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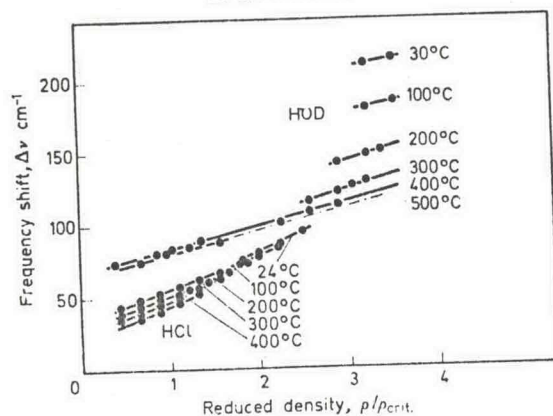


Figure 6. Frequency shift $\Delta\nu = \nu_{\text{gas}} - \nu_{\text{max}}$ of HCl- and OD-vibrations.

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

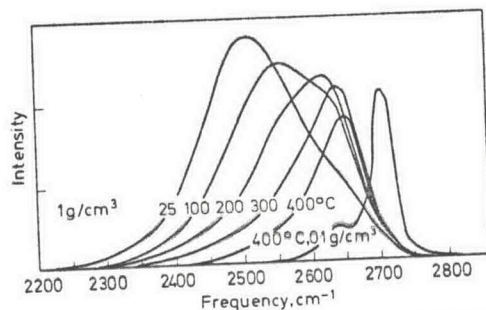


Figure 7. Raman intensity of the OD-vibration of HDO. (6.2 mole/l. D₂O in H₂O; slit width: 18 cm⁻¹; argon laser, 4880 Å).

AQUEOUS SOLUTIONS AT HIGH PRESSURES AND TEMPERATURES

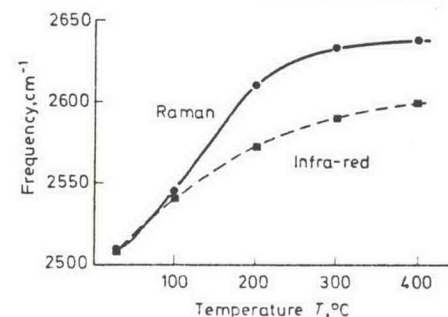


Figure 8. Frequency shift of OD-vibration of HDO in H₂O with temperature at constant density of 1.0 g/cm³.

this band considerably changes. A detailed analysis of numerous spectra at densities from 1.0 to 0.015 g/cm³ has been made. It shows that the band which appears as a shoulder at 2650 cm⁻¹ gradually transforms into a sharp peak at 2710 cm⁻¹ at 400°C and very low density. It is possible that this band indicates non-hydrogen-bonded OD-groups.

The frequency shifts of the maxima discussed above are shown for a constant density of 1 g/cm³ as a function of temperature in Figure 8. Below 100°C the infra-red and Raman curves almost coincide. Above that temperature the Raman shifts are higher and the shape of the curve is different. This may be due to the fact that the Raman curve in Figure 8 actually combines the frequency shifts of the '2507-band' at low temperature with those of the '2650-band' at high temperature. In the infra-red, the absorption of hydrogen bonded OD-groups around 2507 cm⁻¹ and more may be so much stronger than a possible absorption around 2650 cm⁻¹ that this latter is not clearly observed.

III. ABSORPTION SPECTRA OF DISSOLVED COMPLEXES

Spectroscopic evidence is also available for the association of water molecules with dissolved ions and complexes at high temperature and high pressure. Several heavy metals can form complex compounds which are stable enough to exist in aqueous fluids even at supercritical temperatures. In some cases the stability of such complexes can be increased by the addition of high concentrations of alkali halides to the fluid. Such 'hydrothermal' solutions are of importance as transport media for heavy metals within certain areas of the earth's crust¹⁷.

Recently the range of existence of complexes of bivalent cobalt and nickel has been investigated spectroscopically in the visible and near-ultra-violet regions^{18, 19, 20}. For this purpose absorption double cells were designed and built, which could be used with aqueous solutions to 500°C and 6 kbar. The windows were cylindrical rods of synthetic colourless sapphire of 60 mm length. The high temperature inside the cells decreases along the length of