48. *The Infrared Spectra of Liquid and Solid Formic Acid.*

By D. Chapman.

The infrared spectra of liquid and solid formic acid have been obtained between 3500 and 650 cm.$^{-1}$. The former spectrum shows that formic acid does not exist in dimeric units except on dilution with a solvent. The bands in the latter have been assigned to their corresponding molecular vibrations. The spectrum for the solid is reasonably consistent with the information from *X*-ray analysis that it exists as polymer, but not consistent with the measured C–O and C=O bond lengths.

The infrared spectra of formic acid as vapour and in solution have received particular attention.[1] No study of the acid in either the liquid or the solid state has been published, though Randall, Fowler, Fuson, and Dangl [2] have recorded (without comment) the spectrum of the liquid between 3500 and 650 cm.$^{-1}$.

The spectra for these states are of importance since there is evidence to suggest that this acid, unlike most other carboxylic acids, is not dimeric in the liquid or the solid state but is associated as a polymer. Dielectric-polarisation measurements [3] of the acid in the liquid and the solid state indicate that there must be a significant contribution from polar configurations rather than from non-polar dimers; this is in contrast with results for liquid acetic acid where the dielectric values confirm the dimeric condition.

The recent *X*-ray analysis [4] of solid formic acid shows that the molecules of formic acid in this state are linked by hydrogen bonds at both ends, forming infinite chains and not dimeric units. It suggests a considerable decrease (about 0·1 Å) in the C–O bond length in the transition from formic acid vapour to the solid (cf. Davies and Thomas [5]).

Materials and Apparatus.—Anhydrous formic acid was obtained by treating 98% commercial formic acid with a small excess of phosphoric oxide and cooling the mixture. This product was distilled under reduced pressure, and a middle fraction taken.

The liquid-state spectrum was obtained in the usual manner, with rock-salt flats. The solid-state spectrum was obtained by means of a transmission-type, evacuated, low-temperature cell, with liquid oxygen as a refrigerant.

The spectrometer was a Grubb-Parsons double-beam spectrometer with a rock-salt prism. The spectra were obtained between 3500 and 650 cm.$^{-1}$. Duplicate spectra of the liquid were obtained and the spectrum of the solid was obtained a number of times.

Results and Discussion.—Liquid formic acid. This gave bands at *ca.* 3151(s), *ca.* 2999(s), 2768(m), 2571(m), 2361(w), *ca.* 1724(s), 1391(sh), 1362(s), 1195(s), 1067(w), 1019(w), 875(w), and 669(w) cm.$^{-1}$.

The infrared spectra of a considerable number of carboxylic acids and their deuterated derivatives have been investigated between 1500 and 500 cm.$^{-1}$, as dimeric units in the liquid or crystalline solid state.[6] Under these conditions the carboxyl group gives rise to absorption bands in the regions 1420 $\pm$ 20, 1300 $\pm$ 15, and 935 $\pm$ 15 cm.$^{-1}$. The first two of these correspond to closely coupled OH deformation vibrations occurring in the plane of the ring formed by two carboxyl groups, whilst the last is caused by the out-of-plane OH deformation vibration.

In liquid formic acid strong absorption bands occur at 1391 (sh), 1362, and 1195 cm.$^{-1}$ (see Fig. *a*). There are no strong bands in the range 1300 $\pm$ 15 or 935 $\pm$ 15 cm.$^{-1}$. Only

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[1] (*a*) Bonner and Hofstadter, *J. Chem. Phys.*, 1938, **6**, 531; Van Zandt Williams, *ibid.*, 1947, **15**, 232, 243; Herman and V. Williams, *ibid.*, 1940, **8**, 447; (*b*) Orville Thomas, *Discuss. Faraday Soc.*, 1950, **9**, 339; (*c*) Sverdlov, *Doklady Akad. Nauk S.S.S.R.*, 1953, **91**, 503.

[2] Randall, Fowler, Fuson, and Dangl, "Infra-red Determination of Organic Structures," Van Nostrand, New York, 1949, p. 103.

[3] Johnson and Cole, *J. Amer. Chem. Soc.*, 1951, **73**, 4536.

[4] Holtzberg, Post, and Fankuchen, *Acta Cryst.*, 1953, **6**, 127.

[5] Davies and Orville Thomas, *Research*, 1951, **4**, 384.

[6] Hadzi and Sheppard, *Proc. Roy. Soc.*, 1953, *A*, **216**, 247.

a weak absorption centred about 875 cm.$^{-1}$, spreading from 994 to 745 cm.$^{-1}$, occurs, instead of the usual intense out-of-plane OH deformation band found in all dimeric acids.

This evidence suggests that liquid formic acid is not dimeric. Examination of formic acid in solution in carbon tetrachloride confirms this interpretation. The spectra of the liquid, and of concentrated solutions of formic acid, are quite different. A strong band at 927 cm.$^{-1}$ occurs at high concentrations (but vanishes on dilution as the amount of monomer increases), and has been assigned to a dimeric vibration.[1b] Further, with concentrated solutions, there is no band at 1195 cm.$^{-1}$ but on dilution a band appears at 1208 cm.$^{-1}$ which has been assigned to a monomer vibration.[1b]

Thus the infrared evidence shows that formic acid is neither monomeric nor dimeric in the liquid state. On dilution in carbon tetrachloride, the polymer presumably splits to form dimeric units which on further dilution split to give monomers.

It is of interest to consider the frequencies of the absorption bands in the associated OH region of the liquid acid. Davies and Evans[7] have pointed out that the structure of the associated bands in solutions of certain amides and of trichloroacetic acid can apparently be accounted for in terms of sums and differences between the OH (or NH) stretching frequency and low frequencies of the order of 70—200 cm.$^{-1}$. The latter are attributed to the associated molecule.

FIG. *a*.

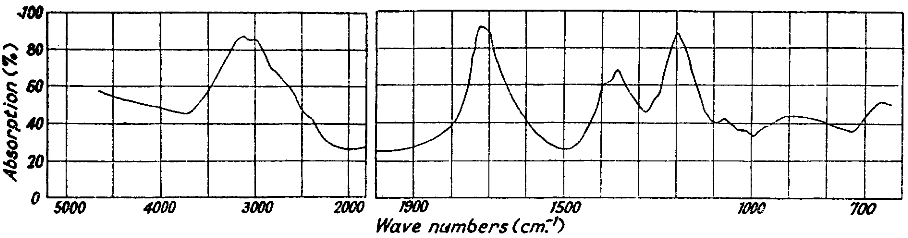
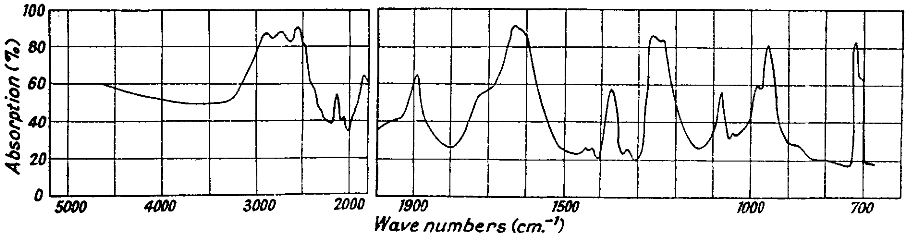


FIG. *b*.



The bands due to association are at 3151, 2768, 2571, and 2361 cm.$^{-1}$. By starting from the 3151 cm.$^{-1}$ feature the others occur at intervals of 383, 580, and 790, which may be expressed revealingly as *ca.* 2 × 190, 3 × 193, and 4 × 195. The hydrogen-bridge frequency (ν_1 of the linear X–H—Y) directly observed in formic acid liquid has been observed in the Raman spectrum[8] at ~180 cm.$^{-1}$. Thus it seems plausible to identify the bands in the "associated OH" region as overtones of this frequency. It should be noted, however, that the extra peaks in the 3μ region in formic acid vapour, and in liquid acetic acid, have been interpreted in terms of summation bands due to appropriate combinations of fundamental vibrations of the coupled carboxyl groups of the dimeric molecules[9]. Davies and Evans[7] suggest that the combination tones may be more clearly resolved the more definite the structure of the associated species, and compare the carboxyl dimer (as in trichloroacetic acid) with the chain-associating alcohols. With liquid formic acid it appears that even in the polymeric form the associated OH region can be clearly resolved.

[7] Davies and Evans, *J. Chem. Phys.*, 1952, **20**, 342.

[8] Hibben, " The Raman Effect and its Chemical Applications," Reinhold Publ. Corp., New York, 1939, p. 180.

[9] Bratož, Hadži, and Sheppard, *Bull. sci. Conseil Acad. R.P.F., Yougoslavie*, 1953, **1**, 71.

Solid formic acid. A theory of the infrared spectra of crystals at low temperatures has been given by Winston and Halford,[10] and by Hornig.[11] Hornig points out from a comparison of experimental results that there is, in general, a correlation between a frequency of the free molecule in the gas and a set of crystalline frequencies, but that both shifts of frequency and coupling effects must be taken into account. Further, he shows that the spectrum for the crystalline state is determined by the site symmetry of the molecules in the unit cell and by the symmetry of the unit cell.

It seems reasonable, as a first approximation, to discuss the spectrum of solid formic acid by analogy with the frequencies of the monomeric vapour (as determined and assigned by Orville Thomas [personal communication (see Table)]. Whilst there is a molecular plane of symmetry in the formic acid molecule in the vapour state, this is not the case for the polymerised molecule in the solid state. Furthermore, allowance must be made for the influence of the V_J' perturbation, *i.e.*, the change in V_J^0 the potential energy function of the free molecule due to the equilibrium field of the crystal, and of the V_{JK}'' perturbation (the interaction between the displacement co-ordinates of the *j*th and the *k*th molecule). Shifts in frequency due to the perturbation V_J' will not be too great, perhaps about 20 or 30 cm.$^{-1}$ (cf. benzene), whilst larger shifts (100 cm.$^{-1}$) such as are reported [11] to occur in hydrogen-bonded substances are almost certainly due to changes in the lengths of the bonds involved in the hydrogen bonding. The V_{JK}'' perturbation is the coupling term and will produce splitting of the frequencies corresponding to each non-degenerate vibration of the free molecule. The number of such components observed in the infrared spectrum of the crystalline solid depends on the number of molecules per unit cell and the symmetry of the point group.

The *X*-ray measurements [5] of the formic acid crystal show that there are four molecules per unit cell, and the space group of the unit cell is Pna(C_{2v}^9). The point group is, therefore, C_{2v} and the site symmetry is C_1. From this it can be deduced that all fundamental vibrations of the molecule will be infrared-active. The number of components for each vibration will be four, of which three will be active in the infrared (A_1, B_1, and B_2) and all of which will be active in the Raman effect (A_1, A_2, B_1, B_2).

The spectrum of the solid differs considerably from that of liquid formic acid, with an increase in the number of absorption bands (Fig. *b*). A closer analogy is usually observed between the spectra of the liquid and the crystalline phase of non-polar molecules. With polar molecules, however, particularly where hydrogen bonding occurs, marked modifications can occur in the spectrum. The frequencies for the solid state are given in the Table.

Three strong bands occur, at 2921, 2744, and 2562 cm.$^{-1}$, which can be assigned to the set of three frequencies associated with the OH stretching vibration, in agreement with the predicted splitting expected for the point and site symmetry deduced from the *X*-ray evidence. The shift in frequency from the monomer frequency in the vapour (3569 cm.$^{-1}$) to the mean position of the three components in the spectrum of the solid is 825 cm.$^{-1}$. Such a considerable shift in this frequency is fairly consistent with the *X*-ray measurements. The O–H–O distance in the polymer is estimated to be 2·58 Å. This distance in the dimer is 2·73 Å, and the OH stretching frequency of the dimer is at 3080 cm.$^{-1}$, $\Delta\nu$ in this case being 489 cm.$^{-1}$.

It is to be expected that the C–H stretching frequency for the solid will not be altered greatly from that observed for the vapour (2943 cm.$^{-1}$) since this bond is not intimately connected with association. Owing to overlapping of the OH absorption in the spectrum, however, it is not possible to observe clearly the C–H stretching frequency. There is an inflexion on the side of the 2921 cm.$^{-1}$ band which may be due to this vibration.

There are a number of unusual weaker bands occurring between the OH and the C=O regions of the spectrum for the solid. Thus, there are bands at 2464, 2387, 2312, 2143, 2074, 1922, and 1894 cm.$^{-1}$. The origin of these bands is obscure. By starting from the 2464 cm.$^{-1}$ feature the others occur at intervals of 77, 152, 321, 390, 541, 551, and 570 cm.$^{-1}$.

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[10] Winston and Halford, *J. Chem. Phys.*, 1949, **17**, 607.

[11] Hornig, *ibid.*, 1948, **16**, 1063; *Discuss. Faraday Soc.*, 1950, **9**, 115.

These do not seem to fit into any marked sequence analogous to that obtained for the " associated OH " band in the spectrum of the liquid and may be combinations of fundamental vibrations and lattice vibrations.

Gas monomer frequencies (cm.$^{-1}$)	Mode of vibration of free molecule: description	symmetry	Crystal (cm.$^{-1}$)	Frequency shift, gas to solid (cm.$^{-1}$)	Splitting (cm.$^{-1}$)
3569	OH	A′	2921 s 2744 s 2562 s	825	177 182
2943	CH	A′	Inflexion on side of 2921 cm.$^{-1}$ band (?)		
	Combination bands (?)		2464 (sh) 2387 (sh) 2312 w 2143 m 2074 w 1922 w 1894 m		
1773	C=O	A′	1723 m 1638 s (sh)	− 93	85
1107	C–O	A′	1265 s 1240 s 1218 s	+133	25 22
658	δ(OCO)	A′	725 s 715	+ 60	10
1380 1232	δ(CH) δ(OH)	A′ (in plane)	1447 w 1426 w 1374 m 1333 w	− 6	
	δ(OH)	A″ (out of plane)	988 s 959 s		29
1033	δ(CH)	A″ (out of plane)	1080 s	+ 47	

The electron diffraction and *X*-ray measurements indicate that the C=O distance is the same (within the limits of error) in the vapour and the solid state. This seems somewhat surprising in view of the considerable decrease observed in the C–O bond length in the transition from vapour to solid. If this is the case, however, then the mean frequency of the components of the carbonyl vibration would be expected to be near the frequency of the analogous vibration in the monomer spectrum. The monomer frequency is at 1773 cm.$^{-1}$. The frequencies for the solid state most reasonably assigned to carbonyl vibration are at 1638 and *ca.* 1723 cm.$^{-1}$. The mean frequency of these components is at 1680 cm.$^{-1}$, a quite considerable shift ($\Delta\nu = 93$ cm.$^{-1}$) from the monomer frequency. The infrared evidence, therefore, indicates that the C=O bond length is not the same in both the solid and the vapour state.

Electron-diffraction and *X*-ray measurements indicate that the C–O bond length decreases by at least 0·1 (±0·03) Å during the transition from formic acid vapour to solid. Calculations by Davies and Sutherland[12] indicate that a transition of this type might result in a decrease in the bond length of the order of 0·04 Å. Holtzberg *et al.*[4] suggest that, if the electron-diffraction and *X*-ray measurements are both correct, then the differences in bond length cannot be attributed entirely to the vapour–solid transition. A very recent determination of the bond length in the vapour state by an electron-diffraction method[13] confirmed the earlier value for the monomer. It is of interest, therefore, to see whether the spectrum of the solid is consistent with a marked decrease of the C–O bond length.

The frequency assigned to the C–O vibration in the spectrum of the monomer is at 1107 cm.$^{-1}$. The most reasonable assignment of this vibration in the spectrum of the solid is to the set of three frequencies at 1265, 1240, and 1218 cm.$^{-1}$. The bond will certainly acquire more double-bond character in the solid state and hence it is unlikely to give rise to the band at 1080 cm.$^{-1}$. Of the bands at *ca.* 1374 cm.$^{-1}$ and those at *ca.* 1240 cm.$^{-1}$ the latter are preferred in view of their greater intensity, since the increase of double-bond character and the fact that the vibration is a stretching mode will be expected to give rise to a set

[12] Davies and Sutherland, *J. Chem. Phys.*, 1938, **6**, 755.

[13] Karle and Karle, *ibid.*, 1954, **22**, 43.

of component bands of high intensity. (A study of the deuterated material could confirm this assignment.)

On this assignment the shift in frequency (Δν) from the C–O frequency in the monomer to the mean component in the solid is +133 cm.$^{-1}$. The shift from the C=O frequency in the monomer to the corresponding mean component in the solid is —93 cm.$^{-1}$. It is not inconsistent that a corresponding increase in the C–O bond frequency should tend to accompany a decrease in the C=O bond frequency.

It is possible by means of Clark's relation[14] to estimate approximately the decrease in bond length of the C–O bond in the solid state from that observed in the vapour state, by using the increase in the C–O frequency in the spectrum of the solid over that obtained for the vapour. This leads to a decrease in value (1240 cm.$^{-1}$ being used as the C–O frequency) of ~0·05 Å in the bond length. This is in fairly good agreement with Davies and Sutherland's calculations.[12]

Note added in Proof.—W. J. Orville Thomas has recently re-examined his assignments of the frequencies in the monomer, and now suggests that coupling occurs between the ν(C–O) and δ(OH) in-plane vibrations. He suggests that the uncoupled ν(C–O) in the monomer may be at ~1180 cm.$^{-1}$. In solid formic acid, owing to the decrease in the C–O bond length, decoupling of these vibrations may be expected. On this new basis Δν for the ν(C–O) frequencies for the vapour to solid transition is ~60 cm.$^{-1}$, and the change in the C–O bond length from vapour to solid is even less than that predicted in the present paper. The less plausible assignment of the band at *ca.* 1374 cm.$^{-1}$ in the solid state spectrum to the ν(C–O) mode, would give a shift more consistent with the *X*-ray evidence.

In the vapour state the δ(OH) A′ frequency occurs at 1232 cm.$^{-1}$. In dimeric formic acid in solution a shift to 1364 cm.$^{-1}$ is observed. This 1364 cm.$^{-1}$ band completely masks the δ(CH) A′ vibration which occurs in the same region. The δ(CH) A′ frequency in the spectrum of the solid will not be altered appreciably from that observed for the vapour since it is not intimately concerned with hydrogen bonding. It seems reasonable to suppose, therefore, that the set of frequencies at *ca.* 1374 cm.$^{-1}$ for the solid could correspond to a superposition of the shifted δ(OH) A′ frequency of the vapour on the δ(CH) frequency.

The δ(OH) A″ frequency has not been observed in the vapour (monomer), but in the dimer is at 927 cm.$^{-1}$. A corresponding shift to the set of frequencies at *ca.* 974 cm.$^{-1}$ seems a reasonable assignment for a δ(OH) vibration in the spectrum of the solid.

In the crystalline state the acids existing in dimeric form (*e.g.*, lauric acid) give an intense broad band associated with the out-of-plane OH deformation vibration at 935 ±15 cm.$^{-1}$. The bands at *ca.* 974 cm.$^{-1}$ in solid formic acid assigned to a δ(OH) vibration are outside this range, and are neither as broad nor as intense.

The δ(CH) A″ frequency for the vapour (monomer) occurs at 1033 cm.$^{-1}$, in solution in carbon tetrachloride at 1064 cm.$^{-1}$, and at 1069 cm.$^{-1}$ in the formate ion. The band at 1080 cm.$^{-1}$ for the solid is, therefore, assigned to a C–H deformation vibration.

Finally the set of frequencies at *ca.* 710 cm.$^{-1}$ in the spectrum of the solid is assigned to the δ(OCO) vibration by analogy with the assignment of this vibration in the monomer to the frequency 658 cm.$^{-1}$.

These conclusions are summarised in the Table, the mean of the component frequencies being used to compute the frequency shift. Both the shift and the splitting effects are greater for the OH stretching vibrations than for any other vibration.

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[14] Clark, *Phil. Mag.*, 1934, **18**, 459.