CHAPTER I
INTRODUCTION

Introduction

The work presented in this thesis is concerned with the Laser Raman spectroscopic and dielectric studies of aromatic Schiff base molecules. This class of molecules is of considerable importance in many spheres of studies. The biological significance and the liquid crystalline behaviour of these molecules deserve special mention in this context. The protonated Schiff bases are found to play central role in controlling the retinal mechanism. One of the significant contribution of Raman studies of the retinal mechanism is the proof\textsuperscript{1-3} that opsin and retinal are joined by a protonated Schiff base linkage as

\[(\text{retinal}) - \text{CH} = \text{N}^+ - (\text{CH}_2)_4 - (\text{opsin})\]

Vibrational studies on protonated Schiff bases such as rhodopsin, bathorhodopsin provided evidence\textsuperscript{4-6} that absorption of light by these systems does not change the state of protonation. Evidence in favour of existence of an unprotonated Schiff base linkage was found\textsuperscript{6} in metarhodopsin II. For a wide variety of such molecular systems, the assignment of the C=N stretching mode was attempted.\textsuperscript{4,7-11} The vibrational studies on these molecules reveal that the site containing the C=N linkage plays a
significant role in governing the processes involved in retinal mechanism. For deeper insight into these mechanism, a detailed spectroscopic study seems to be of significance which may provide information about excited states and the vibronic coupling of vibrational modes. Application of Laser Raman technique is expected to be useful under pre-resonance conditions for such studies. Besides the Schiff base linkage, the interactions at the other sites is also of importance. Therefore, the study of a large number of molecules having substituents of various chemical nature may be of significance in understanding the various processes involving molecules containing the Schiff base linkage. In an attempt to proceed with such investigations, we have selected aromatic Schiff base as the molecular system for Laser Raman spectroscopic studies. We have investigated four aromatic Schiff bases containing substituent groups of varying chemical characters. The spectroscopic studies of these systems are mostly based on Raman data. However, Raman spectroscopic study is assisted by the electronic absorption spectra which are even otherwise required for pre-resonance Raman spectroscopic investigations. The infrared data have also been used to support the band assignments which are required to identify the band due to Schiff base linkage.

The Raman studies, coupled with the electronic absorption studies are of utmost importance in providing information regarding the geometry of the ground as well as
excited electronic states of complex organic molecules. The Raman intensity of the specific bands in pre-resonance region is capable of providing detailed information about the nature of the lowest excited electronic states. An electronic transition between two states is accompanied by simultaneous changes in the vibrational states, so that the absorption due to the electronic transition, in principle, consists of a large number of lines. The rotational fine structures are usually unresolvable in liquids as rotational states are usually not well-defined. The shape of an absorption band due to a single electronic transition may, therefore, be considered to be determined by the spacing of the vibrational subbands and by the distribution of the total intensity of the electronic transition among the vibrational subbands. The intensity distribution among the vibrational subbands is determined by the Franck-Condon principle which states that the most probable vibrational component of an electronic transition is one which involves no change in the nuclear configuration.

In condensed phases, molecules generally cannot rotate freely and as such the rotational energy levels lose their meaning. It is, therefore, not possible to separate rotational lines in the spectra of liquids, solutions and solids. In liquids and solutions, the vibrational levels are broadened because of varying interactions of molecules with their neighbours. This broadening is often quite sufficient to obscure most or all the
vibrational structure of bands. Although in some cases, the equilibrium geometry of a molecule in an excited electronic state can be inferred from theoretical considerations of the electronic structure of the state, it is, in general, difficult to determine experimentally the geometry of a molecule in an excited electronic state. Since the lifetime of excited states is usually quite short, it is not possible to obtain the requisite quantities of molecules in the excited state for the time needed. Thus, customary experimental techniques used for the determination of the geometry of a molecule in its ground state are not applicable in an excited state. We have attempted to utilize the pre-resonance Raman techniques to get some information. The Raman excitation profiles of some specific bands in the pre-resonance region could be used for providing information about the excited electronic states. Such studies are essentially based on the fact that the most prominent vibrational progression, if present in an absorption band may provide information about the geometry of the molecule in the corresponding excited state.

Substitution at different positions on the rings of the aromatic Schiff base molecules brings about changes in the electron cloud of the benzenoid moiety and as such may perturb the coupling between the sensitive vibrational mode(s) and the electronic states. The extent to which coupling phenomena are perturbed depends upon the chemical nature as well as the
position of the substituent groups in the benzene rings. A systematic study of the Raman excitation profile in the pre-resonance region for a particular band corresponding to a mode of vibration, appears to be informative. The choice of chemical groups with high degree of electron donating or accepting ability is therefore expected to be of significant value in such a context. Such substitution-dependent studies are expected to monitor the active moiety of the Schiff base molecules which are mainly responsible for the coupling of vibrational modes to the electronic states. The aromatic Schiff bases in the present study consist of the benzyldiene and the aniline rings linked by the \(-\text{C}=\text{N}-\) linkage. Depending on the geometry of the molecules which may be non-planar due to steric considerations, only a part of the molecule is expected to provide major contribution towards the coupling phenomena. The electron absorption spectrum useful for pre-resonance work may arise due to a segment of the molecule. A comparative study of the Raman spectra of Schiff bases with different substituent-characters assisted by the pre-resonance excitation profile may provide important clues in this direction. Such studies will also be useful in sorting out the vibrational mode which are strongly coupled to the electronic states in these molecules.

Raman scattering can reveal information about the vibronic coupling of excited molecular states through the intensity variation of the scattered Raman radiation as the
frequency of the incident laser light changes. According to Albrecht and Hutley's\textsuperscript{12} theory, under pre-resonance conditions, the significant terms contributing to the polarizability tensor are determined by two terms known as A and B terms. The intensity factors are represented by $F_A^2$ and $F_B^2$ terms. The $F_A^2$ term contains contribution from the single state and depends on the extent of displacement of the excited electronic state potential along the normal co-ordinate. Since for non-totally symmetric modes, the origin shift upon electronic excitation is zero, only the totally-symmetric modes gain intensity via the A-term. The intensity enhancement through $F_B^2$-term, on the other hand, depends on the coupling where two or more energetically nearby electronic excited states are involved. In several conjugated molecular systems, the pre-resonance Raman intensity was found to be better determined by the $F_B^2$-term rather than the $F_A^2$-term. In the molecular systems of aromatic Schiff bases, the extent of conjugation is not expected to be high due to non-coplanarity of the benzylidene and aniline rings of the Schiff bases due to possible steric hindrance. In the pre-resonance region, due to mixing of the electronic transitions, some of the sensitive vibrational bands coupling the excited states are expected to gain intensity. It may, therefore, be interesting to investigate which of the two terms determine the pre-resonance Raman intensity for this class of molecules. A comparative study of the theoretically calculated values of the intensity factors with the experimentally observed values may provide information about the
coupling. It may also lead to better understanding of the excited states in complex molecular systems.

Some of the aromatic Schiff bases are also important for their liquid crystalline behaviour. The nature of the terminal substituent groups are found to influence the liquid crystalline behaviour in some Schiff bases. The high nematic thermal stabilities of the 3-pyridyl compounds suggest that the diminution in conjugation between a terminal phenyl ring and the CH of the Schiff base linkage that must occur when this ring is replaced by 3-pyridyl, are offset by the enhanced axial polarizability resulting from the 3-heteronitrogen. Young et al studied the effect of the presence of terminal 5-membered heterocyclic rings on the liquid crystalline behaviour of Schiff bases. In Schiff bases having hydroxy-substitution in the ortho-position, lateral substitution was found to enhance the Nematic-Isotropic (N-I) temperatures.

At the phase transitions, due to application of fields and with other alignment procedure, the materials exhibiting liquid-crystalline property undergo changes in refractive index and optical constants. Such changes when interpreted from a macroscopic point of view may reveal important conclusions regarding such materials. While drawing conclusions about molecular rotations from a study of vibrational band shapes, it is essential to know the assignment of the mode under
The assignment of vibrational bands, therefore, appears to be of utmost importance for studies of such systems. Vibrational assignments of molecular systems which show structural resemblance to the liquid crystals may therefore be useful. The aromatic Schiff bases, are excellent systems for this purpose and are, therefore, chosen to be systems for the present studies. The Raman spectra in solution phase, the excitation profile in the pre-resonance region and the IR spectral data are expected to provide useful information for assignment of the important vibrational modes in the Schiff bases. A comparative study with the analogous molecules is also of significance for assigning the observed vibrational features in these systems.

From the point of view of molecular Physics and Chemistry, the biological materials are extremely complicated systems. However, these systems function in a systematic way and their functions may be treated in terms of dynamic rather than static properties of molecules. As a next step, one may be tempted to introduce a known interaction between the atoms and ions of the system and based on the known structure, calculate their dynamic properties. This may, however, not result in the general theory of the relevant processes. In looking to Physics for guidance to find a concept capable of describing biological order we are led to the concept of coherence which applies to cases as different as lasers, masers, superconductors and superfluids. In biological systems periodic processes are very
common. Among them the periods may extend from that of life-cycles to very high frequency electric vibrations. In contrast to most physical periodic processes, periods of biological processes often vary from case to case. Thus the period of the life-cycles of cells grown under exactly the same conditions vary with certain limits i.e. each cell exhibits a certain amount of personality. Random energy supplied to certain systems need not lead to heating but may result in the excitation of ordered (coherent) states. In looking for a physical characteristic common to most biological systems, one is at once led to their dielectric properties. High electric fields of about $10^5$ V/cm is present in many biological systems. This field acts in the range of non-linear response and the materials in the system are therefore, strongly non linearly polarized. Many ions contained in biomolecules provide essential contribution to their stabilization, to their interaction as well as to their interaction to the surrounding medium.

The dielectric properties of water associated with biological structures are of considerable relevance to many biological systems. Dielectric measurements on lysozyme have shown that 36 water molecules are so bound to the protein structure that they are prevented from rotating under the influence of applied electric fields and another 70 water molecules are so bound that they exhibit a dielectric dispersion at a lower frequency than expected for normal bulk water.
Measurements at microwave frequencies for DNA at various stages of hydration have shown that around 280 water molecules per helix turn are so influenced by the electrostatic forces associated with the DNA structure that they do not freeze until temperatures of \(-100^\circ\)C and lower, are attained.

Dielectric behaviour of hydrated biological materials exhibits interesting features at low frequency range i.e. at \(<10^6\) Hz. The variation of relative permittivity as a function of frequency in this range shows a fall and is indicative of a dielectric relaxation.

In order to get a deeper insight into the behaviour of complex molecules, time-dependent dielectric studies may be of significant value. Studies related to polarization, dielectric relaxation and dielectric losses in complex molecular systems are capable of providing valuable information in this context. The dielectric behaviour of complex biological molecules in living organism is substantially influenced by the effects associated with dissolved ionic salts and other chemicals. The concentration of ions in biological fluids can be quite high. In some systems such as mammalian plasma, the concentration of \(\text{Na}^+\) is of the order of 0.15M. The typical ionic concentrations for the higher plant cells, in general, are \(\text{K}^+\) (0.119M), \(\text{Cl}^-\) (0.065M), and \(\text{Na}^+\) (0.014M). The presence of ions with such concentration range in the neighbourhood of biomolecules, therefore, greatly
influence the behaviour of biomolecules. As such, it seems logical that systematic studies of complex molecular systems embedded in ionic environment are of utmost significance for better understanding of their behaviour. In an attempt to get better insight into the dielectric behaviour of molecules of biological significance, dispersed in a strong ionic matrix (e.g. KBr matrix), we considered it worthwhile to study the time-dependent dielectric behaviour of aromatic Schiff bases with various substituent groups. The Schiff base molecules, dispersed in KBr matrix may be regarded as randomly oriented and as such the dispersed system may be assumed to be a heterogenous system. In order to avoid possible complications arising due to intermolecular interactions in liquid phase, we prefered to carry out the investigations related to dielectric studies in the solid phase. Studies of these systems in solid phase, however, are more advantageous in the sense that the solid phase properties are sometimes able to explain the biological processes.
References


