CHAPTER 1

MOTIVATION AND STATEMENT OF THE PROBLEM

1.1 Introduction

The pioneering work of Planck, Einstein, de Broglie, Heisenberg, and others finally led to Schrödinger’s discovery of the wave equation in 1926, which today serves not only as the basis for understanding atomic and molecular structure but also as the basis of molecular spectroscopy.

During the last half of the 20th century, the development of both lasers and computers immensely helped to advance the field of molecular spectroscopy.

The commercial availability of Fourier transform spectrometer (FTS), rapidly advanced the field of infrared spectroscopy. Commercial instruments, could cover the entire visible and IR range. During the 20th century, 22 scientists received Nobel Prizes that can be directly or indirectly related to spectroscopy.

As is evident from all of this, spectroscopy is arguably the one most important tool which has taught us the most about the nature of atoms and molecules, much of this coming in the 20th century.

Amazingly, spectroscopy allows us to carry out chemical analysis on objects not just millions of miles away but billions of light years away.
Few concepts capture the imaginations of non-scientists, no less than scientists, than the Big Bang Theory of the origin of our universe which finds its major support in spectroscopic observations such at the (Red) frequency shifts observed for atomic lines in stellar spectra and of course the blackbody contour of the microwave background. Raman spectroscopy seems to have reached a new horizon. Its application now extends over all basic sciences including physics, chemistry, and biology as well as various research fields in industrial, pharmaceutical, medical, and agricultural science and technology.

Recent progress in experimental techniques, the measurement of the finest details of the energy level structure of highly excited Rydberg states of atoms and molecules has become possible. From such measurements, a better understanding of atomic and molecular photoionization can be reached and the role of nuclear spin(s) in atomic and molecular photoionization can be studied for the first time.

Our knowledge of the chemical composition and physical conditions of interstellar clouds is mainly due to high-resolution spectroscopic observations in the cm- and mm-wavelength region.

The development of Fourier transform microwave (FTMW) spectroscopy and - most notably - its combination with supersonic-jet expansion techniques allows for challenging investigations of chemically and physically interesting molecular systems. The combination of Fourier transform MW (FTMW) spectroscopy with supersonic-jet expansions allowed studying the rotational spectra of weakly bound molecular complexes.
New theoretical tools have been developed to fit the spectra and to relate the obtained data to the potential energy functions. Spectroscopy covers a very wide area which has been widened further since the mid-1960s by the development of lasers and such techniques as photoelectron spectroscopy and other closely related spectroscopies. The importance of spectroscopy in the physical and chemical processes going on in planets, stars, comets and the interstellar medium has continued to grow as a result of the use of satellites and the building of radiotelescopes for the microwave and millimetre wave regions.

Spectroscopy is arguably the most fundamental of the experimental physical sciences. After all we obtain most of our knowledge through our eyes and it is via the quest for an in-depth understanding of what light is, and what it can tell us, that all our true understanding of the universe has been obtained.

Answers to questions about light have led to many of our greatest discoveries, not least our present description of the way almost everything works both on a macroscopic and a microscopic scale. In the deceptively simple question “why objects possess colour at all” - such an everyday experience that few think it odd but in it lies the seed for the development of arguably our most profound and far-reaching theory - quantum mechanics.

As we now trek deeper into the twenty-first century, numerous ingenious researchers have resolved many fundamental theoretical spectroscopic problems. Molecular spectroscopy itself has become less of an intrinsic art form, but more of a powerful tool to uncover the ever more fascinating secrets of complex molecular behavior, and has become worthy of fundamental study in its own right.
Most of our notions about structure arise from within the Born–Oppenheimer approximation. The potential energy surfaces that result from this venerable approximation are one of the most useful and ubiquitous paradigms in descriptive chemistry. They give rise to our notions of activation energies and transition states for chemical reactions, force constants to which the strength of various bonds can be related, the equilibrium structure \( \text{re} \). The latter is defined by the geometry that the nuclei adopt when in a minimum.

Photoassociation (PA) of ultracold atoms is a powerful spectroscopic technique that has been used extensively since the advent of laser cooling to make precise measurements of high-lying vibrational levels that are often difficult to access with traditional bound-bound molecular spectroscopy. In addition to improving our knowledge of weakly bound molecular states, PA spectroscopy has also allowed precise determinations of atom-atom scattering lengths and excited atomic state lifetimes. PA resonances have also been used to control atomic interactions via optical Feshbach resonances and for the production of ultracold molecules.

The theoretical study of the properties of atomic and molecular systems involves three steps. Firstly, the Schrödinger Equation \( H \Psi = E \Psi \), must be formulated for the system under study. Next it has to be solved for the family of eigenfunctions and eigenvalues \( E \). Finally the \( \Psi \)'s are used to calculate properties of the system.
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Chapter 2 discusses the potential energy curves in which the review of Rydberg-Klien-Rees (RKR) formalization is taken. The empirical analytical potential energy functions (APEF) are discussed in which Hulbert – Hirschfelder (H-H) and Extended Rydberg (ER) Functions are mentioned but the Extended Lennard-Jones Potential Energy Function (ELJ) is discussed at greater length.

The Near Dissociation Theory (NDT) and its expansion (NDE) are given. The use of Le Roy – Bernstein (LR-B) method in calculation of the physically important quantities in the long range region of the molecular potential energy such as Dissociation energy, vibrational Index at dissociation, the leading dispersion coefficients (van der Waals coefficients), with the Le Roy criterion of validity on such calculations.

Also the calculation of van der Waals coefficients using the static polarizabilities discussed and an example presented for the case of X-state of Beryllium Dimer (Be).

In chapter 3 the new techniques of constructing potential energy curves are explained the Inverted Potential approach (IPA) and Direct-potential-fit (DPF) theories are discussed at length and they applied to different molecules with single minima and double minima. Where DPF models applied mainly to normal molecules with (single minima) and IPA for exotic states with (shelf or double minima).

In chapter 4 the major thrust is on the calculations the Franck-Condon factors (FCF) and r-centroids of few diatomic molecules using recently and available programme. We used 5 different
programmes for these cumbersome calculations and evaluated the FCFs and r-centroids for the molecules CoF, CS, Li₂, VO, CP, HF, LiH, where many of them are having astrophysical significance. The FCFs and r-centroids for all the band systems of CoF are evaluated for the first time. All these details are given in chapter 4 of the thesis with the necessary theory and proper references.

Chapter 5 is on the method of extracting molecular constants using the Parameter-fit models. We discussed some difficulties which came across in using (DPF) results and we presented examples for extracting equilibrium molecular constants from DPF results for many states of different molecules.

In chapter 6, the summary of the work shall be given and the implications of the results obtained in this thesis shall be reviewed. The future scope of the work also will be outlined. Results are discussed at the end of each chapter. Relevant references along with the computer link search digital object identifier (DOI) codes are given at the end of each chapter.