DISTORTION INDUCED IR AND RAMAN ACTIVITY AND RELATED ASPECTS OF VIBRATIONAL DYNAMICS OF MOLECULAR UNITS IN CRYSTALS

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Thesis

to my parents

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I certify that the thesis entitled " DISTORTION INDUCED IR AND RAMAN ACTIVITY AND RELATED ASPECTS OF VIBRATIONAL DYNAMICS OF MOLECULAR UNITS IN CRYSTALS " submitted by Shri Ramendu Bhattacharjee for the degree of Doctor of Philosophy of the North-Eastern Hill University, Shillong, embodies the record of original investigation carried out by him under my supervision. He has been duly registered, and the thesis presented is worthy of being considered for the award of the Ph.D. Degree. This work has not been submitted for any Degree of any other University.

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CERTIFICATE

This is certified that Shri R. Bhattacharjee has cleared the following four Pre-Ph.D. courses obtaining on average 'A' grade (on seven point scale).

Course	G.P.A.	Grade
1) Group theory and Molecular Physics	4.88	A
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DISTORTION INDUCED IR AND RAMAN ACTIVITY AND RELATED ASPECTS OF VIBRATIONAL DYNAMICS OF MOLECULAR UNITS IN CRYSTALS

In the last few years, a significant number of papers (Luty and Rohleder 1972; Pimentel and McClellan 1952; Pimentel et. al. 1955; Suzuki et. al. 1968; Yamada and Person 1964) and reviews (Califano et. al. 1981; Person and Steele 1974) have appeared on the subject of Raman and infrared intensities of bands due to vibrational modes of molecular units in crystals. The main objective of all these reports has been to study : (i) the relative intensity of Davydov splitting (dichroic ratios), (ii) the change in intensity on condensation and (iii) the intensity of bands due to lattice modes. However, no attention seems to have been paid to formulate a quantitative theory of the phenomenon that activates the forbidden modes of a molecular unit which attains distorted structure and occupies a lattice site of symmetry lower than that of its free state. The phenomenon is associated qualitatively with the lowering of local symmetry of the unit and modified selection rules are derived using well known group theoretical techniques viz, the unit cell (Bhagavantam and Venkatarayudu 1939) and local symmetry approaches (Halford 1946; Hornig 1948; Winston and Halford 1949). Thus the main aim of this thesis is to give a quantitative theory of the phenomenon, using group theory and perturbation methods. It has been revealed that these transitions become active due to structural distortion of the unit and they need to be ascribed as distortion induced transitions. Such transitions of different symmetry species are characterised by different order of distortion induced activity (DIA), i.e. DIA-I/DIA-II/..../DIA-h representing first/second/..../higher order effect of distortion. Normally, the transition occuring only as first order effect in the polar type of distortion are expected to gain observable intensity; others may result in perceptible intensity in exceptional situations. Therefore, for the better understanding of the observed IR and Raman spectra it is highly desirable to know the type and order of distortion induced activity (DIA) of the forbidden modes of a molecular unit. The usefulness of the theory in the study of the forbidden modes of molecular units in liquids and gases (under high pressure) has also been discussed. The intensity of such transitions has been quantitatively associated with the type and magnitude of distortion which is useful in understanding the microscopic mechanism of structural phase transition.

The thesis is divided into six chapters. Chapter I, presents various aspects of vibrations of molecules and crystals, IR and Raman spectroscopy, etc. relevant to the present investigation.

Chapter II, reviews the work pertaining to the vibrational selection rules for molecules in their gaseous as well as in crystalline states. It discusses at length the two well known techniques (alongwith their merits and demerits) i.e. the unit cell approach and the local symmetry approach applied to crystalline solids for determining IR and Raman active species. The application of these techniques has been illustrated by an example of our study and analysis of the IR and Raman spectra of Rochelle Salt ($NaKC_4H_4O_6.4H_2O$); this includes the details of experimental set up and techniques used for sample preparation and recording of the spectra.

Chapter III, describes the formulation of the theory of distortion induced activity (DIA) of forbidden modes of molecular units in crystals. The polar and non-polar site symmetry cases are discussed separately. The central idea of the work is that the crystal field which is non-uniform in strength serves as the source of perturbation and distorts the unit and hence modifies its dynamics and selection rules; the results have been analysed using group theory.

Chapter IV, presents the symmetry classification of forbidden modes of molecular units belonging to different point groups attaining first/second/..../higher order of DIA; in each case the results have been analysed for all possible site symmetries.

Chapter V, discusses the usefulness of the theory in the study of structural phase transition in crystals. The scope and the usefulness of the theory in determining the effective symmetry and the IR and Raman activity of molecular units in liquids and gases (under high pressure) has also been discussed.

Chapter VI, presents the summary of the work alongwith the important conclusions.

CHAPTER I

INTRODUCTION

1.1 GENERAL

The vibrational spectroscopy dealing with absorption (IR absorption) and inelastic scattering (Raman scattering) of photons has been used to make significant contributions in understanding the complex structure and dynamical behaviour of polyatomic systems. It provides valuable information pertaining to the nature as well as the magnitude of several physical parameters (such as intra- and inter-molecular forces, bond length, bond angle, identification of functional groups in compounds) and thermodynamic properties (specific heat, entropy, free energy, dissociation energy, heat of formation etc). In order to obtain these informations more importance has generally been given to the allowed modes in comparison to the so called forbidden modes, which generally appear with weak intensity in the spectra, particularly, of solids, liquids and high pressure gases. However, the study of forbidden modes has drawn much more attention in recent years. It would be interesting to study the conditions under which the forbidden modes become active with significant intensity accessible to experimental observation. This type of investigation may shed light on the local effective symmetry of any molecular unit in solids, liquids and gases. It has been found to be of great significance in the study of microscopic mechanism of the structural phase transition in crystals like $(NH_4)_2SO_4$ and $(NH_4)_2BeF_4$. However, no quantitative theory is available for understanding the activity of forbidden modes of molecules in different environments - solids, liquids and gases under high pressure. It is, therefore, the aim of the present thesis to present a systematic quantitative theory of the IR and Raman activity of forbidden modes of molecular units in different states under different conditions. The various topics and concepts related to the present investigation are briefly introduced in this chapter.

1.2 DYNAMICS OF A MOLECULE

The dynamics of a N-atomic molecule can be described in terms of 3N degrees of freedom or modes of motion (3 translations + 3 rotations + (3N-6) vibrations for a non-linear molecule and 3 translations + 2 rotations + (3N-5) vibrations for a linear molecule) (Colthup et. al. 1975; Herzberg 1945; Wilson et. al. 1955). In a crystal, all the 3N degrees of freedom of the molecule become oscillatory. The oscillations arising from translations and rotations of the molecule are known as translatory and libratory lattice vibrations, respectively. These translatory and libratory vibrations are often referred to as external vibrations to distinguish them from the so-called internal vibrations of the individual molecule. In general, all these vibrations in a crystal are governed by inter- and intra-molecular interactions, which decide most of the microscopic and macroscopic properties of the molecule in isolation as well as in bulk. Although, the dynamics of a molecule or a solid appears to be complex, it may be described in terms of simple modes of motion known as normal modes (3N in number).

1.3 NORMAL MODE OF VIBRATION

A normal mode of vibration has the following properties (Chang 1971; Colthup et. al. 1975; Herzberg 1945; Wilson et. al. 1955): Each atom of the system executes simple harmonic oscillation about its equilibrium position with same frequency and phase. The relative amplitude of oscillation and velocity of atoms depend on their mass and the nature of vibration; they may have different magnitude and direction satisfying the fact that the molecule neither rotates nor its centre of gravity translates.

1.4 IR ABSORPTION

The IR absorption is a phenomenon involving interaction between electromagnetic radiation and matter. To a first order approximation, it arises due to change in electric dipole moment ($\vec{\mu}$) of the molecular unit during its excitation to a higher energy state. It may, however, also arise due to change in electric moments of higher order, magnetic moments, etc., but the absorption induced by such interactions is negligibly weak. For example, if a typical transition induced by the electric dipole moment is assumed to take place at a rate of 10^8 sec^{-1}, the transitions induced by magnetic dipole and electric quadrupole moments are expected to take place at a rate 10^3 and 1 sec^{-1}, respectively (Schutte 1976). The intensity of an IR absorption band is proportional to the square of the change in dipole moment caused by the molecular vibration (Herzberg 1945). Since frequencies of vibrations of molecules and solids fall in IR range of electromagnetic radiations, enough informations (such as force constants, nature of intra- and inter-molecular interactions, symmetry and structure, etc.) about these systems can be obtained from IR absorption spectra.

1.5 RAMAN SCATTERING

Raman scattering is an inelastic scattering of photons by molecular systems. In this process the frequency of scattered light shifts from the incident frequency by a quantum necessary for certain kind of excitation of the sample. The excitation may be translational (e.g. lattice modes of crystal), rotational, vibrational or electronic in nature. The importance of the phenomenon lies in the fact that the difference between the frequencies of scattered and incident radiations carries information about the dynamics and structure of the scatterer. When scattered frequencies are found to be lower than the frequency of incident light, the phenomenon is known as Stokes Raman scattering, whereas, if the scattered frequencies are found to be higher than the frequency of incident light it is known as anti-Stokes Raman scattering. These events are shown schematically in Figure 1.1. Since anti-Stokes emission depends on the number of molecules in the initial excited state, which according to Boltzmann statistics is less than that in the ground state, it is weaker than Stokes emission. The Stokes and anti-Stokes Raman scattering can be explained in terms of energy transfer between the scattering system and the incident radiation. When a system (in ground state) interacts with radiation of wavenumber $\tilde{\nu}_i$, it makes an upward transition from its lower energy level E_1 to an upper energy level E_2 (Figure 1.1a) In the process the system gains energy, $\Delta E = E_2 - E_1$, from the incident radiation. If the wave number difference associated with two levels is $\tilde{\nu}_v$, then $\Delta E = hc\,\tilde{\nu}_v$. This energy is made available by annihilation of a photon $(E = hc\,\tilde{\nu}_i)$ of incident radiation and creation of a photon of smaller energy, hc($\tilde{\nu}_i - \tilde{\nu}_v$); in the process the system is excited to a higher state. On the other hand, the interaction of incident radiation with the system in excited state may cause a downward transition from a higher energy level E_2 to a lower energy level E_1(Figure 1.1b). In this case, an amount of energy $E_2 - E_1 = hc\tilde{\nu}_v$ is made available by the system. In the process a photon of energy $hc\tilde{\nu}_i$ is annihilated and another photon of energy hc($\tilde{\nu}_i + \tilde{\nu}_v$) is created; and the system deexcites to its lower energy state.

Raman scattering is usually weak in intensity hence a strong source of incident radiation is needed for its observation. Stimulated interest in its study and applications therefore arose only after the invention of high power and highly monochromatic continuous laser sources. Developments in the field have since been very fast and several new phenomena, such as resonance-, surface-enhanced-, stimulated-, hyper-, inverse-, coherent anti-Stokes-, coherent Stokes-Raman scattering have been discovered. Stimulated Raman gain spectroscopy, photo-acoustic Raman spectroscopy, Raman-induced Kerr effect spectroscopy, asterisk spectroscopy, etc. have also been developed (Beattie and Black 1977; Bist et. al. 1985; Long 1977; Tobin 1971).

1.6 IR AND RAMAN SELECTION RULES

The transition moment M_{fi} for the transition between initial state $|i\rangle$ and final state $|f\rangle$ is given by

$$M_{fi} = \langle f|\tilde{M}|i\rangle \qquad \ldots \qquad (1.1)$$

where, $\tilde{M}$ is the transition operator. An allowed transition is characterised by non-zero value of M_{fi}. In general, it is difficult to find out exact eigenfunctions $|f\rangle$ and $|i\rangle$ of a system, and so the value of M_{fi}. Group theoretical methods are, therefore, used to predict its zero or non-zero value. M_{fi} attains non-zero value when the product of the symmetry species (i.e. $\Gamma^{f} \otimes \Gamma^{\tilde{M}} \otimes \Gamma^{i}$) of the functions appearing in the term $\langle f|\tilde{M}|i\rangle$ have at least one component which is totally symmetric. When this condition is not satisfied M_{fi} vanishes and the transition is said to be forbidden. Generally the transitions which take place from the vibrational ground state are considered to be of prime importance. In such a case $|i\rangle$ belongs to the totally symmetric species. Hence, the transition is allowed only if $|f\rangle$ has the symmetry of one of the several components of $\tilde{M}$.

For IR absorption, $\tilde{M}$ is $\vec{\mu}_{\rho}$ (ρ = x, y or z); where $\vec{\mu}_{\rho}$ is electric dipole moment of the molecule. The symmetry behaviour of $\vec{\mu}_x$, $\vec{\mu}_y$ and $\vec{\mu}_z$ is same as that of $\hat{x}$, $\hat{y}$ and $\hat{z}$ components of a translational vector, respectively (Herzberg 1945).

Therefore, $|f\rangle$ belonging to the symmetry species of $\hat{x}/\hat{y}/\hat{z}$ are IR allowed.

For Raman scattering, $\tilde{M}$ is $\tilde{\alpha}_{\rho\sigma}$ (ρ = x, y or z and σ = x, y or z); where $\tilde{\alpha}_{\rho\sigma}$ is the polarizability tensor. The six components $\tilde{\alpha}_{xx}$, $\tilde{\alpha}_{yy}$, $\tilde{\alpha}_{zz}$, $\tilde{\alpha}_{xy}$, $\tilde{\alpha}_{yz}$ and $\tilde{\alpha}_{zx}$ of the polarizability tensor transform like the products xx, yy, zz, xy, yz and zx respectively (Herzberg 1945) and Raman allowed modes belong to the symmetry species of these products.

It is clear from the above discussion that Raman scattering and IR absorption are governed by different selection rules. They are obviously complementary techniques for getting information about the molecular dynamics. A mode which is not observed in IR absorption may be seen in Raman scattering and vice versa. Thus, for ~~the~~ better understanding of the molecular dynamics a study of both the IR absorption and Raman scattering is necessary.

1.7 IR BAND INTENSITY

The intrinsic absorption corresponding to a transition between $|f\rangle$ and $|i\rangle$ states is given by

$$dI(\nu) = - hc\nu I(\nu)\ B_{fi}(N_i - N_f)dl \quad \ldots \ (1.2)$$

where, B_{fi} is the Einstein co-efficient related with the transition moment as

$$B_{fi} = \left(\frac{8\pi^3}{3c\,h^2} \right) \left| \langle f \mid \vec{\mu}_\rho \mid i \rangle \right|^2$$

$\nu = \nu_{fi} = (E_f - E_i)/hc$, N_i and N_f are the number of molecules per unit volume in the initial and final states, respectively, $I(\nu)$ is the intensity of light beam at frequency ν after traversing a distance dl in the absorbing medium and $dI(\nu)$ is the absorbed intensity at the same frequency.

Since, the population of excited centres N_f can be considered to be negligibly small compared to N_i, equation (1.2) can be recast as

$$dI(\nu) = - hc\,\nu\, I(\nu)\, B_{fi}\, N_i\, dl \qquad \ldots \quad (1.3)$$

Moreover, equation (1.3) can also be expressed in terms of absorption coefficient a_ν at frequency ν as

$$dI(\nu) = - I(\nu)\, a_\nu\, dl \qquad \ldots \quad (1.4)$$

comparing equations (1.3) and (1.4) a_ν can be written as

$$a_\nu = - \frac{1}{I(\nu)} \cdot \frac{dI(\nu)}{dl} = hc\,\nu\, B_{fi} \cdot N_i \qquad \ldots \quad (1.5)$$

On integrating, equation (1.5) becomes

$$I(\nu) = I_0(\nu)\, \mathrm{Exp}\,(-a_\nu l) \qquad \ldots \quad (1.6)$$

where, $I_o(\nu)$ is the total incident intensity at frequency ν. The equation (1.6) is known as Beer-Lambert law (Banwell 1972). From equation (1.5) we have

$$a_\nu = \frac{1}{l} \log_e \frac{I_o(\nu)}{I(\nu)} = \frac{2.303}{l} \log_{10} \frac{I_o(\nu)}{I(\nu)} \qquad \ldots (1.7)$$

and

$$A_\nu = \log_{10} \frac{I_o(\nu)}{I(\nu)} = \frac{1}{2.303} a_\nu . l = k \cdot l \qquad \ldots (1.8)$$

where A_ν is absorbance and k is Bunsen Rascoe extinction coefficient.

In developing equation (1.7), it was assumed that the absorption due to the transition i ⟶ f gives rise to an infinitely sharp spectral line. However, a spectral line is always broadened due to the uncertainty, the Doppler effect, and the influence of intermolecular forces (Turrell 1972). Hence, every transition is having some finite width and the integrated absorption over the full band has more significance than the peak absorption. Consequently, the absorption coefficient, a_ν is usually integrated over the full absorption band and expressed in absolute unit as

$$a_{int} = \int_{band} a_\nu \, d\nu$$

$$= \frac{2.303}{l} \int_{\text{band}} \log_{10} \frac{I_o(\nu)}{I(\nu)} \, d\nu$$

$$= \frac{2.303}{l} A_{int} \qquad \ldots \quad (1.9)$$

where, $A_{int} = \int A_{\nu} \, d\nu$.

Most of the commercially available double beam IR spectrometers measure the quantity $I(\nu)$ (c.f. equation (1.6)), except some spectrometers which measure the quantity A_{ν} (c.f. equation (1.8)). The computation of a_{int} from spectra obtained on either type of the spectrometers becomes complicated because of the difficulties encountered in measurements of $I_o(\nu)$ and/or l. However, A_{int} can easily be deduced from the spectra recorded on the latter type of the spectrometers. A_{int} is only of relative importance. Its approximate value can be found by multiplying peak absorptivity with full width at half maximum intensity (FWHMI). Moreover, A_{int} can also be estimated by counting the squares on the graph paper or measuring the area of bands using a planimeter.

1.8 RAMAN BAND INTENSITY

In terms of polarizability theory of Raman intensity, developed by Placzek (1934), Raman scattering arises from the ground state polarizability which depends on molecular vibrations. Hester (1967) and Woodward (1967) have discussed the band polarizability theory in later years. Tang and Albrecht (1970) have reviewed the subject in detail.

In single crystal studies, the Raman band intensity is generally treated in terms of scattering efficiency S defined as (Sherwood 1972; Smith 1948)

$$S = \frac{N\ (\nu_s)_{d\Omega}}{N\ (\nu_i)} \qquad \ldots \qquad (1.10)$$

where, $N\ (\nu_s)_{d\Omega}$ represents the number of photons of frequency ν_s produced per unit time per unit cross-sectional area of the crystal in the solid angle $d\Omega$ about the direction of observation and $N\ (\nu_i)$ represents the number of incident photons of frequency ν_i per unit time per unit cross-sectional area.

For unpolarized light and right angle scattering Smith (1948) has computed

$$S = \frac{3h\ L\ d\Omega\ (\nu_i - \nu)^4}{2\pi\sigma' C\ \nu} \left| \langle f \mid \tilde{\alpha}_{\rho\sigma} \mid i \rangle \right|^2 \times \left[1 - \mathrm{Exp}\left(\frac{-hc\ \nu}{KT} \right) \right]^{-1} \qquad \ldots \qquad (1.11)$$

where, $\nu = \nu_{fi} = (E_f - E_i)/hc$, L is the effective length of the crystal from which the scattered radiations are received at the slit of the spectrometer, σ' is the density of scattering centres, K is the Boltzmann's constant and T is the absolute temperature.

Although, the experimentally observed Raman band intensity can be correlated to the value of S, it is only of relative importance and better result can be derived by considering the integrated intensity of a band instead of considering only the peak intensity. The approximate value of the integrated intensity of a band can be found out by multiplying peak intensity with full width at half the maximum intensity (FWHMI) of the band.

1.9 DEPOLARIZATION RATIO FOR LIQUIDS

Information regarding the symmetry of normal modes can often be obtained from Raman experiments if we can determine the degree of depolarization ratio ρ, of the scattered light. The depolarization ratio is defined as the ratio of the intensity of the scattered light polarized perpendicular to the XY plane, $I_\perp$, to that polarized parallel to this plane, $I_\parallel$, when the incident light approaches along the Z-axis and the scattered light is observed at right angle to the Z-axis (c.f. Figure 1.2) (Herzberg 1945),

$$\rho = \frac{I_\perp}{I_\parallel} \qquad \dots \qquad (1.12)$$

when the incident light is plane polarized and the required intensities are computed and averaged over all possible orientations of the molecule, for Raman scattering ρ is found to be,

$$\rho = \frac{3(\tilde{\alpha}'_a)^2}{45(\tilde{\alpha}'_s)^2 + 4(\tilde{\alpha}'_a)^2} \quad \ldots \quad (1.13)$$

where, $\tilde{\alpha}'_s$ and $\tilde{\alpha}'_a$ are *respectively, the symmetric (or isotropic)* and asymmetric (or anisotropic) part of derivative of the polarizability. According to equation (1.13), this means that ρ for all vibrations which are not of the totally symmetric species will be 3/4, while only those of the totally symmetric species can have a value of ρ less than 3/4. This property is extremely useful, in identifying the totally symmetric vibrations, particularly in liquid phase spectra.

1.10 BAND SHAPES

For bands well isolated from their neighbouring bands, most commonly used functions for describing band shapes are Gaussian (Tobin 1971) i.e.

$$I(\nu) = I(\nu_o)\ \mathrm{Exp} - \left\{ \frac{(\nu - \nu_o)^2}{\underline{a}} \right\} \quad \ldots \quad (1.14)$$

or Lorentzian i.e.

$$I(\nu) = I(\nu_o)\ \frac{\underline{b}^2}{\underline{b}^2 + (\nu - \nu_o)^2} \quad \ldots \quad (1.15)$$

These functions are symmetrical around ν_0 of the band peak. I (ν_0) is the maximum intensity at ν_0, and a and b are adjustable parameters. For Gaussian band the full width at half the maximum intensity (FWHMI) is $2\sqrt{a \log_e 2}$ while that for Lorentzian is 2b.

1.11 PHONONS

The elastic waves in solids having quantized energy are known as phonons (Beattie 1977; Kittel 1977; Turrell 1972). For any excited mode of vibration of a molecule in liquid or gaseous state, disturbances are confined only to the single molecule, while they propagate in all directions in solids. Thus the vibration of a free molecule lo~~o~~ses its identity to a large extent in solids

The acoustic phonons are those in which all atoms/molecules in unit cell execute vibration with same phase and same amplitude. There are only three such phonon branches in a crystal. On the other hand, the optical phonons are characterized by vibrations of particles in the unit cell causing no movement of centre of mass of the cell. Hence, there are 3N-3 such branches in the N-atomic unit cell.

The longitudinal and transverse phonons are respectively characterized by the displacements of the particles along and perpendicular to phonon wave vector. The energy transfer between a phonon and photon is governed by the law of conservation of momentum and energy. Since, the electromagnetic radiations are transverse in nature, they can not interact with longitudinal phonons. Therefore, only transverse phonons can be studied in transmission spectroscopy. However, in Raman scattering and reflection spectroscopy one can study both types of phonons.

1.11.1 CONSERVATION LAWS FOR PHONONS

The conservation laws pertaining to the momentum and energy of phonons are mathematically expressed by

$$\vec{k} + \underline{n}\vec{G} = \sum_i \pm \vec{q}_i \qquad \ldots \quad (1.16)$$

and

$$hc\tilde{\nu} = \sum_i \pm hc\,\tilde{\nu}_i \qquad \ldots \quad (1.17)$$

where, $\vec{k}$ and $hc\tilde{\nu}$ are the wave vector and energy of the incident photons, respectively; q_i and $hc\,\tilde{\nu}_i$ are the corresponding quantities for an ith phonon; $\vec{G}$ is the reciprocal lattice vector and $\underline{n}$ is an integer. Positive and negative signs represent the emission and absorption processes, respectively. Since for IR photon $\vec{k} \simeq 0$, we have

$$\underline{n}\vec{G} = \sum_i \pm \vec{q}_i \qquad \ldots \quad (1.18)$$

For single phonon process n has to be zero. Obviously, $\vec{k} = \vec{q}_i \simeq 0$ and such a process occurs at the centre of Brillouin zone. On the other hand, for multiphonon processes $n = 0, \pm 1$, etc. and the phonons involved may have finite wave vectors. Therefore, spectra due to multiphonon processes must be continuous; however, some structure may be observed due to singularities in dispersion curves.

1.11.2 LONGITUDINAL AND TRANSVERSE SPLITTING

The longitudinal and transverse phonon branches of a mode have same frequencies except for polar modes where the longitudinal branch generally has higher frequency than the transverse branch. According to Born and Huang (1954) this happens due to the presence of long range electrostatic interaction. Thus large splittings are observed in ionic crystals.

According to Lyddane-Sachs-Teller (LST) relation, the split frequencies are related to the static dielectric constant ϵ_0 and high frequency dielectric constant ϵ_∞ through the relation

$$\prod_i \frac{\nu_i \text{ (LO)}}{\nu_i \text{ (TO)}} = \left(\frac{\epsilon_0}{\epsilon_\infty} \right)^{\frac{1}{2}} \qquad \ldots (1.19)$$

where, the product over i includes every all polar modes.

1.12 APPROXIMATION METHODS

The physics of a system is theoretically described by Schrödinger equation and its solution. The time-independent Schrödinger equation for a system is written as (Ghatak and Lokanathan 1977),

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V \right] u_a(r) = E_a \, u_a \, (r) \qquad \ldots \quad (1.20)$$

or, in short

$$H \, u_a(r) = E_a \, u_a(r) \qquad \ldots \quad (1.21)$$

This equation is also known as an eigenvalue equation. Here the u_a is an eigenfunction defining an eigenstate of energy E_a of Hamiltonian H. There are only few physical situations for which Schrödinger equation can be exactly solved. For the large majority of systems of physical interest, this presents great mathematical difficulties. Therefore, approximation methods are used to find approximate solutions that describe the physics of the system as accurate as possible. There are several such methods (e.g. time-dependent perturbation method, time-independent perturbation method, variational method, the WKB (Wentzel-Kramer-Brillouin) method) which are selectively used depending upon the nature of the problem. These methods are discussed by several authors (Avery 1972; Dicke and Wittke 1973; Dirac 1958; Ghatak and Lokanathan 1977; Gottfried

1966; Landau and Lifshitz 1974; Merzbacher 1961). In the following, we summarize only the technique of the time-independent perturbation, used in the present work.

Time-independent Perturbation Method

In this technique the Hamiltonian is broken into two parts, such that

$$H = H^{o} + H' \qquad \ldots \qquad (1.22)$$

Here, H^{o} is much larger than H', i.e., the energy of the system in its possible states, defined by H^{o}, is much larger than that accounted for by H'. Further, H^{o} is such that the Schrödinger equation can be exactly solved and we have

$$H^{o} | a \rangle = E^{o}_{a} | a \rangle \qquad \ldots \qquad (1.23)$$

Here, $|a\rangle$ stands for an eigenfunction defining a state of eigenvalue E^{o}_{a}. However, $|a\rangle$ is not the correct eigenfunction and does not describe the system accurately. In order to get more accurate description of the system,correction to $|a\rangle$ is necessary. This correction depends upon H' which is treated as perturbation over the system defined by H^{o}. The first order, second order correction introduced by H' in energy eigenvalue and eigenfunction are added together to get more accurate energy eigenvalue and eigenfunction. In otherwords, we have (Avery 1972),

$$E = E^{o} + E^{1} + E^{2} + \qquad \ldots \qquad (1.24)$$

$$|a\rangle = |a^{o}\rangle + |a^{1}\rangle + |a^{2}\rangle + \qquad \ldots \qquad (1.25)$$

here, the superscripts 1,2,...etc. signify correction of first order, second order,...etc. respectively. A simple mathematical derivation leads to (Avery 1972),

$$E_a^1 = \langle a|H'|a\rangle \quad \ldots \quad (1.26)$$

$$E_a^2 = \sum_{k\neq a} \frac{\langle a|H'|k\rangle \langle k|H'|a\rangle}{(E_a^o - E_k^o)} \quad \ldots \quad (1.27)$$

$$|a^1\rangle = \sum_{k\neq a} |k\rangle \frac{\langle k|H'|a\rangle}{(E_a^o - E_k^o)} \quad \ldots \quad (1.28)$$

$$|a^2\rangle = \sum_{k\neq a} \sum_{m\neq a} \frac{|k\rangle \langle k|H'|m\rangle \langle m|H'|a\rangle}{(E_a^o - E_k^o)\ (E_a^o - E_m^o)} - \sum_{m\neq a} \frac{|m\rangle \langle m|H'|a\rangle \langle a|H'|a\rangle}{(E_a^o - E_m^o)^2} \quad \ldots \quad (1.29)$$

The condition for perturbation series (equation (1.24) and (1.25) to converge is that the successive terms must become smaller and smaller i.e., the second order correction must be smaller than the first order correction and so on. In general, the perturbation series will converge when the matrix elements of the perturbation operator are smaller compared with differences in the zeroth order eigen values. In other words, the required condition is that (Avery 1972),

$$|\langle a|H'|k\rangle| \ll |E_a^o - E_k^o| \quad \ldots \quad (1.30)$$

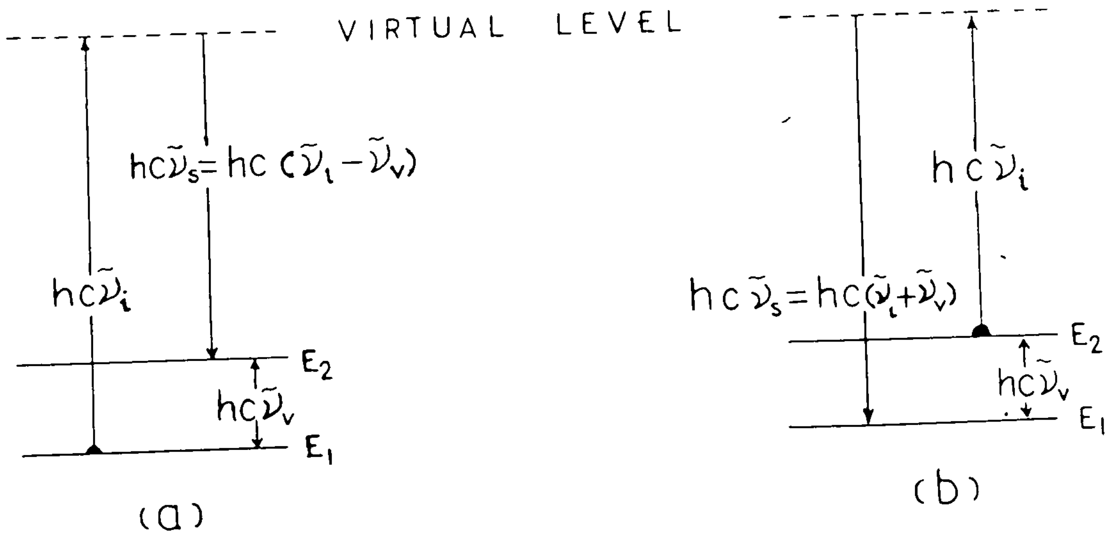

FIGURE 1.1 AN ILLUSTRATION OF (a) STOKES AND (b) ANTI-STOKES RAMAN PROCESSES

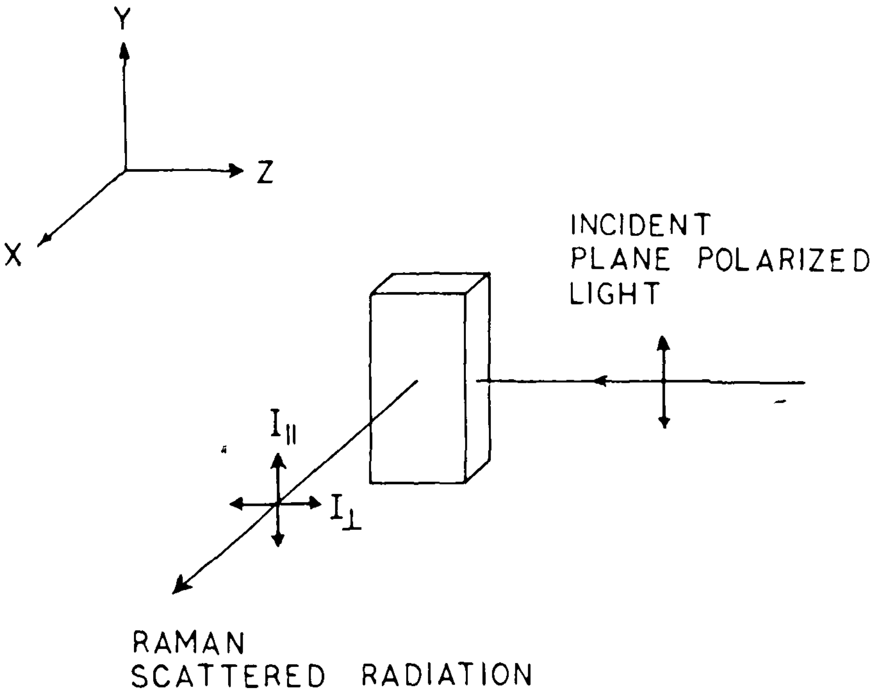

FIGURE 12 AN ILLUSTRATION TO DEFINE DEPOLARIZATION RATIO $\rho = I_{\perp}/I_{\parallel}$; $I_{\perp}$ AND $I_{\parallel}$ STAND FOR THE SCATTERED LIGHT POLARIZED PERPENDICULAR AND PARALLEL TO THE XY-PLANE RESPECTIVELY.

CHAPTER II

SYMMETRY ANALYSIS OF MOLECULAR VIBRATIONS AND SELECTION RULES : APPLICATION TO THE STUDY OF ROCHELLE SALT.*

ABSTRACT

The work pertaining to the vibrational selection rules for molecules in their gaseous as well as in crystalline states is reviewed. The two well known techniques i.e. the unit cell approach and the local symmetry approach, applied to crystalline solids for determining IR and Raman active species are discussed at length. The application of these techniques has been illustrated by an example of our study and analysis of the IR and Raman spectra of Rochelle salt ($NaKC_4H_4O_6.4H_2O$).

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*The work presented in this Chapter has appeared as a brief report in - Proceedings of the Third Symposium on Lasers and Applications (IIT, Kanpur, Dec. 1983) 311.

2.1 INTRODUCTION

If a vibrational mode of a molecule belongs to the symmetry species of some component of electric dipole moment ($\vec{\mu}$) (or translational vector), it is said to be allowed in the IR absorption spectrum. Similarly, if the mode has the symmetry possessed by some component of electric polarizability symmetric tensor ($\tilde{\alpha}$), it is said to be allowed in Raman scattering. These statements describe what are known as IR absorption and Raman scattering selection rules. These rules play an important role in understanding the observed spectra of molecules in gaseous, liquid and solid states. In the light of these rules, the knowledge of the symmetry behaviour (with respect to the symmetry operations of the point group to which the system belongs) of $\vec{\mu}_\rho$ (ρ = x,y,z) , $\tilde{\alpha}_{\rho\sigma}$(ρ,σ = x,y,z) and different vibrational modes become essential. Different methods (with and without use of group theory) of determining the symmetry behaviour of these functions have been discussed in several texts on IR and Raman spectroscopy (Bhagavantam and Venkatarayudu 1939; Dennison 1931; Fateley et. al. 1971, 1972; Halford 1946; Herzberg 1945; Hornig 1948; Rosenthal and Murphy 1936; Winston and Halford 1949). However, only the group theoretical techniques are now-a-days used because they are simple and more informative. In this chapter, we discuss these techniques for isolated molecules as well as for crystals.

We also present our study and analysis of the vibrational spectra of Rochelle salt as an example which illustrates the application of these techniques.

2.2 CHARACTER REPRESENTATION OF THE SYMMETRY POINT GROUP AND MOLECULAR MODES

In order to determine the symmetry species of vibrational modes, the character representation of the molecular point group is determined. This is achieved by using the following facts (Colthup et. al. 1975).

Only those atoms which remain invariant under symmetry operation (R) contribute to the character $\chi(R)$ to which a single invariant atom contributes, $\pm 1 + 2 \cos \phi_R$; where R represents a symmetry operator which could either be a proper rotation (identity or a p-fold rotation) or an improper rotation (inversion, reflection or reflection rotation) defined by an angle ϕ_R; +1 and -1 respectively account for proper and improper rotations. This follows from the following discussion.

We take the example of H_2O molecule. The molecule has C_{2v} point group symmetry as shown in Figure 2.1; this point group has four symmetry operations, i.e. E, C_2, σ_v, σ_v'. Arrows in the figure indicate the cartesian displacements X, Y and Z of a H and O atoms. These displacements are transformed to X', Y' and Z' by the symmetry operations.

For the operator, say σ_v' (the reflection in the plane of the page) we have (c.f. Figure 2.1)

$$\left.\begin{array}{lll} X_1' = -X_1 & X_2' = -X_2 & X_3' = -X_3 \\ Y_1' = Y_1 & Y_2' = Y_2 & Y_3' = Y_3 \\ Z_1' = Z_1 & Z_2' = Z_2 & Z_3' = Z_3 \end{array}\right\} \quad \ldots (2.1)$$

where, co-ordinates X_1, Y_1 and Z_1 stand for one H atom; X_3, Y_3 and Z_3 stand for the other(s) While X_2, Y_2 and Z_2 stand for O atom. These nine equations can be written as

$$\begin{bmatrix} X_1' \\ Y_1' \\ Z_1' \\ X_2' \\ Y_2' \\ Z_2' \\ X_3' \\ Y_3' \\ Z_3' \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} X_1 \\ Y_1 \\ Z_1 \\ X_2 \\ Y_2 \\ Z_2 \\ X_3 \\ Y_3 \\ Z_3 \end{bmatrix} \quad .. (2.2)$$

Thus the symmetry operator σ'_v is represented by

$$\sigma'_v \equiv \begin{bmatrix} -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \qquad \ldots(2.3a)$$

Similarly, the operators E, σ_v and C_2 can be represented as

$$E \equiv \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \qquad \ldots(2.3b)$$

$$\sigma_v \equiv \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad \ldots (2.3c)$$

$$C_2 \equiv \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad \ldots (2.3d)$$

An important property of such matrices is that their trace (i.e. the sum of the diagonal elements) does not change under symmetry transformations. This trace is defined as the character. Thus, the character representation of C_{2v} point group with H_2O co-ordinates as the bases would be

$$\begin{array}{c|cccc} & E & C_2 & \sigma_v & \sigma_v' \\ \hline \chi_{H_2O} & +9 & -1 & +1 & +3 \end{array} \qquad \ldots \qquad (2.4)$$

We clearly notice that only atoms left unmoved by a symmetry operation contribute to the character representation.

In order to evaluate the contribution of a single unmoved atom to $\chi(R)$, we need to examine the transformation properties of X, Y and Z of an atom under R. Figure 2.2 illustrates these components of the displacement vector $\vec{r}$ on the XY plane. If $\vec{r}$ is rotated through an angle ϕ_R about the Z-axis, its Z-component remains unchanged. However, X and Y components change to X' and Y', and we have

$$\begin{aligned} X' &= X \cos \phi_R - Y \sin \phi_R \\ Y' &= X \sin \phi_R + Y \cos \phi_R \qquad \ldots \qquad (2.5) \\ Z' &= Z \end{aligned}$$

These equations can be recast in the matrix form as

$$\begin{bmatrix} X' \\ Y' \\ Z' \end{bmatrix} = \begin{bmatrix} \cos \phi_R & -\sin \phi_R & 0 \\ \sin \phi_R & \cos \phi_R & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} X \\ Y \\ Z \end{bmatrix} \quad \ldots \quad (2.6a)$$

Similarly, for an improper rotation (i.e. rotation followed by a reflection in a plane perpendicular to the axis of rotation), we have

$$\begin{bmatrix} X' \\ Y' \\ Z' \end{bmatrix} = \begin{bmatrix} \cos \phi_R & -\sin \phi_R & 0 \\ \sin \phi_R & \cos \phi_R & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} X \\ Y \\ Z \end{bmatrix} \quad \ldots \quad (2.6b)$$

From equation (2.6a) and (2.6b) R (for proper and improper rotation) can be expressed as

$$R \equiv \begin{bmatrix} \cos \phi_R & -\sin \phi_R & 0 \\ \sin \phi_R & \cos \phi_R & 0 \\ 0 & 0 & \pm 1 \end{bmatrix} \quad \ldots \quad (2.7)$$

Thus, the character contribution for R is

$$\chi(R) = (\pm 1 + 2 \cos \phi_R) \quad \ldots \quad (2.8)$$

Here X, Y and Z, three components of the displacement vector, $\vec{r}$, form the bases of the matrix form of R (equation (2.7)).

2.3 SYMMETRY ANALYSIS OF THE MODES OF ISOLATED NON-LINEAR MOLECULES

In view of section 2.2 the character representation of a point group with 3N normal modes of a N-atomic molecule as bases can be evaluated from

$$\chi(N) = N^R \ (\pm 1 + 2 \cos \phi_R) \qquad \ldots \quad (2.9)$$

where N^R is the number of invariant atoms under the symmetry operator R. The angle $\phi_R = 0°$ for identity (E), $\frac{360°}{p}$ for p - fold rotation (c_p), $\frac{360°}{p}$ for p-fold reflection rotation (s_p), 0° for reflection (σ) and 180° for inversion (i).

To the value of $\chi(N)$, the contributions of the pure translations $(\chi_t(R))$ and pure rotations $(\chi_r(R))$ of the molecule are (Colthup et. al. 1975; Ferraro and Ziomerk 1975)

$$\chi_t(R) = (\pm 1 + 2 \cos \phi_R) \qquad \ldots \quad (2.10)$$

and

$$\chi_r(R) = (1 \pm 2 \cos \phi_R) \qquad \ldots \quad (2.11)$$

The character contribution $\chi_v(R)$ due to vibrational modes is

$$\chi_v(R) = \chi(R) - [\chi_t(R) + \chi_r(R)] \qquad \ldots \quad (2.12)$$

To determine the number of frequencies of each species the reduction formula is used. It is given by (Colthup et. al.

1975; Ferraro and Ziomerk 1975)

$$n^s = \frac{1}{n_G} \sum_i n_i \chi_i \chi_i^s \qquad \ldots \quad (2.13)$$

where, n^s is the number of irreducible representations (corresponding to the symmetry species s) present in the reducible representation; χ_i and χ_i^s are the characters of ith class of operators describing reducible representation and irreducible representation (s^{th} species), respectively. n_i is the order of i^{th} class and n_G is that of the molecular symmetry group.

2.3.1 IR AND RAMAN ACTIVE FUNDAMENTALS

The transition moment M_{fi} for a transition between initial state $|i\rangle$ and final state $|f\rangle$ is given by (c.f. equation (1.1))

$$M_{fi} = \langle f|\tilde{M}|i\rangle$$

where, $\tilde{M}$ is the transition operator. Normally the transitions observed in the spectra are those which take place from the vibrational ground state $|i\rangle$ to some fundamental state $|f\rangle$. The vibrational ground state of a molecule belongs to the totally symmetric species. Consequently, a transition is allowed only if $|f\rangle$ has the symmetry of one of the several components of $\tilde{M}$. For IR absorption, $\tilde{M}$ is the electric dipole moment ($\vec{\mu}$) of the molecule and for Raman scattering it is the polarizability tensor ($\tilde{\alpha}$).

To determine which fundamentals are active in IR absorption we have to determine the symmetry species of $\vec{\mu}_\rho$. In terms of character representation, $\vec{\mu}$ is characterized by

$$\chi_\mu(R) = \pm 1 + 2 \cos \phi_R \qquad \ldots (2.14)$$

when the symmetry of $|f\rangle$ is the same as the symmetry of $\vec{\mu}_\rho$, it is said to be allowed in IR absorption.

Similarly, for Raman allowed fundamentals, we have to determine the symmetry species of $\tilde{\alpha}_{\rho\sigma}$. The character representation of $\tilde{\alpha}$ is given by

$$\chi_\alpha(R) = 2 \pm 2 \cos \phi_R + 2 \cos 2 \phi_R \cdots (2.15)$$

when the symmetry of $|f\rangle$ is the same as that of $\tilde{\alpha}_{\rho\sigma}$, it is said to be allowed in Raman scattering.

2.4 VIBRATIONAL SPECTRA OF CRYSTALS

A molecule in the 'free' state generally has vanishingly small interaction with other molecules. Its potential energy is expressed entirely in terms of the internal parameters. However, in the condensed phase, the molecules interact with each other and the potential energy of the nuclei depends not only on the internal force field but also on its external configuration. As a result, several changes in the vibrational spectrum are induced. (i) New bands of low frequency arising from hindered rotations and freezing of the translations would be observed along with others due to forbidden modes becoming active due to change in structure and symmetry of the molecule. (ii) Changes in width and frequency of bands are also expected.

There are two methods to determine the selection rules of IR absorption and Raman scattering of a crystal. The unit cell approach is developed by Bhagavantam and Venkatarayudu (1939), considering the unit cell as a large molecule and applying group theoretical methods, to predict the vibrational selection rules. The other method known as site/local symmetry approach is developed by Halford (1946) and Hornig (1948) considering the local potentials mainly responsible for the change in the dynamics of the mono- and polyatomic groups in the crystal. Winston and Halford (1949) derived both methods by considering the motions of a crystal segment composed of an arbitrary number of unit cells and subjected to the Born-Van Karman boundary conditions. Fateley et. al. (1971, 1972) tabulated readymade results for most of the crystal symmetries and thus simplified the procedure of determining the species of various phonon modes; the use of these tables does not require rigorous knowledge of group theory.

The potential energy associated with the unit cell can be written, in harmonic approximation, as (Krimm 1963)

$$V = \sum_{j} (V_j^o + V_j') + \sum_{j,k} (V_{jk} + V_{Lj}) + V_L \qquad \ldots (2.16)$$

where, the summation extends over all the molecules in the unit cell.

$\sum_j (V_j^o + V_j')$ represents the sum of internal potential energies of individual molecules in the unit cell. V_j' leads to the static field splitting (site symmetry splitting); V_j^o is the potential energy of the free j^{th} molecule, V_j' represents the perturbation due to crystal field at the molecular site.

V_{jk} contains all cross terms between the internal co-ordinates of different molecules and therefore represents dynamic coupling of the vibrations of different molecules. Both degenerate and non-degenerate vibrations may split, since the potential energy differs if the vibrations of identical units in the cell are in-phase or partly out-of-phase. This splitting is often called the correlation or dynamic field splitting (or Davydov splitting). It is different from the site or static field splitting of degenerate modes.

V_{Lj} represents the interaction between external and internal modes. This may lead to the splitting of degenerate internal modes but generally this term is negligibly small because of large frequency separations between internal and external modes.

V_L represents the lattice potential. It contains terms involving the relative displacements and rotational orientation of molecules with respect to each other and therefore govern the translatory and rotatory (or librational) modes.

2.4.1 THE UNIT CELL APPROACH

In this approach the problem of classification of each $3nN'$ modes of whole crystal (containing n unit cells of N' atoms) is reduced to the problem of classifying $3N'$ modes of the unit cell. This simplification is based on the assumption that atoms or molecules at equivalent lattice positions are in the same state of motion without any phase difference. Following procedure is used for determining the symmetry species of different vibrational modes under this approach.

(i) The unit cell symmetry is known from crystallographic data.

(ii) The total character representation for the unit cell is determined by using equation (2.9); i.e.

$$\chi(N') = N^R\,(\pm 1 + 2\cos\phi_R)$$

(iii) The number of modes of each symmetry species are determined using the standard reduction formula (c.f. equation (2.13)).

In general the unit cell of a crystal may have say N_a atomic units and N_m molecular units. Therefore, the $3N'$ modes of the unit cell account for $3(N_a + N_m)$ translatory modes, $3N_m$ libratory modes and $3N' - 3N_a - 6N_m$ internal modes.

The reducible representation with bases as translational, librational or internal modes can also be obtained separately using

$$\chi(t) = N^R(t) \left[\pm 1 + 2 \cos \phi_R \right] \qquad \ldots \qquad (2.17)$$

for translational lattice modes,

$$\chi(l) = N^R(l) \left[1 \pm 2 \cos \phi_R \right] \qquad \ldots \qquad (2.18)$$

for librational lattice modes, and

$$\chi(i) = \chi(N) - \left[\chi(t) + \chi(l) \right] \qquad \ldots \qquad (2.19)$$

for internal modes.

Where $N^R(t)$, the total number of both atomic as well as polyatomic groups (counting a polyatomic unit as one), and $N^R(l)$, the number of only polyatomic groups, remain invariant under R.

2.4.2 SITE SYMMETRY APPROACH

A site in the crystal is defined as a point which is left invariant by some operations of the crystal space group. These operations form a symmetry group generally referred as site group. The site group is a subgroup of molecular symmetry as well as of crystal symmetry. Each atomic/polyatomic unit occupies some such point in the crystal. In using the above said approach, the site symmetry of each unit is determined from symmetry operations passing through it.

Having determined the site group for each unit, the symmetry classification of the normal modes of the unit into species of local symmetry is determined by correlating the species of free state symmetry to those of the local symmetry. The correlation between the symmetry species of the site group and those of the factor group provide the desired symmetry species of different phonon modes. The number of modes of a particular symmetry species of factor group follows automatically from the multiplicity of equivalent sites in the unit cell. The net classification of modes thus obtained does not differ from that determined from unit cell approach.

2.4.3 MERITS AND DEMERITS OF UNIT CELL APPROACH AND SITE SYMMETRY APPROACH

In the unit cell approach, all the atoms/molecules are considered to form a large molecule. Consequently, the method often becomes cumbersome and sometime even tedious (particularly when the order of the factor group as well as that of reducible representation becomes very large). On the other hand in the site symmetry approach, attention is focussed upon the individual atom/molecule within the crystal. The method is simpler particularly because, the correlation between the species of an isolated molecule and those of crystal through site group can readily be established by comparing character tables of these groups. In the process of this approach, we always have the knowledge about the origin of each mode of the crystal which however does not become apparent in the unit cell approach. Thus the site symmetry analysis makes a better picture of the crystal dynamics. However, since the translatory lattice modes of the crystal can not be attributed to the translatory degrees of freedom of an individual atom or molecule because they are highly mixed modes. Obviously, a better picture is presented by the unit cell approach.

2.5 APPLICATION OF PHONON SYMMETRY CLASSIFICATION IN UNDERSTANDING THE IR AND RAMAN SPECTRA OF ROCHELLE SALT

Rochelle salt (RS), 'Sel de la Seignette' or Sodium Potassium tartrate tetrahydrate, Na.OOC - (OH)CH - CH(OH) - COO.K.$4H_2O$ is one of the most important ferroelectric materials to be discovered. The vibrational spectra of RS have been investigated by several authors (Aleshin 1968; Baker and Webber 1957; Bolard 1965; Chapelle 1946, 1948a,b; Chapelle and Galy 1952; Chavan et. al. 1974; Chisler 1963; Kaneko et. al. 1984; Laroche and Chapelle 1957; Malineau et. al. 1972; Stekhanov and Gabrichidze 1963; Taylor et. al. 1984; Viblyi et. al. 1973; Winterfeldt 1980). Despite this fact, a systematic and complete analysis of its phonon modes in the full spectral region is not available.

In the present investigation, we, therefore, present a detailed analysis of the IR and Raman spectra of RS in view of the symmetry analysis determined through the unit cell and the site symmetry approaches.

2.5.1 CRYSTAL STRUCTURE

The four formula unit cell of RS in para-electric phase (below T_{c1} = -18°C and above T_{c2} = 24°C) belongs to orthorhombic D_2^3 [V^3 ($P\ 2_1\ 2_1\ 2$)] space group symmetry (Frazer et. al. 1954; Känzig 1957; Mazzi et. al. 1956; Rao et. al. 1953).

The unit cell dimensions (above T_{c2}) of RS are given in Table 2.1 which designate the crystal axes in the order b $>$ a $>$ c. The microscopic structure depicting the atomic arrangement in the unit cell projected in (0 0 1) plane is shown in Figure 2.3. For ~~the~~ convenience different atoms (K, Na, C, H, O of COOH, O of OH and O of H_2O) have been shown in the figure by circles of different sizes (not to be related with their atomic sizes).

2.5.2 PHONON BRANCHES IN THE CRYSTAL

The dynamics of RS (NaK $C_4H_4O_6 . 4H_2O$) crystal containing N' (= 112) atoms per unit cell can be described in terms of $3N'$ (= 336) phonon branches (333 optical + 3 acoustical) under the unit cell approach. These branches arise from different normal modes of $C_4H_4O_6^{2-}$, Na^+, K^+ and H_2O.

H_2O molecule in its free state has C_{2v} symmetry. It has three internal modes (ν_1^w (A_1), ν_2^w (A_1) and ν_3^w (B_2)) and six external modes [translational, $t_c (A_1)$, $t_a (B_1)$ and $t_b (B_2)$; and rotational R_c (A_2), R_b (B_1) and R_a (B_2)]. In C_{2v} symmetry, species A_1, A_2, B_1 and B_2 are Raman active; species A_1, B_1 and B_2 are IR active (Herzberg 1945). The number of phonon modes arising from different degrees of freedom of 4 x 4 H_2O molecules in the unit cell are 144.

The structure of tartrate ions have been determined in Sodium tartrate dihydrate (Ambady and Kartha 1968), Rochelle Salt (Frazer et. al. 1954; Känzig 1957; Mazzi et. al. 1956; Rao et. al. 1953), Calcium tartrate tetrahydrate (Ambady 1968) and Ammonium tartrate (Yadava and Padmanabhan 1973) by x-ray diffraction. In all cases the tartrate ion has its chain of carbon atoms almost exactly in a plane as reported also by Kaneko et. al. (1984). The planes of two $C-CO_2$ groups are inclined nearly at 60° to the plane of the carbon atoms. C_2 symmetry has therefore been assumed for the tartrate ion in aqueous solution (Kaneko et. al. 1984). The normal modes of vibrations are then classified into two symmetry species A and B, both active in the IR and Raman spectra. In Raman spectra A-modes appear as polarized bands while B-modes as depolarized bands (Colthup et. al. 1975; Herzberg 1945). The number of phonon modes arising from different degrees of freedom of four $C_4H_4O_6{}^{2-}$ ions in the unit cell would be 168.

The Na^+ and K^+ ions separately have three translational degrees of freedom. These ions would therefore contribute 24 phonon modes.

2.5.3 CLASSIFICATION OF PHONONS

2.5.3a Unit Cell Approach

The classification of 336 phonons using the unit cell approach has been worked out in Table 2.2 for the paraelectric (above T_{c2}) phase of the crystal. The number of atoms found invariant under different operations of D_2 point group are shown against N^R in the table. The crystallographic data (c.f. Table 2.1 and Figure 2.3) reveal that only K^+ goes at $C_2(c)$ site and other atoms at C_1 site. Therefore, 112 atoms remain invariant under E and 4 under $C_2(c)$. Considering each of the atomic as well as polyatomic ions/molecules as single particle, the number of invariant particles are found to be 28 under E and 4 under $C_2(c)$ operations. This accounts for the number ($N^R(t)$) of invariant particles for the external translatory vibrations. Now excluding atomic particles, the number $N^R(l)$ of invariant polyatomic particles is found to be 20 under E and none under other operations. This has been used to determine the number and symmetry of external libratory vibrations. From these values of N^R, $N^R(t)$ and $N^R(l)$ we computed the reducible representations $\chi(N') = N^R(\pm 1 + 2\cos \phi_R)$, $\chi(t) = N^R(t)\ (\pm 1 + 2\cos \phi_R)$ and $\chi(l) = N^R(l)\ (1 \pm 2\cos \phi_R)$. All the 336 phonon modes form the bases of $\chi(N')$ while 84 translatory and 60 libratory external modes form the bases of $\chi(t)$ and $\chi(l)$, respectively.

Reduction of these representations into irreducible representations of D_2 point group provides number of phonon modes belonging to different species (c.f. Table 2.2, column 6- 9).

2.5.3b Site Symmetry Approach

There are two types of crystallographically inequivalent K^+ ions, though both go at C_2 site symmetry. Na^+, $C_4H_4O_6^{2-}$ and H_2O occupy points of C_1 symmetry. The correlation schemes deduced for different symmetry species of relevant molecular and crystal point groups is given in Table 2.3. The symmetry species and the number of phonons arising from a definite mode of Na^+, K^+, $C_4H_4O_6^{2-}$ and H_2O have been summarized in Table 2.4. It may be observed that the total classification of 336 phonon modes of the crystal determined by using unit cell and site symmetry approaches is found to be identical.

2.5.4. THE FORM OF RAMAN TENSOR COMPONENTS

The Raman tensor components of the Raman active species A, B_1, B_2 and B_3 of the symmetry group D_2 of RS have the following form (Tinkham 1974).

$$A = \begin{bmatrix} xx & 0 & 0 \\ 0 & yy & 0 \\ 0 & 0 & zz \end{bmatrix} \qquad B_1(z) = \begin{bmatrix} 0 & xy & 0 \\ yx & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$B_2(y) = \begin{bmatrix} 0 & 0 & xz \\ 0 & 0 & 0 \\ zx & 0 & 0 \end{bmatrix} \qquad , \qquad B_3(x) = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & yz \\ 0 & zy & 0 \end{bmatrix}$$

It shows that all the six components of the symmetric polarizability tensor are independent. Six different spectra having characteristics of these components would, therefore, be sufficient to describe the Raman active phonons in the crystal.

2.5.5 EXPERIMENTAL

2.5.5a Sample preparation

Analar grade RS obtained from 'S.D. fine-chem Pvt. Ltd.' were further purified by recrystallization of aqueous solution at room temperature. Good quality crystals were picked up every time and were dissolved in fresh double distilled water.

The deuterated RS was obtained by crystallization from D_2O solution of the anhydrous salt in vacuum system shown in Figure 2.4. The hydrated compound was first heated in a furnace at 150 °C for about four hours. Then it was taken out of the furnace and transferred soon into a dry flask. The flask was then connected to the vacuum system at F_2 (c.f. Figure 2.4) as soon as possible. Precautions were taken to avoid the absorption of atmospheric water by anhydrated RS.

Using vacuum distillation method, D_2O was then transferred into the flask from the one connected at F_1. When the compound was dissolved completely in D_2O, the D_2O was evaporated and transferred to another flask at F_3 by using the same procedure.

Crystal piece of orthorhombic shape (having sides parallel to the crystallographic axes) and size $\sim$3 x 2 x 1.5 mm^3 was cut from a large single crystal of size $\sim$2.5 x 2 x 2.5 cm^3 (a typical photograph of which is shown in Figure 2.5) for recording the Raman spectra in different orientations. The crystallographic axes were identified by the external morphology of the crystal. The simple seed suspension technique (Holden and Singer 1960) was employed to grow the large single crystals from aqueous solution. The crystal piece was polished on a polishing kit using polishing powders of 302½, 303 and 303½ grades (obtained from British American Optical Company, USA) in succession with CCl_4 drops. The crystal was finally polished with finer alumina powder and glycerene.

2.5.5b Raman Spectra

Raman scattering from the crystal of RS was excited by 514.5 nm radiation from the Spectra Physics 5w Ar^+ ion laser. A Spex 1403 double monochromator equipped with a chilled photo-multiplier-C 31034 tube and a Spex digital photon counting

(DPC-2) system was used to analyse the scattered radiation with the usual right angle geometry. The six different geometries, viz. Z(XX)Y, Z(YY)X, Y(ZZ)X, Z(YY)X, Z(XZ)X and Z(YZ)X were used to record the Raman spectra of the RS single crystal; the laboratory axes, X, Y and Z refer to the crystallographic axes a, b and c, respectively.

The finely ground pure sample taken in a non-fluorescent pyrex capillary was used to record Raman scattering from powdered RS and Deuterated RS (DRS).

A quartz tube was used for recording the Raman spectra of RS in H_2O and D_2O solutions. The spectra for both the parallel (//) and perpendicular (⊥) polarizations were monitored to determine the depolarization ratio of the bands. The usual 90° geometry was used for recording the spectra of both the powder and liquid samples.

The Raman spectra of RS single crystal in different orientations are shown in Figure 2.6(a) and those of RS in H_2O and D_2O solutions, powdered RS and DRS are shown in Figure 2.6(b).

2.5.5c <u>IR Spectra</u>

The IR spectra of RS were recorded on a high performance Perkin-Elmer-983 double beam four-grating IR spectrophotometer covering the 4000 to 180 cm^{-1} range.

The nujol mull technique was used in the present investigation. In this technique, the solid sample is first ground into a fine powder and then dispersed in a mulling agent to get a slurry or mull. The commonly used mulling agent is nujol, which is a high boiling fraction from petroleum. Other mulling agents are hexachlorobutadiene, perfluoro-kerosene (fluorolube), etc. In the present investigation, the mulling agent used was nujol and the plane polished CsBr windows were used for recording the IR spectra.

The IR spectra for KBr pellets were also measured. However, the ion exchange in which Na^+ is replaced by K^+ of KBr seems to affect the observed spectra.

The IR spectra of powdered RS, DRS and anhydrous RS (ARS) are shown in Figure 2.7.

2.5.6 RESULTS AND DISCUSSION

The peak positions of the observed bands are given in Table 2.5 (a) and (b) alongwith our assignments. The estimated error in the frequencies are ± 1 cm^{-1} for well developed bands and ± 5 cm^{-1} for shoulders and diffused bands.

The notations used for internal and external modes of tartrate ion and water molecules and their description as well as expected number of bands for each type are given in Table 2.6.

The three internal modes of H_2O have been represented by standard notations (viz., ν_1^w, ν_2^w and ν_3^w). The bond stretch, angle deformation, bond bending and torsion of a bond/group in the tartrate ion have been represented by ν, δ, β, and τ respectively. The superscripts a and s (wherever they appear) with this notation, refer respectively to the anti-symmetric and symmetric nature of the mode; the subscripts indicate the bond/group mainly involved in the mode.

The interesting feature of the spectra of RS is that the bands due to the internal modes (excluding some skeletal modes) of $C_4H_4O_6^{2-}$ ion appear as doublets. This seems to arise due to interaction between two identical oscillations of two identical groups in $COO.(HO)HC-CH(OH)COO^{2-}$ and/or due to crystallographically distinguishable sites for two identical oscillators. In our discussion we do not distinguish between two such oscillations and represent them by single symbols (c.f. Table 2.5(a) and (b)) against the pair of frequencies corresponding to a doublet.

It is to be noted that the average of all IR and Raman peak frequencies observed for a mode would normally be used as a reference in the discussion pertaining to the assignment of different modes and such frequency numbers have been underlined. FWHMI would refer to the full width at half the maximum intensity of a band. Whenever we talk about the polarization (p)/depolarization(dp) nature of a band it would imply that the inference has been drawn from the Raman spectra of the aqueous solution of RS.

2.5.6a Assignment of ν_{OH}^{t}, ν_1^{w} and ν_3^{w} :

The assignment of ν_{OH}^{t} becomes uncertain due to its overlap with ν_1^{w} and ν_3^{w} expected to fall in the same region. As a whole, under the unit cell approximation 40 OH oscillators are expected to appear in this region; it may be remarked that Winterfeldt's (1980) expectation of a total of 30 OH oscillators is erronious. As stated by others (Kaneko et. al. 1984; Taylor et. al. 1984), it is definitely difficult to identify the bands due to different modes of H_2O molecules and OH groups of tartrate ion. However, very broad and intense band around 3304 cm^{-1} observed in the IR spectrum of ARS gives a clue to the approximate value of ν_{OH}^{t} and we assign this mode to the bands appearing in 3250-3300 cm^{-1} region of the spectra. The bands peaking at about 3521, 3467 and 3393 cm^{-1} are associated with the ν_3^{w} and ν_1^{w} modes. In the light of Glew's (1968) relation, viz.,

$$(3657- \nu_1^{w}) = 0.8333\ (3758- \nu_3^{w})$$

it appears that bands around 3521 and 3467 cm^{-1} (c.f. column 13 of Table 2.5(a) for average frequency) arise, respectively, due to ν_3^{w} and ν_1^{w} modes of one water molecule. These modes of other water molecules seem to fall at 3467 and 3393 cm^{-1} respectively; ν_3^w of this water molecule seems to fall very close to ν_1^w of the former one. We do not observe even eight separate bands as expected for two stretch modes of 4 crystallographically different water molecules. In fact the observations seem to indicate that spectroscopically one pair of H_2O molecules does not differ much from the other pair, though four water molecules are crystallographically different.

The broad structure and large frequency shift of the band due to ν_{OH}^t reveal that OH group in the tartrate ion should exhibit strong hydrogen bonding. The bands of H_2O molecules are, however, found to have low frequency shift and relatively sharp structure which are indicative of weaker H-bonding. Similar inference has been made by Baker and Webber (1957) on the basis of their IR studies. These assignments are in agreement with the observation of 3380 cm^{-1} band due to ν_{OH}^t and at 3516, 3485 and 3415 cm^{-1} bands due to ν_3^w and ν_1^w modes of different H_2O molecules in the spectra of di-potassium tartrate hemi-hydrate (Srivastava et. al. 1982).

Lippincott and Schroeder (1955) have reported some empirical relations and graphs useful for estimating O-H(r) and O...O(R) bond lengths and H-bond energy (E) from the measured frequency shift ($\Delta \nu_{OH}$). In Table 2.7, we have given these characteristic data about H-bonds in RS. It reveals that the

H-bond exhibited by OH-group of tartrate ion is strongest among all H-bonds in the crystal.

2.5.6b Assignment of ν_{CH}:

The CH valence bands are located in the region from 2800 to 3000 cm^{-1}. The two prominent sharp (FWHMI $\simeq$ 20 cm^{-1}) bands observed in Raman spectra of almost all orientations of the single crystal of RS around 2983 and 2939 cm^{-1} arise due to ν_{CH}. In the Raman spectra of aqueous solution of RS only one band is observed at about 2944 cm^{-1}. It is found to be relatively weak in intensity and broad (FWHMI $\simeq$ 60 cm^{-1}) in structure. This assignment is consistent with the results of Winterfeldt (1980), Kaneko et. al. (1984) and Taylor et. al. (1984).

2.5.6c Assignment of ν_2^{w} :

In 1750-1500 cm^{-1} region of the IR spectra, a shoulder at about 1652 cm^{-1} is observed with a strong and broad (FWHMI $\simeq$ 150 cm^{-1}) band peaking at about 1600 cm^{-1}. Corresponding band in Raman spectra gets resolved into three components peaking at about 1665, 1620 and 1592 cm^{-1}; all these components have low intensity. This shoulder does not show up in the IR spectrum of DRS. At about 1665 cm^{-1} there is no band observed in the Raman spectrum of DRS. However, it seems to be related with a weak band appearing at about 1238 cm^{-1} in the Raman spectrum of DRS. This indicates that the bands at about <u>1662</u> cm^{-1} are associated with ν_2^w. This assignment is in line with the observation of Kaneko et. al. (1984).

2.5.6d <u>Assignment of ν_{CO}^a and ν_{CO}^s:</u>

In view of the above observations bands falling around <u>1621</u> and <u>1596</u> cm^{-1} seem to be associated with ν_{CO}^a. This is corroborated by the fact that ν_{CO}^a and ν_{CO}^s modes of carboxylic group in carboxyl salts generally show up in the region 1650-1540 cm^{-1} and 1450-1360 cm^{-1}, respectively (Colthup et. al. 1975). Hence, bands around <u>1433</u> and <u>1411</u> cm^{-1} seem to be due to ν_{CO}^s. These assignments are in line with the fact that ν_{CO}^a mode shows relatively intense bands in the IR and weak bands in the Raman spectra in contrast to those arising from ν_{CO}^s. In the Raman spectra of aqueous solution of RS, only single component bands at about 1600 and 1422 cm^{-1} are observed due to ν_{CO}^a and ν_{CO}^s respectively. The latter band is found to be polarized, while the former one is depolarized. We agree with Kaneko et. al. (1984) that Bolard's (1965) assignment of ν_{CO}^s to 1368 cm^{-1} is in error because this band shifts to around 1050 cm^{-1} in the Raman spectra of RS in D_2O solution.

2.5.6e Assignment of δ_{COH}:

This mode has been assigned to the pair of bands observed around 1390 and 1347 cm^{-1}. These bands shift on deuteration to around 1056 and 1032 cm^{-1}, respectively, as is revealed from the comparative study of Raman spectra of powdered RS and DRS. This assignment is consistent with the nature of this mode. In the IR spectrum of powdered RS these bands are found to be broad (FWHMI $\simeq$ 35 and 40 cm^{-1}, respectively) and intense. The corresponding band observed at about 1374 cm^{-1} in the Raman spectra of aqueous solution of RS is found to be polarized. This assignment is in line with that reported by Kaneko et. al. (1984).

2.5.6f Assignment of β_{CH}:

In the IR and Raman spectra of di-potassium tartrate hemi-hydrate the bands in the region 1325-1208 cm^{-1} are reported to be due to the β_{CH} mode of tartrate ion (Srivastava et al 1982). We also observe two pair of bands in this region of the spectra of RS. These bands are found to be sharp (FWHMI $\simeq$ 10-20cm^{-1}) and moderate to weak in intensity, both in IR and Raman spectra and this observation goes in line with the nature of β_{CH}. Hence the pair of bands observed at about 1316, 1290 and 1245, 1211 cm^{-1} are assigned to β_{CH} modes of tartrate ion.

The Raman spectra of aqueous solution of RS reveals that the corresponding bands at about 1325 cm^{-1} is polarized while those at about 1296 and 1220 cm^{-1} are depolarized; the band at about 1244 is masked by strong neighbouring bands and its polarization character could not be ascertained. Kaneko et. al. (1984) have, however, not reported the observation of 1296 cm^{-1} band which appears clearly in the perpendicular ($\perp$) polarization of the Raman spectra of aqueous solution of RS. We strongly believe that the assignment of these modes to a band at 890 cm^{-1} by Winterfeldt (1980) is in error.

2.5.6g <u>Assignment of $\nu_{C(OH)}$</u>:

This mode is generally observed in the 1075-1150 cm^{-1} range as a strong band in the IR as well as in the Raman spectra (Colthup et. al. 1975) of secondary alcohols, which also have the $>$CHOH group. Hence, the bands observed around <u>1119</u> and <u>1072</u> cm^{-1} in both the IR and Raman spectra as strong bands, are associated with $\nu_{C(OH)}$. These bands shift to around <u>1136</u> and <u>1084</u> cm^{-1} respectively in the spectra of DRS. Apparently this does not go in line with the normal expectation where bands shift to lower frequencies on deuteration. However, such an observation is not unique in itself. We note that $\nu_{C(OD)}$ of CH_3OD (1041 cm^{-1}) is higher than $\nu_{C(OH)}$ of CH_3OH (1034 cm^{-1}) (Hadži 1963). The bands at about 1122 and 1071 cm^{-1} in the

Raman spectra of aqueous solution of RS are observed to be polarized and depolarized, respectively. This assignment is in accord with that reported by Kaneko et. al. (1984). In view of the above discussion we find that the assignment of anti-symmetric CO valence vibration to 1116 cm^{-1} band by Winterfeldt (1980) is also in error.

2.5.6h Assignment of ν_{CC}:

Three sharp bands observed in the IR and Raman spectra around 992, 920 and 892 cm^{-1} seem to be associated with three ν_{CC} modes of the tartrate ion. These peaks have different intensity behaviour. The 920 cm^{-1} peak is found to have very low intensity in Raman but moderate intensity in IR spectra; the remaining two bands have good intensity in Raman, while 992 cm^{-1} peak is very weak in IR spectra. The first and last bands are polarized, while the middle one is depolarized. In the IR and Raman spectra of DRS the 992 cm^{-1} band is observed to shift to a lower frequency i.e. ~943 cm^{-1}. This deuteration shift is not expected from a band due to ν_{CC}. As discussed above, higher frequency shift (15-19 cm^{-1}) is observed in the case of $\nu_{C(OH)}$ mode. It appears that $\nu_{C(OH)}$ and ν_{CC} modes are strongly coupled and this coupling is responsible for the unexpected behaviour of these two modes. Hence, the inference of Kaneko et. al. (1984) that the vibrational modes of 996, 920 and 897 cm^{-1} in a tartrate ion are considerably different from those of 952, 890 and 874 cm^{-1} in a deuterated tartrate ion, seem to be logical because in one case one of the mixing component is $\nu_{C(OH)}$ and in the other case $\nu_{C(OD)}$. The origin of such a significant mixing of ν_{CC} and $\nu_{C(OH)}$ modes seems to rest in the fact that both modes are bond stretch modes falling at close by frequencies.

Following Colthup et. al. (1975) the highest (992 cm^{-1}) and lowest (892 cm^{-1}) frequencies have been associated with $(C\overset{e}{-}C\overset{c}{-}C\overset{e}{-}C)$ and $(C\overset{e}{-}C\overset{e}{-}C\overset{e}{-}C)$ respectively, while the middle one (820 cm^{-1}) is attributed to $(C\overset{c}{-}C\overset{e}{-}C\overset{e}{-}C)$ (e and c stand for expansion and contraction of bonds respectively).

2.5.6i Assignment of δ_{COO}:

This mode has been assigned to bands around 845 and 816 cm^{-1}. This assignment is suggested on the basis of following observations; (i) in anhydrous alkali metal oxalates, where frequencies for δ_{COO} can be more uniquely decided, it is found to fall at about 800 cm^{-1} (Shippey and Shirley 1979) (ii) in lithium formate monohydrate δ_{COO} is identified at 790 cm^{-1} (Galzerani et. al. 1977) and (iii) in di-potassium tartrate hemi-hydrate these bands are observed around 849 and 817 cm^{-1} (Srivastava et.al. 1982). Kaneko et.al. (1984) have also assigned this mode to bands around 845 and 816 cm^{-1} in RS. The former band is observed to be depolarized while the latter one is polarized.

2.5.6j Assignment of Lib.(H_2O), τ_{OH} and τ_{COO}:

In anhydrous alkali metal oxalates, the τ_{COO} modes fall in the 600-450 cm^{-1} range (Shippey and Shirley 1979). The Lib.(H_2O), τ_{OH} and τ_{COO} modes are assigned in the region 735-475 cm^{-1} in di-potassium tartrate hemi-hydrate by Srivastava et. al. (1982). Thus, the Lib.(H_2O), τ_{OH} and τ_{COO} are expected to fall in the region 800-450 cm^{-1} of the IR and Raman spectra of RS.

In the IR spectrum of powdered RS, a broad shoulder at about 765 cm^{-1} is observed with a peak at about 722 cm^{-1}. The intensity of this shoulder is found to be reduced in the IR spectrum of DRS. In the IR spectrum of ARS its intensity is found to be further reduced and it takes the shape of a weak band. The frequency of this shoulder is found to be very well correlated with the weak band observed at around 512 cm^{-1} in the IR spectrum of DRS. Hence, this shoulder is likely to be due to one of the three librational modes of the H_2O molecule. Kaneko et. al. (1984) have also observed this band at the same position.

In the Raman spectrum of powdered RS two bands (not well separated) peaking at about 644 and 612 cm^{-1} are observed; the intensity of 612 cm^{-1} band is more than that of 644 cm^{-1} band. In the Raman spectrum of DRS the intensity of the former one remains almost same, while that of the latter one is found to be reduced; the latter band correlates very well with a very weak and broad new band at about 448 cm^{-1}. In the IR spectrum of powdered RS this band appears as a broad (FWHMI $\simeq$ 40 cm^{-1}) band at about 612 cm^{-1}. In the IR spectrum of DRS, though 612 cm^{-1} band does not show significant decrease in intensity, a new broad and very weak band appears at about 445 cm^{-1}. In the IR spectrum of ARS observable decrease in the intensity of this band is seen. Hence, the band at about <u>613</u> cm^{-1} which correlates very well with the band at about <u>447</u> cm^{-1} may be associated with another Lib.(H_2O). Kaneko et. al. (1984), however, report that the band at 645 cm^{-1} is associated with a Lib.(H_2O); it may be because they did not measure the Raman spectrum of DRS in solid form.

Probably, due to the weak intensity and overlapping by nearby bands, the bands due to τ_{OH} was not observed in our recorded IR and Raman spectra. Kaneko et. al. (1984) also do not report the observation of τ_{OH}. However, at liquid N_2 temperature, they report to observe this mode in the IR spectrum at 545 cm^{-1}.

In view of the above discussion, the remaining bands in 800-450 cm^{-1} region which do not shift on deuteration seem to be associated with the three τ_{COO} modes (i.e. rocking, wagging and twisting of COO group).

In the Raman spectra of aqueous solution of RS, the bands at about 612 and 532 cm^{-1} are observed to be polarized. While, bands at about 704 and 488 cm^{-1} are observed to be **depolarized.**

2.5.6k Assignment of $\beta_{C(OH)}$, δ_{CCC}^{a}, δ_{CCC}^{s}, τ_{CCC} and external lattice modes :

The $\beta_{C(OH)}$ (in-plane and out of plane) modes in phenol are observed at 403 and 242 cm^{-1} respectively (Bist et. al. 1967). In butane the δ_{CCC}^{a} and δ_{CCC}^{s} modes are established at 421 and 271 cm^{-1}, respectively (Colthup et. al. 1975). Thus these modes in RS are expected to be observed in the region 425-240 cm^{-1}.

The τ_{CCC} in tartrate ion, corresponds to the twist of the central C-C bond. To both these C-atoms, heavier groups like -COO and -OH are attached. As a result, the CC-twist is expected to fall at a frequency even lower than those of $\beta_{C(OH)}$ and δ_{CCC}. Hence, the bands observed at about 382, 355, 376, 267, 252 and 240 cm^{-1} are associated with both $\beta_{C(OH)}$ and δ_{CCC} modes. Individual assignments of these modes are not possible because they are expected to intermix considerably. A single broad (FWHMI $\simeq$50 cm^{-1}) and polarized band is observed in this region at about 364 cm^{-1} in the Raman spectra of the aqueous solution of RS.

Bands observed below 240 cm^{-1} are associated with τ_{CCC} mode and external lattice modes of $C_4H_4O_6^{2-}$ ion, H_2O molecules, K^+ and Na^+ ions.

2.5.61 General Observation

As stated earlier internal modes (excluding some skeletal modes) of $C_4H_4O_6^{2-}$ ion appear as doublets in the spectra of RS due to the interaction between two identical oscillators of two identical groups in $COO(OH)HC{-}CH(OH)COO^{2-}$ and/or crystallographically distinguishable sites for two such oscillators. However, the doublets due to ν_{CH}, ν_{CO}^{a}, ν_{CO}^{s}, δ_{COH} and τ_{COO} become singlet having relatively large width in the Raman spectra of RS in aqueous solution. On the otherhand β_{CH}, $\nu_{C(OH)}$ and δ_{COO} modes retain their doublet band structure in the Raman spectra recorded for aqueous solution of RS. This reveals that the doublet structure for the former set of modes arise mainly due to crystallographically distinguishable sites for two identical oscillators. While same for the latter set of modes originates dominantly due to resonance interaction between two identical oscillators of two identical groups.

This inference follows from the fact that in the solution identical oscillators of two identical groups have identical surrounding. Srivastava et. al. (1982) also observed similar doublets in the spectra of di-potassium tartrate hemi-hydrate. They suggested that the resonance interaction between identical oscillators as the cause for this observation without considering the site effect. However, this does not appear to be the case in view of our observations. Identical modes of identical groups in different crystalline environment are known to have different frequencies (Hadži 1963).

The IR and Raman spectra of RS is expected to comprise a large number of peaks because of the large number of atoms ($N' = 112$) in its unit cell. The dynamics of RS crystal can be described in terms of $3N'$ (=336) phonon branches (333 optical + 3 acoustical) under the unit cell approximation. These branches arise from different normal modes of $C_4H_4O_6^{2-}$, Na^+, K^+ and H_2O. The number of phonon modes arising from different degrees of freedom of 4 x 4 H_2O molecules, 4 $C_4H_4O_6^{2-}$ ions are 144 and 168, respectively. The Na^+ and K^+ ions separately have three translational degrees of freedom; thus the 4 ions of each type, contribute a total of 24 phonon modes.

There are two types of crystallographically inequivalent K^+ ions,- both having C_2 site symmetry. Na^+, $C_4H_4O_6^{2-}$ and H_2O occupy points of C_1 symmetry. Hence, all the 333 optical phonon branches are IR and Raman active. However, the observed IR and Raman spectra show only 48 bands in the region in which about more than two hundred bands are expected in view of the unit cell approximation. It appears that the factor group split components of most of the modes do not have frequency separation that can be resolved. As such the single molecule approximation appears to be sufficient to discuss the observed spectra of internal lattice modes, particularly, of powdered samples. One may observe such a situation for several crystalline systems. We thus find that the detailed analysis of the phonon symmetry looses its relevance and one can understand the observed spectra of the powdered samples in terms of the modes of a single molecule. However, to understand the spectra of the single crystal, the detailed symmetry analysis under unit cell approximation remains essential. It is clearly noted that the two approaches are useful to predict which mode would be allowed or forbidden. But at the same time they fail to predict the magnitude of intensity, a mode could be expected to gain. For this aspect one has to rely on correlations with established facts known for identical modes of almost identical molecules, but for forbidden modes one may now use the theory discussed in the forthcoming chapters.

(reference)

TABLE 2.1

Crystal structural data of Rochelle Salt

($NaK\ C_4H_4O_6 \cdot 4H_2O$)

	para electric phase (above T_{c2})
Crystal system	Orthorhombic
Space group	$D_2^3\ [V^3\ (P\ 2_1 2_1\ 2)]$
Unit cell dimensions	
a	11.878 Å
b	14.246 Å
c	6.218 Å

Table 2.2 Classification of phonons in RS (NaK $C_4H_4O_6 \cdot 4H_2O$) (an unit cell approach)

D_2^3	E	C_2(c)	C_2(b)	C_2(a)	Reducible representation			
					A	B_1	B_2	B_3
A_1	1	1	1	1				
B_1	1	1	-1	-1				
B_2	1	-1	1	-1				
B_3	1	-1	-1	1				
$\varnothing_R$	0	π	π	π				
$\pm 1 + 2 \cos \varnothing_R$	3	-1	-1	-1				
$1 \pm 2 \cos \varnothing_R$	3	-1	-1	-1				
N^R	112	4	0	0				
$\chi(N') = N^R(\pm 1 + 2 \cos \varnothing_R)$	336	-4	0	0	83	83	85	85
$N^R(t)$	28	4	0	0				
$\chi(t) = N^R(t)\ (\pm 1 + 2 \cos \varnothing_R)$	84	-4	0	0	20	20	22	22
$N^R(l)$	20	0	0	0				
$\chi(l) = N^R(l)\ (1 \pm 2 \cos \varnothing_R)$	60	0	0	0	15	15	15	15
$\chi(i) = \chi(R) - [\chi(t) + \chi(l)]$	192	0	0	0	48	48	48	48

TABLE 2.3 : Correlation between different symmetry species of C_2, C_{2v}, C_1, D_2 groups

	Symmetry species of			
	Free State		Site	Crystal
$C_4H_4O_6^{2-}$; site C_1	A	B	A	$A + B_1 + B_2 + B_3$
$H_2C(C_{2v})$; site C_1	A_1A_2	B_1B_2	A	$A + B_1 + B_2 + B_3$
Na^+ ; site C_1			A	$A + B_1 + B_2 + B_3$
K^+ ; site C_2			A	$A + B_1$
			B	$B_2 + B_3$
			B	$B_2 + B_3$

TABLE 2.4

Classification of phonons in RS crystal*

(A site symmetry approach)

Modes	Species				
	A	B_1	B_2	B_3	N^b
1	2				3
$C_4H_4O_6^{2-}$					
Internal					
ν_s (A)	4	4	4	4	16
ν_s (B)	2	2	2	2	8
2 x ν_{ns} (A)	15	15	15	15	60
2 x ν_{ns} (B)	15	15	15	15	60
Total	36	36	36	36	144
$C_4H_4O_6^{2-}$					
External					
t_c (A)	1	1	1	1	4
t_a (B)	1	1	1	1	4
t_b (B)	1	1	1	1	4
R_c (A)	1	1	1	1	4
R_a (B)	1	1	1	1	4
R_b (B)	1	1	1	1	4
Total	6	6	6	6	24

Table 2.4 continued

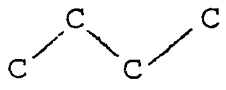
1	2				3
Na^+ t_a, t_b, t_c	3	3	3	3	12
Total	3	3	3	3	12
K^+ t_c	2	2	-	-	4
t_a	-	-	2	2	4
t_b	-	-	2	2	4
Total	2	2	4	4	12
H_2O					
Internal					
$\nu_1^w (A_1)$	4	4	4	4	16
$\nu_2^w (A_1)$	4	4	4	4	16
$\nu_3^w (B_2)$	4	4	4	4	16
Total	12	12	12	12	48
H_2O					
External					
$t_c (A_1)$	4	4	4	4	16
$t_a (B_1)$	4	4	4	4	16
$t_b (B_2)$	4	4	4	4	16

....contd..

Table 2.4 continued

1	2				3
$R_c(A_2)$	4	4	4	4	16
$R_b(B_1)$	4	4	4	4	16
$R_a(B_2)$	4	4	4	4	16
Total	24	24	24	24	96
Grand Total	83	83	85	85	336

$^*N^b$ number of phonon modes,

ν_s represents six skeletal  internal modes, i.e. two $\nu_{cc}(A)$, $\nu_{cc}(B)$, $\delta^{s}_{ccc}(A)$, $\delta_{ccc}^{a}(B)$ and cc-twist (A), three librations corresponding to $R_c(A)$, $R_a(B)$ and $R_b(B)$, three translatory lattice modes corresponding to $t_c(A)$, $t_a(B)$ and $t_b(B)$ of $C_4H_4O_6^{2-}$ ion.

ν_{ns}- represents 30 non-skeletal internal modes, however, these can be grouped into 15 pairs of identical oscillators from pairs of identical groups such as CH, OH etc in $COO.CH(OH)-CH(OH)COO^{2-}$ ion. Thus effectively there are 15 types of different modes, each having an in-phase (A) and an out-of-phase (B) combination of two identical oscillations in identical groups.

Table 2.5 (a) Frequencies (cm^{-1}) of phonon modes of RS single crystal, powdered RS, DRS and ARS.

RAMAN								IR			Assignment	Average frequency
RS Single Crystal						RS	DRS	RS	DRS	ARS		
A			B_1	B_2	B_3	powder	powder	powder	powder	powder		
Z(XX)Y	Z(YY)X	Y(ZZ)X	Z(XY)X	Z(XZ)X	Z(YZ)X							
1	2	3	4	5	6	7	8	9	10	11	12	13
	3522 br,w	3524 vbr,vw			3522 br,vw	3524 vbr,w		3520 br,s	35 br,m		ν_3^w	3521
	3470 br,m	3470 vbr,w	3472 vbr,w		3468 vbr,vw	3472 vbr,m		3460 br,s	3455 br,m		ν_3^w, ν_1^w	3467
3408 br,s	3404 br,m	3406 vbr,m	3408 vbr,w	3406 vbr,m	3408 vbr,w	3404 vbr,m		3382 vbr,s	3384 vbr,s		ν_1^w	3393
3262 vbr,s	3220 vbr,w	3264 vbr,w	3264 vbr,w	3294 vbr,m		3268 vbr,m		3250 vbr,s	3255 vbr,s	3304 vbr,s	ν_{OH}^t	3260
2982 sh,vs	2982 sh,s	2980 sh,s	2982 sh,w	2984 sh,s	2984 sh,vw	2982 sh,s	2990 sh,s	N	N	N	ν_{CH}	2983
2938 sh,w	2940 sh,vs	2936 sh,vw	2940 sh,w		2940 sh,vw	2940 sh,vs	2942 sh,vs	N	N	N		2939

continued.

Table 2.5(a) continued

1	2	3	4	5	6	7	8	9	10	11	12	13
							2586 vbr,m		2580 br,m		$\nu_3(D_2O)$	
									2560 br,m		$\nu_1,\nu_3(D_2O)$	
							2512 br,s		2505		$\nu_1(D_2O)$	
							2414 vbr,m		2423 vbr,s		$\nu_{OD}{}^t$	
	1668 br,vw		1664 vbr,vw	1660 br,vw		1665 br,vw		1652 br,s			$\nu_2{}^w$	1662
	1622 br,vw	1623 br,w				1620 br,vw	1618 br,w				ν_{CO}^a	1621
1592 br,w		1594 br,vw		1596 br,w	1596 br,vw	1592 br,vw	1600 br,w	1600 vbr,s	1601 vbr,s	1594 vbr,s		1596
1436 sh,w	1434 sh,s	1432 sh,w	1434 so	1436 sh,m		1426 sh,m					ν_{CO}^s	1433
1412 br,vw	1412 br,vw	1414 br,w	1414 br,w	1410 br,w	1408 br,vw	1408 br,vw						1411

continued...

Table 2.5 (a) continued

1	2	3	4	5	6	7	8	9	10	11	12	13
1384 sh,vw	1386 sh,vs	1384 br,vw	1388 br,w			1384 br,s	1394 so	1400 br,s	1400 br,m		δ_{COH}	1390
1347 br,w	1346 so	1346 br,m	1352 br,w	1348 br,s	1344 br,vw	1348 br,m	1350 br,w	1343 br,s	1343 br,m	1344 br,vw		1397
		1322 sh,w					1316 sh,s		1315 sh,vw	1312 sh,vw	β_{CH}	1316
1286 sh,vw		1288 sh,w	1292 sh,m	1288 sh,m	1290 sh,vw	1292 sh,w	1292 sh,vw	N	N	N		1290
							1238 br,w				$\nu_2(D_2O)$	
		1246 sh,vw			1244 sh,vw	1244 sh,vw		N	N	N	β_{CH}	1245
1213 sh,vw		1210 sh,m	1213 sh,w	1212 sh,w	1208 sh,w	1208 sh,m	1212 sh,vw	N	N	N		1211

continued..

Table 2.5 (a) continued

1	2	3	4	5	6	7	8	9	10	11	12	13
									1133 sh,m			
	1120 sh,vw	1112 sh,s		1116 sh,w	1120 sh,vw	1116 sh,s	1136 br,w	1116 sh,s	1120 sh,m	1113 br,m	$\nu_{C(OH)}$	1119
1072 sh,m	1074 sh,m	1071 sh,vw	1072 sh,w	1070 sh,s	1070 sh,vw	1072 sh,s	1084 br,w	1069 sh,s	1070 sh,m	1069 br,m		1072
							1056 sh,m		1053 br,m		δ_{COD}	
							1032 so		1029 br,m			
990 sh,vs	990 sh,w	992 sh,vw	992 sh,vw	992 sh,vs	992 sh,vw	992 sh,s	944 br,w	990 sh,vw	941 br,vw	994 sh,w	ν_{CC}	992
	920 sh,s	920 sh,vw	920 sh,vw	922 sh,vw	920 sh,vw	920 sh,vw		919 sh,w		919 sh,w		920
893 sh,s	893 sh,s	888 sh,s	892 sh,w	892 sh,vw	892 sh,vw	892 sh,s	892 sh,m	890 sh,w	888 sh,s	900 sh,vw		892
	849 sh,m	846 sh,vw		848 sh,vw	850 sh,vw	848 sh,w	838 sh,vw	845 br,vw	835 br,vw	850 sh,vw	δ_{COO}	845
812 sh,s	810 sh,m	814 sh,m				812 sh,m	810 sh,s	825 br,vw	820 br,vw	825 sh,vw		816

continued...

Table 2.5(a) continued

1	2	3	4	5	6	7	8	9	10	11	12	13
753 br,vw	760 br,vw			766 br,vw				765 br,m		765 br,w	lib. (H_2O)	761
717 br,vw	720 br,w			716 br,vw				722 br,s	721 br,s	722 br,s	τ_{COO}	719
696 br,vw	700 br,w		700 br,w			702 br,vw	704 br,vw		702 br,s	700 br,w		700
644 br,m		647 br,w	648 br,vw	652 br,vw	644 br,vw	644 br,w	640 br,w	650 so	640 br,m		τ_{COO}	675
612 br,vw	612 sh,m		615 sh,w	613 br,m	612 br,vw	612 br,w	616 so	612 br,s	612 br,s	610 br,m	lib. (H_2O)	613
535 sh,vs	534 sh,w	536 br,vw	535 sh,s	533 br,w		532 sh,m	532 br,w	536 br,w	535 br,w 512 br,w	530 sh,w	τ_{COO}	531
	488 br,vw	487 br,w	488 sh,s		484 br,vw	488 br,w	488 br,vw	483 br,w	484 br,w	490 br,w	τ_{COO}	487
							448 br,vw		445 br,vw		lib. (D_2O)	447

Table 2.5(a) continued

1	2	3	4	5	6	7	8	9	10	11	12	13
380 br,w				380 br,w		376 br,vw	390 br,vw				$\beta_{C(OH)}$ and δ_{CCC}	382
		353 br,w				356 br,vw						355
		376 so										376
267 br,vw												367
				252 br,s								252
242 br,w	242 br,w	242 br,w	242 br,w			236 br,vw	236 br,vw					240
		200 br,vw	200 br,w	196 br,w							$\beta_{C(OH)}$ δ_{CCC}, CC-twist and external lattice modes	199
180 br,m			180 br,w		182 br,m		184 br,vw					182
	160 so		160 br,w	160 so								160
134 so	134 sh,vs	134 sh,vs	132 sh,vs	128 sh,vs	128 sh,m		134 sh,w					132

continued/-..

Table 2.5 (a) continued

1	2	3	4	5	6	7	8	9	10	11	12	13
112 sh,vw		106 sh,vs		106 sh,s								108
			92 br,vs		92 br,s							92
76 sh,vw	76 sh,vs											76
				68 sh,m								68
		56 sh,vw		52 sh,s								54
					40 sh,vs							40

s, m, w, v, sh, br and so stand for strong, medium, weak, very, sharp, broad and shoulder, respectively. N stands for nujol bands.

Table 2.5(b) Frequencies (cm^{-1}) of phonon modes of RS in H_2O and D_2O solutions

RS in H_2O solution			RS in D_2O solution			
Parallel polarization (//)	Perpendicular polarization (⊥)	Depolarization ratio ($\rho = I_{\perp}/I_{//}$)	Parallel polarization (//)	Perpendicular polarization (⊥)	Depolarization ratio ($\rho = I_{\perp}/I_{//}$)	Assignment
1	2	3	4	5	6	7
3420^{*} vbr,vs	3444^{*} vbr,s		3434^{*} vbr,w			
3280^{*} vbr,vs						
2944 br,s	2944 br,w	0.17 (p)	2942 br,s	2944 br,w	0.10 (p)	ν_{CH}
			2510^{*} vbr,vs	2532^{*} vbr,s		
			2422^{*} vbr,vs			
1660 br,w	1660 br,vw	0.27 (p)				ν_2^w
1600 br,w	1600 br,vw	0.60 (p)	1606 br,w	1606 br,w	1.00 (dp)	ν_{CO}^a

continued/-..

Table 2.5 (b) continued

1	2	3	4	5	6	7
1422 sh,s	1422 sh,w	0.20 (p)	1426 sh,s	1428 sh,m	0.21 (p)	ν^{s}_{CO}
				1408 sh,m	? (dp)	
1374 br,s	1374 br,w	0.24 (p)				δ_{COH}
1325 so		0.00 (p)	1326 sh,s	1328 sh,m	0.39 (p)	β_{CH}
	1296 br,vw	? (dp)				
1244 br,w	1244 br,w	? (?)	1246 sh,w	1248 sh,w	0.72 (p)	β_{CH}
1220 sh,vw	1220 sh,vw	0.95 (p)	1210 sh,vw	1206 sh,vw	1.00 (dp)	
1122 sh,w	1122 sh,vw	0.41 (p)	1142 sh,vw	1140 sh,vw	0.70 (p)	$\nu_{C(OH)}$
1071 sh,w	1071 sh,vw	0.93 (dp)	1086 so	1088 sh,vw	4.67 (dp)	

continued...

Table 2.5 (b) continued

1	2	3	4	5	6	7
			1050 sh,m	1046 sh,vw	0.20 (p)	δ_{COD}
			1026 so	1028 sh,vw	? (dp)	
996 sh,s	996 sh,vw	0.16 (p)	958 br,vw	956 br,vw	0.62 (p)	ν_{CC}
	920 sh,vw	? (dp)				
892 sh,s	892 sh,vw	0.15 (p)	892 sh,m	896 sh,vw	0.30 (p)	
814 so	846 sh,vw	4.0 (dp)		842 sh,vw	? (dp)	δ_{COO}
807 sh,s		0.00 (p)	806 sh,s	808 sh,vw	0.08 (p)	

continued.....

Table 2.5 (b) continued

1	2	3	4	5	6	7
704 br,vw	704 br,vw	1.36 (dp)	702 br,vw	704 br,vw	1.20 (dp)	γ_{COO}
612 br,w	612 br,vw	0.29 (p)	616 br,w	616 br,vw	0.40 (p)	Lib (H_2O)
532 sh,s	532 sh,vw	0.33 (p)	530 br,m	530 br,vw	0.53 (p)	γ_{COO}
488 so	488 so	6.67	488 so	488 br,vw	? (dp)	γ_{COO}
364 br,w	364 br,vw	0.28 (p)	360 br,vw	360 br,vw	0.71 (p)	$\beta_{C(OH)}$ and δ_{CCC}

s, m, w, v, sh, br and so stand for strong, medium, weak, very, sharp, broad and shoulder, respectively.

p and dp stand for polarized and depolarized bands respectively

*Bands of H_2O/D_2O

Table 2.6 Notations used for internal and external modes of tartrate ion and water and expected number of each type of such modes.

Notation	Decription	Number of each type of vibration
1	2	3
Internal modes of $C_4H_4O_6^{2-}$ ion		
ν_{OH}^{t}	OH stretch	2
τ_{OH}	OH torsion (out of plane)	2
δ_{COH}	COH angle deformation (in plane)	2
$\nu'_{C(OH)}$	C(OH) stretch	2
$\beta_{C(OH)}$	C(OH) bond bending	
	(a) in plane	2
	(b) out of plane	2
ν_{CH}	CH stretch	2
β_{CH}	CH bond bending	
	(a) in plane	2
	(b) out of plane	2
ν_{CO}^{s}	CO symmetric stretch	2
ν_{CO}^{a}	CO asymmetric stretch	2
δ_{COO}	OCO angle bending	2
τ_{COO}	COO Torsion	
	(a) Twist	2
	(b) Rock	2
	(c) Wag	2

contd....

Table 2.6 continued

1	2	3
ν_{CC}	CC stretch	3
τ_{CCC}	CC twist	1
$\delta_{CCC}{}^{a}$	CCC asymmetric angle deformation	1
$\delta_{CCC}{}^{s}$	CCC symmetric angle deformation	1
External modes of $C_4H_4O_6{}^{2-}$ ion		
R_a	libration along a	1
R_b	libration along b	1
R_c	libration along c	1
t_a	translation along a	1
t_b	translation along b	1
t_c	translation along c	1
Internal modes of H_2O		
$\nu_1{}^{w}$	OH symmetric stretch	1
$\nu_2{}^{w}$	HOH bending	1
$\nu_3{}^{w}$	OH asymmetric stretch	1
External modes of H_2O		
lib. (H_2O)	libration	3
trans. (H_2O)	translation	3
	Total	51

Table 2.7 Characteristic data about O-H ... O bonds

Bond	$\Delta\nu_{OH}$ (cm^{-1})	R (Å)	r (Å)	E ($\frac{kcal}{mol}$)
O-H..O(w)	179	2.96	.982	2.50
	233	2.91	.986	2.56
	307	2.86	.990	2.63
O-H..O(t)	440	2.78	1.006	2.75

O-H..O (w/t) refers to the bond of H_2O/tartrate ion.

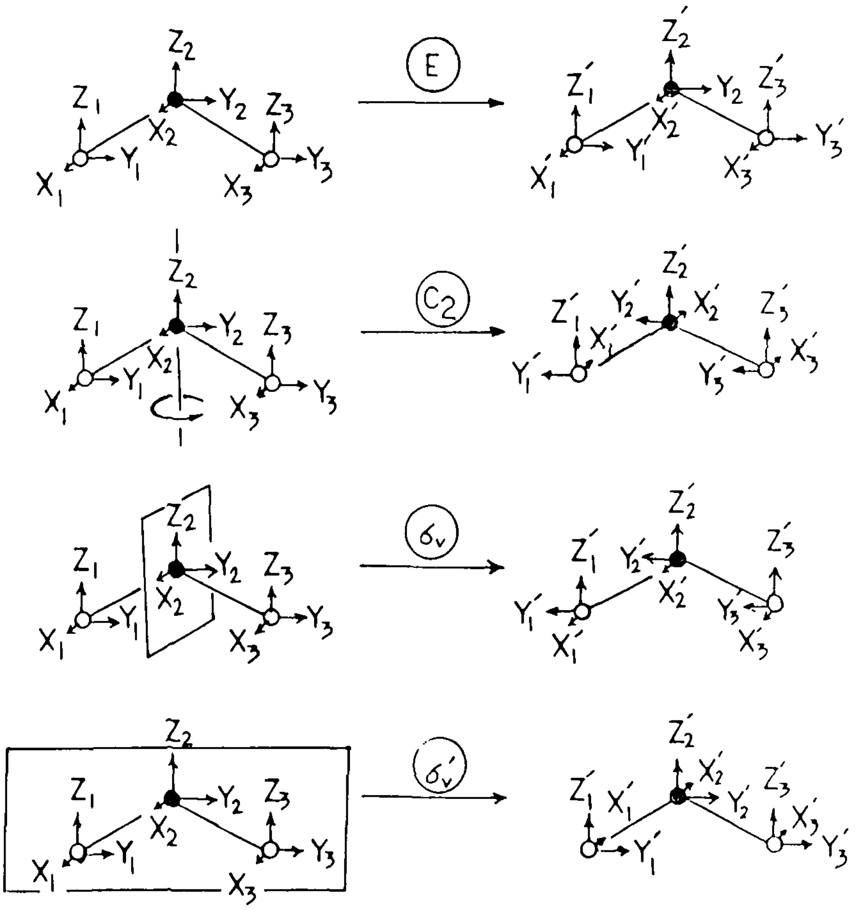


FIGURE 2.1 THE EFFECT OF SYMMETRY OPERATIONS ON CARTESIAN DISPLACEMENT COORDINATES FOR H_2O.

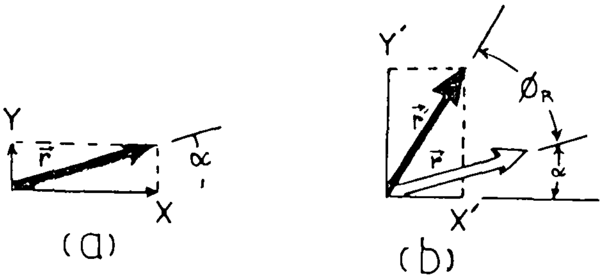


FIGURE 2.2 ROTATION OF VECTOR $\vec{r}$ ABOUT Z-AXIS THROUGH AN ANGLE ϕ_R.

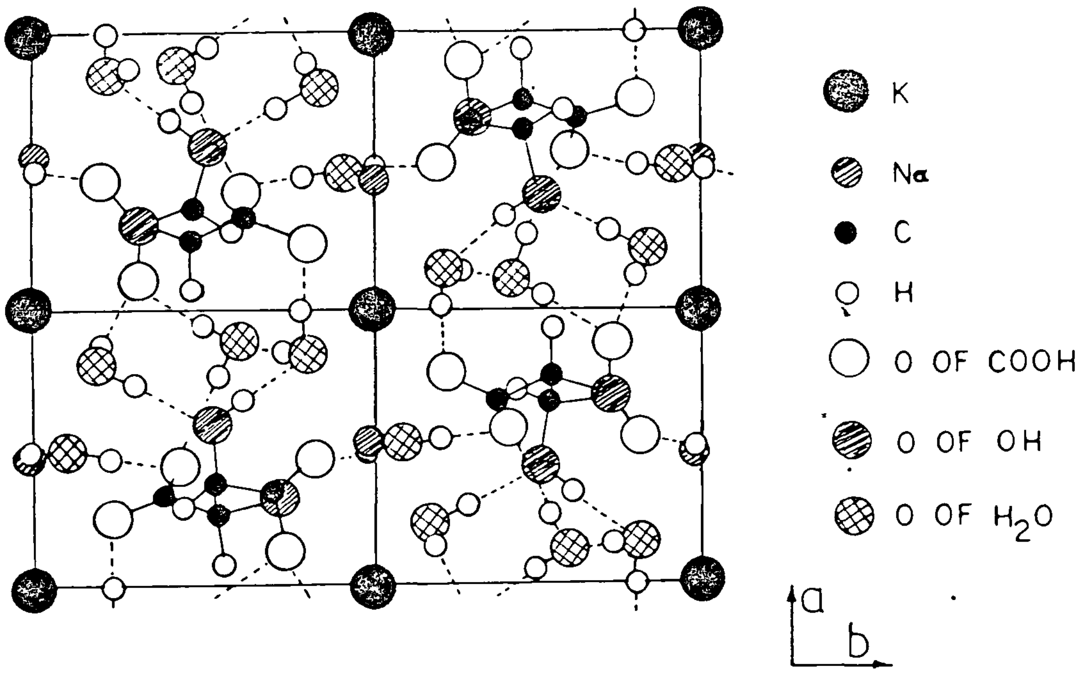


FIGURE 2.3 STRUCTURE OF ROCHELLE SALT PROJECTED ON (001) PLANE.

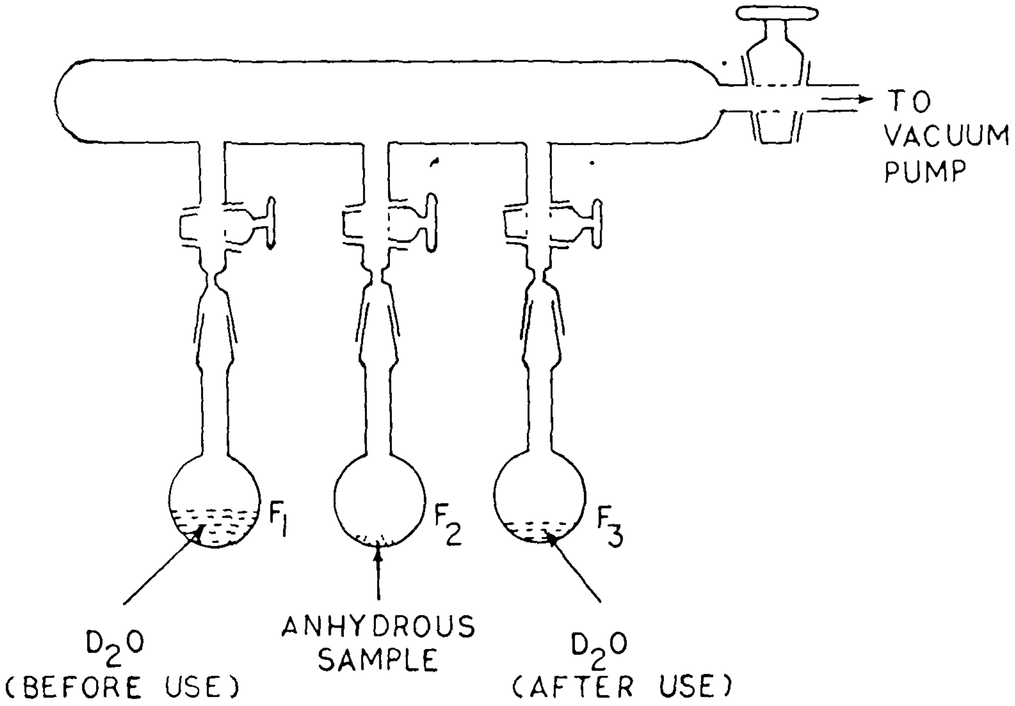


FIGURE 2.4 VACUUM SYSTEM USED TO DEUTERATE THE HYDRATED SALTS.

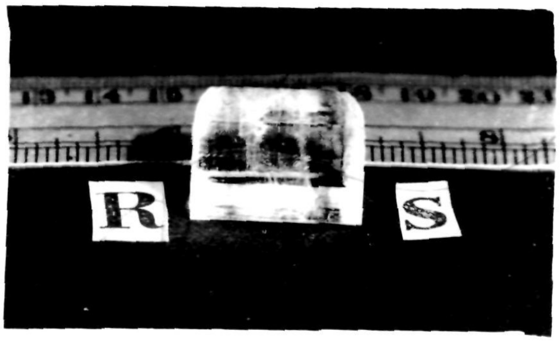


FIGURE 2.5 PHOTOGRAPH OF ROCHELLE SALT SINGLE CRYSTAL.

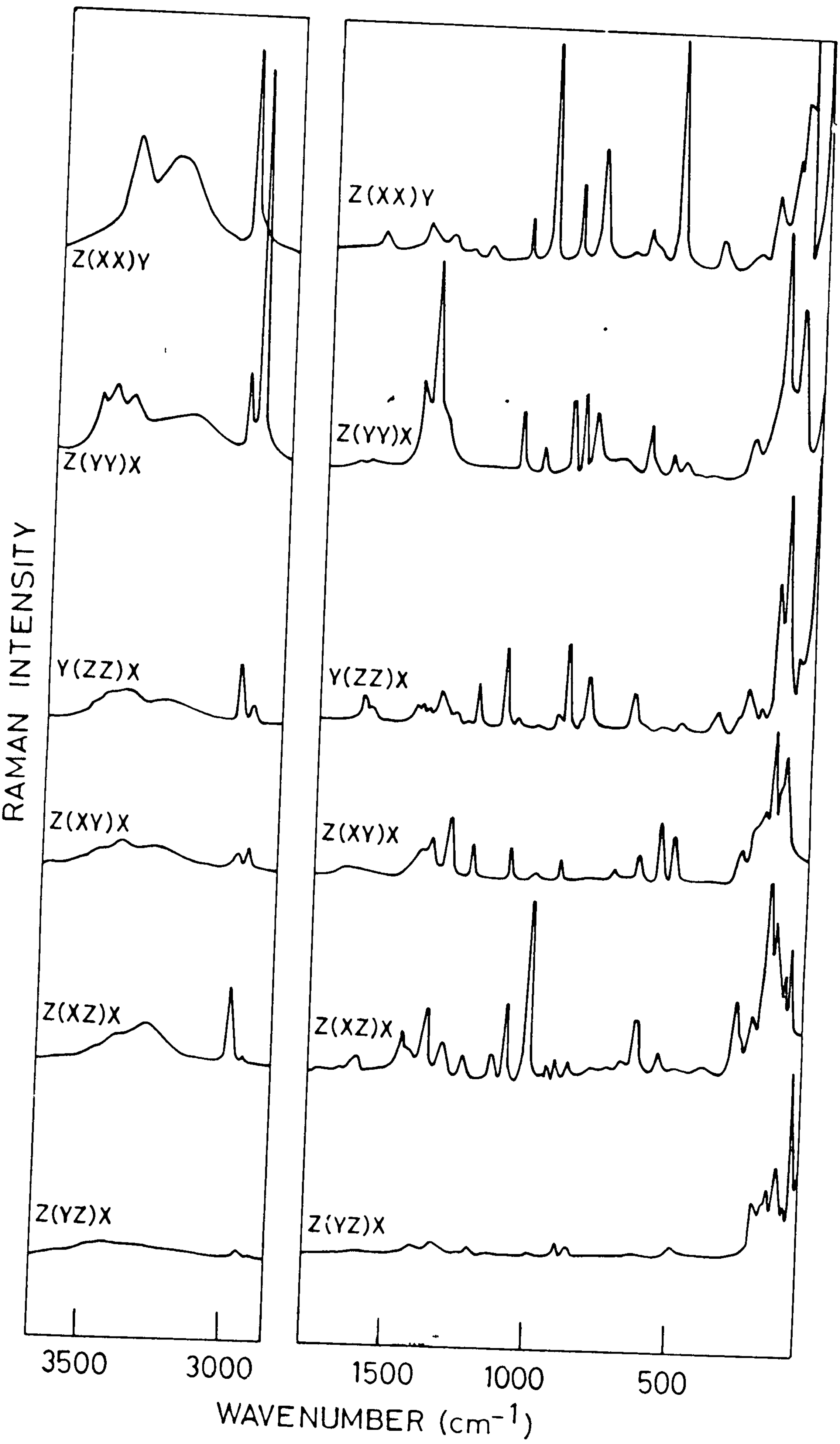


FIGURE 2.6(a) RAMAN SPECTRA OF RS SINGLE CRYSTAL IN DIFFERENT ORIENTATIONS.

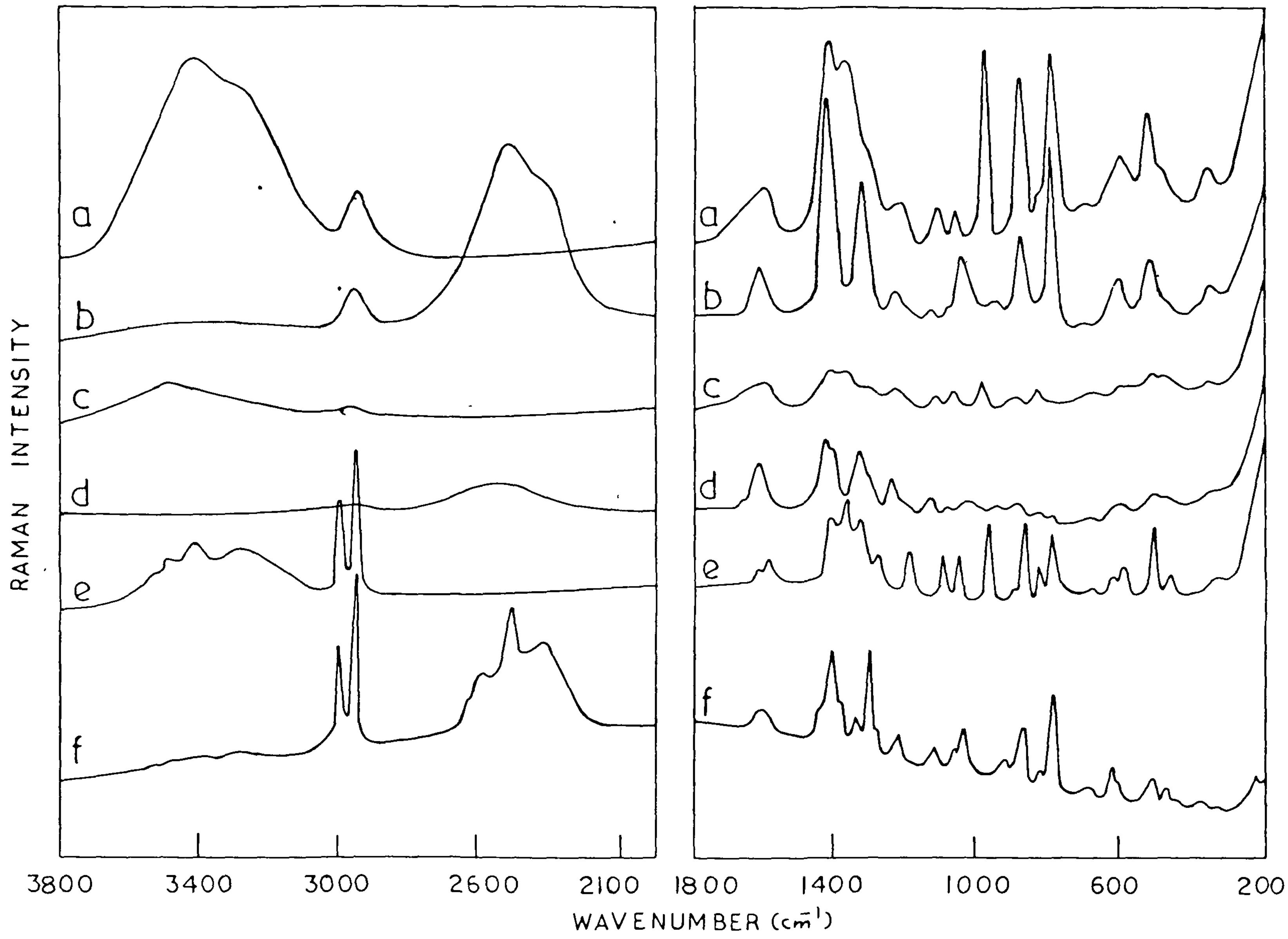


FIGURE 2.6(b) RAMAN SPECTRA OF: a. RS IN H_2O (PARALLEL POLARIZATION); b. RS IN D_2O (PARALLEL POLARIZATION); C. RS IN H_2O (PERPENDICULAP POLARIZATION); d. RS IN D_2O (PERPENDICULAR POLARIZATION); e. POWDERED RS; f. POWDERED DRS.

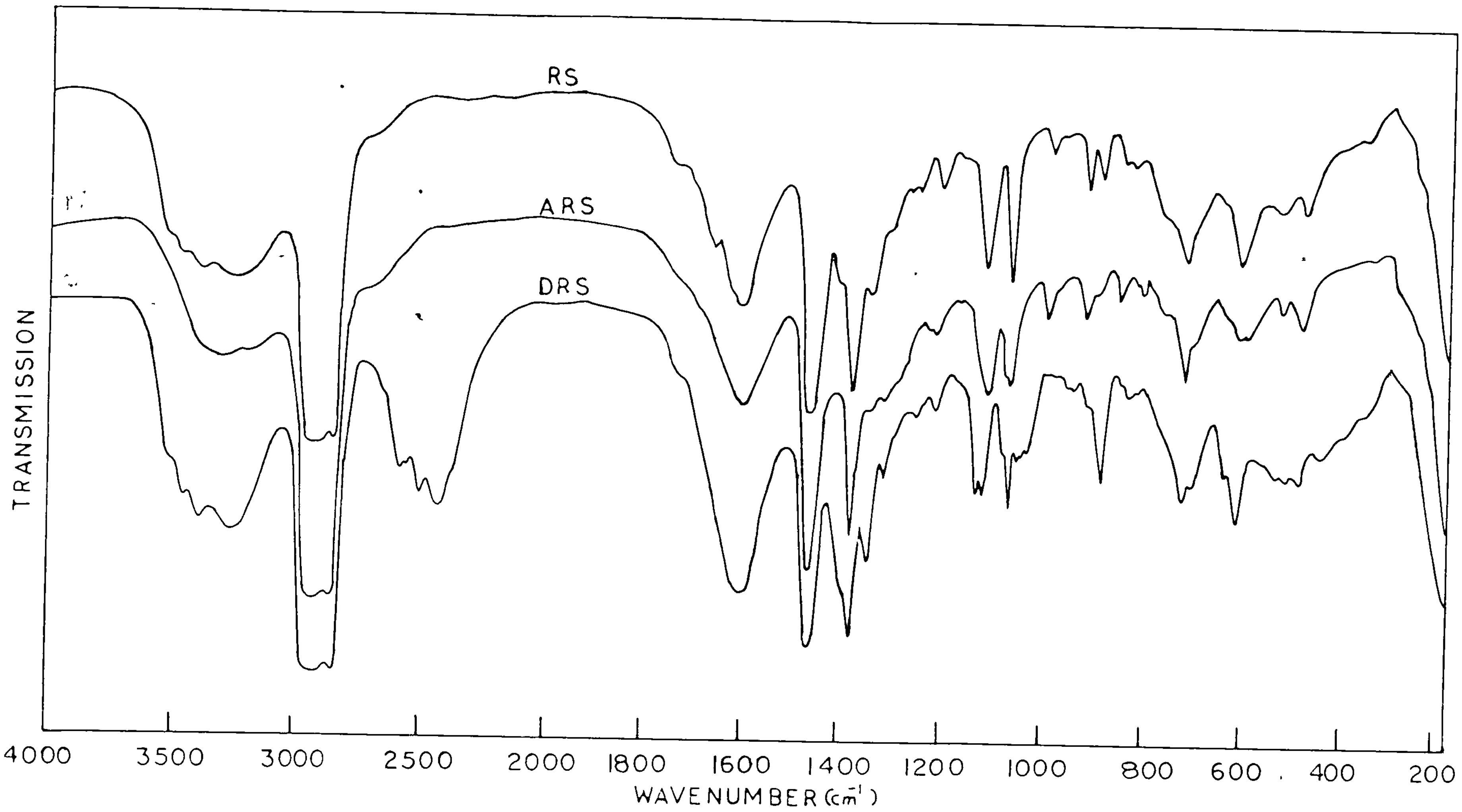


FIGURE 2.7 IR SPECTRA OF POWDERED RS, ARS AND DRS.

CHAPTER III

THEORY OF DISTORTION INDUCED ACTIVITY (DIA) OF FORBIDDEN MODES OF MOLECULAR UNITS IN CRYSTALS.*

ABSTRACT

Using the principles of group theory and approximation methods, a quantitative theory of distortion induced IR and Raman intensity due to forbidden modes of molecular units at polar and non-polar site symmetries in crystals has been discussed. The central idea of the work is that the crystal electric field (generally non-uniform in strength) serves as the source of perturbation which distorts the unit and modifies its dynamics and selection rules. It is inferred that for polar site symmetries the forbidden modes belonging to $\Gamma_{\tilde{M}} \otimes \Gamma_{IR}$

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[*] The work presented in this Chapter has been published in

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[2] Mol. Phys. 57, 379 (1986)

attain distortion induced activity of first order (DIA-I), while those belonging to $\lceil\tilde{M}\rceil \otimes \lceil IR\rceil \otimes \lceil IR\rceil$ attain that of second order (DIA-II). For non-polar site symmetries, modes of $\lceil\tilde{M}\rceil \otimes \lceil\tilde{\alpha}^{an}_{ij}\rceil$ and $\lceil\tilde{M}\rceil \otimes \lceil\tilde{\alpha}^{an}_{ij}\rceil \otimes \lceil\tilde{\alpha}^{an}_{ij}\rceil$ species attain DIA-I and DIA-II respectively, where $\tilde{\alpha}^{an}_{ij}$ is the component of anisotropic polarizability tensor. Forbidden modes, which do not become active as DIA-I and DIA-II, attain DIA of higher order (DIA-h). In general, only the forbidden modes becoming active as first order effect of polar distortion are expected to gain observable intensity.

3.1 INTRODUCTION

In the last few decades, a significant number of papers (luty and Rohleder 1972; Pimentel and McClellan 1952; Pimentel et. al. 1955; Suzuki et. al. 1968; Yamada and Person 1964) and reviews (Califano et. al. 1981; Person and Steele 1974) have appeared on the subject of Raman and IR intensities of bands due to vibrational modes of molecular units in crystals. The main objective of all these reports has been to study : (i) the relative intensity of Davydov splittings (dichroic ratio), (ii) the change in intensity on condensation and (iii) the intensity of bands due to lattice modes. However, no attention seems to have been paid to formulating a quantitative theory of the phenomenon that activates the forbidden modes of a molecular unit that attains distorted structure and occupies a lattice site of symmetry lower than its free state. The phenomenon is associated qualitatively with the lowering of local symmetry of the unit and modified selection rules are derived using well known group theoretical techniques, viz., the unit cell approach (Bhagavantam and Venkatarayudu 1939) and local-symmetry approach (Halford 1946; Hornig 1948; Winston and Halford 1949). Fateley et. al. have simplified the procedure involved in these techniques by devising a method which could easily be used without having rigorous knowledge of group theory (Fateley et. al. 1971, 1972). Jain and co-workers (Jain et. al. 1973; Jain 1974; Jain and Bist 1974, 1975a) made an interesting use of the temperature variation of IR absorbance of bands due to forbidden modes of the SO_4^{2-} ion in $(NH_4)_2SO_4$ and those of the BeF_4^{2-} ion in $(NH_4)_2BeF_4$ to make conclusions about the microscopic mechanism of the structural phase transition in these crystals. They correlated the change in the absorbance with the change in the amount of distortion in the structure of the relevant molecular ion. Although the qualitative character of this relation appears to be rational and correct, its real form has still to be discovered.Using the principles of group theory and approximation methods we have worked out a quantitative theory of the phenomenon being presented in this Chapter.

3.2 FORMULATION OF THEORY

3.2.1 DEFINITION OF POLAR AND NON-POLAR SYMMETRY

If, $\vec{r}$ is the space vector and $|a\rangle$ represents the ground state of the molecular unit, then the site symmetry of the unit commensurate with the relation

$$\langle a | \vec{r} | a \rangle \neq 0 \qquad \cdots (3.1)$$

is known as polar symmetry. Such symmetries are C_n, C_{nv} and C_s. These symmetries are called polar symmetries since a unit in such a case is expected to acquire permanent dipole moment. The remaining symmetries eg. C_{nh}, D_n, D_{nd} etc. are obviously incommensurate with equation (3.1) and they are known as non-polar symmetries. Units at such sites are expected to have any moment higher than the dipole moment.

3.2.2 PERTURBATION

The central idea of the theory is that the crystal field serves as the source of perturbation that distorts the unit and hence modifies its dynamics. In most cases this field is electrostatic in nature and non-uniform in strength. This may be accounted for by a potential V(r), whose interaction with the charge distribution in the unit leading to a first order energy of interaction H', is given by

$$H' = \int \rho(r') \, V(r') \, d\tau \qquad \cdots (3.2)$$

In a space-fixed co-ordinate system we may express V(r) as (Kroto 1975)

$$V(r') = V^{(0)} + \sum_{i}^{3} r_i \left(\frac{\partial V}{\partial r_i}\right)_0 + \frac{1}{2!} \sum_{ij} r_i \, r_j \left(\frac{\partial^2 V}{\partial r_j \partial r_i}\right)_0 + \cdots \qquad (3.3)$$

where, $V^{(0)}$ = uniform constant potential

$\left(\frac{\partial V}{\partial r_i}\right)_0 = E_i$, the ith component of the electric field at $r = 0$

$\left(\frac{\partial^2 V}{\partial r_j \partial r_i}\right)_0 = \frac{\partial E_i}{\partial r_j}$, the field gradient

etc... etc...

From equation (3.2) and (3.3), we have

$$H' = qV^{(0)} + \sum_{i} \mu_i \, E_i + \sum_{ij} Q_{ij} \frac{\partial E_i}{\partial r_j} + \cdots\cdots \qquad (3.4)$$

where, q is the electrostatic charge of the unit

$\mu_i = \int \rho(r) \, r_i \, d\tau$, ith component of the dipole moment of the unit.

$Q_{ij} = \int \rho(r)\ r_i r_j\ d\tau$, the ij component of the quadrupole moment Q of the unit.

etc... etc...

we have that

$$H' = H^{(0)} + H^{(1)} + H^{(2)} + \ldots\ldots \qquad (3.5)$$

$H^{(0)}$, $H^{(1)}$, $H^{(2)}$, etc, can obviously be interpreted as the interaction energy of different multipoles induced in the unit by the crystal field. $H^{(0)}$, the potential of charge q is independent of space coordinate r_i, r_j etc. It should obviously not perturb the structure and the dynamics of the unit. $H^{(1)}$ and $H^{(2)}$ are the interaction energies of the electric dipole and quadrupole moments of the unit, respectively. (a) For the local symmetry of polar nature, the interaction energy of moments other than the dipole moment may be considered insignificant. Thus, the effective perturbation is

$$H^{(1)} = -\sum_{i}^{3} \mu_i E_i \qquad \ldots \qquad (3.6)$$

Here, we define a parameter $\delta\vec{r}$ as the measure of distortion (in magnitude as well as in direction) in the structure of the unit. $\delta\vec{r}$ can be evaluated from the position co-ordinates of the atoms in an appropriately formulated relation. For example, for AB_4 (tetrahedral unit) and AB_6 (octahedral unit) one may use (Jain and Bist 1974)

$$\delta\vec{r} = \sum_{i}^{3} \delta\vec{r}_i = \sum_{i}^{3} \sum_{m} (\vec{A}_i - \vec{B}_i^{\,m}) \qquad \ldots (3.7)$$

where, $\vec{B}_i^{\,m}$ and $\vec{A}_i$ are the i-th component of position vectors respectively of m-th B atom and A atom. Since, the dipole moment $\vec{\mu}$ should be proportional to $\delta\vec{r}$, the effective perturbation equation (3.6) can be recast in the form

$$H^{(1)} = - K \sum_{i}^{3} \delta r_i \, E_i \qquad \ldots (3.8)$$

where K is a constant. (b) For non-polar local symmetry of the unit, the interaction energy of dipole moment vanishes. The effective perturbation should therefore be $H^{(2)}$, the interaction energy of quadrupole moment. We have

$$H^{(2)} = \sum_{ij}^{3} Q_{ij} \left(\frac{\delta E_i}{\delta r_j} \right)_0 \qquad \ldots (3.9)$$

3.2.3 TRANSITION MOMENT

A mode of vibration $|f\rangle$ is said to be forbidden if (Herzberg 1945)

$$\langle f \,|\, \tilde{M} \,|\, g \rangle = 0 \qquad \ldots (3.10)$$

where, $|g\rangle$ is the ground state wave function of the molecular unit and $\tilde{M}$ is the transition operator. When the molecular unit is subjected to a distortion as a result of perturbation H', functions $|f\rangle$ and $|g\rangle$ get modified. The modified functions can be evaluated using perturbation methods, if H' is such that (Avery 1972)

$$|\langle k|H'|a\rangle| \ll |E_a^0 - E_k^0| \qquad \ldots \quad (3.11)$$

where, E^0 (with subscript a/k) stands for the energy in the a/k-th eigen state of the unperturbed Hamiltonian H^0; similar meaning would stand here-after for all E^0 with different subscripts.

The modified functions $|f'\rangle$ and $|g'\rangle$ can be expressed as

$$|f'\rangle = N_f \left[|f^0\rangle + |f^1\rangle + |f^2\rangle + \ldots \right] \qquad \ldots \quad (3.12)$$

and

$$|g'\rangle = N_g \left[|g^0\rangle + |g^1\rangle + |g^2\rangle + \ldots \right] \qquad \ldots \quad (3.13)$$

where, N_f and N_g are the normalization factors; $|f^1\rangle$ and $|g^1\rangle$ are the first order corrections and $|f^2\rangle$ and $|g^2\rangle$ are the second order corrections in the respective functions. The transition moment $\langle f'|\tilde{M}|g'\rangle$ in the changed situation need not be zero. It may rather attain a non-vanishing finite value revealing that the transition becomes active. Such a transition may rightly be called as distortion induced transition. Using the fact that $\langle f|\tilde{M}|g\rangle = 0$ (equation (3.10)), we have

$$\langle f'|\tilde{M}|g'\rangle = N_g\, N_f \left[\langle f|\tilde{M}|g^1\rangle + \langle f^1|\tilde{M}|g\rangle + \langle f|\tilde{M}|g^2\rangle + \langle f^1|\tilde{M}|g^1\rangle + \langle f^2|\tilde{M}|g\rangle + \ldots \right] \qquad \ldots (3.14)$$

The sum of the first two terms in the equation (3.14) gives the first order transition moment,

$$\langle f'|\tilde{M}|g'\rangle^{(1)} = N_g^{(1)}\, N_f^{(1)} \left[\langle f|\tilde{M}|g^1\rangle + \langle f^1|\tilde{M}|g\rangle \right] \qquad \ldots (3.15)$$

while, the sum of the next three terms give second order transition moment

$$\langle f'|\tilde{M}|g'\rangle^{(2)} = N_g^{(2)} N_f^{(2)} \left[\langle f|\tilde{M}|g^2\rangle + \langle f^1|\tilde{M}|g^1\rangle + \langle f^2|\tilde{M}|g\rangle \right] \qquad \ldots (3.16)$$

the sum of the rest of the terms give higher order transition moments and are dropped.

The first and second order distortion induced activity of forbidden modes of molecular units in polar and non-polar site symmetry cases are discussed separately in the following sections.

3.2.4 POLAR CASE

3.2.4a First Order Approximation

The first order correction $|a^1\rangle$ to a wave function $|a\rangle$ is given by (equation V.12 of Avery 1972)

$$|a^1\rangle = \sum_{k \neq a} |k\rangle \frac{\langle k|H'|a\rangle}{E_a^0 - E_k^0} \qquad \ldots (3.17)$$

Following this, equation (3.15) is written as

$$\langle f'|\tilde{M}|g'\rangle^{(1)} = N_f^{(1)} N_g^{(1)} \left[\sum_{i \neq g} \frac{\langle f|\tilde{M}|i\rangle \langle i|H^{(1)}|g\rangle}{E_g^0 - E_i^0} + \sum_{j \neq f} \frac{\langle f|H^{(1)}|j\rangle \langle j|\tilde{M}|g\rangle}{E_f^0 - E_j^0} \right]$$

$$\ldots (3.18)$$

A non-vanishing finite value of $\langle f'|\tilde{M}|g'\rangle^{(1)}$ would represent a distortion induced transition of first order. But this demands that at least one of the several terms in the summation (c.f. equation (3.18) e.g. $\langle f|\tilde{M}|s\rangle \langle s|H^{(1)}|g\rangle$ for a choice $i = s$, should have non-vanishing value. Consequently the terms

$\langle f|\tilde{M}|s\rangle$ and $\langle s|H^{(1)}|g\rangle$ should attain non-vanishing finite value simultaneously. From group theory (Tinkham 1974), we know that a term like $\langle f|\tilde{M}|s\rangle$ or $\langle s|H^{(1)}|g\rangle$ attains non-zero value only when the product of the symmetry species of three functions appearing in the term should at least have one component of totally symmetric species. We note that the $\langle s|H^{(1)}|g\rangle = \langle s|-k\sum_i \delta r_i\; E_i|g\rangle$ has non-zero value only when $|s\rangle$ belongs to the symmetry species of the non-zero component(s) of $\delta\vec{r}$ (i.e. $\delta\vec{z}$ for C_n $(n \geqslant 2)$ and C_{nv}, $\delta\vec{x}$ and $\delta\vec{y}$ for C_s, and $\delta\vec{x}$, $\delta\vec{y}$ and $\delta\vec{z}$ for C_1 site symmetry). Thus $|s\rangle$ should belong to $\Gamma_{(z)}$ for C_n $(n \geqslant 2)$ and C_{nv}, $\Gamma_{(x,y)}$ for C_s, and $\Gamma_{(x,y,z)}$ (full IR active species Γ_{IR}) for C_1 local symmetry. This gives a clear idea of the symmetry of $|s\rangle$ needed for non-zero value of $\langle s|H^{(1)}|g\rangle$. Consequently, for the distortion of symmetry as low as C_1 the term $\langle f|\tilde{M}|s\rangle\langle s|H^{(1)}|g\rangle$ is non-zero only when $|f\rangle$ belongs to a species that appear in the representation $\Gamma_{\tilde{M}} \otimes \Gamma_{IR}$. This implies that a forbidden mode belonging to a species outside the break-up of $\Gamma_{\tilde{M}} \otimes \Gamma_{IR}$ does not become active as first order distortion induced transition. For such modes, we have to consider higher order approximation(s).

3.2.4 .b Second Order Approximation

The second order correction $|a^2\rangle$ in the wave function $|a\rangle$ is given by (equation V.16 of Avery 1972)

$$|a^2\rangle = \sum_{k\neq a}\sum_{l\neq a} \frac{|k\rangle\langle k|H'|l\rangle\langle l|H'|a\rangle}{(E_a^0 - E_k^0)(E_a^0 - E_l^0)} - \sum_{m\neq a}\frac{|m\rangle\langle m|H'|a\rangle\langle a|H'|a\rangle}{(E_a^0-E_m^0)^2} \qquad \ldots \quad (3.19)$$

Using this relation to deduce the second order correction $|f^2\rangle$ and $|g^2\rangle$, and then putting them in equation (3.16), we have the distortion induced transition moment of second order as

$$\langle f'|\tilde{M}|g'\rangle^{(2)} = N_f^{(2)} N_g^{(2)} \Bigg[\sum_{k\neq g}\sum_{l\neq g} \frac{\langle f|\tilde{M}|k\rangle\langle k|H^{(1)}|l\rangle\langle l|H^{(1)}|g\rangle}{(E_g^0-E_k^0)(E_g^0-E_l^0)} - \sum_{l\neq g}\frac{\langle f|\tilde{M}|l\rangle\langle l|H^{(1)}|g\rangle\langle g|H^{(1)}|g\rangle}{(E_g^0 - E_l^0)^2}$$
$$+ \sum_{j\neq f}\sum_{i\neq g}\frac{\langle f|H^{(1)}|j\rangle\langle j|\tilde{M}|i\rangle\langle i|H^{(1)}|g\rangle}{(E_f^0-E_j^0)(E_g^0-E_i^0)} + \sum_{m\neq f}\sum_{n\neq f}\frac{\langle f|H^{(1)}|m\rangle\langle m|H^{(1)}|n\rangle\langle n|\tilde{M}|g\rangle}{(E_f^0-E_m^0)(E_f^0-E_n^0)}$$
$$- \sum_{n\neq f}\frac{\langle f|H^{(1)}|f\rangle\langle f|H^{(1)}|n\rangle\langle n|\tilde{M}|g\rangle}{(E_f^0 - E_n^0)^2} \Bigg] \qquad \ldots \quad (3.20)$$

An analysis of the terms appearing in equation (3.20) (using group theoretical principles) on the same lines that were used in analysing $\langle f'|\tilde{M}|g'\rangle^{(1)}$ reveals that the distortion induced transition of second order is possible if $|f\rangle$ belongs to one of the species that appear in the break-up of $\Gamma_{\tilde{M}} \otimes \Gamma_{\delta r_i} \otimes \Gamma_{\delta r_j}$ or in general that appearing in $\Gamma_{\tilde{M}} \otimes \Gamma_{IR} \otimes \Gamma_{IR}$, for local symmetry as low as C_1.

An analysis of equation (3.18) and (3.20) reveals that the forbidden modes become active due to mixing of different vibrational modes. As such this mixing is a consequence of distortion but, for the fact that $H^{(1)}$, the polar kind of interaction of the unit with the crystal field, is responsible for the phenomenon, it may be called as polar mixing.

For polar distortion, among all forbidden modes only those which belong to $\Gamma_{\tilde{M}} \otimes \Gamma_{IR}$, attain DIA-I($\mu$). Others belonging to $\Gamma_{\tilde{M}} \otimes \Gamma_{IR} \otimes \Gamma_{IR}$ attain DIA-II(μ); however, some of ~~these~~ may be common to $\Gamma_{\tilde{M}} \otimes \Gamma_{IR}$. Modes not included in these two sets may gain only DIA-h (distortion induced activity of higher order).

Specifically, the distortion induced activity of first order, DIA-I, is attained by a forbidden mode when it mixes with allowed modes and/or the ground state mixes with some mode $|i\rangle$ which are connected to $|f\rangle$ through $\tilde{M}$, with $\langle f|\tilde{M}|i\rangle \neq 0$. Similarly, mixing occurs for non-zero value of

DIA-II (c.f. equation (3.20)). However, it comes through an additional mode of the unit. It can easily be seen that more additional modes would be involved as a via medium in the mixing of modes leading to a non-zero value of DIA-h.

3.2.5 NON-POLAR (QUADRUPOLAR) CASE

3.2.5a First Order Approximation

Using the standard form of the first order correction (equation (3.17)) the first order distortion induced transition moment $\langle f'|\tilde{M}|g'\rangle^{(1)}$ (c.f. equation (3.15)) for quadrupolar case can be written as

$$\langle f'|\tilde{M}|g'\rangle^{(1)} = N_f^{(1)} N_g^{(1)} \left[\sum_{i \neq g} \frac{\langle f|\tilde{M}|i\rangle \langle i|H^{(2)}|g\rangle}{E_g^0 - E_i^0} + \sum_{j \neq f} \frac{\langle f|H^{(2)}|j\rangle \langle j|\tilde{M}|g\rangle}{E_f^0 - E_j^0} \right] \qquad \ldots \quad (3.21)$$

we note that

$$\langle s|H^{(2)}|g\rangle = \langle s|Q_{ij} \left(\frac{\partial E_i}{\partial r_j} \right)|g\rangle$$

has non-zero value only when $|s\rangle$ belongs to the symmetry species of the non-zero component (s) of Q_{ij}. [The non-vanishing indepent components of the quadrupole moment are (xx, yy, xy, yz and zx)/(xx, yy and xy)/(zz) for symmetries (C_1, C_i)/(C_s,C_2,C_{2h})/

$\{C_{nv}$ $(n \geqslant 2)$, C_n $(n > 2)$, C_{nh} $(n = 3,4,6)$, D_n $(n = 2,3,4,6)$, D_{nd} $(n = 2,3,4,6)$, D_{nh} $(n = 2,3,4,6)$, S_4, S_6, $S_8\}$ in order (Califano et. al. 1981)]. In other words, $|s\rangle$ should form a basis of $\Gamma_{Q_{ij}}$. For such a choice of $|s\rangle$ the term $\langle f|\tilde{M}|s\rangle \langle s|H^{(2)}|g\rangle$ is non-zero only when $|f\rangle$ belongs to species that appear in the representation, $\Gamma_{\tilde{M}} \otimes \Gamma_{Q_{ij}}$ or $\Gamma_{\tilde{M}} \otimes \Gamma_{\tilde{\alpha}^{an}_{ij}}$ as the components of quadrupole moment and anisotropic polarizability tensor $(\tilde{\alpha}^{an}_{ij})$ transform identically (Long 1977). Hence, $|f\rangle$ should belong to a species falling in $\Gamma_{\tilde{M}} \otimes \Gamma_{\tilde{\alpha}^{an}_{ij}}$. In general, this would imply that a forbidden mode belonging to a species out side the break-up of $\Gamma_{\tilde{M}} \otimes \Gamma_{\tilde{\alpha}^{an}_{ij}}$ does not become active as a first order distortion induced transition. For these cases we have to consider higher order approximation.

3.2.5b Second Order Approximation

Using the standard form of the second-order correction (equation (3.19)), the transition moment, $\langle f'|\tilde{M}|g'\rangle^{(2)}$ (c.f. equation (3.16)), characterising distortion induced transitions of second order in quadrupolar distortion can be given by

$$\langle f'|\tilde{M}|g'\rangle^{(2)} = N_f^{(2)} \, N_g^{(2)} \Big[\sum_{k \neq g} \sum_{l \neq g} \frac{\langle f|\tilde{M}|k\rangle \langle k|H^{(2)}|l\rangle \langle l|H^{(2)}|g\rangle}{(E_g^0 - E_k^0)(E_g^0 - E_l^0)}$$

$$- \sum_{l \neq g} \frac{\langle f|\tilde{M}|l\rangle \langle l|H^{(2)}|g\rangle \langle g|H^{(2)}|g\rangle}{(E_g{}^0 - E_l{}^0)}$$

$$+ \sum_{i \neq g} \sum_{j \neq f} \frac{\langle f|H^{(2)}|j\rangle \langle j|\tilde{M}|i\rangle \langle i|H^{(2)}|g\rangle}{(E_f{}^0 - E_j{}^0)\ (E_g{}^0 - E_i{}^0)}$$

$$+ \sum_{m \neq f} \sum_{n \neq f} \frac{\langle f|H^{(2)}|m\rangle \langle m|H^{(2)}|n\rangle \langle n|\tilde{M}|g\rangle}{(E_f{}^0 - E_m{}^0)\ (E_f{}^0 - E_n{}^0)}$$

$$- \sum_{n \neq f} \frac{\langle f|H^{(2)}|f\rangle \langle f|H^{(2)}|n\rangle \langle n|\tilde{M}|g\rangle}{(E_f{}^0 - E_n{}^0)} \Bigg]$$

$$\ldots \qquad (3.22)$$

An analysis of the terms appearing in equation (3.22) (using group theoretical principles) on the same lines that were used in analysing $\langle f'|\tilde{M}|g'\rangle^{(1)}$ reveals that the distortion induced transition of second order is possible, if $|f\rangle$ belongs to one of the species that appear in the break-up of $\Gamma_{\tilde{M}} \otimes \Gamma_{\tilde{\alpha}^{an}_{ij}} \otimes \Gamma_{\tilde{\alpha}^{an}_{ij}}$.

The mixing of modes responsible for DIA in non-polar case is clearly a consequence of the distortion which is mathematically accounted for by $H^{(2)}$ as perturbation. This mixing may obviously be called as quadrupolar mixing. For quadrupolar distortion, among all forbidden modes only those which belong to $\Gamma_{\tilde{M}} \otimes \Gamma_{\tilde{\alpha}^{an}_{ij}}$ attain DIA-I (Q) while those belonging to $\Gamma_{\tilde{M}} \otimes \Gamma_{\tilde{\alpha}^{an'}_{ij}} \otimes \Gamma_{\tilde{\alpha}^{an}_{ij}}$ attain DIA-II (Q); some of these may be common to both. Modes not included in the two sets may attain DIA-h.

3.3 ORDER OF INTENSITY FOR DIFFERENT ORDERS OF DIA

If a typical transition induced by the electric dipole moment is assumed to take place at a rate of 10^8 sec^{-1}, the transition induced by magnetic dipole and electric quadrupole moments is expected to take place at a rate 10^3 and 1 sec^{-1}, respectively (Schutte 1976). A rough estimate of the strength of distortion induced transitions on this scale can be made as follows. An examination of equations (3.18) and (3.20) reveals that in $\langle f'|\tilde{M}|g'\rangle^{(1)} / \langle f'|\tilde{M}|g'\rangle^{(2)}$ a typical term such as $\langle j|H^{(1)}|k\rangle/(E_j^0-E_k^0)$ appears once/twice in product with the normal transition moment $\langle i|\tilde{M}|j\rangle$. We note that the typical value of frequency separation between different split components of the degenerate modes of most molecular units in crystals fall around 5% value of the fundamental frequency of the modes. This indicates that the typical value of $\langle j|H^{(1)}|k\rangle/(E_j^0-E_i^0)$ should lie around 5×10^{-2}. Obviously, the probability of distortion induced transition of first and second order should, respectively, be 25×10^{-4} and 625×10^{-8} times the normal transition probability. Thus on the scale of 10^8 sec^{-1} for normal dipole transition, the rate of transitions due to DIA-I ($H^{(1)}$) and DIA-II ($H^{(1)}$) should be 10^5 (as $10^8 \times 25 \times 10^{-4} \simeq 10^5$) and 10^3 (as $10^8 \times 625 \times 10^{-8} \simeq 10^3$) sec^{-1}. On the same scale the rate of distortion induced transition (first order approximation with effective perturbation $H^{(2)} = \sum Q_{ij} \frac{\partial E_i}{\partial r_j}$ (equation (3.9)) is roughly estimated to be equal to 10^3 sec^{-1} because $H^{(2)}$ is expected at least to be an order of magnitude weaker than $H^{(1)}$ in strength. In view of these numbers, it can be concluded that the distortion induced transitions due to DIA-I ($H^{(1)}$) (i.e. DIA-I (μ)) are the only transitions that can be expected to appear in the IR/Raman spectra with observable intensity, as the rate of other transitions is equal to or less than 10^3 sec^{-1},—the rate of magnetic dipole transitions which are normally not observed in phonon spectra. In exceptional cases, if DIA-II ($H^{(1)}$) (i.e. DIA-II (μ)) and DIA-I ($H^{(2)}$) (i.e. DIA-I (Q)) transitions could be observed, this observation would be indicative of strong crystalline field and field gradient respectively.

A forbidden mode of a molecular unit in a crystal may also become active due to the effects of lattice vibrations; these effects are linearly related to their amplitude (Hornig 1948). This mechanism becomes uneffective at low temperature because the amplitude of lattice modes reduces almost to a minimum. Thus at low temperature a forbidden mode is only expected to appear due to structural distortion. One could therefore examine whether DIA-II (μ), DIA-I (Q) and

DIA-II (Q) really remain negligibly small or attains perceptible magnitude by studying forbidden modes of molecular units at low temperature.

CHAPTER IV

SYMMETRY CLASSIFICATION OF FORBIDDEN MODES OF MOLECULAR UNITS BELONGING TO DIFFERENT POINT GROUPS ATTAINING DIFFERENT ORDERS OF DIA.*

ABSTRACT

IR and Raman forbidden species of different point groups which are expected to attain first/second/.../higher order of distortion induced activity (DIA) are classified and tabulated in Table 4.1. In each case the results have been analysed for all possible site symmetries. It is revealed that the key component of distortion that affects the selection rules is one which is not present in the free state structure of the molecule. And even for the distortion commensurate with C_1 symmetry not all forbidden modes of the unit attain first order or even second order activity in all cases.

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*Results reported in this chapter, are arranged in the form of a technical report of the department (1986) bearing the same title and are available on request for reference.

4.1 INTRODUCTION

When a molecular unit occupies a site of lower symmetry in a crystal its several modes of vibrations (forbidden in the free state) become active. The well known group theoretical techniques viz. unit cell approach (Bhagavantam and Venkatarayudu 1939) and site symmetry approach (Halford 1946; Hornig 1948; Winston and Halford 1949), provide a way to determine which of these modes become active and which of them remain forbidden. They do not provide any idea pertaining to the order of intensity of such modes and it becomes impossible to decide whether the mode is expected to attain observable intensity or not. The mechanism which activates the forbidden transition of molecular units in crystals also remains unclear. However, the theory discussed in Chapter III helps in solving these problems. It classifies such transitions into categories of DIA-I/DIA-II/etc. and provides the nature of mechanism (polar/quadrupolar/octupolar/etc. type mixing of modes) which activates a given mode. This classification helps in deciding the order of band intensity of the mode in comparison with a normally allowed mode. Obviously, we can have a better understanding of observed IR and Raman spectra, if we know the type and order of distortion induced activity of the forbidden modes of the molecular unit. As discussed in Chapter III, transition allowed as first order effect of polar type of distortion (barring few exceptions) are only expected to gain observable intensity. Thus, the normal techniques of determining the selection rules do not provide effective selection rules for practical purposes. It is in this context that the DIA analysis becomes much more important and useful.

In this chapter, we therefore, provide the detailed results of the DIA analysis for determining the effective selection rules as well as the type and order of DIA mechanism activating a particular forbidden species in case of all important and frequently encountered symmetry point groups which can serve as ready reference. These results are summarized in Table 4.1.

4.2 DISCUSSION

Table 4.1, presents different molecular symmetries, their IR/Raman forbidden species, possible site symmetries alongwith the type and order of DIA that activates a particular forbidden mode. In column 5, the symbol μ/Q refers to polar/quadrupolar distortion for activating the species registered in column 6 and 7; superscript I/II stands for first/second order effect of distortion. Other effects such as DIA-III (μ), DIA-II (Q), DIA-I(O) (first order effect of octupolar distortion), etc. has been identified by symbol h (higher order effect). However, for all practical purposes these effects are not expected to result in observable band intensity as concluded in Chapter III. The symmetry species common in the results of a lower as well as a higher order are only shown in the row of lower order.

It has been inferred in Chapter III that : (i) forbidden modes belonging to $\Gamma_{\tilde{M}} \otimes \Gamma_{\delta r}$ or $\Gamma_{\tilde{M}} \otimes \Gamma_{IR}$ attain DIA-I and those belonging to $\Gamma_{\tilde{M}} \otimes \Gamma_{IR} \otimes \Gamma_{IR}$ attain DIA-II, for polar distortion. Here, Γ_{IR} is $\Gamma_{(z)}$ for C_n $(n \geq 2)$ and C_{nv} $\Gamma_{(x,y)}$ for C_s ; and $\Gamma_{(x,y,z)}$ for C_1 site symmetries. (ii) for quadrupolar distortion, modes belonging to $\Gamma_{\tilde{M}} \otimes \Gamma_{Q_{ij}}$ or $\Gamma_{\tilde{M}} \otimes \Gamma_{\tilde{\alpha}^{an}_{ij}}$ attain DIA-I and those belonging to $\Gamma_{\tilde{M}} \otimes \Gamma_{\tilde{\alpha}^{an}_{ij}} \otimes \Gamma_{\tilde{\alpha}^{an}_{ij}}$ attain DIA-II. Here, $\tilde{\alpha}^{an}_{ij}$ for symmetries $(C_1, C_i)/(C_s, C_2, C_{2h})/$ $\{C_{nv}$ $(n \geq 2)$, C_n $(n > 2)$, C_{nh} $(n = 3,4,6)$, D_n $(n = 2,3,4,6)$, D_{nd} $(n = 2,3,4,6)$, D_{nh} $(n = 2,3,4,6)$, S_4, S_6, $S_8\}$ are (xx, yy, xy, yz and zx)/ (xx, yy and xy)/ (zz) in order and (iii) modes not included in these sets gain DIA-h. These products have been evaluated to generate Table 4.1 for almost all important and frequently encountered symmetries in case of all possible site symmetries.

A distortion does not contribute to the intensity of forbidden modes unless, one of its non-zero components forms the basis of one of the non-totally symmetric species of undistorted structure; because, if the component of distortion* (Δ) belongs to a totally symmetric species, $\Gamma_{\tilde{M}} \otimes \Gamma_{(\Delta)}$ can

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[*] Δ stands for polar as well as for non-polar distortion

not lead to a species other than the allowed species $\Gamma_{\tilde{M}}$. In other words, the key component of distortion that gives rise to the modified selection rules is one which is not present in the free state structure of the molecule. For example, when a molecule of C_{2v} symmetry (c.f. Table 4.1, C_{2v}) goes to C_2 site, the A_2 species does not become active in IR due to DIA (μ) of any order, because, C_2 site does not have other than the z-component of polar distortion already existing in C_{2v} structure. Note that the z-component of polar distortion belongs to totally symmetric species of both C_2 and C_{2v} point groups. Consequently, A_2 species is activated by DIA-I (Q) due to additional quadrupolar distortion Q_{xy} (belonging to A_2 species of C_{2v}) which the molecule acquires in C_2 site. In all such cases of polar sites, results of only first order quadrupolar distortions have been tabulated in the table. As another example of the similar situation one may examine the case of a molecule of D_{2h} structure going to D_2 site. It is observed that no forbidden mode of the molecule becomes active due to quadrupolar distortion (Table 4.1, D_{2h}) since its all non-zero components (xx, yy and zz) in D_2 structure belong to totally symmetric species (A_g) of D_{2h} symmetry. It is further observed that the non-zero component of octupolar distortion O_{xyz} (in D_2 structure) belonging to the non-totally symmetric A_u species of D_{2h} point group, activates the modes. Taking this as a key factor, it can be shown that modes belonging to $\overline{|\text{Raman}|} \otimes \overline{|A_u|}$ (i.e. A_u, B_{1u}, B_{2u} and B_{3u}) species should become Raman active and those belonging to $\overline{|\text{IR}|} \otimes \overline{|A_u|}$ (i.e. B_{1g}, B_{2g} and B_{3g}) species should become IR active as first order effect of octupolar distortion; the modes of A_g and A_u species remain IR forbidden.

The normal group theoretical analysis for the molecular unit attaining C_1 site symmetry reveals that all modes of the unit (without any distinction) should become active in IR and Raman spectra. However, the present work classifies these into categories of modes attaining DIA-I, DIA-II and DIA-h. For example, take a molecule of symmetry O_h going to site C_1 (c.f. Table 4.1, O_h) : In Raman spectrum, forbidden modes of species A_{2u}, F_u, E_{1u} and F_{2u} attain DIA-I; A_{2g} and F_{1g} attain DIA-II; and A_{1u} attains DIA-h. And in IR spectrum, the forbidden modes of species A_{1g}, E_g, F_{1g} and F_{2g} attain DIA-I; A_{1u}, A_{2u}, E_u and F_{2u} attain DIA-II; and A_{2g} attains DIA-h. Thus, even for the distortion commensurate with C_1 symmetry not all forbidden modes of the unit attain first-order or even second-order activity in all cases. This gives a fair idea of the relative intensities of bands arising due to distortion induced transitions. Thus for the first time we note that some modes of certain units particularly of high symmetry may not appear in the IR/Raman spectra even when they are calculated to be allowed according to the conventional selection rules. From this analysis we also get an idea about the relative intensity of such modes; e.g. modes attaining first-order activity should be more intense than those attaining second-order activity. This would obviously help in getting a better understanding of the IR/Raman spectra of complex crystals, and in appreciating, the importance of what we define as effective selection rules.

Table 4.1 Symmetry Species^{+} of forbidden modes (of molecular units belonging to different point groups) attaining first, second, etc., order of DIA for different site symmetries.

Point Group	Forbidden Species in		Site Symmetry	Type and Order of DIA	Distortion induced Raman active species	Distortion induced IR active species
	Raman	IR				
1	2	3	4	5	6	7
C_{2v}	NIL	A_2	C_1	μ^I	NIL	A_2
			C_s (σ_{zx})	μ^I	NIL	A_2
			C_s (σ_{yz})	μ^I	NIL	A_2
			C_2	Q^I	NIL	A_2
C_{3v}	A_2	A_2	C_1	μ^I	A_2	A_2
			C_s	μ^I	A_2	A_2
			C_3	h	A_2	A_2
C_{4v}	A_2	A_2	C_1	μ^I	A_2	A_2 B_1 B_2
		B_1	C_s (σ_d)	μ^I	A_2	A_2 B_1 B_2
		B_2	C_s (σ_v)	μ^I	A_2	A_2 B_1 B_2
			C_2	$\left\{\begin{matrix} Q^I \\ h \end{matrix}\right.$	A_2 -	B_1 B_2 A_2
			C_4	h	A_2	A_2
			C_{2v} (σ_d)	Q^I	A_2	B_2
			C_{2v} (σ_v)	Q^I	A_2	B_1

1	2	3	4	5	6	7
C_{6v}	A_2	A_2	C_1	μ^{I}	A_2 B_1 B_2	A_2 E_2
	B_1	B_1		μ^{II}	–	B_1 B_2
	B_2	B_2	$C_s(\sigma_d)$	μ^{I}	A_2 B_1 B_2	A_2 E_2
				μ^{II}	–	B_1 B_2
		E_2	$C_s(\sigma_v)$	μ^{I}	A_2 B_1 B_2	A_2 E_2
				μ^{II}	–	B_1 B_2
			C_2	Q^{I}	A_2 B_1 B_2	B_1 B_2 E_2
				h	–	A_2
			C_3	h	A_2 B_1 B_2	A_2 B_1 B_2 E_2
			C_6	h	A_2	A_2
			C_{2v}	Q^{I}	A_2 B_1 B_2	B_1 B_2 E_2
			$C_{3v}(\sigma_d)$	h	B_2	B_2 E_2
			$C_{3v}(\sigma_v)$	h	B_1	B_1 E_2
C_{2h}		A_g	C_1	μ^{I}	A_u B_u	A_g B_g
		B_g	C_s	μ^{I}	A_u B_u	A_g B_g
	A_u		C_2	μ^{I}	A_u B_u	A_g B_g
	B_u		C_i	h	NIL	NIL
C_{3h}		A'	C_1	μ^{I}	A''	A' E''
	A''		C_s	μ^{I}	A''	A' E''
		E''	C_3	μ^{I}	A''	A' E''

1	2	3	4	5	6	7
C_{4h}		A_g	C_1	μ^{I}	A_u B_u E_u	A_g B_g E_g
		B_g		μ^{II}	–	B_u
		E_g	C_s	μ^{I}	A_u B_u E_u	A_g B_g E_g
	A_u			μ^{II}	–	B_u
	B_u	B_u	C_2	μ^{I}	A_u B_u E_u	A_g E_g
	E_u			Q^{I}	–	B_u
				h	–	B_g
			C_4	μ^{I}	A_u B_u E_u	A_g E_g
			C_i	Q^{I}	NIL	B_u
			C_{2h}	Q^{I}	NIL	B_u
			S_4	h	A_u B_u E_u	B_g E_g
C_{6h}		A_g	C_1	μ^{I}	A_u B_u E_{1u} E_{2u}	A_g E_{1g} E_{2g}
	B_g	B_g		μ^{II}	B_g	B_u
		E_{1g}		Q^{I}	B_g	B_u E_{2u}
		E_{2g}		h	–	B_g

Contd....

C_{6h} continued

1	2	3	4	5	6	7
	A_u		C_s	μ^I	A_u B_u E_{1u} E_{2u}	A_g E_{1g} E_{2g}
	B_u	B_u		μ^{II}	B_g	B_u
	E_{1u}			Q^I	B_g	B_u E_{2u}
	E_{2u}	E_{2u}		h	–	B_g
			C_2	μ^I	A_u E_{1u} E_{2u}	A_g E_{1g}
				Q^I	B_g	B_u E_{2u}
				h	B_u	B_g E_{2g}
			C_3	μ^I	A_u E_{1u} E_{2u}	A_g E_{1g}
				h	B_g B_u	B_g E_{2g} B_u E_{2u}
			C_6	μ^I	A_u E_{1u} E_{2u}	A_g E_{1g}
			C_i	Q^I	B_g	B_u E_{2u}
			C_{2h}	Q^I	B_g	B_u E_{2u}
			C_{3h}	h	B_u E_{1u} E_{2u}	B_g E_{2g}
			S_6	h	B_g	B_u E_{2u}
D_2	NIL	A	C_1	μ^I	NIL	A
			C_2^x	μ^I	NIL	A
			C_2^Y	μ^I	NIL	A
			C_2^z	μ^I	NIL	A

1	2	3	4	5	6	7
D_3		A_1	C_1	μ^{I}	A_2	A_1
	A_2		C_2	μ^{I}	A_2	A_1
			C_3	μ^{I}	A_2	A_1
D_4		A_1	C_1	μ^{I}	A_2	A_1 B_1 B_2
	A_2		C_2	μ^{I}	A_2	A_1
		B_1		Q^{I}	A_2	B_1 B_2
		B_2	C_2'	μ^{I}	A_2	A_1 B_1 B_2
			C_2''	μ^{I}	A_2	A_1 B_1 B_2
			C_4	μ^{I}	A_2	A_1
			$D_2\,(C_2')$	Q^{I}	A_2	B_2
			$D_2\,(C_2'')$	Q^{I}	A_2	B_1
D_6		A_1	C_1	μ^{I}	A_2 B_1 B_2	A_1 E_2
	A_2			μ^{II}	–	B_1 B_2
	B_1	B_1	C_2	μ^{I}	A_2	A_1
	B_2	B_2		Q^{I}	B_1 B_2	B_1 B_2 E_2
		E_2				

contd......

D_6 continued

1	2	3	4	5	6	7
			C_2'	μ^I	A_2 B_1 B_2	A_1 E_2
				μ^{II}	–	B_1 B_2
			C_2''	μ^I	A_2 B_1 B_2	A_1 E_2
				μ^{II}	–	B_1 B_2
			C_3	μ^I	A_2	A_1
				h	B_1 B_2	B_1 B_2 E_2
			C_6	μ^I	A_2	A_1
			D_2	Q^I	A_2 B_1 B_2	B_1 B_2 E_2
			$D_3(c_2')$	h	B_1	B_2 E_2
			$D_3(c_2'')$	h	B_2	B_1 E_2
D_{2d}		A_1	C_1	μ^I	A_2	A_1 A_2 B_1
	A_2	A_2	C_s	μ^I	A_2	A_1 A_2 B_1
		B_1	C_2	μ^I	A_2	A_1
				Q^I	–	A_2
				h	–	B_1

contd......

D_{2d} contd..

1	2	3	4	5	6	7
			C_2'	μ^I	A_2	A_1 A_2 B_1
			C_{2v}	μ^I	A_2	A_1
			D_2	Q^I	A_2	A_2
			S_4	h	A_2	B_1
D_{3d}		A_{1g}	C_1	μ^I	A_{1u} A_{2u} E_u	A_{1g} A_{2g} E_g
	A_{2g}	A_{2g}		μ^{II}	A_{2g}	A_{1u}
		E_g	C_s	μ^I	A_{1u} A_{2u} E_u	A_{1g} A_{2g} E_g
	A_{1u}	A_{1u}		μ^{II}	A_{2g}	A_{1u}
	A_{2u}		C_2	μ^I	A_{2u} E_u	A_{1g} E_g
	E_u			Q^I	A_{2g}	A_{1u}
				h	A_{1u}	A_{2g}
			C_3	μ^I	A_{2u} E_u	A_{1g} E_g
				h	A_{2g} A_{1u}	A_{2g} A_{1u}
			C_{3v}	μ^I	A_{2u} E_u	A_{1g} E_g
			C_i	Q^I	A_{2g}	A_{1u}

contd.....

D_{3d} continued

1	2	3	4	5	6	7
			C_{2h}	Q^I	A_{2g}	A_{1u}
			D_3	h	A_{1u} E_u	A_{2g} E_g
			S_6	h	A_{2g}	A_{1u}
D_{4d}		A_1	C_1	μ^I	B_1 B_2 E_1	A_1 A_2 E_2 E_3
	A_2	A_2		μ^{II}	A_2	B_1
	B_1	B_1	C_s	μ^I	B_1 B_2 E_1	A_1 A_2 E_2 E_3
	B_2			μ^{II}	A_2	B_1
	E_1					
		E_2	C_2	μ^I	B_2 E_1	A_1 E_3
		E_3		Q^I	A_2 B_1	E_2
				h	–	A_2 B_1
			C_2'	μ^I	B_1 B_2 E_1	A_1 A_2 E_2 E_3
				μ^{II}	A_2	B_1
			C_4	μ^I	B_2 E_1	A_1 E_3
				h	B_1 A_2	A_2 B_1
			C_{2v}	μ^I	B_2 E_1	A_1 E_3
				Q^I	A_2 B_1	E_2

contd....

D_{4d} continued

1	2	3	4	5	6	7
			C_{4v}	μ^{I}	B_2 E_1	A_1 E_3
			D_4	h	B_1 E_1	A_2 E_3
			S_8	h	A_2	B_1
		A_1	C_1	μ^{I}	B_1 B_2 E_1 E_3 E_4	A_1 A_2 E_2 E_5
D_{6d}	A_2	A_2		μ^{II}	A_2	E_3 E_4
	B_1	B_1		Q^{I}	A_2	B_1 E_3 E_4
	B_2		C_s	μ^{I}	B_1 B_2 E_1 E_3 E_4	A_1 A_2 E_2 E_5
	E_1			μ^{II}	A_2	E_3 E_4
		E_2		Q^{I}	A_2	B_1 E_3 E_4
	E_3	E_3	C_2	μ^{I}	B_2 E_1 E_4	A_1 E_5
	E_4	E_4		Q^{I}	A_2 E_3	E_3 E_4
		E_5		h	B_1	A_2 B_1 E_2
			C_2'	μ^{I}	B_1 B_2 E_1 E_3 E_4	A_1 A_2 E_2 E_5
				μ^{II}	A_2	E_3 E_4
				Q^{I}	A_2	B_1 E_3 E_4
			C_3	μ^{I}	B_2 E_1 E_4	A_1 E_5
				h	A_2 B_1 E_3	A_2 B_1 E_2 E_3 E_4

contd.....

D_{6d} continued

1	2	3	4	5	6	7
			C_6	μ^I	E_1 E_4 B_2	A_1 E_5
				h	A_2 B_1	A_2 B_1
			C_{2v}	μ^I	B_2 E_1 E_4	A_1 E_5
				Q^I	A_2 E_3	E_3 E_4
				h	B_1	E_2
			C_{3v}	μ^I	B_2 E_1 E_4	A_1 E_5
				h	E_3	E_2 E_3 E_4
			C_{6v}	μ^I	B_2 E_1 E_4	A_1 E_5
			D_2	Q^I	A_2 E_3 E_4	E_3 E_4
				h	B_1 B_2 E_1	A_2 E_2 E_5
			D_3	h	B_1 E_1 E_3 E_4	A_2 E_2 E_3 E_4 E_5
			D_6	h	B_1 E_1 E_4	A_2 E_5
			D_{2d}	h	B_1 B_2 E_1 E_3 E_4	E_2 E_3 E_5
			S_4	h	A_2 B_1 B_2 E_1 E_3 E_4	B_1 E_2 E_3 E_5

1	2	3	4	5	6	7
D_{2h}		A_g	C_1	μ^I	A_u B_{1u} B_{2u} B_{3u}	A_g B_{1g} B_{2g} B_{3g}
		B_{1g}		Q^I	-	A_u
		B_{2g}	C_s (σyz)	μ^I	A_u B_{1u} B_{2u} B_{3u}	A_g B_{1g} B_{2g} B_{3g}
		B_{3g}		Q^I	-	A_u
	A_u	A_u	C_s (σzx)	μ^I	A_u B_{1u} B_{2u} B_{3u}	A_g B_{1g} B_{2g} B_{3g}
	B_{1u}			Q^I	-	A_u
	B_{2u}		C_s (σxy)	μ^I	A_u B_{1u} B_{2u} B_{3u}	A_g B_{1g} B_{2g} B_{3g}
	B_{3u}			Q^I	-	A_u
			C_2 (z)	μ^I	A_u B_{1u} B_{2u} B_{3u}	A_g B_{2g} B_{3g}
				Q^I	-	A_u
				h	-	B_{1g}
			C_2 (y)	μ^I	A_u B_{1u} B_{2u} B_{3u}	A_g B_{1g} B_{3g}
				Q^I	-	A_u
				h	-	B_{2g}
			C_2 (x)	μ^I	A_u B_{1u} B_{2u} B_{3u}	A_g B_{2g} B_{1g}
				Q^I	-	A_u
				h	-	B_{3g}
			C_{2v} (z)	μ^I	A_u B_{1u} B_{2u} B_{3u}	A_g B_{2g} B_{3g}
			C_{2v} (y)	μ^I	A_u B_{1u} B_{2u} B_{3u}	A_g B_{1g} B_{3g}
			C_{2v}(x)	μ^I	A_u B_{1u} B_{2u} B_{3u}	A_g B_{1g} B_{2g}

contd.....

D_{2h} continued

1	2	3	4	5	6	7
			C_i	Q^{I}	NIL	A_u
			$C_{2h}(z)$	Q^{I}	NIL	A_u
			$C_{2h}(y)$	Q^{I}	NIL	A_u
			$C_{2h}(x)$	Q^{I}	NIL	A_u
			D_2	h	A_u B_{1u} B_{2u} B_{3u}	B_{1g} B_{2g} B_{3g}
D_{3h}		A'_1	C_1	μ^{I}	A'_2 A''_1 A''_2	A'_1 A'_2 E''
	A'_2	A'_2		μ^{II}	–	A''_1
	A''_1	A''_1	$C_s(\sigma_h)$	μ^{I}	A'_2 A''_1 A''_2	A'_1 A'_2 E''
	A''_2			μ^{II}		A''_1
		E''	$C_s(\sigma_v)$	μ^{I}	A'_2 A''_1 A''_2	A'_1 A'_2 E''
				μ^{II}	–	A''_1
			C_2	μ^{I}	A''_2	A'_1 E''
				Q^{I} h	A''_1 A'_2 –	A'_1 A''_1
			C_3	μ^{I}	A''_2	A'_1 E''
				h	A'_2 A''_1	A'_2 A''_1
			C_{2v}	μ^{I}	A''_2	A'_1 E''
				Q^{I}	A'_2 A''_1	A'_2

contd.....

D_{3h} continued

1	2	3	4	5	6	7
			C_{3v}	μ^{I}	A''_2	A'_1 E''
			C_{3h}	h	A'_2	A''_1
			D_3	h	A''_1	A'_2 E''
D_{4h}		A_{1g}	C_1	μ^{I}	A_{1u} A_{2u} B_{1u} B_{2u} E_u	A_{1g} A_{2g} B_{1g} B_{2g} E_g
	A_{2g}	A_{2g}		μ^{II}	A_{2g}	A_{1u} B_{1u} B_{2u}
		B_{1g}	C_s (σ_d)	μ^{I}	A_{1u} A_{2u} B_{1u} B_{2u} E_u	A_{1g} A_{2g} B_{1g} B_{2g} E_g
		B_{2g}		μ^{II}	A_{2g}	A_{1u} B_{1u} B_{2u}
		E_g	C_s (σ_v)	μ^{I}	A_{1u} A_{2u} B_{1u} B_{2u} E_u	A_{1g} A_{2g} B_{1g} B_{2g} E_g
	A_{1u}	A_{1u}		μ^{II}	A_{2g}	A_{1u} B_{1u} B_{2u}
	A_{2u}		C_s (σ_h)	μ^{I}	A_{1u} A_{2u} B_{1u} B_{2u} E_u	A_{1g} A_{2g} B_{1g} B_{2g} E_g
	B_{1u}	B_{1u}		μ^{II}	A_{2g}	A_{1u} B_{1u} B_{2u}
	B_{2u}	B_{2u}				
	E_u					

contd.....

D_{4h} continued

1	2	3	4	5	6	7
			C_2	μ^I	A_{2u} B_{1u} B_{2u} E_u	A_{1g} E_g
				Q^I	A_{2g}	B_{1u} B_{2u}
				h	A_{1u}	A_{2g} B_{1g} B_{2g} E_g A_{1u}
			C_2'	μ^I	A_{1u} A_{2u} B_{1u} B_{2u} E_u	A_{1g} A_{2g} B_{1g} B_{2g} E_g
				μ^{II}	A_{2g}	A_{1u} B_{1u} B_{2u}
			C_2''	μ^I	A_{1u} A_{2u} B_{1u} B_{2u} E_u	A_{1g} A_{2g} B_{1g} B_{2g} E_g
				μ^{II}	A_{2g}	A_{1u} B_{1u} B_{2u}
			C_4	μ^I	A_{2u} B_{1u} B_{2u} E_u	A_{1g} E_g
				h	A_{2g} A_{1u}	A_{2g} A_{1u}
			C_{2v} $(C_2\sigma_v)$	μ^I	A_{2u} B_{1u} B_{2u} E_u	A_{1g} E_g
				Q^I	A_{2g}	B_{2u}
				h	A_{1u}	B_{1g}
			C_{2v} $(C_2\sigma_d)$	μ^I	A_{2u} B_{1u} B_{2u} E_u	A_{1g} E_g
				Q^I	A_{2g}	B_{1u}
				h	A_{1u}	B_{2g}

contd....

D_{4h} continued

1	2	3	4	5	6	7
			$C_{2v}\,(C_2')$	μ^{I}	A_{1u} A_{2u} B_{1u} B_{2u} E_u	A_{1g} A_{2g} B_{1g} B_{2g} E_g
				μ^{II}	A_{2g}	B_{2u}
			$C_{2v}\,(C_2'')$	μ^{I}	A_{1u} A_{2u} B_{1u} B_{2u} E_u	A_{1g} A_{2g} B_{1g} B_{2g} E_g
				μ^{II}	A_{2g}	B_{1u}
			C_{4v}	μ^{I}	A_{2u} B_{1u} B_{2u} E_u	A_{1g} E_g
			C_i	Q^{I}	A_{2g}	A_{1u} B_{1u} B_{2u}
			$C_{2h}\,(C_2)$	Q^{I}	A_{2g}	B_{1u} B_{2u}
				h	-	A_{1u}
			$C_{2h}\,(C_2')$	Q^{I}	A_{2g}	A_{1u} B_{1u} B_{2u}
			$C_{2h}\,(C_2'')$	Q^{I}	A_{2g}	A_{1u} B_{1u} B_{2u}
			C_{4h}	h	A_{2g}	A_{1u}
			$D_2\,(C_2')$	Q^{I}	A_{2g}	B_{2u}
				h	A_{1u} A_{2u} B_{1u} B_{2u} E_u	A_{2g} B_{2g} E_g

contd.....

D_{4h} continued

1	2	3	4	5	6	7
			$D_2(C_2'')$	Q^I	A_{2g}	B_{1u}
				h	A_{1u} A_{2u} B_{1u} B_{2u} E_u	A_{2g} B_{1g} E_g
			D_4	h	A_{1u} B_{1u} B_{2u} E_u	A_{2g} E_g
			$D_{2d}(C_2'-C_2')$	h	A_{1u} A_{2u} B_{1u} E_u	B_{2g} E_g
			$D_{2d}(C_2''-C_2')$	h	A_{1u} A_{2u} B_{2u} E_u	B_{1g} E_g
			$D_{2h}(C_2')$	Q^I	A_{2g}	B_{2u}
			$D_{2h}(C_2'')$	Q^I	A_{2g}	B_{1u}
			S_4	h	A_{2g} A_{1u} A_{2u} B_{1u} B_{2u} E_u	A_{1u} B_{1g} B_{2g} E_g
D_{6h}		A_{1g}	C_1	μ^I	A_{1u} A_{2u} B_{1u} B_{2u} E_{1u} E_{2u}	A_{1g} A_{2g} E_{1g} E_{2g}
	A_{2g}	A_{2g}		μ^{II}	A_{2g} B_{1g} B_{2g}	A_{1u} B_{1u} B_{2u} E_{2u}
	B_{1g}	B_{1g}		h	-	B_{1g} B_{2g}

contd.....

D_{6h} continued

1	2	3	4	5	6	7
	B_{2g}	B_{2g}	C_s (σh)	μ^{I}	A_{1u} A_{2u} B_{1u} B_{2u} E_{1u} E_{2u}	A_{1g} A_{2g} E_{1g} E_{2g}
		E_{1g}		μ^{II}	A_{2g} B_{1g} B_{2g}	A_{1u} B_{1u} B_{2u} E_{2u}
		E_{2g}		h	–	B_{1g} B_{2g}
	A_{1u}	A_{1u}	C_s (σd)	μ^{I}	A_{1u} A_{2u} B_{1u} B_{2u} E_{1u} E_{2u}	A_{1g} A_{2g} E_{1g} E_{2g}
	A_{2u}			μ^{II}	A_{2g} B_{1g} B_{2g}	A_{1u} B_{1u} B_{2u} E_{2u}
	B_{1u}	B_{1u}		h	–	B_{1g} B_{2g}
	B_{2u}	B_{2u}	C_s (σv)	μ^{I}	A_{1u} A_{2u} B_{1u} B_{2u} E_{1u} E_{2u}	A_{1g} A_{2g} E_{1g} E_{2g}
	E_{1u}			μ^{II}	A_{2g} B_{1g} B_{2g}	A_{1u} B_{1u} B_{2u} E_{2u}
	E_{2u}	E_{2u}		h	–	B_{1g} B_{2g}
			C_2	μ^{I}	A_{2u} E_{1u} E_{2u}	A_{1g} E_{1g}
				Q^{I}	A_{2g} B_{1g} B_{2g}	B_{1u} B_{2u}
				h	A_{1u} B_{1u} B_{2u}	A_{2g} B_{1g} B_{2g} E_{2g} A_{1u} E_{2u}

contd....

D_{6h} continued

1	2	3	4	5	6	7
			C_2'	μ^{I}	A_{1u} A_{2u} B_{1u} B_{2u} E_{1u} E_{2u}	A_{1g} A_{2g} E_{1g} E_{2g}
				μ^{II}	A_{2g} B_{1g} B_{2g}	A_{1u} B_{1u} B_{2u}
				Q^{I}	A_{2g} B_{1g} B_{2g}	A_{1u} B_{1u} B_{2u} E_{2u}
				h	–	B_{1g} B_{2g}
			C_2''	μ^{I}	A_{1u} A_{2u} B_{1u} B_{2u} E_{1u} E_{2u}	A_{1g} A_{2g} E_{1g} E_{2g}
				μ^{II}	A_{2g} B_{1g} B_{2g}	A_{1u} B_{1u} B_{2u}
				Q^{I}	A_{2g} B_{1g} B_{2g}	A_{1u} B_{1u} B_{2u} E_{2u}
				h	–	B_{1g} B_{2g}
			C_3	μ^{I}	A_{2u} E_{1u} E_{2u}	A_{1g} E_{1g}
				h	A_{2g} B_{1g} B_{2g} A_{1u} B_{1u} B_{2u}	A_{2g} B_{1g} B_{2g} E_{2g} A_{1u} B_{1u} B_{2u} E_{2u}
			C_6	μ^{I}	A_{2u} E_{1u} E_{2u}	A_{1g} E_{1g}
				h	A_{2g} A_{1u}	A_{2g} A_{1u}
			$C_{2v}(c_2)$	μ^{I}	A_{2u} E_{1u} E_{2u}	A_{1g} E_{1g}
				Q^{I}	A_{2g} B_{1g} B_{2g}	B_{1u} B_{2u}
				h	A_{1u} B_{1u} B_{2u}	B_{1g} B_{2g} E_{2g} E_{2u}

contd....

D_{6h} continued

1	2	3	4	5	6	7
			$C_{2v}(C_2')$	μ^{I}	A_{1u} A_{2u} B_{1u} B_{2u} E_{1u} E_{2u}	A_{1g} A_{2g} E_{1g} E_{2g}
				μ^{II}	A_{2g} B_{1g} B_{2g}	B_{1u} B_{2u}
				Q^{I}	A_{2g} B_{1g} B_{2g}	B_{1u} B_{2u}
				h	-	B_{2g} E_{2u}
			$C_{2v}(C_2'')$	μ^{I}	A_{1u} A_{2u} B_{1u} B_{2u} E_{1u} E_{2u}	A_{1g} A_{2g} E_{1g} E_{2g}
				μ^{II}	A_{2g} B_{1g} B_{2g}	B_{1u} B_{2u}
				Q^{I}	A_{2g} B_{1g} B_{2g}	B_{1u} B_{2u}
				h	-	B_{1g} E_{2u}
			$C_{3v}(\sigma_v)$	μ^{I}	A_{2u} E_{1u} E_{2u}	A_{1g} E_{1g}
				h	B_{2g} B_{1u}	B_{2g} E_{2g} B_{1u} E_{2u}
			$C_{3v}(\sigma_d)$	μ^{I}	A_{2u} E_{1u} E_{2u}	A_{1g} E_{1g}
				h	B_{1g} B_{2u}	B_{1g} E_{2g} B_{2u} E_{2u}
			C_{6v}	μ^{I}	A_{2u} E_{1u} E_{2u}	A_{1g} E_{1g}

contd....

D_{6h} continued

1	2	3	4	5	6	7
			C_i	Q^I	A_{2g} B_{1g} B_{2g}	A_{1u} B_{1u} B_{2u} E_{2u}
			$C_{2h}(C_2)$	Q^I	A_{2g} B_{1g} B_{2g}	B_{1u} B_{2u}
				h	–	A_{1u} E_{2u}
			$C_{2h}(C_2')$	Q^I	A_{2g} B_{1g} B_{2g}	A_{1u} B_{1u} B_{2u} E_{2u}
			$C_{2h}(C_2'')$	Q^I	A_{2g} B_{1g} B_{2g}	A_{1u} B_{1u} B_{2u} E_{2u}
			C_{3h}	h	A_{2g} B_{1u} B_{2u} E_{1u} E_{2u}	A_{1u} B_{1g} B_{2g} E_{2g}
			C_{6h}	h	A_{2g}	A_{1u}
			D_2	Q^I	A_{2g} B_{1g} B_{2g}	B_{1u} B_{2u}
				h	A_{1u} A_{2u} B_{1u} B_{2u} E_{1u} E_{2u}	E_{2u} A_{2g} B_{1g} B_{2g} E_{1g} E_{2g}
			$D_3(C_2')$	h	B_{1g} A_{1u} B_{1u} E_{1u} E_{2u}	B_{2u} E_{2u} A_{2g} B_{2g} E_{1g} E_{2g}
			$D_3(C_2'')$	h	B_{2g} A_{1u} B_{2u} E_{1u} E_{2u}	B_{1u} E_{2u} A_{2g} B_{1g} E_{1g} E_{2g}
			D_6	h	A_{1u} E_{1u} E_{2u}	A_{2g} E_{1g}
			$D_{3d}(C_2')$	h	B_{1g}	B_{2u} E_{2u}

contd.....

D_{6h} continued

1	2	3	4	5	6	7
			$D_{3d}(C_2'')$	h	B_{2g}	B_{1u} E_{2u}
			D_{2h}	Q^I	A_{2g} B_{1g} B_{2g}	B_{1u} B_{2u}
				h	-	E_{2u}
			$D_{3h}(C_2')$	h	B_{1u} E_{1u} E_{2u}	B_{2g} E_{2g}
			$D_{3h}(C_2'')$	h	B_{2u} E_{1u} E_{2u}	B_{1g} E_{2g}
			S_6	h	A_{2g} B_{1g} B_{2g}	A_{1u} B_{1u} B_{2u} E_{2u}
S_4	NIL	A	C_1	μ^I	-	A
			C_2	μ^{II}	-	A
S_6		A_g	C_1	μ^I	A_u E_u	A_g E_g
		E_g	C_i	h	NIL	NIL
	A_u					
	E_u		C_3	μ^I	A_u E_u	A_g E_g

1	2	3	4	5	6	7
T	NIL	A	C_1	μ^{I}	NIL	A E
		E	C_2	μ^{I}	NIL	A E
			C_3	μ^{I}	NIL	A E
			D_2	h	NIL	NIL
T_d		A_1	C_1	μ^{I}	F_1	A_1 E F_1
	A_2	A_2		μ^{II}	A_2	-
		E		h	-	A_2
	F_1	F_1	C_s	μ^{I}	F_1	A_1 E F_1
				μ^{II}	A_2	-
				h	-	A_2
			C_2	μ^{I}	F_1	A_1 E F_1
				μ^{II}	A_2	-
				h	-	A_2
			C_3	μ^{I}	F_1	A_1 E F_1
				μ^{II}	A_2	-
				h	-	A_2
			C_{2v}	μ^{I}	F_1	A_1 E F_1
				μ^{II}	A_2	-

contd.....

T_d <u>continued</u>

1	2	3	4	5	6	7
			C_{3v}	μ^{I}	F_1	A_1 E F_1
			D_2	Q^{I}	A_2 F_1	F_1
			D_{2d}	Q^{I}	A_2 F_1	F_1
			S_4	Q^{I}	A_2 F_1	F_1
				h	-	A_2 E
			T	h	A_2 F_1	F_1
T_h		A_g	C_1	μ^{I}	A_u E_u F_u	A_g E_g F_g
		E_g		μ^{II}	-	A_u E_u
		F_g	C_s	μ^{I}	A_u E_u F_u	A_g E_g F_g
	A_u	A_u		μ^{II}	-	A_u E_u
	E_u	E_u	C_2	μ^{I}	A_u E_u F_u	A_g E_g F_g
	F_u			Q^{I}		A_u E_u
			C_3	μ^{I}	A_u E_u F_u	A_g E_g F_g
				Q^{I}	-	A_u E_u
			C_{2v}	μ^{I}	A_u E_u F_u	A_g E_g F_g
			C_i	Q^{I}	NIL	A_u E_u

contd.....

T_h continued

1	2	3	4	5	6	7
			C_{2h}	Q^{I}	NIL	A_u E_u
			D_2	Q^{I}	A_u E_u F_u	F_g
			D_{2h}	h	NIL	NIL
			S_6	Q^{I}	NIL	A_u E_u
			T	h	A_u E_u F_u	F_g
O		A_1	C_1	μ^{I}	F_1	A_1 E F_2
	A_2	A_2		μ^{II}	A_2	-
		E		h	-	A_2
	F_1		C_2	μ^{I}	F_1	A_1 E F_2
		F_2		μ^{II}	A_2	-
				h	-	A_2
			C_2'	μ^{I}	F_1	A_1 E F_2
				μ^{II}	A_2	-
				h	-	A_2
			C_3	μ^{I}	F_1	A_1 E F_2
				μ^{II}	A_2	-
				h	-	A_2

contd...

O continued

1	2	3	4	5	6	7
			C_4	μ^{I}	F_1	A_1 E F_2
				μ^{II}	A_2	-
			$D_2(3c_2)$	Q^{I}	A_2 F_1	F_2
			$D_2(c_2 2c_2')$	Q^{I}	A_2 F_1	E F_2
				h	-	A_2
			D_3	Q^{I}	F_1	F_2
				h	-	A_2 E
			D_4	Q^{I}	A_2 F_1	F_2
			T	h	A_2 F_1	F_2

O_h		A_{1g}	C_1	μ^{I}	A_{2u} E_u F_{1u} F_{2u}	A_{1g} E_g F_{1g} F_{2g}
	A_{2g}	A_{2g}		μ^{II}	A_{2g} F_{1g}	A_{1u} A_{2u} E_u F_{2u}
		E_g		h	A_{1u}	A_{2g}
	F_{1g}	F_{1g}	$C_s(\sigma_h)$	μ^{I}	A_{2u} E_u F_{1u} F_{2u}	A_{1g} E_g F_{1g} F_{2g}
		F_{2g}		μ^{II}	A_{2g} F_{1g}	A_{1u} A_{2u} E_u F_{2u}
	A_{1u}	A_{1u}		h	A_{1u}	A_{2g}

contd....

O_h continued

1	2	3	4	5	6	7
	A_{2u}	A_{2u}	$C_s(\sigma d)$	μ^{I}	A_{2u} E_u F_{1u} F_{2u}	A_{1g} E_g F_{1g} F_{2g}
	E_u	E_u		μ^{II}	A_{2g} F_{1g}	A_{1u} A_{2u} E_u F_{2u}
	F_{1u}			h	A_{1u}	A_{2g}
	F_{2u}	F_{2u}	C_2	μ^{I}	A_{2u} E_u F_{1u} F_{2u}	A_{1g} E_g F_{1g} F_{2g}
				μ^{II}	A_{2g} F_{1g}	A_{1u} A_{2u} E_u F_{2u}
				h	A_{1u}	A_{2g}
			C_2'	μ^{I}	A_{2u} E_u F_{1u} F_{2u}	A_{1g} E_g F_{1g} F_{2g}
				μ^{II}	A_{2g} F_{1g}	A_{1u} A_{2u} E_u F_{2u}
				h	A_{1u}	A_{2g}
			C_3	μ^{I}	A_{2u} E_u F_{1u} F_{2u}	A_{1g} E_g F_{1g} F_{2g}
				μ^{II}	F_{1g}	F_{2u}
				Q^{I}	A_{2g} F_{1g}	A_{2u} E_u F_{2u}
				h	A_{1u}	A_{2g} A_{1u}

contd....

O_h continued

1	2	3	4	5	6	7
			C_4	μ^I	A_{2u} E_u F_{1u} F_{2u}	A_{1g} E_g F_{1g} F_{2g}
				μ^{II}	A_{2g} F_{1g}	F_{2u}
				Q^I	A_{2g} F_{1g}	E_u F_{2u}
				h	A_{1u}	A_{1u}
			$C_{2v}(c_2\sigma_h)$	μ^I	A_{2u} E_u F_{1u} F_{2u}	A_{1g} E_g F_{1g} F_{2g}
				μ^{II}	A_{2g} F_{1g}	F_{2u}
				h	A_{1u}	A_{2g}
			$C_{2v}(c_2, \sigma_d)$	μ^I	A_{2u} E_u F_{1u} F_{2u}	A_{1g} E_g F_{1g} F_{2g}
				μ^{II}	A_{2g} F_{1g}	F_{2u}
				Q^I	A_{2g} F_{1g}	A_{2u} E_u F_{2u}
				h	A_{1u}	–
			$C_{2v}(c'_2\sigma_h)$	μ^I	A_{2u} E_u F_{1u} F_{2u}	A_{1g} E_g F_{1g} F_{2g}
				μ^{II}	A_{2g} F_{1g}	F_{2u}
				Q^I	A_{2g} F_{1g}	A_{2u} E_u F_{2u}
				h	A_{1u}	A_{2g}

contd...

O_h <u>continued</u>

1	2	3	4	5	6	7
			C_{3v}	μ^{I}	A_{2u} E_u F_{1u} F_{2u}	A_{1g} E_g F_{1g} F_{2g}
				μ^{II}	F_{1g}	F_{2u}
				Q^{I}	F_{1g}	A_{2u} E_u F_{2u}
			C_{4v}	μ^{I}	A_{2u} E_u F_{1u} F_{2u}	A_{1g} E_g F_{1g} F_{2g}
				μ^{II}	A_{2g} F_{1g}	F_{2u}
			C_i	Q^{I}	A_{2g} F_{1g}	A_{2u} E_u F_{2u}
				h	-	A_{1u}
			C_{2h} $(c_2\sigma_h)$	Q^{I}	A_{2g} F_{1g}	A_{2u} E_u F_{2u}
				h	-	A_{1u}
			C_{2h} $(c_2'\sigma_h)$	Q^{I}	A_{2g} F_{1g}	A_{2u} E_u F_{2u}
				h	-	A_{1u}
			C_{4h}	Q^{I}	A_{2g} F_{1g}	F_{2u}
				h	-	A_{1u} E_u
			D_2 $(3c_2)$	Q^{I}	A_{2g} F_{1g}	F_{2u}
				h	A_{1u} A_{2u} E_u F_{1u} F_{2u}	F_{1g} F_{2g}

contd-----

O_h continued

1	2	3	4	5	6	7
			$D_2(c_2 2c_2')$	Q^I	A_{2g} F_{1g}	A_{2u} E_u F_{2u}
				h	A_{1u} A_{2u} E_u F_{1u} F_{2u}	A_{2g} E_g F_{1g} F_{2g}
			D_3	Q^I	F_{1g}	A_{2u} E_u F_{2u}
				h	A_{1u} E_u F_{1u} F_{2u}	A_{2g} E_g F_{1g} F_{2g}
			D_4	Q^I	A_{2g} F_{1g}	F_{2u}
				h	A_{1u} A_{2u} E_u F_{1u} F_{2u}	F_{1g} F_{2g}
			$D_{2d}(c_2 \sigma d)$	Q^I	A_{2g} F_{1g}	F_{2u}
				h	A_{1u} A_{2u} E_u F_{1u} F_{2u}	F_{1g} F_{2g}
			$D_{2d}(c_2 \sigma h)$	Q^I	A_{2g} F_{1g}	F_{2u}
				h	A_{1u} E_u F_{1u} F_{2u}	A_{2g} E_g F_{1g} F_{2g}
			D_{3d}	Q^I	F_{1g}	F_{2u}
				h	–	A_{2u} E_u

contd.....

O_h continued

1	2	3	4	5	6	7
			$D_{2h}(3C_2)$	Q^I	A_{2g} F_{1g}	F_{2u}
			$D_{2h}(C_2 2C'_2)$	Q^I	A_{2g} F_{1g}	A_{2u} E_u F_{2u}
			D_{4h}	Q^I	A_{2g} F_{1g}	F_{2u}
			S_4	Q^I	A_{2g} F_{1g}	F_{2u}
				h	A_{1u} A_{2u} E_u F_{1u} F_{2u}	A_{2g} E_g F_{1g} F_{2g} A_{1u} E_u
			S_6	Q^I	A_{2g} F_{1g}	A_{2u} E_u F_{2u}
				h	-	A_{1u}
			T	h	A_{2g} F_{1g} A_{1u} A_{2u} E_u F_{1u} F_{2u}	F_{1g} F_{2g} F_{2u}
			T_h	h	A_{2g} F_{1g}	F_{2u}
			T_d	h	A_{2u} E_u F_{1u}	F_{2g}
			O	h	A_{1u} E_u F_{2u}	F_{1g}

[+] Symmetry species common in the results of a lower as well as a higher order are only shown in the row of lower order.

μ^I, μ^{II} and Q^I represent DIA-I(μ), DIA-II(μ) and DIA-I(Q) respectively.

CHAPTER V

USEFULNESS AND SCOPE OF THE THEORY OF DISTORTION INDUCED ACTIVITY (DIA) OF FORBIDDEN MODES OF MOLECULAR UNITS IN CRYSTALS*

ABSTRACT

The usefulness and the scope of DIA theory are discussed. This is used to establish a relation between the intensity of forbidden modes with the amount of distortion in the unit. To illustrate its application in understanding the microscopic mechanism of structural phase transition an example of the IR absorbance due to IR forbidden ν_1 mode of SO_4^{2-} ion in $(NH_4)_2SO_4$ crystal has been discussed. We also discuss its scope in determining the effective symmetry of molecular units in liquids and gases (under high pressure). This point is demonstrated by discussing examples of molecules such as C_6H_6 (liquid), C_6D_6 (liquid), CCl_4 (liquid) and CF_4 (liquid) and gas).

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*Part of the work presented in this chapter is included in the publications : J. Phys. C : Solid State Physics 18, 5299 (1985); Mol. Phys. 57, 379 (1986).

5.1 INTRODUCTION

Jain and co-workers (Jain et. al. 1973; Jain 1974; Jain and Bist 1974, 1975a) correlated the temperature variation of the IR absorbance of bands due to forbidden modes of the SO_4^{2-} ion in $(NH_4)_2SO_4$ and those of the BeF_4^{2-} ion in $(NH_4)_2BeF_4$ with the change in the amount of distortion in the structure of the relevant molecular ion. Although, the qualitative character of this relation appears to be rational and correct, its real form remained unclear. In this chapter, we have investigated this relationship using DIA theory.

Forbidden modes of molecular units in liquids and gases (under high pressure) have also been observed by several groups e.g. Bucaro and Litovitz (1971), Fournier et. al. (1968), Gabelnick and Strauss (1967, 1968), Gruebel and Clayton (1967), Ingold et. al. (1936, 1946), Jones (1963), Mair and Hornig (1949), Miller (1956), Narten et. al. (1967), Placzek (1931), Rosenberg and Birnbaum (1968), Wilson et. al. (1955), Woltz and Nielsen (1952). In this chapter we also demonstrate that this observation is related with the distortion in the structure of molecular units. In addition, we discuss the scope of the theory in determining effective symmetry of molecules in these phases by illustrating the examples of the spectra observed for C_6H_6 (liquid), C_6D_6 (liquid), CCl_4 (liquid) CF_4 (liquid and gas).

5.2 INTENSITY OF FORBIDDEN MODES

At a given temperature the band intensity, I_{nm}, of Raman scattering and IR absorption (absorbance scale) may be given by (Overand 1963)

$$I_{nm} = A\,|\langle n|\tilde{M}|m\rangle|^2 \qquad \ldots \qquad (5.1)$$

obviously, the intensity of the forbidden mode to the first order approximation, $I_{fg}^{(1)}$, for polar distortion case would be given by

$$I_{fg}^{(1)} = A\,|\langle f|\tilde{M}|g\rangle^{(1)}|^2 \qquad \ldots \qquad (5.2)$$

In view of the relation, equation (3.18), we have

$$I_{fg}^{(1)} = A\left|N_f^{(1)}\ N_g^{(1)}\sum_{i\neq g}\ \frac{\langle f|\tilde{M}|i\rangle\ \langle i|H^{(1)}|g\rangle}{E_g^{\circ} - E_i^{\circ}} + \frac{\langle f|H^{(1)}|j\rangle\langle j|\tilde{M}|g\rangle}{E_f^{\circ} - E_j^{\circ}}\right|^2$$

$$\ldots \qquad (5.3)$$

It can easily be seen that non-zero magnitude of each term (such as $\langle f|H^{(1)}|j\rangle$, $\langle i|H^{(1)}|g\rangle$, etc. in equation (5.3) should be proportional to the magnitude of distortion parameter $\delta\vec{r}$ (equation (3.7)). Hence

$$I_{fg}^{(1)} = A^{(1)}\,|\delta\vec{r}\,|^2 \qquad \ldots \qquad (5.4)$$

Similarly, I_{fg} for second order approximation would be

$$I_{fg}^{(2)} = A^{(2)}\,|\delta\vec{r}\,|^4 \qquad \ldots \qquad (5.5)$$

where, $A^{(1)}$ and $A^{(2)}$ are constants that depend on the molecular unit and the mode $|f\rangle$ in question. Equations (5.4) and (5.5) are found to be quite useful in as much as they relate the intensity of forbidden modes with the amount of distortion which can be evaluated easily from the crystal structural data using relations such as (equation 3.7).

5.3 STRUCTURAL PHASE TRANSITION

A molecular unit in a crystal may undergo a change in the structure and symmetry when the crystal undergoes a structural phase transition. To detect such change, Jain and co-workers (Jain et. al. 1973; Jain 1974; Jain and Bist 1974, 1975a) used IR absorbance of forbidden modes of SO_4^{2-}/BeF_4^{2-} ion in $(NH_4)_2SO_4$/$(NH_4)_2BeF_4$ crystal (which undergoes a ferroelectric phase transition at 223/165 K) arguing that the absorbance should be a measure of the distortion in the structure of the ions. DIA theory establishes a quantitative relation (between these two quantities (c.f. equation (5.4)) which is in agreement with their contention as discussed below.

Table 5.1 (column 2) gives the IR-absorbance (in arbitrary unit) of ν_1 mode of SO_4^{2-} in the $(NH_4)_2SO_4$ measured by Jain and co-workers (Jain et. al. 1973; Jain 1974) at several temperatures. These data have been used in equation (5.4) to calculate the distortion (in arbitrary unit) as well as relative distortion (c.f. column 3 and 4) in the ion; the relative distortion has been defined as

$$\delta\vec{r}_{\text{rel}} = \frac{|\delta\vec{r}(T)|}{|\delta\vec{r}(133K)|}$$

Use of equation (5.4) for this purpose is justified in view of the facts that (i) ν_1 (SO_4^{2-}) mode can be presumed to be harmonic to a good approximation (ii) the SO_4^{2-} ion occupies polar site symmetry in both phases of $(NH_4)_2SO_4$ crystal. As discussed in Chapter III, distortion in T_d ion can also be calculated with the help of equation (3.7) i.e.,

$$\delta\vec{r} = \sum_i \sum_r (\vec{A}_i - \vec{B}_i^{\,r})$$

using crystal structural data. Recently, Hasebe (1981) measured the crystal structural data of $(NH_4)_2SO_4$ at 233, 224.5, 219.5, 209, 183 and 133K. The values of $\delta\vec{r}$ and $|\delta\vec{r}|_{\text{rel}}$ calculated from these data are given in column 6 and 7 of Table 5.1. The two sets of values of $|\delta\vec{r}|_{\text{rel}}$, so calculated from the two independent experimental results, have been plotted in Figure 5.1(b), we note that they match very closely. This provides not only an experimental support to equation (5.4) but also demonstrates its usefulness in the study of structural phase transitions in crystal like $(NH_4)_2SO_4$. Minor difference between the two curves in the temperature range above T_c can easily be understood. Two important reasons responsible for this are: (i) the proportionality constant $A^{(1)}$, in equation (5.4) has been presumed to remain unchanged at temperatures above and below T_c, (ii) the IR absorption band due to ν_1 (SO_4^{2-}) above T_c is not so well developed as on the other side and the base-line above which the absorption has been evaluated might have not been very accurately chosen.

A molecular unit in the crystal may also attain distortion when the crystal is subjected to pressure. The change in distortion with the change in pressure may be studied by monitoring the change in the IR and Raman intensities of forbidden modes. This may help in understanding the propagation of the effects of pressure down to the molecular level and in discovering a relation between the distortion parameter and the applied pressure. Good systems for such studies may be molecular units doped in crystals such as alkali halides. This shows that equation (5.4) may prove to be useful for studying structural phase transition induced by any parameter such as temperature, pressure, etc. if the crystal has molecular units and the phase transition is triggered by change in the structure of individual unit.

5.4 EFFECTIVE SYMMETRY OF MOLECULAR UNITS

5.4.1 CRYSTALLINE SOLIDS

According to the x-ray crystallographic studies, the crystal structure of benzene is known to belong to the space group D_{2h}^{15}, with four molecules in a unit cell. All the molecules are inferred to occupy C_i site (Cox 1958; Turrell 1972). Consequently, only the ungerade species are expected to appear in IR spectrum and gerade species in Raman spectrum (Herzberg 1945).

According to Swenson and Person (1960) the band observed in IR spectrum of crystalline benzene at 987 cm^{-1} is due to the fundamental band ν_1 (A_{1g}). They have convincingly argued that it is not due to an impurity. In addition, Ito (1965) in his study of the Raman spectrum of benzene crystal at 77 and 195K has observed a weak band at 1012 cm^{-1}; the laser excited spectra also confirm the presence of the band (Gee and Robinson 1969). He (Ito 1965) has attributed it to the fundamental ν_{12} (B_{1u}) mode. These authors (Ito 1965, Swenson and Person 1960) have independently come to the conclusion that these are clear indications of the violation of the selection rules. Swenson and Person (1960) suggest that existing theories of spectra in condensed phase must be modified to predict different behaviour of each fundamental vibrations. Ito (1965) also suggests that the selection rules for the vibrational spectrum of the crystal is not strict for polyatomic substances. Pertaining to these observations, we can make the following comment in view of our theory. The crystal structure of benzene determined by x-ray diffraction method may quite likely have some errors with respect to the position of H-atoms, because of low scattering cross-section. It is possible that C_i site is a correct inference for the positions of C-atoms, while it may not be true for H-atoms. There are several examples of crystals which show this kind of anomalies. It is observed that about fifty compounds (such as $CaBr_2 6NH_3$, $Mg(BF_4)_2 6NH_3$, $CoSO_4 Br 6NH_3$ etc.) have K_2PtCl_6 type cubic structure in which the complex (such as $[M(NH_3)_6]^{2+}$) go to O_h site with C_4 axes along M-N bond; M represents the metallic ion such as Ca^{++}, Mg^{++} etc (Wyckoff 1965). These observations have been analysed by Jain (1982) in a recent report and it has rightly been pointed out that the positions of all atoms other than H-atoms are consistant with O_h site while the positions of H-atoms do clearly not conform to C_4 site for NH_3 molecule. A similar situation has been reported by Jain and Bist (1975b) to conclude the symmetry behaviour of the complex ion $[Ni(OH_2)_6]^{2+}$ in α-$NiSO_4 6H_2O$ crystal. Thus it is quite likely that the positions of H-atoms may not be consistant with C_i site of the benzene molecule; it should obviously have C_1 site with polar distortion. Considering C_1 site, the observation of A_{1g} mode in IR and B_{1u} mode in Raman is clearly understood because these species attain DIA-I(μ) revealing that the bands can have observable intensity. This clearly sets an example of the fact that if IR and Raman spectra are understood without any ambiguity the DIA analysis can help in determining the correct site symmetry of the molecular units and the crystal structure as a whole.

5.4.2 LIQUIDS

Distortion in symmetry and structure of molecules in liquid phase has been invoked in several reports. Wilson et. al. (1955) state that the transition forbidden by symmetry appear in the spectra of liquids presumably due to distortion of symmetry by neighbouring molecules. Jones (1963) believes that molecules in a liquid state have no preferred orientation but a range of environment; they have considerable freedom of movement to change their position and posture. However, it is possible that the molecular symmetry is distorted during close collisions with other molecules and all forbidden vibrations become IR and Raman active to a certain degree (Jones 1963). Studying the dielectric loss in liquid CCl_4 at far-IR frequencies Gabelnick and Strauss (1967) interpreted the observation at 220 cm^{-1} (Raman active and IR forbidden band) and additional absorption, as arising due to structural distortion in the molecule. They concluded that the distortion must be sufficiently large to produce a dipole moment of 0.1 - 0.2 D. In a subsequent study they found that the distortion accounts nicely also for the magnitude of observed Raman intensities. They tried to conclude about the nature of distortion, but they could not present a complete picture. Consequently, they concluded that an understanding of these aspects requires a theory which describes intermolecular motion as well as the postulated distortion in detail. On the basis of x-ray diffraction measurements of liquid CCl_4 it has been concluded, in general, that there is either association of the molecules, preferred packing or distortion of the molecules (Gabelnick and Strauss 1968, Gruebel and Clayton 1967, Narten et. al. 1967), Bucaro and Litovitz (1971) studied Rayleigh scattering in an attempt to investigate collisional motion in several polar and non-polar liquids. They concluded that the origin of the induced anisotropy responsible for Rayleigh scattering is the electronic overlap in the case of noble liquids (viz Ar, Xe) and molecular frame distortion in polyatomic liquids. They argue that the electric field of a molecule induces a dipole moment in other molecule and the field of this dipole induces an additional dipole in neighbouring molecule. Thus we encounter distorted molecules in liquids too.

(i) Fournier et. al. (1968) have observed the activity of forbidden $\nu_1(A_1)$ and $\nu_2(E)$ modes with weak intensity in the IR spectrum of liquid $CF_4(T_d)$. They argued that it is due to the anisotropy of the local field set up by neighbouring molecules which causes a break-down of the selection rules. However, in the frame work of our theory, it can further be concluded that CF_4 molecule in its liquid state has polar distortion. Note that for this kind of distortion only, the $\nu_1(A_1)$ and $\nu_2(E)$ modes are expected to appear with observable intensity in IR spectrum as the first order effect of polar distortion, for the quadrupolar distortion, only F_1 modes become active in the first order (c.f. Table 4.1, T_d). Similarly, the appearance of the far-IR band at 220 cm^{-1} (Gabelnick and Strauss 1967) due to $\nu_2(E)$ mode of CCl_4 (Herzberg 1945) confirms that the distortion in the structure of CCl_4 (T_d) molecule in liquid state is of polar type.

(ii) Several fundamental modes of liquid benzene are found to appear both in IR and Raman spectra (Herzberg 1945, Ingold et. al.1936,1946; Mair and Hornig 1949; Plackzek 1931). In view of this observation Placzek (1931) suggests that the molecule can not be a plane regular hexagon. Ingold et. al. 1936, 1946) infer that the molecule does not retain its D_{6h} structure in the liquid state; The cohesive forces deform the molecule sufficiently to cause a break-down of the selection rules. However, when the coincidence is examined in the frame work of the theory of distortion induced activity, we note that all the Raman forbidden modes [ν_{11}(A_{2u} : 677 cm^{-1}), ν_{16}(E_{2u} : 405 cm^{-1}) ν_{18}(E_{1u} : 1030 cm^{-1}) and ν_{19}(E_{1u} : 1478 cm^{-1})] (Herzberg 1945; Ingold et. al.1936,1946) are allowed as first order effect of polar distortion. Modes allowed as the second order effect of this distortion do not seem to attain observable intensity in Raman spectra. On the other hand forbidden modes observed in IR spectrum (ingold et. al. 1936, 1946; Mair and Hornig 1949) can be classified into categories of first order effect [ν_1 (A_{1g}: 995 cm^{-1}), ν_6 (E_{2g} : 610 cm^{-1}), ν_8 (E_{2g} : 1584, 1604 cm^{-1}), ν_9 (E_{2g} : 1170 cm^{-1} and ν_{10}(E_{1g} : 849 cm^{-1})] and second order effect [ν_{12} (B_{1u} : 1013 cm^{-1}), ν_{14}(B_{2u} : 1310 cm^{-1}), ν_{15}(B_{2u} : 1150 cm^{-1}) and ν_{17}(E_{2u} : 975 cm^{-1})]. The numbering of fundamental frequencies of benzene is done in accordance with Mair and Hornig (1949). Analysing the IR spectrum of liquid C_6D_6 Miller (1956) found it as an interesting observation that four forbidden modes of the molecule appearing in the spectrum at 577, 662, 864 and 945 cm^{-1} were all g-type; no forbidden mode of u-type was observed. In view of the DIA analysis, this observation is not at all surprising because g-type forbidden modes appear as first order effect of polar distortion in this case, while u-modes as its second/higher order effect. As such the theory helps us to conclude that the C_6H_6 and C_6D_6 molecules in liquid state are not only distorted but the distortion is of polar nature. In turn, this reveals that the intermolecular cohesive forces in liquid benzene are basically derived from dipole-dipole interaction. We also understand why all forbidden modes of benzene molecule in its liquid state do not show up with observable intensity.

5.4.3 GASES (UNDER HIGH PRESSURE)

Like in liquid CF_4, forbidden $\nu_2(E)$ mode has been observed as a weak band in the IR spectrum of gaseous CF_4 by Woltz and Nielson (1952); a meter cell with two atmospheric pressure is found to be sufficient to detect this mode with about 10 percent absorption. Fournier et. al. (1968) have explained this phenomenon as a collision-induced transition. The explanation appears to be rational but does not speak about the real change in the molecule. In view of the distortion induced activity this observation reveals that CF_4 molecule attains polar distortion in gaseous state at high pressure because, $\nu_2(E)$ mode becomes IR active as first order effect of polar distortion. Formulating a theory of pressure induced absorption Mizushima (1949) suggests that a molecular unit under consideration, experiences an electric field $\vec{E}$ because of surrounding atoms/molecules which interact with the former through interparticle interactions. Therefore, on an average a molecule in gaseous state has some definite environment (the electric field), though it is free to change its location and posture. This justifies that the DIA theory can be applied to molecules in gases particularly at high pressure. Analysing the far-IR absorption in gaseous CF_4 at the pressure ranging from 10 to 35 atom; Rosenberg and Birnbaum (1968) concluded that the collision induced absorption should occur due to transient dipole moment induced by colliding molecule and by molecular distortion due to overlap interaction. This provides an independent evidence for the existance of polar distortion in the molecule. Thus the DIA theory appears to become relevant for understanding the activity of forbidden modes of molecules in high pressure gases and one should observe that the forbidden modes of only certain species acquire observable intensity, demonstrating once again the relative strength of DIA-I, II etc.

Table 5.1 Distortion and relative distortion calculated from IR-absorbance data (Jain et.al. 1973; Jain 1974) and crystal structure data (Hasebe 1981)

Calculated from IR-absorbance				Calculated from crystal structure		
Temp. (K)	IR-absorbance (arb.Unit)	Distortion (arb.Unit)	Relative Distortion	Temp (K)	Distortion	Relative Distortion
121	40.545	6.367	1.010	133	0.055	1
165	37.572	6.130	0.973			
184	36.491	6.041	0.959	183	0.052	0.951
193	34.463	5.871	0.932			
201	33.517	5.789	0.919			
208	33.517	5.789	0.919	209	0.049	0.897
218	31.760	5.636	0.894	219.5	0.045	0.816
221	29.733	5.453	0.865			
222	22.029	4.694	0.745			
223	9.461	3.076	0.488	224.5	0.021	0.393
230	8.379	2.895	0.459	223	0.019	0.344
239	6.893	2.625	0.417			
254	5.271	2.296	0.364			
260	4.325	2.080	0.330			
297	1.892	1.375	0.218			

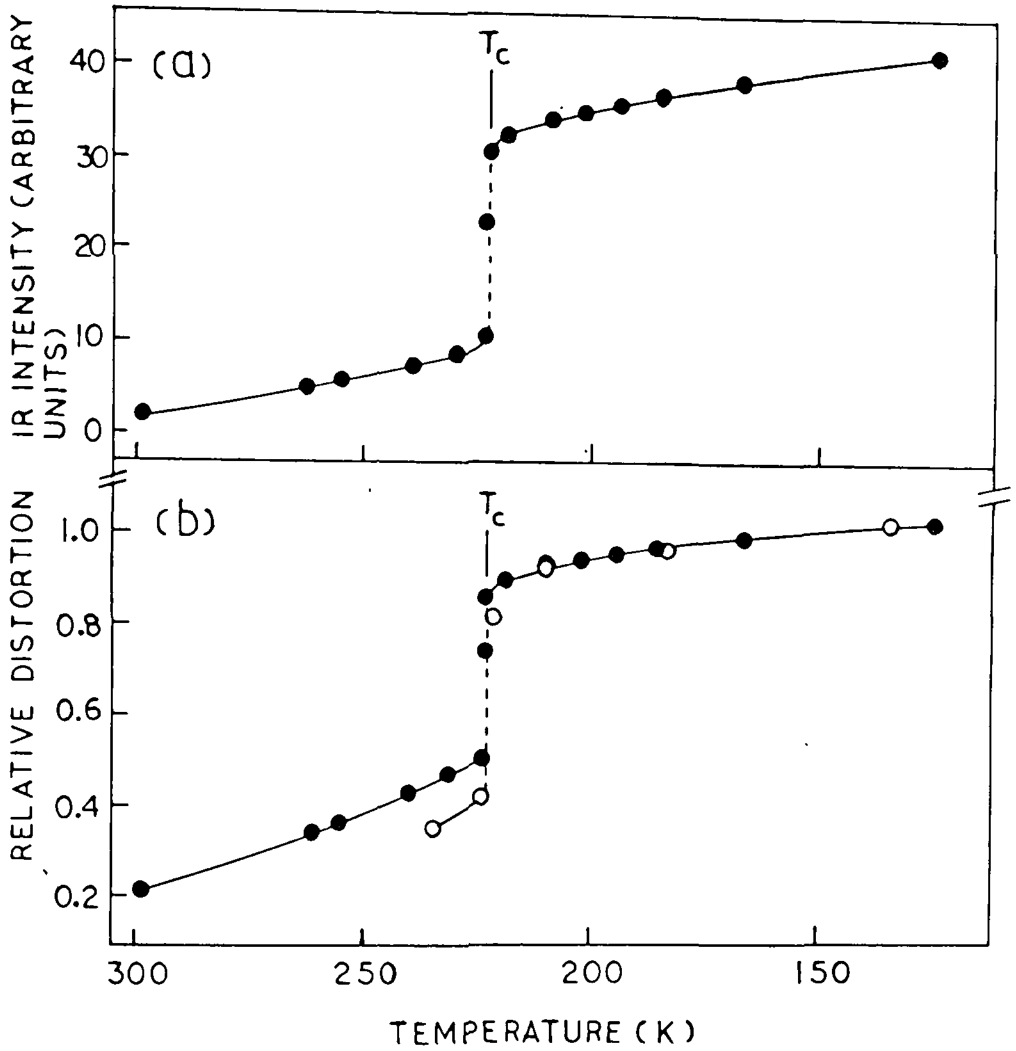

FIGURE 5.1 TEMPERATURE DEPENDENCE OF (a) IR BAND INTENSITY DUE TO THE ν_1 MODE OF SO_4^{2-} ION IN $(NH_4)_2SO_4$ CRYSTAL (DATA FROM JAIN et.al 1973; JAIN 1974) AND (b) RELATIVE DISTORTION $|\delta\vec{r}(T)|/|\delta\vec{r}(133K)|$, DEDUCED FROM IR ABSORBANCE (POINTS SHOWN BY FULL CIRCLES) AND CRYSTAL STRUCTURAL DATA (HASEBE 1981 , POINTS SHOWN BY OPEN CIRCLES).

CHAPTER VI

SUMMARY AND CONCLUSIONS

The present investigation was undertaken with a view to formulate a quantitative theory of distortion induced IR and Raman intensity due to forbidden modes of molecular units at polar/non-polar sites in crystals. It was motivated by the idea of Jain and coworkers (Jain et. al. 1973; Jain 1974; Jain and Bist 1974, 1975a) that the intensity of forbidden modes is the measure of distortion in the molecular units. They measured the temperature dependence of the intensity of IR bands due to forbidden modes of the SO_4^{2-} ion in $(NH_4)_2SO_4$ and BeF_4^{2-} in $(NH_4)_2BeF_4$, and made an interesting use of the idea to understand the microscopic mechanism of phase transition in these crystals.

Group theoretical techniques (Herzberg 1945; Wilson et. al. 1955) are used to decide the IR and Raman activity of different vibrational modes of a molecule. The activity of such modes in a crystal is decided by two well known techniques, viz. the unit cell approach developed by Bhagavantam and Venkatarayudu (1939) and the site symmetry approach developed by Halford (1946), Hornig (1948), and Winston and Halford (1949). Fateley et. al. (1971, 1972) simplified the procedure involved in these techniques and they can be used without having rigorous knowledge of group theory. However, these techniques do not reveal the magnitude of intensity of the allowed modes. The idea of this magnitude in case of certain modes can be obtained from the spectra of these modes of free molecules; however, sometimes this comparison does not work well. The situation remains particularly uncertain for forbidden modes which become active when the unit occupies sites of lower symmetry in crystals and attains distorted structure. Also these techniques do not reveal the explicit nature of the mechanism that activates these modes. In view of all these facts the importance of the present investigation is self evident.

In the course of the present theoretical study we made an experimental investigation of Rochelle Salt (RS) using IR absorption/Raman scattering techniques (c.f. Chapter II). The experimental results have been analysed and discussed in the light of the above referred group theoretical techniques. The spectra are expected to comprise a large number of peaks because of the large number of atoms ($N' = 112$) in its unit cell. The dynamics of RS crystal can be described in terms of 336 phonon branches (333 optical + 3 acoustical) under the unit cell approximation. These branches arise from different normal modes of $C_4H_4O_6^{2-}$, Na^+, K^+ and H_2O. The number of phonon modes arising from different degrees of freedom of 4 x 4 H_2O molecules and 4 $C_4H_4O_6^{2-}$ ions are 144 and 168, respectively. The Na^+ and

K^+ ions separately have three translational degrees of freedom; thus, the four ions of each type, contribute a total of 24 phonon modes. There are two types of crystallographically inequivalent K^+ ions, - both having C_2 site symmetry. Na^+, $C_4H_4O_6^{2-}$ and H_2O occupy points of C_1 symmetry. Hence, all the 333 optical phonon branches are IR and Raman active. However, the observed IR and Raman spectra show about 48 bands in the region in which more than two hundred bands are expected in view of the unit cell approximation. It appears that the factor group split components of most of the modes do not have resolvable frequency separation. As such the single molecule approximation appears to be sufficient to discuss the observed spectra of internal lattice modes, particularly, of powdered samples. However, to understand the spectra of a single crystal, the detailed symmetry analysis under unit cell approximation remains essential.

The IR and Raman spectra of RS reveal that : (i) spectroscopically one pair of H_2O molecules does not differ much from the other pair, though four water molecules are crystallographically different (ii) the H-bond exhibited by OH-group of tartrate ion is strongest among all H-bonds in the crystal. (iii) $\nu_{C(OH)}$ and ν_{CC} modes seem to be strongly coupled (iv) the doublet structure of ν_{CH}, ν_{CO}^{a}, ν_{CO}^{s}, δ_{COH} and τ_{COO} modes arises mainly due to crystallographically distinguishable sites for two identical oscillators, while the same for β_{CH}, $\gamma_{C(OH)}$ and δ_{COO} modes originates dominantly due to resonance interaction between two identical oscillators in $COO.(HO)HC-CH(OH)COO^{2-}$ ion.

The theoretical investigation uses the principles of group theory and approximation methods (c.f. chapter III). The central idea of the work is that the static crystal field which is non-uniform in strength serves as the source of perturbation and distorts the unit and hence modifies its dynamics and selection rules. Thus the transitions become active due to structural distortion of the unit and they need to be ascribed as distortion induced transitions. Such transitions of different symmetry species are characterized by different order of distortion induced activity (DIA), i.e. DIA-I/DIA-II/..../DIA-h representing first/second/..../higher order effect of distortion (c.f. Chapter III). This theory also gives an idea about the mechanism (such as dipolar (μ)/quadrupolar (Q) mode mixing) which activates the modes. The theory reveals that the DIA-I (μ) are the only transitions that could in general be expected to appear in the IR/Raman spectra with observable intensity. In exceptional cases, if DIA-II (μ) and DIA-I(Q) transitions are observed, it would be indicative of strong crystalline field and high field gradiant respectively.

For almost all important and frequently encountered symmetries the type and order of DIA that activates a particular forbidden mode are tabulated for ready reference (c.f. chapter IV). By classifying the IR and Raman forbidden species of different point groups which are expected to attain different order of DIA, it is shown that even for the distortion commensurate with C_1 symmetry not all forbidden modes of the unit attain first/or even second order activity in all cases. It also is revealed that a distortion does not contribute to the intensity of forbidden modes unless, one of its non-zero components forms the basis of one of the non-totally symmetric species of undistorted structure. In otherwords, the key component of distortion that affects the selection rules is one which is not present in the free state structure of the molecule.

A relation between the intensity of forbidden modes and the amount of distortion in the structure of molecular unit has been established (c.f. equations (5.4) and (5.5)). These results can be used effectively in the study of structural phase transitions in crystals (such as $(NH_4)_2SO_4$, $(NH_4)_2BeF_4$, etc) induced by changes in parameters such as temperature, pressure, etc. This point has been demonstrated by taking an example of the change in the IR absorbance due to the ν_1 mode of SO_4^{2-} ion during structural phase transition in $(NH_4)_2SO_4$ crystal.

The results of the theory help in understanding which of the forbidden modes of a molecular unit are allowed as the distortion induced effect may appear as bands of observable intensity. Obviously, it provides with the effective selection rules. It can also help in correct determination of the symmetry of the molecular site and the crystal as a whole.

The results can also be applied to have a better understanding of the IR and Raman spectra of molecular units in liquids and gaseous (particularly under high pressure) states. This point has been demonstrated by discussing examples of molecules such as C_6H_6 (liquid), C_6D_6 (liquid), CCl_4 (liquid) and CF_4 (liquid and gas). It is revealed that these molecules attain polar type of distortion in liquid and high pressure gaseous states (c.f. chapter V).

Finally, it is hoped that this work may serve as a good example of the application of group theory and approximation methods in the text of quantum mechanics and crystal/molecular physics.

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