PREFACE

The investigations presented in this thesis have been carried out in the Department of Physics, Cochin University, where the author has been working as a part-time research scholar during the period 1977-'82.

The major objective of the thesis is essentially to evolve and apply certain computational procedures to evaluate the structure and properties of some simple polyatomic molecules making use of spectroscopic data available from the literature. It must be said that though there is dwindling interest in recent times in such analyses, there exists tremendous scope and utility for attempting such calculations as the precision and reliability of experimental techniques in spectroscopy have increased vastly due to enormous sophistication of the instruments used for these measurements. In the present thesis an attempt is made to extract maximum amount of information regarding the geometrical structure and interatomic forces of simple molecules from the experimental data on microwave and infrared spectra of these molecules.

A notable feature of the present thesis is the use of centrifugal distortion constants for the first time to determine the geometry of symmetric top molecules (Chapter V). The method developed here shows that reliable estimation of the molecular geometry can be carried out even when the microwave
spectroscopic data on isotopic molecule are unavailable. The thesis contains seven chapters in all. The first two chapters are of an introductory nature and the basic background required for the calculation of centrifugal distortion constants is developed here. In the third chapter theory of parametrisation of centrifugal distortion constants in $XY_2$ bent symmetric molecules is discussed in detail. In addition to defining the limits of $\mathbf{T}_{\alpha\beta\gamma\delta}$ elements, this approach helps to fix uniquely the force fields of molecules belonging to the above type. It is also shown that the prediction of fundamental vibrational frequencies is possible from a knowledge of the experimental values of $\mathbf{T}_{\alpha\beta\gamma\delta}$ elements in these molecules. An exhaustive discussion of the parametrised form of $D_J$, $D_{JK}$ for pyramidal $XY_3$ molecule is given in Chapter IV. Certain natural approximation formulas for $D_J$, $D_{JK}$ and $D_K$ are developed and the use of these formulas is demonstrated in Chapter V. The interatomic distances and interbond angles of $PF_3$, $AsF_3$ and $OPF_3$ molecules for which no complete isotopic data are available have been calculated making use of centrifugal distortion constants along with rotational constants and fundamental vibrational frequencies. Excellent agreement with results from electron diffraction studies assures the reliability of the method presented here.

Chapter VI contains a simple formula for the vibrational mixing parameter for $XY_2$ bent symmetric molecules. It also shows how the interbond angle in these molecules can be
estimated from the pair of frequencies of the symmetric vibrations. In the last chapter an attempt is made to solve a third order vibrational problem using pseudo-exact parameter method. The set of force constant elements obtained in the case of CH$_3$F making use of this method is found to agrees very well with the results from more elaborate calculations.

Most of the calculations presented in this thesis have been carried out using the computer facilities available at the Cochin University Computer Centre. A sample programme (BASIC) used for the calculation of the centrifugal distortion constants in XY$_3$ symmetric top molecules is given as an Appendix.

Part of the investigations presented in this thesis has been published in the form of following papers.

1) Use of D$_j$, D$_{jk}$ constants for the unique fixing of intramolecular forces in XY$_3$ pyramidal molecules.

2) Molecular geometry using centrifugal distortion constants.
   Paul C.M. and Girijavallabhan C.P.
   1979 Nat. Acad. Sci. Letters 2 237
3) A note on obtaining vibrational mixing parameter from average bending energy criterion.

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4) Molecular geometry of \( \text{XY}_3\text{Z} \) type molecules using centrifugal distortion constant.

Paul C.M. and Girijavallabhan C.P.

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