



Experimental and Theoretical Investigation to Study the Molecular Structure, Electronic Properties, UV-Vis Spectra of Coumarin 102

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ABSTRACT

In this work, we study the structure, electronic properties and electronic spectra of Coumarin 102 (C102) dissolved in ethanol as an experimental-theoretical investigation. The various properties of the ground and excited electronic states of coumarins 102 using density functional theory (DFT) and time-dependent density functional theory (TDDFT) was calculated by the B3LYP density functional model with 6-31G(d,p) basis set by Gaussian 09 W program. Spectral characteristics of coumarin 102 have been probed into by methods of experimental UV-visible, and quantum chemistry. The UV spectrum was measured in Ethanol. The optimized structures, total energies, electronic states (HOMO-LUMO), energy gap, ionization potentials, electron affinities, chemical potential, global hardness, softness, global electrophilicity, dipole moment and electrostatic potential was calculated. were calculated. We find good agreement between experimental data of UV spectrum and TDDFT excitation energies.

Keywords: DFT, TDDFT, Ionization potential, electron affinity, energy gap and UV spectra

1. INTRODUCTION

Coumarins are broadly happening in nature, with coumarin itself initially separated in 1820 from a particular assortment of bean, and numerous other coumarin subordinates found in an extensive variety of plants [1]. Numerous characteristic and manufactured subsidiaries of coumarin (2H-chromen-2-one) are utilized as a part of various applications in chemistry, biology, medication and material science.

The explanations behind their extensive variety of utilizations are their unearthly properties, for the most part the extraordinary fluorescence watched for some subsidiaries with suitable substitution [2]. These subordinates are vital parts of fluorescence tests, sensors and switches. coumarins show fascinating fluorescence properties, which incorporate a high level of affectability to their nearby surroundings [3].

Coumarin subsidiaries are immense and imperative gathering of concoction mixes. They are described by low lethality, in this way can be utilized as a part of science, solution, perfumery and corrective industry [4].

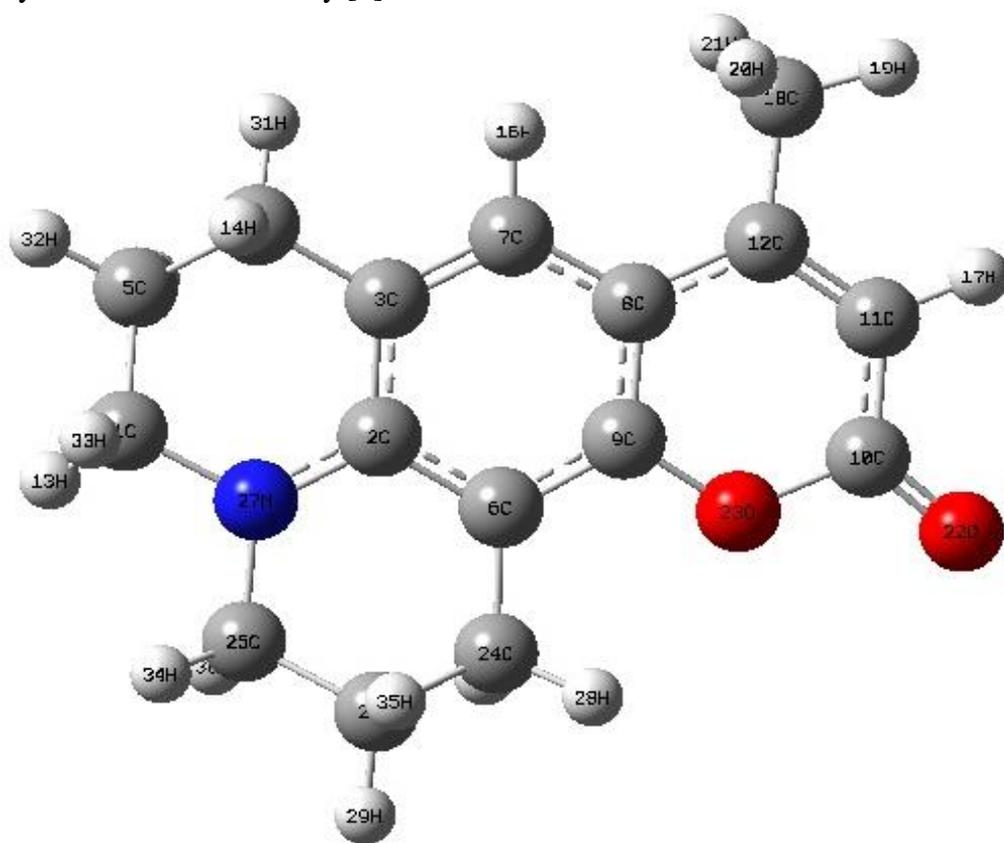


Fig. 1. The optimized structures of C102 obtained by B3LYP/6-31G (d, p)

Hypothetical examinations of the physical and synthetic properties of day sensitizers are vital keeping in mind the end goal to uncover the relationship between the structure, properties and execution, and to help in the outline and union of new color sensitizers [5].

Coumarin 102 (C102) has been known as a solvatochromic color and the fluorescence least wavelength (λ_{max}) of C102 relies on upon the microenvironment encompassing the day [6]. The structure of C102 (C₁₆H₁₇NO₂) is appeared in Figure (1).

Many reviews have demonstrated that the sub-atomic structures and vibration frequencies computed by DFT strategies [7]. Density functional theory (DFT) is these days a standout amongst the most prominent strategies for ground state electronic structure computations in quantum science and strong state material science. Compared to traditional ab initio, contemporary density functional methods show a favorable balance between accuracy and computational sciency [8].

The present work speaks to an exploratory and hypothetical way to deal with study the structure, electronic properties and electronic spectra of Coumarin 102 in Ethanol solvents by utilizing the TDDFT strategy.

2. EXPERIMENTAL

Coumarine dye laser (C-102) supplied from Lambda physics has a molecular mass (255.31 gm/mole), molecular formula (C₁₆H₁₇NO₂) and it can be dissolve in Ethanol, Methanol, Benzene, Acetone, etc. The solvent used in this search was Ethanol from (American Thomas baker com.) with purity (99.9%), molecular formula (C₂H₅OH) molecular mass (46 gm/mole), Polarity (0.654). The materials used in this search without further purification. The coumarin 102 dye a dissolve in Ethanol at three concentrations (10^{-4} , 10^{-5} & 10^{-6} mole /L).

The spectrum of absorbance was taken by Shimadzu spectrometer (UV-Visible, UV-160). This spectrophotometer covers a wide range in EM spectrum from UV to near IR. The absorption spectra of Coumarine 102 have been investigated by using Ethanol solvent in various concentrations. Absorption spectra can give much information related to the molecule under investigated. Absorption spectrum was measured by (UV-VIS spectrophotometer sp-3000 plus), this device operates within the range (200–1100 nm) of the visible and ultraviolet region. Polymer films thickness was measured by using a Japanese aperture. (MITUTOYO) which is measured the thickness of the films ranging between (0-25 mm).

3. COMPUTATIONAL METHODS

In the present study, the ground-state and singlet excited state geometries of C102 dissolved in Ethanol optimized using DFT / TDDFT with B3LYP hybrid functional. Based on optimized ground state geometry, the excitation energies were estimated using TD-CPCM-B3LYP/ 6-31G(d,p). The study of C102 has been carried out by the density functional theory (DFT & TDDFT) using the Gaussian 09 code and Gauss-View molecular visualization program package on the personal computer [9].

The gradient-corrected B3LYP functional form (i.e. Becke's 3-parameter hybrid exchange functional [10] and Lee, Yang, and Parr correlation functional [11]) was employed in the calculations. DFT is the best method to calculate ground state structures and the electronic variables, time-dependent density functional theory (TD-DFT) methods at B3LYP/6-31G(d,p) level were used for the calculation of electronic excitations and UV-Vis

spectra for any molecules. The polarized continuum model (PCM) was used to model the effects of Ethanol solvation. The PCM model used in the DFT calculations takes into account the dielectric constant and the refractive index of each solvent. These parameters describe the solvent fairly well [12]. The energy and oscillator strength calculated by (TD-DFT) result complements with the experimental findings. The geometry optimized structures are obtained by restricted closed-shell formalism and without any symmetry restriction,

In this investigation, the more relevant ionization potential (IP), electron affinities (EA), chemical potential (K) (it is the negative of electronegativity (χ)), hardness (η), softness (S) and electrophilic index (ω) were calculated. These are confirming the charge transfer within the molecule and also the molecular electrostatic potential (MESP) contour map shows the various electrophilic region of the title molecule [13]. The HOMO and LUMO vitality was utilized to evaluate the IP and EA in the edge work of Koopmans' hypothesis:

$$IP = -\epsilon_{HOMO} \text{ and } EA = -\epsilon_{LUMO} \text{ [14,15].}$$

The all parameters are calculated as follows [16,17]:

$$\text{Electronegativity } (\chi): K \approx -\chi = -(IP + EA)/2 \quad (1)$$

$$\text{Hardness } \eta \approx (IP - EA)/2 \quad (2)$$

$$\text{Softness } S = \frac{1}{2\eta} \quad (3)$$

$$\text{Electrophilic index } \omega = \frac{\kappa^2}{2\eta} \quad (4)$$

Density functional theory has also been used to calculate the dipole moment μ , the total dipole moment in a Cartesian frame is defined by [18]:

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \quad (5)$$

The dipole moment in a molecule is an essential property that is fundamentally used to concentrate the intermolecular interactions including the nonbonded sort dipole–dipole interactions, on the grounds that the higher the dipole minute, the more grounded will be the intermolecular interactions [19].

4. RESULTS AND DISCUSSION

4. 1. Molecular geometry

The calculated geometrical parameters (bond lengths and bond angles) were compared with another study [5]. The optimized structural parameters of C102 from B3LYP/6-31G(d,p) calculations and also another study values are listed in Table 1, in accordance with the atom numbering scheme given in Figure (1). The B3LYP method leads to geometry parameters, which are close to another study data [5]. From Table 1, we can find that most of the optimized parameters are agreements with another study.

Table 1. Optimized geometrical parameters of C102 in ethanol obtained by B3LYP/6-31G (d,p) density functional calculations.

bond length	Current Study (Å)	Previous Study [5]	bond angles	Current Study (Å)	Previous Study [5]
R(C ₁ – C ₅)	1.524	1.531	A(C ₅ – C ₁ – H ₁₃)	110.019	110.1
R(C ₁ – H ₁₃)	1.096	1.094	A(C ₅ – C ₁ – N ₂₇)	112.558	113.3
R(C ₁ – N ₂₇)	1.465	1.472	A(C ₅ – C ₁ - H ₃₃)	110.054	109.6
R(C ₁ – H ₃₃)	1.100	1.091	A(H ₁₃ – C ₁ – N ₂₇)	107.711	107.8
R(C ₂ – C ₃)	1.432	1.418	A(H ₁₃ – C ₁ – H ₃₃)	106.793	108.9
R(C ₂ – C ₆)	1.437	1.406	A(N ₂₇ –C ₁ – H ₃₃)	109.515	107.8
R(C ₁ – N ₂₇)	1.465	1.472	A(C ₃ – C ₂ – C ₆)	119.468	120.1
R(C ₃ – C ₄)	1.511	1.512	A(C ₃ – C ₂ – N ₂₇)	120.086	120.6
R(C ₃ – C ₇)	1.380	1.377	A(C ₆ – C ₂ – N ₂₇)	120.445	-
R(C ₄ – C ₅)	1.530	1.537	A(C ₂ – C ₃ – C ₄)	119.121	118.1
R(C ₄ – C ₁₄)	1.099	1.095	A(C ₂ – C ₃ –C ₇)	119.524	120.1
R(C ₄ – H ₃₁)	1.094	1.091	A(C ₄ –C ₃ – C ₇)	121.352	121.7
R(C ₅ – H ₁₅)	1.096	1.091	A(C ₃ –C ₄ – C ₅)	109.923	108.9
R(C ₅ – H ₃₂)	1.094	1.091	A(C ₃ – C ₄ – H ₁₄)	110.175	109.3
R(C ₆ – C ₉)	1.393	1.386	A(C ₃ – C ₄ – H ₃₁)	110.012	109.3
R(C ₆ – C ₂₄)	1.511	1.509	A(C ₅ – C ₄ – H ₁₄)	108.918	108.9
R(C ₇ – C ₈)	1.411	1.403	A(C ₅ – C ₄ – H ₃₁)	111.181	-
R(C ₇ – H ₁₆)	1.085	1.081	A(H ₁₄ –C ₄ – H ₃₁)	106.572	-
R(C ₈ – C ₉)	1.411	1.399	A(C ₁ – C ₅ – C ₄)	109.556	-
R(C ₈ – C ₁₂)	1.440	1.446	A(C ₁ – C ₅ – H ₁₅)	109.717	-
R(C ₉ – O ₂₃)	1.374	1.382	A(C ₁ – C ₅ – H ₃₂)	109.035	-
R(C ₁₀ – C ₁₁)	1.440	1.450	A(C ₄ – C ₅ – H ₁₅)	109.724	-
R(C ₁₀ –O ₂₂)	1.221	1.217	A(C ₄ – C ₅ – H ₃₂)	111.284	110.9

R(C ₁₀ - O ₂₃)	1.391	1.418	A(H ₁₅ - C ₅ - H ₃₂)	107.491	108.9
R(C ₁₁ -C ₁₂)	1.367	1.351	A(C ₂ - C ₆ - C ₉)	118.430	118.7
R(C ₁ - H ₁₃)	1.084	1.094	A(C ₆ - C ₉ - O ₂₃)	116.178	116.7
R(C ₁₂ - C ₁₈)	1.505	1.509	A(C ₈ - C ₉ - O ₂₃)	120.448	120.9
R(C ₁₈ - H ₂₀)	1.095	1.088	A(C ₁₁ - C ₁₀ - O ₂₂)	126.863	127.4
R(C ₂₄ - C ₂₆)	1.530	1.531	A(C ₁₁ - C ₁₀ - O ₂₃)	116.533	115.0
R(C ₂₄ - H ₂₈)	1.093	1.091	A(O ₂₂ - C ₁₀ - O ₂₃)	116.604	117.6
R(C ₂₄ -H ₃₆)	1.099	1.094	A(C ₂₆ - C ₂₅ - N ₂₇)	112.101	111.1
R(C ₂₅ - C ₂₆)	1.524	1.531	A(C ₂₆ - C ₂₅ - H ₃₀)	110.173	109.3
R (C ₂₅ - N ₂₇)	1.463	1.472	A(N ₂₇ - C ₂₅ - H ₃₀)	109.728	110.1
R(C ₂₅ - H ₃₀)	1.101	1.096	A(N ₂₇ - C ₂₅ - H ₃₄)	107.701	107.8
R(C ₂₅ - H ₃₄)	1.096	1.094	A(C ₁ - N ₂₇ -C ₂)	122.878	122.8
R(C ₂₆ -H ₂₉)	1.094	1.090	A(C ₁ - N ₂₇ - C ₂₅)	114.843	117.6
R(C ₂₆ -H ₃₅)	1.093	1.091	A(C ₂ - N ₂₇ - C ₂₅)	122.878	122.0

4. 2. Electronic properties

The essential electronic parameters identified with the orbitals in an atom are the most elevated involved sub-atomic orbital (HOMO) and least abandoned sub-atomic orbital (LUMO) and their subsequent vitality hole [20]. These orbitals not just decide the way the atom cooperates with different species, however their vitality crevice (outskirts orbital hole) portrays the substance reactivity and dynamic security of the particle [21].

The littler the LUMO-HOMO vitality crevices, the simpler it is for the HOMO electrons to be energized; the higher the HOMO energies, the less demanding it is for HOMO to give electrons; the lower the LUMO energies, the less demanding it is for LUMO to acknowledge electrons [22].

Table (2) shows the values of the total energy and electronic states for the analyzed structure and the energy gap ($\mathcal{E}_{LUMO} - \mathcal{E}_{HOMO}$), and dipole moment (μ) of the C102. for the Coumarin-102 in ethanol. The experimental ground-state dipole moment, measured in the presence of chloroform is 6.98 Debye [5]. Along these lines, there is a slight difference between our outcome and the exploratory one that could be brought about by dissolvable impacts.

B3LYP functional used in this study has a high efficient to calculate the electronic properties for the organic studied molecules, such as ionization potentials (IP), electron affinities (EA), chemical potential (K), absolute hardness (η), absolute softness (S), electrophilic index (ω). The results from Crespo-Hernandez et al. [23] for IP and EA are not

directly comparable because they have been calculated in different way (adiabatic, vertical). Thus, there is a slight disagreement between our result and the another study that could be caused by solvent effects and different calculated way (adiabatic, vertical). The experimental ground-state dipole moment, measured in the presence of chloroform is 6.98 Debye [5]. Thus, there is a slight disagreement between our result and the experimental one, that could be caused by solvent effects.

Table 2. Electronic properties of C102 dissolved in Ethanol.

Property	TD-DFT B3LYP/6-31G (d,p)	Previous Study
E_{tot} (a.u.)	-825.21203	-
$\varepsilon_{\text{HOMO}}$ (eV)	-5.059	-
$\varepsilon_{\text{LUMO}}$ (eV)	-1.351	-
E_{Gap} (eV)	3.207	-
IP (eV)	5.059	6.7 ^a 6.8 ^b
EA (eV)	1.351	0.42 ^a
χ (eV)	3.205	
η (ev)	1.854	
S (1/eV)	0.269	-
ω (eV)	2.770	-
μ (Debye)	9.144	6.7 ^c 8.053 ^d

^a adiabatic [23], ^b vertical [23], ^c Exp. [5], ^d from Ref. [5]

4. 3. Frontier molecular orbital analysis

The three-dimensional plot of the molecule HOMO and LUMO orbital of C102 are shown in Figure (2). The electronic cloud of the frontier orbitals of C102 spread over the whole π -conjugated backbone, although C102 dense electronic cloud distributes on the different parts of C102, both shows π -character. LUMO are localized on C2, C3, C6, C7, C8, C9, C10, C11, N27, O22 and O23 whereas HOMO are localized on C1, C2, C3, C6, C6, C7, C8, C10, C11, C25, N27, and O22. The HOMO, of π nature is located over C – C bond and σ nature over C – H and N bond, shows antibonding character, while the LUMO is delocalized over the whole C – C and C – H bond, shows a bonding character. From Figure (3) the most elevated number of degenerate states in the HOMO and LUMO are appeared as 3. Since there are numerous principle peaks in all DOS, there are accessible for occupation at high DOS for

particular energy level and not state can be possessed at zero-density of states for energy level.

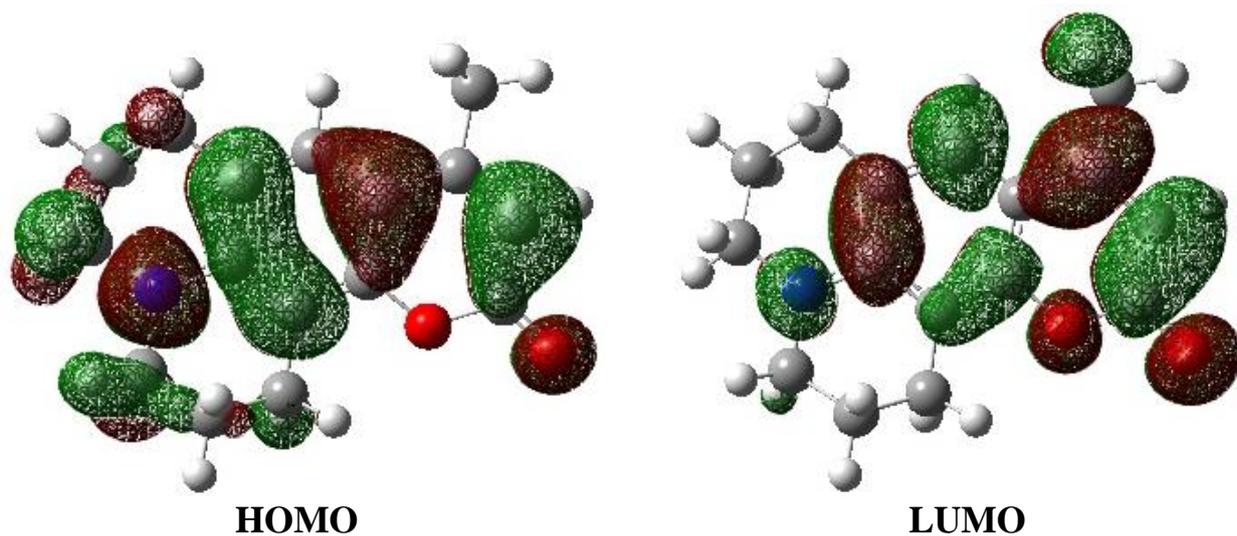


Fig. 2. Frontier molecular orbital's of C102 dissolved in Ethanol

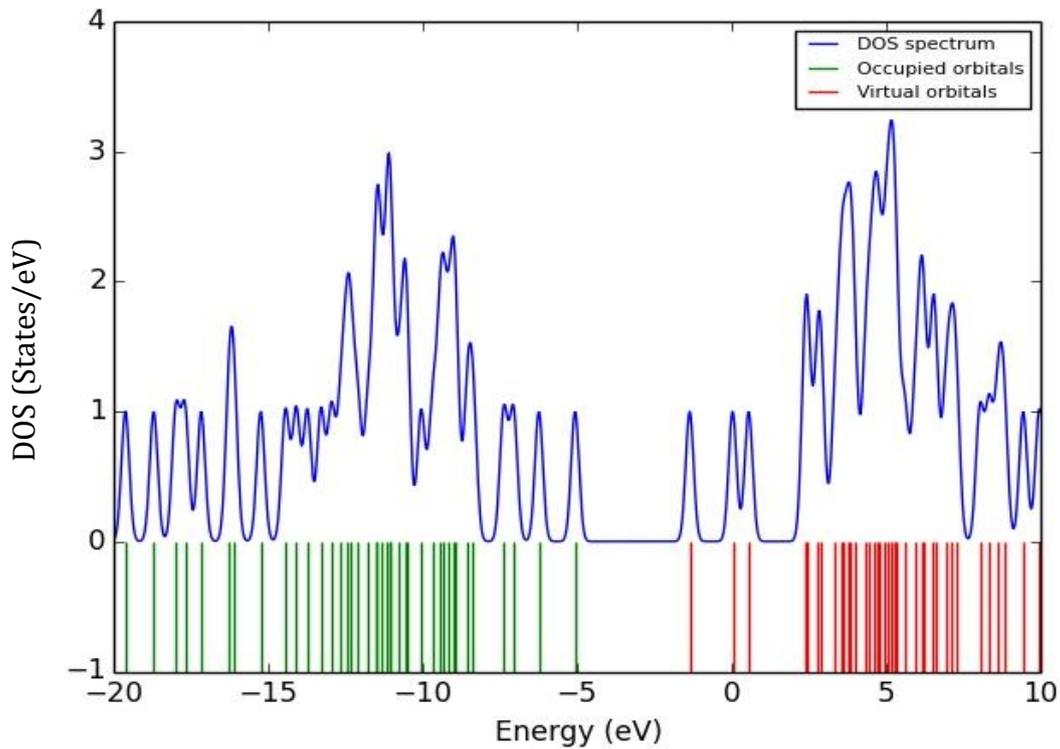


Fig. 3. Density of states (DOS) of C102 dissolved in Ethanol

4. 4. Molecular electrostatic potential (MEP)

Molecular Electrostatic Potential (MEP) at a point in the space around a particle gives a sign of the net electrostatic impact created by then by the aggregate charge conveyance (electron + nuclei) of the Molecular and associates with dipole minutes, electronegativity, partial charges and chemical reactivity of the molecules [24-26].

Learning of the charge dispersions can be utilized to decide how molecules connect with each other. One of the reasons for finding the electrostatic potential is to locate the receptive site of a molecule. The three-dimensional electrostatic potential maps of the C102 dissolved in Ethanol is appeared in Figure (4). A part of the molecule that has a negative electrostatic potential is susceptible to electrophilic assault. The red and blue districts in the EPS outline to the locales of negative and positive possibilities and relate to the electron-rich and electron-insufficient areas separately though the green shading implies the nonpartisan electrostatic potential [27].

As can be seen from the MEP, it was clear that best area (blue) is restricted on the H molecules, which can show a conceivable site for nucleophilic assault. In the interim, a greatest electrostatic potential areas (red) were basically limited over the O22 and O23 atoms, demonstrating the most good site for electrophilic assault. It is clear from figure (4) likewise the zero electrostatic surface potential (green hues) in the focal point of C102.

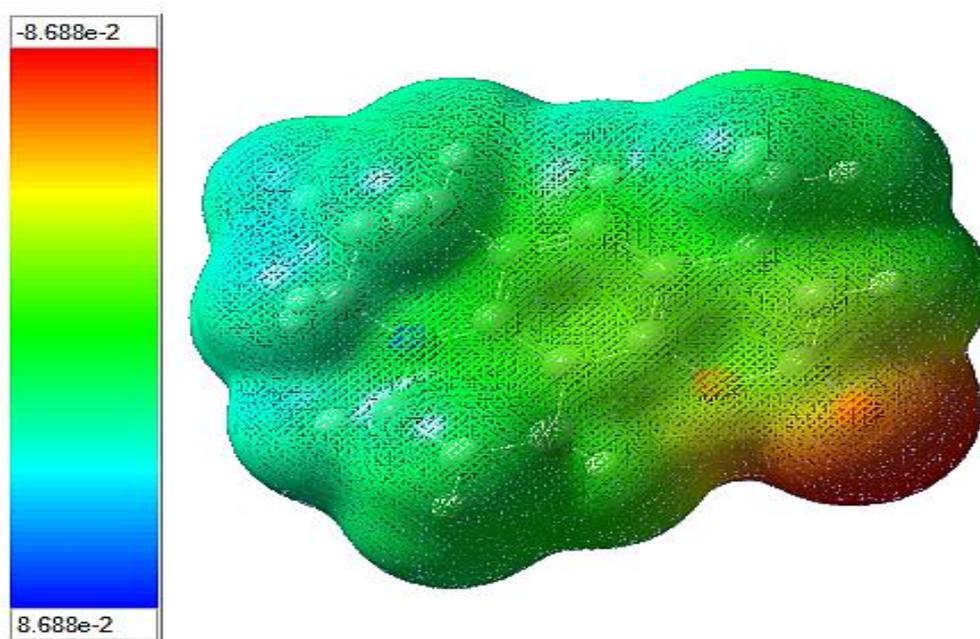


Fig. 4. Molecular Electrostatic potential surface (MEP) mapped onto a surface of total electron density for C102 dissolved in Ethanol (value in a.u.)

4. 5. Adsorption spectra

Figure (5) show the experimental electronic absorption spectra of C102 in the solvent Ethanol in different concentration. The (0-0) bands of the absorption spectra are shifted to shorter wavelengths.

Time-dependent density functional theory (TD-DFT) calculation has been performed for C102 on the basis of fully optimized ground state structure to investigate the electronic absorption properties for the singlet-singlet transition. The max values are obtained from the UV-Vis spectra analyzed theoretically with B3LYP/6-31G(d,p) basis set for 10 excited states.

Table 3. Calculated Absorption (λ_{ma}) wavelength (nm) of C102 in Methanol.

Case	Assignments	Wavelength λ (nm)	excitation energy ΔE (eV)	oscillator strength f (a.u.)	Exp. λ_{max} (nm)
A (Excited State 1)	H \rightarrow L (98%)	366	3.3882	0.442	392 ^a 389 ^b 386 ^c
B (Excited State 7)	H-1 \rightarrow L+1 (84%) H-1 \rightarrow L+2 (7%)	209	5.9529	0.801	220 ^a 216 ^b

^a 10^{-4} , ^b 10^{-5} , ^c 10^{-6} M concentrations

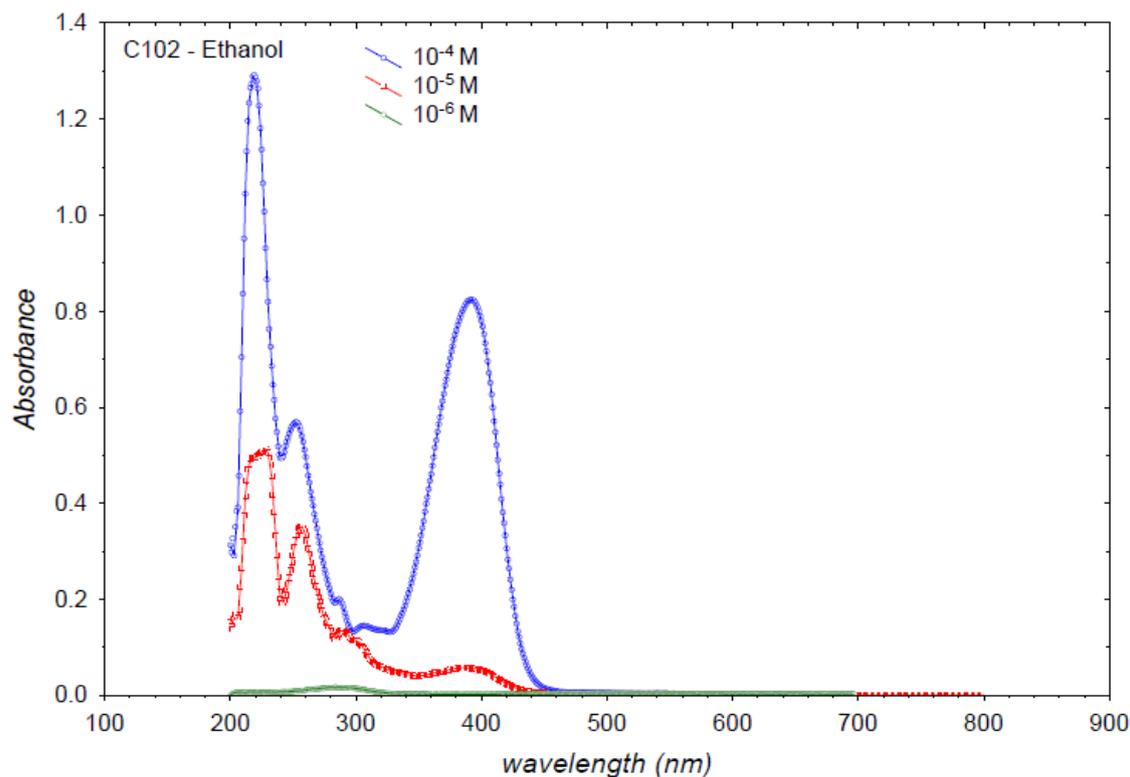


Fig. 5. Absorption spectra for Coumarin 102 dissolved in Ethanol at different concentrations.

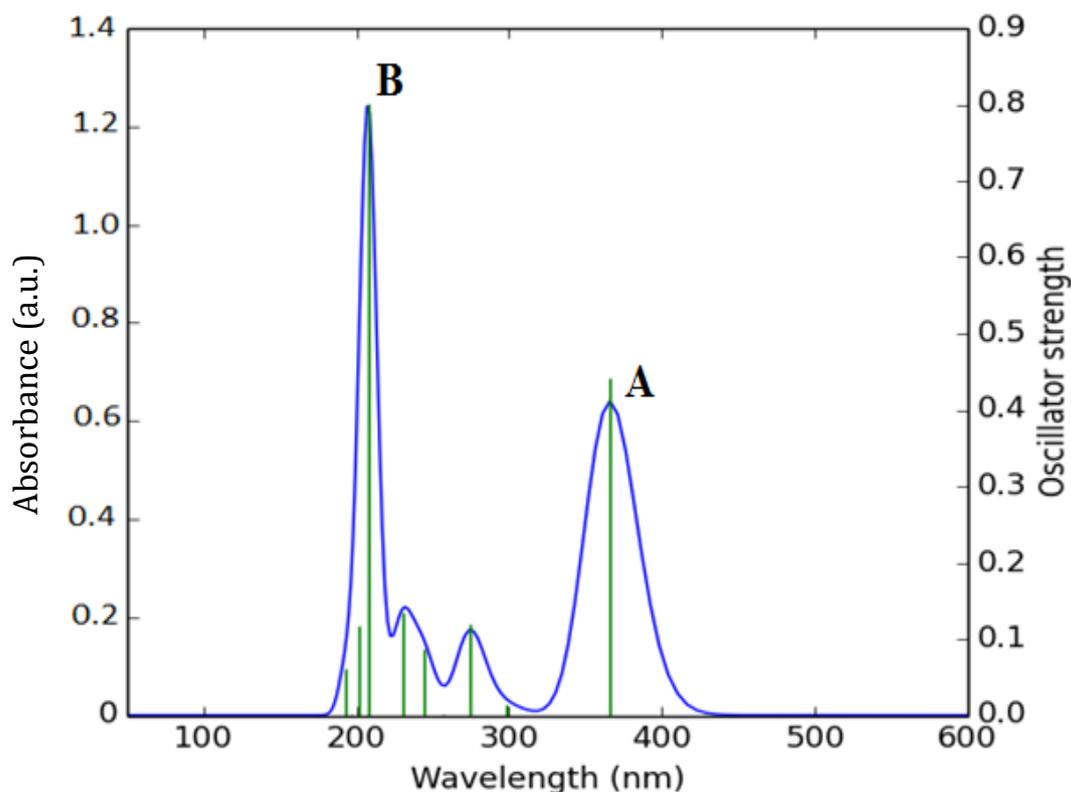


Fig. 6. Theoretical absorption spectra for C102 in Ethanol.

The figured UV-unmistakable assimilation maxima which are a component of electron accessibility hypothetical electronic excitation energies are altogether classified in Table (3). As delineated in Table (3), we can discover the estimations of compute assimilation λ_{\max} (nm) and oscillator quality (f) alongside principle excitation design of the concentrated compound. As appearing in Fig. (5) and Table 4, all mixes display a solid retention band in the UV area. It can be seen from the Table (3) and fig. (6), the ascertained ingestion values for C102 have been observed to be 209 nm (band B) relates to the exploratory estimation of 216 nm (band A) for 10⁻⁵ M focus, this pinnacle basically speaks to excitation from HOMO-1 \rightarrow LUMO+1 (84%), HOMO-1 \rightarrow LUMO+2 (7%). The most extreme λ for band A, whose figured esteem is 367 nm, compares to the test estimation of 389 nm for 10⁻⁵ M. This is basically a HOMO \rightarrow LUMO move, including excitation from π to π^* .

5. CONCLUSIONS

In this work, the structures and electronic spectra of Coumarin 102 broke up in Ethanol are researched utilizing the DFT/TDDFT strategies and the dissolvable impact has been considered utilizing the PCM show. Our outcomes demonstrate that TDDFT is a capable device for treating the spectroscopy and properties of the Excitation condition of the C102.

The outcomes from Crespo-Hernandez et al. [23] of IP and EA are not straightforwardly tantamount in light of the fact that they have been figured in various ascertained way (adiabatic, vertical). Consequently, there is a slight contradiction between our outcome and another review that could be brought on by dissolvable impacts and distinctive ascertained way (adiabatic, vertical).

The energies of critical MOs, retention wavelength (λ_{\max}), oscillator quality, and excitation energies of the compound were additionally decided from TD-DFT techniques and were contrasted and our trial values.

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