

Infrared Spectra of Crystalline Acetic Acid, a Hydrogen-Bonded Polymer

P. F. KRAUSE, J. E. KATON, J. M. ROGERS, and D. B. PHILLIPS

Department of Chemistry, Miami University, Oxford, Ohio 45056

The polarized infrared spectra of crystalline acetic acid and two of its deuterated derivatives, CH_3COOD and CD_3COOD , have been recorded from 400 to 4000 cm^{-1} at cryogenic temperatures. The spectroscopic results have been interpreted on the basis of a factor group analysis based on two structural models: a crystallographic cell composed of four interacting monomer units some of whose vibrational modes are highly perturbed by hydrogen bonding and a unit cell composed of two noninteracting acetic acid chains. The results are discussed in terms of possible interactions between the hydrogen-bonded acetic acid polymeric chains.

Index Headings: Polarized infrared spectra; Crystalline acetic acid; Hydrogen bonding.

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 acids¹⁻³ 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 acid⁴ and acetic acid⁵⁻⁷ crystallize in this manner.

Millikan and Pitzer⁸ 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 cell⁹ 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 Pitzer⁸ detailed analysis of the crystalline spectrum of formic acid has been shown¹⁰ to be incorrect because of polymorphism in crystalline formic acid.¹¹ 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,¹² however.

In analyzing the polarized infrared crystal spectra of acrylic acid,³ 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 fortuitous, the alternative approaches give identical predictions.

Therefore, it seemed worthwhile to investigate the

situation with an acid that crystallized as a hydrogen-bonded polymer. We 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 acid⁴⁻⁷ 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.*¹³ The acetic acid system seems particularly suitable for such a study because of the experimental infrared¹⁴⁻¹⁶ and Raman data¹⁷ available as well as theoretical calculations concerning the structure.¹¹

I. 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 48 h 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 .¹⁴ 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.¹⁸ 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 $\pm 1\text{ cm}^{-1}$ with a precision of $\pm 0.1\text{ cm}^{-1}$. The interpretative ambiguities that arose because of polymorphism in formic acid^{10,11} 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.^{11,19}

II. DISCUSSION

The crystal structure of acetic acid is essentially the same as that of formic acid,^{4,7} i.e., the structure exists as chains of hydrogen-bonded monomers. The structures are both orthorhombic with $\text{Pna}_2\text{1-C}_{2v}^{\text{c}}$ cell. Fig. 1 represents schematically the polymer structure of solid

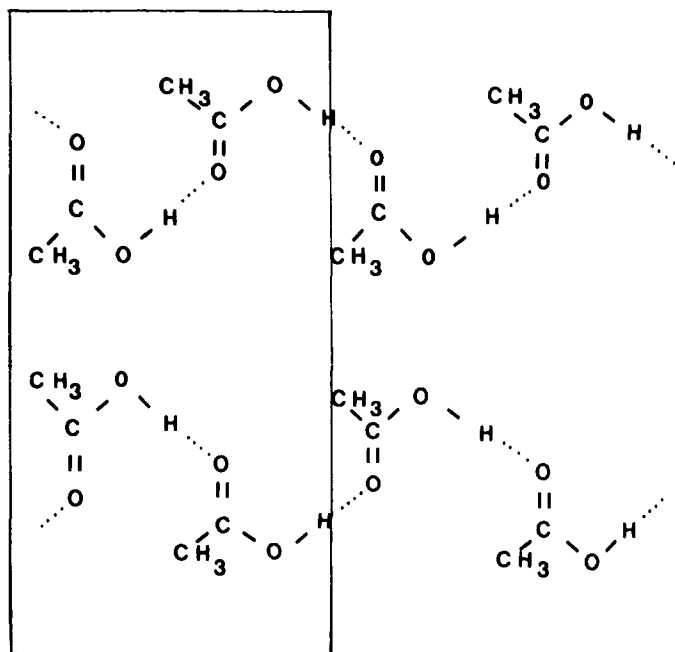


FIG. 1. Projection of the unit cell of acetic acid on the ab plane.⁷ The polymer chains are spiral in nature.

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.¹⁰

The α form, which Millikan and Pitzer⁸ grew by vapor deposition, gives two strong bands in both the ν C=O region and the ν C—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.⁵⁻⁷

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 Fig. 2. 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 Fig. 2. 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 of the A' modes infrared active while only one

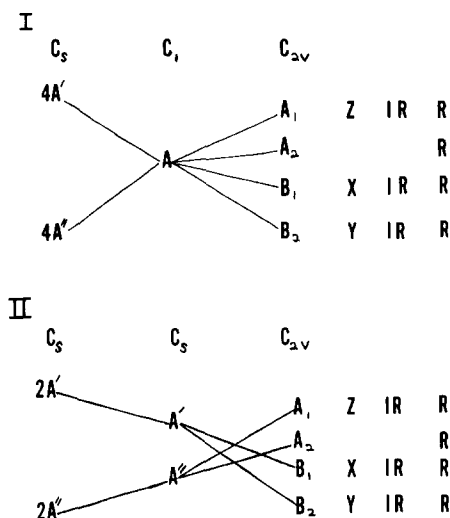


FIG. 2. I. Correlation diagram for the four-molecule Bravais cell of crystalline acetic acid. II. Correlation diagram for two-molecule chain unit cell of crystalline acetic acid.

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 Pitzer²⁰ to conclude that the neglect of interchain interactions is appropriate for their treatment of the solid infrared spectra. (The identical correlation diagrams shown in Fig. 2 may be formulated for formic acid.) Mikawa *et al.*¹² 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 and the specific orientation just mentioned for both the "normal" four molecule Bravais cell and for the two-molecule chain unit cell are summarized in Table I. 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 I 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 I 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

TABLE I. Factor group component predictions.

Vibrational species ^a	General sample orientation		XOO, OXO, OOX orientation ^b		Experimental	
	Normal unit cell ^c F _p ^c	Chain unit cell ^d F _p ^c	Normal unit cell ^c F _p ^c	Chain unit cell ^d F _p ^c	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 C₁ site symmetry, C_{2v} space group symmetry.

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

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

^f P_e = experimental number of unique band polarizations.

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.

Fig. 3 and Table II give the results for the polarized spectrum of crystalline acetic acid-d₀ at 190°K. The two traces in Fig. 3 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 II. In all

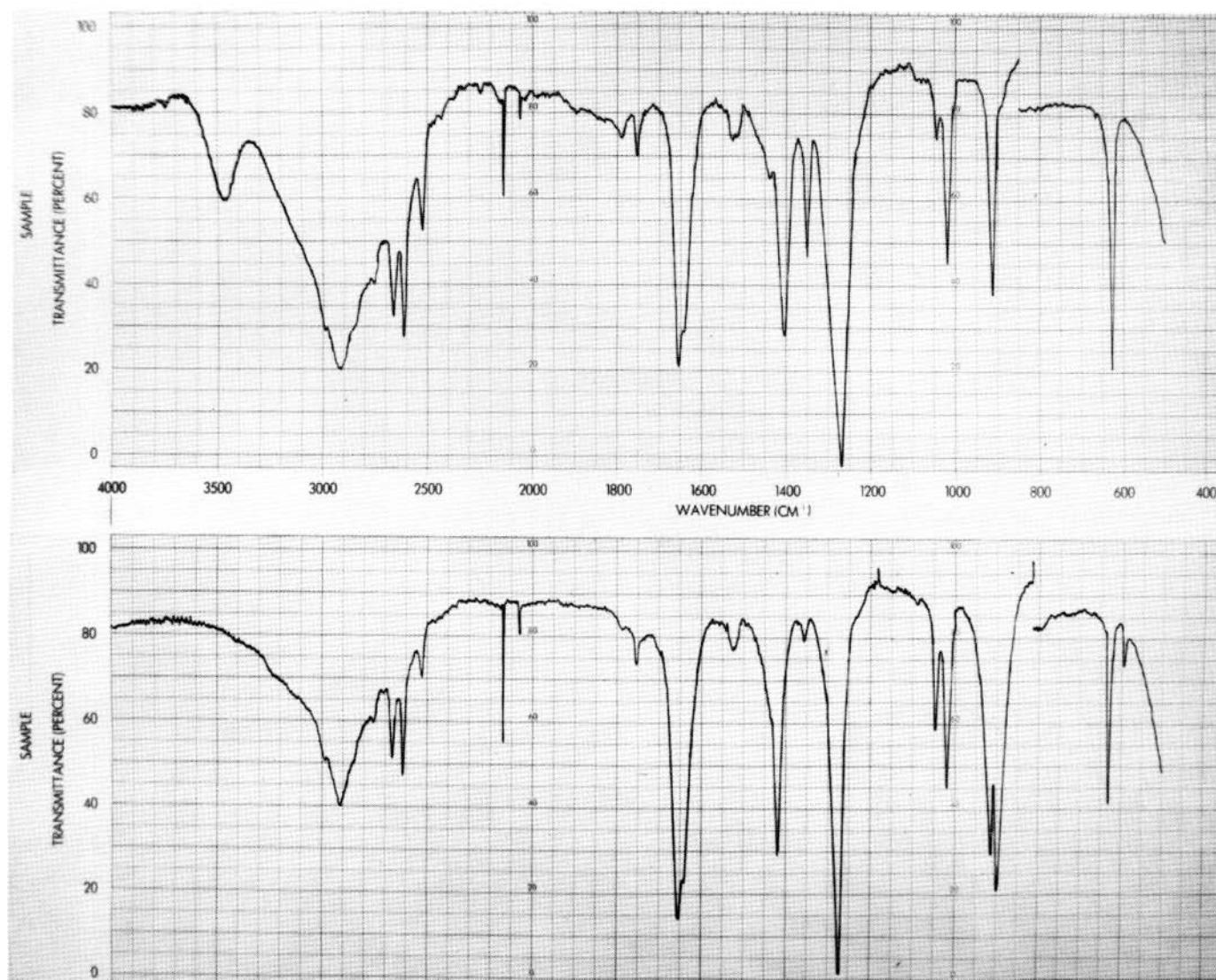


FIG. 3. Polarized infrared spectrum of crystalline acetic acid-d₀ at 190°K. The two traces differ by a 90° rotation of the polarizer.

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 $\pm 0.1\text{ cm}^{-1}$, 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 $-\text{OH}$ stretching mode nor the carbonyl stretching mode yields distinguishable infrared factor group components. In CH_3COOH , the $-\text{OH}$ stretching mode is a broad strong band with frequencies $2921 \pm 2\text{ cm}^{-1}$ 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 hypothesis 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.¹¹ From the latter,¹¹ a crystal splitting of 1 cm^{-1} for the $-\text{OH}$ stretching mode is predicted. Low frequency shoulders exist at 2665 , 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 $-\text{OH}$ 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 $\text{C}-\text{C}$ stretch (911.4 cm^{-1}) and the $\text{O}-\text{H}$ out-of-plane deformation at $\sim 908\text{ cm}^{-1}$. This problem is addressed below. Of particular significance is the out-of-plane CO_2 deformation. In the α spectrum a band was observed at 588.6 cm^{-1} . Upon 90° rotation of the polarizer, this band extinguished completely, and a new band at 593.6 cm^{-1} was observed.

TABLE II. Fundamental vibrational modes^a of crystalline acetic acid- d_6

Assignment	Molecular symmetry species	Reported frequency (Ref. 15)	This work ^b		
			Polarizer out	α	$\alpha + 90^\circ$
$\nu\text{ OH}$	A'	2875	2910	2910	2910
$\nu_s\text{ CH}_3$	A'				
$\nu_s\text{ CH}_3$	A'				
$\nu\text{ C=O}$	A'	1648	1653.2	1652.5	1652.9
$\delta_s\text{ CH}_3$	A'	1448-39			
$\delta_s\text{ CH}_3$	A'	1356	1347.0	1348.0	1354.0
$\delta\text{ OH}$	A'	1418	1415.6	1402.4	1417.9
$\nu\text{ C-O}$	A'	1284	1270.8	1268.3	1272.8
$\rho_s\text{ CH}_3$	A'	1022	1017.6	1018.3	1016.7
$\nu\text{ C-C}$	A'	908	911.4	908.9	911.6
$\delta\text{ COO}$	A'	635	629.6	627.9	631.0
$\delta\text{ CCO}$	A'	450	452.3	452.6	451.4
$\nu_a\text{ CH}_3$	A''				
$\delta_a\text{ CH}_3$	A''	1448-39			
$\rho_a\text{ CH}_3$	A''	1049	1044.2	1043.3	1044.0
$\gamma\text{ OH}$	A''	923	~ 903	908.9	897.1
$\gamma\text{ CCO}$	A''	592		588.6	593.6

^a All frequencies in cm^{-1} .

^b Temperature: 193°K .

This splitting is clear indication of factor group splitting for an out-of-plane mode. This finding 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 Fig. 4 and Table III. Of particular importance are the splittings observed for the OD stretch in CH_3COOD (α : 2204.2 cm^{-1} ; $\alpha + 90^\circ$: 2200.5 cm^{-1}) and the methyl rocking mode (α : 1043.5 cm^{-1} ; $\alpha + 90^\circ$: 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 and $\alpha + 90^\circ$ 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 $\alpha + 90^\circ$ 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 (Table IV). Secondly, the symmetric CH_3 deformation is split by less than 1 cm^{-1} (α : 1007.1 cm^{-1} ; $\alpha + 90^\circ$: 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 $\alpha + 90^\circ$ of CH_3COOD allows us to assign with confidence the 0.8 cm^{-1} splitting to factor group interactions.

The $\text{C}-\text{C}$ stretch raises an interesting question in

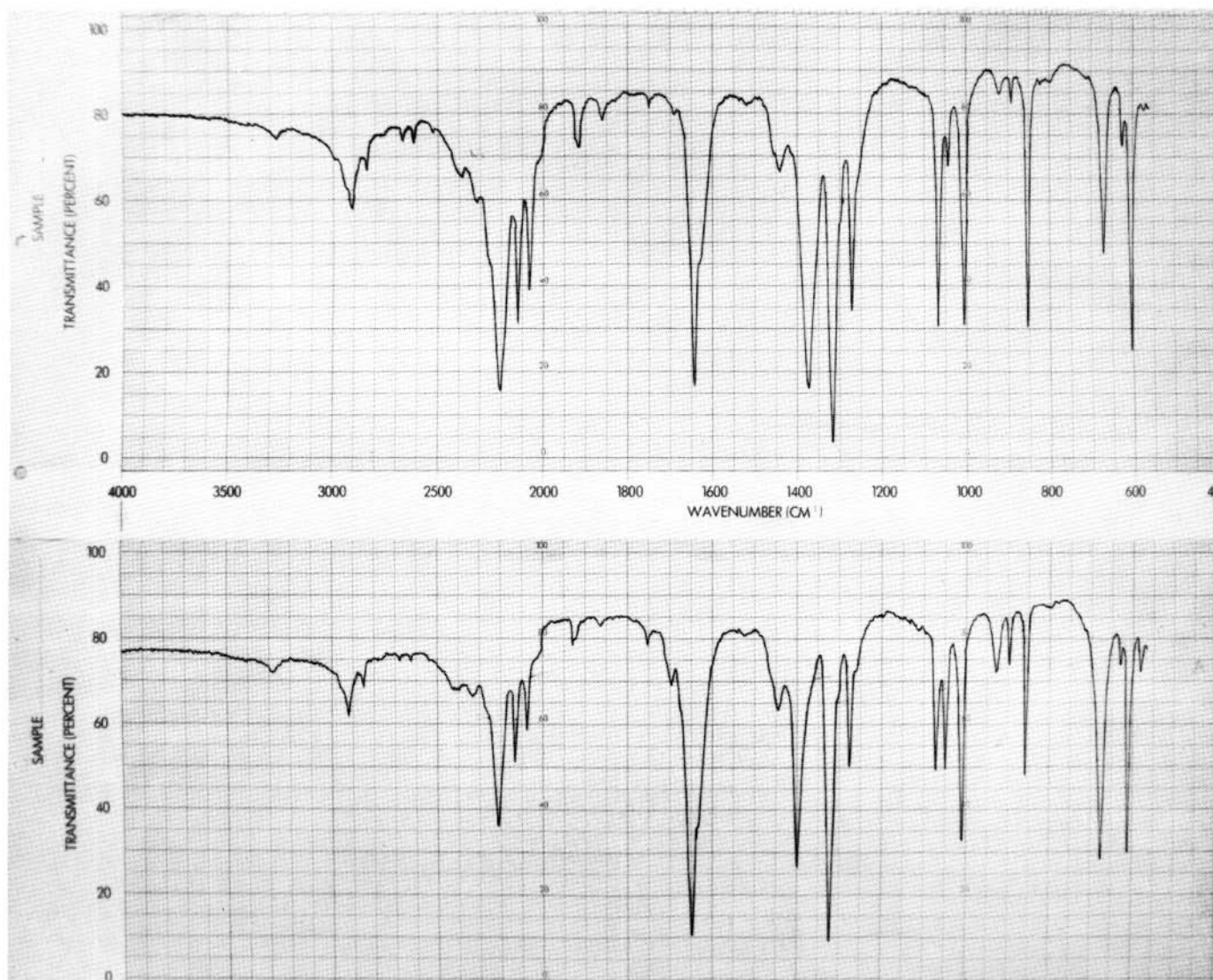


FIG. 4. Polarized infrared spectrum of crystalline acetic acid- d_1 at 147°K. The two traces differ by a 90° rotation of the polarizer.

both the CH_3COOH and CH_3COOD spectra. In the non-polarized d_0 spectrum a broad band ($\sim 908\text{ cm}^{-1}$) 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 $\nu\text{ C—C}$ (A') and the $\sim 908\text{ cm}^{-1}$ band to $\gamma\text{ OH}$ (A''). In the polarized d_0 spectra three bands are observed: 908.9 cm^{-1} (α spectrum), 911.6 cm^{-1} , and 897.1 cm^{-1} ($\alpha + 90^\circ$ spectrum). We have assigned the 897.1 cm^{-1} to one component of $\gamma\text{ OH}$ because of its intensity relative to the 911.6 cm^{-1} band (which is assigned to $\nu\text{ C—C}$). 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}).

Therefore, we 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} , $\alpha + 90^\circ$ spectrum) and the A'' out-of-plane OD bend (671.8 cm^{-1} , α spectrum; 672.1 cm^{-1} , $\alpha + 90^\circ$ 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 $\alpha + 90^\circ$ 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 $\alpha + 90^\circ$ 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.

TABLE III. Fundamental vibrational modes^a of crystalline acetic acid-d₁.

Assign- ment	Molecu- lar sym- metry species	Reported fre- quency (Ref. 15)	This work ^b		
			Polar- izer out	α	$\alpha + 90^\circ$
ν_s' CH ₃	A'	3040			
ν_a CH ₃	A''	3000			
ν_s CH ₃	A'	2950	2927		
ν OD	A'	2194	2202.7	2204.2	2200.5
ν C=O	A'	1644, 1629		1644.4	1644.3
δ_s CH ₃	A'	1395, 1385		1373.8	1394.7
ν C—O	A'	1322	1318.2	1316.8	1318.9
δ OD	A'	1072	1067.8	1067.9	1066.4
ρ_a CH ₃	A''	1046	1044.7	1043.5	1044.8
ρ_s CH ₃	A'	1010	1007.0	1007.1	1006.3
ν C—C	A'	857		854.6	855.1
γ OD	A''	678	671.6	671.8	672.1
δ COO	A'	611, 606	606.2	604.2	607.8
γ CCO	A''	580		581.7	582.4
δ CCO	A'	446		446.6	445.6

^a All frequencies in cm⁻¹.^b Temperature, 147°K.

The polarized spectra of the d₄ derivative (CD₃COOD) were recorded for completeness. The frequencies observed for this compound are given in Table IV. 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°.

III. 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

TABLE IV. Fundamental vibrational modes^a of crystalline acetic acid-d₄.

Assignment	Molecular symmetry species	Reported fre- quency (Ref. 15)	This work ^b	
			α	$\alpha + 90^\circ$
ν OD	A'	2187	~2195	~2190
ν C=O	A'	1640	≈1641	≈1641
ν C—O	A'	1340		
δ OD	A'	1100	1095.5	1101.1
δ_s CD ₃	A'	1045	1043.4	1042.9
δ_s' CD ₃	A'	1035		
ρ_s CD ₃	A'	841	838.7	839.6
ν C—C	A'	808	807.8	809.4
δ COO	A'	591	591.0	592.5
δ CCO	A'	399	399.6	399.4
ν_a CD ₃	A''	1035		
ρ_a CD ₃	A''	924	924.4	926.0
γ OD	A''	672	669.6	669.7
γ CCO	A''	505		

^a All frequencies in cm⁻¹.^b Temperature, 95°K.

spectra sufficiently so as not to allow the resolution of more than a single distinguishable species.

ACKNOWLEDGMENT

This work was supported in part by the U. S. Air Force under Contract F33615-73-C-5013.

1. D. Sinha, J. E. Katon, and R. J. Jakobsen, *J. Mol. Structure* **20**, 381 (1974).
2. D. Sinha, J. E. Katon, and R. J. Jakobsen, *J. Mol. Structure* **24**, 279 (1975).
3. P. F. Krause, J. E. Katon, and K. K. Smith, *Spectrochim. Acta* **32A**, 957 (1976).
4. F. Holtzberg, B. Post, and F. Fankuchen, *Acta Cryst.* **6**, 127 (1953).
5. R. E. Jones and D. H. Templeton, *Acta Cryst.* **11**, 484 (1958).
6. I. Nahringsbauer, *Acta Chem. Scand.* **24**, 453 (1970).
7. P. G. Jonsson, *Acta Cryst.* **B27**, 893 (1971).
8. R. C. Millikan and K. S. Pitzer, *J. Am. Chem. Soc.* **80**, 3515 (1958).
9. T. Shimanouchi, M. Tsuboi, and T. Miyazawa, *J. Chem. Phys.* **35**, 1597 (1961).
10. Y. Mikawa, R. J. Jakobsen, and J. W. Brasch, *J. Chem. Phys.* **45**, 4750 (1966).
11. R. J. Jakobsen, Y. Mikawa, and J. W. Brasch, *Spectrochim. Acta* **23A**, 2199 (1967).
12. Y. Mikawa, J. W. Brasch, and R. J. Jakobsen, *J. Mol. Spectrosc.* **24**, 314 (1967).
13. 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).
14. D. Hadzi and N. Sheppard, *Proc. Roy. Soc. (London)* **A216**, 247 (1953).
15. M. Haurie and A. Novak, *Spectrochim. Acta* **21**, 1217 (1965).
16. M. Haurie and A. Novak, *J. Chim. Phys.* **62**, 146 (1965).
17. R. Foglizzo and A. Novak, *J. Chim. Phys.* **71**, 1322 (1974).
18. P. F. Krause, B. G. Glagola, and J. E. Katon, *J. Chem. Phys.* **61**, 12 (1974).
19. K. E. Zulfargazade, L. A. Guliev and L. M. Imanov, *Zh. Strukt. Khim.* **11**, 776 (1970).
20. T. Miyazawa and K. S. Pitzer, *J. Chem. Phys.* **30**, 1076 (1959).