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Solvent effects on the absorption and fluorescence spectra of coumarins 6 and 7 molecules: Determination of ground and excited state dipole moment

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Abstract

Absorption and fluorescence emission spectra of coumarins 6 and 7 were recorded in solvents with different solvent parameters, viz., dielectric constant ε and refractive index n. The fluorescence lifetime of these dyes were measured in butanol at higher values of viscosity over temperature. Experimental ground and excited state dipole moments are determined by means of solvatochromic shift method and also the excited state dipole moments are determined in combination with ground state dipole moments. It was determined that dipole moments of the excited state were higher than those of the ground state in both the molecules.

Keywords: Solventeffect; Fluorescence lifetime; Dipole moments; Coumarin dyes; Solvatochromic shift

1. Introduction

The conjugated organic dye molecules are recognized to be important materials having novel electronic and photonic properties suitable for many technological applications [1]. Organic dye molecules are attractive laser gain due to its fortunate combination of properties, such as broad tunability, high quantum efficiency and broad spectral band width [2]. Coumarin dyes have found application in various areas of research and coumarins are well known in photobiology as photosensitizing agents in photodynamic actions. These molecules itself is also known show interesting photochemical behavior, particularly dimerization [3] in polar and non-polar solvents. The widespread occurrence of coumarin derivatives in nature and their variety of applications viz., as fluorescent indicator [4], sunburn preventives [5], estimation of enzymes [6], for the study in biological systems [7] and also other interesting areas [8].

Fluorescence and lasing properties of four substituted coumarin dyes studied by Dutt and Ghanty [9]. The photostability characteristics of various silylated coumarin dyes within SiO_2 xeogels and SiO_2 poly, polycream films and neat silylated coumarin dye films have been determined by sol–gel processing method [10]. Intermolecular electron (IE) which occurs faster than solvation dynamics is investigated for coumarins using the fluorescence up-conversion techniques, the ultrafast IE process was also observed from electron-donating solvents and excited coumarin dyes [11]. The dye coumarin 30 is reported to have potential application in different fields. The C30-doped thin film of organic semiconductor, 4,4-di(*N*-carbazole)biphenyl, has been used as a laser medium and has prospective applications and as optical communication, as optical memory materials and as optical sensors [12] .The effect of alkyl chain length and size of the headgroups of the surfactant on the solvation dynamics and rotational relaxation of coumarin 480 has been investigated using dynamic stokes shift of C-480 in different types of alkyltrimethlyammonium bromide micelles and mixed micelles [13].

The effect of solvents on the absorption and fluorescence characteristics of organic compounds has been a subject of several investigations [14]. Dipole moments of short-lived species are of considerable interest because, they provide information of electronic and geometrical structure of these transient. Knowledge of dipole moment of electronically excited species is often useful in the design of non-linear optical materials and elucidation of the nature of the excited state, as well as course of any

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photochemical transformation. Experimental data on excited states are useful in the parameterisation of semi-empirical quantum chemical procedures for these states.

Among the techniques available for the determination of excited state dipole moments, the most popular is that based on the Lippert–Mataga equation [15]. In this technique, absorption and fluorescence shift followed using the solvent polarity, described by dielectric constant ε and refractive index n. Other methods such as Stark splitting of rotational level [16,17] and microwave conductivity [18] are considered to be more accurate in determining excited state dipole moments. However, the experimental determination of this parameter based on the analysis of the solvatochromism of absorption and fluorescence maxima is quite popular. The ground and excited state dipole moments have determined using different methods by Dutt et al. [19], Koti et al. [20], Karunakaran et al. [21], Aaron et al. [22], Nadaf et al. [23], Ghazy et al. [24] and Parkanyi et al. [25]. In this paper we report different solvent parameters, dielectric constant ε, refractive index, fluorescence lifetime and spectral parameters, such as Stokes shift which is useful for determination of dipole moments. We have determined the ground and excited state dipole moments of two coumarin laser dyes by solvent perturbation method [26,27] based on absorption and fluorescence shift in various solvents.

2. Theory

The following equations, that is $\tilde{\nu}_a - \tilde{\nu}_f = m_1 f(\varepsilon, n) + \text{const}$ and $\tilde{\nu}_a + \tilde{\nu}_f = -m_2[f(\varepsilon, n) + 2g(n)] + \text{const}$, which are obtained based on quantum mechanical perturbation theory of absorption ($\tilde{\nu}_a$) and fluorescence ($\tilde{\nu}_f$) band shift in different solvent of varying permittivity (ε) and refractive index (n) [26–28].

Where $f(\varepsilon, n) = \frac{2n^2+1}{n^2+2}\left[\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right]$ is the solvent polarity parameter [29] and $g(n) = \frac{3}{2}\left[\frac{n^4-1}{(n^2+2)^2}\right]$ with

$$m_1 = \frac{2(\mu_e - \mu_g)^2}{hca^3} \tag{1}$$

and

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

h being Planck's constant and c, is the velocity of light in vacuum. μ_g and μ_e are the dipole moments in the ground and exacted states.

The parameters m_1 and m_2 can be determined from absorption and fluorescence band shifts ($\tilde{\nu}_a - \tilde{\nu}_f$ and $\tilde{\nu}_a + \tilde{\nu}_f$) of above equations. If the ground and excited states are parallel, the following expressions are obtained on the basis of Eqs. (1) and (2) [27–29].

$$\mu_g = \frac{m_2 - m_1}{2}\left[\frac{hca^3}{2m_1}\right]^{1/2} \tag{3}$$

$$\mu_e = \frac{m_1 + m_2}{2}\left[\frac{hca^3}{2m_1}\right]^{1/2} \tag{4}$$

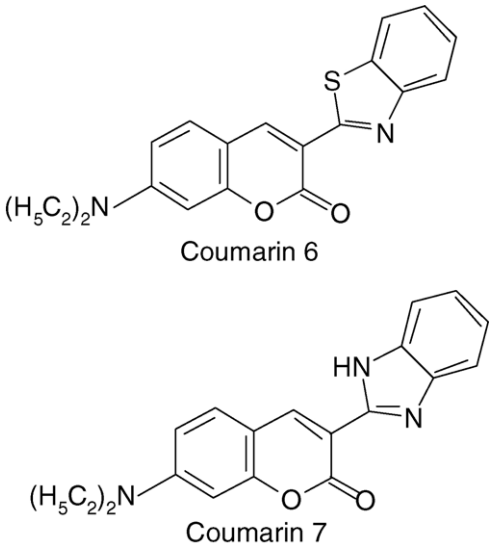

Fig. 1. Molecular structure of coumarins 6 and 7.

and

$$\mu_e = \frac{m_1 + m_2}{m_2 - m_1}\mu_g; \quad m_2 > m_1 \tag{5}$$

The Onsager radius "a" of the solute molecule can be evaluated by using atomic increment method [30] and $f(\varepsilon, n)$ the solvent polarity function is different from Lippert–Mataga function [15,31].

3. Experimental

Coumarins 6 (C6) and 7 (C7) were purchased from Aldrich Chemical Co., and were used without further purification. The molecular structures were given in Fig. 1. All the solvents viz., acetonitrile, methanol, ethanol, acetone, propanol, butanol, ethyl acetate, chloroform, ethylether, toluene, dioxane, cyclohexane and n-hexane, which were of spectroscopic grade. Electronic absorption spectra were recorded on a Hitachi Model 150-20 UV–vis spectrophotometer. Fluorescence spectra were taken by using a Hitachi Model F2000 spectrofluorometer at room temperature.

Fluorescence lifetime was measured using time-correlated single-photon counting technique [32] with the gated hydrogen discharge lamp as the excitation source (Edinbergh Instruments, Model EI-199) and the details have been given elsewhere [33]. The excitation wavelength was 420 nm and a cutoff filter GG455 was used to eliminate the excitation light while collecting the emission decay. In this apparatus, the desired sample temperature was maintained within $\pm 1^\circ$ with the help of temperature controller.

4. Results and discussion

Absorption and fluorescence emission spectra of C6 and C7 were recorded in solvents of different solvent parameters of dielectric constant ε and refractive index n. Figs. 2 and 3 show the typical absorption and fluorescence spectra of C6 and