

Vibration Spectra and Molecular Structure VI. InfraRed Absorption Spectrum of Heavy Formic Acid

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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 1.60Å, the stretching force constants appear to be 4.68 and 0.91×10^5 dynes/cm.

ACKNOWLEDGMENTS

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ful advice. Professors Dougherty and Wallis of the Chemistry Department have very kindly discussed some chemical problems with us. We are thankful to Mr. René Puech for assistance in taking some readings. Professor W. Bleakney has taken an interest in this work which we sincerely appreciate. Finally, we are very grateful to Professor R. Ladenburg for his sustained interest and encouragement.

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Vibration Spectra and Molecular Structure

VI. Infra-Red Absorption Spectrum of Heavy Formic Acid¹

ROBERT HOFSTADTER

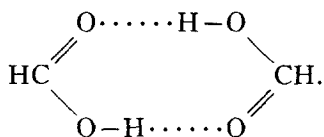
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The infra-red absorption spectra between 1 and 15.5μ of the monomer and dimer of HCOOD have been found with a rocksalt prism spectrometer. The position of the vibration characteristic of the "deuterium bond" in HCOOD has been determined and permits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

INTRODUCTION

SOME time ago Dr. L. G. Bonner and the author² 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 acid³ indicate that the structure of the double molecule is that shown below.



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).

Since the vapor of the acid consists of an equilibrium mixture of double and single molecules⁴ 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-

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

bility seemed more plausible.^{5, 6} It was therefore decided to investigate the deuterium substituted acid (HCOOD). In this case the "deuterium bond" would have a frequency smaller than that of the hydrogen bond by a factor of approximately $\sqrt{2}$. If the band at 3.25μ were really to be connected with the hydrogen bond, then a new one ought now to appear at roughly 4.3μ .

To obtain HCOOD the reaction $D_2S + PbFo_2 = PbS + 2DFO$ was used. Unfortunately only a statistical mixture of the light and heavy acids was produced. Apparently internal exchange occurred on the surface of the $PbFo_2$ column, so that the four forms HCOOH, HCOOD, DCOOH, DCOOD were finally present in equal amounts. CD and OD, of course, behaved exactly as CH and OH; consequently, no more could be learned than from a study of HCOOH. Moreover there was a great complexity and richness of bands in the spectrum.

Recently it has been possible to prepare moderately pure HCOOD, and it is with this compound that the present paper is concerned.

EXPERIMENTAL

Preparation

The first attempt to eliminate the mixed forms was to reduce the temperature of the $PbFo_2$ column from $100^\circ C$ previously used to room temperature. This gave no appreciable improvement so that an entirely different method of preparation was used. At the suggestion of Professor Taylor and Dr. Turkevich, a simple exchange was tried between HCOOH and 99.5 percent D_2O , with subsequent drying of the acid-water mixture with anhydrous $CuSO_4$.⁷ The HCOOD samples obtained by this process were still not entirely pure, probably because of exchange with light water introduced in the drying process. However, the mixtures obtained by this method contained only the two monomeric forms HCOOD and HCOOH as shown by the absence of any CD absorption in the monomer spectrum. The ratios of the amounts of heavy to light forms, denoted by D/H, of several samples

were respectively 3.5, 8, 12.4. The first and last of these ratios were determined by analysis in a mass spectrograph of the H_2-D_2 mixtures obtained by reacting Mg strips with the acid samples.⁸ The middle ratio was found by comparing the depths of the OD and OH bands found in a high pressure run of the monomer spectrum. Good agreement between these two methods was obtained for the ratios $D/H=1.0, 3.5$. This investigation confirmed the earlier conclusions regarding the amounts of the four forms present in the mixed acid.²

The HCOOH was supplied by Kahlbaum and was distilled until the vapor pressure agreed with the determinations of Coolidge.

Analysis

All spectra were obtained with the spectrometer described by Barnes, Brattain and Seitz.⁹ The cells, furnace, etc. were all similar to those used in an investigation of acetic acid.¹⁰ After the high temperature runs were taken, the region $1-5\mu$

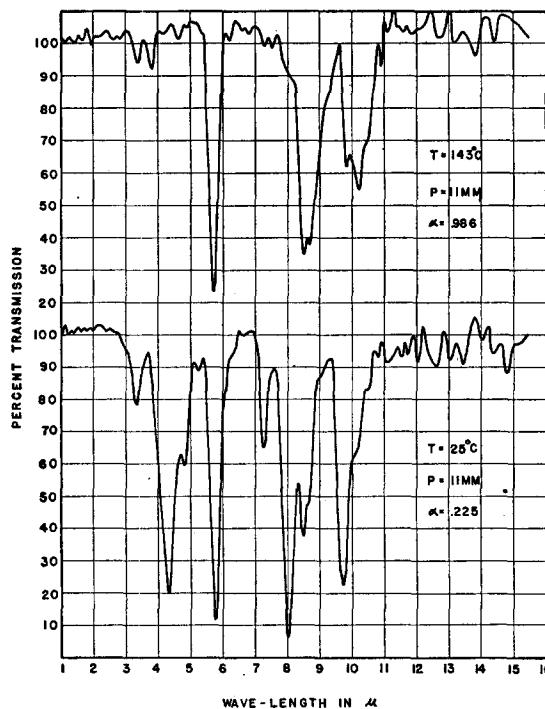


FIG. 1. Absorption spectrum of HCOOD. D/H=8.0. Length of cell=22 cm.

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

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

⁷ That this exchange goes was proved by Münzberg and Oberst, Zeits. f. physik. Chemie B31, 18 (1935).

⁸ I wish to thank Drs. Hipple and Delfosse for kindly doing these analyses.

⁹ Barnes, Brattain and Seitz, Phys. Rev. 48, 582 (1935).

¹⁰ Herman and Hofstadter, Paper No. V in this series.

was re-run at room temperature to see whether any exchange had taken place in the cell. No significant changes were observed other than those which were due to differences in running conditions. Even after several days there were no important changes. This indicates that spontaneous exchange within or between HCOOD molecules is slow, if it exists at all. This is in agreement with the work of Münzberg and Oberst mentioned above.

RESULTS AND DISCUSSION

Figures 1 and 2 show the spectra obtained for two samples with the D/H ratios 8 and 12.4. Even though the samples were run at different pressures one may see from the curves that further purification would probably lead to no serious changes.¹¹ Indeed, the sample for which the D/H ratio was 3.5 presented a very similar set of spectra. The degree of dissociation, α , was determined from the dissociation data of Coolidge.

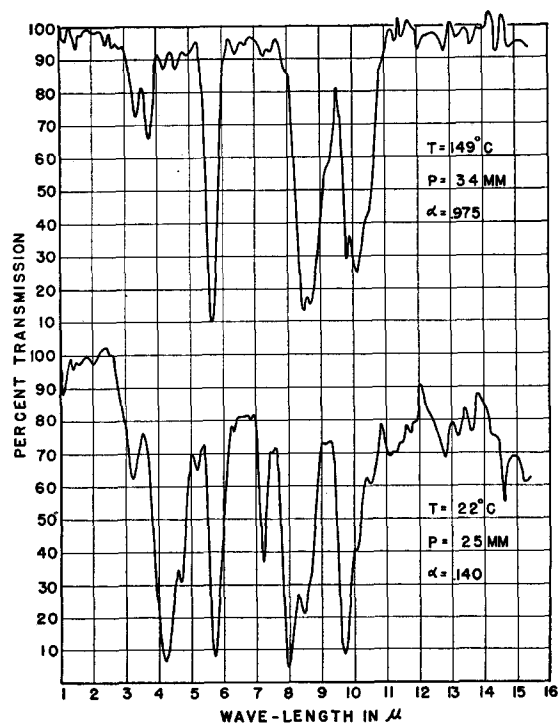


FIG. 2. Absorption spectrum of HCOOD. D/H=12.4. Length of cell=22 cm.

¹¹ The ratios of dimers containing one H and one D to those containing two D's are only half the above values, namely 4 and 6.2.

Since the degree of dissociation at room temperature and the pressures shown is in the neighborhood of 18 percent we may consider the lower curves to represent the dimer. The upper curves are certainly spectra of the monomer for α is very close to 1. Table I lists the frequencies found by averaging the band centers for the corresponding curves in the two figures.

TABLE I. HCOOD.

MONOMER		DIMER	
cm ⁻¹	PROBABLE ASSIGNMENT	cm ⁻¹	PROBABLE ASSIGNMENT
3003±60	C-H	3030±46	C-H
2667 35	O-D		
2347 35*		2347 33	O-D-O
2105 30*		2105 22	
		1916 16	
1764 16	C=O	1736 15	C=O
		1381 11	
		1253 10	
1163 6	C-O?	1181 7‡	C-O?
1081 15†			
1030 5		1030 5	
980 5		985 10‡	
953 8		950 8‡	
		901 7‡	

* Very small and probably due to small amount of dimer.

† Probably due to 7.5 percent impurity of HCOOH.

‡ Probably due to small amount of monomer.

The dimer spectrum of HCOOD shows a strong, broad band at about 4.26μ (2347 cm^{-1}) which is overlapped somewhat by a weaker band on the long wave-length side at 4.75μ (2105 cm^{-1}). The band at 4.26μ must then be that which characterizes the deuterium bond in heavy formic acid. Further proof that this assignment is correct is obtained from the dissociation results, for this band is absent in the monomer and belongs solely to the dimer, where the deuterium bonds occur. No other reasonable choice for such a high frequency can be made. One sees how small the CH bands of the monomer and dimer are. The strong absorption at 3.25μ found in light formic acid may now be explained as being chiefly due to the hydrogen bond, in agreement with the earlier ideas.² Correlated with the disappearance of the bonded band, we see the emergence of a small band at 3.75μ (2667 cm^{-1}). This is to be attributed to a "free" OD valence vibration. Results similar to those just mentioned have been found in light and heavy acetic acids¹⁰

TABLE II.

HCOOH		HCOOD	
Obs.	Calc.	Obs.	Calc.
1740 cm ⁻¹	1744 cm ⁻¹	1764 cm ⁻¹	1741 cm ⁻¹
1093	1093	1162	1083
650?	579	667	572

and in the liquid of ethyl alcohol where a similar association has been assumed to take place.¹²

From the position of the O—D—O band in the dimer, the approximate distance between the D and the nearest oxygen in the dimer ring may be calculated. It is assumed here that the O—D—O vibration frequency in the molecule may be computed from a linear asymmetric triatomic model where the O—O distance is 2.67Å, with force constants evaluated by application of Badger's rule.¹³ A similar calculation can be made using the O—H—O frequency at 3077 cm⁻¹. The best fit for the shorter O—H, O—D distance is 1.07Å. Using this distance the two calculated frequencies check the observed ones to better than 2.6 percent. This same calculation for the acetic acid dimers furnishes the identical value, 1.07Å.¹⁰

The monomer spectrum of HCOOD presents an interesting detail in the appearance of an intense band at 8.6μ (1163 cm⁻¹). In comparison with one of the fundamentals of HCOOH (1093 cm⁻¹), this band is shifted towards higher frequency. The similar shape and approximate position of this band suggest that it is to be attributed to the same bond (C—O), since the band at 1093 cm⁻¹ in HCOOH has definitely been assigned to this vibration. If this assignment for the 8.6μ band be correct, the shift towards

greater frequency cannot be explained as a mere mass effect, for one would expect a decrease in frequency on substitution of a heavier mass in the hydroxyl group (see Table II).

One may calculate the frequencies of a simplified triatomic model of the HCOOD molecule by the method of rigid groups. This method was previously employed in finding the force constants for a similar triatomic model of HCOOH.² The force constants yielded in this way, 11.8, 5.4, 0.4×10⁵ dynes/cm, were used to compute the new frequencies shown in Table II, where for convenience the data on HCOOH are also collected.

In connection with this anomalous behavior it is to be noticed that the calculated frequency for the C—O bond lies about midway in the frequency interval between the bands at 8.6μ (1163 cm⁻¹) and 10.2μ (980 cm⁻¹). No adequate explanation for this behavior has been worked out, although there is a possibility that these two bands furnish another example of an accidental degeneracy.

No interpretation of the dimer spectrum has been made beyond 6.0μ.

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I wish to thank Professors Taylor and Menzies and Dr. Turkevich of the Chemistry Department for suggestions concerning the chemical preparation. I also wish to thank Professor Eyring of the Chemistry Department for a very profitable conversation. I am obliged to Mr. R. C. Newton, who kindly performed a chemical determination. Professors Ladenburg, Bleakney and Smyth have given me encouragement and helpful criticism for which I am grateful. Finally, I am indebted to Mr. R. R. Brattain for his kind assistance and advice.

¹² Errera and Mollet, *Comptes rendus* **204**, 259 (1937).

¹³ R. M. Badger, *J. Chem. Phys.* **2**, 128 (1934).