

Chapter II

THEORY

Crystal Symmetry

A crystal consists of atoms arranged in a pattern that repeats periodically in three dimensions. The pattern may consist of a single atom, a group of atoms or a molecule. The basic pattern of atoms (the unit cell) in the crystal are identical and they have identical orientations in space so that an ideal crystal, which is imagined to extend to infinity in all directions, looks exactly the same when it is viewed from corresponding points in different unit cells.

In dividing space by three sets of planes, unit cells of various shapes can be produced. For example, if the planes in the three sets are all equally spaced and mutually perpendicular, the unit cell is cubic. Only seven different kinds of cells are produced, these correspond to the seven crystal systems. Bravais demonstrated that there are only fourteen point lattices (called Bravais lattices) by the arrangements of atoms in various positions in the unit cell. In Table 1, the symbol P (R used especially for the rhombohedral system) refers to primitive cells which have only one lattice point per cell. Any cell contains additional points in the interior or on faces is nonprimitive. F and I refer to

face-centered and body-centered cells, respectively, while A , B and C for base-centered cells, centered on one pair of opposite faces A , B or C. (The A face is the face defined by the b and c axes, etc.)

Symmetry operation is referred to as some movement after which no change could be detected in an object. The symmetry operations have the property that at least one point of the object is not moved by the operation. In the groups consisting of combinations of such symmetry elements there is also at least one point (center of gravity) that remains fixed, and these groups are , therefore, called point groups.

The symmetry elements of a crystal are limited to 1, 2, 3, 4 and 6-fold rotations. Although all symmetry elements are permissible for isolated molecules, it is not possible for a crystal to have symmetries such as C_5 . The reason is that it is impossible to fill all of space with figures of 5-fold symmetry. Therefore, there are only 32 combinations of symmetry elements possible in a crystal and these are the thirty-two point groups.

The regular arrangement of the unit cells in a crystal permits other symmetry operations besides the point group operations. In any crystal there will be a number of translations through certain distances in definite directions. The symmetry operations of a crystal obtained by combining point group operations with translations can be expressed in terms of two distinct kinds : a screw rotation (a rotation about an axis accompanied by a translation along the axis), and a glide plane reflection (a reflection in a plane accompanied by a translation

along a line lying in the plane). By combining translation to the symmetry elements of the thirty-two point groups, 230 different arrays of symmetry elements (space groups) can be produced.

Table 1. The crystal systems, Bravais lattices and the point groups.

Crystal systems	Unit cell dimensions	Bravais lattices symbol	Point groups	
			Schoenflies symbol	Hermann-Mauguin symbol
Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$	P	C_1	1
			C_i	$\bar{1}$
Monoclinic	$a \neq b \neq c$ $\alpha = \gamma = 90^\circ$ $\beta \neq 90^\circ$	P, C	C_2	2
			C_s	m
			C_{2h}	2/m
Orthorhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	P, I, C, F	D_2	222
			C_{2v}	mm2
			D_{2h}	mmm
Rhombohedral	$a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$	R	C_3	3
			C_{3i}	$\bar{3}$
			D_3	32
			C_{3v}	3m
			D_{3d}	$\bar{3}m$

Table 1. The crystal systems, Bravais lattices and the
(cont.) point groups.

Crystal systems	Unit cell dimensions	Bravais lattices symbol	Point groups	
			Schoenflies symbol	Hermann-Mauguin symbol
Hexagonal	$a = b \neq c$ $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	P	C_6	6
			C_{3h}	$\bar{6}$
			C_{6h}	6/m
			D_6	622
			C_{6v}	6mm
			D_{3h}	$\bar{6}m2$
			D_{6h}	6/mmm
Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	P, I	C_4	4
			S_4	$\bar{4}$
			C_{4h}	4/m
			D_4	422
			C_{4v}	4mm
			D_{2d}	$\bar{4}2m$
			D_{4h}	4/mmm
Cubic	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	P, I, F	T	23
			T_h	m3
			O	432
			T_d	$\bar{4}3m$
			O_h	m3m

Table 2. Space groups in orthorhombic system.

Crystal system	Point groups		Space groups	
	Schoenflies symbol	Hermann-Mauguin symbol	Schoenflies symbol	Hermann-Mauguin symbol
Orthorhombic	D_2	222	$D_2^1 (V^1)$	P 222
			$D_2^2 (V^2)$	P 222 ₁
$D_2^3 (V^3)$			P 2 ₁ 2 ₁ 2	
$D_2^4 (V^4)$			P 2 ₁ 2 ₁ 2 ₁	
$D_2^5 (V^5)$			C 222 ₁	
$D_2^6 (V^6)$			C 222	
$D_2^7 (V^7)$			F 222	
$D_2^8 (V^8)$			I 222	
$D_2^9 (V^9)$			I 2 ₁ 2 ₁ 2 ₁	
	C_{2v}	mm2	C_{2v}^1	P mm2
C_{2v}^2			P mc2 ₁	
C_{2v}^3			P cc2	
C_{2v}^4			P ma2	
C_{2v}^5			P ca2 ₁	
C_{2v}^6			P nc2	
C_{2v}^7			P mn2 ₁	
C_{2v}^8			F ba2	
C_{2v}^9			P na2 ₁	
C_{2v}^{10}			P nn2	
C_{2v}^{11}			C mm2	
C_{2v}^{12}			C mc2 ₁	
C_{2v}^{13}			C cc2	
C_{2v}^{14}			A mm2	

Table 2. Space groups in orthorhombic system.

(cont.)

Crystal system	Point groups		Space groups	
	Schoenflies symbol	Hermann-Mauguin symbol	Schoenflies symbol	Hermann-Mauguin symbol
			C_{2v}^{15} C_{2v}^{16} C_{2v}^{17} C_{2v}^{18} C_{2v}^{19} C_{2v}^{20} C_{2v}^{21} C_{2v}^{22}	A $bm2$ A $ma2$ A $ba2$ F $mm2$ F $dd2$ I $mm2$ I $ba2$ I $ma2$
	D_{2h}	mmm	$D_{2h}^1 (v_h^1)$ $D_{2h}^2 (v_h^2)$ $D_{2h}^3 (v_h^3)$ $D_{2h}^4 (v_h^4)$ $D_{2h}^5 (v_h^5)$ $D_{2h}^6 (v_h^6)$ $D_{2h}^7 (v_h^7)$ $D_{2h}^8 (v_h^8)$ $D_{2h}^9 (v_h^9)$ $D_{2h}^{10} (v_h^{10})$ $D_{2h}^{11} (v_h^{11})$ $D_{2h}^{12} (v_h^{12})$	P mmm P nnn P ccm P ban P mma P mma P mma P cca P ban P ccn P bcn P nnn

Table 2. Space groups in orthorhombic system.
(cont.)

Crystal system	Point groups		Space groups	
	Schoenflies symbol	Hermann-Mauguin symbol	Schoenflies symbol	Hermann-Mauguin symbol
			$D_{2h}^{13} (V_h^{13})$	P mnn
			$D_{2h}^{14} (V_h^{14})$	P bca
			$D_{2h}^{15} (V_h^{15})$	P bca
			$D_{2h}^{16} (V_h^{16})$	P nna
			$D_{2h}^{17} (V_h^{17})$	C mcn
			$D_{2h}^{18} (V_h^{18})$	C nca
			$D_{2h}^{19} (V_h^{19})$	C <u>mmm</u>
			$D_{2h}^{20} (V_h^{20})$	C ccm
			$D_{2h}^{21} (V_h^{21})$	C nna
			$D_{2h}^{22} (V_h^{22})$	C cca
			$D_{2h}^{23} (V_h^{23})$	F mmm
			$D_{2h}^{24} (V_h^{24})$	F ddd
			$D_{2h}^{25} (V_h^{25})$	I mmm
			$D_{2h}^{26} (V_h^{26})$	I bam
			$D_{2h}^{27} (V_h^{27})$	I bca
			$D_{2h}^{28} (V_h^{28})$	I nna

Space Group Notation

1. Hermann-Mauguin Notation. The first symbol is designated by a capital letter which refers to the Bravais lattice (P, A, B, C, F and I).

P, a primitive lattice

A, B, C, lattices which are centered on the A, B, C faces respectively

F, a lattice which is centered on all faces

I, a body-centered lattice

The next symbol denotes the principal axis. Rotation axes and rotation-inversion axes are denoted by 1, 2, 3, 4, 6 and $\bar{1}$, $\bar{2}$, $\bar{3}$, $\bar{4}$, $\bar{6}$ respectively. Thus P2 indicates a primitive lattice with a twofold axis. The screw axis is designated by n_p , n denotes an n-fold axis of rotation associated with a translation of p/n displacement parallel to the axis. Thus $P2_1$ indicates a primitive lattice with a twofold screw axis (2-fold rotation axis with $1/2$ translation). Reflection plane is m, glide planes are a, b, c, d and n. a, b and c are axial glide planes with a glide of one half parallel to crystallographic axes a, b and c, that are $\frac{1}{2}a$, $\frac{1}{2}b$ and $\frac{1}{2}c$, respectively. d is a diamond glide plane with a glide of $\frac{1}{4}(a+b)$, $\frac{1}{4}(b+c)$, or $\frac{1}{4}(c+a)$. n is a diagonal glide plane with a glide of $\frac{1}{2}(b+c)$, $\frac{1}{2}(a+b)$ or $\frac{1}{2}(c+a)$. Thus Pc indicates a primitive lattice with a c-glide plane. If there is a mirror

rotation axis, the symbol is n/m . For example, $P 2/m$ indicates a primitive lattice with twofold axis and a mirror plane perpendicular to it. $P 2_1/c$ means a primitive lattice with a twofold screw axis and a c-glide plane perpendicular to it.

The following symbols are symmetries of secondary axes and mirror planes or glide planes perpendicular to these axes. The symbols are written in an order which indicates the orientation of the symmetry elements in the direction of the three crystallographic axes a , b , c in an order. For example, $Pbcm$ means that, in a primitive orthorhombic lattice, there is a b-glide plane perpendicular to the a -axis, a c-glide plane perpendicular to the b -axis, and a mirror plane perpendicular to the c -axis.

2. Schoenflies Notation. It is the symbol for the corresponding point group obtained by ignoring the translational component of any space operation, plus an arbitrary numerical superscript, for example, C_{2h}^5 (the Hermann-Mauguin symbol is $P 2_1/c$). The symbol denotes the existence of two-fold rotation axis and a reflection plane, so the crystal system is monoclinic. The superscript 5 is the order which is derived by Schoenflies. This notation is rather arbitrary and uninformative, so it is nowadays little use.

Crystallization (24)

The crystallization can be considered to comprise three steps:

1. Achievement of supersaturation
2. Formation of crystal nuclei
3. Growth of the crystals

1. Saturation and Supersaturation

A solution in equilibrium with the solid phase is said to be saturated with respect to that solid. It is possible to prepare a solution containing much more dissolved solid than that represented by saturation condition, such a solution is said to be supersaturated. The supersaturation of a system may be achieved by removing some of the solvent from the solution (evaporation), or cooling the saturated solution. The addition of ions common to the salt in saturated solution will precipitate that salt due to common ion effect. The saturated solution can be made supersaturated by adding a solvent in which the salt cannot dissolve.

2. Nucleation

The condition of supersaturation alone is not sufficient cause for a system to crystallize. Before crystal growth, there must exist in the solution a number of minute solid bodies which are known as centers of crystallization, seeds, or nuclei. Nucleation may occur spontaneously or it may be induced artificially.

2.1 Spontaneous Nucleation

The mechanism of nucleation is as follows: minute structures are formed, first of all from the collision of two molecules, then from that of a third with the pair, and so on. Short chains may be formed initially, or flat monolayers, and eventually the lattice structure is built up. The construction process, which occurs very rapidly, can only continue in local regions of very high supersaturation, and many of these 'sub-nuclei' fail to achieve maturity; they simply redissolve because they are extremely unstable. If, however, the nucleus grows beyond a certain critical size, it becomes stable under the average conditions of supersaturation. The critical size, therefore, represents the minimum free energy of the particle.

2.2 Induced Nucleation

Agitation or bubbling of a gas through a solution can often induce nucleation. Most agitated solutions nucleate spontaneously at lower degrees of supersaturation than quiescent ones. Probably the best method for inducing crystallization is to inoculate or seed the supersaturated solution with small particles of the material to be crystallized. The seeds unnecessarily have to consist of the material being crystallized, unless absolute purity of the final product is required. A few tiny crystals of some isomorphous substance may be used to induce crystallization.

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3. Crystal Growth

As soon as stable nuclei have been formed in a supersaturated system, they begin to grow into crystals of visible size. There are many theories explaining the mechanism and rate of crystal growth, and these are: ' surface energy ', ' diffusion ' and ' adsorption-layer ' theories.

The surface energy theories are based on the postulation that a growing crystal assumes the shape with minimum surface energy. The diffusion theories presume that matter is deposited on a crystal face at a rate proportional to the difference in concentration between crystal face and the bulk of the solution.

Adsorption Layer Theories

The concept of a mechanism of crystal growth based on the existence of an adsorbed layer of solute atoms or molecules on a crystal face was first suggested by Volmer (25).

Atoms or molecules in the vicinity of a crystal face will tend to attach themselves onto the surface in positions where the attractive forces are greatest, i.e. they will migrate towards positions where a maximum number of like elements are located (Figure 1a). This step-wise build up will continue until the whole plane surface is completed (Figure 1b). Before a further layer can be built up again, another ' center of crystallization ' must come into existence on the plane surface, and it is suggested that a monolayer island nucleus, usually called a two-dimensional nucleus, is created (Figure 1c).

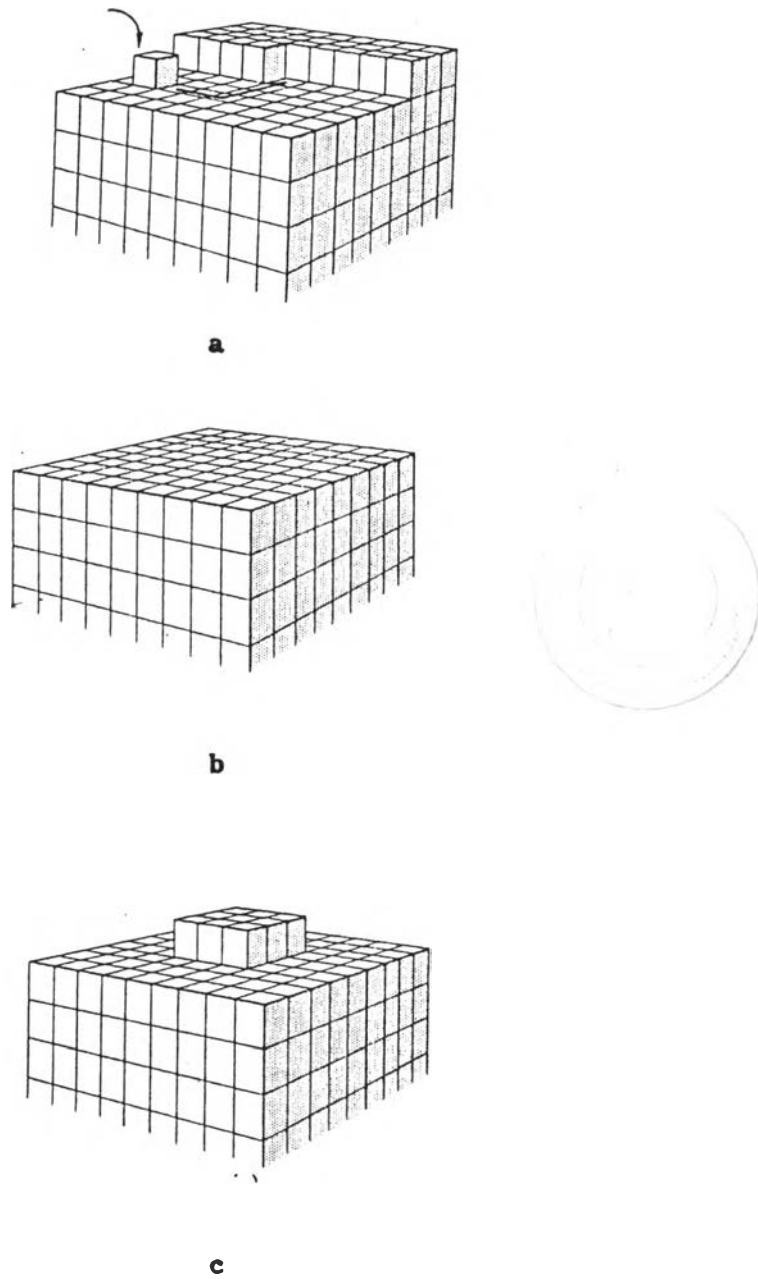


Figure 1. Crystal growth.

- a) Migration towards desired location.**
- b) Completed layer.**
- c) Surface nucleation.**

Solid Solutions

A series of solid solutions is a set of solid mixtures having two (or more) components crystallized in the same lattice arrangement but in which the composition and lattice parameter progressively change together.

Three main types of solid solution are recognized (26) :

1. Substitutional Solid Solution.

Ions or atoms in the structure are replaced by foreign atoms or ions of similar radius without causing serious distortion of the structure. When the charge and radii of substituting ions are similar to the substituted ions, then complete solid solution may exist between the two end-member compounds, for example, substitution of magnesium (II) ion (Mg^{2+}) by ferrous ion (Fe^{2+}) gives a series of products from magnesium silicate (Mg_2SiO_4) through $(Mg,Fe)_2SiO_4$ to ferrous silicate (Fe_2SiO_4). If ions differ markedly in size, then solid solution will occur to a limited extent.

Substitutional solid solution involving different valencies of the substituted and substituting elements is also possible, and is known as altermvalent substitutional solid solution. In order to maintain electrical neutrality in the crystal, one (or more) of the following processes must occur:

a) substitution of a second element of a different, and compensating valency, at the same time.

b) addition of an ion into an interstitial position in the structure.

c) the development of a vacancy.

2. Interstitial Solid Solution.

Foreign atoms or ions do not replace atoms or ions in the structure at the lattice point but fit into interstices (cavities) of the lattice which are sufficiently large to accommodate extraneous atoms. This type is very common in metals, which take up hydrogen, carbon, boron and nitrogen, all of which are small atoms, in interstices of the lattice to form solid solution. If a substance has an open structure, interstitial solid solution may take place even with atoms or ions of a considerable size.

3. Omission Solid Solution.

This type of solid solution is associated with defect lattices, in which some of the atoms are missing from sites in a structure, leaving vacant lattice positions. For example, the mineral pyrrhotite, Fe_{1-x}S , in which analyses show more sulfur than corresponds to the formula FeS . It was, for a long time, described as solid solution of sulfur in FeS . Actually the excess of sulfur shown by analyses is due to the absence of some iron atoms from their places in the lattice; there is a deficiency of iron, not an excess of sulfur. Iron will be ferrous and ferric to provide electrical neutrality.

The Formation of Solid Solutions (Mixed Crystals)

Solid solutions in a sense of mixed crystals are formed when two substances crystallize from a solution or a molten mixture of the two salts, to form a common crystal structure in which the proportions of the components may vary continuously. The phenomenon of mixed crystal formation can occur to substances which are isomorphous. Substances with analogous formulas and in which the

relative sizes of cations and anions are similar often have closely related crystal structures; they are said to be isomorphous, and the phenomenon is known as isomorphism. However, isomorphism is neither necessary to nor sufficient for mixed crystal formation.

It is true that many pairs of substances with similar crystal structures form either a limited or complete range of solid solutions or mixed crystals. There are, however, so many complicating factors that no deductions can be made about the structures of two substances from their ability or failure to form mixed crystals. Compounds with quite different structures such as silver bromide, AgBr (sodium chloride structure) and silver iodide, AgI (wurtzite structure), and even different types of formula such as calcium fluoride, CaF_2 and yttrium fluoride, YF_3 form mixed crystals. On the other hand, substances with the same type of crystal structure do not necessarily form mixed crystals such as calcium carbonate (calcite structure) and sodium nitrate. However, some requirements for the formation of mixed crystals are:

1. Size Factor.

The complete miscibility of similar structurally metals is possible only if the sizes of the atoms do not differ by more than 15 percent. Potassium chloride forms mixed crystals with potassium bromide because the sizes of chloride and bromide ions are quite close.

2. Type of Bond.

The bond in the two compounds must be of similar type, for example, potassium chloride (ionic bond) forms mixed crystals with potassium bromide (ionic bond) but not with lead sulfide (covalent bond) which has the same crystal structure as potassium chloride.

3. Chemical Similarity.

Calcium carbonate (calcite structure) and sodium nitrate cannot form mixed crystals though the cell constants are nearly the same because sodium nitrate is soluble in water while calcium carbonate is insoluble.

Crystal Spectra

An interest in the infra-red and Raman spectra of crystals has been stimulated by recent contributions to the theoretical aspects of their interpretations. The spectra of molecules fixed in a lattice differ from those of free molecules. The selection rules which operate, are affected by the crystal symmetry as well as the molecular symmetry. In crystalline state, the frequency is shifted or splits up into a number of components, otherwise new bands may appear. These spectral changes accompanying solidification may be attributed to two distinguishable influences of the lattice(27).

1. The molecular symmetry may be perturbed by the crystal's potential field, the symmetry is lowered and results in lifting the degeneracy of a degenerate normal mode of an isolated species and leading to a multiplet structure. This splitting is called site group splitting.

2. The molecular vibrations may be perturbed by coupling with identical molecular systems through intermolecular forces. A nondegenerate and degenerate vibrations in an isolated species may exhibit a multiplet structure in a multiply occupied unit cell of a crystal due to the correlation field effects. This splitting is called factor group (correlation field) splitting.

In verifying the theory and experimentally determining the relative importance of the two perturbations, it would be convenient to study these perturbations individually.

Potential Energy of Crystal

Hornig (28) has shown that the potential energy of the crystal is expressed, in the harmonic approximation, as

$$V = \sum_j (V_j^0 + V_j^1) + \sum_j \sum_k V_{jk} + V_L + V_{Lj}$$

where the summations extend over all of the molecules in the unit cell.

The various terms are :

V_j^0 represents the potential energy function of the free j^{th} molecule.

V_j^1 represents the perturbation to V_j^0 due to the field of the crystal at the site of the j^{th} molecule.

V_{jk} represents interactions between vibrations in different molecules.

V_L represents the lattice potential.

V_{Lj} represents interactions between lattice and internal vibrations.

The perturbation V_j^1 causes the potential energy of the molecule in the crystal to differ from that in the vapour phase, the resulting effects are called site group (static field) effects. These effects are a direct measure of the influence which the crystal lattice exerts upon a molecule. Site group effects can produce shifts in frequency and may lead to a splitting of a degenerate vibration and this splitting is called site group splitting.

V_{Lj} is very small (about 0.1 cm^{-1} in 3000 cm^{-1}) so it is neglected. The lattice frequencies V_L are usually small in comparison with the internal frequencies of the molecule. The intermolecular coupling or V_{jk} is much weaker than the intramolecular forces, and so the effects of the crystal field can be treated as a perturbation of the molecular field.

It is possible to eliminate the coupling of the internal modes of different molecules (correlation field effects) by studying molecule A in a dilute solid solution of an isomorphous molecule B or with an isotopic species. This corresponds to partial or complete elimination of the potential term V_{jk} in the potential function which was proposed by Hornig. If the crystal parameters of A and B are close together and they have the same site symmetry, it is possible to study the influence of site symmetry alone on the spectrum of A. Thus the site group splitting can be distinguished from factor group (correlation field) splitting.

The two approaches which are advanced to solve the problem of determining selection rules of crystal spectra are the site-group approximation, which concerns only the first term of the potential energy expression, and the factor-group approximation, which takes the first and the second terms into account. Although each of these approaches is based on a unique set of assumptions, both are founded that the symmetry governing the vibrations in crystals must be the symmetry of the crystal.

The Site-group Approximation and Site Symmetry.

Ralford (29) in 1946 developed this approximation in order to provide a simple model for interpreting the features of vibrational spectra of crystals. The approximation may be carried out if the site symmetries of molecules or ions in the crystal are known.

The point group in the fourteen Bravais lattices represent the full symmetry of the lattice if the lattice points are occupied by structureless points. But in crystals which the unit cells are occupied by molecules, the symmetry of the unit cell will be lower if the molecules do not have the full symmetry of the lattice points. The local symmetry of the molecule in the unit cell is site symmetry. Since one or more symmetry elements pass through each molecule, the site symmetry is described by the symmetry group (called site group).

For example, a cubic system (Figure 2), a structureless point at the center would be unmoved by any of the operations of the O_h point group, so this point exhibits the octahedral symmetry of the system. A cubic object placed at the center would also preserve the octahedral symmetry but an object with less than cubic symmetry would cause the symmetry of the unit cell to be lower.

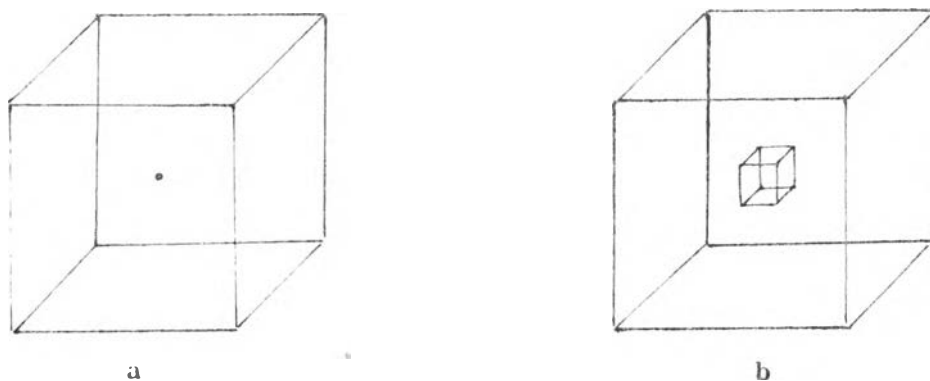


Figure 2 a) Structureless point at the center of a cubic lattice.

b) Cubic structure at the center of a cubic lattice.

The site symmetry of one of the corners of the cube is defined by the identity, the single C_3 axis and the three planes of symmetry which pass through the corner and is thus C_{3v} (Figure 3). The octahedral symmetry of the system is also preserved if the corners of the cube are occupied by objects with C_{3v} symmetry.

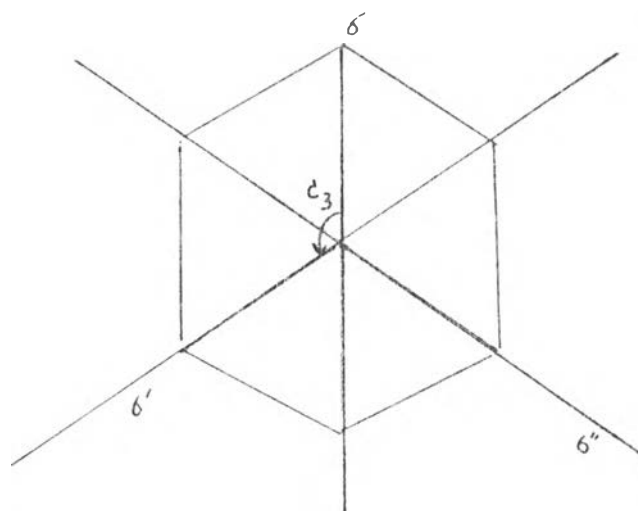


Figure 3 . View along the body diagonal of a cube illustrating the C_{3v} site symmetry at a corner.

The site group is always one of the thirty-two point groups and must be a subgroup of the space group. Since any point in a unit cell is related to one or more other points in the unit cell by at least one element of symmetry, sites of a particular site group symmetry will occur in sets.

It is not necessary to know the site symmetry of each atom since the atoms are grouped into molecules or ions, it is necessary only to know the symmetry of the sites occupied by the centers of gravity of these species. This information is usually, but not always, obtained from the X-ray structure study. In those cases when the site symmetry is not known, it can be deduced by two useful conditions.

1. The site group must be a subgroup of the molecular point group and space group.

2. The positions of centers of gravity of the molecules must occupy a complete set of sites.

These two conditions often, but not always, suffice to fix the site symmetry of the molecules or ions in a crystal for which the space group and number of molecules per unit cell are known.

The assumption of the site group approximation is that in the crystal the intermolecular coupling of vibrational motions is negligible since it is extremely weak. The internal (molecular) modes arise from perturbations of the free-ion modes due to the change in symmetry of the site. Thus, the number and activities of internal modes are found by using the site symmetry of the particular molecule of polyatomic ion in the crystal. Since the site symmetry is usually lower than the symmetry of the free molecule, the effect of the site group approximation for internal modes is to split degeneracies of the normal modes of the free molecule.

An analysis of the spectra of calcite and aragonite will be undertaken as an example of this approximation. The vibrational spectra of calcite and aragonite crystals are different, although both have the same composition (calcium carbonate). This result can be explained if the difference in site symmetry of the carbonate ion between these crystals is considered. According to X-ray analysis, the space group of calcite is D_{3d}^6 and number of molecules per unit cell (Z) is two. Molecular point group is D_{3h} .

Halford's table (29) gives

$$D_3(2), \quad C_{3i}(2), \quad \infty C_3(4), \quad C_i(6), \quad \infty C_2(6)$$

as possible site symmetries for the space group D_{3d}^6 (the number in front of the point group notation indicates the number of distinct sets of sites and that in the brackets denotes the number of equivalent sites for each set). When applying the condition that the positions of centers of gravity of the molecules must occupy a complete set of sites, only $D_3(2)$ and $C_{3i}(2)$ are accepted. The condition that the site group must be a subgroup of the molecular point group and space group eliminates C_{3i} since it is not a subgroup of the molecular point group D_{3h} . Thus the site symmetry of the carbonate ion in calcite is D_3 .

On the other hand, the space group of aragonite is D_{2h}^{16} and the number of molecules per unit cell (Z) is four. Molecular point group is D_{3h} . Halford's table gives

$$2 C_i(4), \quad \infty C_s(4)$$

as possible site symmetries. Since C_i is not a subgroup of molecular point group D_{3h} , the site symmetry of the carbonate ion in aragonite must be C_s . Thus the D_{3h} symmetry of the carbonate ion in an isolated state is lowered to D_3 in calcite and to C_s in aragonite. Then the selection rules are changed as shown in Table 3.

Table 3 . Correlation table for D_{3h} , D_3 and C_s .

Point group	ν_1	ν_2	ν_3	ν_4
D_{3h}	A_1' (R)	A_2'' (I)	E' (I,R)	E' (I,R)
D_3	A_1 (R)	A_2 (I)	E (I,R)	E (I,R)
C_s	A' (I,R)	A'' (I,R)	$A(I,R)+A(I,R)$	$A(I,R)+A(I,R)$

There is no change in the selection rule in going from the free carbonate ion (point group D_{3h}) to calcite (site group D_3): ν_1 is Raman active, ν_2 is infrared active, both ν_3 and ν_4 are Raman and infrared active. In aragonite (site group C_s), ν_1 and ν_2 are both Raman and infrared active, both ν_3 and ν_4 appear as doublets in the infrared and Raman. As Table 3 indicates, the observed spectra are in good agreement with the predictions (30).

The Factor-group Approximation.

Bhagavantam and Venkatarayudu (31) first developed this treatment in 1939. The assumption of the factor group approximation is complete vibrational coupling. This is sometimes called the unit cell approach. The term ' unit cell approach ' arises from further assumption of this method that the frequencies of the crystal may be determined by considering only the atoms contained in a single unit cell. The unit cell is the smallest collection of atoms, all the oscillations of the unit cell represent the smallest set of vibrations. The oscillations of the crystal, then, are the oscillations of a unit cell carried through the crystal by the operations of translation. The observed frequencies in the vibrational spectra of crystals are presumed to result from the

motions of all atoms in the unit cell (and hence the whole crystal), not from the isolated motions of individual molecules.

The group which describes the symmetry of a single unit cell is a finite factor group of the crystal's space group. In terms of the mathematics of group theory, the factor group is formed from the cosets of the invariant subgroup comprised of the translational elements of the space group. The effect is that all the translational elements of the space group form the identity element of the factor group. However, in actual practice one never needs to derive the factor group from the space group, and knowledge of the mathematics involved is not required. The reason is that the factor group is always isomorphous with one of the thirty-two point groups. Furthermore, the isomorphous point group may be identified by deleting the superscript from the Schoenflies notation of the space group. For example, if the space group is C_{2h}^5 , then the factor group is C_{2h} , and the C_{2h} character table would be used as the character table for the factor group. Although the character tables for the factor groups and point groups are identical, the rotation axis and the reflection plane in the point group correspond respectively to the screw axis and the glide plane in the factor group.

The factor group approximation may be accomplished by using correlation chart. The only requirements are knowledge of the space group, site group and molecular point group. For any polyatomic molecules or ions, the number of normal modes and their symmetries are determined first by using the point group for the free species.

The symmetry species under the point group are then correlated to the symmetry species of the site group of the polyatomic molecules or ions, which are then correlated to the symmetry species of the factor group.

For example, potassium chromate, K_2CrO_4 , has space group symmetry D_{2h}^{16} (Pnma) with four formula units per unit cell. The factor group is D_{2h} . The X-ray data reveal that the potassium ions and chromate ions occupy C_s sites so the site group is C_s . The molecular point group is T_d . The correlation of the free chromate ion symmetry species under T_d to the species under site group symmetry C_s and factor group symmetry D_{2h} is shown in the correlation diagram (Table 4).

Table 4 . Correlation diagram of potassium chromate.

Molecular point group	Site group	Factor group
T_d	C_s	D_{2h}
$A_1 (V_1)$ (R)	A' (R,I)	$A_g + B_{2g} + B_{1u} + B_{3u}$
$E (V_2)$ (R)	A' (R,I)	$A_g + B_{2g} + B_{1u} + B_{3u}$
	A'' (R,I)	$B_{1g} + B_{3g} + A_u + B_{2u}$
$T_2 (V_3 + V_4)$ (R,I)	A' (R,I)	$A_g + B_{2g} + B_{1u} + B_{3u}$
	A'' (R,I)	$B_{1g} + B_{3g} + A_u + B_{2u}$

Note. In D_{2h} , modes with subscript g are Raman active, modes with u are infrared active except A_u .

It is noted that the number of frequencies of one species under a particular symmetry may be divided between two or more species under another symmetry, and degeneracies may be eliminated in the correlation process. The splitting of frequencies follows the splitting of the species. It is realized that the number of modes is unaffected by the correlation; only the number of frequencies and their degeneracies are affected.

The relationship between representations of the molecular point group, site group and factor group is found by considering the character tables of them. The character tables of the molecular point group T_d and site group C_s are compared, the symmetry element which occurs in both groups is σ_h . Under this symmetry element, A_1 in T_d corresponds to A' in C_s because they have the same character. E in T_d corresponds to $A' + A''$ in C_s . T_2 in T_d corresponds to $2A' + A''$ in C_s .

Table 5 Character table for C_s .

C_s (h=2)	E	σ_h		
A'	1	1	x, y, R_z	x^2, y^2, z^2, xy
A''	1	-1	z, R_x, R_y	yz, xz

Table 6 Character table for T_d .

T_d (h=24)	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	
A_1	1	1	1	1	1	$x^2 + y^2 + z^2$
A_2	1	1	1	-1	-1	
E	2	-1	2	0	0	$(x^2 - y^2, 2z^2 - x^2 - y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)
T_2	3	0	-1	-1	1	(x, y, z) (xy, xz, yz)

Then the character table of the site group C_s is compared with the factor group D_{2h} . As described above, each representation under σ_h in C_s and σ_{xz} in D_{2h} is correlated and the result is as shown in Table 4.

Table 7. Character table for D_{2h}

D_{2h} (h=8)	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	
A_g	1	1	1	1	1	1	1	1	x^2, y^2, z^2
B_{1g}	1	1	-1	-1	1	1	-1	-1	R_z xy
B_{2g}	1	-1	1	-1	1	-1	1	-1	R_y xz
B_{3g}	1	-1	-1	1	1	-1	-1	1	R_x yz
A_u	1	1	1	1	-1	-1	-1	-1	
B_{1u}	1	1	-1	-1	-1	-1	1	1	z
B_{2u}	1	-1	1	-1	-1	1	-1	1	y
B_{3u}	1	-1	-1	1	-1	1	1	-1	x

The actual spectroscopic data from experiment agree with the predictions from the factor group approximation. The Raman and infrared frequencies for potassium chromate and their assignments are given in Table 8.

Table 8. Vibrational frequencies of potassium chromate(30)

Raman frequencies $\Delta\nu/(\text{cm}^{-1})$	Infrared frequencies $\nu/(\text{cm}^{-1})$	Assignment
918 (B_{2g})	936	
903 (A_g)	910	
881 (B_{2g})	883	ν_3
878 (B_{3g})		
876 (B_{1g})		
867 (A_g)	859	
851 (A_g, B_{2g})	850	ν_1
396 (A_g, B_{2g})	398	
392 (B_{1g})		ν_4
387 (B_{3g})		
386 (A_g, B_{2g})	382	
350 (B_{1g}, B_{2g})		
346 (B_{3g})	342	ν_2
345 (A_g)		

Three types of symmetry: the molecular symmetry (symmetry of the free molecule as given by its point group), the site symmetry (local symmetry of the crystalline environment around the center of gravity of the molecule in the unit cell), and the factor group symmetry (symmetry of a single unit cell) are related to each other. The essential symmetry relationship is that the site group must be a subgroup of both the molecular point group and the factor group. This symmetry restriction leads to some general relationships between site group and factor group selection rules. Thus :

a) A molecular mode cannot be active in the crystal if it is forbidden by the site symmetry.

b) If a mode is active according to the site group symmetry it will give at least one active component under the factor group selection rules.

c) A vibration which degenerates under the site group remains so under factor group.

Classification of the Optical Modes.

The optical modes of vibration of molecular ionic crystals can be classified into three types (32)

1. The Ionic Modes.

The anion and the cation are considered as rigid point ions which are bound to each other by ionic forces. The normal vibrational modes consist of the motions of the anion and the cation, fall in low frequency because of the weak ionic forces.

2. The Covalent Modes.

The atoms are bound together into molecular units by intramolecular forces that are covalent. The normal vibrational modes consist of the internal motions of atoms in the covalently bound molecular units, result in the deformation of the molecular units and fall in high frequency.

3. The Rotational Modes.

The anion is considered as a rigid rotator. These normal modes are due to the rotation of the anion around its center of mass and fall in low frequency. These modes are neither ionic modes since there is no relative motion of the center of mass of the anion and the cation, nor covalent modes since there is no deformation of the anion.

In some cases, the modes of vibration may be classified into two types.

a) The lattice modes or external modes which correspond to ionic and rotational modes. These modes have low frequency.

b) The internal modes which correspond to the covalent modes. These modes have high frequency.

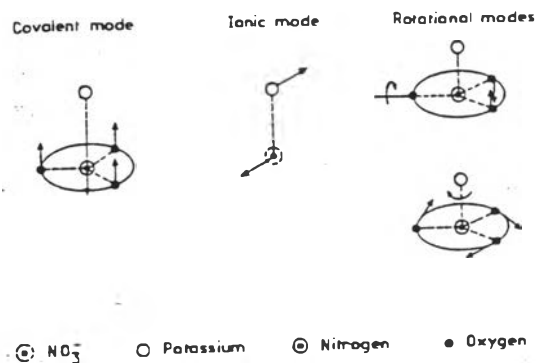


Figure 4. The three types of normal modes of vibration in KNO₃

Theory of Investigation Techniques

Infrared Spectroscopy.

Infrared spectroscopy involves changes in rotational, vibrational energy levels of a molecule, ion or radical after the absorption of energy or the emission of infrared radiation of spectra in the excited states.

From classical theory, a vibrating system can absorb energy from a series of impulses (radiation) only if the impulses strike the system with a frequency that is near the natural frequency of the vibrator. From quantum theory, a molecule will absorb radiant energy if the vibrational frequency of the molecule is the same as the frequency of the radiation, and if the vibration produces a change in dipole moment. The vibrations are not random events but can occur only at specific frequencies governed by the atomic masses and strength of the chemical bonds, this can be expressed as :

$$\bar{\nu} = \frac{1}{2 \pi c} \sqrt{\frac{K}{m_r}}$$

$\bar{\nu}$ is the frequency of the vibration.

c is the velocity of light .

K is the force constant .

m_r is the reduced mass of the atoms.

Selection Rule for Infrared Spectra.

The selection rule for the infrared spectra is determined by the integral :

$$[\mu]_{v'v''} = \int \psi_{v'}(Q) \mu \psi_{v''}(Q) dQ$$

μ is the dipole moment in the ground state.

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ψ is the vibrational eigenfunction.

v', v'' are the vibrational quantum numbers before and after the transition.

Q is normal coordinate.

By resolving the dipole moment into three components in the x, y and z directions, the results are:

$$\begin{aligned} [\mu_x]_{v' v''} &= \int \psi_{v'}'(Q) \mu_x \psi_{v''}(Q) dQ \\ [\mu_y]_{v' v''} &= \int \psi_{v'}'(Q) \mu_y \psi_{v''}(Q) dQ \\ [\mu_z]_{v' v''} &= \int \psi_{v'}'(Q) \mu_z \psi_{v''}(Q) dQ \end{aligned}$$

If one of these integrals is not zero, the normal vibration is infrared active. If all the integrals are zero, the vibration is infrared inactive.

It is possible to decide whether the integrals are zero or not zero from a consideration of symmetry. For fundamental transitions (between ground state $v=0$ and a first excited state $v=1$), $\psi_0(Q)$ is invariant under any symmetry operation, and the symmetry of $\psi_1(Q)$ is the same as that of Q . Thus the integral is not zero when the symmetry of μ_x , for example, is the same as that of Q . If the symmetry properties of μ_x and Q differ in even one symmetry element of the group, the integral is zero. In other words, the integral is not zero when Q belongs to the same species as μ_x .

The normal modes of vibration in carbon dioxide are shown in Figure 5. The individual nuclei carry out a simple harmonic motion in the direction indicated by the arrow. The ν_2 vibrations in CO_2 (ν_{2a} and ν_{2b}) have exactly the same frequency so they are doubly degenerate vibrations.

In the symmetric stretching mode ν_1 , there will be no change in

the dipole moment as the two negative centers move equally in opposite directions from the positive center. The ν_2 and ν_3 vibrations are infrared active, since they result in a change in the dipole moment during the vibration.

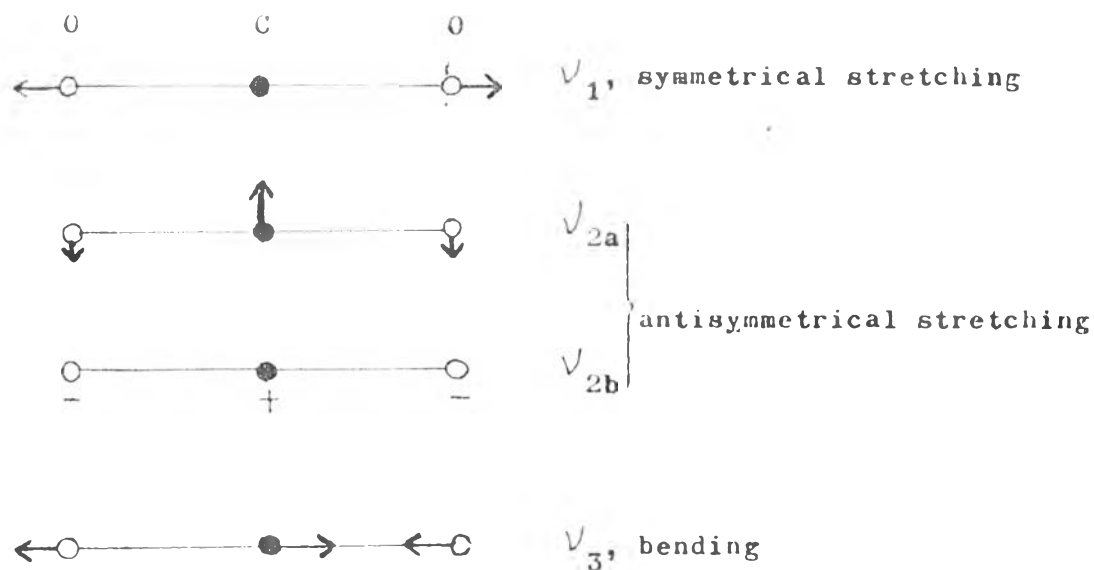


Figure 5. Normal modes of vibration in carbon dioxide.

(+ and - denote the vibrations going upward and downward, respectively, in the direction perpendicular to the paper)

Raman Spectroscopy.

Raman scattering depends on the collision of a quantum of incident light with a molecule. The molecule can be induced by the collision to undergo a pure rotational, a vibrational or a rotation-vibration change. The scattered light has a different frequency from that of the incident light, and the difference corresponds to the energy change which has taken place within the molecule.

Classical Theory of the Raman Effect. (33)

When a molecule is put into a light wave or electric field, it suffers some distortion, the positively charged nuclei being attracted towards the negative pole of the field, the electrons to the positive pole. This separation of charge centers causes an induced electric dipole moment to be set up in the molecule and the molecule is polarized. The magnitude of the induced dipole moment (P) depends on the magnitude of the applied field (E) and the polarizability of the molecule (α) which is a measurement of how readily the electrons are displaced in the field.

$$P = \alpha E$$

If a molecule is not electronically isotropic the magnitude of the induced dipole moment will be different along the electric field component. The induced dipole moments are written:

$$\begin{aligned} P_x &= \alpha_{xx} E_x + \alpha_{xy} E_y + \alpha_{xz} E_z \\ P_y &= \alpha_{yx} E_x + \alpha_{yy} E_y + \alpha_{yz} E_z \\ P_z &= \alpha_{zx} E_x + \alpha_{zy} E_y + \alpha_{zz} E_z \end{aligned}$$

In the α_{ij} elements, the i subscript denotes the direction of the induced dipole moment by the oscillating electric field component in the j direction. $\alpha_{ij} = \alpha_{ji}$.

The polarizability in various directions are represented by a polarizability ellipsoid which is a three-dimensional surface whose distance from the electrical center of the molecule (the center of gravity) is proportional to $1/\sqrt{\alpha_i}$, where α_i is the polarizability along the line joining point i on the ellipsoid

with the electrical center.

For example, a diatomic molecule, H_2 , is shown in Figure 6. The polarizability is anisotropic, the electrons forming the bond are more easily displaced by an electric field applied along the bond axis than one across this direction. The induced dipole moment for a given field applied along the axis is approximately twice as large as that induced by the same field applied across the axis, fields in other directions induce intermediate dipole moments.

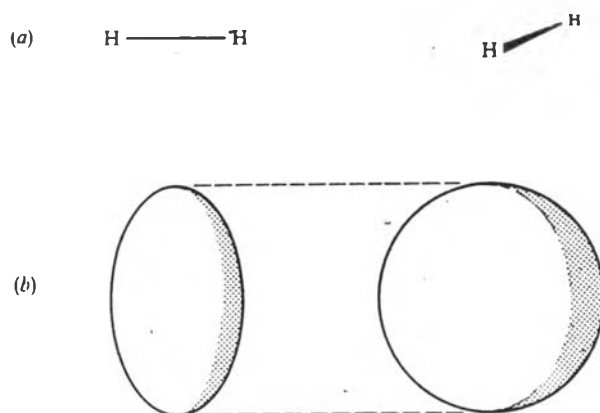


Figure 6. The hydrogen molecule and its polarizability ellipsoid seen from two directions at right angles.

When a molecule is put into an incident beam of frequency ν_0 the electric field (E) is expressed in terms of an amplitude of wave (E_0) and a time dependent term.

$$E = E_0 \cos (2 \pi \nu_0 t)$$

since $P = \alpha E$

so $P = \alpha E_0 \cos (2 \pi \nu_0 t)$

For a vibrating molecule, the molecular polarizability α , also varies with time.

For a diatomic molecule, the polarizability is approximately a linear function of the bond length. In terms of the displacements from the equilibrium bond length,

$$\alpha = \alpha_0 + \left(\frac{\partial \alpha}{\partial Q_1} \right)_0 Q_1 + \dots$$

Q_1 is a displacement coordinate, its value is zero in the equilibrium configuration.

α_0 is the polarizability in the equilibrium configuration of the molecule.

$\left(\frac{\partial \alpha}{\partial Q_1} \right)_0$ is the rate of change of the polarizability with change in the bond length.

Since the molecule is vibrating with the frequency ν_1 , the displacement Q_1 is also a function of time.

$$Q_1 = Q_1^0 \cos(2\pi\nu_1 t)$$

Q_1^0 is the maximum value of the displacement from the equilibrium bond length.

$$\begin{aligned} \text{so, } P &= E_0 \cos(2\pi\nu_0 t) \left[\alpha_0 + \left(\frac{\partial \alpha}{\partial Q_1} \right)_0 Q_1^0 \cos(2\pi\nu_1 t) \right] \\ &= E_0 \alpha_0 \cos(2\pi\nu_0 t) + E_0 Q_1^0 \left(\frac{\partial \alpha}{\partial Q_1} \right)_0 \cos(2\pi\nu_0 t) \cos(2\pi\nu_1 t) \end{aligned}$$

Using the trigonometric identity

$$\cos \alpha \cos \beta = \frac{1}{2} [\cos(\alpha + \beta) + \cos(\alpha - \beta)],$$

$$\text{then } P = E_0 \alpha_0 \cos(2\pi\nu_0 t) + \frac{1}{2} E_0 Q_1^0 \left(\frac{\partial \alpha}{\partial Q_1} \right)_0 \left\{ \cos[2\pi(\nu_0 + \nu_1)t] + \cos[2\pi(\nu_0 - \nu_1)t] \right\}$$

The first term on the right-hand side of equation contains only one frequency ν_0 (the incident radiation). The second term contains two frequencies: $(\nu_0 + \nu_1)$; the Stokes lines and $(\nu_0 - \nu_1)$ anti-Stokes lines. One failure of the classical theory is the prediction that the intensities of Stokes and anti-Stokes lines are the same.

Quantum Theory of the Raman Effect (33)

The Raman effect arises when a beam of intense monochromatic radiation passes through molecules that can undergo a change in molecular polarizability as they vibrate.

The radiation is made up of a stream of photons of energy $h\nu_0$. The scattering of radiation by molecules is pictured in terms of collisions of these photons with the molecules. There are two types of collisions, elastic and inelastic. In the elastic collisions, the photons neither gain energy from nor lose energy to the molecule. The scattered photons still have energy $h\nu_0$. This is called Rayleigh scattering. In the inelastic collisions, the photons gain energy from or lose energy to the molecule. The energy is conserved during the collisions, so

$$h\nu_0 + E_0 = h\nu' + E'$$

The zero subscripts refer to the properties before collision, while primed quantities refer to the properties after the collision.

$$(E_0 - E')/h = (\nu' - \nu_0)$$

In most studies of Raman scattering, the changes in the internal energy ($E_0 - E'$) result from changes in the vibrational energy of the molecules.

A simplified energy level diagram for the Raman effect is shown in Figure 7. The vibrational frequency of a diatomic molecule is designated ν_1 , and the molecule has vibrational energy $(v+1)h\nu_1/2$ where v is the vibrational quantum number.

When the radiation of energy $h\nu_0$ is irradiated on such a molecule, the bulk of the radiation is transmitted. Some may be absorbed, refracted or diffracted. A small fraction of the radiation is elastically scattered in all directions (called Rayleigh scattering). The fraction of the radiation that is inelastically scattered gives Raman effect which involves a quantized exchange of energy between the molecule and the incident radiation. The incident radiation elevates the molecule to a quasi-excited state whose height above the initial energy level equals the energy of the exciting radiation, on the return to the ground state, a vibrational quantum of energy may remain with the molecule. There is a decrease in the frequency of the scattered radiation, $h(\nu_0 - \nu_1)$. This is Stokes Raman scattering. If the scattering molecule is already in an excited vibrational level of the ground state, a vibrational quantum of energy may be emitted from the molecule, leaving it in a lower vibrational level, and thus increasing the frequency of the scattered radiation, $h(\nu_0 + \nu_1)$ which is anti-Stokes Raman scattering.

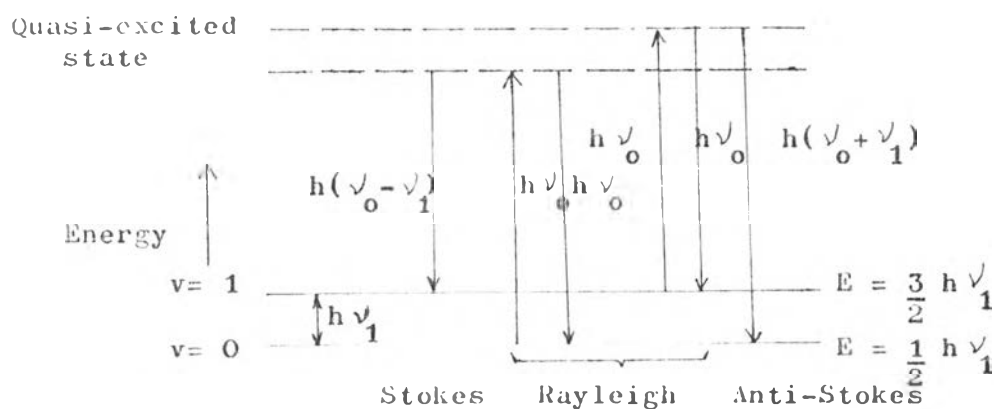


Figure 7. Energy level diagram illustrating the fundamental processes of Raman scattering. The exciting line is of energy $h\nu_0$. Raman bands appear at $h(\nu_0 - \nu_1)$ and $h(\nu_0 + \nu_1)$.

At ordinary temperature the population of molecules in the ground vibrational state is always much greater than in excited vibrational state, and so the intensities of the anti-Stokes lines will always be very much weaker than those of the Stokes lines.

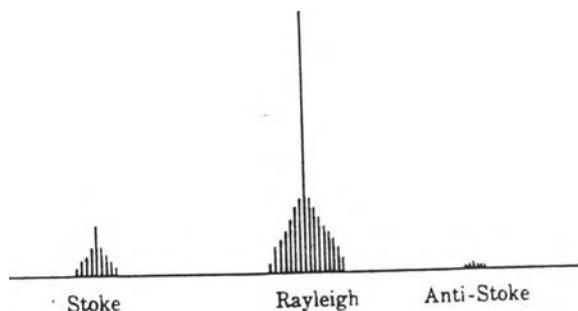


Figure 8. The intensities of the Stokes, anti-Stokes and Rayleigh lines.

Selection Rule for Raman Spectra

The selection rule for the Raman spectra is determined by the integral :

$$[\alpha]_{v'v''} = \int \psi_{v'}(Q) \alpha \psi_{v''}(Q) dQ$$

α is the electronic polarizability of the molecule and consists of six components : α_{xx} , α_{yy} , α_{zz} , α_{xy} , α_{yz} and α_{xz} .

ψ is the vibrational eigenfunction.

v' , v'' are the vibrational quantum numbers before and after the transition.

Q is normal coordinate.

By resolving into six components, the results are :

$$[\alpha_{xx}]_{v'v''} = \int \psi_{v'}(Q) \alpha_{xx} \psi_{v''}(Q) dQ$$

$$[\alpha_{yy}]_{v'v''} = \int \psi_{v'}(Q) \alpha_{yy} \psi_{v''}(Q) dQ$$

$$[\alpha_{zz}]_{v'v''} = \int \psi_{v'}(Q) \alpha_{zz} \psi_{v''}(Q) dQ$$

.....

If one of these integrals is not zero, the normal vibration is Raman active. If all the integrals are zero, the vibration is Raman inactive.

It is possible to decide whether the integrals are zero or not zero from a consideration of symmetry. The integral is not zero when the product of $\psi_{v'}(Q) \alpha \psi_{v''}(Q)$ is totally symmetric (invariant under all symmetry operations of the molecule). In other words, a Raman transition between two vibrational levels v' and v'' is allowed if the product $\psi_{v'}(Q) \psi_{v''}(Q)$ has the same species as at least one of the six components $\alpha_{xx}, \alpha_{xy}, \dots$

Figure 9 shows the polarizability changes with the normal vibrational modes of the carbon dioxide molecule. Only the symmetric stretching ν_1 vibration of carbon dioxide leads to a change in the polarizability, the polarizability ellipsoid becomes larger and then smaller at the frequency of the vibration. For the antisymmetrical stretching ν_2 and bending ν_3 vibrations which lead to a loss in symmetry of the molecule, the polarizability will not change during these vibrations. At the two extremes of a vibration, the vibrational coordinate Q will have the same absolute value but opposite signs. The shape of the molecule will be identical at the two extremes.

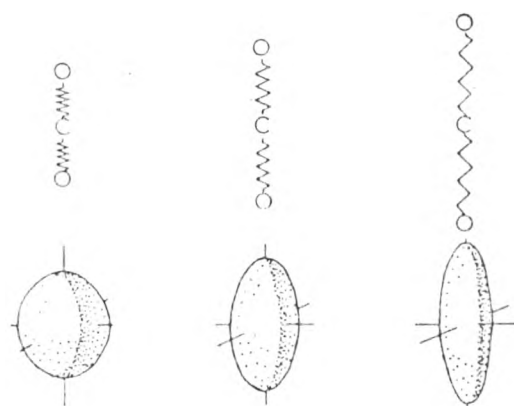
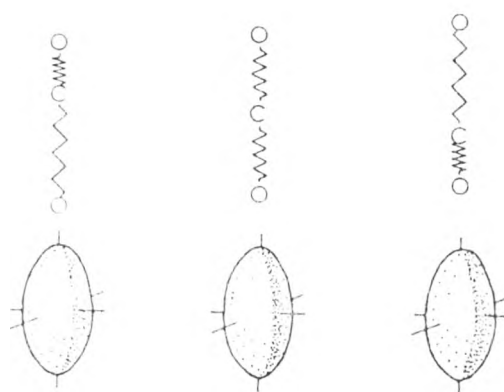
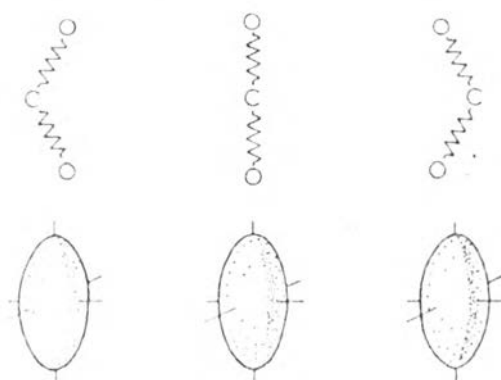
Symmetrical stretching ν_1 Antisymmetrical stretching ν_2 Bending ν_3

Figure 9. Polarizability changes during the vibrations of carbon dioxide.

Diffraction of X-Ray

Diffraction is a scattering phenomenon, a diffraction beam is a beam composed of a large number of scattered rays mutually reinforcing one another.

Diffraction effects with visible light were observed long ago. The geometric principles are demonstrated in Figure 10. A beam of light passes through the clear glass in (a), there is a scratch on the glass which scatters light, in (b), the observer sees a scratch. The two parallel scratches in (c) both scatter light, but interference can occur between the two scattered rays, and the intensity will depend on the angle between the incident ray and the line of observation. Each of the scratches on the glass in (d) will scatter light, but the mutual interference of these scattered rays makes the observed intensity zero except near certain angles.

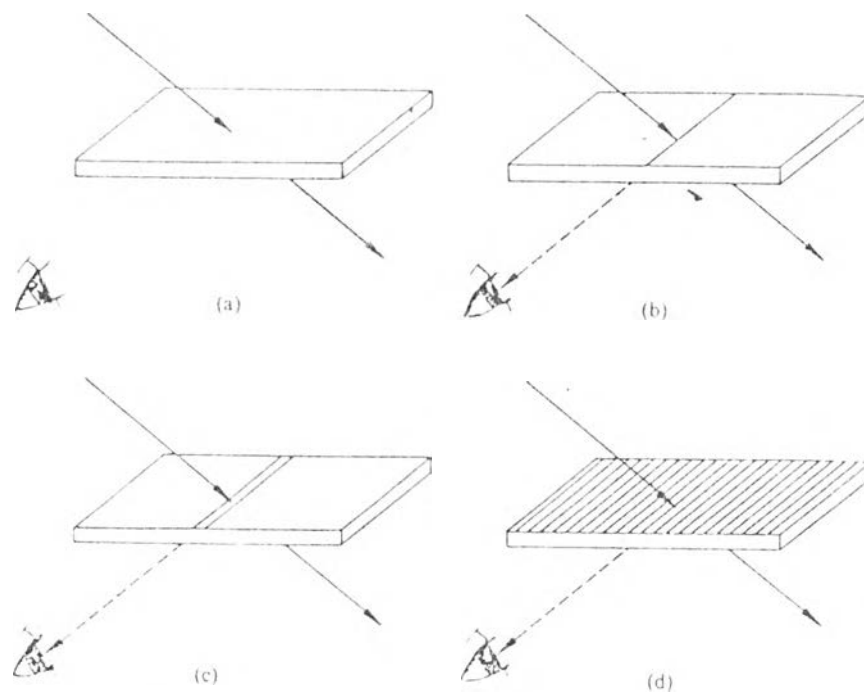


Figure 10. (a) Light passes through clear glass. None scattered to observer. (b) A scratch on the glass scatters light to observer. (c) Radiation scattered by two scratches experiences interference. (d) A diffraction grating. Scattered radiation observed only at certain angles.

The derivation of the angles at which the scattered intensity is maximum is seen on Figure 11. The incident ray makes angle α_0 with the diffraction grating. Before reaching the grating, the incident ray CE travels farther than the incident ray AB, and after passing the grating, the scattered ray BG travels farther than the scattered ray EH. The difference in path lengths of the rays CDEH and ABFG is DE-BF, this difference must be equal to a whole number of wavelengths if the high intensity characteristic of constructive interference is observed at angle α , which is the angle between the scattered ray and the diffraction grating. Therefore, $DE - BF = n \lambda$, where λ is the wavelength of the light and n is an integer. By simple geometry, $DE = a \cos \alpha_0$ and $BF = a \cos \alpha$, where a is the repeating distance, so

$$a (\cos \alpha_0 - \cos \alpha) = n \lambda$$

This is the linear diffraction grating formula.

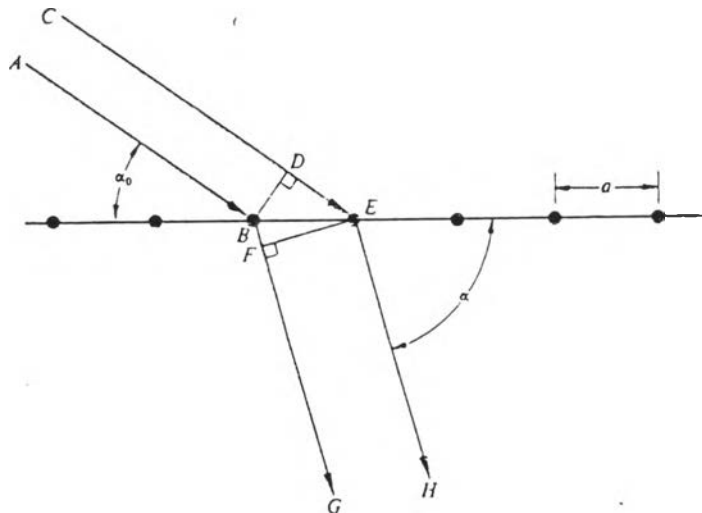


Figure 11. Scattering of light by a diffraction grating with repeating distance a .

When a crystal is in the path of X-rays, electrons will vibrate with the frequency of the incident X-rays, absorbing energy and emitting it as X-rays of the same frequency as the incident rays. The electrons are said to scatter the X-rays. Therefore, the atom as a whole scatters the X-rays. All atoms in the path of X-rays scatter incident X-rays in all directions. In some directions the scattered X-rays interfere with and destroy one other, but in some directions they combine to form diffraction beams.

The diffraction of X-rays by crystals was discovered by Max von Laue in 1912. He suggested that the periodic structure of a crystal might diffract X-rays just as gratings produce diffraction patterns with visible light.

Since crystals are periodic in three dimensions, three equations are required for the diffraction conditions.

$$\begin{aligned} a (\cos \alpha_0 - \cos \alpha) &= h \lambda \\ b (\cos \beta_0 - \cos \beta) &= k \lambda \\ c (\cos \gamma_0 - \cos \gamma) &= l \lambda \end{aligned}$$

α_0 , β_0 and γ_0 are the angles between the incident X-ray beam and the unit cell axes a, b and c.

α , β and γ are the angles between the diffraction beam and the unit cell axes a, b and c.

Constructive interference will occur only when h, k and l are integers. These equations are called the Laue equations.

Shortly after the discovery of X-ray diffraction, Bragg noted that the diffraction of X-rays by a crystal is analogous to the reflection of light by a plane mirror. If a crystal, which has a set of parallel planes with equally spacing d , is in the path of X-rays, (Figure 12), the parallel incident X-rays make an angle θ with these planes, the reflected beams also make an angle θ with these planes. The reflections from the planes will interfere with each other, and there will be constructive interference only when the difference in path length between rays from the planes is equal to a whole number (n) of wavelength (λ). As in Figure 12, the ray striking the second plane travels a distance $AB + BC$ farther than the ray striking the first plane. These two rays will be constructive interfered only when the distance $AB + BC$ is equal to $n \lambda$.

$$\begin{aligned} AB &= BC = d \sin \theta \\ AB + BC &= 2 d \sin \theta \\ n \lambda &= 2 d \sin \theta \end{aligned}$$

This relation is known as the Bragg law.

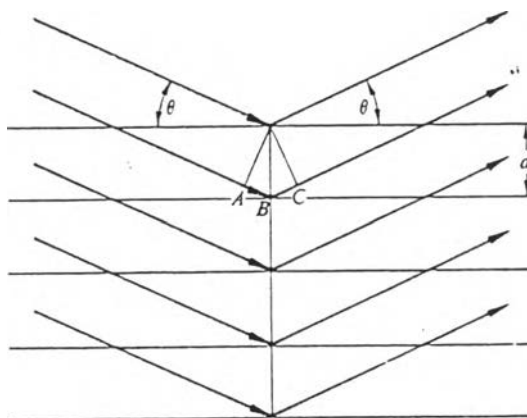


Figure 12. An X-ray beam makes angle θ with a set of planes with interplanar spacing d . For constructive interference $n\lambda = 2d \sin \theta$

The diffraction of X-rays by crystals and the reflection of visible light by mirrors appear similar, since in both phenomena the angle of incident light is equal to the angle of reflected light. However, diffraction and reflection differ in some aspects.

1. The X-ray diffraction beam from a crystal is built up of rays scattered by all the atoms of the crystal which lie in the path of the incident beam. The reflection of visible light takes place in a thin surface layer only.

2. The diffraction of X-rays takes place only at those particular angles of incidence which satisfy the Bragg law. The reflection of visible light takes place at any angle of incidence.

3. The intensity of a diffraction beam is extremely small compared to that of the incident beam. The reflection of visible light by a mirror is almost 100 percent efficient.

X-Ray Powder Diffraction Method.

One of the methods of obtaining diffraction pattern is powder method. This method makes use of a polycrystalline material oriented at random to a monochromatic X-ray beam.

When a tiny crystal in the sample is oriented so that a particular set of lattice planes makes the appropriate Bragg angle to the incident beam, the reflected beam will make an angle with the undeviated beam as shown in Figure 13 (a).

The identical lattice planes of other tiny crystals can be oriented at the same angle θ to the beam and send out the reflected beam in the same angle 2θ around the incident direction. These reflected beams will form a cone (in b). Simultaneously, other lattice planes with different spacing satisfy the Bragg condition and generate other cones (in c) .

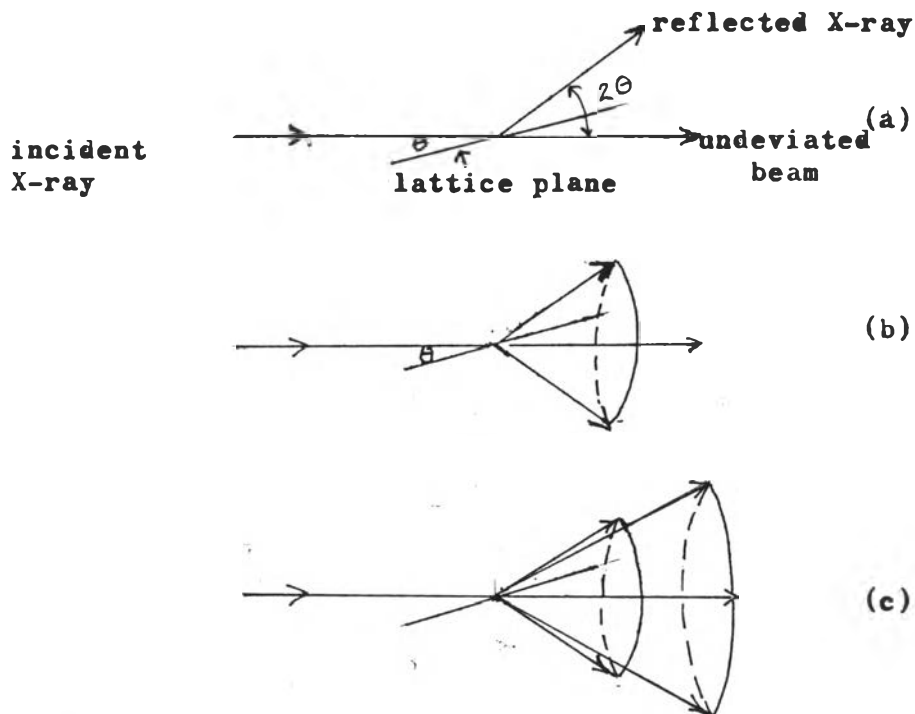


Figure 13. a) Bragg condition for X-ray diffraction.

b) A cone of reflected ray for the identical lattice planes.

c) Cones of reflected ray which have different angles.

The detection of X-ray diffraction can be achieved in one of two ways, by using film method or electronic counting technique. In both cases, the aim is to measure both the 2θ angle and the relative intensity of each reflected beam from the sample.

In film method, a photographic film is placed in the path of reflected radiation, a curved line will be produced for each set of planes of the lattice, and the corresponding θ can be obtained from the position of the line on the film.

In electronic method, proportional counters are used to detect and measure the reflected rays. It yields an electrical pulse from each X-ray photon absorbed in the detector. These pulses are then amplified and counted by a circuit. The powder pattern appears as a series of peaks, the position of each peak corresponds to the position of each line and the intensity of each peak is measured from peak height.

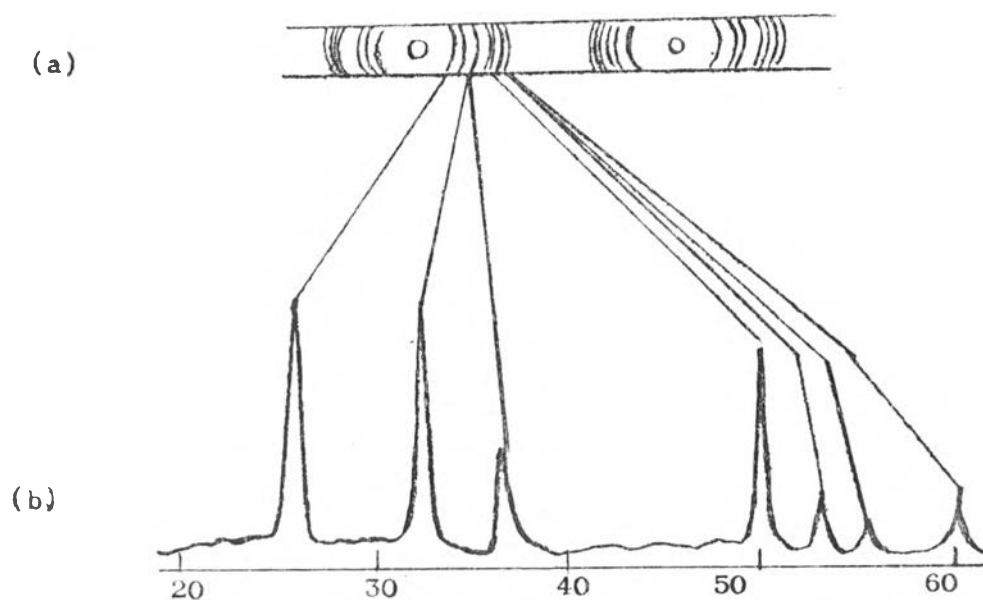


Figure 14. a) The powder photograph pattern.

b) The proportional-counter diffractometer pattern.