Solvatochromic shift and estimation of dipole moment of quinine sulfate

Sunita Joshi, Debi D. Pant *

Department of Physics, Birla Institute of Technology and Science, Pilani 333031, Rajasthan, India

ABSTRACT

The absorption and fluorescence spectra of quinine sulfate (QS) have been recorded at room temperature in wide range of solvents of different polarities. The ground-state dipole moment of QS was obtained from quantum mechanical calculations and the excited state dipole moment of QS was estimated from Bakhshiev's and Bilot–Kawski's equations by means of solvatochromic shift method. Higher value of dipole moment has been observed for excited state as compared to the corresponding ground state value and this is attributed to the more polar excited state of QS.

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1. Introduction

The effect of solvent on the absorption and fluorescence characteristics of organic compounds has been a subject of extensive research [1]. 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. The dipole moment of an electronically excited state of a molecule is important property that provides information on the electronic and geometrical structure 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 [2], elucidating the nature of the excited states and in determining the course of photochemical transformation. For a chromophore, the tunability range of the emission energy as a function of polarity of the medium is also determined by excited state dipole moment [3].

A number of techniques e.g. electronic polarization of fluorescence, electric-dichroism, microwave conductivity and stark splitting [4,5] 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. 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. Several workers have made extensive experimental and theoretical studies on ground (μ_g) and excited state (μ_e) dipole moments using different

techniques in variety of organic fluorescent compounds like coumarins [1,6], indoles [7,8], purines [9,10], exalite dyes [11,12], quinazolines [13] etc.

Quinine sulfate has been the subject of extensive research in the past because of its medical applications as well as its use as fluorescence quantum yield and lifetime standard [14–18]. The photophysical processes in QS and related molecules have been explored for designing fluorescence optical sensors for halides [19,20]. However, to the best of our knowledge there are no reports available in literature on ground and excited-state dipole moments of QS molecule. In this paper we have calculated the ground state dipole moment of QS from the quantum chemical calculations and the excited state dipole moment is estimated by the solvatochromic shift method using Bakhshiev [21] and Bilot–Kawski [22,23] correlations.

2. Experimental

Quinine sulfate (Fig. 1) was obtained from S. D. Fine, Mumbai and was crystallized several times before using. All the solvents used were of HPLC grade or AR. 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 ground state dipole moment for molecule was calculated by quantum chemical calculations using software Gaussian 03 program. The concentration of quinine sulfate in all the solutions prepared in different solvents was 5×10^{-5} M.

* Corresponding author. Tel.: +91 1596515513.
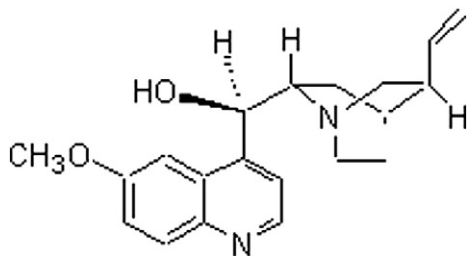E-mail address: ddpant@bits-pilani.ac.in (D.D. Pant).

Fig. 1. Molecular structure of quinine sulfate (QS).

3. Method

3.1. Theoretical calculations of ground state dipole moment

The ground state dipole moment (μ_g) of QS was calculated by quantum chemical calculations. Computations were carried out using the Gaussian 03 program. The basis sets at level of theory HF/6-31G were used for calculations and corresponding optimized molecular geometry is shown in Fig. 2.

3.2. Excited state dipole moment

The following two formulae were used to determine the excited singlet state dipole moment (μ_e) by the solvatochromic method.
Bakhshiev's formula [21]:

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

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

F_1 the bulk solvent polarity function and S_1 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 denotes 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
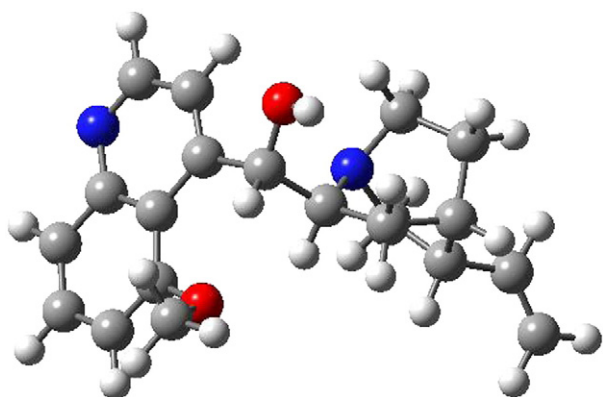
Onsager cavity radius, ε is the solvent dielectric constant and η is the solvent refractive index.

Bilot–Kawski formula [22,23]:

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

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 the ground and excited states are parallel, the following expressions are obtained using Eqs. (3) and (6) [22]:

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

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

and

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

4. Results and discussion

The steady state absorption and fluorescence measurements were made in different solvents at room temperature. The absorption spectrum for QS in water and fluorescence spectrum in four different solvents are shown in Fig. 3. The absorption spectrum shows two bands L_a and L_b at 280 and 330 nm, respectively in all the solvents studied. These two bands correspond to low-lying closely spaced π, π^* states of the main chromophore. The emission spectrum has only a structure-
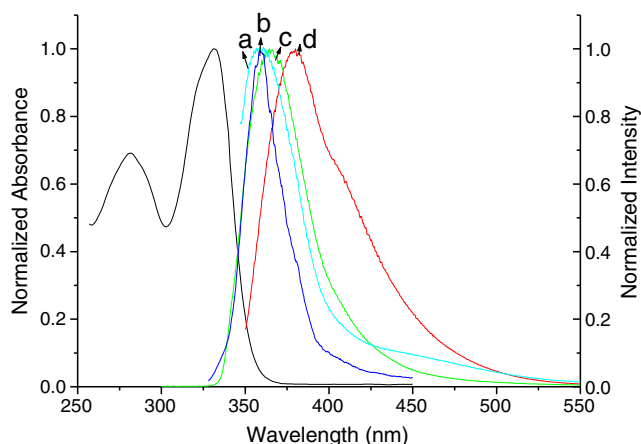

Fig. 2. Optimized molecular geometry of QS using theory HF/6-31G.

Fig. 3. Normalized absorption spectrum of QS in water and fluorescence spectra of QS in (a) benzene (b) cyclohexane, (c) dichloromethane and (d) water.