

AQUEOUS SOLUTIONS AT HIGH PRESSURES AND TEMPERATURES

ference of other vibrations in this frequency range. Thus the HDO-absorption has recently been measured up to 500°C and partly up to 4 kb¹². A special absorption cell of the reflection type, similar in some respects to a cell described by Welsh *et al.*¹³, had been designed for the purpose. It has a single window of colourless synthetic sapphire with a platinum-iridium mirror close to its inner surface. Figure 4 gives a selected number of absorption bands.

Three of these bands at 30°, 200° and 400°C have been obtained at or almost at the normal liquid density of 1 g/cm³. The high absorption intensity at room temperature, which is considered to be caused by the hydrogen bonded structure of the liquid, decreases with temperature but remains relatively high. The frequency of the maximum shifts from 2507 cm⁻¹ to slightly over 2600 cm⁻¹ at 400°C and 0.9 g/cm³. 2720 cm⁻¹ is the value for the Q-branch of this vibration in dilute HDO-gas. The bands, however, become increasingly asymmetric, although a shoulder on the low frequency side is not visible. At a constant temperature of 400°C the rotational structure of the vibrational band appears only at densities below 0.1 g/cm³. This means that even at the supercritical temperature of 400°C and at densities between 0.1 and 1.0 g/cm³ very considerable intermolecular interaction and possibly association must exist, which may be partly caused by hydrogen bonding.

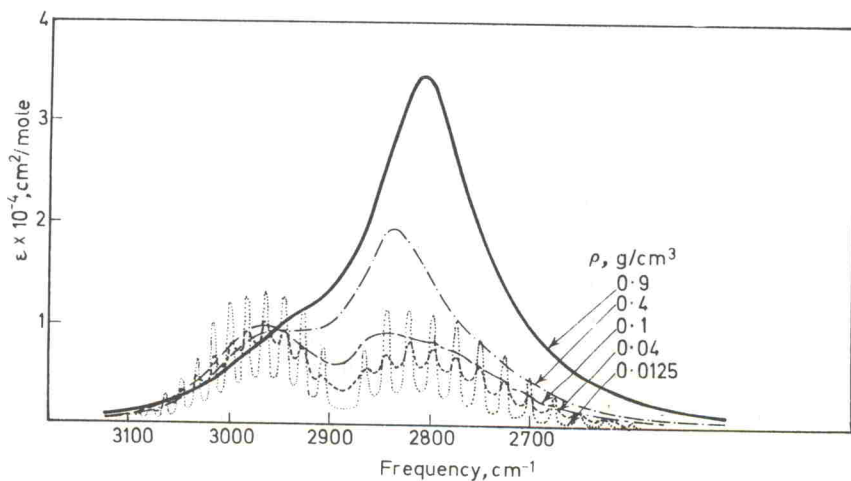


Figure 5. Infra-red absorption of HCl at 150°C for different densities ρ .

For comparison, Figure 5 gives the infra-red absorption of compressed supercritical hydrogen chloride at several densities¹⁴. Although lower in intensity the absorption of the highest density of 0.9 g/cm³ is not very different in appearance from that of HDO. In both cases decreasing density causes a shift of the maximum frequency towards higher values. This behaviour is demonstrated in Figure 6, where the frequency shift isotherms for both compounds have been plotted as a function of the reduced density. Below 400°C the frequency shifts for HDO have a pronounced temperature dependence, while above 400°C the behaviour of the frequency shifts for

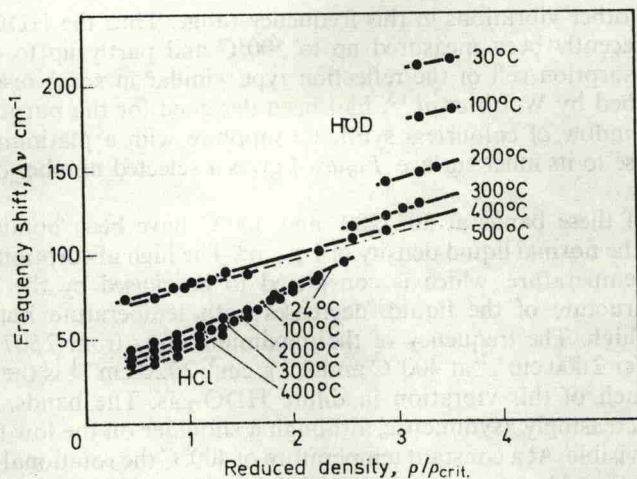


Figure 6. Frequency shift $\Delta\nu = \nu_{\text{gas}} - \nu_{\text{max}}$ of HCl- and OD-vibrations.

HDO and HCl appear to become more alike, suggesting that dipole interactions other than those leading to hydrogen bonds become dominating in dense water above about 400°C.

It is possible that the Raman spectrum of HDO diluted in normal water reveals more information about the hydrogen-bonded structure than does infra-red absorption. In Figure 7 Raman scattering curves are given¹⁵ for temperatures to 400°C and densities between 0.1 and 1.0 g/cm³. The curve for 25°C clearly shows a shoulder at about 2650 cm⁻¹ which has already been observed by other authors¹⁶. If the temperature is increased at almost constant high density to 400°C, a new band seems to appear at the position of this shoulder. Considering the evidence and discussion of Walrafen¹⁶ and other authors⁸, one might take this 2650 cm⁻¹ band as an indication for water molecules which are not hydrogen bonded, but which nevertheless interact strongly with each other. Decrease of density to 0.1 g/cm³ at 400°C

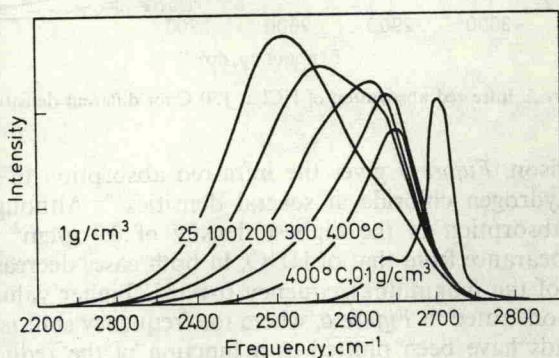


Figure 7. Raman intensity of the OD-vibration of HDO. (6.2 mole/l. D₂O in H₂O; slit width: 18 cm⁻¹; argon laser, 4880 Å).