CHAPTER I

INTRODUCTION
Molecular spectroscopy provides an important method for the determination of molecular structures. Molecular motions involving rotations and vibrations, generally give rise to spectra which lie in the microwave and infrared regions. From a study of these spectra, molecular parameters like the moments of inertia of the molecules, internuclear distances, bond angles, etc. are determined and from them the molecular geometries are derived.

The vibration-rotation spectrum of a polyatomic molecule, for example, benzene is best studied from its infrared and Raman spectra wherein lie the fundamental vibrational frequencies of the molecule. An assignment of the frequencies observed in the infrared and Raman to the different fundamental vibrational modes is made from considerations of certain characteristic features of the vibrational bands such as their intensities, approximate band contours and depolarisation ratios of the Raman bands. The spectral data do not always provide an unique assignment of all the fundamentals and, therefore, these studies are supplemented with a mathematical analysis of the molecular vibrations. Such an analysis requires the use of physically significant force constants.

Experimental data are limited to the observed vibrational frequencies which are always less than the desired number of force constants. The problem, therefore, for molecules like the benzenes considered in the present studies, is to find the requisite number of fundamental vibrational frequencies and the choice of force
constants in order to carry out a normal co-ordinate analysis of the benzenes. As far as the frequency data are concerned, addition of frequencies of isotopic molecules is a great help. The vibrational spectra of the isotopic molecules also contribute, to a large extent, in making the assignments of the original as well as the isotopic molecules unambiguous because the vibrations involving isotopic nuclei shift to a greater extent compared to vibrational modes not connected with these nuclei. Also, the intensity correlation between the frequencies of the isotopically substituted molecules enable one to assign the fundamentals with more certainty. The technique of making use of combined data of isotopic molecules has already been applied to benzene itself by Ingold and co-workers\textsuperscript{(1)} and Langseth and Brodersen\textsuperscript{(2)}. But only relatively little data\textsuperscript{(3)} are available for isotopic molecules of the dihalogenated benzenes. Moreover, a normal co-ordinate analysis using the combined data of the deuterated and undeuterated molecules will also give a better force field for this group of molecules. These force constants could then be transferred to related systems with greater confidence. With these aims, in the present studies, deuterated dihalogenated benzenes - o,m,p-fluorochloro and o,m,p-fluorobromo benzenes - are specially prepared and the spectra are supplemented with those of undeuterated molecules. A normal co-ordinate analysis using the combined data of the deuterated and undeuterated molecules has also been carried out in the present studies.
The experimental techniques employed for deuteration, purification and recording of spectra are discussed in Chapter II.

In Chapter III, the fundamentals of the deuterated molecules are assigned and it is shown that some previously assigned fundamentals for the undeuterated molecules are actually impurity bands, and a reassignment is done for these bands. The interpretations for the remaining observed bands of all the compounds have also been given in terms of the fundamentals.

A normal co-ordinate analysis of the group of 12 molecules have been carried out both for inplane and out-of-plane vibrational modes. For the inplane modes, 33 force constants have been adjusted to fit in all 248 frequencies. For the out-of-plane modes, a 16 parameter force field has been employed to fit 94 frequencies. The results of these calculations and the correlation with benzene modes are discussed in Chapter IV.
REFERENCES

