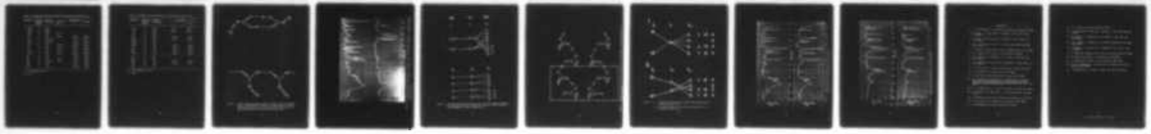
AD-A048 587 MIAMI UNIV OXFORD OHIO DEPT OF CHEMISTRY F/G 7/3
POLARIZED INFRARED SPECTRAL STUDIES OF CRYSTALLINE, HYDROGEN-BO--ETC(U)
MAY 77 J E KATON, P F KRAUSE, K K SMITH F33615-73-C-5013
UNCLASSIFIED AFML-TR-77-89 NL

1 OF 1
ADI
A048587



END
DATE
FILMED
2-78
DDC

AFML-TR-77-89

12
B5

AD A048587

POLARIZED INFRARED SPECTRAL STUDIES OF CRYSTALLINE, HYDROGEN-BONDED ORGANIC ACIDS

ANALYTICAL SERVICES BRANCH
TECHNICAL SERVICES DIVISION

DDC
RECEIVED
JAN 11 1978
F

MAY 1977

TECHNICAL REPORT AFML-TR-77-89
Final Report for Period January 1975 through April 1977

AD NO.
DDC FILE COPY

Approved for public release; distribution unlimited.

AIR FORCE MATERIALS LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

NOTICE

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

This technical report has been reviewed and is approved for publication.

DUANE E. DINWIDDIE, Capt, USAF, Acting Chief
Analytical Services Branch
Technical Services Division
Air Force Materials Laboratory

FOR THE COMMANDER

Duane E Dinwiddie

This report has been reviewed by the Information Office (OI) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

Copies of this report should not be returned unless return is required by security consideration, contractual obligations, or notice on a specific document.

AIR FORCE/56780/16 December 1977 — 50

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

(19) REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS
BEFORE COMPLETING FORM

1. REPORT NUMBER (18) AFML-TR-77-89

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER (9)

4. TITLE (and Subtitle) (6) POLARIZED INFRARED SPECTRAL STUDIES OF CRYSTAL-LINE, HYDROGEN-BONDED ORGANIC ACIDS.

5. TYPE OF REPORT & PERIOD COVERED
Final Rep[redacted]t. [redacted]
Jan [redacted] 75-Apr [redacted] 77

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s) (10) J. E./Katon, P. F./Krause, K. K./Smith [redacted]
J. M. Rogers

8. CONTRACT OR GRANT NUMBER(s) (15) AF F33615-73-C-5013

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Miami University
Department of Chemistry
Oxford, Ohio 45056

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
7360 - Project No.
736005 - Task No.

11. CONTROLLING OFFICE NAME AND ADDRESS
Air Force Materials Laboratory
Air Force Systems Command
Wright-Patterson AFB, OH 45433

12. REPORT DATE (11) May [redacted]77

13. NUMBER OF PAGES 29 (12) 37p.

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)
Air Force Materials Laboratory (TUA)
Air Force Systems Command
Wright-Patterson AFB, OH 45433

15. SECURITY CLASS. (of this report)
UNCLASSIFIED

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

DDC
RECEIVED
JAN 11 1978
F

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

Approved for public release, distribution unlimited.

(16) 7360 (17) 05

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)
Infrared Spectroscopy
Hydrogen Bonding
Crystal Structure
Polarized Infrared Spectra
Acetic Acid
Acrylic Acid

406 312

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Polarized infrared spectra of oriented samples has been shown to be very useful in the study of the structures and properties of crystals. In principle, this method can be used to elucidate crystal structures. It has has not been clear how this method can be utilized with hydrogen-bonded materials, however. This is due to the fact that hydrogen bonds are much weaker than chemical bonds. The method in which such substances should be treated (the size of the unit to be chosen as the molecule, whether to treat they hydrogen-bond differently than chemical bonds, etc.) has not been clear. → over

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

20. This report gives the results of two studies of polarized crystal infrared spectra of hydrogen-bonded organic acids. Acrylic acid exists as a hydrogen-bonded dimer in the crystal and acetic acid exists as a hydrogen-bonded polymer in the crystal. The results are compared with the x-ray data and the theoretical treatment is carried out considering the hydrogen bonding in detail. It is shown that the correlation method is theoretically satisfactory for these hydrogen-bonded materials provided they crystallize in an orderly fashion.

ACCESSION for
White Section ☒
Buff Section ☐
UNANNOUNCED ☐
JUSTIFICATION
DISTRIBUTION/AVAILABILITY CODES
SPECIAL
A

FOREWORD

This report was prepared by the Department of Chemistry, Miami University, Oxford, Ohio under Air Force contract #F33615- 73-C-5013. 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 under the direction of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio. Major J. H. Hauschild and Major K. E. Siegenthaler served as Project Engineers.

The work was performed at Miami University during the period 1 January 1975 to 30 April 1977. The report was submitted by the authors in May, 1977.

Preceding Page Blank - NOT FILMed

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

Preceding Page Blank - Not Filmed

SECTION I

ACRYLIC ACID

1. Introduction

The striking effects on vibrational spectra due to hydrogen bonding have been the subject of many investigations. The general spectral features associated with such spectra are well documented, but neither detailed spectral interpretations nor truly satisfactory theoretical interpretations are as yet available. Polarized infrared spectroscopy has been used only to a moderate extent in vibrational analyses and solid state structural studies. The advantages of this technique, along with the observation that many compounds form highly-oriented polycrystalline films when grown between alkali halide plates, indicates that utilizing the polarized infrared technique with compounds known to hydrogen bond in the solid may lead to further progress in the understanding of their vibrational spectra.

In accord with this, we have been investigating the solid phase infrared spectra of a number of carboxylic acids because of an interest in their structures in condensed states and in the interpretation of their vibrational spectra. Organic acids hydrogen bond rather strongly and may form either hydrogen-bonded dimers or hydrogen-bonded polymers in their condensed states [1-3]. Both of these structures are shown for reference in Fig. 1. It should be noted that the polymer structure shown is given only for comparison purposes, since acrylic acid is not known to form this structure. Both of these basic structures have two or more substructures which are possible, each differing from the others by the detailed conformation of the monomer units.

Structurally, the vibrational spectra of most liquid acids can be best interpreted on the basis of dimeric (C_i or C_{2h}) molecular symmetry. Although this interpretation offers reasonable consistency with the chemistry of such systems and with the group theoretical predictions, the selection rules have been empirically shown not to be rigorous [4]. In this paper we report the infrared spectra of solid acrylic acid.

In attempting to further understand the effects of hydrogen bonding on the vibrational spectra of carboxylic acids, acrylic acid seems a particularly wise choice since (a) its liquid phase vibrational spectra have been reported and interpreted in terms of C_{2h} dimeric symmetry [4]; (b) the crystal structure of acrylic acid has been determined from x-ray diffraction studies [5,6]; and (c) it is one of the simplest acids known to be dimeric in the solid, which is presumed to be the most common type structure for these acids. Since the x-ray results are known, we have examined the consistency of solid state structural results using polarized infrared spectra.

The crystal structure of acrylic acid has been reported by two different groups of workers [5,6]. Both determinations, one performed at 203°K and one performed at 138°K, show the acid crystallizes in the orthorhombic system, space group D_{2h}^{26} (Ibam), with eight monomer units in the crystallographic unit cell. The crystallographic $\underline{c}$ axis is parallel to the $\underline{z}$ molecular axis with a center of symmetry between monomer units. The structure, therefore, consists of planar hydrogen-bonded dimers lying on C_{2h} sites with two such units in the Bravais cell, or alternatively, four monomer units located on C_s sites.

2. Experimental

Acrylic acid was purchased from Matheson, Coleman and Bell and was distilled in vacuo prior to every sample preparation. The fraction boiling at 27°C under a 4 torr vacuum was collected and used in this work.

Our approach to this investigation has been eased by the development of techniques whereby one may grow oriented polycrystalline films of organic compounds suitable for infrared polarization studies. The methods and sample cell employed for growing oriented polycrystals of compounds that are liquids at room temperature have been described previously [7].

Acrylic acid rapidly polymerizes at room temperature once the inhibitor is removed by distillation, and therefore, oriented polycrystalline films were grown immediately after distillation of the liquid. The sample was placed in a closed cycle Cryogenic Technology Inc. Model 20 Cryostat and cooled to a nominal temperature of 20°K, at which temperature the mid-infrared spectra were recorded. The spectra were recorded on a Perkin-Elmer Model 180 spectrophotometer. The reported frequencies are thought to be accurate to $\pm$ 1 cm^{-1} with reproducibilities of better than $\pm$ 0.5 cm^{-1}.

3. Results

Typical polarized infrared spectra of crystalline acrylic acid at 20°K are shown in Figure 2. Temperature dependent spectra were recorded from near the melting point (284°K) to 20°K. The spectra were essentially identical with those shown in Figure 2 indicating no apparent solid-solid phase change. The difference between the two spectra shown is due to a 90° rotation of the polarizer. Each band gave maximum and minimum intensities at these polarizer settings. The spectra indicate a high degree of sample orientation. The frequencies corresponding to the observed bands along with the liquid phase infrared and Raman frequencies [4] are given in Table 1.

The spectra shown in Figure 2 exhibit only two types of polarization which, for a general sample orientation, are inconsistent with an orthorhombic crystal system. A general orientation of an orthorhombic crystal predicts three types of polarization behavior [8]. The in-plane A' modes (C_s molecular symmetry) are assigned to the upper trace while in the lower trace these modes are nearly extinguished and the A" modes are maximized. The single solid state component observed for the A' modes is in disagreement with the factor group analysis prediction of two (see below). If we assume the oriented polycrystalline film has the same structure as that determined by the x-ray diffraction, and there is no reason to believe it is not, these results are indicative of the orientation of the crystal with respect to the substrate. In order not to observe one of the unit cell modes of an orthorhombic crystal, it is necessary that the infrared radiation be normal to a crystal face which can be described by a set of Miller indices where two of the three indices are zero. Since the $\underline{z}$ molecular axis (B_{1u} representation of the D_{2h} factor group) is parallel to the $\underline{c}$ crystal axis, the crystallographic face perpendicular to the beam is either the (010) or (100) plane. This requires that either the B_{2u} or the B_{3u} symmetry species of the D_{2h} factor group be not observed since the dipole moment change for one of them must necessarily be oriented along the direction of propagation of the infrared radiation.

Since the polarized spectra shown in Figure 2 separate the in-plane A' and out-of-plane A" vibrational modes, partial confirmation of the vibrational assignments made on the basis of the liquid phase infrared and Raman spectra [4] is obtainable. In particular, the rather tentative assignments of the out-of-plane modes of acrylic acid (with the exception of the -OH out-of-plane mode at 925 cm^{-1}, which is obvious from the liquid spectrum) may now be confirmed. First of all, the assignments of the three out-of-plane CH modes of the vinyl group may be considered. A strong band in the liquid infrared spectrum at 984 cm^{-1} was assigned to both the CH_2 twist and wag, these being accidentally degenerate. The degeneracy is removed in the polycrystalline spectrum and the two bands, one at 991 cm^{-1} (CH_2 twist) and one at 975 cm^{-1} (CH_2 wag), are both maximized in the lower trace of Figure 2 indicating that both modes have out-of-plane character. The third CH out-of-plane bend of the vinyl group had been assigned to a band at 819 cm^{-1} in the liquid. Potts and Nyquist [9] state that although it is not a good group frequency, the mode is likely to be around 580 cm^{-1} . The assignment of the 819 cm^{-1} band was thought, therefore, to be questionable. The band at 819 cm^{-1} in the lower trace of Figure 2 clearly identifies it as the correct choice. The data also confirm the assignments of the CO_2 deformations at 535 and 505 cm^{-1} in the solid (525 and 512 cm^{-1} in the liquid phase). The higher frequency band is readily assigned as the in-plane deformation (CO_2 rock) and the lower frequency component as the out-of-plane bend (CO_2wag). This order of the rock being higher in frequency than the wag is the reverse of that found in acetic acid [10,11]. A band at 336 cm^{-1} in the liquid spectrum was assigned as a skeletal deformation. Since it is maximized in the upper trace of Figure 2 and totally absent in the lower spectrum, it must be assigned to an in-plane mode. Finally, in the liquid, the infrared active OH bend was assigned to a strong band at 1297 cm^{-1} while the C-C stretch was assigned to a band at 1240 cm^{-1}. From the observed intensities in the solid (the 1258 cm^{-1} band is much stronger than the 1302 cm^{-1} band), it appears that these assignments should be interchanged.

4. Discussion

The approach we have used for the interpretation of the solid state polarized infrared spectra is basically the correlation method of Fateley, et al. [12]. The Bravais unit cell is composed of four monomer units located at sites of C_s symmetry, or alternatively, two hydrogen-bonded dimer units located at C_{2h} sites. Because of the nature of this system one may envision two possible approaches to the interpretation of the vibrational spectra: (1) an interpretation based on a primitive cell composed of two weakly interacting dimer molecules, or (2) an interpretation based on four monomer molecules, some of whose modes are highly perturbed by hydrogen-bonding to a nearest neighbor molecule. In the second case, other intermolecular interactions are assumed to be much smaller. This approach is similar to that employed by Millikan and Pitzer [13] in discussing the crystal spectrum of formic acid which exists as a hydrogen-bonded polymer in its most stable polymorphic form. The correlation diagrams for the factor group analysis for both cases are shown in Figure 3.

As the dimeric structure possesses a center of symmetry, its vibrational spectrum is somewhat easier to interpret. However, the details of the spectra still present a problem. This is particularly apparent when one considers the liquid phase spectra. They appear to be most consistent with a dimer structure, but possibly because of asymmetry of the potential field which the molecule experiences in the liquid state, the selection rules do not hold rigorously. One formally expects no coincidence between Raman and infrared bands when a molecule possesses a center of symmetry. Indeed there does exist non-coincidences in the liquid spectra. A strong infrared band at 1705 cm^{-1} has no Raman counterpart. Strong Raman bands are observed at 1660 cm^{-1} and 1395 cm^{-1} with no counterparts in the infrared. Other examples may be derived from Table 1. On the other hand, a number of bands are observed in both the infrared and Raman spectra, but with a large intensity reversal. This breakdown in selection rules makes the assignment more difficult.

The correlation diagrams shown in Figure 3 both predict that the in-plane modes (A' of C_s and B_u of C_{2h}) should give rise to two infrared active crystal bands. The out-of-plane modes (A" of C_s and A_u of C_{2h}), on the other hand, should give rise to only one infrared active crystal band. The observation of only one component for each species has been discussed earlier. One may argue that the bands which appear in the crystal spectrum which are not readily apparent in the liquid spectrum, e.g., bands at 1680, 1520, 1505, 1380 and 1320 cm^{-1}, are actually the missing factor group components. However, the polarization behavior of these bands is identical to that of the nearby fundamentals. Such results are consistent with the known crystal structure if an (hk0) face is perpendicular to the infrared beam, however, the frequencies of these bands are so different from the nearest fundamentals that their explanation as factor group components is unreasonable. The first three bands would require factor group splittings of 40,94 and 63 cm^{-1}, respectively. The fourth would require that two fundamentals were accidentally degenerate plus a factor group splitting of 14 cm^{-1} and the fifth would require a factor group splitting of 21 cm^{-1}. Such large splittings would require extremely large intermolecular interactions and do not seem reasonable for a dimer molecule with zero dipole moment. These new bands must, therefore, be due to combination modes. It is important to note that although some new bands appear in the solid spectrum because of the better resolution afforded by the low temperature and the polarizer, a few bands that were weak in the infrared spectrum of the liquid with strong Raman counterparts disappear in the solid infrared spectrum. This indicates that the selection rules hold more rigorously in the crystal, at least for these modes.

The broad band at about 3200 cm^{-1} which is present in both spectra shown in Figure 2 is the only band present which is not essentially extinguished at one polarizer setting or another. A number of explanations can be proposed for this observation. The most satisfying accounts for it as arising from water present in the acrylic acid sample, which was not removed by purification. The removal of small amounts of water which are present in many low molecular weight carboxylic acids, is extremely difficult. This is particularly true of acrylic acid since it is so prone to polymerize. Blank experiments were carried out to make certain that the band was not due to a leak in the vacuum system. Other explanations involve ascribing non-linearity to the hydrogen bond or combination bands with the -OH stretching fundamental that have the appropriate symmetry. These are at best, speculative arguments.

5. Conclusion

The following conclusions may be drawn from this study: (1) the polarized infrared spectra of acrylic acid films are consistent with the reported crystal structure. This result helps point out the usefulness of using the polarized infrared technique for solid state structural investigations, particularly of compounds that are liquids at room temperature. (2) It makes no real difference in this case whether the spectra are interpreted in terms of monomer units on C_s sites or dimer units on C_{2h} sites. It may be that this arises from the fact that both the dimeric molecular symmetry and its site symmetry are the same (C_{2h}), and the monomeric molecular symmetry and its site are identical (C_s). The case where this is not true is presently under consideration. (3) The segregation of the in-plane and out-of-plane vibrational modes of acrylic acid through the polarized infrared spectra has led to a rapid confirmation for most of the assignments proposed for the liquid spectrum. In addition, in cases where clarification of assignments were needed or where additional bands were observed, this technique allows classification to be made with ease.

SECTION II

ACETIC ACID

1. Introduction

It is well established that organic acids of fairly high molecular weight crystallize as hydrogen bonded dimers. We have investigated the polarized infrared spectrum of a number of these acids [2,3,14] and have found the increased resolution afforded by this technique extremely useful in making vibrational assignments as well as in making arguments concerning structural details. An alternative structure of organic acids in the solid state is a long polymeric chain of hydrogen-bonded monomers. Formic acid [15] and acetic acid [16,17,18] crystallize in this manner.

Millikan and Pitzer [13] have concluded from the infrared spectrum of crystalline formic acid that it can best be interpreted on the basis of a molecular chain unit cell. Their description assumes a one dimensional lattice for formic acid from which a two molecule Bravais cell [19] can be determined. The implications of this interpretation are that the "weak" Van der Waal's interactions between the two chains in the crystallographic unit cell are neglected. The Millikan and Pitzer [13] detailed analysis of the crystalline spectrum of formic acid has been shown [20] to be incorrect because of polymorphism in crystalline formic acid [21]. The underlying assumption of a two molecule Bravais cell in which the interchain interaction is neglected has been used in a normal coordinate treatment of formic acid, [22] however.

In analyzing the polarized infrared crystal spectra of acrylic acid, [14] which crystallizes with a dimeric structure, we attempted to interpret the results considering the structure as two interacting dimer units or as four monomer units whose interactions significantly perturbed the crystal spectrum particularly in the case of the hydrogen bond interaction. In the case of acrylic acid, although the results may have been fortuitious, the alternative approaches give identical predictions.

It therefore seemed worthwhile to investigate the situation with an acid that crystallized as a hydrogen bonded polymer. We therefore present the polarized infrared spectra for acetic acid and two of its deuterated derivatives CD_3COOD and CH_3COOD. Acetic acid is isomorphic with formic acid [15-18] and we feel that many of the arguments that are valid for crystalline formic acid should also hold for crystalline acetic acid. The method we have employed to distinguish spectroscopically between the chain Bravais model and the normal crystallographic unit cell interactions is the correlation method described by Fateley, et al. [12] The acetic acid system seems particularly suitable for such a study because of the experimental infrared [23,11,24] and Raman data [25] available as well as theoretical calculations concerning the structure. [21]

2. Experimental

Water existing as an impurity in low molecular weight carboxylic acids is very common and extremely difficult to remove. Before sample preparation, attempts were made to purify the acetic acid (99.8% assayed purity) by drying over $CaSO_4$ for two periods of forty-eight hours each, and then distilling from $CaSO_4$. As a check on the purity of the sample, a mid-infrared survey scan was run on the liquid and showed no bands other than those reported for liquid CH_3COOH. [23] In addition, purifications were also carried out on the CH_3COOD (99%, Wilmad Glass Co., Inc.) and CD_3COOD (99.5%, Bio-Rad Laboratories).

The liquid samples were then transferred to the sampling compartment of a CTi Model 20 Cryostat as capillary films and oriented polycrystals were grown by the method described previously. [7] The mid-infrared spectra were recorded at low temperatures with a Perkin-Elmer Model 180 ratio recording spectrophotometer. The reported frequencies are thought to be accurate to within $\pm$ 1 cm^{-1} with a precision of $\pm$ 0.1 cm^{-1}. The interpretative ambiguities that arose because of polymorphism in formic acid [20,21] were of concern to us because of the similarities between the reported crystal structures of formic and acetic acids. It was important that the oriented polycrystals which were grown were of the same structure as that determined by the x-ray diffraction experiment. Polymorphism in acetic acid has been indicated. [21,26]

3. Discussion

The crystal structure of acetic acid is essentially the same as that of formic acid, [15,18], i.e., the structure exists as chains of hydrogen bonded monomers. The structures are both orthorhombic with $Pna2_1 - C_{2v}^9$ space group symmetry, each with four molecules in the crystallographic unit cell. Figure 4 schematically represents the polymer structure of solid acetic acid. A test of our method of growing crystals between alkali halide windows was performed by studying the carbonyl stretching region and the C-O stretching region of crystalline formic acid. At least ten different films of formic acid were prepared and in each case only one strong band was observed in each of the two regions. This is indicative of the β form of formic acid (the crystallographically determined structure) grown previously between CsI plates. [20]

The α form, which Millikan and Pitzer grew by vapor deposition, [13] gives two strong bands in both the νC=O region and the νC-O region. We feel that the above results indicate that our method of growing crystals yields the polymorph of interest to us. By growing the acetic acid films in the same manner and observing again only one strong band in the carbonyl stretching region as well as only one band in the single bond carbon oxygen stretching region, the conclusion was made that the polymorph of acetic acid grown was the one whose crystal structure has been reported. [16,18]

The acetic acid molecules crystallize on sites of C_1 symmetry and, hence, all molecular vibrations are infrared active under the site symmetry approximation. Under the assumption of C_s symmetry for an isolated acetic acid monomer, the "normal" correlation diagram for the four molecule Bravais cell is shown in the top half of Figure 5. The correlation predicts, for a general sample orientation, three infrared active factor group components for each molecular vibrational mode, each having different polarization properties. The correlation diagram for an alternative interpretation which employs the two-molecule chain unit cell of Millikan and Pitzer is shown in the bottom half of Figure 5. The predictions from this diagram are quite different from those of the "normal" correlation. In this case each molecular mode should give rise to two factor group components, with both the A' modes infrared active while only one of the A" modes will be observable in the infrared. Three distinct band polarizations should be observed for a general sample orientation. It is extremely important to note from these correlations that "normal" crystallographic unit cell interactions in the solid will split both the in-plane A' and out-of-plane A" molecular modes into observable infrared factor group components while the chain unit cell will split the A' modes into two observable infrared components while the A" modes will give rise to only one observable infrared factor group species. The observation of no infrared factor group splitting for the out-of-plane vibrational modes in the spectrum of solid formic acid has led Miyazawa and Pitzer [27] to conclude that the neglect of interchain interactions is appropriate for their treatment of the solid infrared spectra. (The identical correlation diagrams shown in Figure 5 may be formulated for formic acid). Mikawa, Brasch and Jakobsen [22] have employed the same assumption for the normal coordinate calculation in solid formic acid.

As in acrylic acid, if the molecules orient themselves between the alkali halide plates in such a manner as to have one of the orthorhombic crystallographic axes parallel to the direction of propagation of the infrared radiation, the number of factor group components observable in the infrared is altered significantly. The predicted number of infrared factor group components for a general sample orientation just mentioned for both the "normal" four molecule Bravais cell and for the two-molecule chain unit cell are summarized in Table 2. It is important to note that since we are assuming that the acetic acid molecules crystallize in the C_{2v}^{9} space group symmetry between the alkali halide plates, the number of factor group components shown in Table 2 also represents the predicted unique band polarizations for each case. Included in the table for comparison are the experimentally observed number of factor group components and band polarizations.

Table 2 shows the prediction that three factor group components should be observed for both the in-plane and out-of-plane molecular species for a general sample orientation in the "normal" unit cell case whereas two unit cell components should be observed for the A' modes in the chain unit cell model and one for the A" modes. Comparing these predictions with the number of experimentally observed components in column 6 leads to discrepancies with both models.

The fourth and fifth columns give the predictions for specific orientations of acetic acid molecules with respect to the incident radiation. The orientations indicated are those in which one of the orthorhombic crystal axes is parallel to the infrared beam. For these cases, two factor group components for both the in-plane and out-of-plane modes should be observed in the infrared for the "normal" unit cell, whereas one or two components, depending on the specific orientation, should be observed for the in-plane A' modes in the chain unit cell and zero or one infrared observable components for the A" species in the chain unit cell. Comparing the experimental results in columns six and seven with these predictions yields a match with the normal unit cell and a specific orientation.

Figure 6 and Table 3 give the results for the polarized spectrum of crystalline acetic acid-d_0 at 190°K. The two traces in Figure 6 differ by a 90° rotation of the grid polarizer. The top trace is arbitrarily assigned a relative polarizer angle of α while the lower trace is $\alpha + 90^\circ$. These orientations are those at which bands showed a maximum or minimum intensity. The frequencies corresponding to these spectra are given in Table 3. In all but three cases, the OH stretching mode, the carbonyl stretching mode at 1653 $cm^{-1}$and a methyl rocking mode at 1044 cm^{-1}, bands present in the α spectrum extinguished completely in the $\alpha + 90^\circ$ spectrum and, conversely, bands present in the $\alpha + 90^\circ$ spectrum disappear as the polarizer is rotated by 90°. As bands disappear in one spectrum or the other, the new bands appear close in frequency (typically 5 cm^{-1} or less). This magnitude coupled with the new band polarization which follows from the correlation method, indicates that we are observing pairs of factor group components whose origin is the same molecular species. Since our experimental frequencies should be precise to ± 0.1 cm^{-1}, the bands at 1043.3 cm^{-1} (α spectrum) and 1044.0 cm^{-1} ($\alpha + 90^{\circ}$ spectrum) could be assigned, on the basis of the 0.7 cm^{-1} splitting, to different components of the 1044.0 cm^{-1} methyl rock. However, we are somewhat cautious about assigning bands that differ by less than 1 cm^{-1} to different bands, and prefer the evidence given below for the solid CH_3COOD spectra factor group splitting for this mode. This is of added significance, it seems, when the vibrational species in question is an out-of-plane mode because of the consequences in assigning observable splittings to such modes.

It is not particularly surprising that neither the -OH stretching mode nor the carbonyl stretching mode yield distinguishable infrared factor group components. In CH_3COOH, the -OH stretching mode is a broad strong band with frequencies 2921 ± 2 cm^{-1} in both the α and $\alpha + 90^{\circ}$ spectrum. The intensities, however, show significant alteration. We feel that if resolved the factor group pair would differ in frequency by a few wavenumbers. This is based on the analysis of the physical nature of the structure itself as well as analogy with the results of the formic acid normal coordinate analysis. [21] From the latter, [21] a crystal splitting of 1 cm^{-1} for the -OH stretching mode is predicted. There exists low frequency shoulders at 2665 cm^{-1}, 2614 and 2521 cm^{-1}. These bands are present in the liquid spectrum of acetic acid, indicating that they are most likely combinations. These are well known combinations in dimeric carboxylic acids and certainly not factor group components.

The carbonyl stretching mode is a fairly broad band with experimentally indistinguishable factor group components in the α and $\alpha + 90^{\circ}$ spectra. As in the case of the -OH stretching mode, the bands do show some intensity alteration possibly indicating bands of different factor group symmetry species. The normal coordinate treatment for formic acid indicates only a 1 cm^{-1} factor group splitting for the carbonyl stretching mode and if this is appropriate for acetic acid, it is not surprising that we do not resolve the pair.

All other fundamental absorptions that were observed for solid CH_3COOH yielded experimentally observable pairs of factor group components. There is some ambiguity associated with the resolution of factor group splittings for the symmetric C-C stretch (911.4 cm^{-1}) and the O-H out-of-plane deformation at $\sim$908 cm^{-1}. This problem is addressed below. Of particular significance is the out-of-plane CO deformation. In the α spectrum a band was observed at 588.6 cm^{-1}. Upon 90^o rotation of the polarizer, this band extinguished completely, and a new band at 593.6 cm^{-1} was observed. This splitting is clear indication of factor group splitting for an out-of-plane mode. This leads to the conclusion that significant interchain interactions do exist.

The polarized spectra of the deuterated derivatives lend additional support to the proposal that all vibrational modes of crystalline acetic acid are split by unit cell interactions. The polarized spectra of crystalline CH_3COOD and the associated frequencies are given in Figure 7 and Table 4. Of particular importance are the splittings observed for the OD stretch in CH_3COOD (α; 2204.2 cm^{-1}; α + 90; 2200.5 cm^{-1}) and the methyl rocking mode (α; 1043.5 cm^{-1}; α + 90; 1044.8 cm^{-1}). The corresponding vibrational modes yielded questionable factor group splitting in crystalline CH_3COOH. The splitting observed for the methyl deformation, an A" out-of-plane mode, gives additional indication of significant interchain interactions in solid acetic acid. The corresponding frequencies in CD_3COOD are α; 924.4; α + 90; 926.0, further confirming these conclusions.

There are bands, however, in the spectrum of crystalline CH_3COOD that do not yield components split by 1 cm^{-1}or more in the α and α + 90^o spectra. Three of these are A' modes: the carbonyl stretch, the symmetric methyl deformation at about 1007.0 $cm^{-1}$and the carbon-carbon stretching mode at 672 cm^{-1}. The weakness of the factor group interaction predicted for the carbonyl stretch along with the broadness of the band accounts for the lack of observable splittings in the spectra of solid CH_3COOH and CH_3COOD. This observation is consistent in that we were unable to resolve factor group components for this mode in the CD_3COOD spectra as well (see Table 5). Secondly, the symmetric CH_3 deformation is split by less than 1 cm^{-1}(α;1007.1 cm^{-} ; α + 90^o; 1006.3 cm^{-1}). The observation of a 1.6 cm^{-1} splitting for this mode in the undeuterated spectrum coupled with the intensity alteration evident in the polarized α and α + 90^o of CH_3COOD allows us to assign with confidence the 0.8 cm^{-1} splitting to factor group interactions.

The C-C stretch raises an interesting question in both the CH_3COOH and CH_3COOD spectra. In the non-polarized d_o spectrum a broad band (~908 cm^{-1}) has associated with it a high frequency shoulder at 911.4 cm^{-1}. Due to the broadness of this background we feel the majority of the intensity is due to the -OH out-of-plane mode. Therefore, the assignment of the 911.4 cm^{-1} band is to C-C (A') and the ~908 cm^{-1}

band to γOH (A"). In the polarized d_0 spectra three bands are observed: 908.9 cm^{-1}, (α spectrum) and 911.6 cm^{-1}, 897.1 cm^{-1} (α + 90° spectrum). We have assigned the 897.1 cm^{-1} to one component of γOH because of its intensity relative to the 911.6 cm^{-1} band (which is assigned to νC-C). The single band at 908.9 cm^{-1} is assigned to accidentally degenerate components of both the 911.6 and 897.1 cm^{-1} band. We would prefer, on the basis of intensity arguments, to assign the single band at 908.0 cm^{-1} in the α spectrum to be due to the other -OH out-of-plane factor group component, but would have no explanation for the missing carbon-carbon stretching mode component. The magnitude of this splitting (12 cm^{-1}) for the observable components of the out-of-plane -OH deformation is of the same order as that observed for the splitting of the in-plane -OH deformation (16 cm^{-1}).

We, therefore, feel that the intensity alteration observed in CH_3COOD for both the carbon-carbon stretching mode (854.6 cm^{-1}; α spectrum; 855.1 cm^{-1}; α + 90° spectrum) and the A" out-of-plane OD bend (671.8 cm^{-1}; α spectrum and 672.1 cm^{-1}; α + 90° spectrum) is indicative of the bands in the two spectra arising from different symmetry species in the factor group. We have no explanation for the decrease in the magnitude of interaction as the carboxylic hydrogen is replaced with deuterium. The other molecular mode in the crystalline CH_3COOD spectra which did not yield splittings greater than 1 cm^{-1} was the out-of-plane CO_2 deformation. In the α spectrum a band was observed at 581.7 cm^{-1} and in the α + 90° spectrum at 582.4 cm^{-1}. The splitting of 0.7 cm^{-1} along with the intensity changes observed in going from the α to the α + 90° spectrum coupled with the fact that a .5 cm^{-1} splitting was observed in the d_0 spectra lends credence to the assignment of the pair as arising from unit cell interactions and, in particular, those between the chains.

The polarized spectra of the d_4 derivative (CD_3COOD) were recorded for completeness. The frequencies observed for this compound are given in Table 5. The spectra yielded no new information but did substantiate some of the arguments presented above. The number of observable factor group components remained constant and all bands yielded significant intensity changes as the polarizer was rotated through 90°.

4. Conclusions

The increased resolution afforded by polarized infrared spectral techniques has allowed us to reach a new conclusion concerning interactions in solid state polymeric carboxylic acids. Our results indicate that both interchain and intrachain interactions must be considered when describing the primitive cell in solid acetic acid. The results are consistent only with a four molecule Bravais cell which is identical to the crystallographic unit cell. The manner in which the acetic acid crystals orient themselves with respect to the alkali halide substrates is extremely fortunate in that one factor component for all species is not observed. This allows resolution of the other two. For a general sample orientation, the third component might complicate the spectra sufficiently so as not to allow the resolution of more than a single distinguishable species.

Table 1. Vibrational Frequencies of Acrylic Acid (in cm^{-1})

Liquid[4]			Oriented Crystals	
R	IR	Assignment	θ	θ + 90°
			3221.2 s	3221 s
				$\sim$3145 sh
	3200-2500 s, vb	νOH	$\sim$3125 s	
3112 m		νCH_2	30.95.0 w, sh	
3076 w, sh		combination		
			3068.8 w, sh	
3039 s, P		νCH_2		
2998 w		νCH		
2935 w		combination		
			1983.4 vw	
			1955.0 w	
			1947.8 w	
			1800.0 w	
			1745.5 m, sh	
1728 m	1725 m	νC=C (op), overtone		
	1705 vs	νC=O (op)	1720.2 s	$\sim$1720 vw
			1680.1 m, sh	$\sim$1680 vw
1660 s, P		νC=O (ip)		
1637 vs. P	1636 s	νC=C (ip)	1634.3 s	1635 w
	1617 s	νC=C (op), combination	1616.3 w, sh	
			1522 w	
			1507 w	
1434 m	1432 s	νCH_2 scissors	1441 m-s	1441 w
	1413 m	νC-O (op)	1396.5 m	
1395 s, P		νC-O (ip)		
	1384 w	νCH bend	1382.5 m	
			1323.5 w-m	

Table 1. (con't.)

R	IR	Assignment	θ	$\theta + 90^\circ$
1295 w	1297 s	OH bend (op)	1302.3m	1302.7 vw
1280 s, P	1279 m	OH bend (ip)		
	1240 s	νCC (op)	1258.5 s	1258.5 w
1232 m, P		νCC (ip)		
1069 m	1068 m	CH_2 rock (op)	1077.8 m	
1048 m	1046 m	CH_2 rock (ip)		
977 m	984 s	CH_2 twist,	993.0 vw	993.4 vs
		CH_2 wag	975.5 vw	976.0 vs
928 w	925 m	OH bend (op)	$\sim$898 vw	896.8 vs
861 s, P	864 m	OH bend (ip)	876.0 w-m	
820 m	810 m	CH bend	815.7 w	815.7 s
643 m	650 m	CO_2 def (op)	655.6 m	655.8 w
625 m	628 w	CO_2 def (ip)		
548 w	552 w	CCO bend (op)	534.8 m	534.5 vw
525 m	525 w	CCO bend (ip)		
512 m	512 w	CO_2 wag		505 w-m
337 m	336 m	skeletal def	355.6 m	

---

s = strong, v = very, w = weak, m = medium, ip = in-phase, op = out-of-phase, P = polarized, sh = shoulder, ν = stretch

Table 2. Factor Group Component Predictions

Vibrational Species[a]	General Sample Orientation		XOO, OXO, OOX Orientation[b]		Experimental	
	Normal Unit Cell[c]	Chain Unit Cell[d]	Normal Unit Cell[c]	Chain Unit Cell[d]		
	F_p[e]	F_p[e]	F_p[e]	F_p[e]	F_e[e]	P_e[f]
A'	3	2	2	2 or 1	2	2
A"	3	1	2	0 or 1	2	2

a = assumed C_s molecular symmetry

b = faces perpendicular to infrared beam

c = C site symmetry, C_{2v}^9 space group symmetry

d = C_s site symmetry, C_{2v}^9 space group symmetry

e $F_{p(e)}$ = predicted (experimental) number of factor group components

f P_e = experimental number of unique band polarizations

Table 3. Fundamental Vibrational Modes[a] of Crystalline Acetic Acid $-d_o$

Assignment	Molecular Symmetry Species	Reported Frequency[15]	This Work[b]		
			Polarizer Out	α	α + 90
νOH	A'	2875	2910	2910	2910
$\nu'_s\ CH_3$	A'				
$\nu_s\ CH_3$	A'				
$\nu C{=}O$	A'	1648	1653.2	1652.5	1652.9
$\delta'_s\ CH_3$	A'	1448-39			
$\delta_s\ CH_3$	A'	1356	1347.0	1348.0	1354.0
δOH	A'	1418	1415.6	1402.4	1417.9
$\nu C{-}O$	A'	1248	1270.8	1268.3	1272.8
$\rho_s\ CH_3$	A'	1022	1017.6	1018.3	1016.7
$\nu C{-}C$	A'	908	911.4	908.9	911.6
δCOO	A'	635	629.6	627.9	631.0
δCCO	A'	450	452.3	452.6	451.4
$\nu_a CH_3$	A"				
$\delta_a CH_3$	A"	1448-39			
$\rho_a CH_3$	A"	1049	1044.2	1043.3	1044.0
γOH	A"	923	∿908	908.9	897.1
γCCO	A"	592		588.6	593.6

a = all frequencies in cm^{-1}

b = 193°K

Table 4. Fundamental Vibrational Modes[a] of Crystalline Acetic Acid $-d_1$

Assignment	Molecular Symmetry Species	Reported Frequency[15]	This Work[b]		
			Polarizer Out	α	α + 90
$\nu'_s CH_3$	A'	3040			
$\nu_a CH_3$	A"	3000			
$\nu_s CH_3$	A'	2950	2927		
νOD	A'	2194	2202.7	2204.2	2200.5
νC=O	A'	1644,1629		1644.4	1644.3
$\delta_s CH_3$	A'	1395,1385		1373.8	1394.7
νC-O	A'	1322	1318.2	1316.8	1318.9
δOD	A'	1972	1067.8	1067.9	1066.4
$\rho_a CH_3$	A"	1046	1044.7	1043.5	1044.8
$\rho_s CH_3$	A'	1010	1007.0	1007.1	1006.3
νC-C	A'	857		854.6	855.1
γOD	A"	678	671.6	671.8	672.1
δCOO	A'	611,606	606.2	604.2	607.8
γCCO	A"	580		581.7	582.4
δCCO	A'	446		446.6	445.6

a = all frequencies in cm^{-1}

b = 147°K

Table 5. Fundamental Vibrational Modes[a] of Crystalline Acetic Acid-d_4

Assignment	Molecular Symmetry Species	Reported Frequency[15]	This Work[b]	
			α	α + 90
νOD	A'	2187	$\sim$2195	$\sim$2190
νC=O	A'	1640	$\approx$1641	$\approx$1641
νC–O	A'	1340		
δOD	A'	1100	1095.5	1101.1
$\delta_s CD_3$	A'	1045	1043.4	1042.9
$\delta'_s CD_3$	A'	1035		
$\rho_s CD_3$	A'	841	838.7	839.6
νC–C	A'	808	807.8	809.4
δCOO	A'	591	591.0	592.5
δCCO	A'	399	399.6	399.4
$_a$CD	A"	1035		
$\rho_a CD_3$	A"	924	924.4	926.0
γOD	A"	672	669.6	669.7
γCCO	A"	505		

a = all frequencies in cm^{-1}

b = 95°K

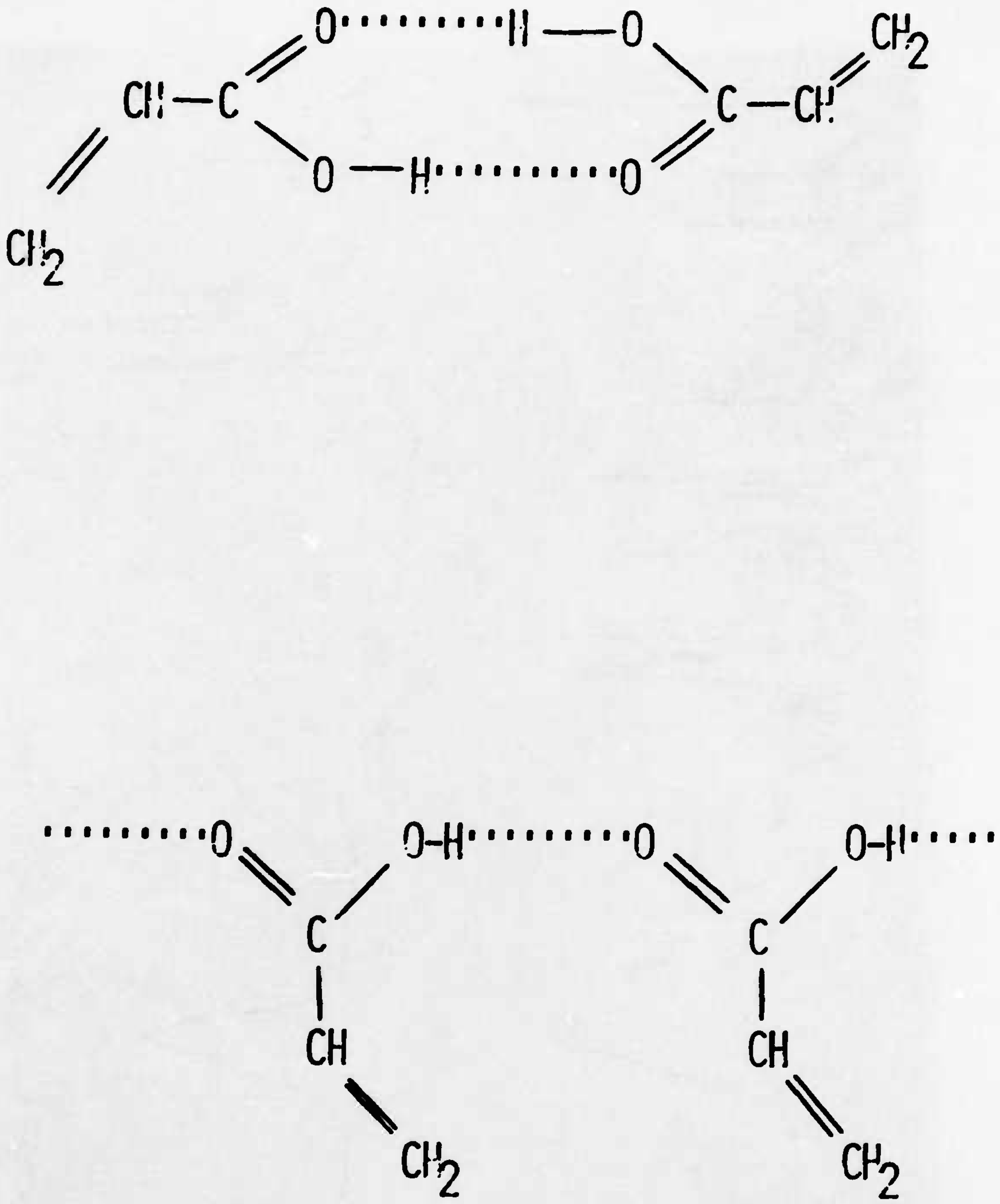


Figure 1. Possible Hydrogen-Bonded Structures of Acrylic Acid in Condensed Phases. Dimer Structures (upper) and Polymer Structure (lower). The polymer structure is not known for acrylic acid, but is the stable crystalline structure for certain other acids.

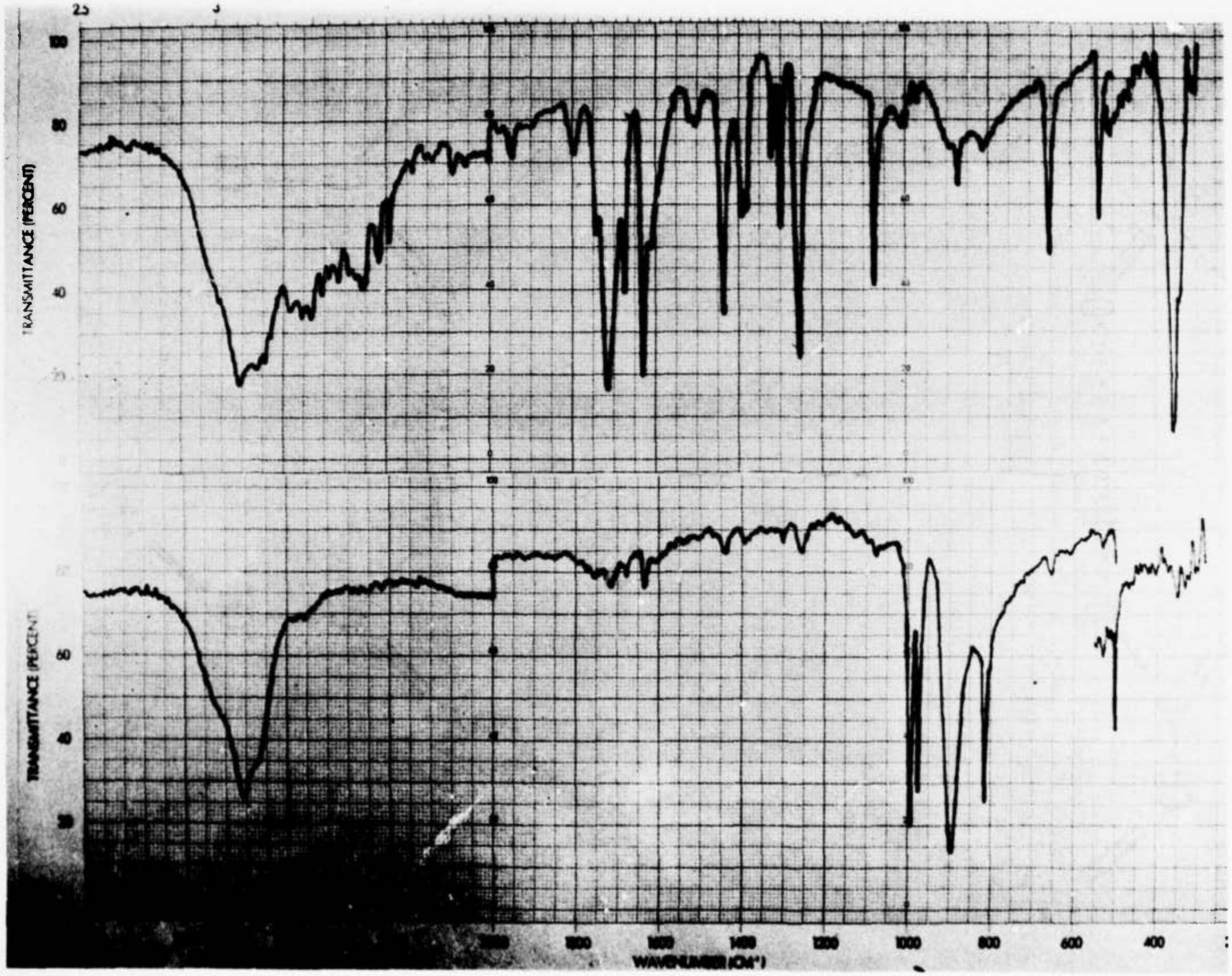


Figure 2. Polarized Mid-Infrared Spectra of Acrylic Acid. The two spectra differ by rotation of the polarizer by 90°. The break in the spectra at about 500 cm^{-1} indicates a longer pathlength below this value.

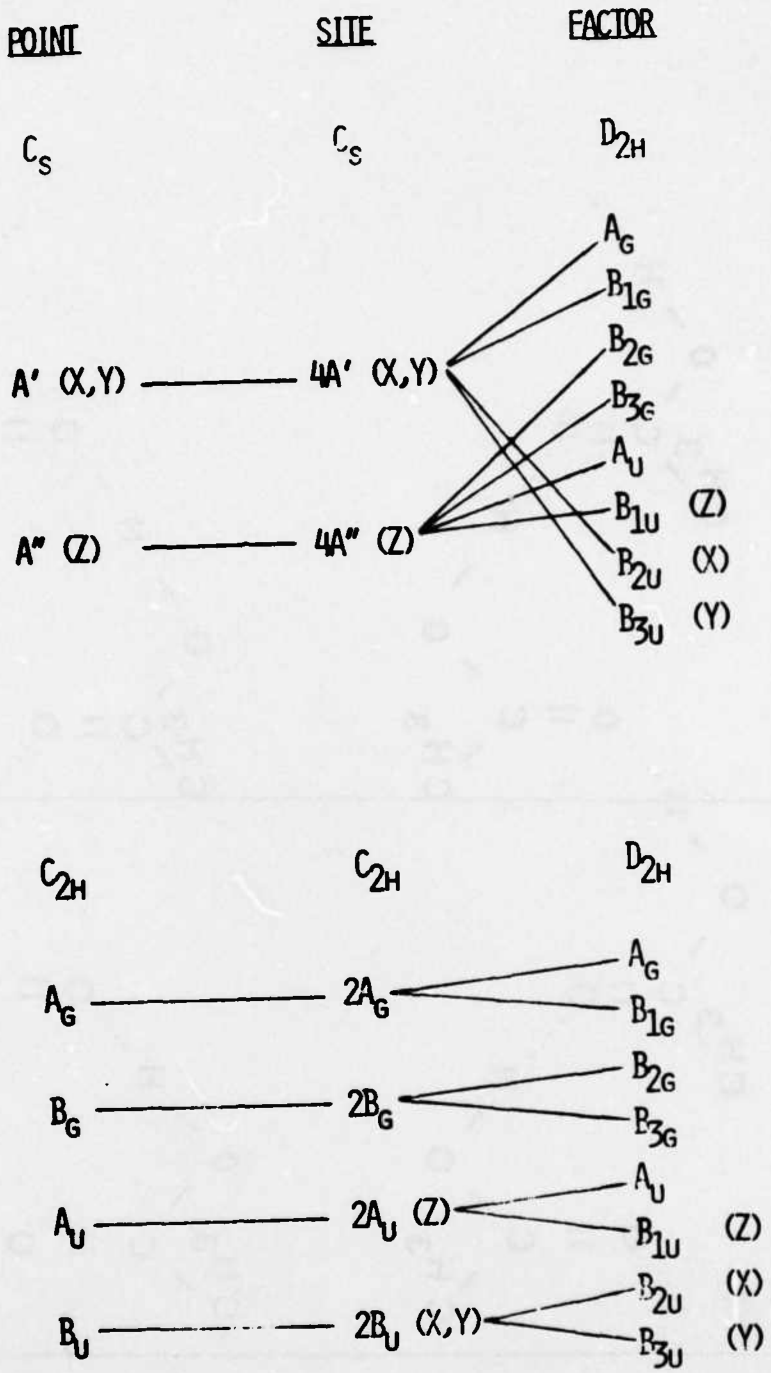


Figure 3. Correlation Diagrams for Acrylic Acid. The upper diagram represents the correlation in terms of monomer units and the lower represents the correlation in terms of dimer units.

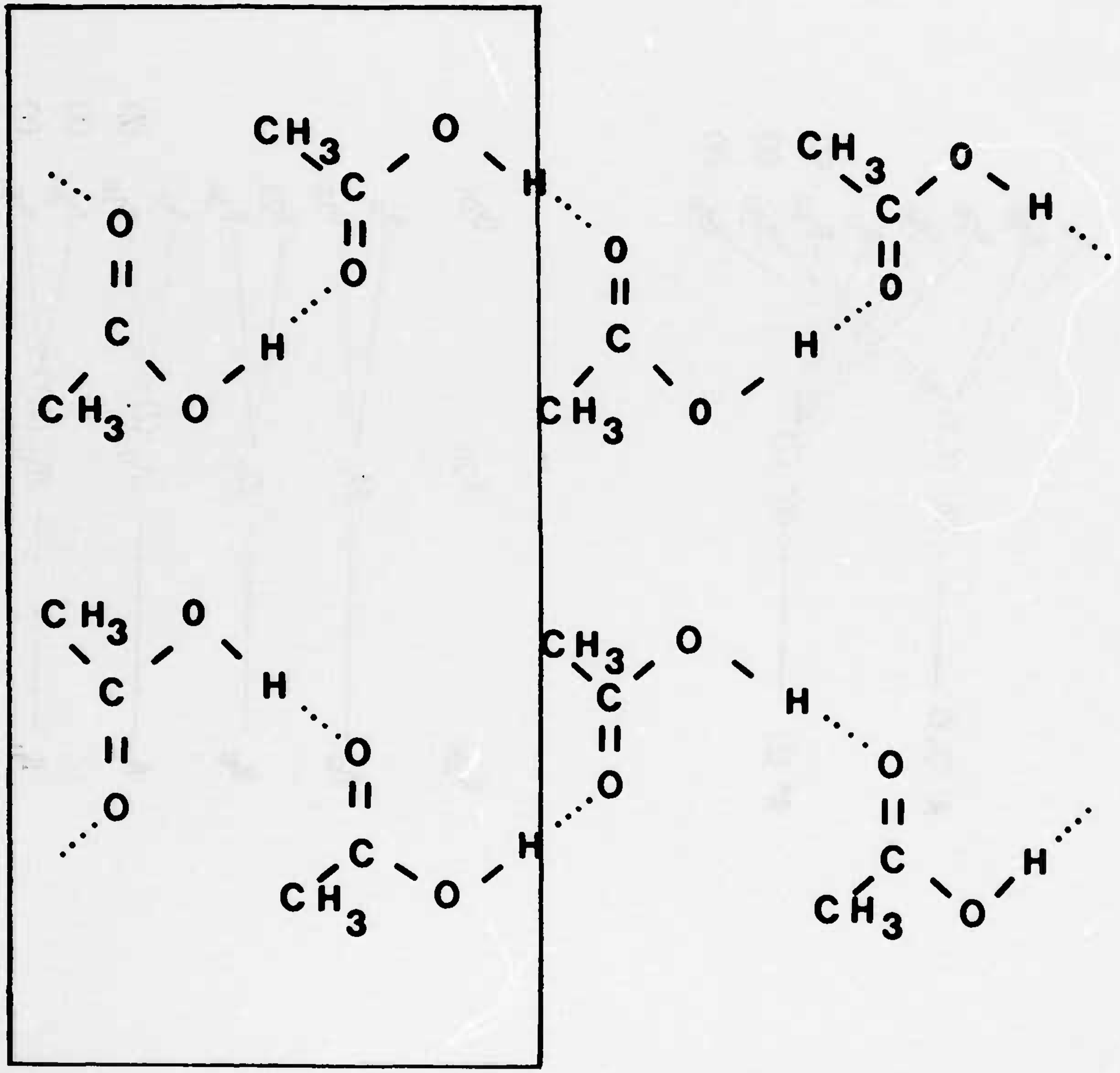


Figure 4. Projection of the unit cell of acetic acid on the ab plane. The polymer chains are spiral in nature.

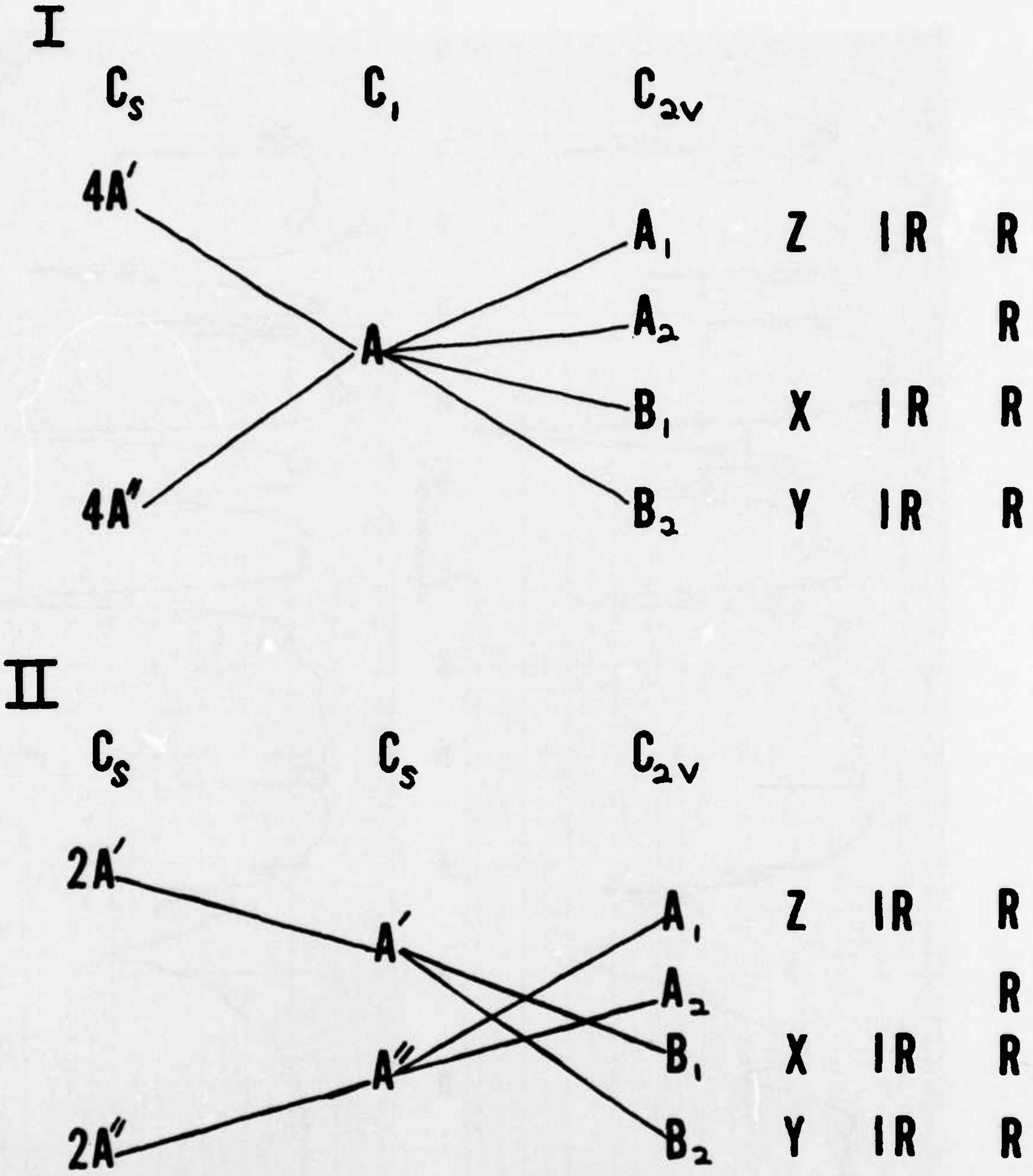


Figure 5. I. Correlation diagram for the four molecule Bravais cell of crystalline acetic acid.

II. Correlation diagram for two molecule chain unit cell of crystalline acetic acid.

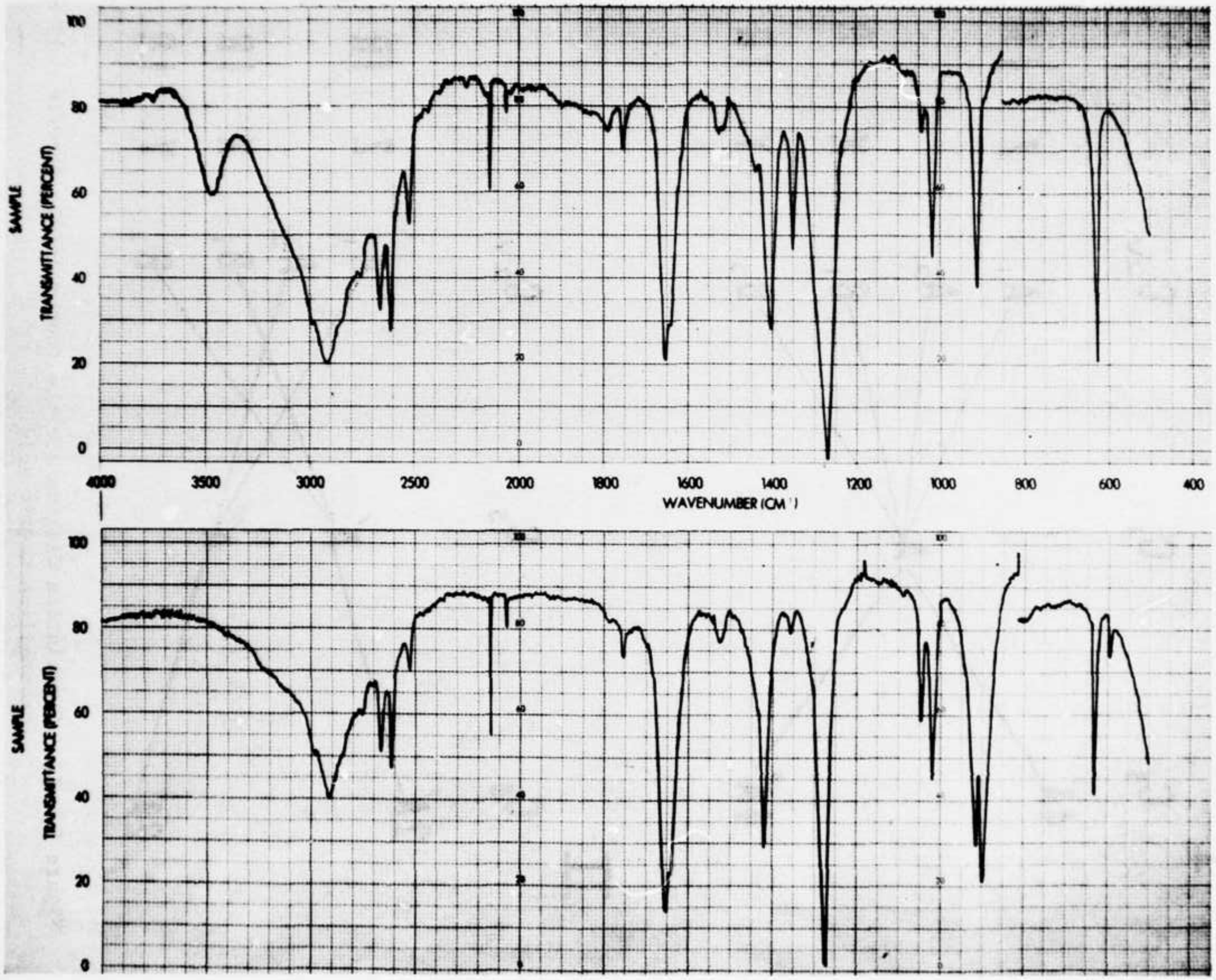


Figure 6. Polarized infrared spectrum of crystalline acetic acid-d_o at 190^{o}K. The two traces differ by a 90^o rotation of the polarizer.

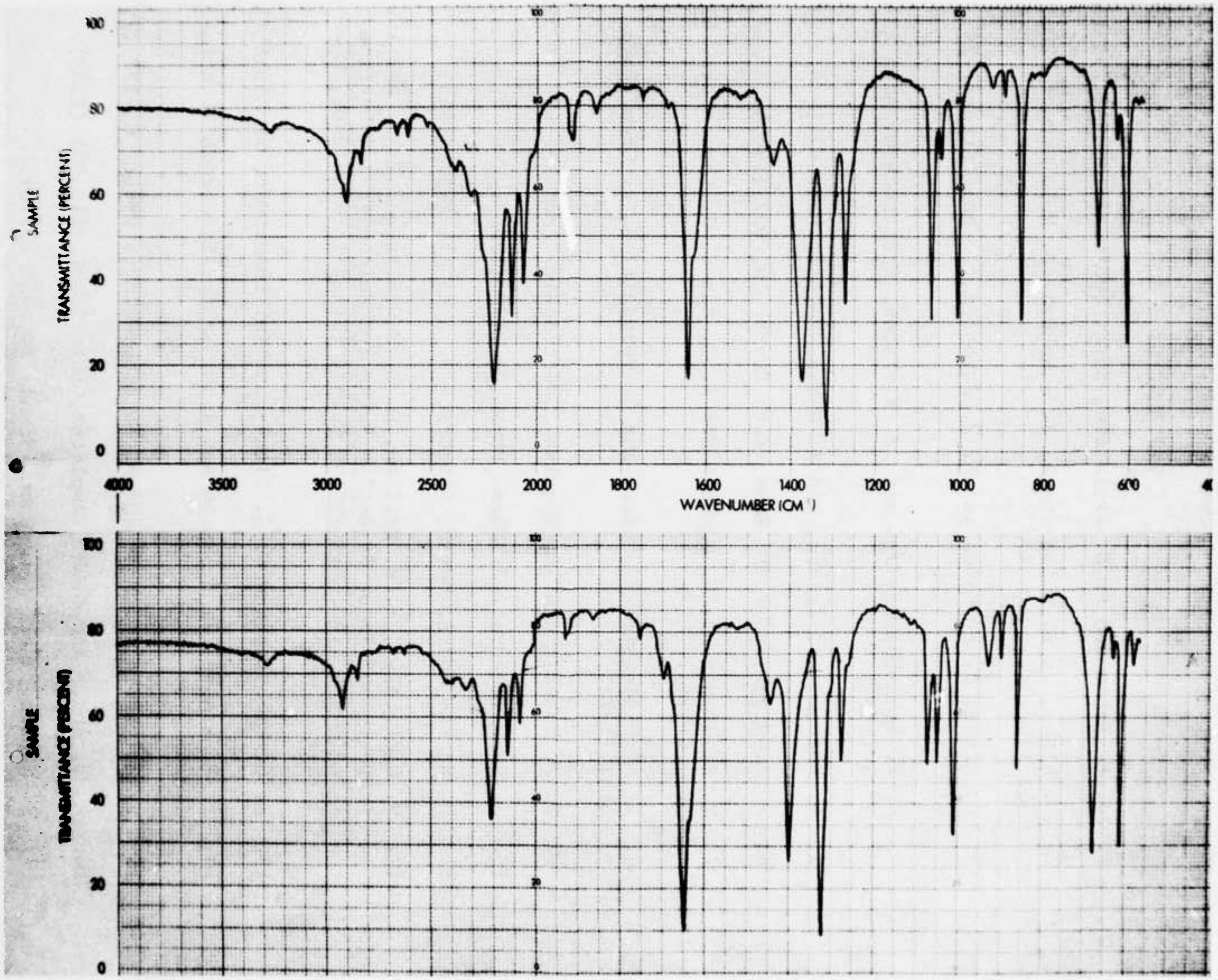


Figure 7. Polarized infrared spectrum of crystalline acetic acid-d_1 at 147°K. The two traces differ by a 90° rotation of the polarizer.

REFERENCES

1. J. E. Katon and R. L. Kleinlein, Spectrochim. Acta 29A, 791 (1973).
2. D. Sinha, J. E. Katon and R. J. Jakobsen, J. Mol. Struct. 20, 381 (1974).
3. D. Sinha, J. E. Katon and R. J. Jakobsen, J. Mol. Struct. 24, 279 (1975).
4. W. R. Feairheller, Jr. and J. E. Katon, Spectrochim. Acta 23A, 2225 (1967).
5. Y. Chatani, Y. Sakata, and I. Nitta, Polymer Letters 1, 419 (1963).
6. M. A. Higgs and R. L. Sass, Acta Cryst. 16, 657 (1963).
7. P. F. Krause, B. G. Glagola and J. E. Katon, J. Chem. Phys. 61, 5331 (1974).
8. E. A. DiAlessio, E. Dodero and C. Pomposiello, J. Chem. Phys. 57, 4137 (1972).
9. W. J. Potts and R. A. Nyquist, Spectrochim. Acta 15, 679 (1959).
10. J. K. Wilmshurst, J. Chem. Phys. 25, 478 (1956).
11. M. Haurie and A. Novak, Spectrochim. Acta 21, 1217 (1965).
12. W. G. Fateley, F. R. Dollish, N. T. McDevitt and F. F. Bentley, Infrared and Raman Selection Rules for Molecular and Lattice Vibrations: The Correlation Method (Wiley-Interscience, New York, 1972).
13. R. C. Millikan and K. S. Pitzer, J. Am. Chem. Soc. 80, 3515 (1958).
14. P. F. Krause, J. E. Katon and K. K. Smith, Spectrochim. Acta 32A, (1976).
15. F. Holtzberg, B. Post and F. Fankuchen, Acta Cryst. 6, 127 (1953).
16. R. E. Jones and D. H. Templeton, Acta Cryst. 11, 484 (1958).
17. I. Nahringbauer, Acta Chem. Scand. 24, 453 (1970).

18. P. G. Jonsson, Acta Cryst. B27, 893 (1971).

19. T. Shimanouchi, M. Tsuboi and T. Miyazawa, J. Chem. Phys. 35, 1597 (1961).

20. Y. Mikawa, R. J. Jakobsen and J. W. Brasch, J. Chem. Phys. 45, 4750 (1966).

21. R. J. Jakobsen, Y. Mikawa and J. W. Brasch, Spectrochim. Acta 23A, 2199 (1967).

22. Y. Mikawa, J. W. Brasch and R. J. Jakobsen, J. Mol. Spectry. 24, 314 (1967).

23. D. Hadzi and N. Sheppard, Proc. Roy. Soc. (London) A216, 247 (1953).

24. M. Haurie and A. Novak, J. Chim. Phys. 62, 146 (1965).

25. R. Foglizzo and A. Novak, J. Chim. Phys. 71, 1322 (1974).

26. K. E. Zul'fugarzade, L. A. Guliev and L. M. Imanov, Zh. Strukt. Khim. 11, 776 (1970).

27. T. Miyazawa and K. S. Pitzer, J. Chem. Phys. 30, 1076 (1959).

☆U.S.Government Printing Office: 1977 – 757-080/207