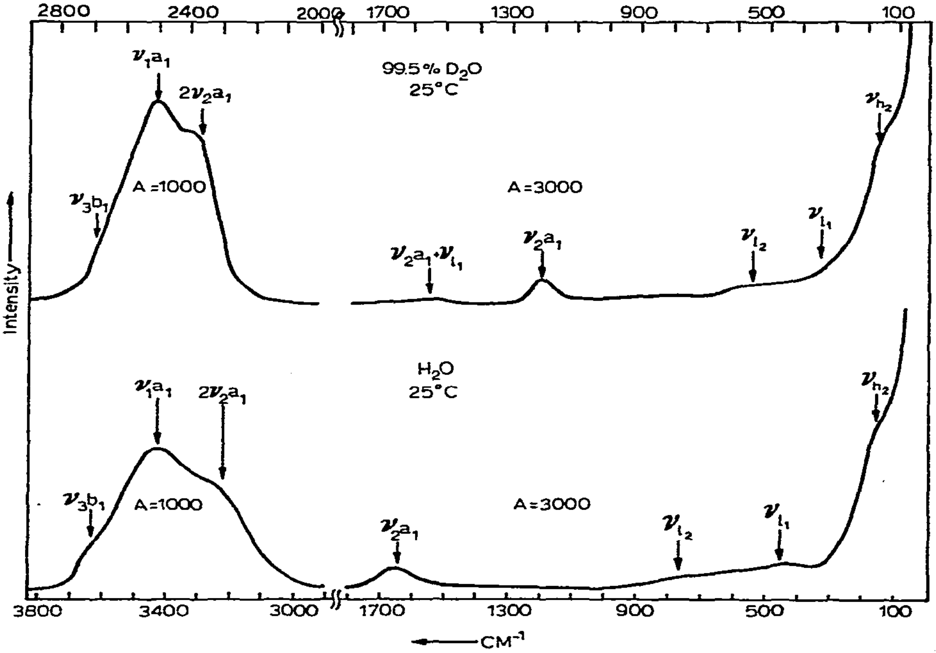

Fig. 6. Photoelectric Raman spectra of water and heavy water. Identical sample geometries were employed in both cases (A = amplification)[90].

TABLE 4

Main features of the vibrational spectrum of liquid water compared to the spectrum of water vapor

Frequency region (cm^{-1})	Water vapor	Liquid water		
			Assignment of the band	Detected by
50–1200	Line spectrum arising from molecular rotation most intense near 200 cm^{-1} at room temperature	Narrow band at 60 cm^{-1}	ν_{T_2} arising from hindered translation	Raman, neutron inelastic scattering
		A prominent shoulder on the 700 cm^{-1} band, maximum near 193 cm^{-1}	ν_T-hindered translations	Raman, IR, neutron inelastic scattering
		Intense band, extends from 300 cm^{-1} to 900 cm^{-1}, maximum near 700 cm^{-1}	Arising from ν_L-hindered rotations	IR, Raman, neutron inelastic scattering
1200–4000	Four vibration-rotation bands: ν_1 = 3657 cm^{-1} ν_2 = 3657 cm^{-1} ν_3 = 3756 cm^{-1} $2\nu_2$ = 3151 cm^{-1}	Broad, asymmetric band Maximum near 3490 cm^{-1} (in the IR spectrum), near 3440 cm^{-1} (in the Raman spectrum)	ν_1, ν_2 associated with the OH stretchings, probable contribution of $2\nu_2$	IR, Raman
		Band near 1645 cm^{-1}	ν_2 bending	IR, Raman
		Very broad and very weak maximum near 2125 cm^{-1}	ν_A may be composed of either overtones of ν_L, ν_T, ν_{T_2} or a combination of the 1645 cm^{-1} with one of the modes mentioned above, or both	IR

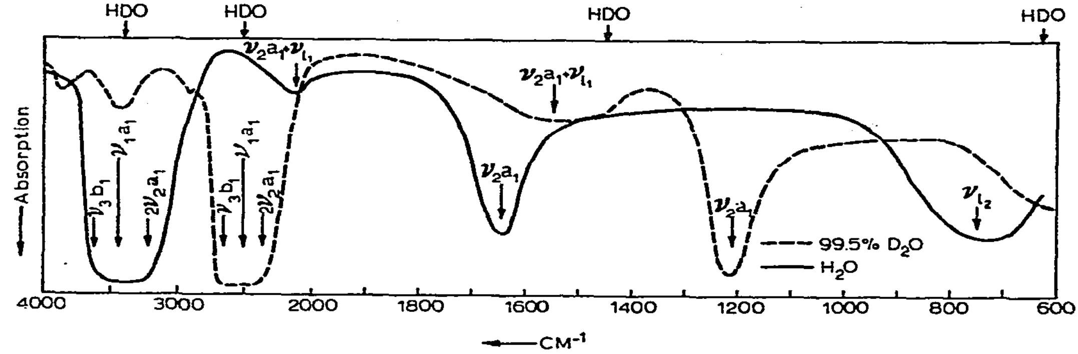

Fig. 7. IR spectra of water and heavy water (weak bands in the spectrum of 99.5% D_2O, which coincide with characteristic HDO frequencies shown by arrows, are indicative of the sensitivity of the IR spectrum to impurities)[90].

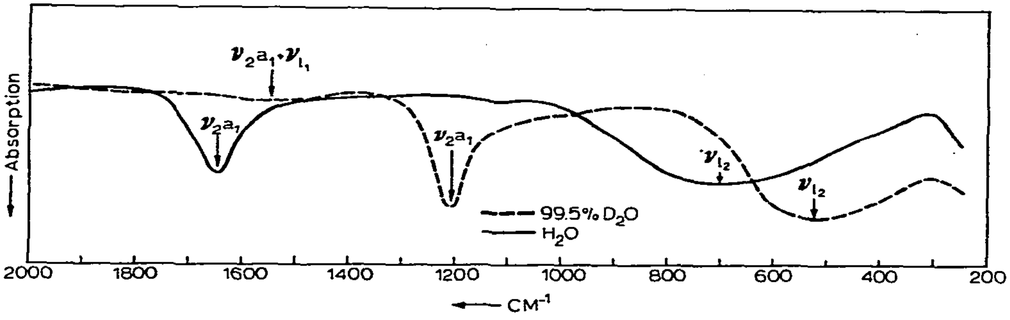

Fig. 8. IR spectra of water and heavy water[90].

the vibrational spectrum of water is referred to the book by Eisenberg and Kauzmann[1].

To give some idea of the difficulty attending non-equivocal assignment of bands in the vibrational spectrum of water, we shall mention two examples of attempts to assign and interpret certain bands in the vibrational spectrum of water.

(1) The uncoupled OH and OD stretching bands of a dilute solution of HDO in D_2O and H_2O were the subject of a Raman spectral study by Wall and Hornig[87]. According to their data these bands showed no structure, and only slight asymmetry (Figs. 9, 10). The large half-width of the OH and OD stretching bands (270 cm^{-1} and 160 cm^{-1}, respectively) was given as evidence that the local environment of the molecules in water varies considerably. It was held that these results show the bands to have a structureless, continuous intensity distribution which passes through a single maximum. This was seen as evidence favoring a "continuum" model of water. For, if there were a small number of distinct species of water molecules, the bands should have been structured. Falk and Ford[88] and Franck and Roth[89] also studied the uncoupled stretching bands in liquid water and arrived at conclusions similar to the above (i.e. favoring a "continuum" model).

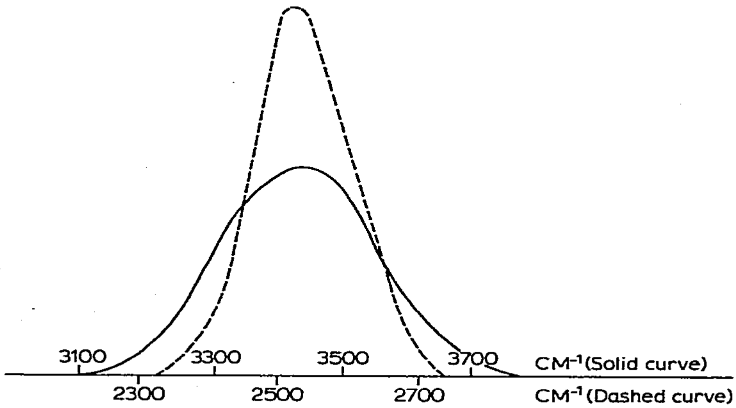

Fig. 9. The O–H (solid curve) and O–D (dashed curve) uncoupled stretching bands in 5 mole-% isotropic solutions of H_2O in D_2O and D_2O in H_2O, respectively (27°C, 30 cm^{-1} [87]; (the uncoupled O–H band may have been inverted through its maximum[133]).

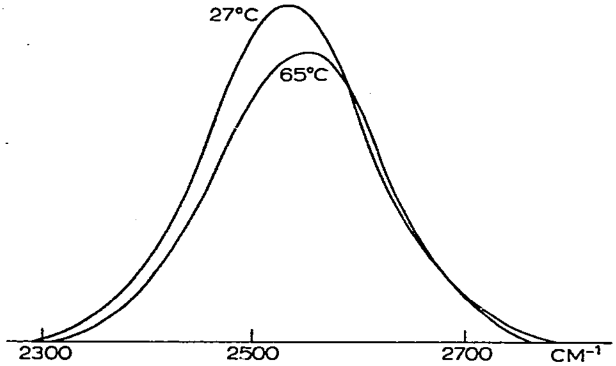

Fig. 10. O–D stretching region in 5 mole-% deuterated water (30 cm^{-1}): effect of temperature on the uncoupled O–D stretching band[87].

Walrafen[90] found shoulders and inflections in the OH and OD stretching contours from HDO solutions which were not observed in the earlier work. These features were held to be incompatible with a "continuum" model. Moreover, the stretching bands of solutions of H_2O-D_2O, H_2O-HDO and HDO-D_2O could be decomposed into Gaussian components. The computed components were found to be separated by isosbestic frequencies. Consequently, Walrafen believes that the components are assignable to non-hydrogen-bonded and hydrogen-bonded OD and OH vibrations. The detection of isosbestic points usually indicates the existence of chemical equilibrium between species. Thus, Walrafen's observation of isosbestic points is strong evidence in favor of "mixture" models.

Considering both the above arguments, the following conclusions may be drawn:

Even if Walrafen's results are accepted, the band half-widths[90] (from 100 cm^{-1} to 240 cm^{-1}) calculated for the components show that molecules belonging to the same species still have a wide range of energies and environments. The overlapping of components shows that the different species have close values of energies and similar environments.

Even if Wall and Hornig's[87] results are accepted, they do not rule out the possibility that non-hydrogen-bonded OH groups (which have environments notably different from most of the OH groups) exist in water. Non-hydrogen-bonded groups are more difficult to detect by IR methods than are hydrogen-bonded OH groups, because the intensity of the absorption of the OH stretching band increases by a factor of about 10 when the OH group forms a hydrogen bond[91,92]. Thus it is possible that a considerable amount of non-hydrogen-bonded OH groups are present in liquid water, but cannot be detected as their absorption is too weak.

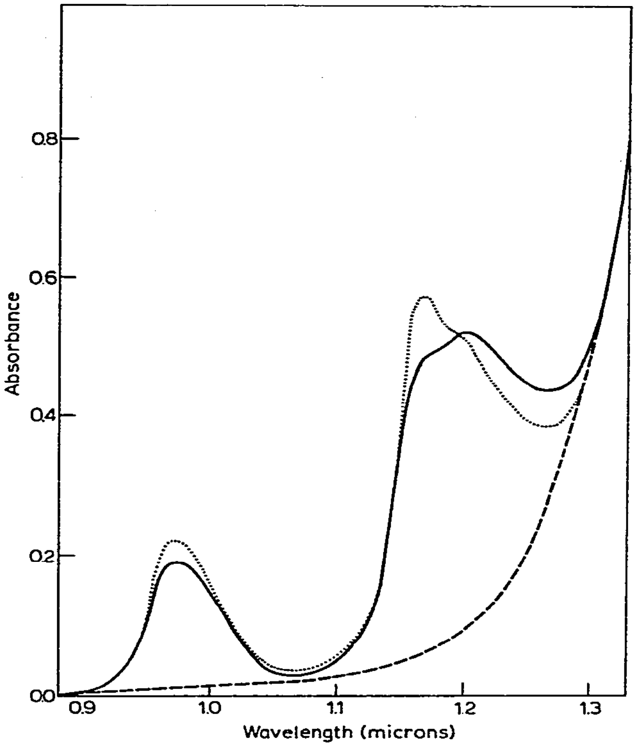

Fig. 11. Near-IR spectra of liquid water between 0.9 and 1.3 μ. The solid curve is the spectrum at 21°C, the dotted curve that at 72°C. The lower dashed curve is the calculated base line[69].

(2) The temperature dependence of the IR spectrum of water in the vicinity of 8000 cm^{-1} was studied by Buijs and Choppin[69,70] (Fig. 11). Thomas et al.[93] repeated this work and also studied the corresponding region of the D_2O spectrum (Fig. 12). A similar study was made by Luck[94]. The absorption in this region was ascribed to the $\nu_1 + \nu_2 + \nu_3$ combination of vibrations. It was suggested that the absorption is due to three component bands, the intensity of which varies with temperature. Each component was assumed to correspond to a different species of water molecules. The species postulated

were (*1*) molecules with both OH groups in hydrogen bonds, (*2*) molecules with one OH group in a hydrogen bond, (*3*) molecules with two free OH groups. It was later argued[95], however, that if three distinct species of water molecules are present, and if their presence causes structure in a combination band, then their presence must also cause a similar structure in the uncoupled fundamental bands.

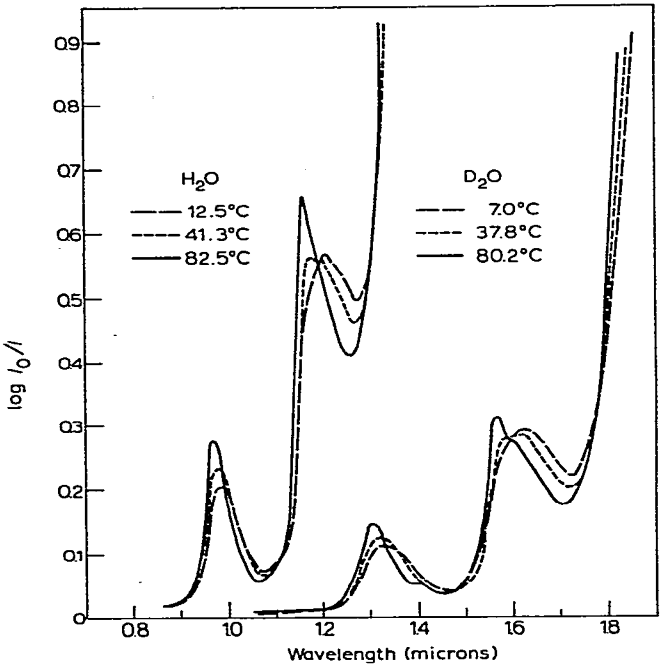

Fig. 12. Near-IR spectra of liquid H_2O and of liquid D_2O at various temperatures[93].

According to Hornig's results[87,95] the fundamental bands do not exhibit a similar structure. The alternative explanation given for the temperature dependence in the 8000 cm^{-1} region was that heating shifts the frequency of the fundamental modes, and these shifts alter Fermi resonances between overlapping overtones and combination bands in this region. However, as mentioned above, Hornig's results have been contested by Walrafen.

(*b*) *Conclusions*

The arguments favoring the "mixture" models or the "continuum" models are detailed in the numerous publications dealing with the vibrational spectrum of water (e.g. Refs. 33, 69, 70, 90, 93, 96–100 for "mixture" and 87–89, 95, 101 for "continuum"). Neither of the two views is generally accepted or generally rejected at present. We see then that we cannot exclude any of the models described in this review on the basis of existing data and interpretation of the vibrational spectrum of water. More than that: even the fundamental question whether different species of water molecules can be detected in the vibrational spectrum of water, cannot be definitely answered as yet and awaits further investigation.

F. "ANOMALOUS" WATER (POLYWATER)

A form of water with properties very different from those of ordinary water, has been reported in a series of papers by Deryagin and coworkers[102–115]. Water in this unusual state has been called "anomalous" water by this group, to distinguish it from ordinary water. Anomalous water has been prepared in two ways: (*a*) secondary columns of "anomalous water" were observed growing near both ends of a column of water sealed in a glass capillary 1–2 mμ in diameter[116]; (*b*) by condensation of incompletely saturated vapors in glass and fused quartz capillaries[103]. The product varies in the degree of anomalous character and is probably contaminated with normal water[102–115,56].

Deryagin[117] assumed that the practical stability of ordinary water must be due to a high value for the work of formation of a critical nucleus of "anomalous water". He also suggested the possibility that the growth of "anomalous water" in contact with ordinary water is a slow process having a high activation energy. He proposed that the transition from ordinary to anomalous water is influenced by the presence of an interface.

Anomalous water is distinguished by the following properties[102–115,56]:

(1) lower vapor pressure than that of ordinary water;
(2) viscosity up to fifteen times that of ordinary water;
(3) greater density (d = 1.2–1.3);
(4) different thermal expansion behavior;
(5) solidification at −40°C or lower temperatures;
(6) stability to temperatures of the order of 500°C, and also stability to cooling and aging.

When anomalous water is mixed with ordinary water, the anomalous water separates out on chilling, or is left behind when the ordinary water is boiled away. Thus anomalous water behaves like a separate substance which is highly soluble in water. In addition, the data[102–115] show that this type of water is not some anomaly due to the structure of the wall of the container. Also, it is not caused by some peculiar structure of water near the surface of the capillary, because the viscosity and thermal expansion of anomalous water are independent of the capillary radius. It also seems unlikely[118–119] that the anomalous properties are due to some contaminants from the walls of the capillaries.

Some of the properties of anomalous water reported by Deryagin and coworkers were checked by Willis et al.[118], and Bellamy et al.[119]. IR and NMR spectra of anomalous water identical with those of ordinary water were obtained by Willis et al.[118]. However, the amounts of material obtained by them were minute, and insufficient for unequivocal characterization. Bellamy et al.[119] obtained Raman and near IR spectra of anomalous water different from those of ordinary water. Lippincott et al.[120] obtained IR and Raman spectra of anomalous water very different from those of ordinary water. The IR spectra appear to be unique with the apparent absence of the O–H stretching bands which are prominent in ordinary water spectra.

Several investigators[119,120,106] have speculated on possible structures of anomalous water (both on the molecular and the supermolecular level) compatible with the reported properties of anomalous water. Erlander[121] and Bolander et al.[122] have specifically advanced two models of the structure of anomalous water. They describe the structure of "clusters" which "constitute" anomalous water. Their propositions seem rather premature, considering the insufficient information available at present[134,135].

G. INTERFACIAL EFFECTS ON THE PROPERTIES OF WATER

Until recently, the majority opinion seems to have been that the ordered region of liquid water near an interface is quite thin – comparable in depth to that of the electrical double layer[123]. However, Deryagin[117] measured the sheer elasticity modulus of water as a function of the distance to an interface of quartz and concluded that the data obtained indicate that there exist boundary layers of water about 500-800 Å thick near the quartz surface. It follows that the traditional conception of liquid structure, i.e. of absence of long range order in the liquid, is an obstacle to recognition of the specific properties in boundary polymolecular layers. This conception leads to the conclusion that no rearrangement of liquid structure under the influence of an adjacent phase can spread into the depths of the liquid, to a distance more than several molecular diameters. This is closely related to the idea according to which the structure and properties in the bulk of the liquid are single-valued functions of the temperature and pressure. Already some time ago, Henniker objected to these ideas[124]. Lately, however, it appears that the above ideas are also in disagreement with two experimental developments: (*a*) the discovery of "anomalous" water as well as "anomalous" forms of other polar liquids (such as acetic acid and methanol), (*b*) the observation that interfacial influences can spread into the depth of the liquid.

It was therefore suggested[117] that the usual state of water and certain other liquids is thermodynamically metastable. Naturally, the assumption of the variability of structure of water and some other liquids makes it easier to understand their ability to change their structure under the influence of an interface. The above assumption together with the possibility that the growth of "anomalous" water in contact with ordinary water is a slow process having a high activation energy, leads one to speculate that the ordered boundary layers near an interface may consist of nuclei of "anomalous" water. Interfacial effects on the properties of water were also reported by Horne et al.[123]. They passed a solution of electrolytes through a column filled with solid particles and compared the electrical conductivity of the eluted solution with that of the original solution (the solid particles are permeated with the solution). Horne et al. concluded that water near an interface tends to exclude electrolytes, thereby increasing the concentration of the solution at some greater distance from the interface.

All the theories discussed in the previous sections of this review regarded all the anomalies of water essentially as pertaining to the properties of bulk water. It was recently suggested[125] that some of those anomalies may owe their existence to specific interfacial effects. Korson et al.[125] measured the dependence of the viscosity of water on temperature (in the range 0-100°C). In contrast with earlier work[126] their data do not indicate thermal anomalies ("kinks") in the viscous flow of water between 8 and 79°C. ("Kinks" in the viscous flow, are abrupt changes at discrete temperatures in the observed energy of activation for the viscous flow of water; "kinks" in the properties of water are usually associated with "higher" structural transitions in liquid water.) It was suggested[125–128] that Korson's data differ from previous data because the measurements were carried out under conditions which minimized surface interferences. Hence the suggestion that the presumed viscosity anomaly of water and possibly other water anomalies may be due to interfacial effects[136].

H. SUMMARY AND CONCLUSIONS

At present, there can be no general acceptance nor general rejection of any of the current models of water. Yet some of the current models are fundamentally contradictory. The main difference in the theoretical basis of "mixture" and "continuum" models lies in their concepts of hydrogen bonding in water. In "mixture" models the hydrogen bond in water is viewed as a linear bond having (much like a chemical bond) a sharp energy minimum about a bending angle of 0°. Such a view leads to the assumption that in water there exist distinct species of molecules, having either "intact" or "broken" hydrogen bonds.

In "continuum" models highly bent hydrogen bond configurations in water, are assumed to have an energy not much higher than linear hydrogen bond configurations. This assumption leads to the view of liquid water as a system consisting of molecules having a continuous and broad distribution of energies and angular correlations (i.e. bending angles of the hydrogen bonds).

The existing theory of the hydrogen bond in water[137] is not developed enough to give an answer to the problem of the angular correlations in water, and to the question whether non-hydrogen-bonded OH groups may be present in liquid water. The estimates of the energy of the hydrogen bond in water range from 1.3 kcal/mole[129] to 6.8 kcal/mole[130]. This is only a prima facie discrepancy, because the different values relate to different definitions of the hydrogen bond. The diverse views on the nature of the hydrogen bond in water lead also to a large variation in the estimates of the percentage of "broken" hydrogen bonds in water. Such estimates range from 71.5%[131] to 2.5%[68] (at 0°C) and from 50%[33] (26°) to 0.1%[132] (25°).

None of the current models of water can be ruled out on the basis of the thermodynamic properties, dielectric properties or results of X-ray scattering measurements of water.

The vibrational spectrum of water is expected to supply the strongest criteria for the judgment of models of water structure. Existing results of vibrational spectroscopic techniques do not exclude "mixture" or "continuum" models of water, but they do indicate that even if different species of water molecules occur in the liquid phase, the distribution of energy and molecular environments within each species are continuous and broad and that the energy and other properties of different species are very close. Also, these results do not rule out the possibility that non-hydrogen-bonded groups of OH bonds (having properties considerably different from those of the rest of the OH groups in liquid water) exist in liquid water. Unfortunately, the controversy extends not only to the interpretation of the vibrational spectrum of water, but also to the experimental data (such as shapes of peaks in the spectra, etc.). Therefore, more definite evidence concerning the structure of water, must await further research in this field. Other examples of controversial experiments are the "anomalies" of liquid water, which though currently attributed to the properties of bulk water, could be due to interfacial effects.

The detection of "anomalous water" by several workers may prove to be of considerable importance to the understanding of the structure of water, and the theory of liquids in general.

After 80 years of research, there is still much uncertainty in the field of water structure. This situation is associated with the present weakness of the theory of the liquid state in general. It may, therefore, be appropriate to conclude this review with the final sentence of Chadwell's review^6: . . . "Let us hope that in the near future rapid progress will be made in this important field of investigation".

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