

CHAPTER 3

NORMAL COORDINATE ANALYSIS OF HIGH TEMPERATURE SUPERCONDUCTORS

3.1 NORMAL MODES OF OSCILLATION

If there are n particles in a molecular model, the configuration of the system at any instant of the time can be represented by $3n$ coordinates. If the centre of gravity does not undergo the translation and the system itself is restricted from undergoing rotation, only $(3n-6)$ coordinates (or $3n-5$ in the case of a linear molecule) will be required. These $(3n-6)$ coordinates correspond to the internal degrees of freedom and relate to the positions of the atoms or mass points relative to each other. Accordingly, there will be $3n-6$ normal modes of oscillation in a molecule consisting of n atoms. Some of these modes may have identical frequencies and will not be counted as independent. Such modes are called degenerate modes, the degree of degeneracy being equal to the number of modes that have identical frequencies.

The classical method of obtaining the normal modes is as follows:

Let the position of the system be represented by the coordinates $q_1, q_2 \dots q_p$. If we regard the oscillations as having infinitesimally small amplitudes in comparison with the nuclear distance, both the kinetic and the potential energies may be expressed as functions of quadratic terms only, as

$$2T = \sum_{i,j} a_{ij} \dot{q}_i \dot{q}_j \quad (i, j = 1, 2 \dots \dots \dots m) \quad 3.1$$

$$2V = \sum_{i,j} b_{ij} q_i q_j \quad (i, j = 1, 2 \dots \dots \dots m) \quad 3.2$$

These two expressions can be reduced to the canonical form as

$$2T = \sum \dot{Q}_k^2 \quad \text{and} \quad 3.3$$

$$2V = \sum \lambda Q_k^2 \quad 3.4$$

by suitable linear transformation of the type

$$q_i = \sum l_{ik} Q_k \quad 3.5$$

The Q 's are called the normal coordinates and each q corresponds to a normal mode. The λ 's of the above expression are the roots of the determinantal equation

$$|b_{ij} - a_{ij}\lambda| = 0 \quad 3.6$$

The λ 's are related to the normal frequencies ν in cm^{-1} units by the equation $\lambda = 4\pi^2 c^2 \nu^2$, c being the velocity of light. If the coefficient of any normal coordinate Q is distinct from other λ 's, the corresponding normal mode is nondegenerate. On the other hand, if two or more Q 's have the same coefficient, the corresponding modes are degenerate and the degree of degeneracy is equal to the number of q 's

having the same frequency. While applying to an actual case, one has to set up the general quadratic forms for the potential and kinetic energies and then find suitable combinations of the variable so that the potential and the kinetic energies expressed in terms of altered variables may not contain cross terms. For complicated molecules, this method is considered to be difficult.

3.2 APPLICATION OF GROUP THEORY

The number and symmetry of the normal modes of oscillation of a molecule can be obtained in a less complicated manner by the application of the theory of groups [1]. Every molecule, by virtue of its symmetry, possesses a set of symmetry operations which transform the molecule into one indistinguishable from itself. The various symmetry operations are:

1. E - identity
2. C_p - rotation about an axis by $2\pi/p$
3. σ_h - reflection at a plane perpendicular to an axis
4. σ_v - reflection at a plane containing an axis
5. S_p - rotation by $2\pi/p$ about an axis followed by reflection at a plane perpendicular to it
6. i - inversion about a centre of symmetry.

The potential and kinetic energies of a molecule in terms

of the normal coordinate may be expressed in the canonical form by equations 3.3 and 3.4. Since, under any of the symmetry operations characteristic of the point group, the molecule remains as it is, the potential and kinetic energies should be invariant under all such operations. The choice of the coordinates is governed by this condition. A configuration of the molecule is considered in which all the normal coordinates except one, say Q_r with frequency ν_r vanish. Let the new configuration obtained by performing a symmetry operation R of the group of symmetry operations be denoted by RQ_k . If by the operation R , the k^{th} atom goes over to the l^{th} atom, then the l^{th} atom remains in its own neighbourhood but gets the motion of the k^{th} atom. By doing this, one obtains a configuration $\bar{R}Q_r$ which is geometrically identical with RQ_r . $\bar{R}Q_r$ represents a normal coordinate having the same frequency ν_r . With these covering operations, all the normal modes of oscillation belonging to the same frequency are obtained. But all these normal modes of oscillation may not be linearly independent. Let Q_1, Q_2, \dots, Q_f be a complete set of linearly independent normal coordinates with frequency ν_r . The oscillation of frequency ν_r is f -fold degenerate. Similarly, the normal coordinates of different frequencies are also obtained. A set of normal coordinates of definite frequency defines an irreducible representation of the group G and the $3n$

cartesian coordinates $x_1, y_1, z_1 \dots x_n, y_n, z_n \dots$ define a reducible representation.

The character of any operation R may be calculated from the reducible representation defined by the cartesian coordinates. If the k^{th} atom is invariant under any operation R, then

$$\bar{R}X_k = X_k \cos\phi + Y_k \sin\phi \quad 3.7$$

$$\bar{R}Y_k = -X_k \sin\phi + Y_k \cos\phi \quad 3.8$$

$$\bar{R}Z_k = Z_k \quad 3.9$$

The axis of rotation is the Z axis and X and Y axis lie in a plane perpendicular to it. The character is obtained as $1+2\cos\phi$ for the operation consisting of a rotation through ϕ radians. If it is a rotation reflection, the character comes out as $-1+2\cos\phi$. Thus an invariant atom under the operation R gives rise to the character $\pm 1+2\cos\phi_R$, the \pm sign being used accordingly, as the operation is a pure rotation or a rotation-reflection. Hence, in the reducible representation, if U_R is the number of invariant atoms, the character of any operation R is $U_R(\pm 1+2\cos\phi_R)$.

From a knowledge of the group characters in any representation Γ_i , n_i -the number of times a particular reducible representation Γ_i contained in Γ is determined using the formula

$$n_i = (1/N) \sum_R X_i(R) \chi'(R) \quad 3.10$$

where $X_i(R)$ and $\chi'(R)$ are respectively the character of R in Γ_i and Γ and N , the order of the group. Γ stands for the reducible representation of the cartesian coordinates. The number n_i of the normal coordinates that belongs to a particular irreducible representation includes translations and rotations of the molecule as a whole. The character arising from pure translation is $(1+2\cos\phi)$ for $C(\phi)$ and $(-1+2\cos\phi)$ for $S(\phi)$ and the character from pure rotation is $(1+2\cos\phi)$ for $C(\phi)$ and $(1-2\cos\phi)$ for $S(\phi)$. Finally, from the equation 3.10, the following results are obtained.

1. The number n_i of the normal modes under the irreducible representation Γ_i including translations and rotations, if

$$\chi'(R) = U_R (1 + 2 \cos\phi_R) \quad \text{for } C(\phi) \quad 3.12a$$

$$\chi'(R) = U_R (-1 + 2 \cos\phi_R) \quad \text{for } S(\phi) \quad 3.12b$$

2. The number of translations occurring in Γ_i , if

$$\chi'(R) = (1 + 2 \cos\phi_R) \quad \text{for } C(\phi) \quad 3.12c$$

$$\chi'(R) = (-1 + 2 \cos\phi_R) \quad \text{for } S(\phi) \quad 3.12d$$

3. The number of rotations coming in Γ_i , if

$$\chi'(R) = (1 + 2 \cos\phi_R) \quad \text{for } C(\phi) \quad 3.12e$$

$$\chi'(R) = (1 - 2 \cos\phi_R) \quad \text{for } S(\phi) \quad 3.12f$$

4. The number n_i' of the normal modes of oscillation excluding translations and rotations in Γ_i , if

$$\chi'(R) = (U_R - 2) (1 + 2 \cos\phi_R) \quad \text{for } C(\phi) \quad 3.12g$$

$$\chi'(R) = U_R (-1 + 2 \cos\phi_R) \quad \text{for } S(\phi) \quad 3.12h$$

Since the character is the same for all operations coming under a particular class j ,

$$\chi_i(R) \chi'(R) = \sum_j h_j \chi_i(R) \chi_j'(R) \quad 3.13$$

The summation on the right hand side extends over all the classes that constitutes the group and h_j represents the number of symmetry elements in the j^{th} class. The above equation can be written as

$$n_i = (1/N) \sum_j h_j \chi_i(R) \chi_j'(R) \quad 3.14$$

If ψ_j' is the character obtained after allowing for pure rotations and translations and is equal to $(U_R - 2)(1 + 2\cos\phi_R)$ for pure rotations and $U_R(-1 + 2\cos\phi_R)$ for rotations accompanied by reflections, then the normal mode excluding pure rotations and translations is

$$n_i = (1/N) \sum_j h_j \chi_i(R) \psi_j'(R) \quad 3.15$$

3.3 SELECTION RULES

In the foregoing paragraphs, it has been shown that every normal mode of oscillation belongs to an irreducible representation of the group symmetry operations of the molecule. The activity or otherwise the modes of oscillation should also be discussed in ascertaining the number of lines that should appear in the infrared absorption or in the vibrational Raman effect. The mode is

active or inactive in the infrared absorption depends whether it causes a variation or not in the electric moment of the molecule. The variation itself may be regarded as a vector. Hence, its character is $(\pm 1 + 2\cos\phi_R)$. From the transformation property of electric moment, the selection rules for the infrared activity are obtained as

$$\sum_R (\pm 1 + 2\cos\phi_R) \chi_i(R) = 0 \text{ inactive 3.16}$$

$$\neq 0 \text{ active}$$

where $\chi_i(R)$ is the character of the irreducible representation Γ_i to which the normal coordinate belongs. The summation extends over all the operations that constitute the group.

The selection rules for the Raman spectra may be derived in a similar manner. The mode is Raman active if it causes a variation in the optical polarizability of the molecule and is inactive if there is no variation. The optical polarizability is a symmetric tensor. By the transformation of the polarizability tensor components, it follows that the character of the operation R in the reducible representation is defined by the polarizability tensor components $2\cos\phi_R(\pm 1 + 2\cos\phi_R)$. The selection rule for the Raman effect is therefore,

$$\sum_R 2\cos\phi_R (\pm 1 + 2\cos\phi_R) \chi_i(R) = 0 \text{ inactive 3.17}$$

$$\neq 0 \text{ active}$$

3.4 NATURE OF MOLECULAR VIBRATIONS

One of the main objectives of the study of vibrational spectra of polyatomic molecules is the investigation of the nature of the forces holding the nuclei in a polyatomic molecule to their equilibrium positions. Most of the Raman and infrared transitions represent the fundamental vibration frequencies of the molecules involved in the scattering and absorption process respectively. A correlation of these frequencies as observed in Raman and infrared spectra may be made with the molecular structure from a knowledge of the characteristic modes of oscillation of the molecule. The fundamental frequencies and the normal coordinate corresponding to them depend on the potential and kinetic energies of the particles.

3.4.1 MATHEMATICAL FORMULATION OF THE MOLECULAR VIBRATIONS

For a system of n particles, such as a molecule in which every particle acts with a certain force on every other one in equilibrium, the resultant of all the forces acting on a given particle is zero. If any particle is displaced from its equilibrium position, the resulting force F' will depend upon the components x_1, y_1, z_1 of the displacement parallel to the fixed coordinate axes. Generally, the force components

may be developed into a power series of these displacements. For sufficiently small amplitudes, however only the linear terms need to be considered. Thus one has for the component parallel to the x direction

$$F_x^{11} = -k_{xx}^{11} x_1 - k_{xy}^{11} y_1 - k_{xz}^{11} z_1 \quad 3.18a$$

and similarly, the components parallel to the other directions are,

$$F_y^1 = -k_{yx}^{11} x_1 - k_{yy}^{11} y_1 - k_{yz}^{11} z_1 \quad 3.18b$$

$$F_z^1 = -k_{zx}^{11} x_1 - k_{zy}^{11} y_1 - k_{zz}^{11} z_1 \quad 3.18c$$

where $k_{xx}^{11}, k_{yy}^{11}, \dots$ are force constants. The above equations will hold good only if all the other particles in the system remain in their equilibrium positions. If they are displaced as well, for small displacements,

$$F_x^1 = -k_{xx}^{11} x_1 - k_{xy}^{11} y_1 - k_{xz}^{11} z_1 - k_{xx}^{12} x_2 - k_{xy}^{12} y_2 - k_{xz}^{12} z_2 \dots \quad 3.19$$

and similarly, expressions for $F_y^1, F_z^1, F_x^2, \dots, F_z^n$ can be expressed. For all the particles in the system, to vibrate in a simple harmonic manner with a frequency ν ,

$$\begin{aligned} F_x^i &= -4\pi^2 c^2 \nu^2 m_i x_i \\ F_y^i &= -4\pi^2 c^2 \nu^2 m_i y_i \\ F_z^i &= -4\pi^2 c^2 \nu^2 m_i z_i \end{aligned} \quad 3.20$$

Thus for certain frequencies defined by the determinant

$$\begin{vmatrix} k_{xx}^{11} - 4\pi^2 c^2 v^2 m_1 & k_{xy}^{11} & k_{xz}^{11} & \dots & k_{xn}^{1n} \\ \dots & k_{yy}^{11} - 4\pi^2 c^2 v^2 m_1 & k_{yz}^{11} & \dots & k_{yn}^{1n} \\ \dots & \dots & \dots & \dots & k_{zn}^{nn} - 4\pi^2 c^2 v^2 m_n \end{vmatrix} = 0 \quad 3.21$$

a simultaneous simple harmonic motion of all particles is possible. The determinant is of $3n^{\text{th}}$ degree and therefore has $3n$ roots. Thus, in principle, the frequencies of the normal vibrations may be determined.

The method described above indicates the general principles but in actual calculation, the law of conservation of energy is most frequently used. The potential energy of the nuclei in a molecule referred to the equilibrium position as $V=0$ is given in first approximation (that is, as long as the displacements are sufficiently small), by

$$\begin{aligned} V = & (1/2) \sum_{i,j} (k_{xx}^{ij} x_i x_j + k_{yy}^{ij} y_i y_j + k_{zz}^{ij} z_i z_j \\ & + \sum_{i,j} (k_{xy}^{ij} x_i x_j + k_{xz}^{ij} x_i z_j + k_{yz}^{ij} z_i y_i) \end{aligned} \quad 3.22$$

Denoting $x_1, y_1, z_1, x_2, y_2, z_2, \dots$ by q_1, q_2, q_3, \dots , the potential energy may be written (with $K_{ij} = k_{ji}$) as

$$\begin{aligned} V = & (1/2) \sum_{i,j} k_{ij} q_i q_j \\ = & (1/2) k_{11} q_1^2 + (1/2) k_{22} q_2^2 + \dots \end{aligned} \quad 3.23$$

The kinetic energy is given by

$$\begin{aligned}
 T &= (1/2) \sum_i m_i (\dot{x}_i^2 + \dot{y}_i^2 + \dot{z}_i^2) \\
 &= (1/2) \sum_{i,j} a_{ij} \dot{q}_i \dot{q}_j
 \end{aligned}
 \tag{3.24}$$

where $a_{ij} = 0$ for $i \neq j$ and $a_{11} = a_{22} = a_{33} = m_1$

$$a_{44} = a_{55} = a_{66} = m_2, \dots$$

Introducing new coordinates $\eta_1, \eta_2, \eta_3, \dots, \eta_{3n}$

$$\begin{aligned}
 x_1 &= q_1 = c_{11}\eta_1 + c_{12}\eta_2 + c_{13}\eta_3 + \dots \\
 y_1 &= q_2 = c_{21}\eta_1 + c_{22}\eta_2 + c_{23}\eta_3 + \dots \\
 z_1 &= q_3 = c_{31}\eta_1 + c_{32}\eta_2 + c_{33}\eta_3 + \dots \\
 q_i &= c_{i1}\eta_1 + c_{i2}\eta_2 + c_{i3}\eta_3 + \dots
 \end{aligned}$$

the potential and kinetic energy can be written as

$$V = (1/2) (\lambda_1 \eta_1^2 + \lambda_2 \eta_2^2 + \dots + \lambda_{3n} \eta_{3n}^2)$$

$$T = (1/2) (\dot{\eta}_1^2 + \dot{\eta}_2^2 + \dot{\eta}_{3n}^2)$$

The λ 's are the roots of the determinantal equation which is called the secular equation of the problem:

$$\begin{vmatrix}
 k_{11} - a_{11}\lambda & k_{12} - a_{12}\lambda & k_{13} - a_{13}\lambda & \dots \\
 \dots & k_{22} - a_{22}\lambda & k_{23} - a_{23}\lambda & \dots \\
 \dots & \dots & k_{33} - a_{33}\lambda & \dots
 \end{vmatrix} = 0
 \tag{3.27}$$

The above equation is of $3n^{\text{th}}$ degree having $3n$ rows and $3n$ columns and therefore has $3n$ roots. Of these, 6 roots (5 roots in the case of linear molecules) are equal to zero and they correspond to nongenuine normal vibrations and consist of translations and rotations. The remaining $3n-6$ (or $3n-5$) roots are real and correspond to $3n-6$ (or $3n-5$) genuine

vibrations in accordance with $3n-6$ (or $3n-5$) vibrational degrees of freedom. Some of these may be repeated twice, thrice, etc. and in such cases they are said to be doubly degenerate, triply degenerate and so on.

3.4.2 SOLUTION OF THE SECULAR EQUATION

In order to determine the force constants included in the potential function chosen for any molecule, it is necessary to solve the secular equation using the observed frequencies. The following are the methods adopted in the solution of the secular equation.

a) Solution in cartesian coordinates:

The secular determinant in terms of the cartesian coordinates will have $3n$ columns and, as such, the resulting equation is of $3n^{\text{th}}$ degree in $\lambda (= 4\pi^2 C^2 \nu^2)$. Thus even in the case of the simplest triatomic molecule, it is of 9^{th} degree. Though this equation has 6 (or 5 for linear molecules) zero roots corresponding to the six nongenuine vibrations, the factor λ^6 (or λ^5) can not be easily separated from the secular determinant. The process of reducing the degree of secular equation to 3, corresponding to 3 genuine vibrations is by no means easy even in such a case. In the case of molecules having more atoms, this method will in general, lead a rather complicated

determinant.

b) Solution in internal coordinates:

The relative positions of the nuclei in a molecule are fixed by $3n-6$ (or $3n-5$) internal coordinates and thus the secular determinant of degree $3n-6$ may be directly obtained. Various choices of the internal coordinates are possible. The deviations Q_i from $3n-6$ equilibrium internuclear distance form one such choice. Such coordinates are called central force coordinates since they are particularly adopted to the central force system. Since for small displacements, these Q 's are linear function of the rectangular displacement coordinates, the potential energy is a quadratic function of Q_i and may be written as

$$2V = \sum_{i,j} b_{ij} Q_i Q_j \quad 3.28$$

The value of b_{ij} will depend on the force constants. The kinetic energy is

$$2T = \sum_{i,j} a_{ij} \dot{Q}_i \dot{Q}_j \quad 3.29$$

Now the secular determinant is

$$\begin{vmatrix} a_{11}\lambda - b_{11} & a_{12}\lambda - b_{12} & a_{13}\lambda - b_{13} \\ & a_{22}\lambda - b_{22} & a_{23}\lambda - b_{23} \\ & & a_{33}\lambda - b_{33} \end{vmatrix} = 0 \quad 3.30$$

and is of degree $3n-6$ only. The value of a_{ij} will depend on

the masses of the nuclei. The calculations by this method are by no means less cumbersome than in the preceding method. But the advantage is that the force constants are more easily visualised.

c) Solution by use of symmetry coordinates:

The utilisation of molecular symmetry has proved to be the most powerful technique in the mathematical analysis of molecular vibrations. The useful procedure consists first in finding the number of genuine vibrations of each species by the group theoretical considerations. Knowing the number of vibrations under each symmetry type, new coordinates are introduced. These new coordinates, called the symmetry coordinates are the linear combinations of the equivalent internal coordinates which are the changes in the bond distances and interbond angles. The potential function is then a quadratic function of the symmetry coordinates as well.

The choice of the symmetry coordinates is not arbitrary but is governed by certain conditions: i) The number of symmetry coordinates corresponding to each symmetry type will be equal to the number of vibrations under each species. For the doubly degenerate vibrations, a pair of symmetry

coordinates are necessary for each and for the triply degenerate vibrations, three such coordinates will be required. ii) They should be normalised and orthogonal. iii) They should transform in accordance with the characters of the symmetry type to which they belong.

The method of Wilson [2] using these symmetry coordinates is the most convenient one for the treatment of complex molecules. In this method, the number of active vibrations under each symmetry type is first determined using the principle outlined in the section 3.2 of this chapter. Corresponding to each vibration, the symmetry coordinates of the form $S_j = \sum U_{jk} r_k$ are constructed from out of the equivalent internal coordinates r_k . These linear combinations are such that $\sum (U_{jk})^2 = 1$ and $\sum (U_{jk})(U_{lk}) = 0$, satisfying the normalisation and orthogonality conditions respectively. Whether the different symmetry coordinates transform in accordance with the character of the vibration species which they represent, can be verified knowing the transformations of the internal coordinates under the various covering operations pertaining to the point group to which the molecule belongs.

Using the above symmetry coordinates, the elements of a matrix F related to the potential energy are obtained. The general expression for the potential energy is

$2V = f_{ik} r_i r_k$ where $f_{ik} = f_{ki}$ is the force constant and r_i and r_k are the internal coordinates. As the symmetry coordinates are of the form $S_j = \sum_k U_{jk} r_k$, the potential energy in terms of the symmetry coordinates will take the form $2V = \sum_j \sum_l F_{jl} S_j S_l$ where j and l extend over all symmetry coordinates. If the above expressions are reduced for the potential energy to matrix notation, then

$$2V = \tilde{r} f r \quad 3.31a$$

$$2V = \tilde{S} F S \quad 3.31b$$

where \tilde{r} and \tilde{S} are the transposes of the r and S matrices.

As $S = Ur, \quad r = U^{-1}S = \tilde{U} S$

$$\tilde{r} = (\tilde{U} S) = \tilde{S} U$$

$$\tilde{r} f r = \tilde{S} F S$$

where $F = U f \tilde{U}$

Sometimes the transpose of a matrix can also be represented by a prime symbol, thus

$$F = U f U'$$

Thus, the elements of the potential energy matrix is calculated using the coefficients of internal coordinates in the various symmetry coordinates and a force constant matrix whose columns and rows are labelled by the internal coordinates. The matrix U will be that formed by the coefficients of U_{jk} 's in the corresponding symmetry coordinate. This form has the advantage of requiring only a single coordinate of each degenerate set.

In terms of cartesian displacement coordinate x_i , the internal coordinate is $r_k = \sum_{i=1}^n B_{ki} x_i$. It is convenient to describe the displacements of the atoms from this equilibrium configuration by using vectors ρ_t one for each atom t instead of x_i which are the components of these vectors. Then the internal coordinate $r_k = \sum_{t=1}^n s_{kt} \rho_t$ in which the vectors s_{kt} are introduced. The three B_{ki} 's belonging to the atom t are then the components of S_{kt} . In this way, a given internal coordinate r_k is characterised by a set of S_{kt} vectors, one for each atom t . Actually, these vanish except for those atoms whose motion changes r_k .

As the kinetic energy is of the form

$$2T = r^{-1} G^{-1} r \quad 3.32a$$

$$2T = F' G F \quad 3.32b$$

where F is the column matrix whose elements are the momenta conjugate to the r_k 's and the prime denotes the transposed matrix,

$$G_{kk'} = \sum_{i=1}^n \mu_i B_{ki} B_{k'i} \quad 3.33$$

where μ_i is the reciprocal mass of the i^{th} atom. Substituting for S_{ki} ,

$$G_{kk'} = \sum_{t=1}^n \mu_t S_{kt} S_{k't} \quad 3.34$$

The above form has the advantage that it requires no

coordinate system. Further, it is possible to express the S_{kt} vectors in terms of unit vectors along the chemical bonds so that, the problem of finding G reduces to one of finding the interbond angles. Very general expressions can be given for the S_{kt} vectors for the important types of internal coordinates r_k . For example, if V_1 is a unit vector directed from atom t to t' along the bond and r_k , the changes in the equilibrium bond distance, then

$$S_{kt} = -V_1 ; S_{kt'} = V_1$$

If r_k is a change in the bond angle t'-t-t", (the atom t being at the apex), the S_{kt} vectors are:

for the end atoms,

$$S_{kt'} = (V_1 \cos\phi - V_2) / d \sin\phi \quad 3.35a$$

$$S_{kt''} = (V_2 \cos\phi - V_1) / d \sin\phi \quad 3.35b$$

for the apex atom,

$$S_{kt} = [(1/D - \cos\phi/d)V_1 + (1/d - \cos\phi/D)V_2] / \sin\phi \quad 3.36$$

The above S_{kt} vectors can not be applied to the case of linear molecules, as the interbond angle becomes 180° and $\sin\phi = 0$. In such cases, the S_{kt} vectors may be obtained from the assumption of unit vectors in a plane.

Wilson et al [3] have given methods for obtaining all the S_{kt} vectors with respect to the other types of coordinates

as well. In terms of the symmetry coordinates of the form $S_j = \sum_k U_{jk} r_k$, what is required for the evaluation of the elements of a modified form of kinetic energy matrix will be S_j^t vectors which are of the form $S_j^t = \sum_k U_{jk} S_{kt}$. The elements G_{j1} will then be $\sum_p \mu_p g_p S_j^t S_1^t$ for nondegenerate blocks and $(1/d) \sum_p \mu_p g_p s_j^t s_1^t$ for degenerate blocks. μ_p is the reciprocal mass of a typical atom, g_p is the number of equivalent atoms in the p^{th} set and d , the degree of degeneracy.

The secular equation is then made up of factors of the form

$$|F - G^{-1} \lambda| = 0 \quad 3.37$$

The above method which utilises the symmetry properties to factorise the secular equation has the great advantage of solving the algebraic equation instead of a secular one.

The normal vibrational frequencies are determined in terms of λ by solving the above equation. It is laborious to solve this secular determinant in this form due to the presence of the term λ and the difficulty in calculating G^{-1} matrix. These inconveniences can be overcome if this equation is multiplied by the determinant of G matrix and we get

$$|GF - E \lambda| = 0$$

Since F and G matrices are symmetrical, this can also be expressed as

The method described above is referred as the Wilson's FG matrix method [3]. This method has been further developed for analysing the optically active lattice vibrations of crystals [4], metal oxides [5] and the same has been adopted for HTSC also [6].

The determination of symmetric potential constants involved in the secular equation, from the vibrational frequencies alone, has been a mathematically undetermined problem so far. The difficulty is due to the fact that a vibration of a type, of order n_i involves $n_i(n_i+1)/2$ potential constant elements F_{ij} in general and their evaluation with n_i vibrational frequencies is mathematically impossible. Hence, any attempt of evaluation of potential constants in a problem of order $n_i > 1$ should require $n_i(n_i-1)/2$ additional data other than n_i frequencies.

The exact force field can be determined using additional data like isotopic frequency shifts, vibrational mean amplitudes, Coriolis coupling constants, centrifugal distortion constants and band intensities etc., On the other hand, for many complex molecules, the additional data are insufficient for determining the unique force field. Hence, the approximation methods are needed.

In the present work, an initial set of force constants for the molecules under consideration is assumed using the transferability of force constants from similar molecules. It is necessary to adjust these force constants in order to reproduce the vibrational frequencies satisfactorily. This is accomplished by a least-square technique similar to that given by Shimanouchi et al [4]. In this method, the Z matrix is constructed out of the elements of the potential energy matrix F and the general quadratic valence force constant so that $F = ZK$. An initial set of force constants K_0 is estimated and $F_0 = ZK_0$ is evaluated. Using F_0 and G, the vibrational frequencies are computed by suitable computer programs and compared with the observed fundamental frequencies. The weighted sum of the squared deviation for the initial set K

$$S = \sum \omega_i (v_{i, \text{obs}} - v_{i, \text{cal}})^2 \quad 3.39$$

is found out. Next step is to estimate the refined set of force constants $K = K_0 + k$ which makes the weighted sum of squared deviation S smaller. This process is repeated by adjusting the force constants each time till a final set of force constants which makes S minimum is obtained.

3.4.3 Potential Energy Distribution

In the normal coordinate analysis, the potential energy distribution (PED) plays an important role to give an

insight into the nature of the normal modes. The PED is usually defined in one of the two ways. The first method determines the contribution of each force constant f_{ij} to the normal frequencies of vibrations, while the second method expresses the PED as a contribution of each internal displacement coordinate to the normal modes. The PED is expressed in terms of the percentage contribution of each force constant or displacement coordinate to the potential energy of each normal mode.

Potential energy is expressed by the equation 3.4 as

$$2V = \sum_i \lambda_i Q_i^2$$

If unit displacements of the normal coordinate Q_i are considered, all other normal coordinate being at rest, then λ_i is a measure of the potential energy.

The normalisation condition $L'fL = \lambda$ gives relations of the form

$$\lambda_i = \sum_{j,k} L_{ji} L_{ki} f_{jk} \quad 3.40$$

and after neglecting the cross terms,

$$\lambda_i = \sum_j f_{jj} L_{ji}^2 \quad 3.41$$

Hence, the normalised PED can be expressed as

$$V_{ji} = f_{ii} L_{ji}^2 / \lambda_i \quad 3.42$$

where V_{ji} is the contribution of the j^{th} symmetry coordinate to the potential energy of the vibration whose frequency is ν_{ji} . The contribution to the potential energy from the individual diagonal elements gives rise to a conceptual link

between the empirical analysis of the infrared spectra of complex molecules dealing with the characteristic group frequencies and the theoretical approach from the computation of the normal modes.

The above procedure is applied to obtain the zone centre phonon frequencies of $\text{RBa}_2\text{Cu}_3\text{O}_7$ (R= Ho, Dy and Sm) and is described in section 3.5. It should be mentioned here that the normal coordinate analysis is carried out only for the modes at the centre of the Brillouin zone (zero wave vector).

3.5 NORMAL COORDINATE ANALYSIS OF THE ZERO WAVE-VECTOR VIBRATIONS OF $\text{RBa}_2\text{Cu}_3\text{O}_7$ (R= Ho, Dy and Sm)

The assignment of the spectral features to specific lattice vibrations would be an important step in understanding their role in superconductivity. Raman and far-infrared studies of these HTSC have contributed significantly to their understanding. Although many reports of superconductivity for rare earth atoms have appeared, systematic investigations for the whole rare earth family are scarce. Raman [7] and infrared reflection spectrum [7,8,9] of $\text{YBa}_2\text{Cu}_3\text{O}_7$ have been reported earlier. Superconducting properties in $\text{RBa}_2\text{Cu}_3\text{O}_7$ (Ho, Dy and Sm) prepared by the

method of powder calcination were studied by Mohan et al [10,11,12]. These compounds showed a sharp superconducting transition width, ΔT , less than 1K. The pressure shift of T_c is studied and a.c. susceptibility measurements were also made.

3.5.1 Symmetry Analysis of $q = 0$ modes

It is well known that the $RBa_2Cu_3O_7$ compounds have an orthorhombic unit cell (Figure 3.1) with lattice constants ($a=3.822 \text{ \AA}$, $b= 3.891 \text{ \AA}$ and $c=11.677 \text{ \AA}$ for $R = Y$) which increase slightly with increasing ionic radius of R^{3+} . They belong to the space group P_{mmm} (D_{2h} in Schoenflies notation) and point group mmm (D_{2h}). These groups have an inversion centre, so that the optical modes near $q = 0$ can not be both Raman and infrared active. There is only one site which has the full symmetry of the point group and this is indeed the case for the sites of the $O1$, $Cu1$ and R atoms. The pairs of atoms $O2$, $O3$, $O4$, Ba and $Cu2$ have lower, C_{2v} symmetry. Permutation of the equivalent atoms in the C_{2v} pairs leads to the irreducible representations A_g and B_{1u} of D_{2h} . The corresponding modes are obtained by multiplying these representations by those of the displacement vectors in a, b and c directions (representations B_{3u}, B_{2u} and B_{1u}). There are three odd (ungerade) modes B_{1u} , B_{2u} and B_{3u} , and three even (gerade) modes A_g , B_{2g} and B_{3g} for each of the members

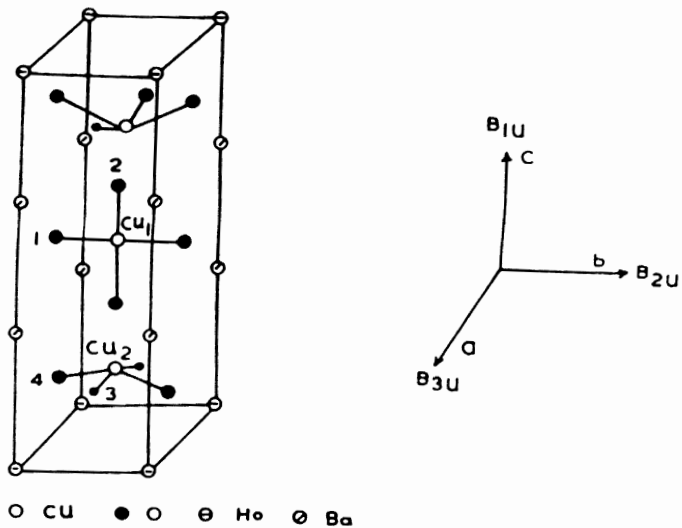


FIG 3-1 ORTHORHOMBIC UNIT CELL OF $\text{HoBa}_2\text{Cu}_3\text{O}_7$

of a pair. For the vibrations involving the atomic positions with full symmetry, only three odd modes are found for each atom. The 13 atoms of the unit cell yield a total of 36 optic vibrational frequency translational modes involving the following sublattice displacements.

$B_{1u}+B_{2u}+B_{3u}$	From the motion of R atoms
$A_g+B_{2g}+B_{3g}+B_{1u}+$ $B_{2u}+B_{3u}$	From the motion of 2 Ba atoms
$A_g+B_{2g}+B_{3g}+B_{1u}+$ $B_{2u}+B_{3u}$	From the motion of 2 Cu atoms sandwiched by R and B atoms
$B_{1u}+B_{2u}+B_{3u}$	From the motion of Cu atom surrounded by 4 Ba atoms
$2A_g+2B_{2g}+2B_{3g}+2B_{1u}$ $+2B_{2u}+2B_{3u}$	From motion of 4 O atoms between the layers of R and Ba
$A_g+B_{2g}+B_{3g}+B_{1u}+$ $B_{2u}+B_{3u}$	From the motion of 2 O atoms on the Cu-O line along the c axis
$B_{1u}+B_{2u}+B_{3u}$	From the motion of O atom on the Cu-O chain in the b-axis direction

Subtracting the translational modes $B_{1u}+B_{2u}+B_{3u}$, the $q=0$ optic modes involve the irreducible representation as follows:

$$\Gamma = 5A_g + 5B_{2g} + 5B_{3g} + 7B_{1u} + 7B_{2u} + 7B_{3u}$$

The species belonging to A_g , B_{2g} and B_{3g} are Raman active modes whereas the B_{1u} , B_{2u} and B_{3u} are infrared active modes. The B_{1u} and A_g modes involve displacement modes along the crystallographic c-axis, the B_{2u} and B_{3g} modes along the b-axis and the B_{3u} and B_{2g} modes along the a-axis.

To find which of the expected modes will actually be observed in an experiment depends on a number of additional physical aspects of these modes. To be observed in infrared spectra, for example, a mode must show a significant charge displacement (dipole moment), a requirement for which group theoretical infrared activity is necessary but not sufficient. It can sometimes be concluded from specific models for the ionic charges and the expected displacement of those ions that a mode is actually nearly silent, i.e., it shows no appreciable activity although it is infrared allowed. An important example is a mode related to the silent (infrared and Raman forbidden) mode of the perovskites. The physical reason for the latter being infrared forbidden is that the oxygen ions situated on contiguous faces of the perovskite unit cell vibrate out of phase in the c direction thus yielding no net dipole moment. A mode similar to this one exists in $RBa_2Cu_3O_7$, but with the

amplitudes for the oxygen displacements somewhat different for the two contiguous oxygen ions. The resulting dipole moment remains small, yielding a nearly infrared forbidden mode in the superconductor. It is the second CuO_2 plane in the superconductor separated by the R-atom that splits the perovskites mode into odd and even components: in one of them, upper and lower CuO_2 planes are out-of-phase (B_{1g}) and in the other, they are in-phase (B_{2u}). The infrared activity is not affected by adding another plane with no dipole moment, and B_{2u} remains silent. The B_{1g} mode, however, becomes symmetry-allowed for Raman activity and is indeed observed.

3.6 RESULTS AND DISCUSSION

The normal coordinate analysis is performed using the Wilson's F-G matrix method along with the modification introduced by Shimanouchi et al [4]. A simple valence force field is used. The structural parameters employed here to carry out these calculations are given in Table 3.1. The initial set of force constants are taken from [6,13] and are adjusted by a least square technique in accordance with the position of the peak in the Raman and infrared spectra. The computer programs CART,GMAT and FPERT [14] are utilised with suitable modifications to carry out the normal coordinate calculations.

A preliminary normal coordinate analysis of $\text{YBa}_2\text{Cu}_3\text{O}_7$ has been performed using the data given in Table 3.1. It is quite interesting to note that the calculated frequencies listed in Table 3.2 agree favourably with the results reported earlier [15]. Hence, the same program [14] has been extended to perform the normal coordinate analysis for the systems under consideration.

The vibrational frequencies for $\text{HoBa}_2\text{Cu}_3\text{O}_7$, $\text{DyBa}_2\text{Cu}_3\text{O}_7$ and $\text{SmBa}_2\text{Cu}_3\text{O}_7$ are given in Tables 3.3, 3.4 and 3.5. The calculated frequencies are compared with the available Raman and infrared experimental data [7,16]. The vibrational assignments belonging to A_g , B_{2g} and B_{3g} of Raman active vibrations and B_{1u} , B_{2u} and B_{3u} of infrared active vibrations are made by referring to the assignment of the $\text{YBa}_2\text{Cu}_3\text{O}_7$ system [17-20] and Raman and infrared intensities. To check whether the chosen set of vibrational frequencies contributes maximum to the potential energy associated with the normal coordinate of the superconducting material, the PED is calculated using the relation given by equation 3.39 and is also tabulated. As an example, the vibrational assignments of $\text{HoBa}_2\text{Cu}_3\text{O}_7$ are discussed here.

Assignments for the Raman active modes:

According to group theory, the atoms involved in the Raman active vibrations are Ba, Cu(2), O(2), O(3) and O(4). The highest calculated mode for A_g symmetry is at 567 cm^{-1} . From the PED, it is clear that this mode is solely due to the symmetric Cu(2)-O(2) stretch. The A_g mode at 487 cm^{-1} is also due to the bond stretching vibrations of O(2) and is associated with the observed mode at 504 cm^{-1} . And it is clear from the tables presented here that this frequency increases with increasing ionic radius of the rare earth. Raman modes observed at 424 and 335 cm^{-1} have been observed consistently in all rare earth superconducting materials and are attributed to pure bond bending vibrations of O(3)-Cu(2) and O(4)-Cu(2) bonds along the c-axis with O(3) and O(4) neighbours moving in-phase and out-of phase respectively. From the normal coordinate calculation, these values are predicted to be 429 and 330 cm^{-1} which agree with the observed values. A feature that appears to be directly related to superconductivity and also seen in the Raman spectra is the anomalous softening of some modes when the temperature is lowered. When the material is cooled below T_c , the phonons associated with stretching-bending vibrations of the Cu-O frames lower their frequency. The observed mode at 335 cm^{-1} is shown to possess such anomaly and this frequency decreases with increasing ionic radius of

the rare earth [7]. According to the present calculations, the wave number at 149 cm^{-1} is the lowest calculated mode for A_g symmetry which corresponds to the experimental value at 155 cm^{-1} and is attributed to the Ba-O vibrations. The relative contribution of the force constants involving Ba-O stretch to the vibrational energy of this mode is 64% .

The phonon frequencies evaluated from this calculation for B_{2g} and B_{3g} symmetries are 552,541,476,320,158 and 549,532,428,280,111 cm^{-1} respectively. The contribution of force constants to these modes are shown in Table 3.3. Although the B_{2g} and B_{3g} modes have different frequencies, they have similar vibration characteristics except the fact that the former mode involves the motion of atoms along the b-axis whereas the latter one is due to the atomic motion in the a-axis. The modes calculated at 552 and 541 cm^{-1} of B_{2g} symmetry and at 549 and 532 cm^{-1} of B_{3g} symmetry are described as asymmetric Cu-O stretches. The observed peak around 580 cm^{-1} was identified as the defect activated mode [15]. Since the infrared active modes around 580 cm^{-1} soften due to oxygen deficiencies, they improbably correspond to the Raman peak at 580 cm^{-1} . But few other reports [21] attribute these modes to the impurity phases of BaCuO_2 . The weak intensity Raman band observed at 271 cm^{-1} has been assigned to the O-Cu-O deformation modes. From the PED, it

is found that this mode is practically due to pure bond-bending vibrations. The observed value is quite close to the calculated value at 280 cm^{-1} . The mode at 320 cm^{-1} is also assigned in the same way.

Assignments for the infrared active modes:

The observed infrared frequencies are at 119, 155, 166, 278, 307, 460 and 573 cm^{-1} respectively. The assignment of the infrared active modes are complicated due to the complexity of the crystal structure. Some weak modes are also observed in the infrared spectrum of these systems. For those modes which involve in-phase and out-of phase types of Cu-O, Ba-O or Ho-O stretches, a strong infrared feature is expected for the in-phase motion of the metal atoms. The lower frequencies at 119, 155 and 166 cm^{-1} are associated with Ba and Ho vibrations. The peak at 166 cm^{-1} is attributed to the vibrations of Ho (infrared allowed, Raman forbidden since there is only one Ho atom per primitive cell) and corresponds to the calculated mode at 170 cm^{-1} . The B_{1u} mode calculated at 262 cm^{-1} agrees well with the observed peak at 278 cm^{-1} and is assigned to Cu(2)-O(3)-O(4) in-plane vibration. The infrared peak at 460 cm^{-1} coincides with the calculated value at 444 cm^{-1} . The rest of the calculated

modes and their corresponding PED are presented in Table 3.3.

Similarly, the normal coordinate treatment is applied to $\text{DyBa}_2\text{Cu}_3\text{O}_7$ and $\text{SmBa}_2\text{Cu}_3\text{O}_7$ systems and the normal mode frequencies are presented in Tables 3.4 and 3.5. The results obtained for these system agree fairly well with the earlier discussed system namely $\text{HoBa}_2\text{Cu}_3\text{O}_7$.

3.7 CONCLUSION

With the aid of the normal coordinate analysis, the evaluated vibrational frequencies of the rare earth superconducting systems in the range $100\text{-}650\text{ cm}^{-1}$ have been assigned. It is significant that the frequencies observed in the Raman and infrared spectra support the present centre of symmetry structure. It is seen from the tables, that the agreement between the calculated and observed frequencies is very good for the systems under consideration. This fact supports that the present vibrational assignments made for the observed infrared and Raman spectra are adequate. Therefore, it can be concluded that normal coordinate analysis of the optically active lattice vibrations is useful for the theoretical interpretation of the vibrational spectra at the centre of the Brillouin zone in ceramic oxides.

TABLE 3.1
FORCE CONSTANTS FOR $\text{RBa}_2\text{Cu}_3\text{O}_7$

Force constants	Bond type	Distance (Å)	Values			
			Y	Ho	Dy	Sm
f_a	Cu(1)-O(1)	1.945	1.4	1.42	1.48	1.46
f_b	Cu(1)-O(2)	1.827	1.6	1.65	1.70	1.69
f_c	Cu(2)-O(3)	1.930	1.4	1.46	1.41	1.49
f_d	Cu(2)-O(4)	1.964	1.4	1.37	1.41	1.43
f_e	Cu(2)-O(2)	2.332	1.1	1.14	1.12	1.26
f_g	Ba-O(1)	2.911	0.8	0.79	0.72	0.74
f_h	Ba-O(2)	2.753	1.0	1.11	1.02	0.98
f_k	Ba-O(3)	2.945	0.8	0.85	0.87	0.89
f_l	Ba-O(4)	2.945	0.8	0.86	0.94	0.92
f_m	R-O(3)	2.421	0.77	0.90	0.87	0.96
f_n	R-O(4)	2.380	0.79	0.88	0.82	0.98
f_p	Cu(2)-Cu(2)	3.374	0.5	0.52	0.51	0.56
f_α	O(1)-Cu(1)-O(2)	---	1.3	1.10	0.99	0.98
f_β	O(3)-Cu(2)-O(4)	---	1.3	1.11	1.03	1.09
f_τ	O-Cu(1)-O	---	0.5	0.33	0.42	0.45

Force constants unit : Stretching 10^2 Nm^{-1}
 Bending $10^{-18} \text{ Nm rad}^{-2}$

TABLE 3.2
CALCULATED OPTICAL FREQUENCIES (cm^{-1}) FOR $\text{YBa}_2\text{Cu}_3\text{O}_7$

A_g	121	B_{1u}	122
	157		209
	351		184
	378		313
	509		417
			527
	565		
B_{2g}	73	B_{2u}	145
	156		104
	351		211
	481		357
	565		451
			548
	573		
B_{3g}	91	B_{3u}	75
	140		120
	440		221
	502		304
	551		369
			548
	142		

TABLE 3.3

CALCULATED PHONON FREQUENCIES FOR $\text{HoBa}_2\text{Cu}_3\text{O}_7$

Symmetry species	Frequency (cm^{-1})	P E D (#)
A_g	567	$f_e(61) f_c(34)$
	487 (504)	$f_e(67) f_d(28)$
	429 (424)	$f_B(41) f_c(21) f_d(24)$
	330 (335)	$f_B(54) f_c(18) f_d(17)$
	149 (155)	$f_l(64) f_h(23)$
B_{2g}	552	$f_d(52) f_c(21) f_g(19)$
	541	$f_c(68) f_d(20) f_e(12)$
	476	$f_d(59) f_c(18) f_h(16)$
	320	$f_B(65) f_d(21)$
	158	$f_h(54) f_B(28)$
B_{3g}	549	$f_d(59) f_e(28)$
	532	$f_c(54) f_d(29)$
	428	$f_d(46) f_e(24)$
	280 (271)	$f_B(54) f_d(20)$
	111	$f_h(48) f_e(32)$

Contd.

(Table 3.3 contd.)

Symmetry species	Frequency (cm ⁻¹)	P E D (%)
B _{1u}	605	f _a (48) f _b (31)
	555	f _a (71) f _b (17)
	472	f _b (41) f _m (22) f _n (20)
	418	f _m (41) f _n (22) f _p (20)
	262 (278)	f _β (56) f _b (24)
	170 (166)	f _m (52) f _h (21) f _α (17)
	114	f _α (34) f _β (30) f _g (15)
B _{2u}	620	f _b (62) f _a (19)
	613	f _b (46) f _a (24) f _g (15)
	561	f _c (41) f _d (32)
	555	f _c (42) f _d (24) f _k (15)
	184	f _g (48) f _m (31) f _n (13)
	170	f _α (38) f _n (30)
	119	f _τ (46) f _α (30) f _β (14)
B _{3u}	622	f _a (39) f _b (28) f _h (21)
	526	f _c (69) f _d (19)
	510	f _d (64) f _b (16)
	444 (460)	f _l (40) f _k (21) f _d (19)
	174	f _g (44) f _n (26) f _p (14)
	156 (155)	f _α (41) f _m (38) f _e (13)
	116	f _τ (39) f _α (20) f _m (24)

Values given in parentheses are experimental values [7]

TABLE 3.4

CALCULATED PHONON FREQUENCIES FOR $\text{DyBa}_2\text{Cu}_3\text{O}_7$

Symmetry species	Frequency (cm^{-1})	P E D (%)
A_g	572	$f_e(48) f_c(44)$
	502 (507)	$f_e(65) f_d(25)$
	430 (436)	$f_B(41) f_c(31) f_d(12)$
	325 (328)	$f_B(62) f_c(20) f_d(15)$
	149 (145)	$f_l(61) f_h(22)$
B_{2g}	559	$f_d(49) f_c(21) f_g(19)$
	539	$f_c(69) f_d(15) f_e(18)$
	514	$f_d(54) f_c(21) f_h(14)$
	310	$f_B(59) f_d(24)$
	158	$f_h(49) f_B(32)$
B_{3g}	541	$f_d(52) f_e(28)$
	538	$f_c(64) f_d(19)$
	455	$f_d(49) f_e(28)$
	280 (271)	$f_B(58) f_d(22)$
	111	$f_h(39) f_e(24)$

Contd.

Table 3.4 contd.

Symmetry species	Frequency (cm ⁻¹)	P E D (%)
B_{1u}	622	f _a (42) f _b (30)
	551	f _a (72) f _b (19)
	452	f _b (46) f _m (31) f _n (19)
	445	f _m (39) f _n (26) f _p (19)
	296 (290)	f _β (58) f _b (17)
	162 (168)	f _m (52) f _h (21) f _α (17)
	92	f _α (28) f _β (18) f _g (14)
B_{2u}	628	f _b (46) f _a (31)
	610	f _b (54) f _a (11) f _g (21)
	554	f _c (46) f _d (29)
	558	f _c (39) f _d (32) f _k (19)
	184	f _g (54) f _m (21) f _n (14)
	172	f _α (55) f _n (28)
	102	f _τ (56) f _α (28) f _β (11)
B_{3u}	621	f _a (46) f _b (21) f _h (15)
	535	f _c (70) f _d (18)
	518	f _d (68) f _b (16)
	478 (480)	f _l (64) f _k (17) f _d (11)
	176	f _g (71) f _n (11) f _p (12)
	153 (148)	f _α (52) f _m (40) f _e (16)
	88	f _τ (68) f _α (21) f _m (12)

Values given in parentheses are experimental values [16]

TABLE 3.5

CALCULATED PHONON FREQUENCIES FOR $\text{SmBa}_2\text{Cu}_3\text{O}_7$

Symmetry species	Frequency (cm^{-1})	P E D (%)
Λ_g	548	$f_e(57)$ $f_c(42)$
	511 (512)	$f_e(68)$ $f_d(28)$
	428 (436)	$f_B(41)$ $f_c(19)$ $f_d(29)$
	317 (308)	$f_B(62)$ $f_c(20)$ $f_d(18)$
	150 (155)	$f_l(62)$ $f_h(21)$
B_{2g}	564	$f_d(42)$ $f_c(21)$ $f_g(17)$
	555	$f_c(76)$ $f_d(12)$ $f_e(12)$
	520	$f_d(64)$ $f_c(21)$ $f_h(18)$
	315	$f_B(59)$ $f_d(24)$
	171	$f_h(62)$ $f_B(21)$
B_{3g}	557	$f_d(59)$ $f_e(24)$
	534	$f_c(62)$ $f_d(21)$
	469	$f_d(58)$ $f_e(22)$
	285 (281)	$f_B(55)$ $f_d(24)$
	108	$f_h(41)$ $f_e(28)$

Contd.

Table 3.5 contd.

Symmetry species	Frequency (cm ⁻¹)	P E D (%)
B _{1u}	611	f _a (57) f _b (19)
	550	f _a (69) f _b (19)
	478	f _b (42) f _m (35) f _n (14)
	430	f _m (40) f _n (18) f _p (21)
	316 (309)	f _β (53) f _b (21)
	179 (171)	f _m (48) f _h (15) f _α (20)
	111	f _α (29) f _β (18) f _g (19)
B _{2u}	620	f _b (54) f _a (21)
	611	f _b (44) f _a (24) f _g (18)
	580	f _c (49) f _d (30)
	562	f _c (48) f _d (24) f _k (17)
	185	f _g (55) f _m (28) f _n (10)
	165	f _α (53) f _n (28)
	110	f _τ (38) f _α (29) f _β (21)
	B _{3u}	618
550		f _c (75) f _d (18)
525		f _d (44) f _b (31)
448 (440)		f _l (65) f _k (25) f _d (10)
180		f _g (40) f _n (21) f _p (14)
136 (146)		f _α (51) f _m (22) f _e (13)
116		f _τ (68) f _α (10) f _m (14)

Values given in parentheses are experimental values [7].

REFERENCES

1. F. Albert Cottton, Chemical Applications of Group Theory, Wiley Eastern Ltd. 2nd Edn. 1971
2. E.B.Wilson, Jr. J.Chem.Phys. 7, 1047, 1939; 9,76, 1941
3. E.B.Wilson, Jr. et al, Molecular Vibrations, McGraw Hill, 1955
4. T.Shimanouchi, M.Tsuboi and T.Miyazawa, J.Chem.Phys. 35, 1597, 1961
5. E.Husson, Y.Replin, H.Brusset, A.Cerez, Spectrochim.Acta, A 35, 1177, 1979 ;
H. Haeuseler, Spectrochim.Acta, 37, 487, 1981
6. F.E.Bates and J.E.Eldridge, Solid State Commun. 64,1435, 1987
7. M.Cardona, R.Liu, C.Thomsen, M.Bauer, L.Genzel, W.Konig and A.Wittlin, Solid State Commun. 64, 727, 1987
8. D.A.Bonn, J.E.Greedan, C.V.Timusk, M.G.Doss, S.L.Kerr, K.Kamras and D.B.Tanner, Phys.Rev.Lett. 58, 2249, 1987
9. S.Onari, T.Hiroaki, K.Onshima, K.Monma, T.Arai, Solid State Commun. 3, 303, 1988

10. S.Mohan and A.Sudha, Proc.Ind.Natn.Sci.Acad. 58 A, 371, 1992
11. S.Mohan, T.Radjakoumar and M.Gal, Mater.Res.Bull. 26, 3, 1991
12. S.Mohan, T.Radjakoumar and K.G.Ravikumar, Bull.Mater.Sci. 14, 247, 1991
13. F.E.Bates, Phys.Rev.B, 39, 322, 1989
14. H.Fuhrer, V.B.Kartha, K.G.Kidd, P.J.Krueger and H.H.Matsch, Computer Programs for Infrared Spectrometry, Normal Coordinate Analysis, Vol.5, 1976
15. R.Liu, C.Thomsen, W.Kress, M.Cardona, B.Gegenheimer, F.W.de Wette, J.Prade, A.D.Kulkarni and U.Schroder, Phys.Rev. B, 41, 2003, 1990
16. M.Cardona, R.Liu, C.Thomsen, M.Bauer, L.Genzel, W.Konig, A.Wittlin, U.Amador, M.Barahona, F.Fernandez, C.Otero and R.Saez, Solid State Commun. 65, 71, 1988
17. Bengang Hu and Ram S.Katiyar, Phys.Stat.Sol (b), 174, 375, 1992
18. Ming-sheng Zhang, Zhen Yin, Gongjian Hu and Qiang Chen, Phys.Rev.B, 41, 2003, 1990

- 19.S.Martinez, A.Zwick, M A.Renucci, R.Enjalbert and
P.Millet, Solid State commun. 82, 619, 1992
- 20.M.stavola, D.M.Krol, W.Weber, S.A.Sunshine, A.Jayaraman,
G.A.Kourouklis, R.J.Cava and E.A.Rietman, Phys.Rev.B,36,
850, 1987
- 21.R.M.Macfarlane, H.J.Rosen, E.M.Engler, R.D.Jacowitz and
V.Y.Lee, Phys.Rev.B, 38, 284, 1988