[CONTRIBUTION FROM THE PHYSICAL CHEMICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN]

The Nature of the Hydrogen Bond. I. Association in Carboxylic Acids

BY R. H. GILLETTE AND ALBERT SHERMAN

Introduction

It has long been known that many organic compounds, especially those containing hydroxyl groups, are associated at ordinary temperatures, both in the gaseous state and in solution in non-polar solvents.[1] The equilibrium was investigated by Auwers,[2] who was able to distinguish two classes of associating substances, those in which the molecular weight increases in proportion to the concentration and those in which the molecular weight approaches a limiting value corresponding to dimer formation. Examples of the former class are alcohols, phenols and amides; of the latter class the carboxylic acids constitute the best example. Much later work using many different methods has yielded discordant results but has largely verified the above conclusions. The present work is concerned with assuming a structure for the dimeric carboxylic acid, and calculating its energy with respect to unassociated molecules. It is mainly for these substances that experimental values for the heat of the association reaction are available. For formic acid Coolidge[3a] obtained the value 14,125 cal., and Fenton and Garner[3b] found 13,790 cal. for acetic acids. The fact that consistent values for the heat of association over a considerable range of temperature and pressure were obtained lends considerable credence to the view that these acids are associated only to dimers, as does also the work of Smyth and Rogers,[4] who showed that associated molecules of acetic acid and butyric acid have an electric moment of zero in benzene solution.

Several mechanisms have been postulated to explain this association, the simplest being that the interaction between two juxtaposed dipoles is responsible for the reaction. This, however, is unimportant in this case, and in general this interaction is insufficient to deal with polar molecules, as has been pointed out by Hildebrand.[5] Williams[6] remarks that the presence of a dipole movement may be a necessary condition for association in general, but it is not sufficient. Phenol and benzoic acid are generally regarded as associated, yet over a considerable range of concentration (benzene solution) these substances show no change in their molar polarizations.

Moore and Winmill[7] were probably the first to postulate a hydrogen bond, *i. e.*, two atoms or groups held together by a hydrogen atom or nucleus between them. Pfeiffer[8] used the idea to explain the weakness of *o*-hydroxyanthraquinone and Huggins[9] used the concept as a theory in regard to certain organic compounds. Latimer and Rodebush[10] were the first to recognize the hydrogen bond as a general phenomenon.

Pauling[11] has considered a hydrogen bond to be polar in nature while Sidgwick[12] as a result of his theory of the coördinate covalent link, postulated that organic acids would associate since an inner coördination would lead to a four-membered ring, which is unstable, whereas two molecules could join together, forming a stable configuration, with carboxyl groups facing one another, the hydroxyl hydrogens acting as acceptors for the formation of coördinate links. This view is, however, untenable, as Sidgwick himself has since stated,[13] since hydrogen cannot be divalent unless some of the electrons are promoted to the 2s state, which is unstable. This argument for the instability of divalent hydrogen assumes that the atomic quantum numbers for hydrogen essentially retain their significance in the molecule.

Sidgwick now regards the hydrogen as first attached to one atom and then to the other, this electronic resonance on a time average amounting to making hydrogen divalent, *i. e.*, the resonance phenomena of wave mechanics. Bell and Arnold[14] come to the same conclusion for dimer formation in the case of trichloroacetic acid molecules.

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(1) W. E. S. Turner, "Molecular Association," Longmans, Green & Co., N. Y., 1915, p. 33.

(2) Auwers, *Z. physik. Chem.*, **12**, 689 (1893); **23**, 449 (1897).

(3) (a) Coolidge, THIS JOURNAL, **50**, 2166 (1928); (b) Fenton and Garner, *J. Chem. Soc.*, 694 (1930).

(4) Smyth and Rogers, THIS JOURNAL, **52**, 1824 (1930).

(5) Hildebrand, *Science*, **83**, 21 (1936).

(6) Williams, *Proc. Nat. Acad. Sci.*, **14**, 932 (1928).

(7) Moore and Winmill, *J. Chem. Soc.*, **101**, 1675 (1912).

(8) Pfeiffer, *Ann.*, **398**, 137 (1913).

(9) Huggins, Undergraduate Thesis, Univ. of California, 1919.

(10) Latimer and Rodebush, THIS JOURNAL, **42**, 1419 (1920).

(11) Pauling, *Proc. Nat. Acad. Sci.*, **13**, 359 (1928).

(12) Sidgwick, "The Electronic Theory of Valence," Oxford University Press, 1929; *Chem. Soc. Ann. Rep.*, **30**, 115 (1934).

(13) Sidgwick, *ibid.*, **31**, 34 (1935).

(14) Bell and Arnold, *J. Chem. Soc.*, 1432 (1935).

W. D. Kumler[14a] discusses the hydrogen bond in relation to dielectric constants and boiling points of organic liquids.

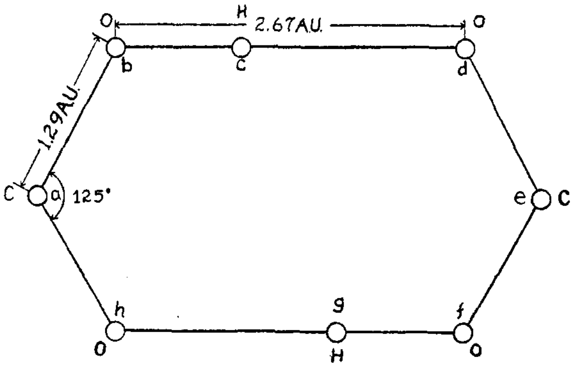


Fig. 1.—The model obtained from electron diffraction experiments for associated dimeric formic acid. The two carboxyl groups form an eight-membered plane ring.

In view of the above facts it is of interest to calculate the energy of the carboxylic acid complex with the aid of wave mechanics in order to throw some light upon the nature of the hydrogen bond, *i. e.*, to determine whether it is polar, homopolar or both.

We shall restrict our considerations for the present to formic acid, partly because it is the simplest acid and partly because accurate experimental data for the substance are available. In order to calculate the energy of the dimer we must assume some particular spacial configuration. The one chosen was that suggested by Latimer and Rodebush[10] and verified experimentally by Pauling and Brockway[15] by electron diffraction measurements. This structure places all the atoms in a plane with carboxyl groups opposite one another, as shown in Fig. 1. Zahn[16] has suggested an alternative model as a result of electric moment investigations, and based on the results of electron diffraction measurements by Hengstenberg and Brú.[17] However, Pauling and Brockway state the model postulated by the latter authors is not in agreement with their electron diffraction pattern and hence can be definitely excluded.

Procedure

All the electrons are considered uniquely paired except those in the ring and the problem is treated in the ordinary way as one of 8 electrons with spin degeneracy. There are in general 14 linearly independent bond wave functions for 8 electrons, a convenient set being the so-called canonical set[18] given below.

The energy of the complex is calculated as a function of the distance between carboxyl groups, *i. e.*, between atoms *b* and *d*. For every distance r_{bd} two cases were considered. In one case the hydrogen atoms are placed midway between the oxygen atoms, as shown in Fig. 1. In the other case the hydrogen atoms are at the normal O–H distance (0.97 Å.) from diagonally opposite oxygen atoms. It is of course immaterial where the hydrogen atoms are located as far as the 14 bond wave functions in Fig. 2 are concerned.

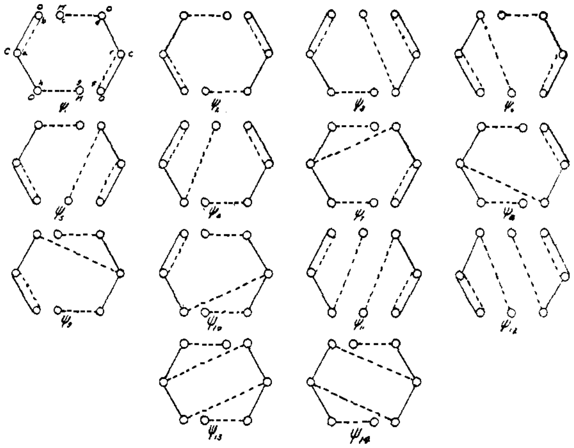


Fig. 2.—Fourteen linearly independent bond wave functions for eight electrons in the ring of dimeric acetic acid.

For the second case we give ψ_3 and ψ_4 the same coefficient in the wave function for the system, and similarly for ψ_5 and ψ_6 and ψ_7, ψ_8, ψ_9 and ψ_{10}. The functions ψ_{11}, ψ_{12}, ψ_{13} and ψ_{14} are neglected. They are what Pauling and Wheland[19] have called second excited structures, and it is evident that they will contribute little to the energy of the system and may be neglected in an approximate calculation. Thus, we define

$$\phi_1 = \psi_1,\ \phi_2 = \psi_2,\ \phi_3 = \psi_3 + \psi_4,\ \phi_4 = \psi_5 + \psi_6,$$
$$\phi_5 = \psi_7 + \psi_8 + \psi_9 + \psi_{10}$$

The matrix components between the ϕ's were computed by first calculating the components in terms of the ψ's, by either Pauling's[18] or Eyring and Kimball's method,[20] and then using the definition of the ϕ's.

In this case $ab = ah = de = ef$; $ac = eg$; $ad = af = be = eh$; $ag = ce$; $bc = fg$; $bd = fh$; $bf = dh$; $bg = df$; $cd = gh$; $dg = ch$ and $bh = df$.

(14a) W. D. Kumler, THIS JOURNAL, **57**, 600 (1935).

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

(16) Zahn, *Phys. Rev.*, **37**, 1516 (1931); **35**, 1047 (1930).

(17) Hengstenberg and Brú, *Anal. soc. españ. fís. quím.*, **30**, 341 (1932).

(18) Pauling, *J. Chem. Phys.*, **1**, 280 (1933).

(19) Pauling and Wheland, *ibid.*, **1**, 362 (1933).

(20) Eyring and Kimball, *ibid.*, **1**, 626 (1933).

The components in terms of the ϕ's are given below.

$$H_{11} = Q + (ab - ac - ag - bc - bd - bf - bg - bh - dg) + 2(cd - ad) - {}^1/_2(ac + cg)$$
$$H_{22} = Q + (ab - ac - ag - bd - bf - cd - bg - bh - dg) + 2(bc - ad) - {}^1/_2(ac + ag)$$
$$H_{33} = 2^1/_2Q + 4(ab - ag - bh) - 2^1/_2(ac + bc + bd + bf + dg) + 2(bg + cd) - 1^1/_4(ac + cg) - 5ad$$
$$H_{44} = 7^1/_2Q + 3(ab + ad) + 6(cd + bc - bg - dg) - 4^1/_2cg - 7^1/_2ac - 10^1/_2(ac + ag) - 12(bd + bh) - 9bf$$
$$H_{55} = 2^1/_2Q + 4(ab - ac - bh) - 2^1/_2(ag + bd + bf + bg + cd) + 2(bc + dg) - 1^1/_4(ae + cg) - 5ad$$
$$H_{12} = {}^1/_8Q + {}^1/_2(ab + ad - ac - bd - ag - bh - bf) + {}^1/_4(bc + cd + bg + dg - ae - cg)$$
$$H_{13} = Q + 2^1/_2(ab - ag - bh) + 2(cd - ad) - (ac + bc + bd + bf + dg) + {}^1/_2(bg - ae - cg)$$
$$H_{14} = 1^1/_2Q + 2^1/_4(ab - ag - bf - bh) + {}^3/_4(ad + bc - cg - bg) + 3cd - 1\,{}^1/_2(ae + dg) - {}^{15}/_4(ac + bd)$$
$$H_{15} = {}^1/_2Q + 1^1/_4(ab - ac - bd - bf - bh - ag) + {}^1/_4(bc + bg - ad - ac) + cd + dg - cg$$
$$H_{23} = {}^1/_2Q + 1^1/_4(ab - ac - bd - bf - bh - ag) + {}^1/_4(cd + dg - ad - ae) + bc + bg - cg$$
$$H_{24} = 1^1/_2Q + 2^1/_4(ab - ac - bf - bh) + {}^3/_4(ad + cd - dg - cg) - {}^{15}/_4(bd + ag) + 3bc - 1^1/_2(ae + bg)$$
$$H_{25} = Q + 2^1/_2(ab - bh - ac) + 2(bc - ad) + {}^1/_2(dg - ae - cg) - ag - bd - bf - bg - cd$$
$$H_{34} = 2^1/_4Q + 4^1/_2(ab - bd - ag - bh) + 1^1/_2(ad + bc + bg) - 6(bf + ac) + 3cd - 2^1/_4(ae + cg)$$
$$H_{35} = 1^1/_4Q + 2(ab - ac - ag - bh - bf) - ad + bc + cd + bg + dg - ae - 2^1/_2cg - 3^1/_2bd$$
$$H_{45} = 2^1/_4Q + 4^1/_2(ab - ac - bd - bh) + 1^1/_2(ad + cd + dg) - 6(bf + ag) + 3bc - 2^1/_4(ae + cg)$$

Here Q is the Coulombic energy of the system, ab the exchange energy between electrons a and b, and similarly for ac, ad, etc.

The Coulombic and exchange energies were evaluated from the various Morse potential energy curves in question, and an approximate formula was used for correcting the Morse values for directed valence. It was assumed that $K'_{ab} = K'_{ab}\cos^2\alpha$ holds for a bond formed from one s and one p electron, where K_{ab} is the exchange energy of a bond determined from a Morse curve, α the angle through which the bond is distorted from its normal value (*i. e.*, from the angle for which the bond energy is a maximum), and K'_{ab} the directed valence exchange energy. The carbon wave functions were considered to be tetrahedral and orthogonal. The Coulombic energy was assumed to be 14% of the total bond value.[21]

The constants used for constructing Morse curves are given in Table I.

TABLE I

Bond	r_0(Å.)	ω(cm.$^{-1}$)	D(kcal.)
O–O	1.32	1304	34.3
C–H	1.12	2930	92.3
C–O	1.43	1030	81.8
H–H	0.74	4375	102.4
C–C	1.54	990	83.0
O–H	0.97	3660	113.1

Results

For every distance between oxygen atoms b and c or h and f the configuration where the hydrogen atoms are placed at the normal distance from diagonally opposite oxygen atoms turned out to be more stable than when they were placed midway between the oxygens. Hence only the matrix component for the more stable configuration was given in the preceding section, since it is the only one of interest for our present problem.[22]

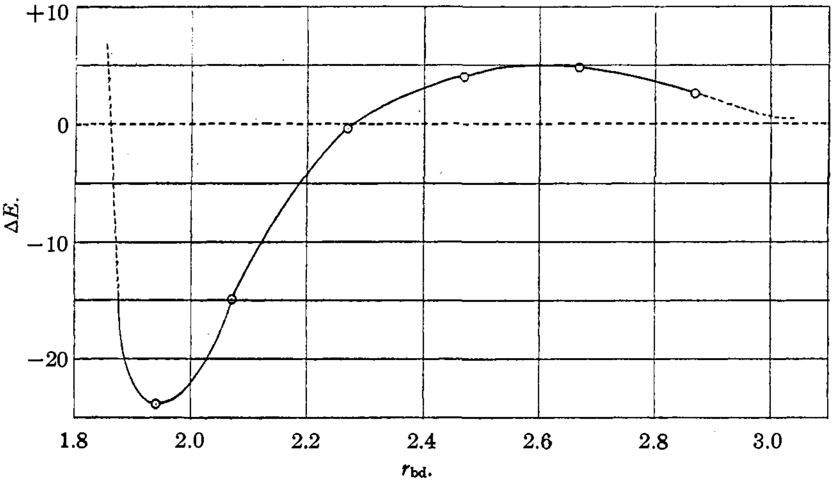
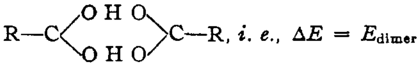


Fig. 3.—The heat of the association reaction of two carboxyl groups as a function of the distance between them. The minimum corresponds to the formation of a stable dimer.

The results of the calculation are shown in Fig. 3.

ΔE is the heat of the association reaction 2R—COOH ⟶



$$R{-}C\begin{matrix}O\ H\ O\\ O\ H\ O\end{matrix}C{-}R,\ i.\ e.,\ \Delta E = E_{\text{dimer}} - 2E_{\text{monomer}}$$

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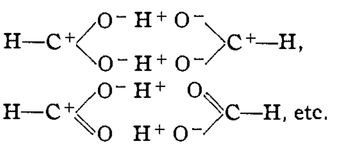
(21) This percentage is taken over from activation energy calculations. See Van Vleck and Sherman, *Rev. Modern Phys.*, **1**, 168 (1935).

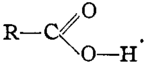
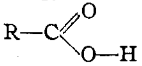
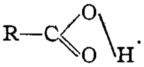
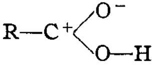
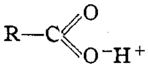
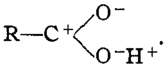
(22) The secular equation for the more unstable configuration was taken as a cubic, defined by the wave functions $\theta_1 = \psi_1 + \psi_2$, $\theta_2 = \psi_3 + \psi_4 + \psi_5 + \psi_6$, $\theta_3 = \psi_7 + \psi_8 + \psi_9 + \psi_{10}$.

Discussion

It is seen from Fig. 2 that the curve has the form to be expected and that for the reaction $2HCOOH \longrightarrow (HCOOH)_2$ we calculate an activation energy of 4.8 kcal., a minimum at $r_{bd} = 1.94$ Å., and a heat of reaction of 23.8 kcal. This is to be compared with the experimental values $r = 2.67$ Å., and ΔE at the minimum equal to 14.1 kcal.

From theoretical considerations we know that a complete wave function for a system should include terms to allow for both polar and homopolar states. It is exceedingly difficult, however, to include polar states in the calculation in any practical way, but it was considered of interest to see to what extent homopolar states alone could account for the results in order to determine, if possible, the relative importance of each. The existence of such states as

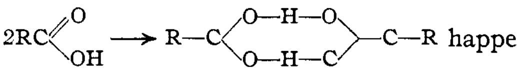


are possible, and the most important cause of the discrepancy between calculated and experimental quantities is undoubtedly to be sought in the neglect of them. Pauling and J. Sherman[23] calculate from thermochemical data that the resonance energy of a carboxyl group is 1.2 v. e. relative to the structure . We have made additional calculations and find the resonance energy to be 0.8 v. e. if it arises from the two states  and . Accordingly other states must be involved, such as ,  and .

To the extent that polar states are important directed valence is unimportant. Since we neglected polar terms we consequently over-corrected for directed valence. This is the main reason why the calculated ΔE was not in numerical agreement with experiment.

Polar terms will come in to the energy expression in an additive way. Although it is not quite correct to infer that they will therefore effectively increase the Coulombic percentage above 14, nevertheless it is interesting to remark that if the importance of directed valence is decreased and the percentage of Coulombic energy slightly increased agreement with experiment is obtained. Thus if directed valence be decreased by 25% and the Coulombic percentage increased from 14 to 17.5 the calculated value of ΔE agrees with experiment.

Resonance between bond wave functions ψ_1 and ψ_2 may be considered to be the resonating hydrogen bond of Sidgwick, mentioned in the introduction. It is to be noticed, however, that if the functions ψ_1 and ψ_2 alone were involved ΔE would be +5 kcal. rather than −23.8 kcal. Thus we see that states ψ_3 through ψ_{10}, although not as important as ψ_1, and ψ_2, must also be considered since they contribute considerable energy to the complex. If all excited states[19] be neglected, both for the dimer and the monomers, the heat of the association reaction turns out to be approximately equal to that found by taking all states into account.[24] Hence it turns out that the ordinary chemical formulation of the reaction



happens to be fortuitously correct if the bonds drawn in the complex are interpreted to represent the functions ψ_1 and ψ_2.

Various assumptions concerning the value of a in the expression $K' = aK \cos^2 \alpha$, together with various choices of the Coulombic percentage all affect the value of ΔE and the activation energy of the association, but many detailed calculations show that the position of maximum stability always occurs at $r_{bd} = 1.94$ Å. The fact that r_{bd} (exptl.) = 2.67 Å. indicates polar states are important, but the discussion above indicates that homopolar states are also important.

Pauling,[11] after remarking that the hydrogen bond in HF_2^- is polar, *i. e.*, $F^-H^+F^-$, says the polar concept of the hydrogen bond explains why only atoms of high electron affinity such as fluorine, oxygen and nitrogen form such bonds. It is not clear, however, why from this viewpoint chlorine which is at least as electronegative as nitrogen[25] forms at best only very weak hydrogen bonds.[26]

We wish to thank Professor Farrington Daniels for his constant interest in this problem. One of us (A. S.) also acknowledges a profitable talk with Professor L. Pauling. He also wishes to thank

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[23] Pauling and J. Sherman, *J. Chem. Phys.*, **1**, 606 (1936).

[24] Pauling and Wheland[19] used this general assumption.

[25] Pauling [THIS JOURNAL, **54**, 3570 (1932)] gives for the coordinates of these elements on his electronegativity scale Cl = 0.94, N = 0.95, O = 1.40, F = 2.00.

[26] Pauling, *ibid.*, **58**, 92 (1936).

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).