PREFACE

The main feature of a molecule is the nature of the chemical bond between its constituent atoms and the force that binds them together in that molecule. Molecular spectra is an important tool in determining the characteristic constants of a molecule.

The present thesis represents a study of molecular constants of seven different types of molecules using their spectral frequencies and structural data. The method of kinetic constants which has thrown new light on molecular constants has been used to study different types of molecules. The force constants, compliance constants, vibrational mean amplitudes, Coriolis coupling constants and centrifugal distortion constants of polyatomic molecules are evaluated in the present thesis. The values of molecular constants agree quite well with literature values. These results are very interesting since they give rise to fresh results of significance.

In the present thesis the laser Raman spectra of inorganic molecules, their vibrational assignments and normal coordinate

analysis have also been reported. Assignment of frequencies from Laser Raman spectra of organic molecules are also done in this thesis. The thesis contains ten chapters in all.

The first chapter gives a brief account of theoretical concept in molecular vibrations. The remaining nine chapters are classified under two parts. Part I gives theoretical analysis of vibrational spectroscopy while Part II illustrates experimental vibrational spectroscopy. The first part consists of six chapters and the second four chapters.

In the second chapter a complete vibrational analysis of methyl mercuric halides and germyl cyanide molecules of tetrahedral structure of XY_3ZW type belonging to C_{3v} point group involving 4 X 4 vibrational problems are given. Valence force constants and a set of molecular constants are evaluated and presented in this chapter by the method of kinetic constants. These constants are in the expected range and compare well with the values available in the literature, thereby proving the validity of the method of kinetic constants.

The third chapter deals with the molecular dynamics of

molecules which belong to planar AXYZ type. The molecules studied are HNSO, DNSO and HClCO. Values of the molecular constants are found to agree well with values obtained by earlier workers.

The fourth chapter gives a detailed study of dynamical model of force constants on the vibrational analysis of two molecules namely trichloro silylisocyanate and trichloro silylisothiocyanate. These molecules form tetrahedral structure of XY_3ZWA type belonging to the C_{3v} point group with fundamental frequencies falling under the irreducible representation $\Gamma = 5A+5E$. The vibrational mean amplitudes and Coriolis coupling constants other than potential constants are also evaluated. The values are compared with literature values.

The fifth chapter is divided into two sections. The first section gives a detailed study of XY_2Z_2 type molecules belonging to C_{2v} point group. The potential constants and other related constants are evaluated. In second part, the Laser Raman spectrum of selenium dioxide difluroride molecule is studied and the frequencies observed are assigned to

different fundamental modes of vibration. The validity of the assignments has been checked by evaluating the potential and other molecular constants. A reasonable set of molecular constants obtained proves that the assignments are in order.

The sixth chapter illustrates an exhaustive study of XYZ type molecules belonging to C_s symmetry. The general quadratic valence force field is applied to obtain potential constants. The Coriolis coupling constants and centrifugal distortion constants for twelve more molecules are estimated for the first time.

The seventh and eighth chapters discuss the spectra of two organic compounds namely α bromotoluene and 2 chloro 6 methyl benzonitrile. The various observed frequencies have been assigned to various modes of vibrations in terms of fundamentals, overtones and combinations assuming C_s point group symmetry for the first time.

The nineth and tenth chapters give the laser Raman spectra and infrared and far Fourier infrared spectra of potassium fluorophosphate potassium fluorosulphonate and potassium

bicarbonate molecules. The observed frequencies are assigned to various point groups and normal coordinate analysis have been carried out. The reasonable set of force constants obtained for the molecules confirm the validity of the assignments.

Although the results of the molecular constants are discussed in each chapter, salient features thrown up in the present study are briefly mentioned here.

Basically kinetic constants are found to be important in the architecture of molecular dynamics. The bond-angle interaction constants are negative for both kinetic as well as potential constants.

The large vibrating masses of the atoms and the low fundamental frequency of the compounds are reflected in the relatively lower values of the potential constants obtained for the molecules and ions.

The mean amplitudes of the bonded as well as non-bonded distances and the shrinkage effects are in the increasing order from lower to higher members of halogen series.

The centrifugal distortion constants are found to be larger in molecules and ions having light ligand atoms because of the small moments of inertia.

In the XYZ_2 (C_{2v}) planar and XYZ_3 (C_{3v}) symmetric top molecules, the negative or positive sign of D_{JK} depends on the position of the centre of mass of the molecule with respect to the central atom.

The weaker bonds with small force constants show larger distortion effects than the stronger bonds with larger force constants.

The major force constants are highly sensitive to the electro negativity of the substituted halagen atom. The major substituting force constant decreases with the decreasing electronegativity of the constituent halogen atom.

Bond stretching and angle bending force constants remain practically the same in relation to isotopically substituted molecule. This statement of Herberg about isotopic substitution is reflected by the unique set of values obtained. Also

a small variation in force constants of isotopic molecules, may be due to the variation of bond-distance because of substitution'-a statement by Jones is also confirmed in this thesis.

An interesting study has been made in the evaluation of force constants adopting kinetic constants approach. The constants obtained are interesting from the point of view of understanding molecular dynamics.

A part of the material presented here have been published in the form of papers in various journals as follows.

1.	Vibrational Analysis of Quasi Linear molecules	Acta.Ciencia Indica (in press)
2.	Dynamical Model of force Constants on the vibrational analysis of Cl_3SiNCS and Cl_3SiNCO molecule	Bull. of Pure & Appl. Sci. (in press)
3.	Laser Raman Spectrum and its vibrational studies of Selenium dioxide difluoride.	Indian J. of Chem. Soc. (1987) (in press)
4.	Laser Raman Spectrum of α - bromotoluene	Proc. of Indian Natl.Science Acad. (1987) (in press)

5.	Laser Raman Spectrum of 2 chloro 6 methyl benzonitrile	Acta. Phys.Pol. (Poland) (1987) (in press)
6.	Infrared and Far Infrared spectra and normal co-ordinate analysis of potassium flurophosphate	Proc. Indian Natn. Sci. Acad. (1987) (in press)
7.	Laser Raman Spectrum of Potassium flurosulfonate and its vibrational analysis	J.Annamalai University (1986) (in press)
8.	Vibrational spectra of $KHCO_3$ and its normal Coordinate analysis	Bull. Pure and Appl. Sci. 3C (Z) 107-110 (1984)

Apart from these papers the following papers have also been published.

9.	Infrared and Fourier far infrared 1 amine 2 naphthaol 4 sulphonic acid	Spectrochim Acta 38B, 230 (1983)
10.	Vibrational Analysis of some axially symmetric XYZ_3 type molecules	National Conference on Vibrational Spectroscopy 86 - 88, (1983)
11.	Molecular constants of some mixed Boron Halides	Bull. of Pure & Appl. Sci. 4C (1) 1985
12.	Vibrational analysis of NO_2 OD and NO_2OH molecules	National Conference on Vibrational Spectroscopy (1985) paper presented and published.