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Infra-Red Spectra of Monomeric Formic Acid and Its Deuterated Forms. I. High Frequency Region*

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The hydrogen and deuterium stretching vibrations of the molecules HCOOH , HCOOD , DCOOH , and DCOOD have been studied with a high resolution echelette-grating infra-red spectrometer. From the rotational structure of these bands parameters which are functions of the moments of inertia have been calculated. From these parameters,

previous data, and assumptions of the hydrogen bond distances and molecular planarity, the following dimensions of the molecule have been derived: $\text{O}-\text{H}$, $0.96 \pm 0.01 \text{ \AA}$; $\text{C}-\text{H}$, $1.08 \pm 0.01 \text{ \AA}$; $\text{C}=\text{O}$, $1.225 \pm 0.02 \text{ \AA}$; $\text{C}-\text{O}$, $1.41 \pm 0.02 \text{ \AA}$; $\text{O}-\text{C}=\text{O}$, $125 \pm 1^\circ$; $\text{C}-\text{O}-\text{H}$, $107 \pm 5^\circ$; $\text{H}-\text{C}=\text{O}$, $122 \pm 5^\circ$.

INTRODUCTION

BECAUSE of the limited resolving power of present day infra-red spectrographs and the half-widths of the rotational bands, complete evaluation of molecular moments of inertia from rotational band structure has been possible for only a few simple or symmetrical molecules. For some heavier molecules which are needle-shaped symmetrical top rotators, i.e., have two large equal moments of inertia and one smaller one, it is often possible to resolve the perpendicular bands even though the parallel band structure cannot be separated. This is also true for a molecule which is an approximate symmetric top, where the two large moments of inertia are comparable and the third is much smaller. Such analyses, unfortunately, offer only one datum for determining the several structural parameters of the molecule. In many cases, particularly if such molecules contain hydrogen atoms, it is possible to prepare isotopic forms for further study. Since the molecular dimensions are not appreciably changed on replacing an atom by its isotope, new data pertaining to the same structure can be obtained.

An example of a molecule to which the above method of analysis can be applied is formic acid, HCOOH . Its rotational fine structure has already been partially examined in the photographic infra-red region by Herzberg and Verleger¹ and

Bauer and Badger² who studied the second harmonic of the $\text{O}-\text{H}$ stretching vibration at $10,203 \text{ cm}^{-1}$ and Thompson³ who photographed the third harmonic of the same band at $13,287 \text{ cm}^{-1}$. These authors showed the structure of HCOOH to be a planar, approximate symmetrical top whose perpendicular bands were such that they could be resolved in the fundamental region. Moreover, it is possible to deuterate the molecule and have four isotopic forms, HCOOH , HCOOD , DCOOH , and DCOOD . These four molecules have been studied with an echelette-grating spectrometer in the region from 4000 cm^{-1} to 800 cm^{-1} . Since the high frequency region of the hydrogen-deuterium stretching vibrations gives all the data from which structural parameters may be calculated, the interval from 4000 to 2000 cm^{-1} forms the subject of this first paper.

EXPERIMENTAL

Instrument

An excellent, automatic recording, echelette-grating spectrometer designed and built by Dr. L. G. Smith⁴ was used in this research. However, at the time of this work the instrument was not free of water vapor nor was the KBr fore-prism in use. Therefore, bands in the water region could not be studied carefully and those below 800 cm^{-1} were not considered.

* This material was presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy, March, 1941. A portion of the material has also been presented before the Physical Society [Phys. Rev. **57**, 1078 (1940), and **58**, 208 (1940)].

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¹ G. Herzberg and H. Verleger, *Physik. Zeits.* **12**, 444 (1936).

² S. H. Bauer and R. M. Badger, *J. Chem. Phys.* **5**, 852 (1937).

³ H. W. Thompson, *J. Chem. Phys.* **7**, 453 (1939).

⁴ L. G. Smith, *Rev. Sci. Inst.* **13**, 54 (1942).

Preparation and Purity of Materials

The HCOOH used was obtained from Kahlbaum and purified by distillation. Its vapor pressure agreed well with the values given by Coolidge.⁵

HCOOD was prepared by repeated exchange with D₂O as described by Hofstadter.⁶

DCOOH and DCOOD were prepared as described by Herman and Williams.⁷ Anhydrous oxalic acid, (COOH)₂, was deuterated by straight exchange and thermally decomposed to DCOOD, CO, CO₂, and D₂O. The CO and CO₂ were removed by pumping. DCOOH was then made by exchange of DCOOD with H₂O. The deuterated forms were freed of water by use of anhydrous CuSO₄ and purified by distillation. All reactions and purifications were carried out in vacuum.

Since two or three lots of each deuterated compound were made as needed, it was not possible to get accurate values of purity at all times. However, some mass spectrographic analyses of D/H ratio were performed by Mr. T. Mariner to determine purity and infra-red spectra and vapor pressure lowerings were used in other cases. It was estimated that HCOOD contained 3 to 4 percent HCOOH; DCOOH, a similar amount of DCOOD; and DCOOD, 6 to 7 percent of DCOOH. All the deuterated samples contained about 5 percent of water.

Cells and Techniques

The absorption cells were Pyrex cylinders with rocksalt windows sealed with Glyptal. As it was necessary to work at 150–160°C to eliminate dimer interference, these cells were contained in a furnace made of sheet metal wrapped with asbestos and a nichrome heating coil. The ends of the furnace were closed with transite slabs with rocksalt window apertures. The sample was contained in a side tube from the cell brought outside the furnace, and the vapor pressure was regulated by the temperature of the side tube. If the pressure desired was greater than could be obtained at room temperature, the side tube was heated with an auxiliary furnace. The pressures quoted are based on the temperature of this side

tube. The vapor was regulated to give good spectral resolution without special regard to its absolute value.

BASIS OF CALCULATIONS

An excellent summary of the theory of the slightly asymmetric top rotator has been given by Dieke and Kistiakowsky⁸ in connection with their study of the formaldehyde molecule. In fact, the degree of asymmetry of HCOOH is very close to that of H₂CO so that the analogy with their results can be followed very closely. The nomenclature used in this work is the same as that of the above authors: γ'' (cm⁻¹) = $h/8\pi^2cC$, δ (cm⁻¹) = $h/8\pi^2cD$, $1/D = 1/2(1/A + 1/B)$ where A , B , and C are the large, middle, and the small moments of inertia, respectively, in gm cm² units. The molecular parameters derived from the perpendicular bands are $\gamma' - \delta$ and $\gamma'' - \delta$, where the single prime refers to the upper vibrational state of the transition and the double prime to the lower. It is assumed that, within the error of measurement, the δ values are the same for each state. These parameters are obtained from the difference equations,

$$\gamma' - \delta = \frac{rQ(K) - pQ(K)}{4K},$$

$$\gamma'' - \delta = \frac{rQ(K-1) - pQ(K+1)}{4K},$$

and the band center from

$$\nu(\text{cm}^{-1}) = \frac{rQ(K) + pQ(K)}{2} + K^2(\gamma'' - \gamma') - (\gamma' - \delta),$$

where $rQ(K)$ and $pQ(K)$ refer to the frequency value in cm⁻¹ of the rotational bands of the r branch and p branch, respectively, arising from the K th energy level of the lower state.

RESULTS

Table I gives a list of the fundamental bands which could be studied thoroughly in the high frequency region and the conditions under which they were observed. These characteristic absorptions are shown in Figs. 1–6. These are the

⁵ A. S. Coolidge, J. Am. Chem. Soc. **50**, 2166 (1928).

⁶ R. Hofstadter, J. Chem. Phys. **6**, 540 (1938).

⁷ R. C. Herman and V. Z. Williams, J. Chem. Phys. **8**, 447 (1940).

⁸ G. H. Dieke and G. B. Kistiakowsky, Phys. Rev. **45**, 4 (1934).

direct photographic records obtained from the spectrograph in which the ordinates are galvanometer deflections representing absorption in an upward direction and the abscissae are cm^{-1} not corrected for vacuum. Above each peak is marked the K -value of the lower state involved in the transition.

All the spectra shown are essentially perpendicular bands consisting of $pQ(K)$ and $rQ(K)$ branches. For K greater than 3 or 4, the peaks are fairly sharp and equally spaced, but for small values of K the asymmetry of the molecule evidences itself as a "washing out" of this characteristic structure. Some of the bands show a small qQ branch at a slightly lower frequency than the computed value of ν_0 indicating a component of dipole moment change parallel to the axis of least moment of inertia. A Fortrat diagram is given (Figs. 1a, 3a-6a) when the bands could be analyzed. With each spectrum there is a table (Tables Ia, III-VI) showing the frequency position of the peaks and wherever possible, individual and average values of $\gamma' - \delta$, $\gamma'' - \delta$, and ν_0 .

An attempt was made to dry the instrument to permit a study of the $\nu(\text{O}-\text{H})$ stretching vibrations of HCOOH and DCOOH . This was sufficiently successful to show that both bands were of the perpendicular type with ν_0 values of $3567 \pm 3 \text{ cm}^{-1}$. However, it was not possible to make a band analysis or to determine whether or not a qQ branch was present.

Figure 1 shows the $\nu(\text{C}-\text{H})$ stretching vibration of HCOOH at 2942.85 cm^{-1} . The pQ and rQ branches are quite sharp and can be traced on each side to the sixteenth member. The irregularities at the high frequency end are caused by water vapor in the instrument. There is no indication of a qQ branch, showing that the change in dipole moment involved in the transition is

practically perpendicular to the axis of least moment of inertia of the molecule.

Figure 2 is the $\nu(\text{C}-\text{H})$ vibration of HCOOD . Unlike the previous picture it does not have quite the regular symmetric appearance expected of a perpendicular band but shows evidence of some perturbing influence. While the bands on the low frequency side are sharp and regular, those on the high frequency half are indistinct and not evenly spaced. The average band separation in the pQ branch is exactly that of the typical pQ branch of $\nu(\text{O}-\text{D})$, HCOOD , Fig. 3, but it does not have the proper convergence. By drawing a line graph of the structure of Fig. 3 and comparing it with one for Fig. 2, the tentative K assignments of Table II are made. This places ν_0 at about 2948 cm^{-1} . Because the assigned K -values are not at all certain, no attempt has been made to determine rotational constants.

Figure 3 is the $\nu(\text{O}-\text{D})$ vibration of HCOOD . It is a regular perpendicular band for which the pQ branch shows twenty-three members and the rQ , sixteen. The large peak at 2681.3 cm^{-1} is a background band and does not belong to the main structure. The band center is at 2631.88 cm^{-1} and just below it there is a small qQ branch.

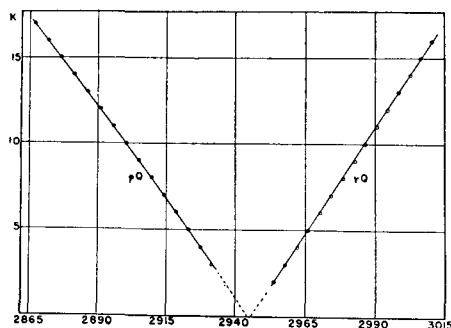
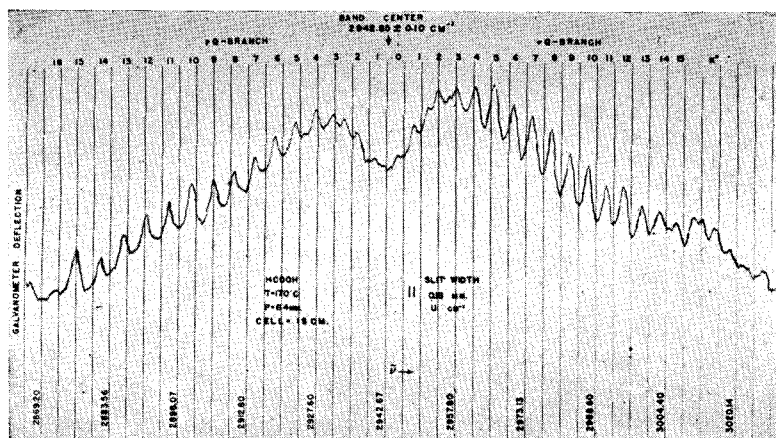
Figure 4 shows the $\nu(\text{O}-\text{D})$ band of DCOOD . Like the preceding bands its pQ branch shows more structure than the rQ . Here there is the added difficulty to analysis that the irregular structure on the extreme high frequency side is mainly caused by the presence of D_2O in the sample. The band center is at 2632.28 cm^{-1} and again there is a small qQ branch.

Figure 5 is the $\nu(\text{C}-\text{D})$ stretching frequency of DCOOH . The band center is at 2219.84 cm^{-1} with a fairly strong qQ branch just below it.

Figure 6 shows the spectrum of the $\nu(\text{C}-\text{D})$ region of DCOOD . Like the $\nu(\text{C}-\text{H})$ of HCOOD , the regular band symmetry is destroyed by some

TABLE I. Important bands studied. All spectra taken in first order.

Fig.	Molecule	$\lambda(\mu)$	$\nu(\text{cm}^{-1})$	$T(^{\circ}\text{C})$	P (mm. Hg)	Cell length (cm)	Grating lines/in.	Spectral slit width (cm^{-1})
1	HCOOH	3.40	2942.85	170	64 ± 10	15	4800	1.1
2	HCOOD	3.40	ca. 2948	170	60 ± 10	15	7500	0.9
3	HCOOD	3.80	2631.88	170	68 ± 10	15	4800	1.1
4	DCOOD	3.80	2632.28	150	58 ± 10	15	4800	1.0
5	DCOOH	4.51	2219.84	150	58 ± 10	15	4800	0.9
6	DCOOD	4.48	2231.83	163	60 ± 10	15	4800	1.0

FIG. 1. $\nu(\text{C-H})$, HCOOH .FIG. 1a. Fortrat diagram $\nu(\text{C-H})$, HCOOH .

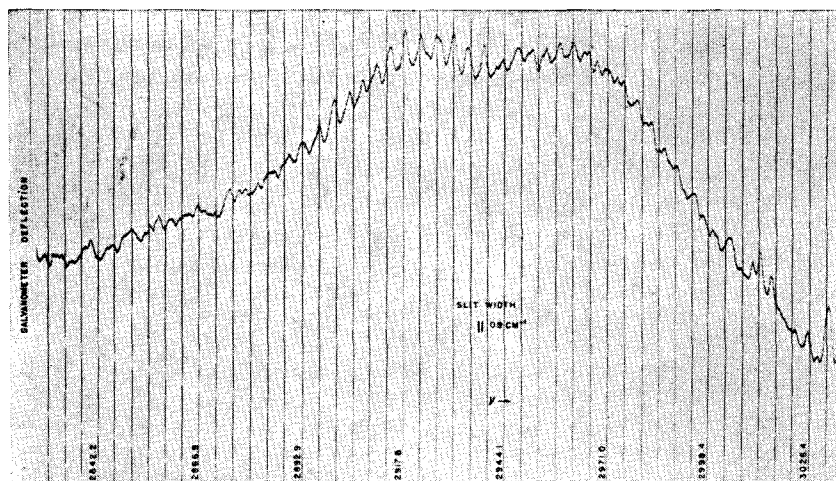
perturbing factor, but it is possible here to identify the $\nu(\text{C-D})$ absorption band. By comparing a line graph of the $\nu(\text{O-D})$, DCOOD , Fig. 4 structure with this band, one finds a very close correspondence if the K -assignments are made as shown. With this analysis, ν_0 can be computed to lie at 2231.83 cm^{-1} and the values of $\gamma' - \delta$, and $\gamma'' - \delta$ are in close agreement with those obtained from the $\nu_0(\text{O-D})$ band. Without a complete knowledge of the spectrum of DCOOD , one cannot with certainty account for the large band at 2195 cm^{-1} and the regular structure at lower frequency. At first the structure was thought to be due to carbon monoxide in the cell, but closer examination showed that neither the exact frequencies nor the convergence of the peaks fitted that molecule. In order to be sure, two or three runs were made with fresh samples of DCOOD , but the structure remained. A possible explanation of this region may be that a combination band of two lower frequencies at 1040 and 1171 cm^{-1} would fall at 2211 cm^{-1} about

TABLE Ia. $\nu(\text{C-H})$; HCOOH .

K''	$\nu(\text{cm}^{-1})$ PQ branch	$\Delta\nu$	$\nu(\text{cm}^{-1})$ RQ branch	$\Delta\nu$	$(\gamma' - \delta)$ (cm^{-1})	$(\gamma'' - \delta)$ (cm^{-1})	ν_0 (cm^{-1})
0							
1							
2			2953.9				
3	2931.0		57.9	4.0			
4	27.2	3.8	62.1	4.2			
5	22.9	4.3	66.1	4.0	2.160	2.170	2942.90
6	18.7	4.2	70.3	4.2	150	63	2.85
7	14.2	4.5	74.5	4.2	54	61	2.88
8	09.8	4.4	78.8	4.3	56	63	3.04
9	05.3	4.5	82.8	4.0	53	69	3.01
10	00.7	4.6	87.0	4.2	58	70	3.09
11	2896.0	4.7	90.8	3.8	55	77	2.94
12	91.2	4.8	94.6	3.8	54	71	2.76
13	86.6	4.6	98.8	4.2	58	71	2.91
14	81.7	4.9	3002.9	4.1	64	84	2.89
15	76.5	5.2	06.6	3.7	68	83	2.54
16	71.9	4.6	10.6	4.0	67	82	2.68
17	66.9	5.0					
Average: 2.158 2.172 2942.85 ± 0.1							

midway between the peaks of Fig. 6. There might be a slight interaction between the combination band and the $\nu(\text{C-D})$ fundamental which would tend to spread the two peaks about the central position.

By comparing the appearance of these bands, one can see the influence of the asymmetry of the molecule. On going from HCOOH to DCOOD , the ratio of the principal moments of inertia changes from 1:7:8 to 1:4.5:5.5. In the spectra, the bands of HCOOH are sharp and well resolved,

FIG. 2. $\nu(\text{C-H})$, HCOOD.TABLE II. $\nu(\text{C-H})$; HCOOD.

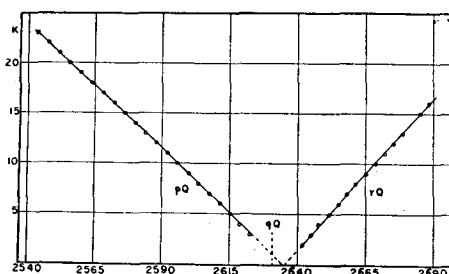
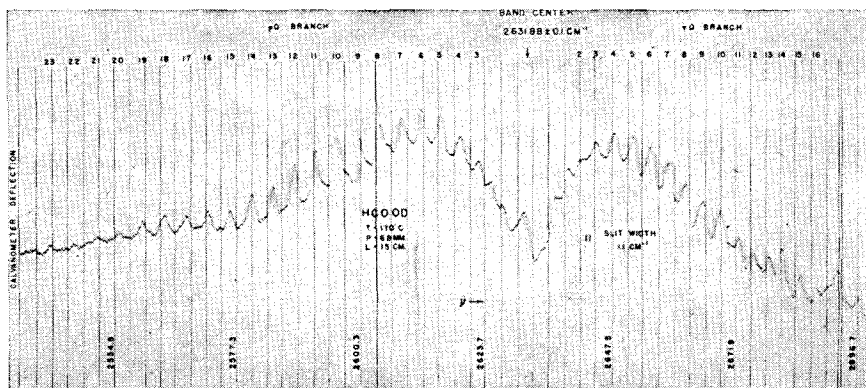
Band center approximately		$\nu_0 = 2948 \text{ cm}^{-1}$	
K''	$\nu(\text{cm}^{-1})$	$\Delta\nu$	
17	2884.7	4.2	
16	88.9	3.5	
15	92.4	3.9	
14	96.3	3.7	
13	2900.0	3.9	
12	03.9	3.5	
11	07.4	3.7	
10	11.1	3.4	
9	14.5	3.9	
8	18.4	4.1	
7	22.5	4.4	
6	26.9	4.0	
5	30.9	3.8	
4	34.7	4.0	
3	38.7		
	43.7		
	47.7		
	51.5		
	55.1		
2	58.6	3.3	
3	61.9	3.8	
4	65.7	2.6	
5	68.3		
	70.7		
	73.4		
7	75.2	3.3	
8	78.5	4.1	
9	82.4	3.7	
10	86.1	3.5	
11	89.6		
	94.3		
	96.7		
	99.8		

while those of DCOOD are smaller and more diffuse.

The values of $\gamma' - \delta$ and $\gamma'' - \delta$ agree well among themselves, the spread in the values being about one percent. The average values are

certainly good to one percent. The quantity $\gamma'' - \delta$ for HCOOH has been previously determined by Herzberg and Verleger,¹ Bauer and Badger,² and Thompson.³ Herzberg and Verleger, with lower dispersion than the other two, gave a rough value of $\gamma'' - \delta = 2.1 \text{ cm}^{-1}$. Bauer and Badger obtain a value of 2.2106 cm^{-1} while Thompson gives an average of 2.202 cm^{-1} . These are to be compared with the value of 2.172 found in this work. Actually, Bauer and Badger had an average value of 2.196 cm^{-1} , but in fitting their data to an energy-level diagram of the form $W/hc = J(J+1)\delta + K^2(\gamma'' - \delta) + \mu K^4$, this was raised to 2.2106 cm^{-1} . No attempt was made to fit the data of this work to an energy expression as the experimental positions of the peaks were not sufficiently accurate to make the resulting values of $\gamma'' - \delta$ more significant than the average value. The value of 2.196 lies slightly outside the limit of error of the 2.172 determination. There is no apparent reason for this discrepancy although it must be remembered that the two values were obtained from different bands. Even so the values determined in this work for DCOOD were on different bands yet were very close, i.e., 1.328 and 1.320 . It would be interesting to compare the value obtained from a study of the $\nu(\text{O-H})$ fundamental with those of the above authors who worked on the $\nu(\text{O-H})$ harmonics.

The spread in the values of ν_0 is approximately 0.3 cm^{-1} . The main inaccuracies in determining the frequency positions of the peaks are (1) the difficulty in setting on the point of maximum ab-

FIG. 3. $\nu(\text{O}-\text{D})$, HCOOD .FIG. 3a. Fortrat diagram $\nu(\text{O}-\text{D})$, HCOOD .

sorption when the peaks are not sharp, and (2) errors in calibration by use of the zero-order spectrums. Since several peaks are used in calculating ν_0 , the first inaccuracy should average out leaving the second as the main source of possible error.

DISCUSSION

The results of this work give four data, the values of $\gamma'' - \delta$, for the four molecules having essentially the same geometric structure. A fifth datum is given by the $\delta = 0.348 \text{ cm}^{-1}$ value of Bauer and Badger.² Since there are more structural parameters than there are data, certain assumptions must be made.

The first assumption is the natural one that the molecule is planar. The $\text{C}-\text{H}$, $\text{C}=\text{O}$, and $\text{C}-\text{O}$ bonds must lie in a plane because the structure

$\text{C}=\text{O}$ is known to be planar. Pauling⁹ has shown that there is resonance in the carboxyl group between the two carbon oxygen bonds which would

⁹ L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1939).

TABLE III. $\nu(\text{O}-\text{D})$; HCOOD .

K''	$\nu(\text{cm}^{-1})$ pQ branch	$\Delta\nu$	$\nu(\text{cm}^{-1})$ rQ branch	$\Delta\nu$	$(\gamma' - \delta)$ (cm^{-1})	$(\gamma'' - \delta)$ (cm^{-1})	ν_0 (cm^{-1})
qQ	2630.8						
0							
1							
2							
3	2622.5		2644.6				2631.85
4	18.8	3.7	47.9	3.3	1.819	1.838	1.74
5	15.2	3.6	51.6	3.7	20	20	1.91
6	11.5	3.7	55.0	3.4	13	21	1.90
7	07.9	3.6	58.4	3.4	04	25	1.97
8	03.9	4.0	61.7	3.3	06	22	1.82
9	00.1	3.8	65.2	3.5	08	25	1.89
10	2596.0	4.1	68.8	3.6	20	28	1.88
11	92.1	3.9	72.3	3.5	23	32	1.96
12	88.2	3.9	75.6	3.3	21	38	1.87
13	84.1	4.1	78.7	3.1	19	37	1.78
14	80.1	4.0				30	
15	80.1	3.9		6.5			
16	76.2	4.1	85.2	3.4	17		1.81
17	72.1	4.0	88.6		20	30	1.86
18	68.1	4.0				31	
19	64.1	4.2					
20	59.9	4.3					
21	55.6	3.8					
22	51.8	4.2			Average: 1.816	1.829	2631.88 \pm 0.1
23	47.6	4.2					
24	43.4						

tend to prevent free rotation of the hydroxyl bond. Moreover the observed vibrations for $\nu(\text{O}=\text{H})$ at 3567 cm^{-1} and $\nu(\text{O}-\text{D})$ at 2632 cm^{-1} are lower than the normal frequencies at 3680 and 2720 cm^{-1} in spite of the fact that the partial double bond character of the $\text{C}-\text{O}$ link would

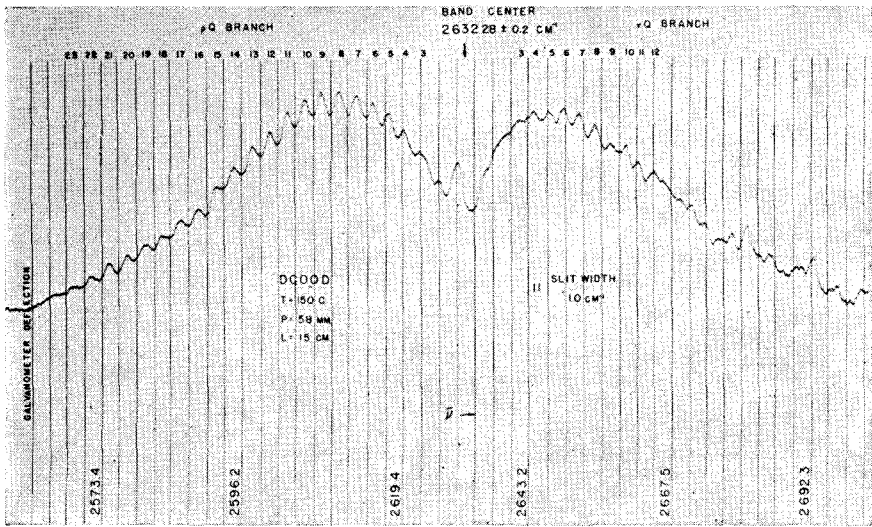


FIG. 4. $\nu(\text{O}-\text{D})$, DCOOD.

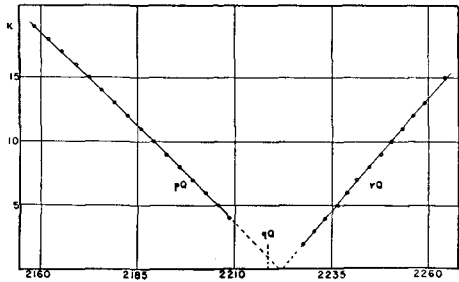


FIG. 4a. Fortrat diagram $\nu(\text{O}-\text{D})$, DCOOD.

tend to increase these frequencies. This decrease implies a weakening of the O—H bond which could be caused by an attraction between the hydroxyl hydrogen and the double bond oxygen. Coop, Davidson, and Sutton,¹⁰ using dipole moment data for HCOOH, infer for the monomer a *cis*- and *trans*-position for the hydroxyl group with the *cis* the dominant form. This *cis*-position of the hydroxyl is strongly supported by the perpendicular band character of the $\nu(\text{O}-\text{H})$ and $\nu(\text{O}-\text{D})$ absorptions. If this linkage were in the *trans*-position, these would be more nearly parallel bands. Karle and Brockway¹¹ doing electron diffraction studies postulate a planar structure for the monomer. Hence all the data, spectroscopic, dipole moment, resonance, and electron diffraction are in agreement on the planarity.

¹⁰ I. E. Coop, N. R. Davidson, and L. E. Sutton, J. Chem. Phys. 6, 905 (1938).
¹¹ J. Karle and L. O. Brockway, J. Am. Chem. Soc. 66, 574 (1944).

TABLE IV. $\nu(\text{O}-\text{D})$; DCOOD.

K''	$\nu(\text{cm}^{-1})$ pQ branch	$\Delta\nu$	$\nu(\text{cm}^{-1})$ rQ branch	$\Delta\nu$	$(\gamma' - \delta)$ (cm^{-1})	$(\gamma'' - \delta)$ (cm^{-1})	ν_0 (cm^{-1})
qQ	2631.5						
0							
1							
2	2628.4						
3	25.6	2.8	2641.9				
4	22.7	2.9	44.1	2.2			
5	20.1	2.6	46.6	2.5	1.325	1.330	2632.19
6	17.5	2.6	48.9	2.3	08	17	.13
7	15.0	2.5	51.6	2.7	07	14	.32
8	12.1	2.9	54.3	2.7	19	22	.33
9	09.3	2.8	57.0	2.6	25	28	.40
10	06.5	2.8	59.6	2.2	28	35	.43
11	03.6	2.9	61.8	2.7	23	39	.23
12	00.7	2.8	64.5		29	31	.29
13	2597.9	2.9				37	
14	95.0	2.9					
15	92.1	2.9					
16	89.2	3.0					
17	86.2	3.0					
18	83.2	2.8					
19	80.4	2.9			Average: 1.321	1.328	2632.28 ± 0.2
20	77.5	2.9					
21	74.6	3.0					
22	71.6	3.0					
23	68.6						

With this assumption there are seven parameters, four bond distances and three angles, for

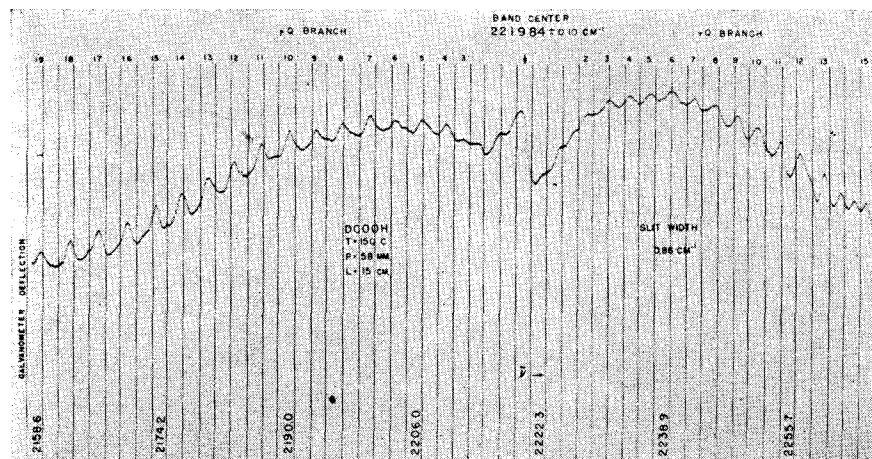
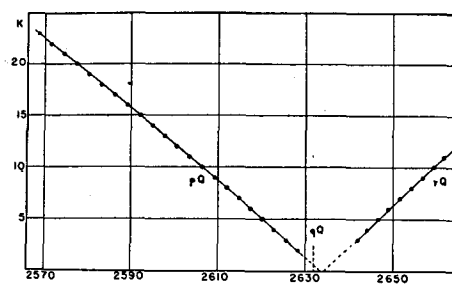

 FIG. 5. $\nu(\text{C}-\text{D})$, DCOOH.

 TABLE V. $\nu(\text{C}-\text{D})$; DCOOH.

K''	$\nu(\text{cm}^{-1})$ pQ branch	$\Delta\nu$	$\nu(\text{cm}^{-1})$ rQ branch	$\Delta\nu$	$(\gamma' - \delta)$ (cm^{-1})	$(\gamma'' - \delta)$ (cm^{-1})	ν_0 (cm^{-1})
qQ	2218.7						
0							
1							
2			2227.7				
3			30.6	2.9			
4	08.9		33.4	2.8	1.531	1.544	2219.86
5	05.9	3.0	36.2	2.8	15	45	19.90
6	02.5	3.4	39.0	2.8	21	38	19.76
7	2199.3	3.2	41.9	2.9	21	39	19.81
8	95.9	3.4	44.7	2.8	25	44	19.73
9	92.5	3.4	47.7	3.0	33	42	19.79
10	89.2	3.3	50.4	2.7	30	48	19.77
11	85.8	3.4	53.4	3.0	36	41	19.89
12	82.6	3.2	56.3	2.9	35	46	20.08
13	79.2	3.4	59.3	3.0	40	46	
14	75.9	3.3				48	20.55
15	72.6	3.3					
16	69.1	3.5	64.8		37		
17	65.5	3.6				52	
18	62.0	3.5					
19	58.4	3.6					
Average: 1.529 1.544 2219.84 ± 0.2							

which there are five data. The two obvious values to assume are the hydrogen bond distances. The C-H distance is assumed to be 1.08Å. It will be shorter than the 1.09Å of methane because the carbon is unsaturated but it will be longer than the 1.07Å of ethylene because the $\nu(\text{C}-\text{H})$ frequency is 2943 cm^{-1} rather than greater than


 FIG. 5a. Fortrat diagram $\nu(\text{C}-\text{D})$, DCOOH.

3000 cm^{-1} as for a typical H-C=linkage. The O-H distance is considered to be 0.96–0.97Å. The normal hydroxyl distance is 0.96Å and Badger's rule,¹² using the frequency lowering, brings this value to 0.97Å. With these assumptions the problem is reduced to five data and five parameters.

The remaining parameters were obtained by calculating the constants δ and $\gamma'' - \delta$ for various tentative structures. The moments of inertia of the assumed structures were first calculated for arbitrary axes in the plane of the molecule, converted to principal moments by principal axes transformation, δ and $\gamma'' - \delta$ calculated and compared with the experimental data which were considered good to ± 1 percent. A structural model was found which would give good agreement between calculated and experimental results. Individual parameters were then varied over a plus and minus range from this model to determine the effect on δ and $\gamma'' - \delta$ of each

¹² R. M. Badger, J. Chem. Phys. **3**, 710 (1935).

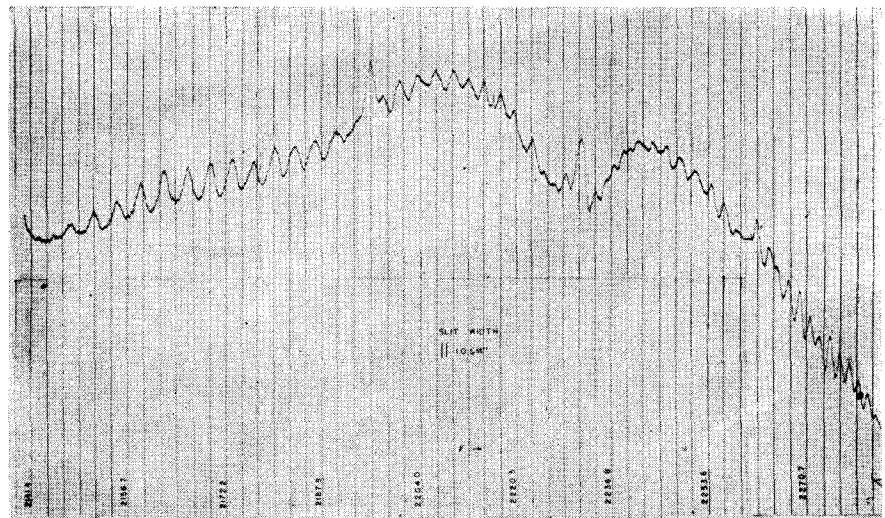


FIG. 6. $\nu(\text{C-D})$, DCOOD.

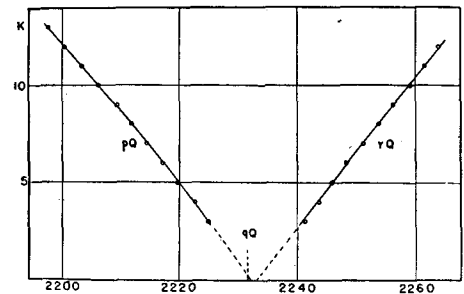


FIG. 6a. Fortrat diagram $\nu(\text{C-D})$, DCOOD.

parameter separately. With this knowledge, it was possible to combine various values of these parameters which would give calculated results within the limits of error. In general, the final structure was chosen to be the median value of the possible variations of these parameters and the extreme values fixed the limits of error. The effect of these variations is given in some detail, and reference to Fig. 7, the final model chosen, will be of aid in following the discussion. In these considerations it should be noted that although the evaluation of $\gamma'' - \delta$ involves all three moments of inertia (A , B , and C), the least moment (C) is the governing factor as a change of six or seven percent in δ represents about one percent change in $\gamma'' - \delta$.

The Angles $\text{H}-\text{C}=\text{O}$ and $\text{C}-\text{O}-\text{H}$

It can be seen that variations in these angles will have but slight effect on the values of $\gamma'' - \delta$. Their contribution to C enters as the sine of the

TABLE VI. $\nu(\text{C-D})$; DCOOD.

K''	$\nu(\text{cm}^{-1})$ pQ branch	$\Delta\nu$	$\nu(\text{cm}^{-1})$ rQ branch	$\Delta\nu$	$(\gamma' - \delta)$ (cm^{-1})	$(\gamma'' - \delta)$ (cm^{-1})	ν_0 (cm^{-1})
qQ	2231.2						
0							
1							
2							
3			2241.3	2.3			2231.79
4	2222.7	3.1	43.6	2.2	1.306		1.95
5	19.6	2.4	45.8	2.5	310	1.320	1.56
6	17.2	2.7	48.3	2.8	296	04	1.69
7	14.5	2.7	51.1	2.8	307	04	1.83
8	11.8	2.5	53.9	2.3	316	06	1.99
9	09.3	3.1	56.2	3.2	303	25	2.00
10	06.2	2.9	59.4	2.3	330	23	2.19
11	03.3	2.9	61.7	2.3	327	41	2.03
12	00.4	3.1	64.0		325	38	1.90
13	2197.5						
	2195.6 (Large peak)						
	90.6	3.7					
	86.9	3.3					
	83.6	3.3					
	80.3	3.5			Average: 1.313	1.320	2231.83 \pm 0.2
	76.8	3.5					
	73.3	3.5					
	69.8	3.5					
	66.3	3.7					
	62.6	3.7					
	58.9	3.6					
	55.3	3.7					
	51.6	3.8					
	47.8						

angle which the hydrogen bonds make with the C axis. This angle must be very close to 90° to give the perpendicular bands observed and the sine is not a sensitive function for an angle near 90° . It was hoped that the relative size of the qQ branches would be of aid in this respect. If the change in dipole moment lies along the bond, the strength of the qQ branch would be proportional to the cosine of the angle formed by the hydrogen bond and the C axis—a very sensitive function when this angle is near 90° . Unfortunately, consideration of Figs. 1, 5, and 7 quickly blasts this hope, because $\nu(C-H)$ of $HCOOH$ shows no qQ branch (Fig. 1) while $\nu(C-D)$ of $DCOOH$ shows a relatively strong (but absolutely weak) one (Fig. 5). It can be seen from Fig. 7 that the carbon hydrogen lies very close to the B axis, so close that a change in its mass from 1 unit in 46 to 2 units in 47 could not possibly rotate the principal axes enough to produce the qQ branch difference shown, assuming the total magnitude of dipole moment change in each case to be similar. Evidently the dipole moment change does not lie strictly along the bond and the qQ branch can be used only as evidence that the bonds must be fairly close to 90° with respect to the C axis.

The value of the $H-C=O$ angle was taken as 122° for which the CH bond makes an angle of 0° with the B axis for $HCOOH$. The variation is taken as $\pm 5^\circ$ to accord with the weak qQ branches. Values of δ for the other three molecules would not help in this determination because the hydrogen is too close to the B axis to produce much variation in δ on isotopic substitution.

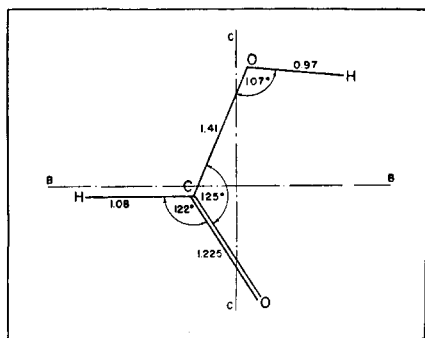


FIG. 7. Structure of the planar molecule $HCOOH$ with principal axes B and C shown.

TABLE VII. Values of various constants of monomeric formic acids.

Molecule	Constant	Experimental values	Model of Fig. 7	Model of Karle and Brockway ¹¹
Moments of inertia ($\times 10^{40}$ g cm ²)				
$HCOOH$	A	86.38	85.99	83.46
	B	75.27	74.89	70.39
	C	11.11	11.10	13.07
$HCOOD$	A		89.84	
	B		76.88	
	C		12.96	
$DCOOH$	A		89.70	
	B		74.92	
	C		14.78	
$DCOOD$	A		93.71	
	B		76.94	
	C		16.76	
Parameters δ and $\gamma - \delta$ (cm ⁻¹)				
$HCOOH$	δ	0.348*	.350	
	$\gamma'' - \delta$	2.172	2.172	
$HCOOD$	δ		.338	
	$\gamma'' - \delta$	1.829	1.822	
$DCOOH$	δ		.343	
	$\gamma'' - \delta$	1.544	1.550	
$DCOOD$	δ		.331	
	$\gamma'' - \delta$	1.328	1.339	
Angles between $C-H$, $O-H$ and B axis				
$HCOOH$	CH		10'	
	OH	4°*	5° 40'	
$HCOOD$	CH		1° 55'	
	OH		3° 55'	
$DCOOH$	CH		30'	
	OH		5° 20'	
$DCOOD$	CH		2° 25'	
	OH		3° 25'	

* Values taken from Bauer and Badger.²

The value of the $C-O-H$ angle was taken as 107° with a variation of $\pm 5^\circ$. An angle of 112° would be large if the hydrogen were attracted to the double bond carbon, and an angle of 102° would show greater qQ branches. Here the other values of δ would be of some aid because this isotopic substitution has a noticeable effect (about 1 percent for 5°) in the intermediate moment.

The Distances $C-O$ and $C=O$

These distances were varied according to Pauling's rule⁹ for single-double bond interaction. The values considered were 1.22A and 1.43A for zero-interaction; 1.225 and 1.40 for 1/20 mixing; and 1.23 and 1.38 for 1/10 mixing. It was found that these bonds could not exceed the limits of 1/10 mixing. Variation over this range produced a 3 percent change in δ so again the other values

of δ would be of importance in fixing the results. The distances chosen were, C=O, $1.225 \pm 0.02\text{\AA}$ and C—O, $1.41 \pm 0.02\text{\AA}$.

The O—C=O Angle

The values of $\gamma'' - \delta$ were exceptionally sensitive to this angle for a 7 percent change results in a variation from 124° to 126° . In fact the variation between the Bauer and Badger value of 2.2106 cm^{-1} and this value of 2.172 cm^{-1} is just the difference between 126° and 125° . Therefore the value of this angle is fairly accurately determined as $125 \pm 1^\circ$.

The structure of the HCOOH monomer is shown in Fig. 7 with the best values designated. The position of the principal axes *B* and *C* are shown. This structure is in fairly good agreement with that given by Bauer and Badger² although it is felt that the present values are more accurate

because of the greater number of data available for the calculations. The structure is considerably different from that obtained by Karle and Brockway¹¹ from electron diffraction data as their results fall considerably outside the limits of error judged for this work. To illustrate this difference, Table VII compares the *A*, *B*, and *C* moments of inertia according to experimental results, the model derived in this work, and that of Karle and Brockway. Table VII also includes the various values for δ , $\gamma'' - \delta$ and the angles which the hydrogen bonds make with the *B* axis.

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