



Solvation of coumarin6 studied by vibrational spectroscopy and density functional theory



Randhir Singh ^{a,*}, Vasant Sathe ^b, Amit Sharma ^c, Sarvpreet Kaur ^d, G.S.S. Saini ^e

^a Applied Science Department, Guru Nanak Dev Engineering College, Ludhiana 141006, India

^b DAE-UGC CSR, University Campus, Khandwa Road, Indore, India

^c Department of Applied Sciences, Bharti Vidyapeeth's College of Engineering, New Delhi 110063, India

^d Department of Physics, Government College for Girls, Sector 11, Chandigarh, India

^e Department of Physics, Panjab University, Chandigarh, 160014, India

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ABSTRACT

Effect of solvation on coumarin6 dye has been studied with density functional theory (DFT). Optimized structure of the dye has been obtained in various solvents and frequencies of various vibrational bands have been calculated in these solvents. Calculations predict shift in the frequency of certain bands in the solvents. Similar shifts have been observed experimentally in the vibrational spectra of the dye in solvents. In order to ascertain the origin of these shifts, the interactions of solvent molecules with the coumarin6 molecule have been studied using various tools of DFT like donor-acceptor interactions, Molecular Electrostatic potential (MEP) and HOMO-LUMO analysis etc.

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1. Introduction

Coumarin dyes have been widely used in a large number of chemical and physiochemical studies like inkjet printing, hetero-junction solar cells, fluorescent probes for local fluidity and polarity of surrounding medium, improving the efficiency of dye lasers, fluorescent microcrystals and molecular dots etc [1–5]. Photo-physical properties of coumarin dyes have been a long standing research topic [6–13]. The molecular structure, fluorescence and photo physics of coumarin dyes are influenced by solvents [7]. Continuous wave emission from coumarin6 in green and blue region have been reported [14]. Acid base properties of coumarin6 have been studied by Corrent et al. [15]. Photophysical, photochemical and photoacoustic properties of coumarin6 have been studied in detail [16–18]. Rotational diffusion of coumarin6 and solvent effects on the absorption and emission spectra have also been studied [19,20]. However we have not noticed any significant work done on the effect of solvation on the vibrational spectra of coumarin6.

Vibrational spectroscopy is an important tool for studying the bonding arrangement in a molecule. Both Raman and infrared (IR) absorption spectroscopic techniques can be used for the study of molecular vibrations. Researchers have used these tools extensively for molecular structure determination and in medical research [21,22]. Density functional theory (DFT) is a computational technique, which can be used to calculate the molecular parameters of a structure and to study the effect substituents and solvents on the molecule in gas phase [23–26]. DFT based normal coordinate analysis of various molecules is very helpful in assigning the observed vibrational bands quite accurately [27–30]. In the present work, we have studied the effect of various solvents on vibrational spectra of coumarin6 using DFT. These calculations predict shift in positions of some vibrational bands in solvents. To verify the results obtained from DFT calculations and in order to investigate the effect of solvents, we have studied IR spectra of coumarin6 dye in KBr and in methanol solvent, while Raman spectra of the dye for crystalline powder and in the methanol, ethanol and CCl₄ solvents. This study may provide a good understanding of the dependence of lasing properties coumarin6 in various solvents. In addition, interaction of coumarin6 with methanol, acetonitrile, Dimethyl Sulphoxide (DMSO), CH₂Cl₂ and CCl₄ has also been studied using DFT.

* Corresponding author.

E-mail address: rsingh@gndec.ac.in (R. Singh).

2. Experimental and computational details

Laser grade coumarin6 from Exciton, USA was used without further purification. However, its purity was checked with electronic absorption spectroscopy on LABINDIA UV 3000 UV/VIS spectrophotometer. Spectroscopic grade solvents, methanol, ethanol, and CCl_4 from Qualigens Fine Chemicals, India, were used without any purification. IR spectrum of coumarin6 crystalline powder was obtained using KBr pellet. For recording of the IR spectra of the dye in methanol, few drops of solution of coumarin6 (conc $\sim 3 \times 10^{-6}$ M) were put on a KBr window. The IR spectra were recorded on a Perkin Elmer PE-Rx1 FTIR Spectrophotometer with spectral resolution 1 cm^{-1} throughout the experiment. Raman Spectra of was recorded on a LabRam JY HORIBA HR 550 and Lab-Ram 800 spectrograph equipped with Olympus Bx41 microscope and CCD detector. The measurements were carried out in either 90° or back scattering geometry with incident light linearly polarized and scattered light was detected unpolarized. Excitation line at 488.0 and 632.8 nm were provided by air cooled Ar^+ and He–Ne lasers respectively. The power of Ar^+ laser at the laser head and the sample were 10 and 3 mW respectively. A lens of 10x was used in the microscope to give a spot size of ~ 3 microns on the sample. Measurement time was varied between 20s to 30s.

DFT calculations using B3LYP functionals [31,32] and basis set of 6-31G(d,p) [33] were carried out to optimize the molecular structure of coumarin6 in gas phase and in various solvents like methanol, ethanol, CCl_4 etc using Polarized Continuum Model (PCM) [34] as well as to study the interaction between coumarin6 and these solvent molecules. Calculations were performed using Gaussian 09 Revision C.01 program package [35]. All calculations on the geometry optimization resulted in convergence and no imaginary frequency was found in the frequency calculations, which means that minima on the potential energy surface were obtained.

3. Results

3.1. DFT calculations

Structure of the coumarin6 [36] along with methanol molecule is shown in Fig. 1. The atomic numbering shown here is same as adopted by Zhao et al. [37].

3.1.1. NBO analysis

Natural Bond Orbital(NBO) Analysis is an important tool for

studying intra and intermolecular bonding and for investigating charge transfer or conjugative interactions in the molecules [38]. The second order perturbation theory analysis of Fock matrix in the NBO basis for coumarin6 is given in the Table 1. It gives stabilization energy for interaction of some electron donor and acceptor orbitals, which produce stronger delocalization of energy density between occupied and unoccupied NBO. Table 1 shows that the intramolecular hyperconjugative interactions are formed by the overlap of $\pi(\text{C}-\text{C})$ and $\pi^*(\text{C}-\text{C})$ bond orbitals in coumarin6, which results in intramolecular charge transfer (ICT) and stabilization of the molecule. Moreover electron donation from the lone pairs $n^\pi(\text{O}1)$, $n^\pi(\text{O}25)$, $n^\pi(\text{S}17)$, $n^\sigma(\text{N}11)$ and $n^\sigma(\text{N}24)$ to neighboring antibonds also give strong stabilization energies. Maximum stabilization of 50.15 kCal/mol is observed in the ICT process due to electron donation from Ref. $n^\sigma(\text{N}11)$ to $\pi^*(\text{C}7-\text{C}8)$. NBO analysis of optimized structure of coumarin6 in various solvents is also done and the data for methanol and CCl_4 solvents is given in Supplementary Tables S1–S2. It has been observed that there is considerable change in the stabilization energy of certain ICT interactions in solvents. For example the value of $E(2)$ for $\pi(\text{C}3-\text{C}4) \rightarrow \pi^*(\text{C}2-\text{O}25)$ increases from 23.34 kCal/mol to 28.17 kCal/mol and 25.05 kCal/mol for methanol and CCl_4 solvent respectively. Similarly the value of $E(2)$ for $n^\pi(\text{O}1) \rightarrow \pi^*(\text{C}2-\text{O}25)$ increases from 34.57 kCal/mol to 37.49 kCal/mol and 35.83 kCal/mol for methanol and CCl_4 solvent, while for the interaction $n^\sigma(\text{N}11) \rightarrow \pi^*(\text{C}7-\text{C}8)$, $E(2)$ increases from 50.15 kCal/mol to 55.39 kCal/mol and 52.34 kCal/mol for methanol and CCl_4 solvent respectively. This means that the electron donating character of $\pi(\text{C}3-\text{C}4)$, $n^\pi(\text{O}1)$ and $n^\sigma(\text{N}11)$ is increased in the solvents. However the electron donating character of $n^\pi(\text{O}25)$ is found to decrease in the solvents, which is characterized by decrease in the stabilization energy from 40.76 kCal/mol to 36.81 kCal/mol and 39.09 kCal/mol for methanol and CCl_4 solvent. The change in stabilization energy is found to be least for CCl_4 solvent. This could be related to the fact that CCl_4 molecule is non-polar and its interaction with the polar coumarin6 molecule is very weak. From this analysis it we were able to predict that the solvent molecules will preferably interact with C–H bonds through hydrogen bonding and with O1, N11, S17, N24 and O25 atoms of coumarin6 due strong electron donating character of lone pair of electrons possessed by these atoms. Therefore if we place solvents molecules near these atoms of the dye molecule and the resulting structure is optimized using DFT, then stable complexes might be formed due to intermolecular charge transfer between solvent and dye molecules.

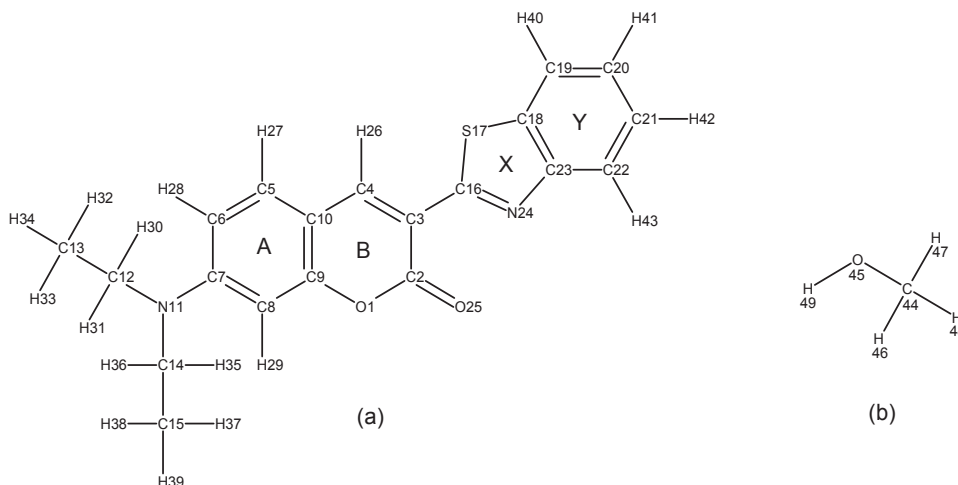


Fig. 1. Structure and atomic numbering scheme of (a) coumarin6 and (b) methanol molecule.

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