probably with a geometry close to that of polyhedra, such as icosahedra. Finally, in the presence of a solid substratum, water may form bonds. This is the case, for instance, of glasses where silanol groups, Si-O-H, are present at the interface water silica. It is worth noting that in presence of biological macromolecules, such as peptides, enzymes, proteins, DNA, all these behaviors can be found depending on the nature more or less hydrophilic or hydrophobic of each site or residue. Bonds, in particular, play certainly a major role in the structure of these macromolecules.

STRUCTURE OF CONFINED WATER

Model Systems-Water Interactions

The choice of porous media as model systems depends on two conditions: a well-characterized pore size distribution and surface details. Among the hydrophilic model systems where the structure of confined water has been studied by neutron diffraction, let us mention clay minerals (11–12), and various types of porous silica (14–22). In the latter case, the authors have interpreted their results in terms of a thin layer of surface water with more extensive hydrogen bonding, lower density and mobility, and lower nucleation temperature as compared with bulk water. Recently, the structure of water confined in the cylindrical pores of MCM-41 zeolites with two different pore sizes (21 and 28 Å) has been studied by X-ray diffraction (21) over a temperature range of 223 to 298 K. For the capillary-condensed samples, there is a tendency to form a more tetrahedral-like hydrogen-bonded water structure at subzero temperatures in both the pore sizes.

The more extensive results concern the structure of water confined in a Vycor glass (47), which is a porous silica glass, characterized by a quite sharp distribution of cylindrical interconnected pores and hydrophilic surfaces. Results have been obtained as functions of level of hydration from full hydration (0.25 g water/g dry Vycor) down to 25% hydration and temperature (48). On the basis of the information that the dry density of Vycor is 1.45 g/cm^3, the porosity 28%, and the internal cylindrical pores of cross-sectional diameter 50 Å, the 50% hydrated sample has three layers of water molecules on its internal surface. A 25% hydrated sample corresponds roughly to a monolayer coverage of water molecules.

Results for two levels of hydration of Vycor demonstrate that the fully hydrated case is almost identical to the bulk water and the partially hydrated case is of little difference (Fig. 2). However, the three site-site radial correlation functions are indeed required for a sensible study of the orientational correlations between neighboring molecules and the results of three neutron diffraction experiments on three different isotopic mixtures of light and heavy water have been reported (49).

It is interesting, however, to comment on the level of supercooling possible for heavy water in Vycor. According to Bellissent-Funel et al. (48), for partially hydrated samples, the deepest supercooling is $-27^{\circ}C$, while for the fully hydrated sample it is $-18^{\circ}C$. As temperature goes below the limit of supercooling, part of the confined water nucleates into cubic ice. The proportion of cubic ice increases with decreasing temperature. This is in sharp contrast to bulk water, which always nucleates into hexagonal ice.