Reports

Polywater: Polymer or Artifact?

Abstract. *Several polywater samples were prepared by the standard methods and have the same physical and spectroscopic properties as those made in other laboratories. However, a variety of chemical analyses show high concentrations of impurities which may account for many of the anomalous properties.*

When water is condensed into fine, freshly drawn capillaries, it has properties very different from that of "normal" water. Deryagin and Fedyakin and their co-workers (*1*), who labeled the new material anomalous water, have shown it to have a low vapor pressure, a low freezing point, a high melting point, a high density, and a high viscosity. Lippincott *et al.* (*2*) have determined its vibrational spectrum and from that study have postulated that anomalous water is a polymer of regular water; hence they termed it polywater. In an attempt to study the infrared and Raman spectrum of polywater in more detail, we have prepared the material by the standard methods. In the course of our investigation several analytical studies were made, and these revealed significant amounts of ionic impurities explaining some, if not all, of the anomalous properties of polywater.

Consistent with reports (*2–4*) that anomalous water is a mixture of "normal" water with the highly polymerized form, measurements of its extraordinary properties vary from sample to sample. Many physical property measurements have been made on freshly prepared samples of anomalous water even though their polywater content was not known. However, as evidenced by the complete absence of O–H stretching vibrations in the infrared spectrum of Lippincott *et al.* (*2*) the spectroscopic evidence has been obtained on samples in which the normal water has been completely removed. The now generally accepted definitions are that in a typical preparation the condensate in the capillaries, *anomalous water,* is a mixture of normal water and polywater. By allowing the normal water to evaporate in a dry atmosphere or by briefly pumping on the capillary, a material of high viscosity, *polywater,* is produced. It is this material that exhibits the more well-defined physical properties and the unique spectroscopic properties. Our spectroscopic and analytical investigations have been made exclusively on this viscous substance.

In our study samples were prepared at unsaturation and at saturation. In the former technique the capillaries were exposed to an atmosphere of water vapor slightly below the saturation pressure by surrounding the capillaries and the doubly or triply distilled water supply with constant temperature baths. The preparations were carried out both at 27° and 30°C, and the capillary chambers were immersed in baths 0.3°C warmer than those of the water supply. In the other preparative technique, carried out at room temperature, the capillaries were placed in a desiccator jar in which there was a supply of water. Since no attempt was made to control the vapor pressure of the water in this method, the vapor surrounding the capillaries was at the saturation pressure. In our experiments salts were never used to reduce the vapor pressure of the water supply.

All of the capillaries were freshly drawn before each preparation and were made of quartz. They ranged from about 10 to 300 μm in diameter. The stock quartz tubing was boiled in aqua regia and thoroughly rinsed with distilled water before the capillaries were drawn. The preparative vessels were cleaned by washing in turn with acetone, distilled water, chromic acid cleaning solution, and again with distilled water. The final rinsing with distilled water was repeated several times to guarantee thorough removal of any soluble residues.

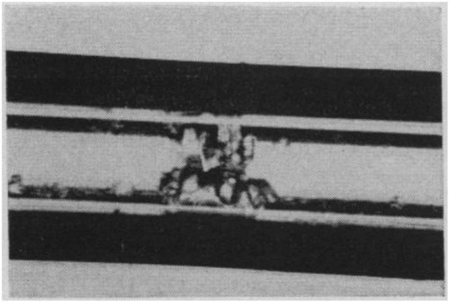

Fig. 1. Vaseline-like polywater sample after removal of normal water. The capillary inside diameter is about 200 μm.

In both types of preparation the evacuated vessels were opened after a few days. Under unsaturated conditions, an average of 1 percent success was achieved. At saturation over 5 percent success was obtained, but generally the anomalous water in these capillaries contained less polywater than in preparations made at reduced vapor pressure. Typically 100 to 500 capillaries were used in a run.

The columns of anomalous water ranged from a few millimeters to 5 cm in length. When these capillaries are placed in a dry atmosphere, the normal water evaporates in about 1 week and a residue is left in the capillaries (Fig. 1). This residue, which at first appeared to be of a Vaseline-like consistency, eventually hardens and becomes saltlike, in agreement with earlier reports (*2, 5*). Furthermore, it is quite deliquescent (*6*). When a capillary containing the residue is exposed to a saturated atmosphere of water vapor, it absorbs about 30 times its weight in water in about a half hour.

A melting point measurement on a sample of anomalous water indicated a broad melting range with an onset that could not be well defined. The melting behavior was characterized by a gradual change in phase, easily noticeable at about −15°C, such that the homogeneously cloudy material separated into a clear liquid phase with small scattering spheres dispersed within it. These particles, also reported by others (*4, 5*), became smaller in size and number upon further warming and eventually disappeared at about 0°C.

The infrared spectra of three samples are shown in Fig. 2. These spectra were obtained on a Beckman IR-12 spectrometer with beam-condensing optics. Scale expansion was used in Fig. 2C only. In each of these spectra we observed vibrational frequencies in the same regions that Lippincott *et al.* (*2*) did—namely, lines near 1600, 1400, and 1100 cm^{-1}. The

Table 1. Vibrational frequencies (cm^{-1}) from infrared absorption data. Sample origins are described in text. Letters in parentheses describe the band intensity (s, strong; m, medium; and w, weak).

Sample A	Sample B	Sample C	Reference *2*
1000 (w)	1000 (w)	1000 (w)	1050 (w)
1080 (s)	1090 (s)		
1120 (s)	1120 (s)	1120 (w)	1120 (m)
1280 (w)			
1320 (w)			
1370 (m)	1370 (s)	1365 (m)	1365 (s)
1425 (m)	1430 (s)		1410 (s)
	1470 (s)		
1615 (s)	1620 (s)	1605 (m)	1595 (s)
2930 (w)	2940 (w)	2930 (w)	
	3210 (s)		
3270 (w)	3350 (s)		

spectra were obtained as follows. The polywater was pushed from the capillary with a piece of wire. The viscous material adhered to the wire which was then immersed in a small droplet of distilled water on a BaF_2 substrate. The polywater dissolved, and, as the regular water evaporated, a homogeneous residue of polywater remained on the BaF_2 window. Sample A in Fig. 2 was prepared in an apparatus at the University of Southern California at reduced vapor pressure. Samples B and C were grown at Bell Laboratories. Sample B, like sample A, was grown below saturation, and sample C was grown at one temperature at saturation conditions. The loss in transmission below 1000 cm^{-1}, which is most pronounced in Fig. 2C where scale expansion was used, is caused by the BaF_2 absorption. It is evident from the spectra that the line at about 1100 cm^{-1}, especially weak in Fig. 2C, behaves very differently from the remaining lines. To a lesser degree, there are also intensity variations among the other lines. A marked variation in the spectrum as a function of the sample's age on the BaF_2 substrate was observed. When the spectrum of sample B was repeated after an interval of 1 week, strong bands appeared at 1280 and 1320 cm^{-1}, similar to those seen in sample A. In Table 1 the frequencies of the absorption bands found in these three samples are tabulated and compared with those reported by Lippincott *et al.* (*2*).

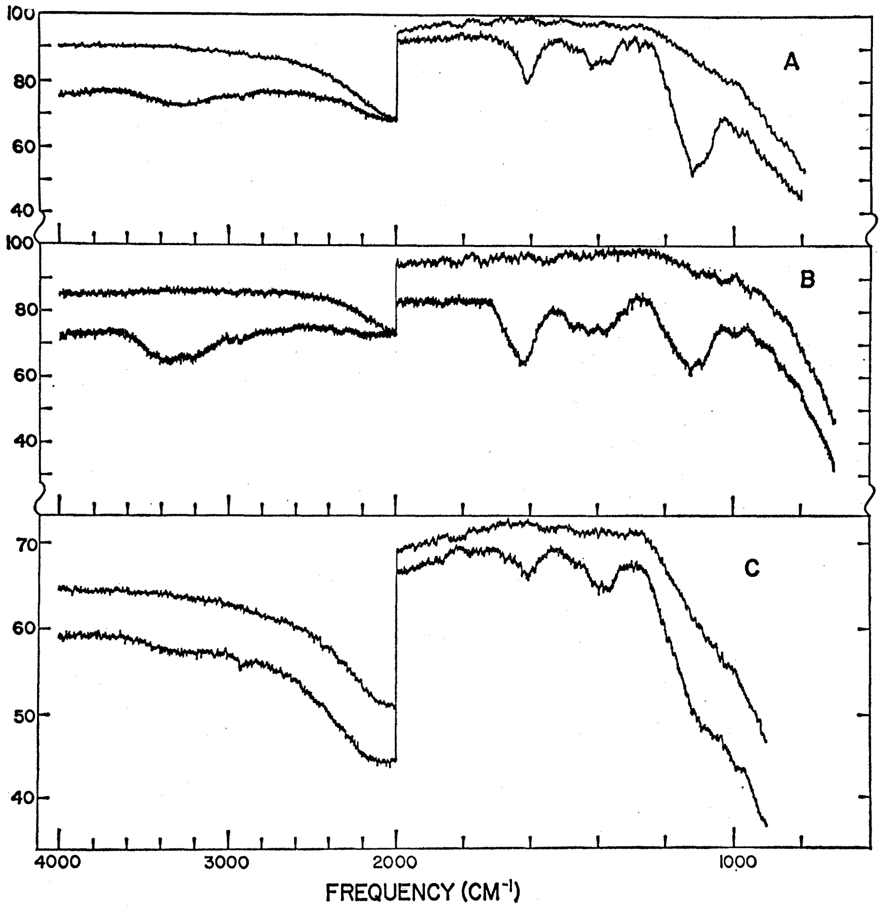

Fig. 2. Infrared spectra of polywater. Above each spectrum are shown background BaF_2 spectra obtained at identical conditions. The discontinuity at 2000 cm^{-1} results from a spectrometer grating change. (A) Sample grown at the University of Southern California by the unsaturation technique; (B) sample prepared at Bell Telephone Laboratories by the unsaturation technique; (C) sample prepared at Bell Telephone Laboratories by the saturation technique.

In principle, Raman scattering should provide the best way to characterize polywater. Generally the analysis is nondestructive and can very suitably be performed within the capillary. We have attempted to obtain argon laser Raman scattering spectra of polywater within the quartz capillary and have found that every sample studied exhibited a very large fluorescent background. This fluorescence clearly came from the polywater and was very intense throughout the vibrational mode region. Furthermore, the intensity diminished under the action of the laser beam, but it was sufficiently great to obscure any discrete bands from being discerned other than those that could be attributed to the quartz capillary. In some spectra we, like Lippincott *et al.* (*2*), were able to find a band at about 620 cm^{-1}. However, fused quartz exhibits a line in this same spectral region with similar structure (*7*). Although the 620 cm^{-1} line reported by Lippincott *et al.* (*2*) appears too strong to originate from quartz in their spectrum, the combination of the intense fluorescence and the overlap with this line makes of the Raman spectrum an ambiguous method of characterizing polywater at present.

The origin of the fluorescence and its relation to the discrete spectrum reported by Lippincott *et al.* (*2*) is not understood. Clearly thermal effects are a factor since in one experiment, at high incident laser powers (about 1 watt), the polywater "burned," that is, the sample turned dark brown, nearly black, in color.

Initially many investigators thought that polywater was a silica gel rather

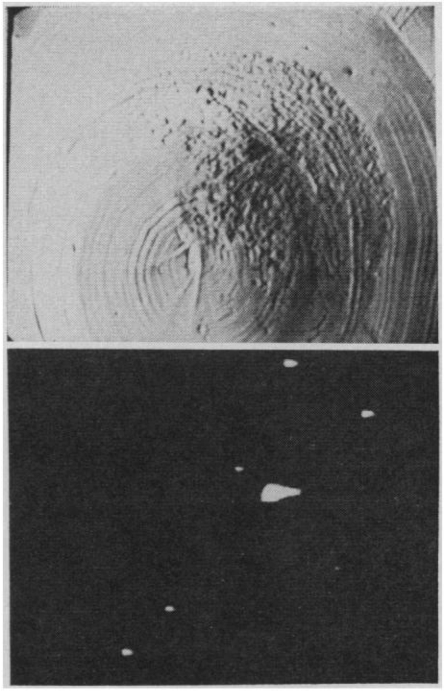

Fig. 3. Electron microprobe analysis for silicon. (Top) Secondary electron photograph of sample; (bottom) Kα silicon emission photograph.

than a polymer of water. To analyze for silicon, we undertook an electron microprobe study. The samples were removed from the capillary by pushing a wire through it so that the polywater adhered to the wire. The sample was then transferred by simply dabbing the wire onto the appropriate substrate. The entire process was carried out under a microscope so that we could ascertain whether a transfer was indeed made. From the results, silicon is not homogeneously present (Fig. 3) in significant amounts (less than 1 percent). The scattered bright areas of silicon, we believe, result from chips of quartz embedded in our sample. In Fig. 4 we present similar photographs in an analysis for sodium, showing on top the secondary electron signal and on the bottom the Kα line of sodium. The strong signal present wherever there is polywater indicates a significant sodium content in the sample.

To determine the approximate percentage of sodium, a neutron activation experiment was performed. From this experiment we have been able to determine that the weight percentage of sodium in our sample is between 20 and 60 percent. This estimate is based on measuring the volume of our sample to calculate its total mass by assuming a density of 1.4.

In a search for other possible contaminants, the x-ray milliprobe, which is sensitive to magnesium and all heavier elements, was used (*8*). The following impurities with the specified weight percentages were found: Ca (1 percent); K (3 percent); Cl (15 percent); and SO$_4^{2-}$ (15 percent). The exact energy of the sulfur emission depends on its valence state, thereby allowing the sulfate determination to be made. Again the weight percentages were determined by measuring the volume of the sample with a microscope then calculating its mass.

To confirm the presence of these contaminants, additional samples were analyzed with a spark source mass spectrometer (*9*). Meaningful absolute concentrations cannot be obtained from this instrument, but it has a high sensitivity for m/e ratios ranging from 10 to 300 and can be used to obtain approximate relative concentrations in an elemental analysis. The densitometer tracing from the photographic emulsion after sparking a polywater sample is shown in Fig. 5. The relative sensitivity of this technique to the various elements involved varies greatly, but from appropriate calibrations and analyses of several samples, we have determined that our samples consisted of approximately equivalent amounts of sodium, potassium, carbon, oxygen, and chlorine each present in the range of 5 to 35 percent of the total ion signal. Furthermore, there are small amounts of calcium, boron, silicon, nitrogen, and sulfur (*10*). This information is tabulated and compared with the other analyses in Table 2.

The low concentration of oxygen and lack of intense bands at $m/e = 18$ or at multiples of 18 indicated that nearly all the material in these samples consisted of the contaminants with relatively few H$_2$O molecules or H$_2$O polymers present. The occurrence of a signal at $m/e = 44$ in the mass spectrum should also be noted because this is the value of the singly ionized CO$_2$ unit. The spark source mass spectrum generally gives an elemental analysis, but small stable species can be observed. The line at $m/e = 44$ may originate from molecular formation of CO$_2$ in the periphery of the spark or it may have originated directly from fragmentation of the sample, indicating carbon-oxygen compounds.

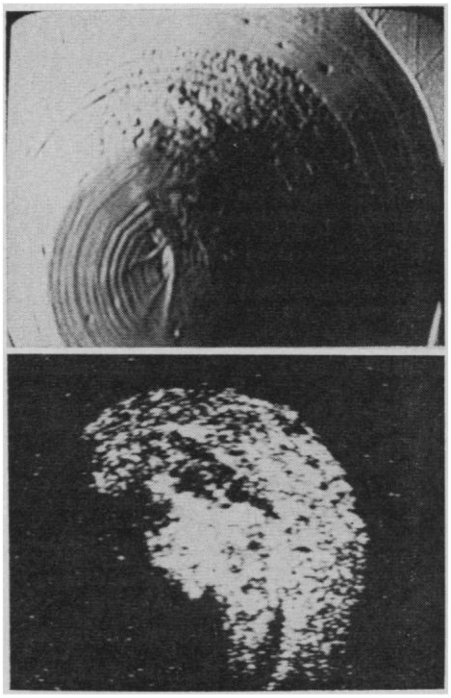

Fig. 4. Electron microprobe analysis for sodium. (Top) Secondary electron photograph of sample; (bottom) Kα sodium emission photograph.

In view of the analytical information, we reexamined the infrared spectrum in an effort to better determine what types of compounds might be present. The strongest mode of the sulfate ion (*11*) occurs at about 1100 cm^{-1}, and the intensity of the 1100-cm^{-1} band varies with the sulfate concentration in our polywater samples. There are no other strong sulfate lines in the range studied in the present investigation or in that of Lippincott *et al.* (*2*). We therefore conclude that the 1100-cm^{-1} band in the infrared spectrum of polywater results from SO$_4^{2-}$ (*12*). The lack of absorptions in the usual hydrocarbon vibrational mode regions rules out the presence of most complicated organic molecules. The strong bands around 1600 and 1400 cm^{-1} is very suggestive of carboxyl groups and bicarbonates which also have strong absorptions in these regions. Furthermore, the line at $m/e = 44$ in the mass spectral analysis is consistent with the presence of such species. Although definitive assignments of these bands from known impurities cannot yet be made, their strength in our highly contaminated samples makes their assignments as bands of a polymer of water tenuous indeed.

The occurrence of ionic nonvolatile species in the capillaries poses an interesting question. In a presumably well-cleaned system with only water of high purity present, how can ionic impurities be found in the capillaries? It should be pointed out that the

Table 2. Summary of analytical results. The letters in parentheses indicate the sample source. The A and C refer to samples simultaneously prepared with those in which the infrared spectra were obtained and they correspond to the labeling in Fig. 2. The percentages, where included, are percentages by weight of the entire sample. The five primary materials listed in the mass spectrum experiment account for about 95 percent of the ion current of the sample.

Electron microprobe (A)	Neutron activation (A)	X-ray milliprobe (A)	Spark source mass spectrum (C)
Sodium No silicon	Sodium (20–60%)	Potassium (3%) Calcium (1%) Chlorine (15%) Sulfate (15%)	Sodium Potassium Carbon Oxygen Chlorine Calcium (trace) Boron (trace) Silicon (trace) Nitrogen (trace) Sulfur (trace)

quantities of polywater formed (up to 1 μg) are too great to result from leaching of impurities from the quartz capillaries. We believe the answer to this question may lie in some experiments by Rabideau (*13*) in which polywater was prepared by adding K_2SO_4 to the supply water to reduce its vapor pressure. Rabideau subsequently found K_2SO_4 in his capillaries and therefore proposed that an electrolytic solution crept along the vessel walls, leaving the salt deposit in the capillaries. He tested his model by suspending his capillaries and his salt solution from wires to reduce the possibility of liquid diffusion into the capillaries. Under these conditions no anomalous water was formed in the several hundred capillaries tested. We believe that a similar diffusion phenomenon occurs even when salts are not used for the vapor pressure reduction. When only pure water is used, it diffuses along the walls of the vessel, leaches impurities from the glass surface, and eventually diffuses into some of the capillaries.

To test the creep model, we performed an experiment in a vessel constructed to house two sets of capillaries simultaneously. One set was in intimate contact with the walls of the Pyrex vessel. The other set was suspended by wires to minimize surface creep effects. The vapor pressure of the water was controlled in the usual manner with a constant temperature bath at 0.3°C below the temperature of the bath surrounding the capillaries. In two experiments totaling about 500 capillaries in each position, we have found five successes from the capillaries in contact with the walls and no successes from those suspended from wires, consistent with the diffusion mechanism. Such a model can account for the seemingly unpredictable success ratios attained in several laboratories since the surface contact between the capillary and the preparative vessel becomes very important. In view of this mechanism, great care must be taken in the construction and the cleaning of the preparative vessels. Salts must not be used for vapor pressure reduction, greases should be avoided, and new cleaning techniques must be devised to eliminate all surface contaminants.

We believe our experiments have very strong implications concerning the existence of polywater. Our material has been carefully prepared in the usual way and has similar physical and spectroscopic properties to that prepared in other laboratories. However, all of our analyses, including the infrared spectrum, show that the material is highly contaminated with impurities (*14*) such that nearly all of the mass can be accounted for. In this complex mixture of impurities only trace amounts of silicon have been found, ruling out the speculation that the anomalous properties result from a silica gel. A high concentration of impurities can account for many of the observed physical properties of polywater such as its reduced freezing point and vapor pressure, its high density and viscosity, and its high stability temperature. Before attributing the unique features of this strange liquid to polymerized water, many more experiments must be carried out

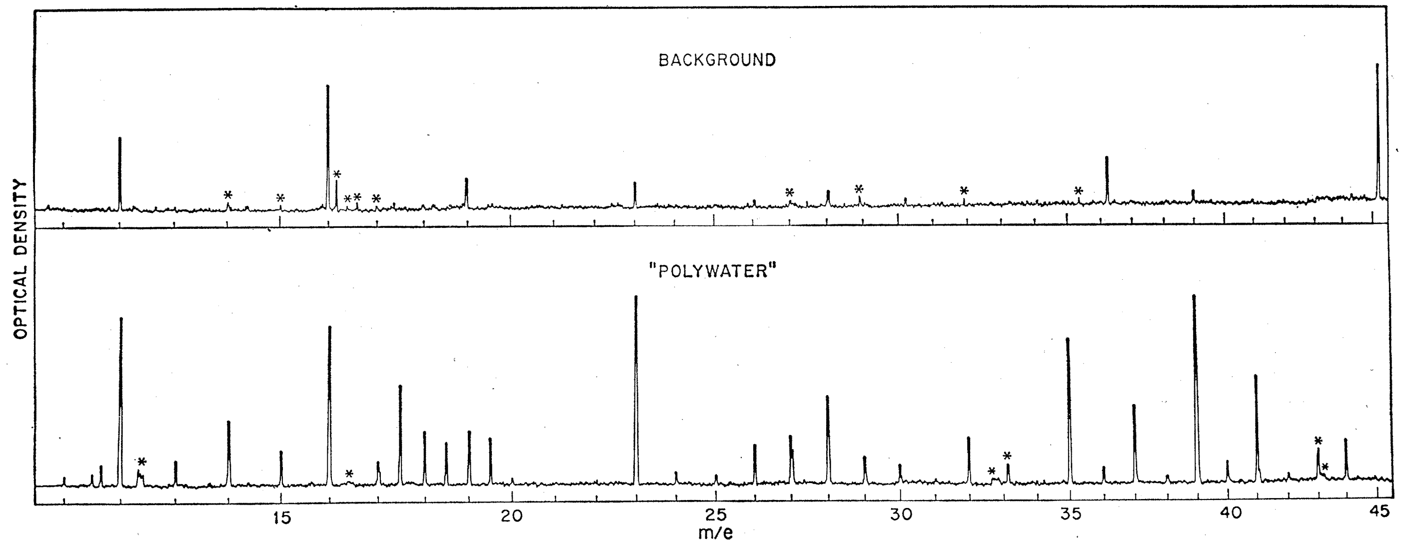

Fig. 5. Densitometer tracing of a photographic plate of a spark source mass spectrum of polywater. The asterisks indicate spurious scratches in the emulsion. The background lines at $m/e = 36.2$ and 45.25 are multiply charged tantalum lines from the substrate. They are absent from the sample since it is preferentially ionized. The ion intensity of each element was determined from the densitometer tracing by the modified two-line Churchill emulsion calibration. No lines beyond $m/e = 44$ could be detected from the sample.

under extremely well-defined experimental conditions to demonstrate precisely which of the anomalous properties may result solely from contaminants. In the meantime our evidence makes it unlikely that the recently reported polymer of water exists.

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References and Notes

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8. T. C. Loomis and K. H. Storks, *Bell Lab. Rec.*, January 1967, p. 2.
9. D. L. Malm, in *Progr. Anal. Chem.* **2**, 148 (1969).
10. The mass spectrum analysis was made on a sample prepared at the same time as the one used to obtain spectrum C in Fig. 2. Its low sulfur content agrees with the near absence of the 1100 cm^{-1} line, which we assign as belonging to SO$_4^{2-}$ in the infrared spectrum.
11. F. A. Miller and C. H. Wilkins, *Anal. Chem.* **24**, 1253 (1952).
12. Although silica gels also have absorption bands in the 1100 cm^{-1} region, the consistent lack of significant amounts of silicon in the analyses suggests that silicon compounds are not responsible for this feature in the infrared spectrum.
13. S. W. Rabideau, private communication.
14. Our microprobe results are in substantial agreement with those of Lippincott *et al.* (*2*) who detected the presence of silicon in trace quantities and of sodium. However, our x-ray fluorescence and mass spectral studies are in sharp contrast to the laser probe and copper spark spectrochemical analyses of Lippincott *et al.* in which no impurities could be detected.
15. We thank H. C. Marciniak for doing the electron microprobe experiment, K. H. Storks for the x-ray milliprobe analysis, D. L. Malm for the mass spectrum analysis, and Dr. C. K. Kim for the neutron activation analysis. We thank Dr. S. W. Rabideau of Los Alamos Scientific Laboratory for communicating his results to us before publication. The portion of this investigation carried out at the University of Southern California was supported by NSF.

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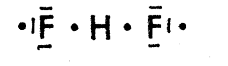
Structure of Polywater

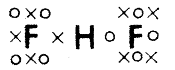
Lippincott *et al.* (*1*) have produced spectroscopic evidence (*2*) that the hydrogen bonds in "polywater" (*3*) resemble the strong hydrogen bonds in the FHF$^-$ ion rather than the more normal ones that exist in ordinary water. The shortness of these stronger bonds will account for the increased density of polywater.

Pimentel (*4*) has suggested that the electronic structure of FHF$^-$ should be described in terms of three center orbitals, two electrons occupying the bonding orbital $(2p_{F'} + k1s_H + 2p_{F''})$ and two the nonbonding orbital $(2p_{F'} - 2p_{F''})$. If this orbital function, which includes no charge correlation between the electrons, is modified to include more electron correlation, an electronic structure which can be depicted by the chemical formula (formula 1)



$$\bullet|\overline{\underline{F}} \bullet H \bullet \overline{\underline{F}}|\bullet \qquad (1)$$

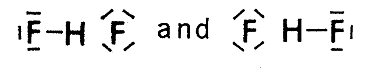
results. The Pauli principle requires that the spins of the electrons in the central region be opposed (or, more precisely, that the probability of their being opposed is greater than one-half). Consequently, one can go further and propose formula 2.



$$\overset{\circ\times\circ}{\underset{\circ\times\circ}{\times F}} \times H \circ \overset{\times\circ\times}{\underset{\times\circ\times}{F\circ}} \qquad (2)$$

According to the double-quartet hypothesis (*5*), which lays particular stress on electron correlation, each atom will possess two spin-sets of electrons, each set of four being accommodated in a tetrahedrally disposed group of four orbitals, one group being staggered relative to the other.

A more accurate description of the electronic structure of FHF$^-$ would be achieved by adding to the wave function corresponding to formula 2, wave functions describing



$$|\overline{\underline{F}}-H\ \widehat{\underset{\vee}{F}}\ \text{and}\ \widehat{\underset{\vee}{F}}\ H-\overline{\underline{F}}| \qquad (3)$$

though their importance would be expected to be lower. The molecular orbital function of Pimentel is obtained if the contributions of formulas 2 and 3 are equal (*6*).

With the double-quartet model it is possible to envisage a three-dimensional network structure for polywater within which all the oxygen atoms are linked to one another by bonds of the FHF type as described by formula 2. This could be achieved, for example, by pseudo-zinc-blende or pseudo-wurtzite structures. In both of these, each zinc is surrounded tetrahedrally by four sulfur atoms and each sulfur tetrahedrally by four zinc atoms. That is, there are two sets of sites, each site in one set being surrounded tetrahedrally by four sites of the other set. The proposal for the structure of polywater would be that every site is occupied by an oxygen atom and that a proton lies halfway between every two adjacent sites. The oxygen atoms on one set of sites would use the electrons of one spin to bind the protons round them (the electrons of the other spin-set being staggered on each atom with respect to the bonding set), while the oxygen atoms on the other set of sites would use the electrons of the other spin to bind the protons. A diagram which portrays this is shown in Fig. 1. The effectiveness of this diagram is limited because the two-dimensional diagram is inadequate to depict fully the three-dimensional structure.

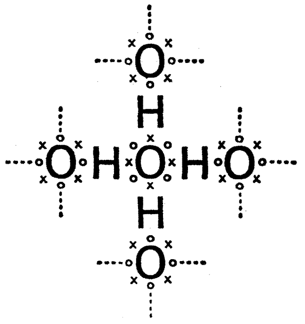


Fig. 1. Diagram indicating proposed electronic structure of polywater.

Each OHO bond is described by

$$\times O \circ H \times O \circ$$

and each oxygen atom participates in four such groupings tetrahedrally disposed. This electronic structure could be described in a corresponding Pimentel-type form incorporating less electron correlation in the following way. Use four sp^3 hybrid orbitals (h) at each oxygen atom. Then for each OHO "bond" there would be an electron pair occupying $(h_{o'} + k1\,s_H + h_{o''})$ which is bonding and another pair occupying $(h_{o'} - h_{o''})$ which is nonbonding (or perhaps slightly antibonding). As with FHF$^-$, the major difference between