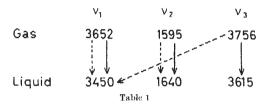
Assignment of the Infra-red and Raman **Bands of Liquid Water**

THE assignment of the fundamental vibrational frequencies of water vapour is well established¹: 3,651.7 $cm^{-1} v_1$ symmetric stretch, 1,595.0 $cm^{-1} v_2$ bending and $3,755\cdot8$ cm⁻¹ v_s antisymmetric stretch, of symmetry species a_1 , a_1 and b_1 respectively for molecular symmetry C_{2v} .

The assignment in the liquid phase is still not properly understood; the bands become very broad in both infrared (IR) and Raman (R) spectroscopy.

Table 1 shows how the frequencies change from gas phase to liquid phase, and the assignments for liquid water made by previous authors.



The dotted arrows in Table 1 represent the conclusions of Fox and Martin² and the solid arrows the assignments of Schultz and Hornig⁸ and Walrafen⁴.

If Fox and Martin (Table 1) are correct, the origin of the 3,615 cm⁻¹ Raman band must be determined; if Schultz and Hornig are correct, the absence of a band corresponding to v_3 near 3,615 cm⁻¹ in the infra-red spectrum must be explained. For a molecule without a centre of symmetry the rule of mutual exclusion is not applicable and there should be a maximum of correspondence between infra-red and Raman spectra.

The assignments of the Raman bands given by Walrafen, and Schultz and Hornig, are based on polarization data. Schultz and Hornig show that the depolarization ratio, p, for the bands at 1,640, 3,225 and 3,450 cm^{-1} respectively is considerably less than 6/7, and, therefore, the major portion of the intensity of these bands must arise from symmetric vibrations. For the 3,615 cm⁻¹ band, $\rho = 0.60$, which is still rather less than $\rho = 6/7$ expected for v_3 . Schultz and Hornig attribute the discrepancy between 0.60 and 6/7 to overlap by the strong 3,450 cm⁻¹ band. However, if ρ were 6/7 at 3,615 cm⁻¹, the band would not necessarily arise from an asymmetric vibration, since even symmetric vibrations may give $\rho = 6/7$. In our opinion, this evidence in favour of the assignment of the 3,615 cm⁻¹ band to v_3 is extremely weak.

In general, in infra-red and Raman spectroscopy, the absolute band intensity arising from a symmetric vibration is a minimum and a maximum, respectively. The converse is true for antisymmetric vibrations. In the gas phase, the infra-red spectrum shows v_1 very weak relative to v_{a} , and in the Raman spectrum the converse is true. It is, therefore, reasonable to suppose that in the liquid the 3,450 cm $^{\scriptscriptstyle -1}$ infra-red band is mainly ν_{0} and that the 3,450 cm⁻¹ Raman band is mainly v_1 . The 1,640 cm⁻¹ band (IR and R) is undoubtedly v_2 from considerations of both frequency and polarization data. Assignment of the 3,225 cm⁻¹ band to 2 ν_2 in Fermi resonance with ν_1 is well supported by its polarization, and variation of intensity with temperatures.

We prefer the overall assignment of Fox and Martin (Table 1) and give our full assignment in Table 2. We

		Table 2		
Phase	cm-1	Symmetry species	Assignment	Observed in IR or R
Gas	1,595 3,052 3,756	$a_1 \\ a_1 \\ b_1$	ν_{1} ν_{3}	IR R IR
Liquid	1,640 3,450 3,450 3,225 3,615	$a_1 \\ a_2 \\ b_1 \\ a_1 \\ a_1 \\ a_1 $		IR, R R IR R R

believe that the best assignment for the 3,615 cm⁻¹ band is a combination, 3,450 + $\nu_{\rm H},$ where $\nu_{\rm H}$ is the stretching vibration of a hydrogen bond. The value of v_H is about 180 cm⁻¹ (there is some doubt about the exact value, but it is between 160 and 200 cm^{-1}). This combination band would be expected to have a low intensity and, therefore, we postulate a second Fermi resonance between v_1 and this band; that is, v_{ff} must have the same symmetry as the 3,450 cm⁻¹ component of the combination. The result is an a-type band. This assignment explains the absence of the 3,615 cm⁻¹ band in the infra-red spectrum, because the main band at 3,450 cm⁻¹ is now v_3 , symmetry b_1 , so that Fermi resonance is not allowed. The same reasoning applies to the 3,225 cm⁻¹ $(2v_2)$ band, and consequently the $3,450 \text{ cm}^{-1}$ infra-red band appears with only a very slight asymmetry on the low-frequency side because of a residual intensity from $2v_2$.

The assignment we propose for liquid water is supported by several other pieces of experimental evidence. Various authors (see ref. 5) have investigated the infra-red spectrum of water in different solvents. The separation Δv between v_1 and v_3 is found to vary with the dielectric properties of the solvent. In carbon tetrachloride Δv is 95 cm^{-1} while in dioxan it is only about 70 cm⁻¹. In pyridine only one band is observed, and this has been interpreted as v_1 and v_3 having the same frequency. However, no polarization investigations have been made on these solutions and assignment of the two bands to more than one hydrogenbonded species of water molecule is not excluded. Walrafen⁴ has examined the variation of intensity of the 175 cm⁻¹ Raman band as a function of temperature and of electrolyte addition. Our results and those of Schultz and Hornig³ indicate that as electrolyte is added the 3,615 cm⁻¹ and 175 cm⁻¹ bands decrease in intensity. When the temperature is raised the 3,615 cm⁻¹ band intensity appears to increase slightly³ while that of the 175 cm^{-1} band decreases⁴. However, this anomaly in the temperature effect is not necessarily in disagreement with our assignment, because a change in the Fermi resonance conditions with temperature could more than compensate for the temperature coefficient of the 175 cm⁻¹ band.

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Mechanisms of Reactions in the Acenaphthene Series. Migration of t-Butyl, and Disproportionation

By a variety of Friedel-Crafts reactions, using t-butyl chloride and acenaphthene, we have synthesized and orientated 1-, 2- and 3-t-butylacenaphthene¹⁻³. A mechanism is now proposed to explain the t-butylation of acenaphthene and the novel migrations of the t-butyl group observed when t-butylacenaphthenes were treated with 0.15 mol. of aluminium chloride at 45°:

