Ever since the Raman effect was discovered and particularly after 1945, there has been an increasing volume of literature pertaining to infrared and Raman spectra of compounds. One important problem confronting physicists has been to understand the nature of the forces holding together the atoms of a compound. Vibrational frequencies obtained from molecular spectra are helpful in this regard. The analysis and interpretation of spectra requires a thorough understanding of the theoretical ideas of molecular dynamics which involves the use of matrix algebra and group theory.

The interpretation of molecular spectra has followed two distinct paths: (i) Spectra of thousands of compounds have been obtained experimentally and empirical relations drawn between the observed frequencies and molecular structure. (ii) Spectra have been subject to vibrational analysis which leads to the determination of potential constants. These constants, called the force constants, are a measure of the forces that resist changes in bond lengths and bond angles.
Since the electronic energy of a molecule does not change during a vibration, the molecular electronic configuration is ignored and a molecule is considered to behave as if it consists of a number of nuclei (or atoms) whose mean relative positions are fixed by molecular force fields. Though the motions of these nuclei are highly complex, they can be understood as a superposition of simple harmonic vibrations, known as normal vibrations. Generally each normal vibration has its characteristic frequency which appears in the spectrum.

A non-linear molecule has \((3N-6)\) normal modes of vibrations while a linear molecule has \((3N-5)\), \(N\) being the number of atoms in it. During a normal vibration all atoms vibrate with the same frequency, pass through their respective equilibrium positions at the same instant and suffer maximum displacement also simultaneously. The form and frequency of a normal vibration is characteristic of (i) the masses of the atoms and their equilibrium geometry and (ii) the forces that tend to restore the equilibrium during a vibration. The equilibrium geometry of a molecule can be obtained from X-ray diffraction studies and studies of rotational spectra.
The vibrational spectrum of a molecule can be deduced from a knowledge of the force constants. But the reverse problem is more important as the vibrational frequencies of a molecule can be determined experimentally to a fair degree of accuracy, whereas the force constants are generally unknown. The reliability or otherwise of calculations of molecular force constants can be tested by the calculation of mean square amplitudes of vibration and coriolis coupling constants for the molecules, and comparing them with the values deduced from electron diffraction, microwave and rotation-vibration studies.

The programme of evaluating the force constants and the normal coordinates of a molecule is called normal coordinate analysis. Though, in principle, it is possible to solve the secular equation with the help of experimental frequencies and the G-matrix to get the force constant matrix, in practice, it is beset with difficulties, since the number of force constants to be determined exceeds the number of frequencies of normal vibration. One has to use additional data such as coriolis coupling constants and mean square amplitudes of vibration to determine force constants. Since such additional information is not always available, some
approximations may reasonably be made to arrive at the
desired solution to the problem. Hence various procedures
have been developed by different workers. A survey of the
relevant theoretical considerations of some methods are
presented in Chapter II.

The first part of this thesis describes studies on
theoretical evaluation of force fields based on spectroscopic
evidence. The method of Herranz and Castano\(^6\) is discussed
in Chapter III. Chapter IV deals with Strey’s method\(^7\). The
quadratic method of Jordanov and Nikolova\(^8\) is presented in
Chapter V. Chapter VI deals with the bond charge method\(^9\)
developed recently by Ken Ohwada.

The second part of the thesis deals with the experimental
IR spectroscopy of some liquid mixtures. The study of
electronic structure of molecular complexes in their ground
state is of considerable importance as they provide insight
into the phenomenon of intermolecular interactions. In this
work systems involving H-bonded interactions are studied
employing infrared spectroscopy and dielectric measurements.

The shifts to lower frequencies of the stretching
vibrations of A-H bonds and spectacular changes in the
IR integrated intensities of absorption associated with the bonding species are observed. They provide valuable information regarding the nature of molecular interactions.

Since formation of H-bond is accompanied by displacement of charges, the dipole moment of the complex may be expected to be different from the vector sum of the components. This aspect is not completely understood. For weak complexes, it may be due to induced polarisation arising out of short range interactions. However, recent dielectric studies on a variety of O-H···N and O-H···O=C type of interactions in a media of non-polar solvents indicate that charge transfer effects\textsuperscript{10}, polarisation effects\textsuperscript{11,12} and partial proton transfer effects\textsuperscript{13,14} could be invoked to explain the enhancement of dipole moment of the complexes.

A perusal of the literature shows that modifications brought about in the carbonyl band should provide a wealth of information on the type of complexes. Hence IR spectra of complexes of the type O-H···O=C were recorded and analysed. Dielectric polarisation measurements were made to obtain additional data. Significant results are obtained. This work is reported in Chapters VII, VIII and IX.
REFERENCES