Vibration Spectra and Molecular Structure V. InfraRed Studies on Light and Heavy Acetic Acids

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An attempt was made to prepare HCOOD by passing D_2S (prepared from D_2O and Al_2S_3*) through a column of powdered lead formate at 100°C. The product was purified by distillation and the spectrum obtained over a temperature range as before. These spectra are reproduced in Fig. 3. It is to be noted that the highest temperature curve shows the presence of about equal amounts of $C-H, C-D, O-H$ and $O-D$ in the monomer. From this we conclude that adsorption and exchange has taken place on the surface of

the hot lead formate powder and that the dimer curves represent the absorption of a statistical mixture of the four possible formic acids. That the exchange took place in the preparation and not in the cell was demonstrated, we believe, by a room temperature run in which the formic acid was placed in a cell sealed with glyceryl phthallate resin. The curve was identical with that obtained using a cell sealed with asbestos and glyptal.

As a result of further experiments by one of us (R. H.) it has been found possible to prepare the pure HCOOD by a different method and to observe its spectrum. These results will be published very shortly.

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* We are indebted to Dr. John Turkevitch, of the Princeton Chemistry Department for supplying us with the pure Al_2S_3.

Vibration Spectra and Molecular Structure

V. Infra-Red Studies on Light and Heavy Acetic Acids[1]

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(Received June 1, 1938)

The infra-red absorption spectra of CH_3COOH and CH_3COOD between 1 and 15.5μ have been obtained with a rocksalt prism spectrometer. The association of CH_3COOD has been studied and a value of the heat of dissociation obtained. Positions of the hydrogen and deuterium bonded $O-H-O$ and $O-D-O$ frequencies are given. Making certain assumptions, a value for the shorter $O-H$ and $O-D$ distances in the dimer rings is found to be 1.07A.

INTRODUCTION

A T room temperature the vapor of acetic acid consists chiefly of double molecules whose structure may be assumed to be similar to that of formic acid. The structure frequently assumed is the following:

in which the two single molecules are linked by two hydrogen bonds. Several years ago Gillette and Daniels[2] studied the effect of association on the infra-red absorption spectrum of acetic acid vapor. By raising the temperature they were able to obtain the spectrum of the single molecules since from recent vapor density measurements[3] it is known that dissociation into single molecules is almost complete at about 150°C. Shifts and changes of intensity of certain bands were reported. However, no changes are mentioned in the high frequency region where vibrations involving hydrogen atoms are known

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[1] Preliminary accounts of this work were given at the Washington meeting of the American Physical Society, April 1938, and in a Letter to the Editor, J. Chem. Phys. 6, 110 (1938).

[2] Gillette and Daniels, J. Am. Chem. Soc. 58, 1139 (1935).

[3] F. H. MacDougall, J. Am. Chem. Soc. 58, 2585 (1936).

to occur.[4] Since the dissociation involves the breaking of two hydrogen bonds, one would expect some changes here if there is an infra-red active band associated with the hydrogen bond. In order to obtain more information concerning this point it was thought desirable to study d-substituted acetic acid (CH₃COOD). Such a substitution would alter the frequency of a band associated with the hydrogen bond, shifting it to about 4.3μ if this hydrogen vibration originally lay in the region of C−H valence vibrations.[5] The suggestion that the hydrogen bond vibration appears fused with the C−H valence vibration was made by Buswell, Deitz and Rodebush.[5] The close proximity of these two bands has also been mentioned by Badger and Bauer.[6] Whereas the "free" O−H valence vibration (fundamental at 2.75μ) has been observed, only weakly if at all, in the spectrum of the double molecule, Badger and Bauer report the second harmonic band to be characteristic of the single molecule of acetic acid. Errera and Mollet[7] have found corresponding results in the liquids of some fatty acids.

EXPERIMENTAL

Heavy acetic acid was prepared in vacuum by reacting Kahlbaum acetyl chloride with 99.6 percent pure heavy water. This method was previously employed by Engler.[8] The DCl as well as a small excess of acetyl chloride were chiefly removed by pumping. The CH₃COOD was further purified by three distillations. In each case all but a middle fraction was rejected. The vapor pressure of the final sample at low pressures (4 to 15 mm), agreed with that of Kahlbaum glacial CH₃COOH. In order to determine the ratio of deuterium to hydrogen in the acid position, the heavy acetic acid was reacted with magnesium and the evolved D_2-H_2 mixture was analyzed in a mass spectrograph.[9]

This analysis yielded a D/H ratio of 95± about 0.1 percent.

The cells employed were constructed from Pyrex cylinders, 22 cm long, having ground glass flanges at either end to which cleaved rocksalt plates were sealed by means of a thin coating of glyptal No. 1201. This technique differs from that of Ebers and Nielsen[10] only in the use of cleaved instead of polished rocksalt windows. The glyptal was usually air dried over night and then baked out for several hours. A second coat of glyptal was then applied and treated in a similar manner. Both the cell for the substance and a similarly constructed vacuum cell were placed in a furnace provided with rocksalt windows. A side tube on the sample cell was led outside the furnace through a hole in one of the end plates. Before distilling the liquid to be studied into the side tube, the sample cell was baked out at about 140°C and simultaneously pumped for several hours. Throughout these experiments, the vapor was in equilibrium with liquid and its pressure was consequently the
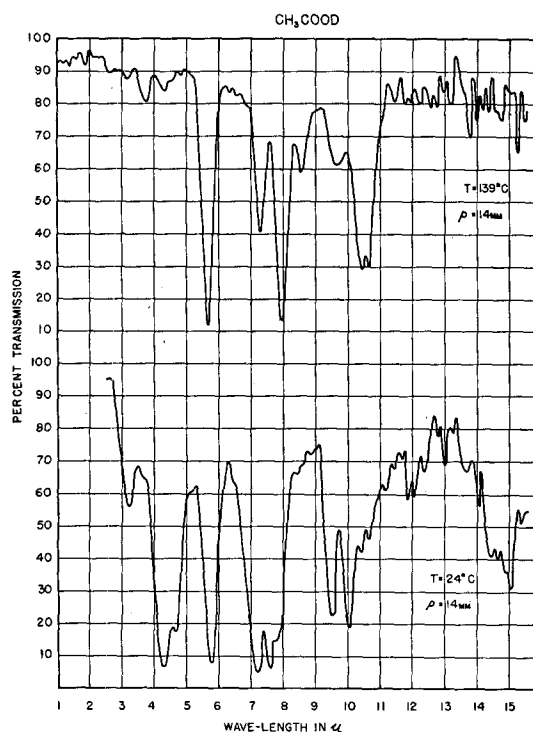

FIG. 1. Absorption spectrum of heavy acetic acid. Length of cell 22 cm.

[4] They report that the band at 2985 cm⁻¹, which they assign to the CH bond, is not affected by increase of temperature.

[5] Buswell, Deitz and Rodebush, J. Chem. Phys. **5**, 84, 501 (1937).

[6] Badger and Bauer, J. Chem. Phys. **5**, 839 (1937).

[7] Errera and Mollet, J. de phys. et rad. **6**, 2811 (1935).

[8] W. Engler, Zeits. f. physik. Chemie **B32**, 471 (1936).

[9] We wish to thank Drs. Hipple and Delfosse for kindly making these analyses.

[10] Ebers and Nielsen, J. Chem. Phys. **5**, 822 (1937).

vapor pressure of the liquid. A temperature bath surrounding the side tube permitted the pressure to be varied. Pressures were measured by means of a mercury manometer. A thermocouple was inserted in the furnace to measure the temperature which did not vary by more than about five degrees over the length of the cells. The furnace could be raised and lowered on ways so that it was possible to place either of the cells in the path of the radiation from the source. The technique described prevented the condensation of liquid on the windows. The rocksalt prism spectrometer employed has been previously described.[11] In obtaining the infra-red curves the transmission of the sample cell was compared to that of the vacuum cell at every tenth of a μ, several readings being taken per point whenever the transmitted energy was low. Certain band centers were located by taking readings about every fiftieth of a μ. All the spectra shown, except the exchange spectrum, have been obtained more than once, in particular at different pressures. Room temperature runs in cells sealed with Picein instead of glyptal gave the same spectra. Likewise, room temperature runs of samples that had previously been run at high temperatures showed no changes.

RESULTS AND DISCUSSION

1. By the method described we have obtained the spectrum of heavy acetic acid at 24°C and at 139°C. These results are shown in Fig. 1. From dissociation data the calculated degrees of dissociation for these two cases are 9 percent and 97 percent, so that these curves very nearly represent the dimer and monomer spectra. It is to be noted that the band appearing at 4.35μ (2299 cm^{-1}) is very sensitive to changes in temperature. This fact alone makes it highly probable that this band is to be attributed to the deuterium bonded $O-D-O$ vibration, since such a high frequency fundamental can be assigned to no other bond. If this frequency is increased by approximately a factor $\sqrt{2}$ which is demanded by a hydrogen replacement one would expect this band to be shifted to about 3.1μ in light acetic acid, and to be temperature

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[11] Barnes, Brattain and Seitz, Phys. Rev. **48**, 582 (1935).

sensitive as well. On comparing this expected behavior with the results reported by Gillette and Daniels,[2] it was felt desirable to restudy light acetic acid. The results of this investigation are shown in Fig. 2. The degrees of dissociation are 9 percent and 98 percent for the low and high temperature runs, respectively. The positions of the observed bands are in good agreement with those found by Gillette and Daniels with the exception of the band at 3.20μ (3125 cm^{-1}) which they report at 3.35μ (2985 cm^{-1}). As the curves show we again find a marked temperature dependence in conformity with the expectation that this frequency is to be associated with the hydrogen bonded $O-H-O$ vibration.[12]

As the temperature is raised the ratio of single to double molecules increases and while the $O-H-O$ or $O-D-O$ bonded frequency diminishes in intensity, the "free" $O-H$ or $O-D$ appears. These frequencies appear at 2.75μ (3640 cm^{-1}) and 3.77μ (2653 cm^{-1}) respectively. The more or less normal values of
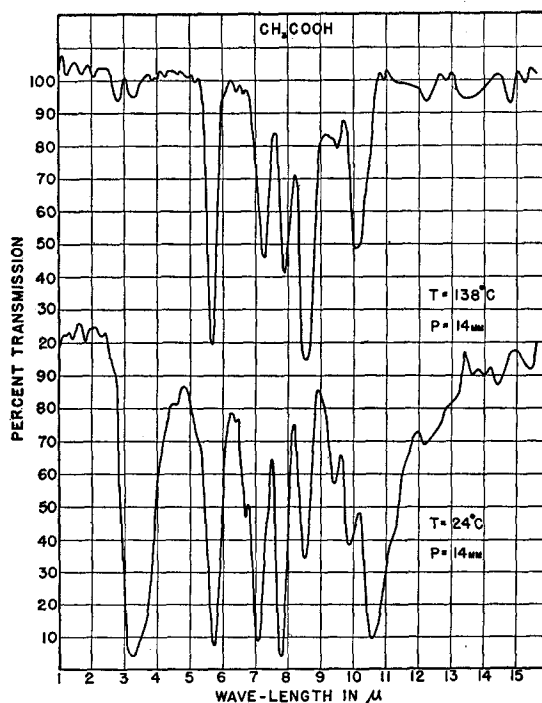

FIG. 2. Absorption spectrum of light acetic acid. Length of cell 22 cm.

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[12] Buswell and Rodebush, J. Chem. Phys. **5**, 296 (1938), from their studies on the carboxylic acids, believe that the hydrogen bond absorption lies near 3.2μ.

these frequencies suggest that the H or D atoms are linked to only one oxygen atom in the single molecule.

In both light and heavy acetic acids the monomer and dimer spectra are quite different. Apart from the changes already mentioned, which are concerned with hydrogen vibrations, we find numerous changes in intensity, the disappearance of certain bands, the appearance of others, as well as shifts.

In Table I we have tabulated our frequency

TABLE I.*

	CH₃COOH			CH₃COOD	
MONOMER	DIMER	PROBABLE ASSIGN-MENT	MONOMER	DIMER	PROBABLE ASSIGN-MENT
			3840 ± 140		
3640 ± 70	3125 ± 19	O$-$H			
		O$-$H$-$O			
3030 ± 45	?	C$-$H	3175 ± 70	3125 ± 50	C$-$H
			2653 ± 15		O$-$D
			2299 ± 15†	2299 ± 11	O$-$D$-$O
				2127 ± 25	
1770 ± 7	1739 ± 9	C$=$O	1770 ± 6	1736 ± 6	C$=$O
	1493 ± 20				
1381 ± 5	1418 ± 4	δC$-$H	1377 ± 3	1387 ± 4	δC$-$H
				1315 ± 9	
1266 ± 8	1282 ± 8	*C$-$O*	1266 ± 8	1258 ± 8‡	*C$-$O*
1176 ± 6	1176 ± 6	*δO$-$H*	1176 ± 6§		
1053 ± 10	1058 ± 5		1042 ± 10	1058 ± 5	
	1010 ± 5			1000 ± 5	
985 ± 10		*C$-$C*	953 ± 5	953 ± 9‡	*C$-$C*
	938 ± 7				
	820 ± 10			840 ± 8	
				667 ± 30	

* The italicized *C$-$O*, *δO$-$H* and *C$-$C* assignments have been suggested by preliminary work on CD₃COOD.
† Probably due to a small amount of dimer.
‡ Probably due to a small amount of monomer.
§ Possibly due to five percent impurity of CH₃COOH.

measurements of the more prominent bands found in CH₃COOH and CH₃COOD with rather generous estimates of probable errors. The complexity of all these spectra make impossible a complete assignment of bands at the present time. However, certain bands may be identified with confidence. These identifications have been noted in the table.

In light acetic acid three bands shift appreciably. The C$=$O frequency which appears at 1739 cm⁻¹ in the dimer shifts to 1770 cm⁻¹ in the monomer, a change of 31 cm⁻¹. A slightly larger shift occurs for the band at 1418 cm⁻¹ in the dimer. The fact that so large a shift is observed in the latter case is surprising if this is really a C$-$H bending vibration. The band at 1282 cm⁻¹ shifts by 16 cm⁻¹, appearing at 1266 cm⁻¹ in the monomer. Gillette and Daniels
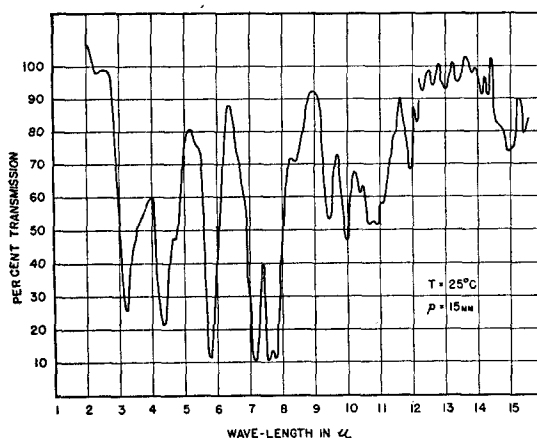

FIG. 3. Exchange spectrum. Length of cell 15 cm.

report two bands in the dimer spectrum at 1740 and 1435 cm⁻¹ which shift by 46 and 37 cm⁻¹, appearing in the monomer at 1786 and 1398 cm⁻¹, respectively. They also find a band in the dimer at 1296 cm⁻¹ which is reported at 1288 cm⁻¹ in the monomer. Thus we find qualitative agreement in the directions and approximate magnitudes of the shifts although the band centers are in slight disagreement. In the region beyond 9.1μ in the monomer spectrum we find the appearance of a new band at 985 cm⁻¹.

It is of interest to note the great intensity of the O$-$D$-$O band in CH₃COOD, which suggests the highly polar character of the hydrogen bond.[13] A smaller band occurs at 2127 cm⁻¹ on the long wave-length side of the O$-$D$-$O band. A similar result has been found in the spectrum of formic acid.[14] The O$-$H$-$O band at 3125 cm⁻¹ is likewise of great intensity and shows an asymmetry on its long wave-length side. The asymmetry can possibly be correlated with the 2127 cm⁻¹ band. The C$=$O frequency in heavy acetic acid is observed at the same position as in light acetic acid and shifts in the same direction by the same amount, within the experimental error. The 1377 cm⁻¹ band shifts by the small amount of 10 cm⁻¹. The new band in the monomer spectrum at 953 cm⁻¹ probably corresponds to the 985 cm⁻¹ frequency of the CH₃COOH monomer. Among the differences between the dimer spectra of the light and heavy acids one

[13] M. L. Huggins, J. Org. Chem. 1, 407 (1936).
[14] R. Hofstadter, Paper No. VI of this series.

further change appears especially noteworthy. The band at 938 cm^{-1} in CH_3COOH appears to shift to 667 cm^{-1} in CH_3COOD and therefore seems to be due to a vibration directly involving a hydrogen atom.

In one run upon CH_3COOD some asbestos paper was present in the form of washers between the windows and cell. After heating the vapor in this cell to 124°C the temperature was reduced to room temperature and a run taken. The curve obtained is shown in Fig. 3. This is clearly the result of an exchange because the superposition of the spectra of light and heavy acetic acids shows all the bands observed in this spectrum. It is not clear whether the exchange occurred catalytically between the methyl and acid group or is a result of impurity within the asbestos.

2. The heat of dissociation of molecules held together by hydrogen bonds can be obtained from the dependence of the equilibrium constant on temperature as determined by means of vapor density measurements. According to Fenton and Garner[15] the heat of dissociation of acetic acid is 13,790 cal. per mole, whereas Nernst and von Wartenburg[16] find 15,000 cal. per mole. Mac-Dougall[3] made what is probably the most careful determination and obtained 16,400 cal. per mole. Since there are two $O-H-O$ bridges in the dimer ring this last value corresponds to a dissociation energy of 8200 cal. per mole for each hydrogen bond. Recently Badger and Bauer[17] investigated the dependence on temperature of the intensity of the second harmonic of the $O-H$ band in acetic acid. They remark that because of the difficulty of making photometric determinations of intensity, their individual determinations do not claim the accuracy of MacDougall's measurements. However, in the region where their accuracy was greatest, the best straight line through their points does not deviate greatly from MacDougall's which is represented by

$$\log_{10} K_p = 11.789 - 3590/T.$$

We have made an attempt to find the heat of dissociation using one of the fundamental bonds of CH_3COOD. Since the hydrogen bonded $O-H-O$ frequency falls in the region of $C-H$ valence vibrations [5, 6, 1, 18] it was not possible to investigate light acetic acid by means of its fundamental bridge frequency. The substitution of a D for an H atom in the acid position shifts this frequency, now the deuterium bonded $O-D-O$ frequency, to a region unoccupied by other bands, making it possible to study the dependence of association on temperature in CH_3COOD.

Setting the spectrometer at the center of the 2299 cm^{-1} band, intensity measurements were made for various total pressures at given temperatures between room temperature and 145°C. In order to obtain a greater percentage of dimer in the vapor than we have worked with, it would have been necessary to cool the vapor below room temperature. This would have been very inconvenient with our experimental arrangement. However, if one were to cool the vapor to 5°C the degree of dissociation would only change from 9 percent to 6 percent. Since it was not possible to obtain 100 percent dimer, we could not directly determine the dependence of transmission on the number of grams of dimer in the cell. This dependence can be obtained by means of the "free" $O-D$ band at 3.77μ, since at or slightly higher than 145°C the vapor is almost completely dissociated. However, the resolving power of the instrument employed was not great enough to study this band; the neighboring 4.35μ band affected the results. Instead, we assumed MacDougall's values for the degree of dissociation α at 38.5°C and calculated the partial pressure of dimer P_D from the relation

$$P_D = \frac{1-\alpha}{1+\alpha}p,$$

in which p is the total pressure. Since our total pressures were low, rarely greater than 22 mm, we may apply the gas law
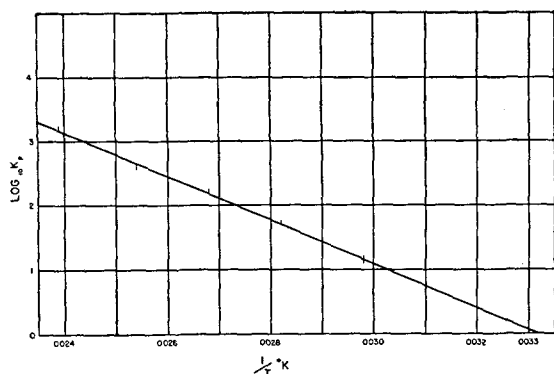
$$P_D V = N_D RT,$$

to find the number of moles of dimer in the volume of the cell, V, at a given temperature T.

[15] Fenton and Garner, J. Chem. Soc. 694 (1930).
[16] Nernst and von Wartenburg, Zeits. f. Elektrochem. u. angew. physik. chemie 22, 37 (1916).
[17] Badger and Bauer, J. Chem. Phys. 5, 605 (1937).
[18] Bonner and Hofstadter, J. Chem. Phys. 6, 531 (1938).

FIG. 4. Equilibrium constant for CH_3COOD.

This leads to a knowledge of the dependence of the transmission on $\rho_D = N_D/V$ since we experimentally determined its dependence on p at a given temperature. Employing this calibration curve it was possible to find α from the relation

$$\alpha = (p - \rho_D RT)/(p + \rho_D RT).$$

At each temperature the dissociation constant K_p can be evaluated from the equation

$$K_p = 4\alpha^2 p/(1 - \alpha^2).$$

K_p is defined as p_M^2/p_D in which p_M and p_D are the partial pressures of monomer and dimer, respectively. Fig. 4 gives the plot of $\log_{10} K_p$ vs. $1/T$. The heights of the vertical lines give the spread in $\log_{10} K_p$, and contain on the average about five points. From the slope of the curve one finds the heat of dissociation to be 15,900 cal. per mole or 7,950 cal. per mole per bond. This is to be compared with MacDougall's value 8200 calories. Our experimental error estimated at roughly ±700 cal. is too large to distinguish between the heats of dissociation of light and heavy acetic acids.

The use of a deuterium substitution for investigating dissociation processes spectroscopically may be of some value in examining other aliphatic or aromatic compounds.

3. The electron diffraction experiments of Pauling and Brockway[19] have shown that in formic acid the O−O distance is 2.67A. Since this work did not locate the hydrogen atoms in the ring some calculations have been made in an

attempt to do so. For instance, a quantum-mechanical calculation by Gillette and Sherman[20] indicated that the dimer ring of formic acid is stable if the hydrogen atoms lie on the O−O line of centers and at the normal O−H distances. The system was shown to be less stable if the hydrogen atoms lie midway between the oxygens. With the H atoms at the normal O−H distances, values of the bridge length and heat of dissociation were calculated and found to be in poor agreement with experiment. Barnes, Bonner and Condon[21] assumed that the hydrogen lies somewhere along the perpendicular bisector of the line joining the oxygen atoms considered stationary and calculated frequencies for various configurations. They obtained an upper limit of 2390 cm^{-1} for the frequency in the case in which the hydrogen atom is situated midway between the oxygen atoms. This does not agree with the experimentally observed bridge frequency of about 3100 cm^{-1}, which was not known at that time.

We have made a similar calculation with the acetic acid dimer ring considered to have a structure identical with that of formic acid. We have assumed that the O−H−O and O−D−O groups in the dimer rings of light and heavy acetic acids can be treated approximately as asymmetric linear triatomic molecules. We have further assumed that the force constants involved vary inversely with the cube of the equilibrium distance according to Badger's formula[22]

$$k = \frac{1.86 \times 10^5}{(r_e - d_{ij})^3} \frac{\text{dynes}}{\text{cm}},$$

in which d_{ij} is a constant depending on the atoms involved. Calculations were made for various O−H and O−D distances. If the shorter O−H or O−D distance is taken as 1.07±0.01A the experimental O−H−O and O−D−O frequencies, 3125 and 2299 cm^{-1}, respectively, are checked to within better than 1 percent. This distance is to be compared with the normal O−H distance of 0.97A. In view of the assumptions

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

[20] Gillette and Sherman, J. Am. Chem. Soc. 58, 1135 (1936).
[21] Barnes, Bonner and Condon, J. Chem. Phys. 4, 772 (1936).
[22] R. M. Badger, J. Chem. Phys. 2, 138 (1934).

made we do not feel that too much confidence can be placed in this value for the distance. However, if we use the distances 1.07 and 1.60A, the stretching force constants appear to be 4.68 and 0.91×10^5 dynes/cm.

ACKNOWLEDGMENTS

Vibration Spectra and Molecular Structure

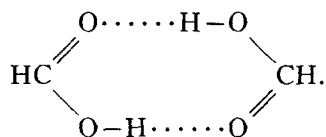## VI. Infra-Red Absorption Spectrum of Heavy Formic Acid[1]

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(Received June 1, 1938)

The infra-red absorption spectra between 1 and 15.5μ of the monomer and dimer of HCOOD have been found with a rocksalt prism spectrometer. The position of the vibration characteristic of the "deuterium bond" in HCOOD has been determined and permits an approximate calculation of the shorter OD distance in the dimer ring. As in CH_3COOD the distance is found to be 1.07A.

INTRODUCTION

SOME time ago Dr. L. G. Bonner and the author[2] were interested in investigating light formic acid vapor (HCOOH) in the infra-red with the hope of finding particulars concerning the hydrogen bond and molecular structure of the acid. Electron diffraction studies of formic acid[3] indicate that the structure of the double molecule is that shown below.

$$
\begin{array}{c}
O \cdots \cdots H-O \\
HC \nearrow \qquad \searrow CH. \\
O-H \cdots \cdots O
\end{array}
$$

Since the vapor of the acid consists of an equilibrium mixture of double and single molecules[4] it was hoped that by raising the temperature and thus promoting the dissociation, the absorption band or bands associated with the hydrogen bond might be recognized and followed as the transition between the double and single molecules progressed. In agreement with these ideas, profound changes were observed in the spectrum on passing from room temperature to higher temperatures. However, these results alone were not sufficient to fix unambiguously either the position or relative intensity of the hydrogen bond band in formic acid, for a very great decrease in intensity of absorption was observed at about 3.25μ where unfortunately the CH commonly appears. One could not say whether this change was due to a changing CH intensity or, indeed, to the hydrogen bond, although the latter possi-

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[1] These results were reported in part in the Washington Meeting of the American Physical Society, April 1938.

[2] Phys. Rev. **51**, 1017 (1937) and Paper No. IV in this series.

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

[4] A. S. Coolidge, J. Am. Chem. Soc. **50**, 2166 (1928).