

## PREFACE AND ACKNOWLEDGEMENTS

The investigations presented in this thesis were carried out by the author as a full-time research scholar in the Physics Department of the Cochin University during 1975-78.

This thesis is divided into two parts. The first part deals with some studies in molecular mechanics using spectroscopic data and has four chapters in it. Certain approximation methods for the evaluation of molecular force fields are herein developed. The second part, which consists of the last two chapters, deals with infrared spectral studies of ternary liquid systems and a polymer film prepared by glow discharge method.

Chapter I is a general introduction in which the various types of standard molecular force fields in use and different methods of calculation of force constant are reviewed briefly.

Chapter II, III and IV present parameter representation of harmonic force fields of some  $XY_3$ ,

$XY_2$  and  $XY_4$  and  $XY_3Z$  type molecules. In Chapter II a graphical method making use of isotopic frequencies is presented. Since it is often not possible to have a unique solution of the force field even with the help of three sets of isotopic frequencies, a new criterion called the "method of equal co-ordinates" is developed to fix the exact force field, in the case of multiple solutions. Using this criterion in the parameter formulation harmonic force fields of ammonia, phosphine and arsine are evaluated. In Chapter III the relationship between the parameter and mass ratio of several molecules is studied. With the help of this, the force fields, mean amplitudes of vibration and coriolis constants of several bent  $XY_2$  and tetrahedral  $XY_4$  type molecules are obtained. Chapter IV presents a new approximation scheme termed "Hybrid High Low Frequency Separation Method" for a third order vibrational problem. This method has been applied successfully to several molecules belonging to the  $XY_3Z$  type model.

The last two chapters report some experimental work. In Chapter V an easy method for the evaluation of association constants for a few ternary liquid systems is developed with the help of ir spectral studies. The fabrication of the experimental set up for the preparation of glow discharge polymers is

described in the last chapter. A glow discharge polymer film of p-toluidine is prepared and the ir spectrum of the film is studied vis-a-vis that of the monomer film. The characteristic lines of the polymer are identified and the probable polymerization mechanism is explained.

The original contributions contained in the present work are the following:

1. A new criterion called the "method of equal co-ordinates" for fixing the exact force field in the case of multiple solutions is identified.
2. A linear relation connecting the parameter and mass ratio is developed which can be made use of for the evaluation of force fields, mean amplitudes of vibration and other molecular constants.
3. An approximation method termed "the Hybrid High Low Frequency Separation Method" is developed and applied to some third order problems and all the twelve force constants are evaluated.
4. An easy and elegant method is presented for the determination of the association constant for ternary liquid systems and the 'K' values for a few cresol-ketone systems are evaluated.

5. A glow discharge polymerization unit and a special ir cell are fabricated and the polymer film prepared is identified with the help of ir spectral studies.

Part of these investigations carried out by the author has been published in the following papers.

1. Parameter Representation of Harmonic Force Field. Method of Equal Co-ordinates Ind. J. of Pure & Appl. Phys. 15 49 (1977).
2. Relation Between Force Field, Parameter and Mass Ratio, Curr. Sci. 45 827 (1976).
3. Hybrid High Low Frequency Separation (HLFS) methods: Harmonic Force Fields of Methyl Halides, Czech. J. of Phys. (In Press).

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