ABSTRACT

The thesis pertains to the study of force fields of molecular systems involving higher order vibrational problems and computation of related molecular constants. The approximation methods used in the present work are Isotani’s method and method of kinetic constants. These methods are applied to compute the force fields in molecular systems, up to eleventh order vibrational problems.

The thesis comprises of seven chapters. In the first chapter, a brief summary of normal coordinate analysis is given. This is the theory of Wilson’s FG matrix formalism for setting up the secular equation. The relevant theories leading to the determination of other molecular constants such as compliance constants, interaction coordinates, mean amplitudes of vibration, Coriolis coupling constants and centrifugal distortion constants are described.

In chapter 2, two approximation methods of solving the secular equation, viz., Isotani’s method and method of kinetic constants are discussed in detail. A few other approximation methods such as Redington’s method, L-matrix approximation method and Herranz and Castano’s method are discussed briefly. A new technique which is applied to fifth, sixth, seventh, eighth, ninth and eleventh order vibrational problems in conjunction with Isotani’s method and Method of kinetic constants to compute force constants and thereby calculate compliance constants, vibrational mean amplitudes, interaction coordinates and Coriolis coupling constants, is explained.
In chapter 3, fifth and sixth order vibrational problems, pertaining to three 1,1,1-trihaloethanes and their deuterium derivatives (CH$_3$CF$_3$, CH$_3$CCl$_3$, CH$_3$CBr$_3$, CD$_3$CF$_3$, CD$_3$CCl$_3$ and CD$_3$CBr$_3$) of the type XY$_2$XZ$_3$ belonging to C$_{3v}$ symmetry, are dealt with. The potential constants have been evaluated using Isotani’s method. The potential constants thus obtained are compared with those obtained from the method of kinetic constants and available literature values. The results are discussed.

Chapter 4 is pertaining to vibrational analysis of planar X$_2$Y$_3$ type molecules belonging to C$_s$ point group. The frequency distribution is 7a$'$ + 2a$''$. The molecules considered are dinitrogen trioxide and its isotope [^{14}N$_2$O$_3$ and ^{15}N$_2$O$_3$]. The force constants are calculated using Isotani’s method and method of kinetic constants. The results are compared with those obtained by other workers. Compliance constants, vibrational mean amplitudes, interaction coordinates and Coriolis coupling constants are computed and the results are discussed.

In chapter 5 vibrational analysis of X$_2$Y$_4$ type molecules, is dealt with. The molecules considered are hydrazine and its tetradeuterated derivative [N$_2$H$_4$ and N$_2$D$_4$]. These molecules belong to C$_s$ point group. The frequencies are distributed as 8a$'$ + 4a$''$. The potential constants are computed using Isotani’s method and method of kinetic constants. The values are compared with those reported in literature and the results are discussed.

Chapter 6 deals with the vibrational analysis of methylamine, methylphosphine and their deuterated derivatives. These molecules belong to the C$_s$ point group. The vibrational analysis of these molecules involves ninth order problem. The approximation methods used for the calculation of force field are those of Isotani
and kinetic constants. The values are compared with those obtained by earlier workers and the results are discussed.

Chapter 7 presents the vibrational analysis of 4,4-Dimethylocyclopentene molecule. It is a planar ring molecule belonging to $C_{2h}$ point group. The frequency distribution is $11A_1 + 6A_2 + 9B_1 + 7B_2$. Isotani’s method is used to compute the force constants. The values are compared with those reported in literature and the results are discussed.

With the aid of the new technique used in the present work, it has been possible to expand the secular equation directly and solve it with the help of fundamental frequencies alone. It appears that there is no limitation to the applicability of the new technique to vibrational problems of any order, provided the initial set of values used for the roots of the secular equation is judiciously chosen.