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produced by the molecules of an association compound. Although it is impossible from the observation of only one absorption band to determine definitely the nature of the mechanism producing it, the authors are inclined toward a belief in the existence of an association compound, since the absorption coefficient at  $2.7\mu$  for an acetone-water mixture is several times greater than the absorption of water at the  $3\mu$  water band.

By comparison with the set of absorption curves in Fig. 3, small amounts of water in

acetone can be determined in a quantitative manner. For example, the absorption curve for the sample of supposedly absolute acetone used for Fig. 2 shows a band which by comparison with the curves of Fig. 3 indicates the presence of approximately 0.3 percent water. Concentrations of water as low as 0.1 percent give rise to appreciable absorption bands in the  $2.7\mu$  region. As a test for the presence of water in acetone this method is more rapid and more accurate than the usual tests involving anhydrous copper sulphate.

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## The Infrared Absorption Spectra of Deuterioxide Solutions in Deuterium Oxide

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The infrared absorption spectra of deuterium oxide and deuterioxide solutions in D<sub>2</sub>O have been measured in the region from  $2.5\mu$  to  $9\mu$ . Also solutions of Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> in D<sub>2</sub>O have been studied in the same region. The spectra of deuterium oxide possess strong bands at  $4.0\mu$  and  $8.2\mu$  and the results agree with those of other workers. The absorption at  $4.0\mu$  is probably composed of several overlapping bands. Intense bands were observed in the NaOD solutions at  $3.1\mu$ ,  $4.95\mu$  and  $7.1\mu$ . The hydrolyzing salts in

D<sub>2</sub>O gave rise to bands in these regions, but with some shifts in wave-length. The changes in the spectra were probably caused by the absorption of the CO<sub>3</sub> ion and D<sub>2</sub>CO<sub>3</sub> which was formed in the solution. The relation of the absorption of NaOD in D<sub>2</sub>O to the absorption of NaOH in H<sub>2</sub>O is discussed. It is concluded that the OD ion has an absorption band at  $3.1\mu$  and that the bands at  $4.95\mu$  and  $7.1\mu$  are produced by hydration.

THE infrared absorption spectra of several hydroxides in aqueous solutions have already been measured.<sup>1</sup> Absorption bands were found at  $3.65\mu$  and  $5.2\mu$ . Grantham<sup>2</sup> had previously found a band at  $2.3\mu$  which was characteristic of all hydroxide solutions. He concluded that this band was due to the absorption of the OH ion. By studying the intensity of the  $2.3\mu$  band in solutions of hydrolyzing salts it has been shown<sup>1</sup> that this band is due to the OH ion. The bands produced by alcoholic solutions of hydroxides have also been measured.<sup>3</sup> There is little difference in the absorption spectra of the hydroxides in solutions of water or alcohol except for the shift of the band at  $3.65\mu$  in

aqueous solutions to  $3.8\mu$  for the alcoholic solutions.

The present work was undertaken to find the change in these bands due to the substitution of deuterium for hydrogen in the aqueous solutions. On account of the increase in mass there should be an appreciable shift to the longer wavelengths of the vibrational frequencies which were observed for the ordinary aqueous solutions. Deuterium oxide, marked 99.5 percent, was obtained from the California Isotope Company, Berkeley, California, and also a solution of NaOD in deuterium oxide. A large type Hilger infrared spectrometer with a fluorite prism was used in the region from  $2.5\mu$  to  $6.9\mu$  and a rocksalt prism from  $6\mu$  to  $9\mu$ . In order to observe the band in the  $7\mu$  region with a single prism the observations with the rocksalt prism were started at  $6\mu$ . The effective slit width at  $4\mu$  was

<sup>1</sup> E. K. Plyler and Walter Gordy, *J. Chem. Phys.* **2**, 470 (1934).

<sup>2</sup> G. E. Grantham, *Phys. Rev.* **18**, 339 (1921).

<sup>3</sup> E. K. Plyler and Dudley Williams, *J. Chem. Phys.* **2**, 566 (1934).

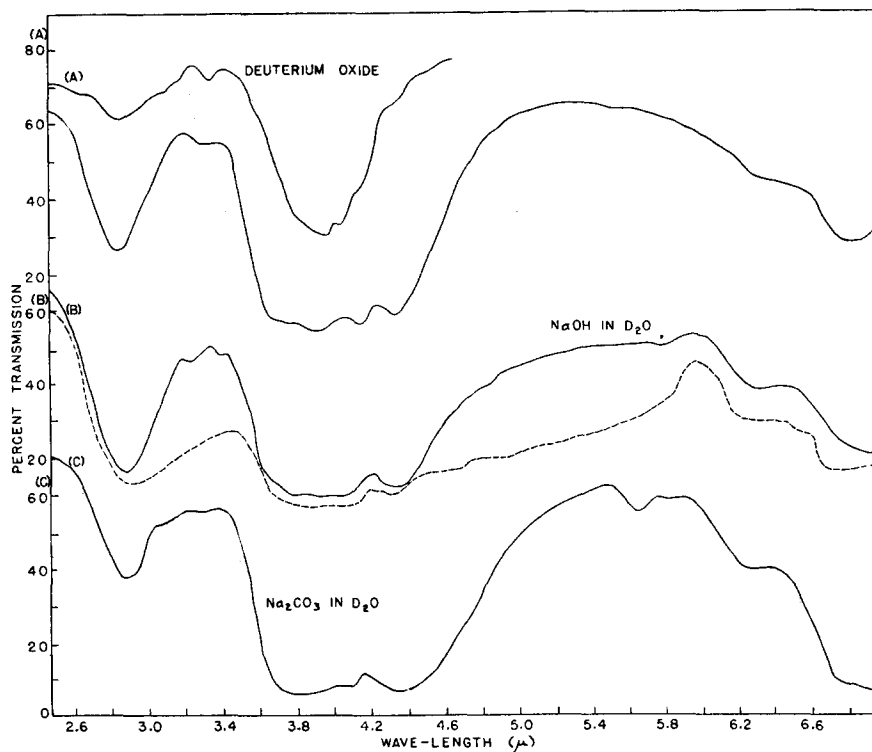


FIG. 1. The percent transmission of deuterium oxide and of certain concentrated solutions from  $2.5\mu$  to  $6.9\mu$ .

$0.03\mu$  and at  $8\mu$  was  $0.04\mu$ . Narrow slits were possible on account of the use of a thermorelay for increasing the deflections. Fluorite windows were used on the cells and they did not absorb very much below  $9\mu$  because they were about 2 mm thick. The absorption cell was made by placing mica washers  $0.03$  mm in thickness between the fluorite plates.

The infrared absorption spectra of deuterium oxide were first measured in order to have a comparison spectra to be used with the hydroxide solutions. The results obtained are represented in Fig. 1 and Fig. 2. Deuterium oxide has already been studied by Ellis and Sorge<sup>4</sup> and also by Casselman.<sup>5</sup> The absorption spectra found in the present work agree well with those previously found. In fact the intensity and position of the stronger bands are markedly similar to those found by Ellis and Sorge. Intense bands were observed at  $2.85\mu$ ,  $4.00\mu$ ,  $6.80\mu$  and  $8.20\mu$ . The broad band in the region of  $4.0\mu$  appeared to have four maxima. A thin

cell was made by placing a drop of deuterium oxide between fluorite windows and pressing them together. The first curve in Fig. 1 shows the transmission through the thin cell. From the intensity of the bands it is estimated that

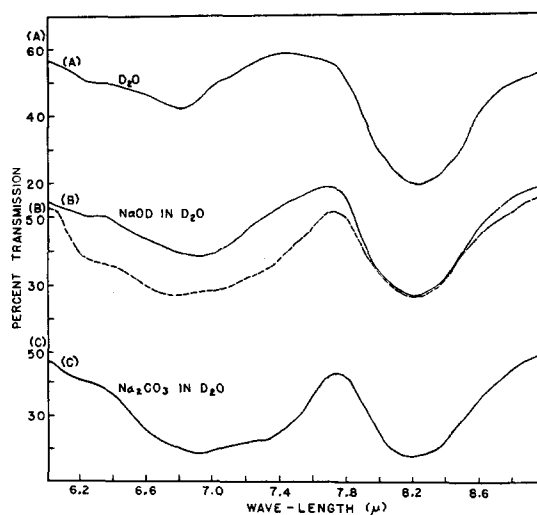


FIG. 2. The percent transmission of heavy water and solutions from  $6.0\mu$  to  $9.0\mu$ . Cell thickness:  $0.03$  mm.

<sup>4</sup> J. W. Ellis and B. W. Sorge, J. Chem. Phys. 2, 559 (1934).

<sup>5</sup> A. L. Casselman, Phys. Rev. 45, 221 (1934).

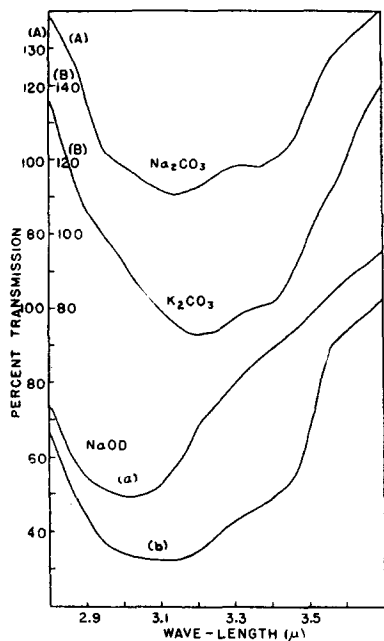


FIG. 3. Ratio of the transmission of certain solutions to that of the solvent. Region:  $2.8\mu$  to  $3.8\mu$ . (a) 0.18 g of NaOD dissolved in 0.66 g D<sub>2</sub>O; (b) 0.18 g of NaOD dissolved in 1.00 g D<sub>2</sub>O. The K<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> solutions were saturated at 26°C.

the cell thickness is 0.01 mm. Weak bands appear at  $2.65\mu$  and  $3.35\mu$ , but it was impossible to separate the bands in the region of  $4.0\mu$ . In ordinary water two fundamental bands occur at  $2.78\mu$  and  $2.92\mu$ . If the absorption at  $4.0\mu$  in D<sub>2</sub>O represents the two similar fundamental bands, they may overlap so that it is impossible to resolve them. Also the first harmonic of the  $8.20\mu$  band falls in the  $4.0\mu$  region. This may in part account for the difficulty in separating the band into its components. Because of the presence of small amounts of H<sub>2</sub>O and HOD many small bands will be present. For example, the absorption band at  $2.85\mu$  may in part be due to H<sub>2</sub>O and the combination of the  $4.0\mu$  and  $8.20\mu$  bands. Also, the region of  $6.8\mu$  appears to have several bands overlapping.

The solutions of NaOD in D<sub>2</sub>O were studied with the same cell thickness as used for D<sub>2</sub>O. The two concentrations were plotted to the same scale and show the regions of increase in absorption due to the presence of NaOD in solution. This absorption is readily observed without the necessity of plotting the ratio of the transmission of the solution to that of water. The greater

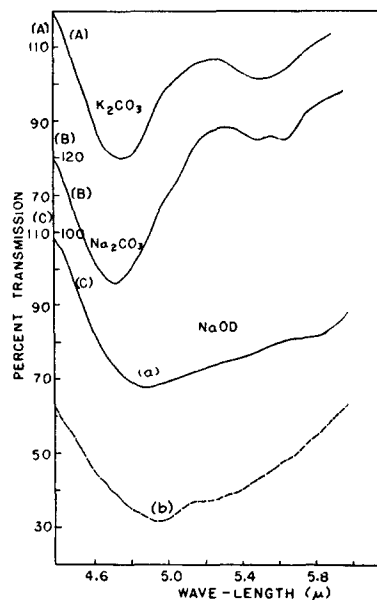


FIG. 4. Ratio of the transmission of solutions in D<sub>2</sub>O to that of D<sub>2</sub>O. Region:  $4.4\mu$  to  $6.2\mu$ . Concentrations of (a) and (b) are the same as in Fig. 3.

absorption is in the regions of  $3.1\mu$ ,  $4.9\mu$  and  $7.1\mu$ . Solutions (saturated at 26°C) of Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> in D<sub>2</sub>O were also studied. Sodium and potassium carbonates were chosen for study because on hydrolysis these salts produce OD ions and because they are easily freed from H<sub>2</sub>O. However, these compounds produce bands arising from the CO<sub>3</sub> group and these bands add to the complexity of the spectra of the solution. For example the strong absorption observed in the region of  $7\mu$  is due in part to the CO<sub>3</sub> group. All compounds containing CO<sub>3</sub> have an intense band in this region, which has only been observed by reflection.

In Fig. 3 the absorption in the region of  $3.1\mu$  is shown. The percent transmission of these curves was obtained by taking the ratio of the transmission of the solutions to that of D<sub>2</sub>O. The transmission of the more concentrated NaOD is about 30 percent at  $3.1\mu$ . Since the cells were of the same thickness (0.03 mm) for solutions and D<sub>2</sub>O, the water content of the solution cells is less than in D<sub>2</sub>O cell. This causes the percent transmission of the solutions, when the ratio to D<sub>2</sub>O is taken, to be greater than the actual value for cells containing equal numbers of D<sub>2</sub>O molecules. The effect due to

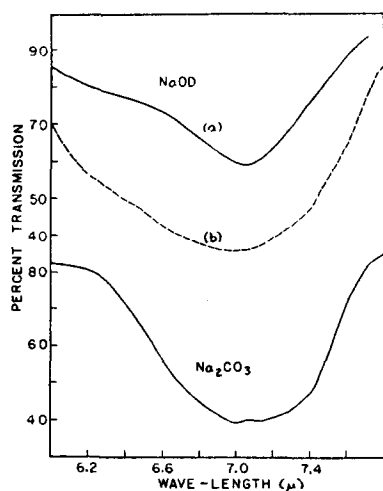


FIG. 5. Transmission of certain solutions compared with  $D_2O$ . Region:  $6.0\mu$  to  $7.8\mu$ . Concentrations of (a) and (b) are the same as in Fig. 3.

effective cell thickness is greatest in the regions of most intense  $D_2O$  absorption and in some of the curves the transmission ratio is greater than 100 percent. On account of the narrow band in  $D_2O$  at  $2.85\mu$ , the absorption band in the solutions of NaOD at  $3.1\mu$  vary in position. In the more concentrated solution of NaOD another band is present at  $3.45\mu$ . This band may be the first harmonic of the absorption in the region of  $7\mu$ . The curve *a* has a weak absorption band in this region. Curves *a* and *b* are plotted to the same scale and show the increase in absorption in this region as the amount of NaOD in the solution is increased.

The absorption bands of  $Na_2CO_3$  and  $K_2CO_3$  are more complex in this region. The maximum absorption occurs at about  $3.2\mu$ . The absorption band at  $3.4\mu$  is in part due to the  $CO_3$  group, which has an intense band in this region. The  $D_2CO_3$  formed by hydrolyzing salts may produce bands in this part of the spectrum. However, the absorption in this region is probably in part due to deuteroxide.

In Fig. 4 the absorption for the  $4.9\mu$  region is plotted. No appreciable absorption bands were observed between  $3.1\mu$  and  $4.9\mu$ . The intensity of the bands in the  $4.9\mu$  region is about the same

as observed at  $3.1\mu$ . The bands observed in  $K_2CO_3$  and  $Na_2CO_3$  solutions are much sharper than in the NaOD solutions and appear at a shorter wave-length. The positions are  $4.75\mu$  and  $4.95\mu$ , respectively. Further differences are shown in the appearance of bands at  $5.5\mu$  for the salt solutions. These bands may have their origin in  $D_2CO_3$  or the  $CO_3$  ion.

In Fig. 5 is represented the absorption in the region of  $7\mu$ . The  $Na_2CO_3$  and  $K_2CO_3$  absorption is here equal to that of the stronger solution of NaOD. This increase in intensity of absorption of the salt solutions is due to the intense absorption of the  $CO_3$  ion in this region. The  $K_2CO_3$  and  $Na_2CO_3$  salt solutions have similar absorption at these wave-lengths and only  $Na_2CO_3$  has been plotted in Fig. 5.

There is a similarity in the absorption spectra of the solutions of hydroxides in ordinary water and that of solutions of deuteroxide in  $D_2O$ . Three intense bands were found at  $3.1\mu$ ,  $4.95\mu$  and  $7.1\mu$  for compounds containing deuterium. The distribution of these bands in the spectra is similar to that of ordinary hydroxides, which have bands at  $2.3\mu$ ,  $3.65\mu$  and  $5.2\mu$ . Also the ratio of the frequencies of the bands in the hydroxide solutions to those appearing in the spectra of deuteroxide solutions is approximately equal to the change calculated by replacing H with D in the OH ion oscillator. The absorption band which is found at  $4.95\mu$  for the NaOD solutions occurs at  $4.75\mu$  in the hydrolyzing salts. This change in position may be produced by decrease in absorption of  $D_2O$  in this region. However, the same effect is found in the hydroxide solutions, the corresponding band being shifted from  $3.65\mu$  in hydroxides to  $3.45\mu$  in the hydrolyzing salt solutions. From the present study it is impossible to determine the origin of the bands. However, on account of the similarity to the absorption of hydroxide solutions it is concluded that the absorption band at  $3.1\mu$  for NaOD is produced by the OD ion. This corresponds to OH band at  $2.3\mu$ . The two bands at  $4.95\mu$  and  $7.1\mu$  are probably due to hydration and correspond to the bands at  $3.65\mu$  and  $5.2\mu$  in hydroxide solutions.