The investigations presented in this thesis have been carried out by the author in the Physics Department, College of Engineering, Anna University, Madras.

Vibrational Spectroscopy plays an important role in the Structure elucidation and in the determination of characteristic groups of polyatomic molecules. Molecules of complex nature can also be exposed to infrared and Laser Raman radiations to observe their spectra. They have been analysed in detail by considering symmetry properties and group theory. An infrared absorption spectrum originates from molecular vibrations which causes a change in the dipole moment of the molecule. It also reflects the structure of the molecule, especially masses of the constituent atoms and the intermolecular forces acting between them. Raman Spectrum arises if there is a change in polarizability during the vibration.

With the advent of Laser Raman Spectroscopy and the advancement in the infrared techniques a considerable amount of experimental data on the vibrational spectra of molecules may be obtained. The current data can be considered more reliable and if they are analysed properly with the help of
group theoretical considerations, valuable information can be obtained regarding the nature and structure of molecules.

Laser Raman and infrared Spectroscopic studies of some polyatomic molecules have been undertaken in this thesis. The thesis consists of eight chapters. The first chapter deals with the experimental and theoretical aspects of molecular spectroscopy briefly. The remaining chapters are divided into two parts, namely Experimental vibrational spectroscopy and Theoretical vibrational spectroscopy. Experimental vibrational spectroscopy consists of five chapters. The rest of the chapters are devoted to theoretical vibrational spectroscopy.

Under the Experimental vibrational spectroscopy, the discussion is confined to infrared and Laser Raman Spectra of some complex molecules. The infrared spectra of compounds have been recorded using Perkin Elmer IR 983 and IR 781 double beam grating spectrophotometer in the regions 200-4000 cm⁻¹ and 600-4000 cm⁻¹ respectively. The Laser Raman Spectra have also been recorded in the region 100-4000 cm⁻¹ on Cary Model 82 grating spectrophotometer using 488 nm radiation from an argon ion laser of 4 watts for excitation. The frequencies for all sharp bands are expected to be accurate to ± 1 cm⁻¹. The chapters under theoretical vibrational spectroscopy are completely devoted to evaluate the molecular constants of two typical molecular types. The
general quadratic valence force field has been employed in the present investigation for both in plane and out of plane vibrations of molecules. The bond length and bond angles have been assumed from Sutton table for most of the molecules under investigation.

Second chapter presents the Laser Raman and infrared spectra of silylgermane. The sample was prepared in the laboratory by the electric discharge method. The spectra were analysed on the basis of fundamentals, combinations and overtones and the frequencies were assigned to various modes of vibration, assuming $C_3v$ symmetry. Further, based on the present assignments a complete vibrational analysis has been carried out for this molecule and the results are briefly discussed. The molecular constants are reasonable and fall in the expected range. This confirms the correctness of the present assignment for this molecule. To check whether the chosen set of assignment contributes maximum to the potential energy associated with normal coordinate of the molecule, the potential energy distribution has been calculated.

Chapter three gives the Laser excited Raman spectrum of sulphuryl chloro fluoride compound. $SO_2FCl$ has been prepared in the laboratory. The aim of the present study is to investigate the vibrational spectrum of $SO_2FCl$ through a
satisfactory vibrational assignment. The observed frequencies have been assigned to the various modes of vibration in terms of fundamentals and combinations assuming C\text{\textsubscript{s}} symmetry. A vibrational analysis has also been carried out using general quadratic valance force field and the results are briefly discussed.

The fourth chapter of the thesis reports the vibrational spectra, assignments and normal coordinate analysis of N,N-Dimethylthioacetamide. The frequencies have been assigned to various fundamental modes on the basis of normal coordinate calculations. A thirty four parameter modified valence force field has been employed for the normal coordinate analysis of N,N-Dimethylthioacetamide. A least square technique has been used to refine the force constants. The potential energy distribution have also been calculated for this molecule. The nature of the absorption bands is discussed in relation to the mixing of vibrational frequencies.

The fifth chapter is devoted to analyse the vibrational spectra of 2-fluro-5-chloro and 3-fluro-6-chlorotoluenes. The vibrational spectra of halogenated toluenes, xylenes dihalogenotoluenes and toluenes have been extensively studied by a number of workers. However the vibrational analysis of 2-fluro-5-chloro and 3-fluro-6-chlorotoluenes using either infrared or Raman data has not
been reported so far. In the present study the results and analysis of the Laser Raman spectra of these compounds are presented. The observed spectra are explained on the basis of $C_3$ symmetry for the molecules under consideration by assuming the CH$_3$ group as a point mass. These assignments are in good agreement with the literature values, thereby projecting the correctness of the assignment for the molecules under investigation.

The study of Laser Raman spectrum of 2-amino, 4-methyl pyrimidine has been undertaken in the sixth chapter of the thesis. The observed frequencies have been assigned to the various modes of vibrations in terms of fundamentals and combinations assuming $C_3$ symmetry. This is possible due to the assumption of NH$_2$ and CH$_3$ groups as point masses. The molecule possesses different group frequencies in addition to planar and nonplanar types of vibrations. The results are briefly discussed in this chapter.

Under theoretical vibrational spectroscopy, molecular dynamics of germylacetylene and silylacetylene have been discussed in chapter seven. A complete vibrational analysis has been carried out for germylacetylene, germylacetylene-d$_3$, silylacetylene and silylacetylene-d$_3$ molecules using the method of kinetic constants and a set of molecular constants is reported. The physical
understanding of the nature of the potential constants and kinetic constants in molecules leads to a stringent application of provisions of group theoretical technique, introduced by Wilson in the study of molecular vibrations. This procedure is applied here to the evaluation of mean amplitude of vibration, Coriolis coupling constants and centrifugal distortion constants of these cases, with satisfactory results. The value of Coriolis coupling constants and centrifugal distortion constants are in good agreement with the observed values for the germylacetylene and silylacetylene molecules, showing the significance of the procedure adopted in the present study.

A complete vibrational analysis has been carried out using kinetic constants for methylethynyl mercury (II) \(-d_0, -d_1, -d_3\) and \(-d_4\) molecules and a set of molecular constants is presented in chapter eight. The calculated values of these molecular constants are further found to be in good agreement with the corresponding observed values, wherever available, thus establishing the merits of the new procedure involving kinetic constants. Such initial studies were confined to \(2 \times 2, 3 \times 3, 4 \times 4\) and \(5 \times 5\) vibrational problems whereas an example of the \(6 \times 6\) vibrational problem has been examined in this chapter with success for the first time.
A part of the material presented in this thesis has been published / accepted as papers in various journals as follows:

1. Laser Raman and Infrared spectra of Silylgermane and its Vibrational Analysis.


3. Laser excited Raman Spectrum and Vibrational Analysis of Sulphuryl cholo fluoride.

4. Theoretical description of infrared and Raman spectra of XY₃ZWAB type molecules.

5. Molecular dynamics of Germylacetylene.
   - J. Mol. Str., 147, 315 - 319 (1986)

6. Laser Raman spectra of 2 fluoro-5 chlorotoluene and 3 fluoro-6-chlorotoluene

7. Laser Raman Spectroscopic studies on 2-amino 4 methyl pyrimidine.

8. Vibrational spectra, Assignments and normal coordinate analysis of N,N - Dimethylthioacetamide.