THE INFRARED SPECTRA OF CRYSTALLINE

CALCIUM AND SODIUM FORMATES

by

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ABSTRACT

The infrared absorption spectra of single crystals of calcium and sodium formate have been recorded between 4000 and 500 cm^{-1}. With the aid of polarized radiation it was possible to carry out an analysis of the spectra. Factor group splitting was observed for the molecular modes of calcium formate. It was possible to assign the origin of the components of any given molecular fundamental to one of the two sets of symmetrically non-equivalent formate ions in the calcium formate unit cell. This assignment was made on the basis of the relative intensities of the components of the fundamentals.

For the sodium formate single crystal spectrum, a combination of factor group and site group analysis was required to satisfactorily interpret the results. The results obtained in this case helped to resolve the controversy surrounding the assignment of the ν_2 and ν_5 molecular modes for the formate ion.

Lattice mode frequencies of 36, 61, 90, 128, 154 and 192 cm^{-1} for calcium formate and 58, 91, 112, 128 and 231 cm^{-1} for sodium formate are inferred from combinations with molecular modes. The analysis was completed by the assignment of several modes to C^{13} formate ion fundamentals and to combination and overtone modes of molecular fundamentals.

ACKNOWLEDGEMENT

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CHAPTER 1. INTRODUCTION

1-1. Preliminary remarks

In the infrared region of the electromagnetic spectrum lie the rotational and vibrational spectra of molecules. That is, the manifestations of the changes in the molecular rotational and vibrational energy that can occur under certain conditions by the interaction of infrared radiation with matter. The frequencies which thus appear are directly dependent on certain molecular constants and a study of these frequencies will give much information concerning the structure of the molecules involved. Up to the present, a vast amount of experimental data has been obtained but very little has been analyzed. Although procedures for this analysis are well developed (39), many workers have been deterred because of the amount and complexity of the work required to satisfactorily complete the analysis.

The major portion of the work that has been done has been concerned with the gas phase where interactions between molecules are limited. It is only relatively recently, after the motions of single molecules were generally well understood, that attention has shifted to the study of molecules in condensed systems and particularly

to crystals. Although a fair amount of work has been done with single crystals in the Raman effect (where comparatively much thicker crystals can be used), little work has been done in the infrared effect because of the difficulty in obtaining single crystals thin enough so as not to be totally absorbing throughout most of the spectrum. The development of better techniques for obtaining very thin single crystals will help to increase the knowledge about intermolecular crystalline forces.

Because of the intermolecular forces in condensed systems, the rotational fine structure associated with the spectra of gases is generally not observed, and if it is, then mainly in the liquid state. (Rotational fine structure has been reported in some solid ammonium salts.) Three main differences between the spectra of vapors and solids occur: (1) usually small changes or shifts in the frequencies of vibrations, (2) the appearance of new vibrational frequencies and (3) splitting of the vapor phase frequencies into two or more peaks.

The first effect is found to be temperature dependent as well as being a function of the electrostatic interaction of an oscillating dipole with its surroundings. The second effect may be explained by the occurrence of polymers or associated molecules in the solid state. The

third effect arises because of a degradation of the symmetry of the molecule concerned when built into a crystal. This degradation can bring about the removal of degeneracy as well as causing some modes, which are inactive in the high symmetry of the free molecule, to be active in the lower symmetry of one or more subgroups of that molecule. In this work, we are concerned with the third effect and a more complete discussion will be given later.

The use of polarized radiation for the analysis of the spectra of crystals is desirable. For substances in non-ordered arrays, the alterations in dipole moments giving rise to absorption bands will take place in all possible directions. Thus, the excitation of all vibrations possible is equally probable. This is also true for polycrystalline samples in which all crystallites are randomly oriented. The situation is entirely different with single crystals. Because of the fixed orientation of the molecules, the oscillating dipoles will also be alligned. By using polarized radiation, the orientation of dipoles in the crystal may be determined. If the crystal structure of the sample is known, then a vibrational assignment may be made by combining the polarization and X-ray results. Similarily, if the crystal structure is

unknown, the infrared spectrum may aid in its determina-
tion. This technique is particularly useful in structure
determinations involving hydrogen atoms, where X-ray
methods are insufficient. Halford (1,2) and others have
determined crystalline space groups by studying the in-
frared spectra of single crystals.

1-2. The problem

A salt of the formate ion was chosen for this study
for several reasons. First, the modes of vibration of
XYZ_2 type systems have been well characterized(3); second,
as a continuation of the work started in this laboratory
by Morrow(4) in his study of barium formate; and third,
as a further test of the theories of vibrations in crystals
developed by Bhagavantum and Venkatarayudu (5,6) and
Halford(7) using a different crystal system than that used
by Morrow. The reasons for the choice of the particular
salts studied will be outlined later.

A considerable amount of previous work involving
the spectra of formates has been carried out in both the
Raman and infrared effects. In 1936, Gupta(8) obtained
the Raman spectra of sodium, barium, and cadmium formates
in the crystalline state and in aqueous solution. An
attempt was made to explain the results on the hypothesis

that the C-H linkage undergoes prototropic change in solution to yield dihydroxymethylene. The explanation is based on an incorrect assumption. The spectra given are rather incomplete with very few frequencies reported. At the same time, Venkateswaran(9) reported more complete spectra for sodium, cadmium, and calcium formates in solution and sodium, cadmium, calcium, and lead formates as crystals. The occurrence of lines corresponding to the HCO deformation and the CH stretch, point to the existence of the CH group. Lecomte(10,11) has reported both the infrared and Raman spectra of several formates with incorrect assignments. Fonteyne(12,13) had done a very complete study of the Raman spectra of aqueous sodium formate and sodium formate-d_1. Force constants for the formate ion have been calculated using a Urey-Bradley potential function.

More recently, Thomas(14), in an attempt to determine the inplane force constants of the formate ion, obtained the infrared spectrum of sodium formate using thin films of the salt melted between sodium chloride plates. The spectrum obtained is in doubt because of the tendency of the formate ion to decompose at the temperatures required to melt the salt. Also, the assignments made for the bands observed are incorrect. Because

of the unreliability of experimental results, the force
constants derived are of similar doubtful accuracy.

Newman(15) in 1952, studied single crystals of
sodium formate using polarized radiation provided by a
silver chloride polarizer. The limited resolving power
of his instrument allowed him to report only the funda-
mental formate frequencies and two combination bands.
He obtained his crystal by evaporation of aqueous solu-
tions of sodium formate. Significant differences, such
as a large shift to higher frequency of ν_4 and an
apparent reversal of Fonteyne's assignment of ν_2 and
ν_5 are noted. He suggests that these discrepancies
are related to a strong influence (that is, hydrogen
bonding) of the aqueous solvent on the Raman frequencies,
although intensity and depolarization measurements of
the Raman lines of the solution support Fonteyne's
assignment.

Ito and Bernstein(16) did an infrared and Raman
study of solid sodium formate and a saturated aqueous
solution (both H_2O and D_2O) of the salt. A rather com-
plete assignment of the observed peaks confirms Fonteyne's
assignments. The solid films of sodium formate were ob-
tained by deposition from water, water-methanol, or water-

acetone solutions on silver chloride plates. A slight change in vibrational frequencies, depending on the method of sample preparation, is noted. Newman's ν_4 band at 1620 cm^{-1} is observed only as a weak shoulder. The presence of two lattice frequencies at 140 and 40 cm^{-1} is assumed for assignment of combination bands.

Harvey, Morrow and Shurvell(17) did a vibrational study of several crystalline formates suspended in pressed potassium bromide pellets. Their assignment of fundamental frequencies is based on Fonteyne's. The occurrence of Fermi resonance is assumed as an explanation for the variations between observed and calculated values of overtone frequencies. The fine structure of the absorption due to the formate internal vibrations is ascribed to crystal-field splitting.

Schutte and Buijs(18), as an extension of work on planar tetra-atomic ions, studied the formate salts of calcium, strontium, barium, and lead. It was found that a second form of calcium formate (labelled β-calcium formate) was crystallized when a water miscible organic solvent was added to an aqueous solution of normal α-calcium formate. The spectrum of β-calcium formate was quite different from the spectrum of α-calcium formate. This second phase of calcium formate might give an

explanation of the variations in the spectrum of sodium formate obtained by Itoh and Bernstein.

Donaldson, Knifton and Ross(19) undertook a study of several formates to determine a relationship (if any) between the frequency of carbonyl vibrations and various properties of the cations concerned. Shifts in the OCO stretching frequencies ν_2 and ν_4 which, if related to the M-O bond strength would imply that some form of co-valent bonding exists. Three types of structure involving co-valent bonding have been suggested.

(A)   (B)   (C)
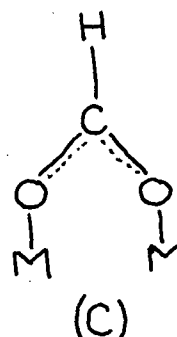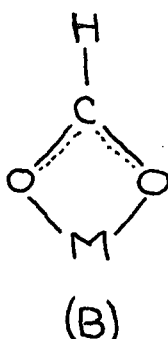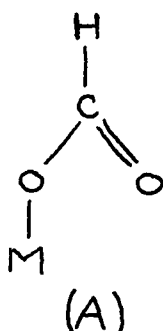
Type (A) can be distinguished from types (B) and (C) in that for type (A) compounds ν_{as} (OCO) increases as the M-O bond strength increases. Three groups of formates were found in which either or both of the frequencies ν_2 and ν_4 differ substantially from those for rubidium formate which is an ionic compound free from crystal-field splitting effects. Some covalent character is thus inferred for some of the formates studied (for

example aluminum, gallium, and tin(IV) formates), although the formates of sodium, potassium, calcium, strontium, and barium appear to be ionic.

Itoh(20) and his co-workers have carried out a study of calcium formate by means of nuclear magnetic resonance. Unlike the N.M.R. results for barium formate, which indicate the reported crystal structure to be in error, the N.M.R. results for calcium formate indicate the reported structure to be correct other than possible small errors in determining the positions of carbon and oxygen atoms by X-ray analysis.

1-3. Methods of investigation

The infrared spectrum of single crystals of sodium and calcium formate were recorded with the aid of polarized radiation. The infrared spectra of polycrystalline sodium and calcium formate and sodium formate-d_1 and calcium formate-d_1 suspended in pressed potassium bromide discs and of these salts in aqueous solution were also recorded. X-ray rotation and Weissenberg photographs were taken in order to confirm reported crystal structures and to unambiguously identify crystal axes.

CHAPTER 2. EXPERIMENTAL WORK

2-1. Materials investigated spectroscopically

The calcium formate used was reagent grade obtained from the British Drug Houses Limited. Slight insoluble impurities were removed from solution by filtration through Whatman number 1 filter paper. The sodium formate used was reagent grade obtained from Baker and Adamson Products, General Chemical Division, Allied Chemical Corporation. Again slight insoluble impurities were removed by filtration.

The calcium formate-d_1 used was prepared by neutralization of formic acid-d_1 with calcium carbonate. The product was filtered and recrystallized three times from solution. The same method of preparation was used to obtain the sodium formate-d_1.

2-2. Growth of single crystals

A salt of the formate ion was chosen for this study as outlined previously. But, because of the complexity of the vibrational analysis, anything that may add to the difficulty is undesirable. Thus salts which are hygroscopic at room temperature or are hydrates when crystallized from aqueous solution are unwanted. Of

the alkali and alkaline earth salts of the formate ion, only calcium and barium formates do not have these undesirable properties. Lead formate may also be included in this group. Strontium and magnesium formates form hydrated salts although a non-hydrated form is known for the strontium salt. Lithium, sodium, and potassium formates are hygroscopic, the potassium salt extremely so.

Large single crystals are most easily grown from a saturated solution by slow evaporation of the solvent. This method essentially eliminated lead formate from this present work because of its low solubility at room temperature although rather imperfect crystals were obtained when grown from a large volume of solution to a size of about 3x3x10 mm. over a period of several months. With a great deal of care, useable crystals could undoubtedly be grown. Because of the extreme hygroscopic nature of potassium formate and the unavailability of sufficient quantities of lithium formate, no attempt was made to grow crystals of these salts. Of the remaining salts, calcium, sodium, and strontium formates seemed to be the most suitable.

It was originally intended to carry out a study of single crystals of sodium formate. The combination of

both a different crystal structure and a monovalent cation
would provide a good basis of comparison with the work of
Morrow. Although sodium formate tends to be slightly
hygroscopic, it was felt that with careful handling, the
method of grinding (to be described later), and flushing
of the instrument with dry nitrogen, most difficulties
arising from this hygroscopic nature could be avoided. To
be of any use the crystals had to be large enough to
cover the slit (10x2 mm.) in the brass plate used for
mounting the crystals. The most obvious way of obtaining
crystals of the appropriate size was to mount a seed
crystal in a saturated solution of the desired salt and
allow growth to proceed with evaporation.

According to Seidell (21), and the International
Critical Tables(22), sodium formate crystallizes as a
dihydrate below temperatures of about 28°C. Therefore,
it was felt that by keeping a saturated solution of the
salt at an elevated temperature, suitable crystals could
be grown. According to the references above, 16.0 moles
of sodium formate should dissolve in 1000 gr. of water at
40°C. To obtain a solution of this concentration, an ex-
cess of salt was added to a volume of water heated to
$60-70^{o}$C. The supernatant liquid was decanted through a
Whatman number 1 filter paper into a 250 ml. erlenmeyer

flask and then placed in a water bath held at $40^{o}C$.
The erlenmeyer flask was used to reduce the surface area
of the solution and thus the rate of evaporation of the
solvent at the elevated temperature used. As the solution
cooled, seed crystals were formed.

Two types of seed crystals were obtained. Long
needle-like crystals approximately 0.5 mm. square and
in various lengths limited only by the dimensions of
the flask were usually obtained. Several times however,
thin flat plates several mm. wide and a few cm. long
were obtained. The formation of the two types appeared
to be dependent on the rate of cooling of the solution,
the flat plates appearing on very slow cooling. Both
types of seeds were used in attempts to grow larger
crystals.

An attempt was also made to grow single crystals
from the melt. A similar method was used by Buchanan
et al. (23) to grow single crystals of normal and deuter-
ated lithium hydroxide. The samples they obtained were
then cleaved to yield crystal plates several hundred
microns thick. In this case a large sample (about 25
grams) was placed in a sealed glass tube one half inch
in diameter and drawn out to a capillary at the lower
end. This tube was then suspended in a furnace by a

system that lowered the tube from the furnace at a slow
rate. As the capillary portion of the tube emerged from
the furnace, the sodium formate contained inside crystal-
lized and acted as a seed for the remaining salt. However,
this method was discarded after a tube exploded in the
furnace because of the decomposition of the salt at the
temperature maintained inside the furnace.

The seeds obtained by evaporation were mounted on
a small coil of plastic-coated copper wire over which a
small piece of spaghetti-tubing was placed. The seed was
held in place by a small amount of C.I.L. Household Cement.

Figure 1. Mounting of seed crystals.

The mounted crystal was then placed in a 250 ml. erlenmeyer
flask filled with a saturated solution of sodium formate,
the flask being held in a water bath at 40°C.

After several seeds had dissolved in the flasks,
it was realized that the vapor pressure of water over the
bath was greater than the vapor pressure over the saturated

solution. Thus water from the bath was being distilled into the flasks. To correct this situation, a small vacuum system was constructed, initially out of glass and then, when the glass proved to be too fragile, out of copper tubing. It consisted simply of a manifold from which several T-joints were made, each joint being connected to the flasks containing the seed crystals by means of rubber pressure tubing. A stop-cock was inserted in each piece of rubber tubing so that individual flasks could be handled without releasing the vacuum on the other flasks. Vacuum was created by means of a water aspirator.

When the vacuum was left on continuously it was found that too rapid evaporation occurred and great masses of crystal meal were precipitated. An attempt was then made to promote growth by applying vacuum for approximately an hour a day. This provided a reasonably low rate of evaporation and also a chance for the crystal to heal. (It is well-known that an imperfect crystal left in a saturated solution will rearrange to form a more perfect crystal). This method proved to be more successful, although the formation of additional crystals on the bottom of the flask and on the crystal mount was encountered.

Growth of crystals of sodium formate by this method was very slow and the resulting crystals were generally

poorly formed, some of them being twinned. Eventually,
(after several weeks), a few crystals of useable quality
were obtained. These crystals were usually about 2 or 3
cm. long and 2 or 3 mm. thick and varying in width from
2 to 10 mm. depending on the type of seed crystal used.
But, because of the possibility of having to abandon
the attempt to obtain reasonable crystals of sodium
formate, an attempt was made to grow single crystals of
calcium and strontium formates.

Seed crystals of both strontium and calcium formate
were obtained by evaporation of a saturated solution of
the salts from an uncovered Petrie dish. Of the seed
crystals obtained, those of strontium formate were by
far the best formed, the calcium formate seeds seeming
very irregular. Therefore seeds of strontium formate
were mounted as above and placed in a saturated solution
on the salt contained in a 2000 ml. beaker. The uncovered
beaker was then placed in a cupboard where air-circulated
dust was at a minimum. The large beaker was used for
several reasons. First, although the rate of evaporation
was fast, the rate of supersaturation of the large volume
of solution was slow and growth proceeded quite evenly.
Second, a large number of crystals (15-20) could be
accomodated in the one beaker. Third, the amount of

handling required and equipment used was reduced to a minimum.

In the course of a few weeks, large (up to 1 or 2 cm. in all directions), well-formed though somewhat imperfect crystals were obtained. Even though the crystals seemed to be cracked, quite suitable portions of the large crystals could be used for further work. However, when ground down, the infrared spectrum of the crystal exhibited a strong band corresponding to the OH stretching frequency, obviously arising from water of hydration. The crystals of strontium formate dihydrate were stored for possible future use and an attempt was made to grow crystals of calcium formate.

The seeds of calcium formate were mounted in the usual manner and place in a 2000 ml. beaker partially filled with saturated solution and stored in a cupboard similar to the procedure used for strontium formate. In this case, the rate of evaporation was slower. As the calcium formate crystals grew, it was readily seen that the crystals were quite symmetrical. Unlike the case with strontium formate, where very few extra crystals grew on the beaker bottom, a thick deposit of crystal meal was formed on the beaker bottom and more importantly, along the mount. As the crystals grew, this crystal meal

was incorporated in the bottom portion of the main crystal giving rise to further centers of deposition leading to highly irregular conglomerations.

To prevent this, the crystals were periodically removed from solution, the crystal meal was scraped off the mount and the crystal was then rinsed in very cold water. Because of the temperature of the water and the physical form of the crystal very little disolution occurred. The rinse removed the last traces of crystal meal from the mount and any that might have adhered to the crystal itself thus preventing these small crystal-lites from acting as centers of crystallization. As the rate of growth proved too slow, a heating tape was placed around the bottom of the beaker and the temperature of the solution was increased by several degrees. This increased the rate of evaporation and thus the rate of growth.

In this manner, several large crystals were obtained, including one 3.5x3.5x4.0 cm., although the others were stopped after they had attained a size of about 2 cm. The crystals grown by this method generally had several flaws consisting of cracks running across the crystals. These cracks could have been caused by the removal of the crystals from the warm solution and the subsequent rinsing in cold water. They may also have been caused by

the removal of the crystals from the warm solution and the subsequent rinsing in cold water. They may also have been caused by stresses created in the crystal when it grew around the mount. In any case the pieces obtained from a cracked crystal provided several convenient specimens which could be ground down.

2-3. Grinding

In order to study the important portions of the infrared absorption spectrum of a single crystal, the crystal must be no thicker than 40 to 50 microns. With this thickness all but a few of the very strongly absorbing vibrational modes (for example, the carbonyl regions in the case of the formate ion) are easily resolved. In order to resolve these bands, crystals of half this thickness are required. Different workers have used various methods of obtaining thin single crystals. Halford(1,2) and his co-workers obtained single crystals by controlled feeding of allene and cyclopropane into a specially constructed potassium bromide cell held at liquid nitrogen temperatures. However, they had no control over the way the crystal axes would be oriented with respect to the window.

Winter, Curnette and Whitcomb(24) obtained single crystals of ferrocene. These were then attached to a potassium bromide window by means of a wax seal. The crystal was then thinned and polished by rubbing on a cloth moistened with acetone. Their crystals however, were of the order of 0.1 mm. thick. Bryant(25,26) grew crystals of sodium and potassium axide from saturated aqueous solutions of the salts, then thinned the crystals to a thickness of 0.09 mm. at the thinnest by grinding and polishing with a jewelers cloth dampened with acetone. Morrow grew large single crystals of barium formate which were partly ground while the crystal was hand-held and then it was attached to a rocksalt window for the final grinding. It is Morrow's general method that was used here.

It is quite easy to obtain crystals in the order of 50 microns thick. As Morrow has pointed out, thinner crystals would be desirable but are usually mechanically unfeasible. However, with a great deal of care, and patience, crystals of the order of 25 microns thick were obtained as described below.

As mentioned earlier, the crystals should have a cross-sectional area of at least 2x10 mm. in order to

completely cover the slit in the mounting plate. Thus
it was necessary to start with a crystal of slightly
larger dimensions than those of the slit. The crystal
fragments obtained when the calcium formate crystals
cracked were of an ideal size. Because of the size of
the sodium formate crystals, a slightly different tech-
nique was required and will be described later.

With calcium formate, the crystal was ground
perpendicular to all three axes. The axes used were those
designated by Groth(27) and shown below.
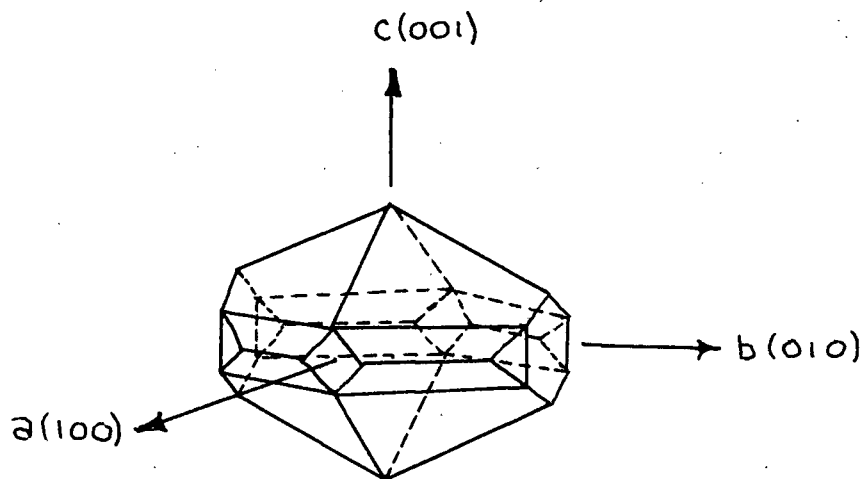
Figure 2. Calcium formate single crystal.

In each case the crystal was ground until a maximum cross-
section was obtained perpendicular to the desired axis.

The grinding proceeded as follows. For the first stage, the crystal or crystal fragment was hand-held and, using 150-C grade emery paper, the major portion of the grinding was done. This rough grinding brought the crystal to within about 100 microns of the desired plane. Then, using 360-A grade emery paper, a rough smoothing of the crystal was obtained by the elimination of the deep scratches inflicted by the coarser emery paper. Finally, a course polishing was done by using 4/0 grade emery polishing paper. At this point, the final smoothing and polishing could be done. For this, a Rocksalt Polishing Kit was obtained from the Research and Industrial Instruments Co. This consisted mainly of a ground glass roughing lap, a ground glass smoothing lap, and a velvet polishing strip.

The coarsely polished crystal was further smoothed on the roughing lap using the alcohol provided in the kit as a lubricant. However, it was found that the alcohol evaporated too rapidly leaving deposits of ground salt which hardened and scratched the crystal. Also, in the second stage of grinding, the alcohol dissolved the glue holding the crystal to a rocksalt window. For these reasons kerosene was used as a lubricant. Kerosene has a fairly low volatility and a low viscosity as well as not

being a solvent for either the crystals, rocksalt windows of glue used. This made it an ideal lubricant for this work.

When all remnants of fine scratches had been removed on the roughing lap, a final smoothing was done on the smoothing lap. The crystal was then polished on the velvet polishing strip using the polishing rouge provided in the kit and kerosene as a lubricant. It was then given a final high polish on a dry velvet strip.

At this stage, the other half of the crystal could be ground. The polished face was glued to a rocksalt window. Initially C.I.L. Household Cement was used but because of the high viscosity of the glue, a thick layer of glue was obtained between the window and the crystal. This thick layer of glue interfered with the infrared spectrum of the crystal so that it was difficult to determine the thickness of the crystal. For this reason, Radio Service Cement, diluted with acetone to reduce its viscosity, was used. Every precaution was taken to ensure that the entire polished surface was cemented down in an effort to reduce the possibilities of chipping when the crystal became very thin. However, this was not completely possible because as the glue's solvent evaporated, small air pockets were formed in the glue between the crystal and the window. These air pockets invariably allowed

chipping to occur. Thus the glue was repeatedly dissolved off and the crystal reglued to the window until a portion of the crystal of sufficient cross-section was obtained that was completely cemented to the window. This generally required several attempts. An ideal glue for this work would be one of very low viscosity and with a very low solvent content.

When the crystal had been satisfactorily glued to the window, the second stage of grinding began. As in the first stage, the crystal was ground to a thickness of about 0.2 mm. using the 150-C grade emery paper and the major scratches removed using the 360-A grade and 4/0 polishing emery paper. At this point the crystals were estimated to be between 50 and 100 microns thick. The roughing lap was then used to reduce the crystal in thickness so that the strongest absorption bands of the formate ion were resolvable in the infrared (ignoring the absorption due to the cement). The very thin section was then reduced further, using #950 bauxite abrasive on the velvet polishing strip. This part of the grinding proceeded very cautiously because it was at this point that the majority of chipping occurred. When fine struc-ture was observable in the resolved absorption bands, the crystal was given a polish using the polishing rouge and

the dry velvet strip. At this point, the crystals were estimated to be approximately 25 microns thick.

The thin crystal section was then removed from the rocksalt window by dissolving the glue in acetone. This generally required several hours. No attempt was made to push the partially glued crystal from the window as severe shattering occurred. Instead, the acetone was periodically stirred, and when the crystal moved slightly over the window it was transferred to the mounting plate. The plate was simply a brass plate with a narrow slit 10x2 mm. in area that would fit into a recepticle in the instrument. A portion of a paper clip was soldered to the plate for use as a handle.

The crystal was very gently pushed from the window to the plate which was held at the same level as the window. Because of the method of glueing the crystal to the window, not much control over the orientation of the crystal section was obtained. Thus no attempt was made to align any particular axis along the slit. Instead the plate and crystal were removed from the acetone and the crystal was glued to the plate using Radio Service Cement.

The directions of the crystal axes were checked using a polarizing microscope and a record kept of the orientation of the axes with respect to the slit. It was noted, using the polarizing microscope, that the crystals were clear and transparent and extinguished sharply and uniformly. No indication was given that any other crystal segments with different orientations were on the crystal.

The crystals were also examined with the polarizing microscope using crossed polars and strongly convergent light for illumination. By viewing between crossed polars not the image of the crystal, or object image, but another optical image formed in the principal focus of the objective by the strongly convergent beam of light, information regarding the direction of the crystal optic axes may be obtained. This image is called the directions image, image in convergent light, or the interference figure. More detailed discussions of this phenomenon are given by Hartshorne and Stuart(28), and by Bunn(29).

To determine how closely the crystals were ground on a plane perpendicular to the respective axes, the isogyres of the interference figures were observed. It was seen that in all cases these isogyres were centered

under the cross-hairs of the microscope indicating that
the crystals were ground exactly perpendicular to the
crystal axes, or at most only one or two degrees from
the perpendicular.

Several crystals of varying thicknesses were
ground perpendicular to each axis. In this way, the
fine structure of the fundamentals could be determined
with the thin crystals and the weaker peaks could be
detected using thicker crystals.

As mentioned earlier, the crystals of sodium
formate obtained were of sufficient length and width
along one axis. However, they were usually fairly thin.
This not only prevented the crystal from being hand-held
in the initial grinding stage but also prevented crystals
from being ground down perpendicular to more than one
axis. This was unfortunate but it was felt that some
useful information could be obtained from just the one
orientation.

The only difference between the grinding techniques
for the calcium formate and the sodium formate was that
for the first stage of grinding, the flat crystal was
glued to the rocksalt window with C.I.L. Household
Cement and one face was ground and polished in the manner

described above. The crystal was then dissolved off the window and the polished face was reglued to the window. The use of kerosene as a lubricant was most convenient in this case. A thin film of kerosene was constantly covering the crystal and no effect of the hygroscopic nature of the salt was noted. Again, crystals of varying thicknesses were obtained, the crystal section being parallel to the plane of the plate.

X-ray photographs of a small seed crystal of calcium formate were taken in order to unambiguously correlate the external crystal axes assigned by Groth (27) and the internal unit cell axes assigned by Nitta and Osaki(30). The crystal was mounted in a Nonius integrating Weissenberg goniometer with the external a-axis horizontal, and perpendicular to the incident X-ray beam. Rotation and oscillation photographs were taken of the a-axis, and Weissenberg photographs of the 0k*l* and 1k*l* planes were taken to determine the b and c-axis lengths. It was confirmed that the axes a, b and c noted by Groth are identical to the axes x, y and z noted by Nitta and Osaki respectively.

A similar set of X-ray photographs were taken of the sodium formate plate-like seed crystals.

Zachariasen's crystal structure was found for a needle-
like crystal and it was thought that the different
crystal modification might be composed of a different
unit cell. However, it was found that the crystal
structure of the flat plates is identical to the structure
previously reported.

2-4. Apparatus

All spectra were recorded on a Perkin-Elmer model
421 dual-grating spectrophotometer. Two dual-grating
interchanges were available which covered the regions
4000-650 cm^{-1} and 2000-200 cm^{-1}. The instrument was
flushed with dry nitrogen to reduce atmospheric absorp-
tion and to prevent attack of moist air on the hygro-
scopic sodium formate.

The polarizer was constructed by mounting two
sets of three 0.5 mm. thick silver chloride plates in
the form of a "V". This arrangement is necessary to
prevent sideways displacement of the beam on passing
through the silver chloride plates. The two sets of
plates were set at Brewster's angles to each other.
The polarizer was similar to that described by Charney
(32). As was pointed out by Brugel(33), with this type
of polarizer, the unwanted component of radiation is

still quite large, but to obtain complete polarization would require a prohibitive number of plates.

Measurements of optical density of the polarizer on a Beckman DU spectrometer using radiation of 6000 Å and a Wollaston prism indicate that the component perpendicular to the desired polarization is greater than 1% but less than 4% of the desired component. Measurements of the convergence of the sample beam show that there would be an unwanted component of not more than 1% of the desired component of polarized radiation due to this convergence.

2-5. Spectra

Table 1 lists the infrared absorption spectra obtained in this study and illustrated in figures 2 - 12. If the spectrum was recorded using polarized radiation, the plane of polarization is indicated as being parallel to axis a, b or c in the case of calcium formate, and as being parallel or perpendicular to the c-axis in the case of sodium formate. Spectral slit widths were calculated using information obtained from the Perkin-Elmer Corporation(42). The average spectral slit width was found to be 0.9 cm^{-1} with a range from 1.2 - 0.6 cm^{-1} depending on the region of the spectrum being studied.

Table 1. Illustrated infrared spectra

Figure no.	Description
3	$Ca(HCO_2)_2$ - polycrystalline in KBr
4	$Ca(DCO_2)_2$ - polycrystalline in KBr
5	$NaHCO_2$ - polycrystalline in KBr
6	$NaDCO_2$ - polycrystalline in KBr
7	$Ca(HCO_2)_2$ - single crystal $(3020\text{-}2680 \text{ cm}^{-1})$ polarized
8	" - " " $(1800\text{-}1000 \text{ cm}^{-1})$ polarized
9	" - " " $(840\text{-}740 \text{ cm}^{-1})$ polarized
10	$NaHCO_2$ - " " $(3100\text{-}2650 \text{ cm}^{-1})$ polarized
11	" - " " $(1800\text{-}1000 \text{ cm}^{-1})$ polarized
12	" - " " $(1050\text{-}750 \text{ cm}^{-1})$ polarized

Tables 2 and 3 list some of the previously reported data for calcium and sodium formate and the observed frequencies and assignments of calcium and sodium formate and calcium and sodium formate-d_1 obtained in this work for polycrystalline samples. Tables 4 and 5 list the observed infrared absorption frequencies of crystalline calcium and sodium formate, along with assignments and polarization properties.

Table 2. Partial summary of infrared and Raman frequencies of

calcium formate and calcium formate-d$_1$

Author assign.	Schutle and Buijs I.R.(mull)	Harvey et. al. I.R.(s)	This work I.R.(s)	I.R.(ag.)	I.R.(s) DCO_2^-	I.R.(ag.) DCO_2^-
ν_3	783	778	782		782	
ν_3	789		788			
ν_3	801	796	800			
ν_3	804		804			
ν_6	1068	1060	1067			
ν_6	1080	1072	1078			
					1086	
		1349	1125		1116	
ν_2	2869	2868	1355	1353	1351	1328
ν_2	2890	2890	1365			
$\nu_1-\nu_3$					1385	
ν_5	1389	1386	1390	1383	1014	
ν_5	1401	1397	1394		1020	1020
ν_5			1403			
$2\nu_3$		1582	1573			
ν_4	1587	1618	1591	1588	1580	1574
ν_4					1609	
	1629		1631			
	1658	1650	1651		1657	
$\nu_1+\nu_6$	2414					
$\nu_1+\nu_6$	2459					
$2\nu_2$	2697	2694	2700		2695	

Table 2 - continued

Author assign.	Schutle and Buijs I.R.(mull)	Harvey et. al. I.R.(s)	This work I.R.(s)	I.R.(aq.)	I.R.(s) DCO_2^-	I.R.(aq.) DCO_2^-
$2\nu_2$	2718					
	2734					
$\nu_2+\nu_5$	2747		2739	2733	2363	
$\nu_2+\nu_5$	2760		2750			
$\nu_2+\nu_5$			2780			
$2\nu_5$	2776	2745			2026	
$2\nu_5$		2775				
ν_1	1353	1359	2872	2832	2164	2123
ν_1	1362		2894			
					2853	
$\nu_2+\nu_4$	2945	2942	2950		2921	
$\nu_2+\nu_4$	2965		2967			
$\nu_1+\nu_3$					2961	
$\nu_4+\nu_5$	3000	3000	3008			

Table 3. Partial summary of infrared and Raman frequencies
of sodium formate and sodium formate-d_1

Author assign.	Ito and Bernstein I.R.(s)	Newman I.R.(s.c.)	Fonteyne R.(aq.) HCO_2^-	Fonteyne R.(aq.) DCO_2^-	This work I.R.(s)	This work I.R.(s) DCO_2^-
						722
ν_3	772	784	773	757	772	751
ν_3						766
						790
$\nu_3 + 60$	840					
$\nu_3 + 2 \times 60$	898					
$\nu_6 - 140$	923					
$\nu_6 - 2 \times 60$	958					
$\nu_6 - 60$	1013					
ν_6	1073	1070	1069	918	1062	915
$\nu_5 - 140$	1226					1312(?)
ν_2	1366	1377	2825	2122	1365	1333
ν_2						1344
ν_5	1377	1365	1386	1028		1014
$\nu_5 + 140$	1514					
ν_4	1567	1620	1584	1580	1601	1610
$\nu_4 + 60$	1620				1685(?)	
$\nu_4 + 140$	1700					
$2\nu_6$			2126	1831		2189(2ν_5?)
$\nu_2 + \nu_3$	2134					2096
$\nu_2 + \nu_6$	2435					

Table 3 - continued

Author assign.	Ito and Bernstein I.R.(s)	Newman I.R.(s.c.)	Fonteyne R.(aq.) HCO$_2$	R.(aq.) DCO$_2^-$	This work I.R.(s)	I.R.(s) DCO$_2^-$
$\nu_2+\nu_6$	2435					
2720-2x60	2599					
$2\nu_2$					2719	
$2\nu_5$			2732	2032		2019
$\nu_2+\nu_5$	2720	2750				
ν_1-60	2791					2074(?)
ν_1	2841	2870	1352	1329	2833	2135
$\nu_4+\nu_5$	2953					
$\nu_2+\nu_4$		2990			2957	2918
$2\nu_4$-60	3070					
$2\nu_4$+60	3190					
$\nu_1+\nu_3$	3611					2897

(?) signifies uncertain assignments

Table 4.   The infrared absorption frequencies of calcium formate

ν (cm^{-1})	a-axis polarized	b-axis polarized	c-axis polarized	calc.(cm^{-1})	other possibilities
$\nu_1 + \nu_6$		3933v.w.	3941w	3958	
$\nu_1 + \nu_3$	3668v.w.	3666w	3669w	3677	
$2\nu_4$	3187v.w.sh.			3196	$2\nu_3 + \nu_4 = 3184$
	3157w	3157w	3158w		
$\nu_1' + 192$		3092v.w.		3087	
$\nu_1''' + 128$	3009w.sh.	3008w.sh.	3010w.sh.	3001	$\nu_1'' + 128 = 3018$
$\nu_4 + \nu_5$	2990w.sh.	2989w.sh.	2986w.sh.	2995	$\nu_1' + 90 = 2985$
$\nu_1''' + 90$	2970w.sh.	2972w.sh.	2973w.sh.	2963	
$\nu_2' + \nu_4$	2951m	2951m	2950m	2945	$\nu_1'' + 61 = 2951$
$\nu_2'' + \nu_4$		2941m	2941m	2935	
$\nu_1' + 36$	2934w.sh.			2931	$\nu_1''' + 61 = 2934$
$\nu_1'' + 36$			2925v.w.	2926	
$\nu_1''' + 36$		2913		2090	
ν_1'	2894s	2895s	2896s		
ν_1''			2890s		
ν_1'''	2874v.w.sh.	2872s	2873s		
$\nu_1''' (C^{13})$		2840v.w.	2838v.w.	2844	$\nu_1''' - 36 = 2837$
$2\nu_5'$	2791w	2793w	2793v.w.	2804	$\nu_1' - 90 = 2805$
$2\nu_5''$	2780w	2780m	2780m	2784	$\nu_1''' - 90 = 2783$
$\nu_1' - 128$		2770w	2766v.w.	2767	$\nu_1''' - 128 = 2762$
$\nu_2 + \nu_5$	2751m	2751v.w.		2752v.w.	$\nu_1''' - 128 = 2745$

Table 4 - continued

ν (cm^{-1})	a-axis polarized	b-axis polarized	c-axis polarized	calc.(cm^{-1})	other possibilities
$\nu_1' - 154$	2739w	2738v.w.	2738v.w.	2741	
$2\nu_2'$		2722v.w.	2724v.w.	2730	
$2\nu_2''$			2713v.w.	2710	
	2701m	2701m	2701w		
$\nu_5 + \nu_6$	2464v.w.	2464v.w.	2464v.w.	2471	
$\nu_2 + \nu_6$	2421v.w.	2419w	2421v.w.	2434	
$\nu_3 + \nu_5$	2185v.w.	2186v.w.	2188v.w.	2190	
$2\nu_6'$	2152v.w.	2152w	2151w	2158	
$2\nu_6'$	2133w	2137w	2135w	2136	
$\nu_4'' + 90$		1667s.sh.	1670w.sh.	1670	$\nu_4' + 61 = 1679$
$\nu_4' + 36$		1650s		1654	
$\nu_4'' + 61$			1642s	1641	
ν_4'	1600s.v.b.	1616s	1618s		
ν_4''		1579s	1580s		
$\nu_4' - 61$			1560v.w.sh.	1557	$\nu_2' + 192 = 1557$
$(c^{13})\nu_4''$			1543w.sh.		$\nu_4''{}^2 - 36 = 1544$
$\nu_4'' - 61$	1506v.w.		1523w.sh.	1519	$\nu_4' - 90 = 1528$
$\nu_2'' + 154$			1507w.sh	1509	
ν_5		1406s			
ν_5	1403s.sh.	1401s			
ν_5	1399s		1400s		
ν_5	1395s.sh.	1395s			

Table 4 - continued

ν (cm^{-1})	a-axis polarized	b-axis polarized	c-axis polarized	calc.(cm^{-1})	other possibilities
ν_5			1392s		
ν_5	1388s	1388s			
ν_5 (c^{13})		1377v.w.			
ν_2	1368s		1369s		
ν_2		1364s	1364s		
ν_2	1362s				
ν_2	1358s				
ν_2			1355s		
ν_2	1352s	1352s			
ν_2 (c^{13})		1336w.sh.	1336w.sh.		
ν_2-36		1330v.w.sh.	1329v.w.sh.	1329	ν_5-61=1333
ν_6'+192		1273w		1271	ν_2-90=1275
ν_6''+192	1260w		1263w	1260	ν_2-90=1265
ν_6''+128		1196v.w.		1196	ν_2-154=1201
	1161v.w.	1156v.w.			
ν_6'	1080m.sp.	1079 m.sp.	1079w.sp.		
ν_6''	1068w.sp.	1067w.sp.	1068m.sp.		
ν_6''-36	1035v.w.			1032	
ν_6'-90		988v.w.	989v.w.	989	ν_3''+192=980
ν_3'+154	972v.w.		967v.w.	957	ν_3''+192=974
ν_6''-128	938v.w.			940	ν_3''+154=942
ν_3'+128		927v.w.	933v.w.	931	ν_6'-154=925

Table 4 - continued

ν(cm^{-1})	a-axis polarized	b-axis polarized	c-axis polarized	calc.(cm^{-1})	other possibilities
ν_6'-192	888v.w.	891v.w.		887	ν_3'+90=893
ν_3'''+90		878v.w.	877v.w.	872	ν_6''+192=876
ν_3'+61	865v.w.	865v.w.		864	
ν_3'+36			844v.w.	839	ν_3''+61=849
ν_3'''+36	817w			818	ν_3''+36=824
	806m	806v.w.sh.	806s.sh.		
ν_3'	803m	802s	803s		
		799s.sh.			
$\nu_3'(c^{13})$		792w.sh.	792v.w.sh.		
ν_3''	788s	788w.sh.	788s.sh		
	786s				
ν_3'''		782s	782s		
$\nu_3'''(c^{13})$	777w.sh.	777w.sh.	778s.sh.		
ν_3'-36	768w	768w	768w	767	
ν_3''-36	761v.w.			752	
ν_3'-61	742v.w.			742	ν_3'''-36=746
ν_3''-61	732v.w.		732v.w.	727	
ν_3'-128	679v.w.		681v.w.	675	
ν_3'-154	650v.w.	646v.w.		649	ν_3'''-128=654

Symbols   s=strong, m=medium, w=weak, v=very, b=broad,

sp.=sharp, sh.=shoulder, c^{13}=carbon 13 formate

ion.

The calculated frequencies are calculated using observed fundamental values.

Table 5. The infrared absorption frequencies of sodium formate

assign.	polarized ll to c	polarized⊥ to c	calc.
$\nu_1 + \nu_6$	3882v.w.		3904
		3690v.w.	
	3190v.w.	3190v.w.	
$\nu_1 + 231$	3061w		3069
	3016w.sh.	3018v.w.sh.	
	2987w.sh.	2990w.sh.	
$\nu_2 + \nu_4$	2958m	2949s	2959
$\nu_1 + 91$		2926m.sh.	2929
$\nu_1 + 58$	2895w.sh.		2986
ν_1	2838w	2836w.sp.	
		2799v.w.	
$\nu_1 - 58$	2776w	2779v.w.	2780
$\nu_1 - 91$		2743w.sh.	2745
$\nu_2 + \nu_5$	2723v.w.sh.	2725m	2735
$\nu_1 - 128$	2704w		2710
		2630w	
$\nu_1 - 231$	2597v.w.		2607
$\nu_2 + \nu_6$	2429w		2427
		2344w	
$\nu_3 + \nu_5$		2146w	2156
	1780w.sh.		
	1746w.sh.	1750w.sh.	

Table 5.- continued

assign.	polarized ‖ to c	polarized ⊥ to c	calc.
ν_4+128	1734m		1738
ν_4+112	1722w.sh.		1722
ν_4+91		1692w.sh.	1701
ν_4	1597w.sh.	1610s.v.b.	
ν_4-58	1542w.sh.		1552
ν_4-112	1493m		1498
ν_5+91	1468w.sh.	1460w.sh.	1466
ν_2+91	1450w.sh.		1450
		1409v.w.	
ν_4-231	1390w		1379
ν_5	1377w.sp.	1375s	
ν_2		1359w.sh.	
ν_2-58	1310w	1303w	1301
ν_5-91	1279w.sh.	1277w	1284
ν_2-128	1228m	1235w	1231
	1169w		
ν_6+58	1130w		1126
ν_6	1068m.sp.	1068w	
ν_6-58	1007w	1013v.w.	1010
ν_6-112	960w	964w	956
ν_3+128	904	913m	908
ν_3+58	839w		838

Table 5 - continued

assign.   polarized 11 to c   polarized ⊥ to c   calc.

ν_3 780w.sp   780w.sp.

         586w

         531w

      Symbols   s = strong, m = medium, w = weak,   v = very,

                 b = broad, sp. = sharp, sh. = shoulder

      The calculated frequencies are calculated using
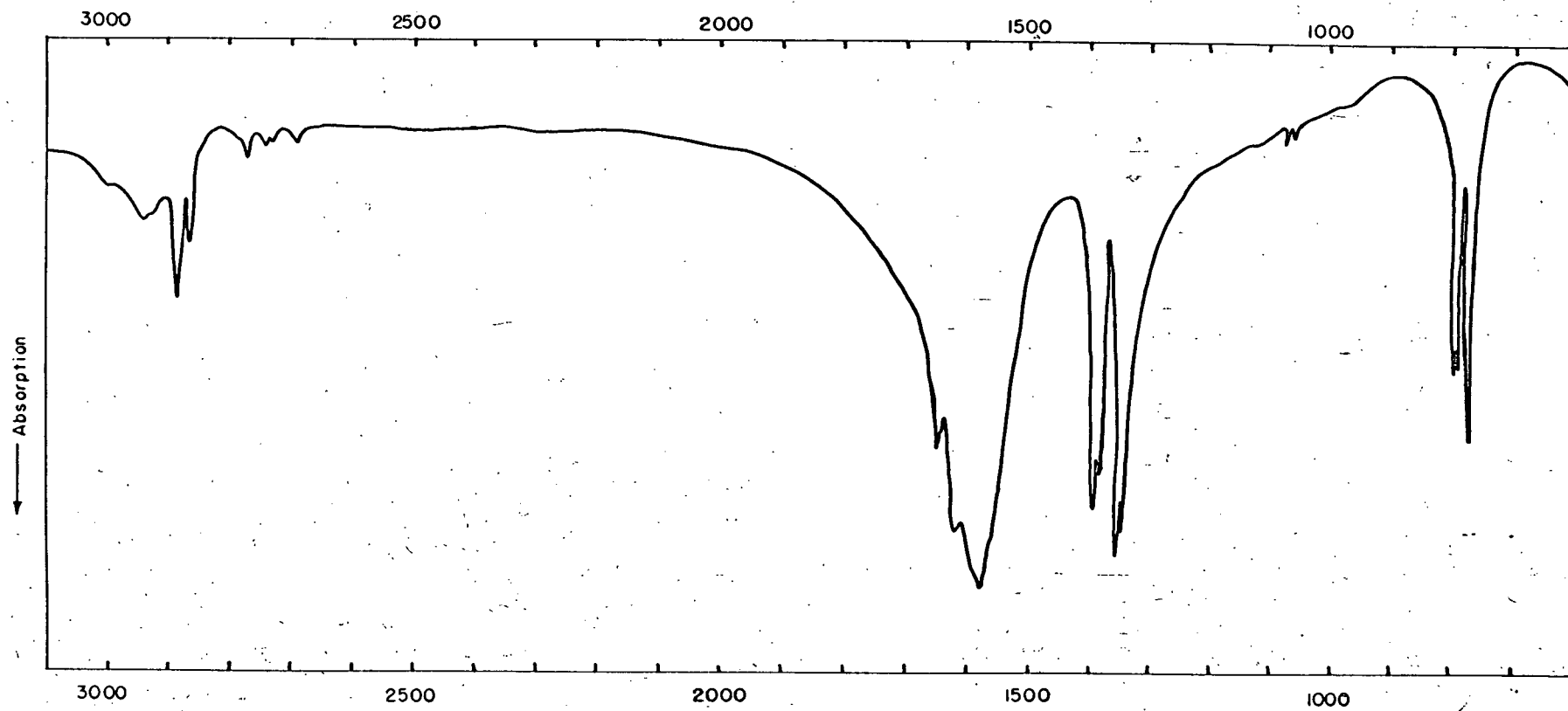   observed fundamental values.

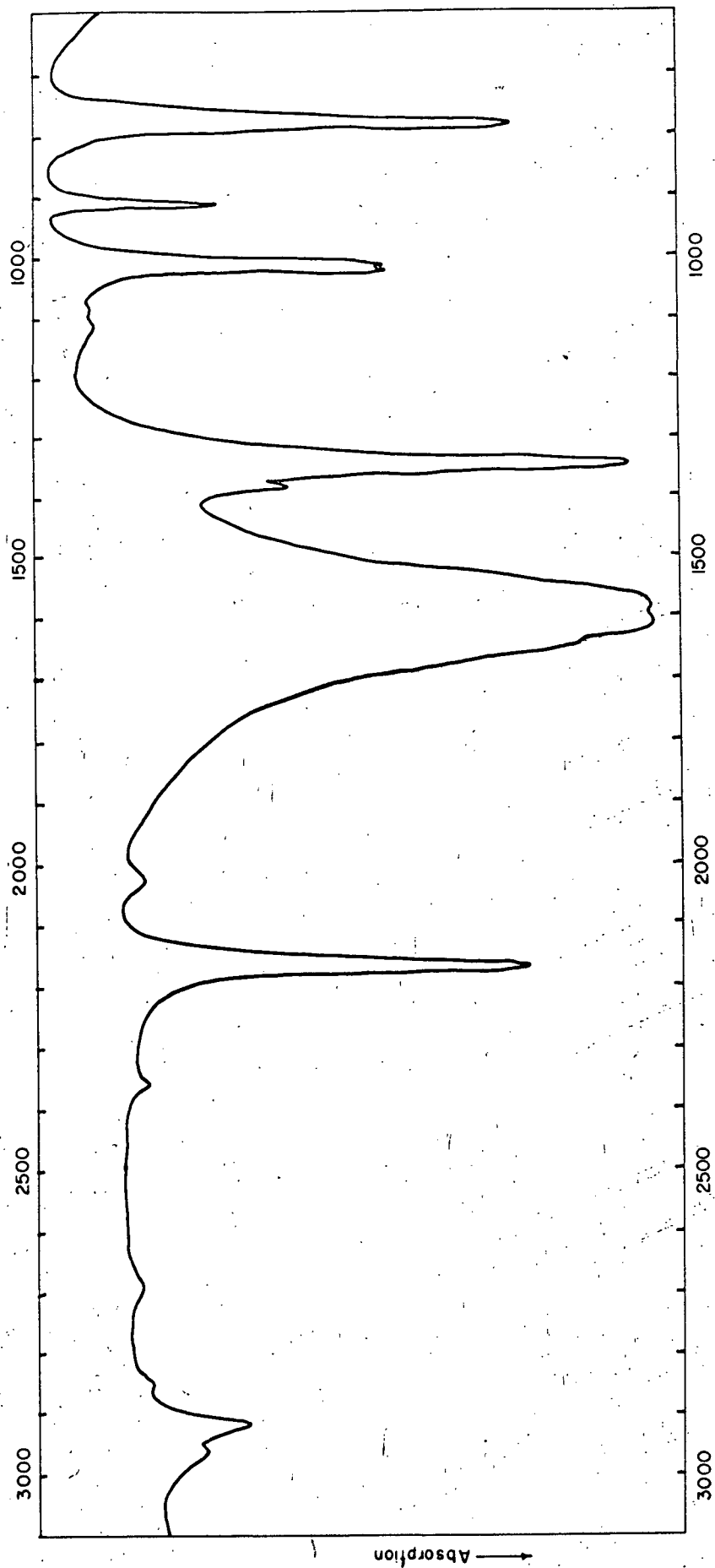Figure 3. Infrared spectrum of polycrystalline calcium formate.

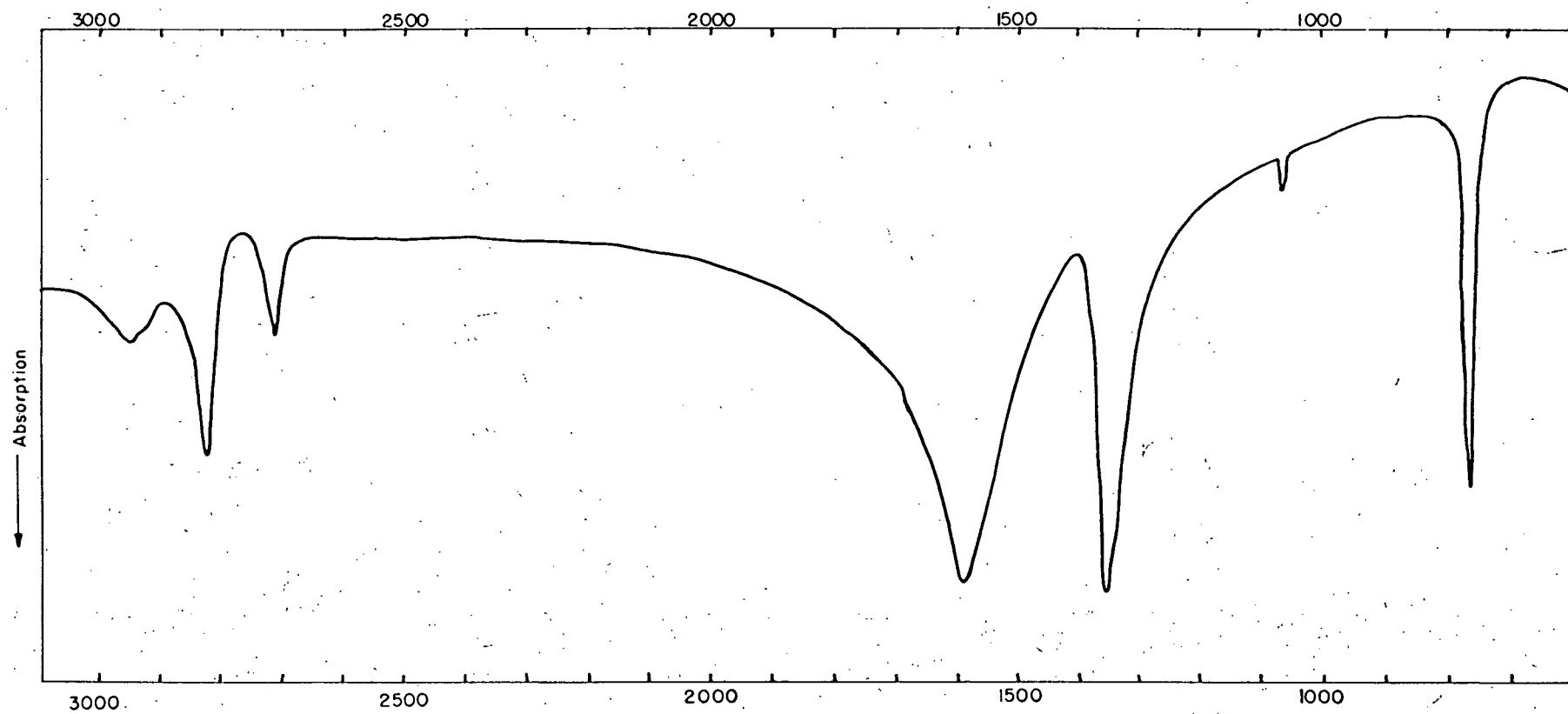Figure 4. Infrared spectrum of polycrystalline calcium formate-d_1.

Figure 5. Infrared spectrum of polycrystalline sodium formate.
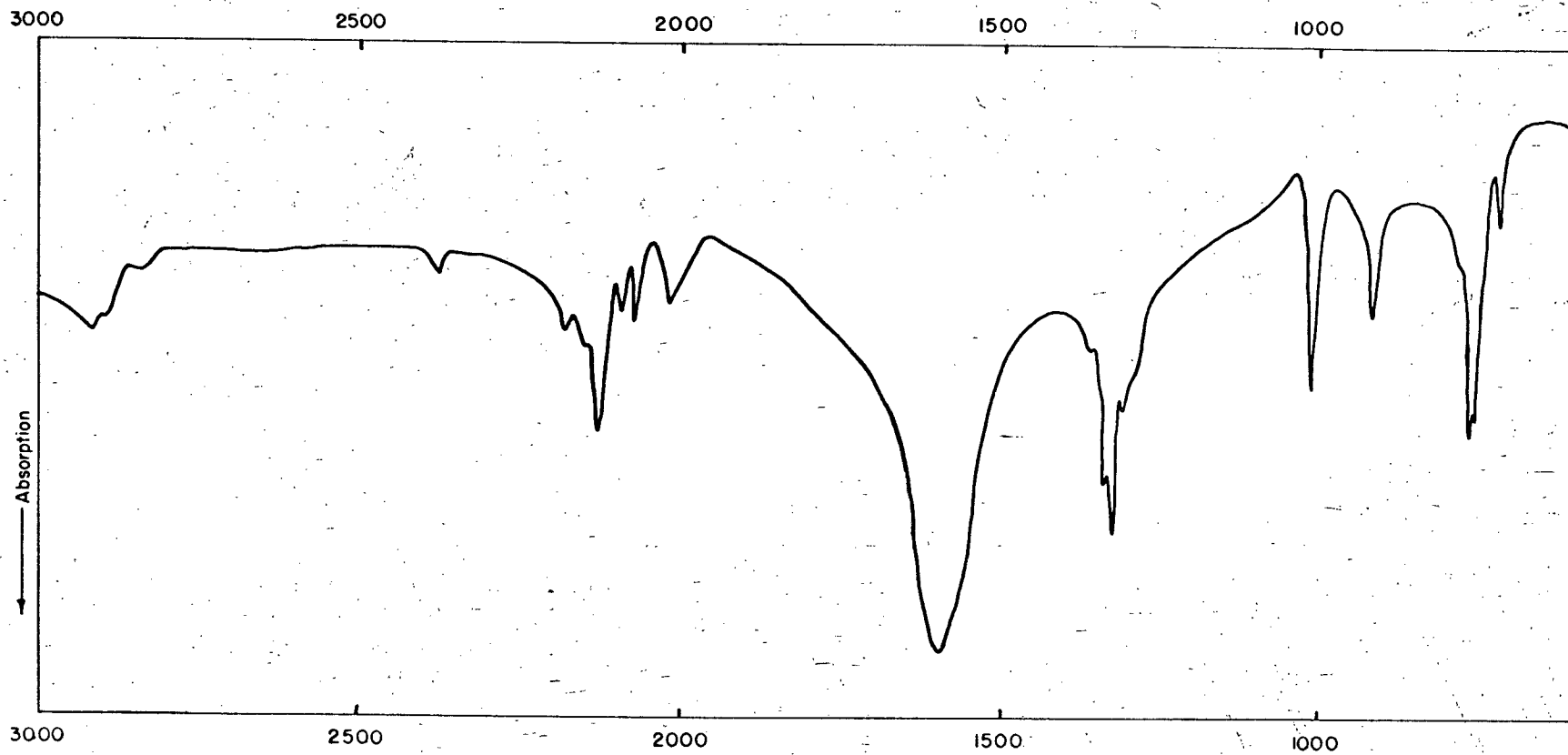
Figure 6. Infrared spectrum of polycrystalline sodium formate-d₁.

Figure 7. Polarized infrared spectrum of calcium formate (3020 - 2680 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.
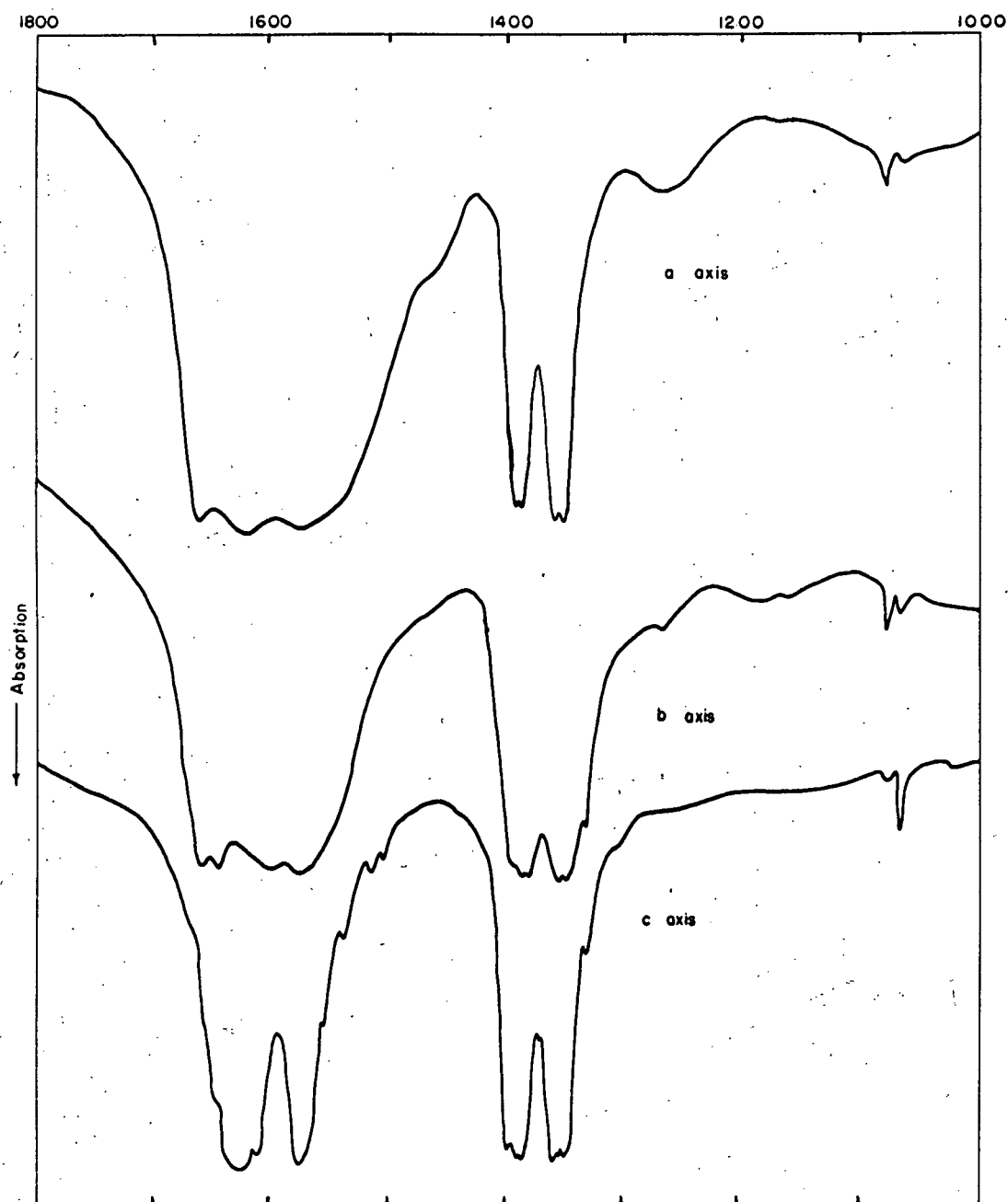
Figure 8. Polarized infrared spectrum of calcium formate (1800-1000 cm⁻¹). The plane of polarization of the infrared light is indicated as being parallel to the a,b, or c axis of the crystal.
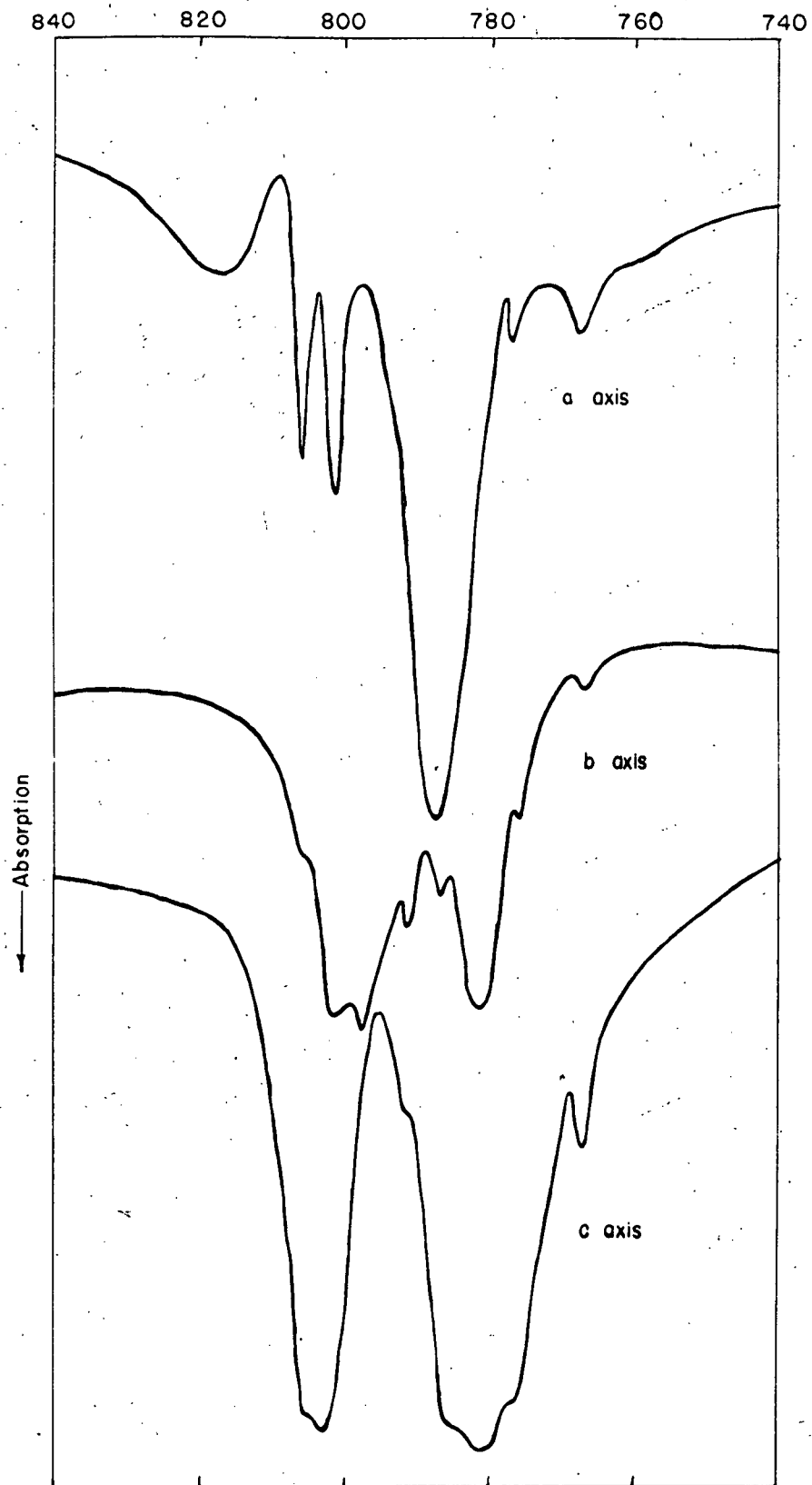
Figure 9. Polarized infrared spectrum of calcium formate (840-740 cm^{-1}). The plane of polarization of the infrared light is indicated as being parallel to the a, b, or c axis of the crystal.

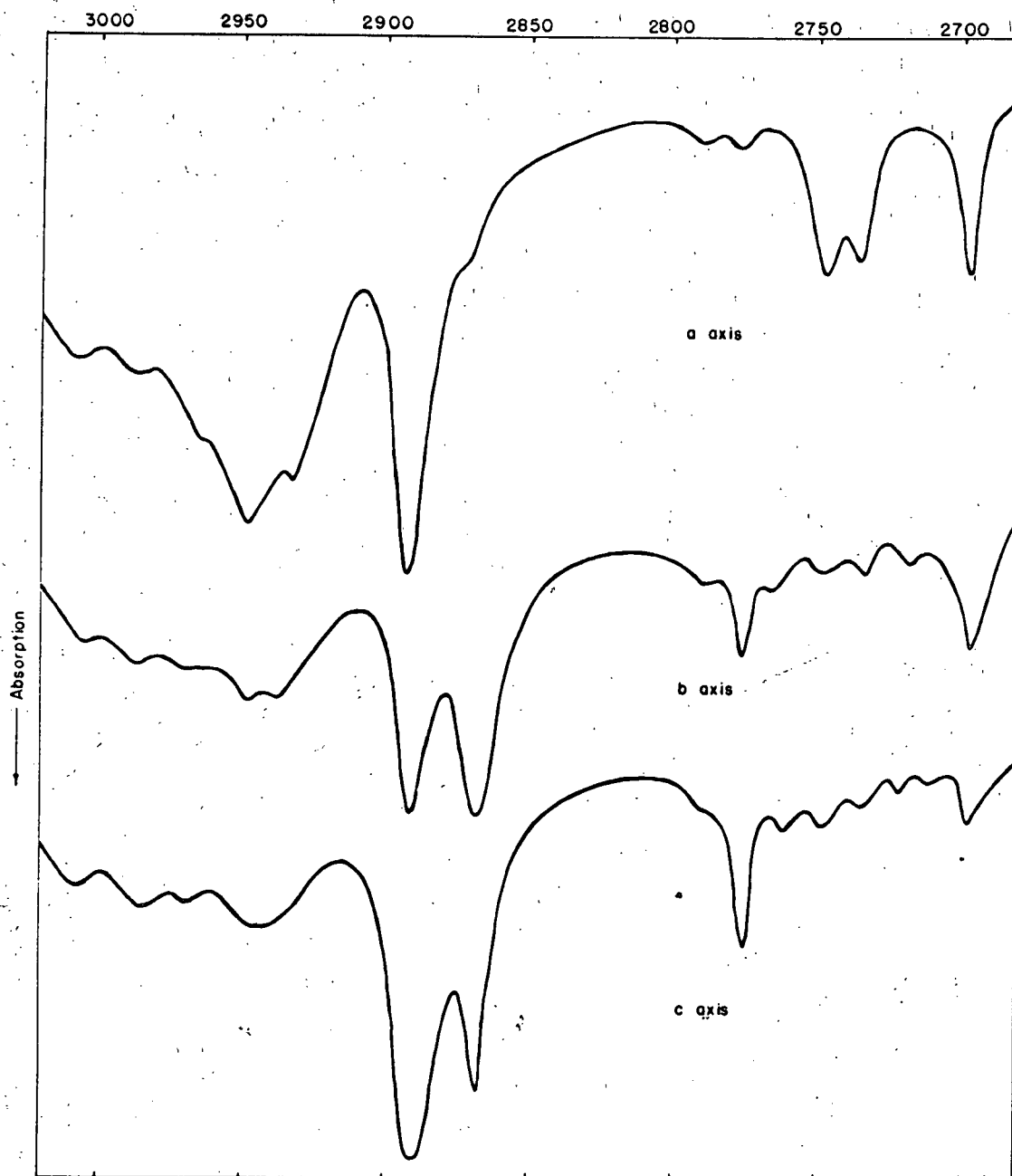Figure 10. Polarized infrared spectrum of sodium formate (3100-2650 cm⁻¹). The plane of polarization is indicated as being perpendicular or parallel to the c-axis.
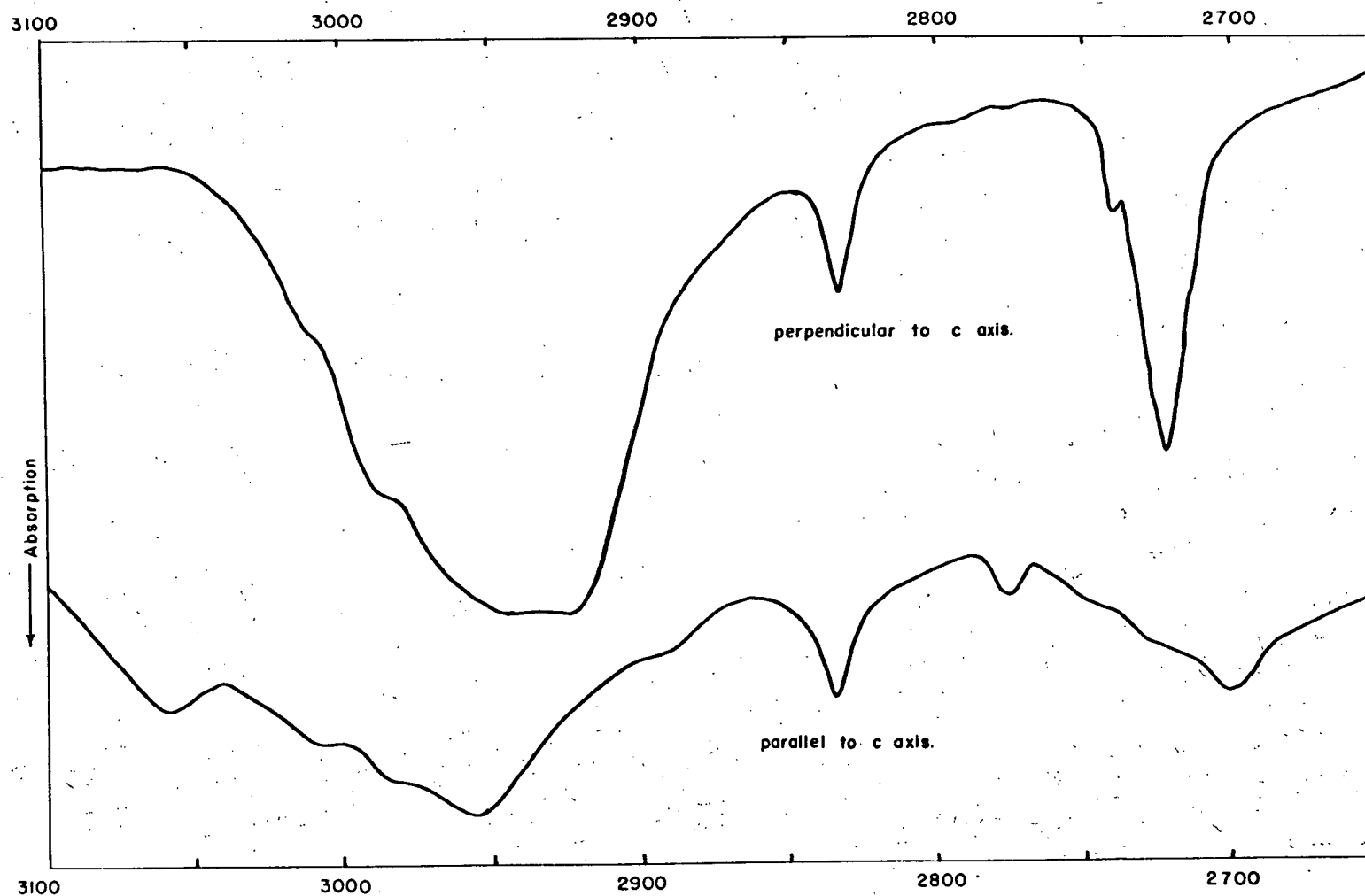
Figure II. Polarized infrared spectrum of sodium formate (1800-1000 cm^{-1}). The plane of polarization is indicated as being perpendicular or parallel to the c axis.
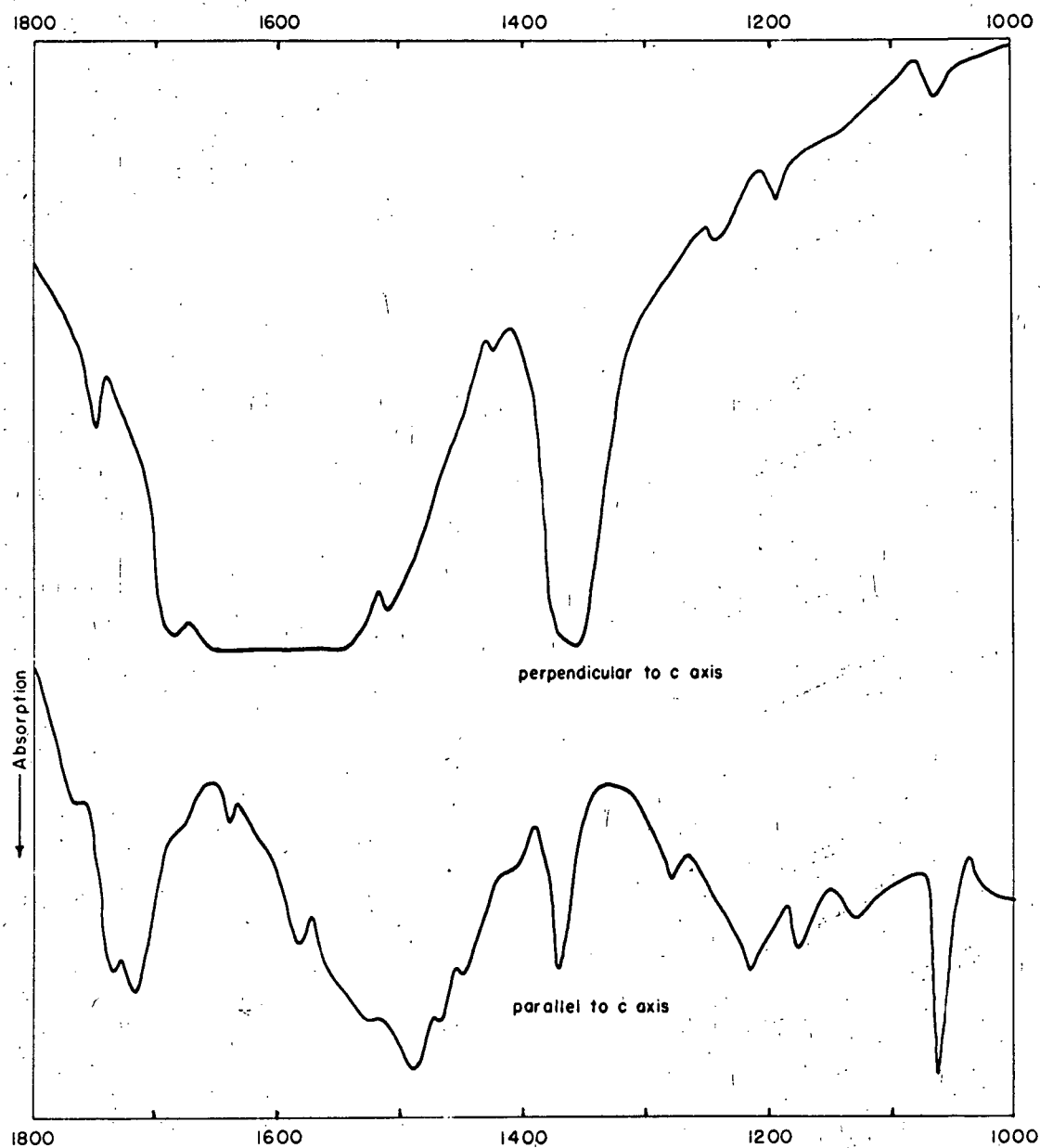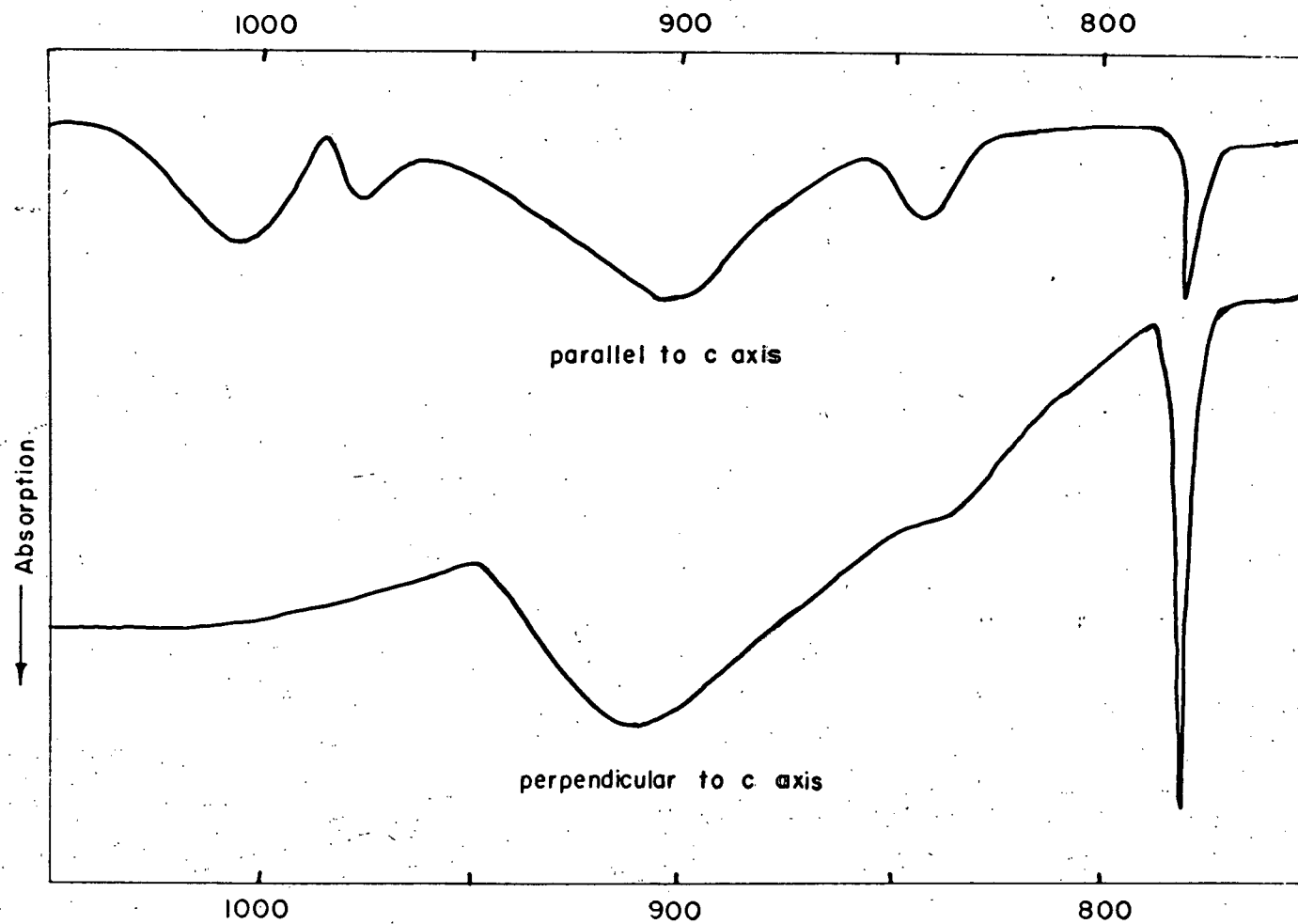
Figure 12. Polarized infrared spectrum of sodium formate. (1050-750 cm⁻¹). The plane of polarization is indicated as being perpendicular or parallel to the c axis.

CHAPTER 3. THEORY

3-1. General theory of vibrations in crystals

In order to study the motions of a polyatomic
system, a set of coordinates is needed to describe the
configuration of the system. For a system of N atoms,
3N coordinates describe the motion of the system as a
whole. Of these 3N coordinates, three describe the
translational motion and three more describe the ro-
tational motion of the system leaving 3N - 6 coordinates
to describe the vibrational degrees of freedom of the
system. Wilson, Decius and Cross(34) discuss a general
method whereby the equations of motion may be written
in terms of the chosen coordinate system. The set of
equations thus derived yields a series of solutions
corresponding to the normal modes of vibration of the
system.

The $3N \times 3N$ secular determinant which must be
solved in order to determine the normal frequencies can,
in most cases, be simplified. This simplification arises
from the fact that the system under investigation generally
possesses some form of symmetry. If, in a molecule, a
symmetry operation is carried out that transforms the
molecule into an equivalent position, the kinetic and
potential energies will be unchanged. The set of symmetry

operations that a molecule possesses which carry it into
equivalent positions is known as a group in the mathe-
matical sense. Each symmetry operation may be represented
analytically by a linear transformation connecting the
old coordinates with the coordinates of the molecule in
its new position. The set of linear transformations is
said to be a representation of the group of symmetry
operations. The coordinates, in terms of which the
transformations are written, are said to form a basis
of the representation.

It is usually possible, by choosing a suitable set
of coordinates, to reduce the square $3N$ x $3N$ transformation
matrices to comparatively simple forms. It is possible
to separate these coordinates into sets which do not mix
with each other in any of the transformations. When the
coordinate system has been found such that it is impossible
to break the coordinates down into any smaller non-mixing
sets, the representation for which these coordinates form
a basis is said to be completely reduced. When it is
possible to do this, the original representation is said
to be reducible. The equations involving the members
of any one non-mixing set can be considered by themselves
as making up transformations which form a representation
of the group. Such a representation is irreducible and
it is seen that a completely reduced representation is
made up of a number of irreducible representations.

It is usually possible to choose several sets of
coordinates to form a basis for the representations,
but in each case the results would be the same. Any
two representations are said to be equivalent when they
differ only in the choice of basis coordinates (the basis
coordinates of one being linear combinations of the basis
coordinates of the other).

The fundamental theorem concerning irreducible
representations states that for each point group there
are only a definite small number of non-equivalent irre-
ducible representations possible. It is possible to
show that the number of times an irreducible representa-
tion appears in a reduced representation is

$$\eta_i = \frac{1}{h} \sum_{R} \chi_R^i \chi_R \qquad (1)$$

where h is the order of the group (equal to the number of
symmetry operations contained in the group), χ_R is the
character of the reducible representation and χ_R^i is the
character of the i th irreducible representation of the
operation R . The sum is taken over all the operations
of the group. The character is defined as the sum of the
diagonal elements of the transformation matrix, the charac-
ters of equivalent representations being identical.

The quantities on the right hand side are easily deter-
mined using a set of simple rules.

Associated with each non-mixing set of normal co-
ordinates is a set of normal modes of vibration, the
number of normal modes being equal to the number of normal
coordinates in the set. Since each normal coordinate
transforms according to one of the irreducible representa-
tions of the group, then by using equation 1, the number
of normal modes of vibration belonging to each irreducible
representation may be determined.

3-2. <u>Selection rules</u>

Group theory may be used to derive the selection
rules for vibrational transitions in the infrared effect.
For a fundamental transition to occur by absorption of
infrared radiation, it is necessary that one or more of
the integrals

$$\int \psi_i^* \mu_x \psi_j \, d\tau \qquad \int \psi_i^* \mu_y \psi_j \, d\tau \qquad \int \psi_i^* \mu_z \psi_j \, d\tau$$

have a non-zero value. Here, ψ_i is the vibrational ground
state, ψ_j is the excited state, and μ_x, μ_y and μ_z are the
components of the electric dipole moment operator. It
may be determined whether the above integrals vanish if
the symmetry properties of $\psi_i, \psi_j, \mu_x, \mu_y$ and μ_z are
known. Since these are definite integrals over the whole
configuration space of the molecule, they should be

unchanged by a symmetry operation $\mathcal{R}$, inasmuch as such an operation merely produces a transformation of coordinates. That is, the integrals must be totally symmetric or the triple direct product of the species of ψ_i^*, μ and ψ_j must contain the totally symmetric species.

Now all wave functions for normal vibrations in their ground states (ψ_i) are bases for the totally symmetric representation of the symmetry species of the molecule (35). Thus for fundamental transitions (from the ground state to the first excited state), the integral will be symmetric if the dipole moment operator and the first excited state belong to the same species since the direct product of a representation with itself is symmetric. It can be shown (34) that the components of the dipole moment operator transform in the same manner as the translational coordinates T_x, T_y and T_z. Thus a normal mode of vibration will be infrared active if ψ_j belongs to the same symmetry species as one of the translational coordinates. Similar symmetry arguments may be applied to determine the activity of overtone and combination type bands.

3-3. Crystal symmetry

All previous theory has pertained to molecules completely isolated from all other molecules. The vibrational states of the isolated molecules have been shown to be dependent on the molecular symmetry. However, in crystals (and in liquids), molecules are in close proximity to other molecules and it is necessary to determine the extent of inter-molecular interactions and the effect they might have on vibrational modes and transitions. To do this, a knowledge of crystal symmetry is required.

For an infinite crystal, there is an infinite number of ways of combining into groups the symmetry operations that carry an atom into an equivalent atom in the crystal. These symmetry operations include rotation, inversion-rotation and screw axes; mirror and glide planes; inversion centers; and simple translations. If we define a unit cell as the smallest repeating unit in the crystal, then the crystal may be built up by translations of this unit cell an infinite number of times. By disregarding simple translations, it has been shown that the remaining symmetry operations of the crystalline state may be combined into 230 different combinations known as space groups.

It is shown in the standard works on space group theory that any space group is the product of an invariant subgroup, consisting of the elements corresponding to pure translations, and a factor group. This factor group is the same for corresponding infinite and finite space groups. The factor groups are always isomorphous with one of the 32 crystallographic point groups, although some of them may involve subgroups containing other than purely point operations combined with lattice translations, that is, screw rotations or glide reflections. Because of this isomorphism, we can use the character table of the crystallographic point group corresponding to the factor group representations. It should be noted that the factor group is necessarily a subgroup of the infinite space group.

Now a site is defined by Halford(7) as a point which is left invariant by some operations of the space group. These operations may be shown to form a group which may be designated as a site group. Thus all points in a crystal are sites with at least the trivial site group involving only the identity operation. Generally, the site group has an order less than the factor group and is isomorphous with a subgroup of the factor group.

In general, a unit cell exhibits several different kinds of sites and sometimes several distinct sets of the same kind of site.

3-4. Analysis of vibrations in crystals

When studying the vibrations in a crystal, because of the large number of atoms in the crystal, it would seem that a most complicated spectrum would result. However, as experimental results have indicated, a spectrum with a finite number of observable bands is obtained. It is thus necessary to consider whether all 3N vibrations in the system are independent.

Since only a small number of absorption bands are observed in the vibrational spectra of crystals in the infrared and Raman effects and since there is a very close correspondence between the spectra of crystals and the spectra of their molten states, it would appear that only a small unit of the crystal is needed in order to determine the nature of the normal modes of the crystal. Bhagavantum and Venkatarayudu(5,6) have considered the unit cell of the crystal.

Within the crystal, there are sets of atoms arrayed in such a manner that each atom in a set is both geo-metrically and physically equivalent to every other atom

in the set. Thus for any given normal mode of vibration,
each atom in a set should undergo the same displacements.
Atoms in any other unit cell in the crystal are related
to the first by simple translation. If each set of
atoms is considered to form a lattice, that is, an
arrangement in which only one atom is located at each
lattice point, then the crystal may be thought of as
a structure in which a group of two or more atoms is
located at each lattice point. That is, the crystal
can be looked upon as being made up of a set of inter-
penetrating lattices. Thus the unit cell of the smallest
possible size will contain as many atoms in it as there
are interpenetrating lattices in the structure. For n
atoms in the unit cell there will be 3n normal oscilla-
tions of which three will be non-geniune oscillations
corresponding to translation of the unit cell.

These 3n possible vibrational modes may be
classified as either pure translations, lattice oscilla-
tions or internal oscillations. The lattice oscillations
are further classified as arising from translatory or
rotatory motions of the molecules in the unit cell.
The forces between one classification and the others
are comparatively feeble whereas the forces that exist
between members of any one classification are quite strong.
The oscillations involving a movement of the molecules as

entities will generall exhibit low frequencies and may be
termed external or lattice vibrations. The oscillations
involving movements of the individual members in each
molecule against themselves will generally exhibit high
frequencies and may be termed internal vibrations. The
factor group analysis as applied to sodium formate and
calcium formate will be explained later.

As Halford(7) has pointed out, while a full con-
sideration of all the consequences of the interactions
between the motions of molecules in a crystal lattice
leads to a very complicated picture, practically all
commonly observed effects of the molecular interactions
can be satisfactorily treated by a less rigorous but
far more manageable idealization.

If the vibrational motions of a molecule are
treated as moving in an environment of fixed symmetry,
the vibrational modes will depend on both the symmetry
of the molecule and its environment. In this case,
point symmetry rather than space symmetry may be used
in the analysis.

In the site group analysis, the symmetries of the
vibrational modes of all equivalent molecules on a given

set of sites is the same and selection rules may be derived using the symmetry of the site group as a basis. In a crystal, the site symmetry can never be such as to contain symmetry elements not belonging to the free molecule and in general, the site symmetry is lower than the molecular symmetry.

Now the center of mass of a molecule is invariant under the operations of the associated molecular group and its equilibrium position in the crystal is called the affix of this group. The molecular group being the group of operations describing the symmetry of the molecule. Generally, the affixes of symmetrical molecules are situated on sites, which requires that the site group be a subgroup of the molecular group. A correlation of the species of the site and molecular groups yields an indication of the activity of the various vibrations in the crystal.

In the case of ionic crystals, it is possible that the anions and cations in the crystal are situated on sites of different symmetry and still belong to the same space group. The site group method neglects the coupling of vibrations between ions of a set and thus gives a rather incomplete picture of the interactions

within the unit cell. Realizing this led Couture(37) to point out that the site group method cannot be applied to ionic crystals even as a first approximation. It should be realized that the site group method is nothing more than a convenient, and often sufficient, first approximation to crystalline spectra. Thus, although the site method may yield an adequate interpretation of the grosser details of the spectrum, complete information may only be obtained by resorting to the unit cell analysis. The activity of molecular modes in the crystal may be determined by the correlation of the species of the molecular group and the site group. The subsequent correlation of the site group into the factor group will give the polarization properties of the molecular modes.

Winston and Halford(36) have used a different approach to the classification of the motions of a crystal on the basis of space symmetry. However, they have shown that equivalent results may be obtained using both their method and the method of Bhagavantum and Venkatarayudu. The former method is derived from a treatment which considers the motions of a crystal segment composed of an arbitrary number of unit cells and subject to the Born-Karman boundary conditions. The latter method considers only one unit cell.

The relationship between the two forms of analysis (site and factor group) may be discussed in terms of the potential energy of the crystal. For crystals containing molecules or complex ions in which the internal motion is only slightly affected by the crystalline field, the complete potential function may be written in the form (38)

$$V = V_L + \sum_j \left(V_j^o + V_j^{'} \right) + \sum_j \sum_k V_{jk}^{''} + V_{Lj}^{''} \qquad (2)$$

where V_L, the lattice potential, contains terms involving the center of gravity and orientation terms of the molecules. V_j^o is the potential energy function of the jth free molecule while $V_j^{'}$ includes those terms containing both internal and lattice coordinates of the jth molecule. The $V_{jk}^{''}$ represents cross terms between internal coordinates of different molecules and $V_{Lj}^{''}$ contains cross terms between internal and lattice coordinates. The terms $V_j^{'}$, $V_{jk}^{''}$, and $V_{Lj}^{''}$ are perturbations of the lattice and free molecule potentials(39). The vibrational problem can be separated into that of the free molecules and of the lattice vibrations if the perturbations are ignored.

By considering the term $\sum_j V_j^o$ only, the secular determinant could be factored into blocks, each associated with only one molecule. This is called the

"oriented gas" model(40). Inclusion of the term V_j'
still permits separation of the secular determinant, but
the frequencies are all shifted. Since the term V_j'
has the site symmetry of the jth molecule, which is
usually lower than that of the free molecule, it may
split degeneracies and change selection rules. In
this approximation, the vibrations may all be classi-
fied under the site groups. Static field effects in-
clude all those effects arising from the fact that
$V_j^o + V_j' = V_j$ for the molecule in the crystal differs
from the potential energy for the corresponding free
molecule. These effects are a measure of the influence
the surrounding lattice has on a given molecule. The
splitting caused by the term V_j' is thus termed the static
field splitting. However, even if the remaining terms
are negligible and the site symmetry is adequate for
calculating frequencies, the polarization properties of
the normal vibrations may not be determined since the
sites may be variously oriented in space, even though
they are symmetrically equivalent.

Dynamic crystal effects arise from the term $\sum_j \sum_k V_{jk}$
and give a measure of the effect internal vibrations
of other molecules have on the given molecule. If the
interaction is small, first order perturbation theory

may be used to calculate the effect, since only couplings between equivalent modes of vibration of the various molecules need be considered, except in the case of accidental coincidence of frequencies. Depending on the number of molecules in the unit cell, each "gas phase" internal mode will be split in the crystal. Splittings associated with the step from site group to unit cell are correlation field or factor group splittings.

After consideration of the above, it is seen that no vibration may be active in the crystal if it is forbidden by the site approximation. Also, every vibration which is active under the site group will give rise to at least one active component in the crystal. Similarily, any vibration which is degenerate under the site group remains so in the crystal. The polarization properties of the molecular modes may thus be determined by the correlation mapping of the site group into the unit cell group.

CHAPTER 4. DISCUSSION

4-1. Crystal structures

Nitta and Osaki have found that crystals of calcium formate are orthorhombic with unit cell dimensions $a = 10.163$, $b = 13.381$ and $c = 6.271$ Å at $18^{\circ}C$. The crystal belongs to space group Pcab (D_{2h}^{15}) with eight molecules per unit cell. Zachariasen found that crystals of sodium formate are monoclinic with unit cell dimensions $a = 6.19$, $b = 6.72$ and $c = 6.49$ Å with $\beta = 121^{\circ}42'$. The crystal belongs to the space group C2/c (C_{2h}^{6}) with four molecules per unit cell. The formate ion has point symmetry C_{2v} with a CO bond length of 1.25 ± 0.03 Å for calcium formate and 1.27 Å for sodium formate. The OCO bond angle is $125^{\circ} \pm 4^{\circ}$ for calcium formate and 124° for sodium formate. In the sodium formate crystal, sodium, hydrogen and carbon atoms are on two-fold rotation axes of the space group. The oxygen atoms are on general positions. For calcium formate, all atoms are on general positions. (See figure 13).

In both cases, the "free" formate ion has six normal modes of vibration, all allowed in the infrared. These modes are distributed among the irreducible

Figure 13.
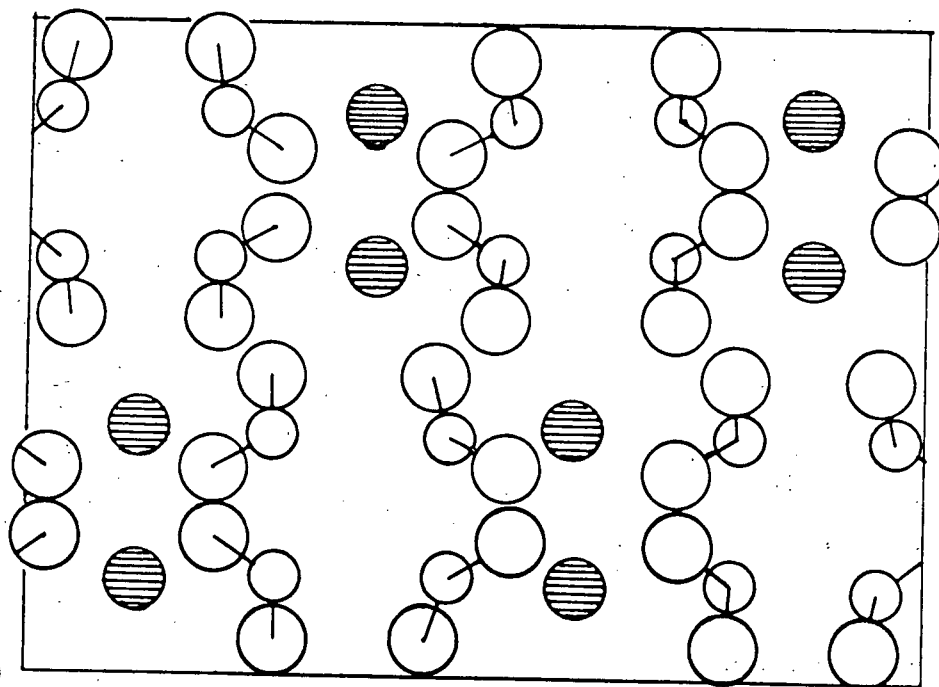
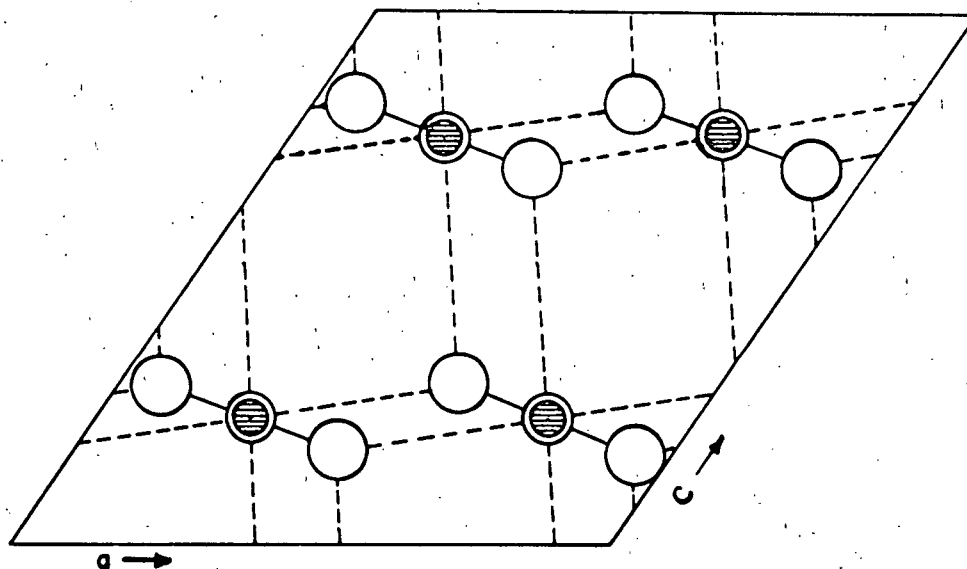Crystal structure of calcium formate projected on the (OOI) plane.
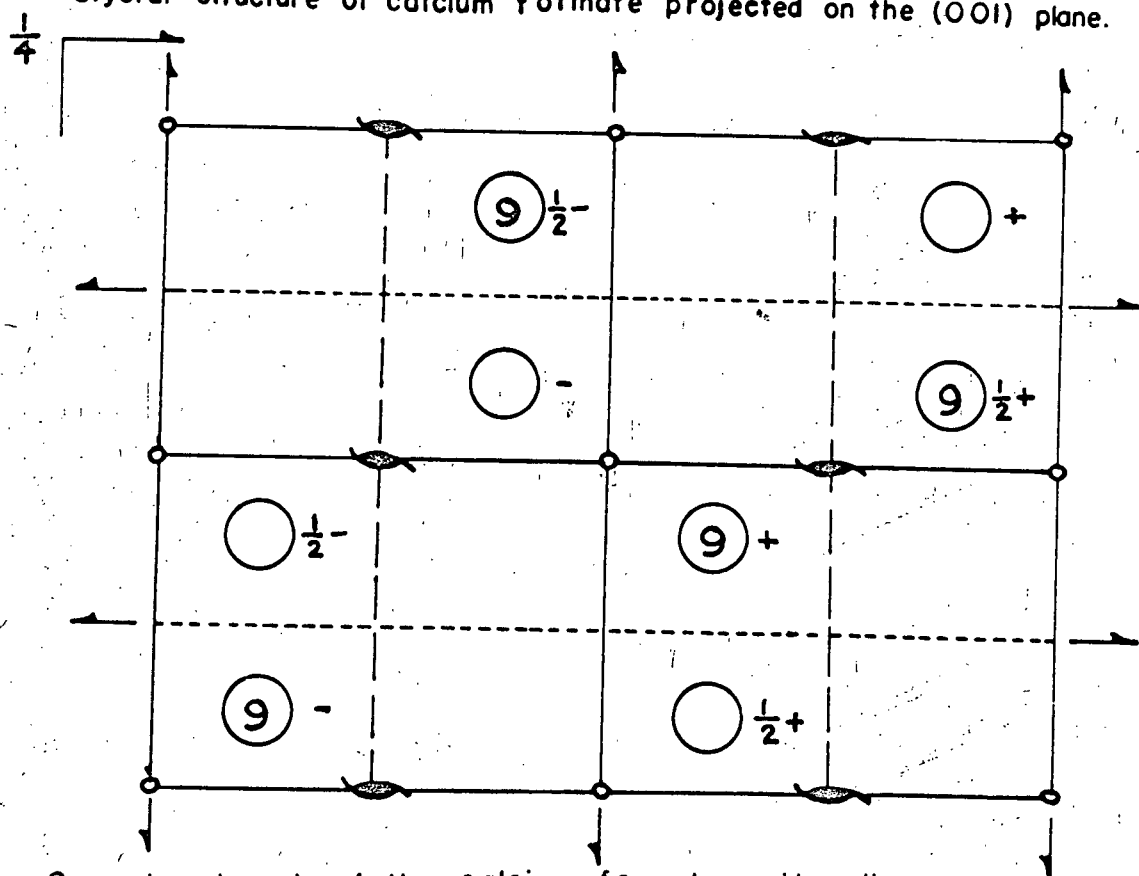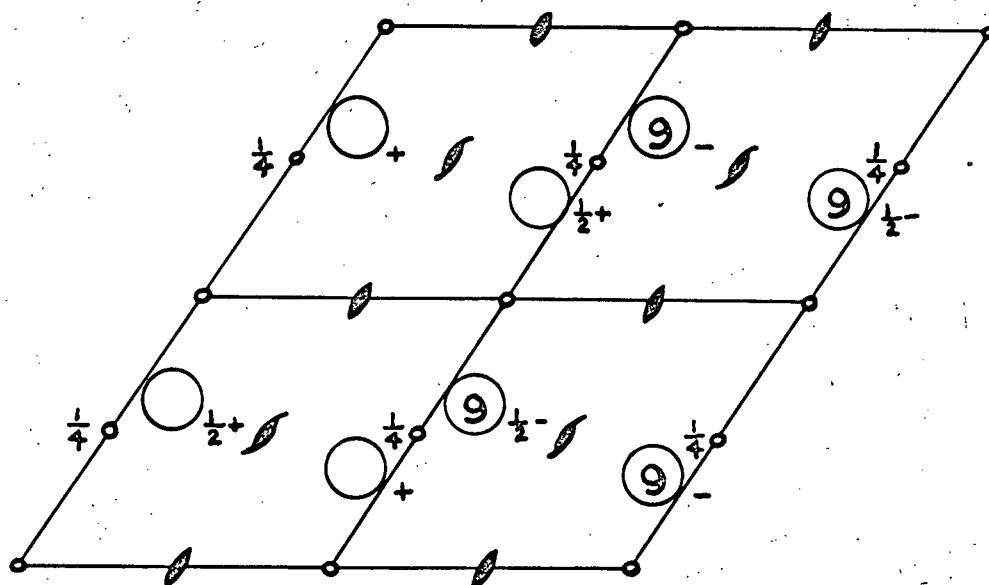

Symmetry elements of the calcium formate unit cell.

Figure 14.

Crystal structure of sodium formate projected on the (010) plane.

Symmetry elements of sodium formate unit cell.

representations of C_{2v} as follows; $3A_1 + 2B_1 + 1B_2$. Since the closest approximation to a "free" formate ion is an aqueous solution of the salt, the Raman and infrared spectra of aqueous solutions of the salts may be used as a basis for further assignments. The observed frequencies for calcium and sodium formate are in good agreement with previously reported Raman and infrared data. Because of the relatively weak forces between ions or molecules in a crystal, the molecular fundamentals should exhibit only slight shifts in frequency from those observed for the corresponding "free" molecular modes.

4-2. Calcium formate

There are no non-trivial subgroups of the factor group Pcab, thus each formate ion in calcium formate is in a general position of site symmetry C_1. This lack of site symmetry has no effect on the spectrum of the crystal since all molecular modes of the formate ion are allowed under the selection rules of the C_{2v} group. There are no degenerate modes in this group, thus no splitting is observed due to static field effects. Because of this lack of site symmetry, the factor group analysis must be employed for the interpretation of the results.

The number of vibrations which can occur in a unit cell can be represented by the expression

$$n_i = \frac{1}{N} \sum_R h_j \chi_j'(R) \chi(R) \tag{3}$$

where n_i is the number of vibrations, N is the order
of the group, h_j is the order of the jth class of opera-
tions R, $\chi_j(R)$ is the character of the operation R
in the irreducible representation and $\chi(R)$ is the
character of the operation R in the reducible repre-
sentation. All terms in (3) can be obtained from the
space group character table except $\chi(R)$. Analytical
expressions for the $\chi(R)$ values have been derived by
Bhagavantum and Venkatarayudu and are summarized below.

Table 6. Summary of expressions for characters of group
operations

Vibrational class	Expression for character of operation
Total number of vibrations $\sum(n_i)$	$\chi(R) = U_R (\pm 1 + 2 \cos \phi)$
Acoustic (T)	$\chi(R) = (\pm 1 + 2 \cos \phi)$
Translatory lattice (T')	$\chi(R) = [U_R(s) - r] (\pm 1 + 2 \cos\phi)$
Rotatory lattice (R')	$\chi(R) = U_R(s-v)(1 \pm 2 \cos \phi)$
Internal (n')	$\chi(R) = [U_R - U_R(s)] (\pm 1 + 2 \cos\phi)$ $- U_R (s-v)(1 \pm 2 \cos \phi)$

Here, U_R is the number of atoms invariant under the opera-
tion R, s is the sum of the number of groups occupying

lattice points and v is the number of single atoms occupying lattice sites.

The character table for the point group D_{2h} isomorphous with the factor group Pcab is given below. By application of equation (3), the number of normal modes for the unit cell associated with each irreducible representation has been determined. The symmetry operations associated with the factor group are the identity operation E, three mutually perpendicular two-fold rotation axes C_2, a center of inversion i and three mutually perpendicular mirror planes σ.

Table 7. Character table and factor group analysis for calcium formate

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(zx)$	$\sigma(yz)$	n	T	T'	R'	n_1'
A_g	1	1	1	1	1	1	1	1	27	0	9	6	12
B_{1g}	1	1	-1	-1	1	1	-1	-1	27	0	9	6	12
B_{2g}	1	-1	1	-1	1	-1	1	-1	27	0	9	6	12
B_{3g}	1	-1	-1	1	1	-1	-1	1	27	0	9	6	12
A_u	1	1	1	1	-1	-1	-1	-1	27	0	9	6	12
B_{1g}	1	1	-1	-1	-1	-1	1	1	27	1	8	6	12
B_{2g}	1	-1	1	-1	-1	1	-1	1	27	1	8	6	12
B_{3u}	1	-1	-1	1	-1	1	1	-1	27	1	8	6	12

The calcium formate crystal has 8 molecules or 72 atoms per unit cell giving rise to 3 x 72 = 216 degrees of freedom. Of these, three correspond to pure translation of the unit cell and the remaining 213 correspond to vibrations within the unit cell. Of the 96 internal molecular vibrations only 36 are allowed in the infrared spectrum of the crystal. The factor group splitting and the origin of this splitting under the space group D_{2h} will now be explained.

In the unit cell of calcium formate, a given formate ion may be transformed into its seven crystallographically equivalent counterparts by the symmetry operations of the D_{2h} factor group. For any internal molecular mode of vibration, eight different combinations are possible in which the ions vibrate in phase or $180°$ out of phase relative to a given ion in the set. Each one of these combinations corresponds to one of the irreducible representations of the factor group. Thus we have a possible eight-fold splitting of each molecular mode. The other crystallographically non-equivalent formate ion also can give rise to an eight-fold splitting of each molecular mode in a manner identical to that above. Even though the two sets are not symmetrically related, the different combinations of the two sets are of the same symmetry species. Thus we have a further two-fold splitting of the eight modes described above, and a total of 16 components for each normal mode of

the formate ion. These 16 components are divided evenly among the eight irreducible representations of the factor group. Only vibrations of the symmetry species B_{1u}, B_{2u} and B_{3u} are active however and thus the infrared spectrum of calcium formate should reveal each fundamental split into six components.

For polarized radiation along any one of the principal crystallographic axes only two of the six components of any one fundamental will be allowed. These two components will correspond to the two non-equivalent sets of formate ions in the unit cell as explained above.

The above paragraphs give the basis for the factor group splitting of the calcium formate fundamentals under the factor group Pcab.

4-3. Infrared spectra of calcium formate

As mentioned earlier, the Raman and infrared spectra of aqueous solutions of calcium formate may be used as a basis of further assignment since these are essentially the spectra of the free formate ion. However, the reported Raman and infrared spectra of calcium formate are incomplete and the reported Raman and infrared frequencies for aqueous sodium formate will thus be used as a basis for further assignment along with the infrared frequencies of aqueous calcium formate.

The three totally symmetric fundamentals of the free formate ion, ν_1, ν_2 and ν_3 occur at 2825, 1352 and 773 cm^{-1} respectively in the Raman spectra of aqueous sodium formate while ν_1 and ν_2 occur at 2834 and 1359 cm^{-1} in the infrared spectra of aqueous calcium formate. There has been some confusion with respect to the assignment of ν_1 and ν_2. The assignment is made here following the convention that for vibrations of the same species, the assignment is made in the order of decreasing absorption frequencies. For calcium formate, the ν_1 mode is split into a triplet at 2895, 2890 and 2873 cm^{-1} in the single crystal spectrum. The ν_2 mode is split into a doublet occurring at 1365 and 1355 cm^{-1} in the poly-crystalline spectrum of calcium formate. The ν_2 region in the single crystal spectrum is quite confused and will be discussed in greater detail later. The ν_3 mode appearing at 773 cm^{-1} in the Raman spectrum of sodium formate is split into a triplet at 803, 788 and 782 cm^{-1} in the single crystal spectrum. The polycrystalline spectrum of calcium formate indicates four components to ν_3 at 804, 800, 788 and 782 cm^{-1}.

The two (C_{2v}) b_2 modes of the formate ion, ν_4 and ν_5 occur at 1584 and 1386 cm^{-1} in the Raman spectrum of aqueous sodium formate and at 1588 and 1383 cm^{-1} in the

infrared spectrum of aqueous calcium formate. In the
single crystal spectrum of calcium formate it is difficult
to determine any splitting in the ν_4 and ν_5 modes because
the crystals were still too thick and these modes were
almost totally absorbing. However, the polycrystalline
infrared spectrum of calcium formate indicates that ν_5
is split into a triplet at 1403, 1394 and 1390 cm^{-1}
while ν_4 appears as a single peak at 1591 cm^{-1}. There
is some indication that this may be split in the single
crystal spectrum into components at 1580 and 1617 cm^{-1}.

The out-of-plane mode, ν_6 , which occurs at 1069
cm^{-1} in the Raman spectrum of aqueous sodium formate is
split into a doublet at 1079 and 1068 cm^{-1} in the single
crystal spectrum. Each fundamental region of the spectrum
will now be discussed in greater detail.

4-4. ν_1 region (3100 - 2700 cm^{-1})

The region around the ν_1 fundamental is quite
complicated since it is in this region that a large number
of overtone and combination bands of the other fundamentals
occur. As was mentioned, the fundamental appears to be
split into a triplet occurring at 2895, 2890 and 2873 cm^{-1}.
All three components, however, are not equally intense
when polarized radiation is used. As can be seen from

figure 7, all three components appear as relatively strong peaks when the direction of polarization is parallel to the c-axis. (Hereafter, for convenience, a, b and c-active modes will mean modes which are active when the direction of polarization of the incident radiation is parallel to the a, b, or c-axis of the crystal). Only the 2895 and 2873 cm^{-1} components are b-active while the 2895 cm^{-1} component is the principal a-active component. A very weak a-active component occurs at 2874 cm^{-1}.

The varying intensities of the various components may be better understood if the direction cosines of the oscillating dipoles are considered. To a first approximation, the ratio of the relative integrated absorption intensities of the various components should be in the same ratio as the squares of the respective cosines. The calculated and observed ratios give a very good qualitative explanation of the spectra. A more quantitative explanation may be possible, depending on the accuracy of the reported crystal structures. The possible errors in the reported atomic positions giving rise to inaccuracies in the calculated direction cosines and the rather crude manner in which intensities were calculated are the two major reasons why there is a relatively large deviation between observed and calculated intensities.

Table 8. <u>Squares of direction cosines of totally symmetric</u> <u>oscillating dipole calculated from the crystal</u> <u>structure of calcium formate</u>

	formate ion 1	formate ion 2	total
ℓ^2	0.0252	0.1105	0.1357
m^2	0.5079	0.2343	0.7422
n^2	0.4666	0.6553	1.1219

ℓ, m and n refer to the direction cosines the totally symmetric oscillating dipole makes with the a, b and c crystal axes respectively.

Table 9. <u>Ratios of calculated and observed total relative</u> <u>intensities for ν_1</u>

calculated	observed
$\ell_t^2 / m_t^2 = 0.183$	<u>a</u> / <u>b</u> = 0.403
$\ell_t^2 / n_t^2 = 0.121$	<u>a</u> / <u>c</u> = 0.373
$m_t^2 / n_t^2 = 0.662$	<u>b</u> / <u>c</u> = 0.940

here <u>a</u>, <u>b</u> and <u>c</u> refer to the observed integrated intensities.

Table 10. Ratios of calculated and observed relative

intensities with various polarizations for ν_1

polarization	calculated	observed
a	$\ell_1^2 / \ell_2^2 = 4.38$	$A / B = 4.28$
b	$m_1^2 / m_2^2 = 0.46$	$A / B = 0.80$
c	$n_1^2 / n_2^2 = 1.40$	$A / B = 1.84$

A and B refer to the 2895 and 2873 cm^{-1} components re-
spectively. In the case of the c-active components,
the 2890 cm^{-1} component is included with the 2895 cm^{-1}
component for the purpose of the above calculations.

On the basis of the above calculations it appears
that the 2895 cm^{-1} component of ν_1 arises from what will
henceforth be called formate ion I, while the 2873 cm^{-1}
component of ν_1 arises from the crystallographically
non-equivalent formate ion II. This result is what is
expected on the basis of the factor group analysis.
There is no obvious explanation of the occurrence of the
2890 cm^{-1} c-active mode. The remainder of the ν_1 region
will be discussed later along with other overtone and
combination modes.

4-5. ν_3 region (820 - 760 cm^{-1})

The ν_3 region is another interesting and com-
plicated region. As indicated earlier, the fundamental

appears to be split into a triplet at 803, 788 and 782 cm^{-1}.
A b-active peak occurring at 799 cm^{-1} in the single crystal
spectrum may be the 800 cm^{-1} component observed in the
polycrystalline spectrum. As with the ν_1 region, all
components are not active along all axes. Thus only the
803 and 788 cm^{-1} components are a-active. The a-active
component at 788 cm^{-1} has a further splitting with a peak
occurring at 786 cm^{-1}. This peak, the b-active 799 cm^{-1}
component and the c-active 2890 cm^{-1} peak are not readily
explained on the basis of the factor group analysis.
There are strong b-active components at 802 and 782 cm^{-1}
and a weak b-active component at 788 cm^{-1}. Similarly,
there are c-active components at 803 and 782 cm^{-1} with
a c-active component occurring as a shoulder at 788
cm^{-1}. The c-active 788 cm^{-1} and the b-active 788 cm^{-1}
component may possibly be due to either a or b and a
or c components respectively arising from one or more
of the following sources: (a) the crystals may not
have been ground absolutely perpendicular to the various
crystallographic axes, (b) the polarizer used was not
100% efficient, and (c) the incident radiation was
not parallel due to the convergence of the light beam
in the instrument. However, measurements and tests
carried out as part of this investigation indicate that

none of these possible sources would allow much more than a 1 or 2% contribution from other components, and certainly less than 5%.

As with the ν_1 region, a comparison of the ratios of the squares of the direction cosines of the oscillating dipole and the relative intensities will give an indication of the origin of the various peaks. Since ν_1 and ν_3 are of the same species, the square of the direction cosines given in table 8 also refer to ν_3. In the case of ν_3, it appears that the low frequency components (that is, the a-active 788 cm^{-1} component and the b and c-active 782 cm^{-1} components) are caused by formate ion I, while the high frequency components are caused by formate ion II. This assignment is made on the basis of calculated and observed intensities.

Table 11. Ratios of calculated and observed total relative intensities for ν_3

calculated   observed

$\ell_t^2 / m_t^2 = 0.183$ $a / b = 0.355$
$m_t^2 / n_t^2 = 0.662$ $b / c = 0.581$
$\ell_t^2 / n_t^2 = 0.121$ $a / c = 0.206$

Table 12. Ratios of calculated and observed relative

             intensities with various polarizations for ν_3

polarization	calculated		observed
$\underline{a}$	ℓ_1^2 / ℓ_2^2	$= 4.38$	$B / A = 3.80$
$\underline{b}$	m_2^1 / m_2^2	$= 0.46$	$B / A = 0.59$
$\underline{c}$	n_1^2 / n_2^2	$= 1.40$	$B / A = 1.85$

A and B refer to the 803 and 782 cm^{-1} (788 cm^{-1} in the
case of the $\underline{a}$-active component) components respectively.
The $\underline{b}$-active 786 cm^{-1} component is included with the 788
cm^{-1} component for the purposes of the above calculations.

Intuitively, it would be expected that a given set
of crystallographically equivalent formate ions would give
rise to either the higher or lower frequency components
of all fundamental modes of the same symmetry species.
In the case of the ν_1 and ν_3 modes there appears to be
a reversal of this expected form. This author believes
that the explanation of this phenomenon lies in the crystal
structure of calcium formate.

Because of the orientation of the formate ions in
the unit cell, the crystal field for the various modes
will differ. Thus the ν_1 mode, which is essentially a
symmetric CH stretch, will be little affected by crystal

field effects since for any group of formate ions all hydrogen atoms are oriented away from the calcium ions. Each hydrogen atom is separated from neighbouring hydrogen atoms by a distance larger than the Van der Waals radius. This lack of crystal field is also an explanation for the relatively small splitting of the ν_1 mode. (Morrow found a splitting of 113 cm^{-1} between the high and low frequency components of the ν_1 mode for barium formate).

However, in the case of the ν_3 mode which is essentially a symmetric OCO bond, the crystal field effects would be expected to be quite large. This comes about since the oxygen atoms of the formate ion are directly neighbouring the calcium ions and any change in the OCO angle would give rise to large crystal field effects. This large crystal field would also explain the relatively large splitting observed in the ν_3 mode. (Morrow observed a splitting of only 11.5 cm^{-1} for the high and low frequency components of the ν_3 mode for barium formate).

4-6. ν_6 region (1100 - 1050)

The out-of-plane b_2 (C_{2v}) mode is the least complicated of all the fundamental regions of the calcium spectrum. The two components at 1079 and 1068 cm^{-1} are

active along all three axes as would be expected from the
factor group analysis. The intensities are in the ratio
expected except for one instance. To a first approximation,
the direction of the oscillating dipole for the ν_6 mode
can be taken as being perpendicular to the plane of the
formate ion. In the case of the b-active modes, the
square of the direction cosines indicate that the com-
ponents due to the two different formate ions should
be of similar relative intensities as the c-active
modes. Instead the b-active components are reversed.
Since the ν_6 mode is the out-of-plane bend it would
be expected that crystal field effects would be re-
latively smaller than for the ν_3 mode. The small
splitting observed (11 cm^{-1}) seems to bear this out.
Hence it would be expected that the high frequency
components would be due to the formate ion I similar
to ν_1 , and the low frequency components due to formate
ion II. Thus, considering the direction cosines of the
oscillating dipole it is expected that the high fre-
quency component (1079 cm^{-1}) should be the most intense
for a-active modes and the low frequency components
(1068 cm^{-1}) should be the most intense for b and c-active
modes. This is observed for the a and c components but,
as mentioned above, is reversed for the b components.
There is no obvious explanation for this anomaly.

Table 13. <u>Ratios of calculated and observed relative</u>

<u>intensities with various polarizations for ν_6</u>

polarization	calculated	observed
<u>a</u>	$\ell_1^2 / \ell_2^2 = 2.397$	A / B = 1.636
<u>b</u>	$m_1^2 / m_2^2 = 0.717$	A / B = 4.238
<u>c</u>	$n_1^2 / n_2^2 = 0.614$	A / B = 0.606

4-7. <u>ν_2, ν_4 and ν_5 region (1700 - 1300 cm^{-1})</u>

Very little information may be obtained from this region of the single crystal spectrum. The major difficulty here was the thickness of the samples used. When the crystal was originally ground, it was considered thin enough when the components of the various modes were resolvable. However, when the polarizer was in place, it reduced the intensity of the signal of the sample beam by 50%. This reduction in signal intensity caused the ν_2, ν_4 and ν_5 modes to be almost totally absorbing. Another difficulty arising in the ν_2, and ν_5 regions was combination and difference modes of lattice and fundamental vibrations. Combinations of ν_2 with a lattice mode of 36 cm^{-1} should appear in the ν_5 region, 1400 - 1390 cm^{-1}, while difference modes of ν_5 with the 36 cm^{-1} lattice mode should appear in the ν_2 region.

The assignment of these lattice modes will be discussed later.

The appearance of these lattice modes is suspected since more components than those predicted by the factor group analysis are observed. In the case of ν_2 and ν_5 there are at least four poorly resolved a-active components for each fundamental. It should be noted that combination modes are generally relatively weak, but since the combination modes and the fundamental components must be of the same symmetry in order to be observed together with the same polarization, Fermi resonance can occur and the relative intensities of the combination modes may be greatly increased. A similar difficulty arises with the ν_4 mode where a combination or difference mode of the 36 cm^{-1} lattice mode with one of the components of ν_4, should fall at almost the same frequency as the other component. Because of the difficulties noted above, this problem could not be satisfactorily resolved.

4-8. 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. The factor group analysis given earlier gives the number of lattice modes belonging to each of the irreducible representations of the factor group C_{2h}. As indicated, these lattice modes undergo a splitting similar to the internal fundamental modes of the formate ion. Generally these modes occur in the region below 300 cm^{-1} and are inaccessible on the spectrometer used for this study. These lattice modes, however, may be observed as combination modes with molecular modes.

In the case of calcium formate, at least 34 frequencies may be assigned to combinations with lattice modes. By determining the frequency separation of the various fundamentals and the weak peaks of the spectrum it is found that six differences occur most often. These differences correspond to lattice modes at 36, 61, 90, 128, 154 and 192 cm^{-1}. Both combination and difference bands are readily observed with lattice modes. This is so because the energy separation of the ground and first excited state of the lattice mode is relatively small and at room temperature the first excited state may have a large population. Since a difference band requires that one mode of those involved be in an excited state, the large population of upper vibrational states of lattice

modes make them ideal for the observation of difference
bands.

Table 14. <u>Population of lattice vibrational states at 20°C</u>

ν_L	36	61	90	128	154	192	793 (ν_3)
n/n_0	0.848	0.741	0.643	0.534	0.477	0.399	0.020

n/n_0 is the ratio of the populations of the upper and
lower vibrational states.

Table 14 also gives an indication why difference bands
are very seldom observed with molecular modes. Even for
a relatively low frequency mode, the population of the
first excited state is very small.

A study of single crystal spectra carried out at
very low temperatures would be very helpful in the assign-
ment of lattice modes since at the lower temperatures,
the upper vibrational states of the lattice modes would
have greatly reduced populations and thus the disappearance
of difference bands would be expected. Because of the
technical difficulties involved, no such investigation
was carried out as part of this study.

4-9. Combinations and overtones

Of the 84 observed frequencies in the spectrum of the single crystal of calcium formate, 16 are attributed to combination and overtones of molecular modes. Since first overtones are totally symmetric, no overtones would be initially expected under the factor group selection rules. However, it must be remembered that each molecular fundamental is split into 16 components under the C_{2h} factor group. Thus any overtone would simply be a combination of one component of the fundamental with another component of the same fundamental. The infrared active components of the overtone arise from combinations of an inactive A_{1g} component with one of the infrared active B_u modes or combinations of an inactive A_{1u} mode with Raman active B_g modes. Thus each overtone should consist of 64 components of which only 12 are infrared active. Table 15 gives the symmetries of possible combination modes. As can be seen from the table, not all combinations of overtones are allowed in the factor group. Of the ones that are allowed, only some are infrared active.

Since the components from which the overtones arise are generally infrared inactive there is no way of knowing whether these components have the same

Table 15. <u>Symmetries of combination and overtone modes</u>
<u>for calcium formate</u>

symmetry of fundamental	symmetry of fundamental of lattice modes							
	A_g	B_{1g}	B_{2g}	B_{3g}	A_u	B_{1u}	B_{2u}	B_{3u}
A_g	A_g	B_{1g}	B_{2g}	B_{3g}	A_u	$B_{1u}^{\dagger}$	$B_{2u}^{\dagger}$	$B_{3u}^{\dagger}$
B_{1g}	B_{1g}	A_{1g}	A_{3g}	A_{2g}	$B_{1u}^{\dagger}$	A_{1u}	A_{3u}	A_{2u}
B_{2g}	B_{2g}	A_{3g}	A_{1g}	A_{1g}	$B_{2u}^{\dagger}$	A_{3u}	A_{1u}	A_{1u}
B_{3g}	B_{3g}	A_{2g}	A_{1g}	A_{1g}	$B_{3u}^{\dagger}$	A_{2u}	A_{1u}	A_{1u}
A_u	A_u	$B_{1u}^{\dagger}$	$B_{2u}^{\dagger}$	$B_{3u}^{\dagger}$	A_g	B_{1g}	B_{2g}	B_{3g}
B_{1u}	$B_{1u}^{\dagger}$	A_{1u}	A_{3u}	A_{2u}	B_{1g}	A_{1g}	A_{3g}	A_{2u}
B_{2u}	$B_{2u}^{\dagger}$	A_{3u}	A_{1u}	A_{1u}	B_{2g}	A_{3g}	A_{1g}	A_{1g}
B_{3u}	$B_{3u}^{\dagger}$	A_{2u}	A_{1u}	A_{1u}	B_{3g}	A_{2g}	A_{1g}	A_{1g}

The dagger (†) denotes infrared active species.

frequencies as the observed active components. For the purpose of calculating overtone and combination frequencies, it was assumed that the inactive components had the same frequency as the active components. It was also assumed that the overtones observed were either combinations of two low frequency components or two high frequency components but never a combination of a low frequency component with a high frequency component since the low and high frequency components arise from different formate ions.

In several cases, the observed peaks were rather broad and diffuse so that they might possibly contain more than one component. In these cases, assignments were made assuming an average frequency for the fundamentals as a basis.

Similar arguments may be advanced for the assignment of combination modes. In the case of combination modes only one instance was observed where an assignment could be made on the basis of separate components of the fundamentals involved. In all other cases, an average value for the fundamental frequency was assumed.

4-10. Isotopic shifts

On the basis of Hammakers results(41) (to be published shortly) from a study of the infrared spectrum of C^{13} enriched sodium formate, the assignment of modes due to the natural abundance of C^{13} in the calcium formate may be made quite readily. Modes arising from C^{13} formate ions are observed for all but the ν_4 mode. This is not unexpected since the ν_4 mode is very weak compared to the other fundamentals. Only in the case of the ν_3 mode is the C^{13} mode of the high frequency component observed. Because of the relatively small isotopic shifts the C^{13} mode of the high frequency component usually

falls in the immediate vicinity of the low frequency comp-
onent and is thus obscured.

The validity of these assignments may be verified
by making use of the product rule (3) which gives a
methematical relationship between the product of the
frequencies of a given symmetry species for two isoto-
pically substituted molecules. For the three a_1 modes of
the formate ion, this rule is given by the expression

$$\frac{\nu_1' \nu_2' \nu_3'}{\nu_1'' \nu_2'' \nu_3''} = \frac{[m(C^{12})\,M']^{1/2}}{[m(C^{13})\,M]^{1/2}}$$

where the primed frequencies refer to the C^{13} species,
m refers to the mass of the two atoms isotopically sub-
stituted, and M and M' refer to the total mass of the
C^{12} and C^{13} ions respectively. Taking the low frequency
component of the C^{12} modes (that is, 2873, 1355 and 782
cm^{-1}) and C^{13} modes at 1336 and 777 cm^{-1}, the frequency
of the C^{13} mode for ν_1 may be calculated as occurring
at 2844 cm^{-1}. The occurrence of a very weak peak at
2839 cm^{-1} may thus be taken as the C^{13} mode for ν_1.
A similar calculation involving the low frequency ν_4
and ν_5 C^{12} components (1580 and 1388 cm^{-1}) and the C^{13}
mode at 1377 cm^{-1} gives a frequency of 1548 cm^{-1} for the
C^{13} component of ν_4. A weak shoulder is observed at
1543 cm^{-1} thus confirming these assignments.

4-11. <u>Infrared spectrum of sodium formate</u>

As stated earlier, crystals of sodium formate are monoclinic with four molecules per unit cell. The crystal belongs to the space group C2/c (C_{2h}^6). However, for the purposes of the factor group analysis proposed by Bhagavantum and Venkatarayudu, the unit cell coinciding with the crystallographic unit cell is not necessarily the unit cell of the smallest possible size. The choice of the smallest possible unit cell is most obvious because of the reduction in the volume of calculations needed to adequately describe the system. As mentioned earlier, if the crystal is regarded as a structure or a set of inter-penetrating lattices, then the unit cell of the smallest possible size will contain as many atoms in it as there are inter-penetrating lattices in the structure. These points may be referred to as the nonequivalent points of the structure for no one of these points may be reached from any other by performing the primitive translations characteristic of the lattice.

As can be seen from figure 14, one half of the sodium formate unit cell may be obtained from the other half by primitive translations. Thus the unit cell of the smallest possible size (on the basis of Bhagavantum's definition of a unit cell) contains only two molecules.

However, the full symmetry of the crystal is retained and
the factor group is still isomorphous with C_{2h}.

The character table for the point group C_{2h} isomor-
phous with the space group C2/c is given below. By
application of equation (3), the number of normal modes
for the unit cell associated with each irreducible re-
presentation has been determined. The symmetry opera-
tions associated with the factor group are the identity
operation E, a two fold rotation axis C_2, a center of
inversion i, and a horizontal mirror plane σ_h .

Table 16. Character table and factor group analysis for
sodium formate

C_{2h}	E	C_2	i	σ_h	n_i	T	T'	R'	n_i'
A_g	1	1	1	1	6	0	2	1	3
B_g	1	-1	1	-1	9	0	4	2	3
A_u	1	1	-1	-1	6	1	1	1	3 (T_z)
B_u	1	-1	-1	1	9	2	2	2	3 (T_x, Y_y)

The sodium formate crystal has two molecules of
10 atoms per unit cell giving rise to $3 \times 10 = 30$ degrees
of freedom. Of these, three correspond to pure translations

of the unit cell and the remaining 27 correspond to the
vibrations of the unit cell. Of the 12 internal vibra-
tions, only 6 are allowed in the infrared spectrum of
the crystal. In the sodium formate crystal, each sodium
formate molecule is situated on a site of symmetry C_2.
Thus a correlation of the symmetry species of the mole-
cular group with the factor group will also show the
basis of the factor group splitting under the factor
group C2/c. The following correlation table shows the
relation between molecular and factor group vibrations.

Table 17. <u>Site group correlation table for sodium formate</u>

molecular group   site group   factor group
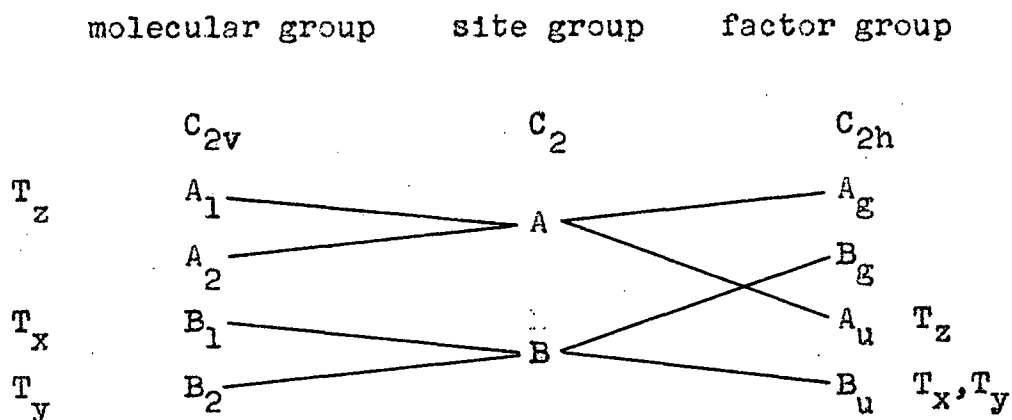
Thus the totally symmetric molecular a_1 modes be-
come a modes in the crystal and the molecular b modes
become b modes in the crystal. From this it follows
that the a_1 molecular modes must be active along one

axis only (in this case the b-axis). Similarly the b modes are active in the ac plane only. Unlike calcium formate, where there is a distinct component active along each axis, the component observed in the ac plane is the same component irregardless of the orientation of the plane of observation.

Following this explanation, it is seen that the polarized sodium formate spectrum will be quite unlike that found for calcium formate. Whereas the most obvious polarization property of the calcium formate single crystal spectrum was an intensity change, the polarized spectrum of the sodium formate single crystal should exhibit inactivity of some modes depending on the direction of polarization.

As was mentioned earlier, the sodium formate crystals were such that they could be ground perpendicular to one axis only. Hence, the crystals were ground parallel to the ac plane only. Thus it was expected that only the b molecular modes would be observed in the infrared spectrum.

As can be seen from table 4, some weak peaks have been assigned to the symmetric a_1 molecular modes which were not expected from the factor group analysis. However, the crystals used for the sodium formate spectra were much

thicker than those used for the calcium formate spectra and partly because of this thickness, unexpected components of the molecular modes may be observed. As mentioned earlier, the convergence of the sample beam, the less than 100% efficiency of the polarizer and the possible misgrinding of the crystal, although contributing a very small unwanted component to the spectrum, these sources, in conjunction with the thick crystal would give rise to a measurable component. A comparison of the intensities of the symmetric modes with the intensity of the active b_u modes shows the former intensities to be much less than 5% of the latter intensities which is in the order of magnitude of unwanted component expected from the above sources.

The three totally symmetric modes were observed as weak extraneous components at 2837, 1359 and 780 cm^{-1}. These are to be compared with the values of Ito and Bernstein for the infrared spectrum of an aqueous solution of sodium formate of 2803, 1352 and 773 cm^{-1}. Similarly, Fonteyne's Raman frequencies of 2825, 1352 and 773 cm^{-1} for an aqueous solution of the salt are in good agreement. Newman's frequencies for the polarized infrared spectrum of a sodium formate single crystal are 2870, 1377 and 784 cm^{-1}. There is some doubt as to the

validity of Newman's values since no other workers have found values for the symmetric frequencies as high as those reported. No polarization properties of the a_1 modes can be inferred from the peaks that were observed.

The ν_4 and ν_5 modes, observed at 1584 and 1380 cm^{-1} by Fonteyne in the Raman spectra of an aqueous solution and at 1585 and 1383 cm^{-1} by Ito and Bernstein of the infrared spectrum of an aqueous solution are observed at 1610 and 1376 cm^{-1} in this work. Newman reports values of 1620 and 1377 cm^{-1} respectively for the polarized infrared spectrum of a sodium formate single crystal. The value of 1610 cm^{-1} for ν_4 is only an approximation. The crystal was totally absorbing over a large region and the band envelope was assumed to be symmetrical so that an average value for the frequency could be determined. This totally absorbing component was observed only when the plane of polarization was perpendicular to the c-axis. A weak peak at 1597 cm^{-1} was observed with the plane of polarization parallel to the c-axis. Similarly, a very strong, almost totally absorbing peak was found at 1375 cm^{-1} for the component of ν_5 perpendicular to the c-axis while only a weak but sharp peak was observed for the parallel component at 1377 cm^{-1}. The ν_6 mode observed at 1069 cm^{-1} by

Fonteyne and by Ito and Bernstein, and at 1070 cm^{-1} by Newman is found at 1068 cm^{-1} in this case.

Since the sodium formate crystal is monoclinic, the angle between two of the axes is not 90°. This obtuse angle, as defined by Zachariasen(31), lies in the ac plane so that the planes of polarization at right angles to each other would not correspond to the crystal axes. It is not necessary, however, to have the planes of polarization parallel to the crystal axes in order to be able to interpret the results. If the directions of polarization and the direction cosines of the oscillating dipole are both known relative to a common coordinate system, the analysis of the results may be readily carried out.

As with the calcium formate single crystal spectrum, a knowledge of the ratios of the direction cosines of the oscillating dipole will give a good approximation of the ratio of the integrated absorption intensities of the different components of one mode. Table 18 gives the calculated and observed intensity ratios. No value is given for the observed ratio of the ν_4 intensities because an accurate value for the integrated intensity could not be readily obtained.

Table 18. Calculated and observed total intensity ratios

for sodium formate

mode	calculated	observed
	$1^2 / n^2 = 0.106$	-
	$1^2 / n^2 = 0.106$	$11 / \underline{1} = 0.066$
	$1^2 / n^2 = 9.41$	$11 / \underline{1} = 7.85$

11 and 1 refer to the plane of polarization being parallel or perpendicular to the c-axis of the crystal.

4-12. Combination and lattice modes; isotopic shifts

As with calcium formate, the external degrees of freedom of the formate ion become translatory and rotatory lattice modes when the ion is in a crystal. In this case, at least 23 of the 47 observed modes may be assigned to combination modes between molecular and lattice vibrations. The lattice frequencies, determined in the same manner as the calcium formate lattice frequencies, were found to occur at 58, 91, 112, 128 and 231 cm^{-1}. Ito and Bernstein assumed lattice frequencies of 60 and 140 cm^{-1} to explain their spectrum of sodium formate. In this case, both sum and difference bands were again observed. Generally, difference bands are seen only with the lower frequency lattice modes as is expected from the

relative populations of ground and first excited vibrational levels.

Unlike the calcium formate spectrum, first overtones of molecular fundamentals sometimes are not allowed under C_{2h} selection rules. Since the a_1 molecular modes become a_g and a_u modes in the crystal and b_1 and b_2 molecular modes become b_g and b_u modes in the crystal, then first overtones would have either a_g or a_u symmetry only. Since the a_u modes are active along the b-axis only (that is, along the axis perpendicular to the plane of the crystal used in this study) they are not observed in this case. Similarly, several combination modes are not observed in this study. A knowledge of the symmetry requirements explains this phenomenon. Table 19 gives the symmetries of possible combination modes.

The most unusual combination mode is that assigned to $\nu_1 + \nu_4$ at 2949 cm^{-1}. This is a relatively strong absorption compared to other combination modes. However, considering the very intense ν_4 fundamental, the combination mode intensity is understandable. On this basis, the $\nu_3 + \nu_4$ combination would also be expected to be prominent, but no peak is observed that could be assigned to the $\nu_3 + \nu_4$ combination. This anomaly is not readily explained.

Table 19. **Symmetries of combination and overtone modes for sodium formate**

mode	symmetry	$\nu_1\nu_2\nu_3$ A_g	$\nu_4\nu_5\nu_6$ B_g	$\nu_1\nu_2\nu_3$ A_u	$\nu_4\nu_5\nu_6$ B_u
$\nu_1\nu_2\nu_3$	A_g	A_g	B_g	$A_u{}^\dagger$	$B_u{}^\dagger$
$\nu_4\nu_5\nu_6$	B_g	B_g	A_g	$B_u{}^\dagger$	$A_u{}^\dagger$
$\nu_1\nu_2\nu_3$	A_u	$A_u{}^\dagger$	$B_u{}^\dagger$	A_g	B_g
$\nu_4\nu_5\nu_6$	B_u	$B_u{}^\dagger$	$A_u{}^\dagger$	B_g	A_g

The dagger (†) denotes infrared active symmetries.

No bands are observed here that could be attributed to C^{13} isotopes as in calcium formate spectrum. Since ν_4, ν_5 and ν_6 are the only active modes, C^{13} isotopic shifts would be expected for these modes only. However, since the ν_6 mode is so weak, the absence of the C^{13} peak is not unexpected. In the case of the ν_4 and ν_5 modes, it is probable that the absorption is so strong that the C^{13} peaks are absorbed in the broad C^{12} peak.

The assignment of peaks in the case of the sodium formate crystal spectrum is rather incomplete compared to that of the calcium formate crystal. A more complete assignment, and the observation of the a_u modes would be

possible if a crystal could be grown large enough to enable a section being obtained in a plane perpendicular to the section already studied. Again, a study of the crystal spectrum at reduced temperatures would be useful and interesting.

4-13. Conclusion

A point has been reached where it can be stated with a good deal of certainty that the infrared spectrum of calcium formate (and to a lesser degree, sodium formate) has been satisfactorily explained in view of the symmetry conditions imposed by the crystal structure. It is seen that a knowledge of the crystal structure can give a quantitative description of the fundamental absorption intensities. It also becomes obvious that the infrared spectrum of a single crystal may be used to help determine the orientations of molecules in a crystal of unknown structure. It is in this manner that infrared spectroscopy could be a powerful tool for the crystallographer. Infrared spectroscopy is also a valuable tool for clarifying crystal structures, especially of hydrogen containing compounds.

Several weak peaks in both the calcium and sodium formate single crystal spectra are still to be assigned.

In both cases, these peaks are probably due to combina-
tion of lattice modes with molecular fundamentals. A
more complete study of the sodium formate single crystal
spectrum would undoubtedly aid in further assignments
as well as providing a better understanding of the rest
of the spectrum. As mentioned earlier, a study of these
spectra at greatly reduced temperatures would aid the
assignment of lattice combination modes. Similarly,
the development of more sophisticated techniques for
grinding thinner crystal sections would be very helpful
in that the splitting of the more intense fundamentals
would be more readily detected.

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