

THE INFRARED SPECTRUM AND STRUCTURE
OF CRYSTALLINE BARIUM FORMATE

by

BARRY ALBERT MORROW

B.Sc. University of British Columbia, 1961

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF
THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

in the Department

of

Chemistry

We accept this thesis as conforming to the
required standard

THE UNIVERSITY OF BRITISH COLUMBIA

September, 1962

In presenting this thesis in partial fulfilment of the requirements for an advanced degree at the University of British Columbia, I agree that the Library shall make it freely available for reference and study. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by the Head of my Department or by his representatives. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Department of Chemistry

The University of British Columbia,
Vancouver 8, Canada.

Date September 7/62.

ABSTRACT

The absorption of polarized infrared radiation by single crystals of barium formate has been recorded between 4000 and 500 cm^{-1} . Factor group splitting has been observed for molecular modes and for some of the overtones and combinations. Lattice mode frequencies are inferred from combinations with molecular modes. The infrared spectrum of polycrystalline lead and sodium formate, and of aqueous barium formate has been similarly recorded and compared with that of crystalline barium formate.

The nuclear magnetic resonance spectrum of barium formate has been recorded, and a discrepancy between the theoretical and experimental second moment indicates that a previously proposed crystal structure is incorrect. However, an X-ray and infrared study of a single crystal confirm that the factor group of barium formate is $P2_12_12_1$ and that there is no degradation of the crystal symmetry due to a possible distortion of the C-H bond of the formate ion. It is concluded that the coordinates of the carbon and oxygen atoms are incorrect in the original crystal structure determination.

The nuclear magnetic resonance spectrum of lead formate also indicates that the crystal structure of this compound is in error, but no attempt is made to elucidate the correct structure.

ACKNOWLEDGEMENT

I sincerely wish to thank Dr. K. B. Harvey for his encouragement and assistance in carrying out this study, and Mr. J. A. Donnan of the Geology Department for donating the materials for grinding and polishing the crystals. The help of the n.m.r. group for recording the n.m.r. spectra, Mr. N. Camerman for assisting with the x-ray analysis, and Mr. R. Muehlchen for the construction of the polarizer is also appreciated. Finally, I would thank the National Research Council of Canada for a Bursary.

Contents

	Page
Acknowledgment	i
Abstract	ii
Contents	iii
List of Tables	iv
List of Figures	v
Chapter 1: Introduction	1
1-1. The Problem	1
1-2. Methods of Investigation	3
Chapter 2: Experimental Work	5
2-1. Materials investigated spectroscopically	5
2-2. Growth of single crystals of barium formate	5
2-3. Grinding	9
2-4. Apparatus	11
2-5. Spectra	12
Chapter 3: Theory	19
3-1. General theory of vibrations in crystals	19
3-2. Application of symmetry	21
3-3. Crystal symmetry	25
3-4. Analysis of vibrations	26
Chapter 4: Discussion	29
4-1. Infrared spectra	29
4-2. N.M.R. results	40
4-3. Crystal structure of barium formate	42
4-4. Conclusion	44
Appendix: Factor group analysis of sodium formate	46
Bibliography	47

List of Tables

	page
Table 1: Infrared Spectra	12
2: The Infrared Absorptions of Barium Formate	16
3: Summary of previously Reported Raman Absorptions and of Observed Infrared Absorptions of Sodium Formate and Barium Formate-d ₁	18
4: Character Table and Factor Group Analysis of Barium Formate Under 222	30
5: Lattice Modes of Barium Formate	35
6: Calculated C ¹³ Frequency Shifts of Formate Ion	38
7: Product Rule Frequency Shifts of C ¹³ Formate Ion	39
8: Factor Group Analysis of Barium Formate Under 2	43

List of Figures

	To follow page
Figure 1: Infrared spectrum of polycrystalline barium formate	13
2: Infrared spectrum of polycrystalline barium formate-d ₁	13
3: Infrared spectrum of barium formate single crystal (<u>bc</u>), 2600-1000 cm ⁻¹	13
4: Infrared spectrum of barium formate single crystal (<u>ac</u>), 2600-1000 cm ⁻¹	13
5: Polarized infrared spectrum of barium formate single crystal, 3300-2500 cm ⁻¹	14
6: Polarized infrared spectrum of barium formate single crystal, 2000-1000 cm ⁻¹	14
7: Polarized infrared spectrum of barium formate single crystal, 800-740 cm ⁻¹	14
8: Infrared spectra of barium formate, 800-740 cm ⁻¹	
(a) <u>ca</u> single crystal	
(b) <u>cb</u> single crystal	
(c) polycrystalline in KBr pellet	15
9: Infrared spectra, 3200-2600 cm ⁻¹	
(a) Aqueous solution of barium formate	
(b) Polycrystalline sodium formate in KBr	
(c) Polycrystalline lead formate in KBr	15
10: (a) Crystal structure of barium formate projected on (001)	
(b) Projection of the positions of the protons of barium formate on (001)	29

CHAPTER 1: INTRODUCTION

1-1 The problem

Investigations of molecular motions by means of infrared and Raman spectroscopy have yielded a vast amount of information about the forces which hold atoms together to form molecules. However, the study of the vibrations of single molecules is limited to the gas phase, where interactions with other molecules are generally small. Procedures for determining force constants and fundamental frequencies of free molecules are well developed (1).

It is only relatively recently that procedures have been developed for analysing the motions of molecules in condensed systems, and in particular, in crystals. The experimental difficulties in obtaining extremely thin single crystals (30 to 100 microns) deterred earlier workers, at least while there was a store of substances which could be conveniently studied as vapors. Some work was done on the Raman spectra of single crystals around 1940, where much thicker crystals can be used than in the infrared technique, but the very slow progress in Raman spectrometer instrumentation has discouraged extensive work in this field. When the experimental difficulties can be overcome, much valuable information can be obtained concerning the nature of crystalline forces.

The most important difference between the spectrum of a substance in the vapor and crystalline state is that in the latter, many of the corresponding vapor phase frequencies are split into doublets and triplets, or may even be broadened into a "band" with considerable fine structure. The nature of this splitting will be discussed later.

When a molecule having a certain degree of symmetry is built into a crystal having a lower degree of symmetry, some of the degenerate modes may

be split in the infrared spectrum of the solid. Since the orientation of a molecule in a crystal is fixed, and if the crystal structure is known from X-ray data, the use of polarized radiation in recording the spectrum of the solid may aid in the vibrational assignments. Conversely, if the crystal structure is not known, the infrared spectrum of the crystal may point to the correct crystal structure. This technique for determining crystal symmetry is particularly useful for small molecules which have low melting points, and for hydrogen containing compounds where X-ray methods may not be applicable. Halford and Hornig have presented several papers in the last decade illustrating the use of infrared spectroscopy in determining the crystal structure of several small molecules. (2-5).

A salt of the formate ion was chosen for this study since the modes of vibration of an XYZ_2 type molecule are well characterized (6). The reasons for the choice of the barium salt are outlined in Chapter 2. The main purpose of this study was to test the theories developed by Bhagavantam and Venkatarayudu (7,8), and Halford (9) for the treatment of vibrations in crystals, and in particular, in a more complicated system than these workers have worked with. Of further interest in the case of barium formate is a discrepancy between the data obtained on the crystal structure from X-ray analysis (11), and that obtained from nuclear magnetic resonance studies on single crystals. (10) X-ray data give no information on the positions of the protons of the formate ion; however, using an average C-H bond length of 1.09 Å, the position of the proton can be estimated in the crystal, assuming the C-H bond is along the line bisecting the OCO angle. Saito et. al. (10) investigated single crystals of barium formate by N.M.R. and did not find agreement between

the predicted line shape and the experimental line shape. These workers concluded that the crystal structure data must be in error. This conclusion is further substantiated by the fact that the calculated distance between the barium ion and its nearest hydrogen is only 1.3 Å using the X-ray data, a value less than the sum of the radius of the barium ion and hydrogen, which is 3.2 Å. Hence, it was hoped that our investigation of the infrared spectrum of barium formate could throw some light on this discrepancy.

As far as could be found from extensive searching of the literature by this author, no report has ever been published on the infrared spectrum of any inorganic formate. However, studies have been carried out on the Raman spectrum of several formates. Gupta (16) reported the Raman spectrum of sodium and cadmium formate in aqueous solution, and of cadmium, barium and lead formates as crystals. But, very few frequencies were reported, most of them being of doubtful accuracy. Lecomte (17,18) has reported the Raman spectrum of aqueous sodium and barium formate, with incorrect assignments, and does not report all the frequencies. Fonteyne (19,20) did a very accurate Raman study of aqueous sodium formate and sodium formate- d_1 , made a complete vibrational assignment, and calculated the force constants of the formate ion, using a Urey-Bradley potential function. This latter work will be referred to in the discussion, as it is the only known vibrational study of any accuracy of the formate ion in either solution or crystal.

1-2 Methods of Investigation

- (a) The infrared spectra of polycrystalline barium formate in KBr, of single crystals of barium formate with polarized radiation, of a solution of

barium formate in water, and of deuterated barium formate in KBr were recorded.

- (b) X-ray photographs with a precession camera were taken to determine the space group of crystalline barium formate.
- (c) Nuclear magnetic resonance studies were carried out on polycrystalline barium formate and lead formate to determine the second moment.
- (d) The infrared spectrum of sodium formate and of lead formate were recorded for comparison with that of barium formate. The crystal symmetry of lead formate is reported to be the same as that of barium formate, and therefore should have a similar infrared spectrum.

CHAPTER 2: EXPERIMENTAL WORK

2-1 Materials investigated spectroscopically

<u>Barium formate</u>	(a) Prepared by the neutralization of formic acid with barium carbonate, filtered, and recrystallized three times from solution.
	(b) Bios Laboratories, reagent grade.
	In both cases there was a slight contamination of insoluble material, probably barium carbonate, which was removed from solution by filtration.
<u>Barium formate-d₁</u>	Prepared as above (a) with formic acid-d ₁ .
<u>Sodium formate</u>	Baker and Adamson reagent grade.
<u>Sodium formate-d₁</u>	Merck Chemical Company
<u>Lead formate</u>	Prepared by crystallization from a solution of sodium formate and lead nitrate, and recrystallized twice.

2-2 Growth of Single Crystals of barium formate

A salt of the formate ion was chosen for this study since it is a small ion whose vibrational spectrum is well characterized. It was desirable to have a salt which is neither a hydrate when crystallized from solution, nor hygroscopic at room temperature. Only the barium, calcium and lead salts had these desirable properties.

The simplest method of growing large single crystals from solution is by slow evaporation of a saturated solution of the material being considered. With this procedure, a small seed crystal is usually mounted in the solution, and growth proceeds with evaporation, Lead

formate was then eliminated as it is relatively insoluble in water at room temperature. However, calcium and barium seed crystals were grown very easily; when a one cm. layer of saturated solution was placed in a 7 cm. (diameter) evaporating dish covered with a filter paper, small seeds up to two mm. in length appeared in two to three days. The crystals of calcium formate were quite irregular, and it was felt that these would be much more difficult to work with than the symmetrical bisphenoids of barium formate. Hence, the choice of barium formate for this study.

Several methods were tried in order to grow a large single crystal, one to two centimeters in length, from the small seeds. In the first attempts, seeds were suspended by thread, hair, or thin platinum wire, into saturated solutions of barium formate, in a 150 ml. beaker. The "support" was tied around a small seed, (1-2 mm. in length) and was suspended from a glass rod placed across the top of the beaker. A paper "tent" was placed over the beaker to keep dust particles out. Fairly large (1-1.5 cm.) but often imperfect crystals resulted; the rate of evaporation was probably too great in an open 150 ml. beaker. Further complications arose from the great clusters of smaller crystals that grew along the support, often growing into the main crystal itself. In order to obtain a suitable crystal by this method, the main crystal would have to protrude at least 10 to 15 mm. on each side of the support, so that there would be a clear section to grind. This was not realized and the method was discarded.

Since it appeared desirable to slow down the rate of evaporation, fifty ml. conical flasks were used in further trials. A seed was placed on the bottom of a flask, containing about one cm. of saturated solution, and the flask was placed in a cupboard where the dust circulation from

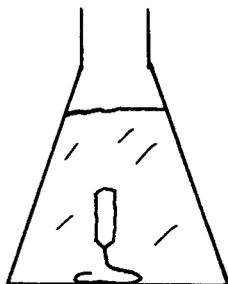
the air was minimized. About one out of five crystals grew to an appreciable size (1 to 1.5 cm. in length) before a mass of smaller seeds grew on the bottom of the flask. However, these larger crystals were not too well developed on the bottom face, and always had many flaws.

The large crystals from the above method grew in about three weeks. However, it was noted that very frequently when a small seed was placed in such a flask, after two to seven days the crystal would have perhaps quadrupled in volume being six or seven mm. in length, by 2mm. wide. These medium size seeds were usually flawless, and were used in further experiments to be described. When reference is made to a medium seed, it will mean one of the type described in this paragraph.

An unsuccessful attempt was made to grow large crystals by a slow cooling method. From the solubility-temperature data for barium formate, it was estimated that about two grams of material should deposit from one hundred ml. of saturated solution in cooling from forty to thirty degrees C. A medium seed was cemented vertically to the end of a small coil of plastic coated copper wire ("CIL" Cement was used) and was placed in a jar (13 cm. high, 7 cm. in diameter) containing four hundred ml. of saturated solution at 45 degrees C. The jar was placed in a thermostatically controlled bath at the same temperature and a rubber stopper with a small hole to allow a glass stirring rod to be inserted was placed over the jar. The solution in the jar was stirred at seven to ten r.p.m., while the temperature of the bath was lowered 0.2 to 0.4 degree C. per day until the temperature was around 30 degrees C. Several attempts were made to grow crystals by this method, but without success. Only slight growth occurred in most cases.

Evaporation procedures were again resorted to. Two methods proved very successful and will be described. Both entailed the vertical mounting of a medium seed on the end of a coil of wire, in the manner described in the last paragraph.

In one method, the coil of wire with the seed was placed in a fifty ml. conical flask, filled nearly to the top with saturated solution. This gave a very small surface area, and hence, very slow evaporation.



After three to six weeks a large crystal (15 to 20 mm. above the end of the wire) grew, which could be broken off at the wire by twisting the crystal slowly. About two out of five crystals grown by this method were completely flawless, and were perfect for grinding. Even some of the others with flaws were usable.

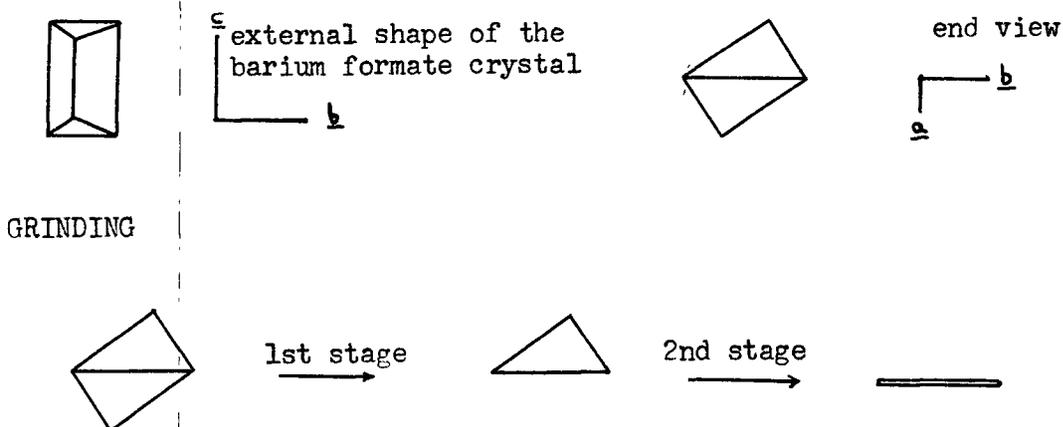
In the second method, the coil with the seed was placed in a jar containing about four hundred ml. of saturated solution. A filter paper covered the top, with a small hole for a stirrer, turning at about seven to nine r.p.m. Due to the large volume of solution, the rate of supersaturation of the solution was slow, even though the rate of evaporation was fast. Hence, after ten to twelve days a large single crystal grew from the seed; one specimen was 25 mm. long, but the others were stopped before this size was reached. The crystals grown by this method frequently had several flaws, but often the top centimeter of the crystal was flawless, and could be broken off from the rest of the crystal. Again, about two

out of five trials were successful.

2-3 Grinding

In order to study the infrared absorption spectrum of a single crystal, the crystal generally must be around forty to fifty microns in thickness. Thinner crystals would be desirable, but this is usually mechanically unfeasible. For this work, the crystal had to have a cross section of 10 mm. x 1.5 mm. in order completely to cover the light beam. Hence, it was necessary to start with a crystal at least one cm. in length, usually being four to five mm. wide. About a dozen suitable crystals were grown, most of them being fifteen to twenty mm. in length.

Grinding was done on a plate glass lap, with a suitable abrasive and lubricant. In barium formate, the crystal was ground perpendicular to the a or b axis, (the crystal axes are those designated by Groth (22), and are shown below) until the maximum cross' section was obtained. Hence, grinding proceeded from two edges, to the center of the crystal.



For the first stage, the crystal was held by hand and was ground by slowly moving it back and forth, over the face of the lap, with slight

pressure applied. Kerosene was used as a lubricant at all times. Initially a carborundum abrasive #600 was employed; this cut very quickly and was used until the crystal was to within ten or fifteen percent of the size desired. Then a finer bauxite abrasive #950 was used for the remainder of the grinding, giving a flat, relatively smooth surface. Finally, the fresh surface was polished on a piece of silk cloth held over a flat glass plate. A drop of kerosene was initially used, but was done away with for the final polishing.

At this stage the other half of the crystal could be ground. The polished face was cemented with Radio Service Cement to a sodium chloride plate. Care was taken to see that the entire surface was cemented down in order to eliminate the possibility of chipping when the crystal became very thin. This particular cement was used as it could be applied in a reasonably thin layer, and is very soluble in acetone, which was used to remove the crystal from the NaCl plate. The reason for using kerosene as a lubricant now becomes clear. Both water soluble barium formate and the cement are insoluble in kerosene. Other liquids have this property, but a desirable lubricant for this work should not have too high a viscosity or volatility.

The grinding with the two abrasives then proceeded in the same manner as described. When the crystal was down to about 150 microns thickness, grinding proceeded very slowly with only slight pressure on the plate, as fracturing easily occurred. Care was taken to ensure that the thickness was as uniform as possible. The grinding continued until the crystal was the desired thickness (40 to 50 microns); it was deemed thin enough when the strongest absorption bands of the formate ion were resolvable in the infrared (ignoring the absorption due to the cement). The thin section

was polished slightly on the silk cloth, but frequently severe fragmentation occurred, and crude polishing only was possible for this surface. Uniformity of thickness and extinction was checked under the polarizing microscope.

The thin crystal section was removed from the NaCl plate by dissolving off the cement in acetone. This usually required one to three days. Shattering occurred if the crystal was "pushed" to remove it from the plate. Instead, the acetone solution was swirled periodically, and eventually the crystal became free, moving slightly over the surface of the NaCl plate.

The crystal was then transferred carefully to a brass plate having a narrow slit for use in the spectrometer. The transfer was done in the acetone solution by placing the brass plate at the same level as the NaCl plate, and slowly pushing the crystal with a wooden toothpick over to the slit. By means of the polarizing microscope, one principal axis of the crystal was aligned parallel to the slit. The crystal was cemented to the brass plate with an acetone insoluble epoxy resin cement, and was washed by dipping in acetone.

The polarizer was constructed by mounting two sets of three $1/2$ mm. thick silver chloride plates in the form of a "V", so that light passed through both stacks of plates at Brewster's angle to each set. It was similar to that described by Charney (12).

2-4 Apparatus

All spectra were run on a Perkin-Elmer dual grating spectrophotometer, model 421. The n.m.r. spectrometer used was a Varian Associates V4200/4300B

instrument operating at 40 megacycles per second and 9395 gauss for proton resonance. For the X-ray analysis, precession photographs were taken of the $h0l$, hll , $0kl$, and lkl zones of a single crystal of barium formate.

2-5 Spectra

Table 1 lists the infrared spectra shown in Fig. 1-9. If the spectrum was recorded using polarized light, the direction of polarization is indicated as being along axis a, b, or c. A crystal section that was ground along the a or b axis is listed as a bc or ac type crystal respectively.

TABLE 1
Infrared Spectra

Fig. No.	Description	Polarization
1	Ba(CHO ₂) ₂ -polycrystalline in KBr	
2	Ba(CDO ₂) ₂ -polycrystalline in KBr	
3	Ba(CHO ₂) ₂ -single crystal, <u>bc</u>	
4	" -single crystal, <u>ac</u>	
5	" -single crystal, 3300-2500 cm ⁻¹	<u>a,b,c</u>
6	" -single crystal, 2000-1000 cm ⁻¹	<u>a,b,c</u>
7	" -single crystal, 800--740 cm ⁻¹	<u>a,b,c</u>
8	" -single crystal <u>ac</u> and <u>bc</u> and polycrystalline in KBr, 800-740 cm ⁻¹	
9	Ba(CHO ₂) ₂ aqueous, Pb(CHO ₂) ₂ in KBr, and NaCHO ₂ in KBr, 3200-2600cm ⁻¹	

Table 2 lists the observed infrared absorption frequencies of crystalline barium formate, along with assignments and polarization properties. Table 3 lists previous data for barium formate, sodium formate, and observed frequencies for sodium formate and barium formate-d₁.

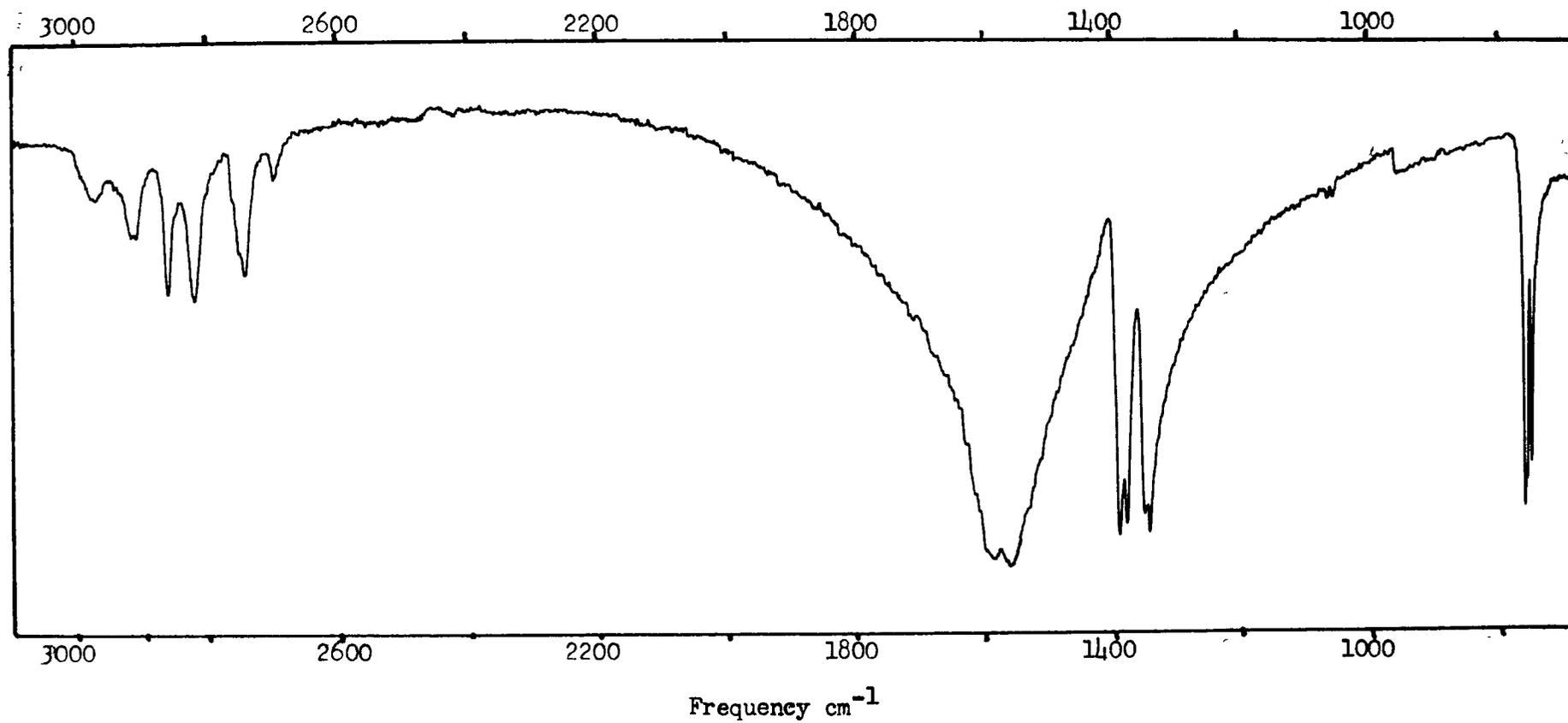


Figure 1: Infrared spectrum of polycrystalline barium formate. Discontinuity at 970 cm^{-1} is part of background.

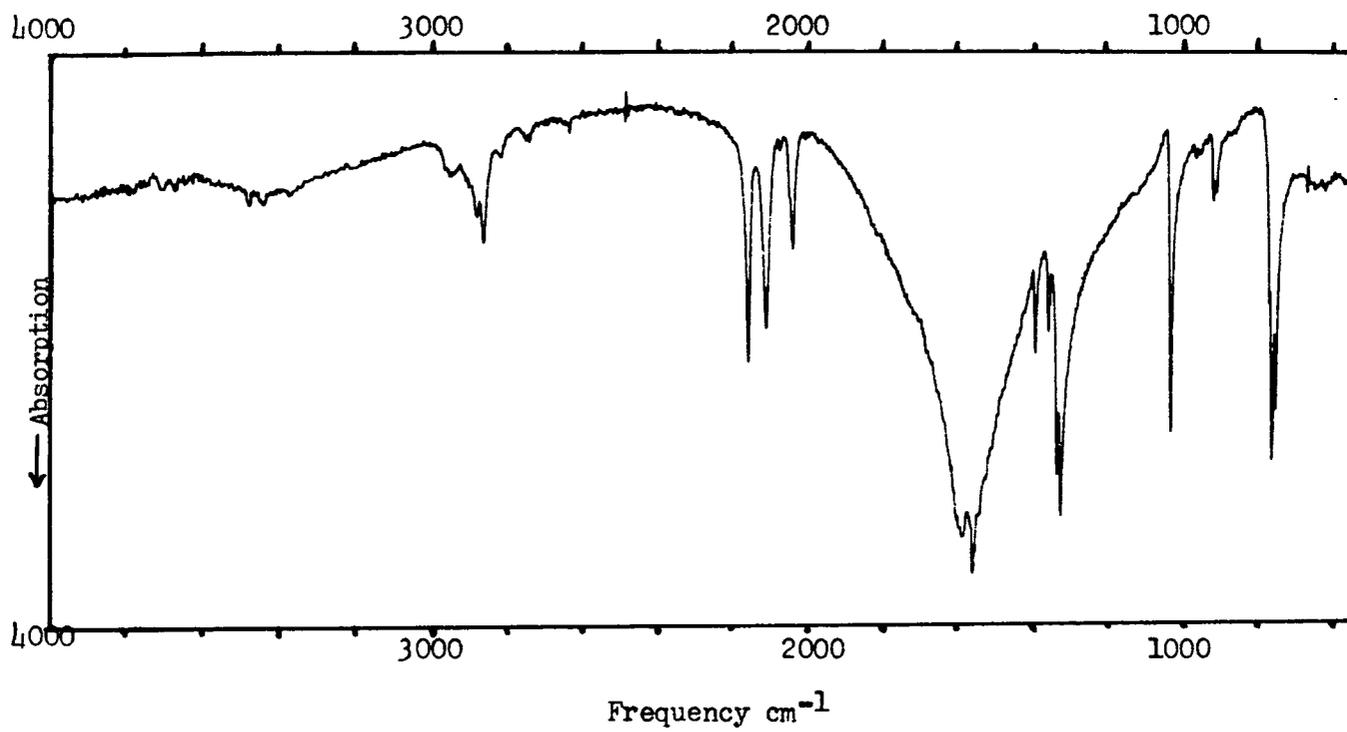


Figure 2: Infrared spectrum of polycrystalline barium formate-d₁

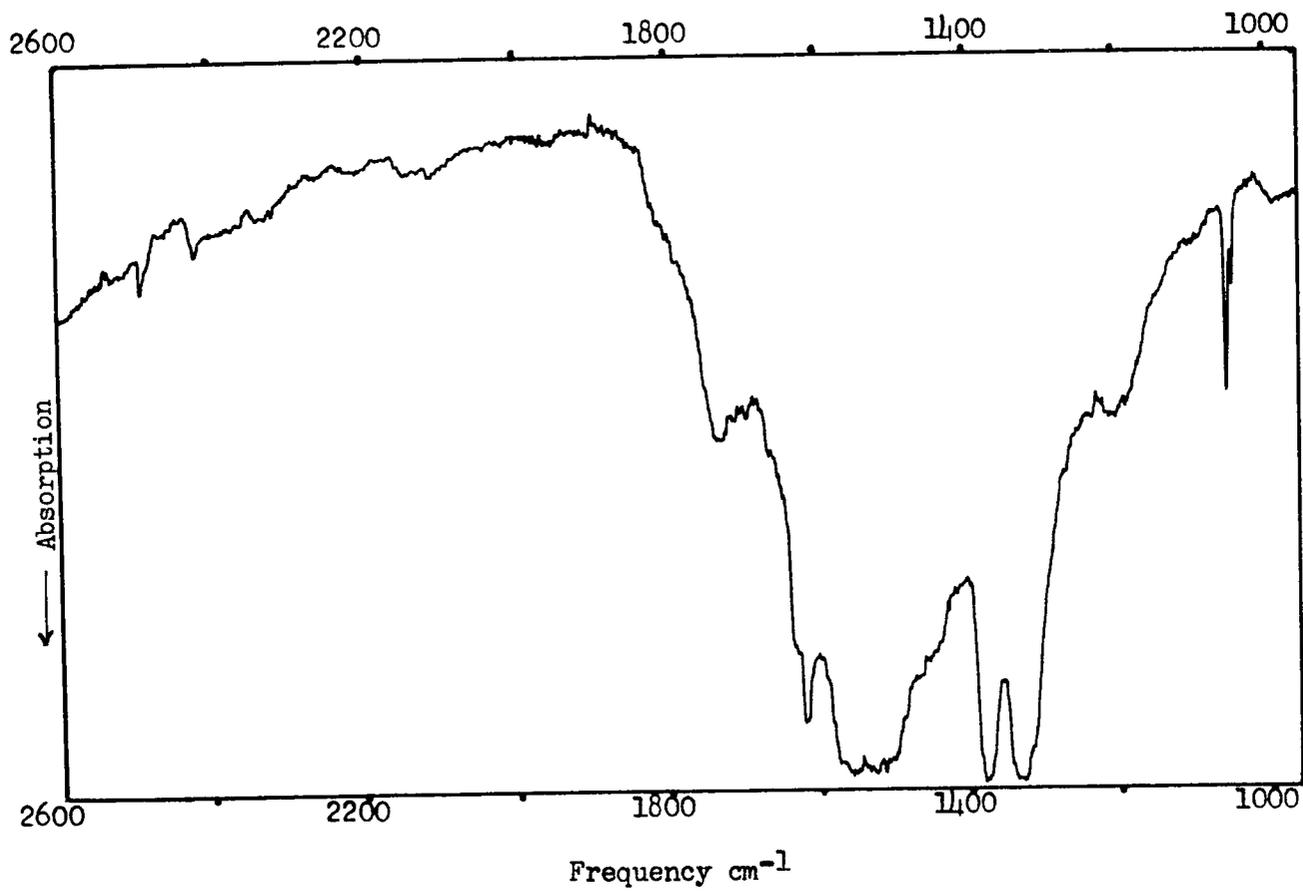


Figure 3: Infrared spectrum of barium formate single crystal (bc)

2600-1000 cm⁻¹

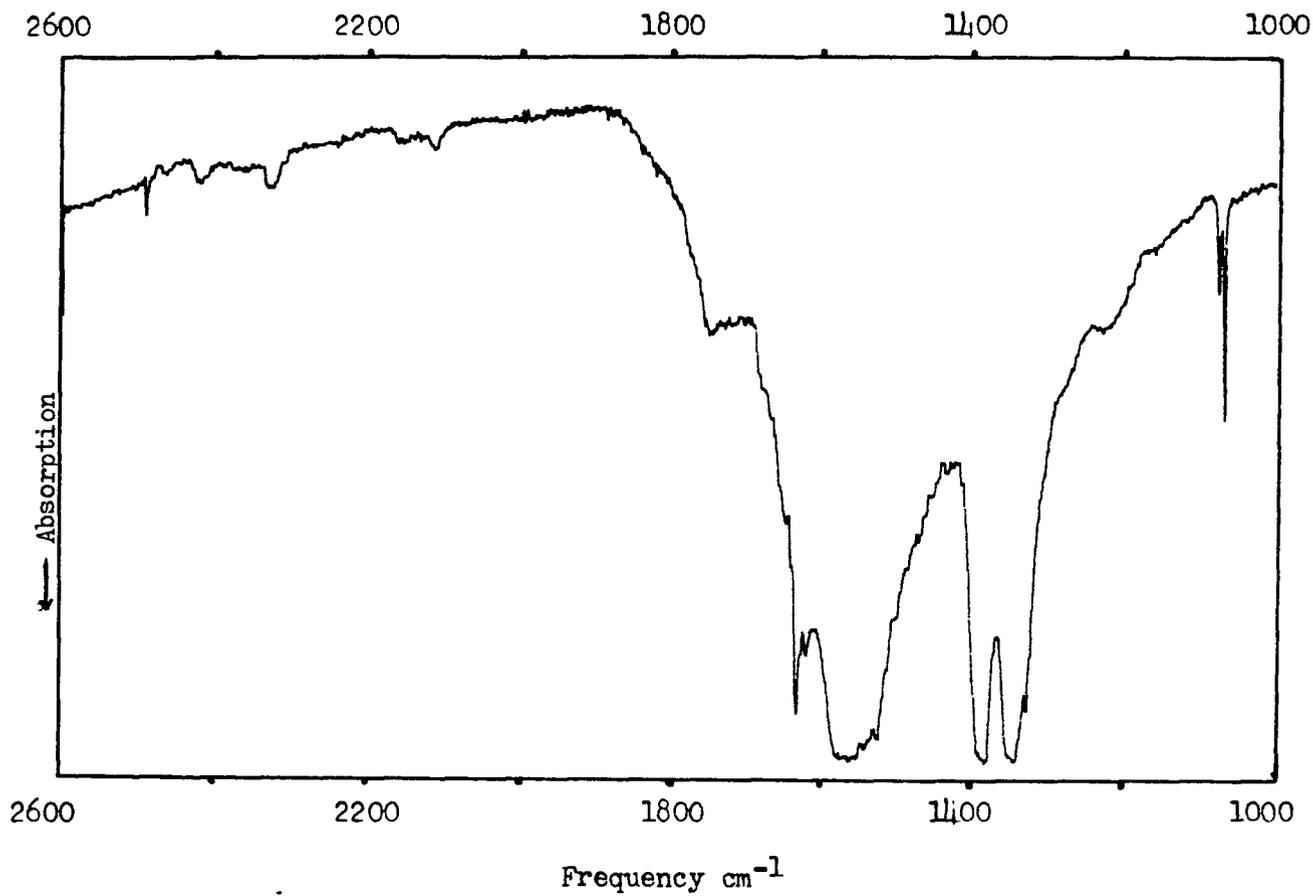


Figure 4: Infrared spectrum of barium formate single crystal (ac)

2600-1000 cm^{-1}

Figure 5: Polarized infrared spectrum of
barium formate, 3300-2500 cm^{-1} .

Figure 6: Polarized infrared spectrum of
barium formate, 2000-1000 cm^{-1} .

Figure 7: Polarized infrared spectrum of
barium formate, 800-740 cm^{-1} .

The plane of polarization of
the infrared light is indicated
as being parallel to the a, b or c
axis of the crystal.

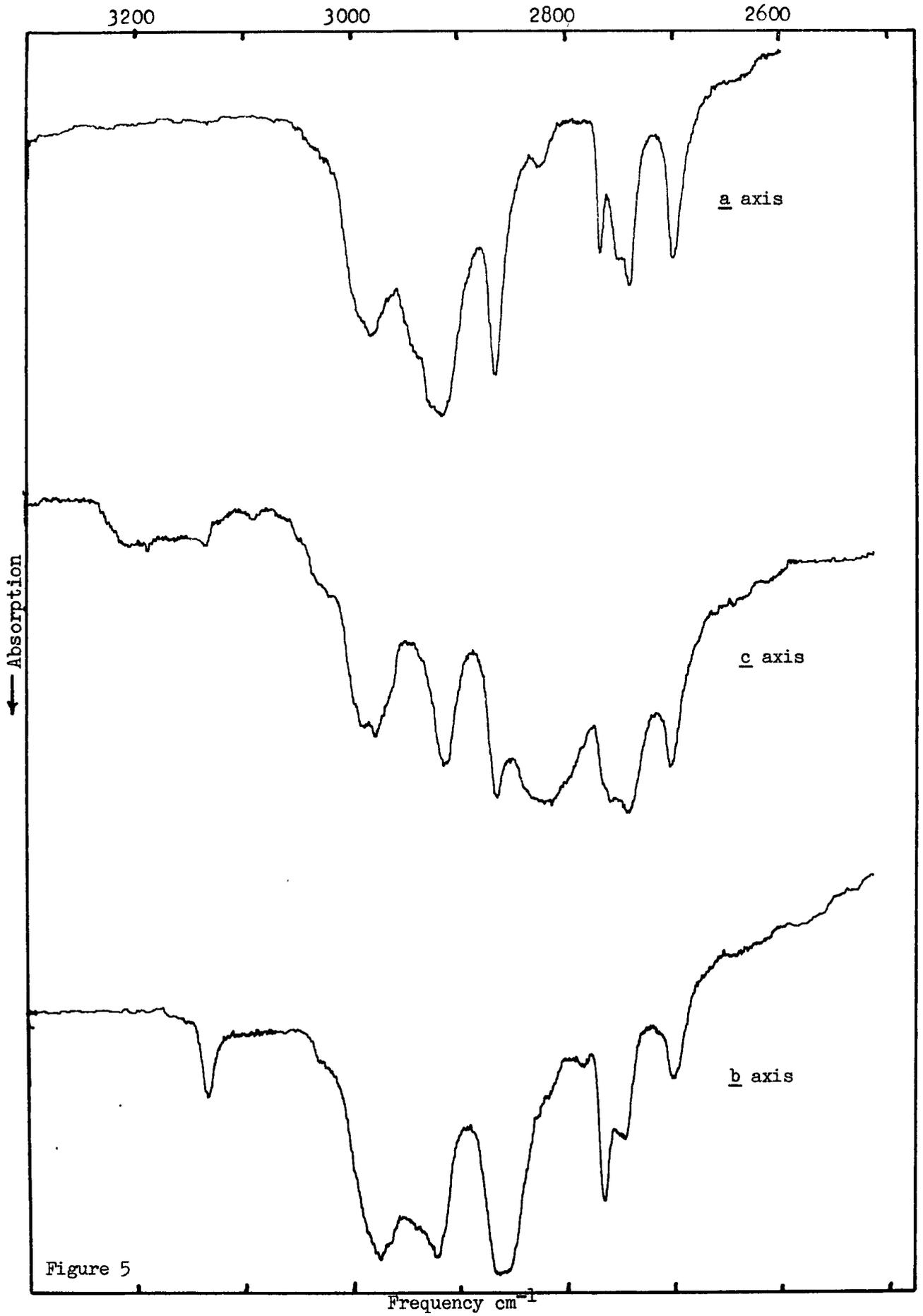


Figure 5

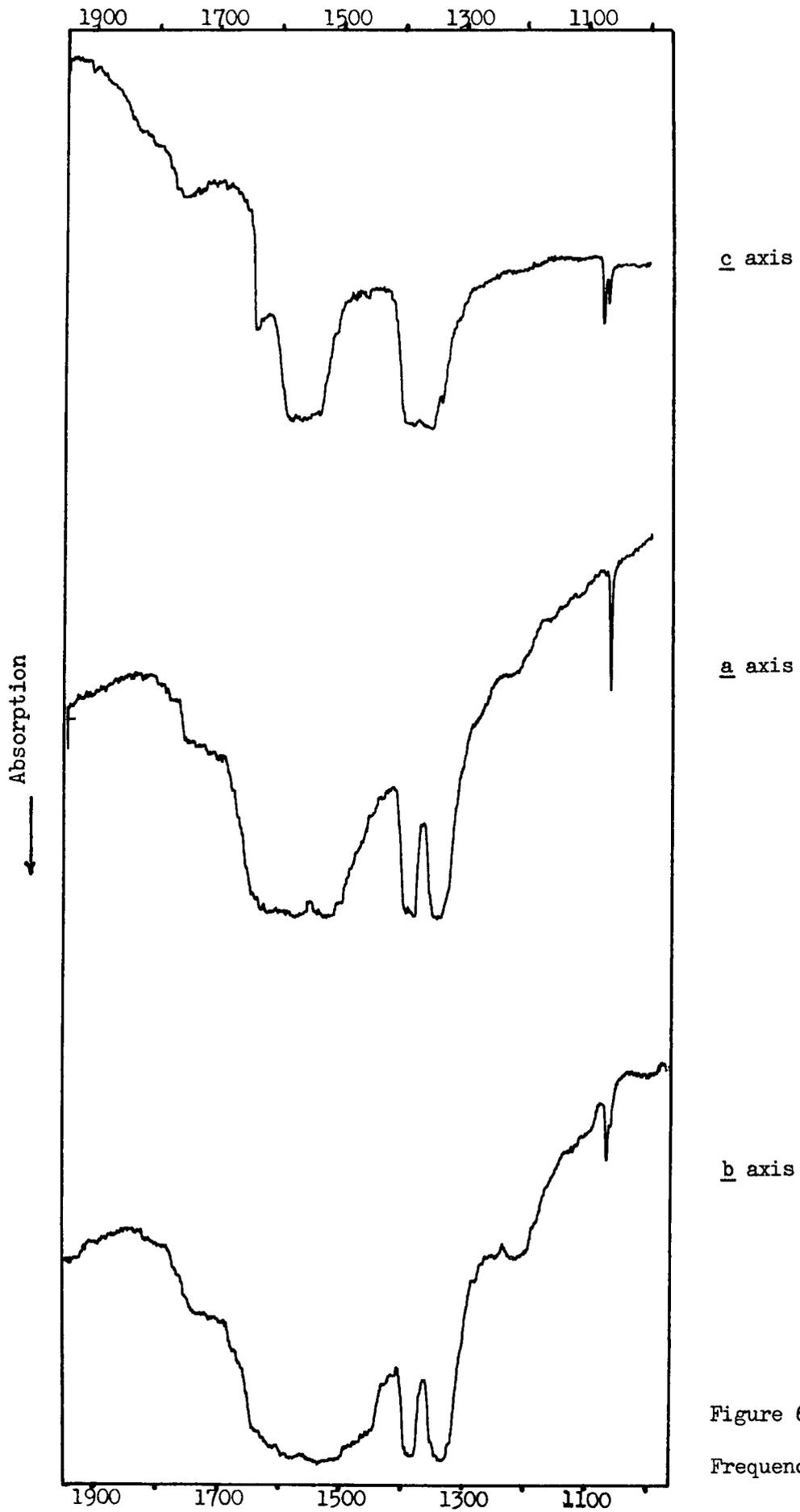


Figure 6
Frequency cm^{-1}

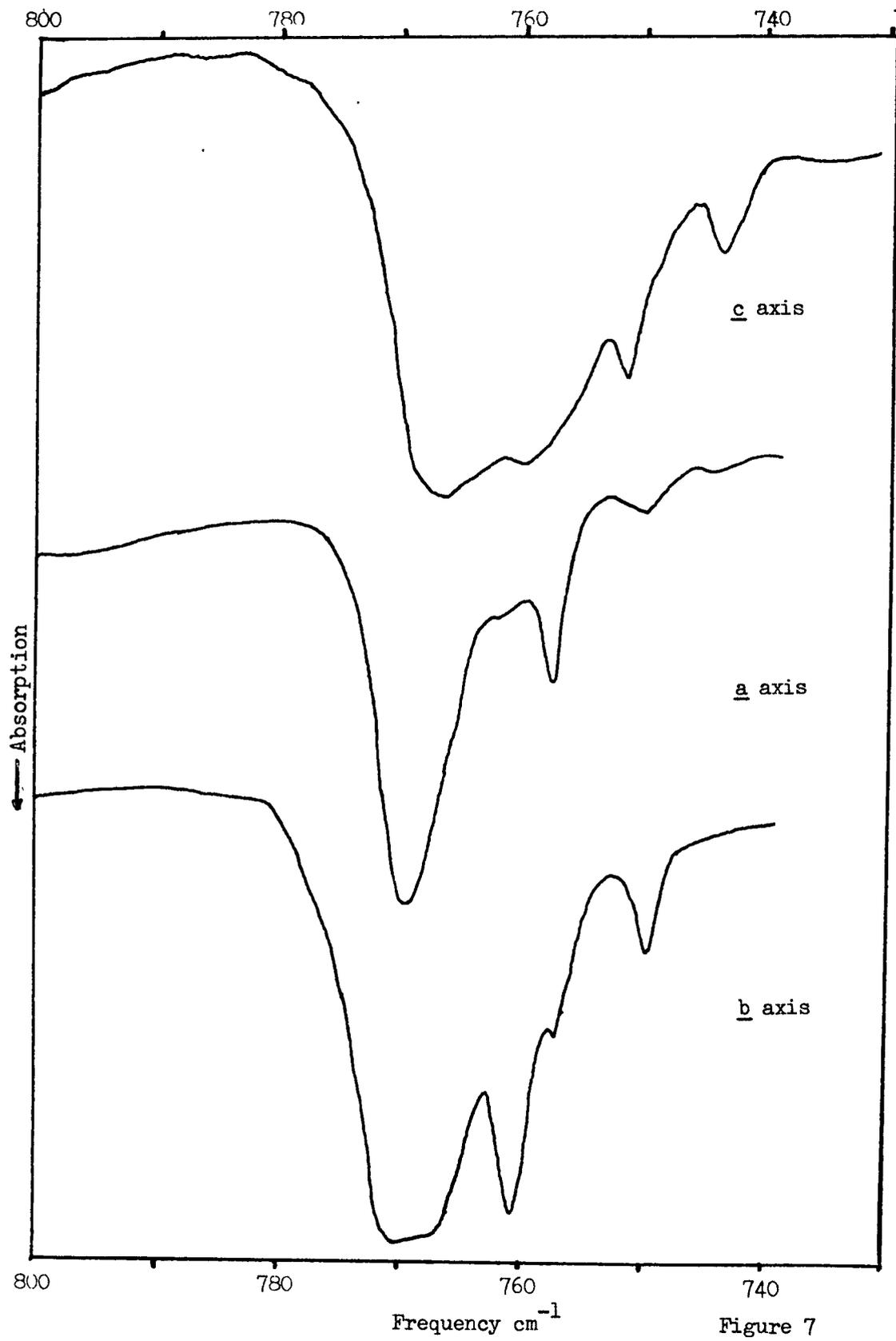


Figure 7

Figure 8: Infrared spectrum of barium formate, $800-740\text{ cm}^{-1}$.

(a) ac crystal

(b) bc crystal

(c) polycrystalline in KBr.

An ac type crystal is one in which both the a and c axes of the crystal are perpendicular to the direction of propagation of light through the crystal.

Figure 9: Infrared spectra, $3200-2600\text{ cm}^{-1}$

(a) an aqueous solution of barium formate

(b) polycrystalline NaCHO_2 in KBr

(c) polycrystalline $\text{Pb}(\text{CHO}_2)_2$ in KBr.

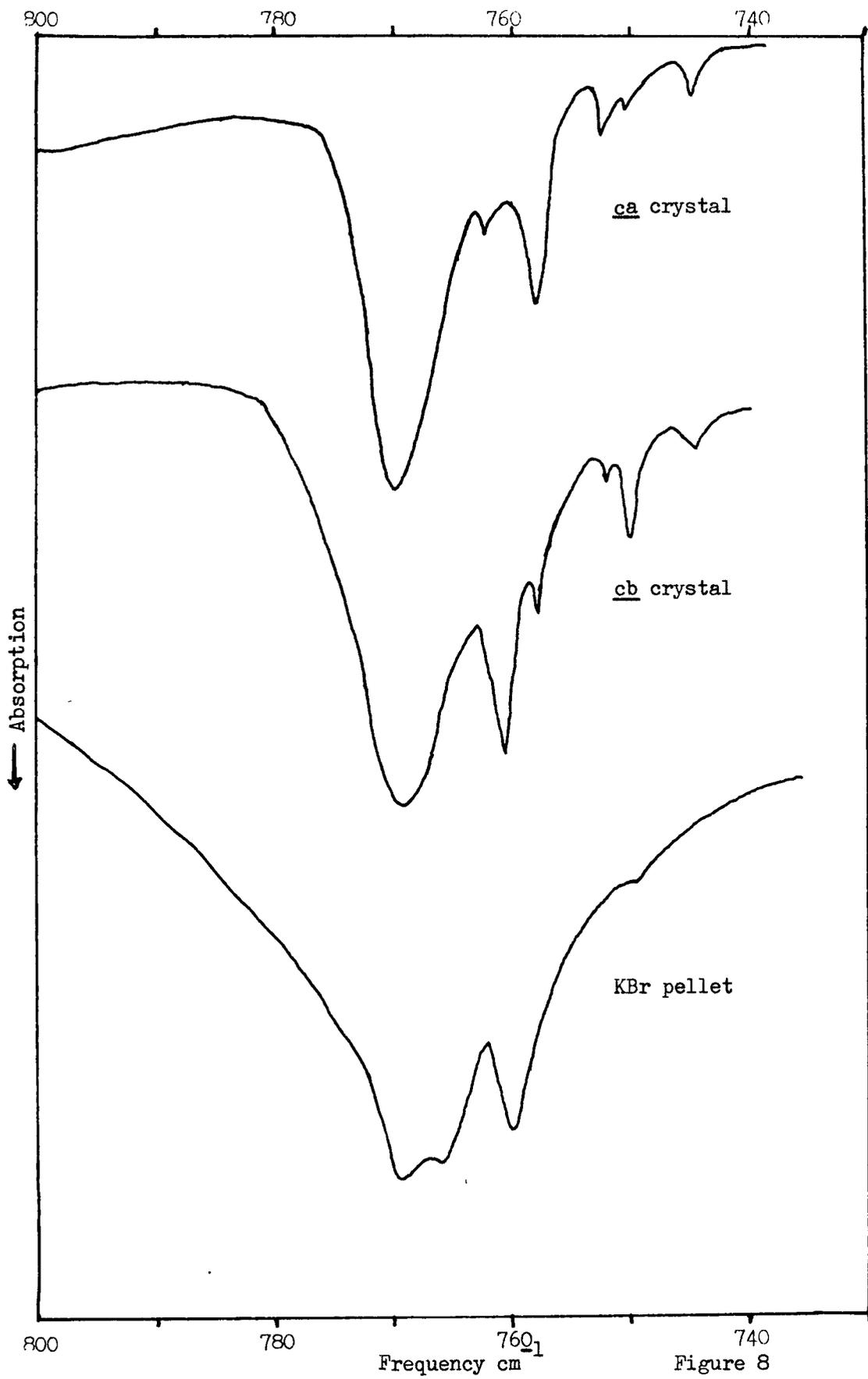


Figure 8

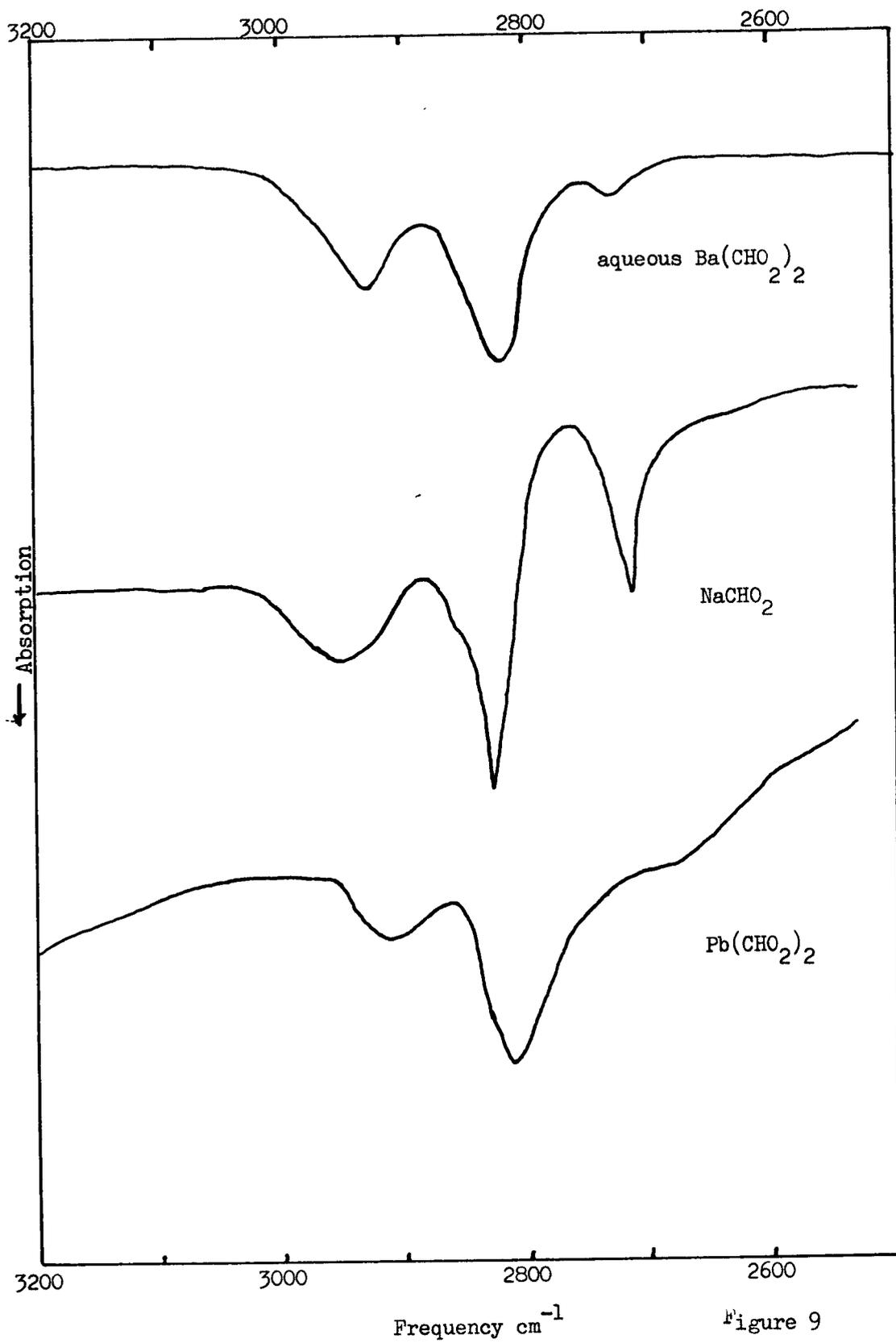


Figure 9

TABLE 2
The Infrared Absorptions of Barium Formate

Frequency cm^{-1}	Polarization	Assignment
744 w	c	ν_3 (C^{13})
749.5 vw	b	ν_3 (C^{13})
752 vw	c	ν_3 (C^{13})
758 m	a	ν_3 (B_3)
761.5 m	c,b	ν_3 (B_1B_2)
766.5 vs*	c	ν_3 (B_1)
769.5 vs*	a,b	ν_3 (B_2B_3)
1000 vw		ν_L
1066 m	c,a	ν_6 (B_1B_3)
1073 m	c,b	ν_6 (B_1B_2)
1110 vw		ν_L
1165 vw		ν_L
1230 m		ν_L
1280 w		ν_L
1334 w		ν_1 (C^{13})
1350 s*		ν_1
1357 s*		ν_1
1386 s*		ν_5
1398 s*		ν_5
1465 vw		ν_L
1535 w		$2\nu_3$ or $\nu_4 - \nu_L$
1570 vs*		ν_4
1590 vs*		ν_4
1630 m	a,b	$\nu_4 + \nu_L$ (B_2B_3)
1640 m	a,b	$\nu_4 + \nu_L$ (B_2B_3)
1680 vw		$\nu_4 + \nu_L$
1720 vw	a,b	$\nu_4 + \nu_L$ (B_2B_3)
1750 m	c	$\nu_4 + \nu_L$ (B_1)
2110 vw		$\nu_3 + \nu_1$
2150 vw		$\nu_3 + \nu_5$

TABLE 2 (con't)

Frequency cm^{-1}	Polarization	Assignment
2325 vw		$\nu_3 + \nu_4$
2420 vw		$\nu_6 + \nu_1$
2645 w		$\nu_6 + \nu_4$
2700 m	a,b,c	$2\nu_1$ ($B_1 B_2 B_3$)
2740 m	a,b(vw)	$\nu_1 + \nu_5$ (B_3)
2750 s	c	ν_2 (B_1)
2763 m	b,a(vw)	$2\nu_5$ (B_2)
2823 s	c	ν_2 (B_1)
2863 s	a,b	ν_2 ($B_2 B_3$)
2910 s	a,c(w)	$\nu_1 + \nu_4$ (B_3)
2920 s	b	$\nu_1 + \nu_4$ (B_2)
2935 b,m	a,b	$\nu_1 + \nu_4$ ($B_2 B_3$)
2975 s	c,b	$\nu_4 + \nu_5$ ($B_1 B_2$)
2985 s	c	$\nu_4 + \nu_5$ (B_1)
3020 w	c	
3134 w	b,c	$2\nu_4$ ($B_1 B_2$)
3200 w	c	

* observed in KBr pellets of barium formate

symbols: vs = very strong, s = strong, m = medium, w = weak, vw = very weak,
 b = broad, ν_L = lattice mode, C^{13} = carbon 13 formate ion.

TABLE 3

Summary of Previously Reported Raman Absorptions and of Observed Infrared
Absorptions of Sodium Formate and Barium Formate-d₁

Ba(CHO ₂) ₂ R(18)	Ba(CHO ₂) ₂ R(16)	NaCHO ₂ R(20)	NaCHO ₂ IR	Ba(CHO ₂) ₂ IR
735			755 (ν ₃ C ¹³)	745 (ν ₃)
790		773 (ν ₃)	772 (ν ₃)	755 (ν ₃)
1070		1069 (ν ₆)	1062 (ν ₆)	908 (ν ₆) 912 (ν ₆)
1290				1025 (ν ₅) 1320 (ν ₁) 1330 (ν ₁)
	1353	1352 (ν ₁)	1355 (ν ₁)	1350 (ν ₁ H)
		1386 (ν ₅)	1385 (ν ₅)	1390 (ν ₅ H)
1520		1584 (ν ₄)	1590 (ν ₄)	1545 (ν ₄)
			1630	1570 (ν ₄) 2046 (ν ₂)
		2126 (2ν ₆)		2054 (2ν ₅) 2080 (ν ₃ + ν ₁) 2116 (ν ₂) 2163 (ν ₂) 2645 (2ν ₁)
		2732 (2ν ₅)	2717	2700 (2ν ₁ H)
		2825 (ν ₂)	2828 (ν ₂)	2745 (ν ₂ H)
	2832			2820 (ν ₂ H) 2862 (2ν ₂ H, ν ₂ +ν ₃) 2881 (ν ₁ + ν ₄) 2900 (ν ₂ + ν ₃)
			2950 (2ν ₄)	2955 3370 (ν ₂ + ν ₁) 3440 (ν ₂ + ν ₁) 3479 (ν ₂ + ν ₁)

symbols: H = hydrogen species of formate-d₁. C¹³ = carbon 13 formate ion.

R = Raman data. IR = Infrared data, this work.

CHAPTER 3: THEORY

3-1 General theory of vibrations in crystals

In studying the dynamics of a system of N particles, it is necessary to specify $3N$ coordinates to describe the configuration of the system. These $3N$ coordinates generally are the three cartesian coordinates of each particle, the coordinates of the i th particle being x_i , y_i , and z_i . Such a system has $3N$ degrees of freedom; three translational, three rotational, and $3N-6$ vibrational degrees of freedom. In a vibrational analysis, of a system of N particles, an expression for the kinetic and potential energy is derived and is substituted into Newton's equations of motion. The solution of the $3N$ equations obtained, depends on a parameter related to a frequency of oscillation of the system, of which there are $3N-6$ possible values. These values are the fundamental frequencies or NORMAL modes of vibration of a system of N particles.

The analysis of the vibrations which can occur in a crystal would appear to be most difficult if the above procedure were to be adopted. An average crystal contains of the order of 10^{23} atoms, which would correspond to 3×10^{23} fundamental modes of vibration. On this basis, one might expect the vibrational spectrum of a crystal to be totally absorbing, there being 10^{23} absorption bands. However, it is observed that there are a finite number of bands in the infrared and Raman spectra of crystals; in fact there are often not too many more than observed in the spectrum of the vapor. It is then necessary to consider whether all of the $3N$ vibrations which a crystal should sustain are physically distinct.

Born's treatment of the dynamics of crystal structures (13) showed that a three dimensional crystal should be able to sustain an infinite number of vibrations, the wave motion being of the nature of a continuum. However, an infinite number of lines is not observed in the infrared or Raman spectra of a crystal. Furthermore, there is often a close correspondence in the spectrum of a melt and that of the crystal of many substances, a fact which suggests small units of atoms or subunits of this are very important in determining the nature of the normal oscillations. As a start in determining the vibrations of crystals, earlier workers considered the unit cell, which is the smallest repeating unit of the crystal. (14) The theory adopted for present day use will be explained briefly in the following paragraph.

Situated on the Bravais lattices of a crystal are sets of equivalent atoms, ordered in such a way that each atom in a set (or lattice) is both geometrically and physically related to its environment in exactly the same way as every other atom of the same set. Hence, the corresponding displacements in a given normal mode of oscillation of every pair of equivalent atoms contiguously situated along any one of the three principal axes of the Bravais lattice should be the same. Thus, a crystal may be considered as a structure or a set of interpenetrating lattices, and the unit cell of the smallest possible size (that is the primitive unit cell) will contain as many atoms in it as there are interpenetrating lattices in the structure. With p atoms in the unit cell, there will be $3p$ oscillations, and three of them will correspond to pure translations. In these modes, the lattices can be regarded as moving in phase with each other.

When treated in this manner, a suitable number of frequencies is usually accounted for, but this is not the most general treatment. One has not taken account of the fact that the Bravais lattices may also vibrate out of phase with respect to each other, and that one should in the most general treatment consider a block of eight unit cells. This is the result of the Born-Karman boundary conditions. The physical significance of this general treatment is that we have considered the effect of the environment and possible interactions from other unit cells surrounding the one we are considering. However, the justification in the simplified treatment lies in the fact that a suitable number of frequencies is accounted for, and there is no need to make the treatment unduly complicated.

3-2 Application of symmetry

In carrying out a vibrational analysis of a dynamical system of N particles, a $3N$ by $3N$ secular determinant has to be solved in order to determine the normal frequencies. However, if the system (or molecule, as is usually the case in infrared spectroscopy) possesses symmetry, the secular determinant can be broken down into the sum of several components. The principle of the application of symmetry to a vibrational analysis is that the potential energy of the equilibrium configuration of a dynamical system must be invariant under the symmetry operations of the system. A group of operations which carry a molecule into a configuration identical with the original configuration are called the symmetry operations of the molecule, and this collection of operations form a group, in the mathematical sense. Associated with a group is a set of irreducible representations, which may be visualized as non-equivalent examples of the

symmetry of the molecule. The number of irreducible representations is limited, and the essence of the application of group theory to a vibrational analysis is that the potential energy of the system may be broken down into a sum of independent contributions. Each contribution is associated with some one irreducible representation of the group describing the symmetry of the configuration. With the above definitions in mind, we will define what is meant by a representation and an irreducible representation of a group.

As stated earlier, a system of N particles may be completely determined by a knowledge of the $3N$ coordinates, usually the Cartesian coordinates. In a vibrational analysis, it is convenient to use displacement coordinates, measuring the displacement from the equilibrium position of the i th particle x_i, y_i, z_i , or to simplify the notation q, q_{i+1}, q_{i+2} , there being $3N$ q 's in all. If the original configuration of a molecule is disturbed, then any new coordinate q' is changed into a linear combination of the original coordinates. Such a disturbance may be a symmetry operation, in which case the new coordinates q' may be represented analytically as:

$$q'_j = \sum_{ij} R_{ij} q_i \quad 3-1$$

or
$$Q' = RQ \quad 3-2$$

where Q' is a column matrix of order $1 \times 3N$, Q is a row matrix of order $3N \times 1$, and R is the square transformation matrix of order $3N \times 3N$. The set of linear transformations defined above for the symmetry operations of a molecule has all the properties of the symmetry group (that is the transformations have the same multiplication properties as the group) belonging to the molecule, and is said to be a representation of the

group. The coordinates q_i are said to form a basis of the representation.

The basis coordinates chosen were arbitrary, and if a different set of coordinates were used (say a different orientation of the Cartesian coordinates) the same results should be obtained. When two representations of a group differ only in that the basis coordinates of one are linear combinations of the basis coordinates of the other, then the two representations obtained are said to be equivalent. The characters of equivalent representations are the same, the character being defined as the sum of the diagonal elements of the transformation matrix R:

$$\chi_R = \sum_i^{3n} R_{ii} \quad 3-3$$

In general, Eq. (3-1) consists of $3N$ equations in $3N$ unknowns. However, it is usually possible by choosing a suitable set of basis coordinates (different from the Cartesian coordinates generally) whereby the number of terms in Eq. (3-1) may be greatly reduced. In fact, in a symmetrical molecule it is possible to choose coordinates which may be separated into sets which do not mix with one another, and the representation for which these coordinates form the basis, is said to be reduced. When it is possible to do this, the original representation is said to be reducible, and when it is not possible to form smaller non-mixing sets, the resulting representation is said to be completely reduced. Since the coordinates which form the basis of the reduced representation separate into sets which do not mix with one another, the equations involving any one set form a representation of the group. Such a representation is irreducible, when the maximum reduction of the reducible representation has been carried out.

A fundamental theory of the representation of finite groups states that for each point group there are only a definite small number of non-equivalent irreducible representations possible. A well known formula shows the number of times a given irreducible representation may appear in a reduced representation;

$$n_i = \frac{1}{h} \sum_{\underline{R}} \chi_{\underline{R}}^i \chi_{\underline{R}} \quad 3-4$$

where h is the order of the group, $\chi_{\underline{R}}$ is the character for the reducible representation, and $\chi_{\underline{R}}^i$ is the character for the \underline{R} 'th operation of the i 'th irreducible representation. The sum is over the \underline{R} operations of the group. All the quantities on the right of Eq. (3-4) are easily deduced.

Associated with any normal mode of vibration of a molecule is its normal coordinate Q which describes the displacement of the atoms of the molecule relative to its equilibrium configuration. Each normal coordinate transforms according to one of the irreducible representations of the group describing the symmetry of the molecule, and with the use of Eq. (3-4), the number of normal coordinates belonging to each irreducible representation may be deduced.

The selection rules for transitions in molecules can also be derived with the aid of group theory (1). A transition from a state i to a state j is allowed or forbidden according as the integral

$$M = \int \psi_i \mu \psi_j d\tau \quad 3-5$$

is equal to zero or not. Since this is a definite integral over the whole configuration of space, it must be invariant to any symmetry operation of the system considered. For fundamentals (from the ground

state which is symmetrical) the integral will be symmetric if the dipole moment operator μ and Ψ_j belong to the same irreducible representation, for the product of a representation with itself is always symmetric. Now the wave function of the first excited state has the symmetry of the normal coordinate for the transition considered (1) and the dipole moment operator belongs to the same irreducible representation as does the translational coordinates T_x , T_y , and T_z . Therefore, a transition from the ground state to a first excited state is allowed if the function Ψ_j belongs to the same symmetry species as μ . Hence, with the aid of group theory, selection rules for vibrational transitions can be conveniently derived.

3-3 Crystal symmetry

If a crystal is assumed to be infinite, the theory of space groups shows that a lattice structure must have the symmetry of one of the 230 space groups. The space group is that group of operations which carry an atom into an equivalent atom in the crystal. The symmetry operations include rotation axes, mirror planes, glide planes, screw axes, inversion centers, inversion-rotation axes, and simple translations; it is the translations which generate the lattice of the crystal, while the other mentioned operations are the familiar space group (in the crystallographer's definition) operations. The smallest unit in which no atoms are equivalent under simple translation is called the primitive unit cell, and the crystal is constructed by translations of this unit cell which when carried out an infinite number of times, builds the infinite crystal.

In this definition the space group is an infinite group; however, if we define translations which carry a point in a unit cell into an equivalent point in another unit cell as the identity operation, we define a finite group, which is a factor group of the space group. This

factor group describes the symmetry of the unit cell, and although not a point group, it is isomorphous with one of the 32 crystallographic point groups. If we define the operations of the translation group, the factor group and the space group by T, F, and S, respectively, we can write

$$S = F \times T$$

3-6

From the group theory it can be shown that an irreducible representation of the factor group F is also an irreducible representation of the space group S.

About any point in a crystal there is a local symmetry, which for most points will consist of the identity operation E. However, if the point in question is situated on one or more of the symmetry elements of the factor* group which do not involve translations, that point will be invariant under certain operations of this group, and will belong to a group which will have an order less than that of the factor group. Such a crystallographic "special position" has been designated by Halford as a site. (9) A given unit cell will in general exhibit several different kinds of sites, and may even have several distinct sets of sites of the same symmetry. The symmetry elements which leave this point invariant form a point group, which is called a site group. As a consequence of its definition, the site group is a sub group of the factor group.

3-4 Analysis of vibrations

Bhagavantam and Venkatarayudu were the first workers to adapt the unit cell method described previously to the determination of the allowed frequencies of vibration in a crystal (7, 14). That is, they considered

* The "factor group" will be used to denote the factor group of the translation group in the space group.

an isolated unit cell as their dynamical system, and using the factor group characteristic of a crystal, derived the selection rules. This is the method used in the treatment of the results for barium formate to be described.

Halford (9) has developed another method for determining the number of modes allowed in a crystal. Instead of treating the motions of one unit cell, he chose to treat the motions of one molecule moving in a potential field reflecting the symmetry of the surrounding crystal. This symmetry will be characterized by the symmetry of the site group. In this method, the frequencies of all equivalent molecules of a given set of sites have the same frequency, and the selection rules are derived by the standard methods, using the site group as a basis. The site group of a molecule in a crystal is a subgroup of the molecular group, and it is well known that symmetrical molecules are usually situated on sites other than the site of trivial symmetry (C_1), which is the most general position.

The site group method is only an approximation when applied to the analysis of the vibrations in a crystal lattice, and complete information of the vibrational modes and their polarization properties can only be obtained from the more complete factor group analysis.

However, the factor group and site group approach are both useful in a vibrational analysis. The relationship between the two can be discussed in terms of the equation for the potential energy of a crystal, which can be written (15)

$$V = \sum_j V_j + \sum_i \sum_j V_{ij} + V_L + V_{Lj} \quad 3-7$$

V_j is the harmonic oscillator function the sum being over all molecules, $\sum_i \sum_j V_{ij}$ contains all cross terms between internal coordinates of different molecules, V_L contains terms involving displacements of the centers of gravity and change of orientation of molecules, and V_{Lj} contains cross terms between internal coordinates and lattice coordinates. When only the first term is considered, we are dealing with the orientated gas model approximation, and V_j reflects the symmetry of the crystal as viewed from the site of the molecule in the crystal. The site symmetry is usually different from the symmetry of the free ion or molecule, and V_j will be different for a molecule in a crystal than the free gas phase molecule. This is the so called static field effect, and is a measure of the effect a surrounding lattice has on the equilibrium configuration of a molecule. If the site group is of lower symmetry than the molecular symmetry, a relaxing of selection rules and removal of degeneracies may result. The latter results in "static field splitting" of degenerate modes.

The "dynamic crystal effect" arises from the $\sum_i \sum_j V_{ij}$ term, and measures the effect of interactions of the internal vibrations of other molecules in the unit cell on the molecule being considered. Depending on the number of molecules per unit cell, each "gas phase" internal mode will be split in the crystal. Such splittings are generally referred to as factor group, or correlation field splittings.

From the above arguments it can be seen that bands which are not allowed in the infrared spectrum of a free molecule may become active in a crystal, depending on the mapping of the molecular group into the site group. The correlation mapping of the site group into the factor group then shows the polarization properties of the molecular modes.

CHAPTER 4: DISCUSSION

4-1 Infrared Spectra

According to Sugawara et. al. (11) barium formate crystals are orthorhombic, $a = 6.80 \text{ \AA}$, $b = 8.89 \text{ \AA}$, $c = 7.66 \text{ \AA}$, belonging to factor group $P2_12_12_1 - D_2^4$, with four molecules per unit cell. An X-ray analysis carried out as part of this investigation indicated that the factor group and unit cell dimensions are as stated.

The formate ion has point symmetry C_{2v} , with a C-O bond length of $1.25 \pm 0.01 \text{ \AA}$, and an OCO angle of 127 degrees (11). The ion has six normal modes of vibration, all allowed in the infrared, and distributed among the irreducible representations of C_{2v} as follows; $3A_1 + 1B_1 + 2B_2$. An infrared spectrum of the "free" formate ion can only be observed with an aqueous solution of the salt, and the observed vibrational frequencies have been reported by several workers from the Raman effect (16-20). Our infrared frequencies are in good agreement with the Raman data of Fonteyne (20) for sodium formate. As the forces between molecules or ions in a crystal are weak, the molecular fundamentals in the crystal are close in frequency to the corresponding "free" molecular modes.

Since there are no non trivial subgroups of the factor group $P2_12_12_1$, the formate ion in barium formate is in a general position of site symmetry C_1 . This lack of site symmetry has no effect on the crystal spectrum since all molecular modes are allowed under C_{2v} selection rules, and there are no degenerate modes to be split due to the static field effect. Hence, the factor group must be considered to interpret the results.

The character table for the point group 222 isomorphous with the factor group $P2_12_12_1$ is shown in table 3. By application of

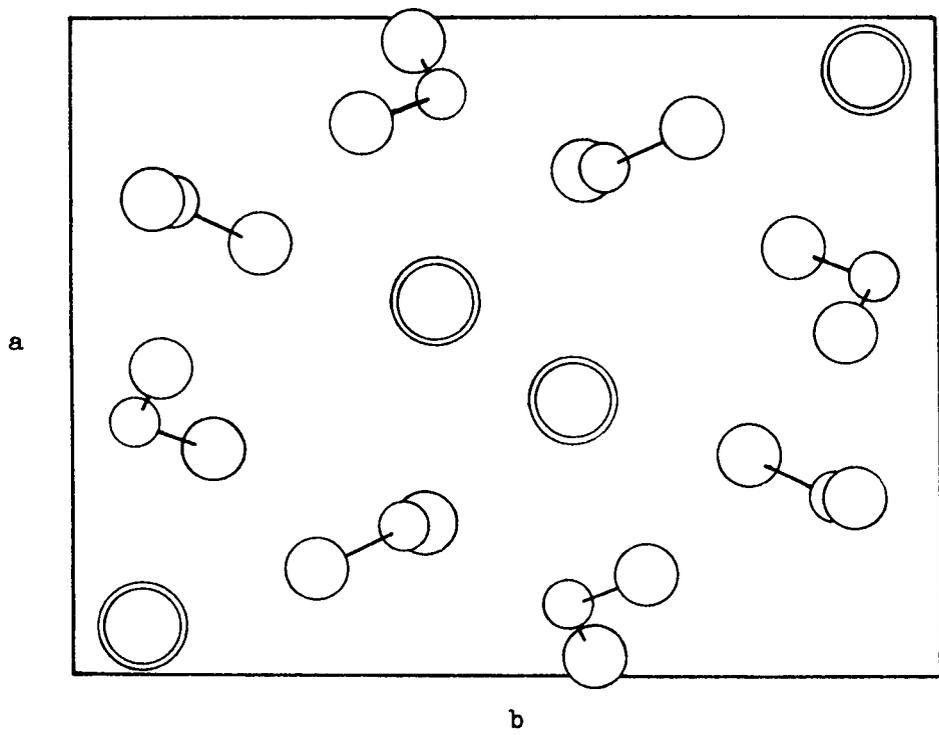


Figure 10a: Crystal structure of barium formate projected on (001)

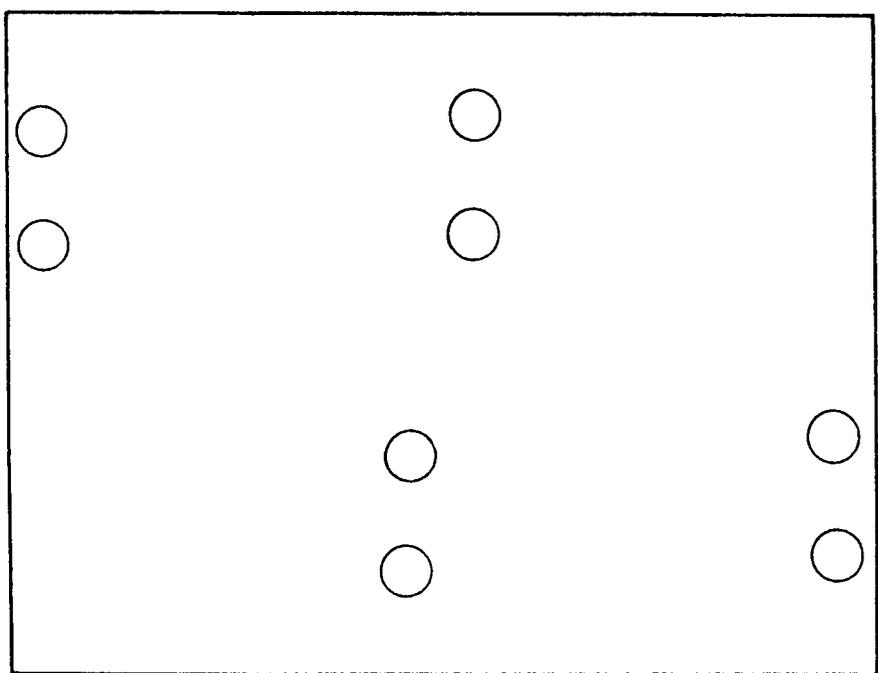


Figure 10b: Projection of the positions of the protons of barium formate on (001)

Eq. (3-4), the number of normal modes for the unit cell associated with each irreducible representation has been determined. $\chi_{\underline{R}}^i$ is given in the left section of the table. $\chi_{\underline{R}}$ in equation 3-4 may easily be derived (see (14) page 138, or (1) page 105), and "h", the order of the group is four for 222. The symmetry operations are the identity operation E, which leaves a molecule unchanged, and the two fold rotation axis C_2 .

TABLE 4

Character Table and Factor Group Analysis of Barium Formate Under 222

222	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	n_i	T	T'	R'	n_i'
A	1	1	1	1	27	0	9	6	12
B ₁	1	-1	-1	-1	27	1	8	6	12
B ₂	1	-1	1	-1	27	1	8	6	12
B ₃	1	-1	-1	1	27	1	8	6	12

n_i is the total number of modes for the unit cell, T gives the symmetry of the translation coordinates, T' is the number of translational lattice modes, R' is the number of rotational lattice modes, and n_i' is the number of internal (or molecular) modes for the unit cell.

The barium formate crystal has 36 atoms per unit cell, corresponding to $3 \times 36 = 108$ degrees of freedom, of which 3 are for translation and 105 are for vibration. Only 36 of the 48 internal molecular vibrations ($\sum n_i'$) are allowed in the infrared. The factor group splitting under the point group 222 will be explained in the following paragraphs.

Under the symmetry operations of the factor group (three mutually perpendicular two fold screw axes) a given formate ion is transformed into its three crystallographically equivalent neighbours in the unit cell. For any internal molecular mode of vibration, any two of these three equivalent ions may be out of phase (antisymmetric) with respect to the generating ion (that is, transform according to one of the three B symmetry species above), or all three may be in phase with the generating ion (A species). This gives rise to a possible four fold splitting of each molecular mode. But the other crystallographically non equivalent formate ion also has the same possible phase relationship for its three other equivalent ions in the unit cell. However, this second set of ions can be symmetric or antisymmetric with respect to the first set and will still have the 222 phase relations among the ions of this set. Thus, a further two fold splitting of each of the four modes described above is possible, giving a total of eight modes for each normal mode of a formate ion. Each molecular fundamental of the formate ion will be split into $2A + 2B_1 + 2B_2 + 2B_3$ modes under the factor group, of which only the B modes are active in the infrared.

For light polarized along one of the principal axes only two of the six components will be allowed. Denote the two non equivalent formate ions by F and F', and their three equivalent ions in the unit cell by $F_z, F_y, F_x, F'_z, F'_y,$ and F'_x respectively, the subscript indicating which screw axis is doing the generating. Consider the ν_1 normal mode of the formate ion, and let F ion have arbitrary phase (+). Any other ion will either be symmetric (+) or antisymmetric (-) relative to F. For the two B_3 factor group components of ν_1 , the other seven ions can have the following phase relationship relative to F:

$$\begin{array}{cccc}
 F (+) & F_z (-) & F_y (-) & F_x (+) & \left. \vphantom{\begin{array}{c} F (+) \\ F' (+) \end{array}} \right\} \\
 F' (+) & F'_z (-) & F'_y (-) & F'_x (+) & \left. \vphantom{\begin{array}{c} F (+) \\ F' (+) \end{array}} \right\} \\
 \text{or} & & & & \\
 F (+) & F_z (-) & F_y (-) & F_x (+) & \left. \vphantom{\begin{array}{c} F (+) \\ F' (-) \end{array}} \right\} \\
 F' (-) & F'_z (+) & F'_y (+) & F'_x (-) & \left. \vphantom{\begin{array}{c} F (+) \\ F' (-) \end{array}} \right\}
 \end{array}
 \begin{array}{l}
 \text{symmetric} \\
 \\
 \text{antisymmetric}
 \end{array}$$

These are the two components of ν_1 that would be allowed for light polarized along the a axis of the crystal. The same type of phase diagram can be drawn for any species of 222, and for any molecular fundamental. This is the basis of the factor group splitting of barium formate under factor group $P2_12_12_1$. The infrared spectrum of each molecular mode will be discussed in turn.

The out of plane mode ν_6 which occurs at 1069 cm^{-1} in sodium formate* is split into a doublet at 1073 and 1066 cm^{-1} in the barium formate crystal. The 1073 cm^{-1} component is active along axis c and b, while the 1066 cm^{-1} component is active along axis c and a (Fig. 6).

The two $B_2(C_{2V})$ modes of the formate ion, ν_4 at 1584 cm^{-1} and ν_5 at 1386 cm^{-1} in sodium formate are both split into doublets in the infrared spectrum of barium formate, located at $1590, 1570 \text{ cm}^{-1}$ and $1398, 1386 \text{ cm}^{-1}$ respectively (Fig. 1). This splitting is only observed for polycrystalline material in KBr pellets, since the single crystals used were thick and totally absorbed over the range of these doublets. As a result, no polarization data is available for these fundamentals.

The three totally symmetric fundamentals of the free formate ion, $\nu_1, \nu_2,$ and ν_3 occur at $1352, 2825,$ and 773 cm^{-1} respectively in the

* The Raman frequencies of aqueous sodium formate provide the closest approximation to a "free" formate ion.

Raman spectrum of aqueous sodium formate. In barium formate, ν_1 is split into a doublet at 1357, 1350 cm^{-1} as can be seen in Fig. 1, but is not resolved in the single crystal spectrum. A weak but very sharp line appears at 1334 cm^{-1} in the spectrum of the crystal which has been assigned to the C^{13} species of barium formate for this vibration. The basis for this assignment will be discussed later. The region of the ν_2 fundamental (3200-2600 cm^{-1}) is complicated due to the presence of at least 15 absorptions of which three only are due to ν_2 . This strong three fold splitting is readily observed in the spectrum of barium formate- d_1 (Fig. 2), where three sharp lines of equal intensity appear at 2163, 2116, and 2046 cm^{-1} . In the region of ν_3 no less than seven distinct components are observed between 770-744 cm^{-1} (Table 2). These two regions of the spectrum are most interesting and will be discussed separately.

Combinations and Overtones

Of the 47 observed frequencies in the spectrum of the single crystal of barium formate 13 are due to combinations and overtones of molecular modes. These are listed in Table 2, along with their polarization properties when observed.

Under 222 selection rules, no first overtones should be allowed. However, it must be remembered that each fundamental has eight components under $\text{P}2_12_12_1$ factor group splitting, and that a first overtone of a fundamental, would in actual fact be just a combination of two different species of the same fundamental, and is therefore allowed under the selection rules. Then each first overtone theoretically consists of $\text{C}_2^8 = 28$ combination components, 27 being allowed. Direct overtones of the same species are not allowed.

Splitting is also observed in some of the high frequency combinations. The $\nu_4 + \nu_5$ combination at 2980 cm^{-1} has two components and the

$\nu_1 + \nu_4$ combination at 2920 cm^{-1} has three (table 2). This splitting is likely due to the factor group components of the fundamentals. This is substantiated by the $\nu_2 + \nu_1$ combination in barium formate-d₁ (Fig. 2) at 3479, 3440, and 3370 cm^{-1} . The intensities are in the same ratio and the splittings between the components are nearly the same for the combination as for the ν_2 fundamental.

Lattice modes

The six external degrees of freedom of the formate ion belong to the following irreducible representations of C_{2v} : $1A_1 + 1A_2 + 2B_1 + 2B_2$. These degrees of freedom become translatory and rotatory lattice modes when the ion is in a crystal. Table 4 lists the number of lattice modes of each type belonging to the various irreducible representations of 222. These modes usually occur in the frequency range between 20 to 400 cm^{-1} , far below the region accessible on the spectrometer used for this study. However, lattice modes can be observed in the near infrared as combinations with molecular modes. Eleven frequencies are listed in Table 2 assigned to combinations with lattice modes. The most prominent of these occur at 1750, 1640, and 1630 cm^{-1} , which have been assigned as sums of lattice modes with ν_4 at 1580 cm^{-1} (mean of the doublet). Another sharp peak at 1535 is possibly the difference mode corresponding to the sum mode at 1630 cm^{-1} , or may be the overtone $2\nu_3$.

TABLE 5
Lattice Modes of Barium Formate

Combination, cm^{-1}	Lattice frequency, cm^{-1}
$\nu_4 + \nu_L = 1750$	170
$\nu_4 + \nu_L = 1720$	150
$\nu_4 + \nu_L = 1640$	60
$\nu_4 + \nu_L = 1630$	50
$\nu_4 - \nu_L = 1535$	45

The difference frequencies corresponding to these modes are listed in Table 5. Other weak absorptions occur at 1465, 1165, 1110, 980 cm^{-1} with a fairly strong one at 1230 cm^{-1} . These are also attributed to combinations of fundamentals with lattice modes, but it is very difficult to ascertain which fundamental is responsible. No lattice frequencies are listed for these latter modes.

ν_2 Region, 3200-2600 cm^{-1}

The region around the C-H stretching fundamental ν_2 is extremely complicated, and at the same time interesting. It was only decided with the aid of deuterated barium formate that the fundamental was split into three components, and from frequency separations, which three these were. The fundamental appears at 2825 in the Raman spectrum of sodium formate (2828 cm^{-1} in the infrared spectrum reported in Table 3) and at 2820 cm^{-1} in the spectrum of aqueous barium formate (Fig. 9). In the spectrum of the single crystal, a and b, active components appear at 2863 cm^{-1} , and c active components at 2823 and 2750 cm^{-1} .

No mention has been made up to this point concerning the infrared spectrum of lead formate or sodium formate. Crystalline lead formate has the same factor group symmetry (11) as does barium formate, $P2_12_12_1$, and since both salts have two formate ions per molecule, they should have a similar infrared spectrum. In all fundamentals except ν_2 this similarity is observed. However, the ν_2 region differs from that in barium formate, and is shown in Fig. 9. On the same diagram is shown the ν_2 region of sodium formate, and of an aqueous solution of barium formate. All three spectra have the same general features; there is no evidence of factor group splitting in lead formate, or, as would be expected, in aqueous barium formate. (It is worth mentioning here that no splitting was observed in any of the other fundamentals of aqueous barium formate either.) The factor group analysis of sodium formate is presented in the appendix, where the theory predicts that each molecular fundamental should be split into two infrared active components in the crystal. This splitting is not observed here for sodium formate, nor is it for any other fundamental.

The remaining 12 of the 15 components in the barium formate spectrum between $3300-2600\text{ cm}^{-1}$ can be assigned to combinations and overtones, as indicated in Table 2. It is then necessary to explain why these other lines do not appear in the spectrum of lead formate.

This author believes the clue is furnished by the disappearance or decrease in intensity of these combinations and overtones in the solution spectrum of barium formate between 3300 and 2600 cm^{-1} . Further, these same bands are extremely weak in the spectrum of crystalline lead formate in KBr, which exhibits no factor group splitting, as does barium formate. The explanation of this intensity behavior is probably due to Fermi resonance between the components of the fundamental

of barium formate, and the overtone and combination frequencies. Due to the factor group splitting, the fundamentals are now close (50 cm^{-1}) in frequency to the overtones, which will produce an equalization of intensity due to a mixing of the wave functions of the two states.

ν_3 Region, 770-740 cm^{-1}

Another interesting region of the spectrum of barium formate lies between 770 and 740 cm^{-1} where seven absorption lines of varying intensity are observed (Fig. 7,8). This "band" is the ν_3 fundamental, which occurs at 773 cm^{-1} in the Raman spectrum of sodium formate. The strong absorption between 770-765 cm^{-1} actually consists of two distinct lines at 769.5 cm^{-1} , and 766.5 cm^{-1} , the splitting being easily observed in KBr pellet of barium formate (Fig. 8c). The polarization properties and frequencies of these lines are shown in Table 2. The polarization properties of the components of the unresolved doublet were inferred from the width and frequency of the absorption maxima, when the polarization was changed. The three lines at 752, 749.5, and 744 cm^{-1} are extremely weak relative to the higher frequency components, and have been assigned to C^{13} barium formate (1% natural abundance). Factor group splitting is again observed in this fundamental, but further discussion of the polarization properties will be left until the isotope effect has been discussed.

Isotopic Shifts

The assignment of the three low frequency modes to C^{13} is questionable, but there is much evidence in its favor. Frequency shifts were calculated for a C^{13} relative to a C^{12} formate ion using a Urey-Bradley potential function and equations developed by Duchesne (21) for an XYZ_2 type molecule. The shifts $\Delta\nu$ for the three A_1 (C_{2v}) modes

are listed in Table 5. These shifts were based on the sodium formate model, since the original force constants used were derived from sodium formate data (20).

TABLE 6
Calculated C¹³ Frequency shifts of the Formate Ion

Mode	Shift cm ⁻¹
$\nu_1(1352)$	27
$\nu_2(2825)$	3
$\nu_3(773)$	6

Assuming the mean of the four components of ν_3 is at about 765 cm⁻¹, this would place the C¹³ barium formate band at about 759 cm⁻¹. There is an absorption line here (758 cm⁻¹) but this would not explain the component at 744 cm⁻¹. Now there is a sharp line at 1334 cm⁻¹, which has been assigned as the C¹³ component of ν_1 at 1353 cm⁻¹ (mean of the doublet). This shift of 19 cm⁻¹ is considerably less than the predicted 27 cm⁻¹ for this mode. Hence, the splitting calculated for the other modes may be in error.

A better approach is to use the product rule (1,6) which gives a mathematical relationship between the product of the frequencies of a given symmetry species for two isotopically substituted molecules. For the three A₁ modes of the formate ion, this rule is given by the expression;

$$\frac{\nu_1 \nu_2 \nu_3}{\nu'_1 \nu'_2 \nu'_3} = \frac{[m(C^{12}) M]^{1/3}}{[m(C^{13}) M]^{1/3}}$$

where the primed frequencies refer to the C^{13} species, m refers to the mass of the two atoms isotopically substituted, and M and M' refer to the total mass of the C^{12} and C^{13} ions respectively.

Now, assuming a C^{13} splitting of 19 cm^{-1} for ν_1 (which is observed), and assuming 3 cm^{-1} for ν_2 (the product of the frequencies is relatively insensitive to a $\pm 3\text{ cm}^{-1}$ change in this high frequency mode), the splitting for ν_3 can be calculated. This turns out to be 12 cm^{-1} , still less than the 17 cm^{-1} observed, but much closer than the previous calculated 6 cm^{-1} .

A further justification in the assignment of these low frequency modes is that the shifts of all three from their corresponding C^{12} mode is constant (Table 7).

TABLE 7

Product Rule Frequency shifts of C^{13} Formate Ion

$C^{12}\nu, \text{ cm}^{-1}$	$C^{13}\nu, \text{ cm}^{-1}$	$\nu_{12} - \nu_{13}, \text{ cm}^{-1}$
769.5	752	17.5
766.5	749.5	17.0
761 *	744	17.0

* weighted mean of 761.5 and 758

Confirmation of the magnitude of this splitting is also found in the infrared spectrum of the same fundamental of sodium formate. A single strong absorption appears at 772 cm^{-1} in the infrared, accompanied by a very weak shoulder at 755 cm^{-1} , a separation of 17 cm^{-1} , which has also been assigned to the corresponding C^{13} mode.

The polarization assignments for the C^{12} components were very difficult to make, especially for the two stronglines at 769.5 and 766.5 cm^{-1} . The former is certainly a active, and the latter c active. However, the b axis spectrum was very broad between 770-766 cm^{-1} since the crystal used for this spectrum was slightly thicker than that for the c and a axis spectra. As a result, it is difficult to ascertain if both components are b active. The high frequency line at 769.5 cm^{-1} , is definitely b active, and it is felt from intensity studies done by rotating the plane of polarization in small increments from c to b axis polarization, that the 766.5 is probably not b active. However, further study with thinner crystals might show this assignment to be incorrect.

Although single crystals of lead formate were not prepared, this region in KBr pellets of lead formate showed five distinct components, whereas only four are detected for barium formate in KBr. (Fig. 8c). No assignments can be made for lead formate.

4-2 N. M. R. Results

It was pointed out in Chapter (1), that an n.m.r. analysis of a single crystal of barium formate failed to give the line shape predicted by the crystal structure of Sugawara et. al. (11). From this structure, the nearest proton-proton distance is 1.81 A, and the next nearest is 4.11 A. The predicted positions of the protons are shown in Fig. 10b, where a C-O bond length of 1.25 A, a C-H bond length of 1.09 A, and an OCO angle of 127 degrees was assumed. The n.m.r. spectrum for proton resonance of polycrystalline barium formate should have a pronounced doublet splitting of 7.13 gauss, and a second moment of 12.3 gauss². The experimental second moment was $1.9 \pm .3$ gauss², and showed no doublet splitting characteristic of two close protons.

A similar analysis for lead formate, with nearest proton-proton distance of 1.78 Å, and next nearest at 3.3 Å, also predicted a doublet splitting of about 7 gauss, and a second moment of 12.2 gauss². The experimental value was 1.6 ± 0.3 gauss².

These results indicate that either both crystal structures are in error or that there is considerable rotation of the formate ion in the crystal. The latter suggestion can be discarded since in order to alter the position of the proton, a hindered rotation or rotational oscillation about an axis other than the symmetry axis (C₂) of the ion would have to occur. It is believed that this type of motion is very unlikely to occur at room temperature.

The first hypothesis is almost certainly correct in view of the fact that the sum of the van der Waals radii of two protons is 2.4 Å, considerably greater than 1.8 Å. Further, the Ba-H distance is only 1.3 Å, whereas the sum of the radius of the barium ion and hydrogen is 3.2 Å. Due to the large scattering power for X-rays of barium and lead relative to that of carbon and oxygen, it is likely that the positions of the formate ions in the unit cell are in error.

Assuming the protons are as close as possible in accordance with their van der Waals radii, say 2.4 Å apart, the second moment should be 1.8 gauss² for two protons only. This is in excellent agreement with the experimental values. It is possible that the C and O positions are correct but that the C-H bond has been distorted from the line bisecting the OCO angle, to give this 2.4 Å separation. However, the infrared evidence to be discussed below indicates that there is no distortion of the formate ion in the crystal.

4-3 Crystal Structure of Barium Formate

A careful study of the infrared spectra and polarization data shows that there is perhaps something unique about the c axis of the barium formate crystal. The c active absorptions are generally more intense than the others, and in the ν_2 and ν_6 fundamentals there are more apparent c axis absorptions than a or b. While this behavior is not inconsistent with the $P2_12_12_1$ factor group predictions, it was felt that it could indicate a different factor group.

As stated at the beginning of this chapter, an X-ray analysis carried out as part of this investigation indicated that the factor group of barium formate was in fact $P2_12_12_1$. Even with extremely long exposures, no evidence could be found to indicate otherwise. Therefore, it appears that the barium, carbon and oxygen atoms are in a $P2_12_12_1$ arrangement in the lattice. But this symmetry may be destroyed when the hydrogen atoms are considered, if there is a distortion of the C-H bond from a line bisecting the OCO angle. The effect of this distortion in destroying the $P2_12_12_1$ symmetry would very likely not show up on an X-ray photograph when one considers the scattering power for X-rays of a barium atom relative to hydrogen. Thus, if the factor group of the crystal is not $P2_12_12_1$, it must be a subgroup of this, of which only $P2_1$ and $P1$ are possible. The latter factor group is the one of trivial symmetry and one would expect no polarization behavior under this group. But polarization properties are possible under $P2_1$. A factor group analysis for barium formate under the point group 2 (isomorphous with $P2_1$) is presented in Table 8.

TABLE 8

Factor Group Analysis of Barium Formate Under 2

2	E	$C_2(z)$	n_i	T	T'	R'	n'_i
A	1	1	54	1	17	12	24
B	1	-1	54	2	16	12	24

If the $C_2(z)$ screw axis is in the direction of the c axis in barium formate, 24_c and 24_{ab} active components are predicted for the six molecular fundamentals in the crystal. By similar reasoning as was applied to the $P2_12_12_1$ factor group analysis, each molecular mode should have $4_c + 4_{ab}$ active components in the crystal. Now when an absorption has dual activity, say active for light polarized along the a and b axes, it is necessary to distinguish between an ab active absorption, which is a single normal mode active along the a and b crystal axes, and two accidentally degenerate modes, one a active, and the other b active. For $P2_1$ symmetry, only c and ab type absorptions should appear. A great many observed absorptions have this property (cf. Table 2) which encourages an interpretation of the results in terms of $P2_1$ factor group. However, there are some conspicuous exceptions to the expected $P2_1$ behavior, namely the 3134 cm^{-1} overtone which is b and c active only, and the ν_6 fundamental which has a c and b active component at 1073 cm^{-1} and a c and a active component at 1066 cm^{-1} . This violates the $P2_1$ predictions where each a active absorption must also be b active and vice versa. However, if we assume that the 1073 cm^{-1} absorption consists of two distinct modes accidentally degenerate, one

mode c active and the other b active, there is no violation of $P2_12_12_1$ predictions. The same consideration applied to other absorptions of dual activity (i.e. that these absorptions are two distinct modes of different activity) is likewise amenable with a factor group of $P2_12_12_1$ for barium formate.

The factor group splitting of the ν_2 , ν_3 , and ν_6 fundamentals under $P2_12_12_1$ is as follows: the ν_2 fundamental has a and b active modes at 2863 cm^{-1} , a c active mode at 2823 cm^{-1} , and a c active mode at 2750 cm^{-1} . The ν_6 fundamental has four distinct components, two c active at 1073 and 1066 cm^{-1} , one b active at 1073 cm^{-1} , and one a active at 1066 cm^{-1} . The ν_3 fundamental has the predicted six $P2_12_12_1$ factor group components; a active lines at 769.5 and 758 cm^{-1} , b active lines at 769.5 and 761.5 cm^{-1} , and c active lines at 766.5 and 761.5 cm^{-1} . The a, b or c activity of an absorption corresponds to a normal mode which belongs to the B_3 , B_2 , or B_1 irreducible representation respectively of the factor group $P2_12_12_1$. The symmetry species of the absorptions of barium formate are then shown in Table 2, when it was possible to determine such.

4-4 Conclusion

Infrared spectroscopy has proven to be a valuable tool in elucidating the crystal structure of a hydrogen containing compound. While X-ray diffraction studies can indicate the symmetry of heavy atoms in a crystal structure, infrared spectroscopy can show if this symmetry is correct when the light atoms, and in particular hydrogen, are also considered. This study has shown that the symmetry of crystalline barium formate is in fact $P2_12_12_1$, and that the error in Sugarawa's

structure is probably due to an incorrect determination of the coordinates of the carbon and oxygen atoms in the unit cell.

Several weak infrared absorption lines in the spectrum of single crystal barium formate are still unassigned, and may be due to sums of lattice modes with molecular fundamentals. It would be very desirable to study the effect of temperature changes on the intensities of these suspected lattice modes. This would aid in assigning these modes since difference combinations appear less intense than corresponding sum modes as the temperature decreases. This effect is due to the decrease in population of the lattice vibrational states at lower temperatures as governed by the Boltzmann factor.

APPENDIX

Factor Group Analysis of Sodium Formate

The sodium formate crystal is monoclinic with factor group symmetry $C2/c - C_{2h}^6$, and has four molecules per unit cell (23). The unit cell dimensions are $a = 6.19 \text{ \AA}$, $b = 6.72 \text{ \AA}$, $c = 6.49 \text{ \AA}$, and $\beta = 121^\circ 42'$. A factor group analysis under point group $2/m$ (isomorphous with $C2/c$) is presented below. The symmetry elements are as follows; E is the identity operation, C_2 is a two fold rotation axis, σ_h is a mirror plane, and i is a center of inversion.

$2/m$	E	C_2	i	σ_h	n_i	T	T'	R'	n'_i
A_g	1	1	1	1	12	0	4	2	6
B_g	1	-1	1	-1	18	0	8	4	6
A_u	1	1	-1	-1	12	1	3	2	6
B_u	1	-1	-1	1	18	2	6	4	6

Sixty normal modes are possible for the unit cell ($\sum n_i$), of which twenty four are internal molecular modes ($\sum n'_i$). T refers to the symmetry of the translation coordinates, T' indicates the number of translational lattice modes, and R' indicates the number of the rotational lattice modes. Only twelve of the twenty four molecular modes are active in the infrared, (that is, belong to one of the translation coordinate symmetry species), and each fundamental of the formate ion should be split into two components in the crystal.

BIBLIOGRAPHY

1. Wilson, Decius, Cross, "Molecular Vibrations", McGraw-Hill, 1955
2. Halford, J. Chem. Phys. 35: 1097, and 1109 (1961)
3. Halford, J. Chem. Phys. 36: 2654 (1962)
4. Hornig, J. Chem. Phys. 36: 2634 (1962)
5. Hornig, J. Chem. Phys. 34: 265 (1961)
6. Herzberg, "Infrared and Raman Spectra", Van Nostrand, 1944
7. Bhagavantam and Venkatarayudu, Proc. Ind. Acad. Sc. 9A: 224 (1939)
8. Bhagavantam and Venkatarayudu, Proc. Ind. Acad. Sc. 13A: 543 (1941)
9. Halford, J. Chem. Phys. 14: 8 (1946)
10. Itoh, Kusaka, Kiriya, Saito, Osaka University, Science and Industrial Research, Memoirs, 14: 1 (1957)
11. Sugawara, Kakuso, Saito, Nitta, X-Sen. (X-Rays), 6: 85 (1951)
12. Charney, J. Opt. Soc. Am. 45: 980 (1955)
13. Born and Huang, "Dynamical Theory of Crystal Lattices", Oxford, 1954
14. Bhagavantam and Venkatarayudu, "Theory of Groups", Andhra University, 1951
15. Hornig, Vedder, "Advances in Spectroscopy" Vol. II, Interscience, 1961
16. Gupta, Indian. J. Phys. 10: 117 (1936)
17. Lecomte, Comptes Rendus, 208: 1401 (1939)
18. Lecomte, Cahiers Phys. 17: 1 (1943)
19. Fonteyne, Naturwisse. 31: 441 (1943)
20. Fonteyne, Natuurwetenschappelijk Tijdschrift, 25: 173 (1943)
21. Duchesne, Physica, 8: 525 (1941)
22. Groth, "Chemische Krystallographie", Vol. 3, Wilhelm Engelmann, 1910.
23. Zachariasen, J. Am. Chem. Soc. 62: 1011 (1945)