Near Infrared Absorption of Solutions of Hydroxides and Hydrolyzing Salts

Walter Gordy

Citation: The Journal of Chemical Physics **2**, 621 (1934); doi: 10.1063/1.1749362
View online: http://dx.doi.org/10.1063/1.1749362
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/2/10?ver=pdfcov
Published by the AIP Publishing

THE JOURNAL
OF
CHEMICAL PHYSICS

VOLUME 2 OCTOBER, 1934 NUMBER 10

Near Infrared Absorption of Solutions of Hydroxides and Hydrolyzing Salts

WALTER GORDY, *Department of Physics, University of North Carolina*
(Received August 9, 1934)

Absorption bands have been observed at 2.60μ, 2.30μ, 1.81μ, 1.30μ, 1.22μ, 1.04μ, 0.87μ, 0.79μ, 0.75μ and 0.67μ in aqueous solutions of hydroxides and hydrolyzing salts. From the behavior of the salt solutions the bands at 2.60μ and 1.81μ were found to be characteristic of the hydroxide molecule, while the band at 2.30μ was found to be characteristic of the OH ion. It was found that if the 2.30μ band, and the 3.65μ and 5.20μ bands previously observed were considered as fundamentals, the remaining bands observed could be classified as harmonics.

RECENTLY a study has been made of solutions of certain hydroxides and hydrolyzing salts[1] in the region from 2.8μ to 6.5μ. All bases showed intense bands at 3.65μ and 5.2μ, and from the absorption of the hydrolyzing salts it was concluded that these bands were due to changes in energy levels of the hydroxide molecules attached to water molecules. Plyler and Barr[2] have studied a number of acid solutions in the region from 1.7μ to 6.5μ and have found absorption bands at 2.4μ, and 5.5μ. Collins[3] observed bands at 0.96μ, 1.10μ and 1.26μ in alcoholic solutions of certain hydroxides, and Grantham[4] observed a band at 2.29μ in aqueous solutions of some hydroxides. A recent study by Plyler and Williams[5] of solutions of hydroxides in alcohol has revealed a number of bands not observed before. The present work was undertaken to see if other bands could be found in aqueous solutions in the near infrared, and to attempt through a study of hydrolyzing salts to obtain more information about the 2.29μ band previously observed.

The experimental method was the same as that used by Plyler and Barr. A quartz prism was used in the region from 0.60μ to 1.26μ and one of fluorite in the region from 1.26μ to 2.8μ. The cell thicknesses were: 2 cm for the range 0.6μ to 1.1μ; 0.5 cm for the range 1.10μ to 1.26μ; 0.01 cm in the range 1.26μ to 2.8μ. Cell windows for the entire region studied were of thin plate glass.

The first two curves in Fig. 1 show the absorption of 10N solutions of NaOH and KOH, the upper curve being for the former. The bottom curve is for 5N LiOH solution. It will be noticed that all of these curves show definite minima at approximately the same positions, at about 0.75μ, 0.79μ, 0.87μ, 1.04μ and 1.22μ. Another band at about 0.67μ was also found but is not shown in the figure. The lower intensity of the LiOH bands is due to the lower concentration. Fig. 2 shows the absorption of the same solutions in the region from 1.26μ to 2.8μ. Here it will be noticed that each solution shows intense bands with minima at 2.3μ and 2.6μ. There are

[1] E. K. Plyler and Walter Gordy, J. Chem. Phys. **2**, 470 (1934).
[2] E. K. Plyler and E. S. Barr, J. Chem. Phys. **2**, 306 (1934).
[3] J. R. Collins, Phys. Rev. **20**, 486 (1922).
[4] G. E. Grantham, Phys. Rev. **18**, 339 (1920).
[5] E. K. Plyler and F. D. Williams, J. Chem. Phys. **2**, 564 (1934).

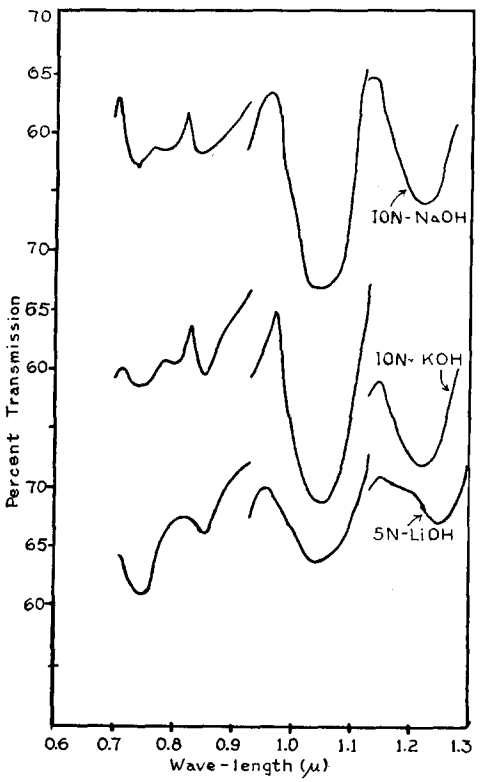

FIG. 1. Absorption in the region of 0.6μ to 1.26μ for aqueous solutions of hydroxides, cell thicknesses being 2 cm for the range 0.6μ to 1.1μ and 0.5 cm from 1.1μ to 1.26μ.

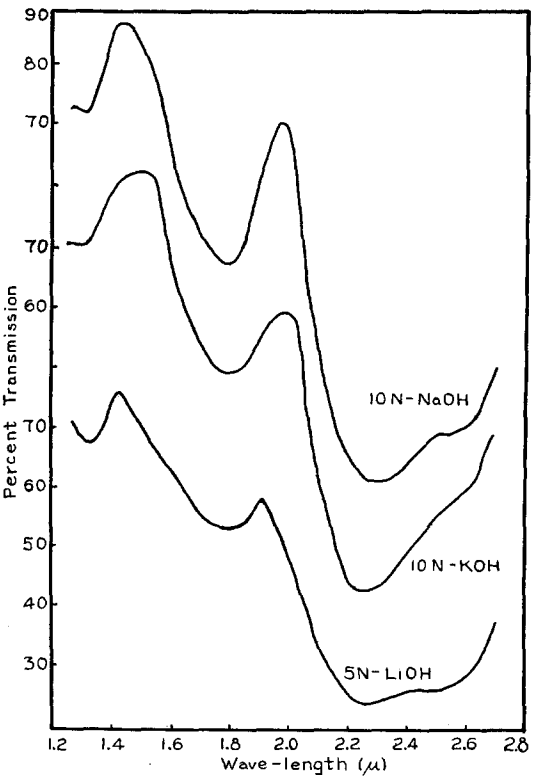

FIG. 2. Absorption in the region from 1.26μ to 2.8μ for aqueous solutions of hydroxides, cell thickness being 0.01 cm.

also definite bands in the regions of 1.3μ and 1.81μ. From the results of the study of hydrolyzing salts, it is possible to draw definite conclusions about the bands at 1.81μ, 2.3μ and 2.6μ. It will be observed in Fig. 3 that the salts which are basic in solution, namely, Na_2CO_3 and $NaC_2H_3O_2$, show strong absorption at 2.3μ; whereas, in the case of salts which give an acid reaction in solution, namely, $ZnCl_2$ and $ZnBr_2$, the absorption is much weaker in this region. Since this band has been shown to be due to the hydroxides the above mentioned variations in intensity of hydrolyzing salts indicate that the absorption is due to changes in energy levels between the OH ions and the water molecule. Oppositely, the bands at 1.81μ and 2.6μ are more intense for the salt solutions giving acid reaction and less intense for those which are basic in solution. This intensity variation is followed by all salts studied except $NaC_2H_3O_2$. The absorption of acetic acid solution was measured in this region, and was found to have bands which account for this discrepancy. This intensity change shows that the 1.81μ and 2.6μ bands are due to the hydroxide molecule. They are in the approximate positions for the first harmonics of the 3.65μ and 5.2μ bands reported by Plyler and Gordy, and shown by them to be due to the undissociated

TABLE I. *Classification of observed bands.*

Term	Frequency in cm^{-1} Cal.	Obs.	Wave-length in microns Cal.	Obs.
ν_1	1923	1923	5.20*	5.20
ν_2	2739	2739	3.65*	3.65
$2\nu_1$	3846	3846	2.60	2.60
ν_3	4348	4348	2.30*	2.30
$2\nu_2$	5494	5524	1.82	1.81
$3\nu_1$	5769		1.73	
$4\nu_1$	7692	7692	1.30	1.30
$3\nu_2$	8196	8196	1.22	1.22
$2\nu_3$	8695		1.15	
$5\nu_1$	9615	9615	1.04	1.04
$4\nu_2$	10989		0.91	
$6\nu_1$	11494	11494	.87	0.87
$3\nu_3$	12987	12645	.77	.79
$5\nu_2$	13698	13333	.73	.75

* Observed values taken as calculated.

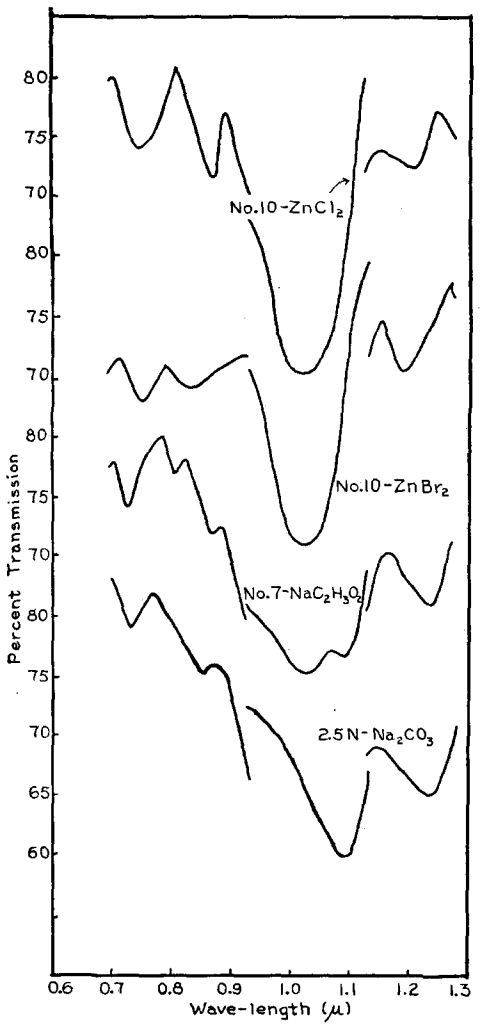

FIG. 3. Absorption in the region of 0.6μ to 1.26μ for aqueous solutions of hydrolyzing salts, cell thicknesses being 2 cm for the range 0.6μ to 1.1μ and 0.5 cm from 1.1μ to 1.26μ. *Note:* The curves No. 10 and curve No. 7 should read 10 N and 7 N, respectively.

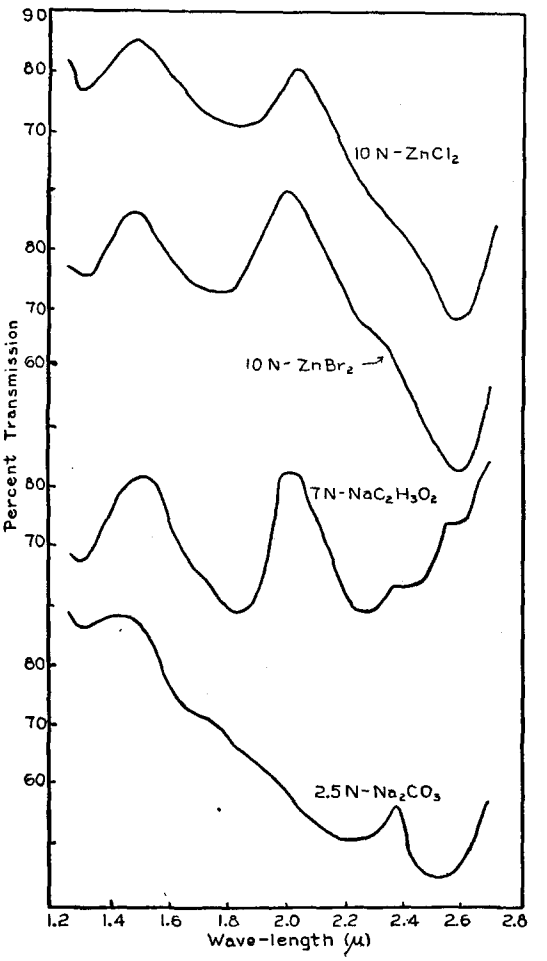

FIG. 4. Absorption in the region of 0.6μ to 1.26μ for aqueous solutions of hydrolyzing salts, cell thickness being 0.01 cm.

hydroxide molecule attached to water molecules. Because the 2.4μ acid band was between the 2.6μ hydroxide molecule band and the 2.3μ OH ion band, it was impossible, from the behavior of the salts, to conclude whether it was the acid molecule or ion attached to water. It was also impossible, because of low intensity and overlapping of higher harmonics, to apply this method of interpretation to the shorter wavelength bands. These harmonics were observed for all the salts and are shown in Fig. 4.

All bands observed for aqueous solutions of hydroxides were classified and are shown in Table I. The 2.3μ, 3.65μ and 5.2μ bands were considered as fundamentals, and it was found that all other bands could be classified as harmonics of these bands, with the exception of a small band at 0.67μ. The second harmonic of the 5.2μ band, the third harmonic of the 3.65μ band and the first harmonic of the 2.3μ band could not be resolved though higher harmonics of these respective bands were observed.

The writer wishes to express his thanks to Dr. E. K. Plyler who offered many helpful suggestions about this work.