

Proton Magnetic Resonance Spectrum of Polywater

Abstract. *With the aid of a time-average computer, the proton magnetic resonance spectrum of anomalous water (polywater) is obtained. The spectrum consists of a single broad resonance shifted approximately 300 hertz downfield from the resonance of ordinary water.*

Anomalous water was first observed by Deryagin and his associates (1) who demonstrated that its physical properties differ from those of regular water. Lippincott *et al.* conclude (2) that the observed Raman and infrared spectroscopic data from water that condenses inside fused quartz capillaries is compatible with a highly ordered polymeric structure composed of H_2O monomer units. Lippincott *et al.* assume this to be the basic structural unit because of an extremely strong O-H-O three-center bond. One structure postulated by Lippincott involves the units being arranged in a plane to form regular interconnected hexagonal rings. These layers of rings tend to stack one on another to build a regular three-dimensional framework. In forming the hexagonal rings, oxygen atoms interact with the s orbital of the hydrogen atoms through sp^2 bonding. The network of rings has a negative charge (the number of rings minus one) which is presumably counterbalanced by hydrated protons. Such a structure implies extensive delocalization of the electrons throughout the network. Previous attempts to observe the proton magnetic resonance (pmr) spectrum of anomalous water [or polywater (2)] failed (3). It is postulated that the regular structure of the quartz surface and the small dimensions of the capillaries (inside diameter, commonly 10 to 50 μm) combine to produce the high degree of association of the water mole-

cules. We decided to obtain a high-resolution pmr spectrum for polywater, in the hope of obtaining further information as to its structure.

Samples of polywater, prepared in the manner described by Lippincott (2) in capillaries of from 50 to 200 μm in diameter, are characterized by their Raman spectrum (2). High-resolution pmr spectra were obtained with a Varian A60A spectrometer equipped with a Varian C1024 time-average computer at ambient temperatures. Reference samples of water both in and out of quartz capillaries were observed and yielded only the normal resonance of water.

The polywater sample remained in the capillary tube during the pmr experiment; water was the external standard. The broad peak which occurs approximately 300 hz downfield from normal water has a line width at half height of approximately 120 hz (Fig. 1).

The spectrum observed may be due to a deshielding by the "ring current" from the delocalized π electrons of the oxygen atoms of the sample, combined with a high degree of hydrogen bonding between molecules, although other explanations are possible. This is in agreement with the hexagonal ring structure (2).

We postulate that the formation of polywater in quartz capillaries involves three steps. (i) Hydrogen bonds form between water molecules and the oxygen of the silicate framework. (ii) Further condensation of water brings the molecules close to each other and hydrogen bonds form between water molecules, combined with the release of a proton from one of the water molecules. If stability of electron delocalization is associated with a six-membered ring structure, then this type of structure will form, although the hexagonal structure of the quartz surface may also be

a factor. (iii) A number of other layers of polywater form, and these stack on top of the first, possibly with further O-H-O hydrogen bonds forming between layers. These bonds might have a near-normal O-O distance of approximately 2.7 Å.

An attractive feature of this mechanism is that, should there be no hydrogen bond formation between the individual layers, the release of the proton provides the cation necessary to counterbalance the negative charge in the ring.

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References and Notes

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4. I thank R. Langridge, L. C. Allen, W. Kauzman, I. D. Kuntz, W. R. Massey, Jr., and E. Samulski for suggestions and advice. I also thank T. Streckas for assistance in recording Raman spectra. Supported by NIH grant GM-165039 and NSF grant GB-7857 to R. Langridge.

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Stalactite Growth beneath Sea Ice

Abstract. *Fresh ice stalactites were observed beneath sea ice in Antarctica. They are hollow, tapering, inverted cones having a base diameter between 10 and 20 centimeters and a tip diameter of 4 to 10 centimeters extending downward about 100 centimeters. The stalactites form when dense, chilled brine drains downward from the ice sheet into seawater of normal salinity and near-freezing temperature.*

A study of sea ice in McMurdo Sound, Antarctica, included the determination of seasonal changes in thickness. One problem in measuring the thickness of sea ice is that a large difference often occurs between measurements taken in the same small area at the same time. Observations made by scuba diving beneath the sea ice indicated that the differences were caused by the irregular skeleton layer at the bottom of the 1.5- to 2-m thick growing ice sheet. Other unusual features consisted of numerous stalactite-like growths extending downward as much as 1 m from the skeleton layer.

In November 1968 it was possible

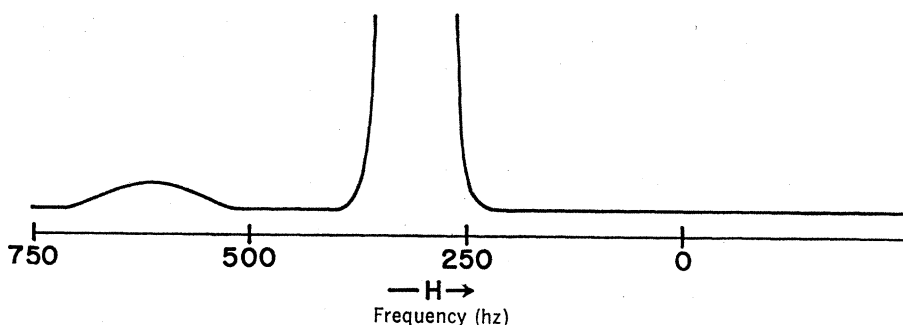


Fig. 1. The proton magnetic resonance spectrum of polywater. The small broad resonance is approximately 300 hz downfield from the resonance due to normal water. The spectrum was obtained with the aid of a time-average computer.