POLARISATION OF THE RAMAN BANDS OF WATER AND DEUTERIUM OXIDE.

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1. *Introduction.*

In two previous communications[1] the author has reported the results of a study of the Raman spectrum of heavy water, and has pointed out the remarkable similarity in the structure and relative intensity of the Raman bands of this substance and those of ordinary water. In order to complete this investigation, it was felt desirable to study the state of polarisation of the Raman bands in the two cases. Results obtained in this direction are communicated in the present paper.

The polarisation of the Raman bands of ordinary water has been studied by Ramaswamy,[2] Cabannes and Rousset,[3] Cabannes and De Riols[4] and Ramakrishna Rao.[5] The results of the different authors are rather conflicting. Ramaswamy found the values 0·6, 0·45 and 0·75 for the depolarisation of the three components of the principal Raman band in the order of increasing frequency. Cabannes and Rousset reported the first component as depolarised and the second one as polarised. Cabannes and De Riols reported quite the contrary result. They found that all the three components are polarised. They gave 0·3 as the depolarisation factor for the central component and remarked that the one of lower frequency is still more polarised. Ramakrishna Rao used a quartz spectrograph in his experiments and got highly anomalous results.

2. *Experimental.*

The liquids (H_2O and D_2O) rendered dust-free by vacuum distillation were contained in suitable Raman tubes of pyrex glass with fused-on end

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[1] R. Ananthakrishnan, *Nature*, 1935, **136**, 551.
R. Ananthakrishnan, *Proc. Ind. Acad. Sci.*, (A), 1935, **2**, 291.

[2] C. Ramaswamy, *Nature*, 1931, **127**, 558.

[3] J. Cabannes and A. Rousset, *Ann. de Phys.*, 1933, **19**, 271.

[4] J. Cabannes and J. De Riols, *C. R.*, 1934, **198**, 30.

[5] I. R. Rao, *Z. f. Phys.*, 1935, **90**, 658.

window. The experimental tube was kept at a distance of about 50 cms. from the slit of the spectrograph and light from a 6-inch quartz mercury lamp was concentrated on it by means of a large glass condenser. The observation window was a circular aperture of 3 mms. diameter. A quartz double image prism with its axes horizontal and vertical was interposed between the slit and the Raman tube and fixed in such a position that the two images of the aperture as viewed through the prism could be seen well separated one above the other. A lens behind the double image prism focussed the two images on the slit of the spectrograph (Hilger two-prism glass optical parts). The time of exposure to get an intense picture was about 2 days in the case of water and 4 days in the case of deuterium oxide using a slit width of 75 μ.

3. *Results.*

The spectra photographed in the above manner are reproduced in the plate. The principal results may be summarised as follows:

(1) The three components of the principal Raman bands of H_2O and D_2O are more and more depolarised in the order of increasing frequency shift. The component of lowest frequency shows a high degree of polarisation, the depolarisation factor being probably of the order of 10 or 15%. The component of highest frequency is highly depolarised, perhaps to the limiting value 6/7. The middle component which is the strongest has a depolarisation factor somewhere between these two values, about 40–50%.

(2) The band $\Delta\nu = 1235$ cm.$^{-1}$ in the case of D_2O is depolarised to the extent of 50–60%. The depolarisation of the corresponding Raman band in the case of H_2O ($\Delta\nu = 1650$ cm.$^{-1}$) could not be ascertained because of its unfavourable position in the spectrum. Cabannes and De Riols have found for it the value $\rho \backsimeq 0{\cdot}4$.

(3) The band $\Delta\nu = 175$ cm.$^{-1}$ which is quite strong with pronounced anti-stokes is depolarised to the limiting extent of 6/7 in both cases.

(4) The diffuse bands $\Delta\nu = 500$ cm.$^{-1}$ and $\Delta\nu = 750$ cm.$^{-1}$ in the case of H_2O seem to be highly depolarised. The corresponding Raman bands $\Delta\nu = 350$ cm.$^{-1}$ and $\Delta\nu \backsimeq 500$ cm.$^{-1}$ recently reported by Magat[6] in the case of D_2O are hardly perceptible in the author's photographs.

4. *Discussion of Results.*

A strict and satisfactory interpretation of the Raman spectra of liquid H_2O and D_2O appears to be very difficult indeed. Nevertheless, there have been certain attempts in this direction, although only of an empirical nature.

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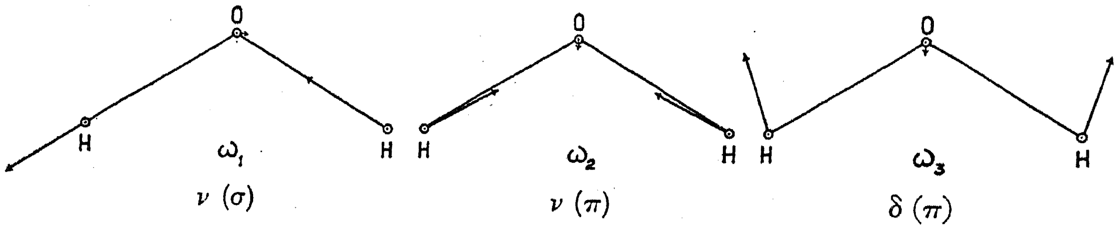
[6] M. Magat, *C. R.*, 1935, **201**, 668.

Mecke's analysis of the vibration-rotation spectrum of ordinary water vapour led him to the choice of the following normal frequencies for the H_2O molecule in the vapour state. $\nu(\sigma) = \omega_1 = 3795$ cm.$^{-1}$; $\nu(\pi) = \omega_2 = 3670$ cm.$^{-1}$; $\delta(\pi) = \omega_3 = 1615$ cm.$^{-1}$ These may be compared with the infra-red absorption maxima at 3756 and 1595 and the Raman line at 3654 cm.$^{-1}$ observed in the Raman spectrum of water vapour.



Normal Vibrations of H_2O.

The infra-red absorption spectra of liquid H_2O and D_2O have been studied recently by Ellis and Sorge.[7] They have identified the absorption maxima at $6 \cdot 2\,\mu$ (1613 cm.$^{-1}$) and $3\,\mu$ (3330 cm.$^{-1}$) in the case of liquid water with the fundamental frequencies assigned by Mecke to the H_2O molecule. The shift in the absorption maxima from the gaseous state to the liquid state is not surprising when it is remembered that many of the molecules contributing to these bands are parts of polymer molecules. Ellis and Sorge have also pointed out that more detailed information about the $3\,\mu$ absorption region is to be sought for from the Raman spectrum which yields three components, the average of the maxima being approximately 3220, 3430, and 3600 cm.$^{-1}$ The effect of temperature on the $3\,\mu$ Raman band of water is to diminish the intensity of the component of lowest frequency and increase the intensity of the component with the highest frequency. This is explained as being due to breaking up of the polymerised molecules. Ellis and Sorge have therefore chosen the Raman bands at 3430 and 3600 to correspond to the vibrational modes $\nu(\pi)$ and $\nu(\sigma)$ respectively *for the H_2O molecules in the liquid state.* Magat[8] on the other hand has suggested that in so far as the component of frequency 3600 is extremely weak if not entirely absent at low temperatures and increases in intensity as the temperature is raised, it should be identified with the Raman line 3654 of water vapour and arises from a small percentage of water molecules which possess free rotation. The two other components 3220 and 3430 which are quite intense at ordinary temperature represent according to him the fundamental frequencies $\nu(\pi)$ and $\nu(\sigma)$ of the liquid molecules. Ramakrishna Rao's suggestion that the

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[7] J. W. Ellis and B. W. Sorge, *Jour. Chem. Phys.*, 1934, **2**, 559.

[8] M. Magat, *Bull. de la Soc. de Phys.*, 1935, **60**, 65.
M. Magat, *C.R.*, 1935, **201**, 669.

component bands at 3220, 3430, and 3600 ought to be attributed respectively to the molecules $(H_2O)_3$, $(H_2O)_2$, and H_2O is only conjectural.

In order to interpret at least in a qualitative fashion the polarisation results, it might be pointed out that the polarisation rules in Raman scattering give the depolarisation factor 6/7 for anti-symmetrical and degenerate modes, and values between 0 and 6/7 for symmetrical vibrations. Thus in the case of H_2O and D_2O, the Raman band corresponding to ν (σ) would be highly depolarised, while those corresponding to ν (π) and δ (π) would show a lesser degree of depolarisation. It is also reasonable to conclude that δ (π) would be much more depolarised than ν (π).

The high depolarisation of the Raman band at 3600 renders it difficult to identify it with the vapour frequency 3654 which presumably corresponds to $\nu(\pi)$. Rather, it supports the view of Ellis and Sorge that it arises from the anti-symmetrical vibration of the liquid molecules. The high degree of polarisation of the component band at 3220 on the other hand suggests that it should arise from a symmetrical vibration.

It appears that the influence of temperature as well as the observed polarisation results could be satisfactorily explained if we postulate that the liquid state is composed of a large percentage of polymerised molecules (di-hydrol) and a smaller percentage of non-polymerised molecules. To the former belong the vibrational frequencies. ν $(\pi) = 3220$ and ν $(\sigma) = 3430$ while to the latter belong the frequencies ν $(\pi) = 3430$ and ν $(\sigma) = 3600$. This assumption will naturally explain the intermediate degree of depolarisation observed for the central component since it is now a superposition of the depolarised anti-symmetrical vibration of the polymerised and the symmetrical vibration of the non-polymerised molecules. The observation of Magat that the intensity maximum displaces itself in the direction of increasing frequency in the two stronger components as the temperature is raised is also not difficult to understand on this assumption since the coupling between two molecules is bound to be influenced by forces of thermal agitation.

If the view suggested above is correct, the same considerations should explain the Raman spectrum of heavy water as well. The vibrational frequencies of the liquid D_2O molecules appear in the Raman spectrum as a sharp band at 1235 cm.$^{-1}$ and a broad and intense band at 2500 cm.$^{-1}$ The latter band shows a structure exactly analogous to the corresponding Raman band of ordinary water, with two strong components at 2360 and 2510 and a fainter one at 2660. Polarisation photographs show quite analogous features.

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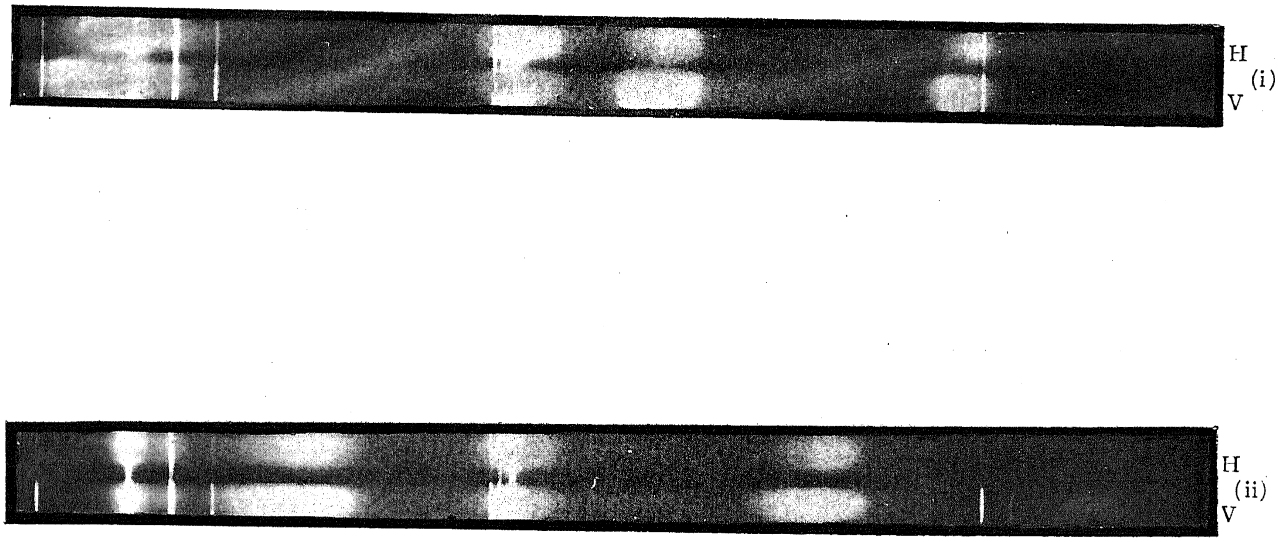

Polarisation of Raman Bands.

(i) D_2O (ii) H_2O

The infra-red spectrum of the liquid investigated by Ellis and Sorge led them to the choice of the absorption bands at $8 \cdot 2\,\mu$ (1220 cm.$^{-1}$) and $4\,\mu$ (2500 cm.$^{-1}$) as corresponding to the fundamental frequencies. The fundamental vapour frequencies in the infra-red observed by Barker and Sleator[9] and by Bartholomé and Clusius[10] are 2775 and 1185, while Rank, Larsen and Bordner[11] found a single Raman line at 2666 cm.$^{-1}$ for the vapour which presumably arises from the symmetric vibration.

The origin of the strong low frequency Raman band at 175 cm.$^{-1}$ has been diversely interpreted. The strong infra-red absorption in practically the same region as well as the high depolarisation exhibited by this Raman band, would seem to favour the view that it arises from the hindered rotation or angular oscillation of the liquid molecules. Magat's suggestion[12] that this band owes its origin to the mutual oscillation of the centres of gravity of two liquid molecules without change of orientation cannot explain the high depolarisation observed for this band.

In conclusion, the author wishes to record his respectful thanks to Professor Sir C. V. Raman for his kind interest and guidance in the present work.

5. *Summary.*

The Raman spectra of liquid H_2O and D_2O have been photographed by interposing a double image prism in front of the slit of the spectrograph. The three components of the principal Raman band in the two cases are more and more depolarised in the order of increasing frequency, the component of lowest frequency being highly polarised, and that of highest frequency being highly depolarised. The band $\Delta\nu = 1235$ cm.$^{-1}$ in the case of D_2O is imperfectly polarised, while the low frequency Raman band($\Delta\nu \approx 175$ cm.$^{-1}$) is depolarised to the extent of 6/7 in both cases. A tentative explanation is suggested to interpret the observed results.

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[9] E. F. Barker and W. W. Sleator, *Jour. Chem. Phys.*, 1935, **3**, 660.

[10] E. Bartholomé and K. Clusius, *Naturwiss.*, 1934, **22**, 40; *Z. f. Elek. Chem.*, 1934, **40**, 530.

[11] D. H. Rank, K. D. Larsen and E. R. Bordner, *Jour. Chem. Phys.*, 1934, **2**, 464.

[12] M. Magat, *loc. cit.*