SUMMARY OF FINAL REPORT
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Major Research Project of UGC, New Delhi
F.No.42-792/2013(SR)
In Physics
Entitled

"Spectroscopic investigations, thermodynamic functions and density functional computation of some substituted N-heterocyclic molecules''

The whole work initiated and completed may be divided into following contents

CONTENTS

1. Introduction

The present work is based on spectroscopic investigation of substituted N-heterocyclic molecules. A heterocyclic compound is a class of organic compounds whose molecules contain one or more rings of atoms with at least one atom (the heteroatom) being an element other than carbon, most frequently oxygen, nitrogen, or sulfur. In case of N-heterocyclic molecule an element other than carbon is nitrogen. Heterocyclic derivatives, seen as a group, can be divided into two broad areas: aromatic and non-aromatic. In general, the reactivity of aromatic heterocycles, which is a combination of that expected from an aromatic system combined with the influence of the heteroatoms involved, is usually more complex, while the reactivity of the non-aromatic systems is not too different from the usual non-cyclic derivatives [1]. The present work deals with derivatives of six membered N-heterocyclic molecules such as pyridines, quinolines, isoquinolines, uracils and pyrimidines. The derivatives of these molecules are used due to their variety of applications which is discussed in literature review.

1.1 Literature review

Heterocyclic chemistry deals with heterocyclic compounds which constitute about sixty-five percent of organic chemistry literature [2]. The best known of the simple heterocyclic compounds are pyridine, pyrrole, furan, and thiophene. A molecule of pyridine contains a ring of six atoms-five carbon atoms and one nitrogen atom. Pyrrole, furan, and thiophene molecules each contain five-membered rings, composed of four atoms of carbon and one atom of nitrogen, oxygen, or sulfur, respectively [3]. Today, pyridine and pyrrole are prepared by synthetic reactions. Their chief commercial interest lies in their conversion to other substances, chiefly dyestuffs and drugs. Pyridine is used also as a solvent, a

waterproofing agent, a rubber additive, an alcohol denaturant, and a dyeing adjunct [4].

Heterocyclic compounds are widely distributed in nature and essential to life; they play a vital role in the metabolism of all living cells. Genetic material DNA is also composed of heterocyclic bases-pyrimidines and purines. A large number of heterocyclic compounds, both synthetic and natural, are pharmacologically active and are in clinical use. Heterocyclic compounds have a wide range of application: they are predominant among the type of compounds used as pharmaceuticals [5], as agrochemicals and as veterinary products. They also find applications as sanitizers, developers, antioxidants, as corrosion inhibitors, as copolymers, dyestuff [6].They are used as vehicles in the synthesis of other organic compounds. Some of the natural products e.g. antibiotics such as penicillin's, cephalosporin; alkaloids such as vinblastine, morphine, reserpine etc. have heterocyclic moiety.

One of the reasons for the widespread use heterocyclic compounds is that their structures can be subtly manipulated to achieve a required modification in function. Many heterocycles can be fitted into one of a few broad groups of structures that have overall similarities in their properties but significant variations within the group. Such variations can include differences in acidity or basicity, different polarity [7]. The possible structural variations include the change of one heteroatom for another ring and different positioning of the same heteroatoms within the ring. An important feature of the structure of many heterocyclic compounds is that it is possible to incorporate functional groups either as substituents or as part of the ring itself. For example, basic nitrogen atoms can be incorporated both as amino substituents and as part of a ring. This means that the structures are particularly versatile as a means of providing, or of mimicking a functional group. Heterocyclic compound is also found as a key component in biological processes. For example the nucleic acid bases, which are derivatives of

the purine, namely adenine, guanine and pyrimidine, namely thymine, cystosine as being crucial to the mechanism of replication. Some purine and pyrimidines can act as antibiotics, by interference with DNA synthesis. Puromycin is an example of such an antibiotic. Many of the pharmaceuticals and most of the other heterocyclic compounds with practical applications are nor extracted from natural sources but are synthesized. The origins of organic chemistry do however lie in the study of natural products. These have formed the basis for the design of many of the useful compounds developed subsequently: examples are the early development of vat dyes based on the structure of indigo and the continuing invention of new antibacterial agents based on the β-lactam structure of penicillin. Some examples of drugs having β-lactam moiety are cephalosporin C**,** amoxicillin, clavuanic acid, penicillin etc.

Some of the biological properties of some heterocyclic compunds, known in literature are summarized as; Anticancer, anti-HIV and antimicrobial [8], Genotoxic active agent [9], Antiviral agents targeting virus proteins[10], COX-2 inhibitors and anti-inflammatory [11], Antitumor activity [12], Anti-oxidant and cytotoxic activity [13], Anticancer agents [14]. Bruno Dominelli et.al. offers an update on phosphine and NHC ligands used in gold complexes with potential anti-cancer, anti-bacterial, anti-parasitic (malaria, leishmaniasis and trypanosomasis) and anti-viral (HIV-1) activity [15].

In view of the importance of the derivatives of N-Heterocyclic compounds in various applications, a combined theoretical and experimental study has been done on selected compounds which have not been reported earlier.

2. Spectroscopic techniques used

Molecular spectroscopy is a means of probing molecules and most often involves the absorption of electromagnetic radiation. The absorbed electromagnetic radiation results in transitions between eigenstates of a molecule. The type of

eigenstates involved in a transition depends on the energy of the radiation absorbed. Figure 2.1 shows an electromagnetic spectrum along with the relative energies, wavelengths, and frequencies associated with each type of radiation. Absorbed ultraviolet and visible radiation generally results in transitions amongst electronic eigenstates. Absorbed infrared radiation results in changes in vibrational and rotational eigenstates. Absorbed microwave radiation results in changes in rotational eigenstates. The specific wavelengths of radiation that are absorbed in each region of the electromagnetic spectrum depend on the energy difference between the eigenstates of a molecule.

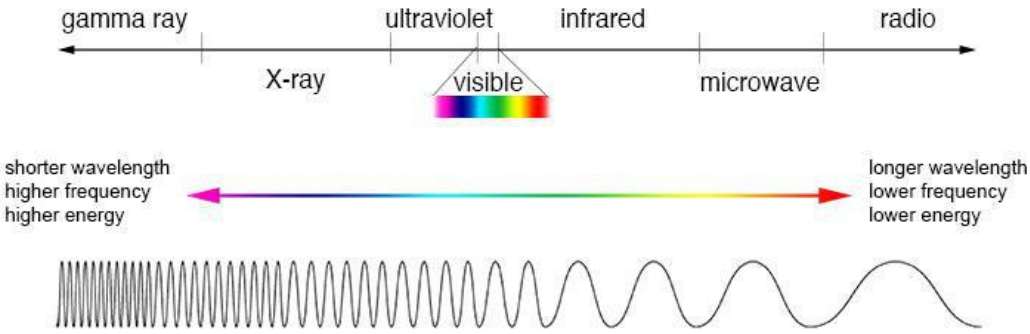

Figure 2.1 The following electromagnetic spectrum indicates the regions used for ultraviolet/visible and infrared absorption spectroscopy.

The types of spectroscopy used in the present study are described below:

2.1 Vibrational Spectroscopy

Vibrational spectroscopy has been used to make significant contributions in many areas of physics and chemistry as well as in other areas of science. Its main applications are to study the intra molecular forces, degree of association in condensed phases and in the determination of molecular symmetries. Other applications include the, identification of functional groups or compound identification, determination of the strength of chemical bond and the calculation of thermodynamic properties.

Modern methods of spectroscopy, in the different regions of electromagnetic spectrum have provided indispensable tools for the investigation of molecular structure. Among which, vibrational spectroscopy is undoubtedly the most powerful physical technique for the elucidation of molecular structure. The vibrational spectrum depends on the intensity radiation absorbed or scattered by a given substance. Due to the complementary nature of infrared Raman spectroscopy, it is interesting to compare the two techniques for studying the vibrational and rotational energies of molecule [16-20]. Vibrational spectroscopy is divided into Infrared and Raman spectroscopy.

2.1.1 Infrared Spectroscopy

The IR region is divided into three regions: the near, mid, and far IR as shown in Fig.2.2. The spectral range for IR spectra used by most physicists is approximately 4000 - 400 cm^{-1}. This range is now called the mid-IR and because it contains the fundamental vibrational modes is most useful for qualitative purposes, but is also much used for quantitative analysis. This is the region of wavelengths between 3 x 10^{-4} and 3 x 10^{-3} cm. Physicists prefer to work with numbers which are easy to write, therefore IR spectra are sometimes reported in μm. Infrared spectroscopy is the measurement of the wavelength and intensity of the absorption of mid-infrared light by a sample. Mid-infrared is energetic enough to excite molecular vibrations to higher energy levels. The wavelength of infrared absorption bands is characteristic of specific types of chemical bonds, and infrared spectroscopy finds its greatest utility for identification of organic and organometallic molecules. The high selectivity of the method makes the estimation of an analyte in a complex matrix possible. The far infrared, approximately 400-33 cm^{-1}, lying adjacent to the microwave region has low energy and is used for

rotational spectroscopy. The mid-infrared, approximately 4000-400 cm^{-1} and is used to the fundamental rotational-vibrational structure. The higher energy near-IR, approximately 12820-4000 cm^{-1} can excite overtone or harmonic vibrations. Like radiant energy the energy of a molecule is quantized too and a molecule can exist only in certain discrete energy levels. Within an electronic energy level a molecule has many vibrational energy levels.

To raise the electronic energy state of a molecule from the ground state to the excited state will cost more energy than to raise the vibrational energy state [21-23]. For some years now, mid-IR spectrometers have been based on an interferometer that produces an interferogram of the sample from which the absorbance spectrum can be calculated. These spectrometers are known as Fourier transform infrared (FTIR) spectrometers. The FTIR approach has a number of advantages in terms of speed, accuracy, reproducibility and sensitivity.

Molecular vibrational frequencies lie in the IR region of the electromagnetic spectrum and they can be measured using the IR technique. In IR, light having different frequencies is passed through a sample and the intensity of

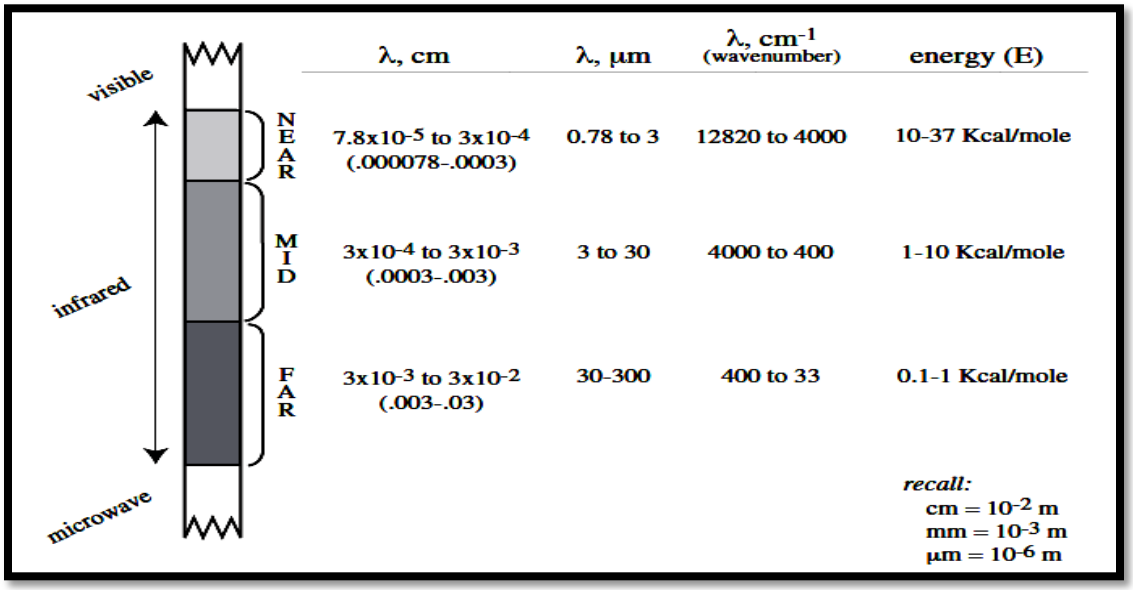

Figure 2.2 IR region.

the transmitted light is measured at each frequency. When molecules absorb IR radiation, transitions occur from a ground vibrational state to an excited vibrational state [23] . In order for a molecule to be IR active there must be a change in dipole moment as a result of the vibration that occurs when IR radiation is absorbed.

2.1.2 Raman Spectroscopy

Raman effect depends upon the polarizability of the molecule, it can be observed for molecules which have no net dipole moment and therefore produce no pure rotational spectrum. This process can yield information about the moment of inertia and hence the structure of the molecule. It is a technique, which explores energy levels of molecules by the scattering of light. Photons of frequency ν_0 are scattered by collision with the molecules of the sample, when new frequencies are added, because photons can acquire or lose energy during collision. If the molecules are excited by light during the collision, molecules withdraw some energy from the photons and so scattered light emerges with a lower frequency ($\nu_0 - \nu_k$). If the molecules are already excited before the photons collide with them, molecules may be able to give up this energy and the emerging photons will have higher frequency, viz. ($\nu_0 + \nu_k$). Raman spectroscopy has recently undergone considerable development because of the availability of lasers, which are so intense that those small samples, and shorter exposures give very good spectra. Further, lasers are associated with very strong electric field, which has shown that scattering is non-linear in nature. Raman spectroscopy differs principally from IR spectroscopy in that it is based on the scattering of photons by molecules rather than on the absorption of photons Fig. 1.3. This six Energy diagram representing the elastic Rayleigh scattering (centre) and the inelastic anti-Stokes (left) and Stokes (right) Raman scattering with ν_0, ν_R, and ν_k referring to the frequencies of

the incident light, the Raman scattered light, and the molecular vibration, respectively. Scattering that leaves the frequency of the incident light unchanged is referred to as elastic or Rayleigh scattering whereas the frequency-shifted (inelastic) scattering is referred to as Raman scattering Fig. 2.3.

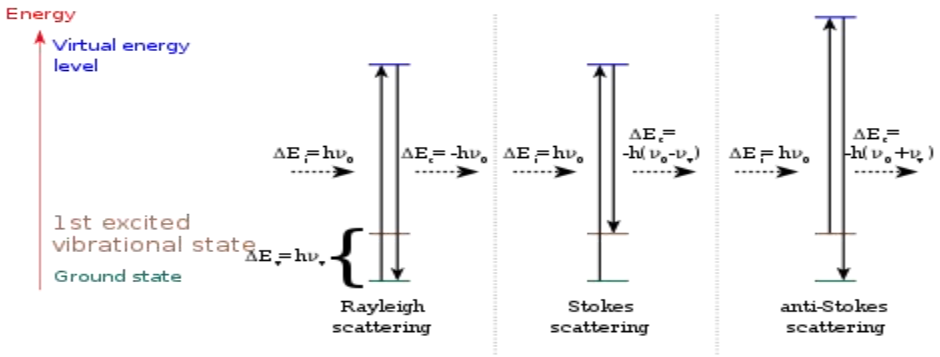

Figure 2.3 Stokes and anti stokes lines in Raman spectra.

When the frequency of the scattered light is lower than ν_0, the molecule remains in a higher vibrationally excited state (m > n for the transition n→m). This process is denoted as Stokes scattering whereas anti-Stokes scattering refers to (ν_0 + ν_k). At ambient temperature, thermal energy is lower than the energies of most of the normal modes, such that molecules predominantly exists in the vibrational ground state and Stokes scattering represents the most important case of Raman scattering [24-26]. Fig.2.4 shows a Schematic Raman spectrum.

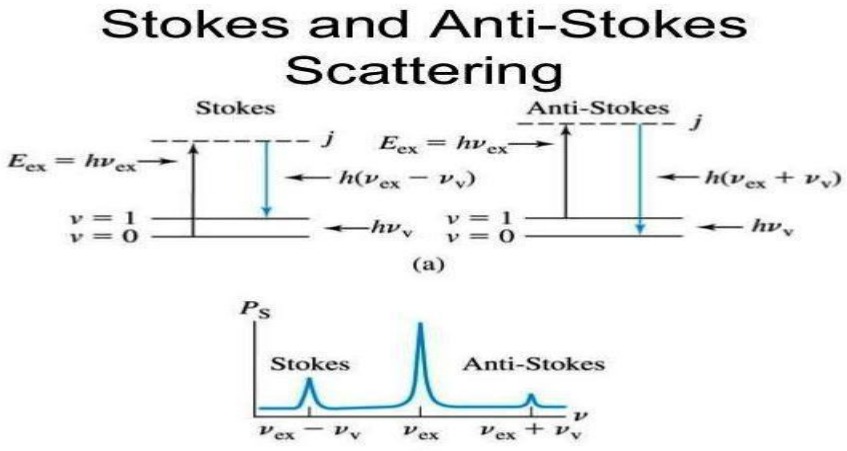

Figure 2.4 Schematic Raman spectrum

2.1.3 Molecular Vibrations

In order to understand IR spectroscopy, we must first consider the motion of atoms in molecules. Atoms in a molecule do not maintain fixed positions with respect to each other, but actually vibrate back and forth about an average value of inter atomic distance with a certain frequency. Organic molecules absorb infrared radiation when the frequency of IR radiation is synchronized with a natural vibration frequency of the molecule. When IR radiation is absorbed, the molecule begins to vibrate with a greater amplitude (but with the same frequency), and thus the molecule has gained energy. The interactions of infrared radiation with matter may be understood in terms of changes in molecular dipoles associated with vibrations and rotations. In order to begin with a basic model, a molecule can be looked upon as a system of masses joined by bonds with spring-like properties.

Taking first the simple case of diatomic molecules, such molecules have three degrees of translational freedom and two degrees of rotational freedom. The atoms in the molecules can also move relative to one other, that is, bond lengths can vary or one atom can move out of its present plane. This is a description of stretching and bending movements that are collectively referred to as vibrations. For a diatomic molecule, only one vibration that corresponds to the stretching and compression of the bond is possible [27,28]. In the cartesian coordinate system, each atom can be displaced in the x, y and z-directions, corresponding to three degrees of freedom. Thus, a molecule of N atoms has in total 3N degrees of freedom, but not all of them correspond to vibrational degrees of freedom. If all atoms are displaced in the x, y and z-directions by the same increments, the entire molecule moves in a certain direction, representing one of the three translational degrees of freedom. Furthermore, one can imagine displacements of the atoms that correspond to the rotation of the molecule. It can easily be seen that a nonlinear

molecule has three rotational degrees of freedom, whereas there are only two for a linear molecule. Thus, the remaining 3N - 6 and 3N - 5 degrees of freedom correspond to the vibrations of a nonlinear and a linear molecule, respectively. For the treatment of molecular vibrations in terms of Cartesian coordinates, the rotational and translational degrees of freedom can be separated by choosing a rotating coordinate system with its origin in the centre of mass of the molecule. The degrees of freedom for polyatomic molecules are summarized in Table 2.1.

Table 2.1: Degrees of freedom for polyatomic molecules

Type of degrees of freedom	Linear	Non-linear
Translational	3	3
Rotational	2	3
Vibrational	3N-5	3N-6
Total	3N	3N

2.1.4 Types of Molecular Vibrations

Diatomic molecule has only one mode of vibration which corresponds to a stretching motion, a non-linear B–A–B type triatomic molecule has three modes, two of which correspond to stretching motions, with the remainder corresponding to a bending motion. A linear type triatomic has four modes, two of which have the same frequency, and are said to be degenerate. According to the character of vibration, normal vibrations can be divided into principal groups.

- **Stretching or bonding vibrations:** A rhythmical movement along the bond axis such that the interatomic distance is increasing or decreasing periodically . As this type of vibrations corresponds to one dimensional motion, it means that there will be (n-1) stretching vibrations for non-cyclic system. During stretching vibrations, bond angles change only if it is required to do so by the centre of gravity resisting displacement.

- **Bending or deformation vibrations:** Alter the bond angles, while the bond lengths remain unchanged i.e a change in bond angle between bonds with a common atom or the movement of a group of atoms with respect to the remainder of the molecule without movement of the atoms in the group with respect to one another. As these vibrations are describing two dimensional motions, there will be (2n-5) bending vibrations for non-cyclic and linear molecules. These appear at lower frequency, whereas stretching vibrations at higher frequencies. The force constants of deformation vibrations are generally less than those of stretching vibrations. Due to the smaller force constants, the deformation vibrations are more sensitive to environmental influence. In a polyatomic molecule, the same bond can perform stretching and deformation vibration simultaneously. Stretching vibrations are of two types**:** symmetric and asymmetric stretching. Deformation vibrations are of two types: in plane deformation and out of plane deformation. In plane deformation vibration includes scissoring and rocking vibrations . Out of plane deformation include twisting and wagging vibrations [28-29].

2.2 Electronic Spectroscopy

The absorption of light is familiar to everyone. The absorption of visible light is what makes things colored. To understand why some compounds are colored and other are not and to determine the relationship of conjugation to color, we must understand electronic spectroscopy. The wavelength of light that a compound will absorb is characteristic of its chemical structure. Specific regions of the electromagnetic spectrum are absorbed by exciting specific types of molecular and atomic motion to higher energy levels. Absorption of microwave radiation is generally due to excitation of molecular rotational motion. Absorption of visible

and ultraviolet (UV) radiation is associated with excitation of electrons, in both atoms and molecules, to higher energy states.

There are many compounds that absorb visible (380-780 nanometers) or ultraviolet (UV) light (10–380 nanometers). The most commonly used part of the UV spectrum is from 200 – 380 nanometers (nm) because below about 200 nm, air absorbs the UV light and instruments must be operated under a vacuum. Many solvents also absorb radiation at the shorter wavelengths of UV light.

2.2.1 Electronic Transitions

Electronic levels in molecules are separated by much greater energy intervals than the vibrational levels, and the spectra originating in transitions from the ground to excited electronics levels occur mainly in the visible and ultraviolet region. The absorption of the light energy by organic compounds in the visible and ultraviolet region involves promotion of electron in σ, π and n-orbitals from the ground to higher energy states [30]. These higher energy states are described by molecular orbitals called as antibonding orbitals. The possible types of electronic transition are

$$n\rightarrow\sigma^*,\ n\rightarrow\pi^* \text{ and } \pi\rightarrow\pi^*,\ \sigma\rightarrow\sigma^*,$$

(where σ^*, π^* are antibonding orbitals). Transitions to antibonding π^* orbitals are associated only with unsaturated centres in the molecule. The energy of the above transitions are in the following order :

$$\sigma\rightarrow\sigma^* > n\rightarrow\sigma^* > \pi\rightarrow\pi^* > n\rightarrow\pi^*$$

The electronic transitions associated with these energy states is depicted in Fig. 1.5. The highest energy transition $\sigma\rightarrow\sigma^*$ (bonding $\rightarrow$ antibonding) generally requires wavelengths below 200 nm and therefore are not seen in typical UV

spectra. The non-bonding → antibonding n→π* transitions, and bonding → antibonding π→π* transitions commonly take place in the useful 200 –700 nm range. In general, bonding π orbitals have higher energies than bonding σ orbitals, and antibonding π orbitals (π* orbitals) have lower energies than antibonding σ orbitals (σ* orbitals). The absorption due to electronic transitions from boning σ orbitals to antibonding σ orbitals (σ-σ* transitions) usually occur in the far ultraviolet region, and the absorption due to electronic transitions from bonding π orbitals to antibonding π orbitals (π-π* transitions) usually occur at longer wavelengths, mostly in the near ultraviolet and visible region.

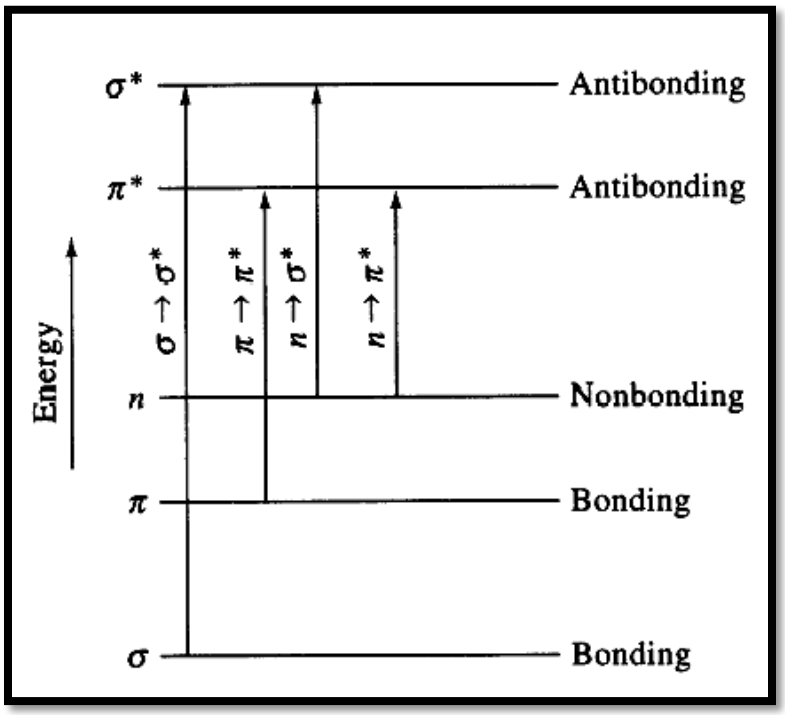

Figure 1.5 Electronic transitions.

In compounds having nonbonding lone-pair electrons, the nonbonding orbital (n orbital) may have a higher energy than bonding π orbitals. The absorption bands arising from electronic transitions from nonbonding n orbitals to antibonding π orbitals (n-π* transitions) usually occur in the near ultraviolet and

visible region. Some of absorption bands due to electronic transitions from nonbonding orbitals to antibonding σ orbitals (n-σ* transitions) occur at about 200mμ or longer wavelengths [31,32]. The σ orbitals are to a first approximation considered to be localized on the respective bonds, and hence the σ-σ* transitions are not characteristic of the overall structure of the molecule, but are rather properties of the respective bonds. On the other hand, the π orbitals are delocalized over the whole conjugated system of the molecule, and hence electronic transitions involving π orbitals, that is, π-π* and n-π* transitions, are characteristic of the whole conjugated system.

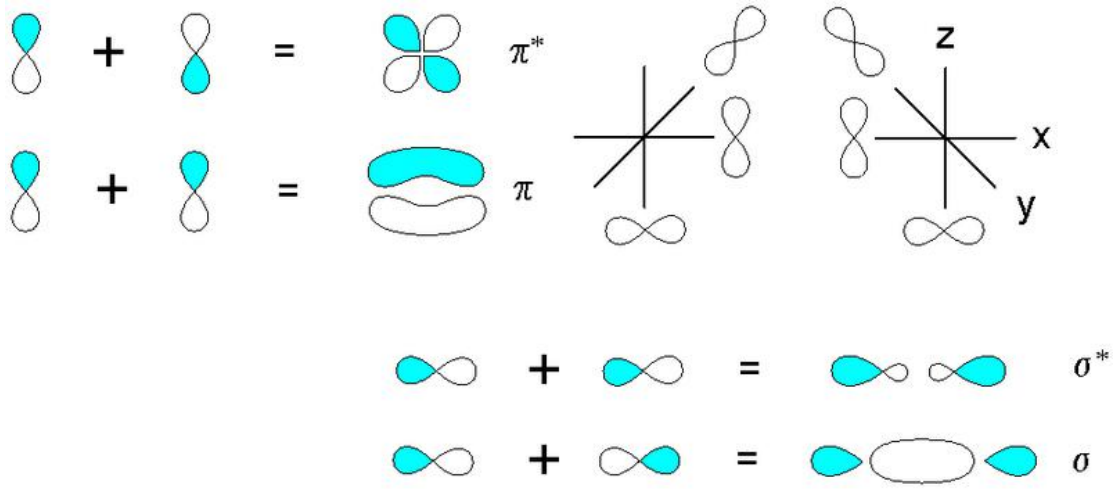

Figure 1.6 Bonding and antibonding orbitals**.**

In addition, while the σ orbitals are not affected by twist of the bonds, the π orbitals, and hence the transitions involving π orbitals, are sensitive to changes in the geometry of the conjugated system, such as twist of bonds. For these reasons, the discussion is confined to the absorption bands due to transitions involving π orbitals in unsaturated, especially conjugated compounds. Shape of different bonding and antibonding orbitals as shown in Fig.1.6.

In practice it is found that the ultraviolet and visible spectrum of most molecules consists of a few humps rather than sharp lines. These humps show than the molecule is absorbing radiation over a band of wavelengths. One reason for this band, rather than line absorption is that an electronic level transition is usually accompanied by a simultaneous change between the more numerous vibrational levels. Thus, a photon with a little too much or too little energy to be accepted by the molecule for a 'pure' electronic transition can be utilized for a transition between one of the vibrational levels associated with the lower electronic state to one of the vibrational levels of a higher electronic state.

2.2.2 Chromophores

A chromophore (literally color-bearing) group is a functional group, not conjugated with another group, which exhibits a characteristic absorption spectrum in the ultraviolet or visible region. Some of the more important chromophoric groups are : nitro, nitroso, azo, azo-amino, carbonyl etc. If any of the simple chromophores is conjugated with another (of the same type or different type) a multiple chromophore is formed having a new absorption band which is more intense and at a longer wavelength that the strong bands of the simple chromophores [32]. This displacement of an absorption maximum towards a longer wavelength (i.e. from blue to red) is termed a bathochromic shift. The displacement of an absorption maximum from the red to ultraviolet is termed a hypsochromic shift.

Substituents may have any of four effects on a chromophore (Fig.1.7).

- Bathochromic shift (red shift) – a shift to longer l; lower energy
- Hypsochromic shift (blue shift) – shift to shorter l; higher energy
- Hyperchromic effect – an increase in intensity

- Hypochromic effect – a decrease in intensity

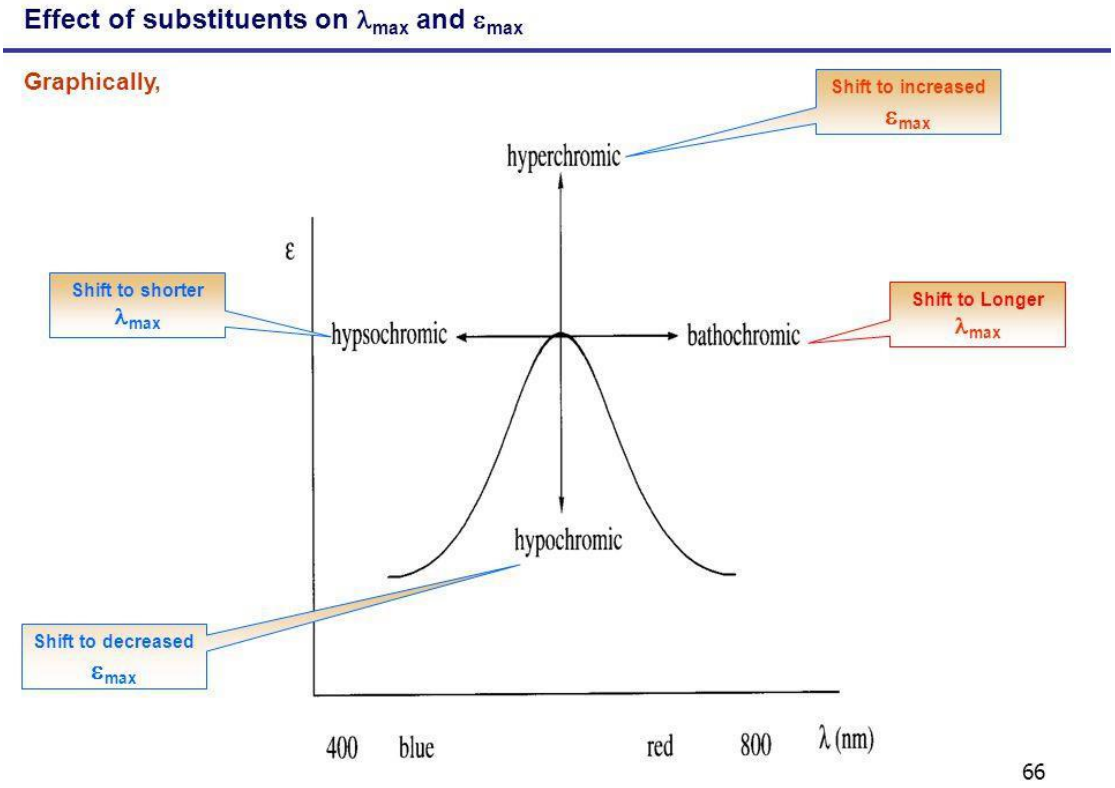

Figure 1.7 Four effects on a chromophore.

3. Computational technique employed

Computational physics is an area of theoretical physics whose focus is the use and development of efficient mathematical approximations and computer programs to obtain results relative to chemical problems. Examples of properties that can be calculated include total energies, molecular geometries, dipole and quadrupole moments, vibrational frequencies, reaction cross-sections, thermochemical data and diverse spectroscopic quantities. Computational quantum physics uses mathematical equations and approximations derived from quantum mechanics. Its necessity arises from the well-known fact that apart from relatively recent results concerning the hydrogen molecular ion , the quantum n-body

problem cannot be solved analytically, much less in closed form. While its results normally complement the information obtained by chemical experiments, it can in some cases predict hitherto unobserved chemical phenomena. It is widely used in the design of new drugs and materials. The field of computational physics helps to explore things that would otherwise be difficult or costly to find because of the tiny nature of molecules, atoms, and nanoparticles. Most of the field is based upon the Schrodinger equation, which models atoms and molecules using mathematics. Computational physicists often attempt to solve the non-relativistic Schrodinger equation with relativistic corrections added, although some progress has been made in solving the fully relativistic Schrodinger equation. It is, in principle, possible to solve the Schrodinger equation, in either its time-dependent form or time-independent form as appropriate for the problem in hand, but this in practice is not possible except for very small systems. Schrodinger's equation is the basis of computational physics, if it could be solved all electronic information for a molecule would be known. Since Schrodinger's equations cannot be completely solved for molecules with more than a few atoms, computers are used to solve approximations of the Schrodinger's equation. While its results normally complement the information obtained by chemical experiments, it can in some cases predict hitherto unobserved chemical phenomena. It is widely used in the design of new drugs and materials. The method employed covers both static and dynamic situations. In all cases the computer time and other resources increase rapidly with the size of the system being studied. That system can be a single molecule, a group of molecules, or a solid.

In theoretical physics, physicists develop algorithms and computer programs to predict atomic and molecular properties and reaction paths for chemical reactions. Computational physicists, in contrast, may simply apply existing

computer programs and methodologies to specific chemical questions [50-52]. There are two different aspects to computational analysis:

- Computational studies can be carried out in order to find a starting point for a laboratory synthesis, or to assist in understanding experimental data, such as the position and source of spectroscopic peaks.
- Computational studies can be used to predict the possibility of so far entirely unknown molecules or to explore reaction mechanisms that are not readily studied by experimental means.

The computational physics process begins by looking at a theory, such as the electronic structure theory. This helps to determine the motion of the electrons within a molecule. At this point, using mathematical equations, a basis set can be determined based upon the calculations. This information can be inputted into computer software to describe such things as the wave function, which can be used to create models of other physical characteristics of the molecule. Physicists can see a model of the orbitals of the molecule, begin predicting experimental structures, and look at the energy of the molecule. Therefore, a great number of approximate methods strive to achieve the best trade-off between accuracy and computational cost [53-56].

3.1 Density Functional Theory

Density functional theory (DFT) methods are often considered to be Ab initio methods for determining the molecular electronic structure, even though many of the most common functionals use parameters derived from empirical data, or from more complex calculations. This means that they could also be called semi-empirical methods. It is best to treat them as a class on their own. DFT has big popularity as a cost effective general procedure for studying the physical

properties of molecules. In DFT, the total energy is expressed in terms of the total electron density rather than the wave function. In this type of calculation, there is an approximate Hamiltonian and an approximate expression for the total electron density. DFT methods can be very accurate for little computational cost. The drawback is, that unlike Ab initio methods, there is no systematic way to improve the methods by improving the form of the functional. Methods in DFT are complicated and diverse but can roughly divide into three classes:

- **Local density approximation (LDA):** It is a fastest method, gives less accurate geometry, but provides good band structures. The LDA is determined solely based on the properties of electron density. The critical assumption of approximation is that, for a molecule with many electrons in a gaseous state, the density is uniform throughout the molecule.
- **Gradient corrected:** It gives more accurate geometries. In this method electron density calculations combine with gradient correction factor. A gradient in mathematics is a function that measures the rate of change of some property.
- **Hybrids (which are a combination of DFT and HF methods):** It also gives more accurate geometries. Methods that are combination of a Hartee-Fock approximation to the exchange energy and a DFT approximation to the exchange energy, all combined with a functional that includes electron correlation. These methods are known as hybrid methods, and are currently the most common and popular method used in practice [59-60].

Density-functional theory can be implemented in many ways. The minimization of an explicit energy functional, discussed up to this point, is not normally the most efficient among them. Much more widely used is the Kohn-Sham approach. The Kohn-Sham approach to Density function Theory allows an

exact description of the interacting many-particle systems in terms of an effective non-interacting particle system. The effective potential in this non-interacting particle system can be shown to be completely determined by the electron density of the interacting system, and is for the reason called a density functional. Interestingly, this approach owes its success and popularity partly to the fact that it does not exclusively work in terms of the particle (or charge) density, but brings a special kind of wave functions (single-particle orbitals) back into the game. As a consequence DFT then looks formally like a single particle theory, although many body effects are still included via the so called exchange-correlation functional [61-62] .

3.2 Basis Sets

The first step in any theoretical calculation of atoms and molecules is the determination of atomic and molecular wave functions, which are usually built up from a set of one-electron one-center functions. The major requirement is that the set has a size that the functions were either a good representation or able to be adjusted to be a good representation of the final function, at least in the most significant regions. The basis set is fixed in a semi empirical way by calibrating calculations on a variety of molecules. A sequence of calculations with improving basis sets is applied to one molecule until the convergence is reached. The error in the calculation is estimated from the sensitivity of the results to further refinements in the basis sets. The existence of such a vast multitude of basis sets is attributable, at least in part, to the difficulty of finding a single set of functions. The basis set should be flexible enough to produce good results over a wide range of molecular geometries and sufficiently small so that the problem is computationally easy and economically reasonable. The truncation of the basis set is an important source of

error in molecular electronic structure calculations. The accuracy of a computational calculation is dependent on both the model and the type of basis set applied to it.

General expression for a basis function = $N * e^{(-\alpha * r)}$

Where, N is the normalization constant, α is the orbital exponent, and r is the radius of the orbital in angstroms. Some common examples of basis sets are:

- The simplest basis sets is STO-3G, an acronym for Slater-Type-Orbitals simulated by 3 Gaussians added together. It is known as a minimal basis set, meaning that it has only as many orbitals as are needed to accommodate the electrons of the neutral atoms and retain spherical symmetry. Thus, STO-3G has only one basis function per hydrogen, five per atom from Li to Ne (1s, 2s, $2p_x$, $2p_y$, and $2p_z$), and nine for the second row elements Na - Ar (1s, 2s, $2p_x$, $2p_y$, $2p_z$, 3s, $3p_x$, $3p_y$, $3p_z$).

- Split valence basis sets use two functions to describe different sizes of the same orbitals. They allow for size variations that occur in bonding.
  Double split valence basis sets: 3-21G, 6-31G.
  Triple split valence basis sets: 6-311G
- Polarized basis sets have higher angular momentum than the occupied AOs. They allow for anisotropic variations that occur in bonding . 6-31G(d) or 6-31G* include d functions on the heavy atoms (non-hydrogen) and 6-31G(d; p) or 6-31G** include d functions on heavy atoms and p functions on hydrogen atoms .
- Diffuse basis functions are additional functions with small exponents, and are therefore have large spatial extent. They allow for accurate modelling of systems with weakly bound electrons, such as: Anions, Excited states. A set

of diffuse functions usually includes a diffuse s orbital and a set of diffuse p orbitals with the same exponent. Examples include 6-31+G which has diffuse functions on the heavy atoms and 6-31++G which has diffuse functions on hydrogen atoms as well.For the theoretical calculation the well known methods are HF and density functional theory [57-60,63].

4. Parameters calculated

In the present study, various parameters are calculated experimentally and theoretically as explained below.

4.1 Biological Study

FUNGI are heterotrophic micro-organism. Fungi cause various diseases in plants, animals and human beings. They are both destructive and beneficial. On one hand, they destroy food, fabrics, leather and other consumer goods manufactured from materials subject to fungal attack, on the other hand they cooperate in the manufacturing of a large number of useful products. In agriculture too, they may damage the crop on one hand, or else increase fertility of the soil by releasing plant nutrient in a form available to the green plants.

Fungal toxins are very widely distributed in nature causing a wide range of effects on living beings, some of these being very harmful. The fungal toxins affecting the plants are of the following two types :

(a) Host-specific Toxins or Pathotoxins : These are highly specific in nature, mimic all function of the producing fungal strains and on susceptible host varieties. They cause all such metabolic, functional and structural changes which are induced by the producing fungal strain.

(b) Non-Specific Toxins : They may not be needed for causing pathogenicity but are required for virulence.

Host specific toxins are mainly produced by the species of Aspergillusflavus, Aspergillusniger, Aspergillusfumigatus and Rizopus. These toxins may be teratogenic, mutagenic and carcinogenic and are called ‘Mycotoxins’. Since a large number of mycotoxins are elaborated on food materials, it is essential that they are regularly checked to ensure that they are free of mycotoxins.

The chemicals used to kill the fungi are known as ‘fungicides’ or ‘antifungal substances’ and their activity is termed as ‘fungicidal activity’ or ‘antifungal activity’. In fact, the term fungicides describes those chemicals which have the ability actual or potential, to control the damages , caused by fungi. Literally speaking, a fungicide would be any agency which has the ability to kill a fungus a temporarily inhibit its growth thus preventing the damage caused by them to the growing crops and their products. A variety of both inorganic and organic compounds have been reported to possess antifungal properties. In earlier days, the inorganic salts were the main fungicides. Later, host of organic fungicides were developed which proved far more effective than the inorganic salts. The year 1934 is regarded as the opening era or organic fungicides introducing dithiocabamates. Since then, the organic fungicides have assumed increasing importance in fungicides usage. They offer the advantage of a greater specificity of action and in many instances, lower toxicity to other form of life.

The possibility of designing organic molecules with superior fungi toxicity, greater margin of safety for use on crops and less hazards led to the rapid preliminary evaluation of a large number of compounds.

The structures carrying one or more acyl residues on shot alkyl chain bearing amino groups are well known for their biological activities. Various heterocyclic compounds like imidazoline, thiazoline oxathiadiazoles and

thiazolidione, condensed oxazoles, substituted iso-oxazolines, thiazoles and a few 2-amino thiazoles have been found to possess good fungicidal activity. The pyridine and their derivatives are reportedly of immense medicinal and physiological importance. Thio-pyridines have reportedly been used in the treatment of tuberculosis, Leprosy and mental disorders. They are also known to act as herbicides, insecticides, redentricides and plant growth regulators. These have been reported to be the precursors of antidiabetic agent. Variation of the substituents may bring characteristic biological activity in the substrate. Thus introduction of hydroxyl group in the aryl substance brings, antiseptic and germicidal properties to the compound while the electron donor substituents such as hydroxyl or fluoro at ortho-position in the ring renders the compound to have better activity than the meta and para-analogus. Substitution of electron attracting group as well as methoxy group on phenyl ring at the ortho position generally increases the antibacterial activity.

Thus, it is obvious that aromatic and N-heteroaromatic compound and their derivatives play a vital role in antimicrobial functions in the biological systems and for this purpose knowledge of their structural activity relationship is to be probed.

4.2 Thermodynamic Functions

Once the vibrational frequencies of a molecule are obtained from the vibrational spectra , it is possible to predict with great precision the values of thermodynamic function [64-68]. The spectroscopically measured frequencies and the moment of inertia are important variables in determining the thermodynamic functions of molecule. This possibility is of great practical

importance, particularly since the direct experimental measurement of these quantities is usually tedious and difficult.

In physics, a partition function describes the statistical properties of a system in thermodynamic equilibrium. They are functions of temperature and other parameters, such as the volume enclosing a gas. Most of the aggregate thermodynamic variables of the system, such as the total energy, free energy, entropy, and pressure, can be expressed in terms of the partition function or its derivatives.

There are actually several different types of partition functions, each corresponding to different types of statistical ensemble. The canonical partition function applies to a canonical ensemble, in which the system is allowed to exchange heat with the environment at fixed temperature, volume, and number of particles. The grand canonical partition function applies to a grand canonical ensemble, in which the system can exchange both heat and particles with the environment, at fixed temperature, volume, and chemical potential. Other types of partition functions can be defined for different circumstances.

Partition function of a molecular system contains all the relevant information of that system [69,70]. It is approximately equal to number of quantum states having energies below the thermal energy available to the molecule in given volume. If the various forms of energy of a molecule may be regarded as completely separable from one another, which is probably justifiable, at least as far as electronic, translational and combined rotational and vibrational energies are concerned, it is possible to write the total energy of the molecule as,

$$E = E_e + E_t + E_r + E_v \qquad \text{..... (4.1)}$$

Where e stands for electronic, t for translational, r for rotational and v for vibrational respectively.

According to Maxwell- distribution law, the number of molecules N having energy is

$$N_i = N_0 e^{-E_i/kT} \qquad \text{..... (4.2)}$$

Where k, known as Boltzmann constant, is equal to molar gas constant R divided by the Avogadro number. N_0 is the number of molecules in this lowest energy state, and N_i is the number in the level in which the energy is E_i.

Although the law was derived from classical mechanics, it has been found that, at all temperatures above the lowest, quantum considerations lead to a result which is almost identical with that given by above equation. One modification is however, necessary: this is the introduction of a statistical weight factor g_i representing the number of possible quantum states having the same, or almost the same, energy E_i. The appropriate form of the energy distribution law is then

$$N_i = \frac{N}{Q} g_i e^{-E_i/kT} \qquad \text{.....(4.3)}$$

Where T is absolute temperature, g_i is the statistical weight and Q is the partition function of the gas given by

$$Q = \sum_i g_i e^{-E_i/kT} \qquad \text{.....(4.4)}$$

All the thermodynamical functions can be expressed in terms of Partition function.

By the help of partition function the various parameters can be calculated by density functional theory using Gaussian software. The calculated parameters at

various basis sets are Heat capacity, Enthalpy, Entropy, Dipole moment, Thermal energy, Vibrational energy and rotational constant.

4.3 Molecular Polarizability

One of the fundamental electrical properties of a molecule is its molecular polarizability. It cannot be measured directly, but can be deducted from the measurement of some bulk macroscopic properties, such as dielectric constant, dipole moment and index of refraction. Polarizability allows us to better understand the interactions between nonpolar atoms and molecules and other electrically charged species, such as ions or polar molecules with dipole moments. Molecular polarizability of a molecule characterizes the capability of its electronic system to be distorted by the external field, and it plays an important role in modeling many molecular properties and biological activities [76].

4.3.1 Computational Polarizability

Two basic lines in the development and application of additive schemes for calculation of polarizability have evolved [72]. In the first case, the dependence of the polarizability parameters of atoms and bonds on their environment leads to additive schemes, which assign specific values to atoms in various valence states and to various types of bonds. Typically, the developed parameter sets take into account the character of substituents at neighbouring atoms. The approach produces a set of polarizability parameters for each fragment, and allows for calculation of average polarizability and its anisotropy in large structural units, automatically including internal interactions within such units. The second direction accepts a relatively narrow additivity scheme and considers deviations from this scheme as manifestation of intramolecular interactions. In this case,

molecular polarizability ellipsoid consists of atomic and bond contributions and, separately, contributions resulting from intramolecular interactions. The polarizability and first order hyperpolarizability of a molecule can be obtained from a Taylor expansion of the energy U about the electric field strength E [73] , the charge density and hence the energy of the system will be changed. The polarizability of a molecule can be obtained from a Taylor expansion of the energy U about the electric field strength E, (i, j and k run over cartesian components, i.e. x, y and z):

$$U = U_0 - \sum_i \mu_i E_i - 1/2 \sum_i \sum_j \alpha_{ij} E_i E_j - 1/6 \sum_i \sum_j \sum_k \beta_{ijk} E_i E_j E_k + \ldots \quad ..(4.1)$$

where U_0 is the energy of the unperturbed molecule; E_i is component of the field in the i direction, μ_i , α_{ij} and β_{ijk} are the components of dipole moment, polarizability and the first order hyperpolarizabilities, respectively. The 27 components of first order hyperpolarizability can be reduced to 10 components due to the Kleinman symmetry [74]. The total static dipole moment μ, mean polarizability $<\alpha>$, anisotropy of the polarizability Δα and total first order hyperpolarizability β_{total} using x, y, z components can be defined as:

$$\mu = (\mu^2_x + \mu^2_y + \mu^2_z)^{1/2} \quad \ldots\ldots\ldots(4.2)$$

$$<\alpha> = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/ 3 \quad \ldots\ldots\ldots(4.3)$$

$$\Delta\alpha = \{1/2 [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6 \alpha_{xx}^2]\}^{1/2} \quad \ldots. \ldots(4.4)$$

$$\beta_{total} = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{xxy} + \beta_{yzz})^2 + (\beta_{zzz} + \beta_{xxz} + \beta_{yyz})^2]^{1/2} \quad \ldots\ldots(4.5)$$

The mean molecular polarizability and total first order hyperpolarizability β_{total} were obtained through the knowledge of above mentioned quantities and with the help of equation (4.3) and (4.5). The molecular structural data, employed in the present computation are taken from the DFT calculations.

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6. Research papers published with Results and Discussion

Paper Sr. No.	Title of Paper	Published in
1.	Combined Experimental and Computational Study of UV-VIS Spectra of 6-bromo-2-methylquinoline	Acta Ciencia Indica, Vol. XXXVIII, No. 4, 2012, pp. 257-266. ISSN 0253-732X
2.	Vibrational Spectral Studies and thermodynamic functions of 6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline-3-carboxylic acid hydrochloride molecule	International Transactions in Applied Sciences, Vol. 6, No. 2, 2014, pp. 189-203. e-ISSN 0975-3761
3.	Molecular Structure, vibrational spectra of 6-amino-1,3-dipropyl uracil by density functional theory and ab initio Hartree-Fock calculations	International Transactions in Applied Sciences, Vol. 6, No. 3, 2014, pp. 301-318. e-ISSN 0975-3761
4.	Role of Spectroscopy Investigations of N-Heterocyclic molecule in Environment	Presented Research paper at the Katholische Akademie der Erzdiozese Freiburg, Germany, 2-5 December, 2014. Published in Academic Journal of Science CD–ROM, Vol-05 No-01, 2016, PP 115-126. ISSN 2165-6282
5.	Solvent Effect on Electronic Transitions, Ph effect, Theoretical UV spectrum, HOMO LUMO analysis of 2,4-dihydroxy-5-fluoropyrimidine	IOSR Journal of Applied Chemistry, Vol. 8, Issue 7, Ver. 1, 2015, pp. 11-17. e-ISSN 2278-5736
6.	Spectroscopic Investigations and role of substituted Pyrimidine in Environment	Review Journal of Political Philosophy, Special Issue , 2015. ISSN No. (E) 2454-3411

7.	Spectroscopic and Vibrational characterization of Fluorinated Pyrimidine, NBO, NLO, Thermodynamic functions, HOMO LUMO analysis based on Density Functional Theory	Global Journal of Advanced Research, Vol. 3, Issue 7, 2016, pp. 601-619. ISSN 2394-5788
8.	Biological activities of some substituted N-Heterocyclic molecules	International Journal of Advance Research in Science and Engineering, Vol. 5, Issue 8, 2016, pp. 726-731. ISSN 2319-8354
9.	Laser Raman and FTIR Spectral Investigation of a Biologically active substituted Pyridine molecule	International Journal of Advance Research in Science and Engineering, Vol. 6, Issue 3, 2017, pp. 300-310. ISSN 2319-8354

Paper 1. "Combined Experimental and Computational Study of UV-VIS Spectra of 6-bromo-2-methylquinoline"

In this paper, UV-VIS Spectra of 6-bromo-2-methylquinoline have been recorded in three solvents of different polarity. Absorption wavelength and oscillator strengths are studied with time dependent density functional theory (TDDFT) at CIS/6-311G(d,p) basis set in conjugation with Polarizable continuum model (PCM). All calculations were carried out with Gaussian 03 software package. The experimental and computed data are in excellent agreement.

Paper 2. "Vibrational Spectral Studies and thermodynamic functions of 6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline-3-carboxylic acid hydrochloride molecule"

In this paper, the FTIR spectra (4000-400 cm^{-1}) and FT-Raman spectra (4000-50 cm^{-1}) of 6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline-3-carboxylic acid hydrochloride molecule were observed. The fundamental bands and vibrational

assignments are discussed. Thermodynamic parameters viz. enthalpy, heat capacity, free energy and entropy have been calculated at various temperatures.

Paper 3. "Molecular Structure, vibrational spectra of 6-amino-1,3-dipropyl uracil by density functional theory and ab initio Hartree-Fock calculations"

In this paper, Quantum chemical calculations of energies, geometries and vibrational wavenumbers of 6-amino-1,3-dipropyl uracil were carried out using Hartree-Fock (HF) and DFT AT 6-311++G(d,p) and 6-31+G(d,p) basis sets respectively. Optimized bond angles and bond lengths were calculated and vibrational assignments are obtained.

Paper 4. "Role of Spectroscopy Investigations of N-Heterocyclic molecule in Environment"

This paper was presented at the Katholische Akademie der Erzdiozese Freiburg, Germany held from 2-5 December, 2014.

This paper was published in Academic Journal of Science. In this paper, infrared and Raman spectra of 6-chloromethyl uracil were studied experimentally and theoretically by HF and DFT at HF/6-311++G(d, p) and B3LYP/6-311++G (d, p) basis sets respectively. The thermodynamic parameters, electric dipole moment (μ), the isotropic polarizability and first order hyperpolarizability of (6-CMU) are also calculated by HF and DFT methods.

Paper 5. "Solvent Effect on Electronic Transitions, Ph effect, Theoretical UV spectrum, HOMO LUMO analysis of 2,4-dihydroxy-5-fluoropyrimidine"

In this paper, the electronic spectra of 2,4-dihydroxy-5-fluoropyrimidine was observed in ethanol, methanol and water to study solvent effect. The HOMO LUMO analysis has been done theoretically using HF and DFT at 6-311++G(d,p) basis set. The mullliken charges have also been computed and discussed.

Paper 6. **"Spectroscopic Investigations and role of substituted Pyrimidine in Environment"**

In this paper, the electronic spectra of 4,6-dihydroxy-5-methylpyrimidine was observed in methanol, water, dimethyl sulphoxide (DMSO) and acetonitrile to study solvent effect. The calculations were also performed using TD-SCF/HF/6-31+G(d,p) basis set.

Paper 7. **"Spectroscopic and Vibrational characterization of Fluorinated Pyrimidine, NBO, NLO, Thermodynamic functions, HOMO LUMO analysis based on Density Functional Theory"**

In this paper, the FTIR spectra (4000-400 cm^{-1}) and FT-Raman spectra (4000-50 cm^{-1}) of 2,4-dihydroxy-5-fluoropyrimidine were observed. The fundamental bands and vibrational assignments are discussed. The calculations were also computed using DFT and HF methods using 6-311++G(d,p) basis set. The HOMO and LUMO analysis has been made using TD-SCF method with 6-311++G(d,p) basis set. The hyperconjugative interactions between the molecule has been evaluated by natural bond orbital (NBO) analysis. The first order hyperpolarizability has been calculated using non linear optical investigation.

Paper 8. **"Biological activities of some substituted N-Heterocyclic molecules"**

In this paper, the antifungal activity of 2-benzylamino-4-methylpyridine, 2-chloro-6-methoxypyridine and 4-amino-3,5-dichloro-2,6-difluoropyridine has been evaluated at different concentrations against Aspergillusflavus, Aspergillusniger, Aspergillusfumigatus and Rizopus by growth method. This study will play an important role in the field of toxicology.

<u>Paper 9.</u> "Laser Raman and FTIR Spectral Investigation of a Biologically active substituted Pyridine molecule"

In this paper, the FTIR spectra (4000-400 cm^{-1}) and FT-Raman spectra (4000-50 cm^{-1}) of biologically active molecule 4-amino-3,5-dichloro-2,6-difluoropyridine were obtained. The vibrational spectra are analysed and assignments of various bands were made.