CHAPTER I

REVIEW OF THE HISTORICAL WORK AND THE PROBLEM

1.1 Introduction

The beginning of spectroscopy could be traced to the dispersion of light through a prism discovered by Newton. The word ‘Spectrum’ was further routinely used for the energy wise distribution of the images of the slit dispersed by prism. Further, spectra of different elements were used as the finger prints of the samples. After a work by Wollaston, Bunsen and Krichoff, Fraunhoffer was first to show the absorption lines in a solar spectrum which was due to the hot background of photosphere and outer cooler layers in chromosphere and corona. These absorption lines are dark where as the emission lines are having color depending on which part of the visible spectrum they appear. The natures of the origin of the spectral lines were not clear until the explanation of Hydrogen spectrum was given by Niels Bohr. Although, the theory was based on postulates, it could successfully explain the quantum nature of transitions. The circular orbits of Bohr were further generalized to elliptical orbits by Sommerfield and the relativistic effects also could be incorporated in the theory. Soon after the discovery of an electron spin angular momentum the interaction with orbital angular momentum was established and a doublet fine structure of the alkalis could be explained. This marked the beginning of detailed studies of atomic spectroscopy.
On an experimental front, the glass prisms were replaced by other materials like dense flint, alkali halide crystals and so on as the glass has a very limited transparency. By this time it was emphatically proved that the electromagnetic spectrum in the visible part extends in the either sides i.e. to IR and UV. These invisible radiations could be sensed by special photographic emulsions for UV and by heat sensing devices used for IR spectroscopy. Due to difficulty in developing homogenous crystals of desired hardness for making prisms set the limit on resolving power of prisms which mainly depends on base length and variation of refractive index with wavelength. Larger base lengths will enhance the apex angle of the prism and hence the reflection will be more dominant in such cases. As a result, gratings were discovered which operate on the multi-slit diffraction patterns. Starting with gratings made by winding fine wires, the ruling engines were discovered which can rule as many as hundreds of lines per mm. Gratings had one disadvantage and that is the falling of intensity in higher orders where the dispersion and resolution is at its full advantage. Slowly, instead of transmission gratings, reflection gratings were discovered which are effective not only in UV, visible but also in IR. The efficiency of gratings was increased by coating the substrate by gold. Ruling on Aluminum is easier and popular but the reflectivity of Aluminum falls in Ultra Violet region. Moreover, due to water vapor present in air it forms Aluminum hydroxide also. Further, the grooves were shaped in a
particular order for particular wavelength in a specific order. Say if the grating rulings are shaped in such a way that the first order spectrum is strong at 6000Å then for the same setting it could be strong also in second order at 3000Å or in third order at 2000Å. This shaping is called Blazing. The blaze angle is also one of the parameter of the grating along with ruled area, grooves per mm etc. Further, in order to avoid the defects of camera lenses the gratings were ruled on concave mirror so that the concave grating itself acts a focusing lens or camera lens. These large radii concave gratings were once very popular for the high resolution – high dispersion studies till 1980.

Compound prism spectrographs like Pellin Broca, were also used for obtaining spectra at low dispersion which were generally used in constant deviation spectrographs.

For concave gratings different types of mountings were suggested from time to time. Mountings like Rowland, Paschen-Runge, and Eagle were popular one time. Concave grating had one advantage that the free spectral range is larger.

A new turn was taken when plane gratings and Echelle’s were used in higher orders. The free spectral range of plane gratings although is small, the overlapping orders were sorted by efficient order sorters or sensitive emulsions or by using quality filters like interference filters. All the details of the instrumentation are discussed in various monographs [1-5]

Today, the concept of high resolution has changed drastically due to
the Fourier Transformation. Based on Michelson Interferometer, these Fourier transform spectrometers can resolve even one wave number and therefore the hyperfine structure could be resolved.

There are various detectors used in various ranges of the electromagnetic spectrum. Eye is sensitive only in the yellow green region of visible spectrum. Large number of photographic emulsions were used for recording the spectra in visible and near IR and UV. Ilford and Kodak companies produced large number of emulsions ranging from 3000 Å to 12000 Å. These emulsions are classified on the basis of sensitivity to a particular photographic range, the grain size, inertia, latitude, speed etc. Finer the grain more is the resolution, but slower is the speed. Thus for a coarse work or for low resolution pictures sometimes fast emulsions are used. The photographic emulsions once popular in last century are slowly replaced by photoelectric detectors like photomultiplier tubes. The response of photographic emulsions to the radiation is also nonlinear and that is why calibration of the emulsion was a major exercise in intensity measurements. In contrast, the photoelectric detectors have a linear response. Besides photoelectric detectors, there are photoconductive and photovoltaic detectors. In the present scenario fast photodiodes, photodiode arrays, photoelectric image intensifiers, photon counting devices are used. They are detailed surveyed by Demtröder [6].
1.2 Atomic and molecular spectra

Atom consists of large number of orbitals. The region in space around the nucleus of an atom where there is maximum probability of finding the electron is called orbital. Each orbital characteristics the energy, shape and orientation designated by three quantum numbers \( n \), \( l \) and \( m \), i.e. principal quantum number, azimuthal quantum number, and magnetic quantum number respectively. Yet another quantum number called the spin quantum number is also necessary to explain the quantum state of an atom. The principal quantum number determines the size of the orbital and also the average distance from nucleus. The different energy states are denoted by 'K', 'L', 'M', 'N' etc depending on \( n' \)=1, 2, 3... respectively. Atom can make transition from one state to another by emitting or absorbing photon of the frequency \( \frac{E_f-E_i}{h} \), where \( E_f \) and \( E_i \) are the energies in the final and initial states. Emission lines are colored whereas absorption lines are dark. For absorption a background source is essential. Absorption spectra can be observed in all phase’s viz. solids (crystals), liquids, and gases. In case of atom only electronic energy exchange is possible. There are three basic rules, known as the building up rules which determine how electrons in large atoms occupy orbitals as given below.

1. Pauli’s principle. - No two electrons in an atom have the same set of value for \( n' \), \( l' \), \( m' \), and \( s' \).

2. Electrons tend to occupy the orbital with lowest energy available.
3. Hund's principle - Electrons tend to occupy degenerate orbital singly with their spins parallel.

When two more atoms combine together a molecule is formed. Molecule can be classified according to the relative values of their three principal moments of inertia. Any body has three principal moments of inertia, one about each axis, usually designated $I_A$, $I_B$, and $I_C$. If $I_B = I_C$, $I_A = 0$ then molecule is called as linear molecule. In this type of molecule all atoms are arranged in a straight line. All the diatomic molecules are linear. If $I_B = I_C \neq I_A$ and $I_A \neq 0$, then molecule is called symmetric top. In this type, if $I_B = I_C > I_A$, then molecule is called a prolate symmetric top, and if $I_B = I_C < I_A$, then it is called as oblate symmetric top. If $I_A = I_B = I_C$, then molecule is called as spherical tops and if $I_A \neq I_B \neq I_C$, then molecule is called as asymmetric top.

When atoms form a molecule along with the nuclei, the peripheral electrons moving around the atoms are also brought together and in fact the governing factor in the stable formation of a molecule is the number of electrons in the valence shell of the atoms constituting the molecules. The molecules can be diatomic, triatomic and polyatomic depending on number of atoms forming the molecules. Diatomic molecules could be further classified as homonuclear and heteronuclear. Homonuclear molecules don’t yield ‘infra red spectrum’ as they don’t possess permanent dipole moment.

The force that keeps the atoms together in a molecule is called a chemical bond. There are different types of bonds
1. Covalent bond
2. Ionic bond
3. Coordinate bond
4. Metallic bond

The molecular orbitals are formed from atomic orbitals. The electrons were filled in molecular orbitals by obeying Pauli's exclusion principle and Hund's rule. Electrons move very fast about the nuclei. We can separate the motion of electrons from nuclei (Born-Oppenheimer approximation). The motion of the nuclei then corresponds to vibration, rotation, and translation. Thus, molecule can have three forms of energy disregarding for the time being the nuclear energy. They are,

1. due to the rotation of the molecule,
2. due to the vibration of molecule,
3. due to electronic motion in molecule.

The first two classes are generally absent in an atom. These motions thus give rise to different energy levels and the transition among these energy levels give rise to different forms of spectra in various regions of the electromagnetic spectrum. Molecular spectra can be classified based on its origin and the region where the transition occurs and whether it is absorption or emission. Thus we can classify the molecular spectra in three different categories.
1. Rotational spectra – This usually observed in microwave region and mainly due to the changes in rotational energy of the molecule. Primary information this type of study gives the value of $r_e$.

2. Vibrational spectra – These usually observed in infra-red region and are mainly due to the changes in the vibrational energy of the molecule. Vibration spectra study tells how stiff is the bond, nature of vibration, curvature of potential and vibrational frequencies etc.

3. Electronic spectra – Usually observed in optical region and are due to changes in the electronic arrangement. Under high resolution one could also observe vibrational-rotational transitions from the levels of the two participating electronic energy states. Study of electronic spectroscopy tells us the detail of electronic states or potential energy curves.

   The s, p, d, f notations represent orbitals in atomic spectra whereas S, P, D, F notations represent the terms. In case of molecules the letter $\sigma$, $\pi$, $\delta$, $\phi$ represent orbitals and the letters $\Sigma$, $\Pi$, $\Delta$, $\Phi$ represent the terms. The projection of orbital angular momentum is conserved and therefore $\Lambda = 0$ represents $\Sigma$ state, $\Lambda = 1$ represent $\Pi$ state and so on. The interactions between vibrational and electronic motion gives rise to Franck-Condon principle and the variation of electronic transition moment, whereas the interactions between electronic motion and rotation gives rise to Hunds coupling schemes.

   There are various selection rules, which govern the transition between various electronic states. The distribution of population in different
vibrational & rotational levels obeys the Boltzmann distribution. The vibrational and rotational temperatures could be calculated from the intensities of the bands and rotational lines respectively.

The spectroscopic constants like harmonic frequency ($\omega_e$), anharmonicity ($\omega_x$), and still higher order vibrational constants ($\omega_y$, $\omega_z$ etc) could be determined from the vibrational analysis of a band system, which results from the transition between two electronic states. The lower state sometimes can be the ground state of a molecule. The rotational analysis of the bands yields rotational constant $B_e$, the rotational-vibrational constant $\alpha_e$ etc. From $B_e$ one can calculate the internuclear distance $r_e$ which is usually expressed in Angstrom units.

The aim of the analysis of the electronic spectra is to determine the vibrational constants and rotational constants. The enrichment of the data is made by repetative studies, either using higher resolution or modified sources or by both. These spectroscopic constants are further used in various studies; one of them is the ‘Construction of potential energy curves’. Several texts have described the Atomic & molecular spectra in detail. [7–14].

### 1.3 Potential energy curves

A potential energy curve is a graphical representation of the change in potential energy of the molecule as a function of the distortion of the bond of the molecule from its equilibrium distance. The atoms forming
diatomic molecules oscillate, resulting in the changes in an internuclear separation. When the bond is stretched more than equilibrium distance ‘r_e’, an attractive force works on them to bring them closer. In case the distance between them is smaller than r_e a repulsive force works and they are pushed apart. If this force is taken to depend on (r-r_e) where r is any internuclear distance between two atoms than the potential depends on the square of (r-r_e). Because of this variation, the curve between the potential energy and distance is a parabola, \( V = \frac{1}{2} k (r-r_e)^2 \). Further consideration reveals that there exists some restoring force and this force also depends on (r-r_e)^2, (r-r_e)^3 etc. Naturally the potential energy curve now assumes a slightly different shape and at higher r-values it is almost asymptotically parallel to r axis. This distance from r axis on ordinate scale is called the dissociation energy. In spectroscopy generally the measurements of energies are in wave numbers (cm\(^{-1}\)). Some workers also use eV or kcal as the units of dissociation energy.

### 1.3.1 RKR Curves

The RKR method is well known procedure for determining potential energy curves of diatomic molecules by calculating classical turning points, r_ and r_+, from experimental spectroscopic constants. This method is developed by Rydberg, Klien and Rees and was further modified by Vanderslice. Sometimes it is also known as RKRV Method. The details of this method are described in [15-20].
1.3.2 Empirical potential Energy Functions

To this date there are large numbers of empirical potential functions used to construct the potential energy curves. A potential energy function is just a mathematical expression involving the molecular constants like $\mu$, $\omega_e$, $\omega_e x_e$, $B_e$, $r_e$, $D_e$ etc. If you substitute these constants of a particular electronic state of any molecule and if you vary $r$, there is a change in potential energy. This potential energy curve matches to RKR curve if the potential function is properly defined.

There are few classic PE functions developed long back. Few of them are the Morse, Rydberg, Kratzer, and Hulbert-Hirschfelder (H-H) etc. The quest of finding of suitable potential function is still going on and in recent years there are some potential functions like the extended Rydberg, Zavitsas, Tietz, etc. which have been suggested and are being applied to different species of diatomic molecules. Detailed surveys are taken by [21-23].

An attempt was made by Birajdar and Behere to see how the arithmetic mean and geometric mean of some of potential functions work. The combinations of Morse, Rydberg and Kratzer functions, which gave new potential functions, were studied by them [24-28]. It was found that the combinations do not give suitable potential functions.

Quite recently a new type of potential function named as Generalized Potential Energy Function (GPEF) is suggested by Surkus [29-39], which was studied by Shelke [40].
Reduced Potentional Energy Curves (RPC) a new type of technique developed by Jenc [41] is also utilized in present studies. All these techniques will be utilized in the context of present studies in the subsequent chapters.

1.4 Intensities of bands, Franck Condon factors and rotational temperature

Franck Condon factor and r-centroids play an important role in finding out the variation of electronic transition moment with internuclear distance.

As it is well known that the Franck Condon Principle governs the intensities of various bands in a band system, a more quantitative way is to calculate the Frank Condon factor of that particular band system. Calculations of FC factors are also associated with r-centroids. Chakraborty and Pan [42] have surveyed various methods of calculating FC factors. These calculations made the overlap integral which is denoted by \( \int \psi_{\nu'}^* \psi_{\nu''} d\tau \) where \( \psi_{\nu'} \) is a wave function of \( \nu' \) th vibrational energy level and \( \psi_{\nu''} \) is wave functions of \( \nu'' \)th energy level to be determined. The TRAPRAB program developed by Jarmain and Nicholls [43] are used to calculate the FC factors.

If the rotational structure of the band is resolved and if the intensities of the rotational lines without overlap of any other lines are measured,
rotational temperature can be determined. These studies are also undertaken in present work.

1.5 The InCl Molecule

The III A group halides are of interest as they are less studied and secondly few of them may be useful for laser transitions. This group contains Boron, Aluminum, Gallium, Indium and Thallium. Since, Thallium salts are poisonous, usually studies are limited to Boron, Aluminum, Gallium and Indium.

The mono-halides of group IIIA elements usually give their main band systems in the range 3000 to 4500 Å.

References [44-69] show the major works on the mono halides of the IIIA group elements. The molecules GaI, GaCl, and AlCl are studied by Saksena et al. [62-64, 67, 69].

Youngner and Winnans [44] first reported the detailed study of InCl. Which was further taken up by Rao et al.[45] and Nampoori et al.[46] Vempati and Jones [49-51] observed some weak bands of InCl in the 3900 – 4100Å region. Few attempts were made to present the vibrational scheme of InCl bands by Rao et al., Nampoori et al. and Perumalswamy et al. [48]. The bands attributed to A′ – X system of InCl were later found to be the bands of B,Σ+ –X,Σ+ system of InCl [57]. It is also suspected that the weak bands of InCl around 5530 to 5830 Å region reported by Perumalswamy et al. [48] may belong to a C,Π –X,Σ band system. Similar electronic states were observed in GaCl, GaBr and InBr.
The bands of InCl, especially at 5530 and 5830 Å, which appeared very strong at low pressure (5 to 10 Torr) by Venkatsubramaniam et al. [61] in microwave excitation can not be fitted in vibrational scheme. In GaCl, GaBr, GaI and InBr there is no such transition reported in which A' state is existing. By many workers A' – X transition is assumed to be the cause of reported perturbations [44, 45, 48, and 53] in $A^3\Pi^0 - X^1\Sigma^+$ transition. This issue was taken by Saxena and Deo [70] and therefore the Fourier transform spectrum of InCl molecule, especially of $A^3\Pi^0 - X^1\Sigma^+$ transition was studied. In these studies, Saxena and Deo concluded that there are no such perturbations and they could show the isotopic spectra of In$^{35}$Cl and In$^{37}$Cl.

1.6. Bibliography

Up to 1975 the references on the work on diatomic spectra are given by Huber and Herzberg [71]. Besides this few other bibliographies like Suchard [72], Rosen [73], Pearse and Gaydon [74], Berkeley News Letters and the website developed by Peter Berenath [75] also very useful source.

1.7 Motivation of Present Study

In order to study the intensity distribution in the rotationally resolved spectrum of InCl the present problem was chosen. With an ordinary spectrographs the resolution is not sufficient. But due to Fourier transform spectrometer with an apodized resolution of 0.025 cm$^{-1}$, the rotational lines
show an intensity distribution, which can be measured as an area under the counter and rotational temperature can be calculated. Secondly, the potential energy (PE) curves of different InCl electronic states, with their derived constants could be constructed. In order to compare the PE curves of other mono-halides of In, the ground state PE curves of InF, InBr, and InI could also be constructed.

Also keeping the Cl radical constant BCl, AlCl, and GaCl molecules could be selected for the study of PE curves of their ground states and can be compared with the PE curve of the ground states of InCl. The combined graphs can help to prove the rules obeyed by Reduced Potential Energy Curves (RPC).

The Frank Condon factors of $A^3 \Pi^0 - X^1 \Sigma^+$, $B^3 \Pi_1 - X^1 \Sigma^+$ band systems also could be computed using the derived constants. All these studies form the work plan of the thesis.