

## **Infrared Absorption Spectra of the Alcohols, Two Acids, and Their Solutions in Carbon Tetrachloride**

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## Infrared Absorption Spectra of the Alcohols, Two Acids, and Their Solutions in Carbon Tetrachloride

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(Received April 3, 1937)

The paper describes the absorption spectra of the first eight alcohols of the aliphatic series and of formic and acetic acids in the regions extending from 0.9 to 2.2 $\mu$  and from 2.0 to 4.0 $\mu$ . The absorptions of the pure liquids are compared with their absorptions in carbon tetrachloride solutions. For methyl and ethyl alcohols and the two acids comparisons are also made with their vapor spectra. In every case solution in carbon tetrachloride modifies the bands characteristic of the hydroxyl group and leaves unchanged the hydrocarbon bands. The modifications are attributed to polymers or lattice structures which are partially destroyed in the solutions. Four bands near 0.96,

1.40, 1.89 and 2.1 $\mu$  for the alcohols and one near 1.40 $\mu$  for the acids which are present in the solution spectra are attributed to single molecules. Each of them in the solution spectra is accompanied by a broad almost continuous region of absorption on its long wave-length side, attributed to polymers, which grows stronger with increasing concentration until in the pure liquid it practically replaces the sharper bands predominating in the solution. The bands of the single molecules can still be detected, however, in each of the pure liquid alcohols. Comparison is made with the spectrum of aniline whose behavior near 1.4 $\mu$  is peculiar.

THE work of several investigators<sup>1-4</sup> has shown that the spectra of liquid organic compounds containing the hydroxyl group undergo modification when these substances are dissolved in nonpolar solvents such as carbon disulfide and carbon tetrachloride. The most striking of the observed changes occurs in the 1.4 $\mu$  overtone band of the hydroxyl group of the alcohols. The liquid alcohols possess in this region a very broad, almost continuous, absorption. When they are diluted with carbon tetrachloride a very strong and narrow band develops, for each alcohol, on the short wave-length side of the broad region, and the broad band itself grows weaker. The existence of these sharp bands in solutions 0.01 molar was first reported by Wulf and Liddell,<sup>1</sup> and they were used by these authors as a means of detecting the presence of hydroxyl groups. Several years ago, before the work of Wulf and Liddell had come to our notice, we began the study of this effect<sup>2</sup> in the region extending from 0.9 to 2.2 $\mu$ , giving our attention to a comparison of the liquid absorption with the absorption produced by the carbon tetrachloride-alcohol mixtures, rather than to the absorption of the solutions themselves. The purpose of this paper is to present these comparisons for the alcohols and

formic and acetic acids, and to indicate their bearing upon the phenomenon of molecular association in the liquid state. For purposes of comparison we have included records of the vapor absorption of methyl and ethyl alcohols, and of formic and acetic acids; and to make a comparison with the behavior of compounds containing the NH<sub>2</sub> group we have included records of the absorption of aniline.

Although the main points of the paper are concerned with the spectra obtained by means of the self-recording quartz spectrograph of the laboratory,<sup>5</sup> which extend from 0.9 $\mu$  to 2.2 $\mu$ , a series of absorption curves comparing the spectra of the liquids with the spectra of the liquids dissolved in carbon tetrachloride are given also for the region extending from 2.0 to 4.0 $\mu$  obtained under the much smaller dispersion and resolving power of a small Hilger rocksalt spectrometer. For the region reached by the quartz instrument, slit widths were equivalent to about 0.003 $\mu$ , and wave-length values are correct to within this accuracy.

The alcohols and the carbon tetrachloride were distilled, in many cases, several times either over calcium sulphate or magnesium perchlorate (anhydron), and the middle fraction of constant boiling point was collected. The solutions consisted of one part by volume of the alcohol or acid and nineteen parts of carbon tetrachloride,

<sup>1</sup> Wulf and Liddell, J. Am. Chem. Soc. **57**, 1464 (1935).

<sup>2</sup> Kinsey and Ellis, Phys. Rev. **49**, 105 (1936).

<sup>3</sup> Freyman, Ann. de physique **20**, 243 (1933).

<sup>4</sup> Naherniac, Comptes rendus **200**, 1742 (1935).

<sup>5</sup> J. W. Ellis, Rev. Sci. Inst. **4**, 123 (1933).

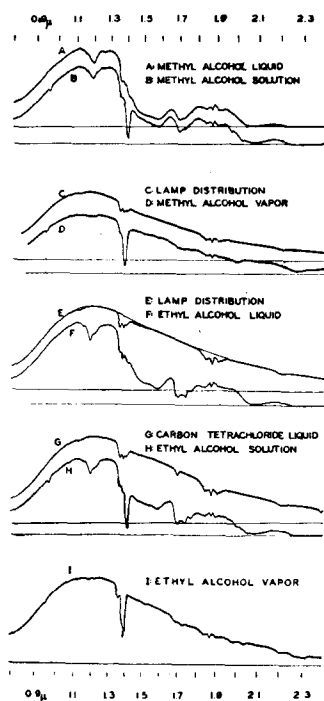


Fig. 1. Self-recorded transmission curves of the vapor, liquid, and  $\text{CCl}_4$  solution states of methyl and ethyl alcohols; liquid cell thickness, 2 mm; solution cell thickness, 4 cm; concentration, 1 : 19 by volume; vapor cell thickness, 96 cm. Vapor approximately saturated at room temperature.

unless otherwise noted, and were contained in a cell 4 cm long. The liquids were contained in a cell 2 mm long so that the solution and liquid records of any one alcohol compare spectra produced by the same total mass of the absorber. Any differences between the spectra produced by the liquids and the solutions will therefore be caused by a change in the character of the molecules of the solute brought about by the solvent or by solvent-solute molecule perturbations. Because of the use of the 1 : 19 ratio for all the solutions the molar concentrations range from 1.0 molar for methyl to 0.3 molar for octyl alcohol.

#### ALCOHOL RECORDS, 0.9 TO 2.2 $\mu$

Figs. 1, 2 and 3 present original records of the transmissions of the first eight alcohols of the aliphatic series obtained by the quartz spectrograph. Galvanometer deflections are automatically recorded and are plotted against wavelengths in  $\mu$ . The curves show, in addition to the

transmissions of the pure liquids and the carbon tetrachloride-alcohol solutions, transmissions of the vapors of ethyl and methyl alcohols. Bands or groups of bands to which it is desired to direct attention lie at 0.96, 1.15, 1.40–1.65, 1.70, 1.89, and 1.95–2.1 $\mu$ , and can be seen easily in the figures. Comparisons of the liquid and solution spectra show that the four of these which lie at 0.96, 1.40–1.65, 1.89, and 1.95–2.1 $\mu$  are strongly modified by solution in carbon tetrachloride and that the two at 1.15 and 1.70 $\mu$ , which are definitely known to be produced by vibrations characteristic of the hydrocarbon groups, are not.

The bands at 1.40 and 0.96 $\mu$  are undoubtedly the first and second overtones of the fundamental characteristic of the hydroxyl group which lies near 3 $\mu$ . The 0.96 $\mu$  band escapes detection in the liquid spectrum and appears as a fairly sharp but weak band in the solution lying at the same wavelength for all the alcohols. Freyman,<sup>3</sup> and later Naherniac,<sup>4</sup> have studied it in the liquid in thicker cells and in carbon tetrachloride solutions

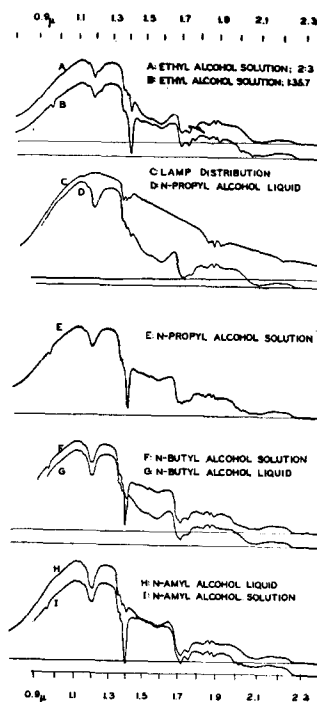


FIG. 2. Self-recorded transmission curves for: A, 5 mm cell of a 2 : 3 by volume  $\text{CCl}_4$  solution of ethyl alcohol; B, 7.5 cm cell of a 1 : 35.7 by volume  $\text{CCl}_4$  solution of ethyl alcohol; D to I, liquid and solution states of propyl, butyl, and amyl alcohols in cell lengths of 2 mm for the liquid, 4 cm for solution.

as a function of the concentration. It appears in ethyl and methyl alcohol vapors at  $0.948\mu$ .

The  $1.40\mu$  region presents features of the greatest interest. As we have mentioned, the broad absorption band so characteristic of the liquid spectrum of all the alcohols, and which stretches almost like a continuous spectrum (with some structure) from about  $1.4$  to  $1.65\mu$ , is considerably weakened in the solution spectrum and is accompanied on its short wave-length edge by a sharp band at  $1.408\mu$  which occurs at this same position in the eight alcohols examined. In every case the sharp band is feebly present at the same position in the liquid spectrum. In methyl and ethyl alcohol vapors it occurs at  $1.387\mu$  and  $1.395\mu$ , respectively. When the alcohols are diluted the broad band of the liquid spectrum, which appears to be double, develops sharper structure, the main features of which are strikingly similar although not exactly alike for all the alcohols.

The band at  $1.89\mu$  falls in a region where the galvanometer deflections are small and in the

midst of a band at  $1.87\mu$  produced by the absorption of the water vapor which was always present in the light path of the spectrograph. Its position in the solution at  $1.895\mu$  is the same for all the alcohols. A careful inspection of the plates shows that it occurs in the spectra of all the solutions, but is absent from the pure liquid records. In these it is replaced by what appears to be a broad continuous absorption on the long wave-length side of its position in the solution spectrum.

In the  $1.95$ – $2.1\mu$  region the same change in the spectrum in passing from liquid to solution occurs. The broad continuous region develops structure and deeper bands on its short wave-length side and becomes weaker toward long wave-lengths.

To show these features more clearly the liquid and solution records for heptyl alcohol, which were chosen as typical of the behavior of the eight alcohols, have been reduced, with the help of the background distribution curve, to give percent transmissions. These were obtained, for the solution, by allowing the radiation to traverse pure carbon tetrachloride contained in the same 4 cm cell which was used for the solution records. The ordinates of the background curve were multiplied by a factor, nearly unity, which was selected to adjust the deflection of the background curve equal to the deflection of the solution curve at a position of the spectrum free from the absorption of the alcohol. Ordinates were measured at intervals of  $0.5$  mm across the plate, that is at approximately every  $0.003\mu$ . In the reduced curves (Fig. 5) the percent transmissions are plotted against plate scale readings which may be converted into wave-lengths by means of the dispersion curve of the instrument, also given in the figure. The wave-length values for the dispersion curve are plotted vertically on the right. The behavior of the broad band of the liquid spectrum at  $1.4\mu$  and of the bands at  $1.89$  and  $2\mu$  perhaps can be followed more clearly in these records. The broad band at  $1.4$ – $1.65\mu$  in the solution has four components, each of which occurs in the spectra of the other alcohols.

#### DISCUSSION OF THE ALCOHOL SPECTRA

It seems to be generally agreed that the changes in the absorption spectra of the alcohols

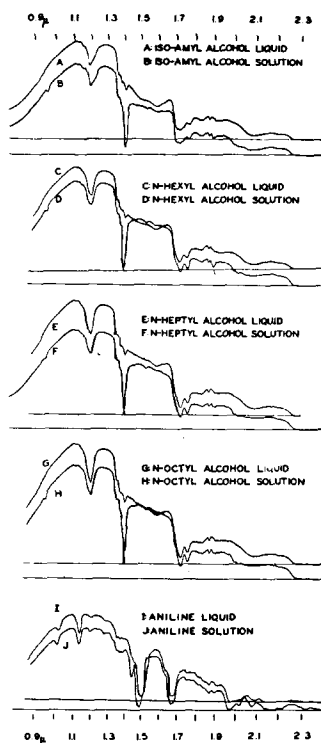


FIG. 3. Self-recorded transmission curves for alcohols from amyl to octyl and for aniline, in liquid and  $\text{CCl}_4$  solution states. Liquid cell thickness, 2 mm. Solution (1:19 by volume) cell thickness, 4 cm.

which are brought about by solution in carbon tetrachloride are caused by the dissociation of polymers which exist in the liquid state, or if definite polymers do not exist, by the weakening of the effects of a liquid lattice which solution in carbon tetrachloride would undoubtedly produce. The sensitivity of the two bands at  $0.96\mu$  and  $1.4\mu$ , which are characteristic of the hydroxyl group, to dilution with a nonpolar solvent, and the absence of a corresponding effect in the bands known to be characteristic of the hydrocarbon groups confirm the belief that the aggregates are held together by forces which arise mainly between the polar hydroxyl groups, and which have little effect upon the hydrocarbon part of the molecule. The existence of the two bands at  $0.96\mu$  and  $1.40\mu$  in the vapor shows that these are probably characteristic of a single unperturbed molecule. The occurrence of the broad absorption which can be attributed to polymers on the long wavelength side of the  $1.40\mu$  band in the solutions along with the sharp band due to single molecules shows that at the dilutions used polymers still exist in considerable concentration. On the other hand, the occurrence of the sharp band at  $1.4\mu$  in the liquids (more pronounced in the higher alcohols) indicates that the liquids themselves are mixtures of free and polymerized molecules. The alteration which solution in carbon tetrachloride produces in the bands characteristic of the hydroxyl group may be used, with some caution, to detect bands characteristic of this group. The band at  $1.89\mu$  which appears only in solution (see solution curve for heptyl alcohol, scale reading 25.20, Fig. 5) is therefore likely to be a "hydroxyl" band. A band that corresponds to the water band which is observed in this region would be expected near this position if the alcohols, like water, possessed characteristic frequencies near  $6.1\mu$ ; for it would be (as it is for water) the combination band ( $\sigma + \delta$ ) formed from the  $3$  ( $\sigma$ ) and  $6.1\mu$  ( $\delta$ ) fundamentals. Although the absorption curves of Weniger<sup>6</sup> show absorption bands near  $6\mu$ , unlike those for water, they are very weak. Moreover, the  $6.1\mu$  or  $\delta$  vibration of water is associated with a change in the angle between the two hydrogen-oxygen bonds and therefore, having as its counterpart in an alcohol an oscillation of the oxygen-hydrogen bond

<sup>6</sup> W. Weniger, Phys. Rev. **31**, 388 (1910).

relative to a bond between an oxygen and a hydrocarbon group, it would involve forces of a different nature and would not be comparable to this type of vibration in an alcohol. Nevertheless, the fact remains that a band at  $1.89\mu$  occurs in all the alcohols which is altered by dilution with carbon tetrachloride and is unaffected by the length of the hydrocarbon chain, so that, like the  $0.96$  and  $1.4\mu$  bands to which in these respects its behavior is similar, it will be regarded as characteristic of the hydroxyl group.

The  $1.95$ – $2.1\mu$  band is unique among those which are affected by dilution because it is the only one which appears to be considerably affected by the length of the hydrocarbon chain. For methyl alcohol it is also the only one which has a different character in the solution than it has in the vapor. It is likely that it is a combination band formed by an intercombination of hydroxyl and hydrocarbon frequencies.

The effect of polymerization or lattice formation in the liquid on the hydroxyl bands of single molecules then is to destroy them and produce on their long wave sides broad and almost continuous absorption. This absorption is most pronounced between  $1.4$  and  $1.65\mu$ , and occurs unmistakably near  $1.89$  and  $2.1\mu$ . There is a definite suggestion of it on the long wave-length side of the weak  $0.96\mu$  band. The polymer band at  $1.4$ – $1.65\mu$  shows four distinct minima which can be found in the records of the solutions of all eight alcohols. Feeble bands in this region appear also in the vapor spectra of ethyl and methyl alcohols, a fact which indicates that the vapors are partially polymerized.

The features exhibited by the fundamental bands of the  $3\mu$  region are not inconsistent with the behavior of the bands in the overtone region described in the previous paragraphs. Absorption spectra of the eight alcohols in the liquid and solution state were obtained for us by Mr. Waldo Lyon, by means of a small Hilger rocksalt instrument. The resolution and dispersion were poor and the slit width, corresponding to  $0.05\mu$ , was large compared to the width used in the overtone region. The transmission curves for the liquid and solution states (Fig. 6) show the two transmission minima that correspond to the hydroxyl and hydrocarbon characteristic frequencies. They lie at  $2.95$  and  $3.45\mu$ , respectively,

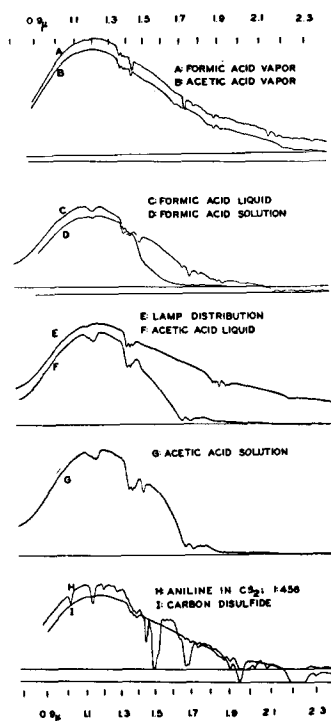


FIG. 4. Self-recorded transmission curves for: *A* to *G*, the vapor, liquid, and  $\text{CCl}_4$  solution states of formic and acetic acids, cell lengths 2 mm for liquids, 4 cm for solutions. Solution concentration, 1 : 19 by volume for acetic acid; saturated solution for formic acid. Vapor, saturated at room temperature. *H*, *I*, aniline in  $\text{CS}_2$ , 1 : 456 by volume, and  $\text{CS}_2$ , cell lengths, 96 cm.

in the solution spectrum, and in the liquid are displaced toward longer wave-lengths. In addition, the hydrocarbon band appears considerably broadened in the liquid. This shift and change in character of the hydrocarbon band is, however, only apparent. The broad polymer absorption that may be expected in this region corresponding to its overtone in the  $1.4\mu$  region should be sufficiently strong to sweep over the hydrocarbon band, especially for the slit width used. The length of the absorbing cell of the liquid alcohol, which was about 0.01 mm, was so small that it could not be controlled to keep the product of concentration and cell length the same for the solution and liquid cases as accurately as it could be for the longer cells which were used in the overtone region. Some variation therefore in the hydrocarbon band in passing from solution to liquid may be expected from this cause.

Errera and Mollet<sup>7</sup> have recently obtained the

<sup>7</sup> Errera and Mollet, *Nature* **138**, 882 (1936).

strong band expected in this region in solutions of the alcohols in carbon tetrachloride as dilute as 0.1 molar. It is clear therefore that in this region the spectra of the solutions which we studied are not characteristic of the single molecules. The band at  $2.95\mu$  is largely produced by polymer absorption which masks the sharp band found by Errera and Mollet at  $2.75\mu$ —the fundamental of the sharp overtone at  $1.4\mu$ .

The vapor absorption of methyl and ethyl alcohols in this region (Fig. 6, curves *C* and *D*) also is evidently not entirely due to single molecules; for although the vapor bands resemble those of the solution much more than they do those of the liquid, the hydroxyl transmission minimum falls at  $3\mu$ , the position of maximum absorption of the polymer band found by Errera and Mollet, and not at  $2.75\mu$ , the position of the band presumably produced by single molecules. The vapors of methyl and ethyl alcohols appear therefore to be partially polymerized. To what extent this is so it is not possible to say on the basis of these records. There is good indication from Errera and Mollet's absorption curves that the hydroxyl absorption probabilities for the associated state are very large compared to those for the single molecules, so that strong absorption in the polymer region relative to the absorption due to single molecules will not necessarily indicate a large proportion of polymers. This is shown by the enormous increase in the polymer absorption and the corresponding small decrease in the single molecule absorption at  $2.75\mu$  which, Errera and Mollet found, occurs in 0.1 molar solutions when the temperature is lowered from  $70^\circ$  to  $0^\circ$ . We have observed this same temperature effect for the solution bands in the  $1.4\mu$  overtone region.

#### FORMIC AND ACETIC ACIDS. ANILINE

We have compared also the absorption of formic and acetic acids in the liquid, solution and vapor states to see whether any of the features which the spectra of the alcohols present are present also in the acid spectra.\* Acid transmissions in the 0.9 to  $2.2\mu$  region are shown in Fig. 4. The transmissions for the liquid and

\* For a discussion of polymer bands in acetic acid vapor from 3 to  $10\mu$  the reader is referred to a paper by Gillette and Daniells, *J. Am. Chem. Soc.* **58**, 1139 (1936).

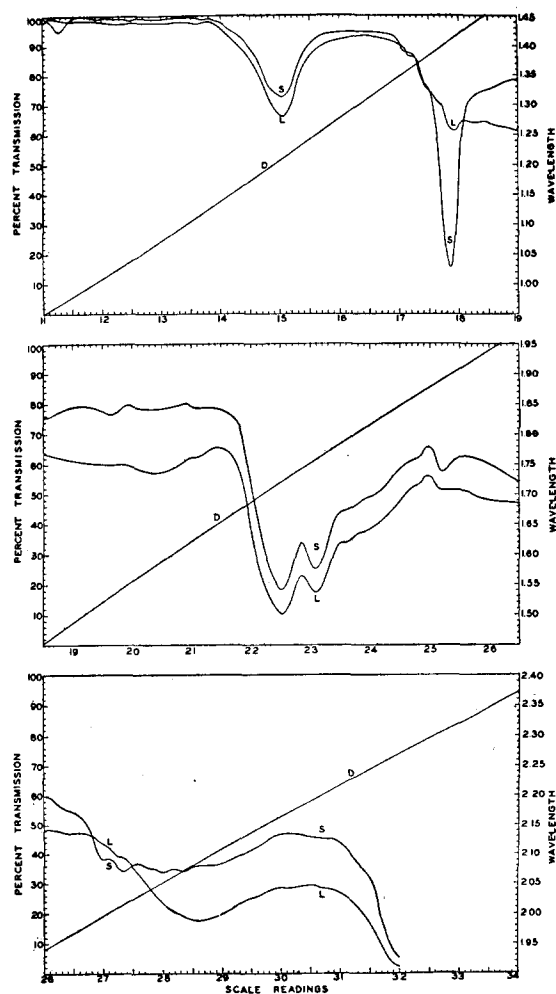


FIG. 5. Percent transmissions for (L) liquid heptyl alcohol, and (S)  $\text{CCl}_4$  solution of it (1 : 19 by volume). Liquid cell length, 2 mm; solution cell length, 4 cm. D, dispersion curve of spectrograph.

solution states of acetic acid at  $3\mu$  are shown in Fig. 6 by curves A and B. The concentrations of formic and acetic acid solutions (1 : 19 by volume) were 1.3 and 0.8 molar, respectively. In the liquid a broad region of continuous absorption begins near  $1.4\mu$  and extends to opacity toward longer wave-lengths. In the carbon tetrachloride solutions this absorption is weakened and is accompanied on its short wave-length edge by the sharp hydroxyl band. The sharp band also occurs in the vapor, but the continuous absorption has been greatly reduced. The continuous absorption in the cell lengths used was so strong that it masked completely the  $1.89$  and  $2.1\mu$  regions in which bands were found for the

alcohols. The weakness of the sharp  $1.4\mu$  overtone band relative to its intensity for the alcohols accounts for the absence of a second overtone corresponding to the alcohol band at  $0.96\mu$ . In the  $3\mu$  region acetic acid behaves like the alcohols. The broad continuous absorption of the liquid is reduced but not extinguished in the solution.

It is interesting to compare this behavior with the behavior of a substance like aniline, which contains the  $\text{NH}_2$  group. Curves I and J of Fig. 3 show the absorption of 2 mm of liquid aniline and 4 cm of a solution of it in  $\text{CCl}_4$  (1 : 19 by volume, 0.5 molar). Curve H, Fig. 4, shows the absorption of 96 cm of a dilute solution in carbon disulfide (1 : 435 by volume, 0.03 molar). The liquid and solution spectra are very similar except in one striking feature. The two bands at  $1.45$  and  $1.495\mu$  reported by Wulf and Liddell to be characteristic of the  $\text{NH}_2$  group in carbon tetrachloride solution appear, but in the liquid the short wave-length component is reduced to a mere shoulder of the other component which remains with its intensity unaltered. Both bands,

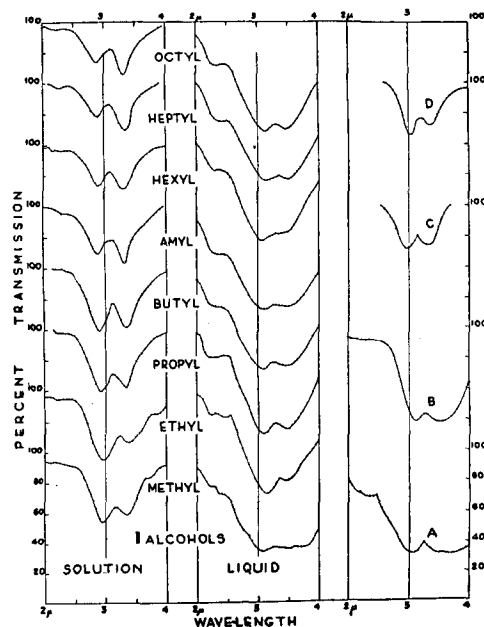


FIG. 6. Left, percent transmissions for liquid and solution states of the alcohols. Liquid cell length, 0.01 mm. Solution (1 : 19 by volume) cell length, 0.2 mm. Right, percent transmissions for: A, 0.01 mm cell liquid acetic acid; B, 0.2 mm  $\text{CCl}_4$  solution of acetic acid (1 : 19 by volume); C, 1 cm cell of methyl alcohol vapor; D, 1 cm cell ethyl alcohol vapor. Vapor approximately saturated at room temperature.

however, are slightly shifted in position. The long wave-length component has a shoulder on its long wave-length side which is more pronounced in the solution than in the liquid. But there is no broad absorption, so characteristic of the alcohols and acids, which is sensitive to dilution with carbon tetrachloride.

It appears therefore that the broad bands of the two acids, like the corresponding bands of the alcohols, are due to a coupling in the liquid state between the hydroxyl parts of the molecules. Since the coupling is very likely of the hydrogen or hydroxyl bond type recently discussed by Bernal and Megaw,<sup>8</sup> a study of these bands may make possible an experimental distinction between the two types of bonds. But if a distinction lies, as Bernal and Megaw suggest it does, in the absence of a characteristic hydrogen vibration

<sup>8</sup> Bernal and Megaw, *Proc. Roy. Soc. A* **151**, 384 (1935).

in the hydrogen bond and, correspondingly, in its presence in a hydroxyl bond, the similarity of the spectra of the alcohols and acids shows that their bondings are alike.<sup>9</sup> And certainly not enough is known about these bonds to say that the apparently greater strength or wider range of the acid polymer bands is sufficient to distinguish between a hydrogen bond in which a proton interchange between oxygens can take place and a hydroxyl bond in which it cannot. For the present the infrared evidence supports the view that, with respect to the behavior of hydrogen, the alcohol and acid polymer bonds are alike.

<sup>9</sup> Compare, for example, Bernal and Megaw's remarks on acetic acid (reference 7, page 420) in which they use the absence of observed Raman lines caused by characteristic hydroxyl frequencies to indicate the presence of a hydrogen bond as distinct from a hydroxyl bond. The same argument based on the evidence of infrared absorption would lead to no such distinction in type between the alcohol and acid liquid lattice bonds.

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## The Potential Function of the Water Molecule

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For use with frequencies corrected for anharmonicity the energy of a molecule is expressed by a complete quadratic form. Reduction of the force constants in Cartesian coordinates to an independent set by relations due to symmetry and mutual forces is carried out by a systematic matrix method which is particularly useful in correcting for anharmonicity and for finding functions of the frequencies and masses invariant in isotopic molecules. For H<sub>2</sub>O and D<sub>2</sub>O these relations being satisfied, the potential function is indeed assumed to be unchanged, all constants are computed, and compared with those of various models. In the S-P<sub>1</sub> picture of the H<sub>2</sub>O molecule the H-H repulsion, ionic terms in OH bonding and exchange integrals in the angular function prove to be the values expected theoretically.

A LARGE number of experimentally determined vibrational levels have been roughly correlated by the use of potential functions of simple models, but satisfactory agreement necessitates the use of a complete potential function. The spectra of a single molecule usually do not yield enough independent data to evaluate all the necessary constants. The many attempts at choosing functions with as many constants as frequencies are by definition only approxima-

tions; cross terms have to be neglected which often turn out to be large. It would be possible to determine all constants by substitution of isotopes provided the potential energy remains unchanged. There are enough experimental data for H<sub>2</sub>O and D<sub>2</sub>O to test whether the isotope makes significant changes in the potential function relative to the vibrational levels, and if not, to determine all the constants of a general quadratic potential expression for energy. It is instructive to evaluate the true values of cross terms of various models showing that it needs an intuitive choice very close to normal coordinates

\* National Research Fellow in chemistry. The author is greatly indebted to Professor W. V. Houston of C. I. T. for his help in the preparation of this and the succeeding papers.