P R E F A C E

The investigations presented in this thesis were carried out by the author in the research laboratory of the Physics department of Kanchi Mamunivar Centre for Post-Graduate Studies, Pondicherry.

The thesis consists of four parts. In the first part, Redington's formalism of restoring force constant $F_k$ [Section 1.5.2] is used for the elimination of multiplicity of solutions in the inverse vibrational problem [Chapter 2] and his formalism of $F_{steep}$ function [Section 1.5.4] to evolve a new criterion for checking the vibrational assignment [Chapter 3]. Also, the physiochemical interpretation of Redington's force field is found to reveal structural information [Chapter 4].

Part two [Chapter 5] proposes a new iterative technique, which permits the use of all the available observed constants (isotopic frequencies, Coriolis coupling constants, rotational distortion constants, mean amplitudes of vibration etc.) for the inverse vibrational analysis. This technique can be used to refine any reasonable approximate force field obtained using any method. When the Redington's force field is refined through this technique, accurate force field, consistent with important molecular constants and of high structure correlation efficiency, is obtained.
Part three [Chapters 6 to 10] deals with the applicability of the new procedure to five different types of molecules \(\text{XYZ} - C_\alpha, \text{XYZ}_2 - C_{2v}, \text{XYZ}_3 - C_{3v}, \text{XY}_5 = D_{3h}\) and \(\text{XY}_2Z_2 - C_{2v}\). In each case, the structure correlation efficiency and the predictive ability of the force field are established. The method has also been successfully applied to ethylene and halogenated ethylenes \(\text{C}_2\text{Y}_4; \text{Y} = \text{H}, \text{F}, \text{Cl}, \text{Br}, \text{I}\), but the results are not reported here as there is no new information either with regard to the structure of the molecules or about any nuances of the application of the method, thereby avoiding the report becoming voluminous.

A method of calculating Coriolis forces on the atoms of a molecule during its rotation is given in Part four [Chapter 11]. The method gives, though not absolute values, at least a quantitative guide to the forces. Calculations done on hypohalous acids \(\text{HOZ; Z} = \text{F}, \text{Cl}, \text{Br}, \text{I}\) are found to yield some encouraging results. A study of these forces is expected to make the elucidation of information about metastable configurations of a molecule possible.

All the experimentally observed molecular constants can be used as input data for the refinement of the force field through the new technique of Chapter 5 and the force field becomes consistent with all of these constants. The possibility of detecting erroneous experimental results by the use of the new method is indicated [Section 8.4.1]. A unique computational procedure based on the mixing of the separately determined force fields of the isotopic species of a molecule is suggested [section 10.4] for the higher order problems, which are not otherwise accurately solvable by the direct application of the method of Chapter 5. Atomic potential energy distribution [Chapter 11], anharmonicity correction [Chapter 10] and Kuczera's idea of the "pure vibrational force field" [Chapter 9] have also been touched upon. The vibrational analysis of the molecules studied here are based on not only
the input data but also the path-length and bond-charge parameters, bond ionic characters, bond distances calculated using established relations and other relevant chemical properties. In this sense, the present approach to vibrational analysis of a molecule is considered to be comprehensive.

Parts of the results presented in this thesis have been published in the form of research papers. A list of five papers published in reputed International Journals, two papers presented in National Conferences and three papers communicated to Journals is given in Chapter 1 [Section 1.9].