Solvatochromatic shift of absorption and fluorescence spectra of 6-methoxyquinoline: Estimation of ground and excited state dipole moments

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ABSTRACT

Electronic absorption and fluorescence spectra of protonated 6-methoxyquinoline ($6MQ^+$) and neutral 6-methoxyquinoline (6MQ) have been recorded at room temperature in wide range of solvents of different polarities. The absorption maximum remains almost unchanged with the increase in solvent polarity, whereas a red shift in fluorescence emission maximum was observed. The ground-state dipole moment and the first excited singlet state dipole moment of $6MQ^+$ and 6MQ were obtained from Bakhshiev's and Bilot–Kawski's equations by means of solvatochromic shift method. High values of dipole moment are observed for excited state as compared to the corresponding ground state dipole moment values of $6MQ^+$ and 6MQ and this is attributed to the more polar excited states of $6MQ^+$ and 6MQ.

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1. Introduction

6-Methoxyquinoline (6MQ) is a parent molecule of spectroscopically well known molecules such as quinine sulfate, quinidine and chinchonine. It is well known that the fluorophore in 6MQ is a quinoline ring with the methoxy group at the sixth position and the vinyl group causes minor changes in the photophysics. The photophysics of 6MQ has been explored in detail in the past [1–5] in order to understand the excited state dynamics. The photophysical processes in 6MQ and related molecules have been explored for designing fluorescence optical sensors for halides [6]. The spectroscopy of 6MQ was earlier reported by Schulman et al. [7]. In case of 6MQ at pH<4 the emission of the mono-cation is observed and from pH 4 to 6, the fluorescence of the cation falls and of neutral 6MQ appears which rises to maximum at pH 12. From pH 6 to 10 the fluorescence of cation and neutral molecule remains constant. In acidic medium only protonated 6-MQ species are observed.

Optical absorption and fluorescence spectroscopic techniques reveal the solute–solvent interactions, which can be characterized from the wavelength, shape and the intensity of the spectrum. The effect of solvent on the absorption and fluorescence characteristics of organic compounds has been a subject of extensive research [8]. Spectral shifts result from the general effects of solvent polarity and due to the specific solute solvent interactions such as hydrogen bonding, acid base reactions or charge transfer interactions. Stoke's shift is the difference (in wavelength or frequency units) between positions of the band maxima of the absorption and emission spectra. The solvent reorganization around the excited state of the solute molecule gives rise to the Stoke's shift. The spectral shift depends on the excited molecule and the nature of the solvent, much larger shifts are observed in polar solvents [9,10]. The increase or decrease of the dipole moment of the excited state to that of the ground state is caused by the redistribution of charges leading to conformational changes in the excited state by photon excitation. The dipole moment of an electronically excited state of a molecule is an important property that provides information on the electronic and geometrical structures of the molecule in short-lived state. Knowledge of the excited-state dipole moment of electronically excited molecules is quite useful in designing nonlinear optical materials [11].

A number of techniques such as electronic polarization of fluorescence, electric–dichroism, microwave conductivity and stark splitting [12,13] are available for determination of excited-state dipole moment, but their use is limited because they are considered equipment sensitive and studies have been related to very simple molecules. Extensive work on experimental and theoretical ground (μ_g) and excited state (μ_e) dipole moments using different techniques in variety of organic fluorescent compounds such as coumarins [8,14], indoles [15,16], purines [17,18], exalite dyes [19,20], quinazolines [21], nile red dye, prodan, laurdan, badan, acrylodan [22–27], thiadiazole [28], bezimidazolone [29], phloroglucinol [30], chalcons [31], 546 laser dye [32] etc. have been reported in the past using different methods.

The solvatochromic method is based on the shift of absorption and fluorescence maxima in different solvents of varying polarity. The solvent dependence of absorption and fluorescence maxima is used to determine the excited-state dipole moments of different molecules. The solvatochromic effect or solvatochromic shift refers to a strong dependence of absorption and emission spectra with the solvent polarity. Since polarities of the ground and excited states of a chromophore are different, a change in the solvent polarity will lead to differential stabilization of the ground and excited states, and thus, a change in the energy gap between these electronic states. Variations in the position, intensity and shape of the absorption spectra can be direct measures of the specific interactions between the solute and solvent molecules. Theoretical description of solvatochromism is based on the Onsager description of non specific electrostatic solute–solvent interactions and the solvent is described as a dielectric continuum hosting solute molecules into Onsager type cavities. The surrounding solvent molecules get polarized due to the electric dipole moment of the solute molecule; as a result, the solute itself experiences an electric field, the reaction field, which is proportional to the dipole moment of the solute.

In our recent papers [33,34] we have reported dipole moments of quinine sulfate dication and quinine sulfate monocation and it was observed that both of these molecules undergo a large change in excited state dipole moment compared to the ground state values. It has been reported that 6MQ undergoes a large change in dipole moment [4] but to the best of our knowledge the ground and excited state dipole moments are not known for 6MQ and 6MQ$^+$. In this paper we have studied ground and excited state dipole moments of 6MQ$^+$ and 6MQ using solvatochromic shift method. We observed a large change in dipole moment of 6MQ$^+$ and 6MQ in the excited state compared to the ground state.

2. Experimental

6-Methoxyquinoline obtained from Aldrich was used as such. All the samples of protonated 6-Methoxyquinoline (6MQ$^+$) were prepared by dissolving the appropriate concentration of 6MQ in 1 N H$_2$SO$_4$ in different solvents and all the samples of neutral 6-Methoxyquinoline (6MQ) were prepared by dissolving the appropriate concentration of 6MQ in different solvents without the presence of acid (H$_2$SO$_4$). The molecular structure of 6MQ$^+$ and 6MQ is shown in Fig. 1(a) and (b) respectively. In dilute sulphuric acid solutions (1 N H$_2$SO$_4$), 6-Methoxyquinoline (6MQ$^+$) is present as a monocationic species. All the solvents were either of spectroscopic grades or were checked for their purity. Absorption spectra were taken with the help of dual beam JASCO V-570 UV/Vis/ NIR spectrophotometer and fluorescence spectra were recorded with the help of Shimadzu, RF-5301PC Spectrofluorometer. The data were analyzed using related software. The spectral shifts obtained with different sets of samples were identical in most of the cases and values were within ± 1.0 nm. Data were analyzed and were fitted to a straight line using origin 6.1 Software. The concentration of protonic 6-methoxyquinoline (6MQ$^+$) and non protonated 6-methoxyquinoline (6MQ) in all the solutions prepared in different solvents was 8×10^{-6} M. For all spectral measurements, the samples were taken in 1 cm × 1 cm quartz cells. The solvatochromic data were analyzed using Origin 6.1 program.

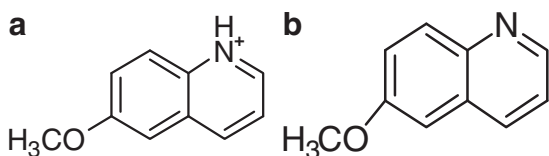**Fig. 1.** (a) Molecular structure of protonated 6-methoxyquinoline (6MQ$^+$). (b) Molecular structure of neutral 6-methoxyquinoline (6MQ).

3. Method

3.1. Ground state and excited state dipole moment

Most theories of solvent effect on the location of absorption and fluorescence spectra, in spite of different assumptions, lead to similar expressions for the Stokes shift. We have used the following two formulae to determine the excited singlet state dipole moment (μ_e) and ground state dipole moment (μ_g) by the solvatochromic method. These equations have been obtained by employing the simplest quantum-mechanical second order perturbation theory and taking into account the Onsager reaction field for a polarisable dipole.

Bakhshiev's formula [35]

$$\overline{v_a} - \overline{v_f} = S_1 F_1(\varepsilon, \eta) + const. \tag{1}$$

Here $\overline{v_a}$ and $\overline{v_f}$ are the wavenumbers of the absorption and emission maxima respectively.

F$_1$ as the bulk solvent polarity function and S$_1$ as the slope are defined as follows:

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

and

$$S_1 = \frac{2\left(\mu_e - \mu_g\right)^2}{hca_0^3}. \tag{3}$$

Here h is the Planck's constant, c is the velocity of light in vacuum, μ_g is the dipole moment in the excited singlet state, a$_0$ is the Onsager cavity radius, ε is the solvent dielectric constant and η is the solvent refractive index.

Bilot–Kawski formula [36,37]

$$\frac{\overline{v_a} + \overline{v_f}}{2} = -S_2 F_2(\varepsilon, \eta) + const. \tag{4}$$

Here the meaning of symbols is same as given above except for F$_2$ and S$_2$ which are defined as follows

$$F_2(\varepsilon, \eta) = \frac{2\eta^2 + 1}{2(\eta^2 + 2)}\left[\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{\eta^2 - 1}{\eta^2 + 2}\right] + \frac{3}{2}\left[\frac{\eta^4 - 1}{(\eta^2 + 2)^2}\right] \tag{5}$$

and

$$S_2 = \frac{2\left(\mu_e^2 - \mu_g^2\right)}{hca_0^3}. \tag{6}$$

The parameters S$_1$ and S$_2$ are the slopes which can be calculated from Eqs. (1) and (4) respectively. Assuming that the ground and excited states are parallel, the following expressions are obtained using Eqs. (3) and (6) [36]

$$\mu_g = \frac{S_2 - S_1}{2}\left[\frac{hca_0^3}{2S_1}\right]^{1/2} \tag{7}$$

$$\mu_e = \frac{S_1 + S_2}{2}\left[\frac{hca_0^3}{2S_1}\right]^{1/2} \tag{8}$$

and

$$\mu_e = \frac{|S_1 + S_2|}{|S_2 - S_1|}\mu_g. \tag{9}$$