

Theoretical Study of Selected Laser Dye Materials

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ABSTRACT

In this work, theoretical calculation of the ground and excited state of coumarin compounds are performed using DFT-B3LYP and CIS methods with 6-31G basis set. IR spectrum, UV/Vis spectrum, molecular orbitals and energy gap are calculated. We use different solvents ethanol, methanol, water, acetonitrile (ACN), dimethyl sulfoxide (DMSO), acetone, and dichloromethane to compare values of UV/Vis absorption spectra. Then the calculated results are compared with the experimental values.

Key words: Coumarin dye, Laser dye, Semi empirical, DFT, CIS, Excited states, solvation models, UV-Vis spectra.

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(ACN)

(UV/Vis)

(IR)

(DMSO)

:

(DFT)

(CIS)

I. Introduction

Organic dyes are large and complex molecular systems, and they show strong absorption bands in UV/VIS region, when excited by suitable wavelength of light. The fluorescence spectrums appear within wide range. Therefore, we found that it is important to study the properties of some materials such as coumarin 4.

Coumarins represent a class of heterocyclic compounds with oxygen ring next to the carbonyl group. Commonly known as the coumarin dyes, which are the well-known laser dyes within the blue-green region. These compounds possess remarkable photophysical properties, which find applications in diverse areas for the following reasons: First, the strong absorption cross sections and large radiative yields of coumarins make them suitable for use as laser dyes [1,2], for the well known tunable laser around 450nm [3]. Second, they are excellent probes to study the solvation dynamics in homogeneous solutions and organized media. The carbonyl dyes owe their success to their ability to provide a wide range of colors covering the entire visible spectrum, and to their capacity to show long wavelength absorption bands when combined with relatively short π -conjugated systems [4].

2. Computational methods

ChemBio3D program was used to draw the molecules [5], Quantum chemical calculations were carried out using the Gaussian 03 package [6] and ChemCraft (post computation program) was used to plot results [7]. Geometrical optimizations of the ground states were done using DFT method [8-19] at B3LYP level with 6-31G basis set. The geometries of the first singlet excited state were optimized using the configuration interaction singles (CIS) [20] method with 6-31G basis set. TD-DFT method [21,22] with 6-31G basis set was used to predict the absorption wavelengths. In the TD-DFT calculations the B3LYP functions were used. The solvent effect on spectrum was considered using the PCM model family [23]. The solvents used in our calculations were ethanol, methanol, water, acetonitrile (ACN), DMSO, acetone and dichloromethane. In this work the molar extinction coefficient [24] were calculated by the TD-DFT method, which are very helpful in assigning the calculated electronic transitions to experimental absorption spectra.

3. Results and discussion

In the current work we have used DFT, TD-DFT and CIS methods to calculate Ground and excited states geometries, IR, UV spectrum and to investigate the effects of different solvents were done using different solvation models.

3.1 Geometric properties of molecules in ground states and excited states:

Structures of chromophore (coumarin) and coumarin4 are shown in Fig.1 and the serial numbers of atoms are also indicated. Bond lengths of two structures are shown in Table 1, where the bond length of coumarin4 (C5-C6) increased by magnitude ($\cong 0.01$) and bond length (C1-C6) increased little due to $-\text{CH}_3$. We compared between ground and excited states, where in excited state bond lengths were larger than ground state bonds (C1=C6, C4=C5, C5-C9, C8-C12, C2-O3). In all cases the values were near optimal values, including the measurement angles, except values of bond lengths that were calculated by AM1 method because it remain semi empirical; therefore, values of angles at two structures are shown in Table 2. Some Dihedral angles were near 180° . This indicate that the molecules are planer (two rings are level within molecule).

Table (1) Bond lengths of coumarin and coumarin4 in the ground and excited states in gas phase.

Coumarin (chromophore)				Coumarin 4			
bond Length (A°)	Ground state		Excited state	bond Length (A°)	Ground state		Excited state
	DFT	AM1	CIS		DFT	AM1	CIS
O(1)-C(2)	1.4278	1.2298	1.4434	C(2)-O(3)	1.4317	1.0995	1.4347
O(1)-C(11)	1.3887	1.3759	1.3464	O(3)-C(4)	1.3845	1.3783	1.3522
C(2)-O(3)	1.2289	1.4107	1.2142	C(2)-O(18)	1.2297	1.3963	1.2176
C(2)-C(4)	1.4553	1.4057	1.4134	C(1)-C(2)	1.4474	1.3869	1.4109
C(4)-C(5)	1.3578	1.4481	1.4070	C(1)-C(6)	1.3652	1.1010	1.4186
C(5)-C(6)	1.4438	1.4808	1.3919	C(5)-C(6)	1.4542	1.3481	1.3986
C(6)-C(7)	1.4111	1.0985	1.4248	C(5)-C(9)	1.4144	1.0997	1.4329
C(6)-C(11)	1.4112	1.4133	1.4624	C(4)-C(5)	1.4124	1.2297	1.4577
C(7)-C(8)	1.3914	1.3714	1.3667	C(9)-C(12)	1.3866	1.1006	1.3642
C(8)-C(9)	1.4080	1.1018	1.4238	C(8)-C(12)	1.4075	1.4092	1.4147
C(9)-C(10)	1.3944	1.0991	1.3800	C(7)-C(8)	1.3945	1.1014	1.3868
C(10)-C(11)	1.3969	1.1180	1.3869	C(4)-C(7)	1.3957	1.4568	1.3758
				C(6)-C(13)	1.5072	1.4426	1.5022
				O(15)-H(19)	0.9767	1.0995	0.9513
				C(8)-O(15)	1.3842	1.3868	1.3592

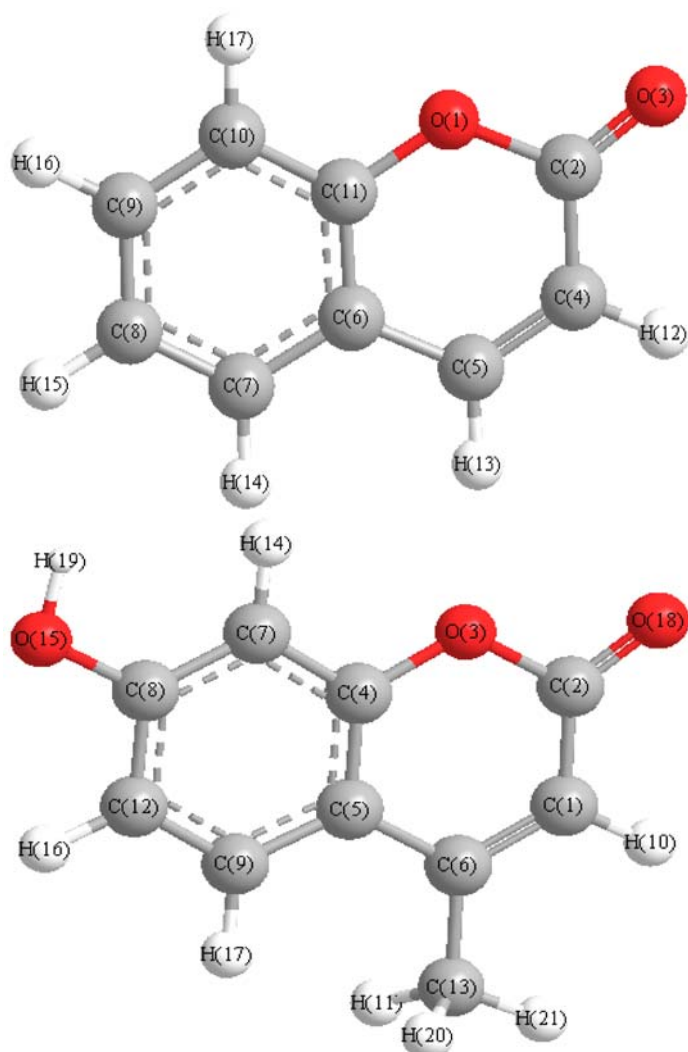


Fig (1) Coumarin molecule (chromophore) and coumarin4 molecule.

From calculations of the ground state of coumarin4 we found that the SCF energy equal to -611.3854 A.U (16636.65 ev) and the SCF energy of the excited state was found as equal to -607.672674 A.U (16535.62 ev). In coumarin4 the dipole moment value for ground state was $\mu_0=4.5785$ Debye, and its value in excited state was $\mu_1=5.8873$ Debye.

Table (2) Angles and dihedrad angles of coumarin and coumarin4 in the ground and excited states in gas phase.

Coumarin (chromphore)			Coumarin 4		
Bond angles(°)	Ground state	Excited state	Bond angles(°)	Ground state	Excited state
	DFT	CIS		DFT	CIS
C(10)-C(11)-O(1)	117.6010	118.2220	C(7)-C(4)-O(3)	116.5141	117.266
C(11)-C(10)-C(9)	118.8394	119.6360	C(8)-C(7)-C(4)	118.7118	119.4013
H(16)-C(9)-C(10)	119.5019	120.1176	O(15)-C(8)-C(7)	122.7168	122.971
H(16)-C(9)-C(8)	119.8111	119.6657	O(15)-C(8)-C(12)	116.4786	116.168
C(10)-C(9)-C(8)	120.6870	120.2167	C(12)-C(8)-C(7)	120.8046	120.861
C(8)-C(7)-C(6)	120.4817	120.7752	C(12)-C(9)-C(5)	121.4365	121.4209
H(13)-C(5)-C(6)	118.4113	119.9036	C(13)-C(6)-C(5)	119.9689	121.7773
H(13)-C(5)-C(4)	120.2594	119.5473	C(13)-C(6)-C(1)	120.7029	119.9684
C(6)-C(5)-C(4)	121.3293	120.5491	C(5)-C(6)-C(1)	119.3282	118.2543
C(5)-C(4)-C(2)	122.0468	122.3070	C(6)-C(1)-C(2)	123.5675	123.764
C(4)-C(2)-O(3)	126.8631	129.4805	O(18)-C(2)-C(1)	127.3071	129.0463
C(4)-C(2)-O(1)	115.4873	115.8237	O(3)-C(2)-C(1)	115.4499	115.9296
O(3)-C(2)-O(1)	117.6496	114.6958	O(18)-C(2)-O(3)	117.243	115.0241
C(11)-O(1)-C(2)	122.6945	122.9994	C(4)-O(3)-C(2)	122.0971	122.2471
C(7)-C(6)-C(5)	123.9497	125.3226	C(9)-C(5)-C(6)	124.4382	124.997
Dihedral angles(°)	Ground state	Excited state	Dihedral angles(°)	Ground state	Excited state
C(9)-C(10)-C(11)-O(1)	-179.9918	179.9788	O(3)-C(4)-C(7)-C(8)	179.9962	179.9782
H(16)-C(9)-C(10)-C(11)	-179.978	-179.987	C(4)-C(7)-C(8)-O(15)	-179.9891	-179.9902
H(16)-C(9)-C(10)-H(17)	0.0046	0.0015	H(14)-C(7)-C(8)-O(15)	0.0065	-0.0034
C(7)-C(8)-C(9)-H(16)	-179.9894	179.9976	O(15)-C(8)-C(12)-C(9)	179.9835	179.9839
C(5)-C(6)-C(11)-C(10)	-179.8907	-179.9372	C(7)-C(4)-C(5)-C(6)	-179.9767	179.9826
C(7)-C(6)-C(11)-O(1)	179.9971	-179.9674	O(3)-C(4)-C(5)-C(9)	-179.9892	-179.9863
H(13)-C(5)-C(6)-C(11)	179.9517	179.9984	C(4)-C(5)-C(6)-C(13)	179.961	-179.9781
C(2)-C(4)-C(5)-C(6)	-0.0406	-0.0435	C(2)-C(1)-C(6)-C(5)	-0.0091	-0.0452
O(1)-C(2)-C(4)-C(5)	0.0365	0.0113	C(6)-C(1)-C(2)-O(3)	0.0428	-0.0578
O(1)-C(2)-C(4)-H(12)	-179.9788	-179.9942	H(10)-C(1)-C(2)-O(3)	-179.9608	179.9638
O(3)-C(2)-C(4)-C(5)	-179.9636	-179.9891	C(6)-C(1)-C(2)-O(18)	-179.9721	179.9342
O(3)-C(2)-C(4)-H(12)	0.0211	0.0054	H(10)-C(1)-C(2)-O(18)	0.0243	-0.0442
C(2)-O(1)-C(11)-C(6)	-0.049	-0.0911	C(2)-O(3)-C(4)-C(5)	0.0113	-0.1203
C(2)-O(1)-C(11)-C(10)	179.8889	179.9016	C(2)-O(3)-C(4)-C(7)	-179.9874	179.9051
C(11)-O(1)-C(2)-O(3)	-179.9915	-179.9423	O(18)-C(2)-O(3)-C(4)	179.9697	-179.8517
C(11)-O(1)-C(2)-C(4)	0.0084	0.0574	C(1)-C(2)-O(3)-C(4)	-0.0436	0.1415

3.2 IR spectrum:

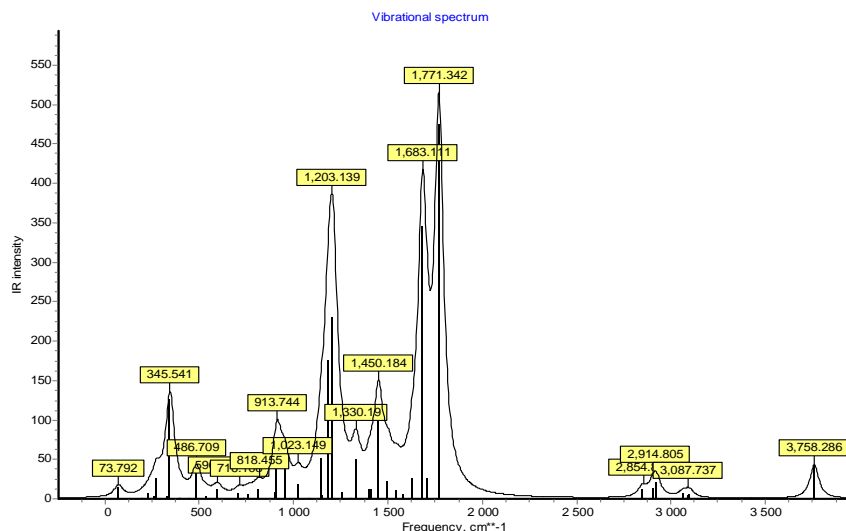


Fig (3) Infrared spectrum (IR) of the Coumarin4 molecule

The infrared spectrum (IR) is displayed in Fig.3. The change in dipole moment ($\Delta \mu = 1.3088$ Debye) should occur for a vibration to absorb infrared energy [4]. Absorption bands associated with C=O band stretching are usually very strong ($\lambda = 5.64 \mu\text{m} \Leftrightarrow \nu = 1771.342 \text{ cm}^{-1}$, IR intensity > 474) because a large change in the dipole takes place in that mode. But the highest frequency ($\nu = 3758.286 \text{ cm}^{-1} \Leftrightarrow \lambda = 2.66 \mu\text{m}$, IR intensity < 50) is due to vibrating swaying motion of O-H bond.

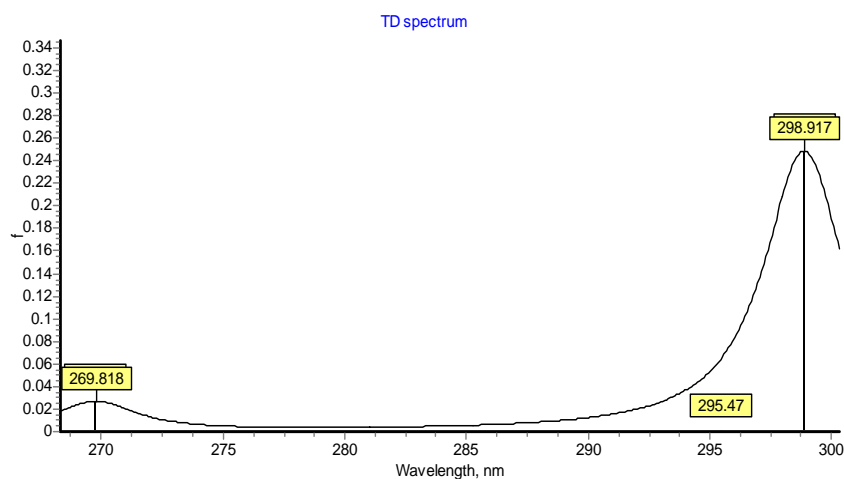
3.3 UV spectrum:

UV absorption spectra of coumarin and coumarin4 were calculated by TD-B3LYP/6-31G method, the comparison of results in gas phase were listed in Table 3. Coumarin 4 is within near-UV rang (wavelength $> 200\text{nm}$) as shown in Fig. 4. The presence of the hydroxyl group in the aromatic nucleus cause bathochromic shifts in the absorption maxima of chromophores To longer wavelength for coumarin 4 [4], UV absorption oscillator strengths f can be expressed by extinction coefficients ϵ cal. The extinction coefficients were calculated by the formula (molar extinction coefficients) [24]:

$$\epsilon \text{ cal} = f * 5.398 * 10^4$$

Table (3) Comparison between coumarin and coumarin4 of absorption spectrum in gas phase.

Coumarin (chromophore)			Coumarin 4		
$\lambda(\text{nm})$	F (Oscillator Strength)	ϵ cal	$\lambda(\text{nm})$	F (Oscillator Strength)	ϵ cal
287.57	0.0839	0.4529×10^4	298.8800	0.2485	1.3414×10^4
273.48	0.0003	0.0016×10^4	269.7700	0.0260	0.1403×10^4
261.34	0.1632	0.8809×10^4	295.4700	0.0002	0.0011×10^4

**Fig (4) UV spectrum of the Coumarin4 molecule in gas phase.**

3.4 Electronic structures of the ground states:

Molecular orbital (MO) calculations were performed using geometrical structures optimized by B3LYP/6-31G method. Shapes of molecular orbitals (MOs) of coumarin4 were presented in Fig. 5. Different orbital energies and energy gaps ($E(\text{HOMO})-E(\text{LUMO})$) of the Coumarin compounds are presented in Table 4, and the values of excited energy, transition, composition and assignment of the S1 state for coumarin compounds are presented in Table 5. So the difference of energy between HOMO and LUMO is reduced, and the transition from HOMO to LUMO need to lower the energy due to $-\text{CH}_3$ and $-\text{OH}$ groups.

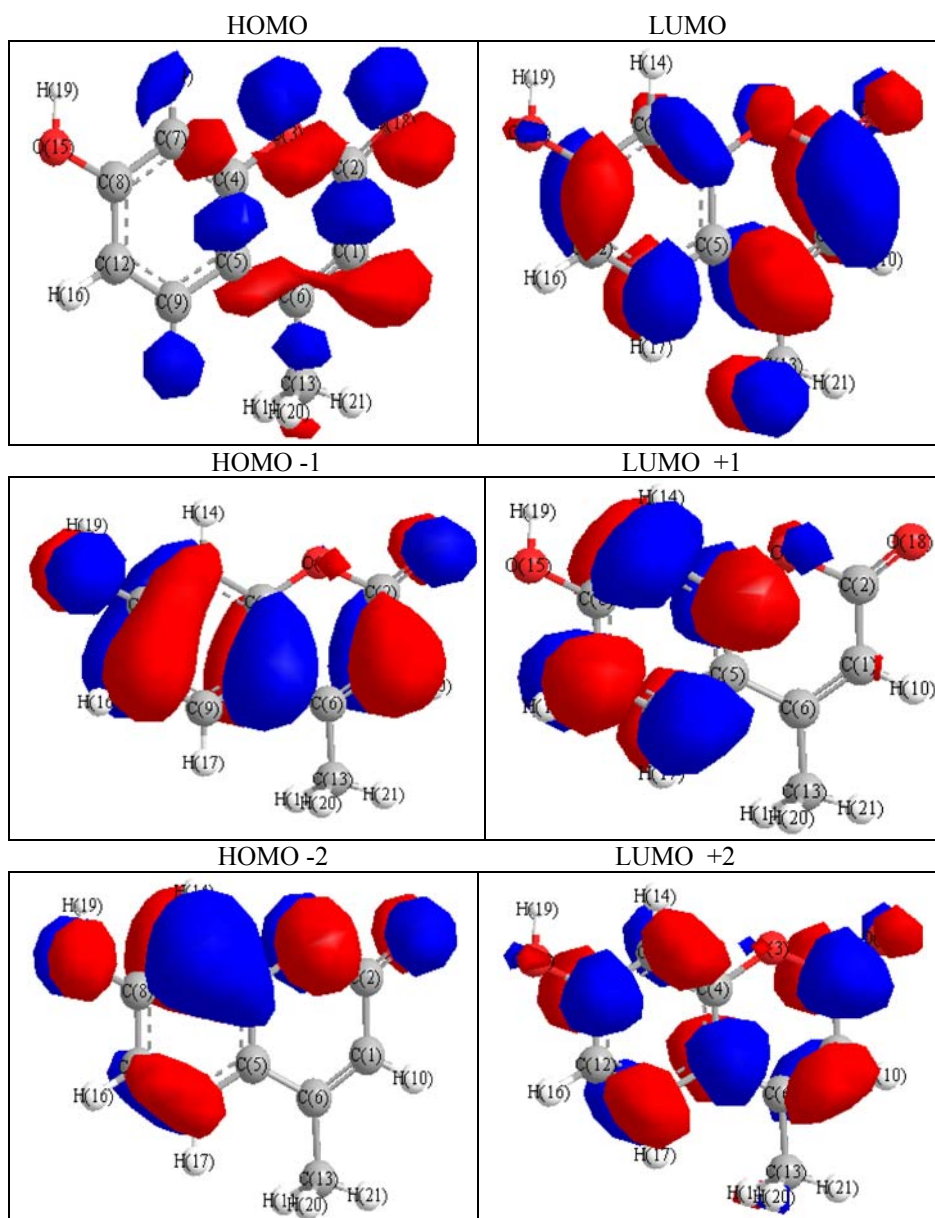


Fig (5) Calculated contour maps of the electronic density in the HOMO and LUMO states calculated by the B3LYP/6-31G method. Note: Positive color: red, Negative color: blue.

Table (4) Energies (ev) of frontier molecular orbitals obtained by B3LYP/6-31G method in gas phase.

	Coumarin	Coumarin4
Molecular orbital	Energy (e v)	Energy (e v)
HOMO -2	-7.546320912	-7.41652158
HOMO -1	-7.184950864	-7.075560232
HOMO	-6.637997704	-6.275811308
LUMO	-2.085224908	-1.836238768
LUMO +1	-0.500965556	-0.066124188
LUMO +2	-0.1428609	-1.269149024
Energy gap	4.552772796	4.43957254

Table (5) The calculated excited energies, transition, composition and assignment of the S1 state for coumarin compounds at the TD-B3LYP/6-31G level in gas phase.

Molecules	excited energy (ev)	Cal. (ev)[1]	Transition	composition
Coumarin	4.3114	-	HOMO →LOMO	38→39
Coumarin 4	4.1483	4.15[1]	HOMO →LOMO	46→47

3.5 Geometric properties of coumarin4 molecule in solvents:

Calculations by TDDFT in solvent were done using CPCM model. The results are also listed in Table 6 and 7, by Perform Equilibrium PCM Solvation made the calculated values nearer to the experimental data and acceptable. By finding solvents the vertical excitation energies made smaller than case without solvent and absorption intensity became larger as shown in Table 7 and Fig.7. Calculations including solvents polarity effects made the absorption spectrum red-shift and results are in very good agreement with experimental measurements. The average errors between the theoretical and experimental values are less than 5 nm in ethanol and methanol, but in water are less than 1.6 nm.

Table (6) Absorption wavelength (λ), oscillator strength (f) and extinction coefficients (ϵ cal) values in different solvents were calculated by TD-B3LYP/6-31G method.

UV spectrum	Ethanol	Water	Methanol	Acetonitrile (ACN)	DMSO	Acetone	Dichloro Methane
λ_{nm} (max)	317.82	319.03	318.25	318.32	318.32	317.36	315.34
f(Oscillator Strength)	0.5355	0.5489	0.5402	0.5411	0.5414	0.5305	0.5065
ϵ cal	2.897×10^4	2.963×10^4	2.916×10^4	2.921×10^4	2.922×10^4	2.864×10^4	2.734×10^4
λ_{nm}	278.11	278.56	278.27	278.3	278.32	277.96	277.19
f(Oscillator Strength)	0.0114	0.0112	0.0113	0.0113	0.0113	0.0114	0.0119
ϵ cal	0.0615×10^4	0.061×10^4	0.061×10^4	0.061×10^4	0.061×10^4	0.0615×10^4	0.064×10^4
λ_{nm}	266.36	265.18	265.93	265.89	265.91	266.82	268.81
f(Oscillator Strength)	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.002
ϵ cal	0.001×10^4	0.001×10^4	0.001×10^4	0.001×10^4	0.001×10^4	0.001×10^4	0.001×10^4
Exp (λ_{nm}) (max)	323[25]	320.6[1]	322[26]	-	-	-	-

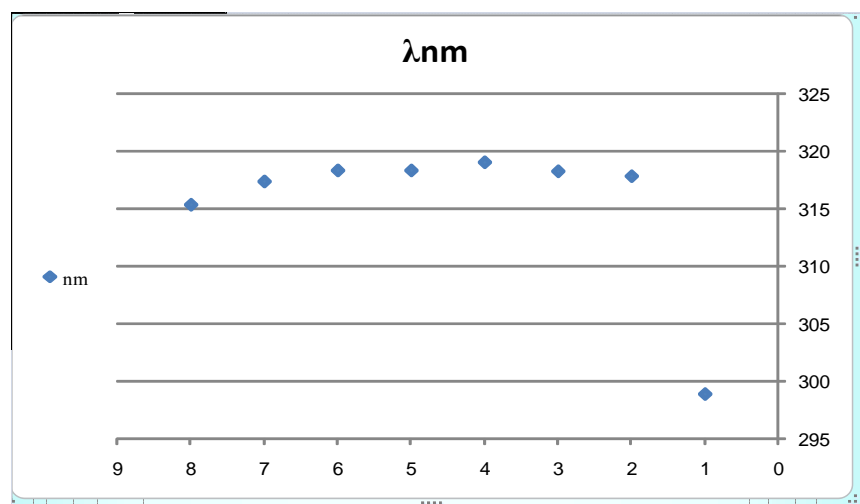
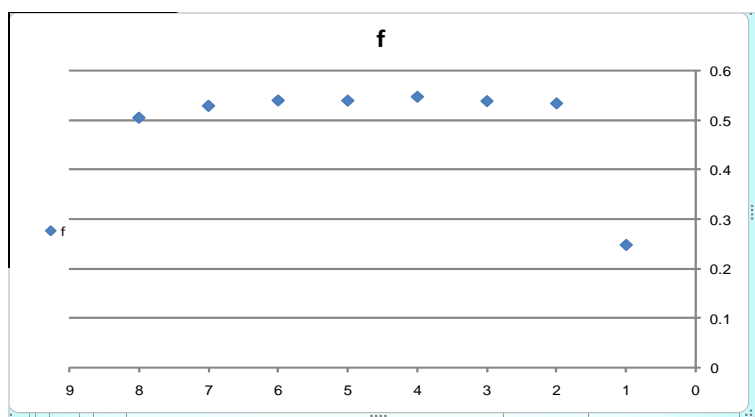


Fig (6) Description change λ_{max} by denotation solvents.

Table (7) The calculated excited energies, transition, composition and assignment of the S1 state for coumarin4 compound at the TD-B3LYP/6-31G level in different solvents.

Solvents	excited energy (ev)	Exp.	Transition	composition
Ethanol	3.9011	3.8313[25]	HOMO →LUMO	46→47
Methanol	3.8958	3.8432[26]	HOMO →LUMO	46→47
Water	3.8863	3.86[1]	HOMO →LUMO	46→47
Acetonitrile(ACN)	3.895	-	HOMO →LUMO	46→47
DMSO	3.8949	-	HOMO →LUMO	46→47
Acetone	3.9067	-	HOMO →LUMO	46→47
DichloroMethane	3.9318	-	HOMO →LUMO	46→47

**Fig (7) Description change f (Oscillator Strength) by denotation solvents.**

4. Conclusions

In this paper, we have investigated the properties of Coumarin4 at the CIS, B3LYP and TD-B3LYP levels of theory. The ground-state geometries were optimized at the B3LYP/6-31G levels of theory and the CIS/6-31G method was adopted to obtain the first excited-state geometries.

Geometrical structures, IR spectrum, molecular orbitals, absorption Spectra of these coumarin compounds have been calculated using DFT methods and have been discussed.

The solvent effect has also been taken into account using CPCM model. The calculated results using TD-B3LYP/6-31G methods agree well with the experimental data. The solvent effect makes the absorption intensity larger than the results without taking solvent into account, we can see that the calculated excited energies agree well with the experimental data, these solvents are suitable for coumarin4. The S1 states are mainly due to HOMO→LUMO transition.

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