QUANTUM CHEMICAL STUDIES ON TRANS-4-(TRIFLUOROMETHYL) CINNAMIC ACID

A phase-II project report submitted to Kalasalingam Academy of Research and Education in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE IN PHYSICS

Submitted By

SIVA K

(Reg. No. 9921127007)

Under the Guidance of

Dr. S. JEYAVIJAYAN

DEPARTMENT OF PHYSICS

KALASALINGAM ACADEMY OF RESEARCH AND EDUCATION

(DEEMED TO BE UNIVERSITY)

KRISHNANKOVIL 626 126

Academic Year(2022-23)

KALASALINGAM ACADEMY OF RESEARCH AND EDUCATION
(DEEMED TO BE UNIVERSITY)
KRISHNANKOVIL 626 126

DECLARATION BY THE STUDENT

I hereby declare that the report entitled "**QUANTUM CHEMICAL STUDIES ON TRANS-4-(TRIFLUOROMETHYL) CINNAMIC ACID**" submitted by me for the Degree of Master of Science in PHYSICS is the result of my original and independent research work carried out under the supervision of **Dr. S. JEYAVIJAYAN** , Department of PHYSICS, Kalasalingam Academy of Research and Education, KRISHNANKOVIL and it has not been submitted for the award of any degree, diploma, associate ship, fellowship of any University or Institution.

K. SIVA

(9921127007)

Date:

KALASALINGAM ACADEMY OF RESEARCH AND EDUCATION
(DEEMED TO BE UNIVERSITY)
KRISHNANKOVIL 626 126

BONAFIDE CERTIFICATE

Certified that this Report entitled "**QUANTUM CHEMICAL STUDIES ON TRANS-4-(TRIFLUOROMETHYL) CINNAMIC ACID**" is the bonafide work of Mr. K. SIVA (Reg. No.: 9921127007) who carried out the research under my supervision. Certified further, that to the best of my knowledge the work reported herein does not form part of any other report or dissertation on the basis of which a degree or award was conferred on an earlier occasion on this or any other scholar.

Dr. S.Saravana Kumar   **Dr. S. JEYAVIJAYAN**

HEAD OF THE DEPARTMENT   RESEARCH SUPERVISOR

 DEPARTMENT OF PHYSICS   **DEPARTMENT OF PHYSICS**

KARE   **KARE**

KRISHNANKOVIL – 626 126   **KRISHNANKOVIL – 626 126**

Project Viva-voce held on _____

Internal Examiner   **External Examiner**

ACKNOWLEDGEMENT

K. SIVA

TABLE OF CONTENTS

CHAPTER – I
INTRODUCTION TO SPECTROSCOPY

1.1. INTRODUCTION

Spectroscopy is the branch of science dealing with the study of interaction of electromagnetic radiation with matter. The most important consequence of such interaction is that energy is absorbed or emitted by the matter in discrete amounts called quanta. The various branches of spectroscopy generally involve measurements of two important experimental parameters:

1. The energy of the radiation absorbed or emitted by the system

2. Intensity of the spectral lines

Molecular spectroscopy is concerned with the interaction of electromagnetic radiation with molecular systems. Modern spectroscopic methods covering the entire electromagnetic spectrum have become powerful tools in the investigations of the physical properties of molecules viz., molecular structure, nature of chemical bonds, hydrogen bonding, isomerism etc.

Vibrational spectroscopy is mainly concerned with vibrational transitions due to absorption and emission of electromagnetic radiations. Vibrational transitions can be observed as infrared and Raman spectra. It also provides important information about the intramolecular forces acting between the atoms in a molecule, the intermolecular forces in condensed phase and the nature of the chemical bond.

1.2. INFRARED SPECTROSCOPY

Infrared spectroscopy is widely used for the identification of organic compounds because of the fact that their spectra are generally complex and provide numerous maxima and minima that can

be used for comparison purposes. Infrared spectroscopy is generally concerned with the absorption of radiation incident upon a sample.

The absorption of infrared radiation depends on increasing the energy of vibration or rotation associated with a covalent bond in a molecule, provided such an increase causes a change in the dipole moment of the molecule. Hence, for IR absorption to take place, the necessary condition is that, there should be a change in the magnitude or direction of the dipole moment of the molecule. Only under these conditions the alternating field of the IR radiation can interact with the molecule and cause changes in its motion.

1.2.1. Selection rule for IR

The selection rule for IR activity is determined by the integral,

$$\left[\mu\right]_{v'v''} = \int \psi_{v'}{}^* \left(Q_a\right) \mu \, \psi_{v''}\left(Q_a\right) dQ_a \qquad \qquad \dots (1.1)$$

Here μ is the dipole moment in the electronic ground state. ψ is the vibrational eigen function, V' and V'' are the vibrational quantum numbers of the states before and after transition respectively and Q_a is the normal coordinate whose activity is to be determined. The dipole moment can be resolved into three components in the x, y and z directions as

$$\left[\mu_x\right]_{v'v''} = \int \psi_{v'}\left(Q_a\right)\left[\mu\right]_x \psi_{v''}\left(Q_a\right) dQ_a$$

$$\left[\mu_y\right]_{v'v''} = \int \psi_{v'}\left(Q_a\right)\left[\mu\right]_y \psi_{v''}\left(Q_a\right) dQ_a$$

$$\left[\mu_z\right]_{v'v''} = \int \psi_{v'}\left(Q_a\right)\left[\mu\right]_z \psi_{v''}\left(Q_a\right) dQ_a$$

For the vibrations to be infrared active, at least one of the components of the derivative of the dipole moment with respect to the normal coordinate, taken at the equilibrium position should be non-zero. If all the integrals are zero, the vibration is infrared inactive [1].

1.3. RAMAN SPECTROSCOPY

A simple method for obtaining vibrational and rotational frequencies of molecule is through observation of Raman Effect. According to Raman, if any substance, gas, liquid or solid is exposed to radiation of definite frequency, then the light scattered at right angles contains frequency different from the incident radiation, and is characteristic of the substance under examination. The scattered light was observed to have a slightly different frequency from that of incident light and there is a change in atomic oscillation within the molecule. If v_i and v_s are the frequencies of incident and that of scattered light respectively, then the difference $\Delta v = v_i - v_s$ is known as Raman frequency. The spectrum of the scattered light is made of lines of the incident light together with series of lines on either side of them. This series of lines in the scattered light is known as Raman Spectra. The Raman lines on the lower frequency side of the incident radiation are called stokes lines i.e., where $v_i > v_s$ and those on the higher frequency side are termed as anti stokes lines i.e., $v_s > v_i$.

1.3.1. Selection rule for Raman spectra

The selection rule for the Raman Spectrum is determined by the integral,

$$[\alpha]_{v'v''} = \int \psi_{v'}{}^{*}\left(Q_a\right)\alpha\ \psi_{v''}\left(Q_a\right)dQ_a \qquad \text{...(1.2)}$$

The polarisability of the molecule α consists of six components α_{xx}, α_{yy}, α_{zz}, α_{xy}, α_{yz} and α_{xz}. For the vibration to be Raman active, at least one of these integrals should be non-zero. If all the integrals are zero, the vibration is said to be Raman inactive.

1.4. QUANTUM THEORY OF RAMAN EFFECT

Quantum mechanics gives a qualitative description of the phenomenon of Raman Effect. The interaction of a photon of the incident light beam with the molecule in its ground electronic and vibrational state (v = 0) may momentarily raise the molecule to a time dependent quasi-excited electronic state (or a virtual state) whose height is above the initial energy level. Virtual states are those in which the molecule has a very short mean life time and hence the uncertainty in energy is large according to the Heisenberg uncertainty principle.

In the case of Stokes line, the molecule at ground electronic state (v = 0) is excited to the virtual electronic state, and then radiates light in all directions except along the direction of the incident light. On return to the ground electronic state, quantum vibrational energy may remain with the scattering species and there will be a decrease in the frequency of the scattered radiation.

Anti-Stokes lines arise when the molecule is already in an excited vibrational state (say v = 1) and is raised to quasi-excited state and reverts to ground electronic state (v = 0) on scattering of photon. Scattered photon is the sum of the energy of incident photon and the energy between the vibrational levels v = 1 and v = 0.

In another instance, a molecule in the ground state on interacting with a photon and attaining the virtual state may leave the unstable electronic state and return to the ground electronic state. In this case, scattered photon has the same energy as the incident radiation and the result is Rayleigh scattering.

For a molecular vibration to be Raman active there must be a change in the polarizability of the molecule during this vibration. This change can be considered as being a change in the shape of the electron cloud surrounding the molecule (Polarization ellipsoid). In a molecule without any symmetry elements, all the normal vibrations are accompanied by polarizability changes and the corresponding frequencies appear in the Raman spectrum. But in a symmetric molecule, some of these vibrations may not produce any change in polarizability and the corresponding normal frequencies are not observed. Such vibrations are Raman inactive [2].

Raman spectrum gives information about molecular symmetry which can then be used to determine the molecular configuration. There are various chemical problems which have been successfully solved with the help of Raman spectra.

The advent of lasers has revolutionalized Raman spectroscopy. Now, with the subsequent development of optical spectrometers and new detection techniques, Raman spectroscopy has developed as an extremely useful tool for material characterization.

1.5. MOLECULAR FORCE CONSTANTS

The vibrational frequencies when supplemented by structural data are significant in estimating the nature of the forces holding the atoms of the molecule and in the evaluation of several molecular constants.

The force constant may be defined as the restoring force per unit displacement, stretching or bending is a measure of the strength of the chemical bonding between the atoms. A molecule and its isotopic analogues have almost the same set of force constant, as isotopic substitution does not alter the nature of the chemical bond. Thus, it is possible to deduce the fundamental wavenumbers of the isotopic substitutes when the force field of a molecule is known. This method is especially useful when the spectrum of the isotopic substitute cannot be easily obtained. Conversely, when the spectra of a molecule and its isotopic substitutes are known accurately, the force constants can be evaluated with greater precision.

Knowledge of force constants help to visualize, certain bonding properties such as electron delocalization and interatomic interactions. The force constants also yield information regarding valence state of atoms in the molecule. This also helps us to know the normal coordinates associated with each vibrational frequency essential for the absolute intensity studies. Infrared and Raman intensities have been used along with the force constants successfully to obtain the bond dipole moments, polarizabilities and their derivatives.

1.6. MOLECULAR FORCE FIELDS

The fundamental vibrational frequencies of a molecule obtained from Raman and infrared spectra can be used to solve secular equations to get the potential energy or force constants. Generally, the number of force constants to be determined is greater than the number of equations and hence it is not possible to obtain unique solutions of such equations. One

way to get over this difficulty is by choosing the initial set of force constants from molecules containing similar bonds and environment, a trial F matrix is set up and iterating them to give a weighted least square fit to all of the observed frequencies. Another method is to make certain assumptions about the forces in the molecules and thereby reducing the number of force constants to be determined. Several such force fields have been assumed, each one having its own merits and limitations.

1.7. MOLECULAR SYMMETRY AND POINT GROUPS

Symmetry is a visual concept as reflected by the geometrical shapes of molecules such as benzene, methane etc. In spectroscopy, the symmetry possessed by a molecule may be used with advantage to simplify the calculation of energy levels of the system and to determine the transitions that are allowed or forbidden. The molecular symmetry is systematized quantitatively by introducing the concept of 'symmetry operation'. It is an action which moves the nuclear framework into a position equivalent to the original one. Related to the symmetry operation is the 'symmetry element'. The symmetry element is a geometrical entity such as a point, an axis or a plane about which action takes place. The symmetry operation is applied to the molecule and the symmetry operation should leave the molecule, physically indistinguishable.

All the axes and planes of symmetry of a molecule must intersect at least at one common point. Thus, the symmetry operation performed on molecule must leave at least one point unaffected. Such groups of operations are called point groups. In a point group, the symmetry of space about a point is uniquely described by a collection of symmetry elements about that point. Point groups are used to describe the symmetry of isolated molecules.

1.8. GROUP THEORY AND MOLECULAR VIBRATIONS

Knowledge of the point group symmetry of a molecule and application of group theory concept is useful in the classification of the normal vibrations, determination of their normal

vibrations and determination of their spectral activity. Molecule of different symmetries has qualitatively different spectra [3].

A very important property of the normal vibrations is that they transform according to the irreducible representations of the molecular point group. Because of their relationship with the normal coordinates, the vibrational wave function associated with the vibrational energy levels also behaves in the same way. Hence, the normal coordinates and the vibrational wave functions can be classified according to their symmetry properties.

1.9. NORMAL MODES OF VIBRATIONS

Normal modes (or fundamental modes) of vibrations of any molecule are internal atomic motions in which all the atoms move in phase with the same frequency but with different amplitudes. The amplitude and direction of each atom may be represented by a displacement vector. The various displacements of the atoms in a given normal mode of vibration may be represented by a linear combination of atomic displacements is known as normal coordinates which are functions of angles and distance. A very important property of this vibration is that for non-degenerate normal modes of vibration, the normal coordinates and the vibrational wave functions are either symmetric or antisymmetric with respect to the symmetry operations of the point group symmetry of the molecule in its mean position. For degenerate normal mode of vibration, the symmetry operation will transform the degenerate set of vibrations into a linear combination of mutually degenerate normal coordinates. A normal mode in a molecule is equivalent to a simple harmonic motion of certain mass and force constant, and can vibrate independently without exciting any other mode for small amplitude motion. The number of molecular vibrations of a chemical compound depends upon the number of atoms in its molecular composition, and the molecular vibration allowed in the IR or Raman depends upon its molecular symmetry.

For a molecule containing N atoms, 3N coordinates are required to describe their motion, i.e. there are 3N degrees of freedom. Of these, for a non-linear, three account for translatory motion of the centre of mass of the molecule and another three account for rotational motion about its centre of mass. The remaining (3N-6) coordinates describe the genuine vibrations of the non-linear molecules. For a linear molecule there are only (3N-5) vibrational degrees of freedom, since the rotation of nuclei about the molecular axis cannot occur, because all nuclei are on the axis. This means that only two degrees of freedom are possible for rotational motion. Thus, the number of vibrational modes is 3N-6 or 3N-5, respectively, depending on whether the molecule is non-linear or linear.

The number of observed bands in the spectra may be less than the number of normal modes, due to various reasons:

- The symmetry of the molecule is such that no change in dipole moment results from a particular vibration.

- The energies of two vibrations may be identical or nearly identical.

- The intensity may be so low as to be detected by ordinary means.

- The vibrational energy may be in a frequency range beyond the range of the instrument.

- The characteristic of a vibration changes as a result of the coupling with another vibration. These couplings are influenced by many factors.

- Strong coupling between two stretching vibrations occur only when there is a common atom of the two vibrations.

- Interaction between two bending vibrations require common bond between the vibrating groups.

- Coupling between stretching and bending vibrations is possible if the stretching bond forms one side of the angle that varies in the bending vibrations.

- If the individual groups have identical energy, the interaction will be large.

- Little or no interaction is possible between groups which are separated by two or more bonds.

- Coupling occurs between vibrations of same symmetry species.

1.10. COMBINATIONS AND OVERTONES

Under harmonic oscillator approximation, only fundamentals contribute to infrared and Raman bands. The deviations of the potential function from the harmonic potential may result in mechanical anharmonicity, while the higher order terms of the dipole moment or polarizability leads to electrical anharmonicity. These anharmonicities lead to the appearance of combinations or overtones arising from simultaneous changes of state by two or more quanta of vibrational energy. The overtones are far weaker than the fundamentals and successive overtones are progressively still weaker. Due to mechanical anharmonicity, overtones of active fundamentals and combination of atleast one active fundamental may appear. Electrical anharmonicity of the molecule can generate overtones and combinations of inactive fundamentals. The combination bands are obtained as sum or difference of two fundamentals or as sum or difference of an overtone and a fundamental frequency. These combination bands and overtones are observed in both the infrared and Raman spectra of molecules. However, the effect of anharmonicity is found to be more in IR than in Raman combinations and overtone bands sometimes gain intensity due to Fermi resonance.

1.11. VIBRATIONAL ASSIGNMENTS AND GROUP FREQUENCY

The normal vibrations of a molecule are associated with appropriate Raman and infrared frequencies and this process is referred to as vibrational assignment. The applications of infrared and Raman spectroscopy rest largely on the correct assignment of the spectra. The assignment of the infrared and Raman spectra is generally made on the basis of the group frequency concept.

By comparison of the spectra of a large number of compounds, it has been observed that the presence of certain groups, for example C-H, O-H, N-H, C=O, C=N etc., in various molecules may

be correlated with a constant occurrence of absorption bands in the infrared spectra whose positions are only slightly altered on going from one compound to another. The atomic group vibrates independently of the other groups in the molecules and has its own frequency. These frequencies are called characteristics group frequencies [4]. The vibration of the group is assumed to occur independently of the rest of the molecule. A number of characteristic group absorptions have been established. The group frequency concept is extremely useful as an aid to the interpretation of vibrational spectra.

CHAPTER – II
QUANTUM CHEMICAL CALCULATIONS

2.1. INTRODUCTION

The philosophy of computational methods of vibrational spectroscopy changed significantly when quantum mechanical programs for optimisation of the geometry of a molecule and for analytical determination of its force field. Harmonic force fields derived from quantum mechanics are widely used at present for the calculation of frequencies and the modes of normal vibrations.

Nowadays sophisticated electron correlation calculations are increasingly available and deliver force fields of high accuracy for small polyatomic. The scaled quantum mechanical force fields [5] are of comparable accuracy with the best purely theoretical results. In addition, the scaling procedure fits the force field to observed (anharmonic) frequencies. Thus, the reproduction of observed spectra will be better with an SQM force field than with the best harmonic field.

2.1.1. Energy minimisation

Molecular mechanics deals with the changes in the electronic energy of the molecule due to bond stretching (v_b) bond angle bending (v_θ), out-of–plane bending ($v_{o\theta}$), internal rotation (torsion) about bonds (v_Φ), interactions between different kinds of motions (v_{int}), van der waals attractions and repulsion between non-bonded atoms (v_{dw}) and electrostatic interactions between atoms (v_{es}). The

sum of these contributions gives the potential energy V in the molecular mechanics frame work for the motion of the atoms in the molecule. It is often called the steric energy or strain energy for the motion of atoms in the molecules.

The mathematical form of this energy function (also called potential energy surface) is given below:

$$V\left(X^N\right) = \sum_{i=1}^{k} V_i \qquad ...(2.1)$$

where V represents the potential energy of the molecular system, which is a function of the Cartesian coordinates of all atoms denoted as X^N. The equation (2.1) can be written as,

$$V = v_{b} + v_{\theta} + v_{\Phi} + v_{o\theta} + v_{es} + v_{dw} + v_{int} \qquad …(2.2)$$

The potential energy calculated by summing up the energies of various interactions is a numerical value for a single conformation. Energy minimisation is usually performed by gradient optimisation. Atoms are moved so as to reduce the net force on them. The minimised structure has small forces on each atom and therefore serves as an excellent starting point for molecular dynamics simulation.

The geometry optimisation starts with the initially assumed geometry and finds the nearest local energy minimum by minimising the steric energy V of the equation (2.2). This equation provides an analytical form for the energy, the first and second derivatives of V can easily be evaluated analytically, which facilitates the energy minimisation. Many programs have built-in searching methods that locate many low energy conformers. Force field methods are primarily geared to predict geometries and relative energies.

2.2. *AB INITIO* METHODS

Ab initio orbital molecular methods are useful to predict harmonic force constants and frequencies of normal modes. The *ab initio* methods first optimize the molecular geometry and then evaluate the second derivative at the equilibrium positions usually using analytical derivatives. Such methods provide reliable values for harmonic vibrational for fairly large sized molecules. Additionally such calculations can be used to predict barriers to internal rotation as well as relative stabilities of

different conformers. The information obtained from structural parameters, conformational stabilities, force constants, vibrational frequencies as well as infrared and Raman band intensities gives significant contributions to the field of vibrational spectroscopy.

Harmonic force constants in Cartesian coordinates can be directly derived from *ab initio* calculations. These force constants can be transformed to force constants in internal or symmetry coordinates. *Ab initio* calculations followed by normal coordinate analysis are very helpful in making reliable vibrational assignments. Band intensities from *ab initio* studies are another important output. Such band intensity data can also be very useful in making vibrational assignments. Two principally different quantum mechanical methods addressing the vibrational problems are namely Hartree-Fock method and Density Functional Theories (DFT). Density functional theory calculation has emerged in the past few years as successful alternative to traditional Hartree-Fock method. The DFT methods, particularly hybrid functional methods [6] have evolved a powerful quantum chemical tool for the determination of the electronic structure of molecules. In the frame work of DFT approach, different exchange and correlation functionals are routinely used. Among these, the Becke-3-Lee-Yang-Parr (B3LYP) combination is the most used since it proved its ability in reproducing various molecular properties, including vibrational spectra. The combined use of B3LYP functional and standard various basis sets, provide an excellent compromise between accuracy and computational efficiency of vibrational spectra for large and medium size molecules. The vibrational frequencies calculated by applying DFT methods are normally overestimated than experimental values by 2-5% on an average. This overestimation is due to the neglect of electron correlation, anharmonicities, and incomplete basis sets.

This overestimation can be narrowed down by empirical scaling factors ranging from 0.8 to 1.0. The scaling factors depend both on method and basis sets and they are partially compensated for the systemic errors in the calculation of frequencies. Selective scaling, multiple scaling are some scaling methods advocated to minimize the overestimation of the frequency differences. *Ab initio* calculation could be performed using GAUSSIAN 09W software package.

If the quantum-mechanical force field is not corrected, especially in the case of large deviations from the experimental results, this omission can complicate the theoretical analysis of the vibrational spectrum of a molecule and lead to errors in the assignment of the experimental frequencies. Therefore, determining empirical corrections to quantum mechanical force fields is important. It is shown that [7] of all the method for empirically correcting quantum-mechanical force fields, the one with the best physical basis is the modern version of the Pulay method.

2.3. DENSITY FUNCTIONAL THEORY

Density functional theory (DFT) is a quantum mechanical method used to investigate the electronic structure of many body systems, in particular molecules and the condensed phases. DFT is among the most popular and versatile methods available in condensed matter physics and computational chemistry.

Traditional methods in electronic structure theory, in particular Hartree-Fock theory and its descendants, are based on the complicated many electron wave function. The main objective of density functional theory is to replace the many-body electronic wave function with the electronic density as the basic quantity. Whereas the many-body wave function is dependent on 3N variables, three spatial variables for each of the N electrons, the density is only a function of three variables and is a simpler quantity to deal with both conceptually and practically.

Although density functional theory has its conceptual roots in the Thomas-Fermi model, DFT was put on a firm theoretical footing by Hohenberg-Kohn theorems. The first theorem demonstrates the existence of a one-to-one mapping between the ground state electron density and the ground state wave function of a many-particle system. The second theorem proves that the ground state density minimises the total electronic energy of the system. The most common implementation of density functional theory is through the Kohn-Sham method. Within the framework of Kohn-Sham DFT, the intractable many-body problem of interacting electrons in a static external potential is reduced to

a tractable problem of non-interacting electrons moving in an effective potential. The effective potential includes the external potential and the effects of the coulomb interactions between the electrons, eg., the exchange and correlation interactions.

2.4. BASIS SET

Quantum chemical calculations are typically performed within a finite set of basis functions. In these cases, the wave functions under consideration are all represented as vectors, the components of which correspond to coefficients in a linear combination of the basis functions in the basis set used. The operators are then represented as matrices, in this finite basis. When molecular calculations are performed, it is common to use basis composed of a finite number of atomic orbitals, centered at each atomic nucleus within the molecule. Initially, these atomic orbitals were typically Slater orbital, which corresponded to a set of functions which decayed exponentially with distance from the nuclei. These Slater-type orbitals could be approximated as linear combinations of Gaussian orbitals. It is easier to calculate overlap and other integrals with Gaussian basis functions and this has led to huge computational savings of the many basis sets composed of Gaussian-type orbitals (GTOs). The smallest are called minimal basis sets and they are typically composed of the minimum number of basis functions required to represent all of the electrons on each atom.

The most common addition to minimal basis sets is the addition of polarisation functions, when polaristion is added to this basis set, a p-function is added to the basis set. This adds some additional needed flexibility within the basis set, effectively allowing molecular orbitals involving the hydrogen atoms to be more asymmetric about the hydrogen. Similarly, d-type functions can be added to a basis set with valance P orbitals, and f-functions to a basis set with d-type orbitals and so on. The precise notation indicates exactly which and how many functions are added to the basis set, such as (d,p).

Another common addition to basis sets is the addition of diffuse functions, denoted by a plus sign, +. Two plus signs indicate that diffuse functions are also added to light atoms (hydrogen and helium). These additional basis functions can be important when considering anions and other large, soft molecular system.

2.4.1. Minimal basis sets

A common naming convention for minimal basis set is STO-XG, where X is an integer. This X value represents the number of Gaussian primitive functions comprising a single basis function. In these basis sets, the same number of Gaussian primitives comprises core and valance orbitals. Minimal basis sets typically give rough results that are insufficient for research-quality publication, but are much cheaper than their larger counter parts. The commonly used minimal basis sets are:

- STO-2G
- STO-3G
- STO-6G
- STO-3G *- polarized version of STO-3G

2.4.2. Split-valance basis sets

During most molecular bonding it is the valance electrons which principally take part in the bonding. In recognition of this fact, it is common to represent valance orbitals by more than one basis function. The notation for these split-valance basis sets is typically X-YZg. In this case, X represents the number of primitive Gaussians comprising each core atomic orbital basis function. The Y and Z indicate that the valance orbitals are composed of two basis functions each, the first one composed of a linear combination of Y primitive Gaussian functions, the other composed of a linear combination of Z primitive Gaussian functions. In this case, the presence of two numbers after the hyphens implies that this basis set is a split-valance, Double-zeta basis sets are also used, denoted as X-YZWg, X-YZWVg etc. The commonly used split-valance basis sets are:

- 3-21G

- 3-21G(p) -polarised

- 3-21+G(d) -diffuse functions.

- 3-21+G(d,p) - with polarization and diffuse function

- 6-31G

- 6-31+G

- 6-31++G

- 6-31G(3df,3pd)

- 6-311G

- 6-311+G

- 6-311++G

2.4.3. Double, Triple, Quadruple Zeta basis sets

Basis sets in which there are multiple basis functions corresponding to each atomic orbital, including both valance orbitals and core orbitals or just the valance orbitals, are called double, triple or quadruple-zeta basis sets. Commonly used multiple Zeta basis sets are:

- CC-PVDZ-Double-zeta

- CC-PVTZ-triple-zeta

- CC-PVQZ-quadruple-zeta

- CC-PVSZ-quintuple-zeta

- aug-cc-pVDz-Augmented versions of the preceding basis sets with added diffuse functions.

- TZVPP-Triple-zeta

- QZVPP-Quadruple-zeta

The 'CC-P' at the beginning of some of the above basis sets stands for 'correlation consistent polarised' basis sets. They are double / triple / quadruple / quintuple-zeta for the valance orbitals only and include successively larger shells of polarisation (correlating) functions (d, f, g etc.,) that can yield convergence of the electronic energy to the complete basis set limit.

2.5. SCALING OF FORCE FIELDS

SQM, the method of scaled quantum mechanical force fields, is a pragmatic approach to the *ab initio* based determination of molecular force fields. Its basis idea is to use relatively low level *ab initio* calculations using small basis sets and combine them with experimental information in the form of an empirical adjustment, 'scaling' of the calculated force constants. SQM force fields are of comparable accuracy with the best purely theoretical results.

Quantum mechanical methods yield harmonic force constants. On the other hand, the observed frequencies are anharmonic, but it is possible to calculate the harmonic frequencies of small molecules from the observed vibrational spectra. The frequencies that are calculated on the basis of quantum mechanical force fields usually differ appreciably from the observed frequencies. This is partly due to the neglect of anharmonicity and party due to approximate nature of the quantum mechanical methods. The scaling procedure fits the force field to observed (anharmonic) frequencies; therefore the scale factors correct, as far as possible, the anharmonicity. Thus, the reproduction of observed spectra may be better with SQM force fields than with the best harmonic field.

The basic features of SQM are as follows:

(1)   For the reference geometry, rather than using the theoretical geometry of the quantum chemical method applied, the ideal choice would be the best experimental geometry. This eliminates a major part of the short comings of the HF method in predicting potential

surfaces [8]. In practice, a reliable equilibrium structure is not always available and the theoretical geometry is corrected based on experience on small molecules.

(2)   Scaling of force constants were proposed to account for the deviation of the calculated and the observed frequencies. They scaled the diagonal internal force constants with different scale factors but used the same scale factors for the cross terms. Later on many people introduced a formula for the scaling of a force constant f_{ij}:

$$f_{ij}' \; = \; \sqrt{S_i S_j f_{ij}} \qquad\qquad \ldots (2.3)$$

where the symbol s_i and s_j denote the scale factors for the diagonal force constants f_{ij} and f_{jj}. Pulay's method makes it possible to calculate scale factors that are transferable between similar molecules. If suitable internal coordinates are chosen.

(3)   For systematic calculations, the same basis set should be used consistently.

CHAPTER – III
INSTRUMENTATION - FTIR AND FT-RAMAN SPECTROSCOPIES

3.1. INTRODUCTION

Infrared and Raman spectroscopic techniques from its early beginning continue to be a complementary fertile research tool in the hands of physicists and chemists. In recent years, Fourier transform (FT) spectroscopic techniques enjoy the advantages over the conventional IR and Raman spectroscopy due to the very intensive developments of FTIR and FT Raman spectroscopy and hence attracted much interest by offering some unique features. The ultimate performance of any infrared spectrometer is determined by measuring its signal-to-noise ratio (SNR). This is best achieved by FT infrared spectrometers. The improved SNR's available with FTIR makes it to become the instrument of choice for obtaining infrared spectra. Frequency precision, good spectral subtractions and high resolution are difficult to achieve with conventional Raman spectroscopy. Hence a new technique, in which the Raman module is an accessory to an FTIR spectrometer, called

FT-Raman spectroscopy. FTIR and FT-Raman technique has been found to be a useful in increasing the spectral sensitivity and thus yielding new information about the atomic or molecular species, or the functional group that exist in the sample.

An instrument for chemical analysis converts information stored in the physical or chemical characteristics of the analytic information that may be manipulated and interpreted by a human. Thus an analytical instrument can be viewed as a communication device between the system under study and the investigator.

Modern spectrometers generally attached with sophisticated computers and high energy sources like lasers, which permit spectrum storage and retrieval, scale expansion, repetitive scanning, spectral comparison, spectral simulation, automatic control of slit, etc. Often these are under the control of a microprocessor and microcomputers. Accessories such as beam condensers, reflectance units, polarizers and microcells can usually be added to extend versatility or accuracy. In this chapter the instrumentation and sample handling techniques of FTIR and FT-Raman spectrometers are presented.

3.2. FOURIER TRANSFORM INFRARED SPECTROMETER
3.2.1. Introduction

Fourier transform infrared spectroscopy (FTIR) is rapidly becoming a common feature in modern spectroscopy laboratories. A wide range of commercial FTIR spectrometers with very different specifications are now available. This has become possible with the availability of sophisticated computers. The absorption spectrum in a Fourier transform infrared spectrometer is obtained through interference technique. Interferometry is therefore known as Fourier transform spectroscopy.

Many laboratory spectrophotometers are the dispersive design, meaning that a prism is used to separate the spectral components in the IR radiation of the source. Most industrial process analysers use non-dispersive infrared (NDIR) designs. With recent improvements in instrumentation,

the infrared radiation refers broadly to that part of the electromagnetic spectrum which lies between the visible and microwave regions. The infrared region of the spectrum encompasses radiation with wave numbers ranging from about 12,800 to 10 cm^{-1} or wavelengths from 0.78 to 1000 µm. From instrumentation and application point of view, the infrared region has been subdivided into near IR region (overtone region) 12800-4000 cm^{-1}, mid IR region (vibration rotation region) 4000-400 cm^{-1} and far IR region (400-10 cm^{-1}). The techniques and the applications of methods based upon the three infrared spectral regions differ considerably. An infrared spectrum shows downward peaks corresponding to absorption, plotted against wavelength (ν) or wave number ($\bar{\nu}$). In the infrared spectrum, apart from the prominent modes of vibrations, there are other vibrations due to coupling and overtones that may lead to additional bands in the spectrum. The various bands can be interpreted according to the characteristics functional groups present in the compound [10].

Infrared absorption, emission and reflection spectra for molecular species can be rationalised by assuming that they all arise from various changes in energy state brought about by transitions of molecules from one vibrational or rotational energy state to another. Absorption of infrared radiation is thus confined largely to molecular species that have small energy differences between various vibrational and rotational states. In order to absorb infrared radiation, a molecule must undergo a net change in dipole moment as a consequence of its vibrational or rotational motion. Only under these circumstances can an alternating electrical field of the radiation interact with the molecule and cause changes in the amplitude of one its motions.

3.2.2. Instrumentation
a. Introduction

The basic components of an infrared spectrometer are shown in Fig. 3.1. A source provides radiation over the entire range of the infrared spectrum. The monochromatic disperses the light and then selects a narrow wave number range. The detector measures the energy and transforms it into an electric signal. This signal is further amplified and registered by a recorder.
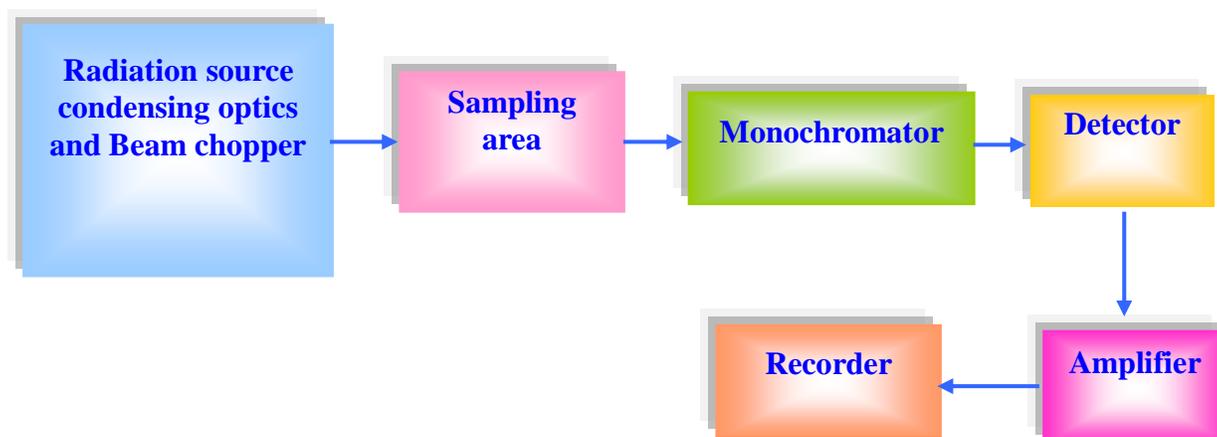
Fig. 3.1: **Block diagram of the major components of a dispersive infrared spectrophotometer**

b. Instrumentation

A FTIR spectrometer consists of two parts: (a) an optical system which uses an interferometer and (b) a dedicated computer which stores data performs computation on data and plots the spectra. Fig. 3.2 shows the optical diagram of a Fourier transform infrared spectrometer. It consists of a movable mirror, a stationary mirror and a beam splitter. Radiation from an infrared source is passed on to the mirrors through the beam splitter and beam splitter partly transmits and partly reflects the incident light. The transmitted and the reflected beams fall on the stationary and movable mirrors respectively. These beams which are sent in two directions at right angles to each other are brought together after reflection, to interfere with each other.

FTIR spectra of all the samples reported in this thesis were recorded on a BRUKET IFS 66 V FTIR spectrometer. This instrument is equipped with an MCT detector, a KBr beam splitter and globar source. Boxcar apodization was used for the 250 averaged interferograms collected for the sample. The far IR spectrum was recorded on the same instrument using polyethylene pellet technique. This instrument has a resolution of ± 1 cm^{-1}.

c. Source

Infrared radiation is produced by electrically heating a source, usually a Nernst filament or a Globar to 1000-1800°C. The Nernst filament is fabricated from a binder and oxides of thorium, cerium, zirconium and yttrium. The Globar is a small rod of silicon carbide usually 5 cm in length and 0.5 cm in diameter. The maximum radiation for the Globar occurs in the 5500-5000 cm^{-1} region. Nichrome wire, carbon arc, rhodium wire and tungsten filament lamp are also used as light source. In a commercial infrared spectrometer either a nichrome wire or a platinum filament contained in a ceramic tube is commonly used as infrared source for the range 4000-400 cm^{-1}.

d. Monochromator

A monochromator is a means of separating wavelengths of the radiation source. Prisms and gratings are used for this purpose. A grating or a prism disperses the radiation from the source into its spectral elements. The monochromators perform three functions, which are basic to the operation of the instrument.

❖ It disperses the radiation according to its wave number component. It restricts the radiation falling on the detector into a narrow wave number range and

❖ It maintains the energy incident on the detector to an approximately constant level when no sample is present throughout the wave number range of the instrument [11].

All infrared monochrometers use mirror optics. Fortunately, the reflection from most metallic surfaces is good in the infrared region and consequently monochromator mirrors are normally worked in glass and finished with a thin reflecting coating of aluminum.

e. Thermal detectors

The detector mostly produces an electrical signal which is proportional to the intensity of the incident radiation over the whole spectral range of the instrument. The most desirable features of the

detectors are the closeness with which they approach the behavior of a black body, high sensitivity, high speed and robustness.

The infrared detectors may be selective or non-selective. The selective detectors are those whose response is markedly dependent upon the wavelength of the incident radiation. Examples of this type are photocells, Photographic plates, photoconductive cells and infrared phosphors. The non-selective detectors are those whose response is directly proportional to incident energy but relatively independent of wavelength. Common examples include thermocouples, bolometers and pneumatic cell. Recent detectors are fabricated from crystals such as lithium niobate, barium, titanate and triglycine sulphate. These crystals are known as pyroelectrics and take less time than other thermal detector. Hence with these crystals, radiation can be chopped at a higher rate. However, these are more expansive and not widely employed.

f. Amplifiers and Recorders

The radiant energy received by the detector is converted into measurable electrical signal and is amplified by the amplifiers. The amplified signal is registered by a recorder plotter. The recorder is driven with a speed which is synchronised with that of a monochromator, so that, the pen moving across the chart, records the transmittance of the sample as a function of the wave number.

g. Beam Splitters

Beam splitters are constructed by transparent materials with refractive indices such that approximately 50% of the radiation is reflected and 50% is transmitted. A widely used material for the far-infrared region is a thin of mylar sandwiched between two plates of a low - refractive - index solid. Thin films of germanium or silicon deposited on cesium iodide or bromide, sodium chloride, or potassium bromide are satisfactory for the mid-infrared region.

3.3. SAMPLE HANDLING

Sample handling is considered as an important technique in the infrared spectroscopy. One of the advantages of infrared spectroscopy is that it can be applied to nearly all types of substances. There are various methods of sample preparation to enable almost any type of sample to be examined. Sample preparation is now the most time-consuming, most error-prone and most labour-intensive step of an analysis. No matter how simple or complex the procedures appear, the same five general principles apply to all sample preparations.

3.3.1. Sample preparation

- The sample preparation should be done without losing any of the analyte(s).

- The sample preparation should include bringing the analyte(s) into the best chemical form to be used.

- The sample preparation should, if necessary, include removing interferents in the matrix.

- The sample preparation should be done without adding any new interferents.

- The sample preparation should include, if necessary, diluting or concentrating the analyte(s) to bring their concentrations into the best range.

Some significant problems arise when trying to construct sample containers for vibrational spectrometry, since every material has some vibrational absorption.

a. Solids

Solids are sampled in a wide variety of ways. If the sample is soluble, it may be dissolved and handled as for a liquid. Solid samples for which no solvent is suitable can be prepared for analysis by incorporating them into a pressed pellet of alkali halide, usually potassium bromide. Sample is mixed with a weighted amount of powdered potassium bromide and the mixture is admitted to a pressure of several tonnes in a die, to produce a highly transparent plate or disc which can be inserted into the spectrophotometer. The use of KBr eliminates the problems of additional

bands due to mulling agent. KBr does not absorb infrared light in the region 2.5 - 15 μm and a complete spectrum of the sample is obtained.

Solid samples have also been examined in the form of a thin layer deposited by sublimation or solvent evaporation on the surface of a salt plate. Another method, called mulling has also been developed, in which the powdered sample is mixed to form a paste with little heavy paraffic oil. The mull is sandwiched between salt plates for measurement. Mulls are formed by grinding 2 to 5 mg of finely powdered sample in the presence of one or two drops of a heavy hydrocarbon oil called Nujol.

b. Liquids

In most instances the spectra of liquids are measured in either a demountable type cell or in fixed thickness or sealed cells. The spectra of pure samples can be measured as very thin films squeezed between two alkali halide windows of a demountable cell. This technique can produce a film of thickness 0.01 mm or less. This method is most useful for qualitative work only because the sample thickness cannot be controlled. Liquid cells consist of two alkali halide windows usually NaCl or KBr, separated by a spacer of suitable thickness made of Teflon or lead which limits the volume of the cell.
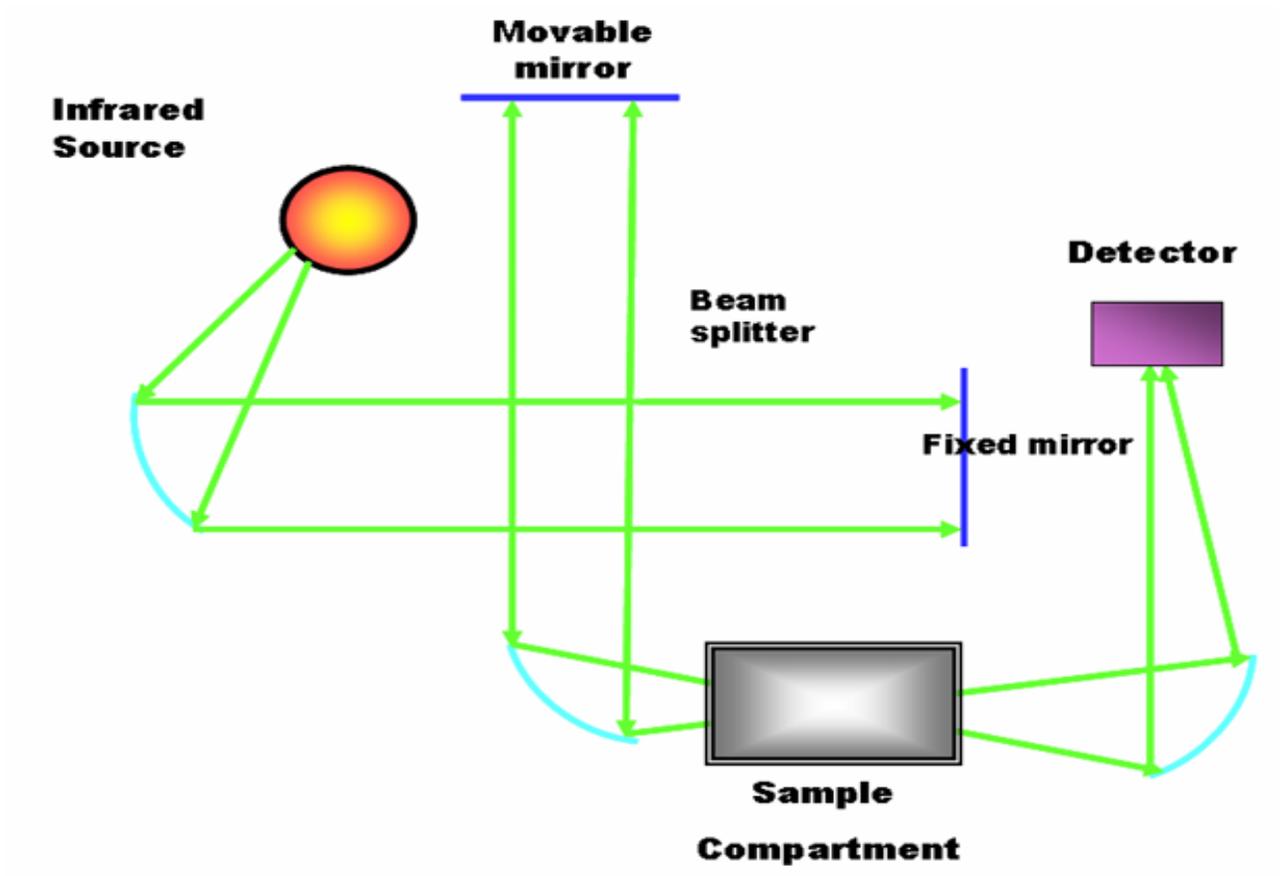
Fig. 3.2: Fourier Transform infrared Spectrometer – Optical arrangement

c. Gases

Absorption spectra of gases can be measured in a wide variety of gas cells ranging from a few centimeters to several meters that can be directly placed in the path of the infrared beam. The end walls of the cell are usually made of sodium chloride which is transparent to infrared. Most organic compounds have very low vapour pressure for this phase to be useful. The low frequency vibrational changes in the gaseous phase often split the high frequency vibrational bands.

3.4. ADVANTAGES OF FOURIER TRANSFORM INFRARED SPECTROMETER

The main advantages of FT spectroscopy are the greater ease and speed of measurement. The entire spectrum can be recorded within few seconds using sophisticated computers. Recent developments in FT infrared spectrometers have thus led to higher resolution, total wavelength coverage, higher accuracy in frequency and intensity measurements. It can also be used in the characterization of all kinds of samples.

a. Jacquinot or throughput advantage

The radiation from the source reaching the detector in an interferometer is not limited by the entrance and exit slits as in a dispersive spectrometer. The circular Jacquinot-stop (J-stop) limits, the total amount of energy passing through the interferometer. This restricts the beam divergence to the maximum acceptable for the required resolution. The optical throughput is thus higher for an interferometer. This is known as the Jacquinot or throughput advantage.

b. Fellgett's or multiplex advantage

The amount of light per spectral element for infrared light multiplexed by an infrared interferometer is far greater than a slit-dependent scanning spectrometer. However, in the infrared range, the noise of the spectrum is detector limited. In a slit-limited scanning instrument, when a single line falls on the detector, the noise of the detector sets the noise of the spectrum. However, when the entire spectrum is gathered at the same time, the detector's noise is, in effect, spread over the entire spectrum. As a result, each line has less noise associated with it than when recorded singly. The improvement in signal-to-noise ratio is called the Fellgett or the multiplex advantage. The higher signal-to-noise ratio in a FT infrared spectrometer is due to both multiplex advantage and throughput advantage.

c. Photometric accuracy advantage (Connes advantage)

Another improvement provided by interferometers is the accuracy of the frequencies assigned to absorption bands. Frequency accuracy in a dispersive instrument is limited by the reproducibility of the scanning mechanism as it sequentially moves through the wavelengths of the mid IR range. In contrast to the mechanical process, the interferometer uses a high frequency laser to very precisely reference the system and provide highly accurate frequency assignments.

3.5. RAMAN SPECTROSCOPY

The Raman spectroscopy is made sophisticated with the advent of gas lasers and computers. The advantages of lasers are their high intensity, high monochromaticity, narrow band width, high resolution and coherence. From the time of invention of Raman Effect, both infrared and Raman spectra of chemical compounds have been effectively used for the determination of molecular structure and also for the quick identification of the presence of the characteristic group frequencies in the compound as discussed in the literature [12]. In order that for a molecular vibration to be

Raman active there must be a change in the polarizability of the molecule. A block diagram of BRUKER, FT-Raman Module Spectrograph is shown in Fig. 3.3.

An important advantage of Raman spectra over infrared lies in the fact that water does not cause interference; indeed, Raman spectra can be obtained from aqueous solutions. In addition, glass or quartz cells can be employed, thus avoiding the inconvenience of working with sodium chloride or other atmospherically unstable window materials. Raman spectra are acquired by irradiating a sample with a powerful laser source of visible or near-infrared monochromatic radiation.
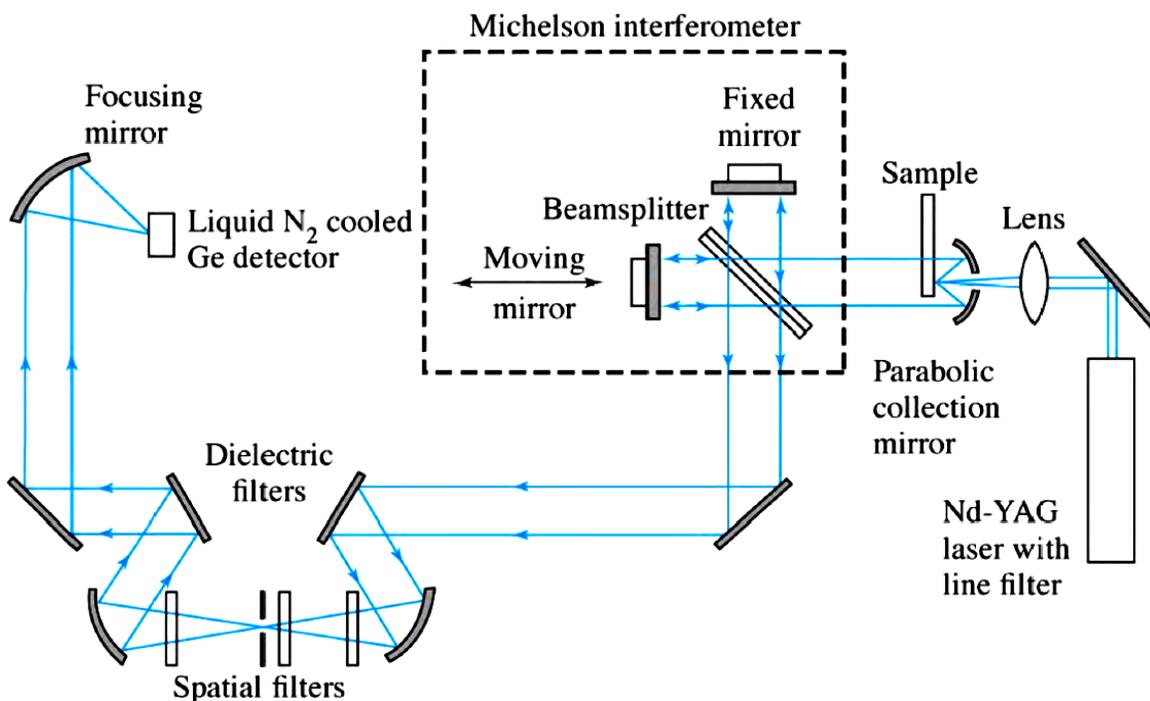

Fig. 3.3: Block Diagram of BRUKER FT-Raman Spectrometer

CHAPTER – IV

VIBRATIONAL AND QUANTUM CHEMICAL STUDIES OF TRANS-4-(TRIFLUOROMETHYL)CINNAMIC ACID

1 Introduction

Cinnamic acid (CA) is known as phenyl acrylic acid or benzal acetate, is a chemical compound, found in cinnamon, a common dietary spice[13]. Aqueous cinnamon extract (ACE), which

35

induces apoptosis in the SiHa cell line via loss of mitochondrial membrane potential, has been previously

reported to have chemo preventative potential in cervical cancer[14]. Many of pharmacological properties

of cinnamon have been reported, including anti-inflammatory, antibacterial[15] and anticancer activities[16].

Recently, the electronic interactions of cinnamic acid derivatives have been carried out by DFT

calculations[17]. *Histone deacetylases (HDACs) are enzymes with a specialized function in tissue*

homeostasis and development[18]. HDACs have been separated into four classes based on their evolutionary

similarity: Class I (HDACs 1, 2, 3, 8); Class II (HDACs 4, 5, 6, 7, 9, 10); Class III HDACs (SIRT1-7); and

Class IV (HDACs 11)[7]. HDACs have significant therapeutic aims for cancer and neurological diseases[19].

Uncontrolled growth occurs in cancer as a result of deregulation of HDAC activity[20]. From the literature,

the DFT based and in vitro mechanisms of cinnamomum exhibit HDAC8 inhibitory activity have

been reported[21].

However, there are no quantum chemical works have been carried out for on *trans-4-*

(trifluoromethyl) cinnamic acid (4TFCA). Therefore, in this study, the analysis on molecular structure

of 4TFCA using DFT method has been performed. The most popular technique for performing

structure calculations in quantum chemistry is DFT, which can yield information about electronic,

vibrational and structural details of the molecule[21,22]. In DFT computations, Becke's three parameter

exchange relations (B3) and the Lee Yang Parr (LYP) functional are very active, which enhances

electron density calculations[23]. The theoretical vibrational assignments, molecular reactivity sites

and the molecular geometric configuration of 4TFCA have been studied using the DFT/B3LYP

method with 6-311++G(d,p) higher basis set, which is useful for enhancing the efficiency of polar

bonds of carbon rings[24]. Initially, the molecular structure was optimized, and after that the

vibrational assignments were done.

2 Experimental Method

2.1 Experimental Characterizations

The 4TFCA was obtained from Sigma Aldrich Chemicals in the United States for the purpose of recording the spectrum. The sample's FTIR was captured using a Perkin Elmer FTIR spectrometer and a KBr pellet with a resolution of 1.0 cm^{-1}. The sample's FT- Raman band was observed using a BRUKER RFS 27 spectrometer model with a resolution of 2 cm^{-1}. The FTIR and FT-Raman scales were investigated in the 4000-400 cm^{-1} and 4000-50 cm^{-1} wavenumber ranges, respectively. The spectroscopic vibrational characterizations are used to check the functional groups of the molecule.

2.2. Quantum Chemical Calculations

The computational studies such as molecular optimization, minimum energy, thermodynamical properties, vibrational wavenumbers calculations, IR intensity, Raman activity and the force field calculations are done by using GAUSSIAN 09W program[25]. DFT calculations of 4TFCA molecule have been achieved by the B3LYP functional with 6-311++G(d,p) basis set and electronic properties have been visualized by Gaussview 05 program[26]. By using a scale factor[27] of 0.9613 for the B3LYP method, the scaled frequencies were obtained which ensures the better agreement between experimental and DFT calculated values. Sundius's MOLVIB software[28] (Adaptation V7.0-G77) is used to calculate the potential energy distribution (PED) for various vibrational modes.

3 Results and Discussions

3.1 Molecular Geometry Analysis

The optimized global energy for 4TFCA is found as -835.50925198 Hartrees. Fig. 1 displays the structure that has been optimized for 4TFCA. It has C_1 symmetry, contains an alkene double bond, a benzene ring and an acrylic acid group in the ring. The computed carbonyl bond lengths for C19-O20, C19-O21 found at 1.202 Å, 1.363 Å which are in well agreement with the corresponding experimental XRD[29,30] data of 1.234 Å, 1.368 Å. In general, the calculated bond distances differ

from the experimental parameters because the experimental results were obtained in the solid state while the computed results were assessed in the gassy state. The bond lengths of C2-H7, C3-H8, C5-H9, C6-H9, C6-H10, C15-H16, C17-H18 are calculated as 1.083 Å, 1.082 Å, 1.082 Å, 1.082 Å, 1.084 Å, 1.087 Å, 1.086 Å by B3LYP and their corresponding experimental values are found at 0.982 Å, 0.978 Å, 1.092 Å, 1.092 Å, 1.087 Å, 0.986 Å, 0.983 Å. The reductions in C-H bond lengths are due to the increase of their force constants. The C-C bond lengths in the aromatic ring have a slight deviation; because of the disorder in the fluorine groups and the electronegativity of oxygen atoms, its values are varied from 1.341 to 1.487 Å. These results show the small amount of electron-delocalization among the π-group of the benzene ring and the rest of the molecule. The C11-F12 bond length is calculated as 1.357 Å by B3LYP and the corresponding XRD data is found at 1.352 Å. The optimized and experimental geometrical parameters of 4TFCA are noted in Table 1. The calculated dihedral angle results clearly specify that the acid group and benzene ring are in the similar plane. The computed bond angles of C2-C1-C6, C4-C3-H8, O20-C19-O21 are calculated as 118.1°, 120.1°, 119.6° (corresponding experimental values: 119.3°, 121.9°, 119.2°). Table 2 provides a description of thermodynamic properties for 4TFCA. In this study, 2.8739 Debye is the extreme dipole moment of 4TFCA, which denotes a greater connection between the atoms of the molecule. The obtained total energy value for 4TFCA is found as 103.812 kcalmol^{-1} and the irrelevant vibrational energy (zero-point) of 95.37866 kcalmol^{-1} is attained. These findings might influence the chemical reactions of 4TFCA.

3.2 Vibrational Assignments

4TFCA has 22 atoms, and leads its 60 normal modes, which are active in both the IR and Raman. Figs. 2 and 3 represent the computational and experimental spectra of 4TFCA. Table 3 illustrates the peak strengths and vibrational wavenumbers of 4TFCA. For heterocyclic compounds, the O-H stretching[31] vibrations are noted in the range 3670-3580 cm^{-1}. As a result, the O-H vibration

is obtained as a weaker band for 4TFCA at 3612 cm^{-1} (99% PED) in the FTIR spectrum. The O-H bending frequencies of 4TFCA are also recognized and are in good consistent with the literature.

The stretching C-H vibrations[32] are formed among 3100-3000 cm^{-1}. The computational frequencies at 3079, 3078, 3061, 3055, 3032 and 3025 cm^{-1} with more than 90% PED are attributed to the C-H stretching vibrations of 4TFCA. The corresponding experimental vibrations are observed in IR at 3066, 3054, 3011, 2957, 2901, 2899 cm^{-1} and in FT-Raman at 3072, 3058, 3017, 2998, 2906, 2893 cm^{-1}. The C-H bending[33] frequencies of 4TFCA are also reported in Table 3. The stretching C-C frequencies play the crucial role in the substituted aromatic structure. Generally, C-C assignments[34] are exhibited in the range 1624-726 cm^{-1}. The experimental peaks in IR at 1619, 1527, 1502, 1477, 1312, 1301, 1299, 1291, 1221, 1122, 1111 cm^{-1} and Raman at 1627, 1529, 1508, 1486, 1321, 1307, 1293, 1286, 1214, 1131, 1102 cm^{-1} are assigned to C-C vibrations with 72-85% PED in 4TFCA. The equivalent DFT wavenumbers are found at 1614, 1589, 1544, 1485, 1387, 1306, 1303, 1287, 1224, 1161, 1118 cm^{-1}. The C=O[35] vibrations are commonly identified in the frequencies range 1780-1700 cm^{-1}. As a result, the experimental stretching C=O vibration of 4TFCA is noted in the FTIR at 1712 cm^{-1} and in the FT-Raman spectrum at 1721 cm^{-1}. The scaled C=O stretching is found as 1743 cm^{-1} for 4TFCA (86% PED). In general, the CF$_3$ stretching[36] vibrations are obtained in the range between 1100 and 1200 cm^{-1}. In this work, the fluorine in-plane stretching wavenumber (72% PED) is computed at 1260 cm^{-1} which matches with the experimental modes at 1253 and 1245 cm^{-1}. The CF$_3$ bending modes for 4TFCA are consistent with the previous report and are reported in Table 3.

3.3 HOMO-LUMO Characterization

The excitation energies can be calculated in a variety of ways and the most basic is the difference among a neutral system's such as highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). The HOMO-LUMO energy values, as well as their

molecular orbital energy gap, reflect the molecule's chemical action. Also, the energy gap among both the HOMO-LUMO has explored intra-molecular charge exchange and bioactivity. Fig. 4 represents the calculated HOMO-LUMO energies for 4TFCA using the B3LYP/ 6-311++G(d,p) basis set. The computed HOMO energy value is -7.4654 eV that reveals the possibility of the electron donor (C-F and C-O bond of ring). The LUMO energy is computed as - 2.8960 eV which suggest the leading most important electron acceptor (C-C bond of ring) and energy gap is calculated as 4.5694 eV. Further, the different molecular properties can be clarified by using Koopman's relations[37]. The chemical characteristics are provided in Table 4. The lowest energy gap and highest electrophilicity implies the strong chemical stability of 4TFCA.

4 Conclusions

Optimized structural parameters and computed normal modes of *trans-4-(trifluoromethyl)cinnamic acid* show well agreement with the experimental data. Molecular orbitals indicate that the molecule has more polarizable and good chemical responses. The electronic absorbance of the molecule has also been matched well with the values of HOMO-LUMO. Therefore, both experimental and computed studies clearly reveal to understand about the vibrational properties of the molecule.

Table 1 — Optimized geometrical parameters of trans-4-(trifluoromethyl) cinnamic acid.

Parameters	Method/Basis set DFT-B3LYP/ 6-311++G(d,p)	Experimental[*]
Bond length (Å)		
C1-C2	1.405	1.412
C1-C6	1.403	1.401
C1-C15	1.463	1.453
C2-C3	1.385	1.372
C2-H7	1.083	0.982
C3-C4	1.398	1.384
C3-H8	1.082	0.978
C4-C5	1.393	1.387
C4-C11	1.505	1.523
C5-C6	1.390	1.378
C5-H9	1.082	1.092
C6-H10	1.084	1.087
C11-F12	1.357	1.352
C11-F13	1.352	1.358
C11-F14	1.350	1.356
C15-H16	1.087	0.986
C15-C17	1.341	1.356
C17-H18	1.086	0.983
C17-C19	1.487	1.492
C19-O20	1.202	1.234
C19-O21	1.363	1.368

O21-H22	0.964	0.982
Bond angle (^{0})		
C2-C1-C6	118.1	119.3
C2-C1-C15	123.3	121.7
C6-C1-C15	118.4	117.2
C1-C2-C3	120.9	121.7
C1-C2-H7	120.2	121.3
C3-C2-H7	118.8	117.2
C2-C3-C4	119.9	119.6
C2-C3-H8	120.1	121.9
C4-C3-H8	119.8	119.8
C3-C4-C5	120.0	121.6
C3-C4-C11	119.6	119.3
C5-C4-C11	120.2	121.7
C4-C5-C6	119.6	118.6
C4-C5-H9	120.1	121.8
C6-C5-H9	120.1	120.3
C1-C6-C5	121.2	122.4
C1-C6-H10	119.2	118.9
C5-C6-C10	119.4	118.9
C4-C11-F12	111.6	110.4
C4-C11-F13	112.0	111.8
C4-C11-F14	112.2	113.3
F12-C11-F13	106.5	105.3
F12-C11-F14	106.6	105.8
F13-C11-F14	107.2	105.4
C1-C15-H16	116.0	115.7
C1-C15-C17	127.8	128.7
H16-C15-C17	116.0	117.8
C15-C17-H18	121.6	122.1
C15-C17-C19	119.9	119.7
H18-C17-C19	118.3	118.6
C17-C19-O20	124.7	123.4
C17-C19-O21	115.5	114.8
O20-C19-O21	119.6	119.2
C19-O21-H22	111.0	111.0
Dihedral angle (^{0})		
C6-C1-C2-C3	-0.0372	-0.0232
C6-C1-C2-H7	179.87	176.87
O20-C19-O21-H22	179.83	177.89
C5-C4-C11-F14	28.8627	30.5679

[*]Experimental values from Ref. [25,26].

Table 2 — The thermodynamic parameters of trans-4-(trifluoromethyl) cinnamic acid.

Parameters	DFT-B3LYP/ 6-311++G(d,p)
Optimized global minimum Energy (Hartrees)	-835.50925198
Total energy(thermal), E_{total} (kcal mol^{-1})	103.812
Heat capacity, C_v (cal mol^{-1} K^{-1})	48.827
Total Entropy, S (cal mol^{-1} K^{-1})	122.612
Translational Entropy (cal mol^{-1} K^{-1})	42.014
Rotational Entropy (cal mol^{-1} K^{-1})	32.680
Vibrational Entropy (cal mol^{-1} K^{-1})	47.918
Vibrational energy, E_{vib} (kcal mol^{-1})	102.034
Zero-point vibrational energy (kcal mol^{-1})	95.37866
Rotational constants (GHz)	
A	2.17377
B	0.19543
C	0.18520
Dipole moment (Debye)	2.8739

Table 3 — The vibrational frequencies (cm^{-1}), IR intensity (Km mol^{-1}) and Raman Activity (Å^4 amu^{-1}) for trans-4-(trifluoromethyl)cinnamic acid.

S. No	Observed wave number		Wave number (cm^{-1})		IR Intensity	Raman activity	Reduced mass	Force constant	Assignment with PED (%)
	FT-IR	FT- Raman	Calculated	Scaled					
1	3612(vw)	-	3816	3668	43.327	72.7073	1.0661	9.1469	vO-H (99)
2	3066(ms)	3072(vw)	3203	3079	0.2405	211.3028	1.0947	6.6201	vC-H (98)
3	3054(ms)	3058(vw)	3202	3078	3.0303	36.5495	1.0935	6.6089	vC-H (96)
4	3011(ms)	3017(vw)	3185	3061	4.1454	29.4368	1.0878	6.5019	vC-H (95)
5	2957(ms)	2998(vw)	3179	3055	3.0311	52.5533	1.0895	6.4879	vC-H (94)
6	2901(ms)	2906(vw)	3155	3032	2.4325	5.8165	1.0863	6.3717	vC-H (90)
7	2899(ms)	2893(vw)	3147	3025	5.2862	58.9441	1.0925	6.3778	vC-H (92)
8	1712(vs)	1721(vw)	1814	1743	307.4326	87.904	9.7008	18.8201	vC=O (88)
9	1619(ms)	1627(vs)	1679	1614	229.8677	1112.539	5.7356	9.5354	vC-C (85)
10	1527(ms)	1529(vs)	1653	1589	0.3063	958.1255	5.6608	9.1198	vC-C (86)
11	1502(w)	1508(vs)	1607	1544	14.4074	25.0912	6.3859	9.7211	vC-C (82)
12	1477(ms)	1486(ms)	1545	1485	0.6274	49.8613	2.4895	3.5052	vC-C (81)
13	1312(vs)	1321(ms)	1443	1387	18.8534	21.788	2.8242	3.4653	vC-O (80)
14	1301(vs)	1307(ms)	1359	1306	66.0758	17.6741	1.82	1.9814	vC-C (83)
15	1299(ms)	1293(ms)	1356	1303	55.4438	49.4591	1.7124	1.8555	vC-C (80)
16	1291(ms)	1286(ms)	1339	1287	3.5049	13.1982	1.7643	1.8658	vC-C (78)
17	1254(ms)	1259(ms)	1320	1268	187.8917	5.0369	3.6416	3.741	CF$_{3ss}$ (75)
18	1253(ms)	1245(ms)	1311	1260	515.8462	66.7317	4.6629	4.7277	CF$_{3ips}$ (72)
19	1221(ms)	1214(ms)	1274	1224	370.3826	49.6264	1.5165	1.4508	vC-C (78)
20	1198(vs)	1199(ms)	1232	1184	38.7658	86.6289	1.7807	1.5942	bO-H (76)
21	1122(vs)	1131(vw)	1208	1161	1.0161	155.9702	1.1997	1.0329	vC-C (74)
22	1111(vs)	1102(vw)	1164	1118	99.4871	9.5234	2.3101	1.8472	vC-C (72)
23	1087(vs)	1094(vw)	1124	1080	71.5974	65.1233	2.6204	1.9513	bC-H (70)
24	1071(vs)	1069(vw)	1117	1073	148.2375	42.4611	2.1466	1.5781	bC-H (71)

25	1061(vs)	1064(vw)	1108	1065	276.7734	14.5729	11.5764	8.3796	bC-H (72)
26	1024(vs)	1012(vw)	1075	1033	203.5658	21.2577	4.0724	2.7754	bC-H (69)
27	998(ms)	991(vw)	1029	989	49.9764	7.7116	3.669	2.2917	bC-H (70)
28	974(ms)	979(ms)	1018	978	30.2859	1.8741	1.2021	0.7352	bC-H (71)
29	950(ms)	948(ms)	990	951	0.5999	0.0307	1.3677	0.7909	Rasymd (68)
30	947(ms)	941(ms)	973	935	7.2736	0.3285	1.3172	0.7355	Rsymd (69)
31	921(ms)	924(ms)	955	918	16.5299	10.4008	4.3183	2.3218	Rtrigd (66)
32	867(ms)	869(ms)	880	845	0.4566	7.7787	1.8436	0.8413	bC-C (68)
33	833(ms)	838(ms)	856	822	11.1926	10.886	5.5631	2.4043	bC-C (65)
34	808(ms)	801(ms)	847	814	43.1803	2.5255	1.5476	0.6547	bC-C (62)
35	791(ms)	799(ms)	844	811	35.5043	0.4456	1.4544	0.6106	bC-C (64)
36	766(vs)	759(ms)	761	731	0.6804	8.3891	5.4402	1.8607	bC=O (65)
37	753(ms)	748(ms)	759	729	8.1651	22.6719	8.5854	2.9152	bC-O (63)
38	698(ms)	691(ms)	704	676	2.4177	0.4012	3.3413	0.978	ωC-H (61)
39	643(ms)	636(vw)	686	659	14.8038	6.1455	8.9185	2.4748	ωC-H (60)
40	621(ms)	624(vw)	650	624	0.4751	8.9268	7.1127	1.775	CF$_{3ops}$ (62)
41	598(ms)	595(vw)	617	593	0.7238	1.6831	8.0024	1.7987	ωC-H (64)
42	552(ms)	557(vw)	589	566	9.9017	0.4919	4.086	0.8377	CF$_{3ipb}$ (67)
43	532(mS)	538(vw)	572	549	0.4291	0.6726	10.3289	1.9964	CF$_{3sb}$ (69)
44	497(ms)	503(vw)	526	505	6.0977	0.5525	4.7599	0.7775	ωC-H (67)
45	491(ms)	496(vw)	504	484	2.1681	0.5675	4.3398	0.6497	ωC-H (68)
46	438(ms)	431(vw)	425	408	35.006	1.2139	2.0113	0.2145	ωC-H (64)
47	391(ms)	396(vw)	410	394	8.2691	1.0614	4.1945	0.4165	CF$_{3ipr}$ (69)
48	386 (ms)	394(vw)	406	390	5.1558	0.4284	3.323	0.3229	tRsymd (59)
49	377(ms)	368(vw)	391	375	55.5613	0.2766	2.5383	0.2295	tRasymd (58)
50	354(ms)	357(vw)	386	371	18.0611	0.3228	5.7775	0.5075	tRtrigd (60)
51	299(ms)	283(vw)	297	285	12.8856	1.0507	6.5755	0.3427	ωO-H (61)
52	231(vw)	241(vw)	256	246	3.7913	0.3267	5.166	0.2008	ωC-C (59)
53	-	188(ms)	205	197	0.3114	4.0889	10.9498	0.2724	ωC-C (58)
54	-	166(ms)	178	171	1.647	1.9283	9.0884	0.1703	ωC-C (56)
55	-	133(ms)	129	124	1.5516	2.3176	8.0592	0.0797	ωC-C (60)
56	-	84(ms)	77	74	4.6556	0.3265	6.5604	0.0234	CF$_{3opr}$ (62)
57	-	78(ms)	75	72	0.6757	0.9731	2.9687	0.01	ωC=O (57)
58	-	47(ms)	45	43	9.5061	0.6033	8.8113	0.0107	ωC-O (58)
59	-	15(ms)	19	18	0.0849	2.0804	5.071	0.0011	CF$_{3opb}$ (56)
60	-	12(ms)	14	13	1.6226	1.7374	6.465	0.0009	CF$_{3torsion}$ (55)

Table 4 — Global reactivity descriptors for trans-4-(trifluoromethyl) cinnamic acid.

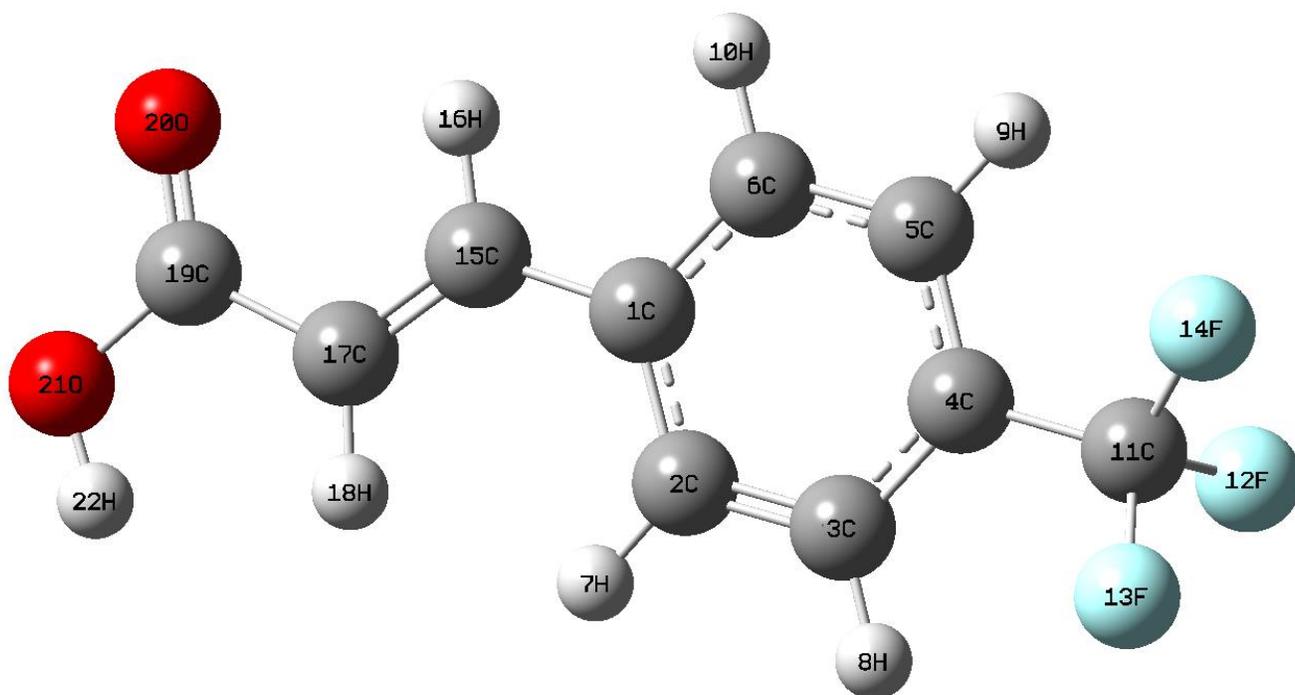| Molecular Properties	B3LYP/6-311++G(d,p)
HOMO (eV)	-7.4654
LUMO (eV)	-2.8960
Homo-Lumo gap (ΔE) (eV)	4.5694
Ionization potential (I) (eV)	7.4654
Electron affinity (A) (eV)	2.8960
Global **hardness (η)** (eV)	2.2847
Global softness (s) (eV^{-1})	0.2188
Electronegativity (χ) (eV)	5.1807
Chemical potential (μ) (eV)	-5.1807
Global electrophilicity (w) (eV)	11.7475

Fig. 1 - Optimized structure of trans-4-(trifluoromethyl)cinnamic acid
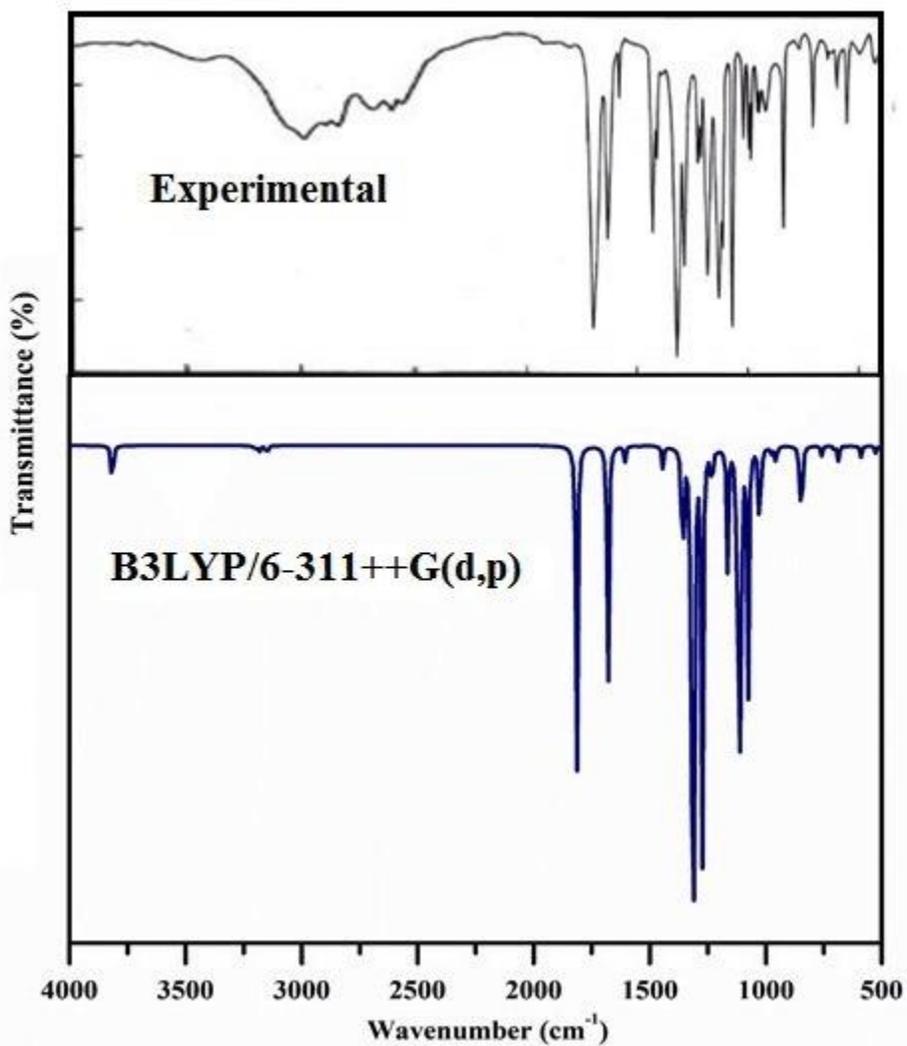
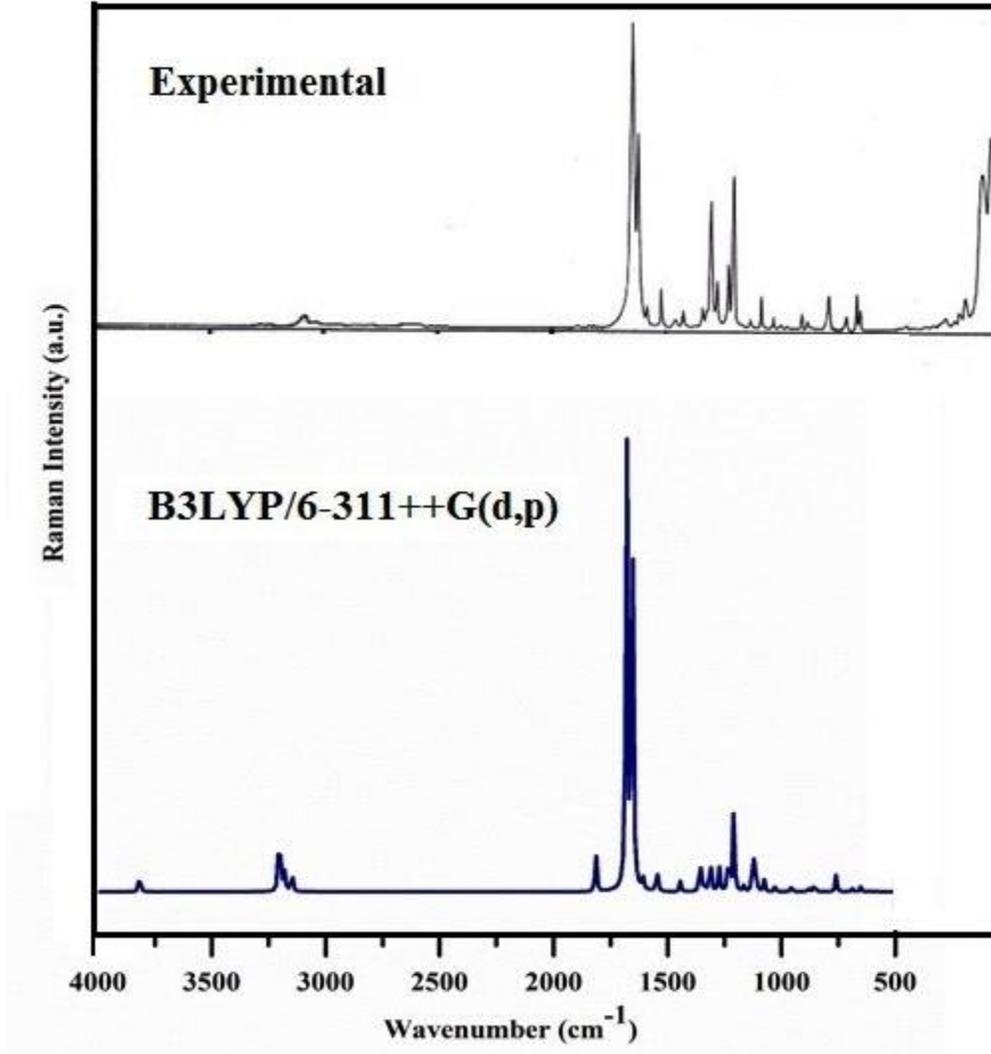Fig. 2 - FTIR spectrum of trans-4-(trifluoromethyl)cinnamic acid

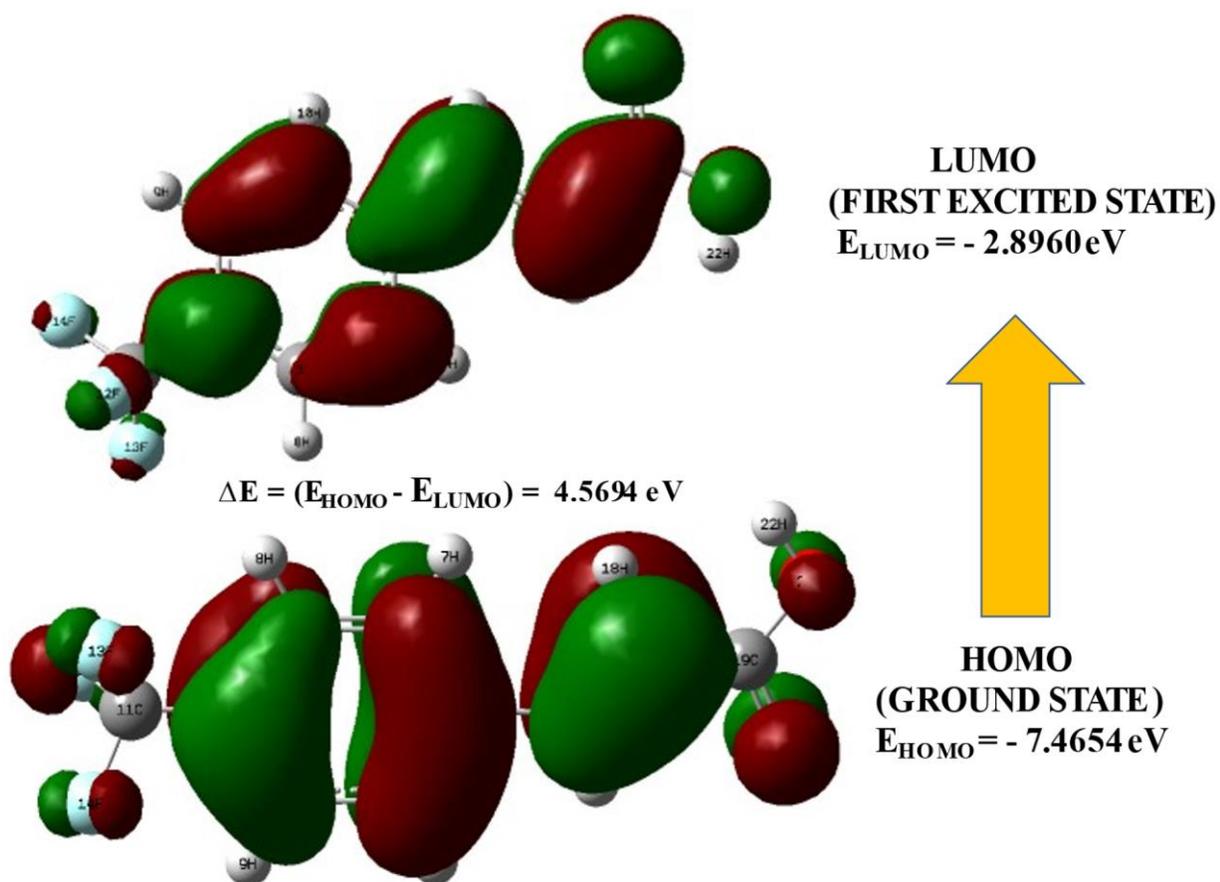Fig. 3 - FT-Raman spectrum of trans-4-(trifluoromethyl)cinnamic acid

LUMO
(FIRST EXCITED STATE)
$E_{LUMO} = -2.8960\,eV$

$\Delta E = (E_{HOMO} - E_{LUMO}) = 4.5694\,eV$

HOMO
(GROUND STATE)
$E_{HOMO} = -7.4654\,eV$

Fig. 4 - HOMO-LUMO plot of trans-4-(trifluoromethyl)cinnamic acid

REFERENCES

1. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Fifth Edition, Part A, John Wiley & Sons Inc., New York, 1977.

2. B.C. Smith, Fundamentals of Fourier Transform Infrared Spectroscopy, CRC Press, Boca Raton, 1996.

3. K.V. Raman, Group Theory and its Applications to Chemistry, Tata McGraw-Hill, New Delhi, 1990.

4. D.N. Sathyanarayana, Vibrational Spectroscopy - Theory and Applications, Second ed., New Age International (P) Limited Publishers, New Delhi, 2004.

5. P. Pulay, G. Fogarasi, G. Pongor, J.E. Boggs, A. Vargha, J. Am. Chem. Soc. 105 (1983) 7037-7047.

6. B. Giese, D. McNaughton, Phys. Chem. Chem. Phys., 4 (2002) 5161-5170.

7. N. Yu. Panchenko, Russ. Chem. Bull., 45(4) (1996) 753-760.

8. G. Fogarasi, P. Pulay, Annu. Rev. Phys. Chem. 35 (1984) 191-213.

9. T. Sundius, J. Mol. Spectrosc. 82 (1980) 138-151.

10. J.R. Durig, S.M. Craven, W.C. Harris, Vibrational spectra and structure, Ed. James R. Durig, Marcel Dekker, Inc., New York, 1972.

11. B.K. Sharma, Spectroscopy, Goel Publishing House (2000).

12. W.G. Fateley, F.F. Bently, F.R. Dollis, Characteristic Raman Frequencies of Organic Compounds, John Wiley and Sons, New York 1974.

13. Mathew S & Abraham, *Food Chem,* 94 (2006) 520.

14. Koppikar S J, Choudhari A S, Suryavanshi S A, Kumari S, Chattopadhyay S & Kaul-Ghanekar R, *BMC Cancer,* 10 (2010) 1.

15. Tung Y T, Chua M T, Wang S Y & Chang S T, *Bioresour Technol,* 99 (2008) 3908.

16. Matan N, Rimkeeree H, Mawson A J, Chompreeda P, Haruthaithanasan V & Parker M, *Int J Food Microbiol,* 107 (2006) 180.

17. Abu-Eittah R H, Khedr M K, Goma M & Zordok W, *Int J Quantum Chem,* 112 (2012) 1256.

18. Fischle W, Dequiedt F, Hendzel M J, Guenther M G, Lazar M A, Voelter W & Verdin E, *Mol Cell,* 9 (2002) 45.

19. Lahm A, Paolini C, Pallaoro M, NardiM C, Jones P, Neddermann P, Sambucini S, Bottomley M J, Surdo P L, Carfí A, Koch U, Francesco R D, Hler C S & Gallinari P, *PNAS*, 104 (2007) 17335.

20. Vannini A, Volpari C, Filocamo G, Casavola E, Brunetti M, Renzoni D, Chakravarty P, Paolini C, Francesco R, Gallinari P, Steinkü C & Marco S D, *PNAS,* 101 (2004) 15064.

21. Senawong T, Misuna S, Khaopha S, Nuchadomrong S, Sawatsitang P, Phaosiri C, Surapaitoon A & Sripa B, *BMC Complement Med Ther,* 13 (2013) 1.

22. Patil M, Choudhari A, Pandita S, M. Islam M A, Raina P & Kaul-Ghanekar R, *Pharmacogn Mag,* 13 (2017) 645.

23. Becke A D, "Density-Functional Thermochemistry. III. The Role of Exact Exchange," *J Chem Phys,* 98 (1993) 5648.

24. Kohn W, Becke A D & Parr R G, *J Phys Chem A,* 100 (1996) 12974.

25. Frisch M J, Trucks G W, Schlegal H B, et al., Gaussian09, Revision A.02, Gaussian Inc, Wallingford CT, 2009.

26. Dennington R, Keith T A & Millam J M, Gauss View, Version 5 (Shawnee Mission, KS: Semichem Inc, 2009).

27. Young D C, *Computational Chemistry: A Practical Guide for Applying Techniques to Real World Problems (Electronic)* (New York, NY: John Wiley & Sons Ltd, 2001).

28. Sundius T, *Vib Spectrosc,* 29 (2002) 89.

29. Howard J A K & Sparkes H A, *Cryst Eng Comm,* 10 (2008) 502.

30. Bryan R F & Freyberg D P, *J Chem Soc Perkin Trans,* 2 (1975) 1835.

31. Pandimeena G, Premkumar R, Mathavan T & A M F Benial, *J Mol Struct,* 1231 (2021) 129996.

32. Jeyavijayan S & Arivazhagan M, *Indian J Pure & Appl Phys,* 50 (2012) 623.

33. Jeyavijayan S, Gobinath E, Viswanathan K & Senthil Kumar J, *Indian J Pure & Appl Phys,* 56 (2018) 108.

34. Sivaraj G, Jayamani N & Siva V, *J Mol Struct,* 1240 (2021) 130530.

35. Ramuthai M, Jeyavijayan S, & Naidu Dhanpal Jayram, *Polycycl. Aromat. Compd.,* 42(10) (2022) 6988.

36. Kreienborg N M & Merten C, *Phys Chem Chem Phys,* 21 (2019) 3506.

37. Sundaraganesan N, Elango G, Meganathan C, Karthikeyan B & Kurt M, *Mol Simul,* 35 (2009) 705.