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The Change in Absorption of Water at 4.7μ Due to Solutions

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A study has been made of the absorption of aqueous solutions of some halogen salts in the region of 4.7μ. It has been found that KF shifts the bands to shorter wave-lengths, while KCl, KBr, and KI shift the band to longer wave-lengths. The effect is explained as due to changes in hindered rotation as produced by the binding forces between the ions and water molecules. The changes in position of the band vary with concentration. The kind of positive ion does not seem to change the effect when the same negative ion is in solution.

STUDIES have been made by several investigators[1] of the effect on the absorption of water when different ions are present. The results obtained may be classified as changes in intensity and position of the water bands due to the presence of ions, other bands are observed which are not characteristic of water or the ions, and bands due to the ions. Some of these investigations on solutions have been made in the near infra-red region. Thicker cells can be used and the intensity of the source is greater. It is more difficult to interpret the results, however, as most of the bands in the near infra-red region are really two or more overlapping combination bands of the fundamental. A change in frequency may be a change in the relative intensities of the component bands, on account of the two fundamental bands of water at 2.72μ and 2.91μ. There is the same difficulty in the study of the 3μ region.

A study of the absorption spectra of liquid water shows bands at about 4.72μ and 5.75μ. These bands are not found in water vapor and are likely due to a combination of the 6.18μ water band and two hindered rotation frequencies at 20μ and 55μ. These bands are readily observed in the water spectrum, as can be seen from the top curve of Fig. 1. Also they have been observed in Raman spectra at 500 cm^{-1} and 170 cm^{-1} by Hibben.[2] The band at 5.75μ under higher resolution shows two parts at 5.56μ and 5.83μ. The angle between the OH and H in water vapor molecule is about 104.5° and in liquid water 107°. The change in the angle is small and the differences in the frequencies observed for the water vapor and liquid water are small. For example, the transverse vibration for water vapor occurs at 6.26μ and 6.18μ for water.

Since the presence of ions will not change the angle of the water molecule very much, it is not likely that the internal frequencies of the water molecule will be considerably altered by their presence. It appears that the effect of ions can best be studied in relation to the hindered rotation type of frequency which occurs at 20μ. In fact the 4.72μ band, which is a combination band with the 6.18μ band, should show the effect of the presence of ions. A study has been made of the effects of certain halogen salts on the absorption of water in this region.

The absorption spectra have been measured by using an infra-red spectrometer with a fluorite prism. At 5μ the effective slit width was 300A. The cells were made by placing a drop of the solution upon a fluorite plate. Another plate was placed over the first one and the two sealed together with wax. The plates were separated by mica washers about 0.02 mm in thickness.

In Fig. 1 is shown the absorption of water and solutions of KF, KCl, KBr, and KI. The cell thicknesses are about the same and the transmission in the region of 4.7μ is about 30 percent. The transmission of the KF is somewhat less than the other solutions. The concentration is greater and the absorption band shows a definite shift to shorter wave-lengths. In fact the shift of the position of maximum absorption in the solution is the important part found in this study. It can be seen from the curves that the band at 4.72μ in water occurs at 4.58μ in 5*N* KF solution, 4.76μ in the 3*N* KCl, 4.80μ in 4*N* KBr, and 5.85μ in 4*N* KI.

The next question considered was the effect on

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[1] G. E. Grantham, Phys. Rev. **18**, 339 (1921).
[2] Hibben, J. Chem. Phys. **5**, 994 (1938).

the position of this band due to the positive ion. Lithium and sodium salts of the halogens gave about the same positions for the different salts as are shown in Fig. 1. Also solutions of NH_4F, NH_4Cl, and NH_4Br were studied, to see the effect of a complex ion on the position of maximum absorption in this region. The results were of the same type as found for the potassium salts. The fluoride band is shifted to shorter wave-lengths, while the chloride and bromide are shifted to longer wave-lengths than the band in water. It appears that the bands for the ammonium salts occur at slightly longer wave-lengths than in the potassium salts. It can be seen in Fig. 2, for example, that the NH_4F band is about 4.62μ compared to 4.58μ for KF. This difference is about equal to the slit width of the spectrometer and may be produced by experimental error.

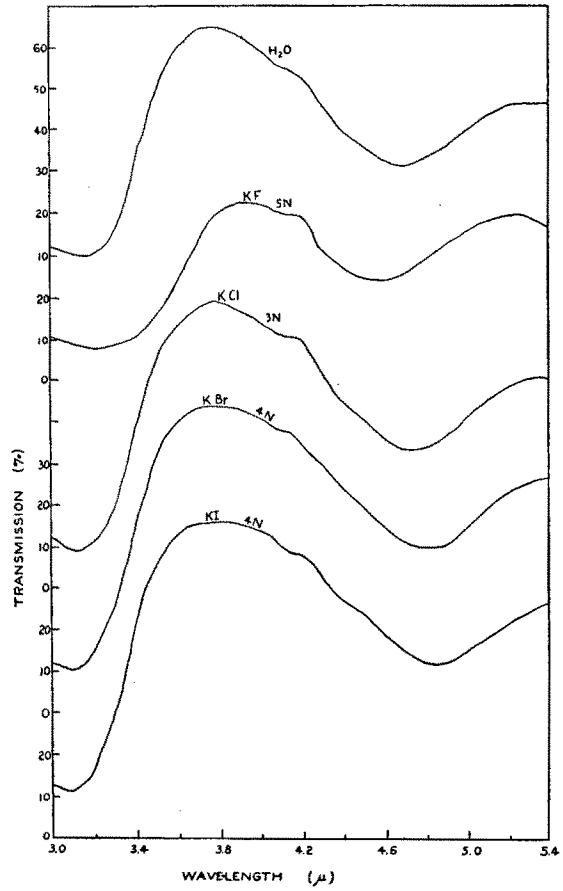

FIG. 1. A comparison of the absorption of water and aqueous solutions of KF, KCl, KBr, and KI in the region from 3.0μ to 5.4μ. The cell thickness is about 0.02 mm.

The next question considered in regard to the absorption of the solutions was the effect of the concentration on the position of the band. Concentrations from $0.75N$ to $6N$ of NaBr were measured in the region from 4.5μ to 6.5μ. The band gradually changed from 4.75μ to 4.88μ in the $6N$ solution. The solutions were also studied on a grating instrument of much higher resolution, but the bands were broad and of the same type as shown in Fig. 3. This shows that the band is not likely due to the overlapping of two bands which change the resultant maximum of absorption as the concentration is increased. The water band at 6.2μ does not change in position and this indicates that the changes observed in the 4.72μ band are due to the vibration of molecule with molecule or hindered rotation.

The structure of liquid water has been studied from various approaches, such as effect of pressure and x-rays. A theoretical study has been made by Bernal and Fowler.[3] They relate

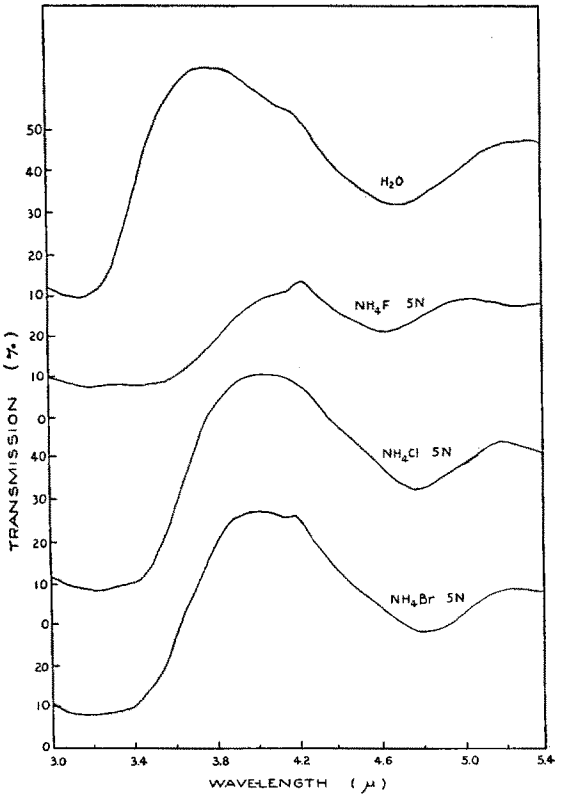

FIG. 2. The absorption of the ammonium salts in solution. The change in absorption at 3.3μ is produced by the NH_4 ion.

[3] Bernal and Fowler, J. Chem. Phys. 1, 515 (1933).

the structure, when ions are present, to a change in temperature. On the basis of their work, the fluorine ion would correspond to a lowering of temperature and the chlorine, bromine, and iodine to a rise in temperature; since it has been shown by Ganz[4] that the water band shifts to the longer wave-lengths when the temperature is increased.

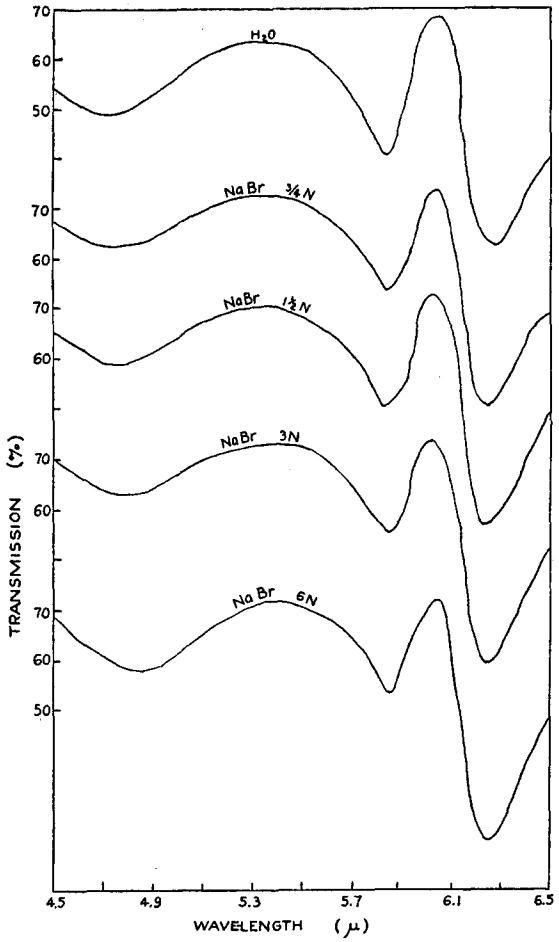

FIG. 3. The effect of concentration on the change in the position of the 4.72μ band.

The structure of water is produced by the linkage of hydrogen and oxygen of the neighboring molecules. For ice the structure is fixed and definite, but in water the linkage may not be so regular and may not extend in a regular way to include a large number of molecules in any group.

We may have a hindered rotation of the molecules in the group and that will give rise to three different frequencies, corresponding to the three principal moments of inertia of the molecule. Unless some force constants are assumed in relation to the forces between molecules, the positions of the three hindered rotations cannot be calculated. When a group of molecules is associated with an ion instead of a water molecule, the force constants will in general be different. When the binding force is increased, we would expect the hindered rotation frequency to be increased. The binding force of an ion will depend on its charge and the size of an ion. The size of the ion from fluorine to bromine is increasing and this is in agreement with the observation of the change in position of the band at 4.72μ. These results also show that the binding force of the fluorine ion is greater than that of water molecule to water molecule, and that the other halogen ions have a binding force less than water for water.

[4] Ganz, Ann. d. Physik **26**, 331 (1936).