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CURRENT PROBLEMS IN RESEARCH

Polywater

Vibrational spectra indicate unique stable polymeric structure.

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A form of water with properties very different from those well established for water has been reported in a series of papers by Deryagin and coworkers (*1*). Water in this unusual state has been called "anomalous water" by this group to distinguish it from ordinary water. It has been prepared in two ways. As described by Fedyakin (*2*), secondary columns were observed growing near both ends of a column of water sealed in a glass capillary 2 to 4 μm in diameter. In subsequent work, the anomalous water was prepared by the condensation of water vapor in glass and fused quartz capillaries at relative pressures somewhat less than unity (*3*). Some of the reported properties of this water are (i) low vapor pressure; (ii) solidification at $-40°$C or lower temperatures to a glass-like state with a substantially lower expansion than that of ordinary water when it freezes; and (iii) a density of 1.01 to 1.4 g/cm^3 and stability to temperatures of the order of 500°C.

Some of the properties of this anomalous water reported by Deryagin and co-workers have been corroborated by Willis, Rennie, Smart, and Pethica (*4*). This group also investigated the infrared spectra of the material in a barium fluoride cell. They reported that they were able to obtain only a poor spectrum, that they were required to use a 5× scale expansion, and that they obtained only absorption bands characteristic of normal water.

Bellamy, Osborn, Lippincott, and Bandy (*5*) also confirmed some of the reported properties of anomalous water. They reported spectroscopic data, in the near infrared region, of distilled samples which they believe consisted of a mixture with normal water. In addition, a Raman spectrum on this material was recorded above 3000 cm^{-1}. Structures consistent with the spectra were discussed.

In all cases, the quantities of material prepared have been extremely minute because the capillaries used for its preparation are of the order of 5 to 100 μm in diameter. This has been a severe limitation in the investigation of the properties of the material and in the analyses of possible contaminants which might account for the remarkable properties. Most of the reported investigations up to now have been carried out in the capillary tubes used for the preparation.

We now report the results of an infrared and Raman spectroscopic study of this "anomalous" water both in and out of the capillaries in which it had been formed. From an interpretation of these spectra we propose that the material is a true high polymer, consisting of H_2O monomer units. The properties, therefore, are no longer anomalous but rather, those of a newly found substance—polymeric water or polywater.

The polywater used was prepared by the condensation of water vapor in freshly drawn, fused quartz and Pyrex capillaries between 5 and 20 μm in diameter. The tubing used to form the capillaries was cleaned by conventional methods and dried. The capillaries were suspended over distilled water in an evacuated and sealed system. Approximately 18 hours or more were allowed for the formation of polywater in the tubes. Saturated salt solutions have also been used for obtaining the water vapor and for preparing samples. However, these were not used for the studies described below.

Infrared Spectra

Infrared spectra of polywater were obtained for samples both in and out of the tubes used for formation. For samples within the fused quartz tubes, the examination was limited to the

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region between 5000 and 10,000 cm^{-1}. Raman spectra were obtained only for samples within the tube.

A double-beam microscope spectrometer (*6*) designed for the study of very small samples was used to examine samples in fused quartz capillaries approximately 20 μm in diameter. The normal water overtone region was considerably altered, being characterized by the disappearance of the combination bands near 6950 cm^{-1} and 5100 cm^{-1}. These bands were either partially or completely removed, depending on the nature of the sample and the amount of ordinary water contaminating the polywater. When samples of polywater are heated to high temperatures these water overtone frequencies again reappear, indicating that the major constituent in the capillaries is a material having the empirical formula H_2O. The disappearance of these overtone bands has been reported (*5*).

The mid-infrared spectra of polywater out of the capillaries was obtained by use of a miniaturized diamond cell with a thin diamond platelet. A commercial double-beam infrared grating spectrometer equipped with a beam-condensing system was used. Spectra are given in Fig. 1a where the solid curves represent the spectrum of polywater from fused quartz capillaries and the dashed curve represents the spectrum of the diamond background.

The infrared spectrum of polywater has a number of remarkable features and appears to be unique; it is not a spectrum of any known substance. As an additional check on the unique character of this spectrum, a search was carried out by means of the "ASTM-Dow SIRCH program" which contains approximately 100,000 infrared spectra. The unusual features include the complete absence of absorption from 2500 to 4000 cm^{-1}, the presence of a strong band near 1595 cm^{-1}, and an intense doublet in the 1400-cm^{-1} region. The region from 2500 cm^{-1} to 1950 cm^{-1} is partially obscured by strong diamond absorption. Close examination of this region, not shown in Fig. 1a, shows that it contains no appreciable absorption bands arising from the polywater. Identical spectra were obtained with samples obtained in separate preparations. Repeat runs of the infrared spectrum after a few days showed no significant changes.

It should be noted that no strong absorption which would indicate the presence of such substances as hydrogen peroxide, silica gel, silicic acids, or silicates was observed. Indeed, there is no evidence in the spectrum for any contamination of silicon-containing compounds, oils, greases, and the like.

Raman Spectra

A laser-excited Raman spectrum of polywater was obtained with a double monochromator and an argon laser at an excitation of 4880 Å. This sample was maintained in a fused quartz capillary. The Raman spectrum is illustrated in Fig. 1b. The spectrum is strikingly different from that of normal water or ice. The most prominent feature is a very strong band centered near 620 cm^{-1} with a shoulder which can be estimated near 640 cm^{-1}. All other bands observed in the spectrum are very weak compared to the band at 620 cm^{-1}. Bands appear near 3940, 3420, 2560, 1865, and 1760 cm^{-1}. The weak band at 1050 cm^{-1} is due to the fused quartz capillary. Below 500 cm^{-1} no bands other than those associated with the fused quartz of the capillary or grating ghosts could be detected. The band at 3420 cm^{-1} could be due to traces of residual water. If so, its very low intensity indicates that very little water is left in this sample, a result which is consistent with a near infrared spectrum taken on the same sample where no ordinary water was observed.

A more intense band at 3440 cm^{-1} reported by Bellamy *et al.* (*5*) would appear to be due to normal water modified by the presence of what has been called anomalous water, as suggested by those authors.

The infrared spectrum for polywater formed in Pyrex capillaries was also obtained. Intense bands near 1600 and 1400 cm^{-1} are still the most prominent features in the spectrum. However, a broad absorption band in the fundamental O–H region can also be observed near 3250 cm^{-1}. Its peak intensity is considerably less than those of the bands near 1600 and 1400 cm^{-1}.

Chemical Analysis

Spectrochemical analyses (*7*) on samples of polywater prepared in Pyrex and fused quartz capillaries were carried out by laser probe excitation. The

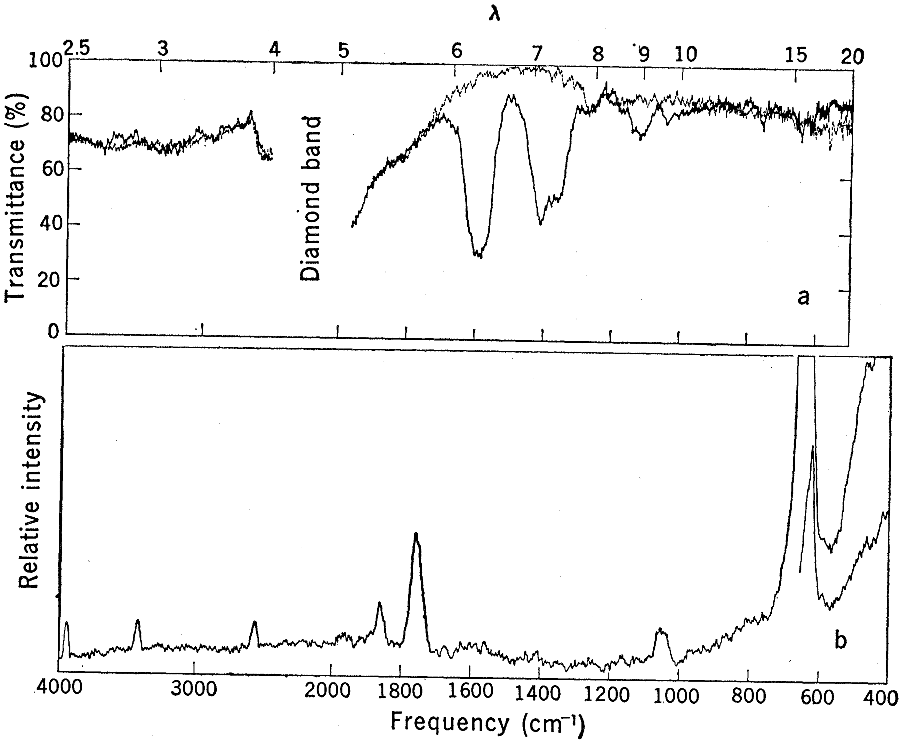

Fig. 1. Infrared and Raman spectra of polywater. (a) Infrared spectrum of polywater after transfer from quartz capillary onto diamond platelets. ——— Polywater; – – – – – – – diamond background. No OH-absorption bands between 4000 and 3000 cm^{-1} are observed. New strong bands appear near 1600 and 1400 cm^{-1}. (b) Raman spectrum of polywater obtained in quartz capillary, with 4880-Å argon laser for excitation. Curve 1 obtained at very high gain, curve 2 at a lower gain sufficient to bring band near 620 cm^{-1} on scale. At this gain, all other bands are extremely weak. The weak band at 1050 cm^{-1} is due to the quartz capillary.

substrate used for this analysis was an acrylic polymer. Only trace quantities of cation contaminants were observed, and there was no significant difference in analytical results, within experimental capability, between the substrate and the sample. A copper-spark method (*7*) was also applied to samples prepared in fused quartz capillaries. No impurities were detected above background or contamination limits of the copper. For the laser probe, the limits of detection are of the order of 10^{-11} g for the elements for which spectrochemical analysis is sensitive, and they are of the order of 10^{-9} g for the copper spark.

Microprobe analysis on samples prepared in fused quartz capillaries showed oxygen (by this technique hydrogen cannot be detected). It also showed the presence of silicon in trace quantities and of sodium. No halogens or other elements were detected. Although the technique was not sensitive for carbon, nevertheless we did ascertain that carbon was not a major component. The quantity of sodium was measured by flame emission spectrometry and was determined to be less than 0.5 percent.

The refractive index of polywater was measured by matching liquids of known refractive index. This measured value is 1.48, in agreement with the value, 1.48, measured by Zorkin, as reported by Deryagin and Churayev (*1*). The latter did not report their method of measurement. The density of polywater can be calculated by the Lorentz-Lorenz equation by assuming that the molar refraction is the same for water and polywater. This assumption should be valid to a first-order approximation. From our data, the calculated density of polywater is 1.39 g/cm^3, in close agreement with the maximum value reported (*1*).

It should also be noted that portions of our material are birefringent, an observation which is consistent with the observation by Fedyakin *et al.* (*8*) and by Willis *et al.* (*4*). In our samples these portions have a refractive index lower than that given above.

Interpretation

The unique spectral data, along with the unusual properties observed for this material, indicate unusual structure and bonding. Previously proposed structures seem less than adequate to explain the thermal stability, high refractive index, and density. In our opinion no structure compatible with the features observed for the vibrational spectra has been proposed. The Raman and infrared spectra are consistent with a structure having a previously unrecognized type of bonding for a system containing only hydrogen and oxygen atoms.

Table 1. Comparison of vibrational frequencies (cm^{-1}) of normal H_2O, alkali bifluorides, and polywater.

Substance	H stretch	H deformation	X • • • X sym. stretch
	*Normal water**		
Vapor	3756† 3651‡	1595	0
Liquid	3450† 3345‡	1645	115
Ice	3370† 3270‡	1655	145
	*Alkali bifluoride **		
KHF_2	1450	1225	595
$NaHF_2$	1570	1205	~600
	Polywater		
$(H_2O)_n$	1595	1410 1360	630

* The frequencies reported for normal water are given in (*17*). Frequencies for alkali bifluoride are given in (*18*). † Antisymmetrical stretch. ‡ Symmetrical stretch.

Although the vibrational spectra of polywater appear completely distinctive and different from those of any known substance, these spectra have a number of features that are strikingly similar to those of hydrogen bond systems which have very strong symmetric hydrogen bonds such as those that occur in KHF_2 and $HCrO_2$. In KHF_2 the bifluoride ion has a linear configuration with an F–F distance of 2.26 Å and an F–H distance of 1.13 Å. The hydrogen bond energy of the FHF^- system has been given as 58 ± 5 kcal/mole in KHF_2 and as 37 ± 2 in $(CH_3)_4N\text{-}HF_2$; it is the strongest hydrogen bond system known to date (*9, 10*). In Table 1 a comparison of the fundamental frequencies of polymeric water with those of the bifluoride ion and normal water (gas, liquid, and solid), is given.

By using the observed vibrational spectra and the observation that the structural unit O–H–O is isoelectronic with the bifluoride ion FHF^-, one can interpret the major features of the observed spectra, on the basis of a structure which would be consistent with the unusual properties observed for polywater. We have concluded that the basic structural unit in polywater is an extremely strong O–H–O three-center bond, isoelectronic with the bifluoride ion. By analogy, therefore, the O • • • O distance must be near 2.3 Å, with the hydrogen atom centered between the oxygens at a distance near 1.15 Å and having a "hydrogen bond" energy of from 125 to 210 kjoule (30 to 50 kcal) per bond unit or 250 to 420 kjoule (60 to 100 kcal) per water formula unit. The O • • • O distance in normal water is about 2.8 Å with a hydrogen bond energy of about 4 kcal/mole.

Given in Figs. 2 and 3 are possible structures which involve the monomer, H_2O, in an extended network system of strong O–H–O bonds. Here the oxygens interact with the *s* orbital of the hydrogen atoms through sp^2 bonding, forming multicenter bonds involving delocalized three-center bonds for the O–H–O unit. Extensive delocalization of the electrons through the network would occur, with the result that each O–H bond has a bond order of ⅔. The remaining *p* orbitals for the oxygen would make a contribution to repulsion between lone pairs in the structure. The bifluoride ion configuration has also been considered as a three-center bond (*11*).

The above structures would be stabilized in that there is delocalization of electrons through the structure and because the effective bond order for an H–O unit in the structures represented in Figs. 2 and 3 for polywater is ⅔, as compared to ½ in the HF_2^- ion. Also, the *s* orbital of the hydrogen forms stronger bonds with the sp^2 orbitals of the oxygen than with a *p* orbital for the fluorine atoms in the FHF^- system. Indeed, it would seem that the H–O bonds in polywater are so strong that they do not fit the normal criteria for hydrogen bonds and that they should really be considered as covalent delocalized single bonds with a bond order near ⅔.

The structure illustrated in Fig. 2 would be one in which the structural units are arranged in a plane and form regular hexagonal rings. In this case one would have to visualize this two-dimensional network as having a negative charge (the number of rings minus one). The network could be held together by the necessary number of protons, cations, or hydronium ions so that the empirical formula of water is maintained. A polymeric structure of this type containing a delocalized negative charge bears marked similarity to polyelectrolytes. It is also possible that no charge occurs, but rather that some oxygen atoms form four coordinated interconnecting hydrogen bonds between layers. For these cases, one would expect that there would be some OH–stretching vibrations which would be more near the normal frequency, although the number of such bonds would be relatively small, compared to the strong bonds. Although the spectra shown in Fig. 1 do not show any OH bands, this portion of the spectra must be examined more critically for the presence of broad weak OH absorption. In addition, when Pyrex capillaries were used the spectra obtained definitely demonstrated the presence of OH in the sample.

The structure shown in Fig. 3, again involving the oxygen atoms in sp^2 bonding with the s orbital of the hydrogen atoms, is typical of that for many long-chain high polymers. The structure would have to be very highly branched in order to maintain the symmetrical O–H–O structural unit and contain relatively few normal O–H groups, consistent with the absence of the absorption band in the 3400-cm^{-1} region for the material formed on a fused quartz surface. Such a structure, however, could account for the appearance of the broad O–H absorption band in the material prepared on Pyrex surfaces. For this surface, the degree of branching in polywater could be considerably reduced. It should also be noted that species of lower-molecular weight, not included in the samples examined by us, possibly could also contain considerable OH, due to the large fraction of end groups. The structure represented in Fig. 3 could also be compared to polyelectrolytes, since it could readily lose protons.

It is possible to assign the most intense bands observed in the infrared and Raman spectra by means of the structures shown in Figs. 2 or 3. These tentative assignments are given in Table 1, along with the corresponding frequencies for normal water and ice where appropriate. The symmetric O $\cdots$ O motion, the antisymmetric hydrogen stretching, and both the inplane and out-of-plane hydrogen bending can be readily assigned.

One would predict that polymeric water would be very stable, since there in an increase in stability within the range of 250 to 420 kjoule/mole (60 to 100 kcal/mole) above that for normal water, which has a hydrogen bond energy of 3 to 4 kcal/mole. This would indeed account for the fact that this material can be maintained at temperatures as high as 500°C. The structures represented in Figs. 2 and 3 are consistent with the very high density reported, the high refractive index, and the extremely high viscosity and low vapor pressure that has been observed by us and others.

A modified electronic spectrum for polywater would also be predicted from a structure of the types shown, since there must be electron delocalization to maintain the configuration O–H–O. Some resonance or canonical forms for the structure given in Fig. 2 are given in Fig. 4. Similar forms can also be drawn for the structure given in Fig.

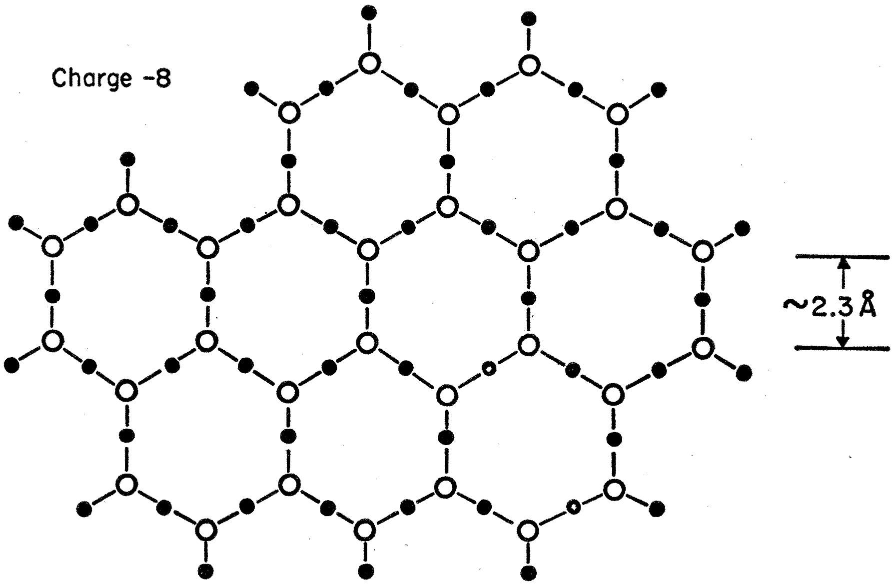

Fig. 2. Structural diagram for polywater consisting of a network of hexagonal units. This structure, as drawn, would have a negative charge. An appropriate number of hydronium ions, protons, or tetra-coordinated hydrogen-bonded oxygen atoms would be required to maintain the empirical formula $(H_2O)_n$.

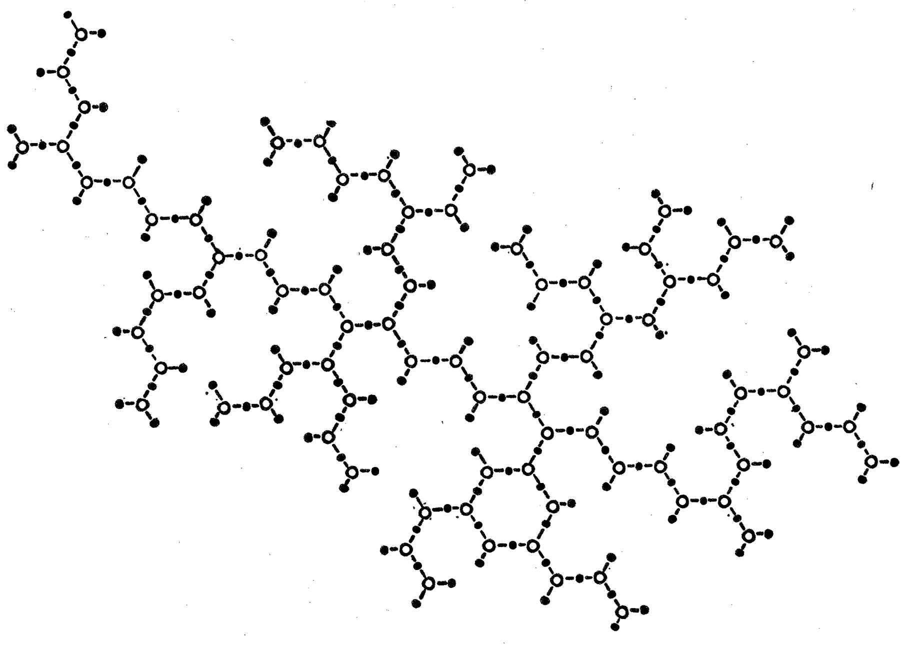

Fig. 3. A proposed structure for polywater consisting of highly branched polymer chains.

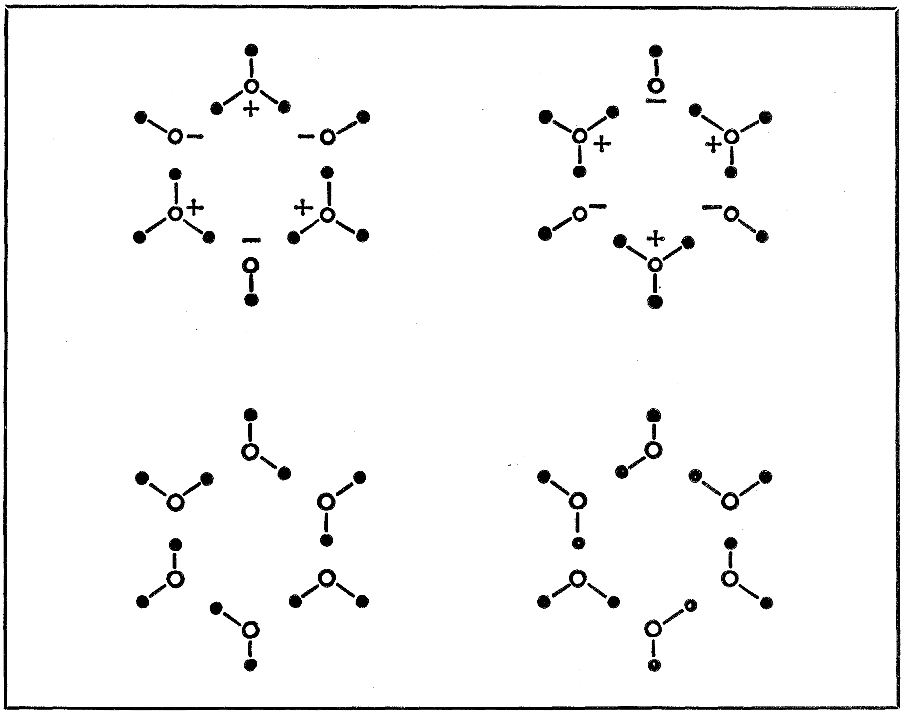

Fig. 4. Some resonance forms for the structure given in Fig. 2.

3. We have observed a modified electronic spectrum by means of a double-beam microscope spectrophotometer (*6*), using samples of polymeric water in fused quartz capillaries.

From the $O\cdots O$ distances of 2.3 Å for the strong hydrogen bonds in the plane of these structures and a van der Waals radius for the oxygen atom of 1.4 Å, one can estimate the maximum density and obtain a value near 1.40. This is a number near the maximum value for the density reported by Deryagin and co-workers (*1*) who reported values ranging from 1.01 to 1.4 "for water of various degrees of anomality."

Another structure that can be considered involves an extended three-dimensional network of O–H–O bonds together in a tetrahedral configuration with each O–H bond having a bond order of ½. Because of the apparent importance of quartz in the formation of polywater, a structure of this type must be seriously considered. In structures of this type all oxygen atoms are equivalent and all hydrogen atoms are equivalent with an $O\cdots O$ distance of approximately 2.3 Å. This structure is related to hexagonal ice or to the metastable cubic ice where the oxygen atoms are located as they would be in a diamond lattice. If polywater should have this type of cubic or hexagonal structure, one might expect that it could be formed by subjecting normal water or one of the known dense forms of ice to high pressures. Since evidence has not been found that pressurizing water or any of the ices produces material analogous to polywater, this type of three-dimensional polymer is not necessarily attractive, as judged from our knowledge of ice structures. The density that can be calculated for this structure is approximately 1.6, which appears to be too high.

The structures and vibrational spectra of all the known forms of ice have been investigated. In all cases the structure is tetrahedral, although in some instances the tetrahedral structure is distorted. For example, ice VII is known to have a body-centered-cubic structure with nearest neighbor $O\cdots O$ distance of approximately 2.85 Å, and a density of 1.51 at 25 kb (*12*). The vibrational spectra reported (*13*) for these ices always show strong OH bands above 3000 cm^{-1}.

An analogy to some of the structures proposed in this paper exists in compounds that contain polyfluoride anions. Cady and co-workers (*14*) have prepared crystalline substances such as KH_4F_5, CsH_6F_7, and CsH_3F_4, containing the H_nF_{n+1} anions. The crystal structure for one of these, KH_2F_3, was determined by Forrester (*15*) and co-workers. They found that the $H_2F_3^-$ ions exist as discrete covalent units in the lattice with the F–H–F bond distance of 2.33 Å, and a F–F–F bond angle of ~ 130°.

Bellamy *et al.* (*5*) have proposed a tetramer structure in which the water units are held together by p^3 bonding of the oxygen atom with the *s* orbital of the hydrogen atoms. In this model, only four strong bonds are used, with four hydrogens remaining unbonded. This model requires a distortion of the O–H–O bond angle. The calculated density for this structure is 1.1 to 1.2. Bellamy and co-workers (*16*) have proposed that such structures would be stabilized because the lone pair orbitals of the oxygen atoms are in a configuration which would minimize the O–O repulsion term in a $O\text{–}H\cdots O$ hydrogen bond. In this tetramer it is not clear whether the hydrogen atoms would be located in a symmetric position between the two oxygen atoms or in an asymmetric position.

On the basis of the foregoing arguments, we believe that water is restructured on the fused quartz or Pyrex surface into a polymeric form with bonds and bond energies completely different from that of ordinary water. Its properties are not those of water, and it should not be considered to be or even called water, any more than the properties of the polymer polyethylene can be directly correlated to the properties of the gas ethylene. In the case of the formation of polyethylene, a bond change occurs. In the case of polywater, a bond change also occurs, although it has previously been unknown.

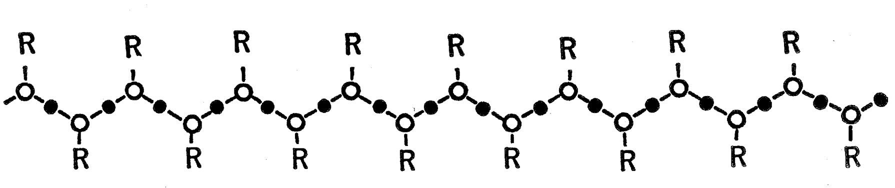

Fig. 5. Proposed structure for polymers of materials such as alcohols, acetone, and acetic acid.

The properties of this material are also consistent with what would be expected from a polydisperse polymer. There would be a distribution of molecular-weight species with both the distribution and average molecular weight dependent on the specific polymerization conditions. Further, any treatment of the sample after polymerization could result in a partial fractionation or degradation of the original sample. Therefore, distillates of this material would consist of components expected from a material of wide molecular-weight distribution. These would include components of low molecular weight, such as tetramers and hexamers (Fig. 4). We believe that the material used to obtain the spectra in Fig. 1 is comprised of species of high molecular weight. Further, the mechanism of polymerization, still unknown, appears to be affected by the conditions of the "catalyst" surface. The spectra obtained from samples prepared in Pyrex capillaries showed residual OH absorption, apparently from incomplete polymerization, possibly from the different structure of the Pyrex as compared to the quartz. Finally, it should be noted that polywater appears to be soluble in ordinary water at room temperature, although under certain conditions separation may occur. We have observed that purity is of primary importance in distinguishing its properties from those of ordinary water.

The formation of columns of other substances containing OH groups—namely, acetone, methanol, acetic acid —(*3*) by the condensation of vapors in capillary tubes has also been reported. The properties of these materials have not been reported in any detail. We believe that the structures given in Figs. 2 or 3 can be modified to describe a structure for these and other materials. This is given in Fig. 5 and represents a linear polymer with bonds similar to those described for polywater.

Summary

The infrared and Raman spectra of a form of water prepared in fused quartz capillaries and previously designated as "anomalous" water have been obtained. The infrared spectra appear to be unique with the apparent absence of the O–H-stretching bands prominent in normal water spectra, and the appearance of new bands near 1600 and 1400 cm^{-1}. The interpretation is that new and previously unreported strong symmetric O–H–O bonds are formed, isoelectronic with FHF^-. The approximate bond distances are given as 2.3 Å for $O \cdots O$, and 1.15 Å for H–O as compared to a $O \cdots O$ distance near 2.8 Å for normal H_2O. These bonds are regarded as responsible for the remarkable properties of the material and have considerable covalent character. They are so strong that they cannot be considered as normal $O \cdots H$ hydrogen bonds. Extensive electron delocalization could occur in structures which involve oxygen atoms in three equivalent bonds, where each O–H unit has a bond order of ⅔. The bond energy per O–H–O unit is given as approximately 125 to 210 kjoule/mole (30 to 50 kcal/mole), and an energy of 250 to 420 kjoules (60 to 100 kcal) per H_2O structural unit. Several structures are proposed which are consistent with the spectral data and the remarkable properties and stability of the material. It is concluded that the material is a true polymer of water, and, therefore, is named polywater.

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