

$\epsilon$  of liquid water at moderate temperatures, Kirkwood<sup>(9)</sup> used the equation

$$(\epsilon - 1)(2\epsilon + 1)/9\epsilon = (4\pi\rho/3)\alpha + (4\pi\rho\mu^2/9kT)g_K \quad (1)$$

Here  $\rho$  is the number of particles per unit volume,  $\alpha$  the isotropic polarizability, and  $\mu$  the strength of the molecular dipoles within the dielectric environment. The quantity  $g_K$  is the *Kirkwood correlation factor*, introduced to take into account short-range ordering between dipoles. Extensive discussions of Eq. (1) and of methods of estimating the dipole strength within the dielectric and of calculating  $g_K$  in liquid water are given elsewhere.<sup>(9,10)</sup>

If neighboring dipoles are uncorrelated, one should find  $g_K = 1$ . At 0°C in liquid water  $g_K$  is about 2.9. The evaluation of  $g_K$  from the experimental  $\epsilon$  data of Fig. 2 shows that  $g_K$  decreases with increasing temperature and decreasing water density, as would be expected.<sup>(8,11)</sup> It appears, however, that even at the critical density and at supercritical temperatures of 400° and 500°C,  $g_K$  is still about 1.6, indicating a considerable degree of dipole correlation.

Very recent experimental results obtained for the dielectric constant of supercritical dense hydrogen chloride with a similar technique<sup>(12)</sup> showed that, at corresponding supercritical conditions,  $g_K$  is only about 1.05 for this

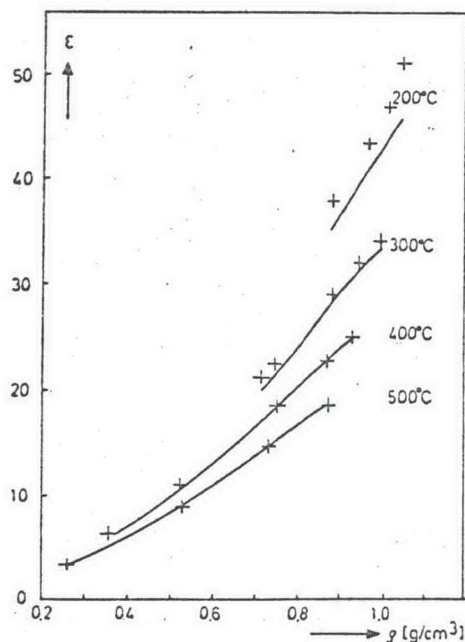


Fig. 3. Static dielectric constant of water  $\epsilon$  as a function of density and temperature. + Experimental values; — calculated.

fluid. One might conclude that the relatively high Kirkwood factors indicate a considerable degree of association by hydrogen bonding in dense supercritical water. Caution is necessary, however, since it has been demonstrated that the experimental  $\epsilon$  data of water between 200° and 500°C and 0.1 and 1.0 g-cm<sup>-3</sup> can be calculated rather well without using the concept of hydrogen bonding.<sup>(13,14)</sup> No adjustable parameters had to be used besides the dipole moment, polarizability, and diameter of water molecules. For such calculations, the general expressions for the dielectric constant of a fluid of hard cores with embedded point dipoles presented by Wertheim<sup>(15)</sup> have been used. This is shown in Fig. 3.

### 3. INFRARED SPECTRA

More detailed information about the association of water by hydrogen bonding can be obtained from infrared and Raman spectra. Particularly well suited for this purpose is the study of the absorption of the OD stretching vibration around 2500 cm<sup>-1</sup> of HDO diluted in H<sub>2</sub>O because of the absence of interference of other vibrations in this frequency range. Figure 4 gives several absorption curves for this vibration of HDO in ordinary water at a constant density of about 1 g-cm<sup>-3</sup> from 30° to 400°C and at 400°C down to 0.01 g-cm<sup>-3</sup>.<sup>(16)</sup> The frequency of the maximum shifts from 2507 to 2720 cm<sup>-1</sup>, the value for the Q Branch of the OD vibration in dilute HDO gas. This shift of the maximum frequency, as well as the decrease of intensity, has been considered as an indication of decreasing association by hydrogen bonds.

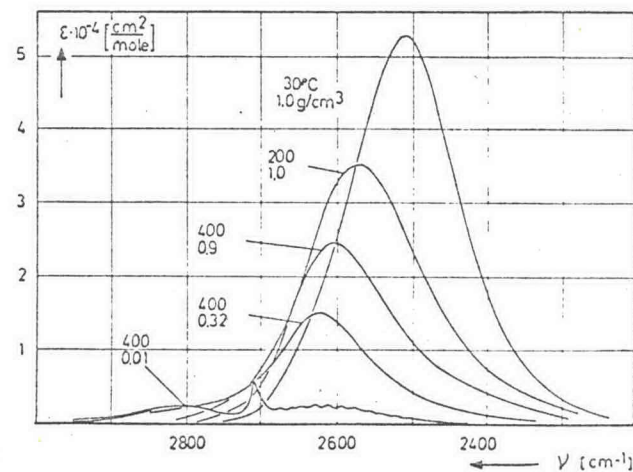


Fig. 4. Infrared OD vibration bands of 9.5 mole % HDO in H<sub>2</sub>O at different temperatures and densities.



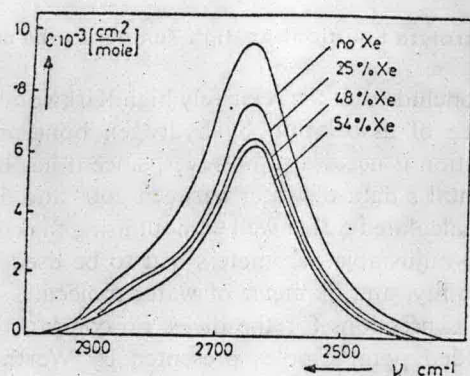


Fig. 5. Infrared OD vibration bands of HDO diluted in  $\text{H}_2\text{O}$  as a function of increasing amounts of added xenon. The temperature is  $400^\circ\text{C}$ , and the total water density for all curves is  $0.17 \text{ g}\cdot\text{cm}^{-3}$ .

It is interesting to investigate the question as to what extent this OD bond at dense supercritical conditions will be affected by the addition of very high concentrations on nonionic but highly polarizable second components to the fluid phase. Experiments of this kind have been made recently with Xe-HDO- $\text{H}_2\text{O}$  and  $\text{CO}_2$ -HDO- $\text{H}_2\text{O}$  mixtures.<sup>(17)</sup> Xe and  $\text{CO}_2$  have been chosen because both particles have similar size, although for  $\text{CO}_2$ , in contrast to Xe, a specific interaction with water molecules even at  $400^\circ\text{C}$  could be expected. Both Xe and  $\text{CO}_2$  are completely miscible with water at  $400^\circ\text{C}$ . Figures 5 and 6 give selected absorption curves at  $400^\circ\text{C}$ , which should be compared with the relevant curves of Fig. 4.

In Fig. 5 the absorption of HDO in  $\text{H}_2\text{O}$  at a total water density of  $0.17 \text{ g}\cdot\text{cm}^{-3}$  is shown. Three other curves demonstrate the influence of added increasing amounts of xenon while the water density remains constant. Two of these curves belong to mixtures with almost equal numbers of Xe and  $\text{H}_2\text{O}$

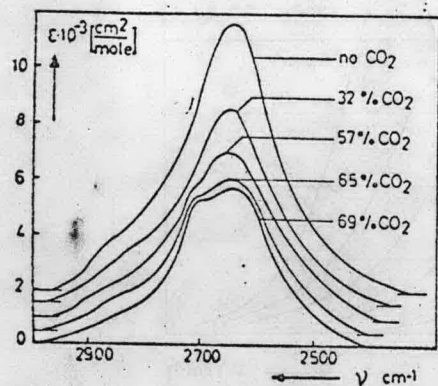


Fig. 6. Infrared OD absorption bands of HDO diluted in  $\text{H}_2\text{O}$  as a function of increasing amounts of added  $\text{CO}_2$ . The temperature is  $400^\circ\text{C}$ , and the total water density for all curves is  $0.17 \text{ g}\cdot\text{cm}^{-3}$ .

particles. Apart from a certain reduction of intensity, the effect of the xenon on the character of the band is insignificant. The bands of Fig. 6, obtained in analogous experiments with  $\text{CO}_2$ , are different. A shoulder at  $2700 \text{ cm}^{-1}$  appears at 57 mole %  $\text{CO}_2$  and develops into a separate band at 69 mole %. This band may be produced by deuterated carbonic acid molecules. PVT data of  $\text{CO}_2$ - $\text{H}_2\text{O}$  mixtures at high pressures and supercritical temperature do not exclude formation of such carbonic acid molecules.<sup>(18)</sup> This assignment is not yet conclusive, however. Investigation of the absorption in the region of C-O vibrations ( $1400 \text{ cm}^{-1}$ ) would be desirable, but the sapphire windows of the high-pressure infrared cell are opaque at such wavelengths. Perhaps Raman measurements would be possible.

It would be interesting to observe the hydrogen-oxygen stretching vibration in a binary system of water and a simple salt from pure water through the region of concentrated solutions to the pure fused salt. Most simple salts have melting points that are too high. Sodium hydroxide, however, melts at  $318^\circ\text{C}$ . Measurements of the absorption of the stretching vibration of normal water in liquid NaOH- $\text{H}_2\text{O}$  mixtures have been made at present at Karlsruhe to 2 kbar and  $350^\circ\text{C}$ , where the two compounds are completely miscible. It appears as if even at this temperature the whole range of compositions from pure  $\text{H}_2\text{O}$  to pure NaOH can be investigated with sapphire windows, although with some difficulty.

#### 4. RAMAN SPECTROSCOPY

The Raman spectra of pure water at high pressure,<sup>(19)</sup> and the conclusions to be drawn from these, have been thoroughly discussed already by G. E.

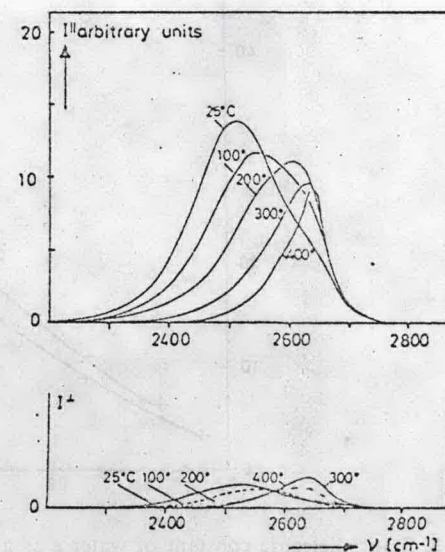


Fig. 7. Raman band of the OD vibration of HDO diluted in  $\text{H}_2\text{O}$  at a constant water density of  $1.0 \text{ g}\cdot\text{cm}^{-3}$  from  $25^\circ$  to  $400^\circ\text{C}$ . Upper part:  $I_{\parallel}$ , parallel polarization relative to laser beam. Lower part:  $I_{\perp}$ , vertical polarization.