Study of dipole moments of some coumarin derivatives

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HIGHLIGHTS

- Dipole moments for 6HMC and 6MMC are estimated from theoretical and experimental method.
- The change in dipole moment estimated experimentally are much less than other family member of coumarin derivatives.
- Two different functional group leads to less change in dipole moment comparative to other coumarin derivatives.

ARTICLE INFO

ABSTRACT

In this paper we report the dipole moments of two coumarin derivatives viz 6-methoxy-4-methyl coumarin (6MMC) and 6-hydroxy-4-methyl coumarin (6HMC). Solvatochromic shift in absorption and emission spectra as a function of different solvent polarity parameter has been analyzed. With the help of this, ground and first excited state dipole moments of two coumarin derivatives have been calculated. Dipole moments are also estimated theoretically. The first excited state dipole moment of both the coumarin derivatives is higher than the ground state dipole moment indicating a substantial redistribution of π-electron density in the excited state.

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1. Introductions

Derivatives of coumarin have various application e.g. food constituents, antioxidants, stabilizers and immunomodulatory substances, as fluorescent markers for use in analyses, in stains, and in clinical use [1,2]. Coumarins possess anti-inflammatory, antiallergic, hepatoprotective, spasmolitic, antiviral, anticarcinogenic and anticoagulant activities [3]. They also constitute an important group of organic compounds that are used as additives to cosmetics, as optical brightening agents, and dispersed fluorescent and laser dyes [4–6]. Due to their inherent physicochemical and photophysical characteristics, such as reasonable relative ease of synthesis, coumarin derivatives have been extensively investigated for electronic and photonic applications such as charge-transfer complexes, laser dyes, fluorescence whiteners, solar energy collectors, and non-linear optical materials [7–10].

Studies on the photophysical properties of the coumarin and its derivative have been the subject of intense research in photochemistry for quite a long time [11]. In spite of significant amount of literature reports, many of the photophysical characteristics are still unresolved [12–19].

Further, excited-state properties of the molecules in condensed phase are quite sensitive towards intermolecular solute–media interactions and in turn affect the energy of the electronic states. As the interaction energy depends on the nature and the property (e.g. charge distribution or the dipole moment) of respective states, it will be different for ground and excited states and thus can give rise to spectral shift. The influence of the solvents on the absorption and emission spectra has been extensively used to determine the magnitude as well as direction of dipole moment in its first electronically excited singlet (S_1) state.

The excited state dipole moment is an important parameter of molecules, as it provides information about the change in elec-

tronic charge distribution upon **excitation.** A prior knowledge of the dipole moments in the excited state is often useful in the design of non-linear optical materials [20]. Solvatochromic technique is a popular way to determine the dipole moments in the ground and the excited states for short-lived states [21–24]. It also provides important information about electronic transitions and is quite useful for assignment of n → π* or π → π* transitions.

To determine the dipole moment in excited state by the solvatochromic method, several approaches have been used including those developed by Lippert [25,26], Bakhshiev [27], Kawski–Chamma–Viallet [28,29,32] and Suppan [30,31]. Other electro optic methods such as electronic polarization of fluorescence [32], electric dichroism [33], microwave conductivity [34] and Stark splitting [35] are generally considered to be very accurate but their use is limited because they are equipment sensitive and hence these methods have been confined to relatively simple molecules [36]. However, the experimental determination of dipole moment based on the analysis of the solvatochromism of absorption and fluorescence maxima is quite popular. Many workers have reported the ground state and excited state dipole moment using different solvatochromic methods [37–39].

The present work deals with the absorption and fluorescence characteristics of 6-hydroxy-4-methyl coumarin (6HMC) and 6-methoxy-4-methyl coumarin (6MMC) in solvents of non polar and aprotic polar character. To the best of our information there are no reports available in literature on the determination of ground and excited state dipole moments of these molecules. Moreover, we studied it in batches of nonpolar and aprotic polar solvents to rule out the interference of specific solvent effects. Significant increase in the dipole moment in the excited state indicates redistribution of charge in the excited state.

2. Experimental

2.1. Material

6MMC and 6HMC (obtained from Sigma Aldrich) of 99% purity were tested for their fluorescence purity and used as such. All the solvents used were either of spectroscopic grades or were checked for their fluorescence purity.

2.2. Instrumentation

Steady state absorption spectra, at room temperature, were recorded by dual beam JASCO V-550 spectrophotometer. The emission spectra were recorded by using JASCO FP-777 spectrofluorimeter and data were analyzed by related software. Transparent quartz cuvette was used for the absorption and emission measurements and frontal geometry was used in recording emission to avoid inner filter effect.

3. Methods

3.1. Theoretical calculations of ground-state dipole moments

Geometry optimization and the ground state dipole moments (μ_g) of 6MMC and 6HMC is estimated by Moller–Plesset perturbation theory (MP2) with the 6-31+G*(d,p). For comparison, similar optimization and estimation of the ground state dipole moment at DFT-B3LYP level with the similar basis set. All the computations are performed by using the Gaussian 03 program. The optimized structure of 6MMC and 6HMC are shown in Fig. 1.

3.2. Experimental calculations of excited state dipole moments

Generally following expression are used for the estimation of dipole moment [32,22]

$$\overline{v}_a - \overline{v}_f = m f(\varepsilon, n) + Constant \tag{1}$$

$$\overline{1/2}(\overline{v}_a + \overline{v}_f) = -M\Phi(\varepsilon, n) + Constant \tag{2}$$

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

And $$m = \frac{2(\mu_e - \mu_g)^2}{hca^3}, \tag{3}$$

$$M = -\frac{2(\mu_e^2 - \mu_g^2)}{hca^3} \tag{4}$$

μ_g and μ_e are the ground and excited state dipole moments of the solute molecule. The symbols h and c are Planck's constant and velocity of light in vacuum respectively, 'a' is the Onsager radius of the solute molecule.

And $$\Phi(\varepsilon, n) = 1/2 f(\varepsilon, n) + g(\varepsilon, n) \tag{5}$$

Where $$f(\varepsilon, \eta) = \frac{\left(\frac{\varepsilon-1}{2\varepsilon+1} - \frac{n^2+1}{2n^2+1}\right)}{\left[1 - \left(\frac{2\alpha}{a^3}\right)\frac{\varepsilon-1}{2\varepsilon+2}\left(\left(1 - \left(\frac{2\alpha}{a^3}\right)\left(\frac{n^2+1}{2n^2+1}\right)\right)\right)^2}\tag{6}$$

$$g(n) = \frac{((n^2-1)/(2n^2+1))(1 - (\alpha/a^3)((n^2-1)/(2n^2+1)))}{\left(\left(1 - \left(\frac{2\alpha}{a^3}\right)\left(\frac{n^2+1}{2n^2+1}\right)\right)\right)^2} \tag{7}$$

If the polarizability of the solute is neglected, i.e. $\alpha = 0$, then Eq. (6) reduces to Lippert–Mataga relation [26]

$$F_1(\varepsilon, n) = \left[\frac{\varepsilon-1}{2\varepsilon-2} - \frac{n^2-1}{2n^2+1}\right] \quad \text{[Lippert's polarity function]} \tag{8}$$

assumes that the fluorophore is a point dipole residing in the center of a spherical cavity with radius in a homogeneous and isotropic

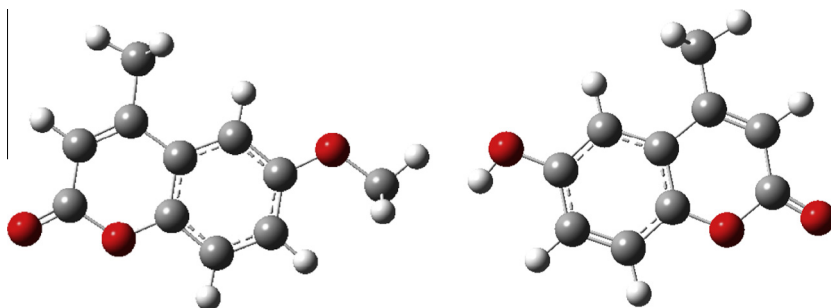

Fig. 1. Optimized molecular structure of 6MMC and 6HMC.