surface, perform very local rotational jumps characterized by D_t and τ_1 like in bulk water, but with a longer residence time τ_0 on a given site before diffusing to an adjacent site along the surface with a diffusion coefficient equal to D_{local}. This diffusion is limited to some volume estimated as spherical. For the 25% hydrated sample, the diffusion coefficient measured by NMR appears to be smaller than D_t, which is smaller than D_{local} (81). This is due to the fact that NMR technique measures the long-time and long-range diffusion coefficient.

The effect of the temperature has been followed down to −35°C. The radius of the spherical volume of confinement varies between 5 and 2 Å; it decreases when the temperature is lowered meaning that water molecules are more localized at low temperatures. The observed trend seems reasonable.

The values obtained for D_{local} are low which demonstrates the influence of the hydrophilic groups when one reaches a monolayer coverage of water molecules. Moreover, these values are close to the values of the diffusion coefficient of water molecules at the immediate hydrophilic interface, as determined in a molecular dynamics simulation by Lee and Rossky (35).

Figure 6 shows the vibrational density of states for confined water (52% hydrated Vycor) as compared with that of bulk water at room temperature (3). The density of states of confined water exhibits striking features. The peak associated with the O-O-O intermolecular rotational motions, centered on 6 meV, is much attenuated indicating the reduction of this degree of freedom upon confinement. There is an up-shift of the librational peak at 70 meV, meaning some hindrance of the librational motions because of the presence of the surface. The hindrance of the motions increases when the temperature is lowered.

In hydrophobic environments, such as activated carbon powder, the vibrational density of states for confined water has been determined by inelastic neutron scattering as a function of temperature and compared with bulk water. For the lowest level of hydration, the translational peak around 6 meV and the

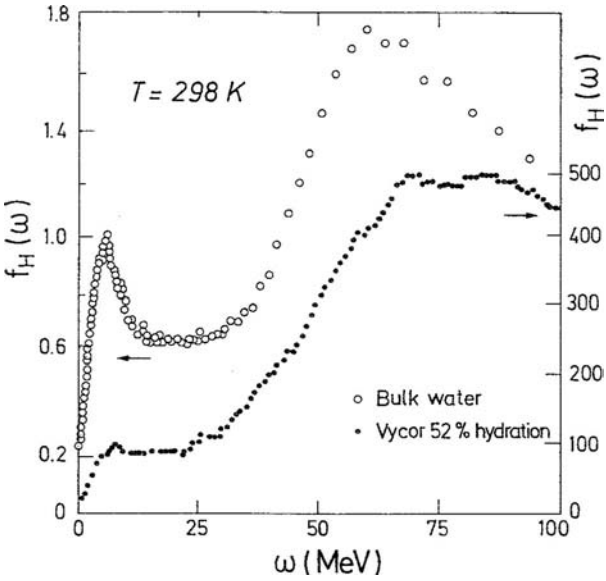

FIGURE 6 Proton vibrational density of states f_H for water contained in 52% hydrated Vycor at 298 K (*solid circles*). For comparison, the corresponding quantity for bulk water (*empty circles*) is also given. *Source*: From Ref. 59.