Ground and Excited State Dipole Moments of a Dye

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Abstract: *Curcumin, the yellow chemical compound found in two forms, keto form and enol form named (1E,6E)-1,7-Bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione (IUPAC), used in food additive, medicine etc. This molecule fluoresces weakly and poorly soluble in water. The absorption and fluorescence spectra of Curcumin dye has been recorded at room temperature (300 K) in solvents of different polarities. The ground state and excited state dipole moments were obtained experimentally from Lippert's, Bakshiev's and Kawski Chamma-Viallet's equations and theoretically from Gaussian 09 software. It was observed that dipole moments of excited state were higher than those of the ground state for the Curcumin dye.*
Keywords: *Excited and ground state dipole moments, Curcumin dye, Solvatochromic method.*

I. Introduction

Determination of the ground and excited state dipole moments of dye molecules is important, because the values of dipole moments provide information about the change in electronic distribution upon excitation. Knowledge of the excited state dipole moments of electronically excited molecules is quite useful in designing nonlinear materials [2], in confirmation of the nature of the excited states and also it reflects the charge distribution in the molecule and allows one to judge the site of attack by electrophilic and nucleophilic reagents in some photochemical reactions. However Curcumin dye molecule fluoresces weakly and we compared the experimental results with theoretical calculations. An attempt is made to estimate the ground and excited state dipole moments of this dye by both experimentally and theoretically. Curcumin dye absorbs more in visible region and it gives fluorescence with low quantum yield. Emission properties highly depend on the polarity of its environment [3].

II. Materials and Methods

Curcumin was obtained from Across Organics and used without further purification. To prepare the stock solution, curcumin was dissolved in spectroscopic grade dichloromethane (Acros Organics). A desired amount of the stock sample was taken in a vial and the solvent, dichloromethane, was evaporated by gentle heating. Final sample solution was prepared by adding required amount of desired solvent into the same vial. Cyclohexane, ethanol, hexane, dichloromethane (DCM), 1,2-dichlorobenzene (DCB), 1,4-dioxane, tetrahydrofuran (THF), methanol, Acetonitrile, n-butyronitrile (nBN), dimethylsulfoxide (DMSO) and N,N-dimethylformamide (DMF) were of spectroscopic grade and obtained from Acros Organics. The solvents were used without further purification [1].

Details of Molecule:
Chemical Name: (1*E*, 6*E*)-1,7-Bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione
Chemical formula: $C_{21}H_{20}O_6$ **Molar Mass**: 368.39 g·mol^{-1}
Colour: Bright Yellow-Orange Powder   **Melting Point**: 183 °C (361 °F; 456 K)

Structure: Enol form
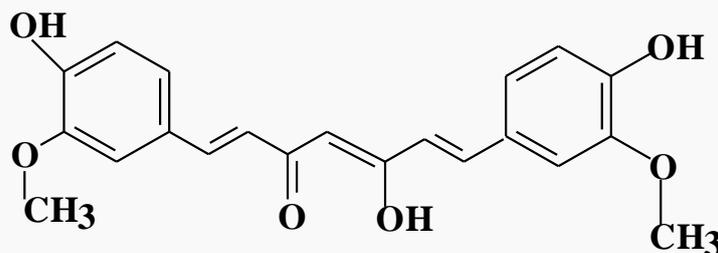
III. Theoretical and Experimental Details

The absorption spectra in various solvents were recorded at room temperature using a JASCO V-570 UV-VIS-NIR Spectrophotometer. Fluorescence measurements were done on a JOBIN YVON Horiba Fluorolog 3 spectrofluorometer. The excitation source was a 100 W Xenon lamp. The detector used was R-928 operating at a voltage of 950 V. The excitation and emission slits width were 5 nm. The synchronous fluorescence spectra were measured at $\Delta\lambda$ = 5 nm, 10 nm, 50 nm, 150 nm and 200 nm. $\Delta\lambda$ = 10 nm was chosen for analytical measurement because of its high sensitivity and narrower spectrum in the synchronous fluorescence wavelength range 250-700 nm. The spectral data were collected using Fluorescence software and data analysis was made using Origin Pro 8 software.

The independent equations used for the estimation of ground state and excited state dipole moment of the fluorescent Curcumin molecule are as follows.

Lippert's equation [5]

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

Bakshiev's equation [6]

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

Kawaski-Chamma-Viallet's equation [7]

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

The expressions for $F_1(\varepsilon, n)$ [Lippert's polarity function], $F_2(\varepsilon, n)$ [Bakshiev's polarity equation] and $F_3(\varepsilon, n)$ [Kawski-Chamma-Viallet's polarity equation] are given as

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

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

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

Where $\overline{\upsilon_a}$ and $\overline{\upsilon_f}$ are absorption and fluorescence maximum wave numbers in cm^{-1} respectively. The other symbol ε and **n** are dielectric constant and refractive index respectively. From equations (4), (5), (7) and (8) it follows that $\overline{\upsilon_a} - \overline{\upsilon_f}$ versus $F_1(\varepsilon, n)$ versus $F_2(\varepsilon, n)$ and $\frac{\overline{\upsilon_a} + \overline{\upsilon_f}}{2}$ versus $F_3(\varepsilon, n)$ should give linear graphs with slopes m_1, m_2 and m_3 respectively and are given as

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

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

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

Where μ_g and μ_e are the ground and excited state dipole moments of the fluorescent Curcumin molecule. The symbols 'h' and 'c' are Planck's constant and velocity of light in vacuum respectively; 'a' is the Onsager radius of the fluorescent Curcumin molecule, with the values evaluated by using atomic increment method [4]. If the ground state and excited states are parallel, the following expressions are obtained on the basis of Eq. (8) and (9).

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

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

$$\mu_e = \left[\frac{m_2 + m_3}{m_3 - m_2}\right]\mu_g \quad \text{for } (m_3 > m_2) \qquad (12)$$

IV. Results and discussion

The absorption maxima ($\overline{\upsilon_a}$) and fluorescent maxima ($\overline{\upsilon_f}$) wave numbers in cm^{-1} for Curcumin fluorescent organic molecule using UV-Visible spectrometer and Fluorometer respectively, from which solvatochromic shifts of Curcumin for different solvents were calculated and these values are tabulated in Table (1).

Lippert's, Bakhshiev's and Kawaski-Chamma-Viallet's polarity functions were calculated using equations [4,5and 6] are presented in Table (2) for Curcumin fluorescent organic molecule. The large magnitude of Stokes shift indicates that the excited-state geometry could be different from that of the ground state. The general observation is that there is an increase in the Stokes shift values with increasing solvent polarity which shows that there is an increase in the dipole moment on excitation. The graphs of ($\overline{\upsilon_a} - \overline{\upsilon_f}$) versus F_1 (ε, n), ($\overline{\upsilon_a} - \overline{\upsilon_f}$) versus F_2 (ε, n) and ½ ($\overline{\upsilon_a} + \overline{\upsilon_f}$) versus F_3 (ε, n) from which slopes m_1, m_2 and m_3 are obtained, respectively. The slopes and intercepts of the fitted lines are given in Table (3). The Optimised structure of Enol Curcumin using 6-311+G (d, p) basis set is shown in Fig (1) and the Homo and Lumo forms of the Curcumin shown in Fig (2). They are obtained from the theoretical calculation of ground and excited state dipole moments of the Curcumin dye using Gaussian 09 software.

V. Figures and Tables
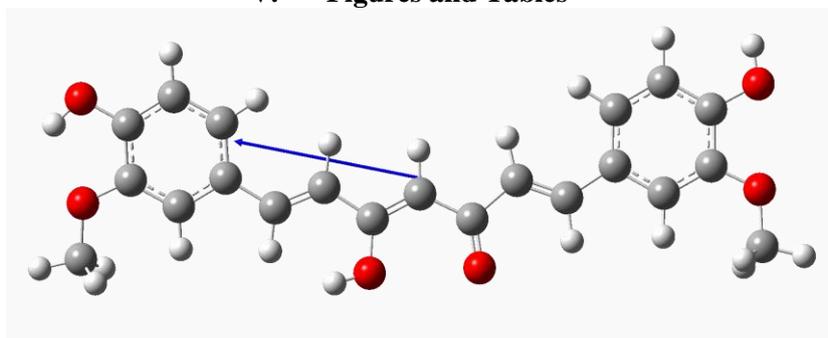
Fig. 1. Optimized structure of Enol Curcumin using 6-311+G (d, p) basis set.
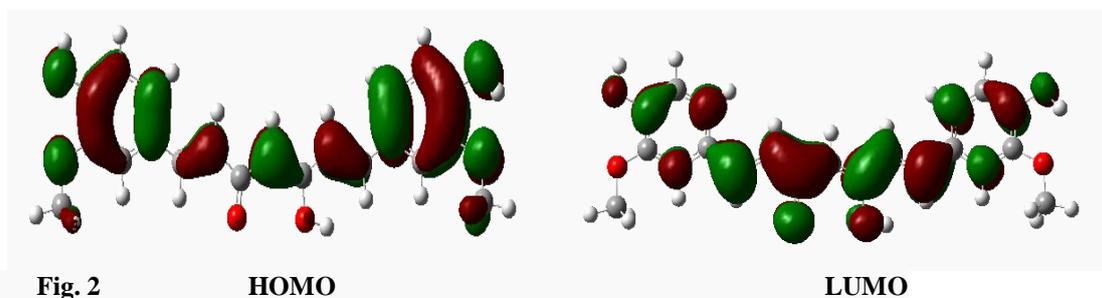
Fig. 2   **HOMO**   **LUMO**
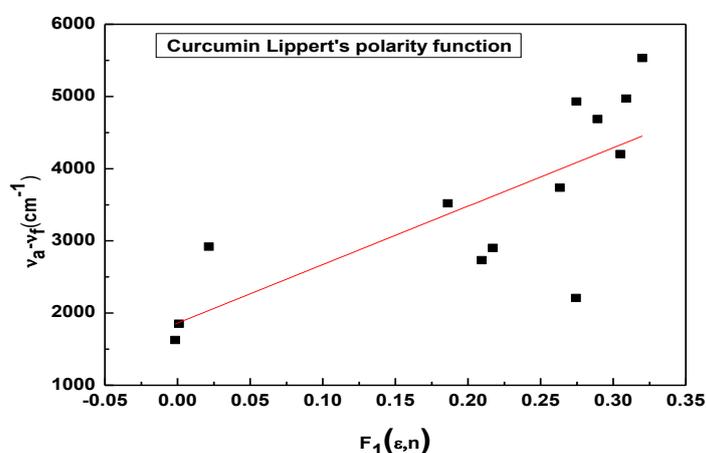
Fig.3. Plot for Stokes shift Vs Lippert's polarity function F_1
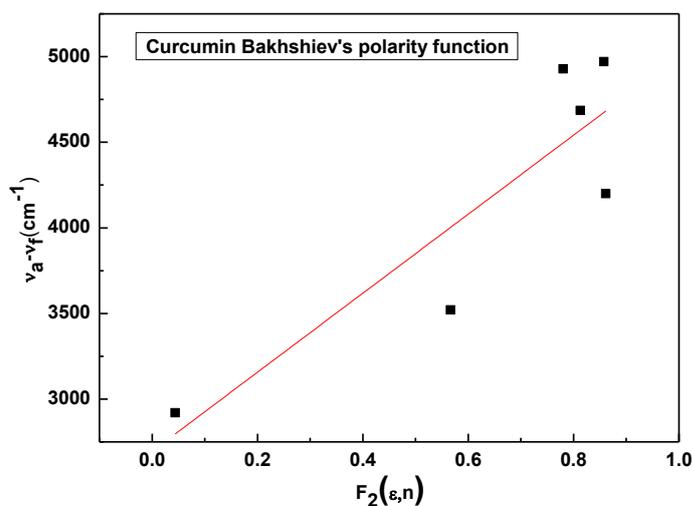
Fig. 4. Plot for Stokes shift Vs Bakhshiev's polarity function F_2
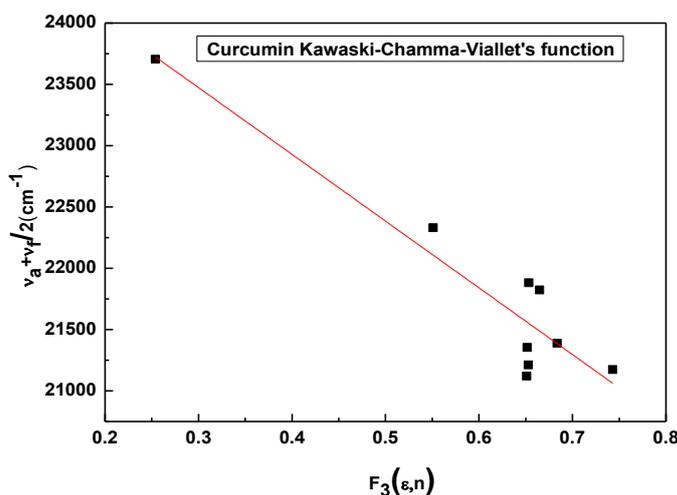
Fig. 5. Plot for arithmetic average of absorption and fluorescence wave numbers Vs Kawaski-Chamma-Viallet's polarity function F_3

Table 1. Absorption maxima and fluorescent maxima wavelengths and wave numbers in nm and cm^{-1} for Curcumin respectively

Solvent	λ_{abs} (nm)	λ_{em} (nm)	$\overline{\upsilon_a}$ (cm^{-1})	$\overline{\upsilon_f}$ (cm^{-1})	$\overline{\upsilon_a} - \overline{\upsilon_f}$ (cm^{-1})	$\frac{\overline{\upsilon_a} + \overline{\upsilon_f}}{2}$ (cm^{-1})
Cyclohexane	408	437	24509.8	22883.3	1626.5	23696.55
Hexane	406	437	24630.54	22779.04	1851.5	23704.79
DMF	425	469	23529.41	21321.96	2207.45	22425.69
THF	422	477	23696.68	20964.36	2732.32	22330.52
DCM	419	477	23866.35	20964.36	2901.99	22415.36
1,4-Dioxane	421	480	23752.97	20833.33	2919.64	22293.15
DCB	423	497	23640.66	20120.72	3519.94	21880.69
DMSO	434	518	23041.47	19305.02	3736.45	21173.25
Acetonitrile	418	507	23923.45	19723.87	4199.58	21823.66
Ethanol	422	526	23696.68	19011.41	4685.27	21354.05
n-Butyronitrile	424	536	23584.91	18656.72	4928.19	21120.82
Methanol	422	534	23696.68	18726.59	4970.09	21211.64
Water	414	537	24154.59	18621.97	5532.62	21388.28

Table 2. Lippert's, Bakhshiev's and Kawaski-Chamma-Viallet's polarity functions of Curcumin

Solvent	ε	n	$F_1(\varepsilon, n)$	$F_2(\varepsilon, n)$	$F_3(\varepsilon, n)$
Cyclohexane	2.02	1.426	-0.001583088	-0.003132161	0.287484
Hexane	1.89	1.372	0.001003179	0.001856707	0.254035
DMF	36.7	1.4305	0.274380237	0.835567608	0.709805
THF	7.58	1.4072	0.209571742	0.549077618	0.551135
DCM	8.93	1.4241	0.217136675	0.590333864	0.582962
1,4-Dioxane	2.22	1.422	0.021637831	0.043870944	0.308341
DCB	9.93	1.5514	0.186104005	0.566340292	0.653368
DMSO	46.7	1.4783	0.263401199	0.84073945	0.743693
Acetonitrile	36.64	1.344	0.304997265	0.861036623	0.664797
Ethanol	24.5	1.36	0.289203269	0.813100025	0.651602
n-Butyronitrile	20.4	1.38385	0.274668589	0.780141919	0.651109
Methanol	33.7	1.329	0.309014678	0.857477941	0.652885
Water	80.1	1.333	0.320091611	0.913632287	0.683667

Table 3. Statistical treatment of the spectral shift of Curcumin

Molecule	Slope	Intercept	Number of data
Lippert's polarity function			
Curcumin	8100.54	1860.58	13
Bakhshiev's polarity function			
Curcumin	2308.03	2695	06
Kawaski-Chamma-Viallet's polarity function			
Curcumin	5442.25	25105.67	09

Table 4. Ground state and excited state dipole moments.

Molecule		Radius 'a' (Å)	μ_g	μ_e
Curcumin	Experimental	4.2135	0.8946	2.20
	Theoretical (Gaussian Software)		4.854	5.7094

VI.   Conclusion

We studied the excited and ground state dipole moments of Curcumin dye molecule. The solvent effect on spectroscopic properties of Curcumin has been analyzed using different polarity parameters. The spectral properties of Curcumin dye are influenced more by polarizibility of solvents. It has been found that excited state dipole moment is greater than that of ground state dipole moment for the Curcumin dye molecule. This increase in dipole moment in the excited state of dye molecule is due to the more polar excited state than the ground state. The effect of solvents on the absorption and fluorescence characteristics of dye molecule has been studied. Excitation of a molecule by photon causes a redistribution of charges leading to conformational changes in the excited state. This can result in increase or decrease of dipole moment of the excited state as compared to ground state. And we noticed that if the radius of the Curcumin dye molecule changes for different forms then the ground state and excited state dipole moments are varying.

Acknowledgement

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