Energy spectra of dyes embedded in SiO_2 sol-gel glass

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Dyes, which are commonly used in the food industry, were incorporated at two different concentrations into SiO_2 coatings prepared using the sol-gel method. The optical absorption, the excitation and emission spectra of the colored glass coatings were used to characterize the optical transitions in the UV-Vis region. The results reveal the existence of discrete energy levels in the systems studied. A simple quantum mechanical model is presented treating the organic molecules as two-dimensional potential wells for electrons. The analysis made give a reasonable agreement with the experimental optical transitions determined from absorption and emission spectra.

Keywords: Dye; sol-gel; coatings; emission and absorption

Pigmentos orgánicos comúnmente usados en la industria alimenticia fueron incorporados en dos concentraciones diferentes a recubrimientos de SiO_2 preparados usando el método sol-gel. Los espectros de absorción óptica, de excitación y emisión de los recubrimientos de vidrios coloreados fueron utilizados para caracterizar las transiciones ópticas en el rango UV-Vis. Los resultados revelan la existencia de niveles de energía discreta en el sistema estudiado. Se presenta un modelo mecánico-cuántico simple que trata a las moléculas orgánicas como pozos de potencial bidimensionales para electrones. Los análisis hechos concuerdan razonablemente con las transiciones ópticas experimentales determinadas de los espectros de absorción y emisión.

Descriptores: Pigmentos orgánicos, sol-gel, recubrimientos, emisión y absorción

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1. Introduction

During the two last decades a considerable amount of investigations have been carried out on sol-gel glasses doped with organic and inorganic dyes. One of the main interests is the application of these systems in the fabrication of new tunable dye lasers [1–11]. An essential progress has been developed in the understanding of the basic properties and in the potential applications of these materials [1–11]. It is now generally accepted that lifetime and stability of dye molecules are enhanced when they are embedded in inorganic matrixes [3]. In particular, the SiO_2 sol-gel glass provides a stable and easily made matrix for this purpose. In the last few years many different types of organic and inorganic dyes have been developed and only few of them have been investigated as active elements inside a stable matrix. To our knowledge, no attempts so far have been made to utilize in this field the well known food dyes which are produced in big quantities, are cheap, and safe in handling.

Several models have been used to correlate the optical properties of organic and inorganic dyes with the energy spectra of the electronic excitations of the molecule. The most frequent approaches are, the free electron molecular orbital (FEMO) and the linear combination of atomic orbital (LCAO) [12–16]. Some authors apply the charge transfer or exciton concepts to analyze the optical electronic transitions in organic dyes [9, 10, 17]. With the exception of the FEMO model, all the approaches mentioned, demand the detailed information about the electronic molecular structure of the dye. These models are technically complicated and require a number of assumptions restricting their usage. Many of the reports describing these models indicate some limitations and point out the need of further investigations.

The purpose of the present work is to demonstrate the possibility of incorporation of some organic dyes, used in the food industry, into SiO_2 coatings prepared by the sol-gel method. The optical properties of these coatings have been investigated by measuring the optical absorption and the emission and excitation spectra of samples having two different concentrations of the dyes. A model is proposed to explain the observed optical electronic transitions, the model considers the organic dye molecule as a two-dimensional quantum well. It is found that the energy spectra of the π-electrons, confined to the box with constant potential inside, agrees well with the electronic transitions observed in the measured optical spectra.

2. Experimental: materials and methods

The colored glass films were prepared by mixing the precursor solution composed of tetraethyl orthosilicate (TEOS), wa-

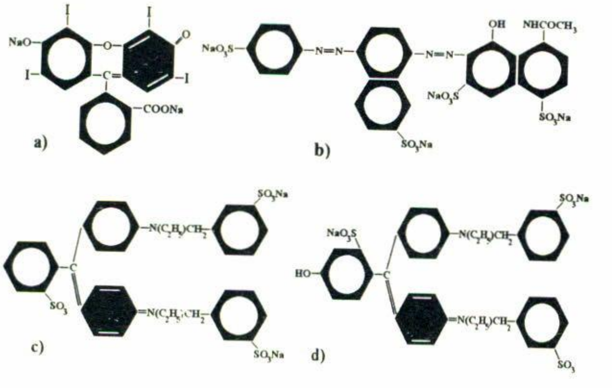

FIGURE 1. Molecular structure of the investigated dyes: The figure shows the structure of the a) R, b) Bk, c) G and d) B dyes.

ter and ethanol. The ethanol to TEOS and water to TEOS molar ratios were 4:1 and 11:1, respectively. The ethanol and TEOS were mixed using magnetic stirrer for 15 minutes. The dye was dissolved in water and added to the ethanol-TEOS and mixed for another 15 minutes.

Four different types of dyes were used, their molecular structures are depicted in Fig. 1, the common names of these dyes are: *a*) FD&C red No. 3 (erythrosine), *b*) brilliant black BN, *c*) FD&C green No. 3 and *d*) FD&C blue No. 1; in the following sections, these dyes will be denoted by R, Bk, G and B, respectively. Notice that the molecular dimensions of dyes G and B are similar. Coatings with two different concentrations of the dyes were used in the starting solutions, for the details see below.

To catalyze the hydrolysis-condensation reactions, the solution was acidified with HCl. After mixing, the colored starting solutions were placed at room temperature inside a closed stainless steel container until its viscosity was of 3 centipoises. We have found that this is a proper viscosity to obtain good quality coatings on glass slides substrates. Two sets of samples were prepared; one with 1 weight percent and the other with 10 weight percent of dye in dry bases, that is, the weight percentage of the dye in the coating after it has been dried. The colored coatings of about 800 nm thick were obtained when the glass substrate was immersed in the solution using a dip coating apparatus and removed at a constant speed of 8.8 mm/s. All films were dried at 90°C for 1 hour in an oven at atmospheric air conditions.

The room temperature emission and excitation spectra were carried out in a Fluorometer Fluoromax SPEX. The optical absorption spectra were obtained using a UV-Vis spectrometer Perkin-Elmer spectrometer Lambda 2.

3. Results and discussion

Figure 2 shows the typical emission spectra, in the range of 300–800 nm, for sol-gel coatings containing the four investigated dyes at the concentration of 1% wt. In order to observe all the emission lines in the near UV and in the visible ranges, the spectra were measured using radiation with a wavelength in the range of 270 to 400 nm, for the excitation. In Fig. 2, the emission spectra is labeled with the letters that identify the dye incorporated in the coating and the number that each letter shows, as subscript, indicates the wavelength, in nanometers, of the radiation used for excitation. In all cases the emission spectra excited with radiation having a wavelength longer than 400 nm, show only the band at about 700 nm. With the increase of the doping levels, the individual molecules interact among them; the general result of this interaction should be a broadening and lowering of the energy levels due to the mutual perturbation. This effect gives a red shift of all the excitation and emission bands. An example of that is shown by the insert at the upper right corner of Fig. 2. In that, the 700 nm emission band excited with the 488 nm line of an Argon laser (Lexel 95 Ion Laser) for the Bk colorant at three different concentrations: 8.5, 4.4 and 1.8% wt is shown. As can be seen, the position of that band moves toward longer wavelengths when the dye concentration is increased.

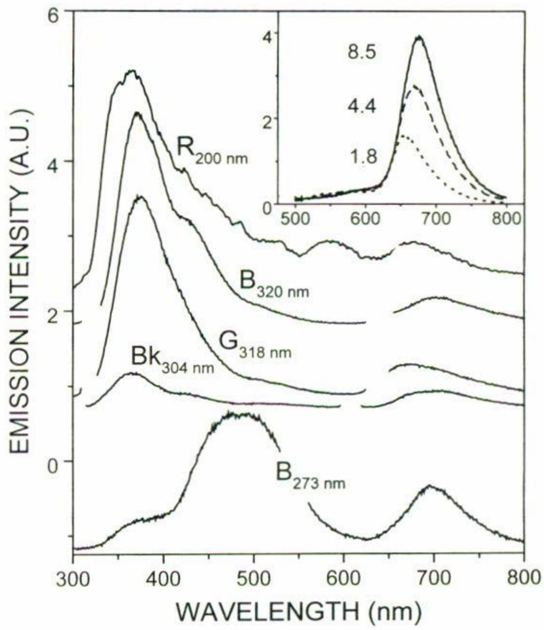

FIGURE 2. Emission spectra of the coatings containing different dyes at 1% wt. concentration. The subscript in the letters that identify the type of dye corresponds to the wavelength (nm) of the radiation used for excitation. The insert at the upper right corner show the 700 nm emission band excited with the 488 nm line of a He-Ne laser for the Bk colorant at three different concentrations: 8.5, 4.4 and 1.8% wt.

Figure 3 shows the excitation and optical absorption spectra, in the range of 230–700 nm for the coatings containing the R, B, G and Bk dyes. Curves corresponding to the excitation spectra have, as a subscript, the wavelength at the maximum intensity of the originated emission band in Fig. 2.

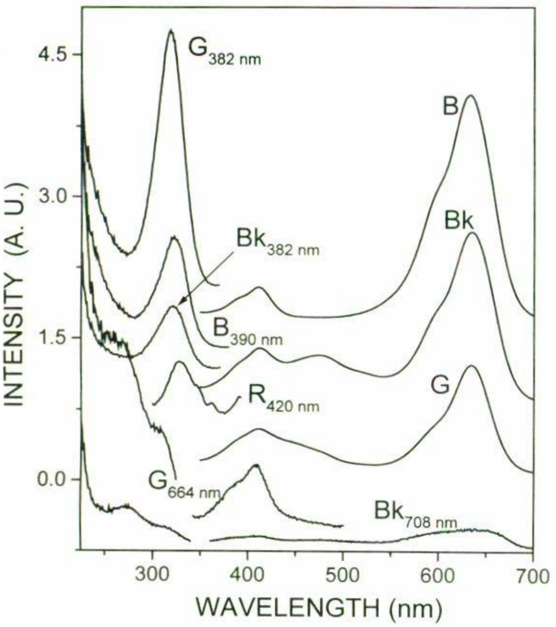

FIGURE 3. Excitation and absorption spectra for coatings containing different dyes at 1% wt. concentration. The subscript in the letters that identify the type of dye, corresponds to the wavelength (in nm) of the originated emission band in Fig. 2. The curves with letters without subscript correspond to the absorption spectra.

TABLE I. Experimental energy spectra (eV) for different dyes in glass coatings. It shows the peak position from excitation (Exc.), absorption (Abs.) and emission (Ex.) spectra.

B	Exc.			3	3.9	4.5^a
B	Abs.	1.9–2.0	2.6	3		
B	Em.	1.95	2.6	3	3.8	
G	Exc.			3	3.9	4.5^a
G	Abs.	1.9	2.6	3		
G	Em.	2	2.5	3.1	3.9	
Bk	Exc.		2.6	3	3.9	4.6
Bk	Abs.	1.9	2.4-2.6	3		
Bk	Em.	1.9	2.6	3.1	3.9	
R	Exc.		3.175	3.43	3.594	3.78
R	Abs.		2.3	2.445	2.88	
R	Em.	1.828	2.11	2.774	3.42	

^{a} The corresponding band isn't observed in all cases

The curves denoted by the letters without subscripts correspond to the absorption spectra measured using optical transmission. These spectra were only obtained in the range of 350–700 nm.

Table I shows the position at the maximum intensity of the bands in the excitation, emission and absorption spectra. Considering a simple absorption and relaxation process, one expects that the energy values in Table I correctly reflect the electronic transition in the organic molecule.

It is widely accepted [3, 4, 7] that the organic molecules embedded in the sol-gel glass matrix are trapped inside the pores serving as the solid dielectric cages. Dye molecules separated from each other exhibit an energy spectrum, determined by the molecular structure, which has to correspond to transitions between the different energy states. Some of these transitions can be determined measuring the absorption and emission spectra of these molecules. The concentration effects could be accounted for on the bases of the perturbation theory.

A simplest model to determine the energy spectra of organic molecules is the "particle in the box" model. This model considers the electrons delocalized inside the molecule, so that the molecular dimensions determine the spectra of the allowed energy values. This model has been used before to estimate the energy spectra of other types of molecules [12–15]. However, in most cases, the one-dimensional approximation is used, with the boundary conditions corresponding to a potential well with infinite depth. We find this approximation to be over-simplified for two reasons: (1) the real depth of the molecular potential well is comparable to the separation between the lower energy levels and thus is finite, and (2) the molecules usually are not linear, so the real shape ought to be taken into account. We will show that taking these factors into account immediately leads to results different than those given by the traditional approximation and in better agreement with the experiment.

In our case (see Fig. 1), we have considered the molecules as two-dimensional potential wells. For the molecule in Fig. 1a, a circular shape has been considered and a rectangular shape for the other three. The depth of the wells is not infinite, so that it is taken into account the finite probability of an electron to be found outside the molecule; this means that the boundary conditions are different from those traditionally used. Below we present a simple description of such a model and its application to the dyes studied.

4. Organic molecule as a two-dimensional quantum well

4.1. The rectangular potential well

Let the potential energy inside the molecule be equal to zero; its size is determined by the values $L_{x,y}$ corresponding to the axes "x" and "y". The Schrödinger's equation for an electron with a mass m in this well is

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}\right)=E\psi. \qquad (1)$$

For rectangular or circular boxes, this equation then has a textbook solution. We shall look for the solution with the variables separated:

$$\psi(x,y) = \psi_1(x)\psi_2(y). \tag{2}$$

Each of the two function $\psi_{1,2}$ has a form

$$\psi = Ce^{ikr}, \tag{3}$$

where C is a constant and r can be x or y in ψ_1 or ψ_2, respectively, the wave vector K is different for the two cases. Furthermore,

$$K_x^2 + K_y^2 = \frac{2m}{\hbar^2}E. \tag{4}$$

One could see that the energy spectrum of the system is determined by the values of $K_{x,y}$; the latter depend on the boundary conditions. Having used the most general Born-Carman (periodic) boundary conditions implying that

$$\psi_1(x) = \psi_1(x + L_x), \qquad \psi_2(y) = \psi_2(y + L_y),$$

we get

$$K_{x,y} = \frac{2\pi}{L_{x,y}} n_{x,y},$$

where n_x and n_y are any integers starting from 1.

The energy levels are given by the equation:

$$E = \frac{h^2}{2m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2}\right), \tag{5}$$

and we must note that this expression gives the energy values which are 4 times larger than those obtained in the "infinite well" approximation [12, 13]; this is the immediate consequence of the boundary conditions used.

4.2. The circular potential well

In some cases, the structure of the molecule is closer to a circular shape, such as the FD&C Red No. 3 dye (Fig. 1a), in this case, the solution of Schrödinger's equation for a circular box is a better approximation. For a circular molecule of radius a, and with the two following boundary conditions for ψ: *i)* $\psi(r < a)$ is finite and, *ii)* $\psi(a) = 0$; the solutions of the Schrödinger's equation are

$$E_{\rm qt} = \frac{h^2}{8\pi^2 m}\frac{u_{\rm qt}^2}{a^2}, \tag{6}$$

where $u_{\rm qt}$ is the t-th root of the regular spherical Bessel function

$$j_{\rm q}(x) = (-x)^{\rm q}\left(\frac{1}{x}\frac{d}{dx}\right)^{\rm q}\left(\frac{\sin x}{x}\right),$$

and $A_{\rm qt}$ is a normalized constant. For the specific case of the dye in Fig. 1a, the circular model gives better results than the obtained using the rectangular model. For this case the estimated a value is 0.919 nm.

TABLE II. Calculated energies of electronic transitions for molecules having rectangular shape (B,G & Bk dyes) and the circular shape (FD&C Red No. 3 dye). Each number represents the energy difference between the levels indicating the corresponding raw and column

Rectangular Well 1.3 × 2.0 nm^2 (B & G Dyes)

	$E_{1,1}$	$E_{1,2}$	$E_{1,3}$	$E_{2,1}$	$E_{2,2}$	$E_{2,3}$	$E_{3,1}$	$E_{3,2}$
$E_{1,2}$	1.128							
$E_{1,3}$	**3.008**	**1.88**						
$E_{2,1}$	**2.67**	**1.542**	0.338					
$E_{2,2}$	**3.798**	**2.67**	0.79	1.128				
$E_{2,3}$	5.678	**4.55**	**2.67**	**3.008**	**1.88**			
$E_{3,1}$	7.12	5.992	**4.112**	**4.45**	**3.322**	**1.442**		
$E_{3,2}$	8.248	7.12	5.24	5.578	**4.45**	**2.57**	1.128	
$E_{3,3}$	10.128	9	7.12	7.458	6.33	**4.45**	**3.008**	**1.88**

Rectangular Well 1.1 × 2.8 nm^2 (Bk Dye)

$E_{1,2}$	0.576							
$E_{1,3}$	**1.535**	0.959						
$E_{2,1}$	**3.729**	**3.154**	**2.194**					
$E_{2,2}$	**4.305**	**3.729**	**2.77**	0.576				
$E_{2,3}$	5.264	**4.689**	**3.729**	1.535	0.959			
$E_{3,1}$	9.945	9.369	8.41	6.215	5.64	**4.681**		
$E_{3,2}$	10.52	9.945	8.985	6.791	6.215	5.256	0.576	
$E_{3,3}$	11.48	10.904	9.945	7.75	7.175	6.215	1.535	0.959

Circular Well $r = 0.919$ nm (FD&C Red No. 3 dye)

$E_{1,0}$	$E_{1,1}$	$E_{1,2}$	$E_{1,3}$	$E_{2,0}$	$E_{2,1}$	$E_{2,2}$	
$E_{1,1}$	**1.862**						
$E_{1,2}$	**4.213**	**2.351**					
$E_{1,3}$	7.031	5.168	**2.817**				
$E_{2,0}$	5.343	**3.48**	1.13	1.688			
$E_{2,1}$	8.988	7.126	**4.775**	**1.958**	**3.645**		
$E_{2,2}$	13.146	11.283	8.933	6.115	7.803	**4.158**	
$E_{2,3}$	17.8	15.938	13.587	10.769	12.457	8.812	**4.158**

According to (5) and (6) the dimensions of the molecule determine the energy spectrum. This model has been previously applied to some hydrocarbon molecules and the theoretical electronic densities have been calculated [18].

From the chemical structures of the food dyes shown in Fig. 1, the estimated dimensions of the molecules were: *a)* the radius $a = 0.919$ nm, *b)* 1.1 × 2.8 nm^2, *c)* & *d)* 1.3 × 2.0 nm^2. We have taken the bond length in the benzene ring as 0.39 nm and added, as it is generally accepted [12], one bond length at each side of the ring. From Eqs. (5) and (6), the energy spectra for the four dyes investigated were calculated and are collected in Table II. The bold numbers in this Table, correspond to energy values that fall within the energy range in which our experimental spectra were taken. As can be seen, there is a good agreement between these values and those in Table I.

TABLE III. The first column shows the experimental values and the second the possible transitions between quantum states that could account for the observed transitions in the photoluminescence spectra.

B & G Dyes		Bk Dye		R Dye	
Energy(eV)	Transition	Energy(eV)	Transition	Energy(eV)	Transition
3.81	22-11	3.74	23-13, 22-12, 21-11	3.594, 3.78	21-20
2.98-3.02	3-12, 14-12, 13-11	3.08–3.16;2.78	15-13,21-12; 22-13	3.42	20-11
2.64–2.68	23-13, 14-13, 21-11	2.35–2.39; 2.2	14-12, 23-14; 21-13	2.88–2.774	13-12
1.85–1.89	13-12, 23-22, 14-22	1.73–1.43	15-14, 23-21, 13-11, 22-14	2.3, 2.11	12-11
				1.828	11-10, 21-13

Analyzing the experimental excitation and absorption spectra of the molecules studied (in Table 1), we can see that the main bands in the spectra can be accounted for by transitions from the ground to one of the excited states calculated from Eqs. (5) and (6). The relatively weak band around 4.5 eV (380 nm), present in part of the spectra for green and blue dyes, could be related with the transition from the first excited state E_{12} to the state E_{14} (second order optical transition); the state E_{12} ought to be reasonably populated not only at the expense of the immediate excitation from the ground state, but also because of the luminescent transitions ending in this state. This state should also take part in the absorption spectra of the colored glass, accounting for the bands in the region 1.7–2.2 eV.

The emission spectra are also in a good agreement with the calculated molecular energy spectra. The energy of the luminescent transitions between higher and lower excited states can be found in Table III. Column one corresponds to the experimental energy values and column two to the possible transitions between calculated energy levels, which could originate the experimentally observed emission bands.

5. Conclusions

We have incorporated some molecular dyes commonly used in the food industry into SiO_2 coatings prepared using the sol-gel process. Samples with a dye weight concentration of up to 10% were prepared. All coatings have a uniform color. The molecular energy levels responsible for the transitions, which produce visible coloration, were determined from the excitation, emission and optical absorption spectra of the coatings. A simple model is proposed to calculate the molecular energy levels. For that, the organic molecules are considered as two-dimensional potential wells for electron, in which they are delocalized. The calculations made on the basis of this model are in good agreement with the results obtained by optical spectroscopy.

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