

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} ν_1 symmetric stretch, 1,595.0 cm^{-1} ν_2 bending and 3,755.8 cm^{-1} ν_3 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 infra-red (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.

	ν_1	ν_2	ν_3
Gas	3652	1595	3756
Liquid	3450	1640	3615

Table 1

The dotted arrows in Table 1 represent the conclusions of Fox and Martin² and the solid arrows the assignments of Schultz and Hornig³ 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 ν_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, ρ , 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 ν_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 ν_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 ν_1 very weak relative to ν_3 , and in the Raman spectrum the converse is true. It is, therefore, reasonable to suppose that in the liquid the 3,450 cm^{-1} infra-red band is mainly ν_3 and that the 3,450 cm^{-1} Raman band is mainly ν_1 . The 1,640 cm^{-1} band (IR and R) is undoubtedly ν_2 from considerations of both frequency and polarization data. Assignment of the 3,225 cm^{-1} band to $2\nu_2$ in Fermi resonance with ν_1 is well supported by its polarization, and variation of intensity with temperature⁵.

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

Phase	cm^{-1}	Symmetry species	Assignment	Observed in IR or R
Gas	1,595	a_1	ν_2	IR
	3,652	a_1	ν_1	R
	3,756	b_1	ν_3	IR
Liquid	1,640	a_1	ν_2	IR, R
	3,450	a_1	ν_1	R
	3,450	b_1	ν_3	IR
	3,225	a_1	$2\nu_2$	R
	3,615	a_1	$\nu_1 + \nu_H$ or $\nu_3 + \nu_H$	R

believe that the best assignment for the 3,615 cm^{-1} band is a combination, 3,450 + ν_H , where ν_H is the stretching vibration of a hydrogen bond. The value of ν_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 ν_1 and this band; that is, ν_H 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 ν_3 , symmetry b_1 , so that Fermi resonance is not allowed. The same reasoning applies to the 3,225 cm^{-1} ($2\nu_2$) band, and consequently the 3,450 cm^{-1} infra-red band appears with only a very slight asymmetry on the low-frequency side because of a residual intensity from $2\nu_2$.

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 $\Delta\nu$ between ν_1 and ν_3 is found to vary with the dielectric properties of the solvent. In carbon tetrachloride $\Delta\nu$ 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 ν_1 and ν_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 hydrogen-bonded 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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¹ Herzberg, G., *Infrared and Raman Spectra*, 280 (Van Nostrand, 1945).

² Fox, J. J., and Martin, A. E., *Proc. Roy. Soc. A*, **174**, 234 (1940).

³ Schultz, J. W., and Hornig, D. F., *J. Phys. Chem.*, **65**, 2131 (1961).

⁴ Walrafen, G. E., *J. Chem. Phys.*, **40**, 3249 (1964).

⁵ Saumagne, P., and Josien, Mlle. M. L., *Bull. Soc. Chim. (France)*, **6**, 813 (1958).

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°:

