

## **InfraRed Spectra of Monomeric Formic Acid and Its Deuterated Forms. II. Low Frequency Region (2200–800 cm<sup>-1</sup>)**

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## Infra-Red Spectra of Monomeric Formic Acid and Its Deuterated Forms. II. Low Frequency Region (2200–800 $\text{cm}^{-1}$ )\*

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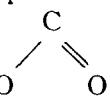
(Received January 14, 1947)

High resolution infra-red studies have been made of monomeric  $\text{HCOOH}$ ,  $\text{HCOOD}$ ,  $\text{DCOOH}$ , and  $\text{DCOOD}$  in the region  $2200\text{ cm}^{-1}$  to  $800\text{ cm}^{-1}$ . Consideration is given to the possibility of the existence of a *trans*-form of the mole-

cule. The bands observed are not sufficiently regular in appearance or absorption frequency to permit assignment of vibrational modes without further knowledge of the spectra.

### INTRODUCTION

PREVIOUS workers<sup>1,2,3</sup> have made infra-red studies of the deuterated forms of monomeric formic acid from  $4000\text{ cm}^{-1}$  to  $650\text{ cm}^{-1}$  with a low dispersion instrument. They had hoped that

vibrational modes associated with the  core of the molecule would maintain fairly constant frequencies of absorption with deuteration while those arising from a motion of the hydrogen atoms would shift by a predictable amount. If this had proved true it might have been possible to assign some of the observed frequencies to characteristic modes. As such behavior was not observed in the low dispersion studies, the

spectra from  $3700\text{ cm}^{-1}$  to  $800\text{ cm}^{-1}$  were studied under high resolution in the hope that the additional band structure would be of further aid in the assignments.

### EXPERIMENTAL

The instrument used, the preparation of samples, and the instrumental techniques have been given in paper I.<sup>4</sup> Table I gives a list of the bands studied, together with the conditions under which each spectrum was observed. Figure 1 shows a schematic summary of all the bands observed (including those in the high frequency region). In Fig. 1, as in all subsequent figures, absorption is shown upward on the ordinate and frequency in  $\text{cm}^{-1}$  on the abscissa. In the

TABLE I. Important bands studied. All spectra taken in first order except Fig. 9 which was in the second order.

| Fig. | Molecule       | $\lambda(\mu)$  | $\nu(\text{cm}^{-1})$   | $T(^{\circ}\text{C})$ | $P(\text{mm Hg})$ | Cell length (cm) | Grating lines/in. | Spectral slit width ( $\text{cm}^{-1}$ ) |
|------|----------------|---|---|-----------------------|-------------------|------------------|-------------------|--|
| 1    | $\text{HCOOH}$ | 8.3   |   | 165                   | $55 \pm 10$       | 15               | 1800              | 1.1                                      |
| 2    | $\text{HCOOH}$ | 9.06  | 1105.3  | 163                   | $10 \pm 1$        | 15               | 1800              | 1.3                                      |
| 3    | $\text{HCOOH}$ | 9.69  | 1033.2  | 165                   | $65 \pm 10$       | 15               | 1800              | 0.8                                      |
| 4    | $\text{HCOOD}$ | 8.50  | 1178.0  | 163                   | $25 \pm 3$        | 15               | 1800              | 1.4                                      |
| 5    | $\text{HCOOD}$ | $\left. \begin{smallmatrix} 9.94 \\ 10.28 \end{smallmatrix} \right\}$ | $\left. \begin{smallmatrix} 1007.0 \\ 972.5 \end{smallmatrix} \right\}$   | 165                   | $25 \pm 3$        | 15               | 1800              | 1.0                                      |
| 6    | $\text{DCOOH}$ | 8.76  | 1142.7  | 163                   | $50 \pm 10$       | 8                | 1800              | 1.3                                      |
| 7    | $\text{DCOOH}$ | 10.30   | 970.6   | 165                   | $30 \pm 3$        | 8                | 1800              | 1.1                                      |
| 8    | $\text{DCOOD}$ | 8.54  | 1171.3  | 163                   | $15 \pm 2$        | 15               | 1800              | 1.1                                      |
| 9    | $\text{DCOOD}$ | 9.62  | 1040.2  | 165                   | $50 \pm 10$       | 15               | 1440              | 0.7                                      |
| 10   | $\text{DCOOD}$ | 10.59   | 945.5   | 165                   | $25 \pm 3$        | 15               | 1800              | 1.2                                      |
| 11   | $\text{HCOOH}$ | 4.55  | 2199.8  | 163                   | $400 \pm 50$      | 15               | 7500              | 0.7                                      |
| 12   | $\text{HCOOD}$ | 4.62  | $\left\{ \begin{smallmatrix} 2142.4 \\ 2178.8 \end{smallmatrix} \right\}$ | 165                   | $400 \pm 50$      | 15               | 7500              | 0.7                                      |
| 13   | $\text{DCOOD}$ | 11.45   | 873.2   | 165                   | $300 \pm 50$      | 15               | 1800              | 1.0                                      |

\* This material was presented in partial fulfillment of the requirement for the degree of Doctor of Philosophy, March, 1941.

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<sup>1</sup> L. G. Bonner and R. Hofstadter, J. Chem. Phys. 6, 531 (1938).

<sup>2</sup> R. Hofstadter, J. Chem. Phys. 6, 540 (1938).

<sup>3</sup> R. C. Herman and V. Z. Williams, J. Chem. Phys. 8, 447 (1940).

<sup>4</sup> V. Z. Williams, J. Chem. Phys. 15, 232 (1947).

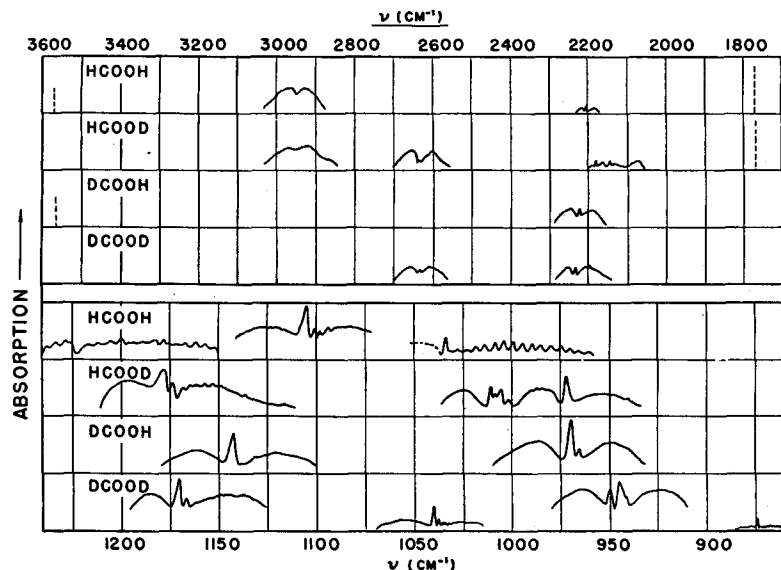


FIG. 1. Schematic representation of the absorption bands of HCOOH, HCOOD, DCOOH, DCOOD 3700–800  $\text{cm}^{-1}$ .

schematic drawing height is roughly proportioned to intensity. Actually an attempt was made to regulate the pressure so that the strongest absorption for each band was of the order of 50–80 percent. This fact combined with the pressures and cell lengths of Table I gives a more accurate conception of relative intensities. The actual recorded spectra of the principal low frequency bands are shown in Figs. 2–11 and are discussed in some detail below. These bands were studied with a fixed fore-prism slit which gave a background energy distribution greater in the middle than at the extremes. This tends to flatten out the observed absorption and is corrected roughly

in Fig. 1. An interesting feature of many of these bands is the occurrence of a sharp satellite very near the  $qQ$  branch of the main band. Whenever possible, these bands were studied at room temperature and the intensity of the satellite was observed to decrease appreciably.

Although the absorption of atmospheric water vapor was very strong from 1900  $\text{cm}^{-1}$  to 1300  $\text{cm}^{-1}$  an attempt was made to study this region. The only bands observed were the expected C=O frequencies. The point of maximum absorption for HCOOH and HCOOD seemed to be about 1770  $\text{cm}^{-1}$ . These bands (like the  $\nu(\text{O}-\text{H})$  bands) are shown as dotted lines in

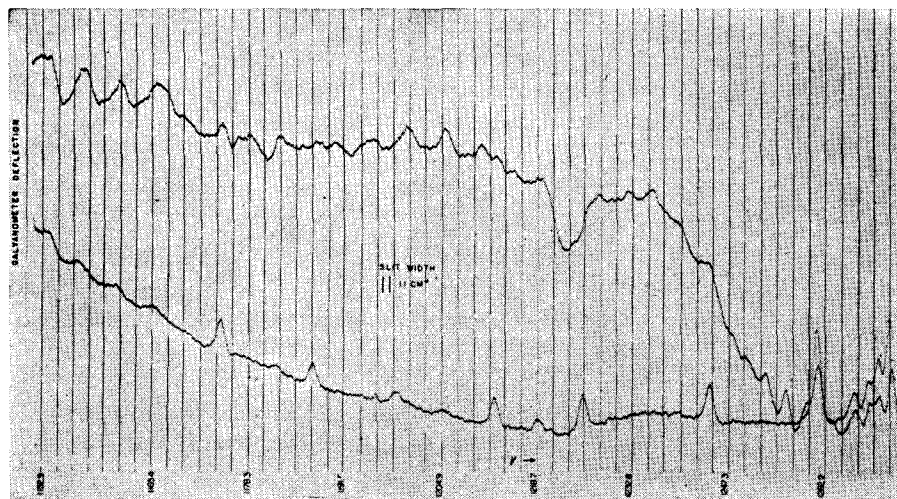


FIG. 2. Absorption of HCOOH ca. 1200  $\text{cm}^{-1}$ .

FIG. 3.  
HCOOH, 1105.3  $\text{cm}^{-1}$

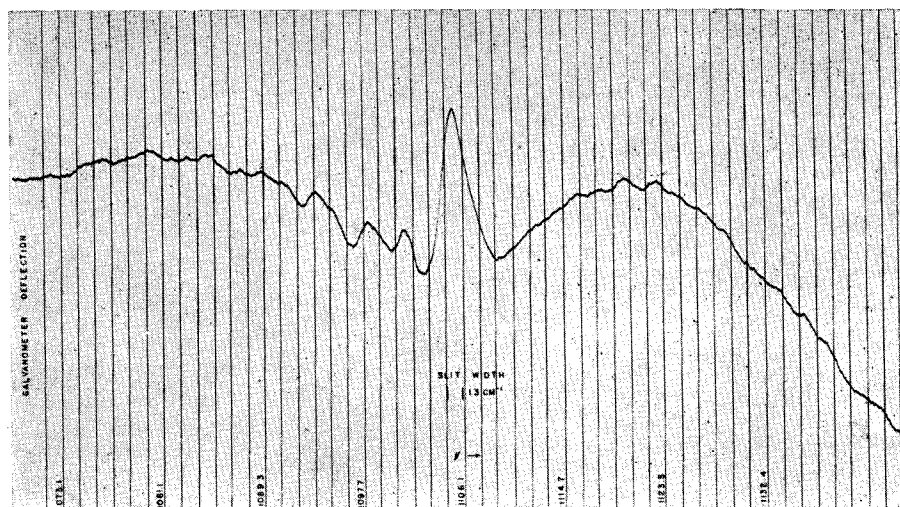


Fig. 1. No tentative values could be determined for the  $\nu(\text{C}=\text{O})$  of DCOOH or DCOOD.

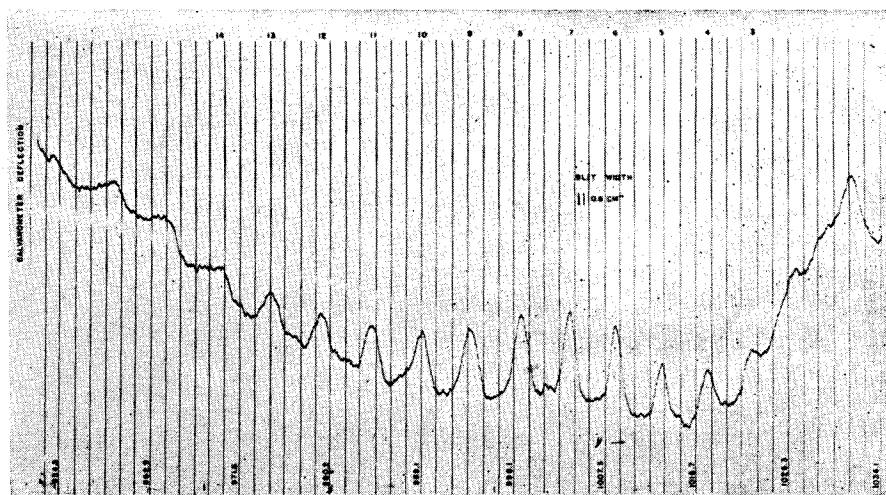
#### HCOOH

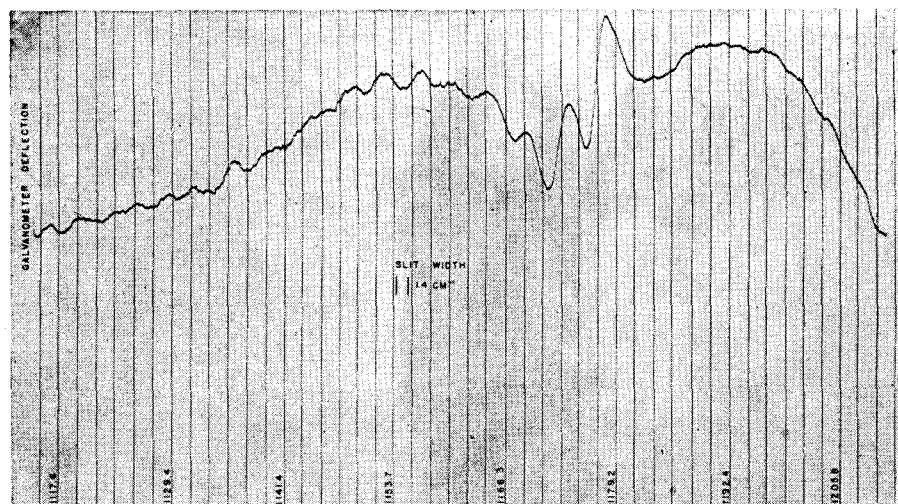
HCOOH has three regions of absorption, *ca.* 1200  $\text{cm}^{-1}$ , 1105  $\text{cm}^{-1}$ , and 1033  $\text{cm}^{-1}$  between 1700  $\text{cm}^{-1}$  and 800  $\text{cm}^{-1}$ . Figure 2 shows the absorption band of HCOOH in the 1200  $\text{cm}^{-1}$  region and the background with the cell evacuated. The spectrum was not continued to lower frequency because of the intense absorption of the adjacent band at the pressure used. The structure is highly irregular and does not conform to the expected pattern of a parallel and/or perpendicular band. Frequency values of the irregularly spaced HCOOH peaks are given in

Table II(a). This band could not be studied at low temperature because the dimer has strong absorption in the same region. However, the structure of Fig. 2 results from the monomer because the dimer band is quite regular and shows no structure.

The strong band at 1105.3  $\text{cm}^{-1}$  shown in Fig. 3 is predominantly a parallel band because of the strong  $qQ$  branch. There is some irregular structure (Table II(b)) superimposed on the  $P$  and  $R$  branches which may arise from a perpendicular component. Of particular interest are the two sharp peaks at 1101.1  $\text{cm}^{-1}$  and 1098.1  $\text{cm}^{-1}$  just to lower frequency of the main  $qQ$  branch. Certainly the 1101- $\text{cm}^{-1}$  peak cannot be a  $pQ$  peak for the bands in the high frequency

FIG. 4.  
HCOOH, 1033.2  $\text{cm}^{-1}$ .





region show that the asymmetry does not permit such a distinct peak so near the band center. Moreover, a study of this band at room temperature shows the higher satellite greatly decreased in intensity with respect to the main  $qQ$  branch so that it must arise from some other transition. The lower satellite seems to decrease also although it is not so obvious because the background slope changes. In addition the main  $qQ$  branch itself becomes sharper because of the loss of the shoulder on its high frequency side.

The third band of HCOOH, Fig. 4, seems to be a combined perpendicular and parallel type with its  $qQ$  branch at  $1033.2\text{ cm}^{-1}$ . Thirteen members of its  $pQ$  branch are identified by the  $K$ -values above the peaks. The seeming lack of

background in the  $P$  branch is caused by an intensity anomaly in the grating used. The  $R$  branch could not be studied because of the strong absorption of the  $1105.3\text{-cm}^{-1}$  band. The frequency values of the  $pQ(K)$  peaks are given in Table II(c). The spacings seem somewhat larger than in the  $\nu(\text{C-H})$  band but, without the  $rQ$  values, it is not possible to determine its significance in terms of the rotational constants.

**HCOOD**

HCOOD also shows three bands in this low frequency region. The spectrum of Fig. 5 is predominantly a parallel band with its  $qQ$  branch at  $1178.0\text{ cm}^{-1}$ . There is definite structure in the  $P$  branch at  $1168.6$ ,  $1164.5$ ,  $1160.6$ ,  $1156.9$ ,

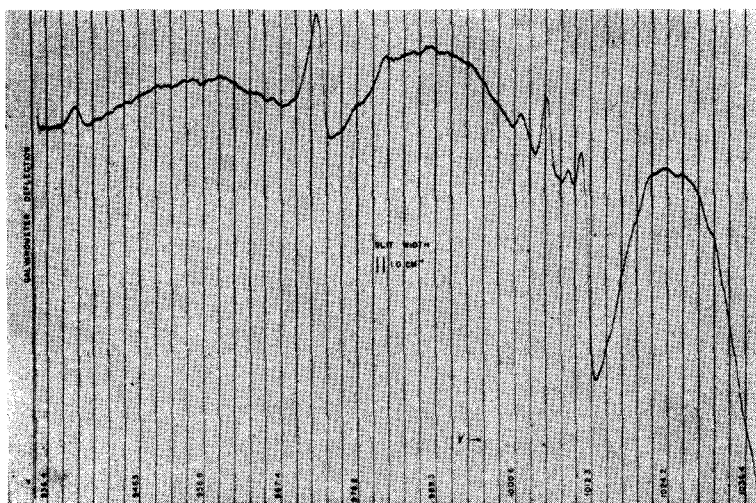
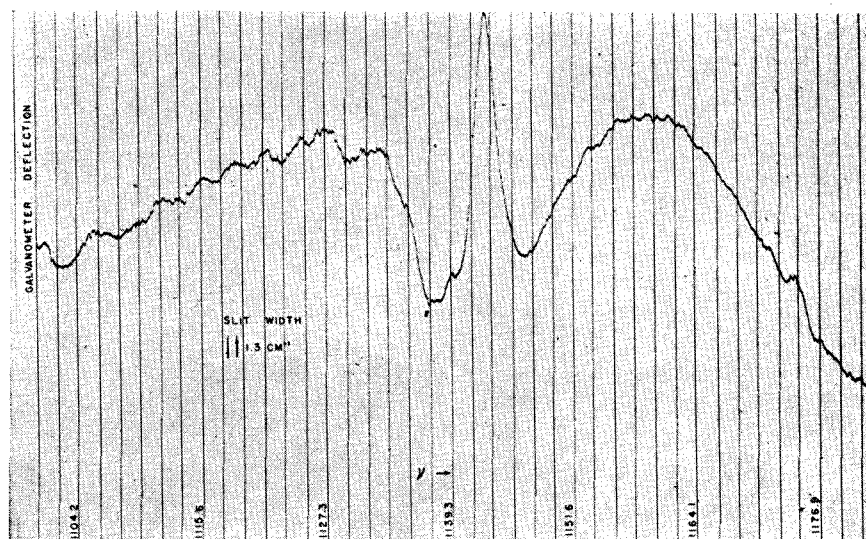


FIG. 7.  
DCOOH,  $1142.7\text{ cm}^{-1}$ .



$1152.8$ , and  $1148.6\text{ cm}^{-1}$  whose fairly regular separation of  $4\text{ cm}^{-1}$  agrees with the value obtained from the  $\nu(\text{O}-\text{D})$  band and implies a perpendicular component. As in the  $1105.3\text{ cm}^{-1}$  band of  $\text{HCOOH}$  there is a lower frequency satellite at  $1173.6\text{ cm}^{-1}$  which decreases greatly in intensity as the temperature of the vapor is lowered.

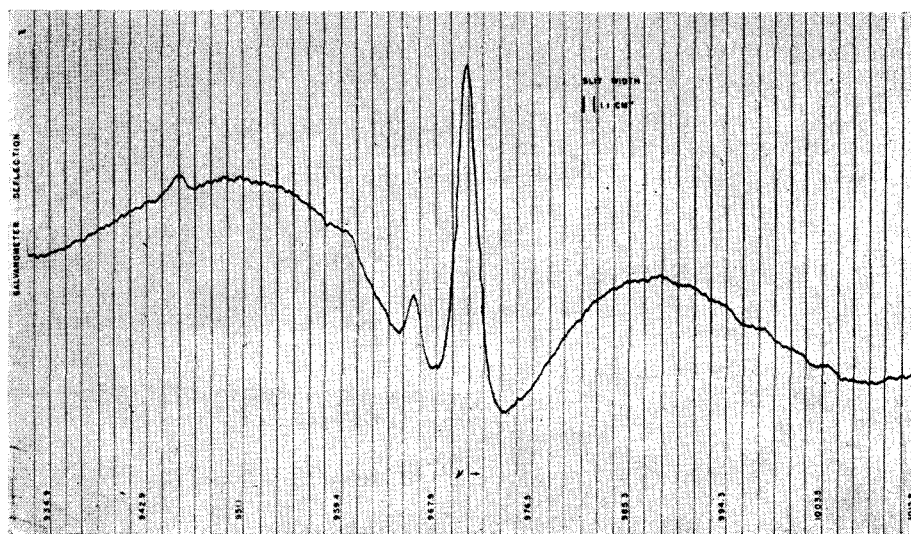
Figure 6 shows two other bands of  $\text{HCOOD}$ , one with a  $qQ$  branch at  $972.5\text{ cm}^{-1}$  with no satellite and the other with two  $qQ$  branches at  $1005.4$  and  $1010.7\text{ cm}^{-1}$  each of which has a lower frequency satellite at  $1001.5$  and  $1008.9\text{ cm}^{-1}$ , respectively. These satellites are greatly

weakened at room temperature. The appearance of this second band is distorted by the above-mentioned intensity anomaly and a better idea of its appearance is gained from Fig. 1. The double peak may be caused by a resonance splitting. The origin of the  $940\text{ cm}^{-1}$  peak is not known.

#### DCOOH

$\text{DCOOH}$  shows only two bands in the region considered. Figure 7 is a parallel band at  $1142.7\text{ cm}^{-1}$  with no appreciable satellite but some evidence of structure in its  $P$  branch. This band is essentially unchanged at lower temperature

FIG. 8.  
DCOOH,  $970.6\text{ cm}^{-1}$ .





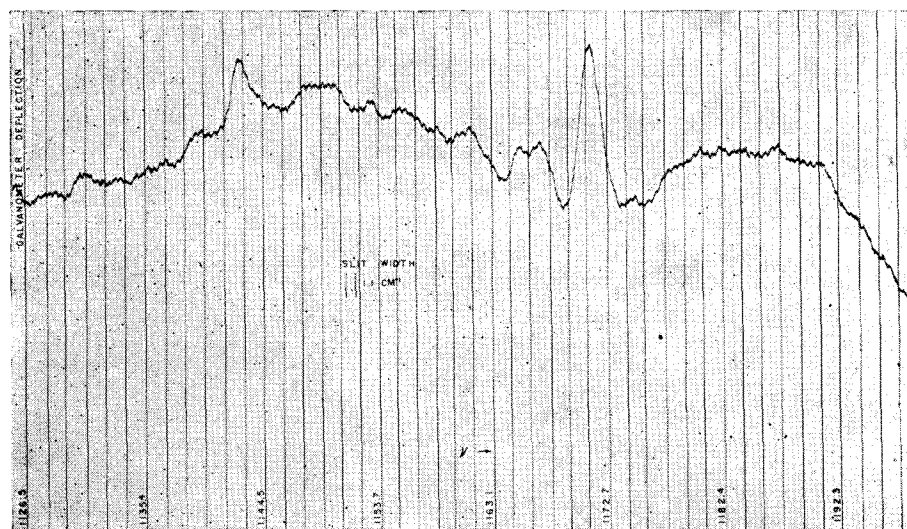


FIG. 9.  
DCOOD, 1171.3  $\text{cm}^{-1}$ .

(80°C). Figure 8 with its  $qQ$  branch at 970.6  $\text{cm}^{-1}$  is an excellent example of a parallel band except for the satellite at 965.7  $\text{cm}^{-1}$  and the small peak at 945.7  $\text{cm}^{-1}$  which results from DCOOD impurity. It was not possible to study this band at room temperature because of dimer interference.

### DCOOD

DCOOD again shows three bands in this region. The spectrum of the 1171.3  $\text{cm}^{-1}$  parallel band of Fig. 9 is somewhat obscured by the  $\text{D}_2\text{O}$  impurity background and the DCOOH impurity peak at 1142.7  $\text{cm}^{-1}$ . Again there is a satellite at 1167.0  $\text{cm}^{-1}$  overlaid by a  $\text{D}_2\text{O}$  peak at 1165.3  $\text{cm}^{-1}$ . The 1167- $\text{cm}^{-1}$  peak practically disappears at room temperature.

A second band of DCOOD, Fig. 10, is a parallel band with a  $qQ$  branch at 1040.2  $\text{cm}^{-1}$  and a satellite at 1038.2  $\text{cm}^{-1}$ . Its unsymmetrical appearance is caused by an intense band at lower frequency. There was insufficient pressure at low temperature to make any studies.

The third band of DCOOD at 945.5  $\text{cm}^{-1}$ , Fig. 11, is also a parallel band but the structure near the center is very interesting. To the low frequency side of the main  $qQ$  branch there are two weaker peaks—one at 943  $\text{cm}^{-1}$  and the other at 944.7  $\text{cm}^{-1}$  which appears as a shoulder on the main branch. In addition, there is a strong peak to higher frequency at 950.2  $\text{cm}^{-1}$ . At low temperature the 950.2 and 944.7- $\text{cm}^{-1}$  peaks become negligible but the 943- $\text{cm}^{-1}$  peak

remains. The peak at 970.6  $\text{cm}^{-1}$  is a DCOOH impurity.

The above bands are all thought to be fundamentals by reason of their intensity. A careful search was made for overtone or combination bands. Three of these were found (see Fig. 1), a parallel band in HCOOH at 2199.8  $\text{cm}^{-1}$  which is probably the first overtone of the 1105.3- $\text{cm}^{-1}$  band; two close lying parallel bands of HCOOD at 2142 and 2179  $\text{cm}^{-1}$  which may be combination bands of the lower frequency fundamentals; and a parallel band of DCOOD at 872.2  $\text{cm}^{-1}$  for

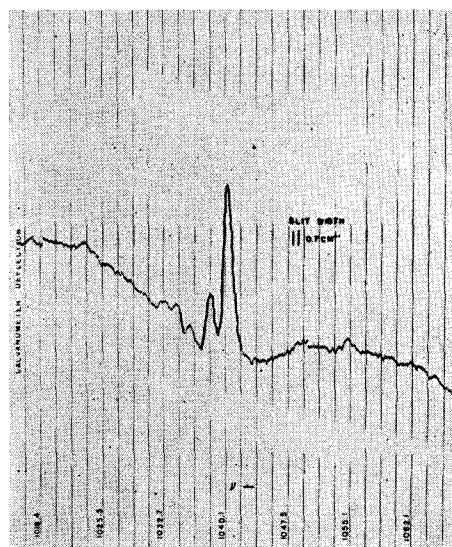
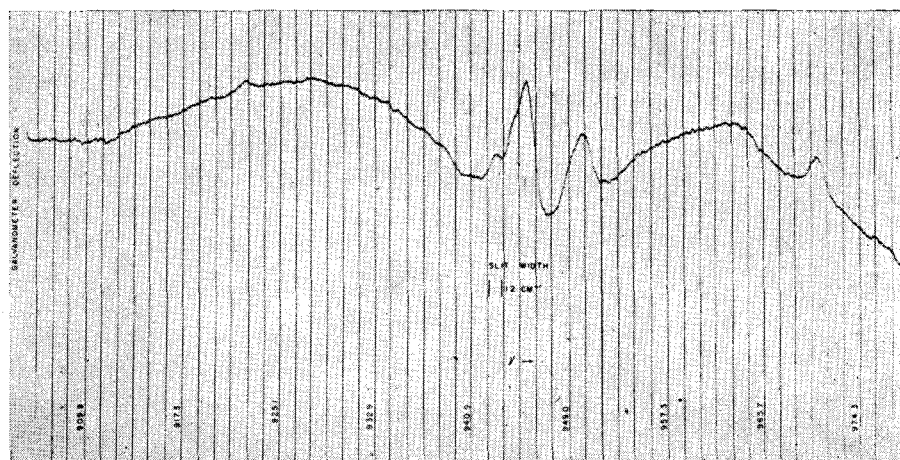


FIG. 10. DCOOD, 1040.2  $\text{cm}^{-1}$ .

FIG. 11.  
DCOOD, 945.5 cm<sup>-1</sup>.



which only the  $qQ$  branch could be observed because of the intense absorption of the adjacent fundamental.

#### ORIGIN OF SATELLITE BANDS

Two possible explanations could be given for these satellite bands. They may arise from a quantum transition similar to the main band but having an excited vibration state as a lower state. This lower state could be the first excited level of the adjacent fundamental or of some lower frequency fundamental. As postulated by

Coop, Davidson, and Sutton,<sup>5</sup> they might also be caused by a *trans*-isomer of HCOOH, in which the hydroxyl hydrogen is bent away from the carbonyl oxygen.

An attempt was made to study the variation of relative intensity of the main and satellite bands in order to determine the energy (or frequency) difference between the states giving rise to the two bands. The expression used for this determination was  $\log(\log T_1)/(\log T_2) = \log \alpha_1/\alpha_2 - (E/k)(1/T)$ , where  $T_1$  and  $T_2$  are the percent transmission of the satellite and main  $qQ$  branches above the background absorption of the bands;  $\alpha_1$ , and  $\alpha_2$  are the absorption coefficients of the two respectively;  $E = h\nu$  is the energy difference, and  $T$  the absolute temperature. The values  $\log(\log T_1)/(\log T_2)$  vs.  $1/T$  should give a straight line from whose slope  $E$  or  $\nu$  can be determined. The pairs of bands used were 1174, 1178 cm<sup>-1</sup> of HCOOD, 1167, 1171 cm<sup>-1</sup>, and 950, 945 cm<sup>-1</sup> of DCOOD over a temperature range from 25°C to 172°C. A portion of this study is illustrated in Fig. 12 where the change in intensity of the two bands is quite marked even over the short range of temperature shown. The use of the above formula is not absolutely correct for the  $\alpha$ -term is itself a function of temperature since the population distribution of the rotational levels of a given vibrational state changes with increasing temperature and causes a change in  $\alpha$ . However, experiments with the 3015-cm<sup>-1</sup> band of methane

TABLE II. HCOOH.

| a                         |                                      | b                                    |       | c                                     |                                 |
|---------------------------|--------------------------------------|--------------------------------------|-------|---------------------------------------|---------------------------------|
| 1200 cm <sup>-1</sup>     |                                      | $qQ$ branch 1105.3 cm <sup>-1</sup>  |       | $qQ$ branch 1033.2 cm <sup>-1</sup>   |                                 |
| $\nu$ (cm <sup>-1</sup> ) | $P$ branch $\nu$ (cm <sup>-1</sup> ) | $R$ branch $\nu$ (cm <sup>-1</sup> ) | $K''$ | $Pq$ branch $\nu$ (cm <sup>-1</sup> ) | $\Delta\nu$ (cm <sup>-1</sup> ) |
| 1151.4                    | 1101.1                               | 1116.0                               | 0     |                                       |                                 |
| 56.2                      | 1098.1                               | 18.0                                 | 1     | 1027.1                                | 4.6                             |
| 61.1                      | 93.6                                 | 20.0                                 | 2     | 22.5                                  | 4.6                             |
| 66.1                      | 90.9                                 | 22.8                                 | 3     | 17.9                                  | 4.6                             |
| 72.0                      | 89.2                                 |                                      | 4     | 13.3                                  | 4.9                             |
| 78.1                      | 87.4                                 |                                      | 5     | 08.4                                  | 4.7                             |
| 82.8                      | 84.6                                 |                                      | 6     | 03.7                                  | 4.9                             |
| 87.7                      | 80.2                                 |                                      | 7     | 998.8                                 | 4.9                             |
| 89.8                      | 76.0                                 |                                      | 8     | 93.9                                  | 4.8                             |
| 94.4                      | 72.3                                 |                                      | 9     | 89.1                                  | 5.0                             |
| 99.9                      |                                      |                                      | 10    | 84.1                                  | 4.9                             |
| 1205.3                    |                                      |                                      | 11    | 79.2                                  | 4.9                             |
| 10.6                      |                                      |                                      | 12    | 74.3                                  | 4.8                             |
| 14.9                      |                                      |                                      | 13    | 69.5                                  |                                 |
| 27.8                      |                                      |                                      |       |                                       |                                 |
| 32.6                      |                                      |                                      |       |                                       |                                 |
| 35.5                      |                                      |                                      |       |                                       |                                 |
| 50.0                      |                                      |                                      |       |                                       |                                 |
| 52.9                      |                                      |                                      |       |                                       |                                 |
| 56.3                      |                                      |                                      |       |                                       |                                 |
| 59.6                      |                                      |                                      |       |                                       |                                 |

<sup>5</sup> I. E. Coop, N. R. Davidson, and L. E. Sutton, J. Chem. Phys. 6, 905 (1938).



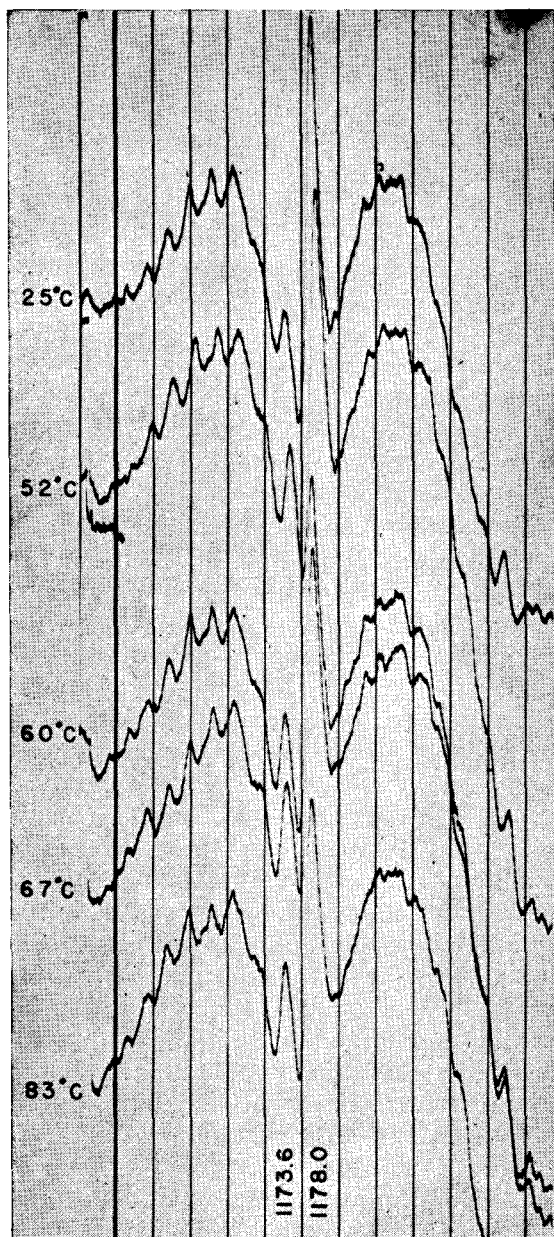


FIG. 12. Disappearance of the  $1174\text{ cm}^{-1}$  satellite of HCOOD with decrease in vapor temperature.

shows that  $\alpha$  can be expressed approximately as  $\alpha = Ke^{-B/T}$ . If this is true for HCOOH and  $B$  is approximately the same for each molecule or state, the above formula can be used.

The points obtained with the bands studied scattered badly but even by choosing extreme points the greatest difference obtained was 1400 calories ( $500\text{ cm}^{-1}$ ). In order to broaden the

range of temperature available the point for  $T = \infty$  was considered. Here the populations should be equivalent and the term  $\log(\log T_1)/(\log T_2)$  would equal  $\log \alpha_1/\alpha_2$ . With the above-mentioned assumptions for  $\alpha$ ,  $\alpha_1$  and  $\alpha_2$  should differ only by the change in dipole moment between the two states. Two possibilities were considered—a minimum of  $\alpha_1(\text{satellite}) = \alpha_2(\text{main } qQ)$  and  $\alpha_1 = 2\alpha_2$ . The first possibility (the more nearly reasonable for a transition from an excited state of the *cis*-form) combined with twelve different band measurements gave a mean value of  $E = 1000 \pm 200$  calories ( $360 \pm 70\text{ cm}^{-1}$ ), while the second gave a mean value of  $1600 \pm 230$  calories ( $570 \pm 80\text{ cm}^{-1}$ ).

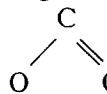
Of the two possible explanations for the origin of the satellite bands, the upper stage transition seems the more logical because in most cases the satellite appears at slightly lower frequency than the main band as would be expected from the usual second-order interaction terms. Although the energy difference measurements obtained from the temperature range studies are very rough, they imply an upper stage of a fundamental at much lower frequency than the adjacent one. The difficulties with this explanation are that there seems to be both lower and higher frequency satellites of the  $1105\text{ cm}^{-1}$  band of HCOOH and of the  $945\text{ cm}^{-1}$  band of DCOOD while some bands show no satellite at all.

Some calculations were made with the data of Coop, Davidson, and Sutton<sup>5</sup> to determine the energy difference between the *cis*- and *trans*-forms. The efforts were not particularly successful because of the limits of error shown, but it was evident that the *trans*-form must have a large permanent dipole and its population must increase rapidly with temperature in order to overcome the natural decrease in polarization with increasing temperature. Quantitatively, therefore, the low energy difference obtained from a measurement of relative band intensities seems in agreement with the isomer hypothesis. Qualitatively, however, this explanation does not seem so likely. It is difficult to believe that an entirely different molecule such as *trans*-HCOOH would give bands so consistently near, and similar to, those of the *cis*-form. Another argument against the *trans*-form is the appearance of the high frequency regions. The  $\nu(\text{O}-\text{D})$  of

*trans*-HCOOD and DCOOD would have a strong parallel component whose *qQ* branch should appear within 100  $\text{cm}^{-1}$  of the *cis*-bands. No such effects were observed.

#### INTERPRETATION OF SPECTRA

Assuming HCOOH to be a planar molecule there will be a total of nine fundamental vibrations, seven planar and two out of the plane motions. If it were possible to assign the modes to specific atomic motions, the seven planar motions would be four stretching vibrations, O-H, C-H, C=O, and C-O, and three angular motions, two hydrogen bending and one



C bending. The two out of the plane vibrations would be essentially hydrogen motions in one of which the two hydrogens move in opposite directions and in the other in the same direction. If the vibrations were so specific, those associated with the hydrogens would give definite shifts on deuteration while those associated with the heavier core of the molecule would maintain fairly constant absorption frequency independent of deuteration. Moreover, the hydrogen stretching and the two out of the plane motions would be essentially perpendicular bands, the in-plane hydrogen bendings would be of a parallel type, and the others would be of mixed structure.

The hydrogen and carbonyl stretching vibrations are easily identified and, within limits of

observation, appear as predicted. For the remaining bands these are observed in this work: HCOOH, *ca.* 1200, 1105, and 1033  $\text{cm}^{-1}$ ; HCOOD, 1178, 1007, and 973  $\text{cm}^{-1}$ ; DCOOH, only two, 1143 and 971  $\text{cm}^{-1}$ ; DCOOD, 1171, 1040, and 946  $\text{cm}^{-1}$ . The possible resonance splitting in HCOOD may imply a fundamental near 500  $\text{cm}^{-1}$  and the possible overtone at 875  $\text{cm}^{-1}$  in DCOOD may mean a band near 440  $\text{cm}^{-1}$ . In addition, there are the low dispersion results of a band in HCOOH at 667  $\text{cm}^{-1}$ <sup>1</sup> and in DCOOH at 678  $\text{cm}^{-1}$ .<sup>3</sup>

As pointed out from the low dispersion results the observed spectra, so far as frequency of absorption is concerned, do not fit the results predicted from the hypothesis of assigning fundamental modes to specific parts of the molecule. The high dispersion results, giving band structure, do not seem to clarify the picture further—neither the position nor the appearance of the bands correspond to the crude vibrational analysis. The peculiar absorption of HCOOH near 1200  $\text{cm}^{-1}$  and the fact that DCOOH shows only two absorptions in the region seem anomalous. Also there may be the possibility that some of the bands denoted as fundamentals in this work may be caused by a *trans*-form of the molecule.

Evidently, explanation of these spectra must await the extension of infra-red and Raman observation, together with careful studies of relative band intensities *vs.* temperature to make certain which bands may be assigned to a single molecular species.