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Water structure and hydration

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Possible structures adopted by bulk water are discussed with special reference to the possible presence of monomeric water and the detection of 'free' –OH groups. The way in which water tends to accommodate small hydrophobic molecules is considered, with particular reference to the clathrate theory and the phenomenon of 'structure making'. Cage-pairing and cage-sharing processes are described.

Consideration of the way water solvates cations and anions is followed by a discussion of the way these solvated ions interact with the bulk medium. Large symmetrical alkylammonium ions probably encourage clathrate cage formation, at least at low temperatures.

Particular reference is made to the use of infrared, Raman, ultraviolet, n.m.r. and e.s.r. spectroscopic techniques to the study of water and aqueous solutions.

Because water is a unique liquid, there is a tendency to shroud its properties in an aura of mystery – a tendency which for example, came to the fore recently in the polywater 'bubble'. I have long maintained that liquid water simply possesses the properties that you would expect it to have, on the basis of the perfectly normal and well understood structure of the monomer molecule (Symons 1972). My present aim is to outline these expectations, and then to examine mainly spectrophotometric data to see to what extent they support the model.

1. THE STRUCTURE OF LIQUID WATER

Good quantum mechanical calculations on water monomer, dimer and oligomers are now available (Del Bene 1970; Hankins, Moscowitz & Stillinger 1970; Diercksen 1970; Kollman & Allen 1972) and it seems that the conventional view of the molecule, in which it is depicted as having a near tetrahedral array of two hydrogen atoms and two 'lone-pairs' of electrons is a good one for structural considerations. Thus the dimer is found to be linear as in figure 1*b*, rather than cyclic. (This is strongly supported by infrared data on matrix isolated dimers (Tusi & Nixon 1970), but the cyclic structure appears to be preferred in fluid carbon tetrachloride (Magnusson 1970). We have suggested (Atkins & Symons 1972) that the cyclic structure is really a metastable transition-state for figure 1*b* interconversions, which may occur rapidly as a collision-induced switch in carbon tetrachloride, thereby modifying the infrared spectrum.)

The key to understanding water is that the molecule is tetra-functional, with an equal number of acidic and basic groups which are ideally placed for three-dimensional growth with no steric resistance to such growth. Thus, it is likely to be present as a giant polymer 'molecule' in the solid or low-temperature liquid states, ordered in the former, but haphazard in the latter. The major difference between water and a tightly cross-linked polymer is that the bonds are weak and are therefore constantly breaking and reforming on a time-scale in the region of 10^{-11} s.

It is important to realize that the acid–base properties of the monomer will be very different from those of the dimer or trimer. This is obvious in the extreme of complete proton loss: thus H_2SO_4 is a very powerful proton donor, but HSO_4^- is weak. To a smaller extent, for H^α—OH - - - OH_2^β, H^α is less, and H^β more, acidic than the protons of the monomer molecules. Similarly, the lone-pairs have varying basicities.

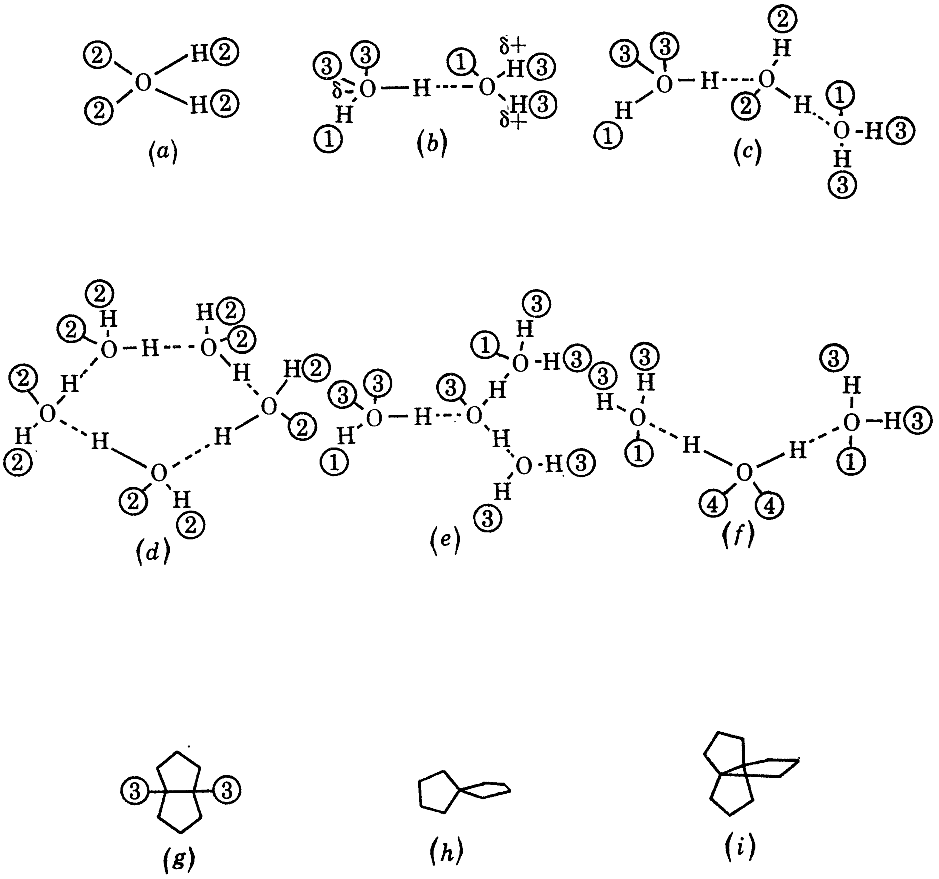
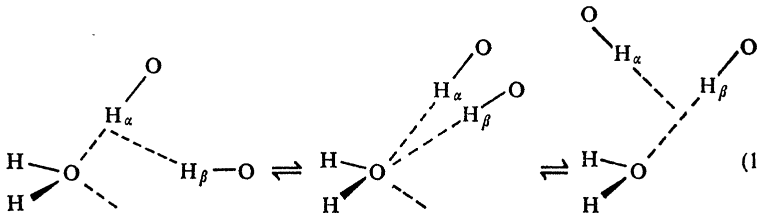


FIGURE 1. Various water oligomers with relative reactivities (1) < (2) < (3) < (4).

As an aggregate of water monomers begins to polymerize, initially, dimers will be formed. These have six growth points instead of four, and linear trimers have eight, so they will tend to scavenge monomer molecules. This increase in functionality will eventually so dominate, that all monomers will be lost, and a single polymeric 'molecule' will be present. However, since growth points have different reactivities, the type of growth will follow certain preferred pathways. The numbers in parentheses for the various structures in figure 1 indicate relative reactivities (acidities or basicities); the smaller the number, the less reactive the centre. Monomers will preferentially add to sites (3) or (4). Cyclization is encouraged because it is a (3) + (3) process, and once cyclization has occurred, the highest reactivity becomes (2) so that further growth is less probable. Again, bond breaking must follow the same pattern, so that ring opening will be energetically unfavourable because it produces two reactive (3) sites. We can therefore predict that unstrained cyclic structures will occur frequently and have relatively long lives.

Once chain-branching as in figure 1*e* has occurred, further growth at the branch-point is encouraged, so that chain-crossing is probable. Structures such as figure 1*f* are improbable, and will have short life-times, both because they will readily fall apart, and also because they have two sites of reactivity (4). For these reasons, multiple ring growth, as in figure 1*g*, *h*, or *i*, will be greatly encouraged, but this will *not* lead to ice structures, because the rings will be of any size, and will be haphazardly placed. This means that there will always be extensive mis-matching, which will result in several protons and lone-pairs being temporarily unable to form bonds. Such 'free' groups represent an extreme but defined limit, with the fully formed linear hydrogen bond as the other extreme. In between, there will surely be a range of bent and stretched hydrogen bonds brought about momentarily and fortuitously because of the demands and constraints of the surrounding three-dimensional structures.

When a free lone-pair or O—H group is present, it need not remain free until another free group of opposite character comes into range. Instead, it may undergo a displacement reaction as in (1), thus generating another such free group,



(1)

and thereby greatly reducing the life-time of a given free O—H unit, and increasing their effective mobility.

One specific conclusion is that there is no reason at all for postulating the presence of many monomer molecules in liquid water at low temperatures. This conclusion is compelling.

There is no reason why any particular water molecule should have C_{2v} symmetry. Indeed, in view of the tendency of one hydrogen donor bond to weaken another, one might guess that many molecules will tend to have one strong and one weak hydrogen bond at a given instant.

2. COMPUTER MODELS

These simple considerations have recently received strong support from computer experiments generally known as 'molecular dynamics' (Rahman & Stillinger 1971, 1973). These start with an ensemble of water molecules (usually a few hundred) and a digital computer solves coupled equations for classical motion, controlled by a specified pair interaction potential. Boundary and initial conditions are chosen to fix the density and temperature. The dynamic system at equilibrium can then be examined from structural and kinetic viewpoints. The reader is referred to the literature for details: here it suffices to say that the results lend strong support to the simple concepts outlined above. Thus non-bonded water molecules are not observed, and indeed, the vast majority form four tetrahedrally arranged hydrogen bonds. These vary considerably in length and direction. Non-stained rings are found to be of considerable significance.

Although the results of molecular dynamics computer experiments are now much quoted, they have been criticized, for example by Lentz, Hagler & Scheraga (1974), and are by no means universally accepted. Probably the most popular alternative view of water, because of its great success in explaining a wide variety of properties of aqueous solutions, is the cluster theory (Frank & Wen 1957; Frank 1958). In its original form, water was envisaged as existing in two states, one comprising large clusters of strongly bonded molecules and the other comprising dense regions of non-bonded molecules. The most recent statistical thermodynamic treatment of the cluster model (Lentz *et al.* 1974) has led to the conclusion that clusters are indeed of great significance, but that these are small, mostly containing less than seven water molecules.

While I agree that ring structures will have long life-times, I find this result very difficult to accept on chemical grounds. Thus, we are asked to envisage a liquid in which most water molecules form only two hydrogen bonds, leaving one proton and one lone-pair free. Why, when these clusters are in continuous close contact, should these sterically available and reactive centres refuse to interact? Of course, once they *are* allowed to interact, the discrete presence of structured clusters is lost. [This particular model must be treated with caution since it requires the presence of about 50% $(O—H)_{free}$ groups, which is ruled out by infrared and Raman studies (§5*a*).]

Another currently popular model involves the concept of interstitial water molecules. This is again useful, when trying to calculate the properties of water, but it seems to be at variance with the expectations outlined above. Of course, there will be $(OH)_{free}$ *groups* and non-bonded lone-pairs which are too far away from each other to interact, but their presence calls for no special structural feature in the neighbouring molecules. Similarly, the much invoked concept of cooperative charges must be correct, but only in the sense that any given water molecule, in addition to its own instantaneous libratory and translatory requirements, will be buffeted on all sides by its moving neighbours to which it is directly or indirectly bound. Its ultimate behaviour will be the sum of all these perpetually varying constraints.

3. Aqueous non-electrolytes

If a solute has acidic or basic groups, it is likely to form hydrogen bonds with water with a consequent modification of the local structure. Some molecules may knit in with no major disruption of structure, but others may generate an excess of $(O—H)_{free}$ groups or of non-bonded lone-pairs, though probably not of both. Water structure is so powerful, that non-interacting solutes are usually rejected. However, if a molecule has interacting and non-interacting regions, as in the example of *tert*-butyl alcohol (which will be used a good deal for illustrative purposes), the non-interacting group will be accommodated in the energetically most favourable manner. Most solvents would simply move in around the solute without any real modification: water, however, can buffer the structural interference by enclosing the unwanted group in a cage of the clathrate type (figure 2*a*). These cages, which are remarkably ubiquitous in shape and size, comprise a set of water molecules all of which have four hydrogen bonds, three lying in the 'sphere' of the cage and the fourth pointing radially outwards. The solute acts as a template for the construction of such cages, which are favoured by enthalpy but disfavoured by entropy factors. Thus they will be most favoured at low temperatures and will be more temperature sensitive than bulk water structure. We (Symons & Blandamer 1968), and others (Glew, Mak & Rath 1968) have invoked this clathrate-cage concept to explain a wide range of observations, but it is by no means universally accepted. The situation differs from that in the solid water clathrates in that the latter structures are in part dictated by the symmetry demands of the continuous structures, in which a thin filigree of water separates each encaged host. Absence of this constraint will, in my view, encourage enclathration in the liquid-state, since a far wider choice of cage shapes and sizes is then permissible.

One possible consequence however, of the tendency of water to form crystalline clathrates is that enclathratable solutes might tend to pair or aggregate as depicted in figure 2*b* (Symons 1972). This form of pairing should be distinguished from the sharing of a single cage, as in figure 2*c*, a situation that we have also postulated previously (Blandamer, Clarke, Hidden & Symons 1968), to explain the ultrasonic relaxation behaviour of relatively concentrated solutions.

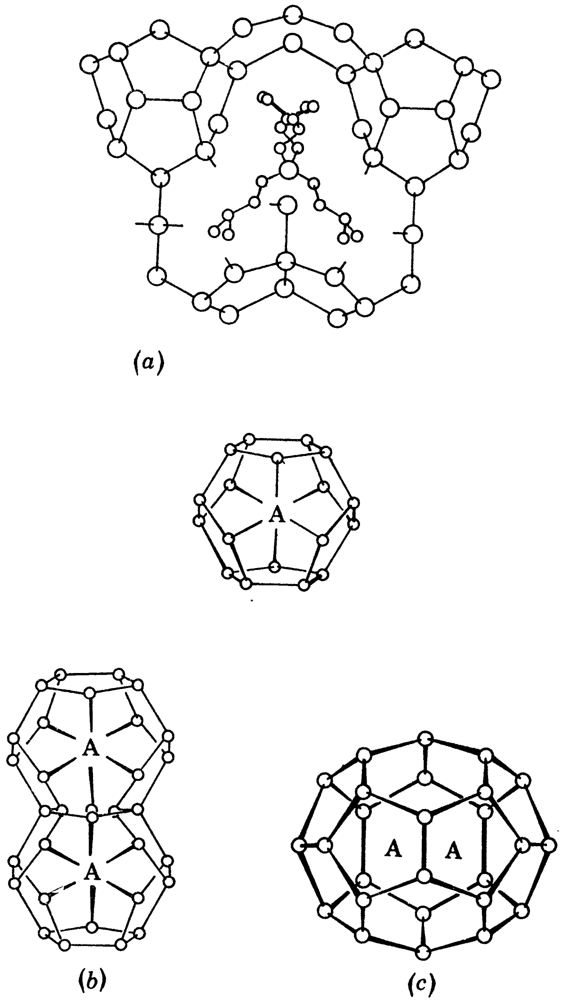


Figure 2. (*a*) Various clathrate cages; (*b*) A possible cage-pair; (*c*) Two host molecules (A) in a single cage.

4. Aqueous electrolytes

Cations are electrophiles and will tend to coordinate to water molecules *via* lone-pairs of electrons. That this is indeed the preferred mode of interaction is amply born out by X-ray studies of salt hydrates and there is no reason to suppose that this will not also occur in fluid solutions. There is, however, a competition for lone-pairs not found in the solid hydrates, and if the charge-density or coordinating power of the cation were to fall sufficiently, these lone-pairs might well be scavenged preferentially by solvent protons. In that case, ultimately, the ion might be treated by water as a large enclathratable unit.

Anions are complimentary, however, and will tend to form hydrogen bonds to water molecules. This again is in competition with solvent lone-pairs. It is probably of importance that there will normally be a rough balance in the numbers of $(O—H)_{free}$ groups generated during cation solvation and $(l.p.)_{free}$ units formed by anion solvation: these will interact and hence any residual free units will remain small. Once again, this cannot be viewed as 'structure breaking' since this term implies the formation of an equal number of $(OH)_{free}$ and $(l.p.)_{free}$ units which no longer tend to recombine.

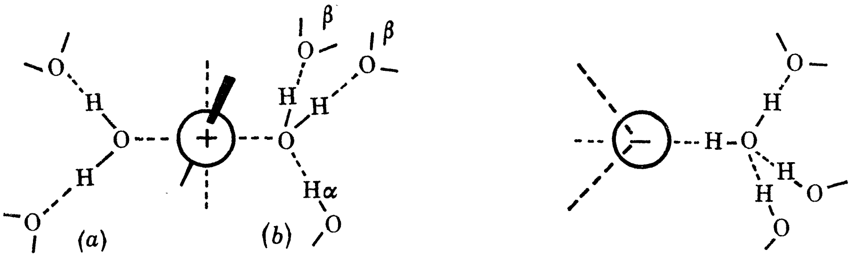


Figure 3. Models for cation and anion hydration: it seems probable that Li^+ is solvated by method *b* (Narten *et al.* 1971).

The way ions are thought to be solvated is depicted in figure 3. It is not, in my view, correct to envisage the ion and its first hydration shell as an entity separated from bulk water. As depicted, these units are closely attached to peripheral solvent and hence to the bulk, in which case the commonly invoked pictures such as that in figure 4, are incorrect.

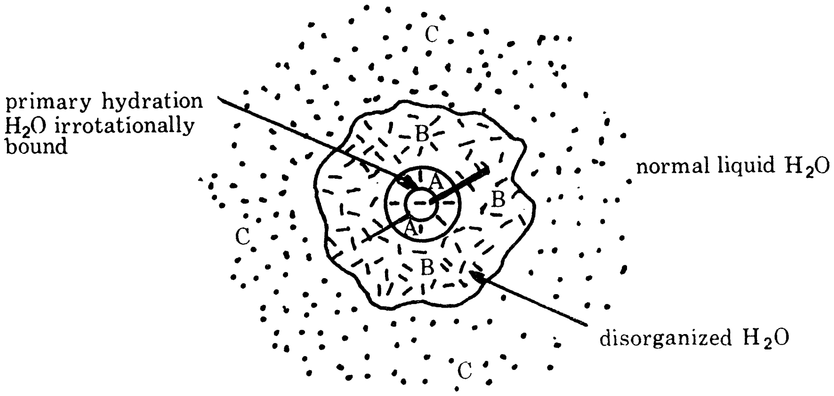


Figure 4. Commonly invoked model for anion or cation hydration including a region of 'non-structured' or 'melted' water.

It is important to realize that in the same way that the properties of a given water molecule are greatly modified by bonding to other water molecules, so also the strength of the interaction between a given water molecule and an ion will depend on how many bonds it forms to other water molecules. For example, in structure *b*, figure 3, strong bonding to $(H_2O)_\alpha$ will weaken the bond to M^+, but will strengthen those to $(H_2O)_\beta$; strong bonding to $(H_2O)_\beta$ will strengthen the bonding to M^+. In the absence of $(H_2O)_\alpha$, bonding to M^+ will be strengthened and this may be the preferred method of solvation for some cations (as in *a* of figure 3). This would have the effect of weakening the hydrogen bonds to $(H_2O)_\beta$.

Large alkylammonium and other symmetrical organic ions are a special case: in the solid state, water enclathrates these ions, and there are reasons to suppose that cold water will also form structures of this type. These ions are interesting probes of the behaviour of water since they are constrained to dissolve largely because of the high solvation energy of the anions and low crystal stabilization energies.

5. Experimental information

The most direct techniques to consult for structural information are X-ray and neutron scattering. Very recent information from a combination of these techniques (Narten & Levy 1971; Narten, Vaslow & Levy 1973) has led to the conclusion that most water molecules are tetrahedrally coordinated, but with no long-range order. Also, for concentrated solutions of lithium chloride, the lithium ions are coordinated to four oxygen atoms in a tetrahedral manner and the chloride ions appear to have six octahedrally arranged hydrogen bonds. The errors in arriving at these important statements concerning ionic solvation are large, however, and it is not certain that they can be extrapolated to dilute solutions. It is therefore informative to turn to spectroscopy for information.

(*a*) *Infrared and Raman spectroscopy*

These techniques are in many ways complimentary to n.m.r. spectroscopy and none yields as much information as might be anticipated. For n.m.r. spectroscopy, this arises because rapid time-averaging hides a wide range of useful pieces of information under a single narrow line.

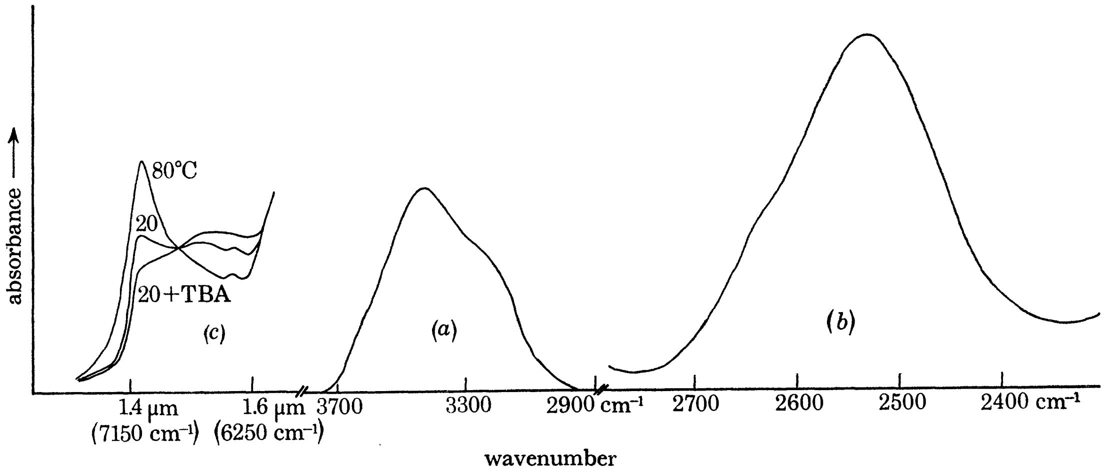


FIGURE 5. The O–H stretching bands for:

(*a*) H_2O in the fundamental infrared region; (*b*) HOD in H_2O (Raman) showing a weak inflexion in the 2640 cm^{-1} region assigned to $(OH)_{free}$ groups; (*c*) HOD in D_2O in the $2\nu_{OH}$ region at 80 °C, 20 °C, and at 20 °C in the presence of 0.05 mole fraction. *tert*-butyl alcohol (TBA).

For infrared or Raman spectroscopy it is largely because potentially informative absorption bands are so broad that they merge into a single almost unresolvable envelope (figure 5*a*). It is therefore necessary to resort to various more devious approaches in order to obtain useful information.

Some band narrowing in the O—H stretching region can be achieved by studying either the isolated O—H stretching band of HOD in D_2O, or the corresponding O—D band for HOD in H_2O. This is because the symmetrical (C_{2v}) water molecule exhibits coupled bands ν_1 (symmetrical stretch) and ν_3 (asymmetric stretch) and there is some residual coupling to equivalent neighbour oscillators causing an extra broadening. These are largely eliminated for the HOD systems. This helps, but not very much. Thus addition in relatively low concentrations, of a range of non-electrolytes to HOD systems has very little effect on its absorption bands.

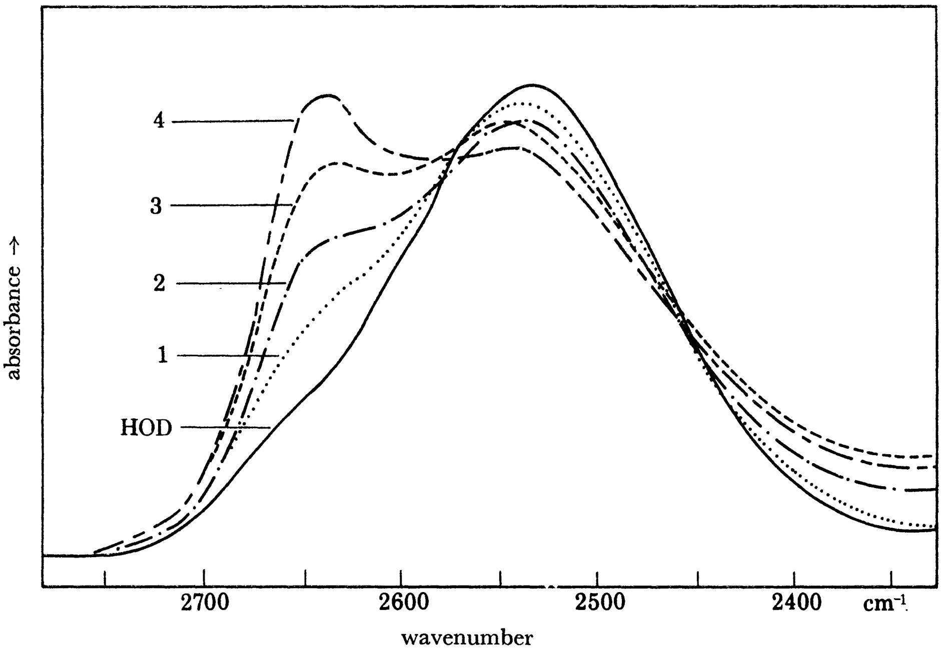


FIGURE 6. Effect of perchlorate ions upon the Raman spectrum (O—D stretch) of HOD in D_2O. ([ClO_4^-] in mol l^{-1} indicated.)

For non-electrolytes, perhaps the most useful information that can be gleaned concerns the concentration of $(O—H)_{free}$ groups. Infrared spectroscopy in the fundamental region is of little use (Senior & Verrall 1969), but Raman spectroscopy is better, because a weak shoulder, assignable to $(OH)_{free}$ groups, can be detected on the high energy edge of the main O—D or O—H stretching bands (figure 5*b*). (The difference is largely a question of selection rules.) The best spectral region for studying $(O—H)_{free}$ groups, however, is the overtone infrared region. This is again a question of relative oscillator strengths: both the $(O—H)_{free}$ and $(O—H)_{bound}$ overtones are greatly reduced in strength, but the loss is relatively greater for $(O—H)_{bound}$. This, coupled with the fact that the separation is greater, leads to a readily detectable, narrow $(O—H)_{free}$ band (figure 5*c*).

The study of factors controlling the presence of $(O—H)_{free}$ groups has been fairly extensive (Worley & Klotz 1966; Luck & Ditter 1969) but the results are not as definitive as might be anticipated. We have found that addition of low concentrations of *tert*-butyl alcohol to cold water causes a systematic fall in the number of $(O—H)_{free}$ groups, but this fall is arrested when the concentration of alcohol approaches the clathrate composition (*ca.* 0.05 mole fraction). This effect, which is equivalent to a cooling, can be taken as supporting the clathrate cage model.

Thus, if the water surrounding the Me_3C-group is more likely to be completely bonded to neighbours, progressively fewer molecules will have the normal probability of having an $(O—H)_{free}$ group, in accord with the spectral information (figure 5*c*).

Added electrolytes also cause slight gain or loss of $(O—H)_{free}$ groups as gauged by their overtone infrared spectra (Luck 1973). Unfortunately, confusion exists regarding the nature of the absorption spectra for solutions containing perchlorate, tetrafluoroborate and similar large anions, so that some of these conclusions are open to question. These salts are unusual in that they give rise to resolvable high energy absorption bands in the fundamental O—H stretching region (Walrafen 1970; Adams, Blandamer, Symons & Waddington 1971; Brink & Falk 1970), (figure 6). These bands are quite close to an unresolved band assigned to $(O—H)_{free}$ groups in pure water (figure 5*b*), and this has led some workers to conclude that these large anions have a unique ability to generate many $(O—H)_{free}$ groups. This would be surprising in view of the fact that large cations have the reverse effect, at least at low temperatures. We have therefore suggested that the discrete band caused by perchlorate and other anions is characteristic of water hydrogen bonded to the anions (Adams *et al.* 1971; Bellamy, Blandamer, Symons & Waddington 1971).

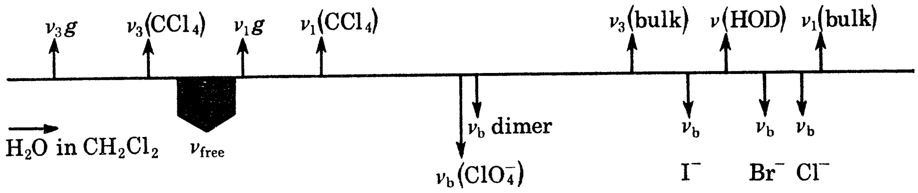


FIGURE 7. Band maxima for water monomers, dimers and for various $A^- - - - HOH$ adducts (ν_{bound}) for solutions of tetraalkylammonium salts in methylene chloride containing low concentrations of water.

That such solvation can occur is clearly illustrated by the infrared spectra of dilute solutions of water or methanol in inert solvents in the presence of tetraalkylammonium perchlorates. Certainly, as is shown in figure 7, this bonding is weak relative even to that for iodide, but nevertheless, it is real. Arguments based upon the measurement of areas under the bands from water 'bonded' to perchlorate ions and the residual bands from water have enabled us to deduce a very approximate solvation number of four for these ions (Symons & Waddington 1974). We therefore postulate the formation of four very weak hydrogen bonds, one to each oxygen, thus knitting these anions into the normal water structure.

This mode of solvation cannot be followed by aqueous nitrate ions, since they show a clear loss of symmetry not exhibited in aprotic solvents (unless ion-pairing occurs). In this case, the O—H stretching region does not exhibit a resolved band similar to that for perchlorate ions, so we can conclude that the hydrogen bonds are stronger. We (Findlay & Symons 1974) consider that this difference stems from the fact that nitrate ions have a far higher polarizability than perchlorate ions. Thus the formation of a hydrogen bond to nitrate causes a drift of negative charge towards the oxygen atom involved and hence a strong bond is formed. This does not occur for perchlorate and hence four much weaker bonds are formed.

If it is accepted that metal perchlorates have a resolved band for water molecules attached to the anions, then the residual absorption (figure 6) must stem from normal water plus water bonded to the cations. Hence, by subtracting the contribution for residual water, the band associated with cation solvation can be revealed. This can be done over a range of concentrations, and hence we (Symons & Waddington 1975) have been able to arrive at the maxima for a range of cations. These are displayed as a function of charge and ion-radius in figure 8, together with similar data for methanolic solutions.

This approach can be extended to anions, but with greater error because separate cation bands are not generally resolved. However, for methanolic solutions, we have been able to check the data by using salts containing large tetraalkylammonium ions which, from our n.m.r. results (Butler & Symons 1969), are known to have an extremely small affect on the solvent. The significance of these results will be discussed after consideration of the complementary n.m.r. information (§5*b*).

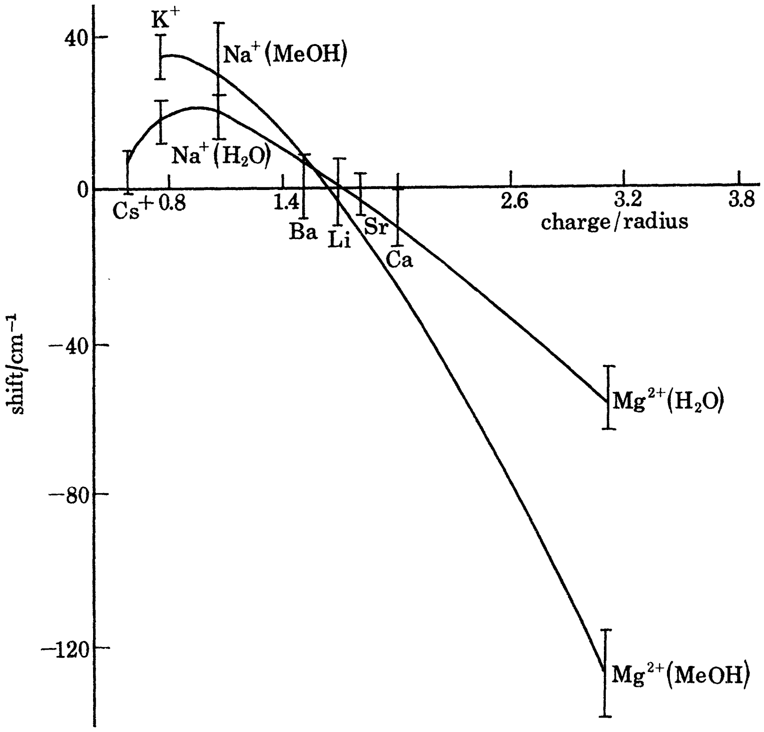


FIGURE 8. Dependence of the band maxima for ν_{OD} (HOD) and ν_{OH} (MeOH) of water and methanol directly bonded to cations upon their charge to radius ratios.

Although this paper is concerned with the behaviour of bulk water, it is of interest to compare the results of infrared studies of dilute water or HOD in various organic solvents (Glew & Rath 1971). Some pertinent results are that in relatively weakly basic media such as dimethylsulphoxide, no $(O—H)_{free}$ groups were detected at 30 °C, whereas in the more strongly basic triethylamine $(O—H)_{free}$ in low concentration was readily discernable. This may arise because mono H-bonding to a strong base deactivates the uninvolved hydrogen of water. This effect is evident when the large shifts induced by bases in the O—H stretch for methanol are compared with the smaller shifts for doubly bonded water.

(*b*) *N.m.r. spectroscopy*

As with infrared spectroscopy, attention can be focused on the solvent nuclei or on various solutes. Most studies have naturally been focused on water protons. These give a single narrow line which shifts monotonically to high field as the temperature is raised. This band is the result of rapid averaging of signals ranging from values for $(\text{O—H})_{\text{free}}$ groups at very high field, down to strongly H-bonded protons on the low-field side of the average. The nearly linear shift on increasing the temperature stems from an increase in the number of $(\text{O—H})_{\text{free}}$ groups together with a general weakening of the hydrogen bonds.

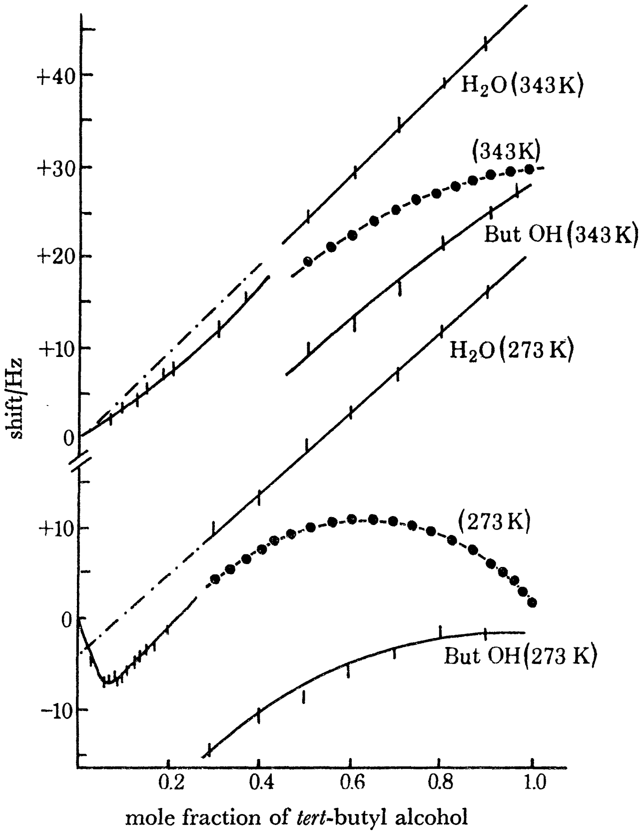


FIGURE 9. Hydroxyl-proton shift (Hz at 60 MHz) for water and *tert*-butyl alcohol as a function of the mole fraction of *tert*-butyl alcohol at 273 and 343 K. The results were averages for all O–H protons in the water-rich regions, but were resolved bands in the alcohol-rich regions. Calculated average curves (-●-●-) are included for comparison.

When a solute is added, there is generally a shift in this resonance. Thus, for example, addition of acetone causes a shift to high-field, to a limiting value associatable with contributions largely from water molecules weakly hydrogen bonded to two acetone molecules. A careful study of aqueous *tert*-butyl alcohol (Kingston & Symons 1973) revealed an initial shift to low-fields (figure 9), and this was interpreted in terms of a slight increase in the extent of hydrogen bonding induced by the bulky Me_3C-group. However, it was subsequently realized that methanol added to water also induced a down-field shift of the averaged hydroxyl proton resonance, so that the original argument became less compelling.

We have succeeded in distinguishing qualitatively between the effect of methanol and *tert*-butyl alcohol on water by studying the effect of temperature. As expected on the clathrate cage model, the effect for *tert*-butyl alcohol was rapidly lost on heating (figure 9). However, for methanol, a relatively minor reduction was observed (Kingston & Symons 1973). For this, and many other reasons, we have assigned the shifts induced by methanol largely to an 'acid-base' affect and that for *tert*-butyl alcohol largely to a clathrate effect, in accord with the infrared information.

In this connexion, it is noteworthy that the n.m.r. and infrared results for pure methanol and pure *tert*-butyl alcohol show that the former contains almost no $(\mathrm{O{-}H})_{\mathrm{free}}$ groups at room temperature while the latter has many. This is largely a steric effect inhibiting chain formation for *tert*-butyl alcohol, whereas the very efficient bonding of O—H groups displayed by methanol, relative to water, arises because there are two available lone-pairs for every proton for methanol, but only one for water. Thus adding methanol to water provides an excess of lone-pairs and hence some $(\mathrm{O{-}H})_{\mathrm{free}}$ groups are scavenged.

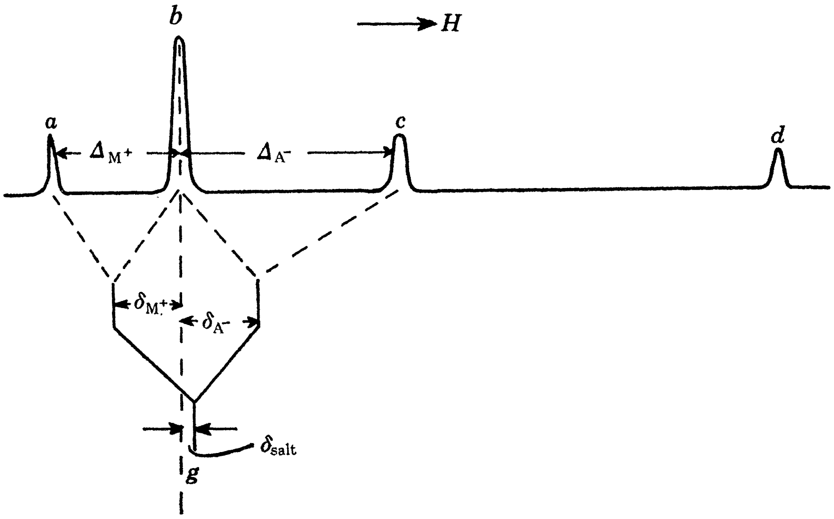


FIGURE 10. Hypothetical n.m.r. spectrum for the ^{1}H resonance of water, showing peaks for water bonded to cations and anions, and the effect of rapid averaging.

Until recently, the task of understanding the effect of electrolytes on the ^{1}H resonance of water has been formidable because of the apparent impossibility of dividing the observed shift into cationic and anionic contributions. The averaging that is occurring, is illustrated diagramatically in figure 10. However, after the discovery (Swinehart & Taube 1962) that low temperature methanolic solutions of magnesium perchlorate displayed a resolved O—H band for solvent molecules directly bonded to Mg^{2+} ions, we realized (Butler & Symons 1969) that any residual shift of the solvent resonance could be largely assigned to anions only. This led to an assignment of individual ionic shifts for methanol, and subsequently for water (Davies, Ormondroyd & Symons 1971).

The pattern of the shifts for cations is qualitatively similar to those displayed in figure 8 (Butler & Symons 1969; Davies *et al.* 1971). My interpretation of this information differs from those of others who usually discuss these shifts in terms of structure making and breaking. Consider the structures in figure 3: ions like Mg^{2+} cause a down-field shift because the solvent bonded to such ions can form stronger hydrogen bonds to the next layer of solvent molecules than are found in the bulk solvent. (This suggestion is born out by our observation that when an aprotic solvent such as acetone is added, the bulk-solvent O—H resonance is shifted to high-field far more rapidly than that for solvent bonded to the cations. Hence bulk solvent hydrogen bonds are broken more readily than those linking the cation's primary and secondary solvent shells. Similarly, the bulk solvent O—H resonance is far more temperature sensitive than is that for the cationic solvent shell (unpublished results).)

Then for, say, Na+ ions, the effect of the cation is reduced so that the resonance from the solvent shell is slightly up-field from bulk solvent. This simply means that H* in $---\overset{|}{\mathrm{O}}\mathrm{H}---\overset{|}{\mathrm{O}}\text{—}\mathrm{H}^*$ forms a stronger bond than in $\mathrm{Na}^+---\overset{|}{\mathrm{O}}\text{—}\mathrm{H}^*$. In the same way, there is no need to postulate major structure making or breaking for the anions, but simply stronger or weaker hydrogen-bonds than the water bonds. To illustrate this point, we have displayed the molal anion shifts as a function of the acidity of the conjugate acids in figure 11.

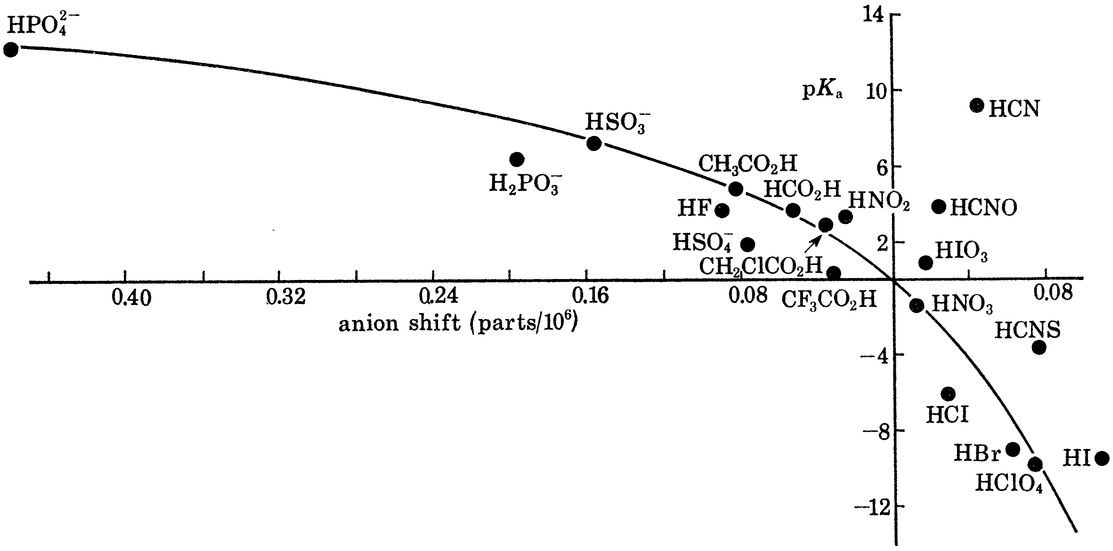


FIGURE 11. Proton resonance shifts for water induced by anions, as a function of the pK_A values for their conjugate acids.

A detailed comparison of the relative shifts obtained by the n.m.r. technique with those from vibrational spectroscopy strongly suggests that they are measuring the same phenomena (Symons & Waddington 1975). In that case, we can confirm that the n.m.r. shifts are a measure of the direct interaction between ions and solvent molecules and that effects involving water structure, such as implied in figure 4, are of minor importance.

(*c*) *Ultraviolet spectroscopy*

In general, this technique has not been very widely or significantly applied to the study of water and aqueous solutions. Perhaps the most studied system is that of aqueous iodide ions (Smith & Symons 1958; Blandamer & Fox 1970). Iodide has an absorption band of high intensity which involves an excited state in which the adjacent solvent molecules (or cations) are directly involved and which is therefore very solvent dependent. The most interesting result from the point of view of water is the effect of low concentrations of additives such as *tert*-butyl alcohol upon the absorption band of aqueous iodide. This is found to shift to high energies and to narrow, the effect closely resembling that of lowering the temperature. This change reaches a limit at about 0.05 mole fraction of alcohol and then no further change occurs until the alcohol is in excess. This sharp high energy shift is interpreted in terms of a tightening of the iodide–hydrogen bonds and an increase in the specificity of solvation (Blandamer, Symons & Wootten 1970). The fact that this new situation is retained for a wide concentration range suggests to us that iodide is satisfactorily incorporated within the filigree of water molecules which are thought to enclathrate the Me_3C-groups.

(*d*) *E.s.r. spectroscopy*

This technique has been used effectively to study the solvation of transition metal ions, but that is outside the scope of this review. Two systems have been studied which do tell us something about water. One concerns the anion of *m*-dinitrobenzene (Jones & Symons 1971). This ion is expected to have a symmetrical structure and indeed this is the case in aprotic solvents. In alcohols, however, a marked line-width alternation indicates that solvation has become asymmetric but that there is a very rapid switch from one form to the other. In water at low temperatures, however, this life-time has become long (*ca.* 10^{-6} s) and the e.s.r. spectrum is characteristic of the asymmetric ion. Addition of low concentrations of *tert*-butyl alcohol actually causes an increase in this life-time, but on further addition there is a dramatic fall, to the fast averaging situation ($< 10^{-8}$ s).

This asymmetric solvation is reminiscent of the nitrate ion and arises because of the very high polarizability of the anion, such that fortuitously strong hydrogen bonding to one nitro-group pulls the charge entirely onto this group leaving the other neutral (Jones & Symons 1971). The interesting feature of this result is the uniquely long life-time of this unit in water. We have interpreted this once again in terms of a relatively well defined clathrate structure around the $O_2NC_6H_5$-group which resists any tendency towards major solvent reorganization.

Finally, I would like to draw attention to some results with di-*tert*-butyl nitroxide (DTBN) radicals that we have obtained from aqueous solutions (Jones 1971). Very low concentrations ($< 10^{-5}$ M) of the nitroxide in water at temperatures below *ca.* 10 °C exhibit e.s.r. spectra characteristic of molecules undergoing rapid, but probably asymmetric rotation. The values for A_{iso} (^{14}N) and g_{av} establish the presence of strong hydrogen-bonding to oxygen, and the asymmetric tumbling is associated with rapid rotation about this bond and somewhat slower rotations perpendicular to it. However, as the nitroxide concentration increases to $> 10^{-4}$ M, the spectral profile changes so that each line becomes asymmetric, indicative of the presence of two species undergoing relatively slow exchange. Superimposed upon this is the normal spin-exchange broadening which usually affects each line equally and in a symmetrical fashion (as indeed is the case for DTBN in all other solvents that we have studied).

We have looked for trivial explanations of this result, to no avail. Relatively low concentrations of *tert*-butyl alcohol destroys the phenomenon which suggests that water structure is playing some role. Very tentatively, we suggest that the marked concentration effect means that at least two DTBN molecules are involved in forming the second species, which we describe as a 'dimer'. For this to have a resolved triplet spectrum in the liquid-phase, the spins have to be at least 1 nm apart, with negligible overlap between the orbitals of the unpaired electrons. Just this situation would occur if two DTBN molecules occupied neighbouring clathrate cages (figure 2*b*), but we need to postulate that this 'dimer' has a life-time of 10^{-8} s or more in order that separate spectra for monomer and dimer appear together. If this interpretation is correct, it is important since it means, as suggested above, that enclathrated molecules may tend to move together to give stable clusters, but in such a way that the molecules are always separated by a layer of structured water.

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Discussion

MARY R. TRUTER (*Molecular Structures Department, Rothamsted Experimental Station, Harpenden*)

I was interested to see your conclusion that the lone-pairs of electrons on coordinated water molecules really are localized in tetrahedral orbitals and oriented towards the cation. This agrees with my expectations but not with the results of my calculations on my own and other people's structure determinations. If the orientation of a water molecule can be fixed either by location of the hydrogen atoms or deduced from hydrogen-bonding the cation may be along a tetrahedral direction, along a trigonal direction or neither, i.e. not in a direction susceptible to theoretical explanation. Recently (Klew, B. & Pedersen, B. 1974 *Acta Cryst.* B **30**, 2363–2371) the structure of sodium chloride dihydrate has been determined by both X-ray and neutron diffraction; although the oxygen atom of the water molecule is tetrahedrally surrounded by two hydrogen atoms and two sodium ions there is no evidence for electron density corresponding to lone-pairs of electrons, the electron density of the water molecule is described as like half a methane molecule stuck to half a fluoride ion.

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On any theory, the extension of the 'lone-pair' orbitals along the (near) tetrahedral axes is extremely small, so one would indeed expect something far closer to fluoride than to methane. Their directional role towards hydrogen-bonding is of great significance because of the short-range 'valence' nature of this interaction As far as the bonding between Na^+ and a *single* water molecule is concerned, one would not expect any strong directional force because of the mainly coulombic nature of this interaction. However, if as envisaged in figure 3 of my paper, there are three water molecules bonded to the one involved in cationic solvation, then these *force* the cation to take up the remaining 'tetrahedral' site.

R. H. Pain (*Biochemistry Department, University of Newcastle upon Tyne*)

Professor Symons has put forward a 'free-sprouting' model in which he suggests that there is no hindrance to the building up of the water lattice on metal ions and on sugar hydroxyls. I should like to ask first, how he reconciles this with the thermodynamic data of ion solvation from which Frank & Evans (1945) derive a 'structure breaking entropy' term which they relate to a shell of relatively disordered water immediately surrounding the inner solvation sphere. Secondly, what is the significance, in terms of Professor Symons' theory, of the dielectric dispersion results which show that for certain sugars, e.g. D-ribose, only 50 % of the sugar hydroxyls are hydrated (Franks, Reid & Suggett 1973)?

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The key to the difference between the approach that I have taken in my paper and that implied in this question is the phrase 'building up of the water lattice'. Only if there is a good deal of 'lattice' nature to water structure will the hydroxyl groups of simple sugar molecules be able to avoid forming hydrogen bonds to water. I see no significant barriers to such bonding, and indeed, our spectroscopic evidence is against the presence of free O—H groups. Similarly for ions that are meant to be 'structure breaking', we see no broken structure, but we *do* see weakened bonds for certain ions and I suspect the entropy factor stems from these, as does the enhanced mobility of water close to such ions.