

## The InfraRed Absorption of Carboxylic Acids in Solution I. Qualitative Features

M. M. Davies and G. B. B. M. Sutherland

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# The Infra-Red Absorption of Carboxylic Acids in Solution

## I. Qualitative Features

M. M. DAVIES AND G. B. B. M. SUTHERLAND

*Departments of Colloid Science and Physical Chemistry, Cambridge, England*

(Received August 22, 1938)

The absorption spectra of solutions of acetic, benzoic and trichloroacetic acids in carbon tetrachloride have been studied at various concentrations and temperatures in the neighborhood of  $3\mu$ ,  $6\mu$ , and  $7\mu$ . At each of these regions is a double band, one component of which is due to the monomeric, the other to the dimeric form of the molecule. The relatively small shift in each case indicates that the molecule is not radically altered on association. The absorptions in the three regions studied were due respectively to the O—H, the C=O and the C—O bonds of the COOH group. It has been possible to make a first estimate of these bond distances in the monomer and dimer, as follows (in A units):

	O—H	C=O	C—O
Monomer	0.9 <sub>81</sub>	1.1 <sub>95</sub>	1.2 <sub>98</sub>
Dimer	1.0 <sub>4</sub>	1.2 <sub>11</sub>	1.2 <sub>85</sub>

The values for the C=O and C—O distances are in satisfactory agreement with those deduced by x-ray methods for oxalic acid but not with those obtained by electron diffraction for formic acid. The general appearance and the temperature variation of the O—H "association" band in these acids appears to be very similar to that of the corresponding band in the alcohols. This is evidence in favor of Badger's explanation of the width of such bands rather than Errera's.

ATTENTION has recently been directed by the work of several authors<sup>1</sup> to the effects of dimeric and polymeric association on the infra-red absorption spectrum of a molecule. The majority of cases so far examined have been concerned with the absorption due essentially to the OH bond in alcohols and in water. The general result of such investigations is, briefly, that the monomeric form of the molecule gives a series of very sharp absorption bands corresponding to the fundamental and overtone frequencies of the OH bond, while the polymeric form gives very broad bands which are consistently shifted to the long wave side of the related sharp monomeric ones. Whatever may be the explanation of the great breadth of these "association bands" it was immediately obvious that the clean-cut distinction between the two types of band provided an excellent means of studying the relative degrees of association under different conditions. One of us (M. M. D.) had been interested in the type of association in the omega-hydroxy carboxylic acids,<sup>2</sup> and the present investigation is the outcome of a suggestion by

Professor E. K. Rideal that the methods of infra-red spectroscopy might be applied to this problem. In order to do this, it was necessary first to investigate carefully the absorption spectra of molecules containing the COOH group in solution. We found on examination that the work already done on such molecules did not provide us with sufficient information, largely because it had been done under too low dispersion. Thus, Gordy<sup>3</sup> had shown that the position of the maximum absorption due to the C=O group varied with concentration in solutions of acetic acid in carbon tetrachloride and in benzene, while Kinsey and Ellis<sup>4</sup> had noted a similar effect in the OH absorption near  $3\mu$ . Gillette and Daniels<sup>5</sup> had studied the effect of association on the spectrum of acetic acid vapor between  $3\mu$  and  $10\mu$ . They noted a shift of  $46\text{ cm}^{-1}$  in the maximum of the C=O absorption near  $5.7\mu$  and a shift of  $37\text{ cm}^{-1}$  in another band (attributed by them to the C—O frequency) near  $7\mu$ . Finally, Badger and Bauer,<sup>1d</sup> working partly in the vapor and also in the liquid and in solution, had found a sharp monomeric and a wide association band in the region of one of the overtone frequencies of the OH group. We decided to reinvestigate the

<sup>1</sup> (a) Errera and Mollet, C. R. Acad. Sci. Paris, **204**, 259 (1937); (b) Fox and Martin, Proc. Roy. Soc. **A162**, 419 (1937); (c) R. Freyman, C. R. Acad. Sci. Paris **204**, 1063 (1937); (d) Badger and Bauer, J. Chem. Phys. **5**, 605 (1937); (e) Badger and Bauer, J. Chem. Phys. **5**, 839 (1937).

<sup>2</sup> Davies, Trans. Faraday Soc. **34**, 410 (1938).

<sup>3</sup> Gordy, J. Chem. Phys. **5**, 284 (1937).

<sup>4</sup> Kinsey and Ellis, J. Chem. Phys. **5**, 399 (1937).

<sup>5</sup> Gillette and Daniels, J. Am. Chem. Soc. **58**, 1139 (1936).

region between  $2.5\mu$  and  $8\mu$  which contains the important fundamental frequencies, using a quartz prism up to  $3.5\mu$  and a fluorite prism between  $3.5\mu$  and  $8\mu$ . A preliminary report of the main results to be described has already appeared in *Nature*.<sup>6</sup>

### EXPERIMENTAL METHODS

The spectrometer employed in the investigation was the standard Hilger model (D.83). Two different sources of radiation were employed. In the quartz region a tungsten filament lamp in a quartz bulb, running at 6.5 volts and 14 amp., proved steadier than, and yet of equal intensity to, a Nernst glower. The latter source was used beyond  $3.5\mu$ , running at 110 volts and 0.95 amp., with the usual hydrogen-filled iron-filament lamp in series. One great improvement in the normal steadiness of the instrument was effected by the introduction of a second exactly similar Moll low resistance thermopile, completely enclosed in a brass case, which was connected in series and in opposition to that being exposed. The zero fluctuations in both were so nearly equal as to result in a very steady reading. The absorption cells for the solutions had fluorite windows 1" in diameter and  $\frac{1}{10}$ " thick, polished to optical flatness. These were cemented into brass collars C, (Fig. 1) the grooves in which were such as to make the window flush with the rim of the collar. An accurately plane brass ring D, pierced by a small hole B for filling and emptying, was then cemented between both windows. A cellulose acetate adhesive (Durofix) was used throughout with complete success as this is unaffected by the solvents used. Cells with washers of 1.3, 3.05, and 6.02 mm were used at different times. A longer cell of 24 mm was also made by cementing windows into the ends of a short brass tube.

An important feature of the work was the measurement of the absorption of solutions at

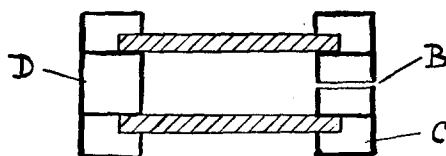


FIG. 1.

<sup>6</sup> Davies and Sutherland, *Nature* **141**, 372 (1938).

temperatures up to  $108^\circ\text{C}$ . For this purpose a length of Nichrome wire was wound on an asbestos covering around the circular edge of the cell. This was protected by further layers of asbestos tape, while loss of heat from the exposed surfaces of the cell was reduced by pasting to them a covering of asbestos board having a circular aperture. The copper-constantan thermocouple inserted through the aperture used for filling the cell, and the millivoltmeter used in conjunction with it, were calibrated with the aid of N. P. L. standardized thermometers. By means of a large scale ammeter and hand-regulation of the rheostat, the temperature of the cell could be maintained constant to  $\pm 0.5^\circ$ .

The radiation was brought to a focus at approximately the center of the cell, which could be moved out of the beam to determine the percentage absorption. The solvent correction was determined by finding the absorption when the cell (without being removed from its mount) was filled with pure solvent. The reason for not moving the cell from the mount between these runs is that the percentage absorption may vary slightly according to the position of the cell in the beam. By pipetting out of B and flushing the cell several times with the solution or solvent about to be examined, the transition from one absorbent to another could safely be accomplished without disturbing the position of the cell in the beam.

The numerical calculation of the solvent effect may briefly be noted. If  $I_0$  is the original intensity,  $I_\alpha$  that after passing through the solution and  $I_\beta$  that after passing through the solvent alone, then

$$I_\alpha = I_0 \cdot e^{-\{K_w d + (c_s K_s + c_t K_t) l\}}$$

and

$$I_\beta = I_0 \cdot e^{-\{K_w d + c_s K_s l\}},$$

where  $K_w$  is the absorption coefficient of the fluorite,  $K_s$  is the absorption coefficient of the solvent, whose conc. is  $c_s$ ,  $K_t$  is the absorption coefficient of the solute, whose conc. is  $c_t$ .

$$\text{Hence, } (I_\alpha/I_0)/(I_\beta/I_0) = e^{-c_t K_t l},$$

or the ratio of the percentage absorptions due to solution and solvent separately gives the practical absorption which would have been given by the solute alone. Since much of the later work

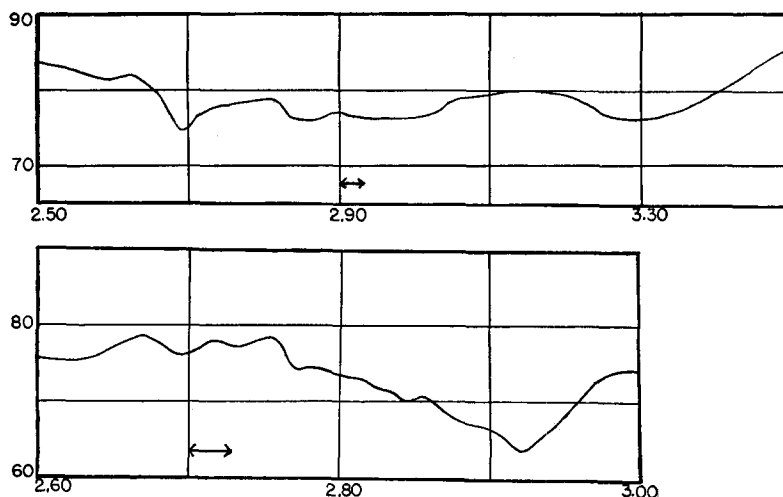


FIG. 2. Transmission curves for  $\text{CCl}_4$  in 6.02 mm cell. Percentage transmission plotted against  $\lambda$  in  $\mu$ . Above at  $18^\circ$ ; below at  $74^\circ$ .

depended on the measurement of relative intensities it was decided to evaluate the integral absorption corresponding to each band, defined by the expression

$$\int \delta d\lambda, \text{ where } \delta = \log_{10} (I_\beta/I_\alpha) = c_l k d.$$

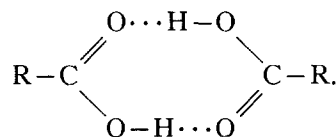
This may be expected to bear a more satisfactory relation to the concentration of absorbing centers than the simple percentage absorption at the center of the band. The  $\log_{10} (I_\beta/I_\alpha) \sim \lambda$  plots were made on squared paper and the areas under the absorption band estimated by counting squares, due allowance being made for background absorption when present. In some cases two adjacent bands overlap and the effect of one on the other had to be taken into account.

The greater proportion of the data refer to carbon tetrachloride solutions. The solvent used was the Analar reagent, given a final drying by refluxing and distilling from sodium in an all-glass apparatus. In the quartz region at room temperatures it showed a reasonably uniform transmission of about 80 percent through a 6 mm layer except for a small band at  $2.70\mu$  probably due to an overtone of a  $\text{C}-\text{Cl}$  vibration (Fig. 2). It is worth noting that even when the solvent correction was determined with considerable accuracy, a slight absorption at  $2.70\mu$  might still be recorded in the corrected curve for the solute, indicating a limitation in the accuracy of the method of applying the correction in such a

region. At longer wave-lengths an intense band in the solvent made it impossible to work in the region  $6.3\mu$  to  $6.8\mu$ : fortunately, this region contained no absorption of the solutes, which was of interest. Carbon tetrabromide was used for temperatures up to  $108^\circ\text{C}$ . It proved somewhat difficult to work with (it does not appear to have been used previously as a solvent in this field) as it melts only at  $90^\circ\text{C}$  and tends to decompose on prolonged heating. Its extremely strong lachrymatory action was also troublesome.

#### THE QUALITATIVE NATURE OF THE RESULTS AND THEIR INTERPRETATION

The association of a carboxylic acid is well known to take place through the medium of the  $\text{COOH}$  group in some such manner as indicated,



It is therefore to be expected that the  $\text{O}-\text{H}$ ,  $\text{C}-\text{O}$ , and  $\text{C}=\text{O}$  bonds of the monomeric molecule will be affected. It is further known from the Raman spectra of series of compounds that any molecule containing a reasonably isolated  $\text{C}=\text{O}$  bond possesses a characteristic frequency in the neighborhood of  $1750\text{ cm}^{-1}$ , while the  $\text{C}-\text{O}$  bond sometimes appears to be associated with a frequency of about  $1400\text{ cm}^{-1}$  and the  $\text{OH}$

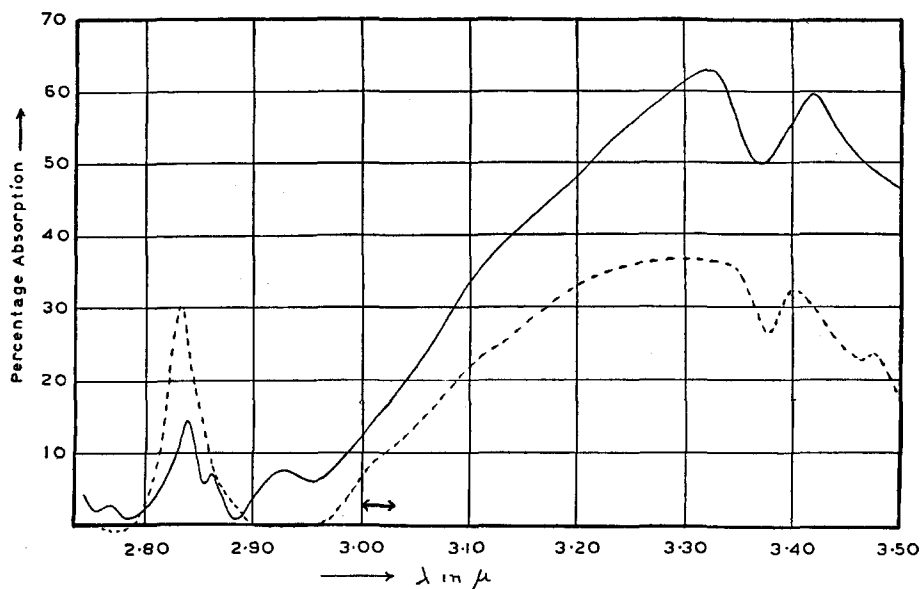


FIG. 3. 0.0100 molar acetic acid in  $\text{CCl}_4$  6.02 mm cell. Full curve at  $18^\circ$ ; dotted curve at  $74^\circ$ .

frequency is always near  $3400\text{ cm}^{-1}$ . Accordingly, we chose the regions near  $2.6\text{--}3.4\mu$ ,  $5.6\text{--}6.2\mu$  and  $6.7\text{--}8.0\mu$  as most likely to yield significant results. In order to vary the proportion of monomer to dimer we either (a) varied the concentration of the acid in the solvent, or (b) varied the temperature keeping the concentration fixed. In discussing the qualitative results we shall confine our attention to (b), since (a) can only be discussed properly if quantitative measures are considered.

#### The region of the OH fundamental

The absorption spectra of acetic and benzoic acids were examined between  $2.7\mu$  and  $3.5\mu$  first at room temperature and then at  $74^\circ\text{C}$ . The result in each case (as shown in Figs. 3 and 4; in these, and in the other figures, the effective slit width is indicated by the horizontal arrow) is that a weak but sharp band at  $2.84\mu$  increases remarkably in intensity with rise in temperature, whereas a broad ill-defined band near  $3.3\mu$  decreases or remains unaffected on raising the temperature. This behavior is very similar to that of the OH absorption in alcohol solutions, with the distinction that there the broad association band can be made to disappear completely by increasing sufficiently the dilution or the temperature. In the case of the alcohols it is

possible to distinguish very easily the association band (which extends roughly from  $2.8\mu$  to  $3.1\mu$ ) from the CH bands occurring between  $3.2\mu$  and  $3.5\mu$ ; in the case of the carboxylic acids it would appear that the association band begins at about  $3\mu$  and extends to at least  $3.3\mu$ . The consequent overlapping of the intense CH absorption would explain why its decrease is difficult to detect in some cases. Accordingly, we have also examined

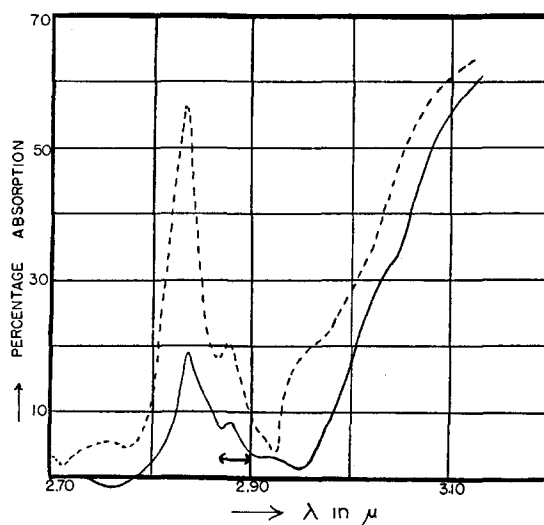


FIG. 4. 0.0167 molar benzoic acid in  $\text{CCl}_4$  6.02 mm cell. Full curve at  $18^\circ$ ; dotted curve at  $71^\circ$ .

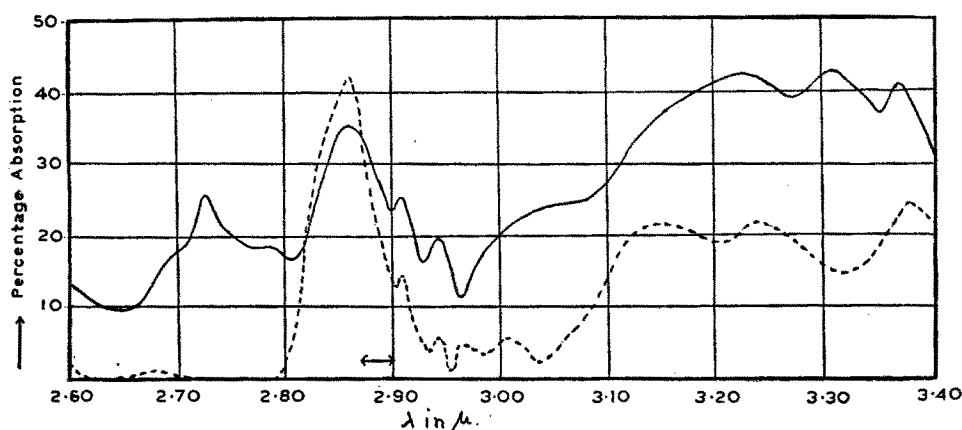


FIG. 5. 0.00565 molar trichloroacetic acid in 6.02 mm cell. Full curve at 18°; dotted curve at 76°.

the absorption of trichloroacetic acid in the same region. Since there is no CH bond in this molecule one would expect the diminution of the association band to be more pronounced if the above explanation is correct. The curves of Fig. 5 show exactly this behavior, and indicate that the association band extends from approximately  $2.9\mu$  to  $3.3\mu$ . This is a greater width than that found in the alcohols—roughly  $420\text{ cm}^{-1}$  as compared with  $350\text{ cm}^{-1}$ . It might be remarked here that the position of the monomeric OH absorption in trichloroacetic acid is at a slightly longer wave-length ( $2.86\mu$ ) than that for acetic or benzoic acid ( $2.835\mu$ ). This will be more fully considered later.

Certain small but important peculiarities in the region of the OH absorption should be noted. The first is that very frequently on the long wave-length side of the sharp OH band there appear minor but very definite peaks. These occur at  $2.86\mu$  and  $2.93\mu$  in acetic, at  $2.88\mu$  in benzoic acid and at  $2.91\mu$  and  $2.94\mu$  in trichloroacetic acid. This phenomenon appears to have no counterpart in the OH absorption of the alcohols. The bands in acetic acid were not recorded at the higher temperatures, but it may be that the broadening of the main monomeric band obscured one of them. The bands in benzoic and in trichloroacetic acid appear to be relatively unaffected by temperature. Again, in the latter acid there is, on the short-wave side of the main monomeric OH absorption, a distinct band at  $2.73\mu$  which disappears on raising the temperature. The possible interpretation of these bands is discussed in a later section.

### The region of the C=O fundamental

In this case we have studied only acetic and trichloroacetic acid. The results for the former are illustrated in Fig. 6. A 0.010 molar solution in carbon tetrachloride showed two distinct bands both at room temperature and at  $73.5^\circ\text{C}$ . At the lower temperature the centers of the bands were at  $5.66\mu$  and  $5.82\mu$ , with the latter much more intense; at the higher temperature the centers seemed to shift to  $5.64\mu$  and  $5.81\mu$ , the bands were more clearly resolved, and their intensities were now almost equal. For a 0.0020 molar solution the  $5.65\mu$  band appeared stronger than that at  $5.81\mu$ . The slight shift of the centers is almost certainly due to the weaker band (at the lower temperature) being "attracted" by the stronger in a well-known way. The shift in the position of this band which was observed by Gillette and Daniels<sup>5</sup> is thus seen to be due to the change in the relative intensities of two bands, one of which is presumably due to the monomeric molecule ( $1768\text{ cm}^{-1}$ ) and the other to the dimer ( $1719\text{ cm}^{-1}$ ). Thus the association may be studied in the region of the C=O fundamental as well as in that of the OH, with the important distinction that here the bands do not differ so greatly in their characteristics as in the OH case.

For trichloroacetic acid the two bands were not resolved at room temperature.

### The region of the C—O fundamental

The absorption of a 0.010 molar solution of acetic acid was examined between the limits of  $6.8\mu$  and  $7.8\mu$  at  $18^\circ\text{C}$  and  $73.5^\circ\text{C}$ . Some of the results are seen in Fig. 7. It will be seen that there

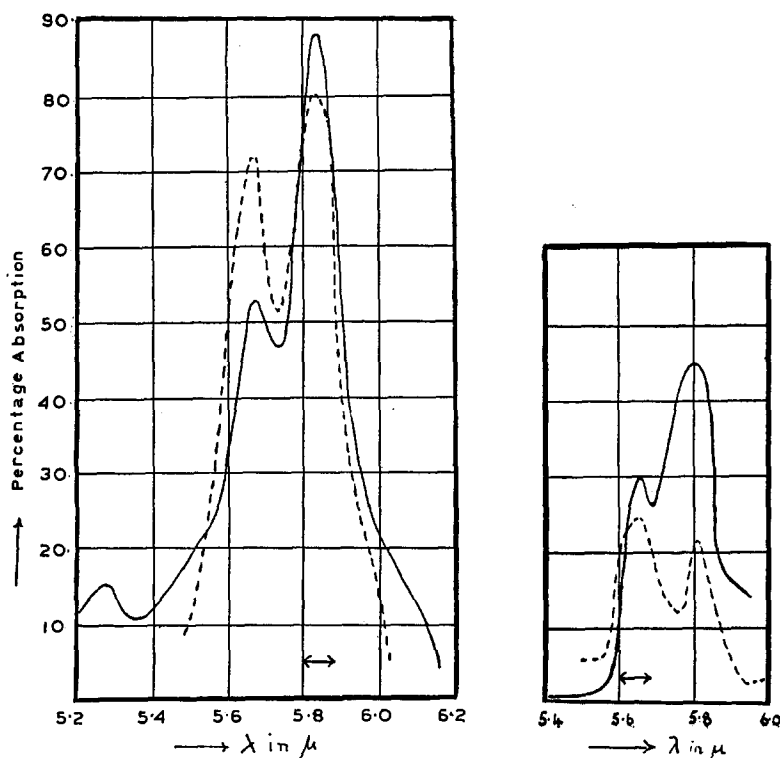


FIG. 6. (a) 0.0100 molar acetic acid in 6.02 mm cell. Full curve at 18°; dotted curve at 73.5°. (b) 0.0020 molar acetic acid.

are four distinct bands at  $6.94\mu$ ,  $7.05\mu$ ,  $7.25\mu$  and  $7.75\mu$ . At the higher temperature the band at  $7.25\mu$  seemed to strengthen relative to that at  $6.94\mu$ , while those at  $7.05\mu$  and  $7.75\mu$  appeared unchanged. Thus the former two exhibit the same behavior as the bands for the C=O frequency, except that in this case it is the one of shorter wave-length which weakens on increasing the temperature. Trichloroacetic acid gave a more marked result (Fig. 8). At ordinary temperatures it was found that there were strong bands at  $6.98\mu$ ,  $7.06\mu$ , and  $7.85\mu$ ; weaker bands were noticeable at  $6.82\mu$  and  $7.36\mu$ . On raising the temperature the  $6.98\mu$  band seemed to disappear, a broad band with center near  $7.2\mu$  coming up with considerable intensity. Presumably the band at  $7.06\mu$  was unaffected although it is difficult to be certain of this in view of the obvious width of the new band. The behavior of the band near  $7.8\mu$  at high temperatures was not examined since the one in this region had shown no change in acetic acid. It might be added, however, that the band probably has a different interpretation

in the two cases. In acetic acid it is probably due to the  $\text{CH}_3$  group, whereas in trichloroacetic acid it probably arises from the  $\text{CCl}_3$  group. We shall not go into the reasons for the assignment as this point is irrelevant to the main discussion.

#### DISCUSSION

The first point of interest is the occurrence of the sharp OH band at a definitely longer wave-length than in the alcohols— $2.84\mu$  as against  $2.76\mu$ , (or  $3521\text{ cm}^{-1}$ , against  $3623\text{ cm}^{-1}$ ). This has proved of great practical value in the later work where a hydroxyacid was studied and it was possible to separate easily the alcoholic OH frequency from that of the carboxylic group. This shift is also important as giving a measure of the change in the OH bond in passing from an alcohol to an acid. Thus we notice from Fox and Martin's work<sup>1</sup> that in a whole series of aliphatic and aromatic alcohols the monomeric OH band shifts only from  $2.750\mu$  to  $2.764\mu$ . In acetic and benzoic acids we find the same band at  $2.84\mu$ , while in trichloroacetic acid (a much stronger acid)

it has moved to  $2.86\mu$ . The decrease in the OH frequency corresponds to a weakening of the OH bond and so it is not surprising to find this qualitative relation between the value of the OH frequency and the acidity of the compound. It is doubtful whether a quantitative relation can be found since the dissociation constant of an acid depends on many other factors besides the immediate energy of dissociation of the H-ion from the rest of the molecule, and it is only to the latter that the vibration frequency can even be approximately related. We have, however, computed the OH distance in the various cases using Badger's relation.<sup>7</sup> While the absolute values obtained cannot be considered reliable, the relative change in them is undoubtedly significant. These results are collected in Table I.

The examination of the association band in trichloroacetic acid, where it is free from the CH absorption, has shown that this band is as broad if not broader, than that found for the alcohols. The cause of this broadening in the alcohols is not yet properly understood. Errera has divided the association band into two bands, one of which

<sup>7</sup> Badger, J. Chem. Phys. 3, 710 (1935).

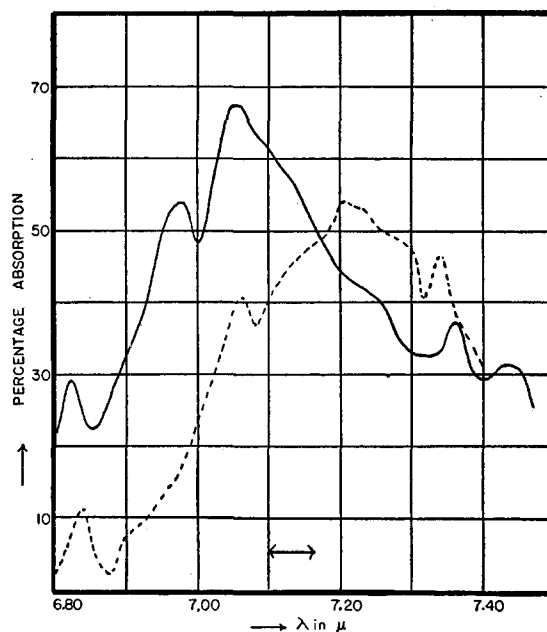


FIG. 8. 0.0195 molar trichloroacetic acid in  $\text{CCl}_4$  3.05 mm cell. Full curve at  $18^\circ$ ; dotted curve at  $72^\circ$ .

he suggests is due to the dimeric form of the molecule, the other to the polymeric molecules.<sup>8</sup>

<sup>8</sup> Errera and Sack, Trans. Faraday Soc. 34, 728 (1938).

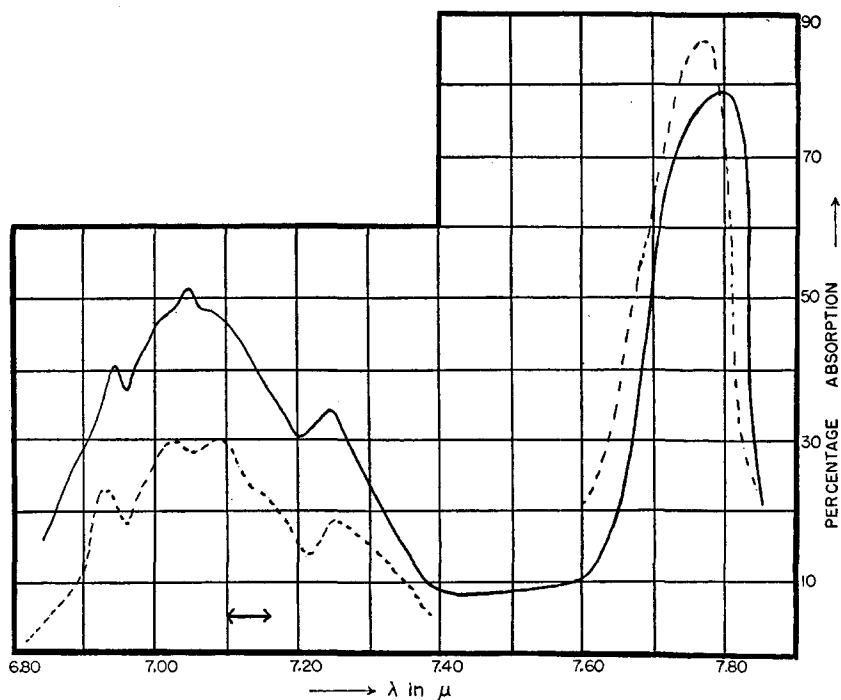


FIG. 7. 0.0100 molar acetic acid in  $\text{CCl}_4$  3.05 mm cell. Full curve at  $18^\circ$ ; dotted curve at  $70^\circ$ .



TABLE I. O—H Distances.

The first column under  $r_{OH}$  was calculated treating the OH group as the vibrating unit, the second column by treating XH as the vibrating unit where X represents the rest of the molecule. The true value lies between those extremes but probably much nearer the former.

MOLECULE	MONOMERIC O—H ABSORPTION		$r_{O-H} \text{ \AA}^\circ$		ACID DISSOCIATION CONSTANT
	$\lambda$ in $\mu$	$\nu$ in $\text{cm}^{-1}$			
<i>n</i> -aliphatic alcohols	2.750	3637	0.9 <sub>88</sub>	0.9 <sub>80</sub>	—
Benzyl alcohol	2.764	3618	0.9 <sub>70</sub>	0.9 <sub>69</sub>	—
Phenol	2.769	3612	0.9 <sub>71</sub>	0.9 <sub>60</sub>	$1 \times 10^{-10}$
Acetic and benzoic acids	2.837	3525	0.9 <sub>81</sub>	0.9 <sub>72</sub>	$1.86 \times 10^{-5}$ and $1.77 \times 10^{-4}$
Trichloroacetic acid	2.86	3496	0.9 <sub>85</sub>	0.9 <sub>73</sub>	$2 \times 10^{-1}$

If Errera's explanation were correct, one would expect in the carboxylic acids (where association has long been accepted as purely dimeric) a narrower association band than in the alcohols, showing no sensible variation in structure with temperature. Actually, the association band is broader than in the alcohols and shows structure of the same type. Again, increase of temperature in the case of trichloroacetic acid moves the position of maximum absorption to shorter wavelengths, which is exactly what Errera found for the alcohols and interpreted as due to the decrease of the polymeric relative to the dimeric form.

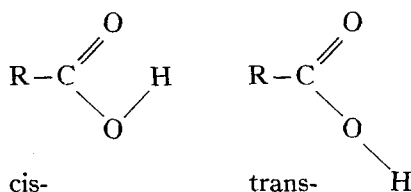
It would seem much more probable that the explanation of the width of these association bands lies in the presence of small combination frequencies arising from the slow vibrations of one-half of the dimer with respect to the other. Since the bond is a weak one, the restoring forces are small, and the masses being large the frequencies must be low. Similar suggestions have already been made by Badger and Bauer.<sup>16</sup> It seems that the present work substantiates this idea in several ways. Thus the fact that the association band is equally broad in the carboxylic acids and in the alcohols is readily understandable on this hypothesis but not on Errera's. The variation of the contour of the association band with temperature is easily explicable as due to the variation in the number of low vibrations excited at different temperatures. Further, Errera's theory would necessitate the polymeric association of acetic acid which would lead to broad "association" bands for the C=O and C—O frequencies; the figures show them to be as sharp as the monomeric ones. This is what would be

expected on the other theory, since the intermolecular bond is through the H-atom and its motion will therefore be most affected by intermolecular vibrations; in other words, the low frequency vibrations should combine strongly with the O—H but not with the C=O or C—O vibrations. The only serious difficulty for the intermolecular vibration theory is the explanation of the variation of the contour of the association band with concentration.<sup>1b</sup> This is not so serious as it might at first appear, since (as we shall show in the following paper) the absorption coefficient for certain vibrations shows variations with concentration. It can therefore happen that at certain concentrations some combination bands will appear more strongly than others. Physically, the effect of concentration on intermolecular vibrations will be rather similar to temperature—an increase of temperature causing increased freedom of vibration in much the same way as does increase of dilution.

The difference between the center of the association band ( $3.25\mu$ ) and that of the monomeric band ( $2.84\mu$ ) *viz.*  $448 \text{ cm}^{-1}$ , is considerably larger than that for the alcohols (about  $230 \text{ cm}^{-1}$ ). This indicates that the OH bond has been more altered by association in the acids than in the alcohols. We are doubtful whether one can use the measurement of this shift to compute the energy of the association bond in the simple way Fox and Martin have employed for the alcohols. We hope to give a detailed discussion of this problem in a later paper.

Finally, an interpretation first considered for the small additional bands on the long-wave side of the main monomeric OH band was that these might arise from *cis* and *trans* forms of the COOH

group in the monomer, thus



Pauling has suggested such an interpretation for the weak subsidiary bands found in many of the substituted phenols.<sup>9</sup> This cannot be the explanation in the present instance since with the *cis* position as the more probable<sup>10</sup> this would require the weak band to be on the short wavelength side of the main one. It seems most likely that they are overtone bands of the C=O frequency. The interpretation of the band at  $2.73\mu$  in trichloroacetic acid is also of considerable interest. It is possibly due to the  $-\text{CCl}_3$  group in this acid. Remembering that such a group possesses several very low fundamentals, one can expect difference bands the intensities of which can be very sensitive to temperature changes. Thus, Fig. 2 shows that in  $\text{CCl}_4$  itself an absorption at  $2.70\mu$  disappears on raising the temperature. The fact that it is only in trichloroacetic acid that its presence has been definitely established tends to support this interpretation. Obviously, more work must be done on these subsidiary bands before their complete elucidation may be properly attempted.

### The C=O frequency

In the foregoing discussion it has justifiably been assumed that one of the normal modes of vibration of any molecule containing an OH group consists essentially of the vibration of the OH group: although there is much evidence that this may also be applied to the C=O and C—O groups, one must be careful about the assignment of definite C=O and C—O frequencies, as the rest of the molecule will now be affected to an appreciable extent. Examination of the Raman spectra of esters, aldehydes, and ketones has shown that they all contain a frequency within  $20\text{ cm}^{-1}$  of  $1740\text{ cm}^{-1}$  and this has very properly been associated with the C=O group. In the

carboxylic acids, however, although some evidence has been found for a frequency near  $1730\text{ cm}^{-1}$  the majority of observers have agreed<sup>11</sup> that the Raman frequency common to all such acids which should be ascribed to the C=O group lies near  $1680\text{ cm}^{-1}$ . Work in the infra-red has revealed no strong absorption in the latter region but instead a very strong absorption at about  $1750\text{ cm}^{-1}$ . This is a serious difficulty which does not seem to have been satisfactorily resolved.

It might be suggested that there is a shift in the C=O frequency in going from the gaseous to the liquid state. Such shifts are well known for other molecules, and the above infra-red data refer either to the gaseous state or to weak solutions in inert solvents, while the Raman data refer to the pure liquid. Indeed, Edsall<sup>12</sup> and Krishnamurti<sup>13</sup> have both remarked on the fact that if the Raman spectrum is done in aqueous solution then a frequency does appear at  $1720\text{ cm}^{-1}$ . In ether solutions frequencies appear at both  $1666\text{ cm}^{-1}$  and at  $1750\text{ cm}^{-1}$ , and Edsall has suggested that one ( $1650\text{ cm}^{-1}$ ) might be associated with the dimeric form of and the other ( $1720\text{ cm}^{-1}$ ) with the monomeric form of the molecule.

It seems that the point that has been overlooked is that one is dealing with a double molecule. There are therefore not one, but two C=O bonds to be considered. Presumably these are identical and are loosely coupled through the hydrogen bond. The result will be not one, but two C=O frequencies arising from the loose coupling of the two identical systems; one frequency lying a little above, the other a little below the individual frequency of either C=O bond taken separately. The best example is another case of a loosely associated molecule which has been investigated in the infra-red *viz.*  $\text{N}_2\text{O}_4$ . Here the frequencies of the two  $\text{NO}_2$  groups are split into pairs, one of each pair being active in infra-red absorption but inactive in Raman scattering, the other having the opposite properties.<sup>14</sup> The essential condition for this separation into complementary pairs is that the molecule has a center of symmetry. In the car-

<sup>9</sup> Pauling, J. Am. Chem. Soc. **58**, 94 (1936).

<sup>10</sup> Bauer and Badger, J. Chem. Phys. **5**, 852 (1937); Morino and Mizushima, Proc. Inst. Phys. Chem. Research, Tokyo **32**, 33 (1937).

<sup>11</sup> Cf. Hibben, Chem. Rev. **18**, 38 (1936).

<sup>12</sup> Edsall, J. Chem. Phys. **4**, 1 (1936).

<sup>13</sup> Krishnamurti, Ind. J. Phys. **6**, 401 (1932).

<sup>14</sup> Sutherland, Proc. Roy. Soc. **A141**, 341 (1933).

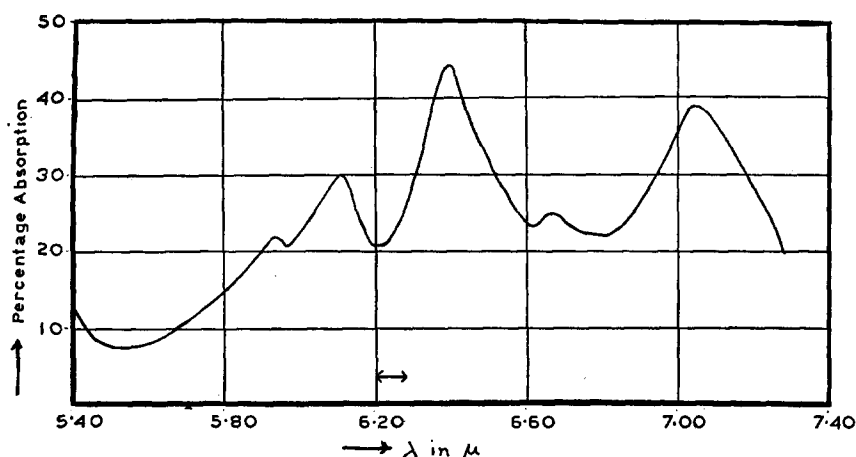
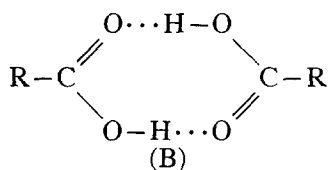
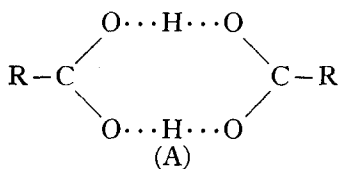


FIG. 9. Absorption of a thin layer of sodium acetate.

boxylic dimer there are two possible structures for the  $(\text{COOH})_2$  group corresponding to the cases of complete resonance<sup>14b</sup> (A) and incomplete resonance (B), and there is a center of symmetry in both cases.



If resonance is complete and all C—O bonds are identical then one of the pairs will closely correspond to the splitting of the unsymmetrical

mode of vibration of the  $\begin{array}{c} \text{O} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{O} \end{array}$  group, and another

pair to the splitting of the symmetrical mode of the same group. If resonance is incomplete, then one of the pairs corresponds to the splitting of the C=O frequency and the other to the splitting of the C—O frequency. We believe the latter alternative is the correct one since the dimeric frequency in each case appears so close to the mono-

meric one. If resonance were complete it seems

improbable that the frequencies of the  $\begin{array}{c} \text{O} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{O} \end{array}$  group should fall so close to the monomeric C=O and C—O frequencies.

A rough calculation may be made for the unsymmetrical mode of the  $\begin{array}{c} \text{O} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{O} \end{array}$  group assuming a

C—O force constant of  $8 \times 10^5$  dynes/cm and an angle of  $120^\circ$  between the C—O bonds. This yields a value of  $1595 \text{ cm}^{-1}$ . In order to obtain a frequency of  $1720 \text{ cm}^{-1}$ , the value of the force constant would have to be  $9.3 \times 10^5$  dynes/cm. The value of the C—O force constant is generally accepted to be very close to  $4.5 \times 10^6$  dynes/cm and that of the C=O bond to be about 12 in the same units. The value of 9.3 therefore cannot be ruled out of consideration. In this connection we have investigated the absorption of a thin layer of sodium acetate where resonance is known to be complete.<sup>15</sup> As Fig. 9 shows there is a particularly strong band at  $6.39 \mu$  or  $1575 \text{ cm}^{-1}$ . Further Edsall<sup>16</sup> from investigations of the Raman spectra of molecules containing the  $\text{COO}^-$  group came to the conclusion that the value for the unsymmetrical mode of

<sup>14b</sup> Pauling and Brockway, Proc. Nat. Acad. Sci. 20, 236 (1934).

<sup>15</sup> Zachariasen, Phys. Rev. 53, 917 (1938); Pauling and Sherman, Proc. Nat. Acad. Sci. 20, 340 (1934).

<sup>16</sup> Edsall, J. Chem. Phys. 5, 508 (1937).

this group is  $1580\text{ cm}^{-1}$ . Although those semi-quantitative arguments cannot be regarded as conclusive without further detailed investigation, the fact that the OH frequency is not altered nearly sufficiently to bring the hydrogen atom midway between the oxygens (the separation of which is  $2.67\text{\AA}$ ) makes it very difficult to see how the carbon-oxygen bond to which a hydrogen is firmly attached can be equivalent to the other to which a hydrogen atom is so very weakly attached.

On the basis of incomplete resonance in the carboxylic dimer, and a frequency in the monomer for  $\text{C}=\text{O}$  equal to  $1768\text{ cm}^{-1}$ , for  $\text{C}-\text{O}$  equal to  $1379\text{ cm}^{-1}$ , one would expect in the dimer two  $\text{C}=\text{O}$  frequencies and two  $\text{C}-\text{O}$  frequencies. The actual value of the  $\text{C}=\text{O}$  frequency in the dimer is consequently the mean of the frequencies observed in the Raman and infra-red. These are, respectively,  $1683\text{ cm}^{-1}$ <sup>17</sup> and  $1719\text{ cm}^{-1}$ , giving a mean of  $1701\text{ cm}^{-1}$ . This approximate method of treatment is only adopted to avoid the complication of a complete dynamical treatment of the problem at this stage. It shows sufficiently well, however, the considerable alteration in the  $\text{C}=\text{O}$  bond which occurs on association. An estimate of the approximate alteration in the interatomic distance during association is also of interest. This may be made using Clark's empirical relation between interatomic distance and vibration frequency for diatomic molecules.<sup>18</sup> We quite realize the approximations involved in such a procedure, and, of course, little reliance can be placed on the absolute values of the interatomic distances derived. However, the relative shift given in Table II must be very near the actual value and is of considerable use until a more complete analysis of the vibrations of the dimer can be achieved.

### The C—O frequency

In the foregoing we have made the assumption that there is a definite frequency which may be associated with the  $\text{C}-\text{O}$  bond in the  $\text{COOH}$  group and that this frequency occurs in the neighborhood of  $1400\text{ cm}^{-1}$  or,  $7\mu$ . Such an assumption is open to criticism on two grounds:

<sup>17</sup> This value is taken from the work of Angus, Leckie, and Wilson on the Raman spectrum of acetic acid. *Proc. Roy. Soc. A* **155**, 183 (1936).

<sup>18</sup> Clark, *Phil. Mag.* **18**, 459 (1934).

specifically, (a) that many authors from examination of the Raman spectra of other compounds (alcohols, glycols, etc.) have assigned a much lower value to this frequency<sup>19</sup> of about  $1050\text{ cm}^{-1}$  to  $1100\text{ cm}^{-1}$ ; more generally, (b) that one cannot associate frequencies with individual bonds. We shall not discuss (b) since this involves either a complete dynamical treatment of the problem or the quotation of a host of empirical data. Concerning (a), however, it may be remarked that the  $\text{C}-\text{O}$  bond is not necessarily the same in the alcohols as it is in the carboxylic acids.

When one comes to examine the spectra of the carboxylic acids one has the following facts to explain. The presence of a  $\text{COOH}$  group in a molecule seems to give rise to four characteristic absorptions in the infra-red, (1) near  $5.8\mu$  (2) near  $7\mu$  and  $8\mu$ , and (3) near  $10.7\mu$ .<sup>20</sup> The first of these we have already associated with the  $\text{C}=\text{O}$  bond; of the remaining three, the first does not seem to vary in position when one forms the ester whereas the other two do show considerable variations. This would indicate that the  $7\mu$  band is due to the  $\text{C}-\text{O}$  link whereas the  $8\mu$  and  $10.7\mu$  come from deformation vibrations (probably of the OH group, (2) in, and (3) out, of the plane of the group). A further argument in favor of the assignment of the  $\text{C}-\text{O}$  frequency at  $1400\text{ cm}^{-1}$  in these acids is that in the Raman spectrum of pure  $\text{Cl}_3\text{C}\cdot\text{COOH}$ <sup>21</sup> there is a line at  $1413\text{ cm}^{-1}$ , which disappears when the acid is in aqueous solution and is also absent in trichloroacetyl chloride. The latter fact provides strong evidence that it is not due to the  $\text{C}\cdot\text{Cl}_3$  group; the trichloro-derivative has been quoted as otherwise there is the great difficulty that  $\text{CH}_3$  and  $\text{CH}_2$

TABLE II. The change in the  $\text{C}=\text{O}$  distance on association.

MOLECULE	POSITION OF ABSORPTION BAND IN $\mu$	VIBRATION FREQUENCY IN $\text{cm}^{-1}$	$r_{\text{C}=\text{O}}$ IN $\text{\AA}$	$\Delta r_{\text{C}=\text{O}}$ $\text{\AA}$
Monomeric Acetic Acid	5.65	1768	1.195	0.016
Dimeric Acetic Acid	5.82	1701	1.211	

<sup>19</sup> Hibben, reference 11; Bonner, *J. Chem. Phys.* **5**, 293 (1937).

<sup>20</sup> Lecomte, "Structure des Molecules" in *Traité de Chimie Organique*, Vol. 2 (Masson et Cie., Paris, 1936).

<sup>21</sup> Magat, "Tables of Raman Frequencies" from Vol. 11 of *Annual Tables* (Gauthiers Villars, Paris, 1936) pp. 26-40, 26-42.

TABLE III. *The change in the C—O distance on association.*

MOLECULE	POSITION OF ABSORPTION BAND IN $\mu$	VIBRATION FREQUENCY IN $\text{cm}^{-1}$	$r_{\text{C—O}}$ IN Å	$\Delta r_{\text{C—O}}$ IN Å
Monomeric Acetic Acid	7.25	1379	1.298	-0.013
Dimeric Acetic Acid	6.94	1425	1.286	

groups each have prominent frequencies in this region.

Accepting this general interpretation of the absorption near  $7\mu$  we identify the band at  $6.94\mu$  as due to the dimeric C—O and that at  $7.25\mu$  as due to the same bond in the monomer. It is to be noted that, as for the C=O frequency, the monomeric absorption is very intense compared with the dimeric. The fact that the dimeric absorption is at a shorter wave-length than the monomeric indicates that the C—O bond strengthens on association, the frequency increasing from  $1393\text{ cm}^{-1}$  to  $1435\text{ cm}^{-1}$ . This shift is correlated with the change in internuclear distance in the same way as for the C=O frequency (Table III). Here it will be observed that for the C—O frequency in the dimer we have taken not the frequency corresponding to  $6.94\mu$  but the mean between this frequency and that

found in the Raman spectrum of trichloroacetic acid *viz.*  $1413\text{ cm}^{-1}$ . The latter is presumably the counterpart of the  $1680\text{ cm}^{-1}$  carboxyl Raman frequency. The result should be compared with that found for the C=O distance. There we found an extension of  $0.016\text{Å}$ : here we get a contraction of  $0.013\text{Å}$  on association. Again, we would stress that the absolute values of the distances must not be regarded as within less than 3 percent of the correct value but the differences are certainly significant and of the correct order of magnitude. It is particularly interesting to compare the distances for the C=O and C—O links with those found by x-ray methods by Robertson and Woodward.<sup>22</sup> They found  $1.24\text{Å}$  and  $1.30\text{Å}$ , i.e., a difference of  $0.06\text{Å}$ ; we get the corresponding figures to be  $1.211\text{Å}$  and  $1.285\text{Å}$ , giving a difference of  $0.074\text{Å}$ . The agreement is very satisfactory considering the nature of the approximations made in our calculations. It may be noted that if a value of  $1080\text{ cm}^{-1}$  is used for the C—O frequency, the corresponding distance comes out as  $1.376\text{Å}$ . This is additional evidence in favor of our assignment.

<sup>22</sup> Robertson and Woodward, J. Chem. Soc. 4, 1817 (1936).