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VIBRATIONAL SPECTRA OF SELECTED MONOHALOGENATED MONOCARBOXYLIC ACIDS

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FOREWORD

This report was prepared by the Chemistry Department, Miami University, Oxford, Ohio under USAF Contract F33615-70-C-1021. This contract was initiated under Project No. 7360, "Chemical, Thermal and Dynamic Properties of Materials", Task No. 736005, "Compositional, Atomic and Molecular Analysis". The work was administered and directed by the Air Force Systems Command, Air Force Materials Laboratory, Materials Physics Division, Analytical Branch (MAYA), Wright-Patterson AFB, Ohio. Mr. Freeman F. Bentley was the Project Engineer.

This report summarizes a portion of the work on the project carried out from May 1969 to April 1970. The work was carried out under the above contract and with Purchase Order D48715, Monsanto Research Corporation under USAF Contract F33615-67-C-1363.

It was submitted by the authors in July 1970.

The work was performed at Miami University. The major participants were Messrs. Thomas P. Carll and Walter Danison and Dr. J. E. Katon. Dr. J. E. Katon served as project leader.

This technical report has been reviewed and is approved.

Freeman F. Bentley

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ABSTRACT

The infrared spectra of sixteen monohalogenated monocarboxylic acids have been recorded in the range 4000-250 cm^{-1}. In addition the infrared and Raman spectra of iodoacetic acid and sodium iodoacetate have been recorded in the 4000-50 cm^{-1} region.

The spectra have been interpreted in terms of group frequencies that would potentially serve to identify and characterize halogenated acids. The approach has been primarily that of determining the effect of halogen substitution on the normal group frequencies of saturated unsubstituted acids. Temperature effects have been investigated in a preliminary manner on several of the acids. In many cases changes in the spectra are noted when the temperature is lowered. In view of the many polymorphic phases in which acids can exist, these temperature effects cannot be completely explained without considerable additional effort.

The vibrational spectra of iodoacetic acid and sodium iodoacetate were investigated in detail and assigned as a model for the spectra of the other acids. The data is most consistent with a hydrogen bonded dimer structure in the liquid and stable solid states. The monomer units are sufficiently strongly coupled so that "pseudo" C_{2h} selection rules are followed. There is no evidence for the existence of more than one rotational isomer at room temperature or below and the data are most consistent with a structure in which the iodine atom is trans, or nearly trans, to the carbon-oxygen single bond of the acid.

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SECTION I

INTRODUCTION

The vibrational spectra of organic acids have been widely studied by numerous investigators. Despite this, only a few of the acids have had their spectra analyzed in any detail. Although acetic acid has been studied by several groups[1-6], substituted acetic acids have received very little attention. Of the monohaloacetic acids, chloroacetic acid has received some study[7-9] and its spectra have been assigned[9]. The spectra of the other haloacetic acids have not been reported in any detail, although the infrared spectrum of iodoacetic acid in the carbonyl stretching region has been published[10] and the far infrared spectra of the monohaloacetic acids have been reported[11]. The vibrational spectra of the iodoacetate ion have been published along with a partial assignment[12].

In addition, the structures of the monohaloacetic acids are of interest from two points of view. Spinner[12] has suggested that the iodoacetate ion exists exclusively as the gauche form in both liquid and solid states whereas the chloroacetate ion exists exclusively as the trans form (the trans form is such that the iodine atom is in, or nearly in the CCO_2 plane. The gauche form is one in which the $-CH_2I$ group is rotated from the trans by approximately

120°). Thus, the conformational behaviors of the closely related iodoacetic acid and chloroacetic acid are of interest. Secondly, although it has been known for some time that solid chloroacetic acid exists in three polymorphic crystal forms, it has only been recently shown[13] that one of these is a hydrogen bonded dimer while the other two are hydrogen bonded polymers. It is therefore of interest to elucidate the nature of the hydrogen bonded structure of the other haloacetic acids.

This paper reports the complete vibrational spectra of iodoacetic acid and sodium iodoacetate along with proposed assignments. The structures of the two compounds are also discussed and it is shown that the observed data are most consistent with the trans conformation for both the acid and the ion and that the acid exists as a hydrogen bonded dimer in its normal solid form and probably in the liquid state.

The dimer structure is concluded to be proper since the infrared and Raman spectra show the large intensity alternations indicative of the presence of a center of symmetry. Although the presence of a center of symmetry (C_{2h} point group) would imply, by the Rule of Mutual Exclusion, that infrared active vibrations would not be Raman active and vice versa, these selection rules do not hold rigorously. This must be due to either intermolecular forces in the condensed phases in which the studies are carried out or to the fact that the hydrogen bonds are not as strong as regular bonds and therefore do not lead to the selection rules predicted by assuming the dimer to be a single molecule.

SECTION II

EXPERIMENTAL

Iodoacetic acid and sodium iodoacetate were obtained from Matheson, Coleman and Bell. The acid was purified by three vacuum sublimations. The salt was purified by dissolving it in absolute methanol followed by precipitation through the addition of absolute ethanol, filtering, washing with ethanol and drying.

Iodoacetic acid-d_1 (oxygen deuterated) was prepared by three successive exchanges of the light acid with heavy water. This procedure yielded a product that had undergone only about 60-70% exchange. This degree of exchange was sufficient, however, to allow assignment of the OH and OD vibrational modes with reasonable surety. The amount of material obtained was insufficient to record a Raman spectrum with the instrumentation available. It is difficult to get good exchange with iodoacetic acid due to its physical and chemical properties. The material tends to decompose at temperatures slightly above its melting point (82°C), but has a significant vapor pressure at room temperature. Separation of iodoacetic acid from D_2O by distillation under reduced pressure could not be accomplished, due either to the vapor pressure of iodoacetic acid or azeotrope formation. Iodoacetic acid is quite soluble in water, presenting further separation difficulties.

Infrared spectra of iodoacetic acid (solid film, Nujol and hexachlorobutadiene mulls, KBr pellet, solution in CCl_4 and CS_2) and sodium iodoacetate (Nujol and hexachlorobutadiene mulls and KBr

pellets) were recorded on Perkin-Elmer Model 225 and 301 infrared spectrophotometers. Raman spectra of the solid acid were obtained on a Spex Ramalog System and those of the solid salt were obtained on a Cary Model 81 Laser Raman Spectrometer. Both Raman spectra were obtained using argon laser excitation. Low temperature infrared spectra were recorded using a RIIC VLT-2 cell with liquid nitrogen coolant.

The vibrational absorption bands of solid iodoacetic acid and sodium iodoacetate along with their proposed assignments are listed in Tables I and II. A typical infrared spectrum (4000-200 cm^{-1}) of a mixed mull of iodoacetic acid is reproduced in Fig. 1 and that of a mixed mull of sodium iodoacetate in Fig. 2 (the breaks in the curves indicate the ranges covered by the two mulling agents). Typical Raman spectra of the two compounds are reproduced in Figs. 3 and 4. A typical infrared spectrum (4000-200 cm^{-1}) of iodoacetic acid-d_1 (about 65% deuterated) in a KBr pellet is reproduced in Fig. 5.

The estimated maximum error in the observed frequencies are $\pm$ 2 cm^{-1} in the infrared spectra and $\pm$ 4 cm^{-1} in the Raman spectra. It is generally assumed that agreement of the two spectra within $\pm$ 6 cm^{-1} corresponds to one vibration or accidental degeneracy of two vibrations. If the frequencies of two bands disagree by more than this amount it is generally assumed that they correspond to two different vibrations.

The solution infrared spectra of iodoacetic acid are essentially identical to those of the solid. The infrared spectra of both the acid and the salt were recorded at about 110°K, but

neither compound showed any additional features at this temperature other than the usual band sharpening resulting in improved resolution of overlapping bands.

SECTION III

VIBRATIONAL ASSIGNMENT

The assignments of the vibrational spectra of iodoacetic acid and sodium iodoacetate are aided by the fact that a number of the vibrations are well-known group frequencies[14]. The technique of comparing the spectrum of an acid with that of its corresponding salt has also been shown to be valuable since many of the vibrations are not greatly shifted in the two compounds[1, 15-16]. Those that do shift considerably (e.g. carbonyl stretching vibration) are mostly understood from previous work. In addition, the replacement of the OH group by the OD group in the acid is useful for the assignment of the acid and the spectral effects which occur upon this substitution are well-known[17].

1. Sodium Iodoacetate

Sodium iodoacetate has been previously assigned by Spinner[12], but his infrared data extended only to 600 cm^{-1} and his Raman data were of an aqueous solution and of rather poor quality. There are, therefore, a number of disagreements between this work and that of Spinner. These will be discussed with regard to each vibration where disagreement exists.

In the 4000-700 cm^{-1} range, the vibrational spectra of sodium iodoacetate have relatively few bands of an intensity expected for fundamental vibrations. It is therefore relatively easy to make a vibrational assignment from group frequencies alone. Some of the vibrations are shifted somewhat from normal group vibrations, but

the intensity situation is such that the present assignment has practically no alternatives.

There are only two bands in the CH stretching region and their assignment is straightforward from their relative intensities in both the infrared and Raman spectra. The higher frequency band is more intense in the infrared and the lower frequency band is more intense in the Raman as expected for antisymmetric and symmetric vibrations, respectively. The two frequencies disagree rather widely from Spinner's values which were taken from the infrared spectrum, but he used a sodium chloride prism instrument with the concomitant poor dispersion in this region.

The antisymmetric CO_2 stretching frequency is certainly the very intense infrared band at 1583 cm^{-1}, but there are difficulties in the Raman spectrum in this region. A medium band occurs at 1618 cm^{-1} and this difference is beyond experimental error. It is exceedingly difficult to rationalize this band as anything except a fundamental, however, because of its intensity. In addition to this band, there is a weak Raman band at 1583 cm^{-1}, which agrees with the infrared value. The proper assignments in the Raman spectrum are not clear, therefore. It is tempting to ascribe the 1618 cm^{-1} band to νCO_2 (antisymmetric) and explain the difference from the infrared as perhaps a crystallinity effect of some sort. It may, however, be an artifact whose origin is unknown and the 1583 cm^{-1} band may be the true fundamental. Both bands can be fitted by a combination, but the fit for the 1583 cm^{-1} band is clearly better.

The assignment of the CH_2 scissors vibration seems clear from its group frequency character. The band possesses the usual intensity and frequency characteristics of the vibration and does not shift on going from the salt to the acid. The υCO_2 (symmetric) assignment is in the normal range and shifts downward in the acid, as expected.

The next two lower frequency bands in the infrared are clearly due to the CH_2 wagging and twisting modes. Spinner has reversed the assignment given here, but it is generally felt that the wag occurs at higher frequencies than the twist[18-23]. These two modes are no doubt highly mixed, however.

The assignment of υCC seems clear from the Raman intensity and agrees with Spinner's assignment, as does the assignment of the CH_2 rocking mode.

The spectra in the 600-700 cm^{-1} region present an interesting problem. There are two infrared bands in this region, one medium to strong at 671 cm^{-1} and one medium at 650 cm^{-1}. There are three Raman bands, all very strong, at 678, 665 and 653 cm^{-1}. Spinner observed only one band in this region in both the infrared (671 cm^{-1}) and Raman (665 cm^{-1}) although he did observe a Raman band at 598 cm^{-1}. Spinner assigned this one band as the CO_2 scissors mode, which is expected to be in this region. By comparison with the C-Cl and C-Br stretching frequencies in the corresponding chloroacetate and bromoacetate ions, Spinner expected the C-I stretch of iodoacetate ion to be in this region. Since he could not observe a second band, he interpreted his results in terms of

a different structure for iodoacetate ion than that of chloroacetate and bromoacetate ions (gauche instead of trans). Our results show clearly that there are at least two vibrations in this region. We interpret the two very strong Raman bands at 678 and 665 cm^{-1} as being crystal splitting components of the C-I stretching mode. The infrared spectrum does not show this splitting well, although there is an indication of it. We then assign the 650 cm^{-1} infrared and 653 cm^{-1} Raman band to the CO_2 scissors mode. The CO_2 scissors is about 20 cm^{-1} lower, then, than the corresponding mode in chloroacetate and bromoacetate ions[12, 24], but is probably shifted by Fermi resonance with the very strong υCI. The only other α-iodocarbonyl compound whose spectra have been studied is iodoacetone[25]. The CI stretching vibrations in this compound, which exists as rotational isomers in the liquid state, are 617 cm^{-1} and 566 cm^{-1}. Spinner reports a very strong Raman band at 491 cm^{-1} which he assigns as υCI. We are unable to confirm this and find no band in either the infrared or Raman spectrum near this frequency.

There are four fundamental vibrations that are expected to occur below 600 cm^{-1}. These are the CO_2 wagging and rocking modes, the CCI bending mode and the torsion. These modes are probably strongly coupled, especially the first three, so that their description must be very qualitative. Spinner assigns the rock at the highest frequency followed by the wag. This is the reverse from the usual relative frequencies of these two vibrations[1, 19, 24].

The CCI bending mode is assigned in agreement with that of iodoacetone[25]. It also has the expected shift to lower frequencies when compared to the chloro- and bromo- compounds[24].

This leaves two observed bands in the low frequency region, at 236 and 127 cm^{-1}. It is felt that the 236 cm^{-1} band is too high to be the torsion and so it is assigned as a lattice mode and the 127 cm^{-1} band is tentatively assigned to the torsion. Spinner assigns a 166 cm^{-1} Raman band to the torsion, but we are unable to find this band. It may, however, correspond to the band we observe at 190 cm^{-1} and which we assign as the CCI bending mode.

2. Iodoacetic Acid

Although it is often thought that organic carboxylic acids in pure condensed phases exist in the hydrogen bonded dimer structure, it has been shown recently that this is not always the case, particularly with respect to the simpler members of the class. Thus, acetic acid exists as a hydrogen bonded polymer in the common solid phase, although it appears to be mostly a dimer in the liquid phase[4]. Chloroacetic acid exists in three polymorphic crystal forms, the most stable of which is a polymeric form, while of the other two, one is polymeric and the other dimeric[13]. As expected, the difference in these two structures is reflected in their vibrational spectra. The main point of differentiation arises from the presence of a center of symmetry in the dimeric structure which is not present in the hydrogen bonded polymer, thus the vibrations occur in pairs which are symmetric and antisymmetric

to the center of symmetry.

Spectrally, this center is reflected by the fact that symmetric vibrations tend to be strong in the Raman spectrum and antisymmetric vibrations tend to be strong in the infrared spectrum. Both vibrations often appear in both spectra because (1) the coupling between monomer units is sufficiently great that they often occur at different frequencies (2) the selection rules do not hold rigorously because of intermolecular forces occuring in the solid state and/or the hydrogen bonds are not as strong as normal chemical bonds. In the discussion of the assignment of such a structure it is convenient to speak of these vibrations as being in-phase or out-of-phase with respect to the two monomer units. The in-phase will be those which are symmetric to the center of symmetry and the out-of-phase those which are antisymmetric to this symmetry element. This situation has been discussed in detail with regard to the spectra of liquid acrylic acid, which is primarily a hydrogen bonded dimer[16].

Consideration of the spectra of iodoacetic acid shows that the Raman-infrared intensity reversals typical of the dimer structure are present. This results in a number of strong bands in the spectra which can only be assigned reasonably on the basis of a dimer structure. The assignment is therefore discussed in these terms.

The υOH band is unmistakeable since it is the broad, intense band commonly observed in acids in the 3000 cm^{-1} region. It is

centered at about 3000 cm^{-1} and somewhat obscures the two υCH_2 modes, but these can be readily observed in the Raman spectrum where hydrogen bonding effects are very much less than in the infrared spectrum.

The carbonyl stretching vibrations clearly occur as an in-phase, out-of-phase pair, a strong infrared band at 1680 cm^{-1} being the out-of-phase carbonyl stretch and a medium Raman band at 1669 cm^{-1} being the in-phase carbonyl stretch. This splitting of the carbonyl stretching vibration was early recognized as evidence for dimer structure by Davies and Sutherland[26].

The CH_2 scissors and wag vibrations seem clear from their positions and their constancy in the spectrum of the oxygen deuterated compound. The scissors vibrations are not split into in-phase, out-of-phase pairs, but they would not be expected to be strongly coupled. The wag appears to be split into pairs and therefore must be somewhat coupled.

The OH in-plane bending and CO stretching vibrations are assigned as in-phase, out-of-phase pairs. This is based on the fact that the infrared band at 1390 cm^{-1} shifts downward in the OD compound to 1025 cm^{-1} and both the 1247 cm^{-1} and 1156 cm^{-1} infrared bands shift upward to 1340 cm^{-1} and 1246 cm^{-1}, respectively. (Note that the band at about 1246 cm^{-1} does not change intensity in the deuterated compound while all others mentioned here do change a great deal in the expected manner. This is interpreted as due to the loss of the 1247 cm^{-1} band of the light compound upon

deuteration with a concomitant gain of the 1246 cm^{-1} band. Both νCO bands are then shifted upward on deuteration by 90 cm^{-1}). It is well known that these two vibrations couple strongly in the OH compound, but uncouple in the OD compound and the observed shifts are approximately those predicted[17]. It is noted that the in-phase OH bending and the out-of-phase CO stretching modes are not observed in both spectra (the former not being observed in the infrared and the latter not being observed in the Raman). It is not unusual for the spectra of dimeric acids to show this effect. The appearance of a formally forbidden band is a strong function of the degree of coupling, the detailed nature of intermolecular forces, the band intensities, etc. which cause experimental observation of selection rule breakdown of a different degree with different vibrations. The spectrum of the OD compound offers strong evidence for the present assignment, however.

Although the 1247 cm^{-1} band is very strongly overlapped by the 1270 cm^{-1} band at room temperature, cooling to about 110°K. resolves these two bands reasonably well. The strong Raman band at 915 cm^{-1} must certainly be the υCC in-phase stretch. The υCC out-of-phase stretch should be observed in the infrared spectrum. Unfortunately, the broad γOH vibration tends to obscure it in most spectra, but there is evidence for a weak band near 910 cm^{-1} in the infrared spectrum of a mixed mull of the acid. The broad 891 cm^{-1} band in the infrared spectrum is certainly the γOH and shifts to 598 cm^{-1} in the OD compound, confirming this assignment.

The in-phase γOH is apparently a part of the broad, weak Raman band at 845-860 cm^{-1}, another part of which is the CH_2 rocking mode, whose out-of-phase component occurs at 850 cm^{-1} in the infrared.

The CO_2 scissors mode occurs as an in-phase, out-of-phase pair at about the expected frequency as does the υCI mode. The latter does not appear to split into an in-phase, out-of-phase pair. Carbon-halogen stretching frequencies are known to be quite constant, however, if their local environment is the same[27, 28].

The CO_2 wagging vibration and the CCO in-phase bending mode are probably strongly coupled, as is the CCI bending mode. The description of these vibrations is therefore very approximate. The latter two appear as in-phase, out-of-phase pairs, but the CO_2 wag does not, within experimental error. The major problem with the present assignment is the very strong Raman band at 488 cm^{-1}. It is considerably stronger than expected for the CO_2 wagging vibrations, but appears to be at too high a frequency for the CCI bending frequency. It is possible that its high intensity is due to coupling with the CCI bending frequency, however. In bromoacetic acid[24] a similar very strong Raman band occurs at 371 cm^{-1}. This also appears to be at too high a frequency for a CCBr bending mode. There is clearly no mass relationship between the two and the high intensities observed must therefore indicate that both bands are due to vibrations which couple strongly, but in

a different manner, with other vibrations.

The remaining two infrared bands at 157 cm^{-1} and 108 cm^{-1} are assigned as a lattice mode and the hydrogen bond stretching mode, respectively. The lower of the two is assigned as the hydrogen bond stretch by comparison with bromoacetic and chloroacetic acids[24] and the known hydrogen bond stretch sensitivity to mass effect of the alpha substituent[29]. The 172 cm^{-1} Raman band could be either the symmetric hydrogen bond stretching mode or a lattice vibration.

SECTION IV

STRUCTURAL CONSIDERATIONS

The lack of agreement between the infrared and Raman spectra of crystalline iodoacetic acid clearly indicate a center of symmetry and therefore that the structure is dimeric in nature. The selection rules do not hold rigorously, but this has been shown to be the case with other dimeric acids in condensed phases[16].

The solution infrared spectrum of iodoacetic acid is not significantly different from those of the crystalline solid at either room temperature of near liquid nitrogen temperature. This indicates that the energy difference between rotamers is too great for more than one to be present in significant concentration at room temperature or below. The results on the sodium salt are on the solid state only, but the frequency agreement of most vibrations with those of the acid indicate that the rotational conformation of the salt is the same as that of the acid.

The rotational conformation of the two compounds is not very clear, but appears to be close to trans (the iodine atom being trans to the C-O bond of the acid). Evidence for this structure is admittedly not very strong and is based only on analogy with other compounds, however. Spinner[12] summarizes the data obtained on other iodo compounds up to 1964. The υCI bands of the trans rotamers are at 620-590 cm^{-1} and those of the gauche rotamers are 570-490 cm^{-1}. Iodoacetone[25] has CI bands assigned at 617 and 566 cm^{-1}, but these are not assigned as a trans-gauche pair, but as more polar-less polar isomers, respectively. Spinners assignment

of υCI for sodium iodoacetate at 491 cm^{-1} falls within the range for the gauche isomer. The present assignment of υCI for the salt and acid at 678 cm^{-1} and 632 cm^{-1}, respectively, does not fall in either range, but is clearly closer to the trans range. We therefore feel that the evidence indicates the trans-like form, as being more probable, in contrast to Spinner's conclusions. It appears that a positive determination of the structure, <u>with respect to the exact conformation</u>, requires an x-ray diffraction study. Attempts to perform this work are currently underway in these laboratories.

Table I

The Observed Vibrational Spectra of Iodoacetic Acid (in cm^{-1}) and their Assignment

Infrared Mixed Mull	Raman Solid	Assignment
3100-2900 m,vb		υOH
3058 m	3058 m	υCH_2 antisym.
	2993 s	υCH_2 sym. (ip)
2985 w		υCH_2 sym. (op)
2630 w		
2300 w		
2160 w		
1810 w		915 + 891 = 1806
1712 w-m		1247 + 458 = 1705
		1270 + 434 = 1704
1680 vs		υC=O (op)
	1669 m	υC=O (ip)
1532 w		2 x 766 = 1532
1427 s	1426 w	CH_2 scissors
	1396 vw	δOH (ip)
1390 m		δOH (op)
	1278 w	CH_2 wag (ip)
1270 m {≈110°K		CH_2 wag (op
1247 s		υC-O (op)
1156 m	1163 vs	υC-O (ip)
1086 s	1091 w	CH_2 twist
910 w	915 s	υCC^2
891 s		γOH (op)
850 w	845-60 w, b	CH_2 rock, γOH (ip)
	766 m	CO_2 scissors (ip)
752 m		CO_2 scissors (op)
632 s	636 vs	υCI^2
483 w	488 vs	CO_2 wag
458 m		CCO bend (op)
	434 m	CCO bend (ip)
	214 s	CCI bend (ip)
188 m		CCI bend (op)
	172 w	υH-Bond (sym.)?
157 w		lattice?
108 w		υH-Bond (antisym.)

s = strong, m = medium, w = weak, v = very, op = out-of-phase, ip = in-phase, sym = symmetric, antisym = antisymmetric, υ = stretch, δ = in-plane bend, γ = out-of-plane bend (the plane is that of the two $-CO_2H$ groups of the cyclic dimer).

Table II

The Observed Vibrational Spectra of Sodium Iodoacetate (in cm^{-1}) and their Assignment

Infrared Mixed Mull	Raman (Solid)	Assignment
2991 m	2990 s	υCH_2 antisym.
2941 w	2940 s	υCH_2 sym.
1583 vs	1618 m (?)	υCO_2 antisym. (678+925=1603
	1583 vw	1395 + 190 = 1585
	1562 vw	1370 + 190 = 1560
1429 s	1431 m	CH_2 scissors
	1398 vw	855 + 548 = 1403
1397 s	1395 m	υCO_2 sym.
1389 w, sh		
1368 s	1370 m	CH_2 wag
1177 s	1177 vs	CH_2 Twist
	1126 w	
1114 w		925 + 190 = 1115
1055 vw		925 + 127 = 1052
972 vw		855 + 127 = 982
923 m	925 s	υCC
	865 vw	678 + 190 = 868
853 m	855 w	CH_2 rock
771 vw		653 + 127 = 780
671 m-s	678 vvs, 665 vs	υCI
650 m	653 vs	CO_2 scissors
548 w		CO_2 wag
359 m	360 vs	CO_2 rock
236 w		lattice (?)
188 w-m	190 s	CCI bend
127 w		torsion(?)

s = strong, m = medium, w = weak, v = very, op = out-of-phase, ip = in-phase, sym. symmetric, antisym. = antisymmetric, υ = stretch.

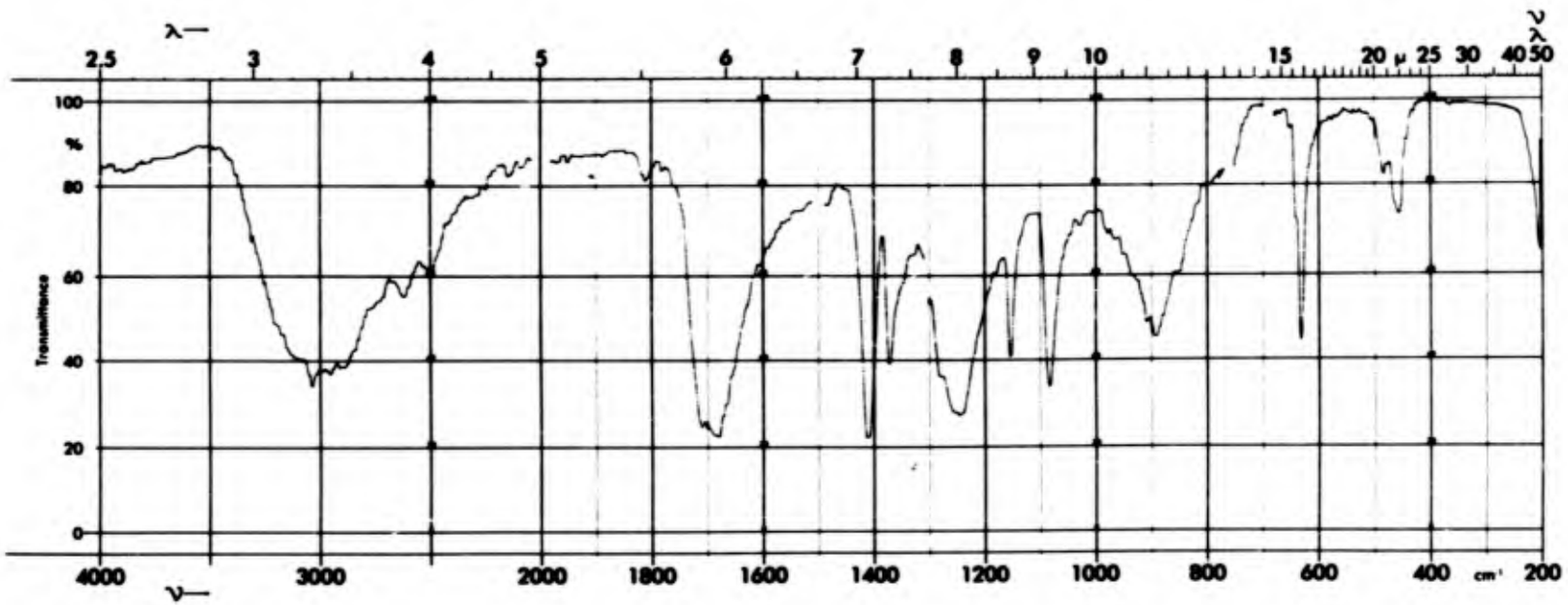

Figure 1. The Infrared Spectrum of Iodoacetic Acid (mixed mull).

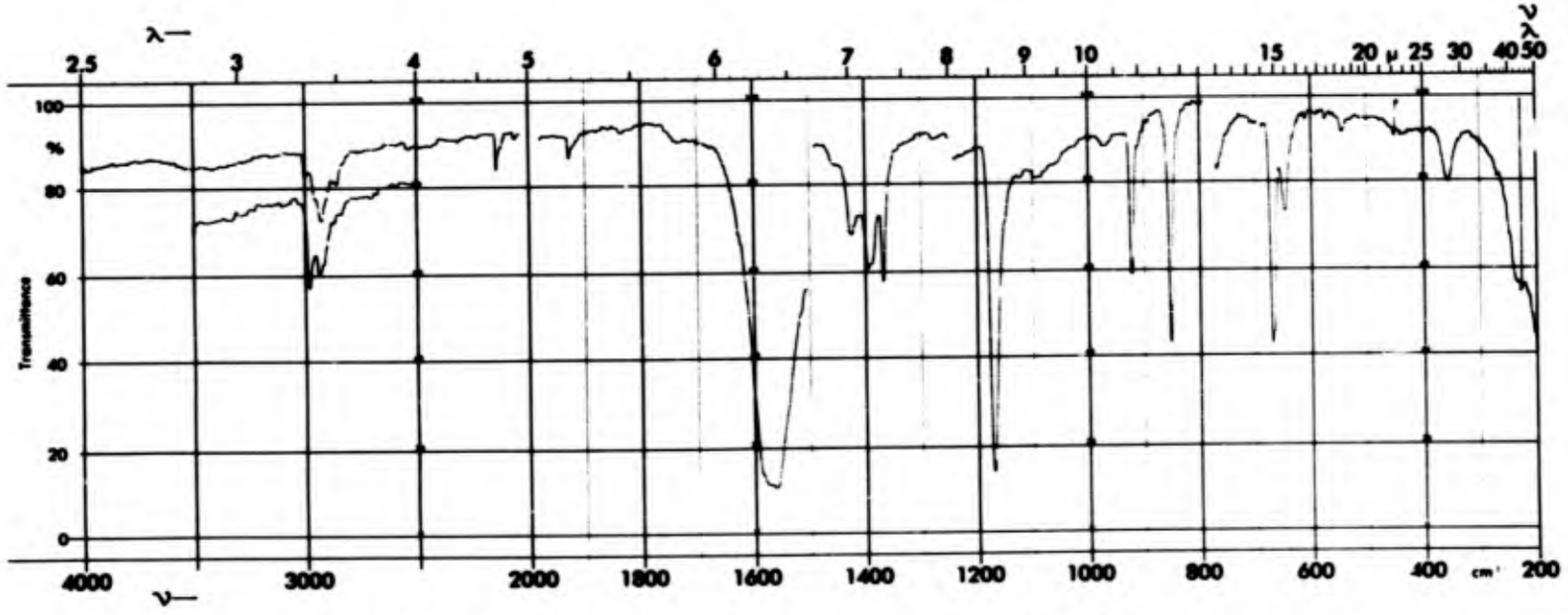

Figure 2. The Infrared Spectrum of Sodium Iodoacetate (mixed mull).

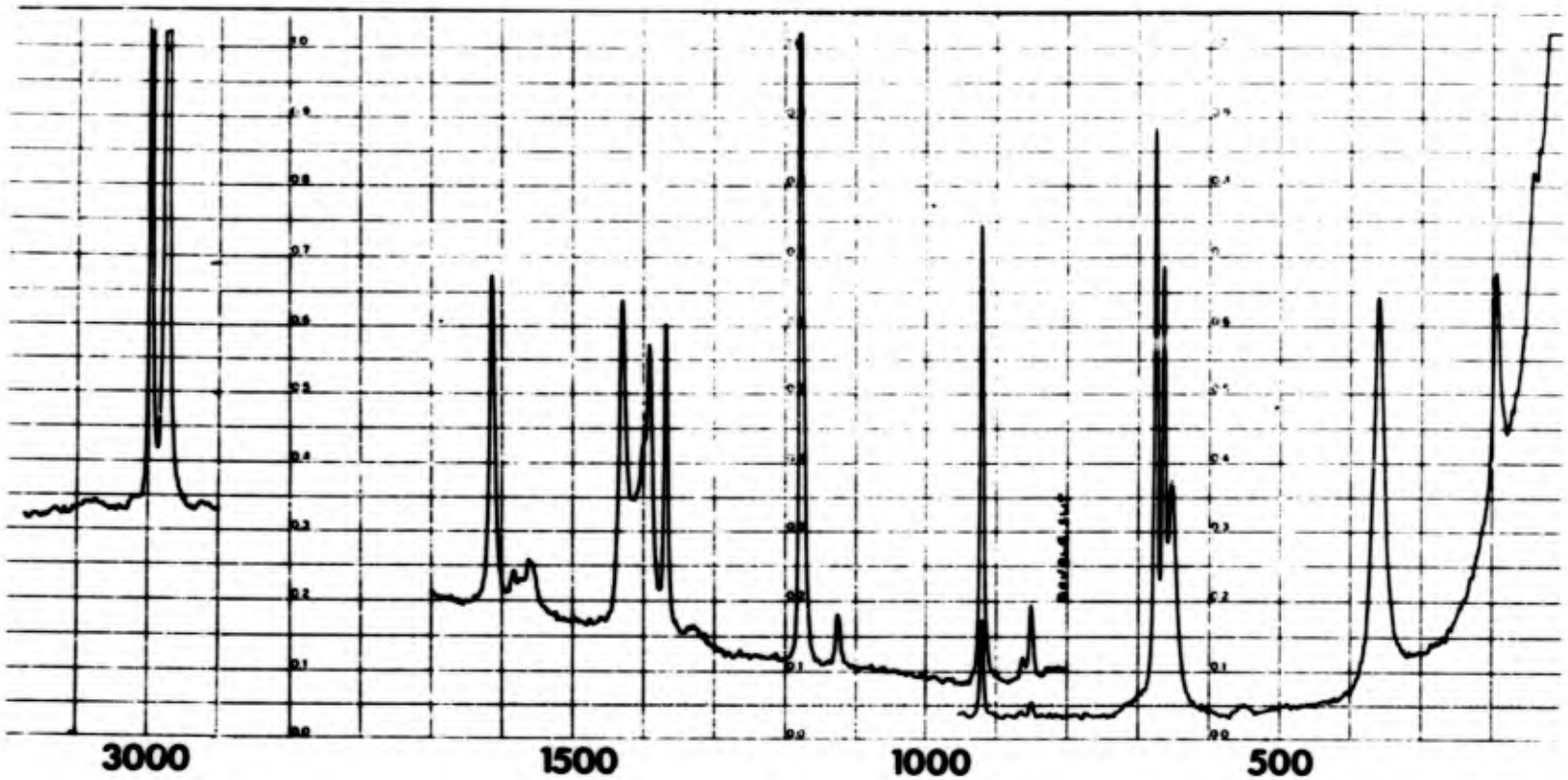

Figure 3. The Raman Spectrum of Sodium Iodoacetate (Powder).

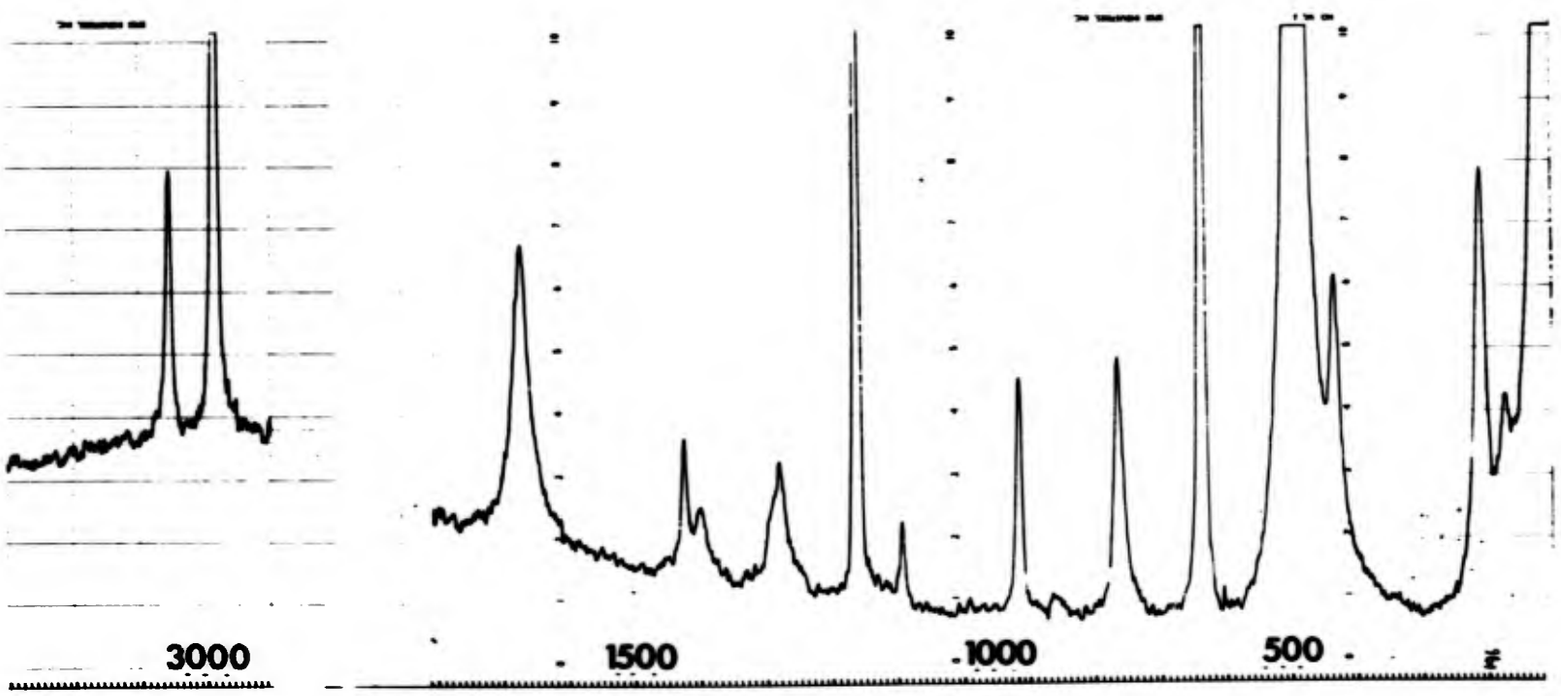

Figure 4. The Raman Spectrum of Iodoacetic Acid (Crystals).

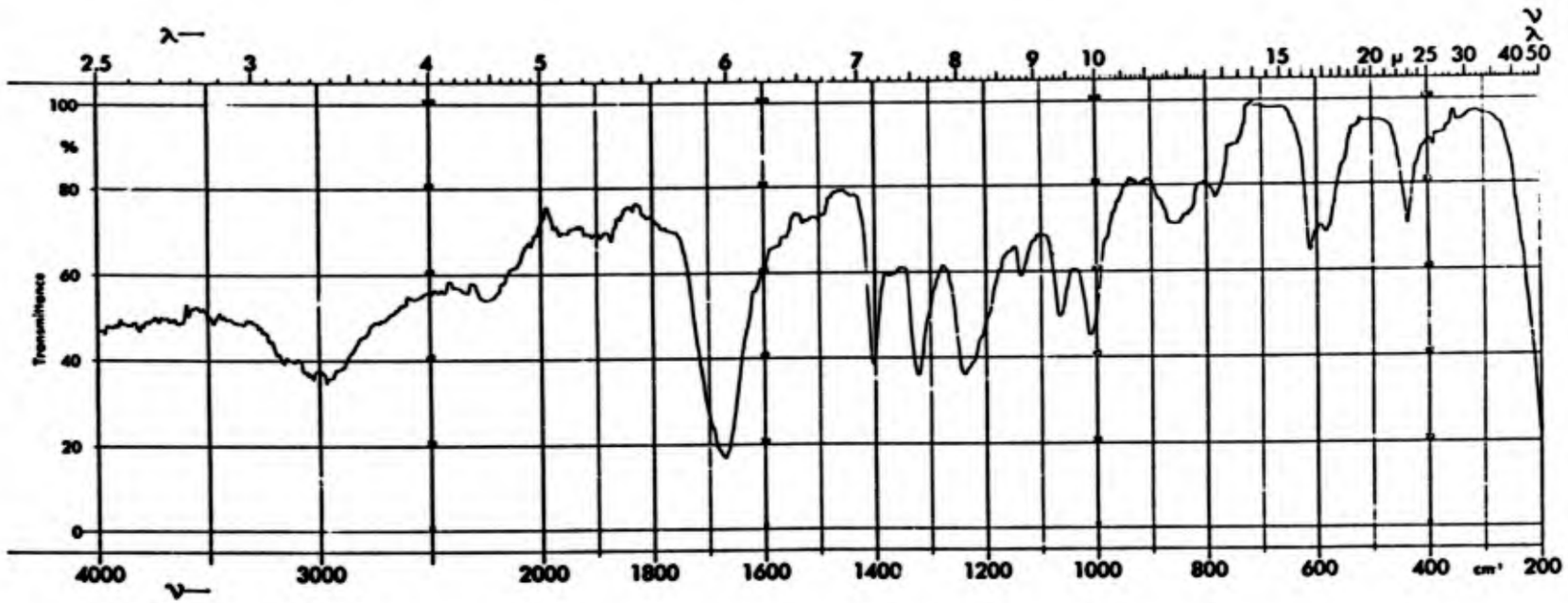

Figure 5. The Observed Infrared Spectrum of

CH_2ICOOD - KBr pellet

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THE CHARACTERISTIC GROUP FREQUENCIES OF MONOHALOGENATED MONOCARBOXYLIC ACIDS BETWEEN 4000 CM^{-1} AND 200 CM^{-1}

SECTION I

INTRODUCTION

The infrared group frequencies of halogenated monocarboxylic acids are of interest as an aid in identifying compounds by means of their infrared spectra. In recent years several studies of aliphatic monocarboxylic acids have been undertaken[1-4]. In addition, the spectra of acetic acid[5-9] and formic acid[10-13] have been studied extensively. There have been isolated infrared and/or Raman spectra determined for several substituted acetate ions[14-21], but no systematic study of the effects of substitutents on the vibrational spectra of monocarboxylic acids has been reported other than the work by Fonteyne[22] on three trihaloacetic ions, Spinner's[23] study of some selected substituted acetate ions, and Randi and Lorenzelli's[24] study of the far infrared spectra of monohaloacetic acids.

This section of this report is concerned with the group frequencies of a number of monohalogenated aliphatic monocarboxylic acids in the range from 4000 cm^{-1} to 200 cm^{-1}. All the acids were studied at room temperature and the liquid acids were also studied at sub-ambient temperatures. The low temperature studies must be viewed as preliminary studies only. Because acids are particularly susceptible to polymorphism, changes observed in

their spectra as a function of temperature must be interpreted with caution. In no cases were low temperature effects studied in detail so that nothing is known about possible polymorphs of these compounds.

SECTION II

EXPERIMENTAL

The acids studied are as follows: chloroacetic acid, bromoacetic acid, iodoacetic acid, 2- chloropropanoic acid, 3-chloropropanoic acid, 2-bromopropanoic acid, 3-bromopropanoic acid, 3-iodopropanoic acid, 2-chlorobutanoic acid, 3-chlorobutanoic acid, 4-chlorobutanoic acid, 4-chloropentanoic acid, 5-chloropentanoic acid, 2-bromohexanoic acid, 2-bromodecanoic acid and 2-chloro-4-methylhexanoic acid. All of the above acids were obtained from commercial sources, and were used without further purification. The infrared spectra were recorded on Perkin-Elmer Models 421 and 225 infrared spectrophotometers using cesium iodide optics to utilize the full range of the instruments.

The low temperature spectra were obtained using a Research and Industrial Instruments Variable Low Temperature Unit, VLY-2, using liquid nitrogen as a coolant. Of the liquid acids, the only one that did not appear to crystallize upon cooling to liquid nitrogen temperature was 2-bromohexanoic acid, and it appeared to form a glass. It is, therefore, not included in the data for the solid state acids.

For the room temperature spectra the solid acid samples were run as Nujol mulls, and the liquid-state acid samples were run neat as capillary films.

SECTION III

RESULTS

The room temperature spectra of the acids are reproduced in Figures 1-15 and their major absorption bands are tabulated in Table I. The low temperature spectra are reproduced in Figures 16-22 and their major absorption bands are tabulated in Table II. The group frequency data are summarized in Figure 23 for the region 4000 cm^{-1} to 200 cm^{-1}.

A Room Temperature Acids

In the region between 4000 cm^{-1} and 2000 cm^{-1} all the acids displayed the typical, broad, hydrogen bonded OH stretching absorption with several sub-maxima. This absorption occurs in the range 3200 cm^{-1} to 2850 cm^{-1} for all the acids. In general the frequency range for a given acid shifts to lower frequencies in the order Cl>Br>I when the halogen appears at the same position in the acid molecule. The range also shifts to lower frequencies as the chain length of the acid increases, i.e., chloroacetic>2- chloropropanoic>2-chlorobutanoic. A further observation is that the span of the range decreases as the chain length increases.

The next group frequency observed is a range from 1740 cm^{-1} to 1705 cm^{-1} for all of the acids studied except 3-iodopropanoic and iodoacetic. These compounds absorb at 1680 cm^{-1}. The range is 1740 cm^{-1} to 1710 cm^{-1} for the α-substituted acids as a group. The α-chloro compounds always absorb at the higher end of the range (1725-1735 cm^{-1}).

The band is observed as being of very strong intensity. For a given acid the frequencies fall Cl>Br>I for substituents at the same position on the acid. In 4-chloropentanoic and 5-chloropentanoic acids there was a slight shift in the frequency of this absorption band. In 2-chloropropanoic and 3-chloropropanoic acids a shift of 20 cm^{-1} was observed with the former being at a higher frequency. In the series of chlorobutanoic acids a 10 cm^{-1} shift was observed between 2-chloro- and 3-chlorobutanoic acids while a 7 cm^{-1} shift was observed between 3-chloro- and 4-chlorobutanoic acids (1725 cm^{-1}>1715 cm^{-1}>1708 cm^{-1}).

As previously noted, it the iodo substituted acids are excluded from the correlation, the range for all the rest of the acids becomes 1740 cm^{-1} to 1705 cm^{-1}. In that no other iodo compounds were studied, it cannot be determined whether iodine substitution in longer chain length acids causes a great lowering of this frequency. It seems more likely, however, that these compounds differ structurally from the others in some manner, which would explain the observed results in a manner consistent with other observations.

The 1400 cm^{-1} region of the spectrum yield another group frequency range. For all the acids studied a range of 1430 cm^{-1} to 1400 cm^{-1} was observed. The band is of medium to strong intensity in all cases. There were no trends observable with respect to either halogen series, halogen position, or chain length. Since this band is probably due to the CH_2 scissors vibration it is not a very useful correlation. Nearly all compounds containing a CH_2 group absorb in this region. There is almost always a second band

very near this band, usually at somewhat lower frequency. In many cases they overlap and in the cases where only one is observed it may be due to failure to resolve the second band due to strong overlap.

A range from 1260 cm^{-1} to 1200 cm^{-1} is another group frequency for the acids studied. The absorption band is of medium to strong intensity in all cases. Here, again, there were no observable trends regarding the halogen atom, or the chain length of the acid molecule. In the bromopropanoic acids two bands appear in this region. They are of strong intensity and are separated by about 10 cm^{-1}.

An additional group frequency range was observed from 940 cm^{-1} to 890 cm^{-1} for all the acids studied. For the α-substituted acids the range is 930 cm^{-1} to 890 cm^{-1}. The band generally occurs as a medium intensity absorption, but is of strong intensity in some cases. It is usually rather broad. Again, there were no observable trends.

The next group frequency range is from 690 cm^{-1} to 575 cm^{-1} and includes all the acids studied. If 3-iodopropanoic acid is excluded from the correlation a range of 690 cm^{-1} to 630 cm^{-1} results. The absorption band is observed as being of medium to strong intensity. For this frequency range too, there were no observable trends with respect to halogen series, halogen placement, or acid chain length.

The frequency range between 525 cm^{-1} to 420 cm^{-1} is also an observed group frequency for the acids studied. The band is of

weak to medium intensity and there are, again no observable trends.

The last group frequency range observed was from 365 cm^{-1} to 320 cm^{-1}. It is a band of medium intensity. The occurrence of this band is restricted to those acids of greater chain length than the haloacetic acids, with 3-iodopropanoic acid also being excluded. For the remaining acids, no trends of any type were observed.

B. Solid-State Acids

This classification includes both the acids that are solids at room temperature, and the acids which are liquids at room temperature, but that crystallize upon cooling to liquid temperature.

The first group frequency is the range from 3200 cm^{-1} to 2800 cm^{-1}. This band is of medium intensity, is broad, and contains several sub-maxima. In most cases the range shifted to lower frequency in the order Cl>Br>I if the halogen is substituted at the same position in a given acid. This trend is most obvious in the halogenoacetic acids. There were no apparent trends with respect to the chain length of the acid molecules.

The frequency range of 1740 cm^{-1} to 1680 cm^{-1} is observed as a group frequency for all of the acids studied. The range is from 1740 cm^{-1} to 1710 cm^{-1} for the α-substituted acids. The absorption band is observed as a very strong band. In most cases the frequencies for a given acid fall Cl>Br>I if the halogen appears at the same position in the acid molecule. This is, however, not the case for the 3-halopropanoic acid series. The compounds which absorb at the lower end of the range might be polymeric rather than dimeric as

previously discussed. The 3-halopropanoic acids would seem to be interesting candidates for structural elucidation work in this regard.

The band also shifts to lower frequency as the chain length of the acid increases, i.e., acetic acid>propanoic>butanoic>pentanoic acid. A shift to lower frequency is also observed as the halogen substitution progresses in the order $\alpha>\beta>\gamma$.

The next group frequency observed is the range from 1440 cm^{-1} to 1410 cm^{-1}. All the acids studied have a medium to strong absorption band in this region. The α-substituted acids all have a medium to strong absorption band in the region between 1430 cm^{-1} and 1410 cm^{-1}. The frequency position of this band showed no apparent dependency upon the halogen position or the chain length of the acid. Again, there is usually a second medium to strong band near the correlation band.

The range from 1260 cm^{-1} to 1220 cm^{-1} is also an observed group frequency for all the acids studied. The above range is the same for all the α-substituted acids, but the range is 1260 cm^{-1} to 1230 cm^{-1} if the acid is substituted at the β or γ positions. In all cases the band is of medium to strong intensity. If the range is extended to 1260 cm^{-1} to 1200 cm^{-1} then all the acids studied show a strong absorption band. A further observation is that all the propanoic acids show two strong bands in this region. There were no other observable trends.

The next group frequency range observed is from 890 cm^{-1} to 950 cm^{-1}. All the acids studied have a medium to strong absorption

band in this region. The range becomes 890 cm^{-1} to 940 cm^{-1} if the α-substituted acids are considered as a group. There are, again, no apparent trends with respect to either halogen series, halogen position, or chain length.

The range from 680 cm^{-1} to 630 cm^{-1} is another group frequency for all the acids studied with the exception of 3-iodopropanoic acid, which lacks an absorption band in this region. The range is narrowed to 660 cm^{-1} to 630 cm^{-1} if the 4- and 5- chloropentanoic acids are also excluded. In all cases the band is of strong intensity. The band appears to be consistent within about 10 cm^{-1} for all haloacids of the same chain length. No other trends were observed, however.

The last group frequency observed for these solid-state acids is from 530 cm^{-1} to 500 cm^{-1}. This range does not include the α-substituted acids. If the α-substituted acids are included the range becomes 530 cm^{-1} to 450 cm^{-1}. In both cases the band is observed as an absorption band of medium to strong intensity. With the α-chloroacids the band is quite consistent at a lower frequency, a strong band being noted at 420-465 cm^{-1} with no absorption in the 530-470 cm^{-1} range. The solidification thus allows ready differentiation of the α-chloro acids from chloro acids substituted at other positions. The other halo acids do not seem to show this behavior, however.

SECTION IV

DISCUSSION

There has been no attempt made to assign the foregoing group frequencies to particular vibrations of the acid molecules. In most cases, there is no real evidence that the bands appearing in the ranges are due to the same vibration in all of the compounds.

It was hoped that a correlation of all the acids in the solid state would yield smaller frequency ranges for the group frequencies, and possibly a greater number of correlations. The solid-state acid correlations did yield frequency ranges of a smaller span than for the room-temperature acids, but the low frequency correlation present in the room-temperature acids is noticeably absent in the solid-state acid correlation, and, with the exception of the chloro acids no useful information can be gained from this region.

In general the group frequency ranges cited in L. J. Bellamy[25], are more broad than those given here. Although there were few trends observed within the group frequencies cited here, the α-substituted acids displayed sufficiently smaller ranges to make their identification easier.

Table I

Major Infrared Absorption Bands of Monohalogenated Monocarboxylic Acids (Room Temperature)

Chloro-acetic	Bromo-acetic	Iodo-acetic	2-chloro-propanoic	3-chloro-propanoic
3200-3000	3150-2960	3100-2900	3120-2920	3100-2900
1734	1725	1680	1730	1710
1417	1427	1427	1450	1440
	1387	1390	1417	1400
				1340
1287				1300
1220	1255	1247	1255	1250
			1210	
1176	1158	1156	1175	1160
	1110			
	1088	1086		1050
			985	975
931	892	891	915	930
		850	855	900
788		752	720	830
644				
633	633	632	665	670
557	540		500	525
	487	483		
423	460	458		
			345	355
235				260

Table I (cont.)

2-bromo-propanoic	3-bromo-propanoic	2-chloro-butanoic	3-chloro-butanoic	4-chloro-butanoic
3120-2960	3090-2880	3110-2880	3100-2920	3050-2920
1710	1710	1725	1715	1708
1435	1412	1460	1430	1425
1400		1420		
1370	1380	1380		
			1300	1302
		1285	1275	
1230	1240	1200	1235	1237
	1230			
1160	1125	1110	1180	1190
1060	1080	1085		
970	940	1030	1020	989
905	910	900	930	927
840	805	825		
		790		
640	635	685	640	650
625	585			
460	500	495	498	490
			408	422
320	330	339	357	335
			304	
				247

Table I (cont.)

3-iodo-propanoic	4-chloro-pentanoic	5-chloro-pentanoic	2-bromo-hexanoic	2-chloro-4-methyl-hexanoic	2-bromo-decanoic
3000-2900	3040-2860	3020-2860	3000-2840	3300-2800	3140-2860
1680	1705	1710	1710	1730	1715
1422	1430	1430		1470	1460
1400	1410	1410	1410	1415	1430
1320					
1280	1280	1280	1280	1280	1290
			1252		
1230	1225	1230	1230	1200	1250
			1185	1185	1175
1150	1130	1135	1160	1120	1110
		1050	1095	1020	
940					
890	930	930	920	920	930
				890	
				840	
	750	750	720	800	720
	650	650	655	680	670
				540	525
575				440	440
460		440	420	365	380
				310	340
	330	330	335		

Table II

Major Infrared Absorption Bands of Monohalogenated Monocarboxylic Acids (Solids)

Chloro-acetic*	Bromo-acetic*	Iodo-acetic*	2-chloro-propanoic	3-chloro-propanoic
3200-3000	3150-2960	3100-2900	3020-2720	3120-2900
1734	1725	1680	1725	1700
			1460	1470
1417	1427	1427	1420	1440
	1387	1390	1370	1395
			1320	1340
1287			1260	1300
				1280
1220	1255	1247	1220	1260
1176	1158	1156	1090	1160
	1110			
	1088	1086	1070	1060
				1050
			985	970
931	892	891	930	930
				900
		850	870	830
788		752	735	
644				
633	633	632	650	660
557	540			530
	487	483		
423	460	458	450	
			350	
235				230

*Room temperature data

Table II (cont.)

2-chloro-butanoic	3-chloro-butanoic	4-chloro-butanoic	3-iodo-propanoic*
3000-2800	3000-2880	2980-2860	3000-2900
1715	1710	1700	1680
1460	1460		
1455			
1440	1445	1445	
1430	1400	1435	1422
		1410	1400
1375	1380	1375	
1350		1335	
1315	1315	1325	1320
1290	1275	1300	1280
		1290	
1230	1250	1250	1230
1220		1230	
	1180	1190	1150
		1170	
	1125	1150	
1090	1090		
1030	1020	1035	
	980	980	
940	935	955	
	910		
900	900	930	890
830		850	
740		780	
710	710	685	
640	635	650	
	590		570
	500	510	
465	410	430	460
380	360		
340	305		
		250	

*Room temperature data

Table II (cont.)

2-bromo-propanoic	3-bromo-propanoic*	4-chloro-pentanoic	5-chloro-pentanoic
	3090-2880		
1710	1710	1690	1685
		1455	1455
1440		1430	1430
1420	1412	1410	1405
1380	1380	1350	1340
1330		1310	1300
1250	1240	1255	1240
	1230	1240	
1175		1200	1200
	1125		
1095	1080		
1070		1035	1030
990			
930	940	950	940
	910		
860	805		
		730	730
		680	680
660	635		
	585		
540	500	530	530
490		400	400
350			
	330	320	320

*Room temperature data

Table II (cont.)

2-chloro-4-methylhexanoic	2-bromodecanoic
3200-2600	3000-2700
1714	1707
1467	1458
1428	1429
1383	
1366	
1290	1292
1262	1252
1210	
1171	1177
1122	1112
1019	
943	940
889	
840	
	719
682	681
	650
541	518
423	445
384	340
235	

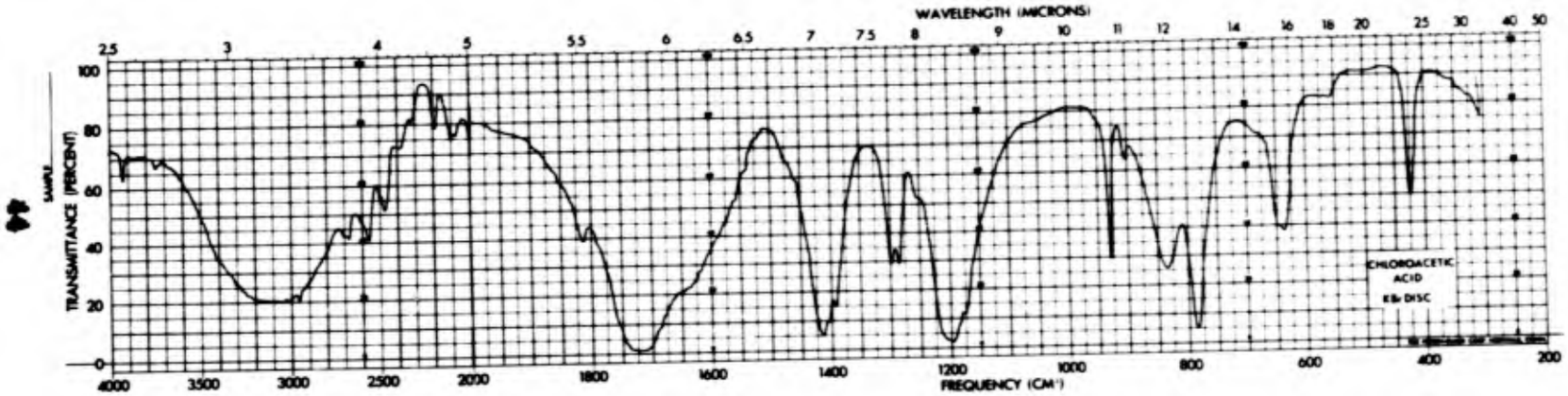

Figure 1. The Infrared Spectrum of Chloroacetic Acid (KBr Disc)

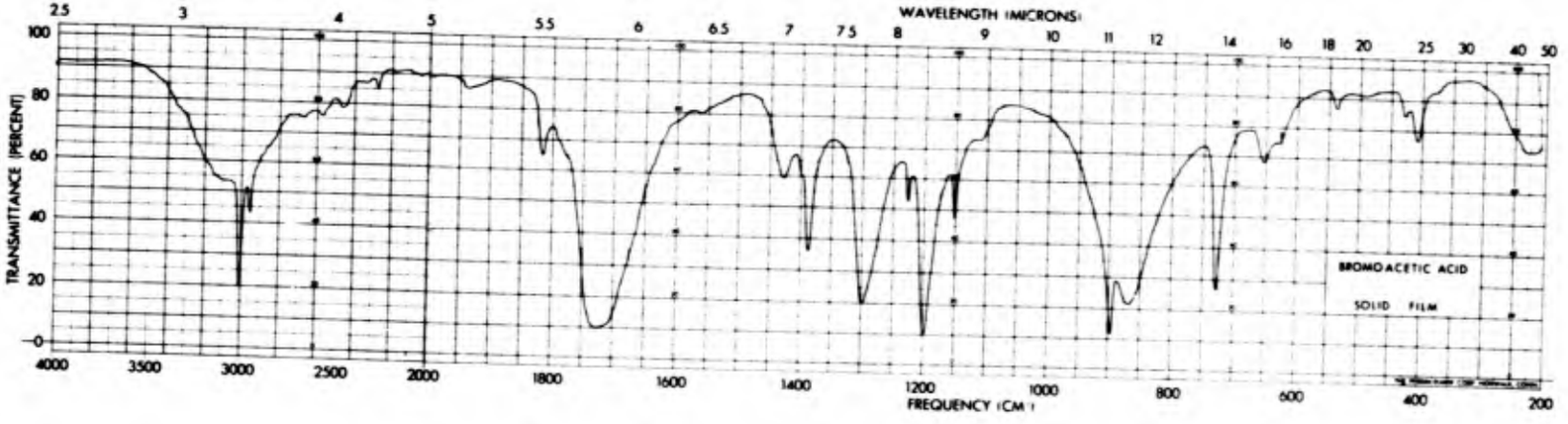

Figure 2. The Infrared Spectrum of Bromoacetic Acid (Solid Film)

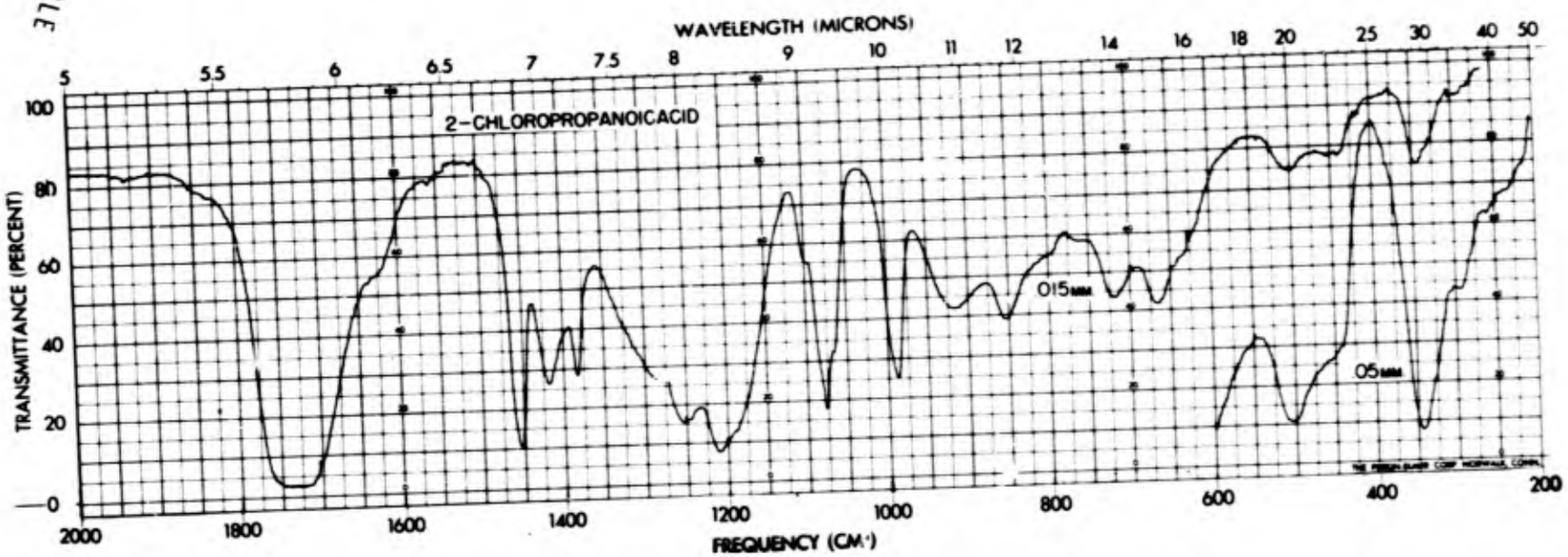

Figure 3. The Infrared Spectrum of

2- Chloropropanoic Acid (Liquid)

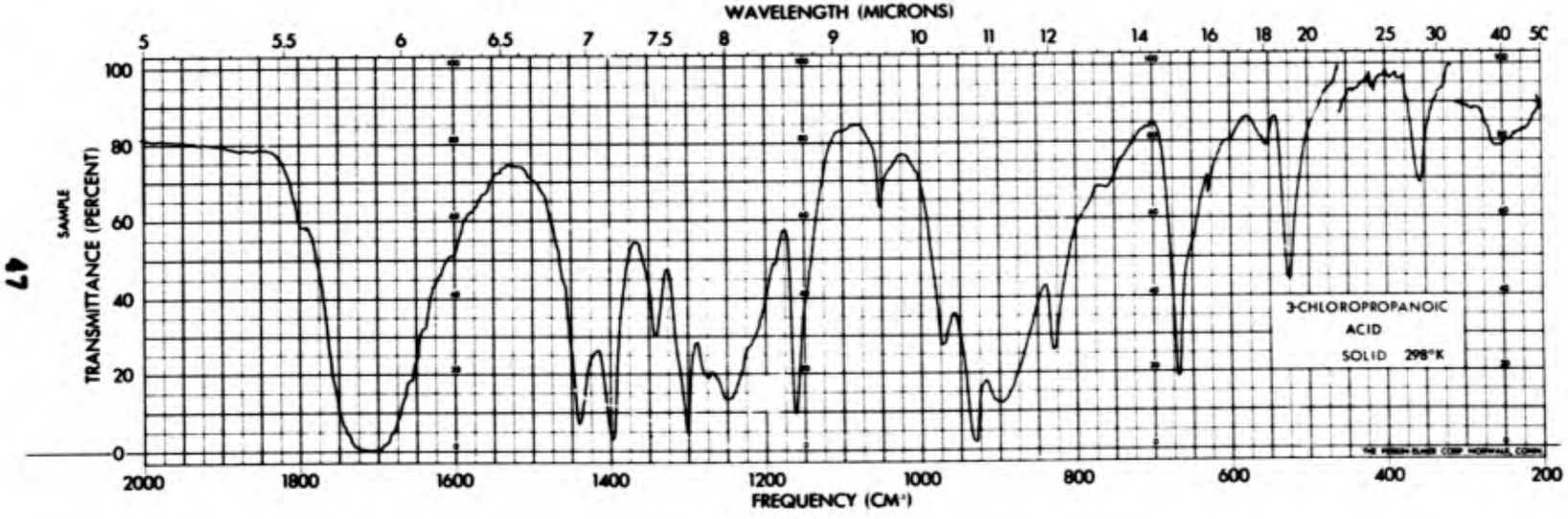

Figure 4. The Infrared Spectrum of

3- Chloropropanoic Acid (Solid Film)

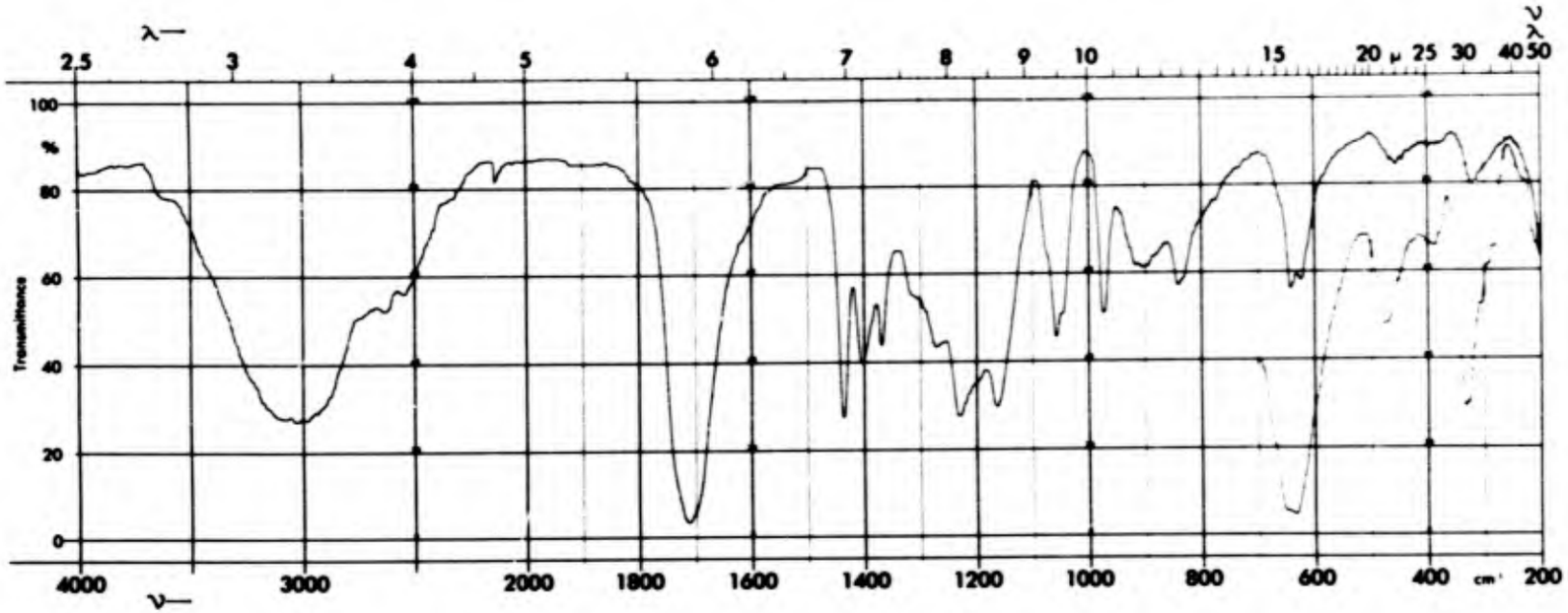

Figure 5. The Infrared Spectrum of

2- Bromopropanoic Acid (Cap Film)

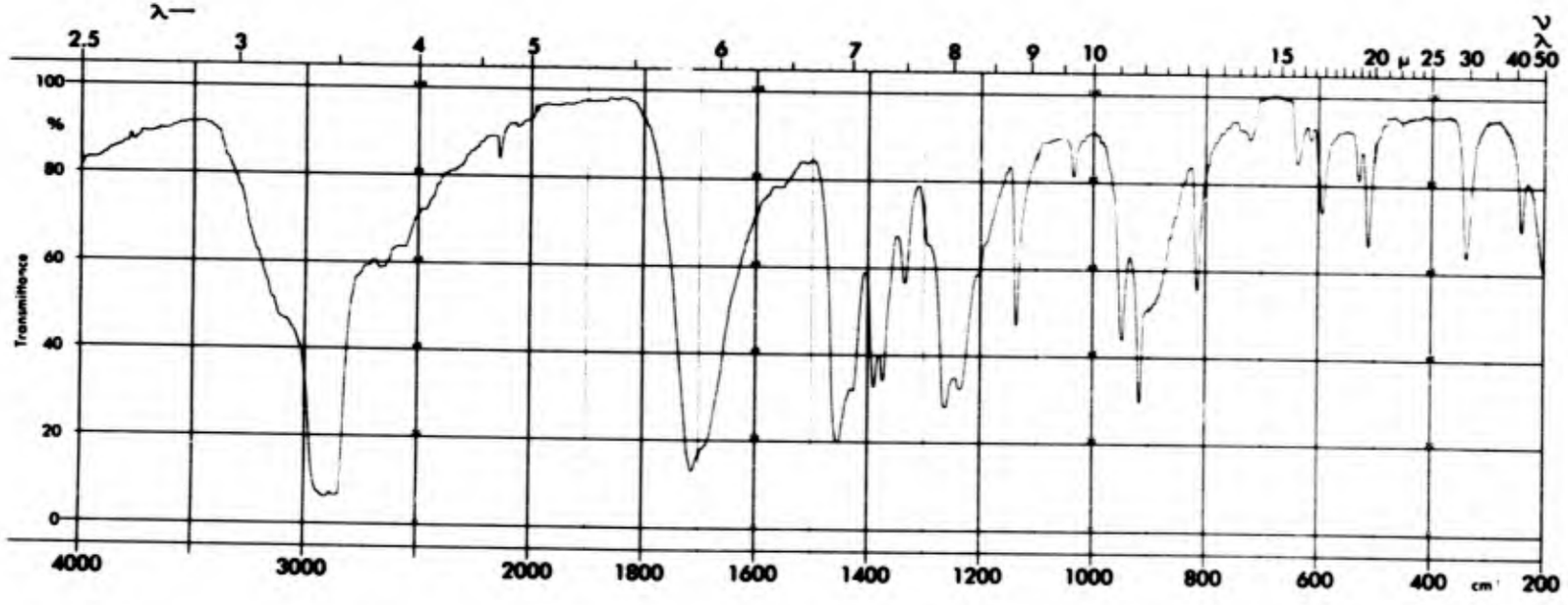

Figure 6. The Infrared Spectrum of

3- Bromopropanoic Acid (Nujol Mull)

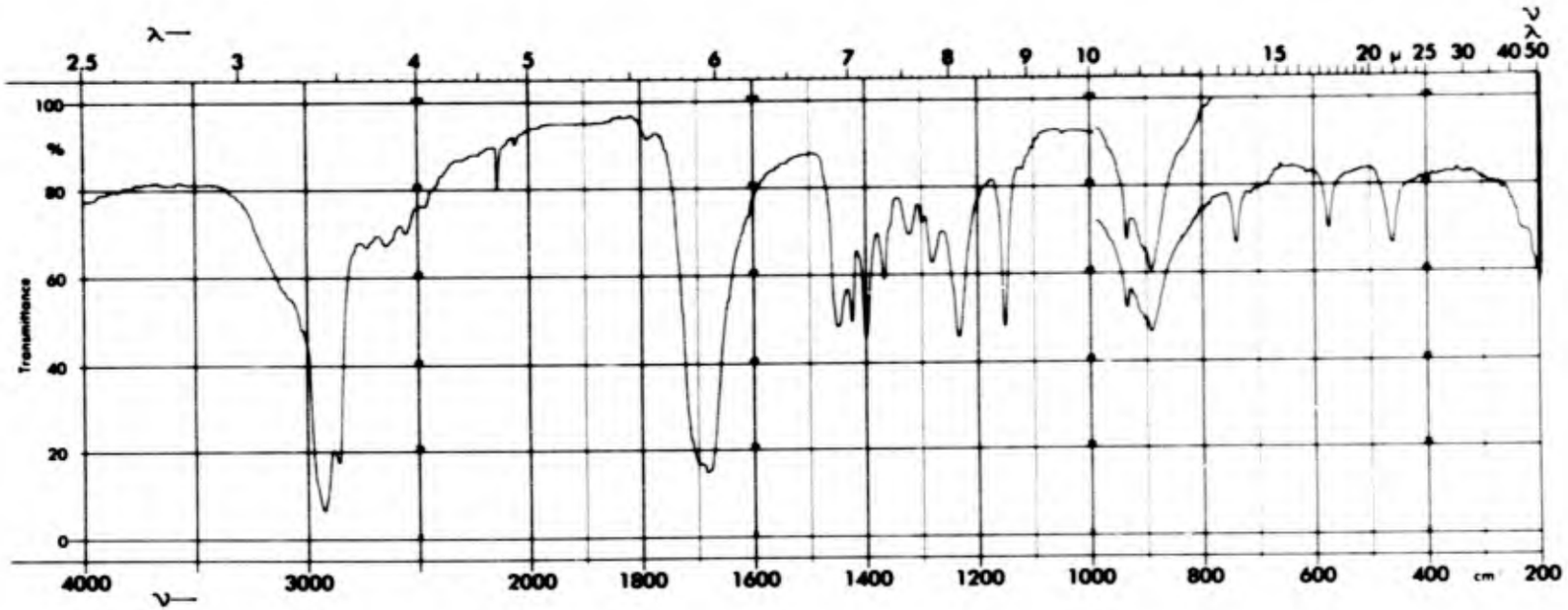

Figure 7. The Infrared Spectrum of

3- Iodopropanoic Acid (Nujol Mull)

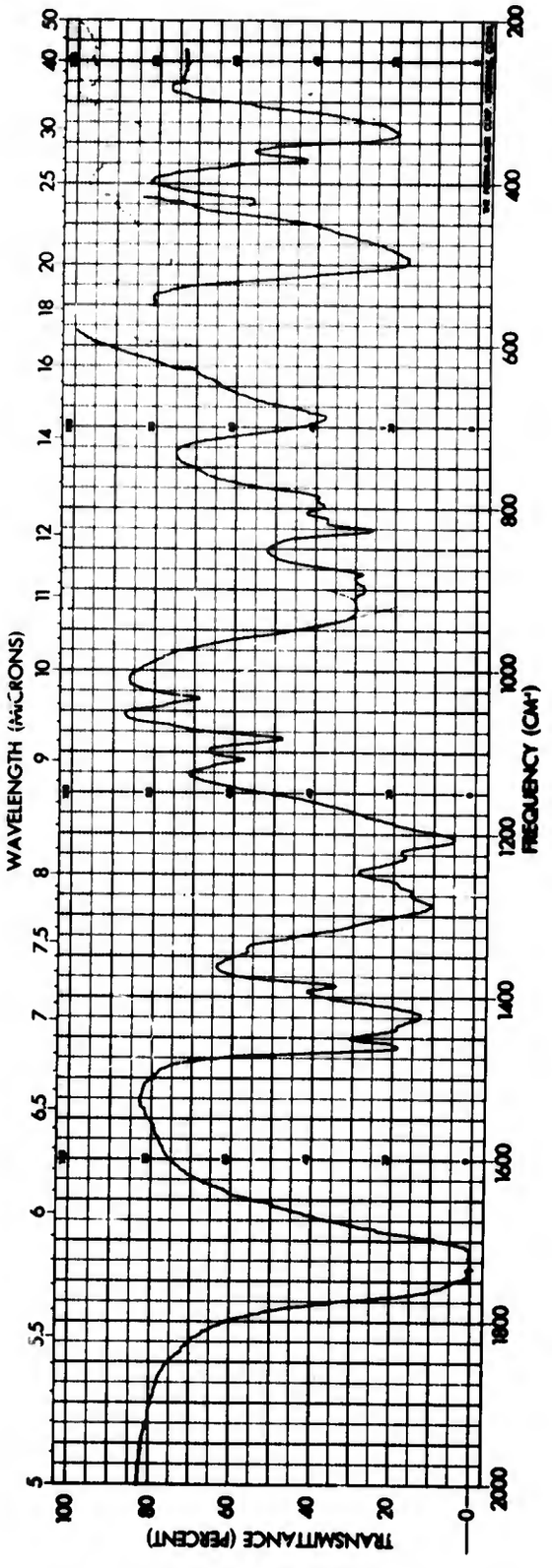

Figure 8. The Infrared Spectrum of
2- Chlorobutanoic Acid (Cap. Film)

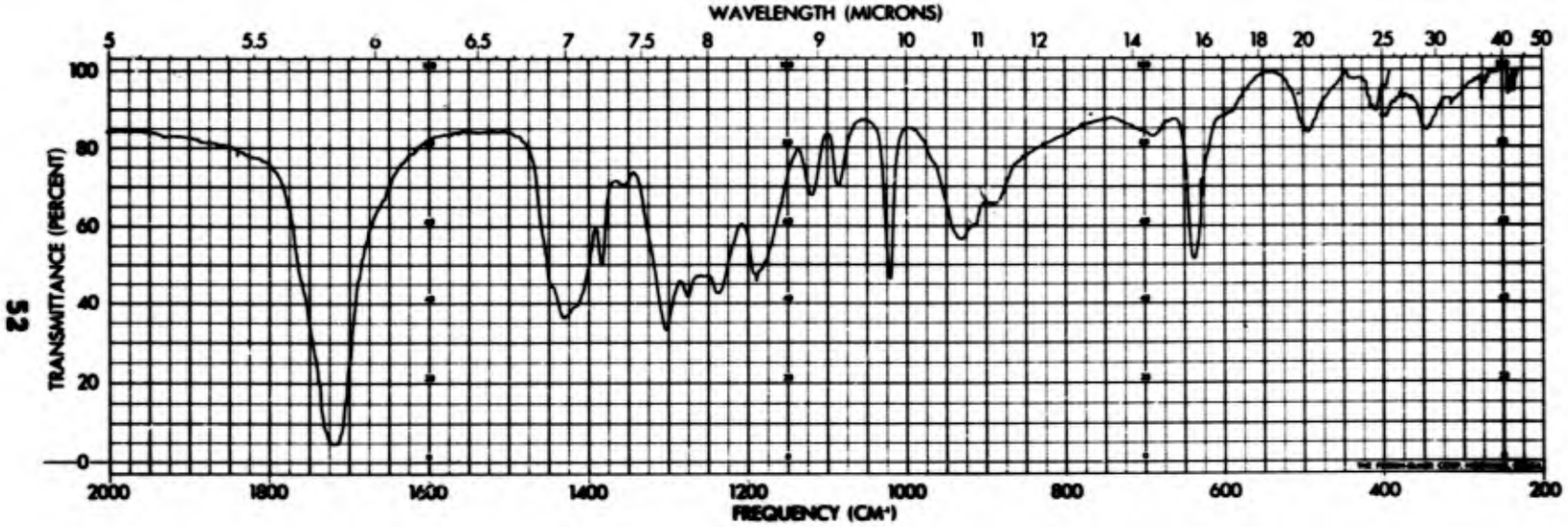

Figure 9. The Infrared Spectrum of

3- Chlorobutanoic Acid (Cap. Film)

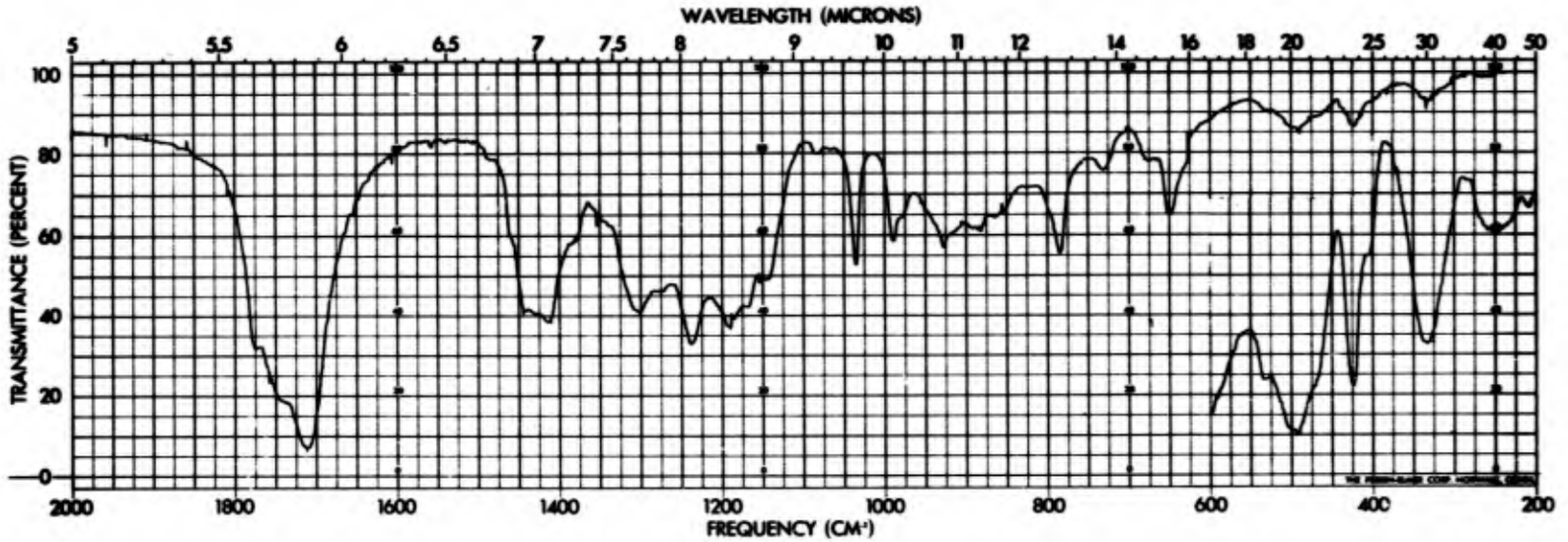

Figure 10. The Infrared Spectrum of

4- Chlorobutanoic Acid (Cap. Film)

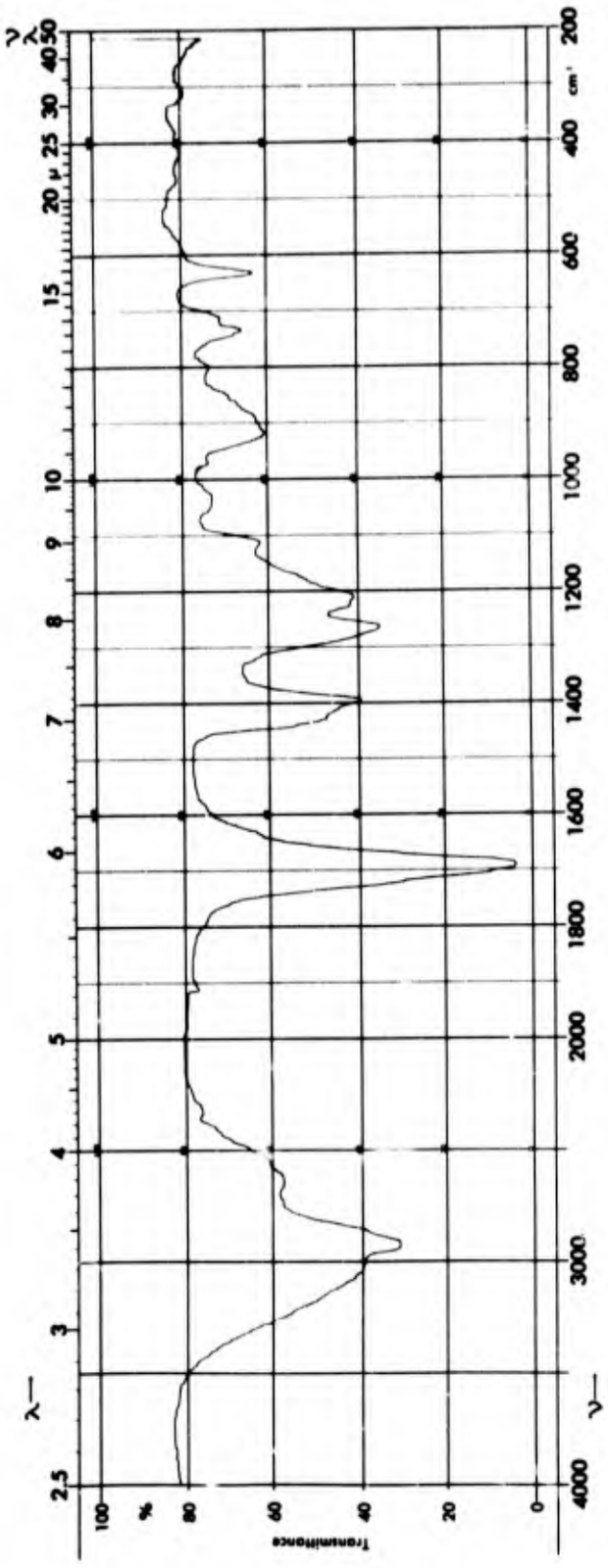

Figure 11. The Infrared Spectrum of
4- Chloropentanoic Acid (Cap Film)

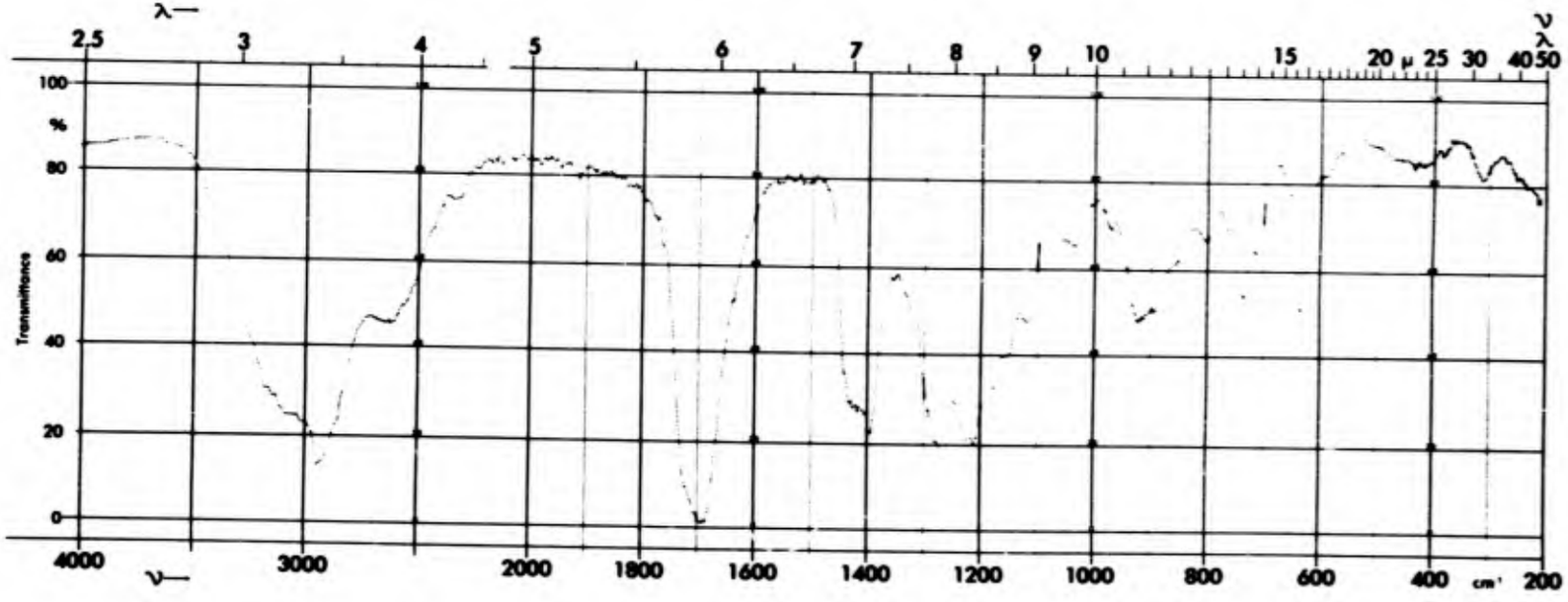

Figure 12. The Infrared Spectrum of

5- Chloropentanoic Acid (Cap Film)

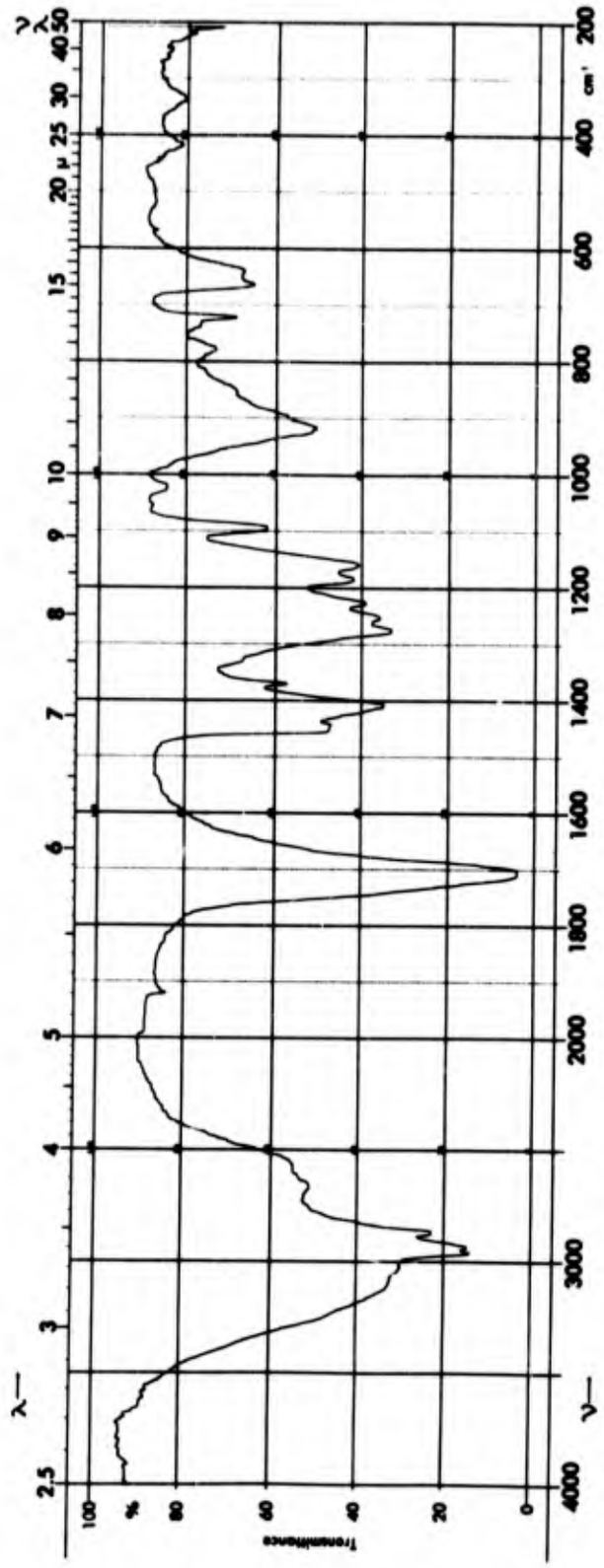

Figure 13. The Infrared Spectrum of
2- Bromohexanoic Acid (Cap Film)

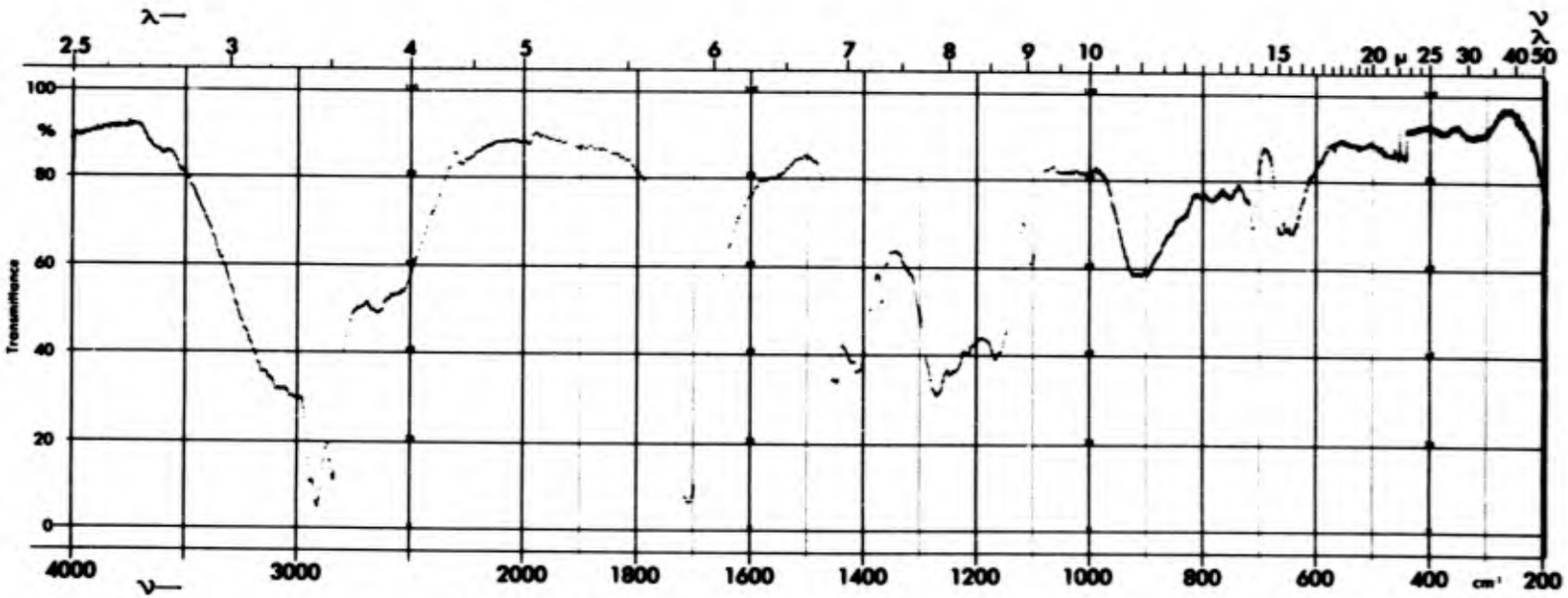

Figure 14. The Infrared Spectrum of 2- Bromodecanoic Acid (Cap Film)

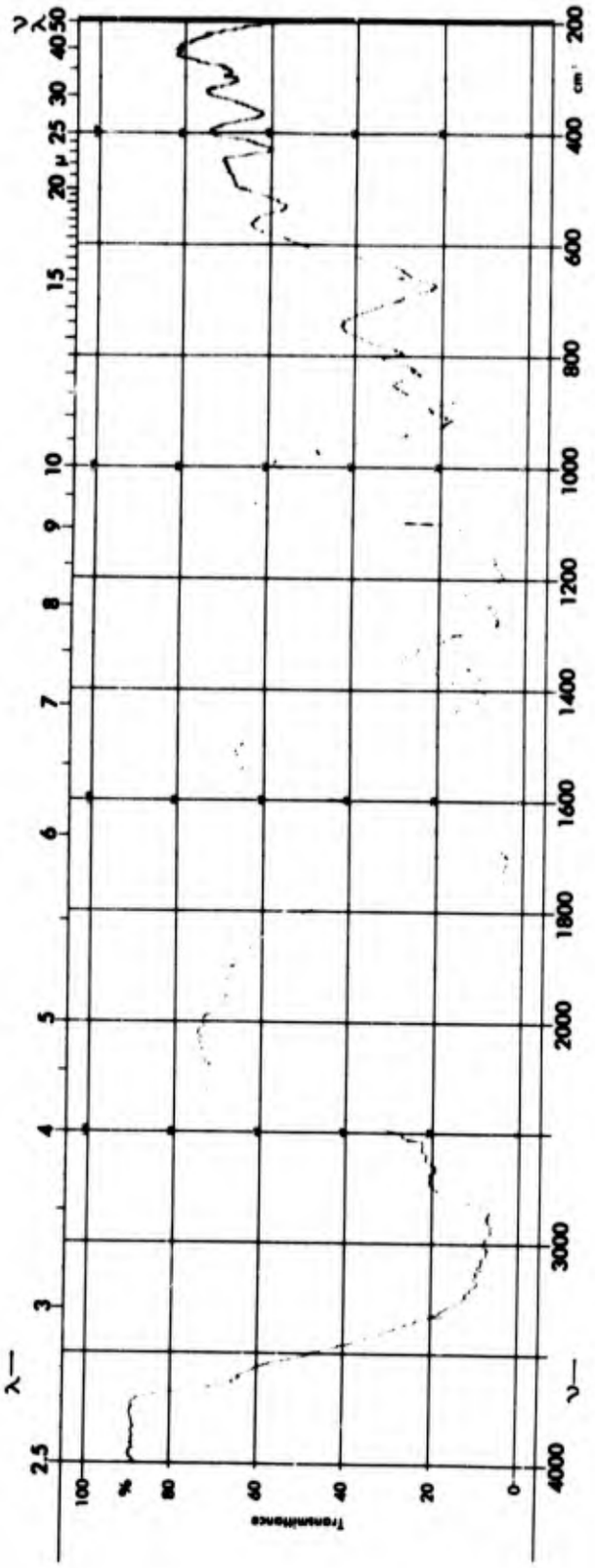

Figure 15. The Infrared Spectrum of

2- chloro- 4- methylhexanoic Acid (Cap Film)

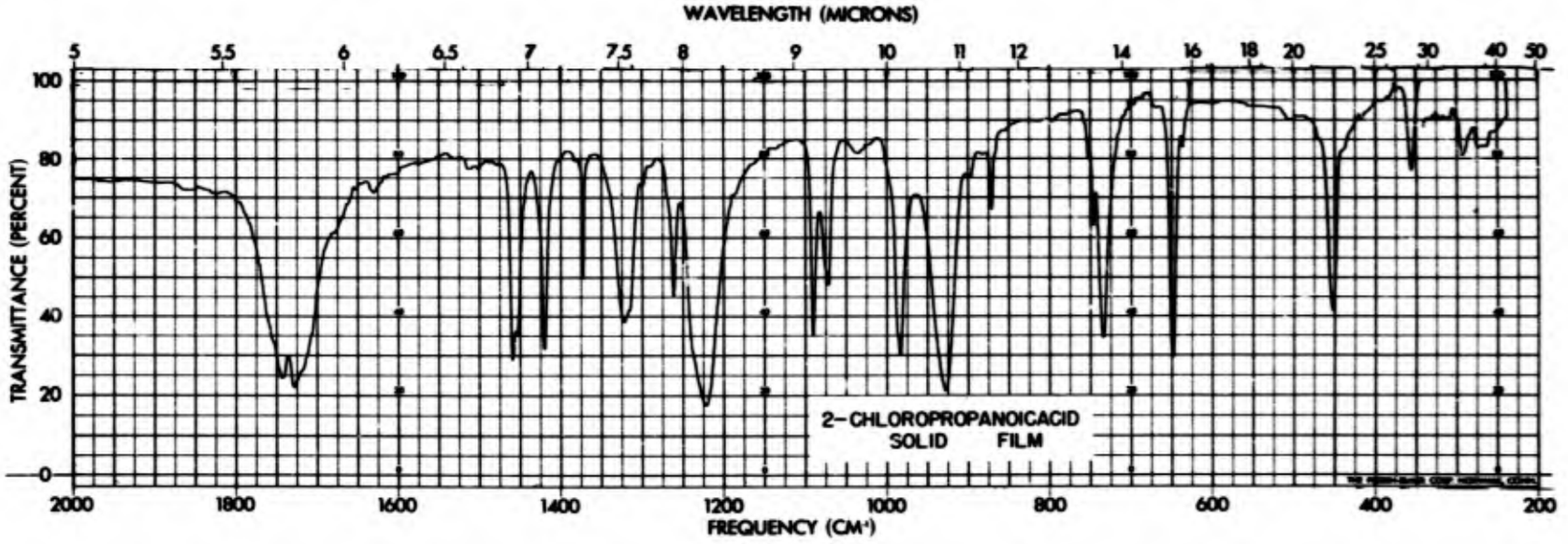

Figure 16. The Infrared Spectrum of

2- Chloropropanoic Acid at Low Temperature (Solid Film)

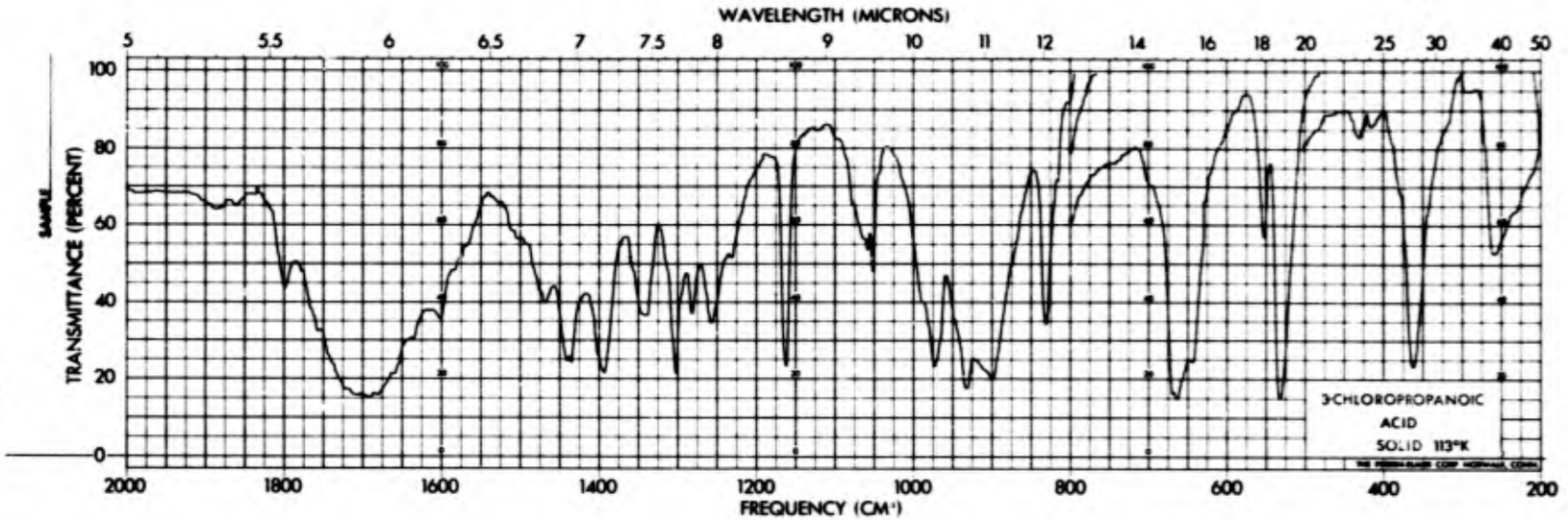

Figure 17. The Infrared Spectrum of

3- Chloropropanoic Acid at Low Temperature (Solid Film)

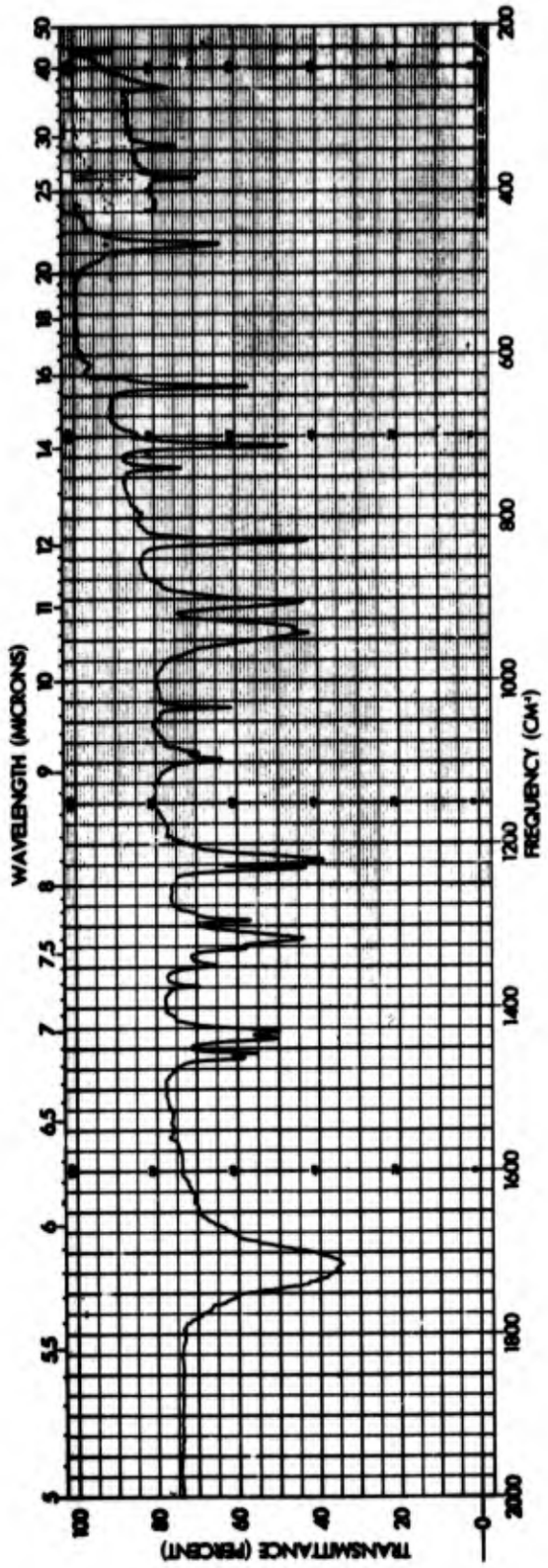

Figure 18. The Infrared Spectrum of
2- Chlorobutanoic Acid at Low Temperature (Solid Film)

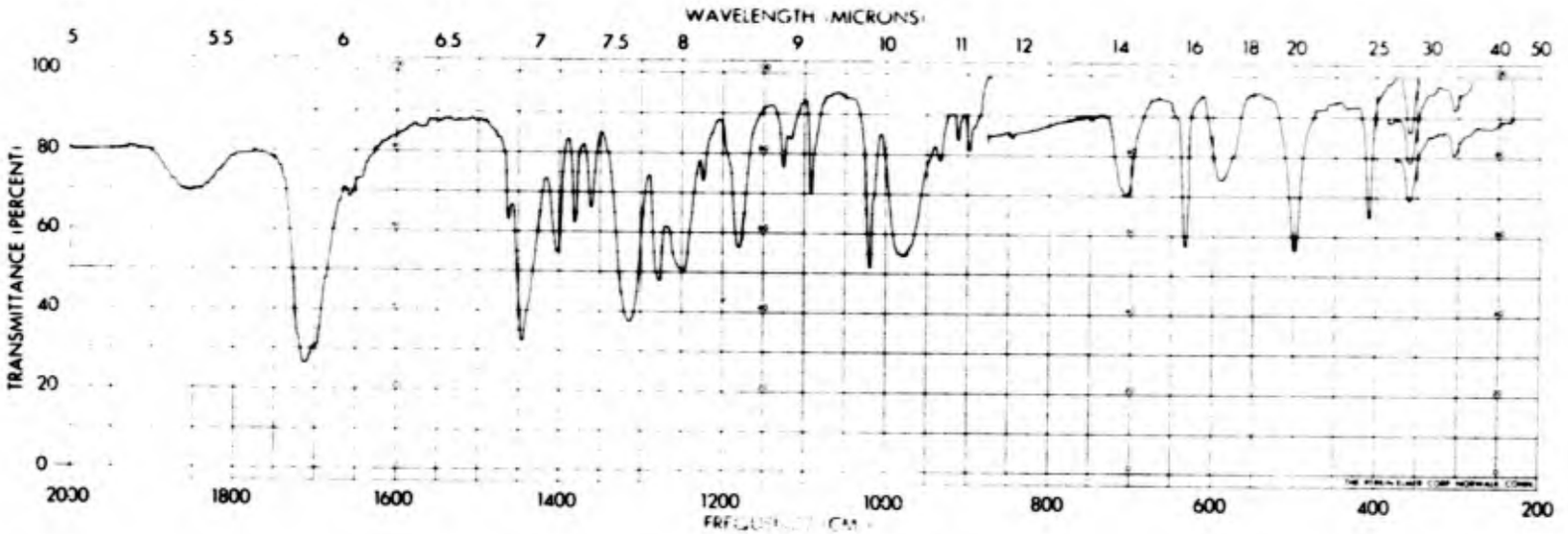

Figure 19. The Infrared Spectrum of

3- Chlorobutanoic Acid at Low Temperature (Solid Film)

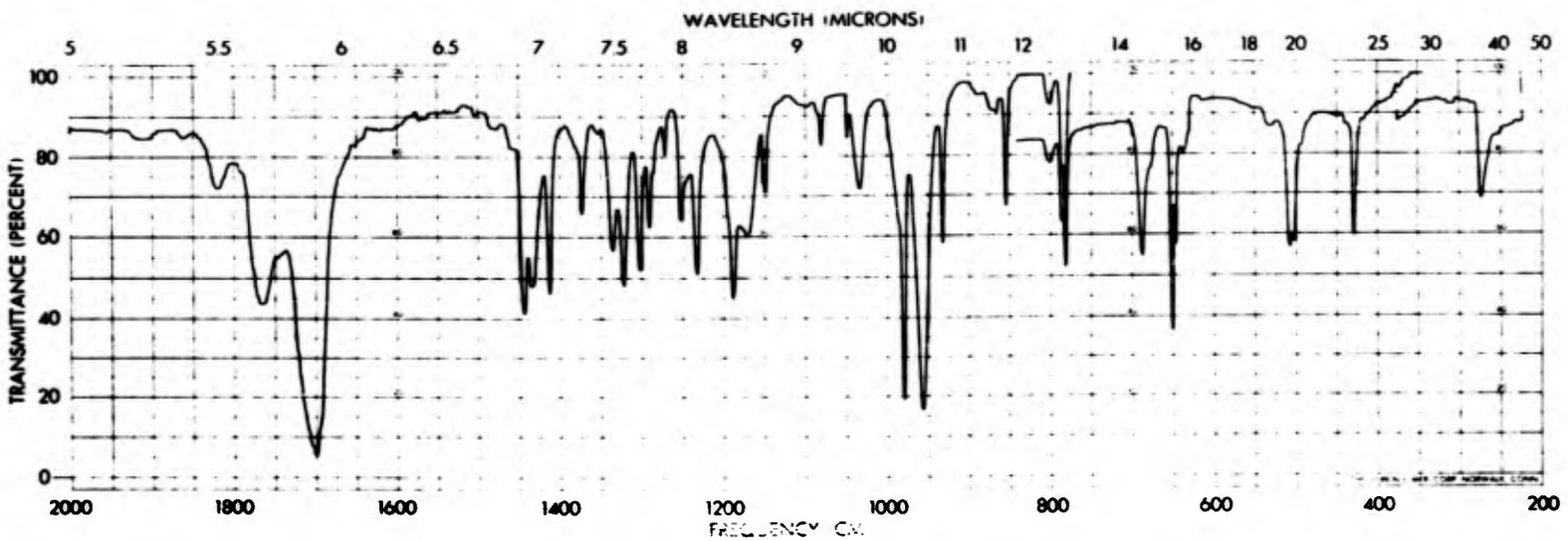

Figure 20. The Infrared Spectrum of

4- Chlorobutanoic Acid at Low Temperature (Solid Film)

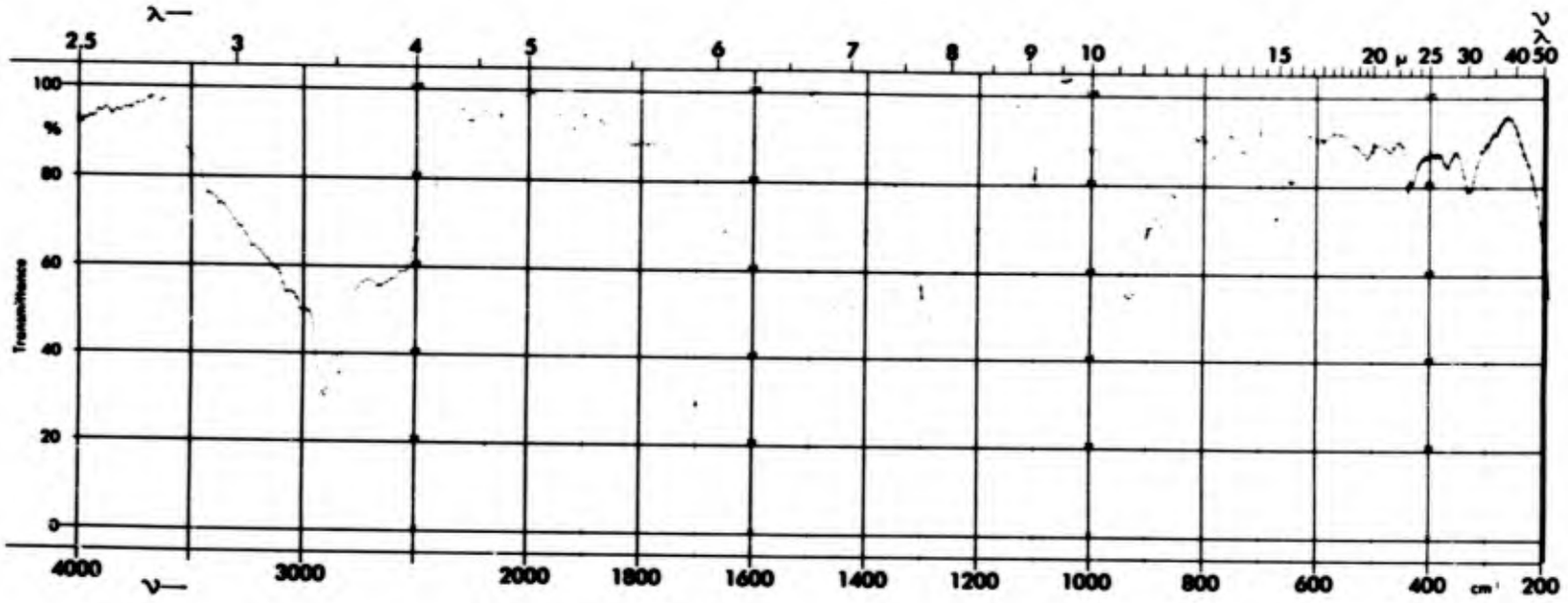

Figure 21. The Infrared Spectrum of

2- Bromodecanoic Acid at Low Temperature (Solid Film)

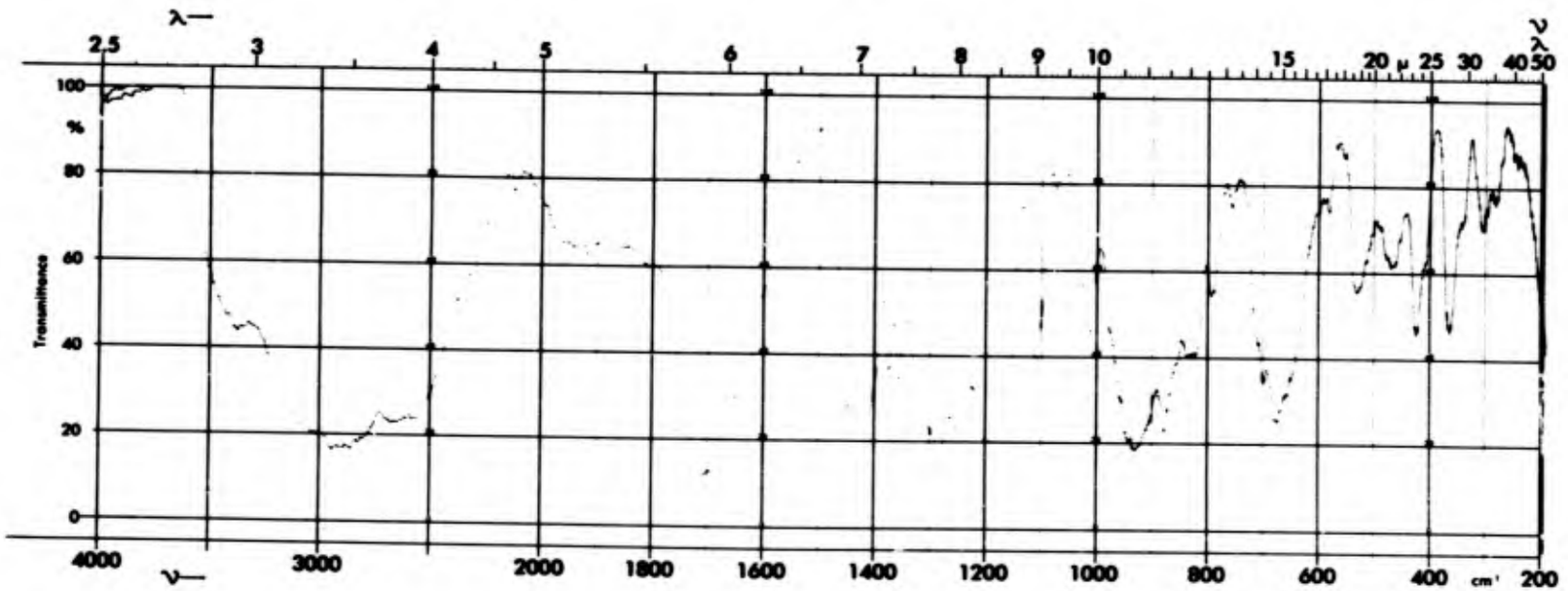

Figure 22. The Infrared Spectrum of

2- Chloro- 4- methylhexanoic Acid at Low Temperature (Solid Film)

CORRELATION DIAGRAM FOR HALOGENATED ACIDS

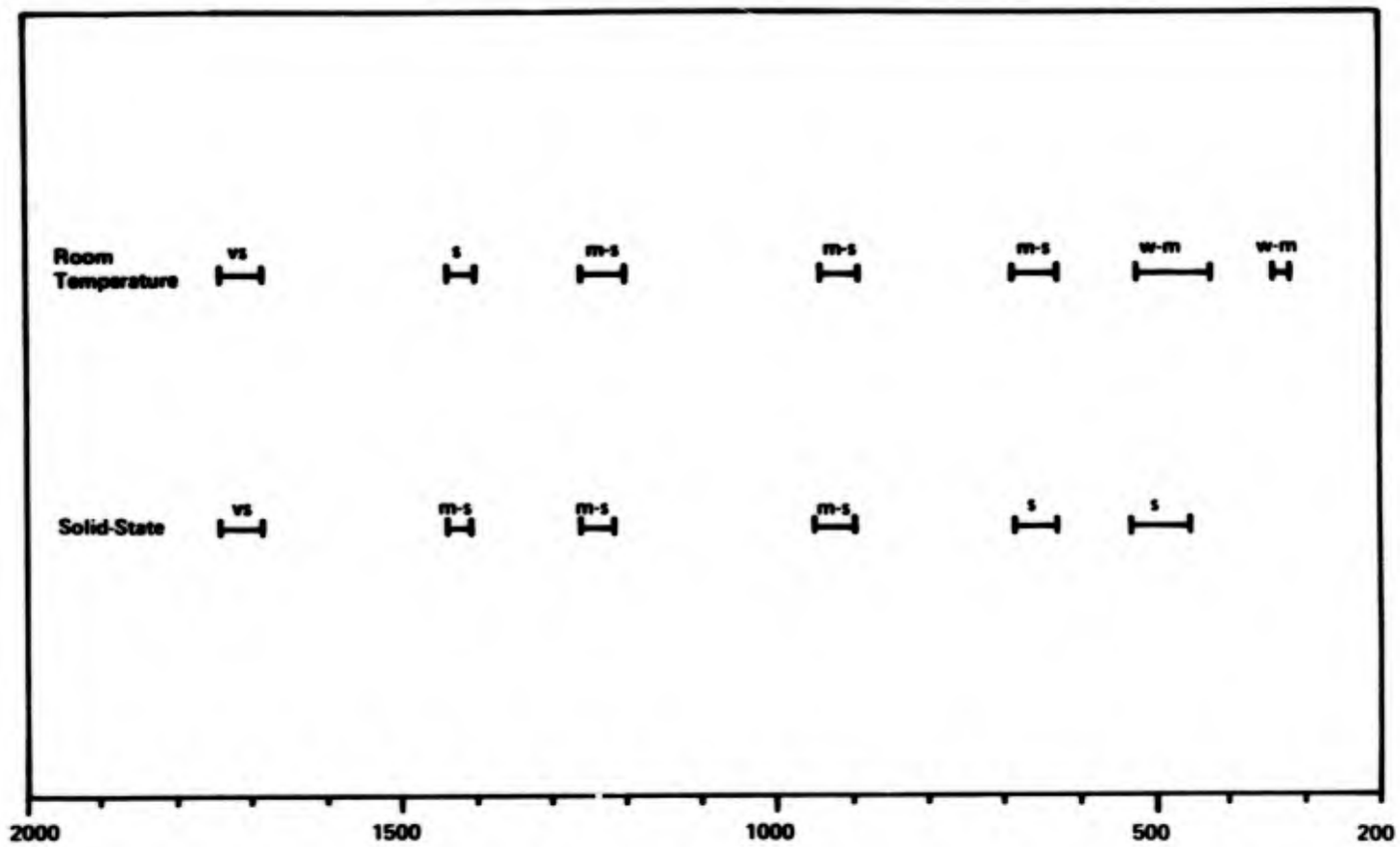

Figure 23.

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13. ABSTRACT

The infrared spectra of sixteen monohalogenated monocarboxylic acids have been recorded in the range 4000-250 cm^{-1}. In addition the infrared and Raman spectra of iodoacetic acid and sodium iodoacetate have been recorded in the 4000-50 cm^{-1} region.

The spectra have been interpreted in terms of group frequencies that would potentially serve to identify and characterize halogenated acids. The approach has been primarily that of determining the effect of halogen substitution on the normal group frequencies of saturated unsubstituted acids. Temperature effects have been investigated in a preliminary manner on several of the acids. In many cases changes in the spectra are noted when the temperature is lowered. In view of the many polymorphic phases in which acids can exist, these temperature effects cannot be completely explained without considerable additional effort.

The vibrational spectra of iodoacetic acid and sodium iodoacetate were investigated in detail and assigned as a model for the spectra of the other acids. The data is most consistent with a hydrogen bonded dimer structure in the liquid and stable solid states. The monomer units are sufficiently strongly coupled so that "pseudo" C_{2h} selection rules are followed. There is no evidence for the existence of more than one rotational isomer at room temperature or below and the data are most consistent with a structure in which the iodine atom is trans, or nearly trans, to the carbon-oxygen single bond of the acid.

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