PART I

THEORETICAL INVESTIGATION
CHAPTER I
INTRODUCTION

ABSTRACT

The essentials of molecular vibrations are briefly discussed. A brief account of the theoretical considerations relating to the evaluation of kinetic constants, force constants, compliance constants, mean amplitudes of vibration, Coriolis coupling constants and centrifugal distortion constants is given.

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1.1 MOLECULAR VIBRATIONS

Molecules in general are associated with symmetry operations like translation, vibration rotation, etc. When a molecule absorbs or emits electromagnetic radiation, molecular spectra arises from transitions between energy states. The spectra lie in different regions of electromagnetic radiation. The rotational spectra occurs in the microwave region (30 cm to 10 cm\(^{-1}\)). Microwave studies provides important informations regarding the structural parameters and rotational distortion constants of molecules. The vibrational spectra lie in the infrared region and the Raman region (10 - 10,000 cm\(^{-1}\)). Infrared spectroscopy is due to the absorption of energy by a molecule and the corresponding change in the dipolemoment. Raman spectroscopy on the other hand depends on the collision of a quantum of incident light with a molecule and the corresponding change in the polarizability during the vibration. The conditions under which vibrations are either infrared or Raman active, are known as selection rules. Wigner has shown that the number of normal mode of oscillation of a molecule may be obtained in a simple manner by the application of the group theory, which has been extensively applied by Wilson (1).
The selection rule for infrared absorption is given as

\[ \sum_{\mathcal{R}} (2 \cos \varphi_{\mathcal{R}} \pm 1) \chi_{\mathcal{I}}(\mathcal{R}) = 0 \text{ inactive} \]

\[ \neq 0 \text{ active}. \]

where \( \chi_{\mathcal{I}}(\mathcal{R}) \) is the character of the irreducible representation \( \mathcal{I} \) to which the normal coordinate belongs, \( \mathcal{R} \) indicates the summation over all the operations that constitute the group.

In a similar way, the selection rule for the Raman spectra may be given as follows.

\[ \sum 2 \cos \varphi_{\mathcal{R}} (\pm 1 + 2 \cos \varphi_{\mathcal{R}}) \chi_{\mathcal{I}}(\mathcal{R}) = 0 \text{ inactive} \]

\[ \neq 0 \text{ active}. \]

In both the cases, the + or - sign indicates whether the operation is a rotation or rotation - reflection.

1.2 STUDY OF POLYATOMIC MOLECULES

In the recent past, there has been remarkable development in the instrumentation for measuring infrared and Raman spectra. A very large number of inorganic compounds were investigated by the analysis of the above spectra - but most of them were in liquid phase. The practice of Raman spectroscopy has been completely revolutionised by the continuous wave laser. The availability of different exciting frequencies, due to various type of gas lasers, has
enabled us to extend our Raman study of opaque or even coloured crystals.

The experimental informations such as vibrational frequencies are of considerable interest to the molecular spectroscopist and chemists, as they are of vital significance in the evaluation of important molecular constants. The present investigation is aimed at to evaluate the molecular constants of polyatomic molecules, by adopting various techniques. A brief account of the molecular constants is given in the following section.

1.3 MOLECULAR CONSTANTS

The fundamental vibrational frequencies of a molecule are governed by
a) the atomic masses and the geometric distribution of the vibrating nuclei.

b) the force field which tends to restore the molecule to its internal equilibrium during any distortion.

The force field arises from the changes in the energy of the electrons which bind the molecule together. The force constant (restoring force per unit displacement of a bond) is a measure of the strength of the chemical bond. In general, the number of vibrational
frequencies associated with a molecule of 'n' atoms is $N = 3n - 6$ ($3n - 5$ for a linear molecule), so that $N(N + 1)/2$ potential energy constants will be required to describe a general quadratic valence force field. Because of this difference, no unique solution is possible. In such cases, the solution is obtained by adopting certain approximations. In isotopic pairs of molecules, the potential function may be assumed to be the same, to a very high degree of approximation. Sometimes the force constant values can be transferred from one molecule to another having similar bond environments. Recently additional experimental data such as Coriolis coupling constants, rotation distortion constants and mean amplitudes of vibration have been successfully used to fix the molecular force field uniquely. When all the available data are not sufficient to provide a unique force field, the problem can be solved either by taking only selected cross terms or by postulating certain specific force fields appropriate to the molecule where the number of force constants to be determined is not large. Some of the force fields used in the evaluation of force constants are the central force field (2), simple valence force field (3), orbital valence force field (4), Hybrid orbital force field (5-6), Urey-Bradley force field (7-10) and
general quadratic valence force field. In the present work, general quadratic valence force field (G Q V F F) is adopted. It gives a more complete picture of the intermolecular forces and takes into account the various possible interactions.

1.3.1 Force constants:

The procedure adopted in the investigation presented in this thesis follows Wilson's F.G. matrix method (11). The first step towards solving the equations of motion lies in deriving expressions for the kinetic and potential energies in terms of some convenient set of coordinates. The chief merit of Wilson's method is that it leads to a breaking up of the vibrational secular equation according to the symmetry species of the molecule. By group theoretical considerations, the number of genuine vibrations in a molecule belonging to each mode is found. From the internal coordinates \( R \), the orthonormalised linear combinations viz: symmetry coordinates \( S \) are formed. They are related as

\[
S = U R
\]

where \( U \) is the orthogonal transformation matrix. In terms of the symmetry coordinates, the potential energy \( V \) becomes
\[ 2V = \tilde{S} f S \]

where

\[ F = U f U \]

\( f \) is the valence force constant and \( F \) is the symmetrized force constant matrix.

Similarly, the kinetic energy may also be given as

\[ 2T = \tilde{S} G^{-1} S \]

where \( G \) is the matrix (12) depending on the position and the reciprocal mass (\( \mu \)) of the atoms consisting the molecule.

The \( S \) matrix is related to the Cartesian displacement coordinates (\( X \)) through a transformation matrix (\( B \)) as

\[ S = BX \]

\( G \) can be evaluated using \( B \) matrix through the relation

\[ G = B \mu B^{-1} \]

1.3.2 Kinetic constants:

The attention of molecular spectroscopists has been drawn to the concept of kinetic constants in molecules. They are the vibrational inertia coefficients involved in Wilson's expression for the kinetic energy relating to molecule vibrations. They are given by

\[ 2T = \tilde{S} G^{-1} S \]

where \( G^{-1} \equiv K \)
The elements of the matrix $K$ are the kinetic constants. These constants are found to be basically important in the architecture of molecular dynamics. In analogy with potential constants, these constants satisfy the relation

$$K = \bar{U} k \bar{U}$$

where $k$'s are the valence kinetic constants.

The study of kinetic constants indicates that the off-diagonal force constants may be linked to the concerned diagonal force constants through the relation

$$F_{ij}/F_{jj} = K_{ij}/K_{jj} \quad (i \neq j)$$

provided the frequencies are ordered. The method of kinetic constants for solving the secular equation has been found to give satisfactory results in various types of polyatomic molecules (13 - 17).

1.3.3. Compliance constants:

The compliance constants are the inverse of the force constants as introduced by Decius (18).

$$N = F^{-1} \quad \text{and} \quad n = f^{-1}$$

where $N$ and $n$ are the compliance constant matrices defined with respect to the symmetry and internal coordinates respectively.
1.3.4 Mean square amplitudes of vibration:

The thermal vibrations of atoms within the molecule can best be studied by evaluating the mean square amplitudes of vibration of the atomic distances. The mean square amplitude for a particular atomic pair is defined as the mean square value

$$\sigma_{ij} = \left\langle (R_{ij} - R_{ij}^e)^2 \right\rangle$$

where $R_{ij}$ and $R_{ij}^e$ are the instantaneous and equilibrium distance between two atoms $i$ and $j$. A thorough study of the problem of computing mean square amplitudes of polyatomic molecules was carried out by Morino and his collaborators (19). The symmetrized mean square amplitude quantities $\Sigma_{ij}$ are defined by the matrix relation

$$\Sigma = \left\langle s \hat{s} \right\rangle$$

The symmetry coordinates and the normal coordinates are connected by the relation

$$s = LQ$$

where $L$ is the normal coordinate transformation matrix. Hence

$$\Sigma = L \Delta \hat{L}$$

where $\Delta$ is a diagonal matrix of mean square values of normal coordinates given by
\[ \Delta_i = \frac{\hbar}{8 \pi^2 \kappa \omega_i} \coth \left( \frac{\hbar c \omega_i}{2 k T} \right) \]

where \( \hbar \) - Planck's constant
\( k \) - Boltzmann's constant
\( T \) - the absolute temperature
\( \omega_i \) - the frequency in cm\(^{-1}\)

The non bonded mean amplitudes are expressed in terms of bonded mean amplitudes. The vibrational amplitudes can be obtained from electron diffraction data.

1.3.5 Coriolis coupling constants:

Coriolis coupling constants occur as a result of the Coriolis forces which arise when a molecule is both rotating and vibrating. The Coriolis forces directed at right angles to the axis of rotation are proportional to the masses of the particles, their apparent velocities with respect to a coordinate system rotating with the molecule and the angular velocity of this rotating coordinate system with respect to a fixed coordinate system (20).

Coriolis coupling of vibration - rotation effect can affect the spectra of linear, symmetric and asymmetric top molecules, although its presence may be more pronounced in symmetric top where first order effects are possible. The Coriolis coupling constants (\( \zeta \) values) for the
coupling between degenerate pairs may be obtained experimentally by measuring the separation between the sublevels of the perpendicular bands in vibration-rotation spectra of molecules. Meal and Polo (21) have developed vector method for the calculation of these constants for both degenerate and non-degenerate couplings.

According to Jahn's rule (22), two vibrational states can couple through a Coriolis interaction, if the direct product of symmetry species of the two vibrational states contains a rotational species. Hence, from the character table, the Coriolis interaction allowed in a molecule may be determined.

The Coriolis coupling constants have been evaluated using the expression

\[ \zeta^\alpha = (L^{-1})^\alpha \mu (L^{-1})^\mu \]

The rows and columns of the \( \zeta^\alpha \) matrix are labelled according to the numbering of the symmetry coordinates. In terms of the \( B \) matrix the \( C^\alpha \) elements are given by

\[ C^\alpha = B^\alpha \beta \gamma \]

where \( \beta \gamma = \mu \beta \gamma \)

\[ I^X = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{bmatrix} \quad I^Y = \begin{bmatrix} 0 & 0 & -1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix} \quad I^Z = \begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \]
A knowledge of even the order of magnitude of these constants is often extremely useful for band assignments, preliminary analysis of rotational structure and prediction of the band shapes.

1.3.6 Centrifugal distortion constants:

When the high resolution infrared and microwave techniques are used to study the pure rotational spectrum of a molecule, it is seen that the molecular energy levels are not predicted exactly by rigid rotor theory, but are influenced by perturbations such as those resulting from vibration - rotation interactions and centrifugal distortion. In reality the molecule cannot be regarded as rigid and bond distances and bond angles will vary due to centrifugal force produced by rotation. Such centrifugal distortions are usually large for light molecules because of their small moments of inertia. In many cases, it can be treated as perturbation of the rigid rotor Hamiltonian, the influence of centrifugal distortion is only a small fraction of the rotational energy.

The general theory with respect to asymmetric rotor molecules has been formulated by Wilson (23), Wilson and Howard (24) and Nielsen (25).
The distortion constants are defined as

$$\tau_{\alpha \beta \gamma \delta} = -(2 \tau^{e}_{\alpha \alpha} \tau^{e}_{\beta \beta} \tau^{e}_{\gamma \gamma} \tau^{e}_{\delta \delta})^{-1} \sum_{ij} \tau^{j}_{\alpha \beta, \gamma \delta, s} N_{ij},$$

where $I^{e}_{xx}, I^{e}_{yy}$ and $I^{e}_{zz}$ are the principal moments of inertia at equilibrium and $\tau^{j}_{\alpha \beta, \gamma \delta, s}$ represent the partial derivatives at equilibrium of the instantaneous inertia tensor components with respect to the symmetry coordinates, $N$ is the inverse force constant matrix.

Cyvin (26, 27) has reformulated the theory defining a new quantity $t^{\alpha \beta \gamma \delta}$ as

$$t^{\alpha \beta \gamma \delta} = -2 \tau^{e}_{\alpha \alpha} \tau^{e}_{\beta \beta} \tau^{e}_{\gamma \gamma} \tau^{e}_{\delta \delta} \tau_{\alpha \beta \gamma \delta},$$

where $t = \tilde{J} S N \tilde{J}$. The centrifugal distortion constants are linear combinations of the $\tau's$ and are given below.

- $D_{J} = -(1/32) \left[ 3 \tau_{xxx} + 3 \tau_{yyy} + 2(\tau_{xxy} + 2\tau_{xyy}) \right] \hbar^{4}$
- $D_{K} = D_{J} - (1/4) \left[ \tau_{zzz} - (\tau_{xzz} + 2\tau_{xzz}) - (\tau_{yzz} + 2\tau_{yzz}) \right] \hbar^{4}$
- $D_{JK} = -D_{J} - D_{K} - (1/4) \tau_{zzz} \hbar^{4}$
- $R_{5} = -(1/32) \left[ \tau_{xxxx} + \tau_{yyyy} + 2(\tau_{xxx} + 2\tau_{xxz}) + 2(\tau_{yyy} + 2\tau_{yzy}) \right] \hbar^{4}$
\[ R_6 = \frac{1}{64} \left[ \tau_{xxx} + \tau_{yyy} - 2(\tau_{xxy} + 2\tau_{xyy}) \right] \hbar^4 \]

\[ \delta_j = -\left( \frac{1}{16} \right) \left( \frac{\tau_{xxx} - \tau_{yyy}}{\tau_{xxx} - \tau_{yyy}} \right) \pi^4 \]

These are the basic concepts of molecular vibrations.
REFERENCES

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