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Study Of Dipole Moments Of Some Fluorescent Molecules

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ABSTRACT

This paper describes the characterization and modulation of photophysical properties of fluorescent molecules in micellar systems. In the introduction part of the thesis, detailed information about different photophysical and photochemical processes of molecules and the structure of micelles is provided. The scope of the present study is briefed by stating the research gap and the work done in this thesis. The materials, methods and instruments used in the present study are also explained.This study is of interest because knowledge of dipole moments is useful in extracting parameters like polarizability in non-linear optical materials, understanding nature of the emitting state and determining the tunability of the emission energy as a function of the medium. There are various techniques available for estimation of ground state and excited state dipole moments of organic molecules. Here, in this study, the solvatochromic method and quantum chemical calculations are employed for estimating the ground and excited state dipole moments of different Quinine Sulfate (QS) and Quinidine (QD) species. These molecules are very sensitive to surrounding solvent, we have estimated dipole moments of these molecules in different forms using solvatochromic shift method and found higher dipole moment in the excited state compared to the ground state.

Keywords: photophysical, solvatochromic an misceller systems.

INTRODUCTION

In recent years, due to fast progress in the field of photophysics and photochemistry, studies of electric dipole moments have gained greater importance. 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 of 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[1], 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.

A number of techniques e.g. electronic polarization of fluorescence, electric- dichroism, microwave conductivity and stark splitting 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 effect of solvent on the absorption and fluorescence characteristics of organic compounds has been a subject of extensive research[7]. Optical absorption and fluorescence spectroscopic techniques reveal the solute-solvent interactions, which can be characterized from the frequency, shape and the intensity of the spectrum. Spectral shifts result from the general effects of solvents polarity and due to the specific solute solvent interactions, such as hydrogen bonding, acid base reactions or charge transfer interactions.

The solvent reorganization around the newly formed excited state of a solute molecule gives rise to the well-known Stokes shift.

Theoretical description of solvatochromism is based on the Onsager description of nonspecific 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. Several workers have made extensive experimental and theoretical studies on ground state dipole moment (μ_g) and excited state dipole moment (μ_e) using different techniques in variety of organic fluorescent compounds like coumarins, indoles, purines, exalted dyes, quinazolines[15] etc. Rabahi et. al. recently estimated ground and excited-state dipole moments of coumarin and iminocoumarins from solvatochromic shift and theoretical methods and found higher dipole moment in excited-state than ground- state. Ground and excited state dipole moments of some α-hydroxy phenyl hydrazone derivatives, Sudan dyes, dipolar laser dyes: coumarin 478 (C478), coumarin 519 (C519) and coumarin 523(C523) by using different solvatochromic shift methods were also estimated recently. Lalithamba et. al. studied, the absorption and fluorescence emission spectra of (9H-fluoren-9-yl) methyl 1-hydroxypropan-2-ylcarbamate [Fmoc-L-alaninol] in solvents of different polarities. By using solvatochromic shift method, experimental ground and excited states dipole moments were calculated. They observed higher dipole moment of excited state compared to ground state. The fluorescence emission peak undergoes a hypsochromic shift with increase in the polarity of the solvent, through which they confirm $n\rightarrow\pi^*$ transition. Sıdır et. al. estimated ground and excited state dipole moments of Oil Red O (ORO) by using solvatochromic shift methods. Fluorescence spectra show positive solvatochromism whereas absorption spectra do not indicate sensitive behavior to solvent polarity. Excited state dipole moment is found as higher than those of ground state for all of the used methods and it is attributed to more polar excited state of ORO.

Quinine Sulfate (QS) 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 The photophysical processes in QS and related molecules have been explored for designing fluorescence optical sensors for halides. On changing pH, various species derived from QS and Quinidine (QD) are: dication (~pH 2), monocation (~pH 7) and neutral molecule (~pH 12).

This paper discusses the estimation of the ground and excited state dipole moments of Quinine Sulfate monocation (QS^+) and Quinine Sulfate dication (QS^{2+}) using solvatochromic shift method (where values of ground state dipole moment were theoretically calculated). We observed a large change in dipole moment of QS^+ and QS^{2+} in the excited state compared to the ground state. Quinidine monocation (QD^+) and Quinidine dication (QD^{2+}) are diastereomers to QS^+ and QS^{2+} respectively.[30] Since diastereomers are non-equivalent in their physical and chemical properties, the dynamic properties of the diastereomers in different environments become essential for understanding the effects of the conformational change on their chemical reactivities.

EXPERIMENTAL

Quinine Sulfate and Quinidine were procured from S.D. Fine Mumbai and Sigma Aldrich, respectively, and 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 related software. The ground state dipole moment for molecule was calculated by quantum chemical calculations using software Gaussian 03 program. The concentration of Quinine Sulfate and Quinidine in all the solutions prepared in different solvents was 5 × 10 M and 10 M respectively. Density of the Quinidine was estimated by ACD/Chemsketch software. For all spectral measurements, the samples were taken in 1 cm × 1 cm quartz cells.

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SOLVATOCHROMIC SHIFT AND ESTIMATION OF DIPOLE MOMENT OF QUININE SULFATE MONOCATION

The absorption and fluorescence spectra of Quinine Sulfate monocation (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 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.

RESULTS AND DISCUSSION

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/ б-31G were used for calculations and corresponding optimized molecular geometry is shown in Figure 1.1.

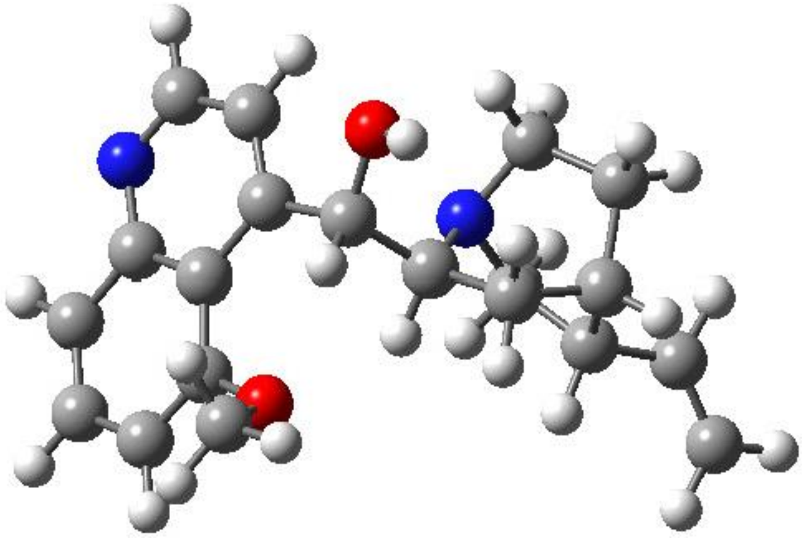


Figure 1.1 Optimized molecular geometries of QS^+ using theory HF/б-31G

STEADY STATE MEASUREMENTS

The steady state absorption and fluorescence measurements of QS^+ (molecular structure shown in Figure 3.2) were made in different solvents at room temperature. The absorption spectrum in water and fluorescence spectrum in four different solvents are shown in Figure 3.3. The absorption spectrum shows two bands L_a and L_b at 330 and 280 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-less broad band with maxima around 357 nm in benzene and 390 nm in water on excitation at 340 nm. The variation of wavenumber of absorption and emission maxima with the solvent polarity function, F_1 (ε, n) are shown in Figure 3.4. The absorption maxima for different solvents studied remains constant with polarity function, whereas the emission maxima shift towards lower frequencies with the increase in polarity of the solvent. The fluorescence spectrum is more red shifted in the case of water as compared to aprotic and nonpolar solvents. This trend in the fluorescence spectra is a bathochromic shift with increase in polarity[31] and is an indication of π , π * transition. Solvent polarity functions F_1 (ε, n) and F_2 (ε, n) have been calculated in order to ascertain the ground and excited state dipole moments of the molecule and are given in Table 1.1.

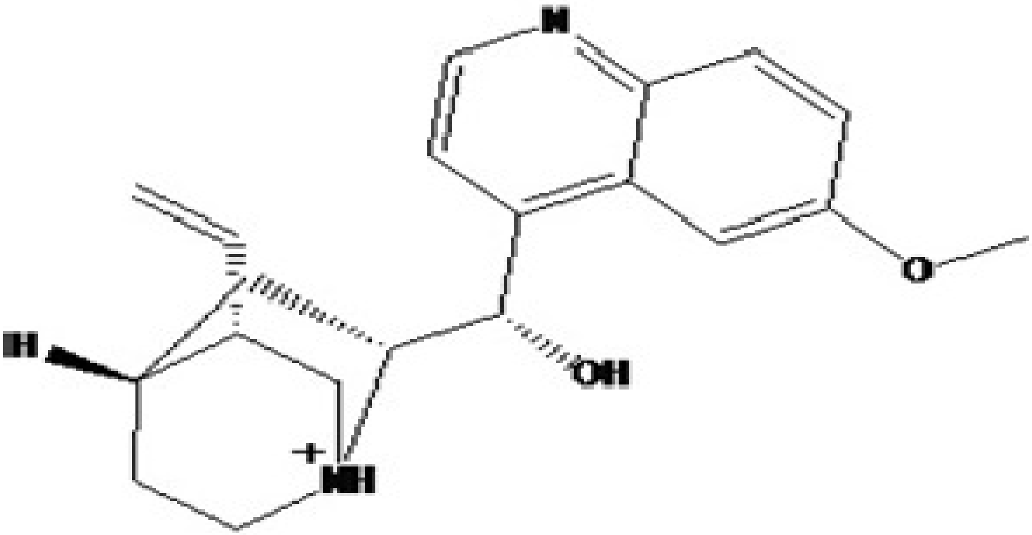


Figure **1.2 Molecular structure of Quinine Sulfate monocation (QS$^+$)**

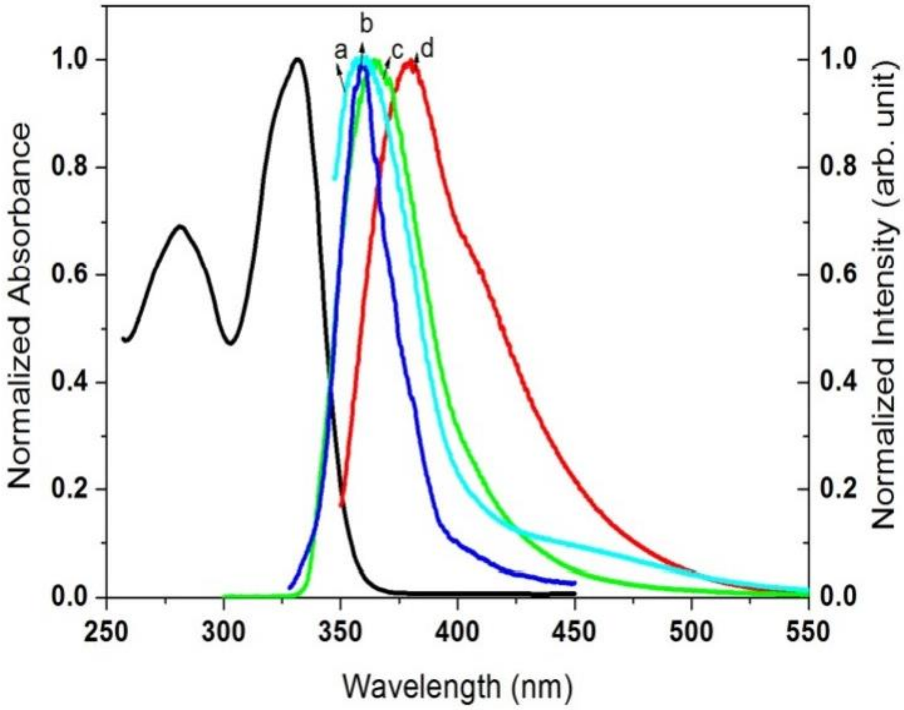


Figure 1.3 Normalized absorption spectrum of QS$^+$ in water and fluorescence spectra of QS$^+$ in (a) Benzene (b) Cyclohexane, (c) Dichloromethane and (d) Water

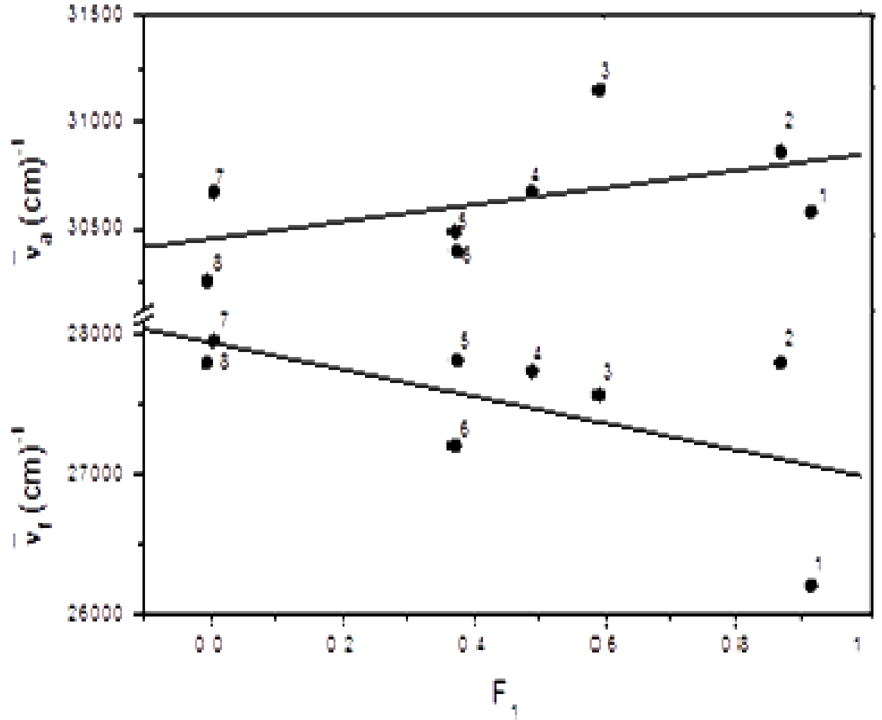
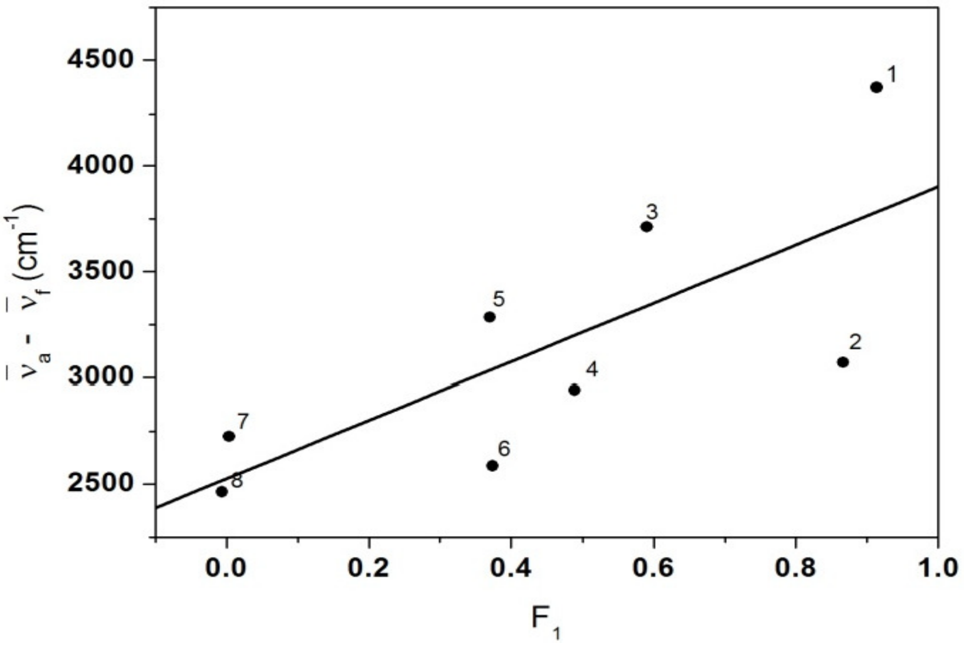


Figure 1.4 Variation of absorption and emission maxima of QS^+ with solvent polarity function. (1) Water, (2) Acetonitrile, (3) Dichloromethane, (4) Ethyl acetate, (5) Chloroform, (б) Diethyl ether, (7) Benzene, (8) Cyclohexane

Table 1.1 Different solvent parameters and spectral data of QS^+ in different solvents



Solvent			n	F_1	F_2	(cm^{-1}) va + v f2
Water	78.3	1.33	0.9134	0.6815	4367	28393.0
Acetonitrile	37.0	1.32	0.8662	0.6568	3071	29328.5
Dichloromethane	8.9	1.42	0.5903	0.5829	3711	29297.5
Ethylacetate	6.0	1.37	0.4891	0.4979	2943	29203.5
Chloroform	4.8	1.44	0.3701	0.4872	3285	28845.5
Diethylether	4.3	1.35	0.3740	0.4267	2586	29100.0
Benzene	2.27	1.50	0.0036	0.3399	2726	29312.0
Cyclohexane	2.0	1.42	-0.0065	0.2845	2464	29025.0

Table 1.2 Dipole moment of QS^+ molecule in ground and excited states Theory $S_1(cm^{-1})$ $S_2(cm^{-1})$
μ_g(D) μ_e(D) ⍰μ(D) μ_e/μ_gHF/6-31G 1375.86 651.57 4.47 12.52 8.05 2.80

Figure 1.5 Plot for Stokes shift versus solvent polarity function F_1. (1) Water, (2) Acetonitrile, (3) Dichloromethane, (4) Ethyl acetate, (5) Chloroform, (6) Diethyl ether, (7) Benzene, (8) Cyclohexane

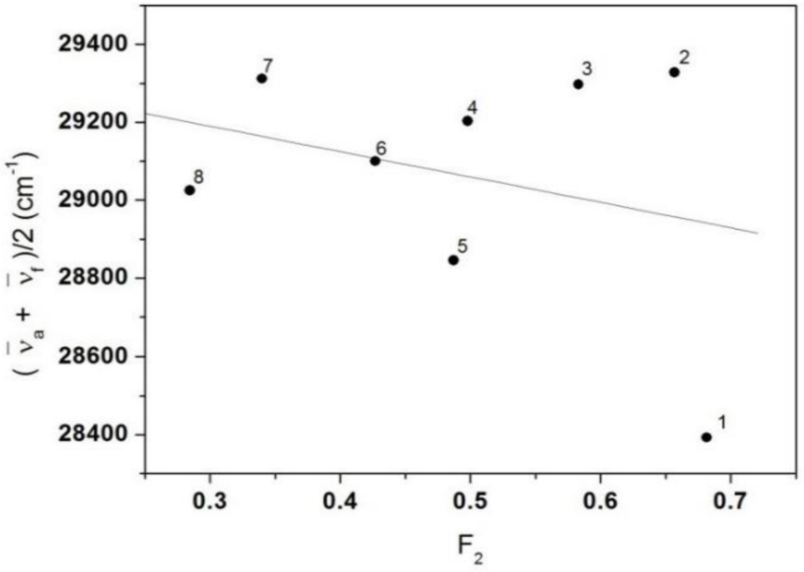


Figure 1.6 Plot for arithmetic average of absorption and fluorescence wavenumbers versus solvent polarity function F_2. (1) Water, (2) Acetonitrile, (3) Dichloromethane, (4) Ethylacetate, (5) Chloroform, (6) Diethyl ether, (7) Benzene, (8) Cyclohexane

CONCLUSIONS

We have calculated ground state and exited state dipole moments of QS$^+$. The μ_g value calculated from quantum chemical calculations is 4.47 D and the estimated excited state dipole moment from the solvatochromic shift method is 12.52 D. This large increase in dipole moment in the excited state of QS$^+$ 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 solvatochromatic method.

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