The Infrared Absorption of Acid Solutions

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A study has been made of the absorption of aqueous solutions of HCl, HF, HBr, H_2SO_4, HNO_3, NaCl and NaBr in the region from 1.7μ to 6.5μ. Also HCOOH, C_6H_5COOH have been studied from 5μ to 6.5μ. No absorption bands were found for HCl and HBr in the regions of 3.5μ and 3.8μ, respectively, where there are strong bands in the gaseous state. All of the acid solutions showed a strong band at about 5.5μ. The position of this band varied slightly with the solute and the sharpness of the band was different for each acid. Another band was found at 2.40μ for the solutes. The 5.5μ band is explained as due to the undissociated molecule attached to a water molecule and the 2.40μ band as due to the same effect or to a hydrogen ion attached to a water molecule.

CONSIDERABLE work has been done on the absorption of solutions in the near infrared by H. C. Jones and his co-workers.[1] These researches did not extend beyond 1.5μ and left a large region of the infrared unexplored. Also very little attention was given to the study of inorganic acids and bases. In many cases the bands were due to harmonics and combinations and thus were difficult to interpret. The work of Collins[2] to 2.2μ on the absorption of 16 inorganic compounds in solution showed that the absorption of water was influenced by the presence of the solute. Collins was not interested in finding bands due to solutes, but he showed that the hydroxides had bands in the regions of 0.96μ, 1.1μ and 1.27μ. Grantham[3] had previously shown than NaOH, KOH, LiOH and CsOH had a band at 2.29μ and NH_4OH had a band at 2.20μ. In view of the agreement in position of this absorption band for the various hydroxides, Grantham concluded that it was due to the dissociated OH ion.

All ions, except those which are monatomic, should have characteristic absorption bands; and a monatomic ion, if attached to a water molecule, may also produce an absorption band. Due to the difficulty in interpreting overlapping bands in the shorter wave-length region, it was felt that further and more definite information could be best obtained by work in the longer wave-length regions. For this reason, the present work has been concentrated in the region from 1.7μ to 6.5μ.

A Hilger infrared spectrometer with fluorite prism was used for resolving the spectra and a thermopile with galvanometer was used for detecting the radiation. The galvanometer was used in connection with a Moll thermorelay with a subsidiary galvanometer, which greatly increased the deflections. The other arrangements were of the usual type.

The greatest difficulty was found in determining the thickness of cell to bring out the bands properly. Because of the intense absorption of water at 3μ and 6μ, extremely thin layers of the solution were used. Below 2.8μ the cells were made of two very thin glass plates, 0.1 mm apart. For the longer wave-lengths either mica or fluorite plates were used. For some of the thicker cells thin mica washers were satisfactory, but a great portion of this investigation was done with thicknesses of solution from 0.001 mm to 0.01 mm. Since washers are impractical for such cells, it was found necessary to make cells of varying thicknesses and test each one until a satisfactory thickness was obtained. The general procedure was to take one of the plates, put a drop or so of the solution on it, place the other plate upon it, and then move the plates one upon the other until the liquid was evenly distributed and the layer sufficiently thin. The plates were then sealed. The plates used had an area of some 4 sq. cm. These extremely thin cells were necessary, for otherwise the intense

[1] Jones, *Absorption Spectra of Solutions*, Carnegie Inst. of Washington, Publication Number 210.

[2] J. R. Collins, Phys. Rev. **20**, 486 (1922).

[3] G. E. Grantham, Phys. Rev. **18**, 339 (1921).

absorption of water at 3μ would have masked any absorption due to the solute.

The first work in this investigation was done in the region between 1.6μ and 2.8μ. In Fig. 1 are shown the transmission curves for H_2O, 36 percent HCl, 65 percent HNO_3, 32 percent HNO_3, and in Fig. 2, those of saturated solution NaCl, 48 percent HBr, 48 percent H_2SO_4, 96 percent H_2SO_4. The cell thickness was very nearly the same in all cases, as may be known from their having approximately the same transmission at 1.6μ. From these curves it can clearly be seen that there is a marked effect in the region of about 2.40μ due to the presence of various acids. In order to determine whether these bands were due in any sense to the negative ion, curves were obtained for NaCl and NaBr in saturated solutions at 23°C. If the absorption in the curves for the solutions of HCl or HBr was due to the negative ion attached to a water molecule, the band at 2.40μ should also appear in curves for these salts. An inspection of Fig. 2 will show that no such absorption has been observed in NaCl. NaBr likewise failed to show any absorption. If there is any modification of the 2μ absorption band of water at all, due to the presence of the solutes, it is not to any great extent. The study of the modification of water bands was not the purpose of this investigation and a careful study of the point has not been made. The percentage transmissions of the solutions as compared with that of water is shown in Fig. 3. All the acids studied give a strong band in the region of 2.40μ, which is attributed to either an undissociated acid molecule or a hydrogen ion attached to a water molecule. The curves have in general the same shape, except that for 65 percent HNO_3. The distortion of this band may be due to the NO_3 ion. It should also be kept in mind that when the percent transmission of a solution is plotted against the transmission of water, small errors in the original data are greatly magnified. In the region from 2.7μ to 4.9μ the transmission of the solutions was practically identical with that of water and, as in the case of the 2μ water band, there was no appreciable modification of the 3μ band due to the presence of the solutes.

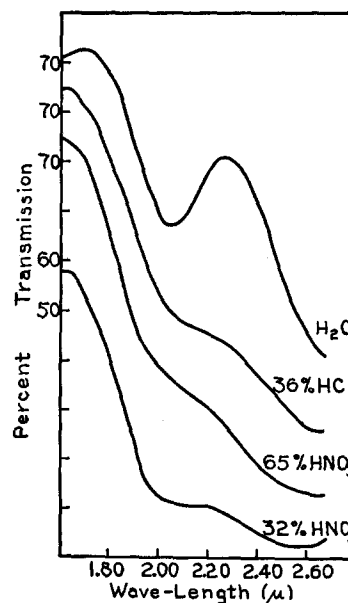HCl in the gaseous state has an intense absorption band at about 3.5μ. This region was

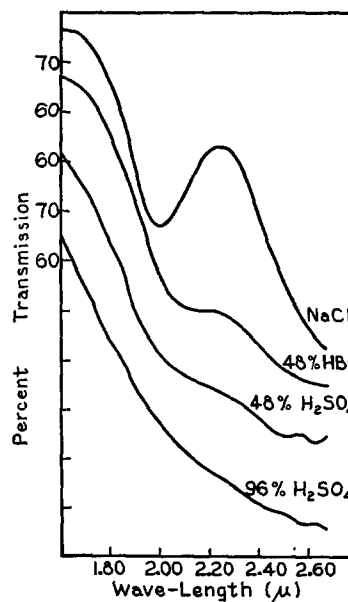Fig. 1. Percent transmission of water, 36 percent HCl, 65 percent HNO_3 and 32 percent HNO_3.

Fig. 2. Percent transmission of NaCl solution saturated at 23°C, 48 percent HBr, 48 percent H_2SO_4 and 96 percent H_2SO_4.

carefully studied in an effort to determine if this band were present in solution. The band was not found, and this non-appearance is taken as an indication that, when in an aqueous solution, there can be only a small percent, if any, of the HCl molecules in a state similar to that of those
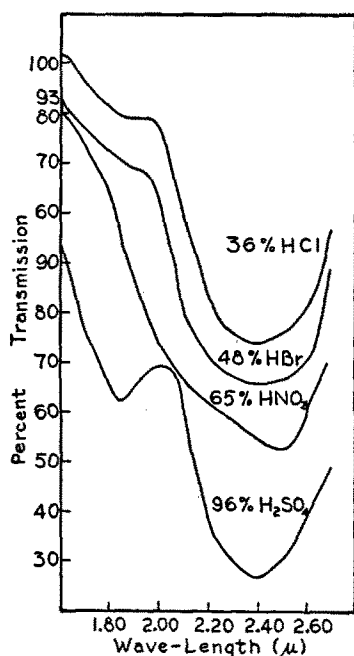
FIG. 3. Transmission in region of 2.40μ of 36 percent HCl, 48 percent HBr, 65 percent HNO$_3$, and 96 percent H$_2$SO$_4$, as compared to that of H$_2$O.

in the gaseous form. The band at about 3.8μ for HBr also failed to appear.

Fig. 4 shows the transmission of H$_2$O and solutions of 45 percent HF, 36 percent HCl, and 48 percent HBr in the region of 5.0μ to 6.5μ. In addition to the bands which are observed in water, there is a strong band at about 5.5μ, which was found for all the acid solutions. The intensity of this band is greater even than that of the strong 6.18μ water band, as can be seen in Fig. 4 by an examination of the absorption maxima for the solutions at 5.5μ as compared with the absorption of water at 6.18μ. The centers of the bands for the solutions correspond only approximately and there is a gradual shift to the longer wave-lengths as the halogen ion increases in atomic weight, the bands for HCl and HBr being much sharper than that of HF. The difference in shape of the HF band may be due to the presence of both HF and H$_2$F$_2$ in the solution. Fig. 5 shows a comparison of the transmission of water with that of solutions of 0.5 percent C$_6$H$_5$COOH, 90 percent HCOOH, 65 percent HNO$_3$, and 96 percent H$_2$SO$_4$. These solutions show absorption in the same region as

TABLE I.

Solutions	Observed bands	Solutions	Observed bands
HBr	5.52μ	HCOOH	5.62μ
HCl	5.48	H$_2$SO$_4$	5.58
HF	5.46	HNO$_3$	5.62
C$_6$H$_5$COOH	5.60		

the other acids shown in Fig. 4, but the bands have been shifted to longer wave-lengths and the maxima occur at about 5.6μ. Table I gives the position of the observed bands. There is a marked difference in intensity for this band in these acids. This difference in intensity is, no doubt, in part due to the difference in concentration of the various solutions, and the very low intensity of the band observed for the benzoic acid solution can be accounted for in this way. The relation between the transmission of H$_2$O, and saturated solutions of NaBr and NaCl was studied. These salts do not show the strong band at 5.5μ which has been observed in the case of the acids. In fact, the curves show only the water bands, and correspond as well as
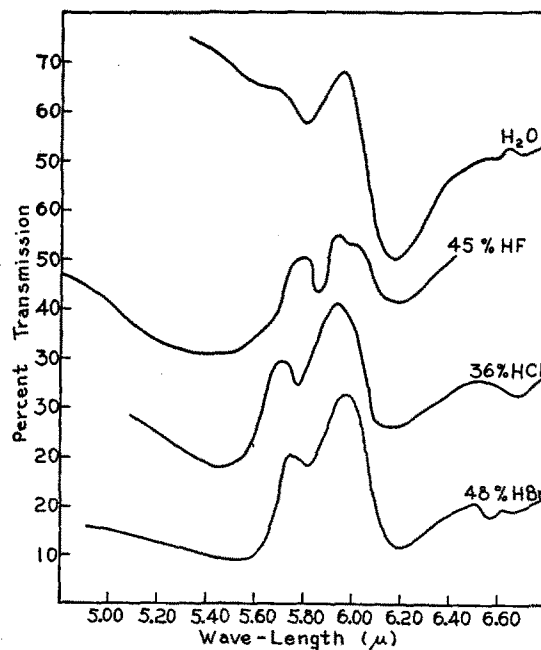

FIG. 4. Percent transmission of H$_2$O, 45 percent HF, 36 percent HCl and 48 percent HBr.
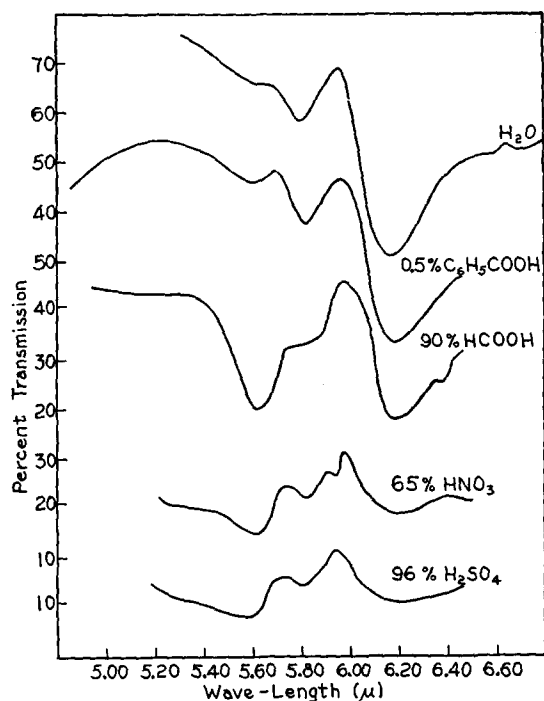
FIG. 5. Percent transmission of H_2O, 0.5 percent C_6H_5COOH, 90 percent HCOOH, 65 percent HNO_3 and 96 percent H_2SO_4.

separate observations made upon water check with each other.

As was noted above, HCl and HBr in solution do not give the strong absorption bands at 3.5μ and 3.8μ, respectively, which are found for these substances in the gaseous form. On account of the general similarity of the absorption bands in the region of 5.5μ due to the acid solutions, it is probable that they have a like origin. Since the only common constituent of the acids is the hydrogen atom, the bands must be caused by either the whole molecule attached to a water molecule through the hydrogen atom, or the hydrogen ion attached to a water molecule. If the latter case is true, then the observed differences in position and shape of these bands must be attributed to the influence of the negative ion at close distances to the $H_3{}^+O$. In order to test this point, a series of observations was taken on the transmission of HBr at concentrations from 1 to 48 percent. These results are shown in Fig. 6. As can be seen, there is no appreciable change in the position of this band with concentration.
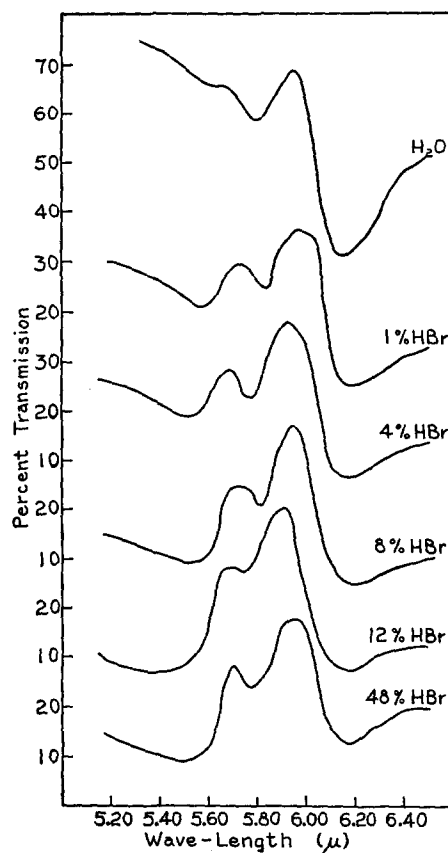

FIG. 6. Percent transmission of H_2O and 1 percent, 4 percent, 8 percent, 12 percent and 48 percent HBr.

From this check and other experimental work,[4] it seems probable that the vibrational energy levels observed in the region of 5.5μ are due to the vibration of the acid molecule as a whole against the water molecule when attached to a water molecule through the hydrogen of the acid. This interpretation may seem inconsistent with not finding the bands at 3.5μ and 3.8μ for HCl and HBr, respectively. However, this inconsistency may be explained by considering the changes in the vibrational energy which take place in the hydrated acid molecule. This may well cause a shift of the band to longer wave-

[4] In hydrolizing salts, such as $ZnCl_2$ and Na_2CO_3, it has been recently found that the 5.5μ acid band is intense when the solution gives a hydroxide test and is of very low intensity when the solution gives an acid test. This indicates that this band is due to the presence of the undissociated acid molecule.

lengths. In work with the Raman effect, shifts have been found[5] in the spectral lines which correspond to the absorption bands at 9.5μ and 11μ for solutions of HNO_3 and H_2SO_4, respectively. These bands may be due to the new vibration of the acid molecule in solution rather than to the vibrational frequency of the molecule in the gaseous state. Further work is now in progress in order to see if all acids have their absorption bands as observed in the gaseous state shifted to longer wave-lengths when in solution.

In Fig. 6 it is of interest to note that the 5.5μ band is still present even with a one percent solution of HBr. The intensity of the band seems to vary directly as the concentration, without any sudden change, but to decide this point more definitely a very detailed study must be made.

[5] S. K. Mukherjee and P. N. Sengupta, Ind. J. Phys. **3**, 503 (1929); I. R. Rao, Nature **124**, 762 (1929).