P R E F A C E

The investigations presented in this thesis have been carried out by the author during 1984 - 1986, in the Department of Physics, Bharathidasan University, Tiruchirapalli - 23.

The thesis is in two parts. In part A, results of complete normal coordinate analysis performed on 22 polyatomic molecules from spectroscopic data are reported. In part B, the frequency assignment based on infrared spectra of four compounds, is dealt with. Wherever possible and feasible, Laser Raman Spectra have also been recorded and analysed to supplement information obtained from infrared spectra. It must be stressed that the investigations reported in part B are of allied nature to that in part A. It is also our humble attempt on the experimental side of molecular spectroscopy, with the available facilities.

Part A consists of six chapters, the first one being an introductory nature, providing a brief discussion on the theory and significance of the molecular constants, such as force constants, mean square amplitudes of vibration, generalized mean square amplitudes of vibration, shrinkage coefficients, Coriolis coupling constants and centrifugal distortion constants.
A brief outline on the thermodynamic functions is also given. The important mathematical formalism and techniques employed for the computation of the above constants have also been outlined.

Chapter 2 describes the normal coordinate analysis of $\text{ReO}_2(\text{CN})_4$, $\text{Re}^{18}\text{O}_2(\text{CN})_4$ and $\text{ReO}_2(\text{CN})_4$, ions. A general valence force field is adopted and all the molecular constants are computed and discussed.

In chapter 3, the molecular constants of 2-butyne and its deuterated analogue are presented. Assuming GVFF, force constants are obtained from vibrational frequencies of the molecules, in the gas phase which are corrected for anharmonicity and Fermi resonance. Using these force constants, other molecular constants are determined. Computed values of heat capacity and Coriolis coupling constants of 2-butyne are compared with experimentally available ones.

Chapter 4 is devoted to the vibrational analysis of propyne and seven of its isotopic substitutes. From the frequency assignment available for some of the isotopes, a precise set of force constants is obtained on the basis of GVFF. Experimental values of Coriolis coupling constants and centrifugal distortion constants are also used as additional parameters to refine the force constants. Making use of the force
constants, fundamental frequencies are predicted for the isotopes for which the experimental values are not known. Other molecular constants are also estimated and compared with the experimental values reported in the literature.

Chapter 5 deals with diazirine molecule and its isotopic modifications including two mixed ones. A set of symmetry coordinates are constructed based on the assignment of vibrational modes. Applying GVFF, a set of force constants is obtained for these molecules, using which other molecular constants are also calculated. Some of these constants are probably reported for the first time. The calculated values of centrifugal distortion are compared with the experimental values available from microwave data.

In chapter 6, normal coordinate analysis of aminoborane BH$_2$NH$_2$ molecule and two of its isotopes are given. A set of symmetry coordinates is constructed, based on a recent assignment of frequencies for $^{11}$BH$_2$NH$_2$ molecule in the gaseous phase and the force field is obtained for the first time. Experimental values of centrifugal distortion constants are also employed in arriving at the force constants. These are used to predict the fundamental frequencies for the other two isotopes and checked by applying isotopic
product rule. The other molecular constants are also calculated. The results are very useful in the structural analysis of the molecule, whose planar structure has been confirmed, only recently. The calculated values of centrifugal distortion constants are compared with available experimental values.

Part B of the thesis consists of three chapters. In the first chapter, application of group theory and band assignments to Raman and infrared spectrum are described. A detailed account of infrared, Raman spectroscopy, a complete information about vibrational assignment and interpretation of spectra are also dealt with.

In chapter 2, the preparation and the structure of β-benzoyl propionic acid and some of its derivatives are outlined along with experimental details and vibrational analysis by laser Raman and infrared techniques.

Chapter 3 deals with the study of vibrational spectra of sulfaguanidine by infrared technique. The vibrational analysis and the interpretation of the spectra are discussed on the basis of the assignments on sulfanilamide and other related compounds.