Figure 3. The Kirkwood correlation parameter from the experimental dielectric constant ε of water as a function of density and temperature (For a discussion of the inserted equation see ref. 8).

may indicate that a certain amount of structure still exists under these conditions. For a detailed discussion see ref. 8. It would be desirable to investigate dense supercritical hydrogen chloride in the same way for comparison.

More detailed information about the association of water by hydrogen bonds can be expected from the infra-red absorption spectrum. Particularly well suited for this purpose is the study of the absorption of the OD-vibration around 2500 cm^{-1} of HDO diluted in H_2O because of the absence of inter-
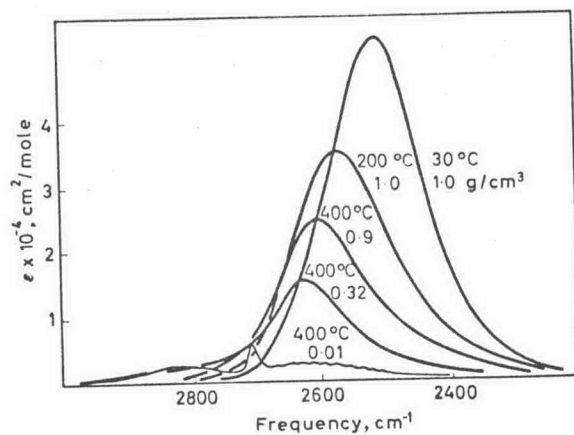

Figure 4. Infra-red OD absorption bands of 9·5 mole per cent HDO in H_2O for different temperatures and densities.

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 kb[12]. 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/cm^3. 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 cm^3. 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 $0·1 \text{ g/cm}^3$. This means that even at the supercritical temperature of $400°C$ and at densities between $0·1$ and $1·0 \text{ g/cm}^3$ very considerable intermolecular interaction and possibly association must exist, which may be partly caused by hydrogen bonding.
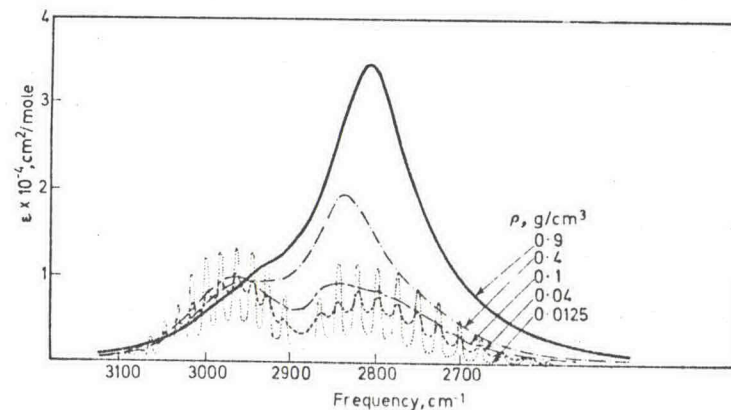

Figure 5. Infra-red absorption of HCl at 150°C for different densities ρ.

For comparison, Figure 5 gives the infra-red absorption of compressed supercritical hydrogen chloride at several densities[14]. Although lower in intensity the absorption of the highest density of $0·9 \text{ g/cm}^3$ 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