value divided by A_p (Table II) represents the fraction of *gauche* isomer present, n_g. $(1 - n_g)$ then gives the fraction of *cis* isomer, n_c, listed in the second column of Table II. The band area for the *cis* isomer divided by *cl* gives the apparent value of intensity for this isomer. This divided by n_c yields the intensity for the *cis* isomer, A_c, listed in the third column of Table II.

The above treatment of the intensity results produces two quantities which are of interest. The first of these is the fraction of *cis* isomer, n_c. It is apparent that there is a direct relationship between this value and the size of the atom or group X attached to the methyl carbon. This is a rather interesting result, because it is not one which could have been predicted on the basis of current knowledge of isomer distribution. The relative stabilities of what are here designated as *cis* and *gauche* isomers is considered to be determined by two factors: the electrostatic effects arising from dipole–dipole interactions and the steric repulsive effect between the group X and the alkoxy oxygen.[10,11] It is generally recognized that in liquid media the more polar *cis* form is relatively more stable than it is in the vapor state, because of dipole–dipole or dipole-induced dipole interactions. In the present work it is clear that the compounds for which the *cis* form is more polar are the more stable in the *cis* configuration. However, since these are also the compounds with the smallest groups X, it is also possible that the van der Waals repulsive force between X and the carbonyl oxygen is a determining factor,[15] although this interaction has in the past been considered unimportant.[11] One bit of evidence which bears on this point is that the monocyano compound, although it would be very polar in the *cis* configuration, nevertheless exists entirely in the *gauche* arrangement, so that polarity alone cannot be the determining factor.

The second quantity which bears consideration is the difference in intensity between the *cis* and *gauche* isomers for each compound, listed in the last column of Table II. This difference varies in a rough way with the size of the group X; the largest, bromine, produces the largest difference. Now if dipole–dipole interactions were responsible for the lower intensity of the *cis* isomer by virtue of their ability to inhibit resonance, as discussed earlier, the difference should be largest for fluorine and not for bromine, since the C–F bond undoubtedly possesses a larger moment than the C–Br bond. The fact that the size of the group seems to be the controlling factor strongly indicates that van der Waals repulsions are responsible for the intensity difference. These latter would surely be larger for the larger groups.

It seems quite likely that the van der Waals forces are also responsible for at least some of the difference in frequency between the *cis* and *gauche* isomer (Table I). The frequency difference does not appear to parallel the polarity of the C–X bond as it should if dipolar interactions were the major factor.[12]

A word might be said on the effect of solvent. First, it is apparent that a solvent as polar as acetonitrile nevertheless does not have a pronounced effect on the intensity; on the other hand, a hydrogen-bonding solvent such as chloroform does cause an increased intensity as a result of specific interaction with the carbonyl. The increased proportion of *cis* isomer in the more polar solvents is in accord with the results obtained by others.[11,12] The more polar *cis* form should be relatively more stable in di-polar solvents because of dipole–dipole interactions.

URBANA, ILLINOIS

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(15) (a) E. A. Mason and M. M. Kreevoy, THIS JOURNAL, **77**, 5808 (1955); (b) M. M. Kreevoy and E. A. Mason, *ibid.*, **79**, 4851 (1957).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA, BERKELEY]

The Infrared Spectra of Dimeric and Crystalline Formic Acid

BY ROGER C. MILLIKAN AND KENNETH S. PITZER

RECEIVED JANUARY 31, 1958

The infrared spectra of gaseous $(HCOOH)_2$, $(HCOOD)_2$, $(DCOOH)_2$ and $(DCOOD)_2$ have been studied in the range 3800 to 625 cm.$^{-1}$. In addition the spectrum of $(HCOOH)_2$ was scanned between 600 and 150 cm.$^{-1}$; a strong band was found at 238 cm.$^{-1}$ with probably a second band at 160 cm.$^{-1}$. The infrared spectra of crystalline formic acid and its deutero forms have been measured. In the spectrum of crystalline HCOOH the center of the O–H...O stretching absorption is shifted 400 cm.$^{-1}$ toward lower frequency relative to its position in the gas phase dimer spectrum. Large crystal splittings were observed in the spectra of the solids. Small temperature dependent band shifts have been observed in the range 20–220°K. An assignment is proposed for the infrared active frequencies of all species. It is based upon an approximate application of the product rule together with the monomer assignment previously given.

Formic acid molecules hydrogen bond into two well characterized configurations, a cyclic dimer in the gas phase and a long chain polymer in the crystalline phase. We have extended our infrared study of the monomer[1] to these polymeric states. This system is advantageous for study since three deuterated derivatives of formic acid can be made easily. By comparing the infrared spectra for the monomer, dimer and crystal for each of the isotopic species, one can obtain a detailed understanding of both the vibrational assignment and the hydrogen bonding effects.

The spectra of the dimeric acids have all been studied previously,[2–4] but the limited resolution available at that time plus the lack of understanding of the monomer assignment precluded detailed

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(1) R. C. Millikan and K. S. Pitzer, *J. Chem. Phys.*, **27**, 1305 (1957).

(2) L. G. Bonner and R. Hofstadter, *ibid.*, **6**, 531 (1938).

(3) R. Hofstadter, *ibid.*, **6**, 540 (1948).

(4) R. C. Herman and V. Z. Williams, *ibid.*, **8**, 447 (1940).

analysis. Chapman[5] has presented a spectrum of solid HCOOH. We have found that annealing of the crystalline sample yields sharper spectra showing fine structure otherwise not observable. His work has been extended to include the deuterated acids.

Experimental

The samples of HCOOH and its deutero forms were those used in work on the monomer.[1] The spectra were obtained in the 4000–625 cm.$^{-1}$ region with a Perkin–Elmer Model 21 spectrophotometer equipped with CaF_2 and NaCl prisms. For the 700–400 cm.$^{-1}$ region a Perkin–Elmer Model 12-C spectrometer with KBr prism was employed. The 400–150 cm.$^{-1}$ region was surveyed using the vacuum grating spectrometer described by Bohn, *et al.*[6] The spectrum of $(HCOOH)_2$ was studied over the entire 4000–150 cm.$^{-1}$ region. The spectrum of crystalline DCOOD was taken between 4000 and 475 cm.$^{-1}$. The remainder of the study covered only the 4000–625 cm.$^{-1}$ region.

The spectra of the dimeric acids were obtained by studying the acid vapors at 26° and 15 mm. pressure in a 5.5 cm. cell fitted with AgCl windows. The crystal spectra were obtained using a cold cell of double dewar construction. It contained an AgCl window clamped in a cooled copper block. The sample was introduced through a side tube as a vapor and sprayed directly on the window. The temperature of both the block and the window were measured with copper–constantan thermocouples. The window temperature during deposition of the sample was found to be important in determining whether a good crystalline sample is obtained. If the acid is sprayed on a window at 77°K., the observed spectrum shows broad, indistinct absorptions, as in the spectrum given by Chapman.[5] Upon annealing a sample prepared in this manner at 145°K. for several hours, many of the spectral features become narrower, and some display fine structure changes attributed to the formation of a more perfect crystalline material. It was found that a good crystalline sample, as judged from the appearance of the spectrum, may be obtained directly by spraying the acid vapor on a window at 145°K. This temperature is just lower than that at which the sample sublimes from the window at about 10^{-5} mm. When the cell was pressurized with argon to reduce sublimation of the sample and warmed to 220°K., no spectral changes were observed. When a crystalline sample of formic acid is cooled from 77° to 20°K., the bands all become slightly sharper and show increased peak intensity. A few bands show small frequency shifts as discussed later, but no gross changes in the spectrum occur.

Measured Spectra.—The infrared spectra of the dimeric acids are presented together in Figs. 1 and 2 in order to show the effect of deuteration. The dashed lines connect analogous vibrational modes; they are based on the interpretation discussed in the next section. Under the conditions used, about 10% monomer is present in the vapor. Some of the stronger monomer bands appear with considerable intensity. These bands are shown with dotted contours in the figure. The far infrared spectrum of $(HCOOH)_2$ is shown in Fig. 3. The region between 300–400 cm.$^{-1}$, while omitted from the figure, was scanned without finding any bands. The spectra of the crystalline acids are shown in Figs. 4 and 5. In order to exhibit the effect of association clearly, the monomer, dimer and crystal spectra of HCOOH are given together in Figs. 6 and 7. Figure 8 shows a similar comparison for DCOOD in the low frequency region. The observed frequencies of the absorption maxima are given in Tables I and II. Certain bands listed in Table II for deuterated species may have been caused by light hydrogen impurities.

Discussion

The structure of the dimer, as determined by electron diffraction,[7] is a cyclic one of symmetry C_{2h}. The structure of the solid was shown by Holtzberg, Post and Fankuchen[8] to comprise long chains of molecules linked by hydrogen bonds. Figure 9 shows the chain structure. We shall presently examine the precise selection rules for both dimer and solid but wish first to make the general assignment so far as possible on the basis of comparison with the monomer. We assume only a loose

TABLE I

OBSERVED FREQUENCIES (CM.$^{-1}$) OF DIMERIC FORMIC ACID

$(HCOOH)_2$		$(DCOOD)_2$	
This work	Bonner and Hofstadter	This work	Herman and Williams
3385sh		2432sh	
3272sh		2372sh	
3210sh		2323s,b	2325
3150sh		2293sh	
3110vs	3080	2248sh	
3028s		2226s	
2957vs		2153m	
2886sh		2073m	
2815sh		1981w	
2735sh		1884w	
2623m		1720vs	1719
2582m	2530	1596w	
2427w	2380	1446w	
		1383w	
2222w		1313w	
2078vw		1246s	1243
1923w	1905	1071sh	1178
1754vs	1740	1055w	1150
1450vw		1040w,sh	1052
1365m	1350	987s	
1283vw			
1218vs	1205	976s	974
1171w		890w,b	927
1030sh[a]	1093	764vw,b	
917s	917	678s	
695m	667	642s	
237s			
~160m			

$(DCOOH)_2$		$(HCOOD)_2$	
This work	Herman and Williams	This work	Hofstadter
3270sh			3030
3173sh		2960m	
3098s	3175	2572w	
3002ms		2455sh	
2889m		2370sh	
2741m		2314s	2347
2626w		2263sh	
2440vw		2162m	
2316w		2080m	2105
2251ms	2248	1914w	1916
2224m		1745vs	1736
2153w		1660sh	
2064vw		1605sh	
1891vw		1387m	
1726s	1730	1380m	1381
1360w	1358	1259s	1253
1239s	1224	1037m	1030
	1150	693m	
1020sh	1121	651m	
996m	990		
930m,b	944b		
890m,b	887		
690m			

[a] This shoulder is on the strong monomer peak at 1105 cm.$^{-1}$. The dimer band center is obscured but is >1030 cm.$^{-1}$.

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(5) D. Chapman, *J. Chem. Soc.*, 225 (1956).

(6) C. R. Bohn, N. K. Freeman, W. D. Gwinn, J. L. Hollenberg and K. S. Pitzer, *J. Chem. Phys.*, **21**, 719 (1953).

(7) J. Karle and L. O. Brockway, THIS JOURNAL, **66**, 574 (1944).

(8) F. Holtzberg, B. Post and I. Fankuchen, *Acta Cryst.*, **6**, 127 (1953).

TABLE II

OBSERVED FREQUENCIES (CM.$^{-1}$) OF CRYSTALLINE FORMIC ACID AT 77°K.

HCOOH				
This work	Chapman	DCOOD	DCOOH	HCOOD
3020w		2907w	2995sh	2969w
2958m		2704w	2896s	2904w
2892s	2921s	2605w	2708s	2725w
2712s,b	2744s	2565w	2597sh	2624sh
2601sh		2343w	2550s	2585w
2532s	2562s	2272m	2421sh	2296w
2459sh	2464sh	2247m	2273w	2175ms
	2387sh	2191m	2246sh	2055s
2359w	2312w	2108s	1935w	1903w
2141w	2143m	2051sh	1881sh	1723sh
2059w	2074w	2041s	1795s	1702sh
	1922w	1992sh	1680s	1694s
1900m	1894m	1800w	1593s	1602s
			~1500sh	
1718sh	1723s	1671s	1258s	1396m
1703s		1590s	1006s	1385m
1683sh		1270s	981s	1277s
1609s	1638s,sh	1253s	899m	1268s
	1447w	1090w	710s	1081m
	1426w	1075m		1070m
1391m		993s		713m
1381w	1374m	899w		674m
1370m	1333w	707s		657sh
1255s	1265s	668s		
	1240s	653sh		
1224s	1218s	No bands: 650–475		
1083w	1080s			
	988s			
974m	959s			
	725s			
721s	715			

coupling of monomer units. Each monomer frequency will have one counterpart in the dimer infrared spectrum and one set of lines in the solid. Crystal effects may split the lines of the solid, but in many cases this splitting is not resolved.

In addition to the vibrations analogous to those of the monomer, the dimer and solid will have low frequency vibrations in which monomeric units move as a whole. These modes lie at very low frequencies and their interaction with the higher frequencies may be ignored as a first approximation. Strict application of the Teller-Redlich product rule to the dimer and solid spectra would involve these low frequency vibrations. A reasonable approximation may be obtained, however, by assuming that these frequencies are determined by the mass and moments of inertia of the whole molecule. Then we may use the theoretical product ratios for the monomer[1] as approximately applicable to the dimer or to the solid. The separation into in-plane and out-of-plane motions is retained also.

Since the coupling is principally through hydrogen bonds, we expect the largest shifts in the frequencies associated with the O–H hydrogen. The stretching frequency is decreased substantially on bond formation and the out-of-plane bending (or torsion) is increased. The in-plane O–H bending motion is usually mixed with C–H bending and C–O stretching motions, hence the situation is more complex. These frequencies are found to increase moderately.

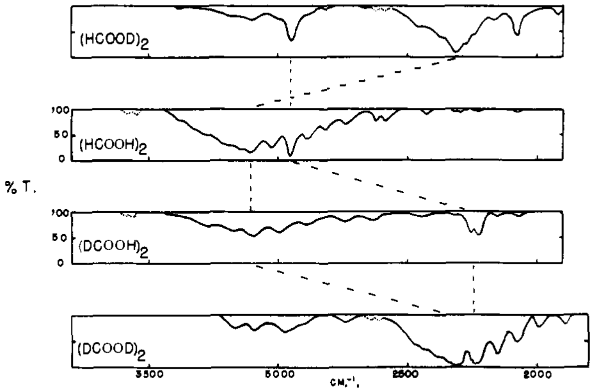

Fig. 1.—The infrared spectra of dimeric formic acid. The dotted contours are monomer bands.

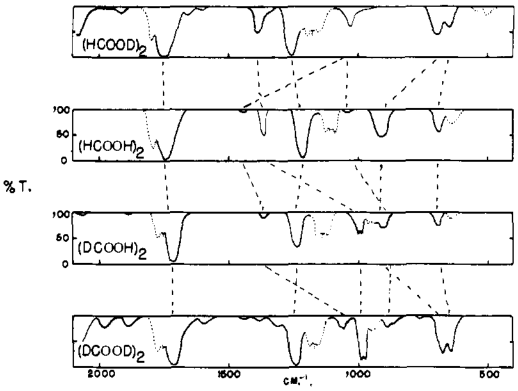

Fig. 2.—The infrared spectra of dimeric formic acid. The dotted contours are monomer bands.

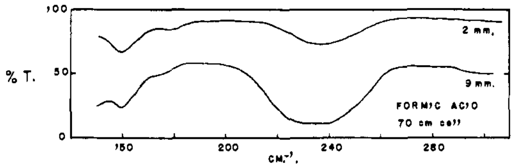

Fig. 3.—The infrared spectrum of dimeric formic acid in the range 150–300 cm.$^{-1}$.

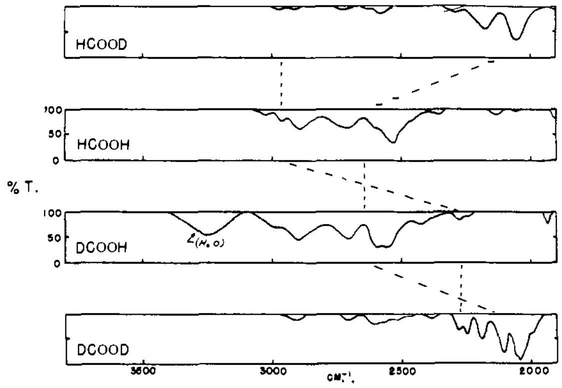

Fig. 4.—The infrared spectra of crystalline formic acid at 77°K.

The hydrogen bonding will affect the two C–O stretching vibrations also. The two C–O bonds

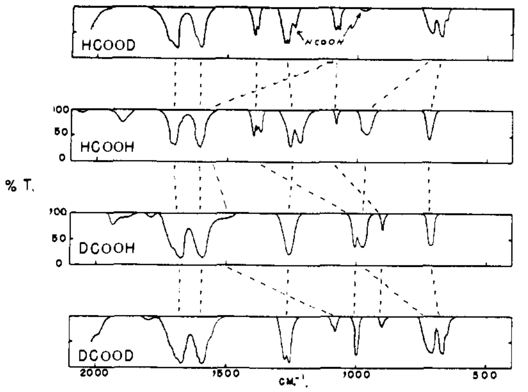

Fig. 5.—The infrared spectra of crystalline formic acid at 77° K.

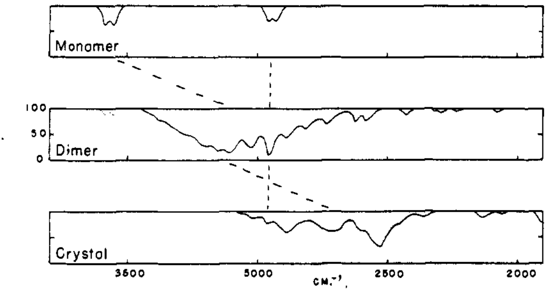

Fig. 6.—The infrared spectra of HCOOH in three states of aggregation.

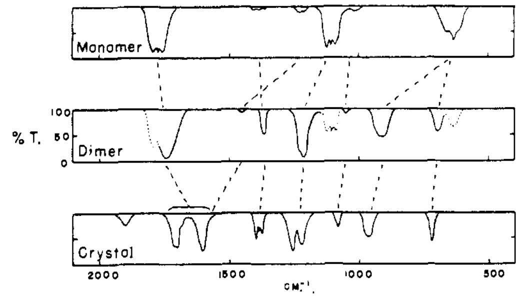

Fig. 7.—The infrared spectra of HCOOH in three states of aggregation.

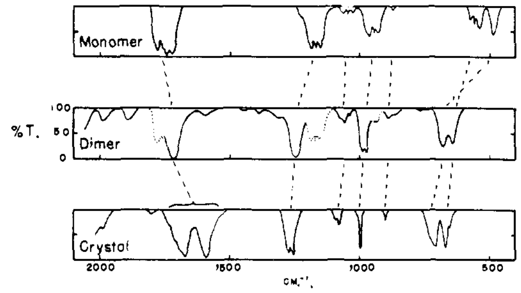

Fig. 8.—The infrared spectra of DCOOD in three states of aggregation.

become more nearly equal in bond character in the sequence monomer–dimer–solid. Thus the carbonyl frequency may be expected to decrease and the C–O "single bond" frequency to increase in this order. Indeed the description as C=O and C–O frequencies is no longer very appropriate for the crystal.

It is best to examine first the spectra of DCOOD because all frequencies appear with substantial intensity for all three states of aggregation. Figure 8 shows the spectra in the 500–2000 cm.$^{-1}$ range. The correlation of the bands is obvious, except for the two lowest frequencies, where the assignment was made as indicated because the O–C–O bending motion would not be expected to shift much with coupling, whereas the out-of-plane OD bending is expected to increase substantially.

From Fig. 7 we see that a very similar pattern is obtained for HCOOH except that the highest in-plane bending frequency is so weak that it is uncertain in the dimer and completely unobserved in the solid. Also the C–H out-of-plane bending frequency in the dimer is obscured by the strong monomer band which cannot be eliminated. The trends are similar for the mixed isotopic species HCOOD and DCOOH, but in almost all cases there are unobserved frequencies. Approximate values have been predicted by use of the product rule. The correlation of these frequencies among the various isotopic species is shown in Figs. 2 and 5.

The C–H and O–H stretching frequencies lie above 2000 cm.$^{-1}$ and the spectra for this region are shown in Figs. 1, 4 and 6. The general pattern is unambiguous and the details will be discussed below.

The frequency assignments are given in Table III for the dimer and Table IV for the solid. Table V gives the product ratios for all states of aggregation. The observed values appear very reasonable except for the out-of-plane motions on OH–OD substitution. The effect of low frequency modes is presumably responsible for this apparent anomaly.

TABLE III

PARTIAL FUNDAMENTAL ASSIGNMENT FOR THE DIMERIC FORMIC ACIDS. COMPARISON WITH THE MONOMER

Monomer			Dimer				
				Frequencies in cm.$^{-1}$			
sym.	HCOOH Mode	cm.$^{-1}$	sym.	$(HCOOH)_2$	$(DCOOD)_2$	$(DCOOH)_2$	$(HCOOD)_2$
	ν(OH)	3570		3110	2323	3098	2314
	ν(CH)	2943		2957	2226	$\begin{cases}2251\\2224\end{cases}$	2960
	ν(C=O)	1770		1754	1720	1726	1745
A′	ν(C—O)	1105	B_u	1218	1246	1239	1259
	δ(CH)	1387		1365	$\begin{cases}987\\976\end{cases}$	996	1387
	δ(OH)	1229		1450	1055	1360	1037
	δ(OCO)	636		697	642	695	651
	δ(CH)	1033		(1050)	890	890	1037
A″	δ(OH)	636	A_u	917	678	930	693

Dimer.—The dimer has symmetry C_{2h} with 24 vibrations. The eighteen higher frequency modes may be considered as nine pairs each comprising a symmetric and antisymmetric combination of a monomer mode. The symmetric modes are only Raman active; the antisymmetric modes are only infrared active. The latter were observed in this study and are listed in Table III. If the loose coupling picture is valid, the Raman active frequencies should be nearly the same. Bonner and Kirby-Smith(9) have observed the Raman spectrum of formic acid vapor. The observed bands of the

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(9) L. Bonner and J. S. Kirby-Smith, *Phys. Rev.*, **57**, 1078 (1940).

TABLE IV

ASSIGNMENT OF THE INFRARED BANDS IN THE CRYSTALLINE FORMIC ACIDS. FREQUENCIES IN CM.$^{-1}$

Type of vibration	HCOOH	DCOOD	DCOOH	HCOOD
In-plane				
OH str.	2532^a	2041^a	2550^a	2055^a
CH str.	2958	2272	2273	2969
		2247	2246	2904
C=O str.	1703	1671	1680	1694
	1609	1590	1593	1602
C–O str.	1255	1270	1258	1277
	1224	1253		1268
C–H bend	1391			
	1381	993	1006	1396
	1370			1385
O–H bend	(1560)	1090	1500	1081
		1075		
O–C–O bend	721	668	710	674
Out-of-plane				
CH bend	1083	899	899	1070
OH bend	974	707	981	713

^{a} The O–H str. bands are very broad and have several submaxima. The most intense peak is listed above.

TABLE V

TELLER–REDLICH PRODUCT RULE RATIOS

Isotopic pair	$\frac{\mathrm{HCOOH}}{\mathrm{DCOOD}}$	$\frac{\mathrm{DCOOH}}{\mathrm{DCOOD}}$	$\frac{\mathrm{HCOOD}}{\mathrm{DCOOD}}$
In-plane motions (sym. A′ in monomer)			
Calcd.	3.66	1.91	1.91
Obsd. monomer	3.52	1.89^a	1.89^a
Obsd. dimer	3.68	1.89	1.91
Obsd. solid	3.5^a	1.86	1.87
Out-of-plane motions (sym. A″ in monomer)			
Calcd.	1.57	1.30	1.23
Obsd. monomer	1.54	1.28^a	1.20
Obsd. dimer	1.6^a	1.37	1.19
Obsd. solid	1.66	1.39	1.20

^{a} Assumed value, used to calculate a missing frequency.

dimer are 2945, 1346, 1049, 981, 232 cm.$^{-1}$. The first four are close counterparts of infrared bands at 2957, 1365, (1050), 917 cm.$^{-1}$.

The Raman spectrum of liquid formic acid has been measured several times but we shall not attempt to use these data because the state of molecular aggregation is uncertain and probably very complex. Clearly the liquid is not primarily cyclic dimers.

The hydrogen bonded O–H stretching absorptions in all the spectra are broad, intense and show much fine structure. The origin and proper interpretation of this sub-structure has concerned many workers. Recently, in an extensive study of associated carboxylic acids, Bratoz, Hadzi and Shephard[10] noted the existence of satellite bands on the low frequency side of the O–H absorption.

In the eight acids studied by them, they observed these satellites centered near 2650 cm.$^{-1}$ for the ordinary acids and near 2100 cm.$^{-1}$ for the deuterated acids. Similar bands can be picked out in the dimeric formic acid spectra shown in Fig. 1. We have made a further study of the 3500-2500 cm.$^{-1}$ spectral region for HCOOH using the matrix isolation technique. The most intense bands for the dimer in a nitrogen matrix at 20°K. lie near the 3100 cm.$^{-1}$ peak observed in the vapor. The matrix bands are considerably sharper, however, and we hope to present a detailed discussion of the substructure of the O–H stretching band in a future paper.

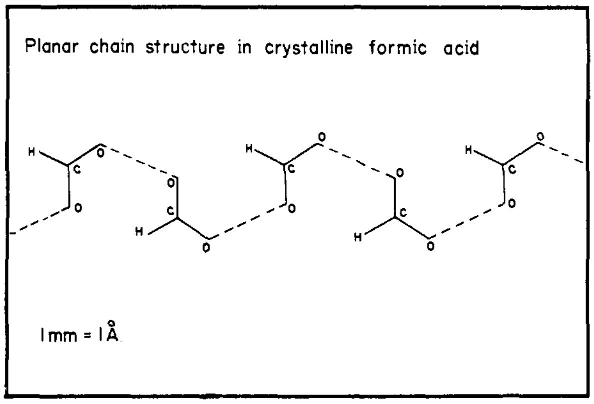

Fig. 9.—The chain structure in the crystal.

Hadzi and Sheppard[11] studied a series of carboxylic acids which they believed to be predominantly dimeric in the liquid state. They concluded that three bands of the COOH group at 1420 ± 20, 1300 ± 15 and 935 ± 15 cm.$^{-1}$ shifted to 1350 ± 50, 1050 ± 10 and 675 ± 25 cm.$^{-1}$ on deuteration. The COOD bands were attributed to C–O "single bond" stretching, and to in-plane and out-of-plane O–D bending modes, respectively. In the case of the COOH derivatives the in-plane bending and C–O stretching were believed to be substantially mixed.

Our results for the formic acid dimer in the vapor are in full agreement for the out-of-plane bending modes and for the in-plane O–D bending. We find the C–O stretching frequencies about 100 cm.$^{-1}$ lower, however. This difference probably arises from the interaction of the C–O stretching with the C–H vibrations in formic acid and with C–C vibrations in all the acids studied by Hadzi and Sheppard. The C–H stretching and in-plane bending frequencies are both above 1300 cm.$^{-1}$ and their interaction tends to depress the C–O frequency to 1218 cm.$^{-1}$ in $(HCOOH)_2$. In $(DCOOH)_2$ the bending frequency has moved down to 996 and the C–O frequency up to 1239 cm.$^{-1}$. Thus it seems reasonable that the interaction of the C–C stretching motion might further increase the C–O frequency to levels found by Hadzi and Sheppard.

The Hadzi and Sheppard assignment of the band which is largely O–H in-plane bending at 1420 cm.$^{-1}$ reassures us in our assignment. This band is extremely weak in both $(HCOOH)_2$ and $(DCOOH)_2$. Since the O–H bending motion itself almost certainly has an appreciable effect on the dipole moment of the molecule, the low intensity must arise from cancelling electrical effects of the C–O stretching and C–H bending motions which also enter in this normal mode.

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(10) S. Bratoz, D. Hadzi and N. Sheppard, *Spectrochim. Acta*, **8**, 249 (1956).

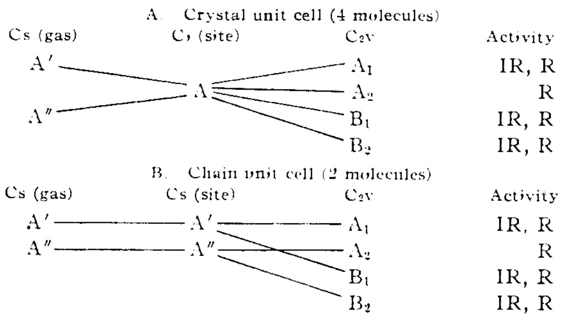
(11) D. Hadzi and N. Sheppard, *Proc. Roy. Soc.* (*London*), **216A**, 247 (1953).

In addition to the eighteen high frequency modes, the dimer has six low frequency modes in which the monomer units may be assumed to move as a whole. Three are Raman active and three infrared active. Slutsky and Bauer[12] have discussed these modes as well as the thermodynamics of the dimerization reaction. Our spectrum clearly shows an intense band at 237 cm.$^{-1}$ and indicates a second absorption around 160 cm.$^{-1}$. Presumably these are two of the three infrared active bands. Further calculations are now being carried out in the hope of deriving detailed force constants for these low frequency motions. If successful, these will be reported in the future.

Crystal Spectra.—The possible interactions between neighboring molecules in crystalline formic acid must be considered in interpreting the spectra shown in Figs. 4 and 5. The crystal structure of formic acid is of the space group C_{2v}^9–P_{na} with four molecules per unit cell. Each formic acid molecule occupies a site of symmetry C_1, hence all molecular vibrations will be infrared active in the site group approximation.[13] As indicated by Chapman,[5] interaction between molecules within the unit cell is expected to split each fundamental into four components, of which only three (A_1, B_1, B_2) will appear in the infrared. These expectations must be modified, however, when the presence of hydrogen bonds in the crystal is taken into account. The acid units are hydrogen bonded together in the form of planar, zig-zag chains whose configuration is depicted in Fig. 9. For some vibrations the interaction between molecules hydrogen bonded to each other will be much more important than the coupling with adjacent molecules which involves only crystalline forces other than H bonding. In such a case the important structural unit for a site group analysis is not the unit cell of the crystal, but rather the unit cell of the molecular chain. The chain unit cell contains two molecules, each of which occupies a site of symmetry C_s. All molecular vibrations will still be infrared active, but the expected splitting of the fundamentals is different when the chain unit cell is considered. The vibrations will be split into two components corresponding to the exactly in-phase and the 180° out-of-plane motions in adjacent chain units. For the in-plane (A′) vibrations, both components will appear in the infrared, but the out-of-plane (A″) fundamentals have only one infrared active component. These conclusions are based on the group representation diagram shown below.

The crystal spectra are shown in Figs. 4 and 5. The C–H bending absorption of HCOOH at about 1390 cm.$^{-1}$ appears to have three components, but the corresponding bands for the isotopic species show fewer components. Thus it is not clear whether or not this is an example of three-dimensional crystal splitting. The most prominent example of the chain type of crystal splitting is seen in the appearance of two strong components of the C=O vibration at 1600 and 1700 cm.$^{-1}$. This unusually large splitting for a C=O band attests to the presence of strong H bonds in the crystal; and this conclusion is confirmed by the large splitting of the O–H stretching band. Interactions within a chain also predominate for the out-of-plane vibrations since the out-of-plane absorptions show no splitting in any of the isotopic species.

SITE GROUP ANALYSIS



The large splittings of the carbonyl and O–H stretching bands may be understood in terms of the electronic structure of the carboxyl unit. Changes in either O–H or C–O distances will tend to shift the π electron density, or in other terms, the fraction of double bond character of each C–O bond. The C–O distances of 1.23 and 1.26 Å. are so nearly the same that each must be nearly a 3/2 bond at equilibrium. The two C–O stretching vibrations of each monomer unit in this case are strongly coupled into symmetrical and antisymmetrical stretching modes.

The unsymmetrical mode, in which one C–O bond stretches while the other shortens, will involve large shifts in double bonding electrons. The shorter the bond distance the greater will be the double bond contribution. If the successive monomer units vibrate in-phase, we may think of the following extreme structures as the limits toward which the motion tends. If the successive mono-

$$\cdots H-O-CH{=}O\cdots H-O-CH{=}O\cdots H-O-CH{=}O\cdots$$

$$-H\cdots O{=}CH-O-H\cdots O{=}CH-O-H\cdots O{=}CH-O\cdots$$

mer units vibrate out-of-phase, however, the extreme structures are

$$-\overset{-}{H}-O-CH{=}O\cdots\overset{+}{H}\cdots O{=}CH-O-\overset{-}{H}-O-CH{=}O\cdots\overset{+}{H}$$

$$\cdots\overset{+}{H}-O{=}CH-O-\overset{-}{H}-O-CH{=}O\cdots\overset{+}{H}\cdots O{=}CH-O-$$

Since hydrogen can form but one covalent bond, the unit written as $-O-\overset{-}{H}\cdots O\cdots$ must be regarded as the resultant of the resonance $-\overset{-}{O}\ H-O-$ and $-O-H\ \overset{-}{O}-$.

Since the second pair of extreme structures correspond to much higher energy than the former set, we may expect the out-of-phase coupled vibration to have the higher frequency, *i.e.*, about 1700 cm.$^{-1}$, and the in-phase motion the frequency of about 1600 cm.$^{-1}$.

In the dimer molecule the same general relationship will apply for the carbonyl vibration. The in-phase motion (A_g symmetry) may be expected to have a lower frequency than the out-of-phase motion (B_u symmetry). The former is Raman active but was not found in the gas phase spectrum. It is probably to be identified with the broad 1670 cm.$^{-1}$ band observed in solution by

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[12] L. Slutsky and S. H. Bauer, THIS JOURNAL, **76**, 270 (1954).

[13] R. S. Halford, *J. Chem. Phys.*, **14**, 8 (1946).

Batuev.[14] The out-of-phase vibration is infrared active at 1754 cm.$^{-1}$. The splitting is about 90 cm.$^{-1}$—similar to that in the crystal.

It should be emphasized that the vibration is over just a small range of configurations which are intermediate between the extremes of the diagrams. Also there is a terminal hydrogen at one end and not at the other end of the chain; consequently there is not complete symmetry between the pairs.

The electronic motions accompanying the in-phase O–H stretching vibration will be similar to those in the upper set of diagrams. The out-of-phase O–H stretching may be regarded as tending toward the extreme structures, $\text{--H-O-}\overset{+}{\text{C}}\text{H-O-H-}$ $\text{-O}\overset{\cdots}{-}\overset{-}{\text{C}}\text{H}\overset{\cdots}{-}\text{O--}$ which may be regarded as formate ion HCO_2^- and the ion $HC(OH)_2^+$. Again the out-of-phase motion tends toward higher energy extreme structures, and we assume it to have the higher frequency. The O–H stretching bands are much more complex than the 1600 - 1700 doublet. Evidently some complication is occurring, for when one compares the corresponding bands for the O–H or O–D stretching motions in the four isotopic species, the observed structure is not the same. The HCOOH and DCOOH spectra show three intense bands (*ca.* 2550, 2720 and 2900 cm.$^{-1}$) while in the HCOOD spectrum the O–D band exhibits only two strong components (2055 and 2175 cm.$^{-1}$) plus a much weaker band on the high frequency side (2296 cm.$^{-1}$). The 2000–2200 cm.$^{-1}$ region of the DCOOD spectrum exhibits three strong peaks whose spacings are quite different from those in the HCOOD spectrum. Chapman[5] has assigned the three HCOOH bands at 2562, 2744 and 2921 cm.$^{-1}$ to the three crystal split components of the O–H stretching fundamental. The appearance of only two strong components in the O–D band of HCOOD is difficult to explain on the basis of such an assignment. It seems much more likely that the hydroxyl stretching motion, like the C=O vibration, is split into two components by the strong H-bond interactions within the chains. The third components appearing in the HCOOH and DCOOH spectra at ~2900 cm.$^{-1}$ may be accounted for by the sum $\nu(C{=}O) + \nu(C{-}O)$ which gains intensity through interaction with the ν(O–H) fundamental. In DCOOD we may assume that resonance with the sum of CD and OD in-plane bending modes yields the extra peak at 2108 cm.$^{-1}$ and shifts the two ν(O–D) frequencies from 2055, 2175 in HCOOD to 2041, 2191 in DCOOD. This combination falls outside the range of the O–D stretching band for HCOOD. But the overtone of OD bending would fall at 2160 cm.$^{-1}$ for both DCOOD and HCOOD. If it interacted strongly with O–D stretching, the single band at 2175 in HCOOD should be split. While the explanation given for the DCOOD spectrum is formally satisfactory, we do not feel very confident of its correctness.

The spectrum of a crystalline sample of HCOOH has been studied at 225, 150, 77 and 20°K. in order to determine the effect of temperature. As the sample temperature was lowered, all of the bands narrowed, and showed slightly increased peak intensities. In addition, a number of bands show appreciable frequency shifts. The O–H stretch absorptions at ~ 2700 and 2532 cm.$^{-1}$ decreased in frequency by 34 cm.$^{-1}$ and the O–H··O out-of-plane bend at 974 cm.$^{-1}$ increased in frequency 15 cm.$^{-1}$ as the temperature was lowered to 20°K. Use can be made of this temperature dependent frequency shift to identify several of the heretofore unexplained bands which appear between the C=O and the O–H stretching absorptions. The band at 1900 cm.$^{-1}$ shifts 30 cm.$^{-1}$ to higher frequency as the temperature is changed from 220 to 20°K., just twice the shift of the 974 cm.$^{-1}$ band. This identifies the 1900 cm.$^{-1}$ absorption as the first overtone of the 974 cm.$^{-1}$ vibration. In a similar manner, since the 2141 cm.$^{-1}$ band shifts upward the same amount as the 974 band, it is interpreted as the sum combination $974 + 1239 = 2213$. No bands other than those just mentioned show temperature dependent frequency shifts. In the case of the unannealed samples, no frequency shifts were noted for any bands when the temperature was lowered.

Acknowledgments.—We want to thank Dr. E. D. Becker, Jr., for his help in performing the low temperature experiments and Dr. G. C. Pimentel and Dr. Tatsuo Miyazawa for many helpful discussions concerning the spectral assignment. The work was aided by a National Science Foundation Fellowship (to R. C. M.) and by the American Petroleum Institute through its Research Project 50.

BERKELEY, CAL.

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(14) M. I. Batuev, *Compt. rend. acad. sci. U.R.S.S.*, **53**, 507 (1946).