

THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 5

NOVEMBER, 1937

NUMBER 11

Spectroscopic Studies of the Hydrogen Bond. II. The Shift of the O-H Vibrational Frequency in the Formation of the Hydrogen Bond*

RICHARD M. BADGER AND SIMON H. BAUER

Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California

(Received July 30, 1937)

The association spectra of a number of acids and alcohols in the region $\lambda\lambda 9000$ – $11,000$ have been observed both in solution and in the pure liquids. In each case a broad band with maximum near $\lambda 10,000$ was observed while in the alcohols an additional weaker band near $\lambda 9000$ appears to be present. Evidence is presented that the $\lambda 10,000$ band is to be identified with the O–H group. This evidence includes the behavior of the association band with change in concentration and temperature and its presence in several substances in which absorption other than that due to the O–H group is practically absent in the region studied. New evidence is given that a weak intermolecular

hydrogen bond is formed between acetone and methyl alcohol. It is pointed out that the presence of absorption in the narrow O–H bands is not to be taken as evidence of the absence of hydrogen bonds in case the absorption is weak. The character of the O–H absorption in the case of intermolecular hydrogen bonds is discussed and the probable nature of the spectrum in the case of an intramolecular bond is indicated. A relation between the energy of the hydrogen bond and the shift of the O–H vibrational frequency is pointed out and its use is suggested in the interpretation of certain spectra.

INTRODUCTION

RECENTLY there has been considerable interest shown in a peculiar form of linkage sometimes known as the "hydrogen bond" in which a hydrogen atom, usually belonging to an hydroxyl or amino group, appears to serve as a connecting bridge between two electronegative atoms. The concept of the hydrogen bond has been most useful in the explanation of many cases of molecular association as well as of the closing of rings within a molecule. It has served in the interpretation of many facts which have come to light in the course of physico-chemical investigations of the ordinary sort, and in other fields has been able to account for numerous results which at first sight would appear to be

rather anomalous. These include certain dipole moments and some internuclear distances, determined by x-ray and electron diffraction measurements, which would be expected to be much larger in the absence of some such bond.¹ Though investigations of the types mentioned appear to have established the existence of some peculiar form of bond and have given information about the conditions under which it is to be expected, and in very few cases an estimate of its energy, there are certain points on which they seem to be incapable of giving information. Indeed the exact nature of the bond is not yet clear and it has not been shown in what way the hydrogen atom is involved.²

* This investigation is a part of a program of research made possible by a grant-in-aid from the National Research Council to one of us (R. M. B.) for which it is desired to express appreciation.

¹ For references, see M. L. Huggins, *J. Org. Chem.* **1**, 407 (1936).

² It has not been shown, for example, that the hydrogen atom lies on a line connecting the two atoms which it appears to join, though this is often assumed.

It has recently become evident that spectroscopic investigations are particularly suitable for clarifying a number of doubtful points, since they do give rather direct information about the condition of the hydrogen atom and the strength of its attachment to the atoms with which it is connected. A number of facts have been made evident but no very systematic interpretation has so far been made of the spectroscopic evidence already available which at the moment presents a somewhat confused picture.

Among the facts known are the following. In a considerable number of compounds containing hydroxyl hydrogen, which for various reasons is supposed to be tied up in a hydrogen bond, O—H bands of the approximate frequency and general narrow character of those found in the vapors or dilute CCl_4 solutions of the simple alcohols are absent from the infrared absorption spectrum. Absence of absorption in the 3600, 7100, or 10,400 cm^{-1} regions has consequently come to be accepted as a spectroscopic criterion for the presence of a hydrogen bond.^{3,4} That this is justified we have demonstrated in a previous paper⁵ in which we showed that in acetic acid vapor the intensity of the sharp O—H bands at 10,240 cm^{-1} is a quantitative measure of the concentration of single molecules and consequently of the number of hydroxyl groups not involved in those relatively strong hydrogen bonds which appear to be responsible for association.

However, in a number of cases in which intramolecular bonds might perhaps have been possible Hilbert, Wulf, Hendricks and Liddel report an absorption band near 7100 cm^{-1} , though it is sometimes rather weak and often accompanied by subsidiary bands on the low frequency side. These workers apparently take any absorption at 7100 cm^{-1} as indicative of the absence of hydrogen bonds.

The absence of normal O—H absorption may be taken as evidence of considerable modification of the hydroxyl group on hydrogen bond formation. How great this is in the intramolecular

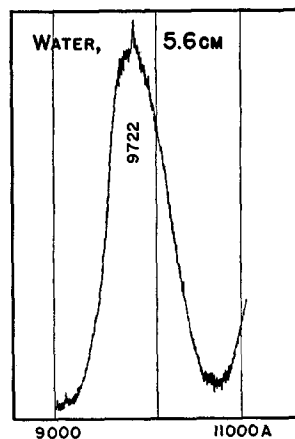


FIG. 1. The absorption band in liquid water at $\lambda 9722$.

bonds has not been made clear since when the 7100 cm^{-1} bands were absent the workers mentioned above did not report whether or not there were other bands on the low frequency side which could be identified with a shifted O—H frequency.⁶ This question is of fundamental importance since in some views of the hydrogen bond it has been regarded that the modification of the O—H, or N—H group may be so great that one could no longer speak of an O—H, or N—H frequency.

In numerous cases of intermolecular hydrogen bonds in associated molecules, or in crystals, absorption bands are present which must be identified with an O—H vibration. In water for example, of which one band is reproduced in Fig. 1, there is no other frequency which could be responsible. It appears not always to have been realized that these bands are decidedly different in appearance from those characteristic of the hydroxyl group in the alcohol vapors, for example, though they are indeed much broader and considerably shifted to lower frequencies. This frequency shift is evidence of a material modification of the O—H group but still not enough to destroy its identity or greatly alter its force constant or internuclear distance.

Numerous studies have been made of the spectra of binary liquid mixtures⁷ in an attempt

³ Hilbert, Wulf, Hendricks and Liddel, *J. Am. Chem. Soc.* **58**, 548 (1936).

⁴ In this paper we shall confine ourselves almost exclusively to the O—H—O linkage but similar investigations have been made of other types of bridge. See M. Freyman and M. R. Freyman, *J. de phys. et rad.* **7**, 506 (1936).

⁵ Badger and Bauer, *J. Chem. Phys.* **5**, 605 (1937).

⁶ In one case of the intramolecular bond a shifted O—H band has been observed in the 3μ region. It has been shown that in *o*-nitrophenol the hydroxyl group is responsible for a considerable part of the absorption near 3300 cm^{-1} . See Buswell, Deitz and Rodebush, *J. Chem. Phys.* **5**, 501 (1937).

⁷ See Williams and Gordy, *J. Am. Chem. Soc.* **59**, 817 (1937). This paper contains references to previous work.

to demonstrate the formation of hydrogen bonds between dissimilar molecules. In a number of cases the spectrum of a mixture, such as of alcohol and acetone,⁸ was found to differ appreciably from the calculated sum of those of the components. The reported shift of the C=O frequency of acetone on mixing with alcohol is very interesting if real. Unfortunately such comparisons of observed spectra with those calculated from Beer's law are likely to be considerably in error unless the observations are made with extreme precision and great resolving power. It would be more convincing if a comparison were made between the spectrum of the mixture and that obtained when the separate components were placed in two absorption cells in series in the absorption path.

The observations on the O-H frequency might at first sight seem to indicate the opposite of that which was intended. In liquid alcohol the hydroxyl hydrogens are presumably almost entirely engaged in hydrogen bonds, and the apparent shift of the O-H band to higher frequencies on dilution with acetone shows that these bonds are broken by a decrease in association and if any new ones are formed between the dissimilar molecules they must be relatively weak. It is evident that additional facts are needed in order to make a satisfactory interpretation of the data on liquid mixtures.

There are numerous gaps in our knowledge which must be filled before we can fully understand what spectroscopy is able to tell about the condition of the O-H or N-H groups involved in hydrogen bonds. There still seems to be some doubt as to whether there may be different kinds of these bonds which may be distinguished in type as well as degree, in particular whether or not there is any essential difference between the intermolecular and intramolecular bonds.

We have consequently undertaken a study of the O-H absorption under a variety of conditions chosen so as to answer some of these questions. This is a very favorable case for investigation since, owing to the fact that the angle between the two oxygen bonds is not greatly different from 90°, the valence frequency

of the O-H group is but little affected by differences of mass in the molecules to which it is attached though it is greatly altered by interaction of the O-H group with other atoms in its immediate environment. We have previously observed small shifts in the O-H frequency in going from the primary to the secondary and tertiary alcohols and much larger ones in going to the unassociated oxy-acid molecules.⁹ In this paper we shall consider some cases in which the O-H group has been considerably modified by entering into a hydrogen bond and shall show what kind of spectrum is generally to be expected in this case.

EXPERIMENTAL

The greater part of the investigation was carried out with the use of a large Littrow glass spectrograph with a dispersion of about 70Å per mm at $\lambda 9000$, though a few exposures were made with higher dispersion to settle some doubtful points. Eastman 1Z plates, sensitized with ammonia, were used throughout. Two different preparations of these plates were used. The earlier one, with which most of the work was done, showed very uniform sensitivity over a wide range, though there was a maximum near $\lambda 10500$ and the sensitivity dropped off very rapidly beyond $\lambda 11,000$, as may be seen in the last section of Fig. 2. The broken curves represent the background blackening at a number of different intensities and were obtained by interposing screens with the transmissivities indicated in the diagram. We have had some difficulty in carrying out any precise photometry with ammonia sensitized plates, but most of the microphotometer curves may be at least qualitatively interpreted by use of the curves of Fig. 2. The second preparation of 1Z plates showed a somewhat different sensitivity curve and had a more pronounced maximum near $\lambda 10500$. Spectra taken with the second emulsion are shown in Figs. 3, 4, 5, and the last section of Fig. 7.

The wave-lengths of most maxima, as well as of some points of inflexion in the curves which are definitely real, are indicated in the diagrams. It is difficult to measure accurately the maxima of broad bands in regions where the plate

⁸ W. Gordy, Phys. Rev. 50, 1151 (1936).

⁹ Badger and Bauer, J. Chem. Phys. 4, 711 (1936).

sensitivity shows a trend, but we do not believe that the errors are great.

In regard to the materials used it does not seem necessary to make any remarks other than that adequate precautions were taken to secure purity. In the investigation of sulfuric acid the fuming acid was used. The phosphoric acid was prepared by adding P_2O_5 to 90 percent acid to make up to the formula H_3PO_4 .

DISCUSSION OF THE RESULTS

In beginning this investigation we were confronted by one difficulty in particular. In searching for bands which may be ascribed to the vibrations of a somewhat modified O—H group, the frequency of which is not precisely known, it is frequently difficult to make a positive identification owing to the possible presence of bands of other origin in the same region. We soon found that in many cases of intermolecular hydrogen bond formation not only is the hydroxyl frequency considerably decreased but the characteristic bands are greatly broadened so that the intensity of absorption at any point is relatively small. Rather great path lengths are required for their study which in organic compounds frequently bring out various weak bands involving C—H and other vibrations. These could easily escape attention under the conditions suitable for observing the normal narrow O—H bands, but are sometimes bothersome in the study of the broad bands. The most certain identification can of course be made when the same substance can be studied both when the O—H group is relatively unperturbed and when it is involved in a hydrogen bond, with other conditions being kept similar and *with the same amount of material in the absorption path* in the two cases. With the alcohols this was possible but with most other substances it was not and we were obliged to use evidence which is somewhat indirect. We have studied several substances in which the region of spectrum under observation must be practically free from any bands not concerning the O—H vibrations, and have compared them with others in which this may not be the case and so have been able to come to rather definite conclusions.

THE ALCOHOLS

A very favorable situation is found in the alcohols since they can be studied at various concentrations in a more or less inert solvent such as CS_2 or CCl_4 and the changes in spectrum as association progresses with increase in concentration are easily followed. There seems little doubt that the association which has been demonstrated by freezing point measurements, for example, is due to hydrogen bond formation. One may make an estimate of the energy of the bond in two different ways which agree very well and are probably not much in error. By comparing the heats of vaporization of the alcohols with those of the paraffins, or by plotting the former against the number of carbon atoms and extrapolating to zero, one concludes that the O—H group contributes about 7500 cal to the energy of vaporization of the lower primary alcohols. The greater part of this energy may be attributed to the hydrogen bond since a more accurate determination in the case of acetic and formic acids gave practically the same value per bond for the dissociation energies of the double molecules.

The characteristic "association bands" which replace the sharp O—H bands at high concentrations of the alcohols have been observed by several workers.¹⁰⁻¹² We have studied them in detail in CH_3OH through a wide range of concentration keeping the amount of alcohol in the absorption path and the temperature constant. As will be seen in Fig. 2 there are two absorption regions which may definitely be designated as association bands. The more intense one is on the low frequency side of the O—H band of the monomer and has a maximum around $\lambda 10,000$; the other, on the high frequency side, is relatively narrow and weak but seems to be quite real. (The fourth harmonic of the C—H frequencies is located in about this region but can only be responsible for a small part of this band since the intensity increases with concentration.) Both bands show some structure which is much more evident in the original plates than in the microphotometer curves. The shoulders on the curves

¹⁰ Errera and Mollett, *Nature* **138**, 882 (1936).

¹¹ Fox and Martin, *Nature* **139**, 507 (1937).

¹² Kinsey and Ellis, *J. Chem. Phys.* **5**, 399 (1937).

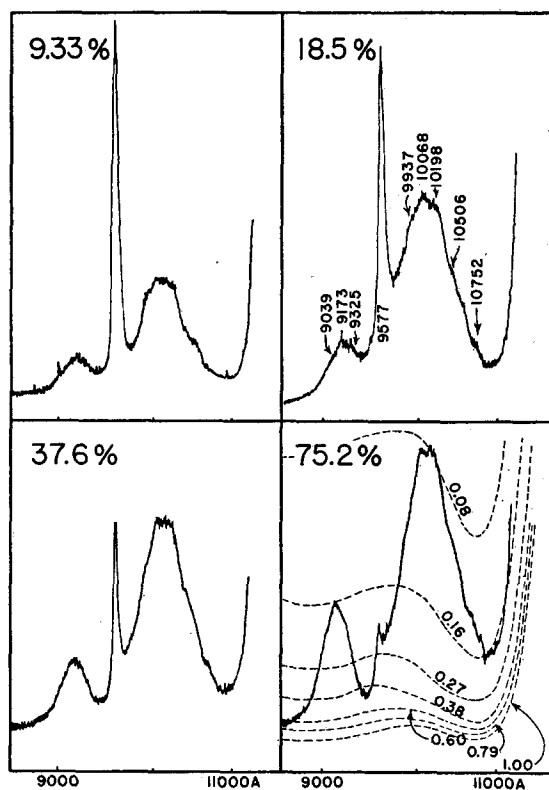


FIG. 2. The absorption spectrum of methyl alcohol in carbon tetrachloride solutions. The concentrations are in mole percent and the path lengths were inversely proportional to the concentration so that the amount of alcohol in the path was constant. The broken curves in the last diagram represent the background blackening with only carbon tetrachloride in the cell and with screens of the transmissivities indicated interposed in the path.

which are designated with wave-lengths are definitely real.

Though the origin of the high frequency association band may be in some doubt we have no hesitation in ascribing the broader and more intense one to a shifted O—H vibration. The behavior of the band on change of temperature is very convincing, as will be shown later. We have made a comparison of the integral molecular absorption coefficient of the narrow O—H band in the state of complete dissociation with the sum of those of the two bands in the associated molecule and find that the latter is certainly not smaller but probably considerably larger. There are difficulties in the way of comparing very narrow with very broad bands but we believe our accuracy is sufficient to show that the total O—H absorption does not decrease greatly on association.

It is of particular interest that the entire association spectrum appears to develop simultaneously and at about the same rate as the concentration is increased. This is quite different from the situation found by Errera and Mollet¹⁰ in their temperature studies of the O—H bands in ethyl alcohol.

Broad association bands with maxima around $\lambda 10,000$ are found also in the spectra of several higher alcohols which we have investigated. Examples are shown in Figs. 3 and 6. The situation on the high frequency side of the sharp O—H bands is more difficult to interpret owing to the presence of the fourth harmonic band of the C—H frequencies. This is evidently very weak in methanol, in ethanol it is quite evident at $\lambda 9098$, and in the higher alcohols becomes quite intense. In ethanol a weak high frequency association band appears at about $\lambda 9400$, distinct from the C—H band, but in the heavier compounds it is entirely obscured, if present. Some observations on temperature effects which will be described below indicate that it is indeed present, superposed on the C—H harmonic.

In the aromatic compounds the situation is very unfavorable since even in the $\lambda 10,000$ region there are bands of appreciable intensity which do not involve the O—H vibration, but presumably result from combinations of the C—H and double bond C=C vibrations.

In the lower primary alcohols the sharp O—H bands are practically absent from the spectra of the liquids, but as the number of carbon atoms increases they show up with appreciable intensity. Note for example *n*-amyl alcohol shown in Fig. 3. This fact need not be ascribed to a weaker hydrogen bond but may well be due to the greater entropy change on dissociation.

In comparing normal, secondary and tertiary alcohols in the liquid state one finds that the intensity of the sharp O—H bands increases in the order given, as shown in Fig. 3, which duplicates observations made by Naherniac¹³ except as regards the wave-lengths of the maxima. These differences may be correlated with data on heats of vaporization. For example the heats of vaporization of *n*-propyl and isobutyl alcohols are greater than those of isopropyl and tertiary-butyl alcohols by about 300 and 500 cal., respec-

¹³ A. Naherniac, Ann. de physique **8**, 528 (1937).

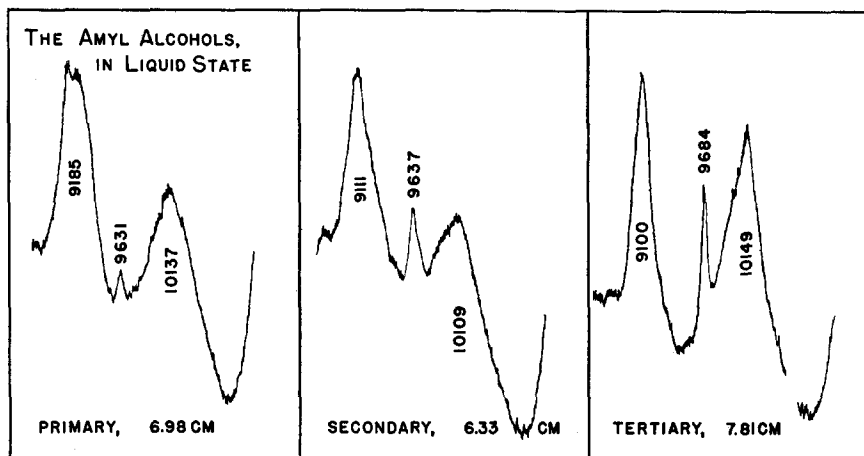


FIG. 3. Comparison of the spectra of the liquid amyl alcohols showing the increase in intensity of the narrow O—H band in going to the secondary and tertiary compounds.

tively. Although these facts point to slightly weaker hydrogen bonds, we are inclined to attribute this entirely to steric factors, namely the crowding of CH_2 or CH_3 groups around the hydroxyl radical which prevents the close approach of two oxygen atoms, since in mixtures of methanol with a secondary or tertiary alcohol the sharp O—H bands disappear. See Fig. 4.

EFFECT OF TEMPERATURE ON THE ASSOCIATION BANDS

Errera and Mollet have studied the effect of temperature on the spectrum of a solution of ethyl alcohol in CCl_4 ,¹⁰ but the results are not simple to interpret. It seems clear that not only a change in the degree of association but also an actual alteration of the spectra of the associated molecules are involved. It is indeed difficult to separate these two effects but it seemed worth while to investigate the temperature changes in the spectra of some of the lower alcohols which in the liquid condition show little absorption in the sharp O—H bands even up to 75°C , and can in a sense be regarded as nearly completely associated.

The spectra of liquid methyl, ethyl and *tert*-amyl alcohol all showed certain changes in common as the temperature was raised. Microphotometer curves of the first two are shown in Fig. 5. In each case absorption decreased in

the vicinity of $\lambda 9000$ but increased markedly in the region between the position of the O—H band of the monomer and the maximum of the $\lambda 10,000$ association band. In methyl alcohol no trace of a sharp O—H band is evident even at 71° , but at the point where it should be expected the long wave association band shows a very sharp edge. At higher temperatures the narrow band becomes quite evident in ethyl alcohol and moderately strong in *tert*-amyl alcohol in which it is present even at 1°C . In each case as the temperature is raised there is a noticeable shift of the maximum of the $\lambda 10,000$ association band to shorter wave-lengths, but it is most evident in methyl alcohol.

As mentioned above, it seems evident that in the $\lambda 9000$ region there is superimposed on the fourth harmonic of the C—H frequency another band which is intimately connected with association. One should not expect the C—H band to be much affected by temperature or association but the $\lambda 9173$ band of methanol is very dependent on both. In this substance the C—H band should be in any case relatively weak. In ethanol two separate bands are evident. The more intense one of shorter wave-length seems little altered by temperature though the other is considerably affected. In *tert*-amyl alcohol the strong and apparently single band in this region must be due in large part to the C—H harmonic but there is nevertheless a considerable decrease in intensity with temperature.

THE SIMPLE ORGANIC ACIDS AND SOME INORGANIC OXY-ACIDS

In the case of the acids we did not find it possible in the $\lambda 10,000$ region to follow the course of the spectrum from the state of complete dissociation to that found in the double molecules. We have been able to follow the weakening in intensity of the sharp O—H band at $\lambda 9760$ in acetic acid vapor as association proceeds,⁵ but the greatest path length which it was convenient to use, though well adapted to the study of the bands in the monomer in which the intensity is concentrated in a narrow region, was not sufficient to make evident any trace of an association spectrum. In solutions of the acids association is practically complete even at the highest temperature which one can use without an apparatus designed for high pressures.

In CCl_4 solutions of a number of monobasic organic acids we have observed broad bands in the $\lambda 10,000$ region, some of which are shown in Fig. 6. They are very similar to the association bands of the alcohols and it seems reasonable to attribute them in part at least to a shifted O—H frequency. However, to make the situation clearer we have investigated a number of substances in which the O—H vibration is the only one of high frequency and in which the $\lambda 10,000$ region should be free of any bands of appreciable intensity for which it is not responsible. These substances include trichloro-acetic acid, fuming sulfuric acid and phosphoric acid, all of which

one should expect to be largely or completely associated by hydrogen bonds. In each case we have observed broad bands similar to those of the organic acids, though there are differences in the distribution of absorption and in the position of the maxima.

HYDROGEN BONDS BETWEEN UNLIKE MOLECULES

We have devised one experiment to see whether the existence of hydrogen bonds between unlike molecules could be demonstrated spectroscopically in a much more direct way than by the studies of liquid mixtures which were mentioned above, and to provide additional information for interpreting those experiments. We have compared the spectra of CCl_4 solutions of methyl alcohol, of acetone, and of the two together. The alcohol solutions were sufficiently dilute that dissociation was great though not complete. On the addition of acetone the narrow O—H band decreased in intensity considerably, as shown in Fig. 7, which demonstrates rather directly the formation of a bridge between the hydroxyl and keto oxygens of the respective molecules. This is a very interesting case since it appears to be one in which resonance is unlikely though it is sometimes supposed to be essential in hydrogen bond formation.

The bond in question seems to be rather weak,

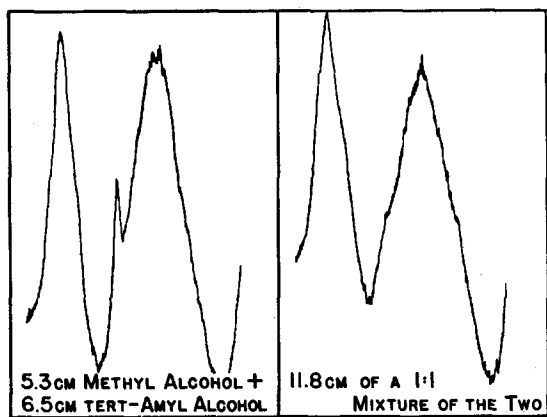


FIG. 4. The disappearance of the narrow O—H band of *tert*-amyl alcohol on addition of methyl alcohol. The spectrum in the first diagram was obtained with the two alcohols in separate cells in series in the light path.

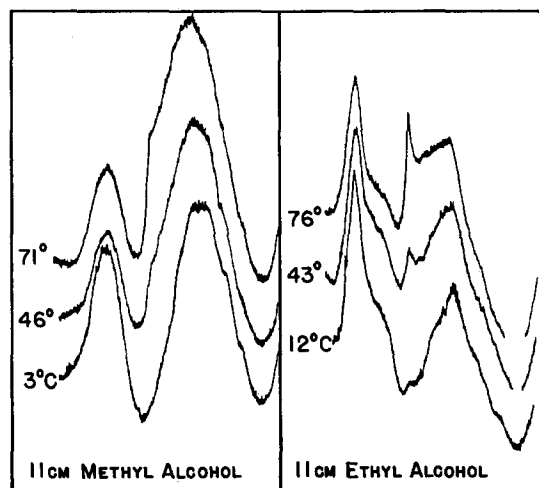


FIG. 5. Temperature dependence of the spectra of liquid methyl and ethyl alcohols. Origins of successive curves are displaced.

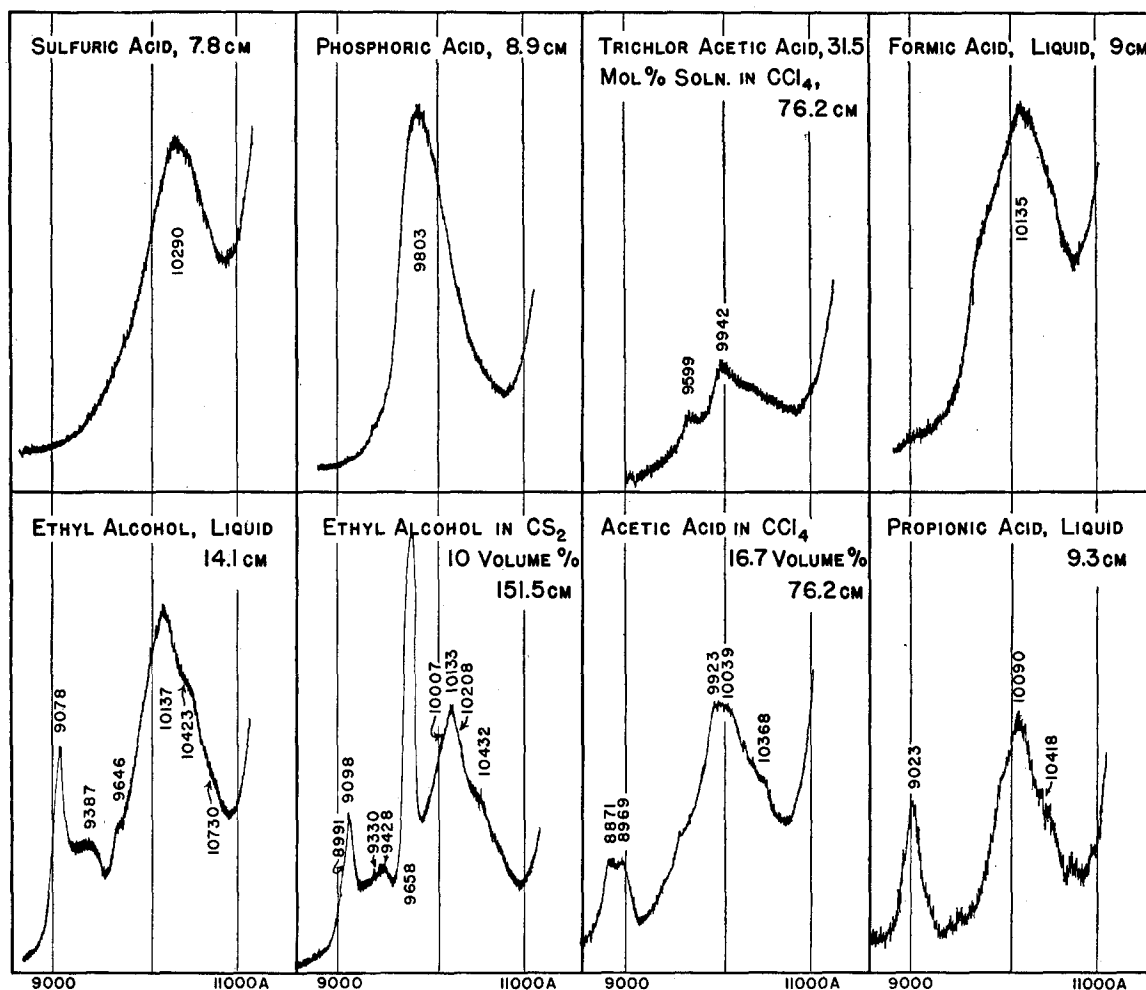


FIG. 6. Association bands in a number of substances. In the upper diagrams the bands must be attributed almost exclusively to a shifted O-H frequency. In the lower diagrams the weaker bands near $\lambda 9000$ are due in part to the fourth harmonic of the C-H vibration.

however, as is indicated by the nature of the association spectrum. This is somewhat difficult to observe in all details since acetone itself has a strong absorption near $\lambda 10,000$, due presumably to a combination of C-H and C=O vibrations; but the essential facts are clear and are especially evident in the spectrum of a solution of methanol in acetone shown in the last diagram of Fig. 7. No sharp O-H band is present such as would be observed in a solution of the same concentration in CCl_4 , but continuous absorption sets in abruptly just at the point where this band would occur and comes to a maximum at considerably shorter wave-lengths than the center of the methanol association band.

THE INTRAMOLECULAR BOND WHICH MAY BE BROKEN BY ROTATION OF SOME GROUP ABOUT A SINGLE BOND

Hilbert, Wulf, Hendricks, and Liddel³ have reported several cases in which an intramolecular bond might perhaps have been expected but was considered to be absent owing to the presence of a band near 7100 cm^{-1} , though this was sometimes weak. This condition has been found in some substances like aldol in which a possible rotation of some group about a single bond could break the hydrogen bond. We have observed one alcohol in which this situation is possible, namely diacetone alcohol, and have compared it with tertiary amyl alcohol in which the immediate

environment of the O—H group is very similar, both substances being studied in CCl_4 solution. See Fig. 8. The former substance indeed shows a sharp band at $\lambda 9700$ but it is very weak compared with the analogous one in the latter, certainly less than one-quarter as strong. We believe therefore that it would be quite unjustified to say that intramolecular bonds are absent in diacetone alcohol. Probably three quarters of the molecules are so bonded though in the remainder the linkage appears to be broken.

From general considerations as well as from known facts it appears to us reasonable to suppose that any hydroxyl group which is so little perturbed that it has about the same vibrational frequency as that found in the monomer alcohols will have also about the same ability to absorb. Consequently if a substance containing these groups has an unusually weak absorption in the regions where the O—H harmonic bands are usually found it is extremely probable that in a considerable fraction of the molecules the hydroxyl group has entered into a hydrogen bond.

GENERAL CHARACTER OF THE O—H BANDS IN CASES ON THE INTERMOLECULAR HYDROGEN BOND

The work which has been described as well as the references which have been cited make it

clear that in cases of the intermolecular bond involving hydroxyl hydrogen there is indeed a rather characteristic spectrum which can be ascribed to the vibrations of a modified O—H group. This differs somewhat in individual cases but in general one finds very broad bands with some structure which are considerably shifted to the low frequency side of the normal O—H harmonic bands. It seems worth while to discuss the probable reasons for the general character of these bands before considering the case of the intramolecular bond.

Now in those instances in which it is possible to observe the narrow O—H bands of the same substance in the two conditions it appears that in going from vapor to liquid or solution they are shifted to longer wave-lengths by an appreciable amount (about 100 cm^{-1} in the case of the third harmonic) but are not greatly broadened. The "association" bands on the other hand are distinguished by a breadth which is from ten to fifteen times greater. There may be several causes for this but the following list of five appears to us to include the more probable ones:

1. The association bands may not be due exclusively to a shifted O—H vibration but may arise in part from an alteration in frequency and intensity of other bands, or may indeed include combinations of C—H frequencies with intermolecular vibrations in the polymer.

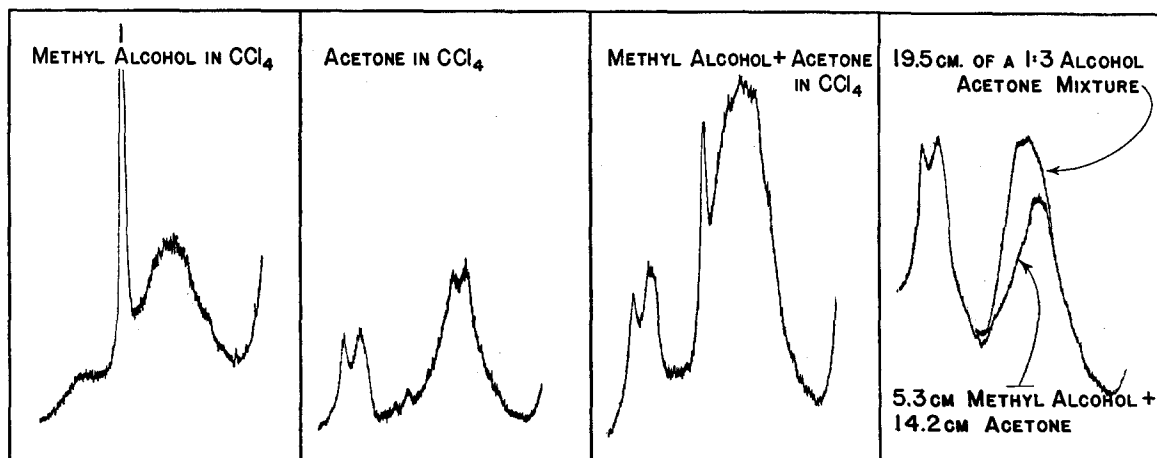


FIG. 7. Microphotometer curves demonstrating the formation of an intermolecular bond between methyl alcohol and acetone and the development of a new association spectrum. In the first three cases the path length was 75.8 cm and the concentrations were: (1) 5 cc methyl alcohol per 100 CCl_4 , (2) 25 cc acetone per 100 cc CCl_4 , (3) 5 cc alcohol and 25 cc acetone per 100 cc CCl_4 . The lower curve of the last diagram was obtained with the two liquids in separate cells in series in the light path.

2. Several different polymers may exist simultaneously in which the situation of the O—H group is slightly different. It is evident from freezing point measurements as well as from vapor densities that in the case of the alcohols we have the situation known as the "continued equilibrium" in which a great number of different kinds of polymer are in equilibrium.

3. There may be combination bands of the O—H vibration with intermolecular vibrations. This would not be surprising since the interaction energy must be appreciable.

4. In the completely dissociated simple alcohols or acids we have a degenerate condition, with only one O—H frequency. When association takes place this degeneracy is partly removed and there exists in each polymer a number of modes of O—H vibration some of which may still be degenerate, but some of which will have different frequencies.

5. Since the hydrogen bridge is relatively very weak in comparison with other bonds there will exist in any polymer low frequency intermolecular vibrations in which the component molecules behave as practically rigid units and oscillate with respect to each other. Since these vibrations almost exclusively involve a stretching or bending of the hydrogen bonds they will interact greatly with the O—H vibration. Being of very low frequency they will on the average be nearly classically excited at ordinary temperatures, especially in the heavier molecules. As they are more and more excited, due to the character of

the potential function the molecules will on the average be farther apart and the mean condition of the O—H groups will approach that in the completely dissociated state. Owing to the presence of polymers in various excited states we should expect at room temperature a greatly broadened band with upper limit near the O—H frequency of the monomer, and lower limit near the position which the band would have at very low temperatures. The absorption maximum, which must be in some way related to the most probable energy in the intermolecular degrees of freedom, would be expected to shift to higher frequencies as the temperature is raised.

It is not possible to give a general discussion of the first two reasons though in regard to the second we call attention to the studies of methyl alcohol at various concentrations. The association bands do not seem to change in character on increasing the concentration, but develop as a whole. It appears to us that even in rather dilute solutions the polymers present in any appreciable concentration are already sufficiently complex to possess practically all possibilities with regard to the O—H group which are found even in the liquid alcohol. Vapor density and freezing point data indicate that the tendency for association is small at the dimer stage but increases with higher polymers.

In any case we have studied some substances in which reasons 1 and 2 can scarcely play any part. In trichloroacetic, sulfuric, and phosphoric acids the absence of C—H vibrations should make the spectrum in the $\lambda 10,000$ region quite free of bands not involving the O—H vibration. In the solutions of the acids and possibly even in the liquid state the dimers should greatly predominate over any other polymer. But even in these cases the same broad character of the association bands is preserved indicating the importance of the remaining reasons. We shall now discuss points 4 and 5 in somewhat greater detail in the case of the organic acids which presents some particularly interesting possibilities.

DEGENERACY OF THE O—H VIBRATIONS IN THE ACID DIMERS

In the monobasic organic acids, which exist principally in the form of double molecules, we have an especially simple situation. In consider-

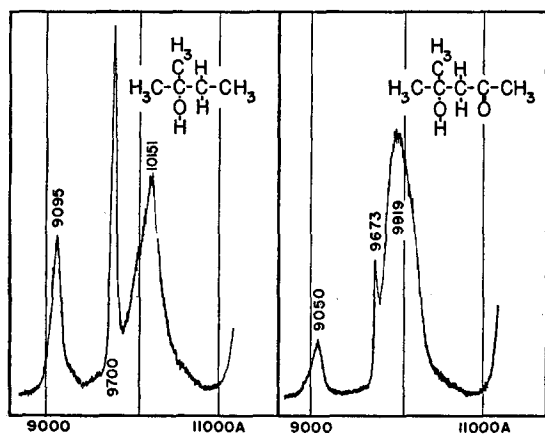


FIG. 8. Spectra of *tert*-amyl and diacetone alcohols in carbon tetrachloride solution. Concentration in each case was about 18.05 mole percent, and path length 75.8 cm.

ing the O—H vibrations appropriate coordinates will be $(x_1+x_2)/2$ and $(x_1-x_2)/2$, where x_1 and x_2 are the displacements of the respective hydrogen atoms from their equilibrium positions, measured in the direction away from the oxygen atoms to which they are most strongly attached. In an approximate treatment we may regard them as normal coordinates since all of the molecule except the hydroxyl hydrogens will be comparatively rigid and motionless. Corresponding to the two coordinates there will be two frequencies which may be designated as ν_s and ν_a . If the double molecule possesses a center of symmetry, which is practically certain in the case of formic acid, ν_s will be infrared inactive while ν_a will be active. We shall expect only those infrared bands roughly given by the formula $\nu = V_s\nu_s + V_a\nu_a$ where V_a is odd, though V_s may take the value of any integer. Thus in the 3μ and 1.5μ regions we shall expect only ν_a and $\nu_s + \nu_a$ respectively, while near 1μ there will be two bands, $2\nu_s + \nu_a$ and $3\nu_a$. This is strictly true in formic acid while in heavier molecules which do not possess a center of symmetry it will be so nearly true that the bands mentioned will probably be the only ones strong enough to observe. It seems fairly clear that the association band of the organic acids near 1μ is a doublet though the temperature broadening makes it difficult to be certain. The 3μ and 1.5μ regions have not been investigated with sufficient dispersion to make the situation clear.

A consideration of the potential function of the molecule brings out some additional facts. See Fig. 9. If the hydroxyl hydrogens are indeed located on the lines joining the oxygen atoms which they link the potential energy will have two minima in $(x_1+x_2)/2$ and one only in $(x_1-x_2)/2$. From this it is clear that ν_a is probably of higher frequency than ν_s . For the development of the theory of the hydrogen bond it is important to have a more exact knowledge of the potential function, in particular of the height of the potential hump separating the two minima in $(x_1+x_2)/2$, but this will probably be rather difficult to obtain. The double minimum will of course give rise to a splitting of the energy levels, but on account of the diffuse character of the spectra it will probably be impossible to observe this except perhaps in the case of one or two

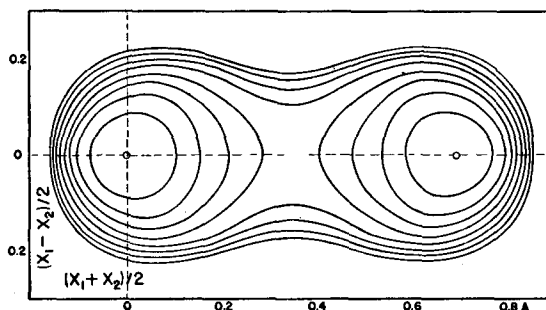


FIG. 9. Topographic diagram showing approximate dependence of the potential energy of the organic acid double molecule on two coordinates. The interval between contours is roughly 10,000 cal.

levels just below the potential hump. If one could make observations on high harmonic bands one might be able to come to some conclusion but there are experimental difficulties in the way.

BROADENING OF THE BANDS DUE TO THE INTERACTION BETWEEN THE O—H AND THE TEMPERATURE EXCITED INTER-MOLECULAR VIBRATIONS

In the simplest case, the dimer of a simple monobasic organic acid, there are six vibrations, which we may call intermolecular, in which the hydrogen bonds due to their extreme relative weakness will be concerned almost exclusively. The two of highest frequency involve in the one case simultaneous stretching or compression of the two bonds (alternate approach and recession of the two component molecules), and in the other the stretching of one bond while the other is compressed. We may estimate force constants for the hydrogen bonds from the distance between the hydrogen atom and the oxygen to which it is weakly attached.¹⁴ This separation must be roughly 1.71A, since the O—O distance is known to be 2.67A in the formic acid dimer¹⁵ and the internuclear separation in the hydroxyl group cannot be much greater than in the water molecule. In the formic acid dimer the two high frequency internuclear vibrations will be of the order of 350 cm^{-1} and will have about 0.4 of classical excitation at room temperature.

In heavier molecules these frequencies will be considerably lower and excitation more nearly

¹⁴ R. M. Badger, J. Chem. Phys. 2, 128 (1934).

¹⁵ Pauling and Brockway, Proc. Nat. Acad. Sci. 20, 336 (1934).

complete while all other vibrations in all cases must be practically completely excited since they involve chiefly a bending of very weak bonds. This means that up to 3600 cal. per mole of dimer may be present in degrees of freedom involving hydrogen bonds even at ordinary temperatures. It is not surprising that the O—H association bands are extremely broad, and that O—H frequencies should so frequently be difficult to observe in the Raman spectrum.

We have attempted to observe temperature changes in the spectra of organic acids in carbon tetrachloride solution but the temperature range in which it was possible to work was somewhat restricted and our results were not conclusive. In the case of the liquid alcohols the shift of maximum with temperature was quite noticeable.

EXPECTED CHARACTER OF THE O—H BANDS IN CASES OF INTRAMOLECULAR HYDROGEN BOND

Unfortunately in the λ 9000–11,000 region we have found it impossible to make any very certain identification of bands due to an O—H group engaged in an intramolecular bond. As mentioned above, the aromatic compounds in which such bonds largely exist have combination bands near λ 11,000, and in some aliphatic substances a similar difficulty was encountered since it was probable that combinations of C—H and C=O vibrations were responsible for a part of the absorption observed. However, in the regions of the fundamental and second harmonic the situation may be more favorable and it seems worth while to make some suggestions as to what may be expected in case observations can be made. The position of a band can probably be fairly accurately estimated if the bond energy is known, as will be shown below, but the character of the band may well be rather different from that of the association bands of the alcohols, etc.

As will be discussed below we see at the moment no spectroscopic evidence that the kind of interaction between the hydroxyl group and other atoms which produces a very considerable lowering of the O—H frequency in orthochlorophenol, or in the single molecules of acids in the vapor state, is to be distinguished from that found in the hydrogen bond in the commonly

accepted sense, except that in the former case steric factors prevent the normal strength of the bond being realized. In the single molecules of formic or acetic acid the O—H bands though of about 300 cm^{-1} lower frequency than the methyl alcohol bands, in the case of the third harmonic, are sharp and of normal character. This is to be expected since there is only one vibration of the molecule which more or less exclusively involves the hydrogen bond and this will not be of very low frequency since it is a torsional motion of the light hydrogen atom about the ordinary O—H bond. In the great majority of the molecules this degree of freedom will not be excited and the factor responsible for the breadth of the association bands is absent.

The cases of intramolecular hydrogen bond in the ordinarily accepted sense will lie intermediate between the two extremes. In some instances there may be vibrations of moderately low frequency within the molecule which if excited will tend to break the bond, but the excitation will in general not be very great and the O—H bands will still be rather sharp. In nondegenerate cases we shall not expect any structure in the bands unless the O—H group is able to be found in more than one situation.

CONCLUSION

The various kinds of evidence which have been used to establish the presence of hydrogen bonds have sometimes led to contradictory conclusions but this should seldom be the case if one establishes really satisfactory criteria which have been compared with each other in a number of cases. In order to establish such criteria one must of course decide what is to be meant by a hydrogen bond. Shall the term be reserved for certain cases in which the O—O or other internuclear distance concerned and the energy required to break the bond lie within rather narrow limits, or shall it be extended to include a great variety of weaker interactions such as are responsible for the low frequency of vibration of the O—H group in single molecules of the acids and in orthochlorophenol, and for a part of the heats of vaporization of HCN and HCl? These latter, of course, merge into the group of interactions known as van der Waals forces.

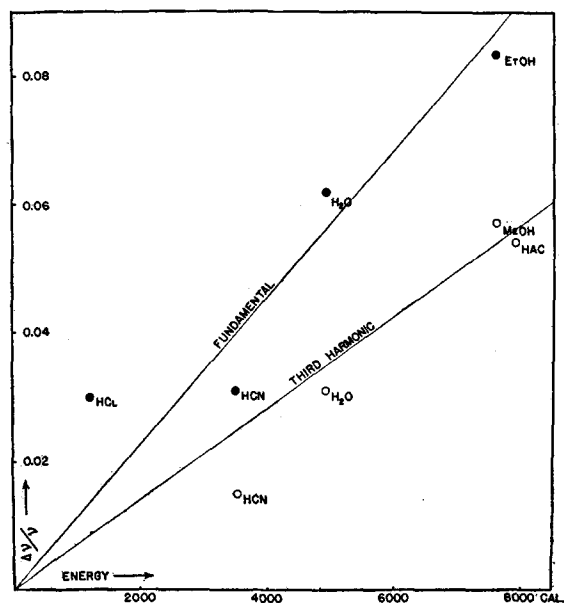


FIG. 10. Relation between frequency shift and interaction energy.

It would appear that the most satisfactory ultimate criterion for the presence of a bond is the energy required to break it, though of course one may decide to distinguish between different hydrogen bonds of the same energy and evidence may be forthcoming to show that this is desirable. So far as spectroscopic information goes we are at present only able to distinguish between cases by the magnitudes of the frequency shifts and by the intensity of absorption. Of the frequency shifts there appears to be a practically continuous series of cases from the small displacement when an alcohol vapor is dissolved in CCl_4 to ones so large that the O—H frequency approaches that of the C—H group.

We have mentioned some qualitative evidence that the shift of the O—H frequency is some measure of the strength of a hydrogen bond, or more generally of the magnitude of some interaction between hydroxyl hydrogen and another atom. It is unfortunate that the energies are known accurately in only a few cases, but we have collected some data which seem to be more or less reliable and present them in Fig. 10. In the organic acids and the alcohols the frequency shift plotted is the difference between the maximum of the respective association band and the

frequency of the narrow band of methyl alcohol vapor, which was taken as standard or normal. In the other cases the shift is that observed in going from vapor to liquid. The energy data for acetic acid were obtained from the work of MacDougall.¹⁶ In the other cases they were estimated from heats of vaporization. The procedure in the case of the alcohols has been outlined above. In water the energy of vaporization was assumed to be due practically entirely to the breaking of hydrogen bonds. In HCl and HCN one-half of the energies of vaporization of Cl_2 and $(\text{CN})_2$ were subtracted from the energies of vaporization of the two liquids, respectively. The frequency shifts of the water band were taken from our own data in the case of the third harmonic, and from the Raman observations of Cross, Burnham and Leighton¹⁷ for the fundamental.

It is seen that the frequency shifts are indeed a semiquantitative measure of the energies. Considering the nature of the bands in the associated acid molecules, for example, it is evident that there will be no very simple general relationship, but even if an approximate proportionality exists, as seems to be the case, it should be very useful. It is interesting that if the percentage frequency shifts of the water band observed by Cross, Burnham and Leighton are plotted against energy of vaporization, instead of against the temperature, the slope of the curve at lower temperatures is nearly the same as in our plot.

The plot in Fig. 10 suggests that corresponding to the series of frequency shifts there is a similar set of energy conditions, which would make it very arbitrary indeed to put definite limitations on the situation which is to be described as a hydrogen bond. If a few more energy data can be obtained to confirm the approximate relationship between shift and energy we believe that it will be very useful in the further discussion of many cases which have already been investigated, particularly those in which a number of subsidiary maxima accompany a weak absorption near 7100 cm^{-1} .

¹⁶ F. H. MacDougall, *J. Am. Chem. Soc.* **58**, 2585 (1936).

¹⁷ Cross, Burnham and Leighton, *J. Am. Chem. Soc.* **59**, 1134 (1937).