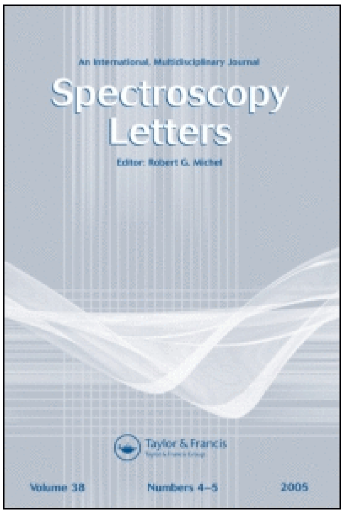

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

SPECTROSCOPIC CHARACTERISTICS OF COUMARIN 540 A IN SOL-GEL

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To cite this Article Farooqui, Asma Sohail and Zaidi, Z. H.(2001) 'SPECTROSCOPIC CHARACTERISTICS OF COUMARIN 540 A IN SOL-GEL', Spectroscopy Letters, 34: 3, 301 — 309
To link to this Article: DOI: 10.1081/SL-100002284
URL: http://dx.doi.org/10.1081/SL-100002284

SPECTROSCOPY LETTERS, 34(3), 301–309 (2001)

SPECTROSCOPIC CHARACTERISTICS OF COUMARIN 540 A IN SOL-GEL

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ABSTRACT

The present paper deals with the spectroscopic study of coumarin 540 A in sol-gel and other liquid solvents in the 190-500 nm wavelength region. The electronic absorption spectra are compared with coumarin and its parent aromatic molecule anthracene. Theoretically, ground state geometries are optimized using the MNDO molecular orbital method. The electronic energy levels have been calculated using the optimized geometries and the CNDO/S-CI method. The role of the sol-gel matrix and the effect of hydrogen bonding is discussed in order to explain the observed spectral characteristics.

Key Words: Electronic absorption spectra; Coumarin 540 A; Sol-gel; CNDO/S-CI.

INTRODUCTION

Sweet clover is grown as a green manure and hay crop in the northern United States and in Canada. In 1920's use of this hay was widespread and it lead to epidemic of "bleeding disease" in cattle. Similar was the case in England when sweet vernal grass which was used as forage caused bleeding disease in cattle. Sweet clover or sweet vernal grass has a distinctive sweet odor similar to vanilla. This is because of its coumarin content. Glucoside melilotoside which is found in sweet clover binds to coumarin to form dicoumarol, a highly toxic and anticoagulant derivative of coumarin (1-3). Furano coumarins are another form of toxic compounds that consist of a coumarin nucleus bonded to a furan ring. Coumarin is found widely distributed in nature and some of its derivatives are of great importance in chemistry and medicine (4-8). Coumarins show a varying inhibiting effect on enzymes (9-10). Recent studies have indicated some antitumour activity of simple coumarins. Coumarin itself has been reported to be a moderately potent inhibitor of chemical carcinogen-induced neoplasia (11-12). Hence, coumarins and many of its derivatives have marked physiological effects such as active hypotoxicity, anticoagulant action and antibiotic activity.

Along with their biological importance coumarins are strong laser dyes. 7-amino coumarin dyes are recognized as an important class of fluorescent dyes emitting in the blue green spectral region. These dyes have been used to probe the effects of pH on sol-gel processing (13). Research activities during the past seven years have established the role of coumarin dyes in tunable solid state sol-gel lasers. Laser materials have been prepared by incorporating the dye directly in the sol or by impregnating the transparent gel with a dye solution (14-15). Furthermore, considerable work has been done on the synthesis, quantum yield, lasing efficiency, lifetime, effect of pH and temperature on the fluorescence characteristics of 7-amino coumarin dyes (16-19). But it appears that a systematic detailed study of the uv-visible electronic absorption spectra is missing within the literature. Understanding spectroscopic properties of these dyes are helpful not only for biological diagnostic purposes but also for predicting their laser action properties. Such information can lead to synthesis of new materials with lower lasing threshold and higher efficiency. Coumarin 540 A is one such strongly fluorescent laser dye and has a laser emission peak at 525 nm and an oscillation bandwidth of 21 nm (FWHM) (15).

The present paper deals with a spectroscopic study of coumarin 540 A in sol-gel and other liquid solvents. The study of electronic transitions of coumarin 540 A is reported in the 190-500 nm wavelength region. The electronic absorption spectra of coumarin 540 A are compared with coumarin and its parent aromatic molecule anthracene. Theoretical side ground state geometries are optimised using the MNDO molecular orbital method (20). The electronic energy levels have been calculated using the optimized geometries and the CNDO/S-CI method (21-22). The role of the sol-gel matrix and the effect of hydrogen bonding is discussed in order to explain the observed characteristics.

EXPERIMENTAL AND COMPUTATION

Coumarin 540 A was obtained from M/S Exciton, INC. Dayton. Ohio. USA and ethanol, cyclohexane, methanol, tetraethoxy silane were also obtained from

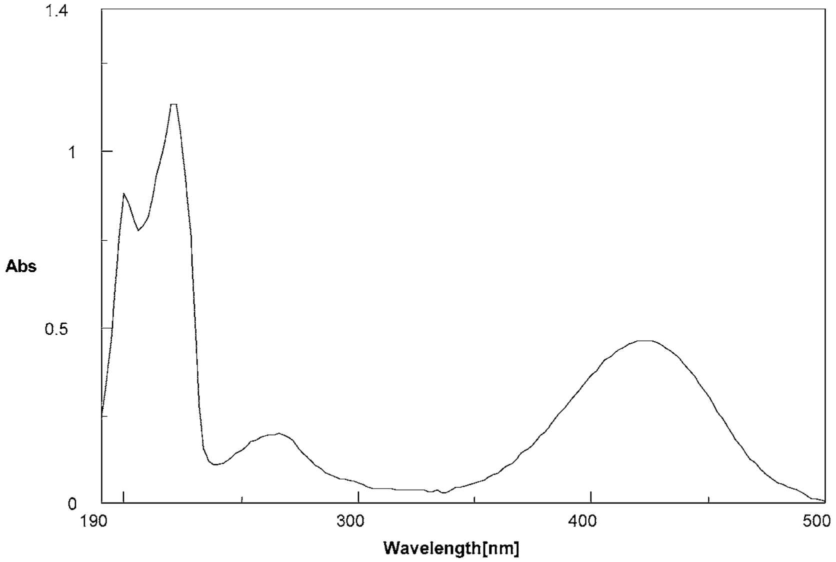

Figure 1. Electronic absorption spectra of Coumarin 540 A molecule in ethanol solution.

M/S. Sol-gel monoliths doped with coumarin 540 were prepared by the method described elsewhere (23). The optical absorption spectra were recorded using a JASCO UV-VIS-NIR spectrophotometer (model V-570). Singlet energies have been calculated using the CNDO/S-CI method (21-22).

RESULTS AND DISCUSSION

The electronic absorption spectra of Coumarin 540 A in ethanol and sol-gel in the region 190-500 nm are displayed in Figures 1-2. Figure 3 shows the spectra of Coumarin 540 A in methanol and cyclohexane. The spectrum of coumarin in ethanol is displayed in Figure 4. Electronic absorption spectra of coumarin 540 A are compared with its parent coumarin molecule in ethanol and the parent aromatic hydrocarbon anthracene. The electronic states are calculated using the optimized geometries and the CNDO/S-CI method (20-22). The positions of absorption maxima together with their assignments on the basis of the molecular orbital calculations using the CNDO/S-CI method are given in Table 1.

In the spectrum of coumarin 540 A in sol-gel an electronic transition marked II is observed at 374 nm. This spectrum corresponds to the electronic transition of type $^1B_{1u}$-^1A_g observed at 378 nm in the anthracene molecule, with the transition moment along the short axis of the molecule. It is observed at 312 nm in the

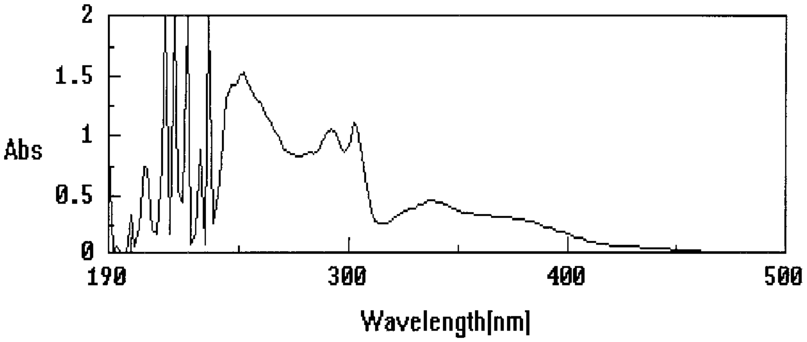

Figure 2. Electronic absorption spectra of Coumarin 540 A molecule in sol-gel.

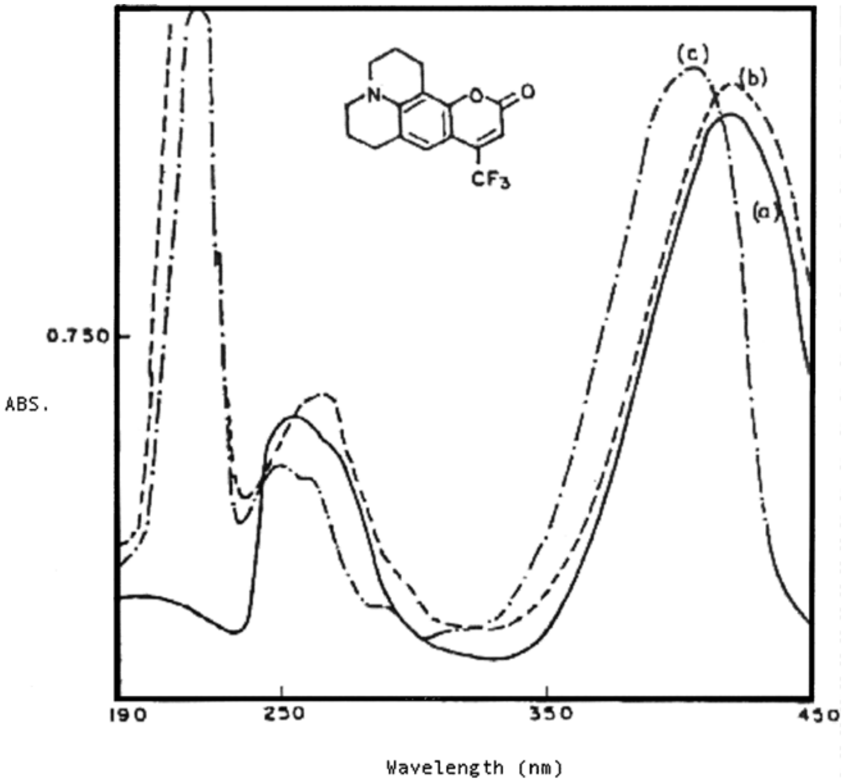

Figure 3. Electronic absorption spectra of Coumarin 540 A in three typical organic solvents: (a) chloroform, (b) methanol, (c) cyclohexane.

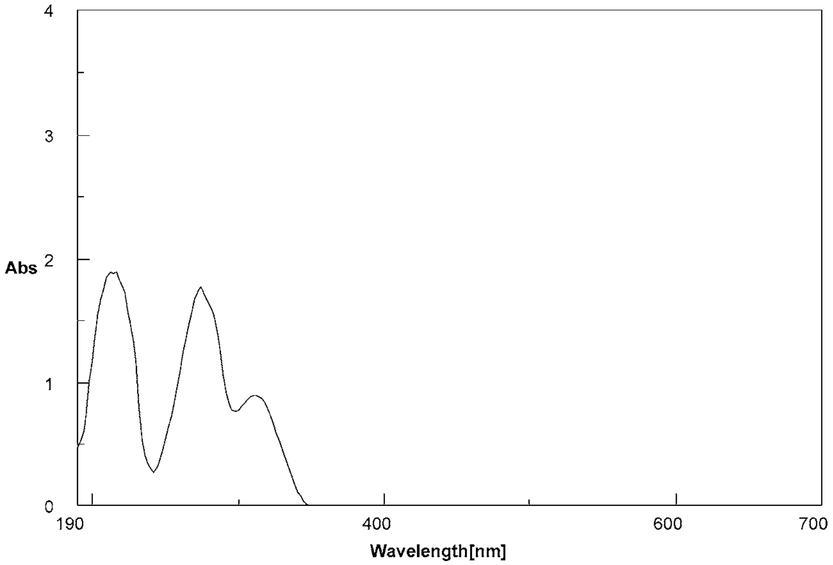

Figure 4. Electronic absorption spectra of Coumarin molecule in ethanol solution.

electronic absorption spectra of coumarin in ethanol, and our calculations predict it at 407 nm. The 29761 cm^{-1} band attached to this band shows a difference of 3024 cm^{-1} from its origin and may be attributed to the aromatic C-H stretching vibrational band.

The structure observed at 332 nm shows a difference of 3383 cm^{-1} from the origin of the second transition. This may correspond to the N-H stretching mode of primary aromatic amines. The second vibrational structure is observed at 328 nm which shows a difference of 3750 cm^{-1} from the origin. This may be due to the combination of aromatic C-H stretching and C-H out-of-plane bendiing mode. A less prominent vibrational structure is observed at 320 nm which may be due to the combination of N-H stretching and strong C-F stretching modes of the carbon–halogen bond.

In the electronic absorption spectra of coumarin 540 A in sol-gel, a new electronic transition not present in the spectrum of anthracene or coumarin is observed at 450 nm. However it is detected at 422 nm in the spectrum of coumarin 540 A in ethanol with much greater intensity. In cyclohexane and methanol it is detected at 395 and 425 nm respectively. CNDO/S-CI calculations predict this band at 504.7 nm as a medium strong band and identify it as $\pi \rightarrow \pi^*$ transition.

The third electronic transition in coumarin 540 A is detected at 302 nm in sol-gel. It is located at 300 nm in ethanol in the spectrum of coumarin 540 A.

CNDO/S-CI calculations do not predict this band. Two vibrational bands are observed attached to it at 292 nm and 282 nm at the difference of 1134 cm^{-1} and 2348 cm^{-1} from the origin, respectively. The first may be due to C-F stretching vibrations of the carbon halogen bond. The second may be due to the combination of C-F stretching and strong C-N stretching vibrations.

Another very intense and prominent electronic transition in the absorption spectrum of coumarin 540 A is found at 252 nm in sol-gel. It shows a large red shift of 14 nm in ethanol and is detectedat 266 nm. In the case of the coumarin molecule it appears at 275 nm as shown in Figure 3. As in the case of the spectrum of coumarin the intensity of this band lies inbetween the short and long wavelength bands. This electronic transition corresponds to the $^1B_{2u}$-^1A_g transition of the anthracene molecule observed at 254 nm. It is noted that the intensity of this band is larger in sol-gel matrix than in ethanol. In cyclohexane the same peak appears at 250 nm. Our calculations predict it to occur at 262.5 nm as a strong band and identify it as $\pi \rightarrow \pi^*$ transition.

A very intense transition is observed at 220 nm in the absorption spectrum of C 540 A in sol-gel. It is observed at 222 nm in ethanol and corresponds to the ^1c_b-^1A band of anthracene at 220 nm. Theoretically this electronic transition is predicted as the most intense peak at 206.7 and is identified as a $\pi \rightarrow \pi^*$ transition. In the spectrum of coumarin 540 A in cyclohexane and methanol it is observed at 212 and 215 nm, respectively . It has an accompanying vibrational band at 216 nm (i.e., $\sim$46296 cm^{-1}) which might be attributed to one of the fundamental modes of anthracene.

A transition observed at 236 nm in sol-gel is extremely sharp and intense. This electronic transition shows a vibrational band at 232 nm. It shows a difference of 731 cm^{-1} from its origin and may correspond to the C–H out-of-plane bending mode. This band has been missed by using CNDO/S-CI calculations.

A very intense sharp peak is observed in the electronic absorption spectrum of coumarin 540 A in sol-gel at 226 nm. This is predicted at 219.7 nm. The medium-strong peak at 206 nm is predicted to occur at 204.9 nm. In the case of the parent coumarin molecule it is observed at 212 nm as the strongest short wavelength band. A medium strong electronic transition is observed at 200 nm in the spectrum C540 A in sol-gel. It is calculated to lie at 197.0 nm. Another very weak transition is observed at 194 nm in the sol-gel matrix which occurs at 192 nm in the spectrum of coumarin 540 A in ethanol. This may correspond to the $^{I}B_a \leftarrow {}^1A_a$ band of anthracene.

Large shifts of electronic transitions observed in the sol-gel matrix leads us to conclude that it is more polar than ethanol. Hydrogen bonding between the solute and the solvent molecules, especially between the ethanol (also used in the preparation of gel) and the amino nitrogen affects the electronic spectra remarkably. This fact has been ascribed to the rearrangement of the hydrogen bond between the

Table 1. Assignments of the Observed Band Maxima of Coumarin 540 A

Transition No.	Corresponding Anthracene Bands Plat Notation	Corresponding Coumarin Bands Ethanol (nm)	Calculated Transition Energy (nm)	Ethanol (nm)	Observed Band Maxima Coumarin 540 A.	
					Sol-Gel (nm)	Sol-Gel (cm^{-1})
I			504.7 (.3311)	422	450 vw	22222
II	374 $^1B_{1u}-^1A_g$	312	407 (.3536)		374 ms	26737
					336 ms	29761
					332	30120
					328	30487
	323				320	31250
III	309			300	302 s	33112
	292				292 s	34246
	285				282	35460
V	256 $^1B_{2u}-^1A_g$	275	262.5 (.2564)	266	252 vs	39682
VI					236 vs	42372
VII					232	43103
VIII		212	219.7 (.4539)		226	44247
IX	220 $^1C_b-^1A$		206.7 (.7653)	222	220	45454
X	217				216	46296
XI			204.9 (.0201)	200	206 s	48543
XII			197 (.0333)		200 ms	50000
XIII	186 $^1B_a \leftarrow ^1A_a$		190.6 (.000079)		194 w	

solute and the solvent molecules during the lifetime of the excited solute molecule. The hydrogen bonding interaction in alcohol solutions of the 7–amino coumarin probably involves the several types of hydrogen bonds.

The hydrogen bond of the −H−H. . .O< type causes a red shift of the absorption spectrum, whereas the −N. . .H−O type hydrogen bond causes a blue shift of the absorption spectrum. This is because the former is favorable while the latter is unfavorable to the charge migration from the substituent to the aromatic ring. Secondly, electronic transitions observed in the case of the spectrum of coumarin 540 A in sol-gel appear with a much increased intensity in comparison to the liquid solvents. This is the result of perfect compatibility between the dye and the host matrix. There are several parameters such as solution pH, temperature, solvent, and relative concentration of the TEOS precursor that influences the hydrolysis and condensation polymerization reactions during sol-gel preparation. The combination of these effects causes an increase in the interaction between the coumarin 540 A molecule and the silica gel. Our experimental results in general are found to be in good agreement with theory.

ACKNOWLEDGMENTS

This research work was supported by grants from the Directorate of Training and Sponsored Research, Defence Research and Development Organization, Ministry of Defence- New Delhi to Jamia Millia Islamia for the project," Preparation and Spectroscopic characterization of Sol-gel glass Laser materials.

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Received August 1, 2000
Accepted January 1, 2001

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