EFFECT OF POLAR SOLVENTS ON ABSORPTION SPECTRA OF COUMARIN 1 : PCM-TDDFT STUDY

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ABSTRACT

Density functional theory (DFT/ Time dependent density functional theory (TDDFT) calculations have been carried out to study the electronic structure and the exited state properties of coumarin 1 dye. The exited state properties have been investigated with inclusion of solvent effect. The B3LYP functional with a cc-pVDZ basis set have been used to compute transition energies. The solvent effects have been described within the polarizable continuum model (PCM). Ground-state geometries are optimized using DFT with B3LYP functional combined with cc-pVDZ basis sets. Vertical absorption energy calculations characterize the lower singlet excited states both in gas phase and in solvents. A large red-shift of the absorption maximum in the polar solvents suggests an intra-molecular charge transfer character of the excited state. The absorption maximum both in gas phase and in polar solvents is discussed in terms of electrostatic interaction energy, oscillator strength and dipole moment.

Key words: DFT, TDDFT, cc-pVDZ, PCM, Coumarin 1.

INTRODUCTION

The 7-aminocoumarins represent an important class of organic compounds with extensive and diverse applications[1-3]. They possess distinct biological activity[4] and have been indicated as agents with potential anticancer, antibiotic and anticoagulant activity. However, the main reason for their popularity lies mostly in their excited state properties. They exhibit a strong fluorescence in the visible region (from 350 nm to 500 nm), which makes them suitable for use as laser dyes and non-linear optical chromophores.

The compound Coumarin 1 (4-methyl-7-diethylaminocoumarin) is one of the most featured dye among the coumarin family. The substitution at the 7-position with an electron-donating group enhances the fluorescence of the dye, which leads to their wide application in blue-green laser dyes and fluorescence probes. Furthermore, 7-aminocoumarin dyes are applied to study solvatochromic properties since the large Stokes shifts of these molecules are very sensitive to the polarity and viscosity of the surrounding solvent environment. Hence, the photophysics of these dyes has been studied intensively[5-28]. In spite of the numerous studies and wide applications of 7-aminocoumarins, further investigation of the excited state properties are essential. The nonradiative deactivation mechanism of 7-aminocoumarins has been debated for the past two decades. The first model describes the nonradiative deactivation process as the 7-aminocoumarin forms the twisted intra-molecular charge transfer state (TICT) from the S_1 singlet excited

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state.[5] The second is the open closed umbrella like motion mechanism.[6] This mechanism ascribes the internal conversion process to a structural change of the amino group from a planar N^+-aromatic configuration (with sp^2 hybridization for the nitrogen atom) to a pyramidal N-aromatic configuration (with sp^3 hybridization for the nitrogen atom).

The time-dependent density functional theory (TDDFT) method combined with the polarizable continuum model (PCM) has been developed and applied to predict the absorption and fluorescence spectra of solvated molecules[29-41]. The TDDFT has been applied to study various 7-aminocoumarins[20,42-54]. In 2002, Cave et al.[20,42] performed a detailed theoretical study on several coumarins using different electronic structure methods and concluded that the TDDFT method was a powerful tool for treating the spectroscopy of 7-aminocoumarins. More recently, the spectra of a series of coumarins[43-54] have been studied using the TDDFT method and the calculated results are in good agreement with various experimental measurements.

In this paper, the structure and electronic spectra of Coumarin 1 in solvents and gas phase using the TDDFT method have been computed. The PCM model is used to evaluate the solvent effect.

Computational details

Ground-state optimization of Coumarin 1 have been performed by using B3LYP hybrid function with cc-pVDZ basis set at a DFT level.[55-60] TDDFT is used for transition energy calculation within a DFT framework using same function and basis set. The effect of the solvents was added using PCM model of solvation. All calculations were performed using GAMESS-US software suit.[61,62]

RESULTS AND DISCUSSION

The optimized structure of the Coumarin 1 has planar geometry, as can be seen in Figure 1. The main optimized parameters of Coumarin 1 of the ground and excited states in four solvents and gas phase are given in Table 1.
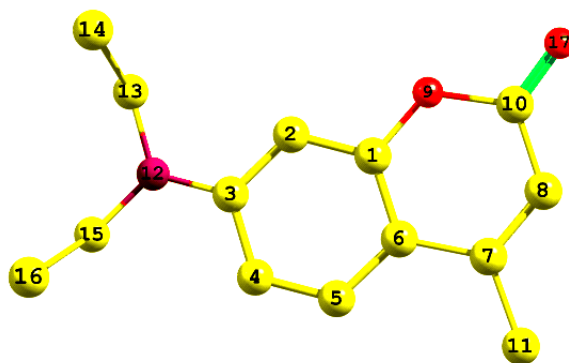

Fig. 1: Optimized structure of Coumarin 1 (Red-O, Magenta-N and Yellow-C)

Ground state geometry

From Table 1, it can be seen that the geometrical parameters are affected by the solvents. The bond lengths of C1-C2, C3-N12, C4-C5, C6-C7, C7-C11, C8-C10,O9-C10, C13-C14,C15-C16 are decreased and C1-O9, C2-C3, C3-C4, C5-C6, C7-C8, C10-O17, N12-C13, N12-C15 are increased by the same amount in all polar protic solvents (H_2O, MeOH, EtOH) where as in polar aprotic solvent (THF), slight variation of the bond length from -0.003Å to 0.003 Å. The bond angles are slightly changes due to solvation (-3.3° to 2.6°). Solvents have no influence on the dihedral angles.

Table 1: Bond lengths (Å) and bond angles (°) for the ground and excited states of Coumarin 1

Bond length/ bond angle	Ground state					Excited state				
	Gas phase	Water	MeOH	EtOH	THF	Gas phase	Water	MeOH	EtOH	THF
R (1-2)	1.393	1.391	1.391	1.391	1.391	1.396	1.387	1.388	1.388	1.388
R (1-6)	1.412	1.412	1.412	1.412	1.412	1.425	1.425	1.425	1.425	1.425
R (1-9)	1.364	1.372	1.372	1.372	1.371	1.348	1.365	1.365	1.365	1.362
R (2-3)	1.414	1.418	1.418	1.418	1.417	1.423	1.430	1.429	1.429	1.428
R (3-4)	1.427	1.431	1.431	1.431	1.430	1.416	1.422	1.420	1.420	1.420
R (3-12)	1.383	1.375	1.375	1.375	1.377	1.398	1.384	1.385	1.385	1.386
R (4-5)	1.385	1.383	1.383	1.383	1.383	1.399	1.392	1.393	1.393	1.393
R (5-6)	1.410	1.414	1.414	1.414	1.413	1.417	1.424	1.424	1.424	1.423
R (6-7)	1.449	1.444	1.444	1.444	1.445	1.461	1.450	1.450	1.450	1.451
R (7-8)	1.363	1.369	1.369	1.369	1.368	1.399	1.407	1.406	1.406	1.405
R (7-11)	1.505	1.504	1.504	1.504	1.504	1.493	1.496	1.496	1.496	1.496
R (8-10)	1.454	1.445	1.445	1.445	1.446	1.425	1.418	1.418	1.418	1.420
R (9-10)	1.403	1.394	1.394	1.394	1.395	1.461	1.436	1.436	1.436	1.439
R (10-17)	1.208	1.219	1.219	1.219	1.217	1.218	1.235	1.235	1.235	1.232
R (12-13)	1.463	1.466	1.466	1.466	1.465	1.462	1.466	1.465	1.465	1.466
R (12-15)	1.462	1.467	1.467	1.467	1.466	1.460	1.466	1.466	1.466	1.465
R (13-14)	1.534	1.533	1.533	1.533	1.533	1.538	1.537	1.538	1.538	1.537
R (15-16)	1.535	1.533	1.533	1.533	1.534	1.538	1.537	1.536	1.536	1.537
A (2-1-6)	122.4	122.9	122.9	122.9	122.8	121.1	121.8	121.8	121.8	121.7
A (2-1-9)	116.0	116.0	116.0	116.0	116.0	115.8	115.7	115.8	115.8	115.7
A (1-2-3)	120.9	120.6	120.6	120.6	120.7	121.3	121.1	121.0	121.0	121.1
A (6-1-9)	121.6	121.1	121.1	121.1	121.2	123.2	122.4	122.5	122.5	122.6
A (1-6-5)	116.3	116.1	116.1	116.1	116.2	116.9	116.4	116.5	116.5	116.5
A (1-6-7)	118.4	118.6	118.6	118.6	118.6	118.5	118.9	118.8	118.8	118.8
A (1-9-10)	122.2	122.1	122.1	122.1	122.1	121.0	120.9	120.9	120.9	120.9
A (2-3-4)	117.0	116.9	116.9	116.9	116.9	118.2	117.7	117.9	117.9	117.8
A (2-3-12)	121.4	121.6	121.6	121.6	121.6	120.0	120.4	120.2	120.2	120.3
A (4-3-12)	121.5	121.5	121.5	121.5	121.5	121.9	121.9	121.9	121.9	121.9
A (3-4-5)	121.1	121.3	121.3	121.3	121.3	119.9	120.4	120.4	120.4	120.4
A (3-12-13)	121.0	121.1	121.1	121.1	121.1	121.7	121.7	121.7	121.7	121.7
A (3-12-15)	121.2	121.2	121.2	121.2	121.2	120.7	121.0	121.0	121.0	120.9

Cont…

Bond length/ bond angle	Ground state					Excited state				
	Gas phase	Water	MeOH	EtOH	THF	Gas phase	Water	MeOH	EtOH	THF
A (4-5-6)	122.3	122.2	122.2	122.2	122.2	122.6	122.5	122.5	122.5	122.5
A (5-6-7)	125.3	125.3	125.3	125.3	125.3	124.6	124.7	124.7	124.7	124.7
A (6-7-8)	118.6	118.6	118.6	118.6	118.6	116.7	116.7	116.7	116.7	116.7
A (6-7-11)	120.2	120.4	120.4	120.4	120.4	120.1	120.6	120.6	120.6	120.5
A (8-7-11)	121.1	120.9	120.9	120.9	121.0	123.2	122.7	122.7	122.7	122.8
A (7-8-10)	123.1	122.7	122.7	122.7	122.8	125.3	124.6	124.7	124.7	124.7
A (8-10-9)	116.1	116.8	116.8	116.8	116.7	115.4	116.4	116.4	116.4	116.3
A (8-10-17)	126.7	126.8	126.8	126.8	126.8	130.0	129.3	129.3	129.3	129.3
A (9-10-17)	117.2	116.4	116.4	116.4	116.5	114.6	114.3	114.3	114.3	114.4
A (13-12-15)	117.8	117.7	117.7	117.7	117.7	117.6	117.3	117.3	117.3	117.3
A (12-13-14)	115.2	115.0	115.0	115.0	115.0	114.6	114.2	114.3	114.3	114.3
A (12-15-16)	115.1	114.9	114.9	114.9	114.9	114.6	114.2	114.2	114.2	114.3

Table 2: Important torsion angles (°) for the ground and excited states of Coumarin 1

State	Chain	Gas phase	Water	MeOH	EtOH	THF
Ground	c4-n18-c19-c20	-83.81	-84.07	-84.07	-84.07	-84.00
	c4-n18-c21-c22	-81.42	-81.33	-81.33	-81.33	-81.36
Excited	c4-n18-c19-c20	-84.75	-85.66	-90.08	-90.03	-86.67
	c4-n18-c21-c22	-79.85	-79.66	-73.04	-73.15	-78.62

Electronic structure

Figure 2 displays the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), both shows π-character. LUMO are localized on C3, C5, C7, C8, C10, O9 and O17 where as HOMO are localized on N12, C2, C3, C4, C6, C8 and O17. The contributions to HOMO and LUMO are mainly from the parent coumarin. However, the composition of 7-amino group is much larger for the HOMO than that for the LUMO. The electronic transition from HOMO to LUMO could lead to the intra-molecular charge transfer from the amino substituent to the parent coumarin.
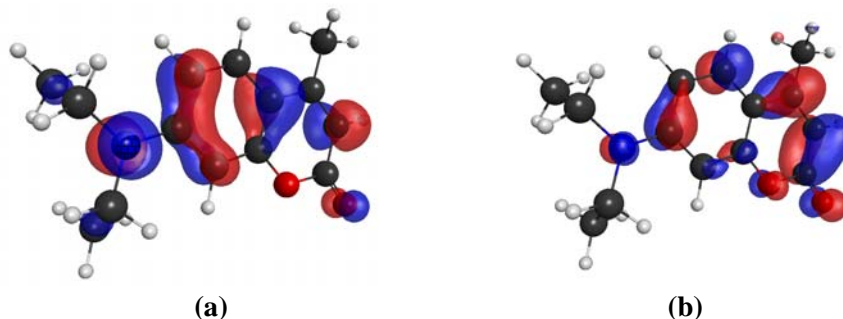

(a)   (b)

Fig. 2(a): HOMO and (b) LUMO of Coumarin 1

Excited state geometry

The geometries of the first excited state were optimized at the TDDFT/cc-pVDZ level of theory and the influence of solvent polarity on the geometry has been taken into account using the PCM method. From Table 1, it can be seen that the geometrical parameters are affected by solvent polarity. The way of bond elongation and contraction from gas phase to solvent phases is similar to that in the ground state. The lowest singlet transition for Coumarin 1 is the transition from the HOMO to LUMO, so the relaxation of bond length can be understood by analyzing the nodal patterns of the HOMO and LUMO orbitals. Taking the geometric parameters of Coumarin 1 in gas phase as an example, the HOMO is bonding in the C1-C6, C2-C3, C3-C4, C7-C8 and C3-N12 bonds, but LUMO has nodes across these bonds except C3-C4. As a consequence, an elongation of the C1-C6, C2-C3, C7-C8 and C3-N12 bonds (+0.013, +0.009, +0.036, and +0.015Å, respectively) is expected. The LUMO is bonding in the C3-C4 and C8-C10 bonds. A shortening of C3-C4 and C8-C10 bonds (0.011 and 0.029Å, respectively) is obtained. Also, LUMO has nodes across O9-C10 bond, due to which the bond length increased by 0.058Å. The maximal values of dihedral angles for the Coumarin 1 (Table 2) in solvents and gas phase are less than 10°, indicating that TICT formation is unlikely for this molecule.

Absorption spectra

The computational UV absorption spectra of Coumarin 1 in polar solvents and gas phase are shown in the Figure 3. Spectra show a similar profile in all phases; they present intense bands in polar solvents than in gas phase. Excitation energy (E), oscillator strength (f), electrostatic interaction energy (E_{int}), dipole moment (D) of Coumarin 1 molecule in polar solvents and gas phase, and total dipole moment (D_T) of solvated system for the ground (S_0) and excited (S_1) states are given in the Table 3. The spectra show absorption energies at 3.723, 3.357, 3.366, 3.418 eV in gas phase, water, methanol and THF respectively. In ethanol, the spectrum presents the absorption peak at 3.371 eV. This is consistent with the experimental result 3.322 eV.[63]

Table 3: Excitation energy (E), oscillator strength (f), electrostatic interaction energy (E_{int}), dipole moment (D) of Coumarin 1 molecule in polar solvents and gas phase, and total dipole moment (D_T) of solvated system for the ground (S_0) and excited (S_1) states

Medium	E (eV)	f	E_{int} (KCal/mol)		D (Debye)		D_T (Debye)	
			S_0	S_1	S_0	S_1	S_0	S_1
Gas phase	3.723	0.395	-	-	6.654	11.431	-	-
Water	3.357	0.666	-10.400	-11.140	9.603	16.176	0.138	7.630
Methanol	3.366	0.660	-10.090	-10.760	9.523	16.083	0.298	7.805
Ethanol	3.371	0.656	-9.850	-10.570	9.554	16.011	0.303	7.849
THF	3.418	0.623	-8.410	-8.980	9.099	15.373	1.189	8.205

The dipole moment of the molecule increases to nearly two fold during excitation in solvents and gas phase. The interaction energies of Coumarin 1 with solvent molecules are negative in all solvents. The excited state dipole moment of Coumarin 1 molecule and the total dipole moment of the system are increase from gas phase to THF via water, MeOH and EtOH. The change in electronic charge distribution between HOMO and LUMO is also indicative of a large dipole moment and is the possible reason for the increase in oscillator strength for the HOMO → LUMO transition in polar solvents. The large dipole moment of the Coumarin 1 molecule in the excited state is additionally stabilized by polar solvent molecules, that lead to the decrease in the excitation energy and the corresponding red shift of the spectral maximum.
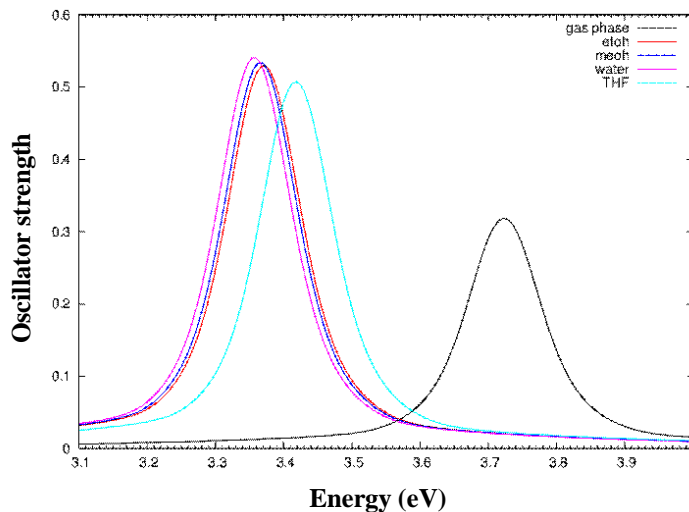
Fig. 3: Calculated UV/Vis absorption spectra of Coumarin 1

CONCLUSION

In this work, the structures and electronic spectra of Coumarin 1 are investigated using the DFT/TDDFT methods and the solvent effect has been taken into account using the PCM model. The observed geometrical relaxation from the ground to the first-excited states can be understood by analyzing the nodal patterns of HOMO and LUMO orbitals. The maximal values of dihedral angles for the Coumarin 1 in solvents and gas phase are less than 10°, indicating that TICT formation is unlikely for this molecule. The absorption energies are calculated using the TDDFT method and the PCM model is employed to evaluate the solvent effect. The solvent makes the absorption spectra red-shift. The calculated absorption energies in polar protic solvents are closely spaced.

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