ABSTRACT

The thesis pertains to the study of the force fields of molecular systems involving higher order vibrational problems and computation of related molecular constants. Also presented in the work is the structure elucidation of Schiff bases using Infrared, Nuclear Magnetic Resonance and Mass spectroscopic techniques.

The thesis comprises nine Chapters of which Chapter 1 is introductory and contains rudiments of the theory of molecular vibrations leading to the determination of force field and other related molecular constants such as compliance constants, interaction coordinates, mean amplitudes of vibration, Coriolis coupling constants and centrifugal distortion constants.

In Chapter 2, methods of solving the secular equation, such as the isotopic substitution method, Isotani's method and kinetic constant method are discussed in detail. A new technique of solving the secular equation using Newton-Raphson's method is evolved. The merits and demerits of the new technique are discussed. The succeeding Chapters excepting the last one, contain the application of this new technique in conjunction with the methods mentioned above.
In the third Chapter, first, second and fourth order vibrational problems pertaining to nine molecules of the type \( XY_5Z \), belonging to \( C_{4v} \) symmetry is dealt with. The potential constants have been determined using Isotani's method. The potential constants thus obtained are compared with those obtained by the method of kinetic constants as well as with the available literature values and the results are discussed.

In the next few Chapters, the new technique is extended to fifth, sixth, seventh and ninth order problems in conjunction with the two approximation methods to compute force constants and other related constants and the results are discussed.

Chapter 4 is devoted to the vibrational analysis of four quasi-linear and two planar \( AXYZ \) type molecules belonging to \( C_s \) point group and involving first and fifth order problems.

Chapter 5 deals with the vibrational analysis of three molecules belonging to \( X_3Y_2Z_2 \) type (\( C_{2v} \) point group) and involving second, third, fourth and sixth order problems.

Chapter 6 is concerned with the vibrational analysis of four molecules belonging to \( XYZUV \) type (\( C_s \) point group) and involving second and seventh order problems.
Chapter 7 presents the vibrational analysis of two molecules (Cs point group) of $X_2Y_3Z$ type and involving third and ninth order problems.

The avowed object of generating the precise force field using the isotopic substitution method in conjunction with the new technique developed in the present work, manifests itself in Chapter 8. In this Chapter three molecules of the type $XY_2Z$ ($C_{2v}$ point group) and involving first, second and third order problems are studied.

In Chapter 9 is presented the preparation and characterisation of Schiff bases using IR, NMR and Mass spectroscopic techniques.

In the present work, the isotopic substitution method to compute the precise force field and two approximation methods (Isotani's method and kinetic constant method) to determine acceptable approximate force field have been used in conjunction with the new technique. It has been demonstrated that the new technique can be applied to any higher order vibrational problem to compute the force field by direct expansion and solution of the secular equation.