PREFACE

Study of molecular structure is helpful in understanding the physicochemical properties of a molecule. The application of spectroscopy in different branches of science is well known.

The mathematical difficulties in the application of purely theoretical ab-initio methods for molecular systems are so great that semi-empirical and qualitative methods are the only available approach at the present time. These methods involve certain empirical parameters, which are adjusted to fit some properties of a particular molecule. Conjugated molecules like benzene form a very suitable testing ground for these theories. The spectral studies of a group of closely related and similar molecules provide a guide to the various possible approximations involved in the formulation of a consistent theory. The group of molecules obtained by replacing one or more hydrogen atoms in the benzene molecule by some other atom or group form a unique ground from this point of view. A large number of investigations on such substituted benzene have been carried out by infrared, Raman and electronic spectral studies.

Organic chemists interpret Raman and infrared spectra in terms of characteristic group frequencies. Group frequency analysis has proved valuable in determination of structure. Some chemist attempt to interpret the vibrational spectra of more complex molecules by a transposition of the results of normal coordinate analysis of simpler molecules. The vibrational assignments of complex molecules should be assisted by zero-order normal coordinate analysis. This requires a good set of initial force constants. This problem is being addressed from both theoretical and experimental point of view. On the
theoretical side, the ab-initio method met with modest success due to the deficiency to available wave functions. Hence, until improved wave functions are available, better results from ab-initio computations cannot be expected. As a result one has to depend on the spectroscopic or experimental force constants. On the experimental side, Snyder and Schchchtschneider proposed the Overlay technique where in a set of related molecules can be treated together to reduce the number of force constants. The problem for the modern molecular spectroscopists is to find a few hundred-force constants that can reproduce the spectra of a few thousand molecules.

Determination of accurate force field for a molecule is of fundamental importance. Force constants are very important molecular parameters. These are used:

(i) In drug design experiments as input parameters and,

(ii) To predict vibrational frequencies of related molecules.

The number of possible observed frequencies for a molecule is usually much less than the number of unknown parameters (force constants) to be determined. Study of the vibrational spectra of isotopic species helps in determining more force constants. Difficulty in deuteration limits the use of this technique to few molecules. However, this difficulty may be overcome using isomers wherein the substituent groups change their position thus enabling a large number of experimentally observed frequencies to fit only a limited (same) number of force constants. This novel approach is adopted in the present study to avail a set of force constants, which are transferable to all the isomers and related molecules.

Hydroxy and amino-phenyl units constitute a functional structural fragment of the molecular framework in a variety of chemically and
biologically interesting systems. A comprehensive selection would include systems as diverse as bio-molecules like proteins, amino acids and various pharmacologically active substances. For systems of such overall complexity hydroxy and amino benzenes and their derivatives may serve as comparatively simple and convenient model compounds.

The present study deals with the determination of force constants for amino and hydroxy benzene derivatives. The thesis is divided into five chapters. Chapter 1 contains a general introduction regarding the aim and outline of the work undertaken along with the theoretical approach used.

Chapter 2 deals with the force field calculations for the planar and non-planar vibrational modes of dimethylaminobenzenes using the vibrational frequencies of three isomers of dimethylaminobenzenes (DMA). A simple valance force field is obtained which is able to successfully fit all the vibrational frequencies of the three isomers of DMA.

Chapter 3 deals with the force field calculation of chloro-methyl aminobenzene when one of the methyl groups (Chapter 2) is replaced by chlorine atom. Focus of the calculation is to obtain a force field, which was able to reproduce the vibrational frequencies of DMA with necessary modification for chlorine.

Chapter 4 covers the force field calculation for hydroxybenzene derivatives. The substitution of methyl and chlorine serve a testing ground for the force field obtained in chapter 2 and 3. Finally a comparative study is presented in chapter 5.