Coordination Chemistry Reviews, 10 (1973) 183–193

A DESCRIPTIVE INTRODUCTION TO ANALYSIS OF THE VIBRATIONAL SPECTRA OF SOLIDS

D.M. ADAMS

Department of Chemistry, University of Leicester, Leicester LE1 7RH (Gt. Britain)

(Received August 18th, 1972)

CONTENTS

A. INTRODUCTION

The use of symmetry theory in analysis of infrared and Raman spectra is now well established. A wide variety of textbooks is available in which these topics are treated at levels varying from semi-pictorial introduction to full-blooded mathematical detail. In the U.K. most students in physical sciences graduate with a working knowledge of "chemical applications of group theory", whilst in North America such courses are among the more heavily subscribed in graduate programmes. The great majority of these books and courses deal with applications of point group theory only, leaving the recipient well-equipped to deal with analysis of gas-phase and (with some qualifications) solution and liquid-phase spectra. In order to deal adequately with the spectra of solids, even at a qualitative level, a simple extension of theory is required. The appropriate procedure, commonly known as "factor group analysis", has been clearly described in several reviews and books but is not as widely understood as it should be. The reason is most probably that some understanding of space group theory seems to be necessary and that various types of mode appear that have no counterpart in point group analysis. The purpose of this article is to show how very simple factor group analysis really is, that almost no knowledge of space groups is required, and to show how, with the aid of Tables[1] readily available, the procedure is in some respects even easier than the currently taught means of handling point group analysis.

We shall begin by relating certain definitions and background material. However, the reader should be assured at this stage that the final outcome will be a procedure that is extremely simple in operation.

It is, of course, a pre-requisite for vibrational analysis of a solid that its crystal structure be known. From knowledge of space group and unit cell occupancy alone valuable information can often be deduced. In the absence of any crystallographic information little more than speculation is possible.

B. CHOICE OF A UNIT CELL

In discussing the vibrations of a molecule we consider the molecule as a whole, but what sized chunk of crystal need we take to work out its vibrational representation? Although many crystal vibrations are cooperative and involve a large number of unit cells we can, in fact, treat the problem on the basis of one *unit cell.* The physical reasoning underlying this assumption is that, because the dimensions of a unit cell are invariably small compared with the wavelengths of radiation used in observing vibrational spectra, all unit cells can be considered as experiencing the same electric field. It is essential to take the *primitive* unit cell in each case as this contains the smallest representative portion of the crystal structure: from it the crystal can be reconstructed by repeated primitive translations along three axes. Crystallographers often describe structures in terms of non-primitive unit cells containing 2, 3 or 4 times as many atoms as the primitive cell. This is done for convenience rather than for any physical reason: it is possible to outline a primitive space lattice for each non-primitive one but the axes of the primitive cell may not then correspond with those used for other cells of the same class.

There is absolutely no objection to working out the vibrational representation for a non-primitive lattice, but the result must be divided by the multiplicity of the cell relative to that of the primitive cell. The method of analysis described below automatically avoids this problem.

We note for reference that an F-centred cell contains 4 times as many atoms as the primitive cell, an I, A, B or C-centred cell twice as many, and an R-type cell three times as many.

C. POINT, SPACE AND FACTOR GROUPS

Space groups differ from point groups in having operations of a translational nature in addition to those associated with point groups. The 230 space groups may be derived by considering combinations of the operations of the 32 "crystallographic" point groups with appropriate Bravais lattices. Since we propose to analyse spectra on the basis of the *primitive* unit cell, it is clear that we should work with the group of operations that derives from the generating crystallographic point group. This is known as the "factor group".

The factor group is very simply identified. For example, $K_2CuCl_4 \cdot 2H_2O$ forms crystals of symmetry *P4/mnm* (Hermann–Mauguin notation)[2]. The equivalent Schoenflies description is D_{4h}^{14}; the factor group is D_{4h}. Lists of space group equivalents in these two notations are found in *International Tables for X-Ray Crystallography* [3] and in many other places.

It has recently been pointed out that we should refer not to "factor group" but to "unit cell group" [4]. However, the term "factor group analysis" (FGA) is so widely used that we shall retain it.

D. PHYSICAL INTERACTIONS IN CRYSTALS

Before launching into a description of the vibrational analysis of crystals let us briefly consider the physical processes which we seek to quantify. When two oscillators couple they yield a higher and a lower frequency as, for example, the two O–H stretching modes of water. If we consider not an isolated molecule but an infinite chain of like atoms, then the equations of motion can be analysed to show that the individual oscillators couple in such a way that the resulting frequencies are either low (the so-called "acoustic" modes) or of higher frequency (the so-called "optic branch" modes). The treatment can be generalised for the case of a three-dimensional lattice. For a primitive unit cell of N atoms there are $3N$ vibrations of which only *three* are acoustic. The acoustic modes involve in-phase motion of all of the atoms in the crystal and correspond to propagation of plane waves along three orthogonal directions. The symmetry species of the acoustic wave functions are the same as those of translational vectors aligned with the same axes and are therefore read directly from the appropriate character table. Acoustic modes are not normally optically active since no dipole change is associated with them.

The $3N-3$ "optical branch" modes may or may not be optically active (i.e. appear in IR and/or Raman spectra) depending upon the factor group and the unit cell occupancy. We discuss examples below. Although "optical branch" modes are higher in frequency than acoustic modes, optic modes *can* be extremely low (e.g. 17 cm^{-1} in red HgI_2).

If a crystal consists of molecules between which there is only weak attractive bonding it is then realistic to divide the optic branch modes into two classes: (*a*) internal molecular vibrations corresponding to those of the free molecule, and (*b*) rotational and translational modes of the whole molecules, referred to collectively as "lattice modes". In complex ionic crystals a similar distinction can often be made. Note, however, that writing down reduced representations for lattice modes in no way validates the process. Vibrational interaction within any one symmetry species may remove the distinction between low-lying internal modes and lattice modes. In semi-ionic crystals it is often difficult to decide a priori whether decomposition into lattice and internal modes is meaningful; copper(II) chemistry provides many such examples.

(i) Site effects

Imagine now that we are dealing with a molecular crystal. In general, the molecules surrounding any given one will create an electric field of lower symmetry than that of the point group describing the isolated molecule. If the magnitude of the field is sufficient to perturb the molecule, then it may be appropriate to discuss its vibrations in terms of the symmetry of the site, the so-called "site-group" analysis of Halford and Hornig. For example, consider a C_{3v} molecule on a crystal site of C_s symmetry. From standard correlation tables[5] we find

C_{3v}	C_s
A_1 (IR + Raman)	A' (IR + Raman)
A_2	A'' (IR + Raman)
E (IR + Raman)	$A' + A''$ (IR + Raman)

As a result of condensing the C_{3v} molecules from (say) gas to solid the E modes now split into doublets and the previously inactive A_2 modes become allowed in both IR and Raman spectra.

(ii) Correlation coupling

If there is more than one molecule in the primitive unit cell their vibrations will interact, coupling in the combinations permitted by the *space group* symmetry. This is generally referred to as "correlation coupling". Its magnitude depends upon the strengths of the interactions between the molecules in the cell. We may illustrate this diagramatically with a simple example. In brucite, $Mg(OH)_2$, there are two hydroxyl groups in the primitive unit cell, aligned along the crystallographic z axis[2]. Their ν(OH) modes are coupled in phase and out of phase yielding *crystal* modes of symmetries A_{1g} and A_{2u} (in D_{3d}) respectively.

←H—O→	H→—←O
←O—H→	←O—H→
A_{1g}	A_{2u}

If the site group is of lower symmetry than the molecular group, correlation coupling is considered as taking place between vibrations labelled according to site group symmetry. Thus, consider a hypothetical unit cell described by a factor group of symmetry C_{2v} in which there are two C_{3v} molecules upon C_s sites. As shown above, the effect of the site field is to lower the symmetry of the vibrational wave functions of the molecule to A' and/or A''. Two A' molecular vibrations (one from each of the two molecules in the cell) will now couple in phase and out of phase to yield $A_1 + B_2$ modes in C_{2v}, whilst A'' molecular motions yield $A_2 + B_1$ modes. The selection rules of C_{2v} then operate.

In addition to any band multiplicity caused by site and/or correlation fields, the molecules in a molecular crystal will also undergo (*a*) rotational motion, and (*b*) translational motion, with three degrees of freedom contributed to each type of motion by each molecule. For each unit cell *three* of the translational modes will be of the acoustic type, as discussed above.

E. DATA NEEDED FOR FACTOR GROUP ANALYSIS

In crystallographic papers a structure is described, inter alia, in terms of its space group and the atomic coordinates. The latter are often given in terms of Wyckoff site occupancy. (All possible sites in all 230 space groups are listed and classified in terms of the Wyckoff notation in *International Tables for X-Ray Crystallography*[3].) If the paper lists only the atom coordinates these must be translated into Wyckoff site occupancy data by reference to the *Tables*[3].

The vibrational analysis can now be carried out very simply using tables of reduced representations[1]. These *Tables* have been adjusted, where necessary, for non-primitive unit cells so that in such cases the analysis yields only the number of vibrations of the primitive cell. Note that where identical lines occur in the *Tables* they have been condensed. For example, in space group No. 2 the rows 1A, 1B, 1C, ... 1H are all identical; they are accordingly listed as 1A–H.

F. EXAMPLES OF FACTOR GROUP ANALYSIS USING THE TABLES OF REDUCED REPRESENTATIONS

We first summarise checks that we shall apply in the analysis.

(*a*) A primitive unit cell containing N atoms has $3N$ modes of vibration. Three of these are acoustic (T_A), leaving $3N-3$ optical branch modes, N_{opt}.

(*b*) If the crystal contains molecules or complex ions there will be:

(*i*) $3Z'$ rotatory modes (R), where Z' = number of non-linear molecules or complex ions in the unit cell ($2Z'$ in the case of linear species);

(*ii*) $(3Z'' - T_A) = 3Z'' - 3$ translatory modes (T), where Z'' = number of monatomic and polyatomic units in the cell. For instance, $Z'' = 3$ for $K_2[PtCl_4]$, which has a monomolecular cell.

(*a*) *Nickel arsenide, NiAs*

This has the symmetry[2] of space group No. 186, *P6mc* (C_{6v}^4). There are two Ni atoms on sites *a* and two As atoms on sites *b*. Turning to Table 2 of *Tables for Factor Group and Point Group Analysis*[1], under space group No. 186 we find

C_{6v}	A_1	A_2	B_1	B_2	E_1	E_2	
Row 2A	1	0	1	0	1	1	
Row 2B	1	0	1	0	1	1	
N_{tot}	2	0	2	0	2	2	(= 3N)
T_A	1				1		(= 3)
N_{opt}	1	0	2	0	1	2	(= 3N − 3)

where T_A is read directly from the C_{6v} character table. The C_{6v} table also shows that A_1 and E_1 modes are IR-active and that A_1, E_1 and E_2 modes are Raman-active. We therefore expect a four-line Raman spectrum and a two-band IR spectrum with one coincidence (E_1). The B_1 modes are inactive.

(*b*) *Zircon, ZrSiO$_4$*

This has a non-primitive cell[2], *I4/amd* (D_{4h}^{19}), No. 141, with $Z = 4$. Sites are occupied as follows: Zr on 4*a*, Si on 4*b*, O on 16*h*. Since the primitive cell has $Z = 2$, we should use only *half* this number of sites in the analysis. Thus

D_{4h}	A_{1g}	A_{2g}	B_{1g}	B_{2g}	E_g	A_{1u}	A_{2u}	B_{1u}	B_{2u}	E_u	
Zr, 2A	0	0	1	0	1	0	1	0	0	1	
Si, 2B	0	0	1	0	1	0	1	0	0	1	
O, 8H	2	1	2	1	3	1	2	1	2	3	
N_{tot}	2	1	4	1	5	1	4	1	2	5	(=36=3N)
T_A							1			1	(=3)
T	0	0	2	0	2	0	1	0	0	0	(=3Z''−3=9)
R	0	1	0	0	1	0	0	1	0	1	(=3Z'=6)
N_{int}	2	0	2	1	2	1	2	0	2	2	(=2×(3n−6)=18)

Some explanation may be required at this point. N_{tot} was obtained, just as in the first example, by summing the rows corresponding to the site occupancy: we checked that the total (including degeneracy) = 3N where N = number of atoms in the unit cell (12). Translatory modes are obtained by considering the representations associated with the sites occupied by the *centres of gravity* of the various ions. Clearly this means that we take 2A for Zr^{4+}, and 2B for $[SiO_4]^{4-}$. Summing rows 2A and 2B yields the total number of translatory modes, $T + T_A$; for convenience we have separated this into acoustic (T_A) and optical branch (T) translatory modes. We note that since there are 4 particles in the primitive cell (i.e. 2 × Zr^{4+} and 2 × $[SiO_4]^{4-}$) there can only be 3 × 4 translatory modes, of which all but three are optical branch.

Rotatory motion in zircon will be associated with the anions only; their representation is obtained by considering rotations about the centre of gravity of the ion, clearly the sites 2B. Thus, we read the row 2B under the "Rotatory" part of the table, on the right-hand side. (Note that the centre of gravity of a complex ion or molecule is not necessarily associated with a site upon which any of the atoms are located. An obvious example is benzene. In such cases the Wyckoff site of the centre of gravity can usually be deduced from *International Tables for X-Ray Crystallography*[3] or from the crystallographic paper. Some particularly difficult situations arise in the working out of lattice modes of polymers and sheet structures: these are discussed in Sect. J).

Finally, N_{int} is obtained by subtracting $T + T_A + R$ from N_{tot}; it is the representation of the *coupled* vibrations of the two anions in the unit cell. We can further examine the meaning of N_{int} by drawing up a correlation between this result, relating to a factor group of D_{4h} symmetry, and the vibrational representation of an isolated $[SiO_4]^{4-}$ anion. Thus

Ion, T_d $\longrightarrow$	Site, D_{2d} $\xrightarrow{\times 2}$	Unit cell, D_{4h}
A_1 (Raman)	A_1 (Raman)	$A_{1g} + B_{2u}$ (inact)
E (Raman)	$A_1 + B_1$ (Raman)	$A_{1g} + B_{2u}$ (inact) $B_{2g} + A_{1u}$ (inact)
$2T_2$ (IR + Raman)	$2B_2 + 2E$ (IR + Raman) (IR + Raman)	$2B_{1g} + 2A_{2u}$ (IR) $2E_g + 2E_u$ (IR)
		g-modes (All Raman-active)

To do this correlation tables[5] were used, beginning with the reduced representation under T_d for an isolated $[SiO_4]^{4-}$ ion. The site symmetry, D_{2d}, is taken from *International Tables for X-Ray Crystallography*[3]. We note that the representation so deduced is exactly that of the row N_{int}. Note that in this particular case it is not possible to tell whether D_{2d} or D_{4h} selection rules apply from the Raman spectrum alone. It *is* possible if both IR and Raman spectra are given, since, for example, non-coincidence of B_{1g} and A_{2u} modes would support D_{4h}, whereas their coincidence would require D_{2d} symmetry.

G. REPRESENTATIONS BASED UPON INTERNAL COORDINATES: USE OF THE "VECTOR" TABLE[1]

It is of great practical convenience in interpreting spectra to have some idea of how the various types of mode will combine. In the case of zircon, consider the Si–O stretches. For an isolated ion they span the representation $A_1 + T_2$ in T_d. Using correlations as above we find for the unit cell

$$A_1 + T_2 \rightarrow A_{1g} + B_{1g} + E_g + A_{2u} + B_{2u} + E_u$$

We can, however, obtain this information much more quickly by using Table 3 of ref. 1, which, for want of a better name, we call "VECTOR". It was constructed by coupling oriented vectors with respect to factor group symmetry, taking *one* (not three) from each Wyckoff site.

We may represent an increment in Si–O bond length by a vector oriented along the bond. This vector can itself be regarded as on a site of the same symmetry as the oxygen atoms, 8H. We find that row 8H of space group number 141 in Table 3 reads exactly the same as the representation (above) deduced from correlation tables. Bending coordinates may be treated similarly. An example is worked in full in the Introduction to ref. 1.

H. STRUCTURES CONTAINING LINEAR SPECIES: BRUCITE

For unit cells with linear molecules or ions only two degrees of rotational freedom per linear ion are allowed[6]. Consider the case of brucite, $Mg(OH)_2$. It has the symmetry of space group $P\bar{3}ml \equiv D_{3d}^3$ (No. 164) with one formula per unit cell. The hydroxil ions are aligned parallel to the crystallographic z axis and are therefore allowed to rotate about the x and y axes only. Both oxygen and hydrogen atoms are on Wyckoff sites d so that in working out lattice modes of the crystal we take sites d as representing the centres of gravity of hydroxyl ions. Note, however, that Table 2, ref. 1, gives under the heading "Rotatory" the *sums* of rotational motions about x, y and z axes. For brucite we need only rotations about x and y axes. The authors of the *Tables* have thoughtfully provided for such eventualities[1]: Table 4 lists separately the reduced representations for rotations about x and z axes where such are appropriate. For brucite, therefore, we take ROTATORY (x+y+z) from Table 2 (ref. 1) less ROTATORY (z) from Table 4, the result being ROTATORY ($x \pm y$) as required. The full analysis is given below.

No. 164	A_{1g}	A_{2g}	E_g	A_{1u}	A_{2u}	E_u	
Mg on 1*a*					1	1	
O on 2*d*	1	0	1	0	1	1	
H on 2*d*	1	0	1	0	1	1	
N_{tot}	2	0	2	0	3	3	$(=3N=15)$
$T+T_A$ (i.e. rows 1*a*+ 2*d*)	1	0	1	0	2	2	$(=3Z''=9)$
$R(x+y+z) - R(z)$	0	0	1	0	0	1	$(=2Z'=4)$
N(internal)	1	0	0	0	1	0	

I. FURTHER REMARKS ON THE USE OF THE "VECTOR" TABLES

Thus far we have proceeded as if it is necessary to work out the full selection rules, including lattice modes if relevant, in every case. As the majority of spectroscopic studies deal with incomplete data and restricted frequency intervals the general need for FGA is sometimes questioned. Its use, even for a single internal coordinate type, helps to quantify the interpretation of spectra and removes the need to make vague comments about "solid state effects".

Consider the example of $Cr(CO)_3$ (π-C_6H_6). If only the ν(CO) part of the spectrum is of concern to us, we can work out the selection rules very simply using the VECTOR tables. This compound crystallises in space group number 11 with two molecules per primitive cell[7]. Each molecule has one set of C,O atoms on sites *e* and two sets on sites *f*. We consider, therefore, a set of *two* C–O vectors on sites *e* and *two sets* of two on sites *f*. Rows 2E and 4F (Table 3) yield the ν(CO) representation for the solid as $2A_g+B_g+A_u+2B_u$, indicating that three bands are expected in the Raman spectrum and three (non-coincident) ones in the IR.

Examples such as this can be multiplied many times over. The case of the ν(Si–O) modes of zircon was dealt with above. The VECTOR tables are so simple to use that it is hoped they will find extensive application in vibrational spectroscopy.

J. LAYER STRUCTURES AND POLYMERS

If there is only one layer or chain per primitive unit cell the only translatory modes will be of the acoustic type. Infinite layers and linear chains have no degrees of rotational freedom but chains in which all of the atoms are not co-linear have *one* degree of rotational freedom about the direction of the chain axis.

For a polymer chain, or a sheet, the concept of "centre of gravity" used in working out lattice modes of molecular and complex ionic crystals is often not quite so simple to apply. For example, in the layer structure form of Ga_2S_3 the "centre of gravity" lies in the median plane of the sheets which does not contain any of the atoms of the structure.

We recall that the "centres of gravity" we have used so far have all been atom sites (in the Wyckoff notation), i.e. sites associated with certain symmetry operations. We follow the same procedure for polymers and other examples. Thus, we list the symmetry elements of the individual polymer chains which are *also* symmetry elements of the space group. (The chains may have additional symmetry elements which are not elements of the space group.) These elements together define a site symmetry; it is this site which we use to work out lattice modes.

The next step depends upon whether the chain or sheet has associated screw axes or glide planes. If it does not, then the sites located by the above procedure will be found to correspond to one of the sets of Wyckoff sites of the space group. They are then used, as above, to work out lattice mode representations. The sites are (for polymers) on the chain axes and equal in number to the number of the chains in the primitive cell.

If the chain or sheet has associated screw axes or glide planes there will not be a set of Wyckoff sites in the space group with symmetry isomorphous with that of the sites located by the above procedure. However, such a set of sites will always be found in a *different* space group having the *same* factor group. We illustrate this procedure by reference to polyethylene.

Polyethylene has the symmetry[8] of space group number 62, *Pnma* = D_{2h}^{16}. There are four formula units in the primitive cell, which contains two chains parallel to the *b* axis. The internal modes are most readily discussed in terms of the line group: we shall consider lattice modes only.

The symmetry elements of *Pnma* which are also those of the chains are: a screw axis along *b*, a centre of inversion, and a mirror plane. The site symmetry is therefore $2/m \equiv C_{2h(y)}$, where *y* indicates the direction of the two-fold axis. There is no Wyckoff site of this symmetry in *Pnma*. However, space group number 51, *Pmma* $\equiv D_{2h}^{5}$, has the same factor group and also contains sites $2/m$ in which the two-fold axis is along *b*, viz. sites 2*a*. Thus

No. 51, *Pnma*	A_g	B_{1g}	B_{2g}	B_{3g}	A_u	B_{1u}	B_{2u}	B_{3u}
2*a*, $T + T_A$					1	2	1	2
Less T_A						1	1	1
Hence, T =					1	1	0	1
2*a*, $R(x, y, z)$	1	2	1	2				
Less $R(x)$	0	1	0	1				
Less $R(z)$	0	1	0	1				
Hence $R(y)$ =	1	0	1	0				

K. CONCLUDING REMARKS

It is clear that the *Tables*[1] can be used for many other purposes beside FGA. For chemists, one of the more useful applications is to bonding theory. Sigma-bonding schemes are readily written down by using the VECTOR tables in a manner identical to that used above for bond-stretching schemes in internal coordinates. Similarly, π-bonding schemes can be obtained by taking the *difference* between representations for equivalent sets of sites in Tables 2 and VECTOR (Table 3)[1].

The author will always be interested to hear of applications of these *Tables*[1] in new or interesting ways and to give any help he can with difficulties.

REFERENCES

1 D.M. Adams and D.C. Newton, *Tables for Factor Group and Point Group Analysis*, Beckman-RIIC Limited, Croydon, Gt. Britain, 1970.
2 R.W.G. Wyckoff, *Crystal Structures*, Vol. 1, Interscience, New York, 1948.
3 *International Tables for X-Ray Crystallography*, Vol. 1, Kynoch Press, Birmingham, 1969.
4 J.E. Bertie and J.W. Bell, *J. Chem. Phys.*, 54 (1971) 160.
5 E.B. Wilson, J.C. Decius and P.C. Cross, *Molecular Vibrations*, McGraw-Hill, New York, 1955.
6 S.S. Mitra, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, 116 (1961) 149.
7 M.F. Bailey and L.F. Dahl, *Inorg. Chem.*, 4 (1965) 1314.
8 C.W. Bunn, *Trans. Faraday Soc.*, 35 (1939) 483.