Synopsis

The first chapter of this dissertation deals with the basic theory of Microwave Spectrocopy. The different types of rigid rotor molecules and the corresponding Hamiltonians have been discussed. Special emphasis has been placed on the asymmetric rotor as all the molecules presented in this dissertation belong to this class. The labelling of and the expressions for the energy-levels of the asymmetric rotor have been discussed, as also the symmetry classification of the energy-levels and the advantages of using this group theoretic analysis. The symmetry classification of the rotational states has also been used to find the selection rules for rotational transitions. Next, the expressions for the quartic centrifugal distortions have been derived and the rotational Hamiltonian including the modifications due to these quartic terms has been presented. The problem of relating the molecular structure to the observed moments of inertia has then been covered, including the three concepts of structure (or bond-length) commonly encountered. Lastly, the iterative least squares fitting procedure, the basis of all the spectral analysis presented in this thesis has been described.

The Microwave Spectrum of an asymmetric top molecule is normally very dense, posing a formidable problem in spectral assignment. This particular disadvantage of conventional or Stark-Modulated Spectroscopy is much reduced by the use of Radio Frequency-Microwave Double Resonance Spectroscopy. The theory of Double Resonance has been dealt with in Chapter 2.

Chapter 3 describes the Stark-Modulated and the Double Resonance-Modulated Spectrometers used in the present investigations. In the first the Stark splitting of the rotational lines on application of an external electric field has been utilised to modulate the zero-field absorption line and hence enhance the Signal-to-Noise ratio. In the Double Resonance-Modulated Spectrometer the same objective is realised by using the Double Resonance splitting of characteristic microwave spectral lines on applying a strong saturating RF field. A performance check on the Double Resonance Spectrometer has also been discussed as well as the sensivity, resolution, and accuracy of both the set-ups.

The Microwave Spectral study of the molecule 2-fluorophenol and its OD species in the ground vibrational state constitutes the fourth chapter. 2-fluorophenol or ortho-fluorophenol should, in principle, exhibit two stable conformers, viz., cis and trans. The study of this molecule acquires added importance due to the presence of strong intramolecular hydrogen-fluorine interaction which stabilises the cis conformer in the gas phase. From the analysis of the parent and the deuterated species the energetically favourable cis-conformation was established. Three bond-lengths were obtained by a structural least-squares analysis and an effective structure for this conformer has been proposed. The technique of the structural least-squares analysis is also described in this chapter.

In chapter 5 the Microwave Spectral studies on ground vibrational states of the two disubstituted benzene compounds, 2-fluorobenzonitrile and 3-fluorobenzonitrile, have been presented. The peripheral substituents to the benzene ring in both cases were the cyano-group and the fluorine atom. The

interest was to see whether the proposed r_o-structures for these molecules, each based on an undistorted benzene ring, could reproduce the observed molecular moments of inertia, inspite of two peripheral substitutions on the benzene ring.