# VIBRATIONAL SPECTROSCOPY OF SOME <br> INORGANIC SINGLE CRYSTALS 

A thesis presented for the degree of

Doctor of Philosophy
in the Faculty of Science
of the

University of Leicester
by

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Learn from others' mistakes - you haven't time to make them all yourself.

Vernon H. Willings.

## Statement

The accompanying thesis submitted for the degree of Ph.D. entitled "Vibrational Spectroscopy of Some Inorganic Single Crystals" is based on work conducted by the author in the Department of Chemistry of the University of Leicester, mainly during the period between October, 1974 and September, 1977.

All the work recorded in this thesis is original unless otherwise acknowledged in the text or by references. None of the work has been submitted for another degree in this or any other University.

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## ABSTRACT

VIBRATIONAL SPECTROSCOPY OF SOME INORGANIC SINGLE CRYSTALS

This thesis contains the results of studies by single crystal vibrational spectroscopy of several materials. In an introduction the essential facts necessary for an understanding of the construction and nature of crystals in relation to single crystal vibrational spectroscopy are summarised. A review of i.r. reflectance spectroscopy is given as this was the major technique used in this research. $A$ brief description of the Raman process is also given as well as methods of crys+al growth used for this work.

Single crystal i.r. and Raman spectra for topaz are reported. A complete assignment is given for the $\nu($ Si-0) region; at lower frequencies there is a more or less continuous range of modes and any assignments in this regicn must be tentative. Some fragmentary data for spodumene are reported.

Single crystal i.r. and Raman spectra for $\mathrm{AlCl}_{3} \cdot 6 \mathrm{H}_{2} \mathrm{O}$ are reported and, together with data collected from the deuteriate, enable an assignment to be given.

The assignment takes note of normal coordinate analysis calculations, deuteriation shifts, and factor group components, as well as solution data. An assignment for the modes due to water motions is given by comparison with previous assignments for mono- and di-aquated complex ions.

Far-i.r. spectra of $\mathrm{HgCl}_{2}$ and $\mathrm{HgBr}_{2}$ are reported at buth ambient and low temperatures. For $\mathrm{HgCl}_{2}$ the translatory modes have been identified from the fundamental modes predicted by theory, all of which have been observed. Al. 1 the fundamental modes of $\mathrm{HgBr}_{2}$ have been observed and assigned to symmetry species.

Far-i.r. spectra of three complex halides with the $\mathrm{CsNiCl}_{3}$ structure are reported at ambient temperature. The results agree well with those reported previously for mulls and an unambiguous assignment is given.

Far-i.r. spectra of five square-planar complexes are reported at both ambient and low temperatures. Complete assignments for $\mathrm{K}_{2} \mathrm{PtBr}_{4},\left(\mathrm{NH}_{4}\right)_{2} \mathrm{PtCl}_{4}$ and $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{PdCl}_{4}$ are given for the first time. In the case of $\mathrm{K}_{2} \mathrm{PtBr} \mathrm{F}_{4} \mathrm{v}_{4}$ and $v_{7}$ are accidentally almost degenerate at ambient
temperature. The lattice mode region of the ammonium salts has been assigned; the breadth of the central region of i.r. mulls of these compounds is due to three bands occurring in close proximity. The occurrence of low temperature features in the chlorides has been confirmed, the possible origin of these modes is discussed.

A simplified factor group analysis scheme is given for the 80 diperiodic groups which lack periodicity in the third dimension. Examples of the use of the Tables are given.

Listings of compt.ter programs used for i.r. reflectance analysis are given in the appendices.

This thesis is dedicated to my wife Linda, and to my mother.

## CONTENTS

Page

Chapter 1 :
The Theoretical Treatment of Crystals
Chapter 2 :
The Practical Investigation of Crystals
(Section A) A Review of I.r. Reflectance
Spectroscopy and Techniques 26
(Section B) The Raman Process, Crystal Growth 60
Chapter 3 :
Vibrational Spectra of Topaz and Some Data
for Spodumene 73
Chapter 4 :
Vibrational Spectra of Aluminium Trichloride
Hexahydrate
90
Chapter 5 :
Far-i.r. Spectra of Mercuric Chlonide and
Mercuric Bromide
Chapter 6 :
$\begin{array}{ll}\text { Far-i.r. Spectra of Three Complex Halides } \\ \mathrm{CsMgCl}_{3}, \mathrm{CsMnBr}_{3}, \mathrm{CsMnI}_{3} & 145\end{array}$
Chapter 7 :
Far-i.r. Spectra of Five Square-Planar
Complexes $\quad \mathrm{A}_{2} \mathrm{MX}_{4}$
154
Chapter 8 :
The 80 Diperiodic Groups in Three Dimensions180
Appendices:
Appendix 1
Kramers-Kronig Analysis Program
Appendix 2
Simple Harmonic Oscillator Program
(for Transverse Optic Mode Analysis)
Appendix 3
Simple Harmonic Oscillator Program
(for Transverse and Longitudinal Optic
Mode Analysis) 237
Loading of Programs : 243

Chapters 3-7 inclusive have Tables and Figures at the end of the text.

## Crystals and Symmetry

A crystal is a periodic three dimensional array of atoms, the smallest representative portion of which is called the "unit cell". The unit cell may be envisaged as a parallelepiped. By stacking a very large number of these unit cells along the three directions in a regular manner, the crystal may be constructed.

Crystals are divided into seven crystal systems by the macroscopic symmetry which they possess. An explanation of symmeiry will not be attempted here, but has been extensively reviewed by Cotton (1971). Figure 1.1 shows the essential symmetry axes of six of the seven systems. The seventh system, triclinic, is characterised by a total lack of symmetry axes. The essential symmetry axes represent the highest symmetry axes present and therefore define the system. Many other symmetry axes and elements are possible; the full cubic symmetry has thirteen symmetry axes and nine symmetry planes. The various combinations of symmetry elements in each system leads to a subdivision into thirty-two crystal classes. One class in each system will possess the full symmetry of the system and is called the holosymmetric class. Detailed accounts of the determination of crystal system by external morphology are given by Dana (1932); Cox, Price and Harte (1967), and Kirkaldy (1968). On a macroscopic scale it is sometimes difficult to distinguish orthorhombic crystals from those of the monoclinic system. In the absence of

Table 1.1

Factor group symbols
Crystal system Unit cell constants Schonflies Herman-Mauguin

| Triclinic | $\alpha \neq \beta \neq \gamma$ | $C_{1}$ | 1 |
| :---: | :---: | :---: | :---: |
|  | $a \neq b \neq c$ | $C_{i}\left(S_{2}\right)$ | $\bar{\jmath}$ |
| Monoclinic | $\alpha=\gamma=90^{\circ} \beta \neq 90^{\circ}$ | $C_{2}$ | 2 |
|  | $a \neq b \neq c$ | $C_{5}\left(C_{I h}\right)$ | m |
|  |  | $C_{2 h}$ | 2/m |
| Orthorhombic | $\alpha=\beta=\gamma=90^{\circ}$ | $\mathrm{D}_{2}(\mathrm{~V})$ | 222 |
|  | $a \neq b \neq c$ | $C_{2 v}$ | mm |
|  |  | $\mathrm{D}_{2 \mathrm{~h}}\left(\mathrm{~V}_{\mathrm{h}}\right)$ | mmm |
| Tetragonal | $\alpha=\beta=\gamma=90^{\circ}$ | $C_{4}$ | 4 |
|  | $a=b \neq c$ | $S_{4}$ | $\overline{4}$ |
|  |  | $\mathrm{C}_{4 \mathrm{~h}}$ | 4/m |
|  |  | $\mathrm{D}_{4}$ | 422 |
|  |  | $\mathrm{C}_{4} \mathrm{~V}$ | 4 mm |
|  |  | $\mathrm{D}_{2 \mathrm{~d}}\left(\mathrm{~V}_{\mathrm{d}}\right)$ | 42m |
|  |  | $\mathrm{D}_{4} \mathrm{~h}$ | 4/mmm |
| Trigonal | $\alpha=\beta=\gamma \neq 90^{\circ}$ | $C_{3}$ | 3 |
| (rhombohedral) | $\mathrm{a}=\mathrm{b}=\mathrm{c}$ | $\mathrm{S}_{6}$ | $\overline{3}$ |
|  |  | $\mathrm{D}_{3}$ | 32 |
|  |  | $C_{3 v}$ | 3m |
|  |  | $\mathrm{D}_{3 \mathrm{~d}}$ | $\overline{3} \mathrm{~m}$ |

contd...

| Hexagonal | $\alpha=\beta=90^{\circ} \cdot \gamma=120$ | $\mathrm{C}_{6}$ | 6 |
| :---: | :---: | :---: | :---: |
|  | $a=b=c$ | $\mathrm{C}_{3 \mathrm{~h}}$ | $\overline{6}$ |
|  |  | $c_{6 h}$ | 6/m |
| Cubic |  | $\mathrm{D}_{6}$ | 622 |
|  |  | $\mathrm{C}_{6 \mathrm{~V}}$ | 6 mm |
|  |  | $\mathrm{D}_{3 \mathrm{~h}}$ | $\overline{6} \mathrm{~m} 2$ |
|  |  | $\mathrm{D}_{6} \mathrm{~h}$ | 6/mmm |
|  | $\alpha=\beta=\gamma=90^{\circ}$ | T | 23 |
|  | $a=b=c$ | Th | $2 / \mathrm{m} \overline{3}$ |
|  |  | 0 | 432 |
|  |  | Td | 43m |
|  |  | Oh | $4 / \mathrm{m} 32 / \mathrm{m}$ |

Figure 1.1

The essential symmetry axes of six of the seven crystal systems.
$\Leftrightarrow$ a two-fold axis

A a three-fold axis
a four-fold axis

- a six-fold axis

FIG.1.1




Monoclinic

Orthorhombic
sufficiently developed faces, or in the case of a very small crystal, the system may be determined by the use of reflection goniometry, an account of which will not be attempted here. The "Barker Index of Crystals" lists common forms of many crystals. An analysis of interfacial angles with the optical goniometer may enable identification of the crystal to be made.

If the external form of a crystal can be said to possess symmetry, but is itself composed of a large number of unit cells, these unit cells must also possess the essential symmetry axes of the crystals.

Six parameters describe a parallelepiped. These are three angles $\alpha, \beta$ and $\gamma$ and three lengths $a, b$ and $c$. Figure 1.2 shows the relation of these parameters to the parallelepiped (which is the unit cell). The variation of these six parameters to create essential symmetry axes in the unit cell leads directly to the microscopic criteria which define the crystal system. The data are summarised in Table l.l. The graduation from triclinic to cubic symmetry describes an ascent in symmetry.

In the crystal, the sides of the unit cell, and the angles between them, determine the stacking directions for the unit cells. The dimensions $a, b$ and $c$ now describe "crystallographic axes" of the crystal. It is obvious from Table 1.1 that cubic, tetragonal and orthorhombic systems have orthogonal axes. Monoclinic crystals have two orthogonal axes,

FIG. 1.2


FIG. 1.3
monoclinic

$\beta \neq 90^{\circ}$
triclinic

$\alpha \neq \beta \neq \gamma \neq 90^{\circ}$
the third axis is inclined towards one of these (see figure 1.3). In this system the b (or y ) axis is sometimes referred to as the "unique axis" and corresponds to the diad axis of symmetry. Triclinic crystals have no specific relation between axes other than that all three angles are different and all three axes have different repeat lengths.

For convenience, in trigonal and hexagonal systems a fourth axis is introduced. The crystallographic $c$ axis contains the three on six fold axis of symmetry. Perpendicular to $c$ are three axes spaced at $120^{\circ}$ to each other, all of equal length and in the same plane.

A knowledge of the relationship of the crystallographic axes to the external morphology is essential to a single crystal vibrational study. A crystal may be oriented in such a way that the crystallographic axes are either parallel or perpendicular to the polarisation of incident radiation. This enables information unique to certain directions within the unit cell to be obtained; a fuller account is given in Chapter Two.

## Symmetry and the Unit Cell

A collection of symmetry elements, each of which corresponds t) a symmetry operation, is called a group. The theory of groups is covered extensively by Cotton (1971) and Bradley and Cracknell (1972), the concepts introduced here are given in outline only.

A symmetry operation may be expressed as a change of Cartesian coordinates from $x_{1}$ to $x_{2} ; y_{1}$ to $y_{2} ; z_{1}$ to $z_{2}$. A change in coordinates for $\mathrm{x}_{1}$ to $\mathrm{x}_{2}$ may be expressed as:

$$
\underline{x}_{2}=\underline{R x_{1}}+\underline{t}
$$

$\mathrm{Rx}_{1}$ represents a rotation of the coordinate system around the origin, and $t$ represents a translational displacement from the origin. If the symmetry operations are restricted to those which preserve bond lengths and bond angles, $R$ is a real orthogonal matrix which can be expressed as:

$$
\underline{R}=\left[\begin{array}{ccc}
-1 & 0 & 0 \\
0 & \cos \theta & -\sin \theta \\
0 & \sin \theta & \cos \theta
\end{array}\right]
$$

The notation commonly adopted to express a rotation followed by a translation is :

$$
\{\underline{\alpha} \mid \underline{t}\}
$$

$\underline{\alpha}$ is the operator for proper or improper rotation, i.e. those which involve a pure rotation, and a rotation plus inversion about a centre respectively; $t$ is the vector of translation.

The combinations of the type $\underline{\alpha} \mid \underline{o}\}$ involve no translational
motion and all symmetry elements pass through a point and form the "point group" of collection of atoms concerned. Combinations involving $t$ are termed "space groups". The vector $t$ is composed of a set of three translations in the $x, y$ and $z$ directions such that:

$$
t_{n}=n_{1} \underline{t}_{1}+n_{2} \underline{t}_{2}+n_{3} \underline{t}_{3}
$$

$\mathrm{n}_{1}, \mathrm{n}_{2}$ and $\mathrm{n}_{3}$ are integers, and $\underline{t}_{1}, \mathrm{t}_{2}$ and $\underline{t}_{3}$ are called the "basic primitive translations". The translations $\underline{t}_{1}, t_{2}$ and $\underline{t}_{3}$ may be used to form a lattice in three dimensions.

Before any further consideration of the unit cell, it is desirable to consider what are known as Bravais lattices. Such a lattice is an infinite collection of points which have exactly the same environment in the same orientation. A real crystal cannot have an infinite lattice but as the sizes of the atoms are very small, a crystal comprises an infinite lattice to a good approximation. It has been shown that there are only 14 such Bravais lattices and they are shown in figure 1.4. It is not necessary that the centre of every atom in a real crystal corresponds to a point of a Bravais lattice, nor is it necessary that Bravais lattice points should be occupied at all. Each Bravais lattice may be assigned to a crystal system. The labels P, I, F and C stand for primitive, body centered, fully face centred, and centred respectively, the label $R$ is also primitive (Rhombohedral).

Each point of a Bravais lattice contains all the symmetry operations of the point group of the holosymmetric class of the

FIG. 1.4

## The 14 Bravais Lattices



Orthorhombic P, Orthorhombic C,Orthorhombic I, Orthorhombic F


Monoclinic $P$


Monoclinic C


Triclinic P


Trigonal R


Trigonal and Hexagonal $C$ (or P)
crystal system. Table l.l contains the point groups of the crystal systems in column 3; the last point group in each system is the holosymmetrical class. There are only 32 point groups, each is a holosymmetrical point group of the crystal class, or a sub-group of one of these.

If we now return to the unit cell, the parallelipiped may be constructed from the basic primitive translational vectors $t_{1}, t_{2}$ and $t_{3}$. If these vectors are selected in such a way that the unit cell exhibits the symmetry of one of the Bravais lattices it is possible that the unit cell, if it contains more than one point, may not then be primitive. Where there exists a possibility of a primitive and a non-primitive unit cell a relationship can always be established becween the two. Unit cells which have labels C, F and I have 2, 4 and 2 times the volume of the corresponding primitive unit cell respectively.

Symmetry elements of a space group which are not pure translations may involve translation and rotation or translation and reflection. Because of the constraints imposed by the ordering within a crystal, it is necessary to introduce additional symmetry elements to relate identical "sites" in the unit cell or in adjacent unit cells. Such symmetry elements are called screw axes and glide planes. An ' $n$ ' fold screw axis consists of a $2 \pi / n$ rotation followed by a translation of $\frac{1}{n}$ times the unit cell length in the direction of the axis. A glide plane consists of a reflection in
a plane, followed by a translation of half a unit cell length along the plane. Figure 1.5 illustrates the concept of screw axes and glide planes. In space groups limitations are placed on the values $\theta$ can take in the rotational matrix $\underline{R}$. The values of $\theta$ allowed are $\pi / 2$ and $\pi / 3$. The result is that the number of different space groups is limited to 230. Each space group can have a "factor group" associated with it. This group is the space groups less the translational elements, and is isomorphous with a point group. The factor group of any space group is imnediately obtained from the Schonflies symbol of the space group. For example, space group P222 (no 16) $\equiv D_{2}^{1}$ in Schonflies notation, the relevant factor group is $D_{2}$ from point group tables.

In addition to the 230 space groups which are concerned with lattices in 3 dimensions, Wood. (1964) has shown that there are 80 "diperiodic groups". These groups are each related directly to a space group (as they are a sub-group of a group). The diperiodic groups, unlike the 17 strictly two-dimensional groups given in volume 1 of "International Tables for X-ray Crystallography", are concerned with lattices which are periodic in only two dimensions but admit that symmetry operations are possible in the third dimension. Such groups are very useful in considering sheet structures, where there are two dimensional lattices which have no chemical bonding between layers. The equivalent of the Bravais lattices, the 5 two-dimensional nets, for these groups are shown in figure l.6. Each of the 80 diperiodic

FIG. 1.5


FIG. 1.6

## The 5 Nets in 2 Dimensions



square $P$

hexagonal $P$
groups can be derived directly from the 230 space groups by inspection. Wood has listed the sites allowed for each of these groups and has retained the nomenclature given in I.T.X.R.C. These groups are considered in more detail in the last chapter of this thesis.

## Modes of Vibration in Crystals

An isolated non-linear polyatomic molecule has $3 n-6$ vibrational modes associated with it, where $n=$ the number of atoms. In considering a crystal it would be necessary to take into account N unit ce-.ls each containing n atoms; this yields 3 nN modes as translations and rotations cannot be ignored in solids. It is immediately obvious that an astronomical number of modes would be predicted. Fortunately, simplifications can be made. The vibrational modes of crystals can be thought of as combinations of identical vibrations in all the unit cells. The quantum of energy which describes unit excitation of one of these standing waves is called the "phonon".

Using the established equation:

$$
\begin{aligned}
& E=m c^{2}=\frac{h c}{\lambda} \\
& m c=\frac{h}{\lambda} \quad \text { mc is a momentum term and is described } \\
& \quad \text { by the vector quantity } \overrightarrow{\mathrm{P}} \\
& \overrightarrow{\mathrm{P}} \propto \frac{1}{\lambda}
\end{aligned}
$$

We can now relate $\vec{P}$ to a generalised vector $(K)$ and describe $K$ by the equation

$$
K=\frac{2 \pi}{\lambda} \quad \text { (1) } K \text { is called the wave vector }
$$

As the velocity of electromagnetic radiation in a vacuum is a constant (C) and is related to frequency ( $W$ ) and wavelength ( $\lambda$ ) by:

$$
C=W \lambda
$$

from (1) above $K \frac{l}{\lambda}$ therefore the frequency of a phonon can be related to K by:

$$
\begin{equation*}
\mathrm{W}=2 \pi \mathrm{CK} \quad \therefore \quad \mathrm{~K} \alpha \mathrm{~W} \tag{2}
\end{equation*}
$$

If a crude model is adopted, and the example of a very simple vibrating system is taken. A restoring force (F) can be expressed in terms of the displacement x .

$$
F=a x+b x^{2}+c x^{3}+\ldots
$$

If x is sufficiently small the first term predominates and the vibration is simple harmonic. Higher terms are used to describe anharmonicity, a description of which will not be attempted here. In the case of atomic lattices, no one vibration may be isolated from the others. These vibrations can then be described in terms of normal modes, each possessing an angular frequency ( $W$ ) and
wave vector (K). Each mode can therefore be quantised into phonons of energy $W$ and momentum $K$.

From (1) above $\lambda$ is the wavelength of the phonon. The relation between frequency and K is called a dispersion relation. Born and Huang (1954) have proved that for unit cells containing more than one atom $K$ has two branches, known as acoustic and optic branches. Figure 1.7 shows such a dispersion relation. The optic branch has three branches, two T.O. (transverse optic), modes, and one L.O. (longitudinal optic) mode. The acoustic branch has two branches, one T.A. (transverse acoustic) mode and one L.A. (longitudinal acoustic) mode. At values of $K$ A $O$ the two T.O. modes are degenerate, this is streated in greater detail in Chapter two; in addition the acoustic branch has effectively zero frequency and corresponds to the bulk translations of the unit cell along the $x, y$ and $z$ directions. At $K=0$ the modes predicted to occur are known as the "fundamental modes of vibration" or "factor group fundamentals"; these correspond to all unit cells vibrating in phase. Figure 1.8 shows that for all cells vibrating in phase the wave vector of the phonon is very small and the wavelength is large.

For the purposes of i.r. and Raman experiments the radiation has a frequency of no more than $2 \times 10^{4} \mathrm{~cm}^{-1}$, so that the wave vector of the radiation is $<2 \times 10^{5} \mathrm{~cm}^{-1}$. When a photon and a phonon interact the wave vector must be conserved, so that

## Figure 1.7

$W_{L}=$ L.O. frequency<br>$W_{T}=T .0$. frequency

L.O. is the longitudinal optic mode.
T.O. is the transverse optic mode.
L.A. is the longitudinal acoustic mode.
T.A. is the transverse acoustic mode.

FIG.1. 7

## A Dispersion relation


the phonon in i.r. or Raman experiments is also $<2 \times 10^{5} \mathrm{~cm}^{-1}$. This is much smaller than the largest phonon wave vector possible ( $\pi / d$ where $d$ is the lattice spacing) which is of the order of $10^{8} \mathrm{~cm}^{-1}$. Figure 1.8 shows that at $K=0$ the phonon will have infinitive wavelength and all unit cells will be vibrating in phase. Phonons with wave vector $\sim 10^{5} \mathrm{~cm}^{-1}$ have a frequency of the same order as the infinite wavelength phonon. The assumption normally made in i.r. and Raman experimentation is that $K=0$. This is the basis of the vibrational analysis used here, where only one unit cell (the primitive unit cell) is considered. The wavelength of the radiation is large in comparison to the size of the unit cell, so this assumption is justified.

In an identical uanner to which the unit cell was constructed from three translational vectors $t_{1}, t_{2}$ and $t_{3}$, it is possible to define a set of reciprocal lattice vectors, $\mathrm{g}_{1}, \mathrm{~g}_{2}$ and $g_{3}$ to construct the first Brillouin zone of the lattice.

$$
\begin{aligned}
& g_{1}=\frac{2 \pi\left(t_{2} \times t_{3}\right)}{\underline{t}_{1}\left(\underline{t}_{2} \times \underline{t}_{3}\right)} \\
& g_{2}=\frac{2 \pi\left(\underline{t}_{3} \times \underline{t}_{1}\right)}{\underline{t}_{2}\left(\underline{t}_{3} \times \underline{t}_{1}\right)} \\
& g_{3}=\frac{2 \pi\left(\underline{t}_{1} \times t_{2}\right)}{\underline{t}_{3}\left(\underline{t}_{1} \times \underline{t}_{2}\right)}
\end{aligned}
$$

the position vector $g$ of any point in reciprocal space may be given in terms of

FIG. 1.8 Unit cell vibrations in a crystal


$$
\begin{aligned}
& k=\pi / d
\end{aligned}
$$



$$
g_{n}=n_{1} g_{1}+n_{2} g_{2}+n_{3} g_{3}
$$

where $n_{1}, n_{2}$ and $n_{3}$ are integers.

A paralellipiped in reciprocal space may therefore be constructed, the coordinates of any point are given in terms of $K_{x}, K_{y}$ and $K_{z}$. The so-called zone centre is the point at which $K=0$ and is given the special symbol. $\Gamma$. The first Brillouin zone or simply Brillouin zone contains all the wave vectors $K$ of the unit cell. Much of the nomenclature relevant to Brillouin zones has been established by Koster (1963), and a mathematical treatment of Brillouin zones is given by Bradley and Cracknell (1972). Just as a unit cell has points of special symmetry, the Brillouin zone also has points of high symmetry each of which is given a special symbol. Multi-phonon modes, i.e. those which are not factor group fundamentals can sometimes be related to these special symmetry sites, a treatment of which will not be attempted here.

## Calculation of Factor Group Fundamentals

The method of calculation was first described by Bhagavantam and Venkataraywdu (1939, 1941, and 1969). The procedure is essentially the same as that of point group analysis. The atoms which comprise a unit cell form the "molecule" for analysis. It is essential only to find the number of equivalent positions under each factor group symmetry operation. It is essential
that only the primitive unit cell is used or more than the required number of modes is predicted.

The method is known as factor group analysis or F.G.A.; it is possible using this method to distinguish between internal modes of the lattice, i.e. vibrations, and the translations and rotations of any complex ions (the external modes). A fuller account of the method is given in the last chapter where a simplified F.G.A. scheme is given for the 80 diperiodic groups in three dimensions. It is obvious that a large amount of tedious arithmetic is involved. A revised method described by Newton (1970) and published as a set of tables (Adams and Newton 1970) is available for the 230 space groups, whereby the irreducible representations for any lattice may be directly read without calculation. It is essential only to know the Wyckoff notation of the sites occupied by the atoms in the structure, and that the axes chosen are the "standard set" given in "International Tables for X-Kay Crystallography". The equivalence between axes is given in the appendices of volume 1 of the I.T.X.R.C. tables.

An alternative approach to the calculation of the factor group fundamentals is to use the correlation method. This method was first described by Halford (1946) and was shown to be equivalent to F.G.A. by Hornig (1948). From the irreducible representation of a complex ion or molecule correlation tables are used
to observe the changes of symmetry species which occur on correlation to the site occupied by the "centre of gravity" of the complex ion. This so-called site field is the symmetry of the field acting on the complex ion by virtue of its environment. Correlation to the factor group symmetry of the lattice then yields the symmetry species for the internal modes. The coupling between complex ions in a unit cell is responsible for this last assignment of symmetry species. In a simple case a bimolecular unit cell will couple to give in phase and out of phase components for the vibrations of the isolated complex ion. Davrdov splitting is the term given to the frequency range of the split between modes of identical type in the crystal. The larger the frequency range the greater the interaction between the complex ions. The correlation method is useful in predicting the intensity of modes expected. A mode which is inactive in a complex ion, but which gains activity by virtue of the site field can reasonably be presumed to be weak; a mode which is active in the complex ion can be presumed to be a strongly allowed mode. F.G.A. gives no indication of the origin of the modes predicted and it is useful to use both methods so that absences in spectra may be explained on the basis of the site field. It is possible in certain circumstances to make the assumption that a distinction between internal and external modes is possible. For the case of molecular crystals where there is very little interaction between molecules; the interatomic forces are very much greater than the long-range
forces between molecules, it may be possible to distinguish the internal modes from the external modes which are expected to occur at much lower frequency. The class of structures which may be called complex ions will have much larger interactions between them and the regions of the spectrum where they occur may well overlap considerably. In addition it is possible that the modes may become mixed, where atomic displacements are similar modes of the same symmetry species may interact. In the extreme case of ionic lattices such a distinction is impossible since the bonding between atoms has very little directional character and the long range forces between atoms may be very large indeed. The notation of translatory, rotatory and internal modes may le reserved only for accounting purposes unless isotopic data is available which proves beyond doubt that a particular mode can be assigned.

## The Indicatrix

Light has a sinusoidal wave motion transverse to its propagation direction in two mutually perpendicular planes. One of these sinusoidal motions is the magnetic vector and will be disregarded for the purposes of this thesis since the effects produced by it are not significant in the work reported here. The other wave motion is the electric vector, the direction of which is hereafter called the polarization direction. The
term light is taken to refer to all parts of the electromagnetic spectrum, not only the visible region.

The optical properties of all crystal systems, excluding in most cases cubic crystals, are anisotropic, i.e. vary with orientation. One property which is particularly dependent upon the symmetry of the lattice is the refractive index ( $n$ ). When light is incident upon the boundary between two layers of differing refractive indices, refraction occurs, unless incidence is normal to the boundary. Crystals have differing refractive indices associated with the crystallographic axial directions, except cubic crystals. However, even in the case of normal incidence for crystals the light is split into two rays. This phenonmenon is known as "double refraction". The refractive indices of crystals show dispersion, i.e. vary with wavelength, however this effect is sufficiently small to be ignored for the purposes of vibrational spectroscopy.

Double refraction may occur in one of two forms for all crystal systems except the cubic system, which is isotropic and does not exhibit double refraction. The two cases are uniaxial and biaxial crystals. For uniaxial crystals the two rays produced are known as the ordinary and extraordinary rays. The ordinary ray is undeviated from its path, the extraordinary ray is deviated from the plane of incidence. Both rays travel through the crystal with electric vectors polarized in mutually perpendicular
directions, and with differing' phase velocities. For biaxial crystals both rays are extraordinary. Both rays are polarized in mutually perpendicular directions and have differing phase velocities. Figure l.9(a) demonstrates the concept of double refraction in uniaxial and biaxial crystals. The two rays may interact to produce interference, this is used as an analytical method by geologists and is known as birefringence; an account is given by Cox, Price and Harte (1967).

The Indicatrix is the term given to the three dimensional representation of the refractive properties of crystals. Walhstrom (1960) has shown that this takes the form of an ellipsoid of revolution. For light incident from any direction the refractive indices and polarization of the two rays produced are given by the magnitudes and directions of the semiaxes of that section of the ellipsoid normal to the direction of incidence.

It is iseful at this stage to introduce a term known as the "optic axis". Uniaxial crystals have one optic axis, biaxial crystals have two optic axes. Optic axes are the directions normal to which the sections of the indicatrix ellipsoid are circular. Light incident along these directions is isotropic and is not doubly refracted. The ellipsoid of revolution for uniaxial crystals has one axis of revolution, which corresponds to the optic axis. The ellipsoid of revolution of biaxial crystals is a triaxial ellipsoid. Figure l.9(b) shows the three

FIG. 1.9 (a)

Uniaxial crystal
Crystal


Biaxial crystals


Ellipses represent the three principal sections
principal sections of the ellipsoid for biaxial crystals. The three axes of revolution may be related to two-fold axes of symmetry in some crystals classes, this is discussed in greater detail later; the optic axes are not fixed by any symmetry and their position is not usually of concern for single crystal spectroscopy.

- The optic axes for uniaxial crystals corresponds to the three, four or six-fold axis of symmetry of trigonal, tetragonal an hexagonal crystal systems respectively. The three two-fold axes of symmetry of the biaxial ellipsoid may be related to twofold axes of symmetry of orthorhombic and monoclinic crystals; triclinic crystals are also biaxial, but the two-fold axes are not related to any symmetry elements as triclinic crystals may have only a centre of inversion as a symmetry element. For orthorhombic crystals the three axes of the ellipsoid are the three two-fold axes of symmetry of the system. For monoclinic crystals one axis of the ellipsoid is the unique axis of the system, the other two axes need not correspond to other two fold axes although they are required to be coplanar with them.

The three two fold axes of the biaxial ellipsoid are directions along which no double refraction occurs, as these correspond to the vibration directions of the extraordinary rays produced by double refraction. Radiation polarised parallel to one of these directions will therefore not be doubly refracted as no component of the radiation exists which can produce another ray.

In conclusion, the optical properties of crystals may be of use to determine the axes of the crystal. A polarising microscope is used to determine the position of axes within a crystal; this is essentially the same as an ordinary microscope but it has two polarisers set at $90^{\circ}$ to each other. One polariser is mounted in the collimator of the light beam which passes through the optics, the other polariser is mounted in the eye-piece. If a crystal is rotated on the microscope stage with both polarisers in place it will be seen that in certain orientations there is total extinction of light passing through the crystal. Along these directions the light is not doubly refracted, therefore the initial polarisation of the light is maintained. This light cannot be observed with the second polariser in place as the polarisation directions are mutually perpendicular. It is clear therefore that these orientations locate the optic axis of uniaxial crystals, and therefore the 3, 4 or 6 fold axis of symmetry, and the two fold axes of symmetry of orthorhombic and monoclinic crystals. Thus it is possible to locate the axes of crystals by a simple experiment; this enables the axes to be related to the external morphology which is essential for oriented studies in polarised light.

For uniaxial crystals: trigonal, tetragonal and hexagonal systems, the axis of symmetry is easily located and other axes are perpendicular to this axis, further confirmation is seldom required. For biaxial crystals: orthorhombic, monoclinic and
triclinic; the indicatrix axes are of use to locate crystallographic axes but they give no indication of which axis is which. A determination in these circumstances must be done by X-ray methods.

An account of X -ray methods of location of axes will not be given here but has been reviewed by Henry, Lipson and Wooster (1954), and Stout and Jensen (1968).

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## Section A

A Review of I.r. Reflectance Spectroscopy and Techniques
I.r. Spectroscopy

A great deal of the i.r. information collected for this thesis was obtained using the method of reflectance spectroscopy.

The following is an account of the reasons for choosing reflectance methods, the experimental advantages of using the technique and the disadvantages inherent in the method. A review of reflectance methods is given, which includes the theory essential to an understanding of the method. Where possible derivations of formulae are given, in the case of exhaustive mathematical treatments to obtain formulae no derivations are given but references are quoted for further reading. Some account of the history of the development of the technique is also given. The final section deals with the problems encountered with reflectance spectra and the subtle adjustments to data which are sometimes necessary to achieve meaningful analyses.

Reflectance and Transmission Methods

All people who have attempted single-crystal transmission experiments will appreciate the extreme difficulty encountered in preparing the sufficiently thin slices of crystal required. If the crystal absorbs radiation very strongly thicknesses of the order of l-2 $\mu \mathrm{m}$ may be necessary, thicknesses of $10-20 \mu \mathrm{~m}$ are common.

If the crystal is air stable, non-hygroscopic and only sparingly solu: ble in a non-toxic, non-volatile solvent (e.g. water) thinning the crystal to the final stages of preparation is not difficult, if perhaps extremely tedious. The last stages of preparation are often achieved by polishing on a soft surface to avoid cracking the very thin sample.

Transmission experiments sometimes fail due to some adhesive between the crystal and the transparent medium onto which it is mounted. This may have the effect of increasing sample thickness beyond a critical value, or it may act as a cut-off filier for the transmitted radiation.

Low temperature work can be a lengthy procedure, nearly all infra-red transmitting materials are poor conductors of heat; thus -ong cooling periods may be necessary to achieve very low temperatures at the sample.

For reflectance measurements, the crystal is mounted directly onto a medium of high thermal conductivity (normally copper) using a quick setting epoxy resin, into which fine aluminium powder has been incorporated in order to increase thermal contact. A crystal once mounted in such a manner is immediately ready for experimental work, unless a small amount of polishing is required first.

If i.r. data are required throughout the entire frequency range ( $10-4000 \mathrm{~cm}^{-1}$ ) transmission measurements would be required
with different transparent media. It would be necessary to remove the crystal from one mount for the high frequency range ( KBr ) and mount again onto the medium for low frequency work (polythene). This can be an extremely perilous operation, the alternative is to mount and thin another crystal. Reflectance does not rely on any transparent media and the same sample may be used for all frequency ranges. Figure 2.1 shows the apparatus used to obtain reflectance data up to $1000 \mathrm{~cm}^{-1}$, using the Beckmann RIIC FS720 interferrometer; other reflectance units are of similar design. The Polyethylene window is removed for ranges above $400 \mathrm{~cm}^{-1}$, when in place, it allows the sample compartment to be evacuated independently of the rest of the machine. This enables beam splitters to be changed during low temperature work.

If hygroscopic or air-sensitive crystals are studied a method is given in this thesis of using reflectance techniques. Hygroscopic samples in extremely thin sections may easily dissolve in the small amount of water produced by evacuating an instrument, by the de-gassing which is encountered. Reflectance spectroscopy has one serious drawback, that is that adsorption frequencies cannot be estimated visually without considerable experience in the technique. However data may be analysed using one of the methods described herein in order to obtain accurate parameters.

FIG. 2.1


Mitra and Gielisse (1964) have extensively reviewed this subject and only an account relevant to this thesis is given here.
I.r. activity is associated with the interaction of the oscillating electric vector of the radiation and the oscillating electric dipole present in a molecule or primitive unit cell. If there is a change in dipole moment, i.r. activity will occur, hence homonuclear diatomics which have no dipole moment are not i.r. active. The irreducible representation of a molecule or primitive unit cell is given in terms of symmetry species. If one or more of these species are associated with the translational vectors $x, y$ and $z$, ir. activity will occur.

If polarised radiation is used, such that the plane of the electric vector of the radiation is incident on a specific orientation of the primitive unit cell; only the component of the dipole which is coplanar interacts strongly. The component of the dipole which is perpendicular to the plane of the radiation has effective $\_$y zero interaction. Thus symmetry species associated with the respective $x, y$ and $z$ vectors of the unit cell can be excited uniquely. This enables the spectrum of a unit cell to be decomposed into bands associated with a symmetry species and a complete assignment is possible.
I.r. activity in crystalline solids is associated with three types of phonons. These are known as Transverse Optic phonons (T.O.) and Longitudinal Optic phonons (L.O.). At the centre of the Brillouin zone where $K=0$ the two T.O. modes are degenerate (See figure 2.3(b)). The two T.O. modes correspond to the vibrations of the primitive unit cell when the plane containing the electric vector of the radiation and the dipole moment is perpendicular to the direction of the propagation of the radiation. (See figure 2.2(a)). The Longitudinal optic phonon can be described as the interaction with the radiation of the charge variation on the surface of the unit cell; this oscillates about a position with its own frequency. L.O. modes can be uniquely observec by the technique devised by Berreman (1963), which has also been used by Hargreave (1971). The method entails using oblique angles of incidence on thin films of substrates, usually in contact with highly polished surfaces. If the angle of incidence is sufficiently oblique the electric vector of the radiation is approximately parallel to the surface of the crystal; and is therefore aligned favourably for strong interaction with the surface charge variation (see figure 2.2(b)). L.O. modes can also gain activity in the Raman process where the factor group is non-centrosymmetric (see Chapter 2, section B).

```
                    If we confine our attention to angles of near normal
    incidence, we might reasonably expect that only T.O. modes will
    be active in the general case. In transmission measurements
    which use normal incidence, only T.O. modes will be active.
```

FIG. 2.2(a)

(normal incidence)

FIG.2.2(b)

(oblique incidence)

FIG. 2.3 (a)


FIG. 2.3 (b)


## Reflectance Spectroscopy

In order to explain the phenomenon of the interaction of radiation at a plane surface, it is necessary to introduce symbols which represent the microscopic physical effects which occur.

The following are given without derivation:
$P$ represents the electric polarisation, defined as the dipole moment per unit volume in the medium.
$E$ is the average electric field within the medium.
D is the electric displacement caused by the electromagnetic
field in the medium.
$D, E$ and $P$ are related by the following equation

$$
D=E+4 \pi P
$$

We now consider the effect of a monochromatic plane wave of angular frequency $w$ and wave vector $K$ travelling through a crystalline medium. The electric field $E$ of the wave will cause forced oscillations of the atomic particules, a linear relationship between $D$ and $E$ will then exist.

$$
\underline{D}=\underline{E}
$$

Because both $\underline{D}$ and $\underline{E}$ are vector quantities $\varepsilon$ is a 2nd rank tensor. $\underline{\varepsilon}$ is called the dielectric tensor and has six components represented by (taking $x, y$ and $z$ orthogonal components, which correspond
to the crystallographic axes in orthorhombic and higher symmetry systems).

$$
\begin{aligned}
& D_{x}=\varepsilon_{x x} E_{x}+\varepsilon_{x y} E+\varepsilon_{y z} E_{z} \\
& D_{y}=\varepsilon_{y x} E_{x}+\varepsilon_{y y} E_{y}+\varepsilon_{y z} E_{z} \\
& D_{z}=\varepsilon_{z x} E_{x}+\varepsilon_{z y} E_{y}+\varepsilon_{z z} E_{z} \\
& \left(\varepsilon_{x y} \equiv \varepsilon_{y x}\right)
\end{aligned}
$$

Using polarised radiation oriented along the principal axes, non-diagonal terms are zero.

Thus the relations reduce to:
$D_{x}=\varepsilon_{x x} E_{x}$
$D_{y}=\varepsilon_{y y} E$

$$
D_{z}=\varepsilon_{z z} E_{z}
$$

For tetragonal, hexagonal and orthorhombic systems $E$ must be either parallel or perpendicular to the crystallographic $z$ direction, if non-diagonal terms are to be excluded. For cubic systems (isotropic) $\varepsilon$ does not vary with orientation. Mostellar and Wooton (1968) have examined the validity of the above relations and reviewed the dielectric theory involved.
$\varepsilon$ can be thought of as the response of the crystal to a perturbing field of frequency $w$ and is therefore itself a function of frequency (see figure 2.3(a)).

If the radiation is absorbed by the medium, there will be a phase difference between $D$ and $E$ by virtue of the finite relaxation time of a vibrational mode. This can be included in the theory by allowing $\varepsilon$ to have complex values. Born and Huang (1954) have produced a mathematical treatment of lattice vibrations in which the proof can be found.

Thus $\varepsilon$ can be expressed as:

$$
\begin{equation*}
\varepsilon=\varepsilon_{1}+i \varepsilon_{2} \tag{2}
\end{equation*}
$$

where $\varepsilon_{1}$ and $\varepsilon_{2}$ are the real and imaginary parts respectively of the dielectric tensor.

The refractive index ( $n^{*}$ ) of a material may be defined as the ratio of the velocity in a vacuum (c) to a phase velocity ( $\mathrm{V}^{*}$ ) in the medium, i.e.

$$
n^{*}=\frac{c}{V^{*}} \quad \text { (3) } \quad \text { i.e. } \quad V^{*}=\frac{c}{n^{*}}
$$

Hodgson (1970) has derived from Maxwell's relations a relationship between wave-vector $K$, dielectric tensor $\varepsilon$ and the velocity of electromagnetic radiation in a vacuum (c), with respect to frequency of the radiation (w).

$$
\begin{equation*}
c^{2}(K \cdot K)=w^{2} \varepsilon \tag{4}
\end{equation*}
$$

This is easily rearranged to give

$$
\begin{equation*}
\frac{\mathrm{W}}{\mathrm{~K}}=\frac{\mathrm{c}}{\varepsilon^{\frac{1}{2}}} \tag{5}
\end{equation*}
$$

as $K=\frac{2 \pi}{\lambda}$ and $c=w \lambda, \frac{w \lambda}{2 \pi}=\frac{c}{\varepsilon \frac{1}{2}}$
$\varepsilon^{\frac{1}{2}}$ is dimensionless. $c / \varepsilon^{\frac{1}{2}}$ is therefore a phase velocity. The similarity with equation (3) may be used to define $n^{*}$ in terms of $\varepsilon$, i.e. $n^{*}=\varepsilon^{\frac{1}{2}}$ or $n^{* 2}=\varepsilon$. (6) from $n^{*}=c / \frac{c}{\varepsilon^{\frac{1}{2}}}$.

We have therefore established a link between microscopic quantities ( $D, E$ and $P$ ) and macroscopic quantities ( $n$ ) via this relation.

However, it follows that if $\varepsilon$ is complex $n$ may also have complex values, i.e.

$$
n^{*}=\left(n_{1}+i n_{2}\right)
$$

which is usually expressed in the form

$$
\begin{equation*}
n^{*}=\left(n_{1}+i k\right) \tag{7}
\end{equation*}
$$

$\mathrm{n}_{1}$ is called the refractive index and k the extinction coefficient. (Hereafter for simplicity the nomenclature $n \equiv n_{1}$ is established) from the form of equations (6) and (7).

$$
\begin{aligned}
& \varepsilon \equiv\left(\varepsilon_{1}+i \varepsilon_{2}\right) \equiv n^{* 2} \equiv(n+i k)^{2} \\
& \therefore\left(\varepsilon_{1}+i \varepsilon_{2}\right)=\left(n^{2}-k^{2}+2 i n k\right)
\end{aligned}
$$

equating real and imaginary parts.

$$
\begin{align*}
& \varepsilon_{1}=\mathrm{n}^{2}-\mathrm{k}^{2}  \tag{11}\\
& \varepsilon_{2}=2 \mathrm{nk} \tag{12}
\end{align*}
$$

It is therefore clear, that a route has been established to enable the dielectric tensor to be calculated from other parameters. If $n$ and $k$ are known for any frequency (w), the real and imaginary parts of $\varepsilon$ may be uniquely established.

Reflectance spectra often include very broad bands, unlike those obtained in transmission measurements. The area of large variation of reflectance with frequency is known as the Reststrahlen region.

During absorption of radiation, the dielectric tensor shows large variations with frequency. Figure $2.3(a)$ shows that at zero frequency $\varepsilon$ has a value denoted by $\varepsilon_{0}$. In the region of absorption (bounded by $\mathrm{w}_{\mathrm{T}}$ and $\mathrm{w}_{\mathrm{L}}$ ) $\varepsilon$ undergoes a catastrophe for the ideal case (a $100 \%$ ionic diatomic lattice). This is explained in classical terms by the introduction of complex values of $\varepsilon$. When the region of absorption has been passed $\varepsilon$ returns to a slowly varying function with respect to frequency, and will
assume a constant value at infinite wavelength denoted by $\varepsilon_{\infty}$. At this limit, it is assumed that $\varepsilon$ has real values only and hence from equation (6)

$$
\varepsilon_{\infty}=n^{2} \quad(k \approx 0)
$$

where $\mathrm{n}=$ visible light refractive index.

Mitra and Nudelman (1969) have reviewed the link between the quantities $\varepsilon_{0}, \varepsilon_{\infty}$ and $\varepsilon$ as a function of frequency. They state (for a one oscillator model):

$$
\begin{equation*}
\varepsilon=\varepsilon_{\infty}+\frac{\left(\varepsilon_{o}-\varepsilon_{\infty}\right) \mathrm{w}_{o}^{2}}{\mathrm{w}_{\mathrm{o}}^{2}-\mathrm{w}^{2}} \tag{13}
\end{equation*}
$$

$\mathrm{w}_{\mathrm{O}}$ and w are frequency terms.
Equation (13) is known as the dispersion formula.

From the Fresnel formula:

$$
\begin{equation*}
R=\left\{\frac{\left(n^{*}-1\right)}{\left(n^{*}+1\right)}\right\}^{2} \tag{14}
\end{equation*}
$$

where $R$ is the observed reflectance at any wavelength (w), and n is the refractive index at that wavelength.

Using

$$
\begin{align*}
& n^{*}=\varepsilon^{\frac{1}{2}} \\
& R=\left\{\frac{\left(\varepsilon^{\frac{1}{2}}-1\right)}{\left(\varepsilon^{\frac{1}{2}}+1\right)}\right\}^{2} \tag{15}
\end{align*}
$$

we have a direct link between $\varepsilon$ and the observed reflectance.

From equation (13) when $w=w_{o} \varepsilon$ will tend to $\infty$ $\therefore \mathrm{R}$ from equation (15) will tend to 1.

When w is infinitesimally greater than $w_{0} \varepsilon \rightarrow-\infty(R=1)$ and will remain negative until a frequency satisfies

$$
0=\varepsilon_{\infty}+\frac{\left(\varepsilon_{0}-\varepsilon_{\infty}\right) w_{0}{ }^{2}}{w_{0}^{2}-w^{2}}
$$

which is $w=\left(\varepsilon_{0} / \varepsilon_{\infty}\right)^{\frac{1}{2}} \mathrm{w}_{\mathrm{o}}$
In this case $\varepsilon=0$ therefore $\mathrm{R} \rightarrow \mathrm{o}$.

Figure 2.4(a) illustrates this theoretical phenomenon $\left(\gamma / w_{0}=0.00\right)$. The values of $w$ for $w_{0}$ and $\left(\varepsilon_{0} / \varepsilon_{\infty}\right)^{\frac{1}{2}} w_{0}$ correspond to $w_{T}$ and $w_{L}$ of figure $\cap .3(a)$ and are the T.O. and L.O. frequencies respectively.

In practice this effect is never seen because of a parameter known as damping. In the absence of anharmonicity, i.e. a system which conforms to classical simple harmonic motion, damping introduces a mechanism whereby energy can leak out of the vibrational modes into other modes, and as such is a function of the lifetime of both T.O. and L.O. modes. Thus it may be reasonably expected that the lifetimes of these modes will influence the shapes of the reflectance curves obtained.

Cochran (1973) has given a brief account of the concept of damping. Damping can be conceived as a frequency dependent

FIG. 2.4 (a)


FIG. 2.4(b)

variable; in the classical sense, it is described however as a single constant value $\gamma$, which is often scaled $\gamma / w_{0}$ for convenience (Mitra 1963).

Figure 2.4(a) shows the effect of changing the value of the constant $\gamma / w_{0}$ in a synthetically generated spectrum, and illustrates the unreliability of visually estimating the T.O. frequency (which remains constant throughout).

The frequency dependence of $\gamma$ has been examined by Gervais and Piriou (1974). Using a semi-quantum model they have deduced the dependence of damping, as a function over all frequencies and temperatures, in this case damping is given by symbol $\Gamma$ to distinguish it from the classical constant value.

Denham and Field et al (1969) have used a frequency dependent damping function, based on quantum mechanical arguments by Cowley (1963). Using the real and imaginary parts of the dielectric tensor, along with the constants $\varepsilon_{o}$ and $\varepsilon_{\infty}$ the damping function can be expressed as

$$
\Gamma_{(w)}=\frac{\left(\varepsilon_{0}-\varepsilon_{\infty}\right) w_{o}}{2} \frac{\varepsilon_{2}(w)}{\left(\varepsilon_{1}(w)-\varepsilon_{\infty}\right)^{2}+\varepsilon_{2}(w)}
$$

Mitra (1963) has shown that for a classical damping ( $\gamma$ ) the values of $\gamma / w_{o}$ are linear to a very good approximation with respect to the maximum value of the reflectance function.

Figure 2.4(b) shows the variation of $\gamma / w_{0}$ with respect to $1 / R_{\text {max }}$ calculated from figure 2.4(a). The concept of a single value for $\gamma$ is the one adopted here for reflectance analysis.

It remains to be established how the exact value of the T.O. frequency can be obtained. The L.O. frequency in the case of centrosymmetric solids does not assume such importance, as these are inactive in i.r. transmission and are therefore not observed.

Two such methods exist for routine analysis of samples.
a) what has become known as Kramers-Kronig analysis ( $k-k$ ), b) slassical dispersion analysis (C.D.).

## Kramers-Kronig Analysis

The phenomena of absorption and the phase shift of waves has been known for some time. Kramers and Kronig independently discussed the application of some of the known relations to optical absorption.

The significance of the real and imaginary parts of the dielectric tensor become apparent when the variation of these with frequency is established. Simon (1951) demonstrated a proof that the maximum of the imaginary part of the dielectric tensor (2nk) corresponds to the T.O. frequency. Similarly the node (=0) of the real part of the tensor corresponds to the L.0. frequency.

Therefore what is required is to establish the variation of n and k with frequency. The functions $\varepsilon_{1}$ and $\varepsilon_{2}$ can then be calculated for any frequency and the T.O. and L.O. established.

Simon (1951) gives one of the first accounts in the literature of the study of materials by reflectance. In the absence of more sophisticated methods, it was necessary to collect data at two angles of incidence. Simultaneous equations were then used to solve unique values for $n$ and $k$ at any particular wavelength. In order to by-pass the tedium of a great deal of routine calculation, Simon used a graphical method of analysis. It is interesting to note that Simon observed distortions of the observed reflectivity at large angles of incidence i.e. $\approx 70^{\circ}$, remembering the Berreman method of establishing L.O. modes at oblique incidence. Simon reported the difficulty of obtaining reflectance measurements at oblique incidence, but concluded that the technique showed promising results.

The determination of the optical constants $n$ and $k$ from one set of data collected at near normal incidence was first discussed in detail by Robinson (1952). The method used to obtain the i.r. spectrum of P.T.F.E. by Robinson and Price (1953); however, graphical solutions were still necessary. The conclusion to the paper indicated that some form of computation was necessary to make the method easier to use in a routine manner.

The one angle of incidence technique is made practical by studying the phase change on reflection of the reflected wave. Bowlden and Wilmshurst (1963) have extensively reviewed the technique and tested the results obtained for errors in the input data. They concluded that the results were of the same order of accuracy as low resolution absorption experiments.

The phase change on reflection $(\theta)$ is related to the observed reflectance ( $R$ ) and the amplitude coefficient ( $r$ ) by:

$$
\begin{equation*}
(R)^{\frac{1}{2}}=r e^{i \theta} \tag{16}
\end{equation*}
$$

Bowlden and Wilmshurst have shown by the application of the Cauchy theorem, that $\theta$ can be related directly to $(R)^{\frac{1}{2}}$ by

$$
\begin{equation*}
\theta\left(w^{-}\right)=\frac{2 w^{-\theta}}{\pi} \int_{0}^{\infty} \frac{\ln (R)^{\frac{1}{2}}(w)-\ln (R)^{\frac{1}{2}}\left(w^{-}\right)}{\left(w^{2}-w^{-2}\right)} \tag{17}
\end{equation*}
$$

using the Kramers-Kronig dispersion relations (Kronig (1926) and (1929)), and that the optical constants $n$ and $k$ can be derived from $\theta$ by the following relations:

$$
\begin{align*}
& \mathrm{n}=\frac{1-\mathrm{R}}{1+\mathrm{R}-2(\mathrm{R})^{\frac{1}{2}} \cos \theta}  \tag{18}\\
& \mathrm{k}=\frac{-2(R)^{\frac{1}{2}} \operatorname{Sin} \theta}{1+R-2(R)^{\frac{1}{2}} \cos \theta} \tag{19}
\end{align*}
$$

The phase angle $\theta$ may show minor discrepancies due to the
magnitude of $(R)^{\frac{1}{2}}$ at all other frequencies. It is here that the small errors in $\theta$ have to be catered for in adjustments to the reflectance spectrum in analysis.

Figure 2.5 shows the parameters obtained from a $K-K$ analysis. The L.O. mode frequencies are established from the real part of the dielectric function (labelled $\varepsilon^{\prime}$ by convention) and the T.O.s from the maximum of the imaginary part function ( $\varepsilon^{\prime \prime}$ by convention). The variation of n and k will be discussed later.

## Classical Dispersion Theory

The dispersion formula (equation 13) may be re-written to include a damping term (Nudelman and Mitra 1969).

For a simple harmonic oscillator:

$$
\begin{equation*}
\varepsilon(\mathrm{W})=\varepsilon_{\infty}+\frac{\left(\varepsilon_{0}-\varepsilon_{\infty}\right)}{l-\left({ }^{W} / \mathrm{W}_{0}\right)^{2}-i\left(\gamma / \mathrm{w}_{0}\right)\left(\mathrm{W} / \mathrm{w}_{0}\right)} \tag{20}
\end{equation*}
$$

This equation is now complex, but will generate realistic reflectance spectra for suitable values of $\varepsilon_{0}, \varepsilon_{\infty}, w_{o}$ and $\gamma$.

Damping must be included or the reststrahlen region would resemble figure $2.4(\mathrm{a})\left(\gamma / \mathrm{w}_{0}=0.00\right)$.

Equation (20) can be expanded in terms of real and imaginary parts to obtain $\varepsilon^{\prime}$ (real function) and $\varepsilon^{\prime \prime}$ (imaginary function) to give

FIG. 2.5

$\varepsilon^{\prime}=n^{2}-k^{2}=\varepsilon_{\infty}+\frac{\left(\varepsilon_{o}-\varepsilon_{\infty}\right)\left(1-\left(w / w_{o}\right)^{2}\right)}{\left(1-\left(w / w_{o}\right)^{2}\right)^{2}+\left(\gamma / w_{o}\right)^{2}\left(w / W_{o}\right)^{2}}$

Seitz (1940) gives an alternative form by introducing a parameter known as oscillator strength. This is effectively a measure of the width of a band between T.O. and L.O. frequencies.

$$
\begin{align*}
& \varepsilon^{\prime}=\varepsilon_{\infty}+\left(\frac{B_{j}\left(w_{o}{ }^{2}-w^{2}\right)}{\left(w_{o}{ }^{2}-w^{2}\right)^{2}+\gamma^{2} w^{2}}\right)  \tag{23}\\
& \varepsilon^{\prime \prime}=\left(\frac{B_{j} \gamma w}{\left(w_{o}^{2}-w^{2}\right)^{2}+\gamma^{2} w^{2}}\right) \tag{24}
\end{align*}
$$

$B_{j}$ is the oscillator strength of an oscillator $j$ at T.O. $=w_{o}$ and damping $=\gamma$.

For multi-oscillator problems this is the more convenient form to use and the bracketed expressions must be summed over all oscillators.

Classical dispersion analysis involves the generation of a spectrum using equations $21-24$, and the subsequent variation of parameters to obtain a good fit with observed data. Final values then correspond to the parameters of the observed oscillator.

It is immediately obvious that this task is almost impossible without the aid of an iterative routine which adjusts parameters automatically in the computer program used. The monitoring of the progress is done by calculating functions $\varepsilon^{\prime}$ and $\varepsilon^{\prime \prime}$ and solving for $n$ and $k$ (a trivial task) and then the reflectivity at any wavelength is calculated via a revised Fresnel formula.

$$
\begin{equation*}
R=\frac{(n-l)^{2}+k^{2}}{(n+l)^{2}+k^{2}} \tag{14b}
\end{equation*}
$$

$n$ * in the original formula (14) is replaced by ( $n+i k$ ). In regions of transparency $k \not \approx 0$ and the equations are identical.

Spitzer and Kleinman (1963) used the damped simple harmonic oscillator model to reproduce the reflectance spectrum of o quartz. Barker and Hopfield (1964) reported however, that the model failed to predict the dielectric behaviour of some Perovskite structure oxides, and determined the reason for failure as the non-dependence of the damping function with frequency.

Andermann, Caron and Dows(1.965) suggested a frequency dependent correction term to $\theta$. The basic assumption was that the phase angle $\theta$ can be split into components.

$$
\theta=\Delta \theta_{\mathrm{L}}+\theta_{\left(\mathrm{W}_{\mathrm{O}}\right)}+\Delta \theta_{\mathrm{u}}
$$

$\theta_{\left(w_{0}\right)}$ represents the contribution to $\theta$ at any frequency, from the reflectivity over the entire range of absorption of radiation and as such is equivalent to equation (17).
$\Delta \theta_{\mathrm{L}}$ and $\Delta \theta_{\mathrm{u}}$ represent respectively the contribution to $\theta$ from the regions below the lowest oscillator and above the highest oscillator, regions of transparency.

$$
\begin{align*}
& \Delta \theta_{L} \text { and } \Delta \theta_{u} \text { were evaluated as: } \\
& \Delta \theta_{L}=\frac{1}{2 \pi} \int_{0}^{w_{0}}\left(\ln r_{1}-\ln r_{2}\right)\left\{\frac{\ln \left(w_{1}-w_{2}\right)}{\left(w_{1}+w_{2}\right)}\right\} \tag{25}
\end{align*}
$$

Subscript 1 represents the first data point. Subscript 2 represents all other data points up to $w_{0}$.

$$
\begin{equation*}
\Delta \theta_{u}=-\frac{1}{2 \pi} \int_{w_{0}}^{\infty}\left(\ln r_{3}-\ln r_{4}\right)\left\{\frac{\ln \left(w_{3}-w_{4}\right)}{\left(w_{3}+w_{4}\right)}\right\} \tag{26}
\end{equation*}
$$

Subscript 3 represents the highest data point. taken. Subscript 4 represents all other data points from $w_{0}$ to the last point.

Use of equations (25) and (26) partially overcomes the difficulties associated with a non-variable damping function, and the imperfections introduced by it.

Verleur in a review (1968) showed how effective the simple harmonic oscillator model can be at determining optical constants over a very limited range. This was effected by assigning additional oscillators (which need not correspond to real oscillators) outside the range studied, in order to fit the observed reflectivity
spectrum and thus obtain the parameters required.

Gervais and Piriou (1974) have extended the simple harmonic oscillator model, using a semi-quantum model. In this system L.O. modes are taken into account along with T.O. modes, thus an estimate of oscillator strength is no longer needed.

$$
\begin{equation*}
\varepsilon=\varepsilon_{\infty} \prod_{j} \frac{w_{j(L . O .)}^{2}-w^{2}-i \gamma_{j(L . O .)^{w}}}{w_{j(T . O .)}^{2}-w^{2}-i \gamma_{j(T . O .)^{w}}} \tag{27}
\end{equation*}
$$

is the form used.
$W_{j(L . O .)}$ and $\gamma_{j(L . O .)}$ are the L.O. frequency and damping term respectively.
$w_{j(T . O .)}$ and $\gamma_{j(T . O .)}$ are the T.O. frequency and damping term. A program has been devised in this laboratory to utilise the method of equation (27) and produced a high consistency with observed data.

An essential pre-requisite of classical dispersion analysis is to do a Kramers-Kronig analysis initially, to establish T.0. frequencies and the damping function. Although $\gamma / w_{0} \alpha \frac{l}{R} \max$ (Mitra 1963), the band width at $\frac{1}{2}$ peak height of the $\varepsilon^{\prime \prime}$ maxima $=2 \Gamma$ and thus the damping term may be calculated accurately. Calculated values can then be compared with those obtained from $\mathrm{K}-\mathrm{K}$ analysis for accuracy.

The programs written as an integral part of this thesis all output the following parameters as a function of frequency.
a) observed reflectance
b) refractive index ( n )
c) extinction coefficient (k)
d) real part of the dielectric tensor ( $\varepsilon^{\prime}$ )
e) absorption coefficient ( $\alpha$ )
f) conductivity ( $\sigma$ )
g) imaginary part of the dielectric tensor ( $\varepsilon^{\prime \prime}$ )

Of these, two have not yet been described.
i) Absorption coefficient ( $\propto$ ): This is calculated from the extinction coefficient (k) by the following equation.

$$
\alpha=4 \pi k / \lambda
$$

where $\lambda=$ wavelength of the radiation in a vacuum and is approximately equal to $c / w$, where $w$ is the frequency of the radiation. $\alpha$ may be used in the familiar Lambert's law:

$$
I_{x}=I_{0} \exp (-\alpha x)
$$

where $I_{o}$ is the intensity of the incident ratiation. $I_{x}$ is the intensity of the radiation after traversing $x \mathrm{cms}$, the depth of penetration can be found if $I_{o}$ and $I_{x}$ are calculated.
ii) Conductivity $(\sigma)$ : This is calculated from the refractive index and extinction coefficient by the relation:

$$
\sigma=n k w=\varepsilon^{\prime \prime} w / 2
$$

The conductivity can be used to calculate T.O. frequencies. However, it has a far more significant use. It has been shown (Hodgson 1970) that $\sigma$ is a complex quantity, the real part of which can be used to calculate power absorbed. Peaks in the conductivity spectrum at greater than the L.O. frequencies, correspond to two phonon processes.

A useful check on the calculated frequencies of the T.O. and L. O. modes can be performed by overlaying the spectra of $n$ and $k$ ( $n$ and $k$ must have the same ordinate expansion factor).

The number of cross-over points locate alternatively the T.O. and L.O. modes (as shown in figure 2.5). This has become known as Drude's rule (Renneke and Lynch 1965). This rule is often abused, as when oscillators of widely varying intersites are present, $n$ and $k$ frequently do not show sufficient points at which they have the same value. Chang and Mitra (1968) have reviewed this method and concluded that it is only suitably applied when a few oscillators of approximately equal strength are present.

If all the T.O. and L.O. frequencies are established using
the methods of $\varepsilon^{\prime \prime}$ maxima, $\varepsilon^{\prime}$ nodes and $n, k$ cross-over points, none remaining unfound, the radio frequency dielectric constant may be calculated ( $\varepsilon_{o}$ ).

The extended Lyddane-Sachs-Teller relationship (Lyddane, Sachs and Teller 1941) (Casselman, Mitra and Spector 1965) relates $\varepsilon_{0}, \varepsilon_{\infty}$ to the T.O. and L.O. frequencies as follows.

$$
\prod_{i} \frac{\mathrm{T.O.i}}{\mathrm{~L} .0 \cdot i}=\left(\frac{\varepsilon_{0}}{\varepsilon_{\infty}}\right)^{\frac{1}{2}}
$$

This is the only reliable method of calculating $\varepsilon_{0}$, as the reflectance at low frequencies is seldom known accurately, therefore equation (15) cannot be strictly applied.

The damping factor $\gamma$ as already stated is found from the width at half-peak height of $\varepsilon^{\prime \prime} . \quad \gamma$ is inversely proportional to the lifetime of the T.O. mode :

$$
\gamma \propto \frac{l}{T} \quad \text { where } T=\text { lifetime of the mode }
$$

Thus ratios of lifetimes may be calculated, which may provide useful data for theoretical studies of the compound.

Reflectance spectroscopy can therefore provide information which would be difficult to obtain by other means, and is useful not only for determining oscillator frequencies, but for collecting
data for theoretical studies on the compound under examination.

## Modification of Data

In order to do either a K-K or C.D. analysis the observed reflectance must be measured as a function of frequency. This is an extremely tedious procedure, and can be made more efficient by the use of a transparent sheet calibrated vertically with lines at $2 \mathrm{~cm}^{-1}$ intervals, and horizontally with lines at $\bullet 1 \%$ reflectance intervals. The value of the reflectance at any frequency can then be read-off directly to a reasonable degree of accuracy. There are certain areas of the reflectance spectrum where either; the reflectance changes greatly over a very short frequency range, or, the reflectance changes only marginally over a wide frequency range. In these areas it may be necessary to introduce an additional scale for greater accuracy.

Figure 2.6(a) shows the "critical" areas of the reflectance spectrum, i.e. areas as mentioned above where a high degree of accuracy in measuring reflectance is required. It will be found on analysis that neglect of accuracy in these areas will have the inevitable result of impossible values for the ouput parameters. The best guide to the accuracy of the results of analysis is the va?ue of $k$. In the regions of transparency, $k$ will assume values very close to zero. In the area of intense reflectance, $k$ will assume fairly large positive values (these rarely exceed 10.0).

Under no circumstances will $k$ ever be negative in correct analyses. Negative values of $k$ will generate negative values of $\varepsilon^{\prime \prime}$, this will induce distortions to the frequency variation, with the result that the T.O. frequency will appear to shift from its true position, thus making the entire analysis void.

It is sometimes found, however, that even on taking the most extreme care in measuring the variation of reflectance (values of $R$ as low as $0.01 \%$ are possible on the high frequency side of the L.O.), that negative values of $k$ are still generated.

The fault lies within the original data, and subtle corrections are needed in order to generate positive values of $k$.

Two general situations frequently generate negative values of $k$ :
a) spectra where very low absorptions occur, i.e. $\leqslant 90 \mathrm{~cm}^{-1}$
b) spectra where there are two or more oscillators in very clcse proximity to one another, of differing intensity.

Other situations arise from time to time. However, the modifications to these two types of spectra can be extended to other examples.
a) The case where low frequency absorptions occur:

The errors arising from these spectra are frequently due to restricted information concerning the value of the reflectance at low wavelengths. The value of $R$ at zero frequency may not be
known to any degree of accuracy due to the lack of energy available. Two principles must be observed.
i) the $\% \mathrm{R}$ spectrum must be parallel to the abscissa in the limit where $\mathrm{w} \rightarrow \mathrm{o}$.
ii) the \% $R$ spectrum must be a smoothly varying function with frequency, sudden increases in $R$ will generate negative values of $k$.

Smoothing of the reflectance shape, and adjustment of the value of $R$ at $w=o$ can then take place. It must be stressed that the exact amount of smoothing is determined largely by experience. However, the area of intense reflectance must not be altered in position, nor must the area where the gradient rises steeply be tampered with. A cure is most often provided by smoothing at the point of largest curvature (see figure 2.6(b)).

The correct value for $R$ at $w=0$ is found from the value of $\varepsilon^{\prime \prime}$ at $w \simeq o$. If the value for $R$ is too high $\varepsilon^{\prime \prime}$ will have values of the order 0.5-1.0. If the value for $R$ at $w=0$ is too low, $\varepsilon^{\prime \prime}$ is slightly negative and changes slowly to positive values as the region of the T.O. is approached. If the value for $R$ is correct, $\varepsilon$ " will have values of the order 0.01 .
b) The case where two or more oscillators are close together:

This situation is by far the most difficult to correct as no hard and fast rules apply. However, certain guide lines have

FIG. 2.6 a


FIG. 2.6b

been established. In the case of a one oscillator analysis, the $\% R$ curve is seen to become parallel to the abscissa as the L. 0 . is passed (see figure 2.5). When two oscillators are widely spaced there is also a region where the $\% \mathrm{R}$ curve may not be parallel to the abscissa, butincreases very gently with increasing frequency until the next oscillator is approached (see figure 2.7(a)).

It can be imagined that as the two oscillators approach each other this region undergoes a steady compression until the L.O. of the first mode tails over and the reflectance begins to rise steeply for the next oscillator (see figure 2.7(b)). A "critical area" is then established, the section of this area which often requires attention, is the part where the gradient begins to rise gently. Some correction may be possible by introducing a small plateau where the reflectance briefly levels out before beginning to rise steeply - as shown. The amount of smoothing here has been exaggerated to show the concept of smoothing in this area. The exact amount of smoothing can only be determined by trial and error, but only the most subtle amounts will not affect the input data. Large distortions of observed data will invariably introduce errors in $\theta$ and hence arrors will arise in the computed values of $n$ and $k$.

In the situation of oscillators in close proximity to each other of widely different intensity (see figure 2.8) another guide line has been established. That is that the \% R before the sharp rise to the T.O. of the weak oscillator must be greater than the

FIG. 2.7a


FIG. 2.7b


FIG. 2.8

$\% \mathrm{R}$ after the tail over from the L. O. of the strong oscillator as shown.
$\Delta \mathrm{R}$ here has been exaggerated to show the concept involved, but in real terms values of $\Delta \mathrm{R}$ \& $3 \%$ are common. Similar results have been deduced previously (Gardner 1974).

All the above guide lines have been deduced empirically with no theoretical justification. If applied carefully, taking note of the cautions mentioned herein, the $\% \mathrm{R}$ curve can be adjusted to give positive values of $k$ (and hence $\varepsilon$ ") with no noticeable distortion to the results obtained, T.O. frequencies being monitored with those obtained from i.r. mulls.

As a final note, cases do occur with multi-oscillator problems, i.e. 9-10 oscillators in each orientation, when no amount of subtle correction will yield positive values of $k$. Unfortunately such cases do not have an easy solution. $\theta$ is calculated over all values of $R$ over all wavelengths and hence distortions to $\theta$ can be cumulative. In the absence of more empirical data, guide lines for such circumstances cannot be given.

Listings of all programs are given in appendices 1-3.

Appendix 1

> , Kramers-Kronig analysis program : optical constants calculated directly from input data.

Appendix 2

Simple harmonic oscillator program : optical constants calculated fron a synthetically generated spectrum, using initial guesses for a) transverse optic mode frequency, b) transverse optic damping term, c) osc.illator strength.

Appendix 3

Simple harmonic oscillator program : optical constants calculated from a synthetically generated spectrum, using initial guesses for $a)$ transverse optic mode frequency, b) transverse optic damping term, c) longitudinal optic mode frequency, d) longitudinal optic damping term.

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## Section B

The Raman Process, Crystal Growth

## The Raman Effect

In the Raman effect an incident photon interacts with the crystal with the creation or destruction of a phonon to produce a scattered photon of a new frequency. This is inelastic light scattering.

The total energy, and hence wave vector, is conserved in the process

$$
k_{i}=k_{s}+k_{p}
$$

$\therefore_{i}, k_{s}$ and $k_{p}$ represent the wave vectors of the incident and scattered photons and the phonon respectively. As $k$ is related to $w$ (frequency) as in Chapter one:

$$
w_{s}=w_{i} \pm w_{p}
$$

The difference between the frequencies of the incident and scattered photons is the phonon frequency.

The process can result in the scattered photon having greater or lesser energy than the incident photon. The former is described as the anti-Stokes effect and the latter as the Stokes effect.

It is seen practically that the Stokes effect results in a more intense spectrum. This is because in the anti-Stokes process a phonon is destroyed and involves the medium in a vibration-
ally excited state. Therefore the intensity will be related to the Boltzmann energy distribution for that state. Gil son and Hendra (1970) have reviewed the Raman process and a detailed account is given. The following is a representation of the facts relevant to this thesis.

The detailed mechanism of the Raman process is still not fully understood. However the essential theory relevant to its use has been well documented. The Raman process can be explained by the introduction of an induced dipole moment in an electron sloud by the oscillating electric vector of the incident radiation. Vibrations are observed if there is a change in the polarisability of the electron cloud due to the displacements of the nuclei involved.

The assumption is made that the energy of the incident radiation is insufficient to promote the system to an electronic excited state. This is valid even in the case of modern lasers which are used as the source of incident radiation.

It may be imagined that a transient intermediate electronic state between the ground and first excited electronic states is created by the absorption of photons by the medium. A photon is then emitted which allows the medium to return to the ground electronic state, but in a higher vibrational level. The result
is that the phonon produced is equivalent to a simple vibrational transition. No order is placed on the vibrational level which the medium returns to, this is determined by a term known as the "probability of transition" a description of which will not be attempted here. A review of the process has been given by Peticolas (1972).

Placzek (1962) describes the theory of the effect in classical terms using the polarisability of the medium ( $\alpha$ ) in relation to a normal coordinate (q).

Placzek has shown that Raman intensity is proportional
to

$$
\left(\frac{\partial \alpha}{\partial q}\right)^{2}
$$

and has shown that this has the form of a second rank tensor.

$$
\left(\frac{\partial \alpha}{\partial q}\right)_{i} \equiv \alpha^{\prime}=\left[\begin{array}{ccc}
\alpha_{x x} & \alpha_{x y} & \alpha_{x z} \\
\alpha_{y x} & \alpha_{y y} & \alpha_{y z} \\
\alpha_{z x} & \alpha_{z y} & \alpha_{z z}
\end{array}\right]
$$

$x, y$ and $z$ are the orthogonal axes. The tensor $\alpha_{x y}$ denotes the magnitude of the $x$ component of the dipole moment, induced by the $y$ component of the oscillating electric field.

Placzek has also shown that the relation:
$\left(\frac{\partial \alpha}{\partial q}\right)^{2} \alpha($ proportional $) \mu_{u m}^{2}$
$\mu_{u m}$ is the transition moment such that:

$$
\mu_{u m}=\Psi_{u} \alpha^{\prime} \Psi_{m}^{\partial} \tau
$$

$\Psi_{u}$ and $\Psi_{m}$ are the eigen states of the initial and final vibrational levels. However it has been shown that

$$
\mu_{u m} \nexists 0 \text { if and only if } \quad \Psi_{u} \alpha^{\prime} \Psi_{m} \text { contains the totally }
$$

symnetric representation $A_{1 g}$. The representation for a product $\Gamma_{u m}$ will only contain $A_{1 g}$ if $\Gamma_{u}=\Gamma_{m}$. Since $\Psi_{u}$ must be totally symmetry (as it is the ground state) the product $\alpha^{\prime} \Psi_{m}$ must contain $A_{l}{ }^{-}$

Thus the final vibrational state will have the same representation as the polarisability tensor if it is Raman active. The species of a polarisability tensor is obtained from the point group table corresponding to the factor group of the crystal.

The nomenclature $\alpha_{x y}$ indicates that if the incident photon is polarised with respect to $x$, the scattered photon will be polarised with respect to $y$. Therefore it is possible to assign symmetry species of a Raman spectrum using polarised radiation and a polariser incorporated into the analyser for the scattered light.

The notation of Porto et al (1966) is used by single crystal spectroscopists therefore $x(z x) y$ represents an incident beam
parallel to the $x$ axis of a crystal polarised with respect to the z axis, and scattered photons parallel to the y crystal axis polarised with respect to the x axis.

If a solid is examined by Raman spectroscopy and the unit cell does not possess a centre of inversion, it is possible in certain orientations to observe the phenonmenon of L.O. T.O. splitting.

## Splitting of Longitudinal and Transverse Optic Modes

I.r. active modes have been discussed in section $A$; it was established that the frequencies of T.O. and L.O. modes differ. The magnitude of the difference depends on the material under investigation. Strongly ionic materials may have a T.O.-L.O. split of $\sim 100 \mathrm{~cm}^{-1}$. "Molecular" materials may exhibit a very small splitting.

The existence of both T.O. and L.O. modes for a symmetry species may be predicted using a vector diagram, (see figure 2.9). If the phonon propagation direction is in the plane of the directions of both incident and scattered photons, and the phonon polarisation direction is also in this plane, bcth L.O. and T.O. may be active, if the species is both i.r. and Raman active.

If the polarisations of both incident and scattered photons are parallel to crystallographic axes in high symmetry species several simplifications can be made. If these conditions are not

FIG. 2.9

observed, it is possible to observe "hybrid" L.O. and T.O. modes, a description of which will not be attempted here but has been discussed by Wilkinson et al (1971).

If the example of $D_{3}$ symmetry is taken, operations of type $E$ are both i.r. and Raman active, the tensor components describing phonon polarisation are given by:

$$
(x) \quad(y)(z)
$$

$\left.E(x):\left[\begin{array}{lll}c & & \\ & -c & d \\ & \text { d } & \end{array}\right] \begin{array}{lll}(x) & E(y): \\ (y)\end{array}\right]$

For a $90^{\circ}$ Raman scattering experiment using the orientations $x(y x) y$ and $x(z x) y$ the phonon polarisation is $y$. In the case of $\mathrm{x}(\mathrm{yz}) \mathrm{y}$ the phonon polarisation is x . In all three cases the phonon polarisation is the $x-y$ plane, and L.O. and T.O. modes may appear. Where splitting is small a band of intermediate frequency may be observed.

## Growth of Crystals

Unless otherwise stated in the text, all crystals were grown by slow evaporation of solutions, the precise conditions being given in the relevant chapters.

In the case of the mercuric halides $\mathrm{HgCl}_{2}, \mathrm{HgBr}_{2}$ these were grown by vapour phase deposition. The apparatus shown in figure 2.10 was mounted inside the oven shown in figure 2.11. The glass tubes were packed with purified compound and sealed by forming a constriction at the end of the tube and fusing a glass rod onto the constriction. The thin wire placed in the capillary was then removed and the apparatus was evacuated by attaching a rubber tube onto the open end and fitted with a tap. A plug of sublimed compound collected in the wide bore of the tube and sealed the apparatus during extrusion.

The apparatus was pulled through a temperature gradient in the oven by means of a sliding rail attached to rotating discs by wire. The discs were fitted with grooves of varying diameter so that the rate of extrusion could be varied. The average rate of pulling consistent with crystals of good optical quality was not greater than 1 cm per day.

## Examination of Crystals

The crystals obtained by either of the two methods described above were frequently different sizes and often showed incomplete development of faces, the face which was in contact with the vessel would be poorly developed. The other faces exposed to either the saturated solution or the vapour of the compound showed a high

FIG. 2.10
tube closed at this point after packing compound. Glass rod is fused to main body for support during extrusion
compound packed here

$$
\begin{aligned}
& \mathrm{g} \\
& \text { od }
\end{aligned}
$$

crystals collect here at"cool" end of apparatus
capillary 0.05"dia. wire inserted while filling
plug of sublimed compound collects here to seal apparatus
rubber tubing with tap attached to seal apparatus under vacuum.

FIG. 2.11

degree of development. If a crystal of a size suitable for spectroscopic work (ca. $5 \mathrm{~mm} \times 3 \mathrm{~mm} \times 2 \mathrm{~mm}$ ) was selected on the basis of a well developed set of faces the "optical quality" could be determined using the polarising microscope. As well as locating crystallographic axes this method enables the distinction between twinned and untwinned crystals. Twinned crystals rarely grow in exactly parallel directions, and thus the presence of a twin is distinguished by incomplete extinction. A series of "growth rings" caused by the intermittant and rapid deposition of material can also be distinguished; these are characterised by small bright spots in the crystal while under extinction. The quality of results obtained is directly linked to the quality of the crystal and thus crystals should be selected showing the highest possible optical quality.

Raman and I.R. Experiments

The layout of the reflectance unit used on the Beckmann RIIC FS720 interferrometer has already been shown (figure 2.1. section A). The principle of operation of this machine has been described by Martin (1966). Some data was also collected using a Perkin-Elmer PE225 grating spectrometer.

Polarised i.r. information was collected using the following polarisers in the frequency ranges shown.
$0-600 \mathrm{~cm}^{-1}$ Perkin-Elmer gold wire grid mounted onto polyethylene
$600-1000 \mathrm{~cm}^{-1}$ KRS5 polariser made by Oxford instruments PE225

200-2000 $\mathrm{cm}^{-1}$ Perkin-Elmer gold wire grid mounted onto silver bromide

Because of the mode of operation of the FS720 it is necessary to use filters for the radiation which cut-off the high frequency (unwanted) part of the radiation. Suitable filters for each of the beam-splitter ranges of the FS720 are:

| Range | Beam Splitter | Filter |
| :---: | :---: | :---: |
| $10-110 \mathrm{~cm}^{-1}$ | $25 \mu \mathrm{M}$ | Teflon |
|  | (100 G) |  |
| 20-200 $\mathrm{cm}^{-1}$ | $\begin{array}{r} 12 \mu \mathrm{M} \\ (50 \mathrm{G}) \end{array}$ | Teflon $\left\{\begin{array}{c}\text { Polyethylene field } \\ \text { lens used }\end{array}\right.$ |
| 40-400 $\mathrm{cm}^{-1}$ | $\begin{aligned} & 6 \mu \mathrm{M} \\ & (25 \mathrm{G}) \end{aligned}$ | None $\quad$ |
| 200-600 $\mathrm{cm}^{-1}$ | 3.6 M M | Beckmann No. 9 |
|  | ( 15 G ) | low pass filter |
| $600-1000 \mathrm{~cm}^{-1}$ | $6 \mu \mathrm{P}$ | Grubb-Parsons |
|  |  | low pass filter |

G refers to the "gauge" of the Melinex (M) (polyethylene terephthalate), P refers to polypropylene.

The three low frequency ranges are examined using a polythene field lens, this shows very strong absorptions above ca. $500 \mathrm{~cm}^{-1}$ and hence no filter is necessary for the range $40-400 \mathrm{~cm}^{-1}$.

A computer program is described elsewhere by Appleby (1977) for computing the results obtained from the FS720.

The PE225 was found to have several drawbacks; the major one being the thermal energy available from the beam. Low temperature work was extremely difficult and some crystals showed a small amount of sublimation or decomposition whilst under examination.

The Raman instrument used in this study is a Coderg T800 triple-monochromator machire. This has four independent slits and two photo-multipliers, one for use at the "blue" end of the visible spectrum, the other for use at the "red" end of the spectrum. The optical layout of this machine has been discussed by Trumble (1974).

Most of che information was collected using a Coherent Radiation Laboratories model 52A argon-ion laser which has two powerful emission lines. $4880 \AA(488 \mathrm{~nm})$ "blue line" and $5145 \AA$ (514.5 nm) "green line".

The optical layout for $90^{\circ}, 180^{\circ}$ and $0^{\circ}$ scattering experiments is shown in figure 2.12. The polarisation of the incident beam is

FIG. 2.12

off axis ellipsoid
$180^{\circ}$ Scattering

off axis ellipsoid
$0^{\circ}$ Scattering
varied by the use of a $\lambda / 2$ plate, this rotates the plane of polarisation of the laser. The analyser enables selection of scattered radiation with respect to crystallographic axes. The $\lambda / 4$ plate effectively "scrambles" the polarisation of the beam of scattered photons to safeguard that the sensitivity of the detection system does not vary with light polarisation.

## Preparation of Samples

As discussed in section $A$, transmission samples must be very thin indeed. A face is selected containing the axes required, or a face is cut containing the axes, this is then mounted directly onto a plate of material transparent to the radiation in the frequency range required. Alternatively, the face may be mounted onto a disc of type shown in figure 2.13(a), the disc is made of brass or copper, different frequency ranges may therefore be studied with the same mount. The conical section acts as a condenser of radiation, "thick" samples may be studied if they are not strongly absorbing.

Figure 2.13(b) shows the arrangement of mounting for reflection measurements. Crystals are polished with a soft cloth to remove any grease or dirt placed on them during handling. The area surrounding the crystal was "masked" using black paper, this is to stop stray reflection from the copper disc. Trial experiments were conducted to deduce the best masking material. Copper

FIG. 2.13a


FIG. 2.13b

sample

FIG. 2.13c

painted with matt black paint was tried, along with black rubber and various other materials. The conclusion was that black paper was far superior to any other material.

Crystals for Raman experiments were mounted onto copper posts as shown in figure 2.13(c). Epoxy resin into which aluminium powder had been mixed was used. The posts were made so that they would easily fit into the cryostat used.

## Cryostats Used

Much of the low temperature work for this thesis was collected using a Cryogenic Technology C.T.I. model 20 closed-circuit liquid helium cryostat. This was fitted with a temperature controller which theoretically allowed any temperature between $300-10^{\circ}$ $K$ to be obtained and maintained. It was discovered early in this program of research that temperatures in the order of $<100^{\circ} \mathrm{K}$ were not being obtained. A cold shield was designed for the purposes of this thesis which was mounted onto the nominal $77^{\circ} \mathrm{K}$ first stage cooling unit of the C.T.I. The cooling block was then surrounded by a copper band at $77^{\circ} \mathrm{K}$ during cooling, although this added to the load to be cooled, the radiation losses were drastically cut. Temperatures in the order of $30^{\circ} \mathrm{K}$ could be obtained subsequently. At all stages temperatures were monitored using a thermocouple.

Some data was also collected using a "home-made" liquid nitrogen cryostat with which temperatures of $115^{\circ} \mathrm{K}$ could be obtained.

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## Chapter Three

Introduction

Both topaz and spodumene are minerals. Problems are frequently encountered in the vibrational studies of minerals, because by definition their compositions may vary within certain set limits. A "solid solution" series may be formed where the variable element may be present in a concentration of 0-100\% of that allowed.

It can be reasonably expected that the two so-called "end-members" of a series (those which contain respectively $0 \%$ and $100 \%$ of the variable element) will show significant differences in their vibrational spectra. In addition, the disordering which occurs due to the presence of variable amounts of an element (different sized ions may well distort the lattice symmetry) will be reflected in the quality of the spectra obtained. Mineral spectra very seldom show any appreciable change on cooling to low temperatures. Therefore resolution of small features, or broad bands is frequently impossible.

Interpretation of mineral spectra and any assignments made can only be tentative, except in the case of well defined and separated regions of the spectra, or if confirmation is available by alternative means such as normal coordinate analysis (N.C.A.).

Although much information about the i.r. spectra of silicate minerals is available, and to a lesser extent their Raman spectra; reviews are given by Farmer (1974), Lazarev (1962),
and Karr (1975), very little work has been done using oriented samples in polarised light. Such studies are essential prerequisites to a full understanding of what are often very complex spectra, since silicate minerals commonly have large unit cells of low symmetry.

Single-crystal data collected for beryl (Adams and Gardner 1975) and benitoite (Adams and Gardner 1976) are examples of how an understanding of the structures, coupled with oriented aralysis by selection rules, can lead to an understanding of the construction of the spectra, thus making a partial or full assignment possible.

## Theory (Topaz)

The X-ray study of topaz $\mathrm{Al}_{2}(\mathrm{OH}, \mathrm{F})_{2} \mathrm{SiO}_{4}$ by Wyckoff (1968) has established the symmetry as Pnma $\left(D_{2}^{16}\right)$ with $z=4$. It is therefore a primitive unit cell of orthorhombic symmetry with four molecules per unit cell.

The silicon atom and half the oxygen atoms occupy $\mathrm{C}_{S}$ sites with all other atoms on general sites. The factor group analysis is shown in Table 3.1.

Topaz is classified as an orthosilicate and contains discrete $\left(\mathrm{SiO}_{4}\right)^{4^{-}}$ions, therefore information concerning the Si-0 modes may be inferred in the absence of Si-0-Si modes.

Adams (1974) has discussed bond directionality and bond character, however the decomposition into internal and external modes should not be taken to infer anything quantitative about the bond character, even though the Si-0-Al bond may be presumed to be very directional.

The Al atom is in octahedral coordination to oxygen from four separate silicate groups, the remaining two positions being occupied by either oxygen from OH groups or F. Porto and Krishnan (1967) have reported optically active T.O. phonons as high as $751 \mathrm{~cm}^{-1}$ for $\alpha-\mathrm{Al}_{2} \mathrm{O}_{3}$ where Al is in a distorted octahedral environment, similar high frequencies for topaz Al-0 may therefore be expected.

## Experimental

The sample of topaz used to collect data was of side ca. $1 \times 1 \times 1 \mathrm{~cm}^{3}$ and was cut from a colourless block of excellent optical quality. Kostov (1968) has reported that topaz commonly exhibits a cl ?avage parallel to the (OOI) faces. This appeared to be the case with our specimen, which on examination under a polarising microscope revealed two orthogonal indicatrix directions in the plane of the original block.

The sample was cut from the block, which was mounted in a goniometer, along these directions using a diamond impregnated saw. The freshly cut piece was then polished, first with boron carbide grit 1000 and then with alumina.

A preliminary study of the single crystal Raman data obtained, revealed significant departures from F.G.A. predictions and indicated an incorrect choice of axes. A Weissenberg photograph of a small chip of the sample clearly showed that in terms of the axis set given by Wychoff, the cleavage plane of the original block was parallel to (010). The indicatrix axes taken were therefore: $\mathrm{x}=\mathrm{a}_{\mathrm{o}}(4.6499), \mathrm{Y}=\mathrm{b}_{\mathrm{o}}(8.7968), \mathrm{Z}=$ $c_{0}(8.3909)$, cell parameters being in parentheses.

## Results and Discussion

The results obtained are shown in figures $3.1,3.2 \mathrm{a}$ and 3.2 b and summarised in Tables 3.2 and 3.3. The presence of hydroxyl is clearly demonstrated by the Raman bands at $1166 \mathrm{~cm}^{-1} \delta(\mathrm{OH})$ and $3655 \nu(\mathrm{OH})$.

The only reliable guide is the representation of optically allowed modes, which is:

$$
N_{\text {opt }}=15 A_{g}+12 B_{1 g}+15 B_{2 g}+12 B_{3 g}+14 B_{1 u}+11 B_{2 u}+14 B_{3 u}
$$

Single crystal i.r. reflectance data and Raman data have been collected by Serroin and Piriou (1973) and Hohler and Fünck (1973) for forsterite $\left(\mathrm{Mg}_{2} \mathrm{SiO}_{4}\right)$ which is also an orthosilicate. On the basis of this data an N.C.A. analysis has been made by Devarajan and Fünck (1975).

The bonding between $\mathrm{Mg}^{2+}$ and $\left(\mathrm{SiO}_{4}\right)^{4-}$ is weaker than that between $\mathrm{Al}^{3+}$ and $\left(\mathrm{SiO}_{4}\right)^{4^{-}}$and results in a region of no absorption in the spectra between ca. $600-800 \mathrm{~cm}^{-1}$. This allows the $v(S i-0)$ region to be treated separately, as these modes are expected to occur $>800 \mathrm{~cm}^{-1}$. However, none of the authors have concluded a fully consistent interpretation of all the data.

The region below $600 \mathrm{~cm}^{-1}$ will contain the $v_{2}$ and $v_{4}$ modes of the $\left(\mathrm{SiO}_{4}\right)^{4-}$ anion, this region is also characterised by lattice modes and the two sets become significantly mixed. An assignment in this region can only be tentative.

The Raman data $r \in$ ported here for topaz shows a much smaller gap in the region below $v(S i-0)$, the i.r. data shows only one very weak peak in this region. Bands in the frequency range $600-800 \mathrm{~cm}^{-1}$ must be considered good candidates for $v(\mathrm{Al}-0)$ where the oxygen is from $\left(\mathrm{SiO}_{4}\right)^{4-}$.

The $v($ SiO $)$ assignment $\left(>800 \mathrm{~cm}^{-1}\right)$

Figure 3.4 shows the modes of vibration of the isolated $\left(\mathrm{SiO}_{4}\right)^{4^{-}}$ion. The correlation table incorporated into Table 3.1 shows how these modes will become mixed in the spectrum of the crystal.

Species $A_{g}$ and $B_{2 g}$ contain identical representations for

$$
v_{1}+v_{2}+2 v_{3}+2 v_{4}
$$

Figures 3.2 and 3.3 show that in $A_{g}$ and $B_{2 g}$ spectra, one band is present at significantly lower energy than the other two in these species, implying that $\nu_{1}<\nu_{3}$. The bands in the $\mathrm{B}_{1}$ g and $B_{3} g$ spectra at 1006 and $984 \mathrm{~cm}^{-1}$ respectively can only originate from $\nu_{3}$, and are significantly higher in frequency than the lower bands in $\mathrm{A}_{\mathrm{g}}$ and $\mathrm{B}_{2 \mathrm{~g}}$ attributed to $\nu_{1}$.

A single mode is predicted in $\mathrm{B}_{2} \mathrm{u}$ originating from $v_{3}$. Figure 3.1 shows a very broad region of reflectance, corresponding to a very intense absorption, with a T.O. frequency of $870 \mathrm{~cm}^{-1}$. Since this is the dominant feature it is regarded as the fundamental, the weak feature at ca. $1000 \mathrm{~cm}^{-1}$ is attributed to a two-phonon mode.

It is not uncommon to observe two-phonon modes in i. $x$. reflectance spectra - not only of minerals. These must be distinguished before an assignment can be made. On present evidence there is no a priori means of making such a distinction, uless a thermal dependence study is done in order to evaluate cubic and quartic anharmonicity. The guide here is internal consistency (backed up by Raman data) and the intuitive experience gained in reflectance spectroscopy.

In the $B_{1 u}$ spectrum 3 modes are predicted $\nu_{1}+2 \nu_{3}$. Three bands are found, these are regarded as fundamentals.

In the $B_{3 u}$ spectrum 3 modes are predicted $\nu_{1}+2 \nu_{3}$. Three bands are found, and are also regarded as fundamentals.

The following assignment has been deduced for the $\nu($ Si-0) region.

Ion $\left(T_{d}\right) \quad$ Site $\left(C_{S}\right) \xrightarrow{x 4}$ Crystal $\left(D_{2 h}\right)$

$\nu_{1}\left(A_{1}\right) \longrightarrow A^{\prime} \quad \begin{array}{cc}A_{g}+B_{2 g}+B_{I u}+B_{3 u} \\ 854 & 908 \\ 875 & 857\end{array}$

The assignment for $v_{1}$ shows a high consistency and a range of $54 \mathrm{~cm}^{-1}$. The assignment for $\nu_{3} A^{\prime}$ components yields a splitting of $70 \mathrm{~cm}^{-1}$ which is regarded as reasonable. The A" assignment is less satisfactory, at first sight a splitting of $136 \mathrm{~cm}^{-1}$ seems rather large. If the weak feature in $B_{2 u}$ at ca. $1000 \mathrm{~cm}^{-1}$ was chosen the splitting would have been very small, perhaps too small.

It is regarded that the $v(S i-0)$ assignment is established.
It is interesting to note that the N.C.A. of forsterite by Devarjan and Fünck presented a similar problem. The final assign-
ment gave $v_{3}$ a range of ca. $130 \mathrm{~cm}^{-1}$ and $v_{1}$ a range of $16 \mathrm{~cm}^{-1}$. The region below $v($ Si-0)

It is impossible to establish a unique assignment for this region in the absence of a full N.C.A. treatment. The $v_{2}$ and $v_{4}$ modes of $\left(\mathrm{SiO}_{4}\right)^{4^{-}}$are mixed with the lattice modes. Comparison of topaz with other orthosilicates suggests that none of the $v_{2}$ and $v_{4}$ components occur above ca. $650 \mathrm{~cm}^{-1}$. Accordingly the very weak i.r. feature at ca. $760 \mathrm{~cm}^{-1}$ and Raman bands at 682,706 and $843 \mathrm{~cm}^{-1}$ can be regarded as either due to Al-0 (Si) bond stretching or to two phonon processes. The fundamentals $v(A l-O H)$ and $v(A l-F)$ are most probably in the region below 650 $\mathrm{cm}^{-1}$.

The region below $400 \mathrm{~cm}^{-1}$ to the Ranan band at $155 \mathrm{~cm}^{-1}$ and i.r. bands down to $175 \mathrm{~cm}^{-1}$ are most probably lattice modes. The absence of bands below $155 \mathrm{~cm}^{-1}$ is consistent with a structure in which only light atoms are involved.

It is useful only to note the number of modes predicted with those found.

|  | $\mathrm{A}_{\mathrm{g}}$ | $\mathrm{B}_{1 \mathrm{~g}}$ | $\mathrm{~B}_{2 \mathrm{~g}}$ | $\mathrm{~B}_{3 \mathrm{~g}}$ | $\mathrm{~B}_{1 \mathrm{u}}$ | $\mathrm{B}_{2 \mathrm{u}}$ | $\mathrm{B}_{3 \mathrm{u}}$ |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| F.g.a. | 12 | 11 | 12 | 11 | 11 | 10 | 11 |
| observed | 11 | 10 | 7 | 10 | 11 | 9 | 10 |

Since the completion of this work an F.G.A. of topaz has been published by Kovaleva (1975). I.r. reflectance data is reported in the region $1200-400 \mathrm{~cm}^{-1}$. Kovaleva reports only reflectance maxima and not T.O. positions, so direct comparison cannot be made. A large degree of agreement is seen between spectra, Kovaleva reported a secondary feature on the highest $\nu_{3}(S i-0)$ band in $B_{1 u}$ which is not regarded as a fundamental here. There is an inconsistency between the labelling of spectra, compatible spectra are found by interchanging Kovaleva's species of $\mathrm{B}_{1 \mathrm{u}}$ and $\mathrm{B}_{2 \mathrm{u}}$ to fit those reported here. This would seem to indicate an incorrect choice of axes, which is interesting in view of the knowledge gained from preliminary Raman experiments reported here. In view of the Raman data and low frequency i.r. reported here, it is believed that this assigument is the correct one (Adams and Hills 1977). Minor deviations in reflectance band shapes etc., are likely to be due to the differing amounts of OH and F in our respective crystals.

Theory (Spodumene)

The X-ray study of Spodumene (LiAlSi $\mathrm{O}_{6}$ ) by Wyckoff (1968)
has determined the symmetry as $C 2 / C \equiv C_{2}{ }^{6}$ with $z=2$. It is therefore a unit cell of monoclinic symmetry with two molecules in the primitive cell.

Spodumene is classified as a Pyroxene and contains chains of $\mathrm{Si}_{2} \mathrm{O}_{6}$ units parallel to the c -axis.

Clarck et al (1969) have shown that there is a șmall distortion of the atom positions which indicates $C 2 \equiv C_{2}^{3}$ symmetry, but conclude that the distortion is sufficiently small to enable C2/C to be safely used.

Gervais, Piriou and Cabannes (1973) have studied the thermal dependence of the $A_{u}$ modes of spodumene, but report no deta for the $B_{u}$ modes. $A_{u}$ was determined as: 295, 314.7, 342, $449,486.7,494,526.5,571,856.5,993,1068,1088$, and $1130.5 \mathrm{~cm}^{-1}$, the bands between and including $342-494 \mathrm{~cm}^{-1}$ being assigned to $v_{2}$ and $v_{4}$ components of the $\left(\mathrm{Si}_{2} \mathrm{O}_{6}\right)^{4^{-}}$ion.

Factor group analysis predicts for the optic branch

$$
N_{o p t}=14 A_{g}+16 B_{g}+13 A_{u}+14 B_{u}
$$

## Results and Discussion

Raman data was collected on the crystal which had a small face ground parallel to the c-axis using boron carbide grit 1000. Unfortunately the crystal showed no significant intensity changes with orientation using all available scattering geometries (90 , $180^{\circ}$, $0^{\circ}$ scatter). In addition, strong fluorescence was observed which remained even on the changing of exciting line used. Using 488 nm radiation the following bands were observed above noise level: $134,190,254,300,360(\mathrm{~m}), 397,446,523,590$, 712 (v.s.), $1076 \mathrm{~cm}^{-1}$, all weak unless otherwise indicated.

Of the $14 A_{g}$ and $16 \mathrm{~B}_{\mathrm{g}}$ modes predicted $v(\mathrm{Si}-0)$ accounts for $3 A_{g}+3 B g_{g}$. Only one band at $1076 \mathrm{~cm}^{-1}$ was observed for this region. Using i.r. reflectance the following bands were located:
$A_{u}\left(E_{\|} C\right) 229,270,444$, ca. 500,1008 , ca. $1050 \mathrm{~cm}^{-1}$ $B_{u}\left(E_{\perp} C\right) 325,358,392,463,619$, ca. $650,890,1085,1205 \mathrm{~cm}^{-1}$. The agreement with Gervais et al for the $A_{u}$ modes seems to be weak except in the cases of the bands at 444, ca. 500,1008 and $1050 \mathrm{~cm}^{-1}$ reported here, and may well be due to the poor sample used. This is shown by the lack of orientation effects in the Raman.
F.g.a. predicts $\left(f v(S i-0) 3 A_{u}+3 B_{u}\right.$, the $B_{u}$ spectrum may be viewed sceptically, however 3 bands may be assigned for $v\left(\right.$ Si-0) at 1085,890 , and ca. $650 \mathrm{~cm}^{-1}$. Bands occurring above $1100 \mathrm{~cm}^{-1}$ are correlated with Si-0-Si bridges.

Further discussion is of little use in the absence of a better specimen.

Table 3.1 Factor group analysis and correlation scheme for topaz.

A : Factor group analysis

| $\mathrm{D}_{2 h}$ | $\mathrm{~N}_{\mathrm{T}} \mathrm{a}^{2}$ | $\mathrm{~T}_{\mathrm{A}}$ | T | R | $\mathrm{N}_{\text {vib }}$ | $\nu($ Si-0) | Activities |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $\mathrm{A}_{\mathrm{g}}$ | 15 |  | 8 | 1 | 6 | 3 | $\mathrm{x}^{2}, \mathrm{y}^{2}, \mathrm{z}^{2}$ |
| $\mathrm{~B}_{1 \mathrm{~g}}$ | 12 |  | 7 | 2 | 3 | 1 | xy |
| $\mathrm{B}_{2 \mathrm{~g}}$ | 15 |  | 8 | 1 | 6 | 3 | xz |
| $\mathrm{B}_{3 \mathrm{~g}}$ | 12 |  | 7 | 2 | 3 | 1 | yz |
| $\mathrm{A}_{\mathrm{u}}$ | 12 |  | 7 | 2 | 3 | 1 |  |
| $\mathrm{~B}_{1 \mathrm{u}}$ | 15 | 1 | 7 | 1 | 6 | 3 | z |
| $\mathrm{B}_{2 \mathrm{u}}$ | 12 | 1 | 6 | 2 | 3 | 1 | y |
| $\mathrm{B}_{3 \mathrm{u}}$ | 15 | 1 | 7 | 1 | 6 | 3 | x |

B : Correlation scheme

| Ion, $\mathrm{T}_{\mathrm{d}}$ | Site, $c_{s}(x z)$ |  |  | Crystal, $\underline{D}_{2} \mathrm{~h}$ |
| :---: | :---: | :---: | :---: | :---: |
| $v_{1} \mathrm{a}_{1}$ | $\mathrm{A}^{\prime}$ ) | 6A' | $\xrightarrow{\mathrm{x} 4}$ | $6\left(A_{g}+B_{2 g}+B_{1 u}+B_{3 u}\right)$ |
| $v_{2} \mathrm{e}$ | $\left.A^{\prime}+A^{\prime \prime}\right\}$ |  |  |  |
| $v_{3}, v_{4} t_{2}$ | $2 A^{\prime}+A^{\prime \prime}$ | $3 A^{\prime \prime}$ | $\longrightarrow$ | $3\left(B_{1 g}+B_{3 g}+A_{u}+B_{2 u}\right)$ |

a $N_{T}=$ total number of unit cell modes; $T_{A}=$ acoustic, $T=$ optic branch modes; $R=$ rotatory modes of $\left(\mathrm{SiO}_{4}\right)^{4-} ; \mathrm{N}_{\mathrm{vib}}=$ internal modes of $\left(\mathrm{SiO}_{4}\right)^{4-}$ of which $v(\mathrm{Si}-0)$ forms part.

Table 3.2 I.r. wavenumbers $/ \mathrm{cm}^{-1}$ for single-crystal topaz.

| $\mathrm{B}_{1 \mathrm{u}}(\mathrm{z})$ | $\mathrm{B}_{2} \mathrm{u}(\mathrm{y})$ | $B_{3 u}(x)$ |  |
| :---: | :---: | :---: | :---: |
| 175w | 178w |  |  |
|  |  | 208w |  |
| 292w | 291vs | 268 vs |  |
| 310w |  | 309 vs |  |
| 336w | 335 vs |  |  |
| 375 ms | 364 m | 389 vs |  |
| 420w |  | 419 ms |  |
| 444 vs | 450ms | 463 ms |  |
| 489 vs | 473w | 489 vs |  |
| 513 vs | 520 ms |  |  |
|  | 545 s | 544wm |  |
|  |  | 572w |  |
| 609 vs | 611 vs | 610 vs |  |
| $\sim 760 \mathrm{vw}$ |  |  |  |
| 875w |  | 857s $v_{1}$ |  |
| 895 vs | 870ms | $936 \mathrm{vs}$ | $v($ Si-0) |
| 995 vs | 995 vw a | $\underline{\mathrm{ca}} .985 \mathrm{sh}\} \underline{\mathrm{b}}^{\nu_{3}}$ | ( |

a Not a fundamental.
上 This region is complicated and appears to contain a further oscillator.
Raman wavenumbers/cm-1 and intensities (arbitrary units) ${ }^{\text {a }}$ for topaz.

Symmetry
$\nu / \mathrm{cm}^{-1}$ species $z(x x) y$ z(yy)x $y(z z) x \quad z(y x) y \quad z(x z) x \quad z(y z) y$

| 155 | $\mathrm{A}_{\mathrm{g}}$ | 6 | 25 | 24 |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 165 | ${ }^{B_{1}} \mathrm{~g}$ |  |  |  | 68 |  |  |
| 171 | $\mathrm{B}_{3} \mathrm{~g}$ |  |  |  |  |  | 6 |
| 191 | $\mathrm{B}_{3 \mathrm{~g}}$ |  |  |  |  |  | 8 |
| 237 | $\mathrm{B}_{2 \mathrm{~g}}$ |  |  |  |  | 100 |  |
| 242 | $\mathrm{A}_{\mathrm{g}}$ | 49 | 100 | 100 | 16 |  | 15 |
| 266 | $\mathrm{B}_{2 \mathrm{~g}}$ |  |  |  |  | 37 |  |
| 270 | $A_{g}$ | 100 | 100 | 100 | 22 |  | 20 |
| 273 | $\mathrm{B}_{2 \mathrm{~g}}$ |  |  |  |  | 40 |  |
| 288 | $A_{g} / B_{1 g}$ | 100 | 100 | 90 | 53 | 14 |  |
| 292 | $\mathrm{B}_{3 \mathrm{~g}}$ |  |  |  |  |  | 20 |
| 315 | $\mathrm{B}_{1 \mathrm{~g}}$ |  |  |  | 68 |  | 10 |
| 334 | $A_{g}$ | 81 | 8 | 38 | 15 | 4 |  |
| 351 | $\mathrm{B}_{3 \mathrm{~g}}$ |  |  |  |  |  | 6 |
| 360 | $\mathrm{B}_{2 \mathrm{~g}}$ |  |  |  |  | 48 |  |

$369 \mathrm{~B}_{1 \mathrm{~g}} \quad 20$
$373 \quad B_{3 g}$
$380 \quad B_{2 g}$
$402 \quad \mathrm{~B}_{1} \mathrm{~g}$
$405 \quad A_{g}$
$424 \quad \mathrm{~B}_{1 \mathrm{~g}}$
18
$441 \quad \mathrm{~B}_{3} \mathrm{~g}$
O
48
$460 \quad A_{g}$
62
$6 \quad 8$
$8 \quad 6$
10
$474 \quad B_{3}$
10
$482 \quad \mathrm{~B}_{3 \mathrm{~g}}$
$\begin{array}{ll}491 & A_{g} \\ 495 & B\end{array}$
$499 \quad B_{1 g}$
$509 \quad B_{1 g}$
$549 \quad \mathrm{~A}_{\mathrm{g}}$
266
$561 \quad A_{g}$
$599 \quad B_{1 g}$
$6 \quad 8$
17
8
22
27

Table 3.3 (contd.)

a ( $x x$ )y, (yy), and ( zz ) spectra recorded at $0.5 \mathrm{~cm}^{-1}$ spectral slit width; ( $x y$ ), ( $y z$ ), and ( $z x$ ) spectra recorded at $3.25 \mathrm{~cm}^{-1}$ spectral slit width. The intensities in the two sets cannot be compared directly.

FIG. 3.1


FIG. 3.2 (a)


FIG. 3.2 (b)


FIG. 3.3 (a)


FIG. 3.3 (b)
Raman Spodumene Unorientated


FIG. 3.4

$v_{1}\left(A_{1}\right)$

$v_{4}\left(T_{2}\right)$

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## Chapter Four

## Introduction

Although much information has been collected on the vibrational motions of the water molecule coordinated to metal ions (reviews are given by Adams, 1967 and Brun 1968), the data is still not satisfactorily understood. Relatively little Raman and fari.r. data has been published on hydrated metal ions in the solid state; the majority of data has been collected in the 250-4000 $\mathrm{cm}^{-1}$ i.r. region, and few data sets contain symmetry information.

The principal experimental evidence given in support of assignments is based upon the frequency changes on deuteriation. The skeletal modes of the molecules, due to metal-oxygen stretches and deformations, are expected to show some sensitivity on deuteriation, the "effective mass" of the ligand being increased from 18 to 20. The external modes of the molecules (translations and rotations) are sensitive only to changes in moments of inertia, and show very small changes due to the extra mass of the deuterium atoms. The modes of the coordinated water molecules, "librations", i.e. restricted rotations and translations may be expected to show large shifts close to the theoretical $\mathrm{V}_{\mathrm{H} / \mathrm{V}_{\mathrm{D}}}=\frac{1}{\sqrt{2}}$.

The assignment of the modes due to water motions has been the subject of great debate. Normal coordinate analysis calculations, such as those of Nakagawa and Shimanouchi (1964), have been published for hydrate complexes $\left[M\left(\mathrm{OH}_{2}\right)_{n}\right]^{2+} n=4,6$; these
may be unreliable in the absence of a unique assignment, because of the large number of modes which can occur. A strict examination of the substantial evidence for hydrate complexes (hexahydrates in particular) show that they are less well-understood than the complex spectra of the many phases of ice.

The approach adopted for this study is the consistency of the evidence accumulated. The isolated water molecule has $C_{2 v}$ symmetry, on coordination to a cation the three rotational and the three translational degrees of freedom of the isolated molecule are incorporated into those of the complex, a description is given by Adams and Lock (1971). For a single coordinated water molecule six modes will occur, these are: a $\mathrm{V}\left(\mathrm{M}-\mathrm{OH}_{2}\right)$ mode; two skeletal modes involving a deformation of the $M-0$ bond; and three "librational" modes, these are described by $\rho_{r}$ (a rocking mode), $\rho_{\mathrm{T}}$ (a twisting mode) and $\rho_{\mathrm{W}}$ (a "wagging" mode). The three forms are shown below.


Rock


Twist


Wag

It is the energy order of these three modes which is often at the centre of the controversy of the assignment in hydrates. It
can be inferred from mono-hydrated anions such as $\left[\mathrm{FeCl}_{5}\left(\mathrm{OH}_{2}\right)\right]^{2-}$ that the order $\rho_{W}>\rho_{r}$ is usually obeyed. This is reasonable when the relative moments of inertia associated with the rotational motions of water are compared. Calculated values for the moments of inertia of the rotational motions which become $\rho_{w}, \rho_{t}$ and $\rho_{r}$ in the coordinated complex are in the ratio 1:1.9:2.9 in the free molecule. Evidence accumulated by Adams and Lock (1971) and Shankel and Bates (1976) would indicate that $\rho_{W}>\rho_{r}$, in mono and di-aquated complexes, is the energy order found. The place of $\rho_{t}$ has not yet been settled, this is because it is likely to be weak in i.r. spectra. This mode originates as the rotation about (z) in the free molecule, and has symmetry $A_{2}$ in the point group $C_{2 v}$, and is not i.r. active. It may gain activity in the complex by virtue of the symmetry subtended by the rest of the complex (see Chapter one).

Hexahydrate complexes have received attention recently, reports are in the literature on the $\left[\mathrm{Ni}\left(\mathrm{OH}_{2}\right)_{6}\right]^{2+}$ ion in the compounds $\left[\mathrm{Ni}\left(\mathrm{OH}_{2}\right)_{6}\right]\left[\mathrm{SnCl}_{6}\right]$ by Jäger and Schaack (1973) and Adams and Trumble (1974) and also $\left[\mathrm{Ni}\left(\mathrm{OH}_{2}\right)_{6}\right] \mathrm{SO}_{4}$ by Jäger and Schaack (1973) and Jani et al (1974). Partial Raman studies of $\left[\mathrm{Mg}\left(\mathrm{OH}_{2}\right)_{6}\right]$ $\mathrm{SO}_{4} \cdot \mathrm{H}_{2} \mathrm{O}$ by Hillaire et al (A) (1971) and $\left[\mathrm{Mg}\left(\mathrm{OH}_{2}\right)_{6}\right]\left[\mathrm{PH}_{2} \mathrm{O}_{2}\right]$ by Hillaire et al (B) (1971) provide a good basis for a survey of the relative magnitudes of the modes predicted. The overall order of $\rho_{\mathrm{W}}>\rho_{\mathrm{r}}>\mathrm{V}\left(\mathrm{M}-\mathrm{OH}_{2}\right)$ has been accepted by all these authors and
as such it seems very reasonable. Jaćger and Schaack (1973) attributed bands at 290,357 and 365 in the complex $\left[\mathrm{Ni}\left(\mathrm{OH}_{2}\right)_{6}\right]\left[\mathrm{SnCl} \mathrm{C}_{6}\right]$ to $\rho_{t}$ modes of the complex. These shifted to 236,272 and 292 respectively on deuteriation, in all cases the bands were only observed at 15 K or below; this assignment cannot be regarded as well substantiated.

An inelastic neutron scattering study of several hydrates by Prask and Boutin (1966) reveals bands attributable to water motions in the range of $300-900 \mathrm{~cm}^{-1}$. This is compatible with most studies both i.r. and Raman on a wide range of hydrates. Prask and Boutin obtained significantly different scattering spectra for $\mathrm{AlCl}_{3} \cdot 6 \mathrm{H}_{2} \mathrm{O}$ and the isomorphous $\mathrm{CrCl}_{3} \cdot 6 \mathrm{H}_{2} \mathrm{O}$, this is attributed to the isomeric form of $\mathrm{CrCl}_{3} \cdot 6 \mathrm{H}_{2} \mathrm{O}\left[\mathrm{Cr}\left(\mathrm{OH}_{2}\right)_{5} \mathrm{Cl}\right] \mathrm{Cl}_{2} \cdot \mathrm{H}_{2} \mathrm{O}$. Modes due to sater motion are highly sensitive to metal oxidation state and hydrogen bonding and often show a large thermal dependence.

Three single-crystal Raman studies of $\mathrm{AlCl}_{3} \cdot 6 \mathrm{H}_{2} \mathrm{O}$ have been reported previously. The studies of Galy (1953) and Weil-Marchand (1955) were confined to the internal modes of the coordinated water molecules. The third study by Champier and Galy (1954) studied the region up to $1000 \mathrm{~cm}^{-1}$. The results reported here confirm the assignments of the stronger bands in most cases, but also reveal more detail. An i.r. study using the KBr pellet technique (Lucchesi and Glasson 1956) did not assign any symmetry labels to the sample, and the low frequency end was not observed.

Some interesting solution work by Mathieu (1950) and by da Silveira et al (1961, 1965) located $v_{1}, v_{2}$ and $v_{5}$ using Raman spectroscopy on solutions of $\mathrm{AlCl}_{3}$.
$\nu_{1}$ was located at $525 \mathrm{~cm}^{-1}$ on account of its polarised behaviour
$v_{2}$ was located at $447 \mathrm{~cm}^{-1}$ (depolarised)
$\nu_{5}$ was located at $340 \mathrm{~cm}^{-1}$

## Experimental

Crystals of $\mathrm{AlCl}_{3} \cdot 6 \mathrm{H}_{2} \mathrm{O}$ were grown by slow evaporation of aqueous solutions of $\mathrm{AlCl}_{3}$ dissolved in $1: 10 \mathrm{HCl}: \mathrm{H}_{2} \mathrm{O}$, the initial small precipitate of alumina was filtered off. The composition of the crystals was verified by thermogravimetric analysis. The crystals had well-developed faces of side ca. $10 \times 5 \times 2 \mathrm{~mm}^{3}$ and w $\in$ re of excellent optical quality. Extinction directions were found using a pclarising microscope and are illustrated in figure 4.1. The deuteriate was prepared similarly using $D_{2} O$ followed by two successive recrystallisations from $\mathrm{D}_{2} \mathrm{O}$.

It proved impossible to obtain sufficiently thin crystal sections for study by i.r. transmission because the material has a slight deliquescent nature and was mechanically unstable in thin sections. So the crystals were studied using reflectance spectroscopy using the method described in Chapter two, section B. Many attempts
were made to obtain reflectance spectra at low temperatures, but were frustrated by a loss of reflectance on cooling. Attempts were also made to obtain spectra at $>1000 \mathrm{~cm}^{-1}$ using a grating spectrometer, but these failed due to partial dehydration of the crystals in the heat of the beam. Cooling these crystals in a cryostat to attempt to overcome this problem were frustrated by loss of reflectivity on cooling.

Samples were prepared for Raman work as in Chapter two, section B, excellent results were obtained. It proved impossible to achieve trmperatures of below 115 K without the aid of the cold shield (see Chapter two, section B) which was designed after the completion of this work.

Theory

The symmetry of $\mathrm{AlCl}_{3} \cdot 6 \mathrm{H}_{2} \mathrm{O}$ was determined by Andress and Carpenter (1934), it crystallises in the trigonal system with space group $R \overline{3} C \equiv D_{3}^{6} d$ with $z=2$. A factor group analysis is shown in table 4.1(a) along with a correlation scheme for the internal modes of the $\mathrm{AlO}_{6}$ octahedron in table 4.l(b). The bands of A and E symmetry should occur in close proximity as they would be degenerate if the complex had $\mathrm{O}_{\mathrm{h}}$ symmetry. The overall symmetry of $\left[\mathrm{Al}\left(\mathrm{OH}_{2}\right)_{6}\right]^{3^{+}}$is $\mathrm{S}_{6}$ which requires that both components of the inactive $v_{6}$ mode are i.r. active. The Al-O bond distance was
confirmed at $1.88 \AA$ from a recent X -ray determination of $\left[\mathrm{Al}\left(\mathrm{OH}_{2}\right)_{6}\right]\left[\mathrm{RuCl}_{6}\right] \cdot 4 \mathrm{H}_{2} \mathrm{O}$ by Hopkins et al (1969).

The vibrational modes of a regular octahedron are shown in figure 4.2. The order of the skeletal modes follows from the dynamical equations:

$$
\begin{aligned}
& v_{1}\left(A_{1 g}\right)>v_{2}\left(E_{g}\right)>v_{5}\left(T_{2 g}\right) \\
& v_{3}\left(T_{1 u}\right)>v_{4}\left(T_{1} u\right)
\end{aligned}
$$

in addition $\nu_{5} \approx \sqrt{2} \nu_{6}$ (from force constant relations) $\nu_{6}\left(T_{2} u\right)$ The position of the $v_{3}$ relative to $v_{1}$ and $v_{2}$ (the other skeletal stretching modes) depends upon the magnitudes of the GF matrix elements, as described by Nakamoto (1963), and may be greater or less than $v_{1}$, but is always greater than $v_{2}$.

## Results and Discussion

Some data which are useful for reference in this discussion are summarised in table 4.2. The data collected is for mono- and dihydrated complexes. The work on $\mathrm{Rb}_{2}\left[\mathrm{NiCl}_{4}\left(\mathrm{OH}_{2}\right)_{2}\right]$ by Shankel and Bates (1976) is very useful as the crystal has a uni-molecular unit cell, so no coupling will be seen; also the data was recorded at very low temperatures. The fact that only two bands were found in both the i.r. and Raman spectra, which could be attributed to water "librations", indicates that $\rho_{t}$ is weak and could well be absent from the spectra.

Results are shown in figures $4.3 \rightarrow 4.7$ and data are summarised in Table $4.3,4.4(\mathrm{a}), 4.4(\mathrm{~b})$ and a comparison with some other hexahydrates is given in Table 4.5. Judging by values quoted for $\rho_{W}$, $\rho_{r}$ and $\rho_{t}$, the only possible mode due to water motion in this region is $\rho_{t}$. All other modes in this region will be either internal modes of the $\mathrm{AlO}_{6}$ group or lattice modes. None of the bands in this region shows a large deuteriation shift and therefore it is assigned as follows.

All ...r. lattice modes are translatory in type (see Table 4.1(a)). The two lowest energy Raman-active lattice modes, i.e. $71\left(E_{g}\right)$ and $78\left(A_{1 g}\right)$ are considered as the predicted rotatory modes, and all others are assigned to translatory in type. This assumption is supported by the observation that there is very little sensitivity to deuteriation, the exception being the highest $A_{1 g}$ mode in this refion which is reduced by exactly the amount calculated for a simple translation of the $\left[\mathrm{Al}\left(\mathrm{OH}_{2}\right)_{6}\right]^{3+}$ ion, 183 to $180 \mathrm{~cm}^{-1}$.

The remaining bands are the $\nu_{4}, v_{5}$ and $v_{6}$ components of the $\mathrm{AlO}_{6}$ skeletal structure. Of these, only $\nu_{5}$ is allowed to have an $A_{1 g}$ component; the only reasonable assignment for it is $295 \mathrm{~cm}^{-1}$, and it is accompanied by one of the required $E_{g}$ components at $310 \mathrm{~cm}^{-1}$, the other component is either degenerate or is absent.

The weighted average of these values places $v_{6}$ at $216 \mathrm{~cm}^{-1}$ (using $\nu_{5}=\left(\overline{2} v_{6}\right.$ ) this is very close to the average of the i.r. bands at $229\left(A_{2 u}\right)$ and $209\left(E_{u}\right)$. The Kramers-Kronig analysis of the $E_{u}$ spectrum of the protiate, and the values of T.O. frequencies estimated visually are in excellent agreement, except for the band at $209 \mathrm{~cm}^{-1}$ which is significantly displaced from its estimated value. It is considered that this inconsistency is due to two modes of vibration which are ca. $10 \mathrm{~cm}^{-1}$ apart, the width of the band could easily incorporate another mode in near coincidence. Accordingly the $E_{u} \nu_{6}$ modes are estimated to be 209 and $218 \mathrm{~cm}^{-1}$. $v_{4}$ is present at $309 \mathrm{~cm}^{-1}$ in $A_{2 u}$, but no $E_{u}$ component was found at ambient temperatures in either the protiate or the deuteriate, a weak band at $327 \mathrm{~cm}^{-1}$ was observed in a mull of the protiate at liquid nitrogen temperatures, this is considered to be one of the missing $E_{u}$ components.

All modes show deuteriation shifts as is required by the forms of their i2 matrix elements, but these shifts are very much smaller than those of the modes due to water motion. $\nu_{5}$ for the deuteriate can be calculated using a crude model as

$$
\begin{aligned}
& v_{5}^{\prime}=v_{5}\left({ }^{\left.\mathrm{M}_{2} \mathrm{O} / \mathrm{M}_{\mathrm{D}_{2} \mathrm{O}}\right)^{\frac{1}{2}} \text { taking masses of } 18 \text { and } 20 \text { respectively. }} \begin{array}{rlrl}
\nu_{5} 310 & v_{5}{ }^{\prime} \text { (calculated) } & 294 & v_{5}{ }^{\prime} \text { (observed) } \\
291 \\
295 & 278 & 284
\end{array}\right.
\end{aligned}
$$

which shows a very reasonable agreement. Other modes can be calculated using the same model, and show a reasonable agreement; thus none of these modes are due to water librations, and are shown to be internal modes.

The Region Above $350 \mathrm{~cm}^{-}$

This region contains all the librational modes of water, since $\rho_{t}$ is shown to be absent $<350 \mathrm{~cm}^{-1}$, in addition to $v_{1}, v_{2}$ and $\nu_{3}$. Theory (Table 4.1 ) predicts that $A_{1 g}$ should contain four bands in this region, and four are observed. Similarly, $E_{g}$ is predicted to contain eight bands, seven are actually observed. Tris is significant in that these bands must contain $\rho_{t}$, and place a lower limit of $524 \mathrm{~cm}^{-1}$ on it ( $A_{1 g}$ component).

All four $A_{l_{g}}$ bands in this region ( $524,584,701$ and $800 \mathrm{~cm}^{-1}$ ) are substantially shifted on deuteriation, but it is not immediately obvious which bands may be paired in the two spectra. The shift of $\nu_{1}$ on deuteriation may be calculated by a crude model as:

$$
v_{1}^{\prime}=v_{1}\left({ }^{M}\left(\mathrm{H}_{2} \mathrm{O}\right) / M_{\left(\mathrm{D}_{2} \mathrm{O}\right)}\right)^{\frac{1}{2}}
$$

applied to each of the four $A_{1 g}$ modes of the protiate we obtain

| $A_{1 g}$ mode | $\nu_{1}{ }^{\prime}$ (calc.) | $A_{1 g}$ mode $\left(D_{2} O\right)$ obs. |
| :---: | :---: | :---: |
| 524 | 497 | 418 |
| 584 | 554 | 504 |
| 701 | 665 | 593 |
| 800 | 759 | 650 |

Since the highest $A_{1 g}$ mode in the deuteriate is 650 $\mathrm{cm}^{-1}$ it is obvious that the bond at $800 \mathrm{~cm}^{-1}$ cannot be $v_{1}$. Similarly the shift for the mode at $584 \mathrm{~cm}^{-1}$ does not correspond sufficiently closely to any observed band in the deuteriate. Selecting $\nu_{1}$ as $524 \mathrm{~cm}^{-1}$ or $701 \mathrm{~cm}^{-1}$ the remaining bands may be paired:
$\nu_{1}(701): 800(593), 701(650), 584(504), 524(418)$
$\nu_{1}(524): 800(650), 701(593), 584(418), 524$ (504)
all of which yield reasonable deuteriation shifts.

Three arguments may be forwarded to resolve the position of $\nu_{1}$. Firstly solution studies of $\mathrm{AlCl}_{3}$ by Silveira et al (1961, 1965) concluded that $\nu_{1}$ was at $525 \mathrm{~cm}^{-1}$, this is justified by the polarised behaviour of the mode. The other modes identified by Silveira et al were $\nu_{2}(447)$ and $\nu_{5}(340) \mathrm{cm}^{-1}$. Values for $\mathrm{AlCl}_{3}$ in $D_{2} \mathrm{O}$ were $\nu_{1}(503), \nu_{2}(433)$ and $\nu_{5}(313) \mathrm{cm}^{-1}$. All these values are very close to observed bands in solid $\mathrm{AlCl}_{3} \cdot 6 \mathrm{H}_{2} \mathrm{O}$ and the deuteriate, and support $\nu_{1}$ at $524 \mathrm{~cm}^{-1}$. The mode at $432 \mathrm{~cm}^{-1}$ ( $\mathrm{ing}_{\mathrm{g}}$ ) is assigned to $\nu_{2}$ which is in a reasonable position relative to $\nu_{5}$. The remaining $\nu_{2}$ component may be either degenerate or of disappearingly weak intensity, $v_{2}$ may be seen to shift to 418 $\mathrm{cm}^{-1}$ in the deuteriate which is a very reasonable shift.

The second line of argument is to perform a simple Normal Coordinate Analysis calculation. As $\nu_{2}$ and $\nu_{5}$ have been established, and only two possibilities exist for $\nu_{1}$, it may be possible to compute values of $\nu_{3}$ and $\nu_{4}$ using these values and compare them with the observed results. The Ur $\in \mathrm{y}$-Bradley field was selected owing to the relative simplicity of the model. Three force constants are necessary to describe all of the modes of vibration of a regular octahedron using this model. These are:
$\left.\begin{array}{l}\text { K, metal-ligand stretching force constant } \\ \text { F, stretch-stretch interaction constant } \\ \text { H, angle bending constant }\end{array}\right\}$ m dymes $/ \AA \times 10^{-5}$

Several assumptions are made. These include that each complex ion is isolated from the lattice, and that all the $\mathrm{Al}-\mathrm{O}_{6}$ skeletal modes are uneffected by removing the interactions associated with the lattice. Using the equation $|G F-E \lambda|=0$ where $G$ and $F$ are $G$ and $F$ matrices respectively and $E$ is the unit matrix. $\lambda$ is related to observed frequencies by:

$$
\lambda_{i}^{\frac{1}{2}} \times 1303.16=w_{i} \quad \text { where } w_{i}=\text { observed frequency in } \mathrm{cm}^{-1}
$$

The following relationships exist:

$$
\begin{array}{lll}
\mathrm{A}_{1 g} & \left.v_{1}\right) & \mu_{\mathrm{x}}(\mathrm{k}+4 \mathrm{~F})-\lambda_{1}=0 \\
\mathrm{E}_{\mathrm{g}} & \left.v_{2}\right) & \mu_{\mathrm{x}}(\mathrm{k}+0.7 F)-\lambda_{2}=0
\end{array}
$$

$\mu_{\mathrm{X}}$ is the reduced mass of the ligand; $k$ and $F$ are force constants.

$$
\begin{array}{lll}
\mathrm{T}_{2 \mathrm{~g}} & \left.\nu_{5}\right) & 4 \mu_{\mathrm{x}}(\mathrm{H}+0.55 \mathrm{~F})-\lambda_{5}=0 \\
\mathrm{~T}_{2 \mathrm{u}} & \left.\nu_{6}\right) & 2 \mu_{\mathrm{x}}(\mathrm{H}+0.55 \mathrm{~F})-\lambda_{6}=0
\end{array}
$$

It can be seen clearly from these two equations that $v_{5}=\sqrt{2} v_{6}$. H is the third force constant required for the analysis.

The $T_{l u}$ components $v_{3}$ and $v_{4}$ can be calculated using the equation:

$$
\left|\begin{array}{ll}
G_{11} & G_{12} \\
G_{21} & G_{22}
\end{array}\right| \quad\left|\begin{array}{ll}
F_{11} & F_{12} \\
F_{21} & F_{22}
\end{array}\right|-\left|\begin{array}{ll}
\lambda & 0 \\
0 & \lambda
\end{array}\right|=0
$$

which simplifies to:
$\lambda^{2}-\lambda\left(G_{11} F_{11}+G_{22} F_{22}+2 G_{12} F_{12}\right)+\left\{\left(G_{11} G_{22}-G_{12}\right)^{2}\left(F_{11} F_{22}-F_{12}\right)^{2}\right\}=0$

This can be solved as a quadratic equation to find the coefficients, yielding values of $\lambda$ for $\nu_{3}$ and $\nu_{4}$.

$$
\begin{aligned}
& G_{11}=\left(\mu_{x}+2 \mu_{m}\right) \\
& G_{12}=\frac{-4 \mu_{m}}{r}=G_{21} \\
& G_{22}=\frac{2}{r^{2}}\left(\mu_{x}+4 \mu_{m}\right) \\
& F_{11}=(k+1.8 F) \\
& F_{12}=0.9 r F=F_{21} \\
& F_{22}=r^{2}(H+0.55 F)
\end{aligned}
$$

where $\mu_{m}$ is the reduced mass of the metal atom, $r$ is the metaloxygen bond distance. A simple computer program was written for the purposes of this thesis to calculate $v_{3}$ and $v_{4}$ from values fed in for $\nu_{1}, \nu_{2}$ and $\nu_{5} ; r$ was taken as $1.88 \AA$ following a recent $X-$ ray structure determination of $\left[\mathrm{Al}\left(\mathrm{OH}_{2}\right)_{6}\right]\left[\mathrm{RuCl}_{6}\right] .4 \mathrm{H}_{2} \mathrm{O}$ by Hopkins et al (1969). The results obtained were:

$$
v_{3}(\text { calc. }) v_{4}(\text { calc. }) \quad v_{4} \text { (obs.) } \quad k \quad F
$$

| $\nu_{1}(701)$ | 591 | 269 | 309 | 1.22 | 0.92 | -0.28 |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $v_{1}(524)$ | 653 | 319 | 309 | 1.79 | 0.26 | 0.09 |

With $v_{1}$ at $701 \mathrm{~cm}^{-1} v_{4}$ was calculated $40 \mathrm{~cm}^{-1}$ below its observed value, in addition, the values of $k$ and $F$ are insufficiently different. $F$ is much too large relative to $k$. With $\nu_{1}$ at $524 v_{4}$ was calculated only $10 \mathrm{~cm}^{-1}$ away from its observed value and $k, F$ and $H$ have reasonable magnitudes. This strongly supports $v_{1}$ at 524 $\mathrm{cm}^{-1}$. A similar calculation for the deuteriate with $v_{1}$ at $504 \mathrm{~cm}^{-1}$ gave $v_{3}$ at $644 \mathrm{~cm}^{-1}$ and $v_{4}$ at $302 \mathrm{~cm}^{-1}$ (observed in the deuteriate at $282 \mathrm{~cm}^{-1}$ ). The exact positioning of $v_{3}$ with either of the above calculations has relative merits and disadvantages. The value of $591 \mathrm{~cm}^{-1}$ for $v_{1}$ at $701 \mathrm{~cm}^{-1}$ places $\nu_{3}$ near to the intense reflectance bands at $560\left(A_{2 u}\right)$ and $580\left(E_{u}\right)$ which is reasonable since $v_{3}$ is reasonably expected to be a strongly allowed vibration in the i.r. However $v_{4}$ is mush too low. The value of 653 with $v_{1}$ at $524 \mathrm{~cm}^{-1}$ places $\nu_{3}$ near to the weak bands at $678 \mathrm{~cm}^{-1}\left(\mathrm{~A}_{2 \mathrm{u}}\right)$ and 664 ( $E_{u}$ ), it is not immediately obvious why $v_{3}$ should be so weak.

The third line of argument by which $\nu_{1}$ may be decided is that for each of the groups $\rho_{r}, \rho_{W}, \rho_{t}$ there should be three bands bearing symmetry labels $A, E, E$. It is most useful here to consider the Raman data since the i.r. is obviously well short of the theoretically predicted number (this is considered in more detail later). How much splitting may be expected can be guessed from the behaviour of $v(\mathrm{OH})$ and $\delta(\mathrm{OH})$. The $\mathrm{A}_{\mathrm{l}} \mathrm{g}$ components of $v(\mathrm{OH})$ seen are the $v_{1}$ and $v_{3}$ modes of the $\mathrm{H}_{2} \mathrm{O}$ molecule. $\mathrm{E}_{\mathrm{g}}$ is missing two bands in this region. If the reasonable assumption is made that the two $E_{g}$ modes observed are $v_{1}$, the total Davydov splitting
is $31 \mathrm{~cm}^{-1}$. Therefore equally modest splittings of the components of $\rho_{W}, \rho_{r}$ and $\rho_{t}$ should be observed. All components of $v(O H)$ are low in frequency compared to situations in which little or no hydrogen bonding is present, e.g. $3300 \mathrm{~cm}^{-1}$ in the Raman spectrum of $\left[\mathrm{NiCl}_{4}\left(\mathrm{OH}_{2}\right)_{2}\right]^{2-}$. If consideration of $v_{3}$ is deferred, two alternative groupings of the modes may be postulated depending on the choice of $v_{1}$.


The i.r. assignment is the same in either case. The total Davydov splitting is rather large for the middle group whichever choice of $v_{1}$ is made.

If the i.r. data are now considered in detail, both $\mathrm{A}_{2} u$ and $E_{u}$ spectra show reflectance bands at similar positions and of similar relative intensities. The $A_{2 u}$ spectrum shows three of the four predicted bands, the $E_{u}$ spectrum shows only three of the theoretical eight bands. An explanation may be given in terms of the coupling between the molecules in the unit cell. If this is weak, as shown by the $v_{1}$ components of $v(\mathrm{OH})$ the selection rules which apply are those of the site group $\mathrm{S}_{6}$. This describes the symmetry of the field which one complex ion experiences in the crystal, and correctiy accounts for the absence of one $\nu_{5}\left(E_{g}\right)$ and one $\nu_{2}\left(E_{g}\right)$ component in the spectra. The coupling between molecules is via the weakly hydrogen bonded chlorides which separate the complex ions and therefore this explanation is plausible. Since $\mathrm{A}_{2 \mathrm{~g}}$ is inactive, no further test of this theory can be made. The behaviour of $v_{6}$ which according to $S_{6}$ symmetry should show only one $E_{u}$ component is undecided. A null spectrum at low temperature showed two components at ca. $210 \mathrm{~cm}^{-1}$; the shape of the $\varepsilon^{\prime \prime}$ function is indicative of two components in this region.

The groupings of the librational modes $\rho_{W}, \rho_{t}$ and $\rho_{r}$ is supported by the consideration of the moments of inertia of the isolated water molecule. For the free molecule, the motions which become $\rho_{W}, \rho_{t}$ and $\rho_{r}$ have moments of inertia in the ratio 1:1.9:2.9. The coordinatedmodes may therefore be reasonably
presumed to follow the order $\rho_{\mathrm{W}}>\rho_{\mathrm{t}}>\rho_{\mathrm{r}}$. There is good evidence that, at least for mono- and di-aquated complexes, $\rho_{\mathrm{W}}>\rho_{\mathrm{r}}$ (see Table 4.2), the position of $\rho_{t}$ is unsettled. It is proposed here that it lies between $\rho_{W}$ and $\rho_{r}$, at least in hexa aquo complexes. The feebleness of the i.r. bands attributed to $\rho_{t}$ is consistent with this assignment, since they arise from the inactive motion $A_{2}$ in $C_{2_{V}}$ and are only made active by the field subtended by the surroundings.

The assignment of $v_{3}$ can no longer be neglected. Since evidence strongly follows $\nu_{1}$ at $524 \mathrm{~cm}^{-1}, \nu_{3}$ must lie close to the region calculated for it, i.e. $653^{\circ} \mathrm{cm}^{-1}$ for the hydrate and $644 \mathrm{~cm}^{-1}$ in the deuteriate. If $\nu_{1}$ is taken at $701 \mathrm{~cm}^{-1}$ $\nu_{3}$ may lie beneath the very intense bands at $560\left(A_{2 u}\right)$ and $580\left(E_{u}\right)$. The assignment of these modes to $\rho_{r}$ cannot be disturbed as both bands show very large shifts on deuteriation to ca. $400 \mathrm{~cm}^{-1}$, yielding ratios of $\sim 0.72$ which is close to the expected 0.72 for librational modes. Unfortunately the i.r. reflectance spectra for the deuteriate in the region $>500 \mathrm{~cm}^{-1}$ were of much lower quality than the protiate. It was not certain whether there were any weak bands at ca. $640 \mathrm{~cm}^{-1}$ which may be attributed to $\nu_{3}$. Although it is not obvious why $\nu_{3}$ should be so weak, the bands at $678\left(\mathrm{~A}_{2 \mathrm{u}}\right)$ and $664\left(\mathrm{E}_{\mathrm{u}}\right)$ are attributed to $v_{3}$ on the basis of evidence accumulated. This explains the absence of one $A_{2 u}$ mode, attributed to $\rho_{t}$, which is expected to be weak in the i.r.

The $E_{g}$ spectrum of the deuteriate is difficult to explain unless some of the observed bands are attributed to more than one mode, since fewer bands are found than in the protiate. All these $E_{g}$ bands are due to water librations since $v_{2}$ has been located at 423 and $418 \mathrm{~cm}^{-1}$ in the hydrate and deuteriate respectively. On the basis of relative intensities the modes are paired as:

| protiate | deuteriate | ${\nu D_{2} O /}_{\nu_{2} \mathrm{O}}$ |
| :---: | :---: | :---: |
| 534 | 408 | 0.78 |
| 563 | 443 | 0.78 |
| 610 | 504 | 0.83 |
| 825 | 617 | 0.75 |

These assignments are not entirely satisfactory. For a definitive assignment a much more detailed experimental approach must be adopted. Data should be collected for a range of temperatures over the i.r. and Raman region between $350-1000 \mathrm{~cm}^{-1}$.

## Conclusion

A comparison of the assignment here with those for other $\mathrm{MO}_{6}$ skeletal modes for $\left[\mathrm{M}\left(\mathrm{OH}_{2}\right)_{6}\right]^{2^{+}}$ions is given in Table 4.5. All frequencies appear to be considerably raised by the greater charge on aluminium, since the masses of aluminium and magnesium are not too dissimilar. For $M=N i$ there is a further reduction
in $\nu_{1}, \nu_{2}$ and $\nu_{3}$ frequencies due to the increased mass of the metal.

The spectrum of $\left[\mathrm{Al}\left(\mathrm{OH}_{2}\right)_{6}\right] \mathrm{Cl}_{3}$ has been almost entirely established; there is some ambiguity about the positioning of $\nu_{3}$. It is not clear why $\nu_{1}$ and $\nu_{3}$ should be so weak, as they should be very strongly allowed modes. Some further experimental work, on the deuteriate in particular, may allow a definitive assignment to be made.

Table 4.1
(a) Factor group analysis for $\left[\mathrm{Al}\left(\mathrm{OH}_{2}\right)_{6}\right] \mathrm{Cl}_{3}$

| $D_{3 d}^{6}$ | ${ }^{\text {A }} 1 \mathrm{~g}$ | $\mathrm{A}_{2} \mathrm{~g}$ | $E_{g}$ | $\mathrm{A}_{1 \mathrm{u}}$ | $\mathrm{A}_{2 \mathrm{u}}$ | $\mathrm{E}_{\mathrm{u}}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Trans. | 1 | 2 | 3 | 2 | 2 | 47 |  |
| Rotatory | 1 | 1 | 2 |  |  | \} | $\mathrm{AlO}_{6}$ Octahedron |
| Internal | 2 | 2 | 4 | 3 | 3 | 6 - |  |
| $\rho_{\text {W }}$ | 1 | 1 | 2 | 1 | 1 | 27 | Modes due to coordinated |
| $\rho_{r}$ | 1 | 1 | 2 | 1 | 1 | 2 | water molecules |
| $\rho_{t}$ | 1 | 1 | 2 | 1 | 1 | 2 \} |  |
| $\delta$ | 1 | 1 | 2 | 1 | 1 | 2 |  |
| $\nu$ | 2 | 2 | 4 | 2 | 2 | 4 J |  |
| Total | 10 | 11 | 21 | 11 | 12 | 23 |  |
| Activity | $\mathrm{x}^{2}+\mathrm{y}^{2}$ |  | $\mathrm{x}^{2}-\mathrm{y}^{2}$ |  | z | X, Y |  |
|  | $z^{2}$ |  | xy, $x z$ |  |  |  |  |
|  |  |  | yz |  |  |  |  |

Trans $=$ optic branch translatory modes, acoustic modes have been subtracted; Rotatory $=$ optic branch rotatory modes; Internal $=$ modes due to Al-0 band stretching and deformations $=$ sum of $a$. $\rho_{W}, \rho_{r}, \rho_{t}$ numbers of wag, rock and twisting modes of coordinated water; $\delta=$ bending modes of coordinated water; $\nu=$ stretching modes of coordinated water.

## Table 4.1

(b) Correlation scheme for $\mathrm{AlO}_{6}$

| Oh | Site, $S_{6}$ | $\xrightarrow{\mathrm{x} 2}$ | $\underset{\text { Crystal, }}{\boldsymbol{a}} \mathrm{D}_{3 \mathrm{~d}}^{6}$ |
| :---: | :---: | :---: | :---: |
| $v_{1}\left(A_{1}{ }_{\mathrm{g}}\right)$ | ${ }^{\text {A }} \mathrm{g}$ |  | $A_{1}{ }_{g}+A_{2} g^{\prime}$ |
| $v_{2}\left(E_{g}\right)$ | $E_{g}$ |  | $2 E_{g}$ |
| $\nu_{5}\left(T_{2} \mathrm{~g}\right)$ | $A_{g}+E_{g}$ |  | $A_{1 g}+A_{2 g}+2 E_{g}$ |
| $v_{3}\left(T_{1}{ }_{u}\right)$ | $A_{u}+E_{u}$ |  | $A_{1 u}+A_{2 u}+2 E_{u}$ |
| $v_{4}\left(\mathrm{~T}_{1} \mathrm{u}\right)$ | $A_{u}+E_{u}$ |  | $A_{1 u}+A_{2 u}+2 E_{u}$ |
| $v_{6}\left(T_{2} u\right)$ | $A_{u}+E_{u}$ |  | $A_{1 u}+A_{2 u}+2 E_{u}$ |

Table 4.2

|  | $\rho_{\text {w }}$ | $\rho_{r}$ | $v\left(\mathrm{M}-\mathrm{OH}_{2}\right)$ |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  |  | I.r. | Raman |
| $\mathrm{K}_{2}\left[\mathrm{Fe}^{\mathrm{III}} \mathrm{Cl}_{5}\left(\mathrm{OH}_{2}\right)\right]$ | 600 | 460 | 390 |  |
| $\mathrm{Cs}_{2}\left[\mathrm{Fe}^{\mathrm{III}} \mathrm{Cl}_{5}\left(\mathrm{OH}_{2}\right)\right]$ | 540 (430) | 460 (340) | 320 (310) |  |
| $\mathrm{Cs}_{2}\left[\mathrm{Mn}^{\text {II }} \mathrm{Cl}_{4}\left(\mathrm{OH}_{2}\right)_{2}\right]$ | 570 (430) | 455 (350) | 295 (282) | 290 |
| $\mathrm{Rb}_{2}\left[\mathrm{Ni}^{\mathrm{II}} \mathrm{Cl}_{4}\left(\mathrm{OH}_{2}\right)_{2}\right]$ | 621 | 471 | 353 | 342 |
| $\mathrm{Cs}\left[\mathrm{MnIII}_{\left.\mathrm{F}_{4}\left(\mathrm{OH}_{2}\right)_{2}\right]}\right.$ | $730^{\text {a }}$ (525) | 665 (470) | 370 (367) |  |

Authors preferred not to distinguish between $\rho_{W}$ and $\rho_{r}$.
Deuteriated data is shown in parentheses.

## Table 4.3

(a) I.r. reflectance data - T.0. frequencies $/ \mathrm{cm}^{-1}$ for single crystal $\mathrm{AlCl}_{3} \cdot 6 \mathrm{H}_{2} \mathrm{O}$ and $\mathrm{AlCl}_{3} \cdot 6 \mathrm{O}_{2} \mathrm{O}$ (in parentheses) at 295 K .

| $\mathrm{A}_{2} \mathrm{u}$ | $E_{u}$ | Assignment |
| :---: | :---: | :---: |
| 82 (80) | 151 (151) | ${ }^{\nu}$ Trans |
| 138 (138) | 167 (167) |  |
| 229 (215) | $\left.\begin{array}{l}209 \\ 218\end{array}\right\}(208)^{a}$ | $v_{6}$ |
| 309 (282) |  | $v_{4}$ |
| 560 (400) | 580 (420) |  |
| 678 | 664 | $\nu_{3}+\rho_{W}+\rho_{r}\left(+\rho_{t}\right)$ |
| 790 | 836 |  |

(b) Mull spectrum of $\mathrm{AlCl}_{3} \cdot 6 \mathrm{H}_{2} \mathrm{O}$ at liquid nitrogen temperature

$\mathrm{m}=$ medium; $\mathrm{sh}=$ shoulder; $\mathrm{s}=$ strong; $\mathrm{w}=$ weak
a Shape of the reflectance band and Kramers-Kronig analyses are inconsistent; this may indicate the presence of an extra band 218 in protiate, mull spectrum shows an additional peak in this region.

Table 4.4
(a) Single crystal Raman data $\mathrm{cm}^{-1}$ and intensities (arbitrary units) for $\mathrm{AlCl}_{3} \cdot 6 \mathrm{H}_{2} \mathrm{O}$, using 514.5 nm radiation at 115 K .
$\begin{array}{rr}\text { Region of table (a) } & A_{1_{g}} \text { modes recorded at slit width } 1.5 \mathrm{~cm}^{-1} \\ & E_{g} \text { modes recorded at }\end{array}$

Region of table (b) $\quad A_{1}$ modes recorded at slit width $3.3 \mathrm{~cm}^{-1}$
$E_{g}$ modes recorded at
$4.7 \mathrm{~cm}^{-1}$
(b) Single crystal Raman data $\mathrm{cm}^{-1}$ and intensities (arbitrary units) for $\mathrm{AlCl}_{3} \cdot 6 \mathrm{O}_{2} \mathrm{O}$, using 514.5 nm radiation at 115 K .
Region of table (a) All modes recorded at slit width $1 \mathrm{~cm}^{-1}$
Region of table (b) All modes recorded at slit width $2.85 \mathrm{~cm}^{-1}$
$\nu_{R}=$ Rotatory modes of $\left[\mathrm{Al}\left(\mathrm{OH}_{2}\right)_{6}\right]^{3^{+}}$
$\nu_{T}=$ Translatory modes

Table 4.4(a) Raman wavelength ( $\mathrm{cm}^{-1}$ ) and intensities (arbitrary units) for single crystal $\mathrm{AlCl}_{3} \cdot 6 \mathrm{H}_{2} \mathrm{O}$.

| $\mathrm{cm}^{-1}$ | Symmetry species | $y(z z) x$ | $y(x y) x$ | $y(x z) x$ | $y(z y) x$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 71 | $E_{g}$ |  | 20 | 40 | 15 |  |
| 78 | ${ }^{A} 1_{g}$ | 15 |  |  |  | $\nu_{R}$ |
| 110 | $E_{g}$ |  | 15 | 22 | 10 |  |
| 128 | $E_{g}$ |  | 74 | 100 | 35 |  |
| 138 | $E_{g}$ |  | 37 | 50 | 20 | $\nu_{T}$ |
| 150 | $E_{g}$ |  | 18 | 30 | 14 |  |
| 183 | $A_{1} g^{\prime}$ | 100 | 8 | 10 | 13 |  |
| 295 | ${ }^{A}{ }_{1 g}$ | 42 |  |  |  | $v_{5}$ |
| 310 | $E_{g}$ |  | 50 | 80 | 33 |  |
| 432 | $E_{g}$ |  | 5 | 14 | 5 | $v_{2}$ |
| 524 | $\left.{ }^{A}\right]_{g}$ | 5 |  |  |  | $\nu_{1}$ |
| 534 | $E_{g}$ |  | 5 | 8 | 3 |  |
| 566 | $E_{g}$ |  | 10 | 10 | 5 |  |
| 584 | ${ }^{A_{1}} \mathrm{~g}$ | 10 |  |  |  |  |
| 610 | $E_{g}$ |  | 8 | 30 | 7 | $\mathrm{H}_{2} \mathrm{O}$ |
| 622 | $E_{g}$ |  | 6 | 35 | 8 | librations |
| 701 | $A_{1}{ }_{g}$ | 15 |  |  |  |  |
| 800 | $A_{1 g}{ }^{+E} g_{g}$ | 30 |  | 5 | 10 |  |
| 825 | $E_{g}$ |  | 15 | 12 | 12 |  |
| 1094 | $A_{1} g_{g}$ | 15 |  |  |  | overtone |
| 1645 | $E_{g}+A^{\prime} \mathrm{g}$ | 3 | 8 | 10 | 6 | $\delta(\mathrm{OH})$ |
| 3045 | $E_{g}$ |  | 13 | 80 | 30 |  |
| 3053 | $A_{1}{ }_{g}$ | 45 |  |  |  | $\nu_{1}\left(\mathrm{H}_{2} \mathrm{O}\right)$ |
| 3076 | $E_{g}$ |  | 18 | 11 |  |  |
| 3162 | $A_{1 g}$ | 3 |  |  |  | $\nu_{3}\left(\mathrm{H}_{2} \mathrm{O}\right)$ |

Table $4.4(\mathrm{~b}) \quad$ Raman spectra of single crystal $\mathrm{AlCl}_{3} \cdot 6 \mathrm{O}_{2} 0$


Table 4.5 Comparison of modes of vibration of $\left[\mathrm{M}\left(\mathrm{OH}_{2}\right)_{6}\right]^{\mathrm{n}+}$

$$
\mathrm{Al}\left(\mathrm{OH}_{2}\right)_{6}{ }^{3+(\mathrm{a})} \quad \mathrm{Ni}\left(\mathrm{OH}_{2}\right)_{6}{ }^{2+(\mathrm{b})} \quad \mathrm{Mg}\left(\mathrm{OH}_{2}\right)_{6}{ }^{2+}(\mathrm{c})
$$

$\begin{array}{llll}\nu_{1} & 524 & 382 & 363\end{array}$
$\begin{array}{llll}\nu_{2} & 432 & 301 & 310\end{array}$
$v_{3}$
570 or 653
333, 381
421
$v_{4}$
316, 327
209, 207
200-215
(4 bands)
$\nu_{5} \quad 295,310$
209, 191
268-285
(5 bands)
$v_{6} \quad 205,224,250 \quad 142,146$
(a) This work.
(b) Jäger and Schaack (1973).
(c) Hillaire et al (B) (1971).

FIG. 4.1


FIG. 4.2


$v_{1}\left(\mathrm{~A}_{1 \mathrm{~g}}\right)$
$v_{2}\left(E_{g}\right)$
$v(X-Y)$

$$
v(X-Y)
$$




$$
\begin{aligned}
& v_{3}\left(T_{1 u}\right) \\
& \delta(Y-X-Y)
\end{aligned}
$$



FIG. 4.3


FIG. 4.4


## $\mathrm{AlCl}_{3} \cdot 6 \mathrm{H}_{2} \mathrm{O}$

Figure $4.5 \quad \mathrm{~A}_{2 \mathrm{u}} \quad 295 \mathrm{~K}$
Figure $4.6 \quad \mathrm{E}_{\mathrm{u}} \quad 295 \mathrm{~K}$



FIG. 4.7


FIG. 4.8

## $\mathrm{AlCl}_{3} \cdot 6 \mathrm{H}_{2} \mathrm{O}$ Mull at Liquid Nitrogen Temperature



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## Chapter Five

Far-i.r. Spectra of Mercuric Chloride
and Mercuric Bromide

Introduction

Both mercuric chloride and bromide have been extensively studied using Raman (reference list l) and i.r. spectroscopy (reference list 2).

The majority of the data obtained has been confined to the positions of the stretching modes allowed in $D_{\infty h}$ molecules, these are: $\nu_{l}, \Sigma_{g}^{+}, v(H g-X)_{\text {sym }}$; and $\nu_{3}, \Sigma_{u}^{+}, v(H g-X)_{\text {asym }}$, and these have been assigned beyond doubt for gaseous, molten, and dissolved samples, mainly on the basis of the Raman polarisation property of $\nu_{1} ; \nu_{3}$ may be assigned by elimination or by using force constant relations.

Information on the position of $\nu_{2}\left(\pi_{u}, \delta\left(\mathrm{HgX}_{2}\right)\right)$ was first obtained from the analysis of the fine structure of the electronic spectra of the vapours of the compounds; (Wehrli 1938, 1940) and Sponer and Teller (1941) calculated values of $v_{2}$ in the region of $70 \mathrm{~cm}^{-1}$ for $\mathrm{HgCl}_{2}$ and $41 \mathrm{~cm}^{-1}$ for $\mathrm{HgBr}_{2}$. These values are very low, and have subsequently been correced after the observation of $\nu_{2}$ in far-i.r. gas phase spectra by Malt'sev et al (1971). Matrix-isolation studies by Loewenschuss, Ron and Schepp (1969) support these values; they obtained values of $v_{2}$ of $107 \mathrm{~cm}^{-1}$ for $\mathrm{HgCl}_{2}$, and $73 \mathrm{~cm}^{-1}$ for $\mathrm{HgBr}_{2}$. These compare favourably with values of $100 \mathrm{~cm}^{-1}$ for $\mathrm{HgCl}_{2}$ and $68 \mathrm{~cm}^{-1}$ for $\mathrm{HgBr}_{2}$ obtained by Malt'sev et al. These values are taken as determined.

Studies of the solids were, until fairly recently, fragmented and incomplete. Rao (1941) first reported low frequency Raman data on $\mathrm{HgCl}_{2}$ observing bands at 73, 95, and $124 \mathrm{~cm}^{-1}$. He concluded that the lowest band may have been the $v_{2}$ mode, the others lattice modes. The complete frequency range single crystal Raman spectrum of $\mathrm{HgCl}_{2}$ was obtained by Brahms and Mathieu (1960), and a few, relatively minor, corrections were added by Poulet and Mathieu (1963). Both studies were conducted at ambient temperature. The frequency shifts on cooling to low temperatures may be inferred from data collected on a polycrystalline sample at $77^{\circ} \mathrm{K}$ by Decamps et al (1973). No single crystal Raman study of $\mathrm{HgBr}_{2}$ has been published to date, however, Decamps et al (1973) list bands observed from a polycrystalline sample at $77^{\circ} \mathrm{K}$.
I.r. information on both $\mathrm{HgCl}_{2}$ and $\mathrm{HgBr}_{2}$ is extremely fragmented; there are many reports in the literature of i.r. absorption experiments (reference list 2); of those which concern the solid state, few give data in the region below the stretching modes $v_{1}$ and $v_{3}$, and none has involved the use of polarised radiation. Accordingly, no firm data is available on which to base a unique assignment of either $\mathrm{HgCl}_{2}$ or $\mathrm{HgBr}_{2}$ in the i.r. In addition, it is doubtful whether the spectra have been fully established in the past.

## Experimental

Samples of commercial grade $\mathrm{HgBr}_{2}$ and $\mathrm{HgCl}_{2}$ were purified by two successive vacuum sublimations. Crystals were grown by vapour-phase deposition of the purified sublimates. A full description of the apparatus used is found in Chapter Two, section B. The tubes were evacuated to a pressure of $10^{-2}$ torr using a rotary vacuum pump, and were pulled through a thermal gradient at a rate of extrusion of ca. 1 cm per day. Peak temperatures were for $\mathrm{HgCl}_{2}\left(130^{\circ} \mathrm{C}\right)$ and $\mathrm{HgBr}_{2}\left(110^{\circ} \mathrm{C}\right)$. Each boule of crystalline sublimate was cut into sections and polished, to expose developed faces which showed indicatrix directions under a polarising microscope. Axes corresponding to indicatrix directions were identified using X-ray methods and labelled according to the standard axis set given in "International Tables for X-Ray Crystallography". Accordingly the axes chosen were :

$$
\begin{array}{ll}
\mathrm{HgCl}_{2} & a_{0}=12.735 \AA ; b_{0}=5.963 \AA ; c_{0}=4.325 \AA \\
\mathrm{HgBr}_{2} & a_{0}=4.624 \AA ; b_{0}=6.798 \AA ; c_{0}=12.445 \AA
\end{array}
$$

The sample of $\mathrm{HgCl}_{2}$ used to collect data by i.r. reflectance measured $5(x) \times 3(z) \times 2(y) \mathrm{mm}$, and the sample of $\mathrm{HgBr}_{2}$ used, also for reflectance, measured $15(\mathrm{z}) \mathrm{x} 6(\mathrm{x}) \mathrm{x} 3(\mathrm{y}) \mathrm{mm}$. Axes are shown in parentheses.

The majority of the data collected was by using reflectance spectroscopy. This is because both compounds are highly
absorbing in the far-i.r. and have measurable vapour pressures at room temperature. As the instrument used (FS720) is a single beam instrument, and therefore has to be evacuated to pressures of $\sim 10^{-2}$ torr for collecting data, it was felt that the sufficiently thin slices of crystal necessary for transmission experiments would probably sublime under the influence of the vacuum at ambient temperatures. Some transmission experiments were conducted using the cleavage fragments of ca. $1.5 \mathrm{~mm}^{2}$ exposing in both cases the ( xz ) face of the crystals. For $\mathrm{HgCl}_{2}$ this face contains the directions which locate $v_{1}$ and $v_{3}$, for $\mathrm{HgBr}_{2}$ only one direction on this face contains $v_{1}$ and $v_{3}$. Repeated attempts to obtain cleavage fragments containing the ( $y z$ ) or ( $x y$ ) faces failed due to the extreme softness of the material.

Samples for reflectance were mounted onto copper blocks using a quick-setting epoxy resin. It was found that if aluminium powder was incorporated into the resin the samples decomposed over a period of $4-5 \mathrm{~h}$, and was therefore not used. Using a home-made liquid nitrogen cryostat temperatures of $115^{\circ} \mathrm{K}$ were obtained at the samples.

Several attempts were made to obtain single crystal Raman data on both compounds, using all 3 scattering geometries and an immersion cell. Neither compound showed any significant intensity changes with orientation. This is attributed to
the existence of micro-domains within the crystals, although this was not evident in the examination with a polarising microscope.

Theory

Wyckoff (1964) has reported the X-ray structure determinations of both compounds, but he uses a non-standard nomenclature. When corrected to the standard setting given in "International X-Ray Tables" this gives:
$\mathrm{HgCl}_{2}$ symmetry Pnma $\equiv \mathrm{D}_{2}^{16}$ with $\mathrm{z}=4$
$\mathrm{HgBr}_{2}$ symmetry $\mathrm{Cmc}_{1} \equiv \mathrm{C}_{2 \mathrm{v}}^{12}$ with $\mathrm{z}=2$
both compounds crystallise in the orthorhombic system.

Both compounds are composed of molecules stacked in planar sheets parallel to one crystallographic axis. The two $\mathrm{Hg}-\mathrm{X}$ bands are not required to be either equal in length or colinear, however, the actual distortions are sufficiently small to allow $D_{\infty h}$ to form the basis of an understanding of the spectra.

The factor group analyses have been reported previously by Adams and Appleby (1977) (6/2230) and (7/079) for $\mathrm{HgCl}_{2}$ and $\mathrm{HgBr}_{2}$ respectively. $\mathrm{HgCl}_{2}$ has all atoms on sites 4 c and the molecular sheets are stacked parallel to the b axis. $\mathrm{HgBr}_{2}$ has all atoms on sites 4 a , molecular sheets are stacked parallel
to the a axis. Factor group analyses are shown in Tables 5.1 and 5.2, and a correlation scheme for both molecules is shown in Table 5.3.

Results and discussion for $\mathrm{HgCl}_{2}$

The f.g.a. in Table 5.1 shows that the vector of optically active modes allows for:
$6 A_{g}+3 B_{1 g}+6 B_{2 g}+3 B_{3 g}+5 B_{1 u}+2 B_{2 u}+5 B_{3 u}$
g modes are Raman active, $u$ modes are i.r. active

If it is assumed, for the purposes of accounting for the number of modes, that these may be decomposed into internal and external modes

$$
\left.\begin{array}{ll}
N_{\text {(internal) }} & =3 A_{g}+B_{1 g}+3 B_{2 g}+B_{3 g}+3 B_{1 u}+B_{2 u}+3 B_{3 u} \\
N_{\text {trans }} & =2 A_{g}+B_{1 g}+2 B_{2 g}+B_{3 g}+B_{1 u}+B_{3 u} \\
N_{\text {rotatory }} & =A_{g}+B_{1 g}+B_{2 g}+B_{3 g}+B_{l u}+B_{2 u}+B_{3 u}
\end{array}\right\} \begin{gathered}
\begin{array}{c}
\text { external" } \\
\text { modes }
\end{array}
\end{gathered}
$$

It can be seen from the correlation scheme (Table 5.3) that $\nu_{2}$ is active in each species, $v_{3}$ and $v_{1}$ are active only in $A_{g}, B_{2 g}$, $B_{1 u}$ and $B_{3 u}$. If attention is confined to i.r. active modes, theory predicts that:
$B_{1} u$ will contain 3 internal modes $\left(v_{1}, v_{2}\right.$ and $\left.\nu_{3}\right)$ as well
as 1 rotatory and 1 translatory mode.

```
B}2u\mathrm{ will contain l internal mode ( }\mp@subsup{v}{2}{}\mathrm{ ) and l rotatory
only.
B}3u\mathrm{ will contain 3 internal modes ( v
translatory and l rotatory (as B iu).
```

Results are shown in figures 5.1, 5.2, and 5.3, and data summarised in Table 5.4.

With the exception of the $\mathrm{B}_{3}$ Davydov component of $v_{1}$, which was only observed in reflectance at low temperature, all the predicted components of $v_{1}$ and $\nu_{3}$ are clearly observed at room temperature (region $>200 \mathrm{~cm}^{-1}$ ). The polarised behaviour of the weak $\nu_{3}$ modes was confirmed by transmission measurements through a thin cleavage fragment containing the ( $x z$ ) face. All other modes showed total adsorption in the range studied. Inco: porating this data with that of Brahms and Mathieu (1960), a full assignment of $\nu_{1}$ and $\nu_{3}$ modes is possible.

|  | $\mathrm{A}_{\mathrm{g}}$ | $\mathrm{B}_{2 \mathrm{~g}}$ | $\mathrm{~B}_{1 \mathrm{u}}$ | $\mathrm{B}_{3 \mathrm{u}}$ | Average | Vapour | $\Delta \nu \mathrm{cm}^{-1}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\nu_{1}$ | 310 | 316 | 312 | 330 | 317 | 360 | -43 |
| $\nu_{3}$ | n.0. | 375 | 379 | 372 | 375 | 413 | -38 |

The frequencies obtained by Klemperer and Lindemann (1956) taken in the gas phase, are used as a standard to calculate the shift $\Delta v$, which is a measure of the effect of taking an isolated molecule and incorporating it into the crystal.

The subscripts 2 and 3 of the data obtained by Brahms and Mathieu (1960) for their symmetry species are interchanged to conform with the standard setting which is used here. The forms of the Davydov components of $\nu_{1}$ are shown in figure 5.7(a).

The region below $\nu_{1}$ and $\nu_{3}$

This region presents a more difficult problem of assignment, as it contains translatory and rotatory modes in addition to components of $v_{2}$. The only adequate far-i.r. data collected on solid $\mathrm{HgCl}_{2}$ is that of Decamps and Hadni (1968). They reported a weak doublet at 32 and $39 \mathrm{~cm}^{-1}$, followed by bands at 75.5 (sharp) and 97 (broad) $\mathrm{cm}^{-1}$, in an unoriented study. Other reports by Mikawa et al (1966) and Adams and Appleby (1977) (6/2230) give various estimates of the band above $75.5 \mathrm{~cm}^{-1}$ which is confirmed in both cases. The reflectance data reported here shows that this region is a composite of five bands with T.O. frequencies of $94,96,108,115$ and $123 \mathrm{~cm}^{-1}$. The modes reported by Decamps and Hadni at 32 and $39 \mathrm{~cm}^{-1}$ were observed as weak features distorted by the neighbouring high intensity reflectance bands. In transmission measurements, these bands were clearly observed and their polarisation behaviour was seen to conform with that seen in the reflectance spectra. The modes above ca. $70 \mathrm{~cm}^{-1}$ showed total absorption and no accurate estimate of their maxima could be taken.

The Raman data of Poulet and Mathieu (1963) in this region, show bands in a similar pattern to the i.r. spectra.

If the i.r. data collected here is considered along with the Raman evidence an assignment can be attempted.

Theory predicts that the $B_{2 u}$ spectrum will contain only $\nu_{2}$ and a rotatory mode. T.O. frequencies were calculated at 94 and $115 \mathrm{~cm}^{-1}$, although which is which cannot be ascertained.

Both $B_{1 u}$ and $B_{3 u}$ spectra are predicted to contain a $v_{2}$ component, one rotatory and one translatory mode each. At ambient temperatures the $\mathrm{B}_{1 \mathrm{u}}$ spectrum contained bands at 40, 74 , and $108 \mathrm{~cm}^{-1}$; however, on cooling to $115^{\circ} \mathrm{K}$, the mode at $108 \mathrm{~cm}^{-1}$ is seen to split into a doublet with $T .0$. frequencies of 113 and $127 \mathrm{~cm}^{-1}$, thus providing one more than the theoretically allowed number. Two aliernatives can be forwarded to account for this behaviour.
i) The three Biu bands at 76,113 , and $127 \mathrm{~cm}^{-1}$ at $115^{0} \mathrm{~K}$ are all fundamentals, this means that in the same region $B_{3 u}$ is accidentally short of one band. This forces the implication that the absorption at 32 and $40 \mathrm{~cm}^{-1}$ are not fundamental modes of vibration.
ii) The band at $127 \mathrm{~cm}^{-1}$ at $1.15^{\circ} \mathrm{K}$ is due to two-phonon processes, all others are fundamental modes of vibration.

The Raman data of Poulet and Mathieu (1963) records
bands at 16,25 and $45 \mathrm{~cm}^{-1}$ as well as higher frequencies;
it is unlikely that they are all due to two-phonon processes. Adams and Appleby (1977) (6/2230) have confirmed these low frequency features. Since $B_{2 u}$ contains no translatory mode, and no band is observed below $90 \mathrm{~cm}^{-1}$, the bands at 32 and $40 \mathrm{~cm}^{-1}$, in $B_{1 u}$ and $B_{3} u$ respectively are taken as being of translatory origin. This fits well with Raman counterparts at $16 \mathrm{~cm}^{-1}$ $\left(B_{3 g}+B_{2 g}\right), 25 \mathrm{~cm}^{-1}\left(\mathrm{~A}_{\mathrm{g}}\right)$ and $45 \mathrm{~cm}^{-1}\left(\mathrm{~B}_{2 \mathrm{~g}}\right)$. There is no a priori evidence on which $\nu_{2}$ modes, and those of rotatory origin can be distinguished, if such a distinction is valid. Gans (1971) has discussed the displacements involved, as they are similar it is possible that these will couple strongly, however, this is not certain. The gas phase data of Malt'sev et al (1971) and the matrix studies of Loewenschuss et al (1969) place $v_{2}$ at ca. $100 \mathrm{~cm}^{-1}$; therefore the modes at $120\left(\mathrm{~A}_{\mathrm{g}}\right), 126\left(\mathrm{~B}_{1 \mathrm{~g}}\right), 108$ $\left(B_{1 u}\right), 115\left(B_{2 u}\right)$ and $123\left(B_{3 u}\right)$ may be considered as having a major contribution from $v_{2}$. Modes at $72\left(\mathrm{~B}_{\mathrm{lg}}+\mathrm{B}_{3 \mathrm{~g}}\right)$, $75\left(\mathrm{~A}_{\mathrm{g}}+\right.$ $\left.\mathrm{B}_{3 \mathrm{~g}}\right), 74\left(\mathrm{~B}_{1 \mathrm{u}}\right), 94\left(\mathrm{~B}_{2 \mathrm{u}}\right)$ and $96\left(\mathrm{~B}_{3 \mathrm{u}}\right)$ can be assigned as being principally rotatory in type. This assignment for $\nu_{2}$ can only be confirmed by a full N.C.A. treatment of the lattice.

Results and discussion for HgBr

The F.G.A. in Table 5.2 shows that the vector of optically active modes allows for:

$$
5 A_{1}+3 A_{2}+2 B_{1}+5 B_{2}
$$

all modes are Raman active and all but $A_{2}$ are also i.r. active.

If it is assumed, for the purposes of accounting for the number of modes, that these may be decomposed into internal and external modes

$$
\begin{array}{ll}
\mathrm{N}_{\text {(internal })} & =3 \mathrm{~A}_{1}+\mathrm{A}_{2}+\mathrm{B}_{1}+3 \mathrm{~B}_{2} \\
\mathrm{~N}_{\text {TRANS }} & =\mathrm{A}_{1}+\mathrm{A}_{2}+\mathrm{B}_{2} \\
\mathrm{~N}_{\text {ROTATORY }} & =A_{1}+A_{2}+B_{1}+B_{2}
\end{array}
$$

It can be seen from the correlation scheme (table 5.3), that $v_{2}$ is active in each species, and that $v_{1}$ and $v_{3}$ are active only in $A_{1}$ and $B_{2}$.

If attention is confined to i.r. activity theory predicts that:
$A_{1}$ will contain 3 internal modes $\left(v_{1}, v_{2}\right.$ and $\left.v_{3}\right)$ as well as 1 rotatory and 1 translatory mode,
$B_{1}$ will contain 1 internal mode $\left(\nu_{2}\right)$ and 1 rotatory only.
$B_{2}$ will contain 3 internal modes $\left(v_{1}, v_{2}\right.$ and $\left.v_{3}\right)$, 1 rotatory and 1 translatory.

Selection rules require that i.r. and Raman components are coincident. The $v_{3}$ components have been established to be in the region of ca. $250 \mathrm{~cm}^{-1}$, and $\nu_{2}$ ca. $180 \mathrm{~cm}^{-1}$. Since all lattice modes and all Davydov components of $v_{2}$ are in the range $<80 \mathrm{~cm}^{-1}$, it is suggestive of a much stronger intermolecular attraction than $\mathrm{HgCl}_{2}$, and there may be no meaningful distinction between the modes labelled above.

Results are shown in figures $5.4,5.5,5.6$ and data are summarised in Table 5.5.

The Raman spectra obtained are of extreme simplicity, showing only 2 major features, one intense band is located at $187 \mathrm{~cm}^{-1}$ which is $\nu_{1},\left(\nu(\mathrm{Hg}-\mathrm{Br})_{\text {sym }}\right)$ and another intense band at $57 \mathrm{~cm}^{-1}$; Adams and Appleby (1977) (7/079) have observed some weak features at 15 and $18 \mathrm{~cm}^{-1}$, and some less well-defined scatter at ca. $40 \mathrm{~cm}^{-1}$. Decamps et al (1973) have shown that tre $57 \mathrm{~cm}^{-1}$ band splits into two components at low temperature 58 and $59 \mathrm{~cm}^{-1}$, also they reported observing the $18 \mathrm{~cm}^{-1}$ band. No single crystal Raman data is available, and this study was unable to obtain any significant intensity changes with orientation. As the factor group is non-centrosymmetric the Raman spectra may show L.O. components (see Chapter Two, Section B) in addition to the T.O. modes predicted by F.G.A. Such features may be identifiable by the coincidence with L.O. mode frequencies obtained from the Kramers-Kronig analysis of the reflectance data.

Decamps and Hadni (1968) obtained some results for the far-i.r. of solid $\mathrm{HgBr}_{2}$ using unpolarised transmission measurements. They observed $v_{3}$ as a single band centred at $250 \mathrm{~cm}^{-1}$, with a very weak feature assigned to $\nu_{1}$ at $185 \mathrm{~cm}^{-1}$. A mull spectrum reported by Nyguist and Kagel (1971) did not show the feature at $185 \mathrm{~cm}^{-1}$, however Décamps et al (1973) did observe this
feature at low temperature, as well as the resolution of $v_{3}$ into a doublet at 230 and $248 \mathrm{~cm}^{-1}$.

In the reflectance results reported here, $v_{1}$ was not seen in either $A_{1}$ or $B_{2}$ spectra even at 115 K . It was observed in the $A_{l}$ spectrum in transmission measurements through a cleavage fragment containing the ( $x z$ ) face at $187 \mathrm{~cm}^{-1}$, which is coincident with the Raman feature of the material.

Analysis shows that the $v(\mathrm{Hg}-\mathrm{Br})$ mode which is prominent in i.r. mulls at $252 \mathrm{~cm}^{-1}$ is the $A_{1}$ Davydov component of $v_{3}$. The much weaker $B_{2}$ component is centred at $220 \mathrm{~cm}^{-1}$. The average of these two values, $236 \mathrm{~cm}^{-1}$, may be compared to the value obtained by Klemperer and Lindemann (1956) from the vapour which is $29.3 \mathrm{~cm}^{-1}$. The static field shift $\Delta \nu$ is $-57 \mathrm{~cm}^{-1}$ in this case. Similarly $\Delta \nu$ for $v_{1}$ can be estimated at $-38 \mathrm{~cm}^{-1}$, as the gas phase value is $225 \mathrm{~cm}^{-1}$. These shifts are comparable to those calculated for $\mathrm{HgCl}_{2}$. The forms of the $v_{1}$ Davydov components are shown in figure 5.7(b).

The region below $\nu_{1}$ and $\nu_{3}$

Decamps and Hadni (1968) obtained values of 35, 53 and 71 (broad) $\mathrm{cm}^{-1}$ in a transmission study using unpolarised radiation. Decamps et al (1973) resolved these features at low temperature and obtained values of $32,55,65,86$ and $113 \mathrm{~cm}^{-1}$, unfortunately no intensities are given.

Theory predicts that the $\mathrm{B}_{1}$ spectrum will be a simple one, containing only a Davydov component of $\nu_{2}$ and a rotatory mode. At both ambient and low temperature two intense - almost coincident reflectance maxima were observed. This appeared to be a doublet with T.O. frequencies of 33 and ca. $50 \mathrm{~cm}^{-1}$. Transmission spectra obtained with the ( $x z$ ) face cleavage fragment, showed only a very intense absorption from ca. $15-90 \mathrm{~cm}^{-1}$. This could be imagined to be resolved into two components, which is consistent with reflectance results. The exact nature of this reflectance spectrum is still not absolutely clear, Kramers-Kronig analyses could not separate the reflectance maxima to give two T.O. frequencies. Simple harmonic oscillator analyses were unable to reproduce the spectrum adequately. It was deduced that two bands were present, and that these are the F.G.A. fundamentals.

Both $A_{1}$ and $B_{2}$ should exhibit three low frequency bands. Each contains a $\nu_{2}$ component, 1 rotatory and 1 translatory mode. The $A_{1}$ reflectance spectrum showed bands with T.O. frequencies of 30 and $70 \mathrm{~cm}^{-1}$. Transmission measurements confirmed the weak band at $29 \mathrm{~cm}^{-1}$, and revealed in addition another sharp band at $15 \mathrm{~cm}^{-1}$, coincident with a weak Raman feature which is accordingly given $A_{1}$ symmetry.

The $B_{2}$ spectrum revealed bands at 42,53 and $79 \mathrm{~cm}^{-1}$, the feature at $42 \mathrm{~cm}^{-1}$ was only clearly seen at 115 K .

Exactly the number of bands predicted by F.G.A. have been observed, apart from $A_{2}$ species. When superimposed they account for all of the observed features of the mull spectrum, although any attempt at a unique assignment is extremely tentative.

It remains to assign the Raman bands not found to be coincident with i.r. bands. The band at $18 \mathrm{~cm}^{-1}$ is assigned to $A_{2}$, which is unique to the Raman spectrum, and could be the required translatory mode. The weak scatter at ca. $40 \mathrm{~cm}^{-1}$ is taken to be the counterpart of the $B_{2}$ band found in the i.r., although :he breadth of this band may be taken to imply an L. O. component in addition. The Raman band at $57 \mathrm{~cm}^{-1}$ is almost coincident with the $B_{2}$ i.r. band at $53 \mathrm{~cm}^{-1}$. The resolution of this into components at low temperatures raises a problem which can only be resolved by a single crystal Raman spectrum of the compound. Three explanations are possible:
i) The $n \geqslant w$ Raman band is an $A_{1}$ L.O. component, and as such it should be coincident with an L.O. determined from the $A_{1}$ reflectance spectrum analysis; it is not, and this theory is therefore rejected.
ii) It is one of the $\mathrm{A}_{2}$ components yet to be identified; this is regarded as probable.
iii) It represents another genuine $A_{1}$ fundamental; if this is so the $15 \mathrm{~cm}^{-1}$ band found in transmission must be rejected and treated as an artefact.

In view of the difficulties in obtaining i.r. spectra at such low frequencies, it is desirable that the $15 \mathrm{~cm}^{-1}$ be confirmed using a lamellar-grating instrument.

It is unlikely that $v_{2}$ will drop in frequency substantially from that calculated for it in a krypton matrix, i.e. $73 \mathrm{~cm}^{-1}$ (Loewenschuss et al 1969) for the crystalline state. It is therefore probable that the bands at ca. $75 \mathrm{~cm}^{-1}$ in the crystal receive a large contribution from $v_{2}$, i.e. 76 ( $\mathrm{B}_{2}$ ), $70\left(A_{1}\right)$ and $50\left(B_{1}\right)$. This automatically describes the features at 53,33 and $30 \mathrm{~cm}^{-1}$ and, in particular, the $57 \mathrm{~cm}^{-1}$ Raman feature as principally rotatory in type. This accords well with the origin of the $57 \mathrm{~cm}^{-1}$ feature in the $\pi_{g}$ (Raman active) species of $D_{\infty} h$, and would therefore be expected to show strong Raman activity.

The implication of this theory is that the coupling between $\nu_{2}$ and rotatory modes is relatively weak and allows a distinction to be made between them. Any assignment can only be confirmed by a full N.C.A. treatment of the lattice.

Table 5.1 Factor group analysis for $\mathrm{HgCl}_{2}$.

| $\mathrm{D}_{2}^{16}$ | $\mathrm{N}_{\mathrm{T}} \mathrm{a}^{\text {a }}$ | $\mathrm{T}_{\text {A }}$ | T | $R(x, y)$ | $N_{\text {int }}$ | Activity |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $A_{g}$ | 6 |  | 2 | 1 | $3\left(\nu_{1}, \nu_{2}, \nu_{3}\right)$ | $\mathrm{x}^{2}, \mathrm{y}^{2}, \mathrm{z}^{2}$ |
| $\mathrm{B}_{1 \mathrm{~g}}$ | 3 |  | 1 | 1 | $1\left(v_{2}\right)$ | xy |
| $\mathrm{B}_{2} \mathrm{~g}$ | 6 |  | 2 | 1 | $3\left(\nu_{1}, \nu_{2}, \nu_{3}\right)$ | $x z$ |
| $\mathrm{B}_{3} \mathrm{~g}$ | 3 |  | 1 | 1 | $1\left(v_{2}\right)$ | yz |
| $A_{u}$ | 3 |  | 1 | 1 | $I\left(v_{2}\right)$ |  |
| $\mathrm{B}_{1 \mathrm{u}}$ | 6 | 1 | 1 | 1 | $3\left(\nu_{1}, \nu_{2}, \nu_{3}\right)$ | 2 |
| $\mathrm{B}_{2 \mathrm{u}}$ | 3 | 1 | 0 | 1 | $1\left(v_{2}\right)$ | $y \quad$ I.r. |
| $B_{3 u}$ | 6 | 1 | 1 | 1 | $3\left(v_{1}, \nu_{2}, v_{3}\right)$ | x |

a $\mathrm{N}_{\mathrm{T}}=$ total number of modes in the unit cell.
$T_{A}=$ acoustic branch modes.
$T=$ optic branch translatory modes.
$R(x, y)=$ rotatory lattice modes.
$N_{\text {int }}=$ number of internal modes and descriptions (see Table 5.3).

Table 5.2 Factor group analysis for $\mathrm{HgBr}_{2}$.
$C_{2 V}^{12} \quad N_{T}-\frac{\mathrm{a}}{} \mathrm{T}_{\mathrm{A}} \quad \mathrm{T} \quad \mathrm{R}(\mathrm{x}, \mathrm{y}) \quad \mathrm{N}_{\text {int }} \quad$ Activity
$A_{1} \quad 6 \quad 1 \quad 1 \quad 1 \quad 3\left(\nu_{1}, \nu_{2}, \nu_{3}\right) \quad z \quad x^{2}, y^{2}, z^{2}$
$\begin{array}{lllll}A_{2} & 3 & 1 & 1 & 1 \\ \left.\nu_{2}\right) & x y\end{array}$

| $\mathrm{B}_{1}$ | 3 | 1 |  | 1 | $l\left(\nu_{2}\right)$ | x | zx |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
|  |  |  |  |  |  |  |  |
| $\mathrm{B}_{2}$ | 6 | 1 | 1 | 1 | $3\left(\nu_{1}, \nu_{2}, \nu_{3}\right)$ | y | yz |

a $N_{T}=$ total number of modes in unit cell.
$\mathrm{T}_{\mathrm{A}}=$ acoustic branch modes.
$\mathrm{T}=$ optic branch translatory modes.
$R(x, y)=$ rotatory lattice mojes.
$N_{\text {int }}=$ number of internal modes and descriptions (see Table 5.3).
$\overbrace{\text { Crystal }}^{\substack{\text { Table } 5.3 \\ L_{2}^{16}}}$
a Approximate geometry, neither molecule has strict $D_{\infty h}$ symmetry in the solid state.
b All g modes are Raman active, $B_{n u}$ modes are i.r. active.
© All modes are Raman active, only $A_{2}$ modes are not i.r. active.

Table 5.4 Transverse and longitudinal optic mode frequencies $/ \mathrm{cm}^{-1}$ for $\mathrm{HgCl}_{2}$, derived from Kramers-Kronig analyses of i.r. reflectance spectra.
$B_{1 u}(z)$
295 K
115 K
Assignment
T.O. L.O.
T.O. L.O.
~39 b ~44
$39 \quad 44$

| 74 | 83 | 76 | 85 |
| :---: | :---: | :---: | :---: |
| $108-$ | $133^{\text {d }}$ |  |  |

$v_{T}$
$v_{2}, \delta\left(\mathrm{HgCl}_{2}\right)$; or $v_{R}$
$v_{R}$ or $v_{2}$
$310-316 \quad 310$
379388
384
392
$\nu_{1}, v(\mathrm{Hg}-\mathrm{Cl})_{\text {sym }}$
$v_{3}, v(\mathrm{Hg}-\mathrm{Cl})_{\text {asym }}$
$B_{2 u}(y)$
295 K
115 K
T.O. L.O. T.O. L.O.

| 94 | $\sim 107 \mathrm{C}$ | 96 | $\sim 112$ c |
| :---: | :---: | :---: | :---: |
| 115 | 132 | 120 | 134 |
| (x) | K |  | K |


| T.O. | L.O. | T.O. | L.O. |
| :---: | :---: | :---: | :---: |
| $30-\mathrm{a}$ | 35 | 32 | 37 |
| 96 | 112 | 99 | 116 |
| 123 | 130 | 127 | 136 |
| n.0. - | n.O. | 330 | 334 |
| 372 | 386 | 380 | 390 |

$v_{\mathrm{T}}$
$\nu_{2}, \delta\left(\mathrm{HgCl}_{2}\right) ;$ or $v_{2}$
$v_{\mathrm{R}}$ or $v_{2}$
$v_{1}, v(\mathrm{Hg}-\mathrm{Cl})_{\text {sym }}$
$v_{3}, v(\mathrm{Hg}-\mathrm{Cl})_{\text {asym }}$
a At $32 \mathrm{~cm}^{-1}$ in single crystal transmission at $295^{\circ} \mathrm{K}$.
b at $40 \mathrm{~cm}^{-1}$ in single crystal transmission at $295^{\circ} \mathrm{K}$, only clearly seen in reflectance at $115^{\circ} \mathrm{K}$.
c Estimated visually.
d Values obtained treating band as due to one fundamental only (see text) with a two-phonon mode at $127 \mathrm{~cm}^{-1}$ at $115^{\circ} \mathrm{K}$ (figure 5.1). e $\nu_{\mathrm{T}}=$ translatory mode, $\nu_{\mathrm{R}}=$ rotatory mode.
f Seen at $330\left(B_{3 u}\right)$ and $312\left(B_{1 u}\right)$ in single crystal transmission at $295^{\circ} \mathrm{K}$.

Table 5.5 Transverse and longitudinal optic mode frequencies $/ \mathrm{cm}^{-1}$ for $\mathrm{HgBr}_{2}$, derived from Kramers-Kronig analyses of i.r. reflectance spectra.

| $A_{1}(z) 295$ |  | 115 K |  | Assignment ${ }^{\text {e }}$ |
| :---: | :---: | :---: | :---: | :---: |
| T.O. | L. 0. | T.O. | L. 0. |  |
| 15 ${ }^{\text {a }}$ | - | - | - |  |
| $30^{\text {b }}$ | $33^{\text {c }}$ | 31 | 33 C |  |
| 70 | 100 | 73 | 104 |  |
| 252 | 258 | 253 | 260 | $v_{3}, v(\mathrm{Hg}-\mathrm{Br})_{\text {asym }}$ |
| $\mathrm{B}_{1}(\mathrm{x})$ |  |  |  |  |
| 295 | K |  | K |  |
| T.O. | L. 0. | T.O. | L. 0. |  |
| 33 | 93 | 35 | 96 | $v_{R}$ or $v_{2} \delta\left(\mathrm{HgBr}_{2}\right)$ |
| $\sim 50$ | - | $\sim 5$ | - | $v_{2}$ or $v_{R}$ |

$B_{2}(y)$
295 K
115 K
$\left.\begin{array}{cccc}\text { T.O. } & \text { L.O. } & \text { T.O. } & \text { L.O. } \\ \text { n.O. } & \text { no. } & 42 & 44^{c} \\ 53 & 70^{-} & 53 & 70^{c} \\ 76 & 92 & 79 & 96\end{array}\right]$
a Found in single crystal transmission only.
b $29 \mathrm{~cm}^{-1}$ in single crystal transmission.
C Estimated visually.
d Additional feature found at $187 \mathrm{~cm}^{-1}$ in single crystal transmission.
e $\nu_{\mathrm{T}}=$ translatory mode, $\nu_{\mathrm{R}}=$ rotatory mode.

FIG. 5.1


FIG. 5.2






FIG. 5.7
(a)

$A_{g}$

$\mathrm{B}_{14}$

$B_{2 g}$

$B_{3 u}$
(b)

$\mathrm{A}_{1}$


FIG.5.8a

Raman spectrum of $\mathrm{HgCl}_{2}$


FIG. 5.8b
Raman spectrum of $\mathrm{HgBr}_{2}$ (Adams and Appleby 1977).
$\int^{186} 16$

FIG. 5.9
$\mathrm{HgCl}_{2}$ Mull
$\mathrm{HgCl}_{2}$ Transmission


FIG. 5.10
$\mathrm{HgCl}_{2}$ Transmission


FIG. 5.11
$\mathrm{HgBr}_{2}$ Transmission


FIG. 5.12
$\mathrm{HgBr}_{2}$ Transmission


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## Chapter Six

## Far-i.r. Spectra of Three Complex Halides <br> $\mathrm{CsMgCl}_{3}, \mathrm{VsMnBr}_{3}, \mathrm{CsMnI}_{3}$

## Introduction

A large number of double salts of the type $\mathrm{AMX}_{3}$, where $X=$ chloride or bromide; $A=$ an alkalie metal (commonly Cs) and $B=a$ divalent metal atom, adopt the CsNiCl 3 structure. This was determined by Tischchenko (1955), and is best described as a trigonal distortion of the perovskite structure adopted by many of the formally analogous complex fluorides - which has been extensively reviewed by Wells (1962). The octahedra share faces (as shown in figure 6.1). Crystals exhibit a good cleavage direction parallel to the c crystallographic axis.

There is to date little detailed spectroscopic data recorded on these compounds, which may be due to their hygroscopic nature. Single-crystal far-i.r. and Raman studies have been reported on some air-stable complex chlorides and bromides: $\mathrm{CsNiCl}_{3}$ and $\mathrm{CsCoCl}_{3}$ (Chadwick et al 1971); $\left(\mathrm{CH}_{3}\right)_{4} \mathrm{NMnCl}_{3}$ (Adams and Smardzewski 1971); and $\left(\mathrm{CH}_{3}\right)_{4} \mathrm{NNiBr}_{3}$ (Adams and Hall 1975). Although the last two crystals are not isomorphous with the first two, the geometries of the $\mathrm{MX}_{3}{ }^{-}$chains are very similar and have almost identical vibrational analyses. In all cases the assignments are unambiguous, frequency changes are due to the different masses of the atoms present. McPherson and Chang (1973) prepared and characterised a large number of chlorides, bromides and iodides of the type $\mathrm{AMX}_{3}$. They found that in the vast majority of cases the $\mathrm{CsNiCl}_{3}$ structure was adopted, except where for example $M=C u^{I I}$, the Jahn-Teller distortion is not
compatible with $C u^{I I}$ in perfectly octahedral sites. An i.r. mull comparison study of those compounds which had the $\mathrm{CsNiCl}_{3}$ structure revealed that a change in cation had a relatively minor effect on the spectra; only the low frequency modes which principally involve cation translations showed significant changes. A change of halogen on the other hand, altered frequencies of all modes in the spectrum. A recent N.C.A. study of $\mathrm{CsNiCl}_{3}$ by Adams, Christopher and Stevens (1977) has determined that the $A_{2} u$ species modes are $98 \%$ pure modes involving only two atom types in each mode.

## Theory

The structural dete.minations of $\mathrm{CsMgCl}_{3}$ (Seifert and Ehrlich 1959), and $\mathrm{CsMnBr}_{3}$ (Goodyear and Kennedy 1972) assign them to the hexagonal system with symmetry $\mathrm{PG}_{3} / \mathrm{mmc} \equiv \mathrm{D}_{6 \mathrm{~h}}^{4}$, which is the CsNiCl 3 structure. The structure of $\mathrm{CsMnI}_{3}$ has not been determined to date, however, comparison with $\mathrm{CsNiCl}_{3}, \mathrm{CsNiBr}_{3}$ and $\mathrm{CsNiI}_{3}$, which are isostructural, infers that it is isostructural with the bromide. The F.G.A. of $\mathrm{CsNiCl}_{3}$ has been reported before (Adams and Smardzewski 1971) and is shown on Table 6.1.

## Experimental

The crystals for this study were forwarded by Dr. G.L. Mcpherson of Tulane University, New Orleans. The crystals in all cases were
extremely water sensitive and readily decomposed into hydrated dihalides and alkali metal halides on contact with the atmosphere. The crystals were received sealed in quartz ampoules under dry nitrogen. It was decided to record i.r. spectra using reflectance techniques. This is because the compounds have been shown to be very strongly absorbing. Previous crystal studies : Chadwick et al; Adams and Smardzewski, and Adams and Hall; all resorted to reflectance techniques to obtain accurate absorption frequencies. Also the crystals may well have proved to be mechanically unstable in thin sections, due to their extreme hygroscopic nature.

Samples were prepared for both i.r. and Raman experiments in a dry box. The crystals used for Raman work were covered with a glass cap which was glued to the copper post (see Chapter Two section $B$ ). An atmosphere of dry nitrogen surrounded the samples at all times and crystals showed no signs of decomposition. Repeated attempts at single crystal Raman spectra were frustrated by an almost total lack of Raman scattered light, no useful data was collected. It has been noticed before in this laboratory that the presence of $\mathrm{Mn}^{\text {II }}$ in a compound often severely reduces the amount of Raman scattered light, the reason for which is not fully understood.

For the purposes of i.r. reflectance work, the samples were transferred from the dry box to the FS720 in sealed bottles.

The sample compartment and golay detector units of the 720 were encapsulated in polythene sheet; this formed a crude, but very effective, dry bag. The bottles were introduced into the bag via a small port which was immediately resealed. A large bowl of silica-gel dessicant was present in the bag at all times. The bag could be successively evacuated and flushed with dry nitrogen (passed over a drying column) by attaching a "T-junction", fitted with taps, into the vacuum line from the rotary pump to the sample compartment. One side of the "T-junction" was then connected to the vacuum line, the other to the nitrogen line; the outlet of the junction was connected to the sample compartment with pressure tubing. By opening the air bleed valve on the side of the sample compartment the atmosphere in the bag could be readily exchanged. After 30 minutes repeated evacuation and flushing, the bottles were opened, and the samples mounted into the holder with black insulation tape. The sample compartment was then immediately evacuated. The samples could be removed by filling the sample compartment with dry nitrogen via the "Tjunction" piece.

Attempts were made with all crystals to collect low temperature data. In all cases the interferrograms recorded were good, however, computed results showed signs of decomposition of the crystals. It can only be concluded that the most minute amounts of water present in the dynamic vacuum of the FS720
sample compartment, were sufficient to cause severe decomposition of the crystal surface used for gathering information. The problem is aggrevated at low temperatures by the fact that any water present will naturally condense onto the coolest part of the apparatus, i.e. the cooling block containing the crystal.

## Results and Discussion

The vector of optically active modes allows for:

$$
A_{1 g}+E_{1 g}+3 E_{2 g}+2 A_{2 u}+3 E_{1 u}
$$

g modes are Raman active, $u$ modes are i.r. active.

In all three cases $2 \mathrm{~A}_{2} \mathrm{u}+3 \mathrm{E}_{1 \mathrm{u}}$ was found. The assignment follows unambiguously. $A_{2 u}$ contains one translatory mode, $v_{7}$ and one out of plane stretching mode, $v_{6} \cdot E_{1 u}$ contains one translatory mode $\nu_{10}$ and two in-plane modes, $\nu_{8}$ and $\nu_{9}$. The results for $\mathrm{CsMgCl}_{3}$ and $\mathrm{CsMnBr}_{3}$ are in good agreement with those obtained from i.r. mulls (Mcpherson and Chang 1973). The high frequency regions of all spectra are characterised by broad strong bands in transmission measurements. Adams and Hall (1975) and Chadwick et al (1971) had noticed that high frequency modes were sometimes significantly shifted in frequency from the estimates of transmission maxima to those obtained from Kramers-Kronig analyses; the latter were taken as the more accurate. It is believed that the values quoted here are the correct ones. Data are summarised in Table 6.2.

The spectra for $\mathrm{CsMnI}_{3}$ are identical in shape to those of the bromide, the frequencies are shifted to lower values, consistent with a change in atom mass. The symmetry of $\mathrm{CsMnI}_{3}$ may reasonably be established as $D_{6 h}^{4}$ with $z=2$. The increase in respective frequencies for $\mathrm{CsMgCl}_{3}$ over those of $\mathrm{CsNiCl}_{3}$ is entirely consistent with the smaller mass of the Mg atom.

The $E_{1 u}$ modes seem more susceptible to a change in halogen than $A_{2 u}$ modes which is difficult to explain in the light of the N.C.A. treatment of $\mathrm{CsNiCl}_{3}$ by Adams et al 1977. The $\mathrm{A}_{2 \mathrm{u}}$ modes are $98 \%$ pure modes involving 2 atom types only in each vibration; $E_{u}$ modes are considerably mixed in character according to this scheme. It can only be assumed that some character involving halogen-halogen motions is significant in determining the frequency of $E_{l u}$ modes. The alternative is that the N.C.A. treatment is in error.

The spectra of three chain structures have been established in the i.r. region. In order to obtain Raman results, a very sensitive syst 3 m is required to overcome the very weak scattering of these materials.

Table 6.1 Factor group analysis of $\mathrm{CsNiCl}_{3}$.

$$
\begin{aligned}
& \begin{array}{llllllllllllll}
D_{6}^{4} h & A_{1 g} & A_{2 g} & B_{1 g} & B_{2 g} & E_{1 g} & E_{2 g} & A_{1 u} & A_{2 u} & B_{1 u} & B_{2 u} & E_{1 u} & E_{2 u}
\end{array} \\
& \begin{array}{lllllllllllll}
N_{\text {TOTAL }} & 1 & 1 & 2 & 0 & 1 & 3 & 0 & 3 & 1 & 2 & 4 & 2
\end{array} \\
& \begin{array}{lllll}
\mathrm{T} & 1 & 1 & 1 & 1
\end{array} \\
& \mathrm{R} \quad 1 \\
& \mathrm{~T}_{\mathrm{A}} \quad 1 \quad 1 \\
& \begin{array}{lllllllllllll}
N_{\text {int }} & 1 & 0 & 1 & 0 & 1 & 2 & 0 & 1 & 1 & 2 & 2 & 2
\end{array} \\
& \text { Activity } \quad\left(x^{2}+y^{2}\right) \\
& y z,\left(x^{2}-y^{2}\right) \quad z \quad x, y \\
& \text { zx } x y
\end{aligned}
$$

I.r. active modes in some $A M X_{3}$ compounds.



$\stackrel{n}{\sim}$

$\mathrm{CsMnBr}_{3} \mathrm{C}$
$\left(\mathrm{CH}_{3}\right)_{4} \mathrm{NMnCl}_{3}-$
$\geqslant \quad$ N
듣 N

ざ | N |
| :---: |
|  |

$\stackrel{\infty}{>} \stackrel{\circ}{>} \stackrel{-}{\rightarrow}$
$\stackrel{7}{4}$
$\overbrace{-}$ $\qquad$

$\mathrm{CsNiCl}_{3} \mathrm{a}$
-
$\begin{array}{lll}\stackrel{\circ}{\sim} & \stackrel{\sigma}{\text { ® }} & \stackrel{\circ}{~}\end{array}$
a Chadwick et al 1971.
b This work.
c Mcpherson and Chang 1973.
d Adams and Smardzewski 1971.

FIG. 6.1

## $\mathrm{CsNiCl}_{3}$ Structure



$$
\begin{aligned}
& 0 \mathrm{Cl} \\
& 0 \mathrm{Ni} \\
& 0 \mathrm{Cs}
\end{aligned}
$$

Normal Modes of $\mathrm{MX}_{3}^{-}$Chain



$E_{2 g}$



$$
v_{6}\left(\mathrm{~A}_{2 \mathrm{u}}^{+}\right)
$$




FIG. 6.3


FIG. 6.4


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## Chapter Seven

## Far-i.r. Spectra of Five Square-Planar

Complexes

$$
\begin{aligned}
& {\underset{2}{2 M X}}_{4} \\
& A=K^{+},\left(\mathrm{NH}_{4}\right)^{+} \\
& M=P t, P d \\
& X=C l, B r
\end{aligned}
$$

## Introduction

There are many reports in the literature of spectroscopic studies on compounds of the type $A_{2} \mathrm{MX}_{4}$ where : $\mathrm{A}=\mathrm{K}^{+}$or $\left(\mathrm{NH}_{4}\right)^{+}$; $M=\mathrm{Pd}^{I I}$ or $\mathrm{Pt}^{I I}$; and $\mathrm{X}=\mathrm{Cl}^{-}$or $\mathrm{Br}^{-}$. A square planar $\left(\mathrm{D}_{4 \mathrm{~h}}\right.$ ) ion such as $\left(\mathrm{PtCl}_{4}\right)^{2^{-}}$executes three i.r. active modes of vibration. They are $: v_{6}\left(E_{u}\right), v(P t-C l) ; v_{7}\left(E_{u}\right), \delta(P t-C l)$; $\nu_{4}\left(A_{2 u}\right), \pi(P t-C l)$, where $\delta$ and $\pi$ represent deformations in and out of the plane respectively. In order to settle the order of the internal modes $\nu_{4}$ and $\nu_{7}$, which are always close to each other, it is necessary to study single crystals in polarised i.r. radiation. This was done in the case of $\mathrm{K}_{2} \mathrm{PtCl}_{4}$ (Adams and Newton 1969) by single crystal transmission through a very thin slice of crystal. The order found was $\nu_{7}\left(E_{u}\right)>\nu_{4}\left(A_{2 u}\right)$, in addition the three i.r. active lattice modes (see Table 7.1) were determined as $E_{u}>A_{2 u}>E_{u}$. The exact value of $v_{4}$ was not determined because of what appeared to be a Fermi-resonance with a combination in the region ca. $170-200 \mathrm{~cm}^{-1}$.

The analogous ammonium salts will be expected to exhibit modes due to ammonium rotation, however these are only active in the Raman effect (see Table 7.1). The intense colour and pleochroic nature of these crystals make Raman studies extremely difficult as the compounds tend to absorb the incident radiation very strongly and are easily decomposed with moderate irradiation. The lattice (translatory) modes of the ammonium salts are expected to occur at higher frequencies than the corresponding
potassium salts, and might therefore be close in frequency to the $v_{4}$ and $v_{7}$ modes of the anion. A single-crystal Raman study of $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{PtCl}_{4}$ and $\mathrm{K}_{2} \mathrm{PdCl}_{4}$ (Beattie and Gilson 1968) established an assignment for both.

The majority of data collected on these compounds is at room temperature on powder and solution samples. The results of Goggin and Mink (1974); Bosworth and Clark (1975); Hendra (1967); Hendra and Stratton (1969); Durig et al (1965); Fertel and Perry (1965); Poulet et al (1964); Sabatini et al (1964); Hiraishi and Shimanouchi (1966) and Perry et al (1967) have confirmed the assignments for the anions $\left(\mathrm{PtCl}_{4}\right)^{2^{-}}$and $\left(\mathrm{PdCl}_{4}\right)^{2^{-}}$unambiguously.

The first work on these compounds at temperatures below 100 K revealed additional bands on cooling (Adams and Berg 1976). These modes cannot be factor group. fundamentals as these are all observed and accounted for at ambient temperature.

## Experimental

Crystals of $\mathrm{K}_{2} \mathrm{PtCl}_{4}, \mathrm{~K}_{2} \mathrm{PdCl}_{4},\left(\mathrm{NH}_{4}\right)_{2} \mathrm{PtCl}_{4}$ and $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{PdCl}_{4}$ were grown by slow evaporation of the respective aqueous solutions containing $10 \% \mathrm{HCl}$. Crystals of $\mathrm{K}_{2} \mathrm{PtBr}_{4}$ were grown in an aualogous manner from a solution containing $10 \% \mathrm{HBr}$.

The crystals grew in the form of thick rods elongated along the c axis. Typical dimensions were $5 \times 3 \times 12 \mathrm{~mm}^{3}$. The
largest face (e.g. $12 \times 5 \mathrm{~mm}^{2}$ ) was used for reflectance measurements. The orientation of the crystals was established by examination with a polarising microscope. An indicatrix direction coincided with the longest side of the crystal in each case and this proved to indicate the $c$ axis.

The lowest temperatures achieved for the single crystal studies was 145 K . The limit was imposed by the impossibility of enclosing the sample completely in a cold shield whilst allowing room for the incident and reflected beams. Mull spectra were obtained at temperatures down to $47.5 \mathrm{~K}(30 \mathrm{~K}$ for $\mathrm{K}_{2} \mathrm{PtBr}_{4}$ ).

## Results and Discussion

The symmetry of $\mathrm{K}_{2} \mathrm{PtCl}_{4}, \mathrm{~K}_{2} \mathrm{PdCl}_{4}$ and $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{PdCl}_{4}$ has been established as $\mathrm{P} 4 / \mathrm{mmm} \equiv \mathrm{D}_{4 \mathrm{~h}}^{\mathrm{l}}$ with $\mathrm{z}=\mathrm{l}$ (Dickenson 1922; Theilacker 1937; Bell et al 1966 and Mais et al 1972). In this structure the primitive unit cell is unimolecular, therefore the selection rules are those of the free ion.
$\left(\mathrm{NH}_{4}\right)_{2} \mathrm{PtCl}_{4}$ is reasonably presumed to be isomorphous, this is supported by the similarity of the spectra. The studies of Kroening et al (1974) and Ito et al (1961) have established that $\mathrm{K}_{2} \mathrm{PtBr}_{4}$ is isomorphous also.

The assignment of $\mathrm{K}_{2} \mathrm{PtCl}_{4} \mathrm{~A}_{2 \mathrm{u}}$ and $\mathrm{E}_{\mathrm{u}}$ species confirm earlier results obtained with i.r. transmission (see Table 7.2).

The assignment of $\mathrm{K}_{2} \mathrm{PdCl}_{4} \mathrm{~A}_{2 \mathrm{u}}$ and $\mathrm{E}_{\mathrm{u}}$ species (295 K) are in good agreement with those for $\mathrm{K}_{2} \mathrm{PtCl}_{4}$ when mass differences are considered. The order $v_{7}>\nu_{4}$ is maintained, in addition the order of lattice modes $E_{u}>A_{2 u}>E_{u}$ is seen to apply. Results are shown in figures $7.2 \rightarrow 7.5$ and data are summarised in Table 7.2. The normal modes of the $\left(M X_{4}\right)^{2^{-}}$ ion are shown in Figure 7.1.

The i.r. spectrum of a chloroform solution of $\left(\mathrm{NBu}_{4}^{\mathrm{n}}\right)_{2} \mathrm{PtBr} 4$ (Goggin and Mink 1974) showed a band at $105 \mathrm{~cm}^{-1}$ with a shoulder at $112 \mathrm{~cm}^{-1}$ in addition to $\nu_{6}$ at $227 \mathrm{~cm}^{-1}$; almost the same frequencies were found for the solid. The assignment of $v_{4}$ at $105 \mathrm{~cm}^{-1}$ and $v_{7}$ at $112 \mathrm{~cm}^{-1}$ was made; only one lattice mode at $88 \mathrm{~cm}^{-1}$ was found. The single crystal reflectance results for $\mathrm{K}_{2} \mathrm{PtBr}_{4}$ shown in Figures $7.6 \rightarrow 7.8$ with data summarised in Table 7.3 , show that $v_{4}$ and $v_{7}$ are almost coincident at 295 K (128 and $129 \mathrm{~cm}^{-1}$ respectively). The two bands appeared as a single mode in mull spectra even at 30 K . The fact that this is a genuine result and not a failure to distinguish properly between orientations is shown by the good extinctions elsewhere in the spectra. The order of lattice modes is seen to obey that of $\mathrm{K}_{2} \mathrm{PtCl}_{4}$ and $\mathrm{K}_{2} \mathrm{PdCl}_{4}$, i.e. $\mathrm{E}_{\mathrm{u}}>\mathrm{A}_{2} \mathrm{u}>\mathrm{E}_{\mathrm{u}}$. There must be considerable Fermi resonance between the $E_{u}$ lattice modes and $v_{7}$, and the $A_{2 u}$ lattice mode and $v_{4}$, to have raised $v_{4}$ by 23 and $v_{7}$ by $14 \mathrm{~cm}^{-1}$ above the values for the $\left(\mathrm{NBu}_{4}^{\mathrm{n}}\right)^{+}$salt.

Mull spectra of the ammonium salts show a single band at ca . $120 \mathrm{~cm}^{-1}$ readily attributable to one, or possibly more, translatory modes, a single $\nu(M-C l)$ absorption ca. $320 \mathrm{~cm}^{-1}$ and a very broad region of absorption in the intermediate range. The single crystal reflectance spectra for $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{PdCl}_{4}$ (Figures 7.11 and 7.12) show that there are two, almost coincident, lattice modes $\left(A_{2} u+E_{u}\right)$ at $\sim 123 \mathrm{~cm}^{-1}$; a similar result is seen for $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{PtCl}_{4}$ (Figure 7.9 and 7.10) with bands at $116 \mathrm{~cm}^{-1}$. Data are summarised in Table 7.4. The $\mathrm{A}_{2 \mathrm{u}}$ spectrum of $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{PdCl}_{4}(295 \mathrm{~K})$ shows in addition a band at $194 \mathrm{~cm}^{-1}$ which is attributed to $v_{4}$ in an analogous manner to $\mathrm{K}_{2} \mathrm{PtCl}_{4}$ and $\mathrm{K}_{2} \mathrm{PdCl}_{4}$. The $\mathrm{E}_{\mathrm{u}}$ spectrum ( 295 K ) shows four modes as predicted by theory, two of these are required to be lattice modes. Two modes occur close to each other in the $150-200 \mathrm{~cm}^{-1}$ range, only one occurs in the range attributed to the lattice modes. Two alternative interpretations may be given:
(i) the single $\mathrm{E}_{\mathrm{u}}$ band at $122 \mathrm{~cm}^{-1}$ in $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{PdCl}_{4}$ represents two, degenerate, lattice modes
(ii) the $163 \mathrm{~cm}^{-1}$ band may be attributed to the other predicted translatory mode.

This explanation is favoured here for the following reasons

It is the simplest explanation of the data. In contrast, if the $122 \mathrm{~cm}^{-1}$ band is taken to represent two $\mathrm{E}_{\mathrm{u}}$ modes it is
necessary to find an explanation for the additional band in the middle region, which can be ignored as the inability to distinguish between orientations as shown by the good extinctions elsewhere and it does not correspond to any $A_{2 u}$ mode. This view conflicts with the assignment of Adams and Berg (1976), based upon single crystal transmission spectra, in which the $122 \mathrm{~cm}^{-1}$ band appeared to split into a doublet at low temperature; this is now regarded as an artefact in view of the difficulty of obtaining transmission measurements with highly absorbing materials such as these. Moreover, it is difficult to envisage the $163 \mathrm{~cm}^{-1}$ band as due to interference from the substrate.

There is evidence from independent sources that translatory modes in ammonium salts are rather higher than in the corresponding potassium salts, as is expected from the relative masses. Thus in $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4}$ and $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{BeF}_{4}$ (Carter 1976, Popkov et al 1975) ammonium translational modes have been assigned in the $145-220 \mathrm{~cm}^{-1}$ region. The associated rotational modes are much higher ( $\sim 350 \mathrm{~cm}^{-1}$ ) and are not i.r. active in these compounds.

The assignment of $E_{u}$ (translatory) at $122 \mathrm{~cm}^{-1}$ and 163
$\mathrm{cm}^{-1}$, a splitting of $41 \mathrm{~cm}^{-1}\left(\right.$ in $\left.\left(\mathrm{NH}_{4}\right)_{2} \mathrm{PdCl}_{4}\right)$, is to be compared with the splitting of $27 \mathrm{~cm}^{-1}$ for the analogous modes in $\mathrm{K}_{2} \mathrm{PdCl}_{4}$. It is now clear that the breadth of the
central feature of the ammonium salts in mull spectra is due to the close proximity of three modes, possibly a reflectance component is included in the transmission envelope. There is also possibly some broadening due to hydrogen bonding with the Cl atoms of the anion.

The $E_{u}$ spectrum of $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{PtCl}_{4}$ shows a similar feature, however the shoulder at $\sim 170 \mathrm{~cm}^{-1}$ is only resolved on cooling to 145 K . If this shoulder is taken to represent the other $E_{u}$ lattice mode a wholly consistent explanation of the data is possible. The $A_{2 u}$ spectrum is easily explained on the basis of a lattice mode and the expected $v_{4}$ mode. It is not immediately obvious why such a large discrepancy should occur in the values calculated from Kramers-Kronig analysis for $\nu_{4}\left(188 \mathrm{~cm}^{-1}\right)$ and the estimated value $\left(200 \mathrm{~cm}^{-1}\right)$. It is possible that this discrepancy is partially due to a lack of smoothing of the reflectance curve (see Chapter Two, section $A$ ); this was not done for any of the spectra in order not to lose any information concerning the features which develop on cooling.

## Low temperature features

Adams and Berg (1976) reported that mulls of $\mathrm{K}_{2} \mathrm{PtCl}_{4}$, $\mathrm{K}_{2} \mathrm{PdCl}_{4},\left(\mathrm{NH}_{4}\right)_{2} \mathrm{PtCl}_{4}$ and $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{PdCl}_{4}$ develop new i.r. absorption features upon cooling. These modes can be immediately dismissed as due to ammonium rotational modes (even though
theory forbids their i.r. activity) because the features are present in the potassium salts in which no cation rotatory modes are allowed.

The fact that these modes are genuine was proven by repeated data collection at a range of temperatures on different samples of the compounds. The results for $\mathrm{K}_{2} \mathrm{PdCl}_{4}$ (mull) are shown in Figure 7.13.

The low temperature reflectance spectra of $\mathrm{K}_{2} \mathrm{PdCl}_{4}$ clearly show new features at 145 K in both $\mathrm{A}_{2 \mathrm{u}}$ and $\mathrm{E}_{\mathrm{u}}$ species; these correspond fairly well with those reported by Adams and Berg. The new strong features in the mull spectrum in the $250-320 \mathrm{~cm}^{-1}$ range appear to have $E_{u}$ symmetry. Mulls of $\mathrm{K}_{2} \mathrm{PtCl}_{4}$ whilst showing some new absorption at low temperature in this range never developed the structure or intensity shown in $\mathrm{K}_{2} \mathrm{PdCl}_{4}$ spectra. The reflectance spectra confirm this: there is a clear change of shape of the reflectance curve in the $200-300 \mathrm{~cm}^{-1}$ region but no structure develops. This change in shape appears to affect the Kramers-Kronig analysis making the $v\left(P_{t-C l}\right)$ mode $\left(E_{u}\right)$ appear abnormally weak in the $\varepsilon^{\prime}$ and $\varepsilon^{\prime \prime}$ functions, although it is strong in the reflectance curve.

Both $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{PdCl}_{4}$ and $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{PtCl}_{4}$ develop new features in their respective reflectance spectra at low temperatures, which are in close agreement with those reported by Adams and Berg.
$\left(\mathrm{NH}_{4}\right)_{2} \mathrm{PdCl}_{4}$
(1)

312
308
298
(2)
-
$309\left(E_{u}\right)$
$295\left(A_{2 u}+E_{u}\right)$

$$
\left(\mathrm{NH}_{4}\right)_{2} \mathrm{PtCl}_{4}
$$

(1)

305
284
$304\left(E_{u}\right)$
$282\left(\mathrm{~A}_{2} \mathrm{u}\right)$
(2)
(1) denotes the results of Adams and Berg (1976).
(2) denotes this work.

It is obvious that an explanation to these phenomena needs to be given. The effect is strongest for the $\left(\mathrm{PdCl}_{4}\right)^{)^{-}}$ anion, $\left(\mathrm{PtCl}_{4}\right)^{2^{-}}$shows a pronounced structure only in the ammonium salt; in contrast $\left(\mathrm{PtBr}_{4}\right)^{2^{-}}$shows no additional structure of any description either in mulls at low temperature or in reflectance spectra at low temperature.

The possibility that these modes are due to two-phonon processes cannot be ruled out, although it is unlikely since the modes are seen to gain intensity on cooling, this is the reverse of that expected. In both $\mathrm{K}_{2} \mathrm{PtCl}_{4}$ and $\mathrm{K}_{2} \mathrm{PdCl}_{4}$ no zone centre overtones are allowed since $u x u=g \times g=g$ but the following combinations can, in principle, result in i.r. activity, i.e. yield $A_{2 u}$ or $E_{u}$ in the direct product:
$A_{2 u}: A_{1 g} \times A_{2 u} ; A_{2 g} \times A_{1} ; B_{1 g} \times B_{2 u} ; B_{2 g} \times B_{1 u}$
$E_{u}: E_{g} \times A_{1 u}, A_{2 u}, B_{1 u}$ or $B_{2 u} ; E_{u} \times A_{1 g}, A_{2 g}, B_{1 g}$ or $B_{2 g}$ $E_{g} \times E_{u}$ does not contain $A_{2 u}$ and is therefore rejected.

Inserting known frequencies, the following are the only combinations for $\mathrm{K}_{2} \mathrm{PtCl}_{4}$ and $\mathrm{K}_{2} \mathrm{PdCl}_{4}$ capable of giving frequencies in the $250-330 \mathrm{~cm}^{-1}$ region:

$$
\begin{aligned}
& A_{2_{u}}: v_{2}\left(B_{1_{g}}\right)+T\left(B_{2_{u}}\right) \quad \text { (translational mode) } \\
& \approx 300 \mathrm{~cm}^{-1} \text { for } \mathrm{K}_{2} \mathrm{PtCl}_{4} \approx 305 \mathrm{~cm}^{-1} \text { for } \mathrm{K}_{2} \mathrm{PdCl}_{4} \\
& E_{u}: v_{2}\left(B_{1_{g}}\right)+T\left(E_{u}\right) \quad \text { (translational mode) } \\
& \approx 313 \mathrm{~cm}^{-1} \text { for } \mathrm{K}_{2} \mathrm{PtCl}_{4} \quad \approx 310 \mathrm{~cm}^{-1} \text { for } \mathrm{K}_{2} \mathrm{PdCl}_{4} \\
& : v_{2}\left(B_{l_{g}}\right)+T\left(E_{u}\right) \quad \text { (other translational mode) } \\
& \approx 289 \mathrm{~cm}^{-1} \text { for } \mathrm{K}_{2} \mathrm{PtCl}_{4} \quad \approx 287 \mathrm{~cm}^{-1} \text { for } \mathrm{K}_{2} \mathrm{PdCl}_{4} \\
& : v_{7}\left(E_{u}\right)+R\left(A_{2}\right) \quad \text { (rotational mode for }\left(\mathrm{MCl}_{4}\right)^{2^{-}} \text {) } \\
& \approx 276 \mathrm{~cm}^{-1} \text { for } \mathrm{K}_{2} \mathrm{PtCl}_{4} \quad \approx 262 \mathrm{~cm}^{-1} \text { for } \mathrm{K}_{2} \mathrm{PdCl}_{4}
\end{aligned}
$$

The $\mathrm{T}\left(\mathrm{B}_{2}\right)$ mode is inactive and is estimated at $100 \mathrm{~cm}^{-1}$ for $\mathrm{K}_{2} \mathrm{PtCl}_{4}$ and $110 \mathrm{~cm}^{-1}$ for $\mathrm{K}_{2} \mathrm{PdCl}_{4}$ and hence is unlikely to generate appreciable i.r. activity in combination with a Raman-activis mode. $R\left(\mathrm{~A}_{2} g\right)$ is also inactive and is estimated at $80 \mathrm{~cm}^{-1}$ for $\mathrm{K}_{2} \mathrm{PtCl}_{4}$ and $71 \mathrm{~cm}^{-1}$ for $\mathrm{K}_{2} \mathrm{PdCl}_{4}$. This leaves only two reasonable combinations, $v_{2}\left(B_{l g}\right)$ with the two $E_{u}$ lattice modes; these are insufficient to account for either the number of or the correct frequency range for the new low temperature features of $\mathrm{K}_{2} \mathrm{PdCl}_{4}$. For the ammonium salts similar arguments apply. Identical combinations are feasible, in addition the combination of $v_{4}\left(A_{2}\right)+R\left(E_{g}\right)$ (rotational mode for $\left(\mathrm{MCl}_{4}\right)^{2^{-}}$) yields a reasonable figure. The inactive $\mathrm{T}\left(\mathrm{B}_{2}\right)$ was estimated at $118 \mathrm{~cm}^{-1}$ for $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{PtCl}_{4}$
and $128 \mathrm{~cm}^{-1}$ for $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{PdCl}_{4}$. Rotational modes of ammonium must be considered also, a value of $250 \mathrm{~cm}^{-1}$ was taken as an estimate. Although for the case of ammonium several modes could be inferred to have some activity none of them occurred in the correct frequency range. These results are taken as evidence to reject the theory that the features are not due to two-phonon processes.

The above argument implies that the new features cannot be adequately accounted for on the basis of the parent $D_{4}^{1} \mathrm{~h}$ structure. The possibility of a phase transition must be considered. If the principle that new structures adopted will have the symmetry of a sub-group of $D_{4 h}$ is followed some new structures can be postulated. In addition it is necessary to consider structures in which:
(i) anions are rotated about the $z, x$ or $x^{\prime}$ axes ( $45^{\circ}$ to $x$ and $y$ axes)
(ii) cations and anions are shifted relative to each other
(iii) the anions have a permanent distortion in the form of one of the out-of-plane modes. Square planar geometry for $\mathrm{Pd}^{I I}$ and $\mathrm{Pt}^{\mathrm{II}}$ is the norm but structures such as cis $\left[\mathrm{PtCl}_{2}\left(\mathrm{PMe}_{3}\right)_{2}\right]$ which has a tetrahedrally
distorted square planar structure are possible
(Messmer et al 1967).

Phase transitions are to be expected in ammonium salts by comparison with the behaviour of the ammonium halides (except the fluorides) which show complicated structural behaviour. It must be considered that at low temperatures a periodic hydrogen bonded array is formed. Such possibilities for the $\mathrm{K}_{2} \mathrm{PtCl}_{4}$ structure were considered by Adams and Berg, they concluded that for a unimolecular unit cell there were only two possibilities: $D_{4}^{l}$ and $D_{2}^{l}$. It is desirable that a consistent explanation for all the data is found, so that the new features in $\mathrm{K}_{2} \mathrm{PdCl}_{4}$ may be explained on the same basis of "hose of the ammonium salts. Adams and Berg reported that the $\mathrm{D}_{2 \mathrm{~d}}^{\mathrm{l}}$ structure could be adopted by these structures for both a hydrogen bonded array and a $\mathrm{B}_{\mathrm{l}}$ distortion of the square planar anion. This represents a very good explanation of the data and explains the trend that the intensity of the new features follows the order

$$
\left(\mathrm{NH}_{4}\right)_{2} \mathrm{P} l \mathrm{Cl}_{4}>\mathrm{K}_{2} \mathrm{PdCl}_{4}>\left(\mathrm{NH}_{4}\right)_{2} \mathrm{PtCl}_{4}>\mathrm{K}_{2} \mathrm{PtCl}_{4}
$$

If the resistance of PdII to out of plane deformation is intermediate between that of $\mathrm{Ni}^{\mathrm{II}}$ and $\mathrm{Pt}{ }^{\mathrm{II}}$, any deformations would be reinforced by the hydrogen bonded array (where present.) Correlation from $D_{4} h$ to $D_{2}$ shows that few Raman active modes can gain i.r. activity, too few to account for the number of new modes. For the ammonium salts where cation rotatory modes can gain activity it is doubtful if these occur in the correct frequency range.


The modes could only be explained on the basis of two-phonon modes in the $\mathrm{D}_{2 \mathrm{~d}}$ structure. Adams and Berg tabulated various possibilities for the correct frequency range.

An X-ray study of the $\mathrm{K}_{2} \mathrm{PtCl}_{4}$ structure at various low temperatures in this laboratory (Appleby 1977) and a neutron diffraction study by Berg (1977) have revealed no evidence whatsoever for a phase change. It must be assumed that this hypothesis, although attractive, is in error. Although Adams and Berg are inclined to the view that this is the only feasible explanation of the data it must now be rejected.

Another possible explanation is that the new features are derived from critical points in the Brillouin zone. Although i.r. photons have wavevector $k \approx 0$ they can interact with lattice phonons from throughout the zone in second order processes providing that

$$
\sum_{i} k_{i} \approx 0
$$

This can be achieved by the creation and annihilation of pairs of phonons with equal and opposite (but non-zero) wavevectors from critical points throughout the zone. The first Brillouin zone for $\mathrm{K}_{2} \mathrm{PtCl}_{4}$ is shown in Figure 7.14. This zone for a simple tetragonal Bravais cell contains many critical points; these are, with their respective point group symbols:

| $\Gamma$ | $\Lambda$ | $\Delta$ | $\Sigma$ | M | X |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{D}_{4} \mathrm{~h}$ | $C_{4}{ }_{v}$ | $\mathrm{C}_{2} \mathrm{~V}$ | $\mathrm{C}_{2 \mathrm{~V}}$ | $C_{2}{ }_{V}$ | $C_{2}$ |
| (zone centre) |  | (y) | ( $\mathrm{y}^{\prime}$ ) | ( $\mathrm{y}^{\prime}$ ) | (y) |
|  | Y | $\mathrm{R}, \mathrm{U}, \mathrm{W}$ | A, V |  |  |
|  | $\mathrm{C}_{S}$ | $\mathrm{C}_{5}$ | $C_{s}$ |  |  |
|  | ( xy ) | (zy) | (zy) |  |  |

Iqbal et al (1972) have established a method of analysis to determine the origin of modes which are not factor group
fundamentals in the single crystal Raman spectrum of KNCS. The accuracy of this method has not yet been established. In outline the method entails the selection of external modes for the suitability of combination with an internal mode. Correlations are performed from the factor group of the structure to the point groups of the critical points of the zone. The representation of acoustic, translatory and rotatory modes are then obtained from the factor group analysis of the parent structure by correlation. The species of the point group which contain a contribution to the internal mode in this revised factor group analysis scheme are then selected as candidates for combination modes. I.r. activity is predicted on the basis of direct products between the species of the point group of the critical points (denoted $G_{k}$ ) which have a contribution to the internal mode. If any of these products is one of the i.r. active species of $G_{k}$ the species is a candidate for a combination mode, for example:

$$
\begin{aligned}
& \text { The critical point } \Lambda\left(C_{4 v}\right) \text { in } \mathrm{K}_{2} \mathrm{PtCl}_{4} \\
& \text { Correlation from } D_{4 h} \rightarrow C_{4 v} \text { gives } \\
& A_{1}=A_{1 g}+A_{2 u} ; A_{2}=A_{2 g}+A_{1 u} ; B_{1}=B_{1 g}+B_{2 u} \\
& B_{2}=B_{2 g}+B_{1 u} ; E=E_{g}+E_{u}
\end{aligned}
$$

In $C_{4 v} A_{l}(z)$ and $E(x, y)$ are the i.r. active species.
From the F.G.A. scheme of the parent structure (see Table 7.1):

|  | $\mathrm{T}_{\mathrm{A}}$ | T | R | $\nu_{i}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{A}_{1}$ | 1 | 1 | 0 | 2 | $\left(A_{1}{ }_{g}+A_{2_{u}}\right)$ |
| $\mathrm{A}_{2}$ | 0 | 0 | 1 | 0 | $\left(A_{2}{ }^{\prime}+A_{l_{u}}\right)$ |
| $\mathrm{B}_{1}$ | 0 | 1 | 0 | 1 | $\left(B_{1 g}+B_{2 u}\right)$ |
| $\mathrm{B}_{2}$ | 0 | 0 | 0 | 2 | $\left(B_{2 g}+B_{1 u}\right)$ |
| E | 1 | 2 | 1 | 2 | $\left(E_{g}+E_{u}\right)$ |

$\mathrm{A}_{2}$ has no contribution to an internal mode and is therefore rejected. Direct products which yield $A_{1}$ from the remaining species are:

$$
A_{1} \times A_{1}=A_{1} ; B_{1} \times B_{1}=A_{1} ; B_{2} \times B_{2}=A_{1} ; E \times E=A_{1}
$$

In each case the representation of $T_{A}, T, R$ is read for the second component of the direct product, i.e.

|  | $T_{A}$ | $T$ | $R$ |
| :--- | :--- | :--- | :--- |
| $A_{1}$ | 1 | 1 | 0 |
| $B_{1}$ | 0 | 1 | 0 |
| $B_{2}$ | 0 | 0 | 0 |
| $E$ | 1 | 2 | 1 |

The possibilities of combination with an internal mode are then acoustic and translatory components of $A_{1}$; a translatory component of $\mathrm{B}_{1}$; an acoustic, two translatory components and cie rotatory component of E .

A similar calculation will yield possibilities for combinations via the $E$ i.r. active species of $C_{4 v}$.

It is obvious that if this calculation is performed for each critical point of the zone a very large number of possibilities emerge. The decision of the origin of each combination feature must be open to debate.

Although this theory cannot be rejected, much more work on these crystals is required before a definitive assignment can be made.

Some possibilities have been forwarded as to the origin of these new features on cooling, none of which yields an entirely satisfactory answer. In the absence of further experimental evidence there is no alternative but to admit that the origin of these modes is unknown.

## Conclusion

The frequencies derived from the reflectance data reported here are preferred to those of mull spectra reported previously (Adams and Berg 1976). This is because it is felt that a reflectance component may distort the strongest bands. The data obtained for $\mathrm{K}_{2} \mathrm{PtCl}_{4}$ by single crystal transmission is open to suspicion because of the complications of Fermi resonance in the middle region of the $A_{2}$ spectrum.

Both the lattice mode values and the $\nu(M-C I)$ values obtained from the reflectance analysis are in very close agreement with values quoted for mull spectra.

There is a drop in $v(\mathrm{Pt}-\mathrm{Cl})$ in passing from $\mathrm{K}_{2} \mathrm{PtCl}_{4}$ to the ammonium salt, and a considerable increase in $v_{4}$ $\left(+40 \mathrm{~cm}^{-1}\right)$ and $v_{7}\left(+19 \mathrm{~cm}^{-1}\right)$, due to the hydrogen bonding in the ammonium salt, see Table 7.5. This is entirely expected since the $\mathrm{Pt}-\mathrm{Cl}$ bond will be weakened but deformations of the $\mathrm{Pt}-\mathrm{Cl}$ bond will become more difficult. Similar results are shown for the palladites. Simultaneously the $v_{4}\left(\mathrm{~A}_{2 \mathrm{u}}\right), \pi(\mathrm{Pt}-\mathrm{Cl})$ and $\nu_{7}\left(\mathrm{E}_{\mathrm{u}}\right), \quad \delta(\mathrm{Pt}-\mathrm{Cl})$ modes move closer together because these motions are both damped by hydrogen bonding. The effect of decreasing the temperature at the sample is to raise all the internal mode frequencies. The greatest shifts are seen in the ammonium salts (as expected) and is attributed to the increased strength of the hydrogen bonding. Similarly the lattice modes show a larger increase in frequency with decreasing temperature in the ammonium salts than in the potassium salts. The relative intensities of the lattice modes in all five complexes shows the same order and this supports the assignment of the lattice modes in the ammonium salts.

Table 7.1 Factor Group Analysis for $A_{2} M X_{4}$.

| $\mathrm{D}_{4} \mathrm{~h}$ | $\mathrm{T}_{\text {A }}$ | T | $\mathrm{R}^{-}$ | $\mathrm{R}^{+}$ | Ni | Activities |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| ${ }^{A_{1} \mathrm{~g}}$ |  |  |  |  | 1 | $\operatorname{Raman}\left(\mathrm{x}^{2}+\mathrm{y}^{2}\right), \mathrm{z}^{2}$ |
| $\mathrm{A}_{2 \mathrm{~g}}$ |  |  | 1 | 1 |  |  |
| ${ }^{B} 1_{1 g}$ |  |  |  |  | 1 | Raman ( $\mathrm{x}^{2}-\mathrm{y}^{2}$ ) |
| $\mathrm{B}_{2 \mathrm{~g}}$ |  |  |  | 1 | 1 | Raman ( xy ) |
| $E_{g}$ |  |  | 1 | 2 |  | Raman (xz, yz) |
| $\mathrm{A}_{1 \mathrm{u}}$ |  |  |  |  |  |  |
| $\mathrm{A}_{2 \mathrm{u}}$ | 1 | 1 |  |  | 1 | I.r. (z) |
| $\mathrm{B}_{14}$ |  |  |  |  | 1 |  |
| $\mathrm{B}_{2 \mathrm{u}}$ |  | 1 |  |  |  |  |
| $E_{u}$ | 1 | 2 |  |  | 2 | I.r. ( $\mathrm{x}, \mathrm{y}$ ) |

Internal modes of A (where applicable) have been omitted. $T_{A}=$ acoustic branch modes ; $T=$ optic branch translatory modes ; $R^{-}=$optic branch rotatory anion modes ; $\mathrm{R}^{+}=$optic branch rotatory cation modes $\left(\left(\mathrm{NH}_{4}\right)^{+}\right.$only) ; $\mathrm{N}_{\mathrm{i}}=$ internal modes of $\left(\mathrm{MX}_{4}\right)^{2^{-}}$.

Table 7.2 I.r. wavenumbers ( $\mathrm{cm}^{-1}$ ) for single crystal $\mathrm{K}_{2} \mathrm{MCl}_{4}$ obtained from Kramers-Kronig analyses of spectra.

| $\mathrm{K}_{2} \mathrm{PtCl}_{4}$ |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 295 | K | 145 | K | a |  |
|  | т.0. | L. 0. | т.o. | L.O. | т.O. |  |
| $\mathrm{A}_{2 \mathrm{u}}$ | 98 | 110 | 100 | 112 | 98 | Lattice mode |
|  | 160 | 196 | 165 | 201 | $\sim 170$ | $v_{4}$ |
| $E_{u}$ | 86 | 96 | 88 | 100 | 87 | Lattice mode |
|  | 113 | 126 | 114 | 128 | 112 | Lattice mode |
|  | 185 | 204 | 186 | 208 | 194 | $v_{7}$ |
|  | 325 | 338 | 326 | 341 | 323 | $v_{6}$ |
| $\mathrm{K}_{2} \mathrm{PdCl}_{4}$ |  |  |  |  |  |  |
|  | 295 | K | 145 | K |  |  |
|  | T.O. | L.O. | T.O. | L.O. |  |  |
| ${ }^{\text {A }}{ }_{2 \mathrm{u}}$ | 106 | 120 | 110 | 122 |  | Lattice mode |
|  | 162 | 200 | 162 | 200 |  | $v_{4}$ |
|  |  |  | $222{ }^{\text {b }}$ | - |  | (see text) |
|  |  |  | $246{ }^{\text {b }}$ | - |  | (see text) |
| $\mathrm{E}_{\mathrm{u}}$ | 92 | 100 | 94 | 105 |  | Lattice mode |
|  | 114 | 134 | 118 | 137 |  | Lattice mode |
|  | 178 | 196 | 184 | 196 |  | $v_{7}$ |
|  | - | - | $272{ }^{\text {b }}$ | $\sim 278$ |  | (see text) |
|  | - | - | $288{ }^{\text {b }}$ | 300 |  | (see text) |
|  | 334 | 350 | 338 | 358 |  | $v_{6}$ |



Table 7.3 I.r. wavenumbers $\left(\mathrm{cm}^{-1}\right)$ for single crystal $\mathrm{K}_{2} \mathrm{PtBr}_{4}$ obtained from Kramers-Kronig analyses of spectra.
$295 \mathrm{~K} \quad 145 \mathrm{~K}$
T.O. L.O. T.O. L.O.

| $A_{2 \mathrm{u}}$ | 90 | 94 | 91 | 96 | Lattice mode |
| :---: | :---: | :---: | :---: | :---: | :--- |
|  | 128 | 156 | 129 | 157 | $v_{4}$ |


| $E_{u}$ | 75 | 96 | 78 | 97 | Lattice mode |
| :--- | :--- | :--- | :--- | :--- | :--- |
| 102 | 109 | 106 | 113 | Lattice mode |  |
| 129 | 145 | 133 | 142 | $v_{7}$ |  |
|  |  |  |  |  |  |
|  | 231 | 246 | 236 | 247 | $v_{6}$ |

Table 7.4 I.r. wavenumbers $\left(\mathrm{cm}^{-1}\right)$ for single crystal
$\left(\mathrm{NH}_{4}\right)_{2} \mathrm{MCl}_{4}$ obtained from Kramers-Kronig analyses of spectra.
$\left(\mathrm{NH}_{4}\right)_{2} \mathrm{PtCl}_{4}$

|  |  | K |  | K |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | T. 0. | L. 0. | T.O. | L. O. |  |
| ${ }^{A_{2}} \mathrm{u}$ | 116 | 123 | 118 | 125 | Lattice mode |
|  | $200^{\text {a }}$ | 270 | 207 | 250 | $v_{4}$ |
|  | - | - | 282 | - | (See text) |
| $E_{u}$ | 116 | 133 | 124 | 133 | Lattice mode |
|  | sh | - | 178 | - | Lattice mode |
|  | 204 | 240 | 217 | 244 | $v_{7}$ |
|  | - | - | 304 | - | (See text) |
|  | 319 | 336 | 324 | 340 | $v_{6}$ |

$\left(\mathrm{NH}_{4}\right)_{2} \mathrm{PdCl}_{4}{ }_{295 \mathrm{~K}} \quad 145 \mathrm{~K}$

|  | T.O. | L.0. | T.0. | L.0. |  |
| :---: | :---: | :---: | :---: | :--- | :--- |
| $\mathrm{A}_{\mathrm{u}}$ | 123 | 131 | 127 | 134 | Lattice mode |
|  | 194 | 280 | 200 | 266 | $v_{4}$ |
|  | - | - | 295 | 303 | (See text) |
| $E_{u}$ | 122 | 137 | 128 | 141 | Lattice mode |
|  | 163 | - | 178 | 188 | Lattice mode |
|  | 204 | 241 | 211 | 241 | $v_{7}$ |
|  | - | - | 295 | - | (See text) |
|  | - | 309 | - | (See text) |  |
|  |  |  | 337 | 355 | $v_{6}$ |

a estimated visually $K-K$ analysis gives $188 \mathrm{~cm}^{-1}$
sh denotes a shoulder
Table 7.5 I.r. wavenumbers $\left(\mathrm{cm}^{-1}\right)$ for $\left(\mathrm{PtCl}_{4}\right)^{2^{-}}$and $\left(\mathrm{PdCl}_{4}\right)^{2^{-}}$in solution, potassium
and ammonium salts.

|  | $\left(\mathrm{PtCl}_{4}\right)^{2-}$ |  |  |
| :---: | :---: | :---: | :---: |
|  | $\mathrm{CHCl}_{3}$ <br> soln. ${ }^{\text {a }}$ | $\mathrm{K}^{+\mathrm{b}}$ | $\left(\mathrm{NH}_{4}\right)^{+} \mathrm{b}$ |
| $\nu_{4}\left(A_{2}{ }^{\prime}\right) \pi(M-C l)$ | 147 | 160 | 200 |
| $v_{7}\left(E_{u}\right) \delta(M-C l)$ | 165 | 185 | 204 |
| $v_{6}\left(E_{u}\right) \quad v(M-C l)$ | 313 | 325 | 319 |

[^0]FIG. 7.0
Morphology of $\mathrm{A}_{2} \mathrm{MX}_{4}$ Crystals


$v_{3}\left(B_{2}\right)$ (in plane)

$v_{4}\left(\mathrm{~A}_{2 u}\right)$ (out of plane)

$v_{5}\left(\mathrm{~B}_{1 \mathrm{u}}\right)$ (out of plane)
$v_{6}\left(E_{u}\right)$ (in plane)

$v_{7}\left(E_{u}\right)$ (in plane)

FIG. 7.2


FIG. 7.3


FIG. 7.4


FIG. 7.5


Figures 7.6-7.8

$$
\mathrm{K}_{2} \mathrm{PtBr}_{4}
$$



Figure 7.7 (c) $\quad \mathrm{A}_{2 \mathrm{u}} \quad 145 \mathrm{~K}$

Figure $7.8 \quad$ (d) $\quad E_{u} \quad 145 \mathrm{~K}$

FIG.7.6


FIG. 7.7


FIG. 7.8


FIG. 7.9


FIG. 7.10


FIG.7.11


FIG.7.12


FIG. 7.13


FIG. 7.14


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## Chapter Eight

A brief introduction was given in Chapter One to the 80 groups. In addition to the 230 space groups, which are used to describe structures which have periodicity in three dimensions, there are 80 diperiodic groups which can be used to describe structures which are, or approximately correspond to, planar structures. Such structures use the third dimension as a stacking direction between layers. Wood (1964) has derived these groups from the 230 space groups. Symmetry operations which are allowed in space groups may not also be allowed in the diperiodic groups owing to the loss of periodicity in the third dimension. The following symmetry operations are excluded from these groups : screw axes normal to the plane of periodicity; glide panes with glide directions out of the plane of periodicity; ' $n$ ' fold rotation axes which are not normal to the diperiodic plane; a special case for this last exclusion is where $n=2$ and the axis is in the diperiodic plane, since the upper side of the plane may be like or unlike the lower side these rotations may be allowed. Mirror planes, glide planes and screw axes may lie in the diperiodic plane.

Each group may be derived from one of the five twodimensional nets (see Chapter One) in an analogous manner to which the 230 space groups are generated from the 14 Bravais lattices. These nets are indeed the two-dimensional equivalents
of the Bravais lattices. Only the rectangular net may be primitive or centred, all other nets are primitive. The 230 space groups given in "International Tables for X-ray Crystallography", hereafter called I.T.X.R.C., have setsof symmetrically equivalent sites given in terms of "Wyckoff notation", and the point symmetry of the sites given in terms of Hermann-Mauguin symbols, in addition to the number of equivalent sites. Wood has retained the notation of the sites as that of the space group from which the diperiodic group (D.G.) is derived. Each diperiodic group may be assigned a "Schonflies notation" factor group which is identical to the factor group of the corresponding space group. Table 8.1 lists the 80 groups with the full HermannMauguin symbols of the group and the Schonflies symbol of the space group from which it was derived, along with the space group number as given in I.T.X.R.C. Each diperiodic group has a unique direction in the plane normal. It is found on inspection that if this direction is placed along two non-equivalent directions of certain single orthorhombic groups two non-equivalent diperiodic groups are generated; one of these may have the I.T.X.R.C. standard axis set, the other will always have a non-standard set. Both groups generated have equivalent point symmetry for their respective "Wyckoff sites". An example is given by D.G. 23 and D.G. 24 , both are derived from space group 25 , sites 'a' in both cases have point symmetry mm. It is important to remember that, in such cases, symmetry operations are identical but are performed on different site coordinates.

The diperiodic groups are particularly useful in dealing with "layer" structures; the confusion between diperiodic groups and space groups can be avoided by nomenclature, adopted here, of D.G. to describe a diperiodic group. It was decided to derive a set of simplified factor group analysis tables for the 80 groups. Similar tables for the 230 space groups have been derived previously (Adams and Newton 1970). Such tables would allow the irreducible representation of the structure to be given in terms of symmetry species without any lengthy calculation. All the information required is a knowledge of the symmetry of the diperiodic group adopted by the structure, and the sites occupied; such information is available from a variety of sources (e.g. Wjckoff 1968).

## Calculation of Irreducible Representations

The method of Bhagavantam and Venkatarayudu (references Chapter 1) is acopted for the calculation. In outline the method entails the calculation of the atoms of the structure which are unmoved by the symmetry operations of the factor group. An atom will not be moved by a mirror plane or rotation axis if and only if the atom lies along the symmetry axis; similarly it will not be moved by an inversion centre or improper rotation if and only if the atom lies at the respective centre. Screw axes and glide planes involve translation by a fraction of the primitive translation (which are used to construct the net) and any atoms
operated on do not remain invariant. Any atom on a particular site is not moved by operations of the site symmetry, but is moved by any other operations of the factor group.

It is at this stage that a simplification can be applied to the method. Sites remaining invariant for each of the 80 groups are tabulated in Table 1 at the end of the chapter. The Wyckoff notation is used for simplicity. A reducible representation may be calculated for each site using:

$$
X_{j}(R)=W_{R} \wedge_{R}
$$

$X_{j}(R)$ is the character of the $j$ th class having symmetry operation R. $W_{R}$ is the number of atoms invariant under operation $R$. $\Lambda_{R}$ is the trace of the transformation matrix for operation $R$ which is given by:

```
2Cos}0\pml where 0 = the angle of rotation for operation \(R\)
```

+1 is added for pure rotations, -1 is added for rotation plus inversion. This representation is then reduced by the usual method.

$$
\begin{equation*}
n_{1}=\frac{1}{N} \sum_{j} h_{j} X_{i}(R) X_{j}(R) \tag{1}
\end{equation*}
$$

$n_{1}$ is the number of times the irreducible representation $\Gamma_{i}$ is contained in the reducible representation $\Gamma_{j}$.
$X_{i}(R)$ and $X_{j}(R)$ are the characters of operation $R$ in $\Gamma_{i}$ and $\Gamma_{j}$ respectively. $N$ is the order of the group (total number of symmetry elements). $h_{j}$ is the number of operations in the $j$ th class.

Another way of doing the same thing is to multiply the elements of each row of the site symmetry table for the diperiodic group (Table l) by the number of equivalent sites in the primitive net, and by the contribution each makes to the representation $2 \operatorname{Cos} \theta \pm 1$. The reducible representations can then be reduced by:

$$
\begin{equation*}
n_{1}=\frac{1}{N} \sum_{j} X_{i}(R) X_{j}(R) \tag{2}
\end{equation*}
$$

all symbols are as in (1).

The irreducible representation for the 3 N normal modes of any structure can then be obtained by summation of the rows of table 2 for the sites cccupied in the diperiodic group. In the case of the absence of a diperiodic group isomorphous with a space group, the irreducible representation may be obtained from another diperiodic group, of the same factor group, by summation of the appropriate rows which correspond to the point symmetries of the three dimensional structure.

For layer structures the only translatory modes allowed are of the acoustic type. These are easily found from the point group table of the isomorphous factor group. Layer structures have no rotational degrees of freedom; the modes calculated from Table 2 are therefore the internal modes of the layer plus the acoustic modes.

In considering whether a structure is a layer structure or not it is important to inspect the distances between sets of atoms. If the distances are greater than the Van der Waal's radii for the atoms the structure may be described as a layer structure. If the inter-atomic distances are less than the Van der Waal's radii, i.e. there is interaction between them, the structure is best described by a space group and not a diperiodic group.

The use of the tables is best illustrated using examples.
j.) Red PbO is a layer structure comprising 1 layer per unit cell. The 3-dimensional space group for the structure is $\mathrm{D}_{4 \mathrm{~h}}^{5}$, inspection of Table 8.1 shows that the corresponding 2-dimensional group is D.G. 63.

Pb atoms lie on sites 2 c and 0 atoms on sites 2 a .

Table 2 D.G. 63 lists the following.

|  | ${ }^{A_{1}} \mathrm{~g}$ | ${ }^{A_{2}} \mathrm{~g}$ | ${ }^{B} 1_{g}$ | ${ }^{B} 2 \mathrm{~g}$ | $\mathrm{E}_{\mathrm{g}}$ | ${ }^{A_{1}} \mathbf{u}$ | $\mathrm{A}_{2} \mathrm{u}$ | $B_{1 u}$ | $\mathrm{B}_{2} \mathrm{u}$ | $E_{u}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 2c | 1 | 0 | 0 | 0 | 1 | 0 | 1 | 0 | 0 | 1 |
| 2 a | 0 | 0 | 1 | 0 | 1 | 0 | 1 | 0 | 0 | 1 |
| Total | 1 | 0 | 1 | 0 | 2 | 0 | 2 | 0 | 0 | 2 |
| TA |  |  |  |  |  |  | 1 |  |  | 1 |
| Int. | 1 | 0 | 1 | 0 | 2 | 0 | 1 | 0 | 0 | 1 |

TA are the acoustic translatory modes found from the point group table for $\mathrm{D}_{4}$. Int. are the internal modes of the layer.
ii) $\quad \mathrm{CdCl}_{2}$ is a layer structure comprising layer per unit cell. The 3-dimensional space group of the structure is $D_{3}^{5}$, inspection of Table 8.1 shows that there is no corresponding 2-dimensional group. Inspection shows that the layer symmetry is also $\mathrm{D}_{3 \mathrm{~d}}$. We may therefore take another $D_{3 d}$ 2-dimensional group and use this to calculate the representation, but it is important to use sites of equivalent symmetry, e.g. D.G. 71 ( $D_{3 d}^{l}$ ) may be used.

In $D_{3 d}^{5} \mathrm{CdCl}_{2}$ has Cd on sites la $\overline{3} \mathrm{~m}$. Cl on sites 2c 3m.

In $D_{3 d}^{l}$ the equivalent sites are la $\overline{3}$.
2e 3m.

|  | ${ }_{7}$ | $\mathrm{A}_{2 \mathrm{~g}}$ | $E_{g}$ | ${ }^{A} \mathrm{l}_{u}$ | ${ }^{A_{2}} \mathrm{u}$ | $E_{u}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| la | 0 | 0 | 0 | 0 | 1 | 1 |
| 2 e | 1 | 0 | 1 | 0 | 1 | 1 |
| Total | 1 | 0 | 1 | 0 | 2 | 2 |
| TA |  |  |  |  | 1 | 1 |
| Int. | 1 | 0 | 1 | 0 | 1 | 1 |

iii) Red $\mathrm{HgI}_{2}$ is a layer structure comprising 2 layers per unit cell. The 3-dimensional space group which describes the structure is $D_{4 h}^{15}$, inspection of Table 8.1 shows no corresponding 2-dimensional group.

In order to obtain the internal modes for layer
the symmetry of the layer must be determined,
inspection shows that this is $\mathrm{D}_{2}$ d. Selecting
D.G. 57 ( $\mathrm{D}_{2 \mathrm{~d}}^{1}$ ).

In $\mathrm{D}_{4}^{15} \mathrm{~h} \mathrm{HgI}_{2}$ has Hg on sites $2 \mathrm{a} \overline{4} 2 \mathrm{~m}$.
I on sites 4 dmm .

This is for 2 layers; for 1 layer:
$\mathrm{D}_{2 \mathrm{~d}}^{\mathrm{d}}$ has sites la $\overline{4} 2 \mathrm{~m}$
2 g mm

|  | $\mathrm{A}_{1}$ | $\mathrm{~A}_{2}$ | $\mathrm{~B}_{1}$ | $\mathrm{~B}_{2}$ | E |
| :--- | :--- | :--- | :--- | :--- | :--- |
| la | 0 | 0 | 0 | 1 | 1 |
| 2 g | 1 | 0 | 0 | 1 | 2 |
| Total | 1 | 0 | 0 | 2 | 3 |
| TA |  |  |  |  | 1 |

This agrees with the cumbersome calculation of Hiraishi (1976). The choice of a non-primitive net for vibrational analysis leads to more than the predicted number of modes. The tables have been calculated using equivalent primitive nets and automatically give the correct number of modes.

Table 8.1 The 80 Diperiodic Groups in 3 Dimensions

Oblique
D.G.

| 1 | Pl | $\mathrm{C}_{1}^{l}$ | $(1)$ |  |
| :--- | :--- | :--- | :--- | :--- |
| 2 | $\mathrm{P} \overline{1}$ | $\mathrm{C}_{\mathrm{i}}^{1}$ | $(2)$ |  |
| 3 | P 211 | $\mathrm{C}_{2}^{1}$ | $(3)$ | lst setting |
| 4 | Pmll | $\mathrm{C}_{\mathrm{s}}^{1}$ | $(6)$ | lst setting |
| 5 | Pbll | $\mathrm{C}_{\mathrm{s}}^{2}$ | $(7)$ | lst setting |
| 6 | $\mathrm{P} 2 / \mathrm{mll}$ | $\mathrm{C}_{2}^{1}$ | $(10)$ | lst setting |
| 7 | $\mathrm{P} 2 / \mathrm{bll}$ | $\mathrm{C}_{2 h}^{4}$ | $(13)$ | lst setting |

Rectangular

| 8 | Pll2 | $C_{2}^{1}$ | (3) | 2nd setting |
| :---: | :---: | :---: | :---: | :---: |
| 9 | Pl121 | $\mathrm{C}_{2}^{2}$ | (4) | 2nd setting |
| 10 | Cll2 | $c_{2}^{3}$ | (5) | 2nd setting |
| 11 | Pllm | $\mathrm{c}_{\mathrm{s}}^{1}$ | (6) | 2nd setting |
| 12 | Plla | $c_{s}^{2}$ | (7) | 2nd setting |
| 13 | Cllm | $C_{S}^{3}$ | (8) | 2nd setting |
| 14 | Pll2/m | $c_{2 h}^{1}$ | (10) | 2nd setting |
| 15 | Pll21/m | $C_{2 h}^{2}$ | (11) | 2nd setting |
| 16 | $\mathrm{Cll} 2 / \mathrm{m}$ | $c_{2 h}^{3}$ | (12) | 2nd setting |
| 17 | Pll2/a | $c_{2 h}^{4}$ | (13) | 2nd setting |
| 18 | P1121/a | $c_{2 h}^{5}$ | (14) | 2nd setting |
| 19 | P222 | $\mathrm{D}_{2}^{1}$ | (16) |  |
| 20 | P222 1 | $\mathrm{D}_{2}^{2}$ | (17) | bca |
| 21 | P22121 | $\mathrm{D}_{2}^{3}$ | (18) |  |
| 22 | C222 | $\mathrm{D}_{2}^{6}$ | (21) |  |
| 23 | P2mm | $\mathrm{C}_{2}^{1}{ }_{\mathrm{v}}$ | (25) |  |


| 24 | Pmm2 | $C_{2 v}^{1}$ | (25) | bca |
| :---: | :---: | :---: | :---: | :---: |
| 25 | Pm2 ${ }^{\text {a }}$ | $c_{2 v}^{2}$ | (26) | $\overline{\mathrm{cba}}$ |
| 26 | $\mathrm{Pbm} 1_{1}$ | $C_{2 v}^{2}$ | (26) | acb |
| 27 | Pbb2 | $c_{2 v}^{3}$ | (27) | $\overline{\mathrm{acb}}$ |
| 28 | P2ma | $c_{2 v}^{4}$ | (28) |  |
| 29 | Pam2 | $c_{2 v}^{4}$ | (28) | acb |
| 30 | Pab21 | $C_{2 v}^{5}$ | (29) | $a \overline{c b}$ |
| 31 | Pnb2 | $C_{2 v}^{6}$ | (30) | bca |
| 32 | Pnm21 | $C_{2 v}^{7}$ | (31) | $\overline{\mathrm{acb}}$ |
| 33 | P2ba | $c_{2 v}^{8}$ | (32) |  |
| 34 | C2mm | $C_{2 v}^{11}$ | (35) |  |
| 35 | Cmm2 | $C_{2 v}^{14}$ | (38) | bca |
| 36 | Cam2 | $\mathrm{C}_{2 \mathrm{v}}^{15}$ | (39) | bca |
| 37 | $\mathrm{P} 2 / \mathrm{m} 2 / \mathrm{m} 2 / \mathrm{m}$ | $D_{2 h}^{1}$ | (47) |  |
| 38 | $\mathrm{P} 2 / \mathrm{a} 2 / \mathrm{m} 2 / \mathrm{a}$ | $\mathrm{D}_{2}^{3} \mathrm{~h}$ | (49) | cab |
| 39 | $\mathrm{P} 2 / \mathrm{n} 2 / \mathrm{b} 2 / \mathrm{a}$ | $\mathrm{D}_{2}^{4} \mathrm{~h}$ | (50) |  |
| 40 | $\mathrm{P} 2 / \mathrm{m} 21 / \mathrm{m} 2 / \mathrm{a}$ | $\mathrm{D}_{2}^{5}$ | (51) | a $\overline{c b}$ |
| 41 | $\mathrm{P} 2 / \mathrm{a} 21 / \mathrm{m} 2 / \mathrm{m}$ | $\mathrm{D}_{2 \mathrm{~h}}^{5}$ | (51) |  |
| 42 | $\mathrm{P} 2 / \mathrm{n} 2 / \mathrm{m} 2 \mathrm{l} / \mathrm{a}$ | $\mathrm{D}_{2 \mathrm{n}}^{7}$ | (53) | $\overline{\mathrm{acb}}$ |
| 43 | $\mathrm{P} 2 / \mathrm{a} 2 / \mathrm{b} 21 / \mathrm{a}$ | $\mathrm{D}_{2} \mathrm{~h}$ | (54) | cab |
| 44 | $\mathrm{P} 2 / \mathrm{m} 21 / \mathrm{b} 21 / \mathrm{a}$ | $\mathrm{D}_{2}^{9} \mathrm{~h}$ | (55) |  |
| 45 | $\mathrm{P} 2 / \mathrm{a} 21 / \mathrm{b} 1_{1} / \mathrm{m}$ | $\mathrm{D}_{2}^{11}$ | (57) | bca |
| 46 | $\mathrm{P} 2 / \mathrm{n} 2_{1} / \mathrm{m} 2_{1} / \mathrm{m}$ | $\mathrm{D}_{2}^{13}$ | (59) |  |
| 47 | $\mathrm{C} 2 / \mathrm{m} 2 / \mathrm{m} 2 / \mathrm{m}$ | $\mathrm{D}_{2} \mathrm{l}$ h | (65) |  |
| 48 | $\mathrm{C} 2 / \mathrm{a} 2 / \mathrm{m} 2 / \mathrm{m}$ | $\mathrm{D}_{2 \mathrm{~h}}^{21}$ | (67) |  |

Square

| 49 | P 4 | $\mathrm{C}_{4}^{1}$ | $(75)$ |
| :--- | :--- | :--- | ---: |
| 50 | P 4 | $\mathrm{~S}_{4}^{1}$ | $(81)$ |
| 51 | $\mathrm{P} 4 / \mathrm{m}$ | $\mathrm{C}_{4 \mathrm{~h}}^{1}$ | $(83)$ |
| 52 | $\mathrm{P} 4 / \mathrm{n}$ | $\mathrm{C}_{4 \mathrm{~h}}^{3}$ | $(85)$ |
| 53 | P 422 | $\mathrm{D}_{4}^{1}$ | $(89)$ |
| 54 | P 42 l 2 | $\mathrm{D}_{4}^{2}$ | $(90)$ |
| 55 | P 4 mm | $\mathrm{C}_{4}^{1} \mathrm{v}$ | $(99)$ |
| 56 | P 4 bm | $\mathrm{C}_{4 \mathrm{v}}^{2}$ | $(100)$ |
| 57 | P 42 m | $\mathrm{D}_{2}^{1} \mathrm{~d}$ | $(111)$ |
| 58 | $\mathrm{P} 42 \mathrm{~m}_{1} \mathrm{~m}$ | $\mathrm{D}_{2 \mathrm{~d}}^{3}$ | $(113)$ |
| 59 | P 4 m 2 | $\mathrm{D}_{2 \mathrm{~d}}^{5}$ | $(115)$ |
| 60 | P 4 b 2 | $\mathrm{D}_{2 \mathrm{~d}}^{7}$ | $(117)$ |
| 61 | $\mathrm{P} 4 / \mathrm{m} 2 / \mathrm{m} 2 / \mathrm{m}$ | $\mathrm{D}_{4 \mathrm{~h}}^{1}$ | $(123)$ |
| 62 | $\mathrm{P} 4 / \mathrm{n} 2 / \mathrm{b} 2 / \mathrm{m}$ | $\mathrm{D}_{4 \mathrm{~h}}^{3}$ | $(125)$ |
| 63 | $\mathrm{P} 4 / \mathrm{m} 21 / \mathrm{b} 2 / \mathrm{m}$ | $\mathrm{D}_{4 \mathrm{~h}}^{5}$ | $(127)$ |
| 64 | $\mathrm{P} 4 / \mathrm{n} 21 / \mathrm{m} 2 / \mathrm{m}$ | $\mathrm{D}_{4 \mathrm{~h}}^{7}$ | $(129)$ |

Hexagonal

| 65 | P 3 | $\mathrm{C}_{3}^{1}$ | $(143)$ |
| :--- | :--- | :--- | :--- |
| 66 | $\mathrm{P} \overline{3}$ | $\mathrm{C}_{3 \mathrm{i}}^{1}$ | $(147)$ |
| 67 | P 312 | $\mathrm{D}_{3}^{1}$ | $(149)$ |
| 68 | P 321 | $\mathrm{D}_{3}^{2}$ | $(150)$ |
| 69 | P 3 ml | $\mathrm{C}_{3 \mathrm{~V}}^{1}$ | $(156)$ |
| 70 | P 31 m | $\mathrm{C}_{3 \mathrm{~V}}^{2}$ | $(157)$ |
| 71 | $\mathrm{P} \overline{3} 12 / \mathrm{m}$ | $\mathrm{D}_{3 \mathrm{~d}}^{1}$ | $(162)$ |
| 72 | $\mathrm{P} \overline{3} 2 / \mathrm{ml}$ | $\mathrm{D}_{3 \mathrm{~d}}^{3}$ | $(164)$ |
| 73 | P 6 | $\mathrm{C}_{6}^{1}$ | $(168)$ |


| 74 | $\mathrm{P} \overline{6}$ | $\mathrm{C}_{3 \mathrm{~h}}^{1}$ | $(174)$ |
| :--- | :--- | :--- | :--- |
| 75 | $\mathrm{P} 6 / \mathrm{m}$ | $\mathrm{C}_{6 \mathrm{~h}}^{1}$ | $(175)$ |
| 76 | P 622 | $\mathrm{D}_{6}^{1}$ | $(177)$ |
| 77 | P 6 mm | $\mathrm{C}_{6 \mathrm{v}}^{1}$ | $(183)$ |
| 78 | $\mathrm{P} \overline{6} 2 \mathrm{~m}$ | $\mathrm{D}_{3 \mathrm{~h}}^{1}$ | $(187)$ |
| 79 | $\mathrm{P} \overline{6} 2 \mathrm{~m}$ | $\mathrm{D}_{3 \mathrm{~h}}^{3}$ | $(189)$ |
| 80 | $\mathrm{P} 6 / \mathrm{m} 2 / \mathrm{m} 2 / \mathrm{m}$ | $\mathrm{D}_{6 \mathrm{~h}}^{1}$ | $(191)$ |

$\mathrm{m}=$ mirror plane
$2,3,4,6=$ rotation axes $\overline{2}, \overline{3}, \overline{4}, \overline{6}=$ inversion axes
$2_{1}=2$ fold screw axis
$\mathrm{a}, \mathrm{b}, \mathrm{n}=$ glide planes
nomenclature relates to cab axes respectively, e.g.
D.G. $46 \mathrm{P} 2 / \mathrm{n} 2_{1} / \mathrm{m} 2_{1} / \mathrm{m}$

2 fold axis parallel to c with diagonal glide plane normal to c.

2 fold screw axis parallel to a with mirror plane normal to a.

2 fold screw axis parallel to b with mirror plane normal to b .

$$
\text { PABTIE } 1
$$

```
D.G. }
IO.ON WYCKORP E
POSINS MOTATIOM
    1
    A }
    1
```

    P 1 OBLTQUE
    D. 6.2
NO. OE WYCTOOPT E i
POSTS NOMATIOH
1
1
1
1
2

| A 1 | 1 | 1 |
| :--- | :--- | :--- |
| C2 | 1 | 1 |
| D3 | 1 | 1 |
| E4 | 1 | 1 |
| I5 | 1 | 0 |

                                    P.千 OBLTQUF
    D. G. 3
P211 ORLIQUE

| MO. OF | WYOKOFR | फ | $C_{2}$ |
| :---: | :---: | :---: | :---: |
| POSNS | MOTATION |  |  |
| 1 | A1 | 1 | 1 |
| 1 | B2 | 1 | 1 |
| 1 | C3 | 1 | 1 |
| 1 | D4 | 1 | 1 |
| 2 | B5 | 1 | 0 |

D.G. 4
$\begin{array}{cccc}\text { WO. OE } & \text { MYOKOPE } & \text { B } & \text { on } \\ \text { POSNS } & \text { MOTAPTOT } & & \\ 1 & \text { A1 } & 1 & 1 \\ 2 & \text { C2 } & 1 & 0\end{array}$
D. G. 5
P 511 OPLIQUTE
$\begin{array}{lccc}\text { NO. OP WYOEOEP } & \mathrm{E} & \sigma_{h} \\ \text { POGIS } & \text { TOTAMTON } & & \\ 2 & \text { A1 } & 1 & 0\end{array}$
Pm 11 OBLIQUE

| D.G. 8 |  |  | P 112 RECTAITGULAR |  |
| :--- | :--- | :--- | :--- | :--- |
| NO. OR | NYCROHF | E | $\mathrm{C}_{2}$ |  |
| POGMS | NOTATION |  |  |  |
| 1 | A1 | 1 | 1 |  |
| 1 | C2 | 1 | 1 |  |
| 2 | E3 | 1 | 0 |  |


| D.G. 9 |  |  |  | P 112, RECTANGUIAR |
| :---: | :---: | :---: | :---: | :---: |
| 170. OR | WYCKOEA | E | $\mathrm{C}_{2}$ |  |
| Posns | NOTATION |  |  |  |
| 2 | A 1 | 1 | 0 |  |
| D. G. 10 |  |  |  | 0112 mectangutar |
| NO. OP | WYCTOH? | E | $\mathrm{C}_{2}$ |  |
| POSAS | motatum |  |  |  |
| 2 | A 1 | 1 | 1 |  |
| 4 | C2 | 1 | 0 |  |


| D.G. 9 |  |  |  | P 112, RECTANGULAR |
| :---: | :---: | :---: | :---: | :---: |
| 170. OR | WYCROEA | E | $\mathrm{C}_{2}$ |  |
| PUSNS <br> 2 | $\begin{gathered} \text { NOTATION } \\ \text { A1 } \end{gathered}$ | 1 |  |  |
| D. G. 10 |  |  |  | 0112 merangular |
| NO. OP |  | E | $\mathrm{C}_{2}$ |  |
| posas | notariun |  |  |  |
| 2 | A 1 | 1 | 1 |  |
| 4 | C2 | 1 | 0 |  |

D. G. 6

## POSTS

1
1
1
1
2
2
2
2
2
4
D. G. 7
$\begin{array}{llllll}\text { INO. OF } & \text { MYCKOFF } \\ \text { POSUS } & \text { MOTATION }\end{array} \quad \mathrm{E} \quad{ }_{2} \begin{array}{ll}\text { i } & \sigma_{h}\end{array}$

| 2 | A1 | 1 | 0 | 1 | 0 |
| :--- | :--- | :--- | :--- | :--- | :--- |
| 2 | D2 | 1 | 0 | 1 | 0 |
| 2 | E3 | 1 | 1 | 0 | 0 |
| 2 | F4 | 1 | 1 | 0 | 0 |
| 4 | G5 | 1 | 0 | 0 | 0 |

D. G. 10


MTO. OF WYCKORP $\mathbb{E} \quad \mathrm{C}_{2}$ i $\sigma_{h}(x, y)$

## NOTATIOR

$\begin{array}{lllll}A 1 & 1 & 1 & 1 & 1\end{array}$
$\begin{array}{lllll}0 & 1 & 1 & 1 & 1\end{array}$
$\begin{array}{lllll}\text { D3 } & 1 & 1 & 1 & 1\end{array}$
$\begin{array}{lllll}\text { G4 } & 1 & 1 & 1 & 1\end{array}$
$\begin{array}{lllll}\text { I5 } & 1 & 1 & 0 & 0\end{array}$
$\begin{array}{lllll}\text { J6 } & 1 & 1 & 0 & 0\end{array}$
$\begin{array}{lllll}\text { K7 } & 1 & 1 & 0 & 0 \\ \text { L8 } & 1 & 1 & 0 & 1\end{array}$
$\begin{array}{lllll}18 & 1 & 1 & 0 & 0\end{array}$
$\begin{array}{lllll}49 & 1 & 0 & 0 & 1\end{array}$
010
1000

P2/b11 OBLIQUE

| D.G. 11 |  |  |  |  |  | P17m Recravgular |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 110. 0 P1 | WYOKOPE | E | $\sigma$ |  |  |  |
| posis | POTATION |  |  |  |  |  |
| 1 | A 1 | 1 | 1 |  |  |  |
| 1 | 32 | 1 | 1 |  |  |  |
| 2 | C3 | 1 | 0 |  |  |  |
| D.G. 12 |  |  |  |  |  | P11a RECRANGULAR |
| NO. OR | WYCROPF |  |  |  |  |  |
| POSIS | MOTATION | E | $\sigma_{h}$ |  |  |  |
| 2 | A 1 | 1 | 0 |  |  |  |
| D.G. 13 |  |  |  |  |  | C1m RECTANGULAR |
| NO. Or | WYCKOPF |  |  |  |  |  |
| POSNS | NOTATION | E | $\sigma_{h}$ |  |  |  |
| 2 | A 1 | 1 | 1 |  |  |  |
| 4 | B2 | 1 | 0 |  |  |  |
| D. G. 14 |  |  |  |  |  | P 112/m PECTAMGULAR |
| NO. OF | WYCKOFE | B | $\mathrm{C}_{2}$ | i | $\sigma_{h}$ |  |
| Posits | NOTATION |  |  |  |  |  |
| 1 | A 1 | 1 | 1 | 1 | 1 |  |
| 1 | B2 | 1 | 1 | 1 | 1 |  |
| 1 | D3 | 1 | 1 | 1 | 1 |  |
| 1 | E4 | 1 | 1 | 1 | 1 |  |
| 2 | I5 | 1 | 1 | 0 | 0 |  |
| 2 | J6 | 1 | 1 | 0 | 0 |  |
| 2 | M7 | 1 | 0 | 0 | 1 |  |
| 2 | N8 | 1 | 0 | 0 | 1 |  |
| 4 | 09 | 1 | 0 | 0 | 0 |  |
| D.G. 15 |  |  |  |  |  | P112 /m RECTANGULAR |
| 1\%O. OP | WYCKOEF | E | $\mathrm{C}_{2}$ | i |  |  |
| POSNS | notation |  |  |  |  |  |
| 2 | A 1 | 1 | 0 | 1 | 0 |  |
| 2 | B2 | 1 | 0 | 1 | 0 |  |
| 2 | E3 | 1 | 0 | 0 | 1 |  |
| 4 | P4 | 1 | 0 | 0 | 0 |  |


| 170. OP | WYCROEF | E | C | i | . $\sigma$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| POSTS | IO:A IUM |  |  |  |  |
| 2 | A 1 | 1 | 1 | 1 | 1 |
| 2 | B2 | 1 | 1 | 1 | 1 |
| 4 | E3 | 1 | 0 | 1 | 0 |
| 4 | G4 | 1 | 1 | 0 | 0 |
| 4 | I5 | 1 | 0 | 0 | 1 |
| 8 | J6 | 1 | 0 | 0 | 0 |


| D.G. ${ }^{17}$ |  |  |  |  |  |
| :--- | :--- | :--- | :--- | :--- | :--- |
| WO. OF | WYCKOEF | I | $C_{2}$ | i | $\sigma_{h}$ |
| POSNS | IOTAIION |  |  |  |  |
| 2 | A1 | 1 | 0 | 1 | 0 |
| 2 | C2 | 1 | 0 | 1 | 0 |
| 2 | E3 | 1 | 1 | 0 | 0 |
| 4 | G4 | 1 | 0 | 0 | 0 |


| D. G. ${ }^{18}$ |  |  |  |  |  |
| :--- | :--- | :--- | :--- | :--- | :--- |
| NO. OF | WYCKOER | E | $C_{2}$ | i | $\sigma_{h}$ |
| FOSNS | NOTARION |  |  |  |  |
| 2 | A1 | 1 | 0 | 1 | 0 |
| 2 | C2 | 1 | 0 | 1 | 0 |
| 4 | E3 | 1 | 0 | 0 | 0 |


| D.G. ${ }^{19}$ |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| IVO. OR | WYCTORF | E | $\mathrm{C}_{2}(z)$ | $\mathrm{C}_{2}(\mathrm{y})$ | $\mathrm{C}_{2}(\mathrm{x})$ |
| POSNS | NOTATION |  |  |  | 1 |
| 1 | A1 | 1 | 1 | 1 | 1 |
| 1 | B2 | 1 | 1 | 1 | 1 |
| 1 | C3 | 1 | 1 | 1 | 1 |
| 1 | I4 | 1 | 1 | 1 | 1 |
| 2 | I5 | 1 | 0 | 0 | 1 |
| 2 | K6 | 1 | 0 | 0 | 1 |
| 2 | H7 | 1 | 0 | 1 | 0 |
| 2 | 08 | 1 | 0 | 1 | 0 |
| 2 | Q9 | 1 | 1 | 0 | 0 |
| 2 | R10 | 1 | 1 | 0 | 0 |
| 2 | S11 | 1 | 1 | 0 | 0 |
| 2 | T12 | 1 | 1 | 0 | 0 |
| 4 | U13 | 1 | 0 | 0 | 0 |

$$
\begin{aligned}
& \begin{array}{cccccc}
\text { POSNS } & \text { TOAAION } & & 2 & 2 & 2 \\
2 & \text { A1 } & 1 & 1 & 0 & 0 \\
2 & \text { B2 } & 1 & 1 & 0 & 0 \\
4 & \text { C3 } & 1 & 0 & 0 & 0
\end{array}
\end{aligned}
$$



| D.G. 23 |  |  |  |  | P2mm RECTANGULAR |
| :---: | :---: | :---: | :---: | :---: | :---: |
| NO. OP | WYCKOEs | E | $\mathrm{C}_{2}(z)$ | $\sigma_{\bar{t}}(x z)$ | $\sigma_{V}^{\prime}(y z)$ |
| POSNS | MOTATION |  |  |  |  |
| 1 | A 1 | 1 | 1 | 1 | 1 |
| 1 | B2 | 1 | 1 | 1 | 1 |
| 1 | C3 | 1 | 1 | 1 | 1 |
| 1 | D4 | 1 | 1 | 1 | 1 |
| 2 | 25 | 1 | 0 | 1 | 0 |
| 2 | F6 | 1 | 0 | 1 | 0 |
| 2 | G7 | 1 | 0 | 0 | 1 |
| 2 | H8 | 1 | 0 | 0 | 1 |
| 4 | I9 | 1 | 0 | 0 | 0 |



```
\begin{tabular}{|c|c|c|c|c|c|}
\hline D.G. 25 & & & & & Pm2 a DECTANGULAR \\
\hline 110. OP & WYCKOPr & E & \(\mathrm{C}_{2}(z)\) & \(\sigma_{V}(x z)\) & \(\sigma_{V}^{\prime}(y z)\) \\
\hline POSNS & MOTATION & & & & \\
\hline 2 & A 1 & 1 & 0 & 0 & 1 \\
\hline 4 & C2 & 1 & 0 & 0 & 0 \\
\hline
\end{tabular}
\begin{tabular}{|c|c|c|c|c|c|}
\hline D.G. 26 & & & & & Pom2, RECTANGULAR \\
\hline NO. OP - & WYCKOPF & E & \(\mathrm{C}_{2}(\mathrm{z})\) & \(\sigma_{V}(x z)\) & \(\sigma^{\prime}(y z)\) \\
\hline POSNS & NOTATION & & & & \\
\hline 2 & A 1 & 1 & 0 & 1 & 0 \\
\hline 2 & B2 & 1 & 0 & 1 & 0 \\
\hline 4 & C3 & 1 & \(\checkmark\) & 0 & 0 \\
\hline
\end{tabular}
```

| D.G. 27 |  |  |  |  | Pbo 2 RECTANGUIAR |
| :---: | :---: | :---: | :---: | :---: | :---: |
| NO. OF | WYCKORE | E | $\mathrm{C}_{2}(\mathrm{z})$ | $\sigma(x z)$ | $\sigma^{\prime}(y z)$ |
| POSNTS | NOTATION |  |  |  |  |
| 2 | A 1 | 1 | 1 | 0 | 0 |
| 2 | C2 | 1 | 1 | 0 | 0 |
| 4 | E3 | 1 | 0 | 0 | 0 |



| D.l. 29 |  |  | Pam2 RECTANGULAR |  |  |
| :--- | :--- | :--- | :--- | :--- | :--- |
| NO. OR | WYCKOR | E | $C_{2}(z)$ | $\sigma_{V}(x z)$ | $\sigma_{V}^{\prime}(y z)$ |
| POSNS | NOTATION |  |  | 0 | 0 |
| 2 | A1 | 1 | 1 | 0 | 0 |
| 2 | C2 | 1 | 0 | 0 | 1 |
| 4 | D3 | 1 | 0 | 0 | 0 |

$$
\begin{aligned}
& \text { D.G. } 30 \text { WYCKORE } \quad C_{2}(z) \cdot \sigma_{V}(x z) \quad \sigma_{V}^{-1}(y z)^{\text {Pab2 }} 1 \text { TECTANGULAR } \\
& \text { DOSNS MOTATIOH } \\
& \begin{array}{llllll}
4 & \text { A1 } & 1 & 0 & 0 & 0
\end{array}
\end{aligned}
$$

| D.G. 33 |  |  |  |  |  |
| :--- | :--- | :--- | :--- | :--- | :--- |
| NO. OF | WYCKORE | I | $C_{2}(z)$ | $\sigma_{V}(x z)$ | $\sigma_{V}^{\prime}(y z)$ |
| POSIS | NOTATION RECTANGULAR |  |  |  |  |
| 2 | $A 1$ | 1 | 1 | 0 | 0 |
| 2 | B2 | 1 | 1 | 0 | 0 |
| 4 | C3 | 1 | 0 | 0 | 0 |


| D.G. 34 |  |  |  |  | C2mm RECTANGULAR |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| NO. Of | WYckore | E | $\mathrm{C}_{2}(z)$ | $\sigma^{-}(x z)$ | $\sigma^{\prime}(y z)$ |  |
| POSMS | WOTATION |  |  |  |  |  |
| 2 | A 1 | 1 | 1 | 1 | 1 |  |
| 2 | B2 | 1 | 1 | 1 | 1 |  |
| 4 | C3 | 1 | 1 | 0 | 0 |  |
| 4 | D4 | 1 | 0 | 1 | 0 |  |
| 4 | E5 | 1 | 0 | 0 | 1 |  |
| 8 | F6 | 1 | 0 | 0 | 0 |  |


| D.G. 35 |  |  |  |  |  | Cma rectangular |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| ITO. OP | WYCKOR | I | $\mathrm{C}_{2}(z)$ | $\sigma_{V}(x z)$ | $\sigma^{\prime}(y z)$ |  |
| Pusns | HOPATION |  |  |  |  |  |
| 2 | A 1 | 1 | 1 | 1 | 1 |  |
| 4 | C2 | 1 | 0 | 1 | 0 |  |
| 4 | D3 | 1 | 1 | 0 | 1 |  |
| 3 | F4 | 1 | 0 | 0 | 0 |  |



D.G. 40 P2/m2/m2/a RECTANGUIAR NO. OF WYCKOFE $\mathrm{EC}_{2}(z) \mathrm{C}_{2}(y) C_{2}(x)$ i $\sigma(x y) \sigma(z x) \sigma(y z)$

## POSNS NOTAIION

| 2 | A 1 | 1 | 0 | 1 | 0 | 1 | 1 | 0 | 0 |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| 2 | C2 | 1 | 0 | 1 | 0 | 1 | 1 | 0 | 0 |
| 2 | E3 | 1 | 0 | 1 | 0 | 0 | 1 | 0 | 1 |
| 4 | G4 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| 4 | H5 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| 4 | I6 | 1 | 0 | 0 | 0 | 0 | 1 | 0 | 0 |
| 4 | K7 | 1 | 0 | 0 | 0 | 0 | 0 | 1 | 0 |
| 8 | L8 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |


| D.G. 41 |  |  |  |  |  |  |  |  | PAT |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| NO. Or | WYCROEF | E |  | 2 |  | i |  | $\sigma(z$ | yz) |
| POSITS | NOTATION |  |  |  |  |  |  |  |  |
| 2 | A 1 | 1 | 0 | 1 | 0 | 1 | 0 | 1 | 0 |
| 2 | B2 | 1 | 0 | 1 | 0 | 1 | 0 | 1 | 0 |
| 2 | E3 | 1 | 1 | 0 | 0 | 0 | 0 | 1 | 1 |
| 2 | F4 | 1 | 1 | 0 | 0 | 0 | 0 | 1 | 1 |
| 4 | G5 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 |
| 4 | I6 | 1 | 0 | 0 | 0 | 0 | 0 |  | 0 |
| 4 | J7 | 1 | 0 | 0 | 0 | 0 | 0 | 1 | 0 |
| 4 | K8 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 1 |
| 8 | $\pm 9$ | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |


| D. G. 42 |  |  |  |  |  | $\mathrm{P} 2 / \mathrm{n} 2 / \mathrm{m} 2$ /a RECTA |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 10. OF | WYCKOEP | E | $\mathrm{C}_{2}(\mathrm{z})$ | $\mathrm{C}_{2}(y)$ | $\mathrm{C}_{2}(\mathrm{x})$ | i | o( xy ) | $\sigma(z x)$ |  |
| Posits | NOTATION |  |  |  |  |  |  |  |  |
| 2 | A 1 | 1 | 0 | 0 | 1 | 1 | 0 | 0 | 0 |
| 2 | B2 | 1 | 0 | 0 | 1 | 1 | 0 | 0 | 0 |
| 4 | E3 | 1 | $\checkmark$ | 0 | 1 | 0 | 0 | 0 | 0 |
| 4 | 44 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| 4 | H5 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |  |
| 8 | I6 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |  |

```
D.G. 43 P'C/a2/02/a RECTANGULAR
NO. OH WYCKOPY E C C (z) C C (y) C
pOSNS NOPATION
\begin{tabular}{llllllllll}
4 & A1 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
4 & C2 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
4 & D3 & 1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
8 & F4 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0
\end{tabular}
```

D.G. 44
$\mathrm{P} 2 / \mathrm{m} 2 \sqrt{\mathrm{~b}} 2 / \mathrm{a}$ RECTANGUIAR
NO. OF
WYCKO PE $E \mathrm{C}_{2}(\mathrm{z}) \mathrm{C}_{2}(\mathrm{y}) \mathrm{C}_{2}(\mathrm{x})$ i $\sigma(\mathrm{xy})$ of $(\mathrm{zx})$ o(yz) POSNS NOTATION

| 2 | A1 | 1 | 1 | 0 | 0 | 1 | 1 | 0 | 0 |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| 2 | C2 | 1 | 1 | 0 | 0 | 1 | 1 | 0 | 0 |
| 4 | H3 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| 4 | F4 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| 4 | G5 | 1 | 0 | 0 | 0 | 0 | 1 | 0 | 0 |
| 3 | I6 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

D. G. 45
$\mathrm{P} 2 / \mathrm{a} 2 / \mathrm{b} 2 / \mathrm{m}$ RECTANGULAR
NO. OP WYCKOPF $\mathrm{E}_{\mathrm{C}_{2}}(z) \mathrm{C}_{2}(y) \mathrm{C}_{2}(x)$ i $\sigma(x y) \quad \sigma(z x) \quad \sigma(y z)$
POSNS NOTATION

| 4 | A1 | 1 | 0 | 0 | 0 | 1 | 0 | 0 | 0 |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| 4 | C2 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| 4 | D3 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 1 |
| 8 | E4 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

D.G. 46


| 2 | A. 1 | 1 | 1 | 0 | 0 | 0 | 0 | 1 | 1 |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| 2 | B2 | 1 | 1 | 0 | 0 | 0 | 0 | 1 | 1 |
| 4 | C3 | 1 | 0 | 0 | 0 | 1 | 0 | 0 | 0 |
| 4 | E4 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 1 |
| 4 | F5 | 1 | 0 | 0 | 0 | 0 | 0 | 1 | 0 |
| 8 | G6 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

D.G. 47 C2/m2/m2/m RECTANGULAB

NO. OR WYCKO $\mathrm{IN}_{2}(z) \mathrm{C}_{2}(y) C_{2}(x)$ i of $\left.x y\right) \sigma(z x) \sigma(y z)$
2
2
4
4
4
4
4
8
8
8
8
16

| A 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| B2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| E3 | 1 | 1 | 0 | 0 | 1 | 1 | 0 | 0 |
| G4 | 1 | 0 | 0 | 1 | 0 | 1 | 1 | 0 |
| I5 | 1 | 0 | 1 | 0 | 0 | 1 | 0 | 1 |
| K6 | 1 | 1 | 0 | 0 | 0 | 0 | 1 | 1 |
| L7 | 1 | 1 | 0 | 0 | 0 | 0 | 1 | 1 |
| IT8 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| N9 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 1 |
| 0 10 | 1 | 0 | 0 | 0 | 0 | 0 | 1 | 0 |
| P11 | 1 | 0 | 0 | 0 | 0 | 1 | 0 | 0 |
| I 12 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |



| D.G. 49 |  |  |  |  |  |
| :--- | :--- | :--- | :--- | :--- | :--- |
| NO. OP | WYCKOPE | E | $\mathrm{C}_{4}(z)$ | $\mathrm{C}_{2}$ | $\mathrm{C}_{4}^{3}$ |
| POSTS | NOTAMION |  |  |  |  |
| 1 | A1 | 1 | 1 | 1 | 1 |
| 1 | B2 | 1 | 1 | 1 | 1 |
| 2 | C3 | 1 | 0 | 1 | 0 |
| 4 | D4 | 1 | 0 | 0 | 0 |


| D.G. 50 |  |  |  |  |  |
| :--- | :---: | :---: | :---: | :---: | :---: |
| NO. OR | WYCROPE | E | $\mathrm{S}_{4}$ | $\mathrm{C}_{2}(z)$ | $\mathrm{S}^{3}$ |
| POSNS | NOTATION |  |  |  |  |
| 1 | A1 | 1 | 1 | 1 | 1 |
| 1 | C2 | 1 | 1 | 1 | 1 |
| 2 | E3 | 1 | 0 | 1 | 0 |
| 2 | E4 | 1 | 0 | 1 | 0 |
| 2 | G5 | 1 | 0 | 1 | 0 |
| 4 | $H 6$ | 1 | 0 | 0 | 0 |

P4 SQUARE
D.G. 51

NO. OR WYCRORE E $\mathrm{C}_{4}(z) \quad \mathrm{C}_{2} \quad \mathrm{C}_{4}^{3}$ i $\mathrm{S}_{4}^{3} \sigma_{\mathrm{h}} \quad \mathrm{S}_{4}$
POSNS

| 1 | A1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| 1 | C2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| 2 | E3 | 1 | 0 | 1 | 0 | 1 | 0 | 1 | 0 |
| 2 | $G 4$ | 1 | 1 | 1 | 1 | 0 | 0 | 0 | 0 |
| 2 | H5 | 1 | 1 | 1 | 1 | 0 | 0 | 0 | 0 |
| 4 | I6 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 |
| 4 | J7 | 1 | 0 | 0 | 0 | 0 | 0 | 1 | 0 |
| 8 | I8 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |



| D. G. 56 |  |  |  |  |  | P40 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| N0. 0 | VYCKOEP | E | $2 \mathrm{C}(\mathrm{z})$ | $\mathrm{C}_{2}$ | $2 \sigma^{-}$ | $2 \sigma$ |
| Pusits | NOTA IUT |  |  |  |  |  |
| 2 | A 1 | 1 | 2 | 1 | 0 | 0 |
| 2 | B2 | 1 | 0 | 1 | 0 | 2 |
| 4 | C3 | 1 | 0 | 0 | 0 | 1 |
| 8 | D4 | 7 | 0 | 0 | 0 | 0 |


| D. G. 57 |  |  |  |  |  | P $\overline{4} 2 \mathrm{~m}$ SQUARE |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\therefore 0.01$ | WYCKOHF | E | $2 S_{4}$ | $\mathrm{C}_{2}(z)$ | 2 C | $2 \sigma_{d}$ |
| POSNS | NOTATION |  |  |  |  |  |
| 1 | A 1 | 1 | 2 | 1 | 2 | 2 |
| 1 | D2 | 1 | 2 | 1 | 2 | 2 |
| 2 | E3 | 1 | 0 | 1 | 2 | 0 |
| 2 | G4 | 1 | 0 | 1 | 0 | 2 |
| 2 | H5 | 1 | 0 | 1 | 0 | 2 |
| 4 | Ij | 1 | 0 | 0 | 1 | 0 |
| 4 | LT | 1 | 0 | 0 | 1 | 0 |
| 4 | M8 | 1 | 0 | 1 | 0 | 0 |
| 4 | N9 | 1 | 0 | 0 | 0 | 1 |
| 3 | 010 | 1 | 0 | 0 | 0 | 0 |



1
1
2
2
2
4
4
4
8

| A 1 | 1 | 2 | 1 | 2 | 2 |
| :--- | :--- | :--- | :--- | :--- | :--- |
| D2 | 1 | 2 | 1 | 2 | 2 |
| E3 | 1 | 0 | 1 | 0 | 2 |
| F4 | 1 | 0 | 1 | 0 | 2 |
| G5 | 1 | 0 | 1 | 0 | 2 |
| H6 | 1 | 0 | 0 | 1 | 0 |
| T7 | 1 | 0 | 0 | 0 | 1 |
| W8 | 1 | 0 | 0 | 0 | 1 |
| L9 | 1 | 0 | 0 | 0 | 0 |


| D.G. 60 |  |  |  |  |  | P-62 | SQUARE |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| NO. OR | WYCKOEE | E | $2 \mathrm{~S}_{4}$ | $\mathrm{C}_{2}(z)$ | $20 \cdot 1$ | $2 \sigma^{2}$ |  |
| POSISS | NOTATION |  |  |  |  |  |  |
| 2 | A 1 | 1 | 2 | 1 | 0 | 0 |  |
| 2 | C2 | 1 | 0 | 1 | 2 | 0 |  |
| 4 | 23 | 1 | 0 | 1 | 0 | 0 |  |
| 4 | F4 | 1 | 0 | 1 | 0 | 0 |  |
| 4 | G5 | 1 | 0 | 0 | 1 | 0 |  |
| 8 | I6 | 1 | 0 | 0 | 0 | 0 |  |


| D. G. 61 |  |  |  |  |  |  | 4/m | $2 / \mathrm{m} 2$ | /m | SQU |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| NO. OF | WYCKOFF | E | $2 \mathrm{C}(z)$ | $\mathrm{C}_{2}$ |  | 2C:' | $i$ | 2 S |  | $2 \sigma$ | $2 \sigma^{-}$ |
| POSNS | NOTATION |  |  |  |  |  |  |  |  |  |  |
| 1 | A 1 | 1 | 2 | 1 | 2 | 2 | 1 | 2 | 1 | 2 | 2 |
| 1 | C2 | 1 | 2 | 1 | 2 | 2 | 1 | 2 | 1 | 2 | 2 |
| 2 | F3 | 1 | 0 | 1 | 2 | 0 | 1 | 0 | 1 | 2 | 0 |
| 2 | G4 | 1 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 2 | 2 |
| 2 | H5 | 1 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 2 | 2 |
| 4 | I6 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 2 | 0 |
| 4 | J7 | 1 | 0 | 0 | 0 | 1 | 0 | 0 | 1 | 0 | 1 |
| 4 | I 8 | 1 | 0 | 0 | 1 | 0 | 0 | 0 | 1 | 1 | 0 |
| 4 | N9 | 1 | 0 | 0 | 1 | 0 | 0 | 0 | 1 | 1 | 0 |
| 8 | P 10 | 1 | 0 | 0 | 0 | 0 | 0 | $\bigcirc$ | 1 | 0 | 0 |
| 8 | R 11 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 |
| 8 | S 12 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 |
| 8 | T 13 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 |
| 16 | U 14 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | $\bigcirc$ |


| D.G. 62 |  |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| NO. OF | WYCKOPE | E | 2 C (z) | $\mathrm{C}_{2}$ | 2C: | $2 \mathrm{C}^{1 \%}$ | i | 2S | $\sigma^{\sim}$ | $2 \sigma^{2}$ | $2 \sigma^{\prime}$ |
| POSNS | HOTATION |  |  |  |  |  |  |  |  |  |  |
| 2 | A 1 | 1 | 2 | 1 | 2 | 2 | 0 | 0 | 0 | 0 | 0 |
| 2 | C2 | 1 | 0 | 1 | 2 | 0 | 0 | 2 | 0 | 0 | 2 |
| 4 | E3 | 1 | 0 | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 1 |
| 4 | G4 | 1 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 4 | H5 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 2 |
| 8 | I6 | 1 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 |
| 8 | K7 | 1 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| 8 | M8 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 |
| 16 | N9 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |


D.G. 64

P4/m2/m2/m SQUARE
MO. OF WYCKORE E $2 C_{4}(z) C_{2} 2 C_{2}^{\prime} 2 C_{2}^{\prime \prime}$ i $2 S_{4} \sigma_{h} 2 \sigma_{V} 2 \sigma_{d}$

| 2 | A 1 | 1 | 0 | 1 | 0 | 2 | 0 | 2 | 0 | 2 | 0 |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| 2 | C2 | 1 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 2 | 2 |
| 4 | D3 | 1 | 0 | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 1 |
| 4 | T4 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 2 | 0 |
| 8 | G5 | 1 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 |
| 8 | I6 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 |
| 8 | J7 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 |
| 16 | K8 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

D.G. 65

P3 HETAGONAL

| D.G. 65 |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
| MO. OR | WYCKORF | E | $C_{3}(z)$ | $C_{2}^{2}$ |
| POSNS | NOTATIUT |  |  | 3 |
| 1 | A1 | 1 | 1 | 1 |
| 1 | B2 | 1 | 1 | 1 |
| 1 | C3 | 1 | 1 | 1 |
| 3 | D4 | 1 | 0 | 0 |

$$
\begin{aligned}
& \text { D.G. } 66 \text { a } 5^{\text {P }} \text { HEKAGONAI } \\
& \begin{array}{lllllll}
\text { MO. OP WYCROFP } \\
\text { POSAS } & \mathrm{C}_{3}(\mathrm{z}) & \mathrm{C}_{3}^{2} & \text { i } & \mathrm{S}_{6}^{5} & \mathrm{~S}_{6}
\end{array} \\
& \begin{array}{llllllll}
1 & \text { A. } & 1 & 1 & 1 & 1 & 1 & 1 \\
2 & C 2 & 1 & 1 & 1 & 0 & 0 & 0 \\
2 & D 3 & 1 & 1 & 1 & 0 & 0 & 0 \\
3 & \text { D4 } & 1 & 0 & 0 & 1 & 0 & 0 \\
6 & G 5 & 1 & 0 & 0 & 0 & 0 & 0
\end{array}
\end{aligned}
$$

| D.G. 67 |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
| 170. OP | \#YCKOPL | E | $2 \mathrm{C}_{3}(z)$ | . 301 |
| Puster | NOTATION |  |  |  |
| 1 | A 1 | 1 | 2 | 3 |
| 1 | C2 | 1 | 2 | 3 |
| 1 | E3 | 1 | 2 | 3 |
| 2 | G4 | 1 | 2 | 0 |
| 2 | H5 | 1 | 2 | 0 |
| 2 | I6 | 1 | 2 | 0 |
| 3 | J7 | 1 | 0 | 1 |
| 6 | I8 | 1 | 0 | 0 |


| D. G. 68 |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
| MC. OR | WYCKORF | E | $2 \mathrm{C}_{3}(z)$ | 3 C |
| POSNS |  |  |  |  |
| POIATION |  |  |  |  |
| 2 | A1 | 1 | 2 | 3 |
| 2 | C2 | 1 | 2 | 0 |
| 2 | D3 | 1 | 2 | 0 |
| 3 | E4 | 1 | 0 | 1 |
| 6 | G5 | 1 | 0 | 0 |

D.G. 69

NO. OF WYCKOBT
POSNS NOTATION $\quad E \quad 2 C_{3}(z) \quad 3 \sigma_{V}$

| 1 | A1 | 1 | 2 | 3 |
| :--- | :--- | :--- | :--- | :--- |
| 1 | B2 | 1 | 2 | 3 |
| 1 | C3 | 1 | 2 | 3 |
| 3 | D4 | 1 | 0 | 1 |
| 6 | E5 | 1 | 0 | 0 |

D.G. 70

NO. OF WYCKOFP E $2 \mathrm{C}_{3}(z) \quad 3 \sigma_{v}$
1
2
3
A 1
$\begin{array}{lll}B 2 & 1 & 2\end{array}$
6
$\begin{array}{llll}\text { C3 } & 1 & 0 & 1 \\ \text { D4 } & 1 & 0 & 0\end{array}$

P3M 1 TEXAGONAL
P3 12 HEXACOTAI

P321 HEXAGONAL

P3 1m HEXAGONAL



| D.G. 78 |  |  |  |  |  | р6m2 |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| TO. OE | WYCKOR | E | $\mathrm{CO}_{3}$ | $3 \mathrm{C}_{2}$ | $\sigma_{h}$ | $2 S_{3}$ | $3 \sigma_{V}$ |
| POSIS | IVOTATION | 1 | 2 | 3 | 1 | 2 | 3 |
| 1 | 02 | 1 | 2 | 3 | 1 | 2 | 3 |
| 1 | E3 | 1 | 2 | 3 | 1 | 2 | 3 |
| 2 | G4 | 1 | 2 | 0 | 0 | 0 | 3 |
| 2 | H5 | 1 | 2 | 0 | 0 | 0 | 3 |
| 2 | I6 | 1 | 2 | 0 | 0 | 0 | 3 |
| 3 | J7 | 1 | 0 | 1 | 1 | 0 | 1 |
| 6 | $\pm 8$ | 1 | 0 | 0 | 1 | 0 | 0 |
| 6 | N9 | 1 | 0 | 0 | 0 | 0 | 1 |
| 12 | 010 | 1 | 0 | 0 | 0 | 0 | 0 |

D.G. 79

P $\overline{6} 2 \mathrm{~m} \mathrm{HEXAGONAL}$
$\begin{array}{lllllllll}\text { NO. OF } & \text { WYCKONF } \\ \text { POSNS } & \text { NOTATION }\end{array} \quad \begin{array}{lllllll} & C_{3} & 3 C_{2} & \sigma_{h} & 2 S_{3} & 3 \sigma_{V}\end{array}$

| POSTS | NOTATION |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | A 1 | 1 | 2 | 3 | 1 | 2 | 3 |
| 2 | C2 | 1 | 2 | 0 | 1 | 2 | 0 |
| 2 | E3 | 1 | 2 | 0 | 0 | 0 | 3 |
| 3 | F4 | 1 | 0 | 1 | 1 | 0 | 1 |
| 4 | H5 | 1 | 2 | 0 | 0 | 0 | 0 |
| 6 | I6 | 1 | 0 | 0 | 0 | 0 | 1 |
| 6 | J7 | 1 | 0 | 0 | 1 | 0 | 0 |
| 12 | I8 | 1 | 0 | 0 | 0 | 0 | 0 |

D. G. 80

P6/m2/m2/m HEXAGONAL


| 1 | A1 | 1 | 2 | 2 | 1 | 3 | 3 | 1 | 2 | 2 | 1 | 3 | 3 |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| 2 | O2 | 1 | 0 | 2 | 0 | 0 | 3 | 0 | 2 | 0 | 1 | 3 | 0 |
| 2 | E3 | 1 | 2 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 3 | 3 |
| 3 | F4 | 1 | 0 | 0 | 1 | 1 | 1 | 1 | 0 | 0 | 1 | 1 | 1 |
| 4 | H5 | 1 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 3 | 0 |
| 6 | I6 | 1 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 1 |
| 6 | J7 | 1 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 1 | 0 | 1 |
| 6 | L8 | 1 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 1 | 1 | 0 |
| 12 | N9 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 |
| 12 | 010 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 |
| 12 | P 11 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 |
| 24 | R12 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |



| D. $\therefore .7$ | $\mathrm{C}_{2 \mathrm{n}}$ |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
| WYCROPS | $\mathrm{A}_{\mathrm{g}}$ | $\mathrm{B}_{8}$ | $A_{u}$ | $B_{u}$ |
| $2 \mathrm{~A}-\mathrm{D}$ | 0 | 0 | 3 | 3 |
| $2 \mathrm{E}-\mathrm{F}$ | 1 | 2 | 1 | 2 |
| 4 G | 3 | 3 | 3 | 3 |
| D. G. 8 | $\mathrm{C}_{2}$ |  |  |  |
| WYCEOEF | A | B |  |  |
| $1 \mathrm{~A}-\mathrm{C}$ | 1 | 2 |  |  |
| 2 E | 3 | 3 |  |  |
| D.G. 9 | $\mathrm{C}_{2}$ |  |  |  |
| WYCKOrs | A | B |  |  |
| 2 A | 3 | 3 |  |  |
| D.G. 10 | $\mathrm{C}_{2}$ |  |  |  |
| WYCEOPF | A | B |  |  |
| 1 A | 1 | 2 |  |  |
| 2 C | 3 | 3 |  |  |
| D.G. 11 | ${ }^{\text {c }}$ |  |  |  |
| WYCKOPI | $A^{\prime}$ | A'' |  |  |
| $1 \mathrm{~A}-\mathrm{B}$ | 2 | 1 |  |  |
| 2 C | 3 | 3 |  |  |
| $\text { D. G. } 12$ | ${ }_{5}$ |  |  |  |
| WYCROFP. | $A^{\prime}$ | A' ${ }^{\prime}$ |  |  |
| 2 A | 3 | 3 |  |  |
| D. G. 13 | $\mathrm{C}_{\mathrm{S}}$ |  |  |  |
| WYCROFP | $A^{\prime}$ | A'' |  |  |
| 1 A | 2 | 1 |  |  |
| 2 B | 3 | 3 |  |  |


D.G. 16

## ${ }^{C} 2 h$

| WYCKGFF | $A_{g}$ | $B_{g}$ | $A_{u}$ | $B_{u}$ |
| :--- | :--- | :--- | :--- | :--- |
| 1 A-B | 0 | 0 | 1 | 2 |
| 2 E | 0 | 0 | 3 | 3 |
| $2 G$ | 1 | 2 | 1 | 2 |
| 2 I | 2 | 1 | 1 | 2 |
| $4 J$ | 3 | 3 | 3 | 3 |

D.G. 17
$\mathrm{C}_{2 h}$

D.G. 18 WYCKOPF $2 \mathrm{~A}-\mathrm{C}$ 4 E $\mathrm{C}_{2 h}$

| $A_{g}$ | $B_{g}$ | ${ }^{A}{ }_{u}$ | $B_{u}$ |
| :--- | :--- | :--- | :--- |
| 0 | 0 | 3 | 3 |
| 3 | 3 | 3 | 3 |

D. G. $19 \quad D_{2}$ WYCKORE

| 1 | $A-E$ | 0 | 1 | 1 | 1 |
| :--- | :--- | :--- | :--- | :--- | :--- |
| 2 | $I-X$ | 1 | 2 | 2 | 1 |
| 2 | $I-O$ | 1 | 2 | 1 | 2 |
| $2 Q-T$ | 1 | 1 | 2 | 2 |  |
| $4 U$ | 3 | 3 | 3 | 3 |  |

D.G. 20
$D_{2}$
WYCKORE
$2 A-B$
2 C
4 E
$\begin{array}{cccc}\mathrm{A} & \mathrm{B}_{1} & \mathrm{~B}_{2} & \mathrm{~B}_{3} \\ 1 & 2 & 2 & 1 \\ 1 & 2 & 1 & 2 \\ 3 & 3 & 3 & 3\end{array}$
D.G. 21
$D_{2}$
$\begin{array}{lcccc}\text { WYCKOPT } & \mathrm{A} & \mathrm{B}_{1} & \mathrm{~B}_{2} & \mathrm{~B}_{3} \\ 2 \mathrm{~A}-\mathrm{B} & 1 & 1 & 2 & 2 \\ 4 \mathrm{C} & 3 & 3 & 3 & 3\end{array}$
D.G. 22
$D_{2}$
WYCKOFE
$1 A-B$
2 E
2 G
2 I-K
4 I
D. G. 23 WYCKOFT

1 A-D
$2 \mathrm{~B}-\mathrm{F}$
2 G-H
4 I

## ${ }^{C}$ 2v

| $A_{1}$ | $A_{2}$ | $B_{1}$ | $B_{2}$ |
| :---: | :---: | :---: | :---: |
| 1 | 0 | 1 | 1 |
| 2 | 1 | 2 | 1 |
| 2 | 1 | 1 | 2 |
| 3 | 3 | 3 | 3 |

D.G. 24
${ }^{6} 2 \mathrm{~V}$
WYCKORT
$1 \mathrm{~A}-\mathrm{D}$
$2 \mathrm{~F}-\mathrm{F}$
2 G $\begin{array}{cccc}A_{1} & A_{2} & B_{1} & B_{2} \\ 1 & 0 & 1 & 1 \\ 2 & 1 & 2 & 1 \\ 2 & 1 & 1 & 2 \\ 3 & 3 & 3 & 3\end{array}$
4 I
D. G. 25

$$
\mathrm{c}_{2 \mathrm{v}}
$$

WYCKOFE
2 A
$\begin{array}{cccc}A_{1} & A_{2} & B_{1} & B_{2} \\ 2 & 1 & 1 & 2 \\ 3 & 3 & 3 & 3\end{array}$
D. G. 26 WYGKOFP

$$
{ }^{0} 2 v
$$

$$
\begin{array}{llll}
\mathrm{A}_{1} & \mathrm{~A}_{2} & { }^{\mathrm{B}} & \mathrm{~B}_{2}
\end{array}
$$

$$
\begin{aligned}
& 2 \mathrm{~A}-\mathrm{B} \\
& 4 \mathrm{C}
\end{aligned}
$$

$\begin{array}{llll}2 & 1 & 1 & 2 \\ 3 & 3 & 3 & 3\end{array}$
D. G. 27
WYCKOFE
$2 \mathrm{~A}-\mathrm{C}$
4 E $\mathrm{C}_{2 \mathrm{v}}$

| WYCKOFE | $\mathrm{A}_{1}$ | $\mathrm{~A}_{2}$ | $\mathrm{~B}_{1}$ | $\mathrm{~B}_{2}$ |
| :--- | :---: | :---: | :---: | :---: |
| $2 \mathrm{~A}-\mathrm{C}$ | 1 | 1 | 2 | 2 |
| 4 E | 3 | 3 | 3 | 3 |

D.G. $28 \quad \mathrm{C}_{2 \mathrm{v}}$

| WYCKOFF | $A_{1}$ | $A_{2}$ | $B_{1}$ | $B_{2}$ |
| :--- | :---: | :---: | :---: | :---: |
| $2 \mathrm{~A}-\mathrm{B}$ | 1 | 1 | 2 | 2 |
| 2 C | 2 | 1 | 1 | 2 |
| 4 D | 3 | 3 | 3 | 3 |

D. G. 29

WYCKOFi
2 A
2 C
4 D
$\mathrm{C}_{2 \mathrm{~V}}$
D.G. 31

MyCHOES
$2 A$
4 C
D.G. 32

WYCKOET
2 A
$4 B$
D.G. 33

| MYCKOFP | $\mathrm{A}_{1}$ | $\mathrm{~A}_{2}$ | $\mathrm{~B}_{1}$ | $\mathrm{~B}_{2}$ |
| :--- | :---: | :---: | :---: | :---: |
| $2 \mathrm{~A}-\mathrm{B}$ | 1 | 1 | 2 | 2 |
| 4 C | 3 | 3 | 3 | 3 |

D.G. 34

WYCKO
$1 \mathrm{~A}-\mathrm{B}$
2 C
2 D
2 E
4 F
D.G. 35

WYCKOFI
1 A
2 C
2 D
$4 F$
D.G. 36

WYCKOEE
2 A
2 C
4
$\begin{array}{cccc}\mathrm{A}_{1} & \mathrm{~A}_{2} & \mathrm{~B}_{1} & \mathrm{~B}_{2} \\ 1 & 1 & 2 & 2 \\ 2 & 1 & 2 & 1 \\ 3 & 3 & 3 & 3\end{array}$
$\mathrm{C}_{2 \mathrm{~V}}$

| $\mathrm{A}_{1}$ | $\mathrm{~A}_{2}$ | $\mathrm{~B}_{1}$ | $\mathrm{~B}_{2}$ |
| :---: | :---: | :---: | :---: |
| 1 | 0 | 1 | 1 |
| 2 | 1 | 2 | 1 |
| 2 | 1 | 1 | 2 |
| 3 | 3 | 3 | 3 |

$$
\mathrm{C}_{2 \mathrm{~V}}
$$



$$
3
$$

$$
3
$$

$$
3
$$

| D. G. 37 | $D_{2 h}$ |  |  |  |  |  |  |  |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| WYCKORT | $A_{g}$ | $B_{1 g}$ | $B_{2 g}$ | $B_{3 g}$ | $A_{u}$ | $B_{1 u}$ | $B_{2 u}$ | $B_{3 u}$ |
| $1 \mathrm{~A}-\mathrm{T}$ | 0 | 0 | 0 | 0 | 0 | 1 | 1 | 1 |
| $2 \mathrm{I}-\mathrm{K}$ | 1 | 1 | 1 | 0 | 0 | 1 | 1 | 1 |
| $2 \mathrm{H}-0$ | 1 | 1 | 0 | 1 | 0 | 1 | 1 | 1 |
| $2 \mathrm{Q}-\mathrm{T}$ | 1 | 0 | 1 | 1 | 0 | 1 | 1 | 1 |
| $4 \mathrm{U}-\mathrm{V}$ | 2 | 1 | 1 | 2 | 1 | 2 | 2 | 1 |
| $4 W-X$ | 2 | 1 | 2 | 1 | 1 | 2 | 1 | 2 |
| 4 Y | 2 | 2 | 1 | 1 | 1 | 1 | 2 | 2 |
| $8 \alpha$ | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 |

D. G. $38 \quad D_{2 h}$
$\begin{array}{lllllllll}\text { WYCKOAE } & \mathrm{A}_{g} & \mathrm{~B}_{1 g} & \mathrm{~B}_{2 g} & \mathrm{~B}_{3 g} & \mathrm{~A}_{u} & \mathrm{~B}_{1 \mathrm{u}} & \mathrm{B}_{2 \mathrm{u}} & \mathrm{B}_{3 \mathrm{u}} \\ 2 \mathrm{~A}-\mathrm{D} & 0 & 0 & 0 & 0 & 1 & 1 & 2 & 2 \\ 2 \text { E-F } & 0 & 1 & 1 & 1 & 0 & 1 & 1 & 1 \\ 4 \text { I } & 1 & 2 & 2 & 1 & 1 & 2 & 2 & 1 \\ 4 \text { K-L } & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 \\ 4 \text { M-P } & 1 & 1 & 2 & 2 & 1 & 1 & 2 & 2 \\ 4 \text { Q } & 2 & 2 & 1 & 1 & 1 & 1 & 2 & 2 \\ 8 \mathrm{R} & 3 & 3 & 3 & 3 & 3 & 3 & 3 & 3\end{array}$
D.G. $39 \quad D_{2 h}$

| WYCKOF | $\mathrm{A}_{\mathrm{g}}$ | $\mathrm{B}_{1 g}$ | $\mathrm{~B}_{2 g}$ | $\mathrm{~B}_{3 g}$ | $\mathrm{~A}_{u}$ | $\mathrm{~B}_{1 \mathrm{u}}$ | $\mathrm{B}_{2 \mathrm{u}}$ | $\mathrm{B}_{3 \mathrm{u}}$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $2 \mathrm{~A}-\mathrm{B}$ | 0 | 1 | 1 | 1 | 0 | 1 | 1 | 1 |
| 4 E | 0 | 0 | 0 | 0 | 3 | 3 | 3 | 3 |
| 4 G | 1 | 2 | 2 | 1 | 1 | 2 | 2 | 1 |
| 4 J | 1 | 2 | 1 | 2 | 1 | 2 | 1 | 2 |
| $4 \mathrm{~K}-\mathrm{I}$ | 1 | 1 | 2 | 2 | 1 | 1 | 2 | 2 |
| 8 M | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 |

D. G. $40 \quad D_{2 h}$
$\begin{array}{lllllllll}\text { WYCKOFP } & A_{g} & B_{1 g} & B_{2 g} & B_{3 g} & A_{u} & B_{1 u} & B_{2 u} & B_{3 u} \\ 2 \mathrm{~A}-\mathrm{C} & 0 & 0 & 0 & 0 & 1 & 2 & 1 & 2 \\ 2 \mathrm{E} & 1 & 0 & 1 & 1 & 0 & 1 & 1 & 1 \\ 4 \mathrm{G}-\mathrm{H} & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 \\ 4 \mathrm{I} & 2 & 1 & 2 & 1 & 1 & 2 & 1 & 2 \\ 4 \mathrm{~K} & 2 & 1 & 1 & 2 & 1 & 2 & 2 & 1 \\ 8 \mathrm{~L} & 3 & 3 & 3 & 3 & 3 & 3 & 3 & 3\end{array}$
D. G. $41 \quad D_{2 h}$
$\begin{array}{lllllllll}\text { WYCKOF } & A_{g} & B_{1 g} & B_{2 g} & B_{3 g} & A_{u} & B_{1 u} & B_{2 u} & B_{3 u} \\ 2 \text { A-B } & 0 & 0 & 0 & 0 & 1 & 2 & 1 & 2 \\ 2 \text { I-F } & 1 & 0 & 1 & 1 & 0 & 1 & 1 & 1 \\ 4 \text { G } & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 \\ 4 \text { I-J } & 2 & 1 & 2 & 1 & 1 & 2 & 1 & 2 \\ 4 \text { K } & 2 & 1 & 1 & 2 & 1 & 2 & 2 & 1 \\ 8 \text { L } & 3 & 3 & 3 & 3 & 3 & 3 & 3 & 3\end{array}$
D. G. $42 \quad D_{2 h}$

| WYCKOFF | ${ }^{A}{ }_{g}$ | ${ }^{B}{ }_{1 g}$ | ${ }^{B}{ }_{2 g}$ | $B_{3 g}$ | ${ }^{A}{ }_{u}$ | $B_{1 u}$ | $B_{2 u}$ | $B_{3 u}$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $2 A-B$ | 0 | 0 | 0 | 0 | 1 | 2 | 2 | 1 |
| 4 E | 1 | 2 | 2 | 1 | 1 | 2 | 2 | 1 |
| 4 G | 1 | 2 | 1 | 2 | 1 | 2 | 1 | 2 |
| 4 H | 2 | 1 | 1 | 2 | 1 | 2 | 2 | 1 |
| 8 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 |

D. G. $43 \quad D_{2 h}$
$\begin{array}{lllllllll}\text { WYCKOEF } & \mathrm{A}_{\mathrm{g}} & \mathrm{B}_{1 g} & \mathrm{~B}_{2 g} & \mathrm{~B}_{3 g} & \mathrm{~A}_{u} & \mathrm{~B}_{1 \mathrm{u}} & \mathrm{B}_{2 u} & \mathrm{~B}_{3} u^{2} \\ 4 \mathrm{~A} & 0 & 0 & 0 & 0 & 3 & 3 & 3 & 3 \\ 4 \mathrm{C} & 1 & 2 & 1 & 2 & 1 & 2 & 1 & 2 \\ 4 \mathrm{D} & 1 & 1 & 2 & 2 & 1 & 1 & 2 & 2 \\ 8 \mathrm{~F} & 3 & 3 & 3 & 3 & 3 & 3 & 3 & 3\end{array}$
D. G. 44
$\mathrm{D}_{2 \mathrm{~h}}$
$\begin{array}{lllllllll}\text { WYCKOFP } & \mathrm{A}_{\mathrm{g}} & \mathrm{B}_{1 g} & \mathrm{~B}_{2 g} & \mathrm{~B}_{3 g} & \mathrm{~A}_{u} & \mathrm{~B}_{1 \mathrm{u}} & \mathrm{B}_{2 \mathrm{u}} & \mathrm{B}_{3 \mathrm{u}} \\ 2 \mathrm{~A}-\mathrm{C} & 0 & 0 & 0 & 0 & 1 & 1 & 2 & 2 \\ 4 \text { L-F } & 1 & 1 & 2 & 2 & 1 & 1 & 2 & 2 \\ 4 \text { G } & 2 & 2 & 1 & 1 & 1 & 1 & 2 & 2 \\ 8 \text { I } & 3 & 3 & 3 & 3 & 3 & 3 & 3 & 3\end{array}$
D.G. $45 \quad D_{2 h}$
$\begin{array}{lllllllll}\text { WYCKOFT } & A_{g} & B_{1 g} & B_{2 g} & B_{3 g} & A_{u} & B_{1 u} & B_{2 u} & B_{3 u} \\ 4 \text { A } & 0 & 0 & 0 & 0 & 3 & 3 & 3 & 3 \\ 4 \text { C } & 1 & 2 & 2 & 1 & 1 & 2 & 2 & 1 \\ 4 \text { D } & 2 & 2 & 1 & 1 & 1 & 1 & 2 & 2 \\ 8 \text { H } & 3 & 3 & 3 & 3 & 3 & 3 & 3 & 3\end{array}$


| WYCKOT: | $\mathrm{A}_{\mathrm{g}}$ | ${ }^{B} 18$ | ${ }^{1} 2 \mathrm{~g}$ | $\mathrm{B}_{3 \mathrm{~F}}$ | ${ }^{\text {a }}$ | ${ }^{\text {B }} 10$ | ${ }^{B} 2 u$ | ${ }^{3} 30$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $2 \mathrm{~A}-\mathrm{B}$ | 1 | 0 | 1 | 1 | 0 | 1 | 1 | 1 |
| 4 C | 0 | 0 | 0 | 0 | 3 | 3 | 3 | 3 |
| 4 T | 2 | 1 | 1 | 2 | 1 | 2 | 2 | 1 |
| 4 F | 2 | 1 | 2 | 1 | 1 | 2 | 1 | 2 |
| 8 G | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 |

D. G. $47 \quad D_{2 h}$

| WYCKOFF | $\mathrm{A}_{\mathrm{g}}$ | $\mathrm{B}_{1 g}$ | $\mathrm{~B}_{2 g}$ | $\mathrm{~B}_{3 g}$ | $\mathrm{~A}_{u}$ | $\mathrm{~B}_{1 \mathrm{u}}$ | $\mathrm{B}_{2 \mathrm{u}}$ | $\mathrm{B}_{3 \mathrm{u}}$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $1 \mathrm{~A}-\mathrm{B}$ | 0 | 0 | 0 | 0 | 0 | 1 | 1 | 1 |
| 2 E | 0 | 0 | 0 | 0 | 1 | 1 | 2 | 2 |
| 2 G | 1 | 1 | 1 | 0 | 0 | 1 | 1 | 1 |
| 2 I | 1 | 1 | 0 | 1 | 0 | 1 | 1 | 1 |
| $2 \mathrm{~K}-\mathrm{I}$ | 1 | 0 | 1 | 1 | 0 | 1 | 1 | 1 |
| 4 M | 1 | 1 | 2 | 2 | 1 | 1 | 2 | 2 |
| 4 N | 2 | 1 | 1 | 2 | 1 | 2 | 2 | 1 |
| 4 O | 2 | 1 | 2 | 1 | 1 | 2 | 1 | 2 |
| 4 P | 2 | 2 | 1 | 1 | 1 | 1 | 2 | 2 |
| 8 R | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 |


| D. G. 48 | $\mathrm{D}_{2 \mathrm{~h}}$ |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| WYCKORE | $\mathrm{A}_{\mathrm{g}}$ | ${ }^{B} 1 \mathrm{~g}$ | ${ }^{B}$ | ${ }^{B} 3 \mathrm{~g}$ | ${ }^{\text {a }}$ | ${ }^{\text {B }}$ 14 | ${ }^{\text {B }} 20$ | ${ }^{B} 3 \mathrm{u}$ |
| 2 A | 0 | 1 | 1 | 1 | 0 | 1 | 1 | 1 |
| 2 C | 0 | 0 | 0 | 0 | 1 | 2 | 2 | 1 |
| 2 E | 0 | 0 | 0 | 0 | 1 | 2 | 1 | 2 |
| 2 G | 1 | 0 | 1 | 1 | 0 | 1 | 1 | 1 |
| 4 H | 1 | 2 | 2 | 1 | 1 | 2 | 2 | 1 |
| 4 J | 1 | 2 | 1 | 2 | 1 | 2 | 1 | 2 |
| 4 L | 1 | 1 | 2 | 2 | 1 | 1 | 2 | 2 |
| 4 M | 2 | 1 | 1 | 2 | 1 | 2 | 2 | 1 |
| 4 N | 2 | 1 | 2 | 1 | 1 | 2 | 1 | 2 |
| 80 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 |


| D. G. 49 | $C_{4}$ |  |  |
| :--- | :--- | :--- | :--- |
| WYCROP | A | B | E |
| 1 A-B | 1 | 0 | 1 |
| 2 C | 1 | 1 | 2 |
| 4 D | 3 | 3 | 3 |

D. G. 50 WYCKOIT

1 A-C
2 E-G
4 H
$\mathrm{S}_{4}$
$\begin{array}{ccc}A & B & E \\ 0 & 0 & 1 \\ 1 & 1 & 2\end{array}$
333
D.G. $51 \quad \mathrm{C}_{4 h}$

WYCKOPF
1 A-C
2 E
2. G-H

4 I
$L_{r}$ J
$A_{g} B_{g} E_{g} A_{u} B_{u} E_{u}$

8 I
$\begin{array}{llllll}C & 0 & 0 & 1 & 0 & 1 \\ 0 & 0 & 0 & 1 & 1 & 2 \\ 1 & 0 & 1 & 1 & 0 & 1 \\ 1 & 1 & 2 & 1 & 1 & 2 \\ 2 & 2 & 1 & 1 & 1 & 2 \\ 3 & 3 & 3 & 3 & 3 & 3\end{array}$
D. G. 52
$\mathrm{C}_{4} \mathrm{~h}$

| FYCKORE | $A_{g}$ | $B_{g}$ | $E_{g}$ | $A_{u}$ | $B_{u}$ | $E_{u}$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| 2 A | 0 | 1 | 1 | 1 | 0 | 1 |
| 2 C | 1 | 0 | 1 | 1 | 0 | 1 |
| 4 D | 0 | 0 | 0 | 3 | 3 | 3 |
| 4 F | 1 | 1 | 2 | 1 | 1 | 2 |
| 8 G, | 3 | 3 | 3 | 3 | 3 | 3 |

D. G. 53

WYCERPF
1 A-C
2 E
2 G-II
4 I
4 J
4 I-0
8 P
$D_{4}$
$\begin{array}{lllll}\mathrm{A}_{1} & \mathrm{~A}_{2} & \mathrm{~B}_{1} & \mathrm{~B}_{2} & \mathrm{E} \\ 0 & 1 & 0 & 0 & 1 \\ 0 & 1 & 0 & 1 & 2 \\ 1 & 1 & 0 & 0 & 2 \\ 1 & 1 & 1 & 1 & 4 \\ 1 & 2 & 2 & 1 & 3 \\ 1 & 2 & 1 & 2 & 3 \\ 3 & 3 & 3 & 3 & 6\end{array}$
D.G. 54
mycrore
2 A
2 C
4 D
4 E
8 G
D.G. 55
${ }^{\mathrm{C}} 4 \mathrm{~V}$

| WYCKOFF | $\mathrm{A}_{1}$ | $\mathrm{~A}_{2}$ | $\mathrm{~B}_{1}$ | $\mathrm{~B}_{2}$ | E |
| :--- | :--- | :--- | :--- | :--- | :--- |
| $1 \mathrm{~A}-\mathrm{B}$ | 1 | 0 | 0 | 0 | 1 |
| 2 C | 1 | 0 | 1 | 0 | 2 |
| 4 D | 2 | 1 | 1 | 2 | 3 |
| $4 \mathrm{E}-\mathrm{F}$ | 2 | 1 | 2 | 1 | 3 |
| 8 G | 3 | 3 | 3 | 3 | 6 |

D. G. 56
$\mathrm{C}_{4 \mathrm{v}}$
WYCKOPT
2 A
2 B
4 C
8 D
D.G. 57

WYckofe
1 A-D
2 E.
$2 \mathrm{G}-\mathrm{H}$
4 I-I
4
4 N
80
D.G. 58
$D_{2 d}$
wyckoff
2 A
2 C
4 D
4 E
8 F
${ }^{D} 2 d$
$\begin{array}{lllll}\mathrm{A}_{1} & \mathrm{~A}_{2} & \mathrm{~B}_{1} & \mathrm{~B}_{2} & \mathrm{E} \\ 0 & 0 & 0 & 1 & 1 \\ 0 & 1 & 0 & 1 & 2 \\ 1 & 0 & 0 & 1 & 2 \\ 1 & 2 & 1 & 2 & 3 \\ 1 & 1 & 1 & 1 & 4 \\ 2 & 1 & 1 & 2 & 3 \\ 3 & 3 & 3 & 3 & 6\end{array}$

| D.G. 59 | ${ }^{\text {D }} 2 \mathrm{~d}$ |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| WYMTOFP | $\mathrm{A}_{1}$ | $\mathrm{A}_{2}$ | $B_{1}$ | $B_{2}$ | E |
| $1 \mathrm{~A}-\mathrm{B}$ | 0 | 0 | 0 | 1 | 1 |
| 2 -G | 1 | 0 | 0 | 1 | 2 |
| 4 H | 1 | 2 | 1 | 2 | 3 |
| $4 \mathrm{~J}-\mathrm{K}$ | 2 | 1 | 1 | 2 | 3 |
| 8 L | 3 | 3 | 3 | 3 | 6 |

D.G. $60 \quad D_{2 \alpha}$

| WYCKOEF | $\mathrm{A}_{1}$ | $\mathrm{~A}_{2}$ | $\mathrm{~B}_{1}$ | $\mathrm{~B}_{2}$ | E |
| :--- | :--- | :--- | :--- | :--- | :--- |
| 2 A | 0 | 0 | 1 | 1 | 2 |
| 2 C | 0 | 1 | 0 | 1 | 2 |
| 4 I-r | 1 | 1 | 1 | 1 | 4 |
| 4 G | 1 | 2 | 1 | 2 | 3 |
| 8 I | 3 | 3 | 3 | 3 | 6 |

D.G. 61
$D_{4 h}$
$\begin{array}{lllllllllll}\text { WYCKORF } & { }^{A_{1 g}} & A_{2 g} & B_{1 g} & B_{2 g} & E_{g} & A_{1 u} & A_{2 u} & B_{1 u} & B_{2 u} & E_{u} \\ 1 \mathrm{~A}-\mathrm{C} & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 1 \\ 2 \mathrm{~F} & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 2 \\ 2 \mathrm{G}-\mathrm{H} & 1 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 1 \\ 4 \mathrm{I} & 1 & 0 & 1 & 0 & 2 & 0 & 1 & 0 & 1 & 2 \\ 4 \mathrm{~J} & 1 & 1 & 1 & 1 & 1 & 0 & 1 & 1 & 0 & 2 \\ 4 \mathrm{I}-\mathrm{N} & 1 & 1 & 1 & 1 & 1 & 0 & 1 & 0 & 1 & 2 \\ 8 \mathrm{P} & 2 & 2 & 2 & 2 & 2 & 1 & 1 & 1 & 1 & 4 \\ 8 \mathrm{~B} & 2 & 1 & 1 & 2 & 3 & 1 & 2 & 2 & 1 & 3 \\ 8 \mathrm{~S}-\mathrm{I} & 2 & 1 & 2 & 1 & 3 & 1 & 2 & 1 & 2 & 3 \\ 16 \mathrm{U} & 3 & 3 & 3 & 3 & 6 & 3 & 3 & 3 & 3 & 6\end{array}$

| D. G. 62 | ${ }^{3} 4 \mathrm{~h}$ |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| WYGKOrr | ${ }^{\text {A }} 19$ | $\mathrm{A}_{2 \mathrm{~g}}$ | $B_{1 g}$ | $\mathrm{B}_{2 g}$ | $\mathrm{E}_{\mathrm{g}}$ | ${ }^{\text {A }}$ 1u | ${ }^{\text {A }} 2 \mathrm{u}$ | ${ }^{\text {B }} 10$ | ${ }^{\text {B }}$ u | $E_{u}$ |
| 2 A | 0 | 1 | 0 | 0 | 1 | 0 | 1 | 0 | 0 | 1 |
| 2 C | 0 | 0 | 0 | 1 | 1 | 0 | 1 | 0 | 0 | 1 |
| 4 E | 0 | 0 | 0 | 0 | 0 | 1 | 2 | 2 | 1 | 3 |
| 4 G | 1 | 1 | 0 | 0 | 2 | 1 | 1 | 0 | 0 | 2 |
| 4 H | 1 | 0 | 0 | 1 | 2 | 0 | 1 | 1 | 0 | 2 |
| 8 I | 1 | 2 | 2 | 1 | 3 | 1 | 2 | 2 | 1 | 3 |
| 8 K | 1 | 2 | 1 | 2 | 3 | 1 | 2 | 1 | 2 | 3 |
| 8 等 | 2 | 1 | 1 | 2 | 3 | 1 | 2 | 2 | 1 | 3 |
| 16 | 3 | 3 | 3 | 3 | 6 | 3 | 3 | 3 | 3 | 6 |


D. G. 64
$D_{4 h}$
$\begin{array}{lllllllllll}\text { WYCKOFE } & { }^{A}{ }_{1 g} & A_{2 g} & { }^{B}{ }_{1 g} & B_{2 g} & E_{g} & A_{1 u} & A_{2 u} & { }^{B} 1 u & B_{2 u} & E_{u} \\ 2 \mathrm{~A} & 0 & 0 & 1 & 0 & 1 & 0 & 1 & 0 & 0 & 1 \\ 2 \mathrm{C} & 1 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 1 \\ 4 \mathrm{D} & 0 & 0 & 0 & 0 & 0 & 1 & 2 & 2 & 1 & 3 \\ 4 \mathrm{~F} & 1 & 0 & 1 & 0 & 2 & 0 & 1 & 0 & 1 & 2 \\ 8 \mathrm{G} & 1 & 2 & 2 & 1 & 3 & 1 & 2 & 2 & 1 & 3 \\ 8 \mathrm{I} & 2 & 1 & 2 & 1 & 3 & 1 & 2 & 1 & 2 & 3 \\ 8 \mathrm{~J} & 2 & 1 & 1 & 2 & 3 & 1 & 2 & 2 & 1 & 3 \\ 16 \mathrm{~K} & 3 & 3 & 3 & 3 & 6 & 3 & 3 & 3 & 3 & 6\end{array}$
D. G. $65 \quad C_{3}$

| WYCKOFF | A | E |
| :--- | :--- | :--- |
| $1 \mathrm{~A}-\mathrm{C}$ | 1 | 1 |
| 3 D | 3 | 3 |

D. G. $66 \quad \mathrm{C}_{3 i} \quad\left(\mathrm{~S}_{6}\right)$

| WYCKOFF | $A_{g}$ | $E_{g}$ | $A_{u}$ | $E_{u}$ |
| :--- | :--- | :--- | :--- | :--- |
| 1 A | 0 | 0 | 1 | 1 |
| 2 C-D | 1 | 1 | 1 | 1 |
| 3 E | 0 | 0 | 3 | 3 |
| 6 G | 3 | 3 | 3 | 3 |

D.G. $67 \quad D_{3}$

| WYCKOFF | $A_{1}$ | $A_{2}$ | I |
| :--- | :--- | :--- | :--- |
| $1 \mathrm{~A}-\mathrm{E}$ | 0 | 1 | 1 |
| $2 \mathrm{G}-\mathrm{I}$ | 1 | 1 | 2 |
| 3 J | 1 | 2 | 3 |
| 6 L | 3 | 3 | 6 |

## D.G. 68 MYCROPE <br> $1 A$ 2 B B <br> 3 E <br> 6 G <br> $1 A$ 2 B C

$D_{3}$
$A_{1} \quad A_{2} \quad E$

G 3
1
3
D.G. 69
$\mathrm{C}_{3 \mathrm{v}}$
mYCKOPF
$1 \mathrm{~A}-\mathrm{C}$
3 D
$\begin{array}{lll}\mathrm{A}_{1} & \mathrm{~A}_{2} & \mathrm{E} \\ 1 & 0 & 1\end{array}$

6 E
$\begin{array}{lll}2 & 1 & 3 \\ 3 & 3 & 6\end{array}$
D. G. 70
$\mathrm{C}_{3}$
WYCKOPI
1 A

| $A_{1}$ | $A_{2}$ | $E$ |
| :---: | :--- | :--- |
| 1 | 0 | 1 |
| 1 | 1 | 2 |
| 2 | 1 | 3 |
| 3 | 3 | 6 |

D. G. 71
$D_{3}$
WYCKOPR
1 A
2 C
2 E
3 F
4 H,
6 I
6 K
12 I
$\begin{array}{llllll}A_{1 g} A_{2 g} & E_{g} & A_{1 u} & A_{2 u} & E_{u} \\ 0 & 0 & 0 & 0 & 1 & 1 \\ 0 & 1 & 1 & 0 & 1 & 1 \\ 1 & 0 & 1 & 0 & 1 & 1 \\ 0 & 0 & 0 & 1 & 2 & 3 \\ 1 & 1 & 2 & 1 & 1 & 2 \\ 1 & 2 & 3 & 1 & 2 & 3 \\ 2 & 1 & 3 & 1 & 2 & 3 \\ 3 . & 3 & 6 & 3 & 3 & 6\end{array}$
D. G. 72
wiydions
1 A
$2 \mathrm{C}-\mathrm{D}$
3 B
6 G
6 I
12 J
$\begin{array}{llllll}{ }^{A_{1 g}}{ }^{A_{2 g}} \mathrm{E}_{\mathrm{g}} & { }^{\mathrm{A}}{ }_{1 u} & { }^{A_{2 u}} \mathrm{E}_{u} \\ 0 & 0 & 0 & 0 & 1 & 1 \\ 1 & 0 & 1 & 0 & 1 & 1 \\ 0 & 0 & 0 & 1 & 2 & 3 \\ 1 & 2 & 3 & 1 & 2 & 3 \\ 2 & 1 & 3 & 1 & 2 & 3 \\ 3 & 3 & 6 & 3 & 3 & 6\end{array}$

| D.G. 73 | $\mathrm{C}_{6}$ |  |  |  |
| :--- | :--- | :--- | :--- | :--- |
| WYCKOPA | A | B | $\mathrm{P}_{1}$ | $\mathrm{~B}_{2}$ |
| 1 A | 1 | 0 | 1 | 0 |
| 2 B | 1 | 1 | 1 | 1 |
| 3 C | 1 | 2 | 2 | 1 |
| 6 D | 3 | 3 | 3 | 3 |


| D.G. 74 | $C_{3 h}$ |  |  |  |
| :--- | :--- | :--- | :--- | :--- |
| WYCKOFI | $A^{\prime}$ | E' | $A^{\prime \prime}$ | E'' |
| $1 \mathrm{~A}-\mathrm{E}$ | 0 | 1 | 1 | 0 |
| $2 \mathrm{G}-\mathrm{I}$ | 1 | 1 | 1 | 1 |
| 3 J | 2 | 2 | 1 | 1 |
| 6 L | 3 | 3 | 3 | 3 |

D.G. 75

| WYCKOPF | $\mathrm{A}_{\mathrm{g}}$ | ${ }^{\text {B }}$ | $\mathrm{E}_{1 \mathrm{~g}}$ | $\mathrm{E}_{2 g}$ | ${ }^{\text {a }}$ | $B_{u}$ | ${ }^{\text {E }}$ fu | $\mathrm{E}_{2 \mathrm{u}}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 A | 0 | 0 | 0 | 0 | 1 | 0 | 1 | 0 |
| 2 C | 0 | 1 | 0 | 1 | 1 | 0 | 1 | 0 |
| 2 2 | 1 | 0 | 1 | 0 | 1 | 0 | 1 | 0 |
| 3 F | 0 | 0 | 0 | 0 | 1 | 2 | 2 | 1 |
| 4 H | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| 6 I | 1 | 2 | 2 | 1 | 1 | 2 | 2 | 1 |
| 6 J | 2 | 1 | 1 | 2 | 1 | 2 | 2 | 1 |
| 12 L | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 |

D. G. $76 \quad D_{6}$

| WYCKOFF | $\mathrm{A}_{1}$ | $\mathrm{~A}_{2}$ | $\mathrm{~B}_{1}$ | $\mathrm{~B}_{2}$ | $\mathrm{E}_{1}$ | $\mathrm{E}_{2}$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| 1 A | 0 | 1 | 0 | 0 | 1 | 0 |
| 2 C | 0 | 1 | 1 | 0 | 1 | 1 |
| 2 E | 1 | 1 | 0 | 0 | 2 | 0 |
| 2 F | 0 | 1 | 1 | 1 | 2 | 1 |
| 4 H | 1 | 1 | 1 | 1 | 2 | 2 |
| 6 I | 1 | 1 | 2 | 2 | 4 | 2 |
| 6 J | 1 | 2 | 1 | 2 | 3 | 3 |
| 6 I | 1 | 2 | 2 | 1 | 3 | 3 |
| 12 N | 3 | 3 | 3 | 3 | 6 | 6 |

D.G. $77 \quad \mathrm{C}_{6 \mathrm{v}}$

| WYCKOR | $\mathrm{A}_{1}$ | $\mathrm{~A}_{2}$ | $\mathrm{~B}_{1}$ | $\mathrm{~B}_{2}$ | $\mathrm{~B}_{1}$ | $\mathrm{~B}_{2}$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| 1 A | 1 | 0 | 0 | 0 | 1 | 0 |
| 2 B | 1 | 0 | 1 | 0 | 1 | 1 |
| 3 C | 1 | 0 | 1 | 1 | 2 | 1 |
| 6 D | 2 | 1 | 1 | 2 | 3 | 3 |
| 6 E | 2 | 1 | 2 | 1 | 3 | 3 |


D. G. 79
$D_{3 h}$
WYCKOPF

| 1 | A | 0 | 0 | 1 | 0 | 1 |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| 2 | 0 | 0 | 2 | 1 | 1 | 0 |
| 2 E | 1 | 0 | 1 | 0 | 1 | 1 |
| 2 F | 1 | 1 | 2 | 0 | 1 | 1 |
| 3 H | 1 | 1 | 2 | 1 | 1 | 2 |
| 6 I | 2 | 1 | 3 | 1 | 2 | 3 |
| 6 J | 2 | 2 | 4 | 1 | 1 | 2 |
| 12 L | 3 | 3 | 6 | 3 | 3 | 6 |

D. G. $80 \quad D_{6 h}$


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$$
\text { Appendix } 1
$$

Kramers-Kronig analysis program.

```
        DROGSAM FIHOE1 (TNNIT, DUTOUT, TAPE1, TAPES=INPUT,TAPEE=OUTOUT)
```

    COH:10ti A1 (00), Bi (D0), C1 ( 400 ), E1 (400), F1 (. 00 ),
    \(1 \vee 1(1:), W 1(15), Z 1(1), T(L 00), A 2(100), C ?(L 00)\),
    \(1 V 1(1),, W 1(15), Z 1(1),, T(L D 0), A 2(00), C ?(L O 0)\),
    $2 P, Q, Q D, P, P, N, M M, D E, V, V V, Y Y, Z Z, X X, F W, W I, M, K, Y M A X, Y M I N$

$I N T E G E$
$I=3.1,15326.236$
$\mathrm{P} I=3.1 .153$
C THIS DROGOA IS FOR COMPUTINS KK VALUES OF OBSEOVED OATA OMLY
C HLS IS TO SS VE AS A CHECK ON VALUES SALCULATED FSOH "ECHOES" ENO "FCHOEZ"
ALL SYMBOSS A E THE SAME IS TH ECHOES OSCILLATOE DAZAMETF S S NEED NOT RE SUPPL
OZSERVEJ JATAU ONLY FHE FDLLOWI NG PARAMEYERS FED BE SUPPLIED
$N, M Y, 31(I), A 1(I), R, Q$,
1 民EAT ( 100 ) if, MH
292 FO?MAT (1)NOOF POINTS=, IJ, $2 X$, ?OH NO OF OSCILLATORS=,IE)

$N=H O$ OF P I VIS IU SOE
FREQUENCIES REQUI EED.
$\therefore$ PEAO(S, 101), (31(I), $=1, N)$

293 FOP:1厶T(19才 WAVELFNGTHS TAKEN=, 5 (2X,F12.5))
100 KEKD (5, 103) (A1 (I) , I=1, N 1 )

Q COITROI $10^{\circ}$ R SPECTRUM OF LEII F F FREQUENCIES
Q COITROL 10
WZITE $1=303) ?$
303 FOEYAT $111+1$, S.L.F. $=$, I5
READ(5,10T)
30. FOSM4T(13H SONTROL NO=,IS)
Q2 $=7+1$
HRITE ( 5.5 万7) QO
550 FOTMOT 4,4 QQ=, I5)
RRER-1
WOITE (
$00=01$ - $=1$ N
$\begin{array}{ll}A 1(T)=A 1(T) / 100.007 I)) \\ C 1(T) & =A L O C(S Q T(A 1(I))\end{array}$
501
501
1 (I) = ALO
ORITNUE
()/100.007
$0 ; 1$ FOGif $(T H \quad \geqslant マ=, I 5)$
10 FOMMTR
10
FOAT
107 FOFMAT (I
$101 \mathrm{FO}=1 \mathrm{~T}(3 \mathrm{~F} 1 \mathrm{n}$, 5$)$
CGLL KKUYGLE (01)
$C A L L ~ C I A G I S(D 1)$
$C A L L G L O H E(0, D 1)$

```
            SUBOOUT VNE KKCYCLF(O1)
            ComtaN &1 ( 00),01( 00),C1(1000), F1(&00), F1(i00),
            1V1(1: ), M1(1\vdots),Z1(1, ), T(400),A2(400),r2(400),
            2P,O,ZO, ,, U,M1,P,V,VV,YY,ZZ,XX,FW,WT,M,K,YMOX,Y:MIN
            OINELSOH,O1(.00),XOSC(L00),Y0SC(L00),G1(100),H1(-00),Q1(400),
            1X1(t00), Y1(400), Th1(:00)
            INTESE: P,R,QO,D,R=,M,MM, YN,K
```



```
    F201VGAJES FODINESTIMATED FROA EXPARIMENTAL DATA
    308 FOFMG Y(30H ENTERIVG KFLME`S KPONIG CYCLE)
            002 I=2R, 又 
            H=0;0
            K=J+1
            TF\+1
            IF(K.EO.T)G2 TO i
    z
C B=C1(<)-C1(I)
C=81(J)*31(j)-B1(T)*81(T)ERVEO KEFLECTIVITIES A1
    C=B1(J)*31(J)-31(I)*81(I)
    E=31(K)-31(J)
    GO TO }
    + K=J+?
    3 F=B
    3 F=8/0
    5 F=(F+G)*E
    H=H+F
    2. cONTINUE
    U=H*31(I)*y
    LOW =2EQUENOY CORRFCTION TERM AA
    A A = AL O5(A1(I)/A1(I))
    BO=ALOG((31(1)-B1(R))/(B1(I)+B1(Q)))
    AA=7. ©*AA* 30*V
C HIGH'FFERUENCY COESECTION TERM CC
    CC=A 05(41(P)/A1(I))
    DD={L0う((B1(R)-B1(I))/(B1(R)+B1(I)))
    CC=-0.*CC*OD*V
    1 1
    u=11+0i+4f
    B=02(K)-5?(I)
    21
    W=CDS(J)
    UU=S5ミT(A1(I))
    X SHJ Y GOPRESPOND TD OPTHOGL CONSTAVTS N GND K
    x=(1.000-11(I))/(1.000+A1.(I)-2.000*UU*H)
    Y=-2.00*リJ*N⿱亠凶禸
    JV=100.0 00*1J*V
    YOO CQPRESOOVOS TO ASSORPTION COEFFISIENT
    YOO=, OOD*DI*Y* (E1 (TI))
    H1(I)=.000*DI*Y*(1(I))
    XXYY EDRZESPONOS TO =EAL DART DIELECTEIC PARDMETEF
    XXYY = X* X-Y*Y
    G1(I) =x*X-Y*Y
C XY2 O OORESOOYDS TO IMAGINA PY D&DT OIELECTPIR PARAMETEF
    XYZ OOERESOOYDS TO TMAGINAPY D&DT OIELECTRIC PA
    XYB=X*Y* S 1(I)
    a1(i) =x*y*31 (I)
    01(I) =2.00年X*Y
    x1(1)=x
    2シ
    Y1(I)=Y
    l
    WRETE (130) (TH1(T),TEEN,RR)
    901 FO.1.T(13H EXT. COEFF=,E(2X,F1].E))
    O03 FO=14T(13H ASS. COFFF=25(2X,F1,O5%)
    90-FOEMAT(6H SIOMA=, (2X,F,150 O))
    FO
    FOEMAT (GHGHETA=,',
    CALL GPAPHO(-1,Y1)
    EM丁
```

```
                SUR-OUTIAE CLADIS(01)
```



```
            1V1(1:), W1 (1 5\(), 71(1-), T(400), A 2(60), 02(400)\),
            \(2 P, R, R O, R, N, M M, D_{-}, V, V V, Y Y, Z Z, X X, F H, W I, M, K, Y M X, Y M I N\)
                IMTE EP P, T, QD, R, RE, M, MY, MN, K
                    CAL GULATE THTEGRLL FKOM KPAMERS KRONIG OUTPUT SPECTRA
                        \(\mathrm{E}=0.000\)
                        \(0020 I=Q Q, R P\).
            PFI F +1.GT. PP)GOTO 20
            \(A=01(\tau) / B 1(I)\)
            \(\mathrm{B}=31(\mathrm{P}) / \mathrm{is} 1(\mathrm{P})\)
            \(C=B 1(P)-31(I)\)
            \(0=V \times\left(C^{*} A+C^{*} \frac{3}{3}\right)\)
            \(E=E+D\)
            T(I) =E
    0 CONTINJE
    WRITE ( 203 ) ( \(T(T), I=Q Q, ? Q)\)
    FORMAT(2OH THE KK OSC. ST \&ENGTH V1=,3(2X,F10.4))
    ENO
    SUBROUTTME GOADHIC(MN,O1)
    COMMON A1 ( 00 ), S1 ( \(=00), C 1(+00), F_{1}(100), F 1(\div 00)\),
    1V1(15), W1 (15), 之1(1-), T(Ln0), A2 (400), C \(2(400)\),
    \(2 P, O, A D, P, F-N, M M, D, V, V V, Y Y, Z Z, X X, F H, W I, H, K, Y M A X, Y M I N\)
```



```
DATA FD?
C TAKES MAVELENGTUS, AND VARILBLES, FIHDS MAX ANH MIN AHD ADJUSTS
    VELUES ACOZRD NGLY TO GYVE AFBITRAOY UMITS WHEN MIN=O - 1
    WHEHMVE1 HO SOZLING VALUES ARE PLOTTEO \(A S\) CALCULATED
    \(K=\) HU:13E OF SETS OF GATA
    \(M=\) NUMZE OF OUTPUT POINTS
    FH = FINAL WAVENUMBEF.
    \(W I=I M I T E A L\) HVVNUNBE:
        \(k=\)
            \(M=(8 マ-a n)+1\)
            \(F W=31(=2)\)
            \(W I=B 1\) (QQ)
            WTYE (1, 31)FW, HI, M, K
            WPITE \((1,30)(31(1), I=Q Q, 2 F)\)
            IF (11) 500,40+, くすこ
    40.
    YMi \(x=000\)
    \(Y M I N=10: 0\)
    00 in \(0 \quad=27, ~ P R\)
    IF(OI(I):LT.YMN) GO TO 1011
    GO TO -00
    401 YMIN=01 (I)
    402 YMi \(X \equiv 91\) (I)
    +00 Cont 1
    500 y y y \(x=1\)
    \(\begin{array}{ll}Y M-V=0 \cdot I \\ 00 \quad 01 & I=Q Q, ~ P D\end{array}\)
```



```
    GOTO 01,
    502 YHIM=71(I)
    \(03 Y+x=31(-)\)
    301 coit vis
    \(100-\overline{0}=27,8 ?\)
```





```
    31 FDCMIT(F:.O, \(2 x, F L .0,2 x, I 3,2 x, I 2,60 x)\)
        PCT:IFN
            END
```

```
Appendix 2
Simple harmonic oscillator program
(for Transverse Optic mode analysis)
```

```
            PROGQAY EEYJES (FNDUT,OUTHUT, TAPE1,TAPES=INPUT,TADEE=OUTPUT)
            COM(1ON &1( DO),51(00),C1(400), E1(*00),F1(&00),
            1V1(1:),自(1:), Z1(1:),T(K00), A己( 00), C2(100),
            ZP,R,QO,P,R, H,N11,P, V,VV,YY,ZZ,XX,FW,WI,M,K,YMAX,YMIN
            INTFGF=O,O,QO,F,FF,N,MM, YN,K
            PI=3.1:1-925538
            V=1.000/j
C
O()
    UYTVFHH ECHOE DEVELOPED LNO RESTPUCTUSED GY D HILLS WITH ASSTSTANCEFFOM
    E?HUES INOSPORATES AN GUTOMATIC CUPVE FITTINGPPOCEOURF AND MUST BE SUDPLIER
    TH THE FOLLONEMG DAYA
    TOTAL NJMBE OF POINTS (ORSEEVATIONS) ? NUMEFE OF OSCJLLATORE (VIBRATIONS)
    3 FSEQUENSY FANGE OSCILSATOR DARDMETERSITNITIAL GUESSES
    OBSEVYESELEOTIVITTES }5\mathrm{ VV,YY,ZZ SET TO 1
    1 PEAO(, 100)M,:1M
    292 FO,MAT(1:H NO OF POTNTS=,I\Xi,2X,2OH NO OF OSCILLATORS=,I5)
N=NO OF PGYYS IN SPECTPUM M=NO OF OSCILLATOES
    FREQUENCTES PEQUIPFD.
        ? READ(S,1T1) (31(I), I=1,N)
    298 FOF,HST(IGH GAVELENGTHS T\triangle\angleEN=,5(2X,F12.6))
    29? FO=MAT(2;H ENTERING CLASS. OSC. CYCLE)
S
    102 FO=:13 T(F3,1)X
        WNITE(E,270) XX
        REAO(,103) (V1(J),W1(J,,Z1(J),J=1,MM)
O
    10:FOMM:T(3F-10.
```



```
    Q COITTOL HO R SPECTRUY JF LIMIT FREQUENCIES
    W=TE (=,303)=
    303 FOE.HST(11H S.O.L.F.=, I5)
        Q=1
        MPTTE(,30)\
    30+FOFATIIBH SONTROL NO=,IS)
    QQ=n+1
    M~ITE(5,050)RQ
    ES0 FOF:HAT(LLH QO=,I5)
    W゙スシー-1
    WRITE (S,5%1)PR
    CALL GOAPH= S(1, A1)
    00 01 I=1, M
    A1(I)=么1(T)/100.000
    C1(I)=&LOG(SQRT(A1(I)))
501 COHTこNJE
    CALL C!JVE
651 FO=MTT(&4 こマ=,エミ)
103 FO-M保T(?IS)
101 FOEMAT (3F10.0)
200 FOFMYT 31 THE OSCTLLATO? PAPANETEOS AFE, 2X,
    11OH EPSILOU THFIH!TY=,F3.11
201FOFMT(1, OSC.ST ENGTH=,F10.1, 2X, 1EH EST. FRFQUENCY=,F10.3,
103 FOF.MAT(3F1?.S)
    COLL KKCYCL5171)
    CHLL CL\mp@code{M)N(01)}
    CALL G?APH: こ(0,D1)
    EHO
```

```
        SUBOOUTINE CLASOSG
        C01M0N 41 (100),B1(400),C1(400), E1(400),F1(400),
        1V1(15),W1(15),Z1(1-),T(400),A2(400),C2(400),
        2P, ,, DO,R,RO,N,MM, DI,V,VV,YY,ZZ,XX,FW,WI,M,K,YMAX, YMIN
    INTEGFR P,O,Q2,R,R2,Y,MH,YN,K
C THIS SUSROUTIHE IS VEPY TMPOरTANT, REFLECTIVITY VALUES AOE
G GGLGULATEO USING OSCILLATOR PARAMETEPS SUPPLIED BY THE USEE
C VOLUES OF THE LOG FUNTIOHS ARE THEN FED INTO AN AUTOMATIC CURVE
C FITTING ROUTIVE AND THE DIFFERENCE MINIMISED THESE VALUES ASF THEN SUPPLIEO
TO SUBROUTINE KKCYCLE THE BEST INITIAL GUESS DECEEASSES COMPUTER TIME
    00 14, T=1::
    B=31(I)*31(I)
    C=0.000
    O=0:000
    0013 J=1,MM
    =W1(J)*Wi(J)
    Z =Z1(J)*Z1(J)
    F=L.000*PI*V1(J)*W*W-L.000*PI*V1(J)*W*B
    G=W*h+C*B+Z*3*M-2.000*B*W
    E=4.009*口I*V1(J)*N*W1(J)*Z1(J)*S1(I)
    C=C+F/S
    O=T+E/G
        1 3 \text { GONTINUE}
    C=C.+XX
    CC=SQRT (C*C+O*O)
    EE=SNFT(2.000*CC+2.000*C)
    A2(I)=(CS+1.000-EE)/(CC+1.000+EE)
    E1(T)=0
    C.2(I) =ALOS(SQPT(A2(I)))
    A2(I)=A2(I)*100.00
    14 CONTINUE
    AZ VALUESGFSOM REFLEGTTVITY CLASS. OSCCYCLE
    WRITE (5,701) (A2(I),I=1,N
    701 FOFMAT(32H GALCULATED REFLECTAHCE VALUES=,5(2X,F10.6))
    GALL GPAPHEO(1,A2)
    H?ITE(0,7口2)
    RETIPN
    ENO
```

```
            SU:MOUT IVE KKCYOGF(nI)
            G0M1j!1 A1 (:00),01( 00),C1(+00),E1(400),F1(100),
            1V1(1"),W1(1,),/1(1-),T(L00), &?(-00), C2(400)
            2P,O,כT, 2, DZ,N,NH,D,V,VV,YY,ZZ,XX,FW,WT,M,K,YMAX,YMTN
            OIENSOM 1(%00), X(G) (400), YOSC(400),G1(,00),H1(-00),Q1(400),
            1X1(%00),Y1(-00),TH1(:1]0)
            INEQEO,Q,QD,吕,S,GM, MN,K
        AMEOS KOHGELATTOHSHTP CALCULATES VALUFS OF OPTICAL CONSTANTS
        FQOM VGLUES FFD INGFSTINGTED FKOPEXPG?IMENTAL DATA
            N#TTE (=,305)
    303FO, H1亻T (3OH ENTERING KRHMERS KRONIG CYCLE)
            OO 2: I=QQ, रR
            H=0.000
            10 2 J=R,?
            k=J+1
            IF(K.ER.I)SO TO 4
            IF(K:Gi:S) GO T0 2
            #
                    C=B1(J)*B1(J)-51(I)*31(I)
                            O=31(K)*51(K)-B1(I)*31(I)
                            E}=E1(K)-B1(J
                    GOTO 3
            GOT0
            3 F=E/D
            G=A/N
            FF=(F+G)*E
            H=H+=
            2 CONTINUE
            U=H*S1(I)*V
            LOW FREQUEICY CORRECTION TERM AA
            AA=ALOF(A2(Q)/A2(I)
            BB=ALOG ((B1(I)-31(D))/(B1(I)+B1(Q))
            AA=0.5*AQ* 3 **V
            HIGH FRERUENCY CORREOTION TERM CC
            CC=ALOS(A?(P)/A2(I))
            OD=A1OS((B1 (R)-81(Z))/(B1(R)+81(I)))
            GC=-0.:*CU* DO*V
            1 1
            TH1(%)+A
            TH1(OM)=U
            M=CUS
            UU=S\RT (12(I))
    X AND Y CORESPONO TO DPTICAL COHSTANTS N LND K
    X=(1.000-A2(I))/(1.000+A2(I)-2.000*リリJ*N)
    Y=-2.000*11j*WW/(1.000+A2(I)-2.000*UU*W)
    UV=103.000%U*V
    YOO 弓OGRESDJNOS TO &BSORPTION COEFFICIENT
    Y09=, 000*RI*Y*(B1(I))
    H1(T)=,000*DI*Y*(?1(I)
    XXYY GOREESPONDS TO PFFFL PART DIELESTEIC PAPAMETER
    XXYY= X* X-Y* Y
    T,1(I)=X*X-Y*Y
    XY?=?.000*X*Y
    XY2 COPOESNONDS TO IMAEINARY PART DIELECTOIC PADAMETES
    XY8 COJRESONOS TO CONOUCTIVITY, SIG:AA=UJKFFEQ
    XY(=x*y*31(I)
    Q1(I) =X*Y*31(I)
                            CLASSISAL BISDERSIDN OUTPUT
```



```
    2.
    WFTTE (=,On0) (X1(I),I=Q2, रR 
    NRITE (S,CO,) (Q1(I),I=QQ, 2R
```



```
    G00 FOR仏T(13H ЗEF. SNTEX=,5(2X,F10.6))
    902 FOSMAT(1S4 REAI EOSIICHI, (2X,Fi= E))
```



```
    90+ FOSM4T(3, SIGMA=,J!2X,F1T.O))
    90ミFO`MAT(?H THETA=,5(2X,F10.5))
    CALL GRADHE(-1,x1)
```

```
                SU3%OUTINE 2LADIS(O1)
                C0M101S A1(00), E1( 00),C1(400), E{1L00),F1(400),
                1V1(1.),W1(15),21(1,),T(400),A2(,00),O2(400)
                2P,O,ON,P,
                INTEF P,O,Q2,R,R,M,MM,YN,K
                CALGULITE -NTEGRAL FROM KRAMERS KRONIG OUTPUT SPECTRA
                GO20 Y = 2Q, R2
                P=+1
                IF(P.GT.RE)GO TO 2O
                A=01(I)/01(I)
                3=01(P)/01(0)
                C=31(P)-31(I)
                0}=\textrm{V}*(C*A+C*B
E=E+0
20 coitINUE
WRITE(%,203) (T(I),I= QQ,R又)
    203 FOMMT(2らH THE KK OSC.STRENGTH V1=,5(2X,F10.4))
    ENO
```

$\qquad$
SUBROUTIME GRADHIC（MN，D1）

1V1（15），H1（15），71（15），T（400），A2（1400），C2（400），
O，Q，AS， $2, N, M M, P I, V, V V, Y Y, Z Z, X X, F W, W I, M, K, Y M A X, Y M I N$
INTEGERP， 1 （2OD
C DATA FOR DLOTTE， $2 R, R, R$ ， $1, M M, Y N, K$ FIS

WHEH：MN NO SCCLIVG VALUES ARE PLOTTED AS CALCULATED
$K=$ MHBER OF SETS OE DATA
$M=$ WUIBER OF OUTPUT POIVTS
$F A=$ FTAL WAVENUMBE

$K=\hat{S}$
$M=(R 2-2 a)+1$
FW＝31（2．）
WRIE（1，31）FW，WI，M，K
WITE（1，30）（31（T），$I=Q Q, ~ 又 ~ 2) ~$
IF（Mi） $500,404,405$
+0 ＋
YHEN＝10．0
$00 \quad i=00 \quad I=Q Q, R D$
IF（D1（I）．LT．YMIN）GO TO iO 0

401 YYIN $=01\left(\frac{1}{9}\right)$
402 YMA $X=01$（エ）
60 B
y $4=0$
YM－N＝0．
TF（D1（I）．LT．YMIM） 50 T0 502
$\begin{array}{ll}\text { IF } \\ \text { GO TO } & 01\end{array}$
502 YMEH＝01（
$\begin{array}{ll}50 T 0 \\ Y & 01 \\ x=01\end{array}$

$100<03=27, ~ 2=$
$01(=1=(01(I)=Y M I N) * 100.001($ YMAX－YMIN $)$


31 FO
RETUR

```
    SUBROUTTNE CURVE
COIMON A1 ( OOI, B1 \((: 00), C 1(400), F 1(400), F 1(\angle 00)\),
```



```
    2P, Q, ZQ, R, ?, M, MM, P , \(V, V V, Y Y, Z Z, X X, F W, W I, M, K, Y M \Delta X, Y M I N\)
    EXTE NIAL FUNCT, FUNSET, MONIT
```



```
G THIS SOUT NE SETS UP CURVE FTT USTNG N.A. G ROUT NE EOLCDF
CHHIS IS AN ITTERATIVE MFTHOD MINYHISATION IS DONE SY LEAST SDUARES METHOD
C PROGRAI WAS INSOSDORATFD RY CJMPUTEQ LABODATODY
CDETAILS LVAILABLE IN N.A.G. MONUALS NO INFORMATION AVAILABLE CONCEPNING
C ROUTINE WHICH IS UNDER GOPYOISHT
    II=HYT PARAMETER VALUES IN \(X\)
    \(11=M+1\)
\(M 2=M M+M 1\)
    \(13=M M+M 2\)
    D0 \(10 \mathrm{~J}=1,11 \mathrm{M}\)
    \(x(J+1)=v 1(J) / 1000.0\)
    \(x(M 1+J)=W 1(J)\)
    10 CONIT NUE
    CaNT
\(\mathrm{x}(1)=\mathrm{x}\)
x
- IVITIDL OUTPUT
    CALL FUNST (M3, X,F)
    WRITE \((5,100)\)
    WRITE \((\hat{0}, 120)(X(I), \overline{=}=1, \mathrm{M} 3)\)
    1LO FOFMATMi BHGGADIEMTVGCTOR, (10E12.4)
C SET SOME PAYANETERS NFEDED QY THE HINIMI ZATION EOITTINE
    DO \(20 J=1, \mathrm{~N}_{3} \mathrm{~J}\)
    20
    COMIIMIE
            IFAIL=1
            CALL EC4CDF \(10, \mathrm{M}, \mathrm{F}, \mathrm{G}, \mathrm{HFSL}, 1033, H E S O\), TPUE \(, 2,0^{*} *(-23)\), DELTA,
            \(10.1,10.0, W, 323, F U N T, F U N S=T, M O N I T,=3000, I F A T L J\)
C SET FINCL PARMYETEP V LIESLYYTOXX,V1, W1, Z1
            \(00,30 J=1,44\)
\(V 1(J)=x(J+1) * 1000.0\)
            \(V 1(J)=x(1+1)\)
\(W 1(J)=x(1+j)\)
\(Z 1(J)=x(12+j)\)
    \(x \times=x(1)\)
    CALL CLASOSE
    WFITE (, 130) (A2(I):I=1,N)
    CALL GOAPHEC(1, Aट)
```




```
    i. 0
    WRITE ( \(=207\) )IFAIL
    200 FJ, 1ET (SH IFAIL=, I1)
    100
    \(110 \mathrm{FO} 14 \mathrm{~T}(2 \mathrm{CH}\) INITIAL FUNTTTJN VALJE=, F2O.10)
```



```
    130 FOFMAT (32H CFLLCULATET FEFLECTAMCE VALUES=, (11OE12...))
    END
```

```
            SUSOO!TTINE FUNCT(M3,X,F)
            C0410N A1(100),811,00),C1(%00),E1(400),F1(400),
            %p,om(1\nu),Z1(1,),T(400),A?(400),C2(400)
            IMTEGE,O,O,MM,P+,V,VV,YY,ZZ,XX,FW,WI,M,K'YYAX,YMIN
            DIMENSION'र(M3)
    SET CUROENT PG_aMETER VALUES INTO XX,V1,W1,ZZ1
            M1=MM+1
            M2=MM+M1
            00 10 s=1, 1:1
            1(J) =x(J+1)*1000.0
            W1(J) =x (M1+J)
            10 COYTINUE
C CALCULATE ARPAY C2
* CALCULATE ERRO? FUNCTION TO उE MINIMIZED
            F=0.0
            Co 20 I=1,:
    2 0
        COUTINUE
            QETU
            SUBRO'ST IIE XUNSET(MZ,X,STEO,FVEC(
O CALCULATES FUNITION VALJES SJ THAT DERIVATIVES MAY BE ESTIMATED
            OO}10,I=1,4
            Y=X(I)
            X(I)=Y+STED(I)
            CALL FIINCT(M3,X,Z)
            FVES(T)=Z
            0 X
            GONTINJE
        _ _.............................................................................
            SUEROUTINE MOMIT(M3,X,F,G,HFSL,ILGHESO,IFC)
            < MJNITOPINJ SUFRDUTYNE
            IF(IFC.LT.B)GOTO1O
            WPITE (U,120)(x(I),I=1,M3)
            PETUFN
            10 COMTNNE
            WRITE (j,110) IFG,F
            WRITE (5,120) (XI', I, I=1,M3)
            WEITG(:, 130) (G\hat{(I),I}=1,M3)
            100 F% UAT(13H NO OF EVALS S=, I=,15H FUNCTTION VALLUE=,E20.10)
            120 FOSMAT(1%H MINIMUM DJINT,/(10E12.4))
            130 FOSHAT(16& GSAOIENT VECTOマ,ノ(10E12.4))
```


## Appendix 3

## Simple harmonic oscillator program

(for Transverse and Longitudinal Optic mode analysis)

```
            PROGRAM ECHOE? (INPUT,OUTPUT,TAPE1,TAPE5=INPUT,TAPEG=OUTPUT)
            C0140N A1(400), E1 ( }400),C1(400),E1(400),F1(400)
1W1(1E),Z1(15),W2(15),Z2(15),T(L00), A2(L00),C2('00),
ZP,Q,QO,R,RP,N,MM,PI,V,VV,YY,ZZ,XX,FK,KI,M,K,YMAX,YMIN
    DIMENSION O1(400)
            INTEGER P,R,QO,R,RP,N,MM,MN,K
            PI=3.1415926536
            V=1.0 (0/PI
    THIS PROGPA, IS SIMILAR TO "ECHOES" EXCEPT THAT VALUES CORRESPONDTNG TO
    BOTH LO ANO TO FPEQUEVCIES ARE TAKEN THE METHON EMPLOYED IS TOENTICAL TO
    "ECHOES" IN PFINCIPAL ONLY SUBROUTINE "CLASOSC" IS DIFFERENT THIS USES THE
    M-THOD OF GERVAIS AND PIPIOU TO CALCULATE VALUES OF "R.OBS."
    ALL PAFAMETERS LISTEO HAVE IDENTICAL MAENINGS TO THOSE OF "ECHOES"
    THIS PROGPA 1 SHOULD ONLY BE USED WHEN WIDE REFLEGTANCE BANDS APE
C OBTAIM=O FOR FULLER DESCIPTION OF PARAMETRS AND USE OF SUBRDUTINES SEE
            1 READ (5,100)N,MM
            WRITE (5,292)N,MM
    292 FORMAT(1SH NO OF POINTS=,IS,2X,2OH NO OF OSGILLATORS=,I5)
            N=NO OF POINTS IN SPECTRUM M=NO OF OSCILLATORS
            FREQUENCIES REOUITRED.
            REAO(5,101) (21(I), I=1,N
            WRITE (5,2.38) (B1(I),I=1,N)
    295 FORHÄT(19H WAVELENGTHS TAKEN=,5(2X,F12.6))
            WRIT (6,239)
    293 FORMAT127H ENTERING CLASS. OSC. CYCLE
    C
    CLASSICAL OSCILLATOES PANAMETERS
    IS EPSILON INFINITY, W1 IS FREQ. OF TO MODE Z1 DAMP. CONST. OF TO MOOS
    FREO. OF LO MOOE ZZ DAMP. CONST. OF LO MODE.
    READ(5,102) XX
    FOFMAT(F3.1)
        WRIT = (6,200) xx
        READ(5,104) (W1(J),Z1(J), J=1,MM)
        READ(E,10'+) (WZ(J),Z2(J),J=1,M:1)
        WRITE(0,201) (W1(J),71(J),J=1,(1:1)
        WRITE(0,202) (W2(J),22(J),J=1,MM)
        READ(5,103) (A1(I),I=1,N)
    103 FOFNAT(3F10.b)
        WRITE(0,30E) (A1(I), I=1,N)
    30j FOFMAT(22H REFLECTIVITIES TAKEN=,5(2X,F10.6))
    C
        Q CONTROL NO SPSCTRUM OF LIMIT FREQUENCIES
        WRITE (5,300)
    300 FOFMLT(53H CLASS. OSC. CYCLE VALUES TAKEN AODITIONAL PARAMETERS)
        2=N-3
        Q=1
        WRITE (O,303)R
    303 FORMAT(11H S.O.L.F.=,I5)
        WRITE (5,304)0
    304 FORMAT(13H CONTROL NO=,I5)
        QQ=2+1
        WRITE (5,550)Q2
    650 FOPMAT(4H Qu=,I5)
    RR=P-1
    WRITE(0,651)PR
    CALL GRAPHIC(1,A1)
    00}501 I=1,
    A1(I)=41(I)/100.000
        C1(I)=ALOG(SQ2T(A1(I)))
    cONTINUE
    CALL CURVE.
    104 FOFMGT(2F15.3)
    051 FOPM4 T(4H रR=,IE)
    100 FORM4 T(2I5)
    101 FOFMAT(3F10.5)
    200 FOR YATS31H THE OSOTLLLATDP PARAMETERS ARE, 2X,
    119H E.3SILOM INF INITY=,F3.1)
    201 FOFMAT(15H TO FEEQUENCY=,F10.6,2X,20H TO DAMP. CONSTANT=,F10.5)
    202 FORHAT(14H LO FREQUENCY=,F10.6, \X,20H LO DAMP. CONSTGNT=,F10.5)
    103 FOR:1AT(3F1:.5)
    CALL KKOYOLEOD1)
    CALL CLADIS(O1)
    STOP
    ENO
```

```
    SUEPOIMTINE CLASOSC
    C0:140% A1(-06), S1(400),C1(400),E1(400),F1(400),
    1%1(15),Z1(15),*:2(15),Z2(15),T(400),A2(400),C2(400),
    ZP,O,OD,P,R=,N,MM,P ,V,VV,YY,ZZ,XX,FW,WI,M,K,YMAX,YMIN
    COMPLEX C, X1,X2,EPSILON
    INTEGEZ P,Q,QO,R,RP,M,MM,MN,K
    00 10 I=1,N
    3=B1(II*S1(I)
    C=CMPLX(1.0,0.0)
    00 2G J=1,MM
    WO=W1 (J)**1(J)
    WN=W2(J)*W2(J)
    x=wo-e
    Y=Z1(J)*B1(I)
    X1=CMPLX(X,Y)
    A=WN-B
    0=Z2(J)*B1(I)
    X2=CMPLX(A,D)
2 0
COHTINUE
EDSILON=CMPLX(EPREAL,-EPIMAG)
PSIL ON = X X +C
    EPFEAL=REAL (EPSILON)
    EPIMAG=-1.000*AIMAG(EPSILON)
    E1(I)=EPREGL
    E=S行T(-1(I)**2+F1(I)**2)
    F=SOTT(2.000*E+2.000*E1(I))
    A2(I)=(E+1:000-F)/(E+1.000+F)
    CZ(II)=ALOG(SQPT(AR(I)))
    A2(I) =A2(I)*100.00
10 CONTINUE
    RETURN
    END
```

```
            SUBROUTINE KKCYCLE(D1)
            C0M4011 A1(400),61(-00),C1(400), E1(400),F1(400),
            1W1(15), Z1(15),W2(15),72(15),T(400), A2 (400), C2(400),
            ZP,Q,QO,R,R2,N,MM,PI,V,VV,YY,ZZ,XX,FW,WI,Y,K,YMAX,YMIN
            DIMENSION D1(400), XOSC(400),Y0SC(400),G1(400),H1(400),Q1(400),
            1X1(600),Y1(400),Td1(400)
            INTEGER P,O,QQ,R,R,M,MY,MN,K
                            KRAMEPS KRONIG CYCLEGHIP CALCULATES VALUES OF OPTICAL CONSTANTS
                            KRAMERS KFONIGRPELATIONHIP CALCULATES VALUES OF OPT
            WRITE(5,308)
    30%
                            OP.MAT (SIN ENTERING KRAMERS KRONIG CYCLE)
                            OO 25 I=QQ,RR
```



```
                            OO 2 J=Q,R
                            K=J+1
                            IF(K.ER.I )GO TO 4
                            F(K.GI., G) GO ?
    5
C
    B=C2(k)-C2(1)
    CT ARE CALCULATED FROM OBSERVED REFLECTIVITIES A1
    C=B1(J)+B1(J)-B1(I)*31(I)
    O=B1(K)*31(K)-B1(I)*B1(I)
    E=01(K)-B1(J)
    GO T0 3
    4K=J+2
    G0T0 j
    3F=8/D
    G=A/C
    - F=(F+G)*E
    H=H+F
    2 CONTINUE
    U=H*B1(T) *V
    TH1(I) =H*B1(I)*V
C LOW FOERUENCY CORRECTION TERM AA
    AA=ALOG(A2(Q)/A2(I))
    BB=ALOG((31(I)-B1(Q))/(B1(I)+B1(Q)))
    A A =0.5*AA*BB*V
    HIGH FRERUENCY CORPECTION TERM CC
    CC=ALOG(AR(R)/A2(IN))/(B1(R)+B1(I)))
    CC=-0.5*C,C*DD*V
    1 1
    U=U+CC+KA
    YH1(I)=\
    21 }\textrm{W}=\textrm{COS}(U
    WW=SIN(U)
    UUUSORT (AZ(I))
    X AND Y COFRESPOND TO OPTICAL CONSTANTS N AND K
    x = (1.000-A2(I))/(1.000+A2(I) -2.000*UU*W)
    Y=-2.000*UU*WH/(1.000 +A2(I) -2.000*UU*W)
    UV=100.000+U*V
C YOO CORRESPONOS TO ABSORPTION CDEFFICIENT
    YOO=4.000*PI*Y*(B1(I))
    H1(I) = 4.00j*PI*Y*(B1(I))
    XXY COREESPONDS TO REAL PART DIELECTRIC PARAMETER
    XXYY=X*X-Y*Y
    G1(I) =X*X-Y*Y
    XY2COFRESPONDS TO IMAGINARY PART OIELECTRIC PARAMETEF
    XYB CORRESFONOS TO CONDUCTIVITY, SIGMA=UUFFREQ
    XYB=X+Y*B1 (I)
    Q1(I)=X*Y*E1(I)
    CLASSIEAL OISSDERSION OUTPUT
    O1(I) =2.000*X*Y
    x1(I) = 
    Y1(I) = Y
    25 CONTINUS
    WRITE(5,900) (X1(I),T=00,RO)
    WRITE (5,7`1) (Y1(I), ==0Q, 2N)
    WRIT (0,902) (G1(I), (H=0Q,R又)
    WRITE(S,904) (01(I),I=00,RF)
    WROTE (5,50E) (01(I),I=20, 2又)
    900 F0, 位T(13H REF. INDEXX,三(2X,F10.E))
    G01 FORMAT(13M EXT. COFFF=,5(2x,F10:O))
    962 FORMAT(15H REAL EPSILON=,う(2X,F15.6))
    903 FO\M4T(13H ABS.COEFF=,S(2X,F15.0.)
    304 FOCMAT(5H SIG44=,5(2x,F15.0))
    505 FOKMAT(39H IMAGINAEY PART OF OIELEGTRIC CONSTANT=,5(2X,F15.5))
    905 FOSMAT(7H THETA=,j(2X,F10.6))
    CALL GPAPUCY-1,*1)
    CALL GRAPHFC(-1,\1)
    CALL GPAPHIC(0,G1)
    CALL GRAPHTC(J,H1)
    RETUZN
    ENO
```

```
                SUBROUTINE CLADIS(131)
                    COMHON A1 (L00), B1 (400), C1 (400), E1 (400), F1 (400),
                    1W1(15), Z1 (15), W2(15), Z2(15), T(400), A2 (400), C2 (400)
                    \(2 P, Q, Q Q, R, R Z, N, M M, P I, V, V V, Y Y, Z Z, X X, F W, W I, M, K, Y M A X, Y M I N\)
                    OIMENSION O1(400)
                            INTEJER \(P, 0, Q \cap, R, R R, M, M M, M N, K\)
                            CALGULATE INTEGRAL FROM KRAMERS KRONIG OUTPUT SPECTRA
            \(\mathrm{E}=0.000\)
            \(0020 \mathrm{I}=Q 2, R \mathrm{R}\)
            \(P=I+1\)
            IF(P.GT.RP)GO TO 2ù
            \(\mathrm{A}=01\) (I) \(/ \mathrm{Bi}(\mathrm{I})\)
            \(B=01(\rho) / 81(P)\)
            \(C=31(P)-31(I)\)
            \(0=V *(C * A+C * B)\)
            \(\mathrm{E}=\mathrm{E}+\mathrm{D}\)
            (1)
            WRITE (E,203) (T (I), I=QQ,RR)
    203 FOEMAT(2GH THE KK OSC. STRENGTH V1=,5(2X,F10.4))
    QETURN
    ENO
SUGROUTINE GRAPHIC（MN，O1）
COMMON A1（ 400 ），E1（L00），C1 \((400), E 1(400), F 1(400)\)
            1W1(15), Z1(15), W2(15), Z2(15), T(400), A2 (400), C2 (400)
            \(2 P, Q, Q Q, R, R F, N, M M, P I, V, V V, Y Y, Z Z ; X X, F W, W I, M, K, Y M L X, Y M I M\)
                    DTHENSONDI LOO
                            INTEGEP P, O,QQ,R,RR, M, MM, MN, K
C OATA FOR PLOTT:R
TAKES WAV LENGTHS, ANO VARIABLES, FINOS MAX AND MIN ANG ADJUSTS
VALUES ACCORDINGLY TO FIVE ARBITRAPY UNITS WHEN MN=0, -1
    WHEN MN=1 NO SCALING VALUES ARE PLOTTEO AS CALCULATED
    \(K=\) NUMBER OF SETS OF JATA
    \(M=\) NUMBE OF OUTPUT POINTS
    FW = FINAL WAVENUMBER
    \(W I=\) INITIAL WAVENUMBEP
    \(K=8\)
            \(M=(3, R-2 Q)+1\)
            FW=31 (尺ス)
            \(W I=31\) (02)
            WRITE \((1,31)=W, W I, M, K\)
            WRIT (1, 30) ( \(31(I), ~ I=Q Q, R 2)\)
    IF (㺄) SO \(0,404,405\)
    \(Y 410\)
    DO \(400^{\circ}=27, R R\)
    IF (D1 (I). LT.YMIN) GO TO 401
    IF(DI (I). GT:YMAX) GO TO 402
    GO TO 400 ,
    401 YMIN=01 (I)
    402 YMAX= 41 1
    400 CONTINU:
    00 GOTO 1
    YMAX \(=4.0\)
YMIN \(=0.0\)
    \(Y M I N=0 \cdot 2\)
    \(00501 \quad I=20, R R\)
    IF (D1(I).LT. YMIN) GO TO 502
    IF (D1 (I). GT. YMAX) GO TO 503
    GO TJ 501
    502 YMIM=01 (I)
    GOTO 101
    503 YMAX \(=01\) ( 1 )
    501 COITINU
    \(100403 \mathrm{I}=20, R \mathrm{R}\)
    \(01(I)=(01(I)-Y M I N) * 100.00 /(Y 4 A X-Y M I N)\)
403 CaITIVUE
405 WRITE (1, 30\()(01(I), I=00, R R)\)
    30 FO俊T(OF9.3)
    31 FORMAT(Fう.0.,2X,F4.0,2X,I3,2X,I2,60X)
    RETUEN
    ENO
```

```
            SUgROUTINE GURVE
            Comion A \(1(400), B 1(400), C 1(400), E 1(400), F 1(400)\)
    1W1(1シ), 71(15), W2(15), Z2(15), T(400), A2 (400), C2 (400)
    \(2 P, Q, Q Q, R, R, N, M M, P I, V, V V, Y Y, Z Z, X X, F W, W I, H, K, Y M A X, Y M I N\)
    INTEGER \(P, O, Q Q, R, R Z\)
    EXT ERINAL FUNCT, FINSET, MONIT
    OIMENSIDN \(\times(46), G(6)\), HESL (1035), HESD (46), DELTA (4E), W(323)
C THIS POUTINE SETS UP CURVE FIT USING N.A.G. ROUTINE EOLCDF
C THIS IS AN ITTERATIVE HETHOD MINIMISATIO\& IS DONE BY LEAST SOUARES METHOJ
C PROGRGM WAS MCORPORAT O GY COMPITER LABORAATODY
C DETAILS AVAILABLE IN N.A.G. MANUALS NO INFORMATION AVAILABLE CONCEPNING
C ROUTIN WHICH IS UNDER COPYRIGHT
    \(M 1=M+1\)
    \(M 2=M 1+M 1\)
    \(M 3=14+M 2\)
    \(M_{4}=11 M+M 3\)
    \(0010 \mathrm{~J}=1\), 14 M
    \(x(J+1)=W 1(J)\)
    \(x(M 1+J)=Z 1(J)\)
    \(x(M 2+J)=N 2(J)\)
    CONTINU
C INITIAL OUTPU
    CALL FUNCT (M4, X,F
    WRITE \((5,10 己)\)
    WRITE (今, 110)F
    WRITE \((5,120)\) (X(I), \(I=1, M 4)\)
    140 FORMÁTIUH GRADIENT VECTOR, (10E12.4))
C SET SOME PARAMETERS NEEOED BY' THE MINIMIZATION ROUTINE
    \(\begin{array}{ll}\mathrm{F}=\mathrm{C} & \mathrm{j} 0 \\ \mathrm{~J}=1, \mathrm{H}\end{array}\)
    20
    このはTINU三
```



```
            \(16.1,10.0, W, 323, F\) UNST, FUNS T, MONIT, 5, 3000 , IFAALI
C SET FALLAL PARAMET ER, VALUES INTOXX,WI, Z 1, W2, Z2,
            \(0030 J=1, M M\)
            N1 (J) \(=x(J+1)\)
            \(W 2(J)=x(M 2+J)\)
            \(W 2(J)=x(M 2+J)\)
\(Z 2(J)=x(M 3+J)\)
        30 colvivue
            \(x \mathrm{x}=\mathrm{x}(1)\)
            CALL CLASOSC
            WRITE (5,130) (A2(I), I=1,N
            CALL GRAPHIC(1, A2)
            WRITニ( 0,702 )
        702 FORMAT (2TH CLASS. OSC. CYCLE COMPLETE)
            \(00710 \quad I=1, N\)
            A2(I)=42(I)/100.00
    710 CONTINU=
    QETUEN
    100 FOEMAT 3 BH \({ }^{* * * * * * * * * * * ~ I N I T I A L ~ S I T U A T I O N * * * * * * ~}\)
    110 FORMAT(24H INITIAL FUNCTION VALUE 2 , E20.10)
    120 FORMT (25H INITIAL MIMIMUM ESTIMATE, (110E12.4)
    133 FOFMAT(32H CALCULATED REFLECTANCE VALUES=, 1 (10ミ12.4))
    END
SUBPOMTIME FUNSET (ML, X, STEP, FVEC)
OIMENSI
C CALCULATES FUHCTION VALLUES SO THAT JERIVATIVES MAY BE ESTIMATED
    \(\mathrm{O}=\mathrm{x}, \mathrm{I}=1, \mathrm{M} 4\)
    \(Y=x(I)\)
    \(X(I)=Y+S T E P(I)\)
    CALL EUNCT (M4, \(x, z\) )
    FVEC(I) \(=Z\)
    \(x(I)=y\)
    10 CONTINUE
    RETURN
ENO
```

```
                    SUBROUTINE FUNCT(M+,X,F)
                    COHMON A1(400),B1(400),C1(400),E1(400),F1(400),
            1W1(15),Z1(15),W2(15),Z2(15),T(400), A2(400),C2(400),
            ZP,Q,QQ,R, RF,N,MH,PI,V,VV,YY,ZZ,XX,FW,WI,M,K,YMAX,YMIN
                INTEGER P,Q,QQ,R,RR
                DIMENSION'X(H4)
    C SET CURRENT PGRAMETER VALUES INTO XX,H1,Z1,H2,Z2,
            M1 =MM+1
            M2= 1:1+M1
            M3=MM+M2
            00 10 J=1,MM
            W1(J) =x (J+1)
            Z1(J) =x(11+J)
            Z2(J)=x(m3+J)
            10 CONTINUS
                            C CALGULATE ARPAY C2
                            C CALCULATE ERROF. FUNCTION TO BE MINIMIZED
                            F=0.0
                            F=F+(C1=1
        20 CONTINUE
            RETUFN
                            SUBROUTINE MONIT (:ML,X,F,G,HESL,IL,HESO,IFC)
                            DIMENSION X(M4),G(%14),HESL'IL), HESD(M4)
    C MONITORING SUBROUTINE
            IF(IFC.LT.0)GOTO10
            WRITE (5, 10U)IFC,F
            WPIT(S,120) (X'(I), I=1,M4)
            10 CONTT NUE
            WFITE (0,110)IFC,F
            WRITE(0,12i) (X (I),I=1,M4)
            WRITE(今,'13心) (G(I),I=1,M4)
            WRITE
            100 FOFMAT(13H VO OF FVALSS,I5,15H FUNCTION VALUE=,E20.10)
    120 FORMAT(14H MINIMUM POINT,/(10E12.4))
    130 FOF.MAT(16H GR.AOI=NT VECTOF,/(10ミ12.4))
        END
```

All three programs have data input formats identical. This enables the same punched card deck to be used for any of the three programs. The data is fed into the programs in the following order:

1. Total number of data points taken; number of reflectance bands (2I5 format).
2. Frequencies of the data points used (3F10.6 format).
3. Oscillator parameters (see section on oscillator parameters).
4. Reflectivities (in \%) of the data points used (3Fl0.6 format).
5. Highest reliable data point (limit of observed data before extrapolation) (I5 format).
6. $\quad$ (first data point) (I5 format).

For the meaning of output parameters, see Chapter Two, section A.

Oscillator parameters

For a meaning of each parameter and methods of estimating them see Chapter Two, section A.

Appendix 1 does not use oscillator parameters and no estimates are required. For Appendix 2 estimates of the following are required:

1. visible light refractive index $\left(\varepsilon_{\infty}\right)$ (F3.1 format).
2. Oscillator strength; Transverse optic mode frequency; damping constant (3F10.6 format).

For Appendix 3 estimates of the following are required:

1. Visible light refractive index $\left(\varepsilon_{\infty}\right)$.
2. Transverse optic mode frequency; damping constant (2Fl0.3 format).
3. Longitudinal optic mode frequency; damping constant (2F10.3 format).

[^0]:    a Goggin and Mink (1974).
    

