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.

D. L. Rousseau

Bell Telephone Laboratories, Murray Hill, New Jersey

S. P. S. Porto

Department of Physics and Electrical Engineering, University of Southern California, Los Angeles

References and Notes

1. A summary of these investigations has been given by B. V. Deryagin and N. V. Churaev, *Priroda (Moskva) No. 4* (1968), p. 16; translation in *Joint Pub. Res. Serv. No. 45* (1968), p. 989. N. N. Fedyakin, *Colloid. J. USSR Engl. Transl.* **24**, 425 (1962). An extensive list of references has also been given by L. J. Bellamy, A. R. Osborn, E. R. Lippincott, A. R. Bandy, *Chem. Ind. London* **1969**, 686 (1969).
2. E. R. Lippincott, R. R. Stromberg, W. H. Grant, G. L. Cessac, *Science* **164**, 1482 (1969).
3. L. J. Bellamy, A. R. Osborn, E. R. Lippincott, A. R. Bandy, *Chem. Ind. London* **1969**, 686 (1969).
4. B. V. Deryagin, N. V. Churaev, N. N. Fedyakin, M. V. Tolaev, I. G. Ershova, *Bull. USSR Chem. Sci.* **1967**, 2095 (1967).
5. E. Willis, G. K. Rennie, C. Smart, B. A. Pethica, *Nature* **222**, 159 (1969).
6. Similar observations have been made on samples grown at Tyco Laboratories by S. B. Brummer.
7. M. C. Tobin and T. Baak, *J. Opt. Soc. Amer.* **58**, 1459 (1968); M. Haas, *J. Phys. Solids*, in press.
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.

29 December 1969; revised 17 February 1970 ■

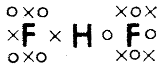
Structure of Polywater

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 $(2p_{\mathrm{F}'} + k1s_{\mathrm{H}} + 2p_{\mathrm{F}''})$ and two the nonbonding orbital $(2p_{\mathrm{F}'} - 2p_{\mathrm{F}''})$. 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)

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

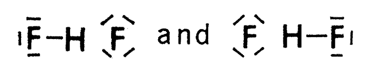
results. The Pauli principle requires that the spins of the electrons in the central region be opposed (or, more precisely, that the probability of their being opposed is greater than one-half). Consequently, one can go further and propose formula 2.



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

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



$$|\overline{\underline{\mathrm{F}}}-\mathrm{H}\;\;\langle\mathrm{F}\rangle\;\;\text{and}\;\;\langle\mathrm{F}\rangle\;\;\mathrm{H}-\overline{\underline{\mathrm{F}}}| \qquad (3)$$

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.

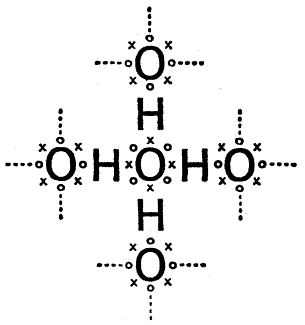


Fig. 1. Diagram indicating proposed electronic structure of polywater.

Each OHO bond is described by

$$\times\mathrm{O}\circ\mathrm{H}\times\mathrm{O}\circ$$

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 $(h_{\mathrm{o}'} + k1\,s_{\mathrm{H}} + h_{\mathrm{o}''})$ which is bonding and another pair occupying $(h_{\mathrm{o}'} - h_{\mathrm{o}''})$ which is nonbonding (or perhaps slightly antibonding). As with FHF$^-$, the major difference between

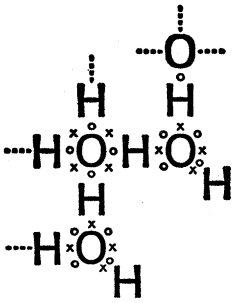


Fig. 2. Diagram indicating a way of terminating the continuous lattice.

the two formulations lies in the amount of electron correlation included.

The structure proposed, which is potentially unlimited in its spatial extent, could be terminated in the manner shown in Fig. 2. As for all other oxygen atoms (and hydrogen atoms) in the lattice, the formal charge on the terminating oxygen atoms is zero since they are forming one two-electron bond and two one-electron bonds to protons. It should be noted that the terminating oxygen atom is joined to two hydrogens of the main structure in such a way that the tetrahedral angle of HOH is maintained. That is, at the terminating oxygen atom the

$$H \times O \times H$$

angle remains tetrahedral as required by the overall structure, one normal electron-pair bond is formed, and the orbitals for the other six electrons remain noncoincident without any distortion from the tetrahedral conformation for either of the spin-sets.

This model would therefore suggest that polywater consists of micelles having the internal structure shown in Fig. 1. These would presumably be contained in a small amount of ordinary water to which they would be hydrogen bonded in a conventional way. So the material would be colloidal in character, which is a description used by Willis *et al.* (*7*). This model accounts for the spectroscopic properties, the density, and the viscosity. Perhaps the surface initiation of the formation of polywater results from the presence of some oxygen atoms in the surface of the silica or silicate glass which have structures in which the two spin-sets of electrons are staggered with respect to one another. Such atoms could provide centers for initiating the structure indicated in Fig. 1. Moreover, once formed the micelles would be expected to be stable because the individual bonds are strong and this model requires that there would have to be a considerable cooperative change to disintegrate a micelle. On the other hand, the micelles would also not be easy to form particularly if ions or molecules were present which held the water molecules by conventional hydrogen bonds. This feature results from the fact that the structure proposed which is depicted by formula 1 is essentially different from those depicted by formula 3.

J. W. Linnett

Department of Physical Chemistry,
University of Cambridge,
Cambridge, England

References and Notes

1. E. R. Lippincott, R. R. Stromberg, W. H. Grant, G. L. Cessac, *Science* **164**, 1482 (1969).
2. L. J. Bellamy, A. R. Osborne, E. R. Lippincott, A. R. Bandy, *Chem. Ind. (London)* **1969**, 686 (1969).
3. B. V. Derjaguin, N. V. Churaev, N. N. Fedyakin, M. V. Talaev, I. G. Ershova, *Izv. Akad. Nauk SSSR* **10**, 2173 (1967); *Bull. USSR Chem. Sci. (Eng.)* 2095 (1967); V. I. Anisimova, B. V. Derjaguin, I. G. Ershova, D. S. Lychnikov, Y. I. Rabinovich, U. K. L. Simanova, N. V. Churaev, *Russ. J. Phys. Chem.* **41**, 1282 (1967); N. N. Fedyakin, B. V. Derjaguin, A. V. Novikova, M. V. Talaev, *Dokl. Akad. Nauk SSSR* **165**, 862 (1965).
4. G. C. Pimentel, *J. Chem. Phys.* **19**, 446 (1951).
5. J. W. Linnett, *J. Amer. Chem. Soc.* **83**, 2643 (1961); *Electronic Structure of Molecules* (Methuen, London, 1964).
6. R. Harcourt, A. Harcourt, J. W. Linnett, in preparation.
7. E. Willis, C. K. Rennie, C. Smart, B. A. Pethica, *Nature* **222**, 159 (1969).

29 January 1970

"Polywater": A Hydrosol?

Abstract. *Measurements of the dielectric constant and the effective parallel conductance of a specimen of anomalous water suggest that anomalous water is a hydrosol consisting of finely divided particulate matter suspended in ordinary water. Scanning electron micrography confirms the presence of particulate matter. These new experimental data provide an alternative explanation for the properties of anomalous water.*

Condensate of nominally pure H_2O, allowed to form below atmospheric pressure in freshly drawn quartz or Pyrex capillaries, has been shown to possess physical properties very different from those of ordinary water (*1*). Lippincott *et al.* (*2*) have recently proposed that this condensate (known as anomalous water) contains a polymer consisting of H_2O monomeric units—polymeric water or "polywater." The possible existence of a previously unknown, stable, polymeric form of water has stimulated much interest in the properties of anomalous water.

Anomalous water has thus far been produced only in extremely small quantities. The lack of a sample large enough for detailed chemical analysis has hindered investigators from performing those experiments which would allow them to unequivocally determine the nature of anomalous water. Thus the "polywater" proposal must be considered as one possibility among many. To aid in assessing these possibilities, we report here new measurements of some of the physical properties of anomalous water. Our study reveals the presence of highly dispersed particulate matter in anomalous water. Hydrosols (*3*) (aqueous systems containing highly dispersed particulate matter) exhibit many of the physical properties of anomalous water. Hence, our experiments suggest that a suitable alternative explanation for the unusual properties of anomalous water may be found in the phenomenon of sol formation.

Anomalous water was prepared by the condensation of water vapor in freshly drawn Pyrex capillaries $\lesssim 50$ μm in diameter (*1, 2*). Pyrex tubing was rinsed in flowing distilled water for 3 hours before being drawn into capillaries. The resulting capillaries were then allowed to stand for several days suspended over distilled water in a partially evacuated system. Condensate that formed within these capillaries was removed by centrifugation. Two microliters of fluid were thus obtained. This fluid possessed the mechanical properties previously reported for anomalous water (*1*). Furthermore, analysis by transmission infrared spectroscopy in the region from 1000 to 4000 cm^{-1} indicated absorption bands characteristic of both normal H_2O and "polywater." In particular, the characteristic "polywater" absorption near 1400 cm^{-1} [as reported by Lippincott *et al.* (*2*)] was observed. Therefore, we proceed on the basis that the sample under discussion is indeed anomalous water and that it contains, in dilute form, that material which has been proposed to be polymeric water. All experiments described below were performed on the same specimen.

Dielectric measurements are a powerful tool for the determination of the symmetry of molecular species; the dielectric constant of a substance is, in general, a measure of the dipole moment of its constituent molecules. Hence, application of techniques for