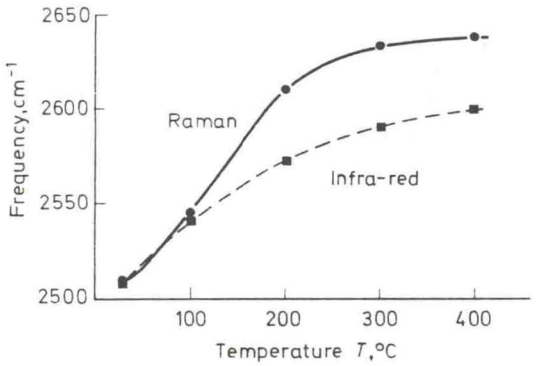

Figure 8. Frequency shift of OD-vibration of HDO in H_2O with temperature at constant density of 1·0 g/cm^3.

this band considerably changes. A detailed analysis of numerous spectra at densities from 1·0 to 0·015 g/cm^3 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/cm^3 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 crust[17].

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

these windows. The cells were of a non-corrosive high strength alloy and in some cases lined with gold–palladium or platinum.

Dilute solutions of bivalent cobalt chloride were investigated to 500°C. The pink solution at 25°C has a maximum of absorption at 515 nm. At 300°C and the relatively low pressure of 350 bar a blue solution with a much

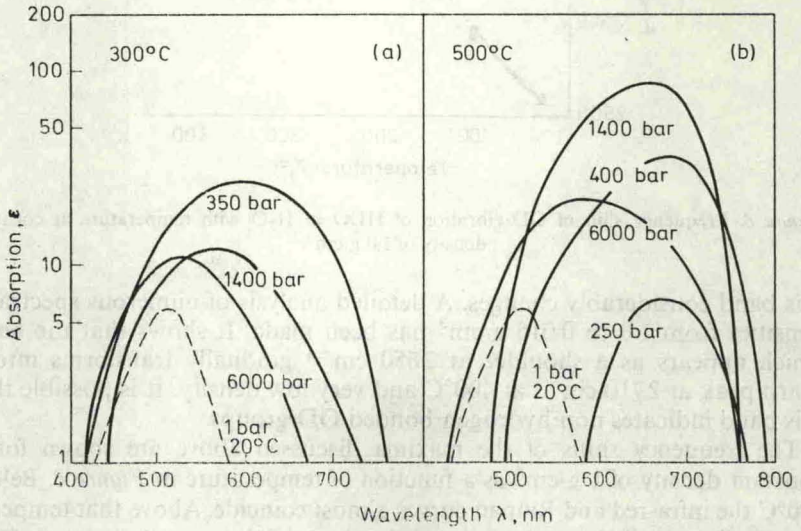

Figure 9. Absorption spectrum of $CoCl_2$ in water (Molality: 0·01) at (a) 300°C and (b) 500°C between 250 and 6000 bar.

stronger absorption having a maximum around 600 nm is formed. Increasing the pressure to 6 kb reduces the absorption and shifts the maximum to about 520 nm [*Figure 9*(a)]. This shift in absorption is explained by assuming an equilibrium between bivalent positively charged hexaquocobalt complexes, absorbing at shorter wavelengths and neutral dichlorodiaquocobalt complexes. The first have an octahedral and the second a tetrahedral structure. Increase of temperature favours the lower coordinated complex with four ligands, increase of pressure favours the higher coordinated complex with six ligands. This is even more obvious at 500°C [*Figure 9*(b)]. At 1400 bar the tetrahedral complexes with their strong absorption predominate. A pressure of 6 kb cannot shift the equilibrium towards the octahedral structure to the same extent as at 300°C. It is suggested that the reduction of absorption caused by a pressure decrease to 250 bar indicates a growing proportion of only slightly hydrated cobalt chloride molecules which are known to exist in the gas phase at high temperatures even without the presence of water.

Similar observations can be made with nickel(II) chloride if a high concentration of chloride ion is added. *Figure 10* gives absorption curves at 300°C in 4-molal sodium chloride solution as examples. The curve for 25°C corresponds to the light green normal solution with two absorbing electron transitions. Temperature increase to 300°C produces blue solutions with a