VIBRATIONAL SPECTROSCOPIC INVESTIGATIONS,DFT COMPUTATIONS AND NON LINEAR OPTICAL PROPERTIES OF 7-HYDROXY COUMARIN

Msc Project Report (2019-2021)

submitted to **MES KEVEEYEM COLLEGE,VALANCHERRY** affiliated to **University of Calicut** in partial fulfillment of the requirement for the award of degree of

Master of Science in Physics.

Department of Physics

MES KEVEEYEM COLLEGE

2019-2021

SUBMITTED BY

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CERTIFICATE

This to certify that the project report entitled **"VIBRATIONAL SPECTROSCOPIC INVESTIGATIONS,DFT COMPUTATIONS AND NON LINEAR OPTICAL PROPERTIES OF 7-HYDROXY COUMARIN"** submitted by **FATHIMATH NIHALA SAFREEN PT**, in partial fulfilment of the requirements for the award of Master of Science Program in Physics at the **MES KEVEEYEM** college, valanchery is an authentic work carried out by her under my supervision and guidance during the year 2019-2021.

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External Examiners

1.

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DECLARATION

I hereby declare that the project entitled **"VIBRATIONAL SPECTROSCOPIC INVESTIGATIONS,DFT COMPUTATIONS AND NON LINEAR OPTICAL PROPERTIES OF 7-HYDROXY COUMARIN "** is submitted by me under guidance of **Dr. SHINEY.A,** Assistant professor, Department of physics, PSMO College, Tirurangadi. I also declare that the information in this project is correct to the best of my knowledge and belief, and this project does not form a part of any other degrees of any university.

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ABSTRACT

In this study the FTIR and FT-Raman spectra of Umbeliferone have been recorded in the regions infrared and microwave respectively. Utilizing the observed FT-Raman and FTIR data, a complete vibrational assignment and analysis of the fundamental modes of the compound have been carried out . In the calculations performed to determine the optimum molecular geometry,harmonic vibrational frequencies,IR intensities and Raman scattering activities,the Density functional theory(DFT/B3LYP) method with 6-311++G(d,p) basisset has been used.The theoretical optimized geometric parameters and vibrational frequencies are found to be in good agreement with corresponding experimental data.The NLO properties such as polarizability ,first hyperpolarizability,electron affinity,ionisation potential,chemical potential,energy gap,chemical softness and chemical hardness of the molecule have been calculated. The effects of Frontier orbitals,HOMO , LUMO and MEP have been discussed.

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CHAPTER 1

1.1 INTRODUCTION

Materials science is an interdisciplinary field involving the properties of matter and its applications to various areas of science and engineering. It includes elements of applied physics and chemistry, as well as chemical, mechanical, civil and electrical engineering. The basis of all materials science involves relating the desired properties and relative performance of a material in a certain application to the structure of the atoms and phases in that material through characterization. **Materials Science centers on the relationships among the processing, structure, properties and performance of six major classes of materials:**

- Metals.
- Ceramics.
- Polymers.
- Composites.
- Semiconductor
- Biomaterials

Beginning in the 1940s, materials science began to be more widely recognized as a specific and distinct field of science and engineering, and major technical universities around the world created dedicated schools for its study. Materials scientists emphasize understanding, how the history of a material (*processing*) influences its structure, and thus the material's properties and performance. The understanding of processing-structure-properties relationships is called the materials paradigm. This paradigm is used to advance understanding in a variety of research areas, including nanotechnology,biomaterials, and metallurgy. Materials science is also an important part of forensic engineering and failure analysis – investigating materials, products, structures or components, which fail or do not function as intended, causing personal injury or damage to property. Such investigations are key to understanding, for example, the causes of variousaviation accidents and incidents.

DFT calculations have recently become an efficient tool in the prediction of geometry of molecular structure. Mulliken structure and vibrational wavenumbers(FTIR and Raman) predict relatively accurate molecular structure and vibrational spectra with moderate computational effort. From the spectroscopic point of view,in recent years numerous experimental and theoretical studies have been made on the umbelliferone and its derivates.However the detailed B3YLP studies on the complete FTIR and FT-Raman Spectra of umbelliferone have not been reported so far.Hence in the present investigation,molecular geometry,optimized parameters and vibrational frequencies are computed and the performance of the computational method for B3LYP with 6-311++G(d,p) basis set is made.

Vibrational spectroscopy has immense importance as an important tool in the pharmaceutical application, where this spectroscopy technique encompasses Fourier Transform infrared (FT IR), Raman and near-infrared spectroscopy. These techniques are sensitive to the chemical structure of the compound and to the environment, where the bond vibrations are measured as an analyzing parameter (Jamieson and Byrne, 2017). Thus, the changing of vibration can help in the determination of solid-state characterization behavior of API and also as a potential probe to determine intermolecular interaction among different ingredients (Volpati et al., 2014). Therefore, any pharmaceutical interaction type, including dehydration or hydrate formation, desalting, morphological changes, or interchange between amorphous and crystalline can easily be identified by this technique. Vibrational Spectroscopy includes Raman spectroscopy, infrared spectroscopy and near infrared spectroscopy.

Raman spectroscopy is commonly used in chemistry to provide a structural fingerprint by which molecules can be identified. A source of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range is used, although X-rays can also be used. The laser light interacts with molecular vibrations, phonons or other excitations in the system, resulting in the energy of the laser photons being shifted up or down. The shift in energy gives information about the vibrational modes in the system.Raman scattering is a phenomenon in which photons incident on a sample are inelastically scattered after interacting with vibrating molecules within the sample. The effect was first discovered by Chandrasekhara Venkata Raman in 1928, for which discovery Prof. Raman received the 1930 Nobel Prize in Physics. While Raman spectroscopy is now used in biology and medicine, Raman spectroscopy found its first applications in physics and chemistry and was mainly used to study vibrations and structure of molecules. One early factor limiting the implementation of Raman spectroscopy was the weak scattering signal. Large intensities of monochromatic light are required to excite a detectable signal. This requirement became much easier to realize following the invention of the laser in 1960. Soon thereafter, lasers were used to drive Raman scattering and the number of applications increased rapidly, particularly in the analysis of biomolecules. Other important developments accelerating the progress of Raman spectroscopy include the digitization of spectra using charge-coupled devices (CCDs), the confocal Raman microscope, and improved filters to remove light at the laser wavelength. These inventions allowed a rapid increase in the popularity of using Raman to study biological samples in the early 1990s. Over the last years, there has been tremendous technical improvement in Raman spectroscopy, as overcome by the problems like fluorescence, poor sensitivity or reproducibility. New trends of applications of Raman spectroscopy ranges from ancient archaeology to advanced nanotechnology. Raman spectroscopic measurements is also used for the analysis of various substances categorized into distinct application areas such as biotechnology, mineralogy, environmental monitoring, food and beverages, forensic science, medical and clinical chemistry, diagnostics, pharmaceutical, material science, surface analysis, etc. Advances in the instrumental design of Raman spectrometers coupled with newly developed sampling methodologies have also been described which enable trace level detection and satisfactory analysis.

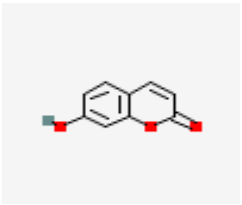
Fourier-transform infrared spectroscopy (FTIR) is a technique used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas. Fourier Transform Infrared (FTIR) spectroscopy is an analytical methodology used in industry and academic laboratories to understand the structure of individual molecules and the composition of molecular

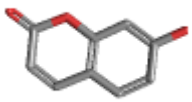
mixtures. FTIR spectroscopy uses modulated, mid-infrared energy to interrogate a sample. The infrared light is absorbed at specific frequencies directly related to the atom-to-atom vibrational bond energies in the molecule. When the bond energy of the vibration and the energy of mid-infrared light are equivalent, the bond can absorb that energy. Different bonds in a molecule vibrate at different energies, and therefore absorb different wavelengths of the IR radiation. The position (frequency) and intensity of these individual absorption bands contribute to the overall spectrum, creating a characteristic fingerprint of the molecule. FTIR spectroscopy equipment has broad use and applicability in the analysis of molecules important in the pharmaceutical, chemical and polymer industries. FTIR analysis is used in both industry and academic laboratories to better understand the molecular structure of materials as well as reaction kinetics, reaction mechanism and pathways in chemical reactions and catalytic cycles. FTIR spectroscopy is used to ensure that raw materials, intermediate compounds and final products are within specification. In chemical and pharmaceutical R&D, in-situ FTIR spectroscopy is used to help scale-up chemical reactions, optimize reaction yield and minimize by-product impurities. In chemical and pharmaceutical production, FTIR spectroscopy functions as a process analytical technology (PAT), ensuring that processes are stable, in control, and achieve final product specifications.

Umbelliferone, also known as 7-hydroxycoumarin, hydrangine, skimmetine, and beta-umbelliferone, is a natural product of the coumarin family.It absorbs ultraviolet light strongly at several wavelengths.It is a yellowish-white crystalline solid that has a slight solubility in hot water, but high solubility in ethanol.Umbelliferone occurs in many familiar plants from the Apiaceae (Umbelliferae) family such as carrot, coriander and garden angelica, as well as in plants from other families, such as the mouse-ear hawkweed (Hieracium pilosella, Asteraceae) or the bigleaf hydrangea (Hydrangea macrophylla, Hydrangeaceae, under the name hydrangine).It is also found in Justicia pectoralis.It used as a sunscreen agent, and an optical brightener for textiles. It has also been used as a gain medium for dyelasers. Umbelliferone can be used as a fluorescence indicator for metal ions such as copper and calcium. It acts as a pH indicator in the range 6.5-8.9.

1.2 LITERATURE REVIEW

Umbelliferone is a coumarin widely spread in plants and is a benzopyrone in nature. The coumarin name originates from ‘Cou- marou’, the vernacular name for the tonka bean (Dipteryx odorata Willd, Fabaceae), from which coumarins were isolated in 1820 . The umbelliferae family is inclusive of economically important herbs such as sanicle, alexanders, angelica, asafoetica, celery, cumin, fennel, parsley and giant hogweed. The name Umbellifer- one on the other hand was derived from the umbelliferae family of plants, and the latter were named for their umbrella-shaped inflorescences . UMB is a 7-hydroxycoumarin that is a pharmacologically active agent. By virtue of its structural simplicity UMB has been generally accepted as the parent compound for the more complex coumarins and is widely used as a synthon for a wider variety of coumarin-heterocycles. It is widely used as anti- bacterial and anti-fungal, for the treatment of diabetes, cancer, hepatocellular carcinoma, has antioxidant property, in the treatment of cerebral ischemia, Parkinson ’s disease, in the treatment of bronchial asthma.





2D 3D CRYSTAL

Fig1: Structure of umbelliferone

Its molecular formula is C9H6O3. It is a yellowish-white needle-like crystal that has a slight solubility in hot water, but high solubility in ethanol, dioxane . It has a molecular weight of 162.144g/mol, melting point: 230-233^{0}C, log P value: 1.58. It absorbs ultraviolet light strongly at several wavelengths. The absorbance maximum in acid is 325 nm while in alkaline solution it shifts to 365 nm. The fluorescence excitation maxima in acid and alkali solutions are 330nm and 370 nm respectively, while the emission maxima is 460 nm .The optimized geometry is planar and the OH group lies on the same plane as the whole molecule.

UMB has broadly circulated inside the Rutaceae and Apiaceae (Umbelliferae) families and is extracted utilizing methanol. Additionally, present in angelica, coriander, carrot and in addition in plants from different families , for

example, the huge leaf (*Hydrangea macrophylla*, Hydrangeaceae, under the name hydrangine) or the mouse-ear hawkweed (*Hieracium pilosella*, Asteraceae).

Source	**Part of plant**	**Family**	**Extracting solvent**
Acacia nilotica	Bark	Mimosaceae	MeOH
Coriandrum sativum	Aerial	Umbelliferae	MeOH
Ferula communis	Peduncles	Umbelliferae	MeOH
Ferula asafoetida	Rhizomes	Umbelliferae	MeOH
Glycyrrhiza glabra	Rhizomes	Fabaceae	MeOH
Ipomoea mauritiana	Tuber	Convolvulaceae	MeOH
Platanusacerifolia	Stem	Planataceae	EtOH

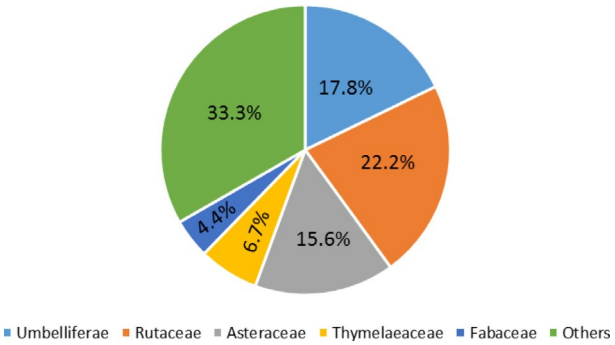


Fig2:Plant families containing umbelliferone

Umbelliferone and HP-a-CD solution are mixed and stirred for 48hrs in a magnetic stirrer.The solid unclusion complex was obtained as a yellow powder.Umbelliferone -HPa-CD complex prepared by inclusion method showed increasing the solubility and dissolu- tion rate in comparision with the plain Umbelliferone. we can synthesize some new coumarins derived from umbelliferone (7-hydroxycoumarin) with predictable biological activities. Umbelliferone is a phenylpropanoid and as such is synthesized from LPhenylalanine. Umbelliferone is traditionally synthesized using the Pechmann condensation, from resorcinol and formylacetic acid. Biosynthetically it is synthesized using the phenylpropanoid pathway. Umbelliferone is the parent compound for a large number of natural products.

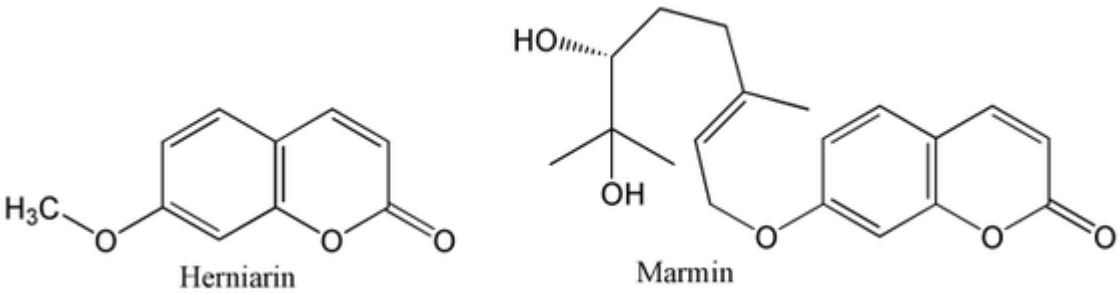


Fig3:umbelliferone derivatives

Umbelliferone has been shown to exhibit various pharmacological applications against various health-related conditions, including conditions related to pro-oxidants and reactive oxygen species such as inflammation, degenerative diseases, microbial infections and cancer cells.Lipid nanoparticles [n-hexadecyl palmitate (CP) and glyceril stearate (GS)] were used to entrap umbelliferone and the hydrodynamic diameters varied from 120 nm to 220 nm. The umbelliferone-loaded solid lipid nanoparticles prepared with Tween 80 surfactant exhibited good entrapment efficiency (60.70%) and antioxidant property (75%) using chemiluminescence method involving luminol. Umbelliferone is a weak monoprotic Brönsted acid that is not fluorescent in acid solutions below pH = 8. The coumarin in a solution exposed to the UV radiation exist as singly charged, green fluorescent anion. Thus, a slightly acidic solution has no visible green fluorescence. When aerosols from the slightly acid and basic (pH = ∼12) solutions were mixed a green fluorescence typical of the umbelliferone anion was reported. This shows that uncharged droplets collide, merge and produced a product with the expected fluorescent properties and a narrow distribution of nanoparticle sizes. Umbelliferone exhibits anti-inflammatory activities where the significant activities were the protection of DNA against gamma irradiation damage and protection from the diclofenac side effects. An anti-hyperglycemic effect was reported on streptozotocin rats. An effective fluorescent probe for hydrogen peroxide was also reported. Umbelliferone has potential as a protector against the side effects of anti-inflammatory agents.

CHAPTER 2

THEORY

THEORY

Spectroscopy played a key role in the development of quantum mechanics and is essential to understand molecular properties and the results of spectroscopic experiments.Molecular spectroscopy is based on the interaction of radiation and matter. It is the powerful tool for learning about nature of atoms and molecules.Molecular spectroscopy is a subject of quantum physics. **Spectroscopy** is **used** as a tool for studying the structures of atoms and **molecules**. The large number of wavelengths emitted by these systems makes it possible to investigate their structures , including the electron configurations of ground and various excited states. There are three basic **types** of spectrometer systems that are commonly used for **molecular spectroscopy**:

- Emission
- monochromatic radiation absorption
- Fourier transform.

Each of these methods involves a source of radiation, a sample, and a device for detecting and analyzing radiation.The principle of **molecular spectroscopy** is the excitation of atoms and **molecules** by photons. Atoms and **molecules** excited from the ground state undergo either resonant vibrations or electronic transitions, depending on the nature of the induced quantum mechanical changes.

Molecular spectroscopy involves the interaction of electromagnetic radiation with materials in order to produce an absorption pattern (i.e. a spectrum) from which structural or compositional information can be deduced. **Spectroscopy** is the study of the interaction between matter and electromagnetic radiation as a function of the wavelength or frequency of the radiation.

2.1 SPECTROSCOPIC METHODS

2.1.1 RAMAN SPECTROSCOPY

Raman Spectroscopy is a non-destructive chemical analysis technique which provides detailed information about chemical structure, phase and polymorphy, crystallinity and molecular interactions. It is based upon the interaction of light with the chemical bonds within a material. **Raman spectroscopy** is used to determine vibrational modes of molecules, although rotational and other low-frequency modes of systems may also be observed. Raman spectroscopy is commonly used in chemistry to provide a structural fingerprint by which molecules can be identified. During an experiment using Raman spectroscopy, light of a single wavelength is focused onto a sample. Most commonly a laser is used as it is a powerful monochromatic source. The photons from the laser interact with the molecules of the sample and are scattered inelastically. The scattered photons are collected and a spectrum is generated from the scattered photons.Photons interacting with molecules most commonly scatter elastically. This is called Rayleigh scattering. Rayleigh scattered photons have the same wavelength as the incident light. However, approximately 1 out of a million photons are inelastically scattered.This effect was first described by Sir Chandrasekhara Raman in 1922. This is the principle from which Raman spectroscopy derives.

Factors influence Raman scattering:

- The polarization state of the molecule (which determines the Raman scattering intensity) must be considered.
- The greater the change in polarizability of the functional group, the greater the intensity of the Raman scattering effect.

This means that some vibrational or rotational transitions, which exhibit low polarizability, and will not be Raman active. They will not appear in a Raman spectra. It should be noted that Raman scattering is a very weak effect as most photons are Rayleigh scattered. However, the intensity of the effect can be dramatically increased using resonance Raman spectroscopy.

2.1.1.1 Classical Theory Of Raman Effect

The classical theory of the Raman effect is based upon polarizability of molecules, which reflects how easy an electron cloud of a molecule can be distorted by an electric field (light). The technique is based on molecular deformations in electric field E determined by molecular polarizability α. The laser beam can be considered as an oscillating electromagnetic wave with electrical vector E. Upon interaction with the sample it induces electric dipole moment P = αE which deforms molecules. Because of periodical deformation, molecules start vibrating with characteristic frequency.The scattered light can have a frequency equal to the incident light (Rayleigh), equal to the incident light minus the vibrational frequency (Stokes) and equal to the incident light plus the vibrational frequency (anti-Stokes).

2.1.1.2 Ramanshift

The Raman shift is the energy difference between the incident (laser) light and the scattered (detected) light. This difference is then only connected to the energetic properties of the molecular vibrations studied and hence independent of the laser wavelength. The Raman shift is usually expressed in wavenumbers,which has a unit of inverse length(cm-1). In order to convert between spectral wavelength and wavenumbers of shift in the Raman spectrum, the following formula can be used:

$$\Delta\tilde{\nu} = \left(\frac{1}{\lambda_0} - \frac{1}{\lambda_1}\right)$$

Where lamda0 is the excitation wavelength,lamda1is the Raman spectrum wavelength.

2.1.1.3 Applications

1. Raman spectroscopy is used in chemistry to identify molecules and study chemical bonding and intramolecular bonds. Because vibrational frequencies are specific to a molecule's chemical bonds and symmetry.
2. In solid-state physics, Raman spectroscopy is used to characterize materials, measure temperature, and find the crystallographic orientation of a sample.
3. In nanotechnology, a Raman microscope can be used to analyze nanowires to better understand their structures, and the radial breathing mode of carbon nanotubes is commonly used to evaluate their diameter.

4. In solid state chemistry and the bio-pharmaceutical industry, Raman spectroscopy can be used to not only identify active pharmaceutical ingredients (APIs), but to identify their polymorphic forms, if more than one exist.
5. Raman spectroscopy has a wide variety of applications in biology and medicine. It has helped confirm the existence of low-frequency phonons in proteins and DNA, promoting studies of low-frequency collective motion in proteins and DNA and their biological functions.
6. Raman spectroscopy has been used in several research projects as a means to detect explosives from a safe distance using laser beams.

2.1.2 FT-IR SPECTROSCOPY

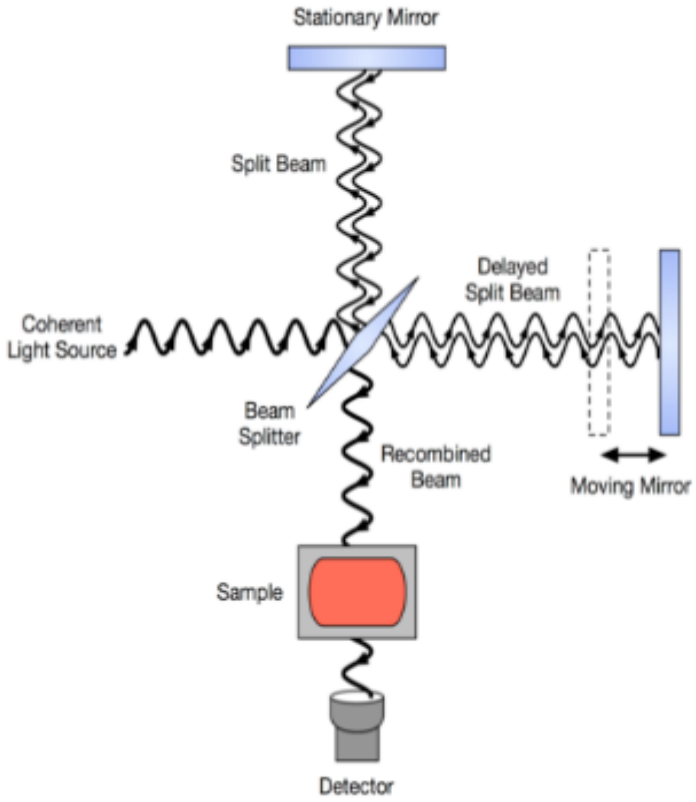
Fourier transform infrared spectroscopy (FTIR) is a technique which is used to obtain infrared spectrum of absorption, emission, and photoconductivity of solid, liquid, and gas. It is used to detect different functional groups. FTIR spectrum is recorded between 4000 and 400 cm^{-1}. For FTIR analysis, the polymer was dissolved in chloroform and layered on a NaCl crystal and after evaporation of chloroform, the polymer film was subjected to FTIR. Fourier transform infrared spectroscopy (FTIR) uses the mathematical process (Fourier transform) to translate the raw data (interferogram) into the actual spectrum. FTIR method is used to obtain the infrared spectrum of transmission or absorption of a fuel sample. FTIR identifies the presence of organic and inorganic compounds in the sample. FTIR is useful in identifying and characterizing unknown materials, detecting contaminants in a material, finding additives, and identifying decomposition and oxidation.

Rather than shining a monochromatic beam of light (a beam composed of only a single wavelength) at the sample, this technique shines a beam containing many frequencies of light at once and measures how much of that beam is absorbed by the sample. Next, the beam is modified to contain a different combination of frequencies, giving a second data point. This process is rapidly repeated many times over a short time span. Afterwards, a computer takes all this data and works backward to infer what the absorption is at each wavelength.

The beam described above is generated by starting with a broadband light source—one containing the full spectrum of wavelengths to be measured. The light shines into a Michelson interferometer—a certain configuration of mirrors, one of which is moved by a motor. As this mirror moves, each wavelength of light in the beam is periodically blocked, transmitted, blocked, transmitted, by the interferometer, due to wave ionterference. Different wavelengths are modulated at different rates, so that at each moment or mirror position the beam coming out of the interferometer has a different spectrum.

As mentioned, computer processing is required to turn the raw data (light absorption for each mirror position) into the desired result (light absorption for each wavelength). The processing required turns out to be a common algorithm called the fourier transform. The Fourier transform converts one domain (in this case displacement of the mirror in cm) into its inverse domain (wavenumbers in cm^{-1}). The raw data is called an "interferogram".

2.1.2.1 Michelson Interferometer



In a Michelson interferometer adapted for FTIR, light from the polychromatic infrared source, approximately a black-body radiator, is collimated and directed to a beam splitter. Ideally 50% of the light is refracted towards the fixed mirror and 50% is transmitted towards the moving mirror. Light is reflected from the two mirrors back to the beam splitter and some fraction of the original light passes into the sample compartment. There, the light is focused on the sample. On leaving the sample compartment the light is refocused on to the detector. The difference in optical path length between the two arms to the interferometer is known as the retardation or optical path difference (OPD).An interferogram is obtained by varying the retardation and recording the signal from the detector for various values of the retardation. The form of the interferogram when no sample is present depends on factors such as the variation of source intensity and splitter efficiency with wavelength. This results in a maximum at zero retardation, when there is constructive interference at all wavelengths, followed by series of "wiggles". The position of zero retardation is determined accurately by finding the point of maximum intensity in the interferogram. When a sample is present the background interferogram is modulated by the presence of absorption bands in the sample.

2.1.2.2 Applications

1. FTIR is also used to investigate various nanomaterials and proteins in hydrophobic membrane environments.
2. Microscopy and imaging.
3. FTIR as detector in chromatography.

4. FTIR analysis is used to determine water content in fairly thin plastic and composite parts

CHAPTER 3

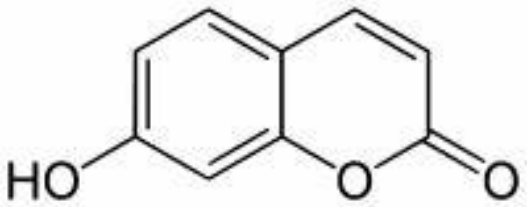
EXPERIMENTAL METHODS AND MATERIALS

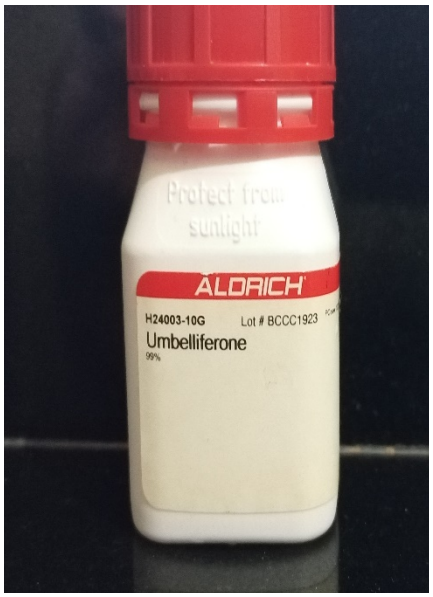
3.1 SAMPLE USED:UMBELLIFERONE

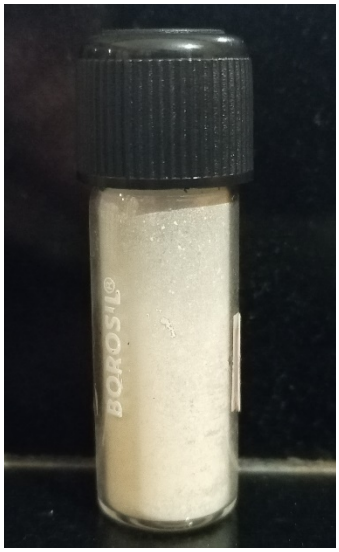
The compound under investigation namely Umbelliferone was purchased from Sigma Aldrich,a global science and technology company, which is of spectroscopic grade and hence used for recording the spectra as such without any further purification. The FTIR spectrum of the compound were recorded in the range393.41-4003.525cm^-1.The FT-Raman spectrumof the title compound have been recorded in the range 162-1982cm^-1.

Umbelliferone (UMB) is 7-hydroxycoumarin (otherwise called as skimmetine, hydrangine) is a coumarin widely spread in plants and is a benzopyrone in nature. The coumarin name originates from 'Coumarou', the vernacular name for the tonka bean (Dipteryxodorata Willd, Fabaceae), from which coumarins were isolated in 1820. The umbelliferae family is inclusive of economically important herbs such as sanicle, alexanders, angelica, asafoetica, celery,cumin, fennel, parsley and giant hogweed. The name Umbelliferone on the other hand was derived from the umbelliferae family of plants, and the latter were named for their umbrella-shaped inflorescences. UMB has broadly circulated inside the Rutaceae and Apiaceae (Umbelliferae) families and is extracted utilizing methanol .The main feature for Apiaceae (Umbelliferae) is the inflorescence gathered within the compound umbels, a parasol-like inflorescence. The plant-derived phenolic coumarins have been purported to play a role as dietary antioxidants because of their consumption in the human diet in fruits and vegetables .It is widely used as antibacterial and anti-fungal, for the treatment of diabetes, cancer, hepatocellular carcinoma, has antioxidant property, in the treatment of cerebral ischemia, Parkinson 's disease, in the treatment of bronchial asthma. Also used as a sunscreen agent and optical brightener in textiles. Umbelliferone is less soluble in water this will decrease functions of the Umbelliferone and create problems. UMB is incorporated into biodegradable polymers to form SLNS and phytosomes and deliver the drug easily into the body. UMB having the capacity to be a defender against the adverse effects of anti-inflammatory agents.

By virtue of its structural simplicity UMB has been generally accepted as the parent compound for the more complex coumarins and is widely used as a synthon for a wider variety of coumarin-heterocycles .







Physical characteristics

Umbelliferone yellowish-white needle-like crystals are slightly soluble in hot water, but have good solubility in ethanol. UMB molecular formula is C9H6O3 and the needle crystals recrystallized from chloroform melts at 224–227 C. It has a molecular weight of 162.144g/mol, melting point: 230-233θC, log P value: 1.58.The dimensions of a single crystal grown by the cryostat process are 5.4 mm 4.2 mm 1.85 mm. The optimized geometry is planar and the OH group lies on the same plane as the whole molecule. The IR spectra of UMB shows bands at 3165 (Ar-OH), 1715–1690 and 1628–1603 (lactone), 1575, 1109 (C@C) and 835 (CH)cm1

When UMB form strong interactions with hydroxypropyl-a-cyclodextrin the IR bands shift to higher wavenumbers [13–15].The UV spectra (MeOH) knm (log e) shows maxima's at 339 (0.50), 294 (0.36), 242 (0.77) nm. The absorbance maxima in acid is 325 nm while in alkaline solution it shift to 365 nm. The fluorescence excitation maxima in acid and alkali solutions are 330 and 370 nm respectively, while the emission maxima is 460 nm. Another report states that umbelliferone shows blue emission band at kmax = 460–480 nm and a positive test with FeCl3 indicated by the deep blue colour. The typical umbelliferone bright blue spot under UV/Vis Rf values reported for authentic and isolated

Sources and extraction

UMB is popularly seen in Rutaceae and Apiaceae (Umbelliferae) families and is extracted utilizing methanol.Additionally, present in garden angelica, coriander, carrot and in addition in plants from different families, for example, the huge leaf (Hydrangeamacrophylla, Hydrangeaceae, under the name hydrangine) or the mouse-ear hawkweed (Hieracium pilosella, Asteraceae).

Silica gel column chromatography eluted with n-hexane and ethyl acetate or CHCl3/MeOH solvent mixtures of increasing polarity were employed for the fractionation and isolations. The extraction efficiency of MeOH was reported to increase when the MeOH concentration increased from 10 to 80%, extracting increasing amounts of coumarin, 1.5–1.8 g/100 g dry extract, which dropped to 0.6 g/100 g dry extract at 100% MeOH. The ideal proportion of plant matter (in grams) to solvent volume was 1:15, which had 1.7 g/ 100 g dry extract UMB content.

Successful separations were reported using high speed counter current chromatography solvent system n-hexane/ethyl acetate/methanol/water (4:6:4:6, v/v) with a partition coefficient (K) value of 0.64. The HPLC-UV (254 nm) analysis of umbelliferone content in n-hexane/ethyl acetate (6:4 v/v) fraction from the ethyl acetate extract on ODS C18 column using acetonitrile-water linear gradient elution at 0.6 mL/min the retention time was reported to be 10 min. The Edgeworthia chrysantha umbelliferone crude extract

content was 6.89% [23]. Umbelliferone from the tubers of Ipomoea mauritiana were quantified by the HPLC method using water acetonitrile mobile phase (77:23) on C-18 RP column, flow rate 1 mL/min and detected at 325 nm. The mean peak area, retention

time of umbelliferone was reported to be 316.1 and 8.9 min respectively. The HP-TLC method mobile phase was toluene, isopropanol and ammonia (8:2:0.1 v/v/v). The mean peak area and retention factor (Rf) of umbelliferone for HP-TLC method was reported to be 5940.92 and 0.55 respectively [26]. A 20 min retention time was reported for the HPLC analysis of umbelliferone from grapefruit (Citrus paradise) on a C-18 RP column using MeOH/H2O mobile phase, flow rate 1 mL/min and detecting at 254 nm. 7-

hydroxycoumarin, and a number of its methyl derivatives are found in plants of the family Umbelliferae.

Biological activities

The key steps in the biosynthesis of umbelliferone coumarin are the cinnamic acid synthesis or para and ortho hydroxylations, trans-cis isomerization of the double bond and finally lactonization.

Umbelliferone has been shown to exhibit various pharmacological activities against various health-related conditions, including conditions related to pro-oxidants and reactive oxygen species such as inflammation, degenerative diseases, microbial infections and cancer cells.

It plays important fungicidal roles in plants. The antimicrobial properties of umbelliferone isolated from Rhododendron lepidotum were examined against different bacterial strains at 0.5 McFarland standard. The minimum inhibitory concentration (MIC)

using microdilution methods were 500 lg/mL against Staphylococcus aureus and Pseudomonas aeruginosa, while activity against methicillin resistant S.aureus (MRSA) and E. coli was shown by MIC value of 1000 lg/mL

UMB β-D-galactopyranoside has antidiabetic property ,it diminishes raised blood glucose. Umbelliferone isolated from Coriandrum sativum methanol extract was assayed against A-549 (Human Small Lung Carcinoma), HT-29 (Human Colon Carcinoma), HeLa(Human Cervical Carcinoma) RPMI (Human Nasal Septum Carcinoma) and HEp G2 (Human Liver Carcinoma) cell lines for cytotoxicity test on MTT assay. Umbelliferone exhibits anti-inflammatory activities where the significant activities were the protection of DNA against gamma irradiation damage and protection from the diclofenac side effects. An anti-hyperglycemic effect was reported on streptozotocin rats. An effective fluorescent probe for hydrogen peroxide was also reported. Umbelliferone has potential as a protector against the side effects of anti-inflammatory agents. UMB having the capacity to be a defender against the adverse effects of anti-inflammatory agents.

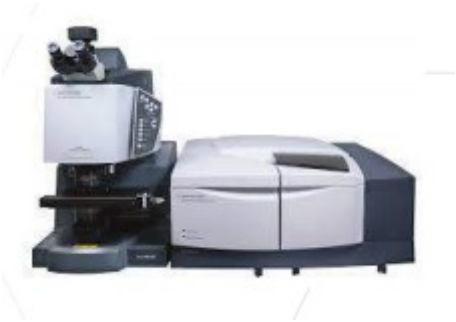
3.2 EXPERIMENTAL SECTION

a) FTIR

FTIR analysis were carried out from CSIF (Calicut university) .The instrument is from Agilent Technologies (It's an American analytical instrumentation development and manufacturing company), MODEL; Cary 620; Cary 660.

Specification includes: High spatial resolution, Live FPA imaging , Large field of view , Range of multi measurement modes-transmission, reflection, attenuated total reflectance (ATR) and grazing angle. , Chemical imaging.

It has Applications in Pharmaceuticals , Food and cosmetics , Materials polymers , Live cell imaging in water, Forensic and Biological and bio medical.



b) RAMAN

It is carried out from B&W Tek. Portable Raman spectrometer delivers a high signal to noise ratio without inducing auto-fluorescence, making it possible to measure a wide range of

natural products, biological samples such as cell cultures, and colored samples. The i-Raman EX provides a spectral coverage range from 100-2500 cm-1, enabling you to measure the entire fingerprint region. The system’s small footprint, lightweight design, and low power consumption provide research-grade Raman capabilities anywhere. The i-Raman EX comes is equipped with a fiber optic probe, and an XYZ positioning stage probe holder. It can be used with a range of sampling accessories to facilitate measurements of samples in many forms.

Laser	
1064nm Excitation	>430mW at laser port (499 mW max)
Laser Power Control	0 to 100%
Spectrometer	
Range	100 cm^{-1} - 2500cm^{-1}
Resolution*	< 10 cm-1 @1296nm
Detector	
Detector Type	TE Cooled InGaAs
Integration Time	200 µs to 5 minutes
CCD Cooling Temperature	-15°C
Electronics	
Computer Interface	USB 2.0 / 1.1
Trigger	Yes (Compatible with B&W Tek Probes)
Power Options	
DC Power Adaptor	Input: 110-240 VAC/ 50-60 Hz Output: 12V DC @ 6.6 Amps
Battery	Optional
Physical	
Dimensions	6.7 x 13.4 x 11in (17 x 34 x 28 cm)
Weight	Main Unit ~7.6 lbs (3.4kg)
Operating Temperature	0ºC - 35ºC
Storage Temperature	-10ºC - 60ºC
Humidity	10% - 85%

3.3 COMPUTATIONAL DETAILS

3.3.1 GUASSIAN 9.0

It's a computer program used by chemists, chemical engineers, biochemists, physicists and other scientists. . It is released in 1970 by John Pople and his research group at Carnegie-Mellon University as Gaussian 70. It has been continuously updated since then and **Gaussian09** is the latest version in the Gaussian series of programs. Fundamental laws of quantum mechanics is used to predict energies, molecular structures, spectroscopic data (NMR, IR, UV, etc) and much more advanced calculations. It provides state-of-the-art capabilities for electronic structure modeling. Gaussian09 is licensed for a wide variety of computer systems.

Gaussian 09W (G09) runs on any modern Windows 32-bit PC. If you want to install G09 on a 64bit PC, there is a special procedure you must follow:

1. Insert the CD with G09 and copy its content onto you computer. Any folder will do; I copied directly into the: C\ directory.
2. Open directory containing G09
3. Find the g09w.exe file
4. Right click on exe file, select Properties, a new window should appear
5. Go into the Compatibility menu
6. Put a checkmark next to: Run as administrator (this should enable other checkboxes)
7. Put a checkmark next to : Run this program in compatibility with (select Windows version that you are using)

The installation requires the Gaussian CD and a registration key

VISUALIZATION SOFTWARE ChemDraw (ChemBio 3D Ultra) and Avogadro (v.1.0.3) softwares can be used for visualization

Gaussian09 offers new features and performance enhancements which will enable you to model molecular systems of increasing size, with more accuracy, under a broader range of real world conditions. Some of these features includes;

- Model Reactions of Very Large Systems with ONIOM.
- Study Excited States in the Gas Phase and in Solution.
- Additional Spectra Prediction.
- New and Enhanced Methods and Algorithms
- Ease-of-Use Features.
- Performance Improvements.

Advanced Calculations Using Gaussian09:

- Comprehensive Investigations of Molecules and Reactions:

predict the structures of transition states, and verify that the located stationary points are in fact minima and transition states. You can go on to compute the reaction path by following the intrinsic reaction coordinate (IRC) and determine which reactants and products are connected by a given transition structure.

- Predicting and Interpreting Spectra:

Gaussian09 can predict a variety of spectra including IR and Raman, NMR, UV/Visible, Vibrational circular dichroism (VCD), Raman optical activity (ROA), Electronic circular dichroism (ECD), Optical rotary dispersion (ORD), Hyperfine spectra (microwave spectroscopy), Franck-Condon, Herzberg-Teller and Franck-Condon/Herzberg-Teller analyses.

- Explore Diverse Chemical Arenas:

Gaussian09 offers a variety of very accurate energy methods for predicting thermochemical quantities, Photochemistry and other Excited State Processes, and Solvent Effects can be taken into account when optimizing structures and predicting most molecular properties.

GaussView is a graphical user interface designed to help you prepare input for submission to Gaussian and to examine graphically the output that Gaussian produces. GaussView is not integrated with the computational module of Gaussian, but rather is a front-end/back-end processor to aid in the use of Gaussian. GaussView provides three main benefits to Gaussian users.

1). GaussView offers you an advanced visualization facility.

2). GaussView makes it easy to set up many types of Gaussian calculations.

3). GaussView lets you examine the results of Gaussian calculations using a variety of graphical techniques.

3.3.2 ORIGIN

Origin offers broad range of plotting options. It's a data analysis and graphing software of choice for over half a million scientists and engineers in commercial industries, academia, and government laboratories worldwide. Origin offers an easy-to-use interface for beginners and has the ability to perform advanced customization as you become more familiar with the application.

Origin graphs and analysis results can automatically update on data or parameter change, allowing you to create templates for repetitive tasks or to perform batch operations from the user interface, without the need for programming. OriginPro offers advanced analysis tools and Apps for Peak Fitting, Surface Fitting, Statistics and Signal Processing

3.3.3 MICROSOFT EXCEL

Microsoft Excel is a spreadsheet developed by Microsoft for Windows, macOS, Android and iOS. It features calculation, graphing tools, pivot tables, and a macro programming language called Visual Basic for Applications (VBA). Microsoft Excel has the basic features of all spreadsheets, using a grid of cells arranged in numbered rows and letter-named columns to organize data manipulations like arithmetic operations. In addition, it can display data as line graphs, histograms and charts, and with a very limited three-dimensional graphical display.

Steps to plot graph using Microsoft excel includes;

1. Open Microsoft excel.
2. Click on blank workbook.
3. Consider the type of graph to be made, it can be bar ,line or pie.
4. Add graph headers. Usually first cell(A1) is kept empty,then add graphs labels.
5. Enter the data in corresponding column.
6. Select the data and click insert button,select the graphs type and format.
7. Finally save the document.

3.3.4 GNU PLOT

Gnuplot is one of the best-established graphing tools, popular among intermediate and advanced users. It works in Windows, Linux and Mac, its primary function is the visualization of mathematical data and functions .It is a portable command-line driven graphing utility,it's a Open source and Used as the plotting engine of applications such as Octave ,it Can be used with various languages such as Perl and Python.

Compared to Excel Gnuplot Can be readily embedded in a program , Allows the batch processing of many files with simple scripting and has many different terminal types.All the data sets you use in gnuplot should be typed into a text file first. There should be one data point per line. Each data point will consist of several numbers: the independent variable, the dependent variable, and optionally error bars. Each of these fields should be separated by a tab.

Actually, any number of fields may be specified on each line; this is useful if you have multiple measurements for each data point, for instance. For information about how to access this additional information in your plots, see (fixme: add section) below.You may include any extra information you want in the file, such as a description of the data, headings for each of the data columns, and so on, as long as each such line begins with the comment character, #.

Plotting functions in gnuplot is really quite easy. Suppose you want to plot the function f(x) = exp(-x^2 / 2). In gnuplot, exponentiation uses **, not ^. So, after starting up gnuplot, at the gnuplot> prompt you would type:

plot exp(-x**2 / 2)

Usually, you'll want a little more control over your plot, at least specifying the ranges for the x- and y-axes. You can specify these in a **[minimum:maximum]** form before the function. Specify the x range first, then the y range. You may leave off the y range, or both. We can revise our previous plot command to:

plot [-4:4] exp(-x**2 / 2)

Here, the y range will be automatically determined. If there is more function list all of them.X label,Y label and title can be given ,for eg

set title "Some Sample Plots"

set xlabel "Independent Variable (no units)"

set ylabel "Dependent Variable (no units)"

After plotting function we can plot data.The syntax is almost the same, except that instead of specifying a function, you must specify the name of the file containing the data to plot, enclosed in double quotes.

CHAPTER 4

RESULT AND DISCUSSION

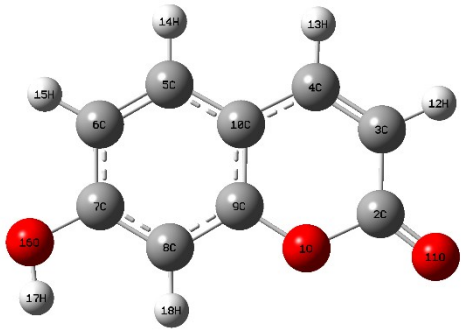
RESULT AND DISCUSSION

4.1 Molecular Geometry

The molecular structure of Umbelliferone is shown in fig.

The title molecule containsOH,C=C,0-C=O, etc atoms attached with the benzene ring.

The optimized structural parameters such as bond lengths ,bondangles and dihedral angles of the Umbelliferone is presented in the table given below.



1. BOND LENGTH

Trial no:	Name Of Bond	Theoretical Value Of Bond Length
1	O1-C2	1.378
2	O1-C9	1.422
3	C2-C3	1.416
4	C2=O11	1.43
5	C3=C4	1.3733
6	C3-H12	1.1
7	C4-C10	1.4217
8	C4-H13	1.1002
9	C5=C6	1.3729

10	C5-C10	1.4221
11	C5-H14	1.1003
12	C6-C7	1.4162
13	C6-H15	1.1
14	C7-C8	1.3729
15	C7-O16	1.43
16	C8-C9	1.422
17	C8-H18	1.1003
18	C9-C10	1.4189
19	O16-H17	0.96

2.BOND ANGLE

No	Name of bond	Theoretical bond angle
1	C2-O1-C9	120.5099
2	O1-C2-C3	120.3763
3	O1-C2=O11	120.6417
4	C3-C2=O11	118.976
5	C2-C3=C4	120.3516
6	C2-C3-H12	119.0027
7	C4=C3-H12	120.6457
8	C3=C4-H10	120.4559
9	C3=C4-H13	120.8999
10	C10-C4-H13	118.6441
11	C6=C5-C10	120.5491
12	C6=C5-H14	120.8596
13	C10-C5-H14	118.5913
14	C5=C6-C7	120.3669
15	C5=C6-H15	120.6492
16	C7-C6-H15	118.9839
17	C6-C7-C8	120.3239
18	C6-C7-O16	118.991
19	C8-C7-O16	120.685
20	C7-C8-C9	120.4968
21	C7-C8-H18	120.8623
22	C9-C8-H18	118.6409
23	O1-C9-C8	121.7004
24	O1-C9-C10	119.0959

25	C8-C9-C10	119.2037
26	C4-C10-C5	121.73
27	C4-C10-C9	119.2103
28	C5-C10-C9	119.0596
29	C7-O16-H17	109.4712

3.DIHEDRAL B0ND ANGLE

No	Name of bond	Theoretical bond angle
1	C9-O1-C2-C3	-0.011
2	C9-O1-C2=O11	179.9952
3	C2-O1-C9-C8	-179.9875
4	C2-O1-C9-C10	0.0171
5	O1-C2-C3=C4	-0.0029
6	O1-C2-C3-H12	-179.9936
7	O11=C2-C3=C4	179.991
8	O11-C2-C3-H12	0.0003
9	C2-C3=C4-C10	0.0104
10	C2-C3=C4-H13	179.9938
11	H12-C3=C4-C10	-179.999
12	H12-C3=C4-H13	-0.0516
13	C3=C4-C10-C5	179.9916
14	C3=C4-C10-C9	-0.004
15	H13-C4-C10-C5	0.0078
16	H13-C4-C10-C9	-179.9878
17	C10-C5=C6-C7	0.0027
18	C10-C5=C6-H15	179.9839
19	H14-C5=C6-C7	-179.9941
20	H14-C5=C6-H15	-0.013
21	C6=C5-C10-C4	-179.9942
22	C6=C5-C10-C9	0.0014
23	H14-C5-C10-C4	0.0027
24	H14-C5-C10-C9	179.9984
25	C5=C6-C7-C8	-0.0078
26	C5=C6-C7-O16	-179.9982
27	H15-C6-C7-C8	-179.9872
28	H15-C6-C7-O16	0.0203
29	C6-C7-C8-C9	0.0084
30	C6-C7-C8-H18	-179.9773
31	O16-C7-C8-C9	179.9987
32	O16-C7-C8-H18	0.013
33	C6-C7-O16-H17	179.5901
34	C8-C7-O16-H17	-0.4003
35	C7-C8-C9-O1	-179.9995

36	C7-C8-C9-C10	-0.0042
37	H18-C8-C9-01	-0.0135
38	H18-C8-C9-C10	179.9818
39	O1-C9-C10-C4	-0.0096
40	O1-C9-C10-C5	179.9947
41	C8-C9-C10-C4	179.995
42	C8-C9-C10-C15	-0.0008

From the theoretical values, it is found that most of the optimized bond lengths are slightly larger than the experimental values,due to the fact that the theoretical calculations belong to isolated molecule in gaseous phase while the experimental results belong to molecule in solid state.The calculated geometrical parameters represent a good approximation and they are the bases for calculating other parameters, such as vibrational frequencies and thermodynamic properties.

4.2 Vibrational Assignment

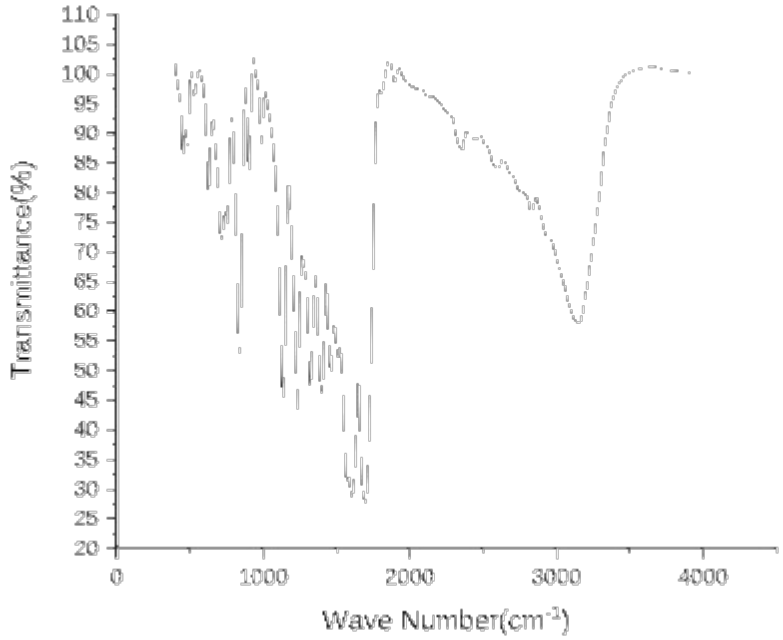
The compound consist of 18 atoms,hence undergoes 48 normal modes of vibrations.

Number Of Frequencies=3N-6 ;N=No of atoms

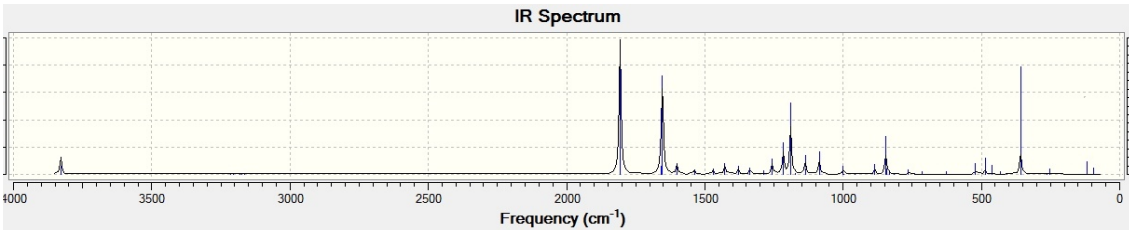
=3*18-6

=48

FTIR SPECTRUM:

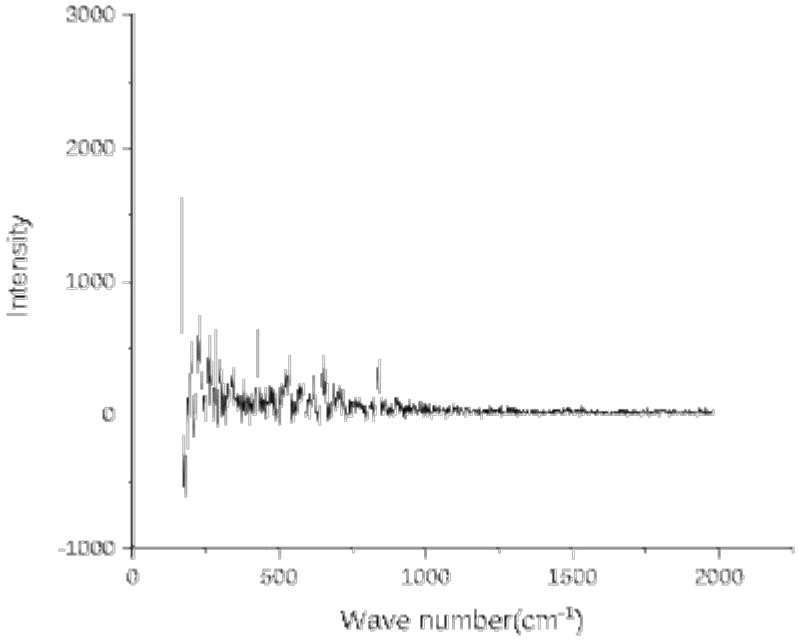


OBSERVED SPECTRUM

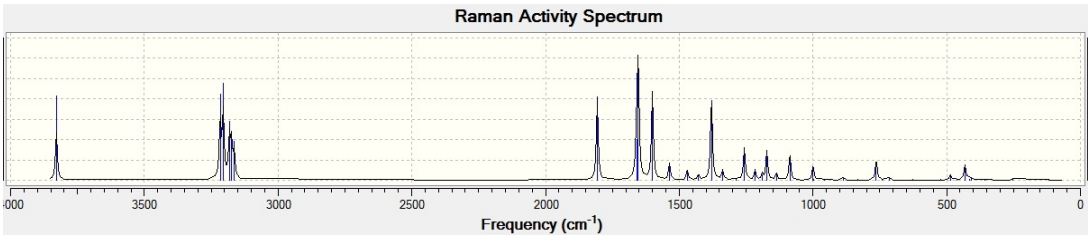


THEORETICAL SPECTRUM

RAMAN SPECTRUM:



OBSERVED SPECTRM



THEORETICAL SPECTRUM

Table: vibrational assignments of fundamental modes of umbelliferone with calculated IR intensity,Raman activity based n quantum mechanical calculations using DFT method.

THEORETICAL WAVENUMBER (CM^{-1})	IR INTENSITY	RAMAN INTENSITY	OBSERVED WAVENUMBER(CM^{-1})		MODE OF VIBRATION
			FTIR	RAMAN	
93.1179	1.6831	0.0444			
118.8339	4.4055	0.8642			
				165.996,196.3,207.8	
252.3298	0.0656	0.8202			
252.6499	4.330	2.0098			
263.8879	0.0086	0.1170			
				264.3,269.26,303.5,332.93	
358.2498	113.2990	1.5223			
				377.386	
406.8054	0.6276	3.3331			
415.555	0.2493	2.3097			
				426.36	
431.6773	3.7450	20.7409			
			448.35	445.952	
460.4229	12.1363	0.0965			
			483.242		
486.404	23.2762	8.3729			
				509.621	
520.65	16.2070	1.8872			
			530.43	539.006,563.4,617.36	
626.3544	5.0625	0.9877			
626.8575	4.4761	0.4672			
			630.98	651.651	
679.4749	0.8439	0.0456			
				705.525	C-C AROMATIC
713.7480	4.7400	4.0591			
			714.090		

741.88	2.1190	0.5611			
			761.28		C-H BENDING
763.3098	9.9165	30.8163			
				769.194	
814.3559	0.5312	0.2891			
833.5175	5.4101	1.8333			
			838.235	837.76	
843.3910	13.2147	0.0512			
846.4625	94.5529	0.2722			
				867.146	C-H BENDING
884.9002	26.4029	4.1550			
			902.872	896.9,945.88	
958.0938	1.2754	0.1306			
			991.108	989.963	C-O-C ANTISYMMETRIC
998.5391	0.8430	2.1718			
999.4997	24.0809	21.1956			
				1019.348	C-C AROMATIC
1086.2750	72.4297	40.8007			
				1097.710	C-C AROMATIC
1136.95	64.1994	11.1179		1122.191	C-O-C ANTISYMMETRIC
			1138.850		C-OH STRETCHING
1172.4966	4.5511	46.2281			
1189.8771	250.1941	9.6385			
				1210.355	C-C AROMATIC
1216.3017	113.39	15.5666			
			1233.242	1222.7878,1239.36	C-OH STRETCHING
1256.568	57.2063	51.9306			

				1274.02	C-C AROMATIC
1286.942	13.7771	206286			
			1321.477		
1337.083	25.54	17.4465			
1379.57	31.8796	140.5097			
			1404.58	1382.148	C-C AROMATIC
1427.573	45.9804	9.4014			
			1463.064	1445.817	C-C AROMATIC
1470.2136	25.0901	17.4386			
			1510.259	1529.076	C=C(RING)
1536.855	21.8309	29.0917			
			1575.923	1587.847	C=C(RING)
1600.339	49.6987	153.7254			
			1604.651	1607.69	C=C(RING)
1653.368	478.1182	204.1407			
1659.1583	40.81	72.3417			
			1693.912	1690.69,1744.57	C=O STRETCHING
1806.3775	713.1502	146.9028			
			1893.9,2348.4,2620.3,2832.7,3158.002	1842.52,1896.77,1960.442	
3164.27	6.9217	68.2651			
3174.1638	7.7518	85.7696			
3181.85	2.6859	103.5296			
3205.1339	2.2421	170.1866			
3216.38	0.2135	151.9466			
3828.72	93.0357	148.2626			

The FTIR SPECTRA OF UMBELLIFERONE shows peak at 761.28(C-H Bending),991.108 corresponds to C-O-C ANTISYMMETRIC(the theoretical value lies between 911-

1150),1138.850,1233.242 corresponds to C-OH Stretching(theoretical value lies between 1020-1200),1404.58,1463.064 corresponds to C-C Aromatic(theoretical value lies between 1400-1564.26),1510.259,1575.259,1604.651 corresponds to C=C Ring(theoretical value lies between 1500-1604.8),1693.912 corresponds to C=O Stretching(theoretical value lies between 1680-1715).

The RAMAN SPECTRA of UMBELLIFERONE shows peak at 867.146 corresponds to C-H Bending(theoretical value:862-870),989.963,1122.191 corresponds to C-O-C Antisymmetric(theoretical value:1000-1123),1019.348,1097.710,1210.355,1274.02, corresponds to C-C Aromatic(theoretical value:1000-1280),1222.7878,1239.36 corresponds to C-OH stretching,1529.070,1587.84,1607.69,1842.52,1896.77,1960.442,corresponds to C=C Ring(theoretical value:1500-1900),1690.69,1744.57 corresponds to C=O Stretching(theoretical value:1641.22-1791.3).

4.3 VIBRATIONAL CONTRIBUTION TO NLO ACTIVITY AND FIRST HYPERPOLARISABILITY

Linear and nonlinear optical properties of molecular crystals have attracted considerable attention for both practical and theoretical reasons.The potential application of the title compound in the field of nonlinear optics demands the investigation of its structural and bonding features.The first hyperoplarizability (β) of this molecular system is calculated using B3LYP/6-311++G(d,p)b method based on the finite field approach. In the presence of an applied electricfield the energy of a system is a function of the electric field.

The total static dipole moment μ,the mean polarizability α_0 ,and the mean first hyperpolarizability β_0 using the x,y,z components are defined as follows

$\mu=(\mu_x^2+\mu_y^2+\mu_z^2)^{1/2}$

$\alpha=1/3(\alpha_{xx}+\alpha_{yy}+\alpha_{zz})$

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

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

The components of dipole moment,polarizability and first hyperpolarizability of the title compound can be seen in the table

Table: calculated dipole moment(μ),polarizability(α)and the first hyperpolarizability (β)components of Umbelliferone

DIPOLE MOMENT

COMPONENTS	VALUES
μ_X	-1.3421178
μ_Y	0.9329186
μ_Z	0.00025731

POLARISABILITY

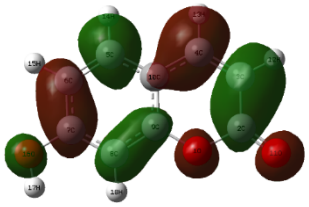
COMPONENTS	VALUES
αxx	184.717899
αxy	2.8498184
αyy	117.74912
αxz	-0.0006356
αyz	0.0000373
αzz	58.596063

FIRST HYPERPOLARISABILITY

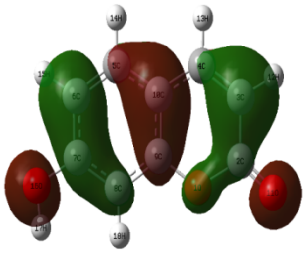
COMPONENTS	VALUES
βxxx	660.91242
βxxy	370.30474
βxyy	26.812574
βyyy	-4.0055601
βxxz	0.056535
βxyz	-0.002943
βyyz	0.019987
βxzz	-13.846705
βyzz	55.122635
βzzz	0.0180043

HOMO-LUMO Analysis

The most important Frontier molecular orbital(FMO) such as highest occupied molecular orbital(HOMO) and lowest unoccupied molecular orbital(LUMO) plays a crucial part in the chemical stability of the molecule.The HOMO represents the ability to donate an electron and LUMO represents the ability to accept an electron. The energy gap between HOMO and LUMO also determines the chemical reactivity,optical polarizability,and chemical hardness-softness of a molecule.A molecule with a small frontier orbital gap is more polarizable and is generally associated with a high chemical reactivity,low kinetic stability and is also termedas soft molecule



LUMO ENERGY (E_{LUMO}= -0.07875a.u)

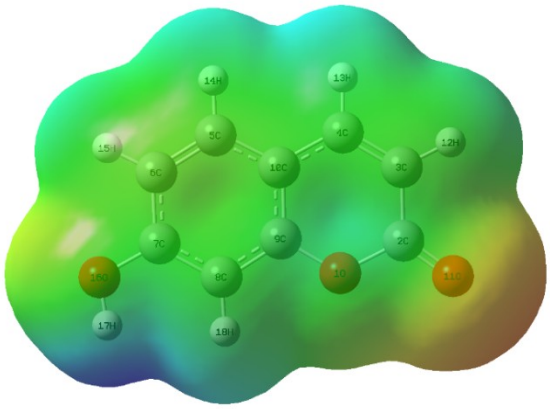


ΔE=0.16252

HOMO ENERGY (E_{HOMO}= -0.24127a,u)

Molecular Electrostatic potential(MEP)

Molecular electrostatic potential(MEP) at a point in space around a molecule give information about the net electrostatic effect produced at that point by total charge distribution(electron+proton) of the molecule. The interaction between the positive charge and some point in the molecule will be attractive if the point is negative charged: repulsive if it is positive charged,and the strength of interaction will depend on the magnitude of the charge.It is convenient to display this map using the colours of the rainbow from red to blue.Red is the negative(electron-rich)end and blue is the positive(electron-poor) end.



MEP

DIFFERENT PARAMETERS	UMBELLIFERONE VALUES
Homo Energy	-0.24127
Lumo Energy	-0.07875
Energy Gap	-0.16252
Electron Affinity	0.07875
Ionisation Potential	0.24127
Chemical Potential	-0.16001
Electro Negativity	0.16001
Chemical Hardness	0.08126
Chemical Softness	12.306

CHAPTER 5

5.1 CONCLUSION

FTIR and FT-Raman spectra of Umbeliferone have been recorded and utilising the observed ftir and ft-raman data in the complete vibrational assignment and analysis of modes have been carried out.The results have been compared with the experimental values.The difference between the observed and the scale wavenumber values of the most of the vibrational modes is very small. The NLO properties such as polarizability ,first hyperpolarizability,electron affinity,ionisation potential,chemical potential,energy gap,chemical softness and chemical hardness etc of the molecule are calculated. The effects of Frontier orbitals ,HOMO , LUMO and MEP are also studied.

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