

Molecular Interaction and InfraRed Absorption Spectra PART I. METHYL ALCOHOL

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n-pentane, have been stated by Pitzer.³² In fact the column labeled ∞ in Pitzer's table of steric energies (Table VI of the first paper cited) gives the number of configurations for each of the normal paraffins listed that have at least one pentane type interaction and are therefore prohibited. In this simplified counting it is assumed that each ϕ may assume only three values, 0 and $\pm 2\pi/3$, corresponding to the three minima in the potential. As a result there is only a finite number, 3^m , of discrete configurations, where m is the number of ϕ 's ($m=n-2$, where n is the number of bonds). Since the pentane type of interaction is the simplest example of steric hindrance, it will be instructive to consider the fraction F_m of the 3^m configurations which are allowed when this type of steric effect is considered. It is not difficult to establish the recursion formula,

$$F_m = \frac{2}{3}F_{m-1} + \frac{1}{3}F_{m-2}, \quad (14)$$

where $F_0 = F_1 = 1$. This leads to the following explicit formula

$$F_m = \frac{3}{2} \left[\left(\frac{\sqrt{2}+1}{3} \right)^{m+1} \pm \left(\frac{\sqrt{2}-1}{3} \right)^{m+1} \right], \quad (15)$$

where the plus and minus signs apply to *odd* and *even* values of m , respectively. This yields the values $F_0=1$, $F_1=1$, $F_2=(7/9)$, $F_3=(17/27)$, $F_4=(41/81)$, and $F_5=(99/243)$, which agree with Pitzer's table. It is clear that as m increases

indefinitely, F_m , the fraction of all configurations that are not prohibited by steric hindrance, approaches zero exponentially.⁴¹ Furthermore, configurations with steric hindrance will on the average be more coiled than configurations without steric hindrance. It is therefore clear that in the derivation of Eqs. (2) and (3), in which no account is taken of steric hindrance in the present sense, the highly coiled configurations have been weighted too heavily, and as a result the calculated values of $\langle L^2 \rangle$ and $\langle R^2 \rangle$ will be too small. An estimate of the magnitude of this error is difficult, although a method of calculation that appears promising is being investigated.⁴² There is another effect of opposite sign, namely the attractive Van der Waals forces between different segments of a long chain, which will tend to make the chain coil. There may also be solvent effects for molecules in solution.⁴³

⁴¹ It is interesting to note that the decrease in the entropy caused by the pentane-type interaction (neglecting other factors than the decrease in the number of configurations) is $-R \ln F_m$, and is therefore *linear* in the number of carbon atoms in the chain (if the small alternating term in Eq. (15) is neglected).

⁴² Steric effects for short paraffin chains with free rotation have been considered by R. M. Melaven and E. Mack, Jr., J. Am. Chem. Soc. **54**, 888 (1932), and L. Laskowski and R. E. Burk, J. Chem. Phys. **7**, 465 (1939). The effect of steric hindrance in long chains has also been considered by R. Simha, J. Research Nat. Bur. Stand. **40**, 21 (1948).

⁴³ For a general discussion see T. Alfrey, Jr., *Mechanical Behavior of High Polymers* (Interscience Publishers, Inc., New York, 1948), pp. 94-98.

Molecular Interaction and Infra-Red Absorption Spectra

PART I. METHYL ALCOHOL

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A study has been made of the absorption spectra between 3μ and 15μ of methyl alcohol at varying concentrations in solution. Clear indications are obtained of at least two new bands outside the 3μ region which arise from the associated molecules. The data allow of a further discussion of the vibrational assignments in methyl alcohol and it is hoped that some of the uncertainties in that respect have now been removed.

THE influence of various inter- and intramolecular forces upon the normal vibra-

tions of particular atomic groupings has received considerable attention on the basis of infra-red absorption studies. In particular, interactions of the nature of "hydrogen bonding" have been re-

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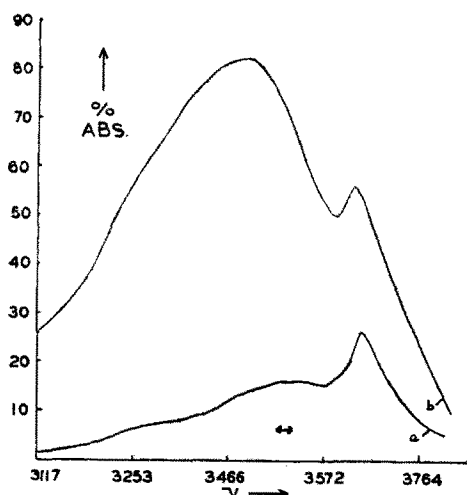


FIG. 1. CH_3OH in CHCl_3 , 0.10-mm cell. (a) = 0.79 molar; (b) = 1.70 molar.

peatedly studied for molecules having O—H, N—H, C=O, groups, etc.¹ While the values of the vibration frequencies observed for these groups in the infra-red are found to provide a sensitive criterion of the occurrence and magnitude of such interactions, it would be anticipated that the potential field governing all the vibrations of the group will be influenced simultaneously. Thus, in the case of a hydroxyl group, while interaction with another molecule will stretch the O—H bond and so cause a decrease in the valence frequency, it will tend to tie the hydrogen more firmly in its angular orientation. Accordingly, the deformation frequency can be expected to rise on association. This has been confirmed in a number of instances: e.g., the 6μ water absorption, which principally involves the angular deformation of the molecule, moves to shorter wave-lengths on going from vapor (single molecules) to liquid (associated molecules).² A similar shift has been reported on the association of methyl alcohol³ and of phenol⁴ molecules.

The present observations relate to the influence of molecular association upon the vibrations of the methyl alcohol molecule. The infra-red absorptions of the single molecules (in the vapor

¹ See *inter alia*, Davies, Chem. Soc. London, Ann. Reports **43**, 1 (1946).

² See especially J. J. Fox and A. E. Martin, Proc. Roy. Soc. A **174**, 234 (1940).

³ G. Bosschieter, J. Chem. Phys. **5**, 992 (1937).

⁴ V. Williams, R. Hofstadter, and R. C. Herman, J. Chem. Phys. **7**, 802 (1939).

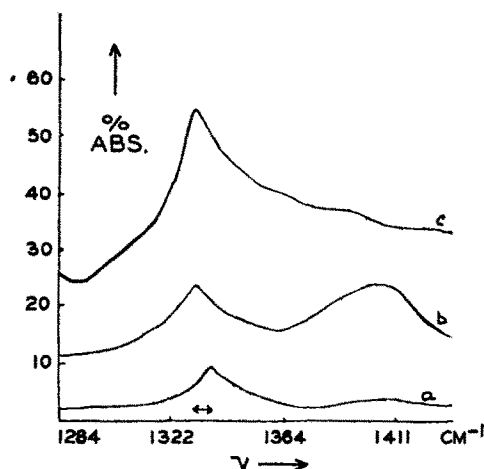


FIG. 2. (a) and (b) CH_3OH in CHCl_3 , 0.10-mm cell. (a) = 0.256 molar. (b) = 1.28 molar. (c) CH_3OH in CCl_4 , 3-mm cell, 0.155 molar.

phase) have been thoroughly studied by A. Borden and E. F. Barker;⁵ their assignment of the observed frequencies is assumed in describing the present results and its validity is discussed in a later section.

Experimental

The spectra were all obtained on a recording instrument (the Beckman Model I.R. 2) which plots on a 11-inch linear scale the energy available in the transmitted beam. A rocksalt prism of 60-mm base was used throughout and the equi-angular wave-length scale checked and corrected where necessary on the basis of well-known gas or vapor absorptions, including those of CO_2 , NH_3 , CH_4 , H_2O , C_6H_6 . The response time of the detector-amplifier, the speed of traverse, and the slit widths were chosen so as to give maximum resolution consistent with stability to ± 0.5 unit in the energy scale of 0 to 100 units. The usual procedure was to record the transmission through the solvent cell and, retaining the same conditions, to superimpose upon that record the transmission of the solution. Coincidence of the wave-length scales on the record could be ensured by preliminary adjustments outside the range actually being studied. Occasionally, transmissions were taken manually on a potentiometer scale readable to 0.1 percent of its total range.

The results are presented in the form of curves

⁵ A. Borden and E. F. Barker, J. Chem. Phys. **6**, 553 (1938).

showing percentage absorptions by the solute under various conditions. Unless otherwise stated the cell temperature was within two or three degrees of 30°C. A limitation to the accuracy of the percentage absorptions ascribed to the solute is noteworthy for the more concentrated solutions. At the highest concentration studied (7.9 g mole CH₃OH per litre) the volume concentration of solute is about 30 percent. Apart from the possible influence of this amount of alcohol on the solvent absorptions, correction has been applied for the latter at 100 percent volume concentration in the cell of equal width. This over-correction will not lead to any significant error in the form of the reported absorptions provided the solvent has no pronounced absorption features in the range considered; we have established that this is the case for the relevant regions.

Methyl alcohol of 99 percent purity was placed over silica gel and freshly distilled before use; the middle third was taken. Analar solvents were distilled from the same drying agent—the chloroform was first repeatedly shaken with water to remove ethyl alcohol and placed over calcium chloride before distilling from silica gel. No trace of alcohol was detected in its absorptions.

Results

3 μ Region

The feature of interest here is, of course, the shift of the O—H valence vibration absorption from a sharp band at 3650 cm⁻¹ for the monomer, to the broad absorption near 3400 cm⁻¹, characteristic of the associated molecules. Figure 1 illustrates this well-known change which has been studied in detail by many workers.⁶ The only reason for reproducing the results for this region here is to help define the concentration range over which the transition from mainly monomeric to mainly associated molecule absorptions may be expected in these solutions. In CHCl₃ at about 30°C it is seen that the change-over will occur between 0.5 molar and 1.5 molar concentrations.

7 μ Region

Three fundamental vibrations of the CH₃OH molecule are found here. Two of them, ν_4 and ν_3

of Borden and Barker, are at 1477 cm⁻¹ and 1455 cm⁻¹ in the vapor and correspond to vibrations within the methyl group. Unlike these, the third (ν_6) would be expected to respond to the forces called into play by the molecular association. It is located in the vapor at 1340 cm⁻¹ and arises from a vibration between the methyl and hydroxyl groups principally determined by the force required to bend the C—O bond. As such a vibration can be resolved into two perpendicular components—one in the COH plane, the other perpendicular to it—the frequency might be expected as a close doublet. The single absorption center found in the vapor, although somewhat broad, indicates that degeneracy is almost complete in the monomeric CH₃OH molecule.

In dilute CHCl₃ solutions this vibration gives rise to a sharp absorption centered at 1331 cm⁻¹, i.e., shifted by about 9 cm⁻¹ from its position in the vapor (Fig. 2). On increasing the concentration (Fig. 3) the absorption apparently shifts to higher frequencies, the peak at 2.44 molar actually being located at 1339 cm⁻¹, but what is more significant and, indeed, the probable cause of this apparent shift, is the relatively increasing importance of a new absorption at about 1401 cm⁻¹. The latter is not detectable at the lowest concentrations but at 2.44 molar it is already notably stronger than the 1331-cm⁻¹ absorption, and in the 7.9 molar solution it has increased in intensity and breadth to such an extent as al-

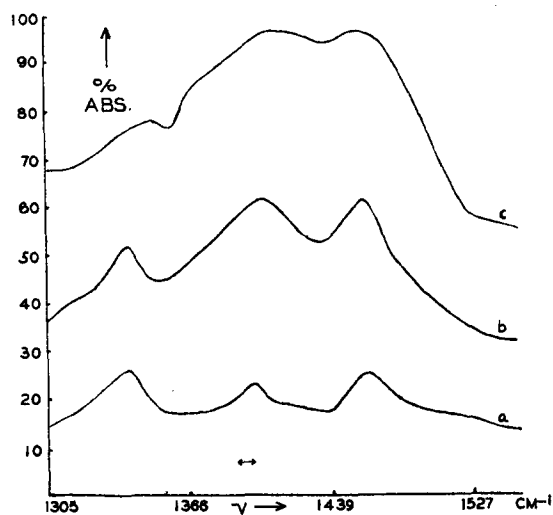


FIG. 3. CH₃OH in CHCl₃. 0.10-mm cell. (a) = 0.079 molar. (b) = 2.44 molar. (c) = 7.90 molar.

⁶ See especially J. Errera, R. Gaspart, and H. Sack, *J. Chem. Phys.* **8**, 63 (1940); J. J. Fox and A. E. Martin, *Trans. Faraday Soc.* **36**, 897 (1940).

most to obliterate the band due to the single molecules. The obvious interpretation of this new and broader absorption is that it represents the frequency for the same vibration as it occurs in the associated molecules. The general correctness of this interpretation is supported by the preliminary study of temperature effects on the absorption intensities, and also by reference to the 1455-cm^{-1} absorption in Fig. 3. This is at exactly the same frequency as that found by Borden and Barker for ν_3 (one of the CH_3 vibrations) in the vapor; being practically unaffected by the association process, this absorption is initially somewhat less intense than the 1331-cm^{-1} peak, but increases relative to this monomer band as the concentration rises.

The change here ascribed to the $\delta(\text{C}-\text{O})$ vibration on association of the alcohol molecules is in the sense that would be anticipated, i.e., to higher frequencies. By careful analysis of the results in the 3μ region⁶ it has been possible to separate the absorption due to the dimeric molecules from that of the other polymolecular species. As yet, no indications are available that this is also possible for the $\delta(\text{C}-\text{O})$ vibration. The latter might well have lost its degeneracy in the associated molecules and, apart from that, the coupling of two oscillators with a common fre-

quency might have resulted in a multiplication of the absorption bands. However, the observations suggest that any such splitting of the frequency as does occur is insufficient to give resolvable components under the present conditions.

9 μ Region

The only absorption reported here by Borden and Barker is that from the parallel vibration, ν_5 , between the methyl and hydroxyl groups, i.e., $\nu(\text{C}-\text{O})$, giving a very intense absorption centered at 1034.18 cm^{-1} in the vapor. In dilute CHCl_3 solutions the center is at 1017 cm^{-1} and the absorption is sufficiently intense for an amount of $3 \times 10^{-5}\text{ g}$, or $1 \times 10^{-6}\text{ g mole}$ of methyl alcohol to be determinable to within 10 percent. Figures 4 and 5 show some of the results in this region as the concentration is increased. Two features evoke immediate comment: the unsymmetrical broadening of the main absorption in its spreading to higher frequencies as the concentration increases, and the appearance of new peaks at 1074 cm^{-1} and at 1110 cm^{-1} .

The center of the intense ν_5 absorption is displaced from 1017 cm^{-1} to about 1025 cm^{-1} as the concentration increases in CHCl_3 . While it is possible that the attendant broadening may arise from general causes (e.g., the crowding of lines

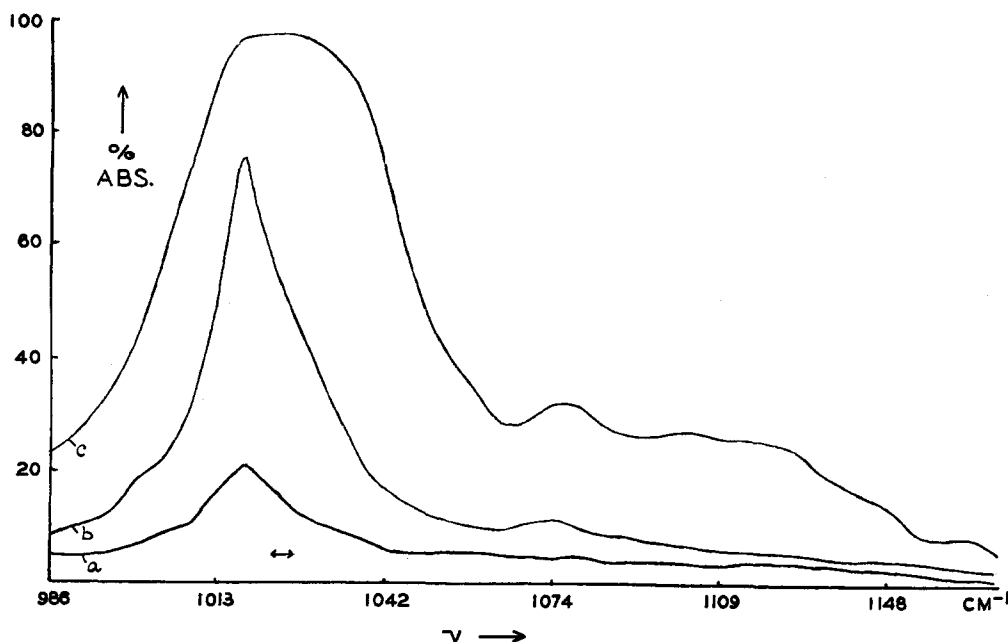
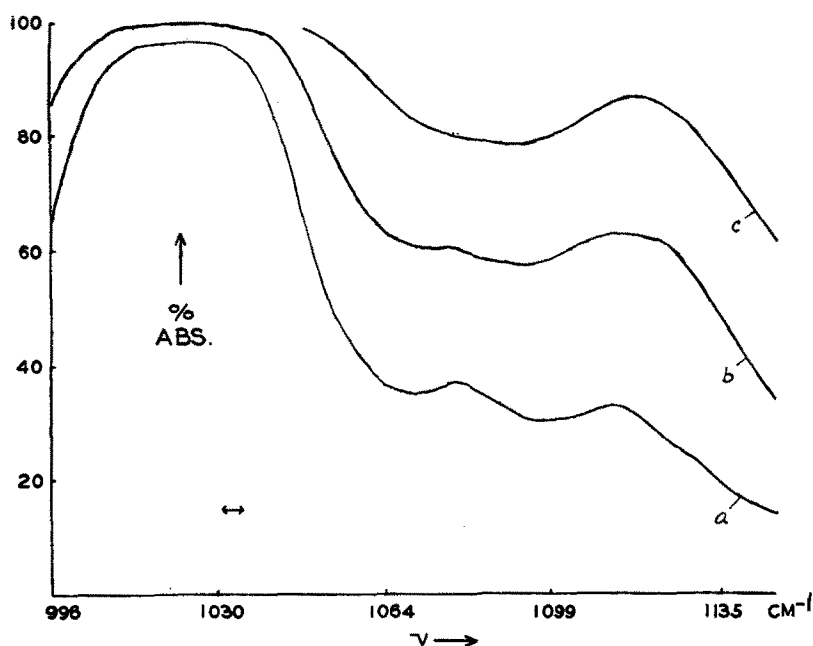


FIG. 4. CH_3OH in CHCl_3 , 0.10-mm cell. (a) = 0.051 molar. (b) = 0.256 molar. (c) = 1.28 molar.

FIG. 5. CH_3OH in CHCl_3 . 0.10-mm cell. (a)=1.98 molar. (b)=3.95 molar. (c)=7.90 molar.



in an unresolved *R*-branch giving it relatively greater intensity than the low frequency side as the total intensity increases), this is not confirmed by a further examination of the absorptions, in particular in CS_2 solutions. In that solvent the CH_3OH is only very sparingly soluble, and the most concentrated solution was prepared by separating the disulfide layer after shaking with excess of alcohol at room temperatures. The solutions examined were obtained by dilution from this saturated phase. Using a 1-mm cell, intensities comparable with those for much higher concentrations in CHCl_3 were obtained (Fig. 6). The absorption spreads symmetrically about its center which, incidentally, is now at 1019 cm^{-1} and so a little nearer the gas value than in CHCl_3 solutions. Thus, the indications are that the unsymmetrical spreading to higher frequencies arises principally from conditions in the concentrated solutions where the most important new feature is the association of alcohol molecules.

An alternative interpretation which has to be considered in this instance is that another almost coincident absorption, which has been missed in dilute solutions, makes its presence known when the concentration is increased. It has been shown that the deformation vibration in which the H-atom moves in the plane of the COH group

should occur for the single molecules near 1030 cm^{-1} ,⁵ although it was not established in the CH_3OH vapor absorptions; neither can it be resolved in the solutions examined. In CHCl_3 the dilute solutions always showed a regular, almost exactly symmetrical, peak at 1017 cm^{-1} . Using a 0.10-mm cell, for which the solvent transmission is particularly uniform over this region, the almost saturated CS_2 solutions showed a slight irregularity on the short wave-length side of the absorption center. (Figure 7.) However, the incidence of this feature has been correlated with the occurrence of alcohol association in these CS_2 solutions, for when it appears, an association band at 3380 cm^{-1} also makes its appearance. It thus seems to be established that the slight shift of the 1017-cm^{-1} absorption to higher frequencies on increasing the concentration is the influence of the association process on the $\nu(\text{C}-\text{O})$ frequency.

The separate absorptions at 1074 cm^{-1} and 1110 cm^{-1} are inherently weak and have not been reported for the vapor.^{5,7} The former fits quite closely the frequency for a difference tone between two fundamentals, $1340 - 270 = 1070\text{ cm}^{-1}$. The two deformation vibrations combined here are both prominent features in the spectrum, the

⁷ H. D. Noether, J. Chem. Phys. 10, 693 (1942).

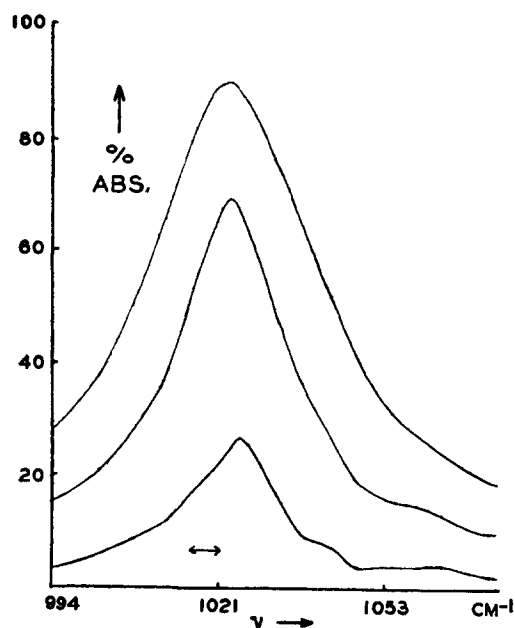


FIG. 6. CH_3OH in CS_2 . Diluted solutions in 1-mm cell.

low frequency one being the $\delta(\text{O}-\text{H})$ vibration in which the H atom moves out of the COH plane. It has been located in the 40μ region by Lawson and Randall.⁸

The 1110-cm^{-1} absorption is very probably the $\delta(\text{O}-\text{H})$ vibration within the COH plane, as it occurs in the associated molecules. It has frequently been observed in the Raman spectrum of the liquid alcohol as 1111 cm^{-1} . The peak of this absorption definitely moves to shorter wavelengths as the concentration rises—from 1111 cm^{-1} to 1116 cm^{-1} in passing from 1.98 to 7.90 molar CHCl_3 solutions. As this is away from the nearby intense $\nu(\text{C}-\text{O})$ band, it represents a real change in the absorption center. A far more pronounced progressive shift of the $\nu(\text{OH})$ absorption in the associated molecules occurs in the opposite direction, e.g., from 3510 cm^{-1} at 0.8 molar to 3430 cm^{-1} at 1.7 molar, and 3350 cm^{-1} at 5.0 molar.

Over the concentration range for which it can be estimated with any accuracy, i.e., 1.28 to 7.8 molar, the 1110-cm^{-1} absorption coefficient, κ , calculated from $\log_{10} I_0/I = \kappa cd$, (where c is the total molar concentration) shows only an increase of about 30 percent. This would suggest

that the associated molecules already formed about 70 percent of the total at 1.28 molar concentration. This is a reasonable estimate judging from the results at 2.7μ to 3.2μ . Insofar as its temperature variation has been studied (i.e., between 16° and 36°C) the intensity of the 1110-cm^{-1} feature shows the expected decrease with rise in temperature. Unfortunately, it is not easy to choose conditions which will show a pronounced temperature change, as the high concentration needed to show the absorption as a separate band leads to large degrees of association over the whole of the convenient range. For large path lengths of more dilute solutions the solvent absorptions cause difficulty.

Beyond 10μ

The range from 10.0μ to 12.4μ was conveniently explored using CHCl_3 solutions in a 0.10-mm cell. Here the vapor shows part of an extended but very weak absorption arising from the first overtone of the $\delta(\text{O}-\text{H})$ 270-cm^{-1} fundamental. A flat, featureless absorption covering the whole of this range was found in the solutions, its level being, in terms of percentage absorption, about 40 percent for 5.0 molar, 20 percent for 1.7 molar, and 10 percent for 0.8 molar.

5μ Region

In CHCl_3 solutions, the single sharp absorption at 2044 cm^{-1} , due to the overtone $2\nu_6(\text{C}-\text{O})$, was readily measured. It showed no signs of structure, nor were any other absorptions in its immediate neighborhood noticed.

Discussion

In the foregoing paragraphs the absorptions have been described on the basis of the assignments made by Borden and Barker. As a result of certain observations made for the deuterated alcohols, changes in these assignments have been made by Noether⁷ and by Herzberg.⁹ The most important suggestion is that of ascribing the 1340-cm^{-1} frequency to $\delta(\text{O}-\text{H})$ rather than to $\delta(\text{C}-\text{O})$, as is done above. Observational factors which are critical of Borden and Barker's assign-

⁸ See J. S. Koehler, D. M. Dennison, *Phys. Rev.* **57**, 1006 (1940).

⁹ Herzberg, *Molecular Spectra and Molecular Structure* (D. Van Nostrand Company, Inc., New York, 1945), Volume II, p. 334.

ment are the failure to detect the $\delta(\text{O}-\text{H})$ frequency in gaseous CH_3OH , the strength of the 1340-cm^{-1} absorption in CH_3OH , and its apparent disappearance in CH_3OD . However, it is agreed by all that $\delta(\text{O}-\text{D})$ in CH_3OD vapor lies at 863 cm^{-1} ¹⁰ and that this is shifted to about 940 cm^{-1} on association of the deuterated alcohol.³ Placing the $\delta(\text{O}-\text{H})$ monomer frequency at 1340 cm^{-1} then gives an isotope factor $\delta(\text{OH})/\delta(\text{OD}) = 1.55$, i.e., significantly larger than $\sqrt{2}$. While this value cannot be finally rejected without a calculation based on an acceptably complete force field for the molecular vibrations, its deviation from $\sqrt{2}$ is in the more unusual direction and is quite unsupported by the data for similar vibrations in other molecules. Some of the observed $\delta(\text{O}-\text{H}) \rightarrow \delta(\text{O}-\text{D})$ frequency changes in other structures may be tabulated¹¹ (Table I).

TABLE I.

Molecule	$\text{C}_6\text{H}_5\text{OH}$	CD_3COOH		$\text{C}_2\text{H}_5\text{COOH}$	
		Monomer	Dimer	Monomer	Dimer
$\delta(\text{O}-\text{H})\text{ cm}^{-1}$	1175	1162	1285	1137	1234
$\delta(\text{O}-\text{D})\text{ cm}^{-1}$	913	984	1046	985	1041
$\frac{\delta(\text{O}-\text{H})}{\delta(\text{O}-\text{D})}$	1.29	1.18	1.23	1.16	1.19

Accepting the 1110-cm^{-1} band described above as the $\delta(\text{O}-\text{H})$ frequency in the associated CH_3OH molecules, an approximate estimate of the corresponding frequency in the monomer can be made by assuming the same percentage change on association as in CH_3OD , i.e., on the basis of the ratio $(\delta(\text{OD}) \text{ associated})/(\delta(\text{OD}) \text{ monomer}) = 940/863 = 1.090$. This gives 1025 cm^{-1} as the estimated monomer frequency. This is so near the center of the very intense $\nu(\text{C}-\text{O})$ band as to explain its non-detection. Relative to the frequencies in CH_3OD , the isotope frequency changes are then $1025/863 = 1.19$ for the monomer, and $1116/940 = 1.18$ for the associated molecules. These ratios are seen to compare well with those previously quoted.

Noether assigns his (non-degenerate) $\delta(\text{C}-\text{O})$ vibration to minor features in his absorption

curves at 1209 cm^{-1} and 1250 cm^{-1} . Absorptions at these values have not been reported otherwise—neither in the vapor^{5,12} nor in the liquid¹³ or solution—and these frequencies are absent in the careful Raman studies made on liquid CH_3OH ,¹⁴ although the corresponding vibrations appear in the Raman spectra of CH_3F and CH_3Cl . In conformity with the latter occurrence and Borden and Barker's assignment is the appearance of a weak Raman line at 1370 cm^{-1} in liquid CH_3OH and CH_3OD . Herzberg, after taking the $\delta(\text{O}-\text{H})$ frequency at 1340 cm^{-1} , assigns $\delta(\text{C}-\text{O})$ to two Raman lines at 1056 cm^{-1} and 1171 cm^{-1} ; these frequency values are in the region that would be expected from a comparison with the methyl halide vibrations, but, for the alcohol they do not appear in the infra-red although their counterparts are medium strong absorptions in the halide vapors. Further, if the assignment of $\delta(\text{O}-\text{H})$ to about 1030 cm^{-1} is accepted, there is little question but that 1340 cm^{-1} represents the $\delta(\text{C}-\text{O})$ vibration.

Some further aspects of the data available for other molecules containing the $\text{C}-\text{O}-\text{H}$ group provide relevant indications supporting the assignment favored. The values of the $\delta(\text{O}-\text{H})$ frequencies in phenol and a number of carboxylic acids—where they may be recognized both by the effect of deuterium substitution and by the influence of association—are in the neighborhood of 1170 cm^{-1} (compare Table I). From the intra-

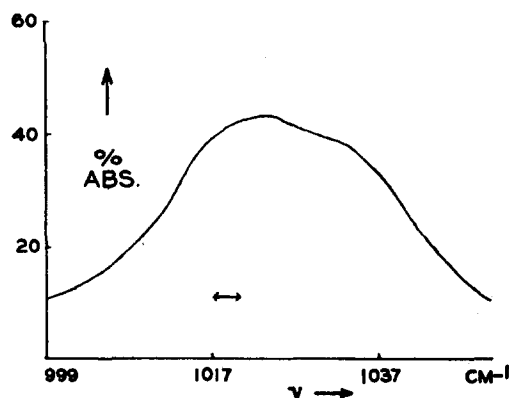


FIG. 7. CH_3OH in CS_2 . Almost saturated solution in 0.10-mm cell.

¹² R. Titeica, *Comptes Rendus* **196**, 391 (1933).

¹³ J. Lecomte, *Comptes Rendus* **180**, 825 (1925).

¹⁴ (a) J. O. Halford, L. C. Anderson, and G. H. Kissin, *J. Chem. Phys.* **5**, 927 (1937); (b) Mizushima, Morino, and Okamoto, *Bull. Chem. Soc. Japan* **11**, 698 (1936).

¹⁰ E. F. Barker and G. Bosschieter, *J. Chem. Phys.* **6**, 563 (1938).

¹¹ (a) Reference 4; (b) R. C. Herman and R. Hofstadter, *J. Chem. Phys.* **7**, 460 (1939).

molecular forces present in these structures, it is to be anticipated that this vibration would have a higher frequency here than in CH_3OH . Again, the values of the frequency ratio, $r = (\delta(\text{OH}) \text{ in monomer} / \delta(\text{OH}) \text{ in associated molecule})$, are given in Table II.

TABLE II.

Molecule	$\text{C}_6\text{H}_5\text{OH}$	CD_3COOH	$\text{C}_2\text{H}_5\text{COOH}$	CD_3COOD	$\text{C}_2\text{H}_5\text{COOD}$
r	1.035	1.104	1.084	1.064	1.056

In these instances the association has produced a frequency shift in $\delta(\text{O}-\text{H})$ of the order of 7 percent; in CH_3OD the observed value is 9 percent and, in the evaluation given, this has been assumed to hold in CH_3OH .

The carboxylic acids have likewise long been known to show absorption changes in the 7μ region on association.¹⁵ Davies and Sutherland ascribed the 1379-cm^{-1} frequency of monomeric CH_3COOH , which becomes 1425 cm^{-1} on association, to the $\nu(\text{C}-\text{O})$ vibration in this structure. It now seems very probable that this would be described more correctly as the $\delta(\text{C}-\text{O})$ frequency, as it is certain that the $\nu(\text{C}-\text{O})$ frequency changes only to a very minor extent on association in CH_3OH and, similarly, almost negligible changes occur on association in the 1060-cm^{-1} frequency common to many of the carboxylic acids. On this basis, the following fre-

quencies can be ascribed to $\delta(\text{C}-\text{O})$ infra-red absorptions in a number of these cases.^{11b} (See Table III.)

TABLE III.

Molecule	CH_3COOH	CD_3COOH	CD_3COOD	$\text{C}_2\text{H}_5\text{COOH}$	$\text{C}_2\text{H}_5\text{COOD}$
(a) $\delta(\text{C}-\text{O})$ monomer:	1379	1335	1280	1378	1360
(b) $\delta(\text{C}-\text{O})$ associated:	1425	1408	1360	1419	1380
(b/a)	1.034	1.054	1.064	1.036	1.015

Association produces here a frequency change of the order of 4 percent; in CH_3OH the present observations give a frequency change of 4.4 percent. It may be noted (compare Table II and Table III) that the influence of association is greater on $\delta(\text{O}-\text{H})$ than on $\delta(\text{C}-\text{O})$. This is certainly the expected order of the effects; anticipation might well have proposed a larger difference in the same direction.

Thus, the evidence accumulated here goes to support the assignments of Borden and Barker in CH_3OH . A more complete picture of the influence of association on the vibrations of this structure is now available, and it is hoped that this will be of service in unravelling the details for more complicated systems. For the present it suffices to repeat that the changes confirm general anticipations, and fall into line with the accumulating spectroscopic data on intermolecular interactions.

PART II. PHENOL

The absorption spectra of phenol in solution, between 6.5μ and 15μ , have been studied with particular attention to the qualitative changes on varying the concentration and temperature. Prominent features appearing only in the more concentrated solutions are ascribed to vibrations in associated molecules. The results are compared with those for methyl alcohol, and their general significance is discussed.

A study, similar to that of methyl alcohol described in Part I, has also been made of phenol. In addition to CCl_4 and CHCl_3 , Analar C_6H_6 has been used as solvent, particularly in the 12μ to 14μ range; it was redistilled before use after being kept over SiO_2 . The solute was the dry Analar reagent.

It is convenient to describe the absorptions in the sequence of increasing wave numbers from

the lower limit of 660 cm^{-1} (15μ) measured with the use of the rocksalt prism, and to divide the range covered into three sections.

15μ to 9μ

Over this range the following absorption peaks, which may be taken as the centers of separate bands, have been located (a rough indication of their relative intensities is appended).

$\nu\text{ cm}^{-1}$	689	729	753	810.4	826.4	882	993	1020	1064	1101
I	<i>s</i>	<i>vw</i>	<i>vs</i>	<i>s</i>	<i>m</i>	<i>m</i>	<i>m</i>	<i>m</i>	<i>ms</i>	<i>w</i>

¹⁵ (a) Gillette and Daniels, J. Am. Chem. Soc. **58**, 1139 (1936); (b) Davies and Sutherland, J. Chem. Phys. **6**, 755 (1938).

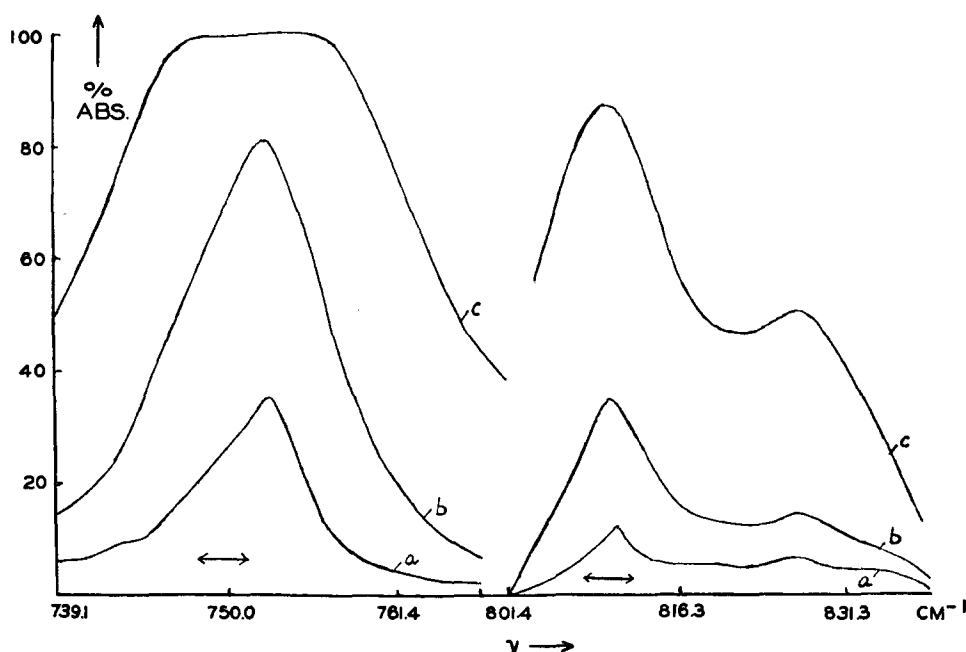


FIG. 1. $\text{C}_6\text{H}_5\text{OH}$ in C_6H_6 , 0.10-mm cell. (a) = 0.073 molar. (b) = 0.290 molar. (c) = 1.45 molar.

From 660 cm^{-1} to 740 cm^{-1} too, a generally featureless background absorption is noticeable: for a 1.5 molar solution in a 0.10-mm cell its intensity is about 25 percent absorption. Its occurrence has been reported previously¹ and it very probably arises from the same source as the similar absorption in CH_3OH , i.e., a $\delta(\text{O}-\text{H})$ vibration.

From a study of the intensity changes with concentration and, in a number of cases, with temperature, it can be stated that none of these absorptions is notably influenced by the molecular association of the phenol. This result may be taken to indicate that, with one probable exception, these frequencies do not prominently involve the force constants within the $-\text{COH}$ group. While it is no part of the present study to assign these absorptions to the proper vibrations of the phenol molecule, the following notes on them may be added:

689 cm^{-1} . In his discussion of the absorptions of mono-substituted benzene derivatives,¹ Lecomte ascribed the 689-cm^{-1} band to a vibration of the benzene ring (having trigonal symmetry).

753 cm^{-1} , 810.4 cm^{-1} , 826.4 cm^{-1} . (See Fig. 1.) Lecomte reported absorptions at 751 cm^{-1} and

819 cm^{-1} —the second apparently corresponding to the latter two features recorded here, whose unresolved center would be 818 cm^{-1} . They were assigned to further vibrations of the carbon ring. Brattain's curves for solid and liquid phenol² show two strong absorptions at 725 cm^{-1} and 794 cm^{-1} practically uninfluenced by temperature changes; these are almost certainly the centers now found at 753 cm^{-1} and 818 cm^{-1} , i.e., at $\Delta\nu + 28\text{ cm}^{-1}$ and $+24\text{ cm}^{-1}$ away. The present observations provide no grounds for supposing that this frequency change on passing from solution to liquid is real.

885 cm^{-1} , 998 cm^{-1} . These absorptions were given by Lecomte as 883 cm^{-1} and 998 cm^{-1} ; a molar solution in a 0.10-mm cell failed to reveal his (weak) absorption at 949 cm^{-1} . In phenol vapor they have been reported at 876 cm^{-1} and 1010 cm^{-1} and the latter frequency is apparently only slightly changed in $\text{C}_6\text{H}_5\text{OD}$ vapor.³ As observed in CCl_4 solutions, these absorptions are insensitive to variations in either concentration or temperature. Benzene itself has an inactive fundamental at 890 cm^{-1} ,⁴ while the hydrocarbon and most of its mono-substituted derivatives

¹ J. Lecomte, J. de phys. et rad. (7) 8, 489 (1937).

² Brattain, J. Chem. Phys. 6, 298 (1938).

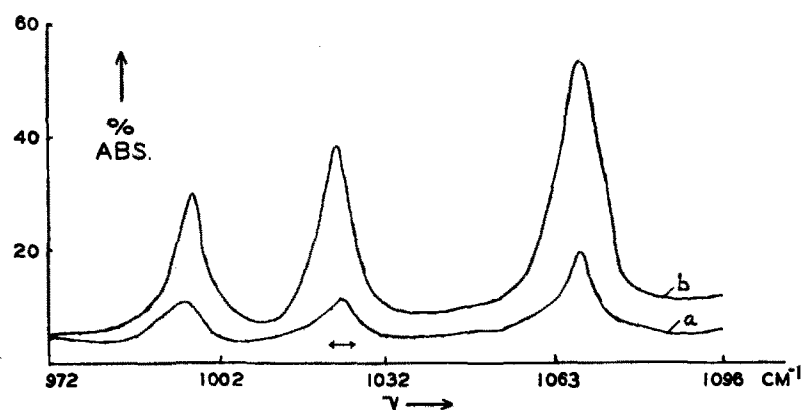


FIG. 2. C_6H_5OH in CCl_4 .
0.10-mm cell. (a)=0.197 molar.
(b)=0.983 molar.

have a well-known Raman line very near 1000 cm^{-1} .⁵

1024 cm^{-1} , 1067 cm^{-1} (see Fig. 2). Of these the 1067-cm^{-1} band has about double the absorption coefficient of the other and it is the only feature mentioned explicitly in the earlier accounts of phenol absorptions quoted above. It may be taken as identical with the 1057-cm^{-1} frequency given for C_6H_5OH vapor and 1070 cm^{-1} in C_6H_5OD vapor. Again, Lecomte reported it as 1056 cm^{-1} and identified it as either a combination band or an overtone.

It will be recalled that the C—O valence vibration in CH_3OH is near 1030 cm^{-1} . It is to be anticipated that this will occur in the same region for C_6H_5OH . However, the identification of this frequency in phenol is not obvious. None of the absorptions in the immediate neighborhood of 1000 cm^{-1} are comparable in intensity with the $\nu(C-O)$ band in the alcohol and $1024 \pm 5\text{ cm}^{-1}$ is, again, a Raman frequency characteristic of mono-substituted benzenes which is independent of the substituent.⁵ Unless the $\nu(C-O)$ frequency is notably lower here (e.g., 885 cm^{-1} ?) than in methyl alcohol, the 1064-cm^{-1} absorption is its most likely identification in the spectrum.

9.0 μ to 7.8 μ

This is a region of considerable interest. (See Fig. 3). In the most dilute solutions (~ 0.05 molar) only three absorptions are recorded—at

⁵ V. Williams, R. Hofstadter, and R. C. Herman, *J. Chem. Phys.* **7**, 802 (1939).

⁴ Ingold *et al.*, *J. Chem. Soc.* 971 (1936).

⁵ J. H. Hibben, *The Raman Effect and its Chemical Applications* (Reinhold Publishing Corporation, New York, 1939), p. 231.

1147 cm^{-1} , 1174 cm^{-1} , and 1249 cm^{-1} ; these must, without question, be ascribed to vibrations in the monomeric molecules. It is equally certain that the somewhat broad absorption centered at 1214 cm^{-1} , which becomes the most intense feature at 1.52 molar, arises from associated molecules. Less certainty attaches to the remaining absorption at 1163 cm^{-1} , but the indications are that this may likewise come from associated molecules. It is difficult to make satisfactory quantitative estimates of the intensity changes with concentration or temperature as the bands overlap to such an extent that, although their peaks are clearly resolved, considerable uncertainty is involved in deducing the individual intensities. Nevertheless, the 1163-cm^{-1} center is not detectable in a 0.10-mm cell at 0.049 molar and provides a shoulder of the same intensity as the 1147-cm^{-1} band at 0.197 molar, and at 0.98 molar or more is distinctly stronger than that "monomeric" absorption. This suggestive sharp intensity increase with concentration is supported by a comparison of the absorption of a 1.52 molar solution at 21° and $37^\circ C$. While raising the temperature notably increases the intensity of the 1147-cm^{-1} band, relative to this the 1163-cm^{-1} peak is decreased. At the same time, and as is required by the foregoing assessment, the 1174-cm^{-1} absorption is much stronger and better defined at the higher temperature. Careful examination of a dilute solution (0.045 molar) in a 1.0-mm cell, however, reveals a slight shoulder in the absorption curves near 1163 cm^{-1} —i.e., the possibility that this frequency is present in the monomeric molecules cannot be finally eliminated.

At best, Brattain's curves show only two peaks in the range of the above five but, consistent with the present results, the center of the unresolved absorptions moves to shorter wave-lengths as the temperature decreases—the increasing predominance of the 1214-cm^{-1} band as the concentration (i.e., association) increases. In the vapor of $\text{C}_6\text{H}_5\text{OH}$ absorptions are recorded at 1250 cm^{-1} and 1170 cm^{-1} , the latter being almost certainly double. In $\text{C}_6\text{H}_5\text{OD}$ vapor there are absorptions at 1250 cm^{-1} and 1166 cm^{-1} .³ These and other results indicate that the 1249-cm^{-1} absorption found above does not arise from the OH group and the present results show it is not influenced by the association process. Similarly, Lecomte has given good reason to suppose that the 1147-cm^{-1} band is really a combination tone involving two "nuclear" frequencies.

There is little doubt that the 1174-cm^{-1} absorption is a $\delta(\text{O}-\text{H})$ band for the monomer molecules in solution which is shifted to 1214 cm^{-1} on association ($\Delta\nu = +40\text{ cm}^{-1}$) and it may be that the 1163-cm^{-1} band also arises from essentially the same group in the associated species. Pauling⁶ has given reasons for supposing that in phenol the hydroxyl hydrogen is tied in the plane of the benzene ring; it can at least be accepted that there will be a certain potential

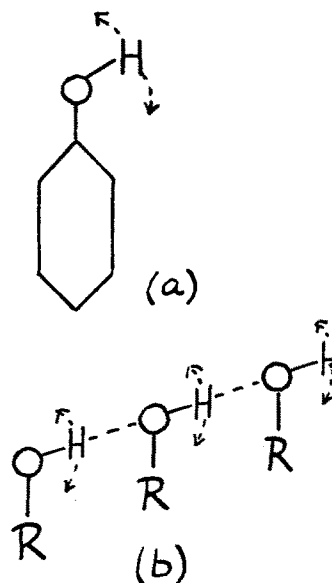


Diagram of (a) single in-plane $\delta(\text{O}-\text{H})$ vibration; (b) hydrogen bonding.

minimum for it in that rotational position. This leads to the single in-plane $\delta(\text{O}-\text{H})$ vibration in monomeric phenol (a). (The out-of-plane vibration will be of much lower frequency and is the likely cause of the extended general absorption below 14μ .) In the dimer and higher molecular species, however, there are clearly two environments for the $\text{O}-\text{H}$ groups, the terminal member

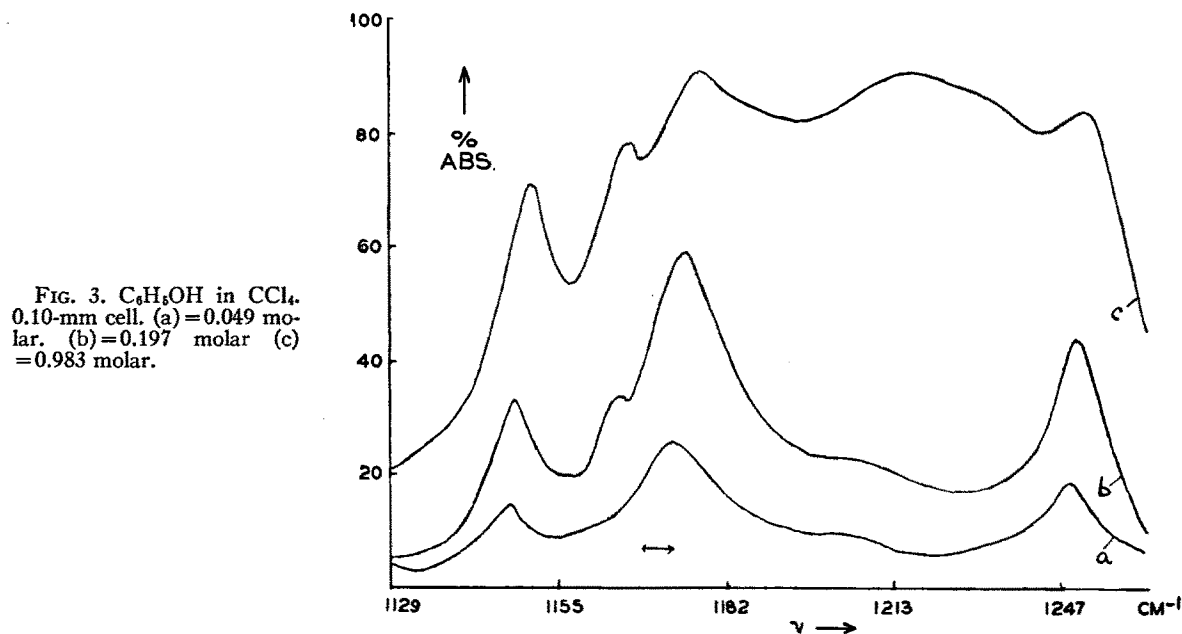


FIG. 3. $\text{C}_6\text{H}_5\text{OH}$ in CCl_4 . 0.10-mm cell. (a)=0.049 molar. (b)=0.197 molar (c)=0.983 molar.

⁶ L. Pauling, J. Am. Chem. Soc. 58, 94 (1936).

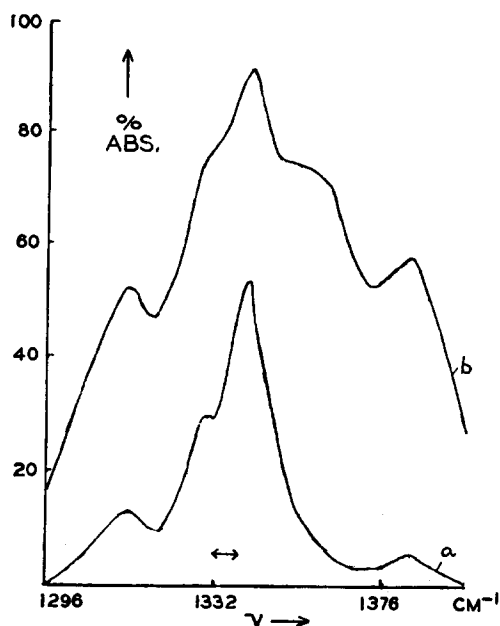


FIG. 4. C_6H_5OH in CCl_4 . 1.0-mm cell.
(a) = 0.045 molar. (b) = 0.224 molar.

being virtually "free," the others involved in "hydrogen bonding" (b). It is certain that for the latter the deformation O—H frequency will be increased with respect to the monomer—owing to the greater constraint on the angular movement when the H atom is between two oxygens. For the terminal O—H group it is quite plausible to suggest a slight relaxation of the restoring force, i.e., a reduced frequency, as for instance would occur if some of the "bonding power" of its

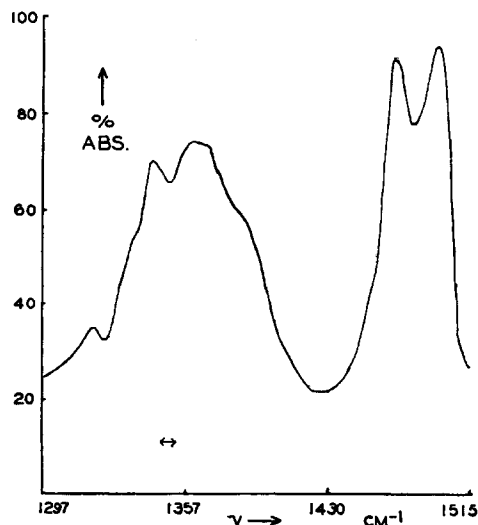


FIG. 5. C_6H_5OH in CCl_4 . 0.10-mm cell. 1.52 molar.

oxygen is involved in the formation of the "hydrogen bridge."

These suggestions are in sensible agreement with the form and intensities of the respective features. The 1214-cm^{-1} band is not only the strongest absorption at concentrations above 1.0 molar, but it is also the broadest even when less intense. As might be anticipated for the comparatively "free" terminal O—H group, the corresponding band (1163-cm^{-1}) appears as sharply defined as that of most monomeric absorptions.

While this scheme provides a consistent account of the region, it should be emphasized that the splitting of the $\delta(O-H)$ absorption, which appears to be established in the associated molecules, could well arise from more general factors than those favored in the above interpretation—e.g. from the presence of two or more groups of similar frequencies in the same molecule. However, the simple explanation given is susceptible to direct experimental test when intensity measurements made under higher resolution become available.

7.8 μ to 6.5 μ

Atmospheric water absorptions are involved in the background of this section from 1340-cm^{-1} to higher frequencies. The following absorption centers are clearly present in dilute solutions and so arise from isolated molecules.

$\nu\text{ cm}^{-1}$	1314	1332	1342	1382	1471	1497
I	w	ms	s	w	vs	vs

The distinctive feature appearing in more concentrated solutions is the strong absorption centered near 1361-cm^{-1} . This is entirely absent in the dilute solutions but at 1.5 molar it is stronger than the neighboring sharp 1342-cm^{-1} peak which is an outstanding feature at low concentrations (see Figs. 4 and 5). Temperature change from 20° to 34°C reduces the intensity of this new absorption relative to that ascribable to the monomeric molecules and so confirms its assignment to associated molecules. While the situation is complicated by the presence of a larger number of absorptions from the simple molecules, we clearly have here the analog to the changes in the methyl alcohol spectrum in the same region. The 1361-cm^{-1} band is that corresponding to the

$\delta(\text{C}-\text{O})$ vibration in the associated molecules. It is not immediately obvious which of the observed frequencies in this neighborhood should be assigned to the same vibration in the simple phenol molecules. For the monomeric alcohol molecules in solution it was located at 1331 cm^{-1} . How this frequency would vary as a result of the change in structure and bonding in passing from methyl alcohol to phenol is not predictable. In dilute solutions, as already mentioned, the strongest feature is the (incompletely resolved) doublet at 1332 cm^{-1} , 1342 cm^{-1} . It is the only band reported in this region for $\text{C}_6\text{H}_5\text{OH}$ vapor ($\sim 1330\text{ cm}^{-1}$) and it is probably also present at about 1316 cm^{-1} in $\text{C}_6\text{H}_5\text{OD}$. Thus, quite possibly $1332\text{--}1342\text{ cm}^{-1}$ represents the $\delta(\text{C}-\text{O})$ absorption in the monomer phenol molecules; its doublet nature would conform to the anticipation that the degeneracy in this vibration, apparently complete in CH_3OH , is removed in the phenol structure. One aspect of this assignment is that the change in $\delta(\text{C}-\text{O})$ on association in methyl alcohol was 70 cm^{-1} , while this choice in phenol gives $\Delta\nu = 24\text{ cm}^{-1}$. This is not a fatal objection. Applying the former value for the change to the 1361 cm^{-1} associated phenol frequency suggests $\sim 1290\text{ cm}^{-1}$ for the monomer absorption. The 1314 cm^{-1} band is the nearest to this figure. However, the changes in intensity with concentration and temperature at present observed indicate the 1337 cm^{-1} feature as the more likely $\delta(\text{C}-\text{O})$ monomer frequency.

In comparison with the seven centers picked out above, Brattain's curves for liquid and solid phenol show only two absorptions between 8.0μ and 6.5μ . The diminution of the 1361 cm^{-1} band with decreasing association accounts for the wave-length shift in his main absorption peak. The strong absorptions at 1471 cm^{-1} and 1497 cm^{-1} are due to the benzene ring—benzene itself having a single fundamental at 1485 cm^{-1} . The 1382 cm^{-1} feature is a weak absorption and may well be a combination band or overtone.

Discussion

The foregoing observations have served to indicate the changes in two of the deformation vibrations when simple hydroxylic molecules become associated. One point of significance is that these changes are more pronounced in methyl alcohol than in phenol (see Table I). This fact

TABLE I.

Vibration	$\delta(\text{C}-\text{O})$		$\delta(\text{O}-\text{H})$	
	CH_3OH	$\text{C}_6\text{H}_5\text{OH}$	CH_3OH	$\text{C}_6\text{H}_5\text{OH}$
Monomer (cm^{-1})	1331	1337	1030	1174
Associated (cm^{-1})	1401	1361	1110	1214
$\Delta\nu/\nu \times 100$	5.3	1.8	7.8	3.4

can be connected with the greater initial flexural rigidity of the bonds in phenol compared with the alcohol, i.e., the higher force constants for these vibrations in the former case. The higher values in phenol of the frequencies themselves suggest such conditions. This is particularly true for the $\delta(\text{O}-\text{H})$ frequency for, other things being equal, the mass factor change would tend to reduce it in $\text{C}_6\text{H}_5\text{OH}$ compared with CH_3OH . However, the much higher polarizability of the phenyl group heightens the angular constraint on the motion of the (polar) H-atom. On this consideration the relative positions of the corresponding absorptions in CH_3OH and $\text{C}_6\text{H}_5\text{OH}$ is only what would be expected.

For the vibration referred to here as $\delta(\text{C}-\text{O})$, the mass factor would very probably show a much greater variation than for the $\delta(\text{O}-\text{H})$ vibration in the two molecules. Thus, despite the changed force constant, the apparent coincidence of the phenol and alcohol frequencies is not precluded.

A comparison of these changes with those in other related simple molecules will be of further interest.

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