

Extreme Infra-Red Absorption of D₂O, Ice and D₂O in Dioxane

THE broad absorption band observed in liquid water at about 160 cm.⁻¹ might be attributed to a free rotation of individual molecules, a combination frequency of near infra-red bands, or to a quasi-crystalline structure. The difference between the absorption of H₂O in the liquid and vapour states suggests the latter, and we can attribute it to either (1) hindered rotation or (2) hindered translation. This frequency being strongly infra-red active I interpreted it as due to a hindered rotation of the molecules¹. Bernal and Tamm², using the model described by Bernal and Fowler³, predict a fundamental frequency of hindered translation near 160 cm.⁻¹ and a fundamental frequency of hindered rotation at 480 cm.⁻¹. Measurements on D₂O permit us to decide between phenomena (1) and (2): for hindered rotation the frequency should be shifted by $\sqrt{2}$, for hindered translation by $\sqrt{20/18}$, or about 5 per cent.

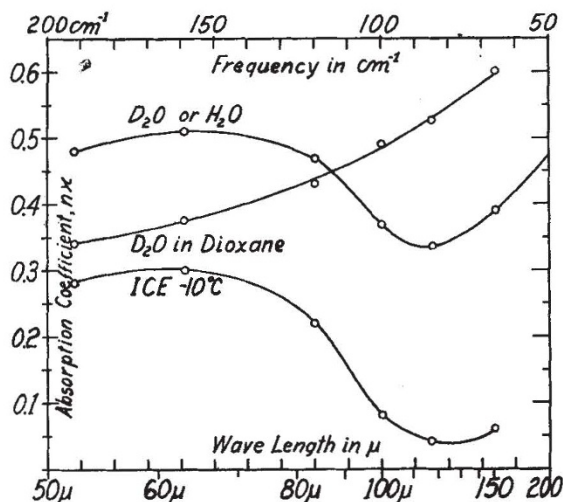


FIG. 1.

Within our experimental limits, D₂O and H₂O had the same absorption between 60 cm.⁻¹ and 200 cm.⁻¹. The absorption band near 160 cm.⁻¹ can therefore be assigned to a hindered translational frequency of D₂O or H₂O molecules as predicted by Bernal and Tamm. However, if this frequency were due only to a vibration of water molecules in a quasi-crystalline structure, it should be neither infra-red active nor Raman active. The difficulty might possibly be removed (using the model proposed by Bernal and Fowler³) by assuming that some of the four surrounding molecules are forced to follow the vibrations of the molecule at the centre by turning. This could in effect make a hindered translational motion infra-red active and also weakly Raman active, as is observed^{4, 5}.

The existence of the 160 cm.⁻¹ band in ice at -10° C., as shown in Fig. 1, is additional evidence for a quasi-crystalline structure in water, and indicates that the intermolecular forces are about the same in water and ice. As is also shown in Fig. 1, the 160 cm.⁻¹ band disappears for water dissolved in dioxane, which confirms that its presence was due to a structure in water rather than to the individual molecules. The absorption of dioxane has been subtracted in calculating the curve in Fig. 1.

Bolla⁴ reports a feeble Raman band near 60 cm.⁻¹. If this frequency is infra-red active, it is masked by the absorption due to the orientation of the permanent dipoles, as is best seen for water dissolved in dioxane. The absorption coefficient of water increases⁶ to a maximum of 2.7 at 0.6 cm.⁻¹.

Absorption measurements of the hindered rotation band predicted by Bernal and Tamm² at 480 cm.⁻¹ would be experimentally difficult, but the measurements of the reflecting power⁷ show a distinct maximum about 500 cm.⁻¹ (much stronger than that for the 160 cm.⁻¹ band). This frequency, if it were due to a hindered rotation, should indeed be strongly infra-red active; however, an accompanying distortion of the configuration of the surrounding water molecules seems necessary to explain the feeble Raman band observed in this region^{4, 5}.

I wish to thank Prof. E. K. Rideal for kindly supplying the D₂O used in these experiments.

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June 4.

¹ C. H. Cartwright, NATURE, 135, 872, May 25, 1935.

² J. D. Bernal and J. G. Tamm, NATURE, 135, 229, Feb. 9, 1935.

³ J. D. Bernal and R. H. Fowler, J. Chem. Phys., 1, 515; 1933.

⁴ Bolla, Nuovo Cimento, 10, 101; 1934.

⁵ Magat, J. Phys., 5, 347; 1934.

⁶ H. Rubens, Verh. d. phys. Ges., 17, 315; 1915.

⁷ H. Rubens u. E. Ladenburg, Verh. d. phys. Ges., 10, 226; 1908.

Molecular Polarisation of Solutes and Dielectric Constant of Solvents

EXPERIMENTALLY it is indicated that the different total polarisations shown by the same solute when dissolved in different solvents are to be related to alterations in the orientation polarisations (${}_0P$) caused by replacement of one dielectric environment by another, the atomic and electronic polarisations being constant throughout such changes. Therefore the expression given by Raman and Krishnan¹ for the volume polarisation of a dielectric, namely :

$$\frac{\epsilon - 1}{\epsilon + 2} = v \left(\frac{4\pi}{3} \frac{\alpha_1 + \alpha_2 + \alpha_3}{3} + \frac{\epsilon - 1}{\epsilon + 2} \psi \right) + \frac{v}{3kT} \left(\frac{4\pi}{3} \mu^2 + \frac{\epsilon - 1}{\epsilon - 2} \Theta \right)$$

(cf. reference for definition of symbols) can be rewritten to show the molecular orientation polarisation (${}_0P_{\text{sol}}$) of a polar solute at infinite dilution in a non-polar medium of dielectric constant ϵ as :

$${}_0P_{\text{sol}} = \frac{N}{3kT} \left(\frac{4\pi}{3} \mu^2 + \frac{\epsilon - 1}{\epsilon + 2} \Theta \right).$$

Now, dividing throughout by the true orientation polarisation as observed in the gaseous state (${}_0P_{\text{gas}} = 4\pi N \mu^2 / 9kT$) we have

$${}_0P_{\text{sol}} / {}_0P_{\text{gas}} = 1 + 3 \Theta / 4\pi \mu^2 \frac{\epsilon - 1}{\epsilon + 2}.$$

We wish to direct attention to two points of interest which arise from this result :

(1) The sign of Θ being inversely that of the Kerr constant for the substance, this quantity is for most substances negative, and therefore their polarisations in solution should be, and in many instances have