the Wisconsin Alumni Research Foundation for financial support.

Conclusions

From the preceding discussion we conclude that the wave function for a hydrogen bond should include both polar and homopolar terms. Although we are not able to decide quantitatively the relative importance of each it seems safe to conclude that both are important. Most simply, therefore, the hydrogen bond must be considered as consisting of at least the three states $X^-H^+X^-$, X—H X and X H—X.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Effect of Association on the Infra-red Absorption Spectrum of Acetic Acid

BY R. H. GILLETTE AND FARRINGTON DANIELS

The effect of interactions between various groups on the infra-red absorption of organic molecules has been investigated recently by a number of workers.[1] The work, however, has been confined chiefly to the study of the intensities of overtones of vibrations involving hydrogen linked to carbon, nitrogen or oxygen. Acetic acid is particularly interesting in this connection because one can observe the effect of association on the spectrum of the carboxyl group. It has, in fact, proved possible to measure a considerable portion of the spectrum of both the monomeric and dimeric acid and to interpret it so as to bring it into accord with the results of electron diffraction measurements and, perhaps less certainly, of electric moment measurements.

Several investigators have used Raman data to obtain such information.[2] Dadieu and Kohlrausch[3] have determined the Raman spectra of several binary liquid mixtures of acetic acid in different solvents and have found that only the lines associated with the C═O group are affected by the solvent. Leitman and Ukholin[4] have shown that the Raman line at 623 cm.$^{-1}$ in acetic acid becomes much weaker when the acid is dissolved in water, and finally, as the concentration is decreased, fades out entirely. They interpret this to mean that the association of acetic acid leads to molecules of quite definite configuration.

Experimental

The spectrometer of the Wadsworth type using a rock salt prism, Nerst glow lamp, and Paschen galvanometer has been described before.[5] The absorption cells were made by cementing polished rock salt windows onto both ends of Pyrex tubes 8 cm. long. Glyptol cement was found to be excellent for attaching the windows to the glass—much better than fish glue. The cells were heated electrically with a constancy of ±1°.

The acetic acid, obtained from the Niacet Chemical Company, was carefully purified by distillation *in vacuo*. Different samples always gave the same absorption spectrum.

Results

The vapor of acetic acid was studied at room temperature and at 172° from 1100 to 10,000 cm.$^{-1}$, the results being shown in Table I and Fig. 1 (to conserve space the high frequency region containing only the band ν_1 was omitted in Fig. 1). In both cases the acid was present at a partial pressure of 19 mm. in an atmosphere of air.

TABLE I

Band	25° C.	172° C.
ν_1	2985 cm.$^{-1}$	2985 cm.$^{-1}$
ν_2	1740 cm.$^{-1}$	1786 cm.$^{-1}$
ν_3	1435 cm.$^{-1}$	1398 cm.$^{-1}$
ν_4	1296 cm.$^{-1}$	1288 cm.$^{-1}$
ν_5	1190 cm.$^{-1}$	1185 cm.$^{-1}$

Five sharply defined bands occur in the region studied, their shape suggesting that the rotational fine structure is completely blotted out, as might be expected at the high pressure of foreign gas. Of these, three are not shifted by the increase in temperature although the band at 1190 cm.$^{-1}$ (ν_5) is greatly intensified. The remaining two bands, at 1740 cm.$^{-1}$ (ν_2) and 1435 cm.$^{-1}$ (ν_3) at room temperature, are shifted considerably fur-

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[1] Errera and Mollet, *J. Phys. Radium*, **6**, 281 (1935); Liddel and Wulf, THIS JOURNAL, **55**, 3574 (1933); **57**, 1464 (1935); Hilbert, Wulf, Hendricks and Liddel, *Nature*, **135**, 147 (1935); Pauling, THIS JOURNAL, **58**, 94 (1936).

[2] Mayer, *Physik. Z.*, **30**, 170 (1929); **32**, 293 (1931); Pringsheim and Schlivich, *Z. Physik*, **60**, 582 (1931).

[3] Dadieu and Kohlrausch, *Physik. Z.*, **31**, 514 (1930).

[4] Leitman and Ukholin, *J. Chem. Phys.*, **2**, 825 (1934).

[5] Cross and Daniels, *ibid.*, **2**, 6 (1934).

ther apart at 172°—occuring at this temperature at 1786 and 1398 cm.$^{-1}$, respectively.

Since the temperature shifts are appreciably larger than the shifts produced by substitutions in the acetic acid molecule itself,[6] it was felt that some type of chemical reaction must be involved which changes bonds between atoms. It is well known from the work of Ramsay and Young[7] and Fenton and Garner[8] that acetic acid is almost completely associated into double molecules even at the boiling point, and at 183° and 400 mm. pressure is still 9% associated. If this association is responsible for the observed shifts, it would be expected that at intermediate temperatures where both monomeric and dimeric forms are present both bands should appear. This is strikingly borne out in Fig. 2 where the absorption of the C=O group is shown at various temperatures. As is to be expected the weaker band drifts toward the stronger one due to the fact that the width of the spectrometer slit is finite and some overlapping occurs.

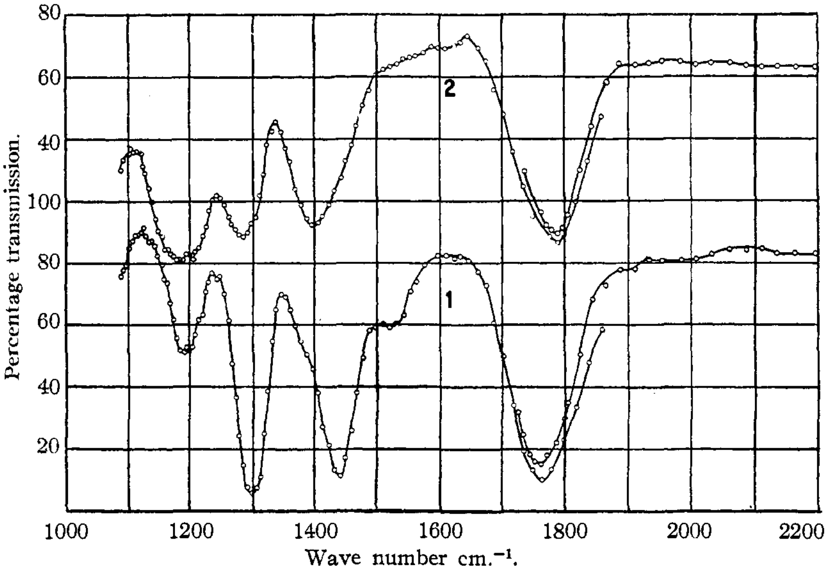

Fig. 1.—The infra-red absorption spectrum of acetic acid vapor. Curve 1 at 25°; Curve 2 at 172°.

Discussion

In order to assign the bands to definite vibrations within the molecule, it is necessary first to consider the nature of the single and double molecules. The former cannot vary greatly from the planar model assumed by Mecke[9] for formaldehyde. There is some arbitrariness in the choice of fundamental modes of vibration for this molecule, but since the molecule is completely unsymmetrical a possible set is shown in Fig. 3, where ω's are used to indicate modes of vibration of the model to be associated with the fundamental frequencies in the absorption spectrum (ν's) having the same subscript. The usual assumptions that interactions between bonds can be neglected and that only the valence vibrations will lie in this region are made.[10] It is apparent that these modes correspond essentially to the vibration of a C=O, a -C-O-, and a C-C bond. At 172° under the conditions of our experiments acetic acid is almost completely dissociated into single molecules and hence the spectrum at this temperature should correspond to that of the model of Fig. 3.

One of the most firmly established frequencies in infra-red spectroscopy is that of the C=O group which occurs in the same region in aldehydes, ketones, acyl halides, amides, esters and acids and has been investigated extensively[11] by both Raman and infra-red measurements. This is clearly to be associated with the ν_2 and ω_2 described here.

Bands occurring in the vicinity of 2960 cm.$^{-1}$ are well known to be produced principally by a valence vibration of the C-H bond.[12] In this region occur also bands due to overtone and combination vibrations of the carboxyl group as well as the fundamental of the O-H vibration. It is also well established that a deformation vibration of the C-H group occurs in the vicinity of 1300 cm.$^{-1}$. To these two vibrations we assign our ν_1 and ν_4, respectively.

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[6] Bennett and Daniels, THIS JOURNAL, **49**, 50 (1927); Gillette, **58**, 1143 (1936).

[7] Ramsay and Young, *Sci. Proc. Roy. Dublin Soc.*, **12**, 374 (1910); see also Drucker and Ullman, *Z. physik. Chem.*, **74**, 604 (1910).

[8] Fenton and Garner, *J. Chem. Soc.*, 694 (1930).

[9] Mecke, "Leipziger Vorträge" (English Edition. Debye, "Structure of Molecules," Blackie and Son, London, 1932, p. 47.

[10] Bartholomé and Teller, *Z. physik. Chem.*, **B19**, 367 (1933).

[11] Roth, *Z. Physik.*, **87**, 192 (1934); Weniger, *Phys. Rev.*, **31**, 388 (1910); Kohlrausch and Pongratz, *Z. physik. Chem.*, **B27**, 176 (1935).

[12] Ref. 11; also Easly, Fenton and Spence, *Astrophys. J.*, **67**, 185 (1928); Morton, *Z. physik. Chem.*, **117**, 97 (1925).

The remaining two vibrations are assigned as shown in Fig. 3. This assignment is in qualitative agreement with the fact that the frequency of a C–O vibration is in general higher than that of a C–C frequency, and will be further justified by a consideration of the double molecule.

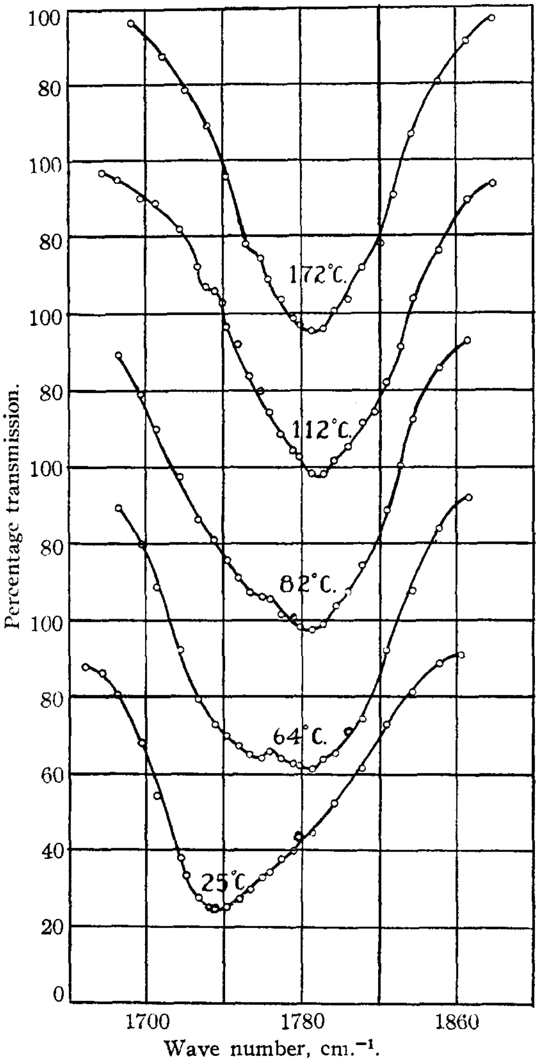
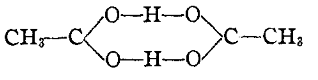


Fig. 2.—The infra-red absorption spectrum of the carbonyl group of acetic acid.

That the association of acetic acid involves hydrogen bonds was first suggested by Latimer and Rodebush.[13] This view was later verified by Pauling and Brockway[14] who determined the configuration of the double molecule of formic acid by electron diffraction measurements. It was found to be a monoplanar ring, the two molecules being joined by two hydrogen bonds



$$CH_3-C\begin{matrix}O-H-O\\ O-H-O\end{matrix}C-CH_3$$

We shall assume that this same structure is also found in acetic acid.

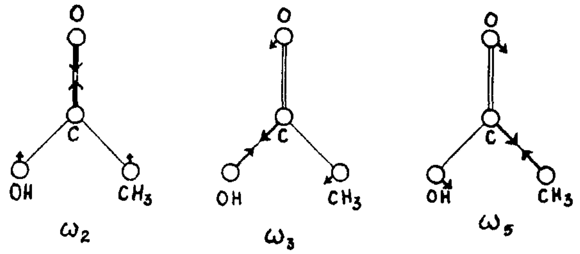


Fig. 3.—Fundamental modes of vibration of the single molecule of acetic acid. (The deformation vibrations have been omitted.)

In formulating the fundamental modes of vibration the hydrogen in the ring is neglected since the electric moment changes associated with its vibration are undoubtedly small as shown by the fact that the formation of hydrogen bonds blots out the characteristic O–H absorption. Again making the assumption that interaction between bonds is negligible we are able to separate the two vibrations of the methyl groups against the ring from vibrations of atoms in the ring itself.

The usual requirement that vibrations be symmetric or antisymmetric with respect to the symmetry elements present leads to the formulation for the double molecule shown in Fig. 4, where the

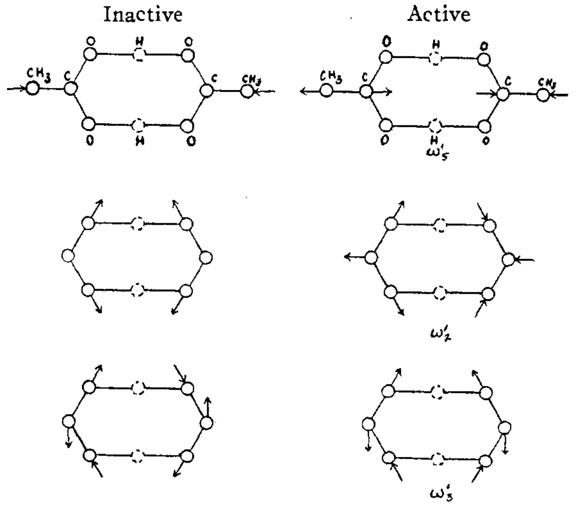


Fig. 4.—The fundamental valence vibrations of dimeric acetic acid.

primes are used to distinguish the vibrations of the dimer from those of the monomer. It may be seen that the frequencies in the first column are

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[13] Latimer and Rodebush, THIS JOURNAL, **42**, 1419 (1920).

[14] Pauling and Brockway, *Proc. Nat. Acad. Sci.*, **20**, 336 (1934).

inactive since they produce no change in the electric moment of the molecule.

It will now be shown that the active frequency ω_5' of the dimer should be the same as ω_5 of the single molecule. Denote by M the mass of the ring exclusive of the methyl groups and by m the mass of a methyl group. Then the reduced mass for the vibration ω_5' is

$$\mu = \frac{2m_1M}{2m + M} = \frac{2m}{1 + (2m/M)}$$

while that for ω_5 is

$$\mu_5 = \frac{m(M/2)}{m + (M/2)} = \frac{m}{1 + (2m/M)}$$

But since there are two methyl groups involved in the vibration ω_5' the force constant f_5' will be twice as large as f_5. Thus the frequency of vibration calculated from the relation $\nu = {}^1/_{2\pi}\sqrt{f/\mu}$ will be the same in both cases. This indicates that it is justifiable to assign the frequency at 1190 cm.$^{-1}$ to this vibration. The greater intensity of absorption in the single molecule may be correlated with the splitting of the band upon association into an active and an inactive vibration.

The frequencies ν_1 and ν_4 associated with carbon to hydrogen vibrations should not, of course, be affected by the increase in temperature. This is, in fact, found to be the case, although the band ν_4 is slightly displaced at 172°, probably because of overlapping with ν_5 which becomes much more intense.

The remaining two frequencies ν_2 and ν_3 are more difficult to attribute to the definite modes of vibration of the associated molecule. Qualitatively they should be closer together in this case than in the single molecules since their separation is merely the result of similar modes of vibration of the ring which cannot have greatly different force constants. Since it appears plausible that a greater electric moment change is to be associated with the active vibration ω_2' than with ω_3' (Fig. 4) it may be tentatively assigned to the more intense band at 1740 cm.$^{-1}$ (ν_2).

The Raman spectrum of acetic acid has been examined most accurately by Kohlrausch, Köppl and Pongratz.[15] The Raman lines occurring in this region are 1275, 1363, 1429, 1663 ± 7.5 cm.$^{-1}$. These are to be compared with the maxima of the infra-red absorption bands recorded here at room temperature: 1205, 1296, 1435, 1740 cm.$^{-1}$.

The findings of this investigation suggest that in the single molecule it is safe, at least as a good approximation, to assign a definite band in the spectrum to a definite bond in the molecule. In the double molecule, on the other hand, because of the highly symmetrical structure this approximation fails completely. A similar case is discussed by Cross and Van Vleck,[16] who show that because of mass symmetry in ethyl alcohol it is no longer possible to apply the approximation which was found to hold well for the ethyl halides.

In all the above reasoning it has been assumed that the association of acetic acid, and undoubtedly of carboxylic acids in general, takes place through the formation of hydrogen bonds. The fact that it has been possible to interpret the spectra on this assumption yields additional evidence that this is the actual mechanism of association. The fundamental nature of this hydrogen bond is discussed by Gillette and A. Sherman.[17]

Summary

1. The infra-red absorption spectrum of acetic acid has been obtained at 25 and at 172°—corresponding to the single and the associated molecule. At intermediate temperatures both spectra appear.

2. Three of the fundamental frequencies are the same in both molecules and two are shifted. These two must be intimately connected with the association process.

3. Modes of vibration of the two molecules are suggested, corresponding to the fundamental frequencies.

4. The results of this investigation suggest that the association of carboxylic acids to give dimers occurs through the formation of hydrogen bonds leading to ring structure which gives rise to different absorption frequencies.

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[15] Kohlrausch, Köppl and Pongratz, *Z. physik. Chem.*, **B21**, 242 (1933).

[16] Cross and Van Vleck, *J. Chem. Phys.*, 1, 350 (1933).

[17] Gillette and A. Sherman, THIS JOURNAL, **58**, 1135 (1936).