

Solvatochromic Shift and Estimation of Dipole Moment of Quinine Sulphate Dication

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II. EXPERIMENTAL

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

Keywords—Dipole moment, Quinine sulphate dication, Solvatochromic shift

I. 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 determined by excited state dipole moment [3]. tunability range of the emission energy as a function of polarity of the medium is also determined by excited state dipole moment. Quinine sulphate 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 explored for designing fluorescence optical sensors for halides [19,20]. However, to the best of our knowledge there is no report available in literature on ground and excited-state dipole moments of QSD molecule. In this paper we have calculated the ground by the solvatochromic shift method using Bakhshiev [21] and Kawski-Chamma-Viallet[22,23] correlations.

Quinine sulphate (Fig.1) was obtained from sd 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 sulphate in all the solutions prepared in different solvents was 5×10^{-5} M.

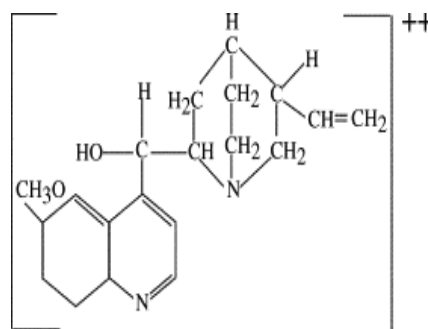


Fig. 1 Molecular structure of quinine sulphate dication(QSD)

III. RESULTS AND DISCUSSION

A. Theoretical calculations of ground state dipole moment

The ground state dipole moment (μ_g) of QSD was calculated by quantum chemical calculations. Computations were carried out using the Gaussian 03 program. The basis sets at level of theory B3LYP was used for calculations and corresponding optimized molecular geometry is shown in Fig. 2.

B. 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]

$$\bar{\nu}_a - \bar{\nu}_f = S_1 F_1(\epsilon, \eta) + \text{const} \quad (1)$$

Here $\bar{\nu}_a$ and $\bar{\nu}_f$ are the wavenumbers of the absorption and emission maxima respectively.

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F_1 the bulk solvent polarity function and S_1 the slope are defined as follows:

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

$$S_1 = \frac{2(\mu_e - \mu_g)^2}{hca_0^3} \quad (3)$$

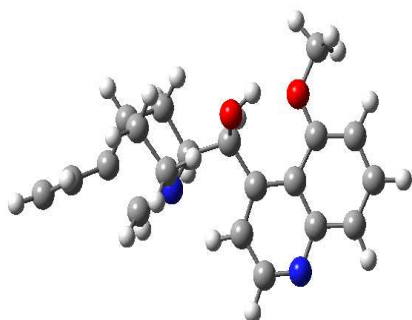


Fig. 2 Optimized molecular geometry of QSD using theory B3LYP

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.

Kawski – Chamma- Viallet's formula [22,23]

$$\frac{\bar{\nu}_a + \bar{\nu}_f}{2} = -S_2 F_2(\epsilon, \eta) + \text{const} . \quad (4)$$

here the meaning of symbols is same as given above except for F_2 and S_2 which are defined as follows

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

and

$$S_2 = \frac{2(\mu_e^2 - \mu_g^2)}{hca_0^3} \quad (6)$$

The parameters S_1 and S_2 are the slopes which can be calculated from equations (1) and (4) respectively. Assuming the ground and excited states are parallel, the following expressions are obtained using equations (3) and (6) [22].

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

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

and

$$\mu_e = \frac{|S_1 + S_2|}{|S_2 - S_1|} \mu_g \quad (9)$$

The steady state absorption and fluorescence measurements were made in different solvents at room temperature. The absorption spectrum in water and fluorescence spectrum in three different solvents are shown in Fig.3.

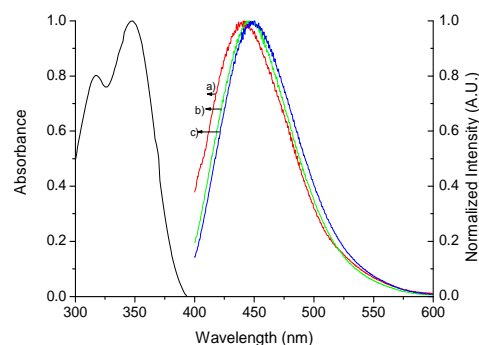


Fig. 3 Normalized absorption spectra and fluorescence spectra of quinine sulphate dication in (a) cyclohexane, (b) acetone and (c) methanol

Absorption spectrum shows two bands L_a and L_b at 317 and 346 nm, respectively in all the solvents studied. These two bands correspond to low-lying closely spaced π , π^* states of the main chromophore. The variation of wavenumber of absorption and emission maxima with the solvent polarity function, whereas the emission maxima shifts towards lower frequencies with the increase in polarity of the solvent. The fluorescence spectrum is more red shifted in the case of polar protic solvents as compared to aprotic and non polar solvents. This trend in the fluorescence spectra is a bathochromic shift with increase in polarity [24] and is an indication of π , π^* transition. Solvent polarity functions $F_1(\epsilon, \eta)$ and $F_2(\epsilon, \eta)$ have been calculated in order to ascertain the ground and excited state dipole moments of the molecule and are given in

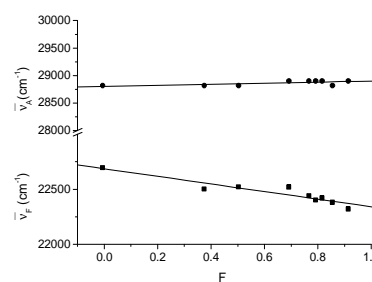


Fig. 4 Variation of Absorption and emission maxima of QSD with solvent polarity function

TABLE I
DIFFERENT SOLVENT PARAMETERS AND SPECTRAL DATA OF QSD IN DIFFERENT SOLVENTS

Sol	ϵ	η	F_1	F_2	$\overline{\nu_a - \nu_f}$ (cm ⁻¹)	$\frac{\overline{\nu_a + \nu_f}}{2}$ (cm ⁻¹)
Water	78.3	1.33	0.9134	0.6815	6580.3	25611.6
Metoh	32.6	1.33	0.854	0.6518	6437	25599.9
Ethanol	24.3	1.35	0.8152	0.6459	6480.2	25661.6
Aceton	20.7	1.357	0.791	0.6386	6460	25671.7
Isop	18.3	1.375	0.766	0.6381	6389	25707
Hexa	13.3	1.4178	0.69108	0.62916	6295.9	25670.5
Hept	6.7	1.423	0.50252	0.53833	6500.3	25651.6
DEE	4.3	1.352	0.374	0.4267	6316.1	25660.5
Cycloh	2.0	1.424	-0.0065	0.28448	6122.1	25757.4

Metoh = methanol, Aceton= acetone, Isop = isopropanol; Hexa = hexanol, Hept = heptanol, DEE= diethylether, cycloh = cyclohexane.

Table I The spectral shifts $\overline{\nu_a} - \overline{\nu_f}$ versus the solvent polarity function $F_1(\epsilon, n_r)$ and $\frac{\overline{\nu_a} + \overline{\nu_f}}{2}$ versus $F_2(\epsilon, n_r)$ are shown in Figs. 5 and 6, respectively. The linear behaviour of Stokes shift versus solvent polarity function indicates general solvent effects as a function of dielectric constant and refractive index. Using software origin 6.1 the data fitted to a straight line. Slopes were found to be $S_1 = 442.35 \text{ cm}^{-1}$ and $S_2 = -251.64 \text{ cm}^{-1}$ from Figs. 5 and 6, respectively. Using software Gaussian 03 we calculated ground state dipole moment for probe QS using level of theory B3LYP. The ground -state dipole moment obtained was 3.2 D.

From Equation (9) we have evaluated the value of μ_e using the above value of μ_g without a need to know the Onsager radius [10,25,26] of the quinine sulphate dication.

The value of μ_e thus obtained is 11.65D. The change in dipole moment from excited state to ground- state is 8.54D. All the data related to dipole moment are summarised in Table 2. Clearly the dipole moment in excited state is significantly larger than the dipole moment in the ground state for the probe studied. The dipole moments of a molecule in the ground and excited states are different due to changes in electron densities in these states.

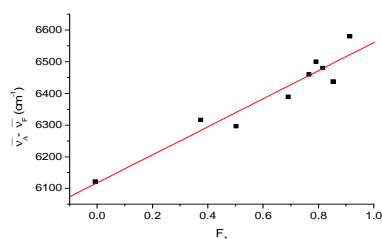


Fig. 5 Plot for stokes shift versus solvent polarity function F_1

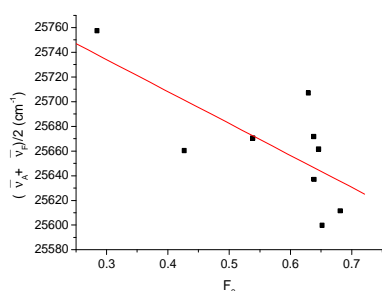


Fig. 6 Plot for arithmetic average of absorption and fluorescence wavenumbers versus solvent polarity function F_2

IV. CONCLUSION

We have calculated ground state and excited state dipole moments of QSD. The μ_g value calculated from quantum chemical calculations is 3.2D and the estimated excited state dipole moment from the solvatochromic shift method is 11.65D. This large increase in dipole moment in the excited state of QSD is due to the more polar excited state than the

ground state. The present study permits one to estimate the value of μ_e from the pre knowledge of μ_g , without the need of knowing the Onsager radius of the molecule, which is often chosen rather arbitrarily and impairs the popularity of solvatochromic method.

TABLE II
DIPOLE MOMENT OF QSD IN GROUND AND EXCITED STATES

Theory	$S_1(\text{cm}^{-1})$	$S_2(\text{cm}^{-1})$	$\mu_g(\text{D})$	$\mu_e(\text{D})$	$\Delta\mu(\text{D})$	μ_e/μ_g
B3LYP	442.35	251.64	3.2	11.65	8.45	3.64

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