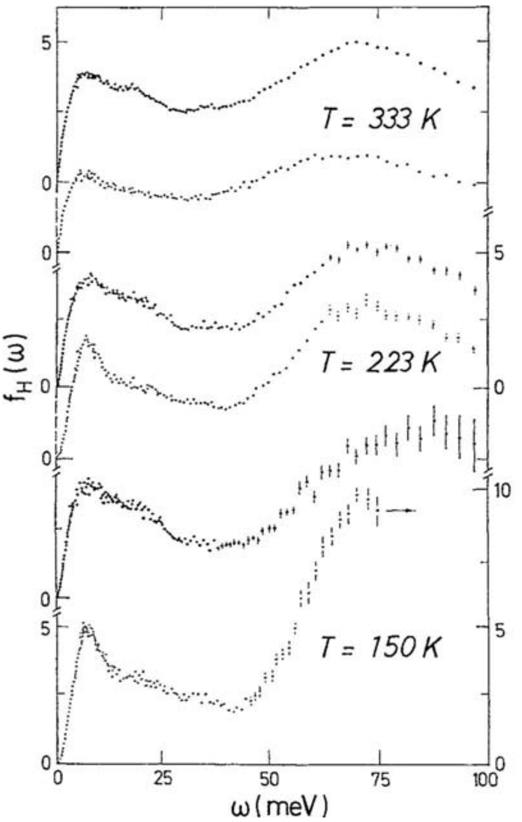

FIGURE 10 Proton vibrational density of states f_H for water at surface of H_2O-hydrated d-CPC protein $\theta = 27.5°$, at three temperatures, 333, 223, 150 K and two levels of hydration $h = 0.50$ (*crosses*) and 0.25 (*solid circles*). *Source*: From Ref. 59.

Moreover, in the case of the low level of hydration ($h = 0.25$) the evolution of the density of states of the hydrated protein as a function of the temperature is less pronounced than in the case of $h = 0.5$. This is in agreement with the structural study (53) at the lower hydration ($h = 0.175$), which only detected small changes when the temperature is lowered from room temperature down to 77 K, and with further structural studies of low-hydrated Vycor samples. Low temperatures do not affect significantly the overall structure of the protein or the bound water molecule and no crystallization of water has been observed. This could reflect the fact that at room temperature the interfacial water behaves like a dense, supercooled liquid.

The study of an artificial peptide formed by five molecules of alanine and capped at both extremities, gave information above the very different behavior of water at the vicinity either of the only hydrophilic site of the protein or on its global hydrophobic surface (85). In the first case, the hydrogen bond formed between water and the hydrophilic site is relatively stable and the only detectable motion is the rotation of the water molecule. Instead, the diffusion is important for the water molecules at the vicinity of the hydrophobic surface.

More recent studies focused on the comparison of amino acids that differ only by the existence of a hydrophobic chain, such as glycine (Gly) and leucine (Leu). A detailed comparison of a large number of experiments performed with