Estimation of ground and excited state dipole moments of newly synthesized coumarin molecule by Solvatochromic shift method and Gaussian software

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Abstract: Absorption and fluorescence spectra of newly synthesized coumarin molecule namely 4-((3-methoxyphenoxy)methyl)-7-hydroxy-2H-chromen-2-one [3-MPHC] have been recorded at room temperature (300 K) in solvents of different polarities. The effects of solvents on the spectral properties are discussed. Using Lippert's, Bakshiev's and Kawski-Chamma-Viallet's equations the ground (μ_g) and excited state (μ_e) dipole moments were estimated. Variation of Stokes shift with the solvent dielectric constant along with refractive index was made use of to estimate dipole moments. Density Functional Theory (DFT) was studied using Gaussian software 16. It was observed that excited state dipole moment was higher than the ground state dipole moment. Further we have analyzed microscopic solvent polarity parameter.

Keywords: Coumarin, Dipole moment, Gaussian Software, Stokes shift, Microscopic solvent polarity parameter

I. INTRODUCTION

Estimation of the ground and excited state dipole moments of newly synthesized coumarin molecule is important, because the values of dipole moments provide information about the change in electronic redistribution upon excitation. Coumarin is the most important naturally occurring oxygen containing heterocyclic compound. From few decades coumarin and its derivatives are well recognized for their biological traits such as anticoagulant, antibacterial, anti-microbial, analgesic anti-pyretic, anti-neoplasm, anti-metastatic and fungicidal activity [1-3]. Coumarin compounds are also used as food preservatives, additives and cologne in cosmetics. Therefore, determination of the coumarin content in different pharmaceutical and commercial products has become an interesting field of research. Coumarin molecules are very good media for efficient optical brighteners, laser molecules and broad–band dye lasers in blue-green domain of radiation. These compounds are used as rodenticides, fluorescent indicators. Using different methods many researchers worked on the ground and excited state dipole moments by experimentally and theoretically for coumarins, fluorescent molecules, organic dyes and laser dyes [4-9]. We observed there is a blue shift in Iron doped ZnO nanoparticles at different molarities by Wet Chemical Method [20]. However, there are no reports available in the literature on the estimation of ground and excited state dipole moment values of the coumarin molecule   4-((3-methoxyphenoxy)methyl)-7-hydroxy-2H-chromen-2-one [3-MPHC]. This prompted us to carry out the present work to estimate and compare the μ_g and μ_e of 3-MPHC.

II. MATERIALS AND METHODS

The coumarin derivative 3-MPHC was synthesized as per the procedure mentioned in the reference [10]. The molecular structure of 3-MPHC is as shown in **Fig.1**. Sample solutions were prepared by adding required amount of solute into different solvents. The solvents used were, Ethyl acetate (EA), Acetone, Dimethyl sulfoxide (DMSO), Acetonitrile (AN), 1-Butanol, Ethanol, Methanol, Toluene, Tetrahydrofuran (THF) and Dichloromethane (DCM) all were of spectroscopic grade. The solvents were used without any further purification. The required solutions were prepared at a fixed solute concentration (10 μ M/L). The concentration of solute was kept sufficiently low in order to minimize the effect of self absorption. Absorption spectra were recorded on a PG Inst. Ltd., model T-90+, UV-Vis. absorption spectrophotometer and fluorescence spectra on a Fluorolog-3 spectrofluorometer (Horiba-Jobin-Yvon). Linear fit was done by using Origin pro 8 software.
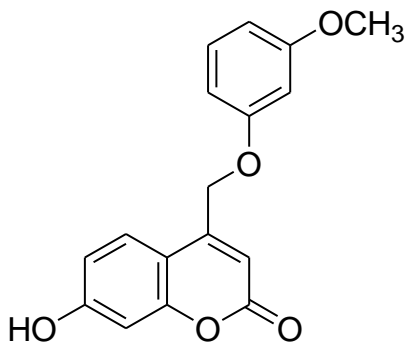
Fig. 1. Molecular structure of 3-MPHC

III. EXPERIMENTAL ESTIMATION OF GROUND AND EXCITED STATE DIPOLE MOMENTS

The independent equations used for the estimation of ground state and excited state dipole moments of the 3-MPHC molecule are as follows,

Lippert's equation [11]

$$\overline{\upsilon_a} - \overline{\upsilon_f} = m_1 \, F_1(\varepsilon, n) + \text{Constant} \qquad (1)$$

Bakshiev's equation [12]

$$\overline{\upsilon_a} - \overline{\upsilon_f} = m_2 \, F_2(\varepsilon, n) + \text{Constant} \qquad (2)$$

Kawski-Chamma-Viallet's equation [13, 14]

$$\frac{\overline{\upsilon_a} + \overline{\upsilon_f}}{2} = m_3 \, F_3(\varepsilon, n) + \text{Constant} \qquad (3)$$

where $\overline{\upsilon_a}$ and $\overline{\upsilon_f}$ are absorption and fluorescence maxima wavelength in cm^{-1}, respectively. The other symbols 'ε' and 'n' are dielectric constant and refractive index respectively.

The expressions for F_1 (ε, n) [Lippert's polarity function], F_2 (ε, n) [Bakshiev's polarity function] and F_3 (ε, n) [Kawski–Chamma–Viallet's polarity function] are given as

$$F_1(\varepsilon, n) = \left[\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \right] \qquad (4)$$

$$F_2(\varepsilon, n) = \left[\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right] \frac{(2n^2 + 1)}{(n^2 + 2)} \qquad (5)$$

$$F_3(\varepsilon, n) = \frac{2n^2 + 1}{2(n^2 + 2)} \left[\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right] + \frac{3(n^4 - 1)}{2(n^2 + 2)^2} \qquad (6)$$

From equations (4), (5), (7) and (8) it follows that $\left(\overline{\upsilon_a} - \overline{\upsilon_f} \right)$ versus F_1 (ε, n) and F_2 (ε, n), also from equations (6) and (9) it follows that $\left(\overline{\upsilon_a} + \overline{\upsilon_f} \right)/2$ versus F_3 (ε, n) should give linear graphs with slopes m_1, m_2 and m_3 respectively and are given below,

$$m_1 = \frac{2(\mu_e - \mu_g)^2}{hca^3} \qquad (7)$$

$$m_2 = \frac{2(\mu_e - \mu_g)^2}{hca^3} \qquad (8)$$

$$m_3 = \frac{2(\mu_e^2 - \mu_g^2)}{hca^3} \qquad (9)$$

Where μ_g and μ_e are the ground and excited state dipole moments of the coumarin molecule, respectively. The symbols 'h' and 'c' are Planck constant and velocity of light in vacuum, respectively and 'a' is the Onsager's cavity radius of the coumarin molecule. The value of 'a' is evaluated using atomic increment method by Edward [15]. In general case, the dipole moments μ_g and μ_e are not parallel but they form certain angle [16]. By assuming the ground state and excited state dipole moments are parallel, the following equations are obtained on the basis of equations (8) and (9).

$$\mu_g = \frac{m_3 - m_2}{2} \left[\frac{hca^3}{2m_2} \right]^{\frac{1}{2}} \text{For } (m_3 > m_2) \qquad (10)$$

$$\mu_e = \frac{m_3 + m_2}{2} \left[\frac{hca^3}{2m_2} \right]^{\frac{1}{2}} \qquad (11)$$

Difference in Dipole Moment Using Molecular

Microscopic Solvent Polarity Parameter

Understanding the polarization dependence or hydrogen bonding effect on spectral characteristics, it may be worthwhile to use molecular microscopic solvent polarity E_T^N function proposed by Reichardt [17]. The theoretical basis for the correlation of the Stokes shift with E_T^N was proposed by Reichardt and developed by Ravi et al. [18]. Accordingly equation (13) is obtained and E_T^N is given as follows:

$$E_T^N = \frac{E_T(solvent) - 30.7}{32.4} \qquad (12)$$

and E_T (solvent) = 28,591/λ_{max} corresponds to the peak wavelength in the red region of the intramolecular charge transfer absorption of the pyridinium-N-phenolatebetaine dye. Using this method, change in dipole moment is calculated from the plots of Stokes shift versus E_T^N. According to the following equation:

$$\overline{\upsilon_a} - \overline{\upsilon_f} = 11307.6 \left(\frac{\Delta\mu^2 a_D^3}{\Delta\mu_D^2 a^3} \right) E_T^N + \text{Constant} \qquad (13)$$

Where $\Delta \mu = (\mu_e - \mu_g)$ and 'a' are the change in dipole moment and Onsager cavity radius of the coumarin molecule of interest respectively. In the expression, the Onsager radii of the both Betaine dye (a_D) and coumarin derivative (a) enter as a ratio, as the values of a_D and $\Delta\mu_D$ are known (6.2 Å and 9 D, respectively [17]).

IV. RESULTS AND DISCUSSION

Effect of Solvents on Absorption and Fluorescence Emission Spectra

Absorption spectra and emission spectra of 3-MPHC molecule in different solvents are shown in **Fig. 2** and **Fig. 3** respectively. It is observed that the absorption wavelength found nearly in the range 275-350 nm and emission wavelength is nearly in the range 375-425 nm. Absorption maxima, emission maxima, Stokes shift and arithmetic mean Stokes shift wave numbers in cm^{-1} of 3-MPHC are given in table 1. The band shift occurred in the emission spectra and there is increase in the Stokes shift values with increasing solvent polarity which indicates that there is an increase in the dipole moment on excitation. Polarity functions values like Lippert's [F_1 (ε, n)], Bakshiev's [F_2 (ε, n)], Kawski-Chamma-Viallet's [F_3 (ε, n)] and E_T^N parameters are tabulated in table 2.
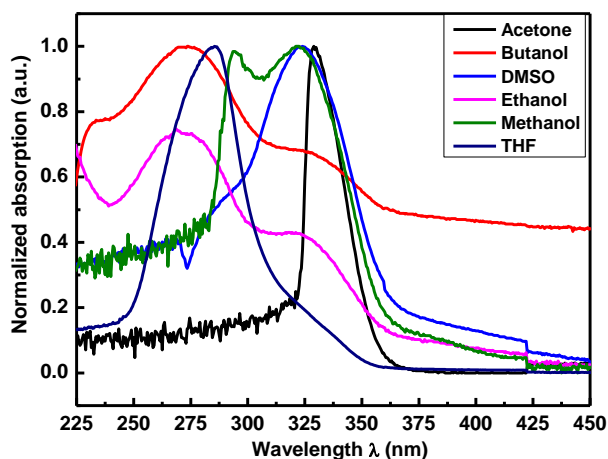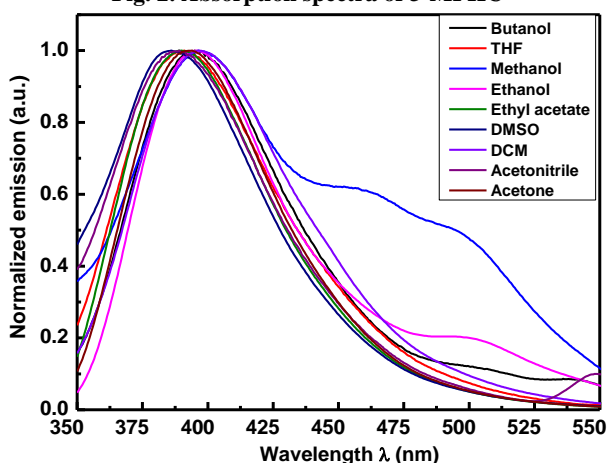

Fig. 2. Absorption spectra of 3-MPHC

Fig. 3. Fluorescence emission spectra of 3-MPHC

Table 1. Absorption maxima, fluorescent maxima wave numbers in cm^{-1}, Stokes shift and arithmetic Stokes shift data

Solvents	$\bar{\upsilon}_a$	$\bar{\upsilon}_f$	$(\bar{\upsilon}_a - \bar{\upsilon}_f)$	$\frac{\bar{\upsilon}_a + \bar{\upsilon}_f}{2}$
Toluene	33085.19	28977.11	31031.15	4108.09
EA	32646.67	27300.03	5346.64	29973.35
THF	32974.46	28538.81	4435.65	30756.64
Acetonitrile	36295.01	25806.45	31050.73	10488.55
DCM	32431.73	26532.24	5899.49	29481.98
Butanol	30601.63	26164.31	4437.32	28382.97
Acetone	30412.70	25458.25	4954.45	27935.47
Ethanol	32755.20	27700.83	5054.37	30228.02
Methanol	32864.47	28113.58	4750.89	30489.02
DMSO	32538.84	26910.66	5628.19	29724.75

Table 2. Polarity functions and microscopic solvent polarity parameter for respective solvents

Solvents	$F_1(ε,n)$	$F_2(ε, n)$	$F_3(ε, n)$	E_T^N
Toluene	0.0132	0.0291	0.3499	0.099
EA	0.1996	0.4891	0.4979	0.228
THF	0.2096	0.5491	0.5511	0.207
Acetonitrile	0.1583	0.4784	0.6313	0.461
DCM	0.2184	0.5955	0.5857	0.321
Butanol	0.2633	0.7494	0.6459	0.586
Acetone	0.2848	0.7925	0.6404	0.355
Ethanol	0.2887	0.8129	0.6525	0.654
Methanol	0.3086	0.8546	0.6510	0.762
DMSO	0.2630	0.8400	0.7420	0.444

Estimation of ground and excited state dipole moments

The graphs obtained for Lippert's polarity function versus Stokes shift (**Fig. 4**), Bakshiev's polarity function versus Stokes shifts (**Fig. 5**) and Kawski-Chamma-Viallet's polarity functions versus arithmetic mean Stokes shifts (**Fig. 6**) are found to be linear. From these graphs we obtained slopes to estimate the ground and excited state dipole moments using the relevant formulae. We also analyzed the change in dipole moment using microscopic solvent polarity parameter (E_T^N). The variation of Stokes shift with microscopic solvent polarity parameter is shown in **Fig. 7**. Onsager cavity radius, statistical correlation values, dipole moments in ground and excited states and change in dipole moments of 3-MPHC are given in table 3.
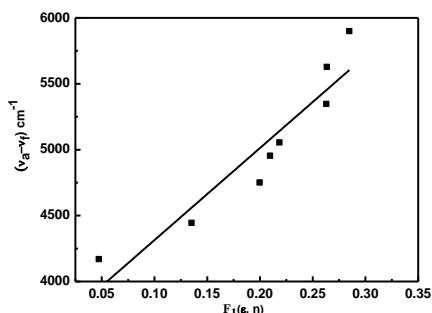
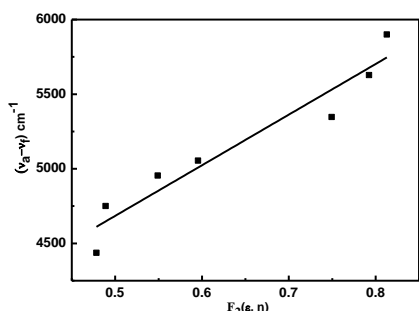Fig. 4. Variation of Stokes shift with Lippert's polarity function for 3-MPHC

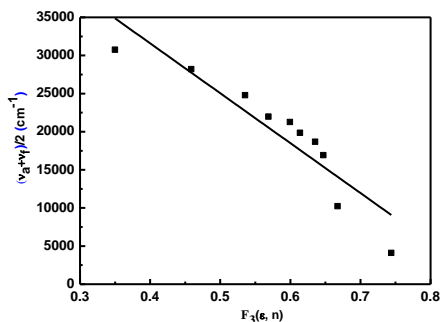Fig. 5. Variation of Stokes shift with Bakshiev's polarity function for 3-MPHC

Fig. 6. Variation of arithmetic mean Stokes shift with Kawski-Chamma-Viallet's polarity function for 3-MPHC
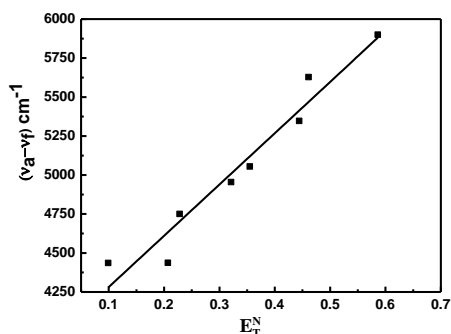

Fig. 7. Variation of Stokes shift with E_T^N for 3-MPHC

Table 3. Radius, statistical correlation values and dipole moments of 3-MPHC in the ground and excited states (in Debye)

Coumarin	Radius a (Å)	Statistical correlation			Dipole moments						
		Slope (cm^{-1})	r	n	μ_g^a (D)	μ_e^b (D)	μ_e^c (D)	μ_e^d (D)	μ_e^e (D)	$\Delta\mu^f$ (D)	$\Delta\mu^g$ (D)
3-MPHC	3.891	m_1=6981.9 m_2=3392.51 m_3=-8634.1 m =3388	0.86 0.91 0.97 0.94	8 7 10 8	3.44	7.90	9.83	7.90	10.62	4.45	2.41

(1 Debye = 3.34 X 10^{-30} cm = 10^{-18} esu cm.)
r- Correlation coefficient.
n- Number of data points.

a) Ground state dipole moment calculated using equation (10)

b) Excited state dipole moment calculated using equation (11)

c) Excited state dipole moment calculated from Lippert's equation (7)

d) Excited state dipole moment calculated from Bakshiev's equation (8)

e) Excited state dipole moment calculated from Kawski-Chamma-Viallet's equation (9)

f) Change in dipole moment calculated using equations (10) and (11).

g) Change in dipole moment calculated using E_T^N equation (12).

Theoretical studies using Gaussian 16 software

From the theoretical calculations using Gaussian-16 program for the ground state optimized geometries, the estimated ground state dipole moment and Time dependent DFT studies, excited state dipole moments of the 3-MPHC molecule is tabulated in table 4. The optimized molecular geometry of the corresponding molecule is shown in **Fig. 8**; the arrow mark indicates the direction of dipole moment. The HOMO, LUMO and total density matrix of the molecule 3-MPHC are as shown in **Fig. 9**, **Fig. 10** and **Fig. 11** respectively. From these figures, it is apparent that the HOMO of 3-MPHC molecule mainly localized on the electron donating aliphatic chain, whereas the LUMO level shifted to peripheral electron accepting moiety results to an obvious spatial separation of frontier orbital's. The polarity of a molecule depends on its electron distribution over the molecule. The absorption of a suitable electromagnetic radiation will cause transition of an electron from HOMO to LUMO orbital. Consequently, the movement of an electron from the low energy orbital to the higher energy orbital

results in a change of dipole moment with respect to the ground state dipole moment [19].
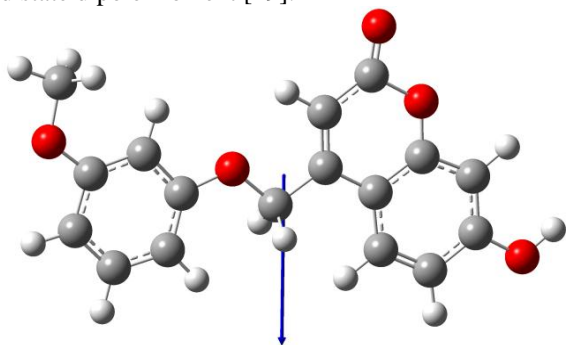

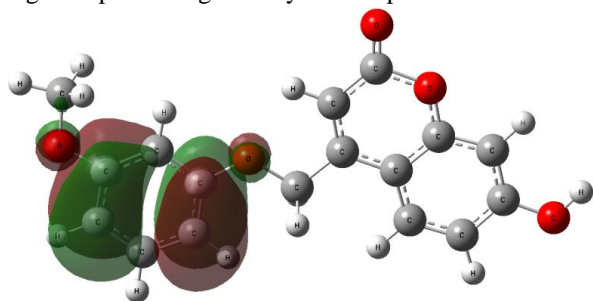Fig. 8. Optimized geometry with Dipole moment vector
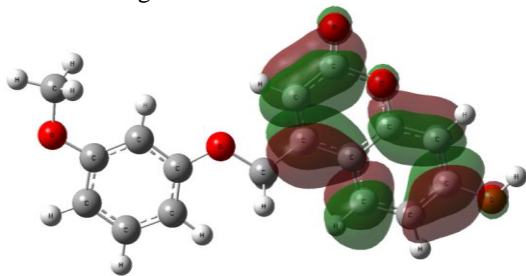

Fig. 9. HOMO structure
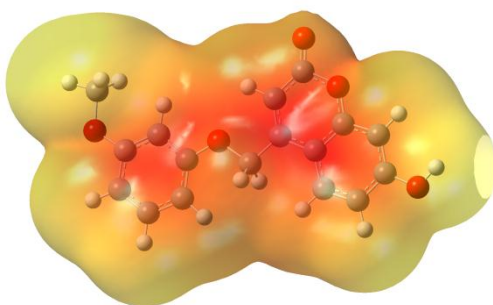

Fig. 10. LUMO structure

Fig. 11. Total Density matrix

Table 4. Photo physical parameters obtained from DFT studies of 3-MPHC

Coumarin	HOMO (eV)	LUMO (eV)	ΔE (eV)	μ_g (D)	μ_e (D)
3-MPHC	-0.33285	-0.04352	0.28933	3.443	8.791

V. CONCLUSION

We studied the effect of solvents on photophysical parameters for 3-MPHC molecule by experimentally and theoretically. We observed that 3-MPHC molecule undergo positive solvatochromism with increase in solvent polarity, indicates that the involvement of $\pi \rightarrow \pi^*$ transition. The dipole moment of 3-MPHC molecule is more in the first excited singlet state than in the ground state. This indicates the existence of a more relaxed excited state, due to intramolecular charge transfer. We compared the experimental values of dipole moments with theoretical values; it is found that the ground state dipole moment is same in both the case. Experimentally the solvent effect is more on 3-MPHC molecule rather than the theoretical value. From microscopic solvent polarity function we estimated the difference in dipole moment and are compared. This is the first report on extensive study of photophysical characteristics of biologically active 3-MPHC molecule which helps to understand the usage of this molecule in various fluorescence applications as well as in the field of medicine.

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