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The Effects of Various Ions on the Infra-Red Absorption of Water

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The effects of various non-hydrolyzing salts on the infra-red spectrum of water have been studied in the region between 1μ and 7μ. Variations in the positions of the absorption maxima at 1.46μ, 1.79μ, 1.96μ, 3.0μ, 4.7μ, and 6.1μ have been observed. The changes produced by the solutes have been compared with existing data on the effects of temperature variation on the absorption of water. The results indicate that, in general, large ions produce changes similar to the changes produced by increasing the temperature of the pure solvent, whereas small ions produce the reverse effect. These results are in agreement with data on the other physical properties of water and aqueous solutions.

ON the basis of x-ray diffraction data, Bernal and Fowler[1] have developed a theory of the intermolecular structure of water and aqueous solutions. According to this theory, the molecules of water in the liquid state are arranged in local crystalline lattices. The extent of these lattices and the regularity of the arrangement of the molecules within the lattices are greatest at low temperatures. The effects of the presence of ions in the water depend upon the polarizing powers of the ions, polarizing power being defined as the ratio of ionic charge to ionic radius. In a sequence of ions of equal charge, the larger ions decrease the regularity of molecular arrangement and produce changes similar to those produced by elevation in the temperature of pure water; smaller ions tend to enter into the crystalline lattices and preserve regularity.

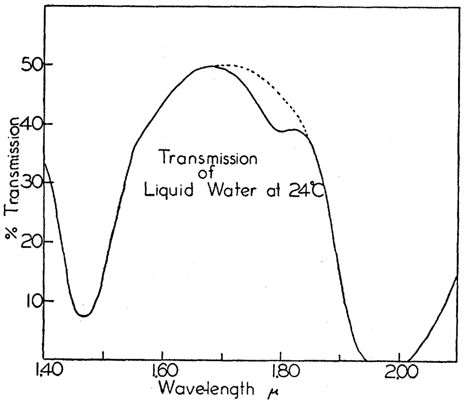

FIG. 1. The transmission spectrum of water in the vicinity of the 1.79-μ band.

As the infra-red absorption bands of water have been found to change in position as the temperature is varied,[2,3] it has been of interest to study the influence of various ions on these bands in order to compare the observed effects with the effects predicted on the basis of the Bernal-Fowler theory. Such studies have already been made for the 4.7μ band.[4,5] The purpose of the present investigation has been to extend these studies to include all the major infra-red bands between 1μ and 7μ.

The spectrometer used was an instrument of the Wadsworth-Littrow type equipped with a large glass prism for use between 1μ and 2μ and a rocksalt prism for use at longer wave-lengths. Absorption cells with glass windows were used at wave-lengths shorter than 2μ and fluorite cells were used between 2μ and 7μ. Cell thicknesses were adjusted to give optimum measurable absorption for each band. The bands studied were located at 1.46μ, 1.79μ, 1.96μ, 3.0μ, 4.7μ, and 6.1μ. Assignment of these bands to various types of molecular vibration have been made by earlier investigators.[6]

The compounds chosen for study were the alkali and alkaline-earth halides.[7] The ions pro-

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[1] J. D. Bernal and R. H. Fowler, J. Chem. Phys. **1**, 515 (1933).

[2] J. R. Collins, Phys. Rev. **26**, 771 (1925).

[3] E. Ganz, Ann. d. Physik **28**, 445 (1937).

[4] E. K. Plyler and E. S. Barr, J. Chem. Phys. **6**, 316 (1938).

[5] D. Williams and T. N. Gautier, Phys. Rev. **56**, 616 (1932).

[6] J. W. Ellis, Phys. Rev. **38**, 693 (1931).

[7] All compounds were obtained from Eimer and Amend;

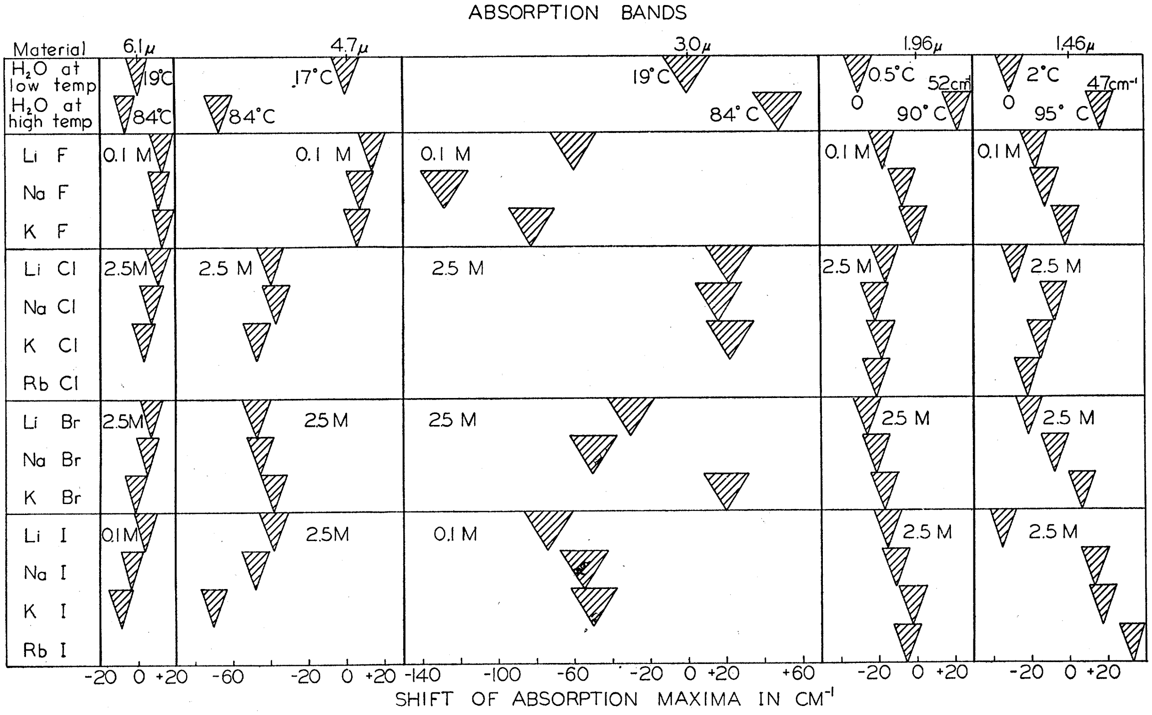

FIG. 2. Changes in the characteristic vibrational frequencies of water: The plots show frequency changes produced by various positive ions in the presence of common negative ions.

duced are monatomic and hence have no absorption in the region being investigated. In order to determine the effects of various cations on a given band, a sequence of solutions of compounds containing these cations in combination with a common anion was studied. The reverse procedure was used to ascertain the effects of various anions. The same molar concentration was used for each solution in a given sequence. In general, the concentration was made as large as possible, but it was found desirable to use less concentrated solutions in the thin cells employed for the 3.0-μ and 6.1-μ bands.

Definitely measurable shifts produced by solutes were observed for all bands except the weak band at 1.79μ. The absorption of water in this region is shown in Fig. 1. It will be observed from this figure that the 1.79-μ band appears as a small depression, on the side of the intense band with maximum at 1.96μ. As indicated by Collins,[8] the location of the 1.79-μ maximum can be determined satisfactorily by taking the ratio of the observed transmission to an assumed background such as that given by the dotted curve in Fig. 1. However, the background absorption changes when solutes are introduced, since the solutes produce changes in the intense 1.96-μ band. Hence, it is necessary to assume a different background for every solution studied and it is felt that the shifts detected by such methods are not sufficiently quantitative to warrant publication. However, it can be asserted that the changes produced by the fluoride and iodide ions are of the type to be expected from the Bernal-Fowler theory. No definite statements can be made about the effects of ions of intermediate size.

The results obtained for the other bands are summarized in Figs. 2 and 3. In these figures the shifts of absorption maxima are plotted. The observed shifts are indicated by the vertices of the shaded triangles and the uncertainties in the location of the maxima are indicated by the length of the bases of the triangles. Concentrations are given for each sequence of solutions.

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only small quantities of the cesium and rubidium compounds were available and these were used for work in the short wave-length region.

[8] J. R. Collins, Phys. Rev. 52, 88 (1937).

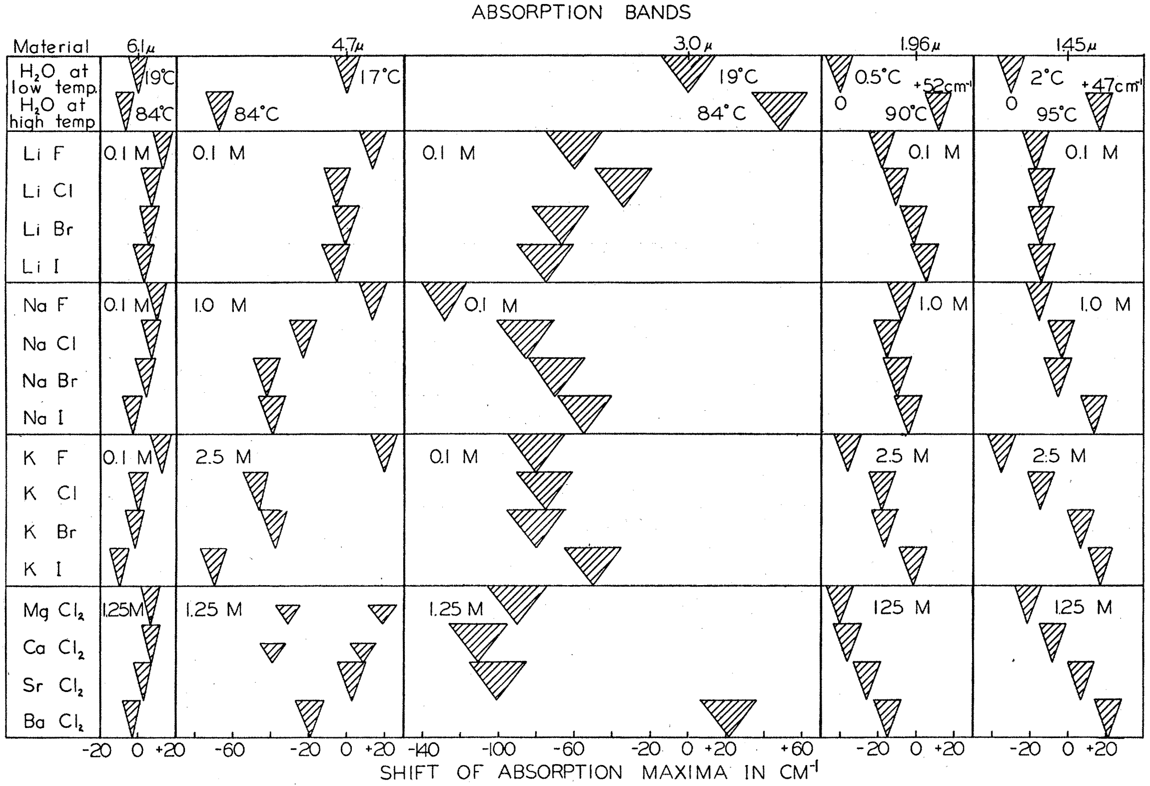

FIG. 3. Changes in the characteristic vibration frequencies of water: The plots show frequency changes produced by various negative ions in the presence of common positive ions.

The data for water at various temperatures are taken from Ganz' work on the 6.1-μ, 4.7-μ, and 3.0-μ bands and Collins' work on the 1.96-μ and 1.46-μ bands.

Figure 2 gives the shifts produced by various positive ions in the presence of common negative ions. According to Bernal and Fowler, increasing ion size should produce effects similar to those produced by increasing the temperature. Of the 20 sequences summarized in Fig. 2, 14 sequences exhibit shifts of the type predicted from the theory, 3 sequences show shifts in the opposite direction, and 3 sequences show no definite trend.

In Fig. 3 are shown the shifts produced by various negative ions in the presence of common positive ions. Of the sequences shown, 16 show shifts of the predicted type, one has a shift to the opposite direction, and three show no definite shift. It should be noted that $MgCl_2$ and $CaCl_2$ produce a definite splitting of the 4.7-μ band.

Six of the sequences for which the shifts were not in agreement with those predicted from the theory were for data obtained in the 3-μ region. The broad band in this region is produced by three overlapping bands. Hence, it is probably desirable to repeat the measurements in this region with an instrument of higher resolving power and with thinner absorbing layers than could be obtained with the type of cells used in this study. It would also be desirable to make a thorough study of the effects of concentration on the changes produced by the solutes.

The results obtained are in general agreement with the predictions made on the basis of the Bernal-Fowler theory. However, the fact that there are some exceptions probably indicates that there are factors other than the polarizing power of the ions which should be considered in developing a more complete theory.

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