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THE EFFECT OF VARYING CONCENTRATIONS OF CERTAIN ELECTROLYTES ON THE VIOLET BAND OF THE RAMAN SPECTRA OF WATER

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Abstract

A Hilger E-1 spectrograph was used to study the Raman scattering by pure water excited by the 3650A group of the mercury arc. Photometric measurements of the plates were made with a Moll microphotometer. The violet band at about 4150A appears to consist of three components. The effect on this band of various concentrations of aqueous solutions of KCl, NaOH, and KOH was examined. In all cases the energy appears to shift toward the long wave-length side and in addition the top of the curves grows sharper with increasing concentrations.

A GREAT amount of work has already been done on the Raman spectra of pure water[1,2,3,4] and a still greater amount has been done on the effect produced on the Raman bands by various concentrations of different substances in aqueous solutions.[5,6,7]

In spite of the amount of work that has been done there is yet quite a bit of uncertainty and some conflicting data as to the structure of these bands. Some have found broad continuous bands[8] showing no real structure while others have found two[9,10] or three[11] and even a higher number[12] of components. Of the bands excited by different lines, Kinsey[13] found the band excited by the 3650A group to be a double band while that excited by the 4047A group was found to be a triple band.

The present work was undertaken with the aim of helping to clarify this situation and to add to the present available data on the changes produced in the water bands by the addition of varying amounts of easily ionized substances.

The major part of the previous work has been confined to the most con-

[1] Raman and Krishnan, Ind. Jour. Phys. **2,** 399 (1928).
[2] Rao, Nature **125,** 600 (1930); Proc. Roy. Soc. **127,** 279 (1930).
[3] Dadieu and Kohlrausch, Naturwissen. **17,** 625 (1929).
[4] Ellis, Nature **123,** 205 (1929).
[5] Carrelli, Pringsheim and Rosen, Zeits. f. Physik **51,** 511 (1928).
[6] Dickinson and Dillon, Proc. Nat. Acad. Sci. **15,** 334 (1929).
[7] Daure, Compt. Rendus **187,** 940 (1928).
[8] Meyer, Phys. Zeits. **31,** 510 (1930).
[9] Dadieu and Kohlrausch, Cf. Ref. 3.
[10] Gerlach, Phys. Zeits. **31,** 695 (1930).
[11] Rao, Cf. Ref. 2.
[12] Ganesan and Venkteswaran, Ind. Jour. Phys. **4,** 195 (1929).
[13] Kinsey, Phys. Rev. **34,** 541 (1929).

spicuous band of water, namely, the one shifted from the exciting line by about 3400 wave-numbers, which corresponds to about 3μ.

The violet band at about 4150A excited by the 3650A group was selected in this work, in spite of its composite nature, because of its intensity and also because fewer data are available concerning this band than concerning the one at about 4700A.

It seemed worthwhile to determine what effect is produced on the water band by a solution of some of the hydroxides. Ten photographs were taken with each of the following as the scattering substance: distilled water, aqueous solutions of KOH varying in concentration from 9.74N to 0.27N, and aqueous solutions of NaOH varying from 13.5N to 1N. In addition three photographs were taken for aqueous solutions of KCl at 2.5N, 0.25N and 0.025N.

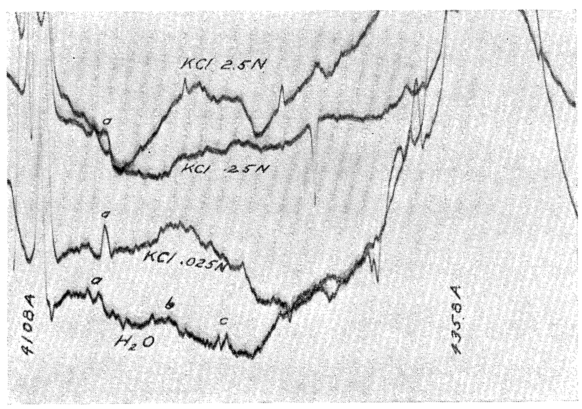

Fig. 1.

The scattering tube and water jacket were of glass. The tube was similar to that described by R. W. Wood.[14] The end farthest from the spectrograph slit was drawn out into a cone, curved upward and painted black. A Hilger E-1 quartz spectrograph was used with special astronomical green sensitive plates. The photometric measurements of these plates were made with a type A Moll microphotometer. The source, for all photographs except those of NaOH, was a Hanovia quartz mercury arc operated at three amperes with 150 volts directly across the lamp terminals. The NaOH photographs were made at an earlier date with the same lamp operating at a lower temperature. The time of exposure for each plate was about 30 hours except in the case of NaOH solutions and in that of pure water where exposures of 48 hours were made. The temperature of the scattering substance was held at 30°C within 2°.

An inspection of the microphotometer curves taken from these plates will give the best idea of the form of the band and also of the effect on the band of various concentrations of the above mentioned substances. It was

[14] R. W. Wood, Phil. Mag. **6**, 729 (1928).

thought best to record a curve for pure water and a number of curves for the same electrolyte at different concentrations on the same microphotometer film. An effort was made to have these curves so placed that corresponding points of all curves on any one film should lie in the same vertical line. How nearly this was accomplished may be judged from the 4108A line near the left in the figures and best seen in the curves for the NaOH solutions. The heavy line seen at the right of the figures is the 4358A line from the arc.

In Fig. 1 the H_2O curve was made from a plate exposed for 48 hours with a spectrograph slit width of 0.02 mm, the microphotometer thermocouple slit being correspondingly narrow. The curve seems to indicate a triple structure

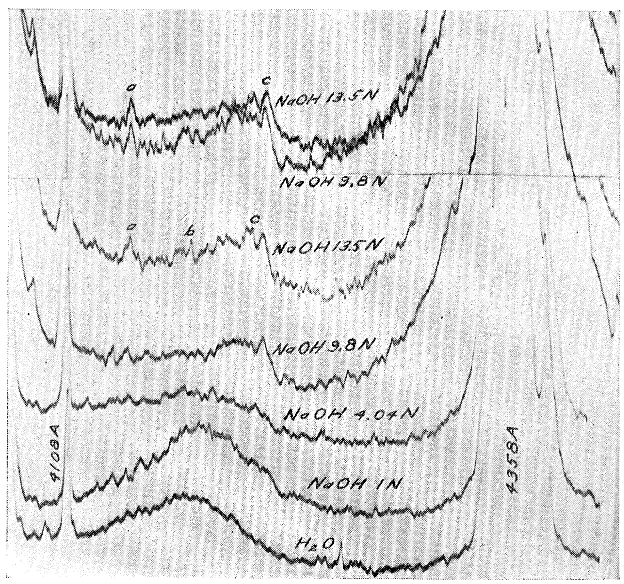

Fig. 2.

for the water band. The components are indicated by letters (a), (b), and (c). These represent shifts from the exciting line of approximately 3228, 3435 and 3624 wave-numbers corresponding to 3.10, 2.91 and 2.76μ. The wave-lengths of the components of the band are 4137A, 4173A and 4206A respectively. This curve shows the components of the water band better than either of the other two curves for water which were made with a wider slit for both spectrograph and microphotometer. Some uncertainty is introduced in regard to component (a) due to the fact that there is in the mercury arc a weak line at 4145A. The gear ratio of the microphotometer for all curves shown was such that 1 mm of film corresponded to 2A closely. The distance between the two outer components measures 35 mm, the inner component being located about midway between the outer ones. The overlapping of the bands due to the different lines of the 3650A group and the general Raman scattering combined with the continuous radiation from the arc make it impossible to determine the wave-length of the individual components with much precision. However, since a large percent of the energy of this groups is associated with the two closely lying lines 3650 and 3655A, the scattering due to these two lines should stand out prominently.

The other three curves for different concentrations of KCl show that for low concentration, 0.025N, there is an increase of energy in all the components, (a) becoming quite sharp. Further concentration shifts the energy more and more toward the long wave-length component (c) and at the same time renders the peak of the curve sharper. Gerlach[15] has reported a like energy shift for a number of the chlorides including KCl. He also reports the disappearance of the short wave-length component of the 4700A band of water for concentrated solutions. Woodward[16] has recently reported a Raman band

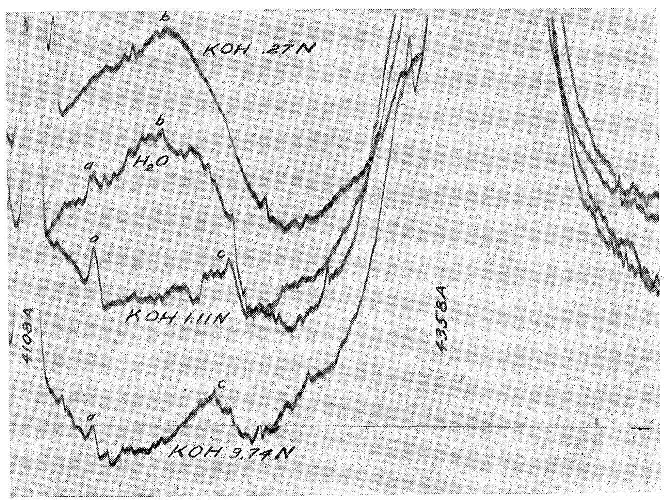

Fig. 3.

which corresponds to a shift of 3615 wave-numbers for very nearly concentrated solutions of both NaOH and of KOH.

In Fig. 2 are shown curves obtained with different normalities of NaOH. At the bottom is shown the poorly resolved curve for water. For 1N the scattering increases while the center of gravity of the curve is shifted toward the long wave-length side. For better comparison the curves for 9.8N and 13.5N are repeated in juxtaposition at the top of the figure. These two curves were made at a later date with a different slit width for the thermocouple. For high concentrations the (c) component becomes most prominent and shows a steep curve on the long wave-length side.

The data are hardly sufficient to enable one to decide whether the individual centers of (b) and (c) shift or whether the energy increase in the locality of (c) shifts the center of gravity of the more or less poorly resolved

[15] Gerlach, Naturwissen. **18,** 68 (1930).
[16] Woodward, Phys. Zeit. **32,** 261 (1931).

curve. It might be pointed out in this connection that the (a) component while suffering a decrease in energy shows little if any shift with change in concentration. With some degree of uncertainty the curves for higher concentrations of NaOH shows signs of the unshifted (b) component.

The effect of different concentrations of KOH is shown in Fig. 3. It can be seen that with increasing concentration there is again a shift of energy away from the center toward the (c) component. The curve for 9.74N, the base of which has been supplied from another curve made from the same plate, shows a marked sharpening of the top of the curve near the location of the (c) component.

The difference in general appearance of the curves for NaOH and those for KOH may be explained in part by the fact that the latter were taken with the arc at a much higher temperature and with slightly wider slit.

Further work along this line is in progress using as a source a helium hot cathode arc described by Wood.[17] It is hoped that with this arrangement, which gives practically monochromatic light, the components of the water band may be located with higher precision and the effect of solutes on this band may be better determined.

[17] R. W. Wood, Phys. Rev. **35**, 670 (1930).

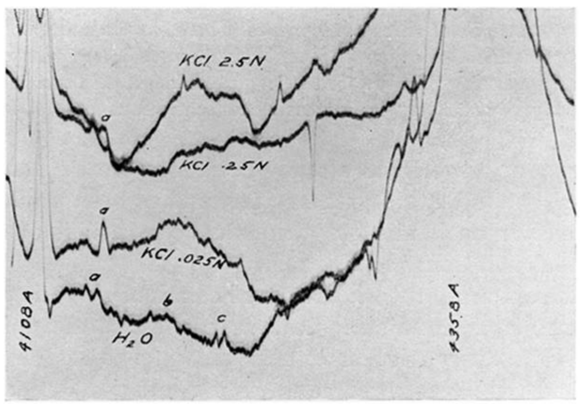

Fig. 1.

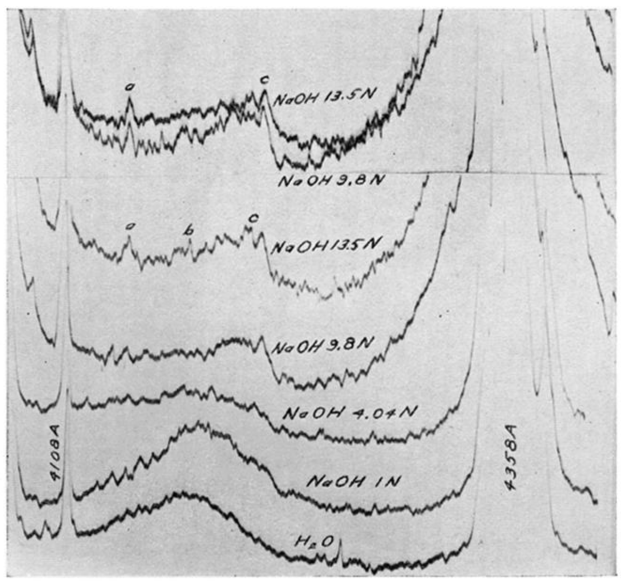
a
c
NaOH 13.5N
NaOH 9.8N
a
b
c
NaOH 13.5N
NaOH 9.8N
NaOH 4.04N
4108A
NaOH 1N
4358A
H₂O

Fig. 2.

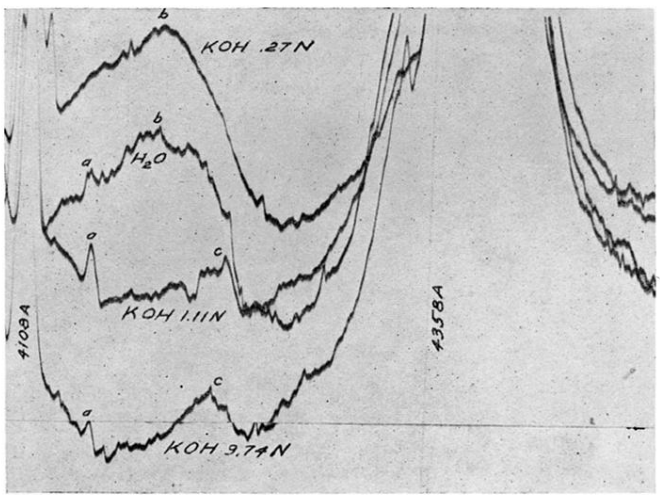

Fig. 3.