

## Formation of Fluorescent Rhodamine B J-Dimers in Sol–Gel Glasses Induced by the Adsorption Geometry on the Silica Surface

Francisco del Monte and David Levy\*,†

*Instituto de Ciencia de Materiales de Madrid, CSIC, Cantoblanco, 28049 Madrid, Spain*

*Received: May 28, 1998; In Final Form: August 10, 1998*

Rhodamine B (RB) dimers were observed in doped gel glasses made by sol–gel processing in a wide range of dye concentrations. The photophysical properties such as excitation/fluorescence spectra and lifetimes of the studied doped gel glasses within a high dye concentration range are characteristic of adsorbed fluorescent J-dimers. To our knowledge, this is the first time that these species have been reported at the xerogel state of doped sol–gel glasses. The formation of fluorescent J-dimers rather than nonfluorescent H-dimers has been studied and was attributed to the geometry that the dimers adopt upon adsorption on the silica gel surface. Geometry is also related to the specific concentration of RB molecules inside the pores. Through the study of the photophysical properties of the doped gel glasses, conversion from fluorescent J-dimers to nonfluorescent H-dimers was observed over a defined RB concentration range. The appearance of these fluorescent J-dimers, even at high dye concentrations, demonstrates the improved capability of these matrices to be used as solid dye lasers.

### Introduction

Inorganic oxide matrices made by sol–gel processing are very attractive systems<sup>1–5</sup> for the incorporation of organic active components. The resulting organic–inorganic hybrid matrix is called ormocer (organically modified ceramic).<sup>6</sup> An ormocer classification has been recently done, according to the type of the bond linking the organic group to the silica surface.<sup>7</sup> Ormocers having a specific formulation can be prepared from a range of different monomer/comonomer precursors, giving the resulting matrix the required properties. There is a large list of organic compounds that can be incorporated into these inorganic matrices,<sup>1,8–17</sup> yielding gel glasses to be used in a wide range of applications, especially in optics.<sup>18–21</sup>

Although the incorporation of organic dyes into silica gel glasses has been largely achieved, there are numerous experimental works reporting on the impediments to retain the optimum spectroscopic properties of these organic dyes.<sup>9–11,22–25</sup> The problems are usually related to the interactions of the dye with the surrounding porous surface, usually called the “cage effect”.<sup>1,8,11,22–25</sup> However, there are important scientific questions about the relation that these molecules can establish with neighbor molecules inside of the pores.

The aim of this work is to find a correlation between the specific allocation of the dye molecules incorporated into porous gel glasses to its spectroscopic properties, through the preparation of doped gel glasses in a wide range of dye concentrations. Specific preparations and measurements were done for the precise assignation of fluorescent species to a specific geometry inside the pore. This geometry is established by the angle formed between the longitudinal axis of the molecule and the silica surface. Rhodamine B was the organic fluorescent molecule chosen to perform this study due to its well-known spectroscopic properties, in solution as well as adsorbed on solid surfaces.<sup>26–33</sup> RB is also adequate because of its capability to

form fluorescent dimers.<sup>32</sup> The formation of RB nonfluorescent or fluorescent dimers (called H-dimers and J-dimers, respectively) is mainly determined by the type of interaction forces between the monomeric constituents, although sometimes is also determined by the surrounding environment. While H-dimers have been observed in solutions of polar and low-viscosity solvents (i.e., water at room temperature), J-dimers may be formed in weakly polar solvents or in the adsorbed state.<sup>30,32,34–37</sup> Whereas dimer formation in solution is mainly due to hydrophobic interactions,<sup>38</sup> these forces do not play a dominant role on a solid surface, where the electrostatic interaction of the molecule with the polar surface and with other monomer molecules prevails.<sup>30,32,36</sup> Thus, the geometry adopted by the monomers during adsorption on a solid surface is a very important factor that will determine the feasibility of the H-dimer or J-dimer formation. As a consequence, the fluorescence properties (both spectral and dynamic properties) of the resulting adsorbed species may serve as an indicator of the specific geometry that RB molecules adopt with respect to the surface of the silica gel cage.

In many works performed on RB doped sol–gel matrices, the photophysical properties such as excitation and fluorescence spectra, and/or fluorescence decay kinetics have been extensively used to characterize the arrangement of the molecule into the porous matrix.<sup>8,39,40–43</sup> However, the modification of the fluorescence properties, as a consequence of the variation of the concentration of RB molecules incorporated into these gel glasses, has not attracted such a large interest. On the other hand, high dopant concentrations have been usually avoided because of the well-known appearance of nonfluorescent dimers, which would result in a loss of the fluorescence properties.<sup>27,35,44</sup> To our knowledge, only a few works were performed using high RB concentrations. These works reported on the observation of J-dimers in the starting sol–gel solution, as well as at the early stages of the sol–gel transition,<sup>43,45</sup> but there are not reported results about the formation of J-dimers at the xerogel state.

† Also with National Aerospace Institute, INTA, Space Instrument Laboratory. Torrejón de Ardoz, 28850 Madrid, Spain.

**TABLE 1: RB Concentrations Used for the Preparation of Gel Glasses 1–7**

	gel						
	1	2	3	4	5	6	7
moles of RB $\times 10^7$	0.03	0.075	0.3	1.2	2.4	4.2	4.8

In this paper, we focused on the formation of J-dimers at the xerogel state, and we investigated the effect of the RB concentration on the fluorescence properties of doped gel glasses. We also associated the specific formation of RB fluorescent J-dimer and nonfluorescent H-dimers to their adsorption angle with respect to the porous surface. Other alternatives, such as “acid equilibria effects”<sup>46–48</sup> or “reabsorption processes”,<sup>30,49–52</sup> may show a similar fluorescent behavior pattern than that observed for J-dimers formation and have also been considered in this work.

## Experimental Section

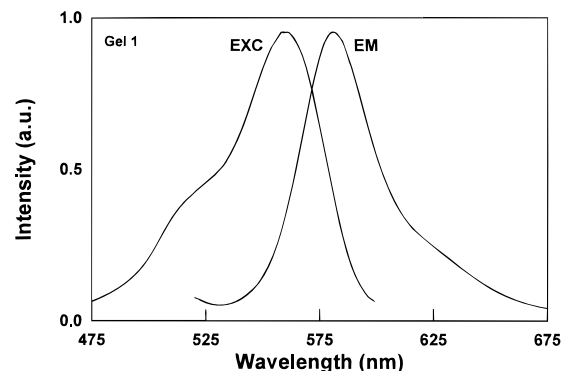
**Materials.** Rhodamine B, from Aldrich, was used as received without further purification. Tetramethyl orthosilicate (TMOS), from Aldrich, spectrophotometric grade methanol, from Merck, and distilled and deionized water (DDW) were used for sample preparation.

**Sample Preparation.** Gel glasses were prepared from 9.1 mmol of TMOS, 36.4 mmol (water to monomer molar ratio,  $r_{w/m} = 4$ ) of  $H_2O$ , and 33 mmol of methanol. A variable amount of RB was added to the solution without further prehydrolysis (Table 1). The polymerization was carried out at room temperature in glass bottles covered with aluminum foil. The mixture was allowed to stir during half an hour to become an homogeneous phase. After gelation occurred, the aluminum foil was perforated to allow the slow evaporation of the solvents until the formation of dried xerogels. The samples were kept in the dark along the study.

**Instrumentation and Lifetimes.** UV–vis spectroscopy was performed on a Varian 2300 spectrophotometer. The samples finely ground were placed in quartz cells with 1 mm path length. Absorption measurements of the samples were recorded in reflectance mode.

Multifrequency modulation, phase analysis, and fluorimetric measurements at 25 °C were performed on a 48000s (T-Optics) spectrofluorometer from SLM-Aminco. The instrument is configured for software controlled variable frequency light modulation from 100 Hz to 120 MHz. A front face sample holder for the samples was used for data collection and oriented at 60° in order to minimize light scattering from the excitation beam on the cooled R-928 photomultiplier tube. A D-glycogen scatter solution was used as the reference for lifetime measurements. Appropriate filters were used to eliminate Rayleigh and Raman scatter from the emission. Excitation and emission spectra were corrected for the wavelength dependence of the 450 W xenon arc excitation, but not for the wavelength dependence of the detection system. Spectroscopic and temporal properties were measured by reflection (*front face mode*) on finely ground samples and placed in quartz cells with 1 mm path length. No attempt was made to remove adsorbed or dissolved molecular oxygen from the doped materials. Reference samples that do not contain any fluorescent dopant were used to check the background and optical properties of the gel glasses.

Phase-resolved fluorescence spectroscopy<sup>53</sup> (PRFS) was used for lifetime measurements.<sup>54</sup> The method provides two sepa-



**Figure 1.** Excitation ( $\lambda_{em} = 640$  nm) and emission spectra ( $\lambda_{exc} = 420$  nm) of RB doped gel 1.

rated determinations of the fluorescence lifetimes due to the phase and modulation, which are independent measurements. Each phase and modulation value is the average of 100–200 readings. The frequency-dependent phase and modulation data were analyzed using a nonlinear least-squares procedure that minimizes the squared deviations between the observed and the expected phase and modulation values. The values of the floating parameters (lifetimes and fractional intensities of each fluorophore contributing to the total fluorescence intensity) are varied in a direction that minimizes the value of the deviations between the model and the data  $\chi_R^2$  (the reduced error). Computation is finished with a number of iterations through the fitting algorithm, when a minimum is found. The uncertainty in any phase or modulation measurement could be decreased to very small levels averaging in minutes. Specifically, values of  $\chi_R^2$  greater than unity may indicate either the presence of systematic errors<sup>55</sup> or an inappropriate model. We collected phase and modulation data measured at 20–25 modulation frequencies, and additional measurements did not seem to improve the resolution. An uncertainty of 0.5 was applied to the resolution of the phase and 0.005 to that of the modulation for the calculation of the  $\chi_R^2$ . The accuracy of the lifetime values measured was determined according to the lower  $\chi_R^2$  value found in each individual measurement.<sup>56</sup>

## Results and Discussion

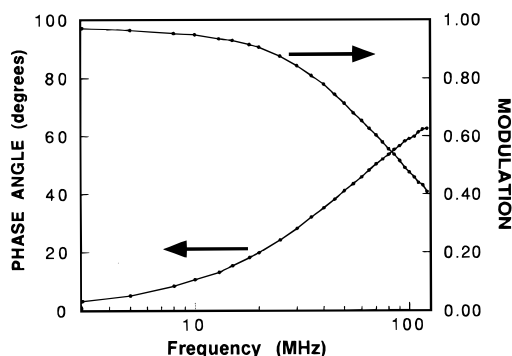
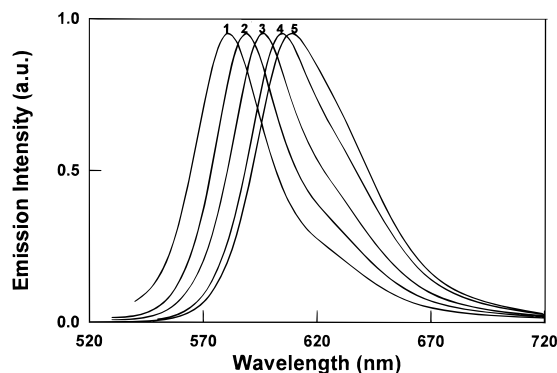
**Formation of Fluorescent J-Dimers on Porous Silica Gel Glasses.** The excitation and emission spectra of doped silica gel glass having a low RB concentration (gel 1, Figure 1, Table 2) were red-shifted compared to the RB excitation/emission spectra in ethanol solution.<sup>28</sup> The different environment of the dye in an ethanolic solution or in a gel glass determines the observed spectroscopic differences (cage effect).<sup>1</sup> The slightly less polar nature of the silica cage (composed of Si–OH and Si–O–Si groups) as compared to the solution affects the fluorescent properties of the RB.<sup>29,40,41,57–59</sup>

Through the application of PRFS, the lifetime of different emitting species can be resolved (Figure 2). In gel 1, a single lifetime was observed, denoting a very homogeneous environment around the dye molecules (heterogeneous environments yield multiple lifetimes<sup>60</sup>). Moreover, the value of this lifetime for gel 1 was markedly higher than the lifetime observed in ethanol/water RB solutions (Table 2),<sup>61,62</sup> denoting a more rigid environment of the RB molecules, which prevents the free arrangement of the molecules. The lack of mobility of the RB molecule limits its intramolecular rotation modes with the subsequent reduction of the deactivation processes or quenching

**TABLE 2: Maximum of Excitation and Emission Spectra, Lifetimes, Experimental Reduced Chi-Squared, and Experimental  $\phi$  Angle of Adsorption of RB in Gel Glasses 1–7**

	$\lambda_{\text{mex}}$ (nm)	$\lambda_{\text{mem}}$ (nm)	$\tau$ (ns) <sup>a</sup>	$\chi_R^2$ <sup>b</sup>	$\phi$ (deg)
RB in solution <sup>28</sup>	552	580	2.38		
gel 1	559	581	3.58 ± 0.29	1.1	monomers
gel 2	560	589	4.16 ± 0.10	1.2	49.0 ± 1.6
gel 3	508–562	596	4.85 ± 0.12	1.1	52.6 ± 1.4
gel 4	507–565	605	5.27 ± 0.18	0.9	54.3 ± 0.9
gel 5	506–570	609	5.52 ± 0.17	0.7	55.3 ± 0.9
gel 6	506–565	617	4.91 ± 0.14	0.3	H-dimers
gel 7	506–566	620	4.69 ± 0.13	0.4	H-dimers

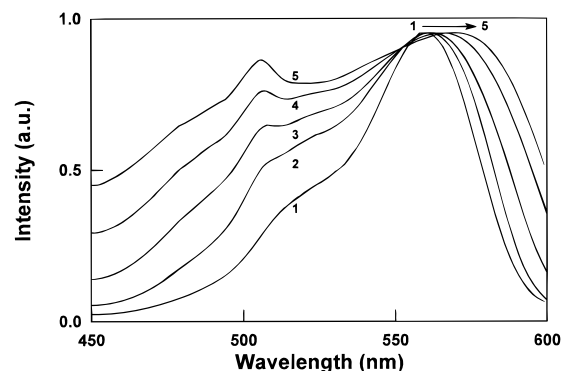
<sup>a</sup> Errors were calculated from refs 55 and 56. <sup>b</sup> Values of  $\chi_R^2$  greater than unity may indicate either the presence of systematic errors or an inappropriate model.

**Figure 2.** Lifetime measurement of RB doped gel 1 by the PRFS method.**Figure 3.** Emission spectra ( $\lambda_{\text{exc}} = 420$  nm) of RB doped gels for different increasing RB concentrations from gel 2 to gel 5.

( $S_1 \rightarrow S_0$ , internal conversion processes).<sup>63,64</sup> The observed lifetime value was in accordance with lifetimes values found by other authors for RB molecules adsorbed on solid surfaces, whether or not prepared through a sol–gel process.<sup>30,36,38,63–65</sup>

When increasing the concentration of RB molecules incorporated into the silica gel glasses (gel 1 to gel 5), two important changes were observed in the spectroscopic properties of the gel glasses: a progressive red shift in the emission maximum spectra (Figure 3) and an increase in the lifetime values (Table 2). The photophysical properties of such spectra are characteristic of RB fluorescent J-dimers<sup>32,36,65–71</sup> and are further discussed for gel glasses 1–5.

Regarding the emission spectra, J-dimer emission bands have been reported at 610 and 625 nm.<sup>72</sup> The observation of these bands (Figure 3) will explain the red shifts observed for the emission maximum of the nonaggregated species toward the gradual formation of the aggregates as the RB concentration

**Figure 4.** Excitation spectra ( $\lambda_{\text{em}} = 640$  nm) of RB doped gels for different increasing RB concentrations from gel 2 to gel 5.

increases (gels 1–5). In addition, the excitation spectra recorded for gels 1–5 show the appearance of a new band at 506 nm and a shoulder of the principal band slightly red-shifted to 560 nm, which are also characteristic of fluorescent J-dimers (Figure 4).<sup>43</sup> Moreover, the possibility to perform the excitation spectra supports by itself the fluorescent character of these aggregates, since nonfluorescent species do not show any type of excitation spectrum.

Concerning the lifetime analysis (Table 2), the increase observed for the lifetime values is also correlated to the formation of fluorescent J-dimers. Usually, the increase of the concentration has been accompanied by a decrease in lifetime values, because the formation of nonfluorescent RB dimers (H-dimers) or contact pairs, which due to the increase of intermolecular interactions, causes the quenching of the excited states by a Foster type energy transfer.<sup>30,73–75</sup> However, inhibition of the formation of contact pairs as quenching centers is expected in our samples because of the adsorption of the RB molecules on the silica surface.<sup>27,30,76</sup>

#### Geometry of RB upon Adsorption on Silica Gel Glasses.

Formation of H-dimers or J-dimers has been related to the adsorption geometry adopted by the RB molecules on the silica surface.<sup>32,36,71</sup>  $\phi$  being the angle between the longitudinal axis of the molecule (defined by the monomer transition moments) and the adsorption surface, it is agreed that values of  $\phi$  angle between  $0^\circ$  and  $55^\circ$  resulted in J-dimers formation, while values of  $\phi$  angle higher than  $55^\circ$  lead to the formation of H-dimers.<sup>32,36,71</sup> Thus, according to simple exciton theory,<sup>77</sup> the radiative rate constant of the fluorescent dimers ( $kr_D$ ) is related to the radiative rate constant of the monomer ( $kr_M$ ) and to the geometry adopted by the monomer species as follows:

$$kr_D = 2kr_M \cos^2 \phi$$

By the calculation of  $kr_M$  from the lifetime of gel 1 (the excitation spectrum of gel 1 did not show any trace of dimers, Figure 1) and of  $kr_D$  of the gels 2–5 from their respective lifetime values (gels 2–5 excitation spectra show the appearance of fluorescent dimers species, Figure 4), the experimental  $\phi$  angle values for gels 2–5 can be calculated from the equation described above (Table 2). The calculated  $\phi$  angles for the adsorption of RB molecules in gels 2–5 were lower than  $55^\circ$ , and accordingly these were ascribed to the presence of J-dimers in these gels.

It was observed that the  $\phi$  angle value increases with the increase of the RB concentration, which is in agreement with the recently published results in ref 78, where it has been

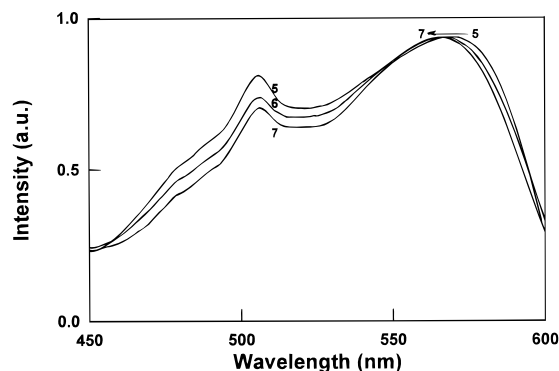


Figure 5. Excitation spectra ( $\lambda_{em} = 640$  nm) of doped RB gels 5–7.

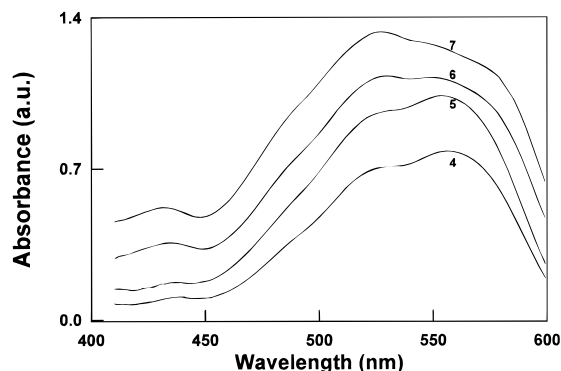


Figure 6. Absorbance spectra of RB doped gels 4–7.

concluded that the adsorption of rhodamine molecules on a surface tends to be perpendicular.<sup>78</sup> Moreover, it has to be pointed out that the  $\phi$  angle calculated for gel 5 is at the limiting value accepted for the formation of J-dimers ( $\phi \approx 55^\circ$ , Table 2). Thus, an increase of the concentration over gel 5 would yield in the conversion from J-dimers to H-dimers.<sup>32,36,71</sup> In fact, the excitation spectra of gels 6 and 7 showed a decrease in the 506 nm band intensity as well as a hidden shoulder at 560 nm (Figure 5); both observations reflect the decrease of the number of the fluorescent species related to the J-dimers. In addition, the absorption spectrum of the gels 6 and 7 showed an increase of the typical band ascribed to H-dimers around 506 nm (Figure 6).<sup>43,45,79</sup> The opposite behavior observed for the band placed at 506 nm in the excitation and absorption spectra (the intensity decreases in the excitation while increases in the absorption) reflects the fluorescent nature of the J-dimers, as well as the nonfluorescent properties of the H-dimers.

The decrease in the lifetime values of gels 6 and 7 can be addressed to a quenching effect on the excited state of the RB molecules through an intersystem crossing process caused by the appearance of H-dimers (Table 2).<sup>35,80</sup>

All these experimental facts indicate that, for the specific concentrations used in the preparation of gels 2–5, the formation of J-dimers is achieved due to the geometry conditions imposed by the silica gel cage, while over this concentration (gels 6 and 7) there is a gradual conversion from J-dimers to H-dimers. Regarding the “remaining” red shifts observed in the emission spectra for gels 6 and 7 (Figure 7), these could induce confusion because, as mentioned above, the number of J-dimers is decreasing. However, because J-dimers to H-dimers transformation is not fully completed, remaining J-dimers will be able to shift the emission spectrum as far as to 610–625 nm, where the emissions of the fluorescent J-dimer band are centered.<sup>72</sup>

**Acid Equilibria Effects.** Rather than formation of fluorescent J-dimers, other authors based their explanations for the red

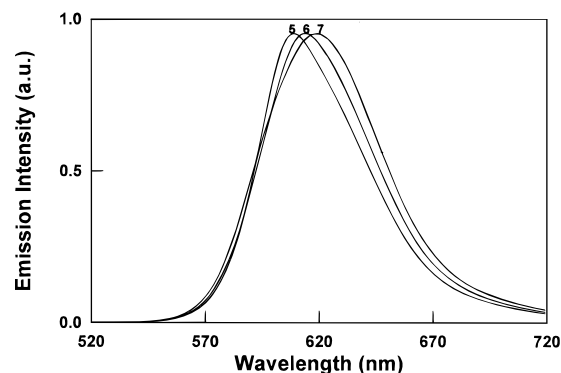
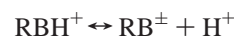


Figure 7. Emission spectra ( $\lambda_{exc} = 420$  nm) of RB doped gels 5–7.

shifts observed in the absorption and emission spectra of the acid equilibrium that take place between the protonated and the zwitterionic forms of the RB ( $RBH^+/RB^\pm$ )<sup>46–48</sup> on the presence of a carboxylic group in the RB molecule.



However, in gel glasses the maximum emission wavelength of RB remains unmodified (555 nm) over a wide pH range (pH = 1–9).<sup>41</sup> The stability of the  $RBH^+$  form over such a wide range of pH values is due to the charge restrictions that the presence of  $SiOH/SiO^-$  groups at the silica surface impose on the transition from  $RBH^+$  to  $RB^\pm$ .<sup>41</sup> Only under the isoelectric point (2.2) of the silica could formation of  $Si-OH_2^+$  groups stabilize the zwitterionic form of RB ( $RB^\pm$ ).<sup>41</sup> Furthermore, other authors have pointed out that the phenyl ring is constrained to be roughly perpendicular to the xanthene ring, which would determine the noninfluence of the carboxylic group ionization on the xanthene fluorescence properties.<sup>38,81</sup>

In addition, acid equilibria effects are not valid to justify the increase of the lifetime values, which let us assume that this is not a useful explanation for the experimentally observed behavior of gels 1–7.

**Reabsorption Processes.** A different approach also checked to explain the overall photophysical behavior described above (emission spectra red-shifted and increase of the lifetime values) is based on the reabsorption of the emitted photons (interaction between excited monomer and neighboring RB monomers) that may takes place in highly concentrated samples along the optical path way.<sup>26–30,38,49–52,75</sup> This effect requires the effective overlapping between the absorption and the emission spectra. This overlap allows the reabsorption of the low wavelengths of the emission spectrum, which determines a shift in the whole emission spectrum toward higher wavelengths (red shift). Moreover, light reabsorption may increase the lifetime values due to the promotion of a radiating trapping phenomenon.<sup>50</sup>

Although theoretically light reabsorption processes would be able to explain our experimental results, the *front face* setup (reflection mode) used to achieve the experimental measurements (for emission spectra as well as for lifetimes measurements) minimizes the reabsorption processes by the practical reduction of the optical path length.<sup>51</sup> The lack of reabsorption effects in the excitation spectra, as well as in the absorption spectra (Figures 4 and 6),<sup>51</sup> confirms that light reabsorption does not have any influence on the emission spectra and lifetimes of the RB doped gels 1–7.

## Conclusions

A determined high concentration range of RB molecules incorporated into porous silica gel glasses induces the formation



of fluorescent J-dimers. It is the first time that these species have been observed in xerogels made by the sol–gel process. The identification of these species has been carefully achieved by the analysis of the emission and excitation spectra and supported by lifetime resolution of different gel glasses containing high RB concentrations. We examined possible explanations and eliminated other mechanisms based on acid equilibrium or reabsorption processes.

The study points to the  $\phi$  angle in which the RB molecules are adsorbed on the porous surface as the most important parameter, which determines the formation of fluorescent J-dimers. Experimental lifetimes of gel glasses with different concentrations were used to calculate  $\phi$  angle in each case. The increase of the RB concentration yields an increase of this angle. The J-dimer to H-dimer transformation was clearly observed by spectroscopy and lifetimes over a concentration range.

The ability to prepare RB J-dimers doped gel glasses opens the possibility to prepare systems where a high number of emission centers would be required, without losing the fluorescence properties. Moreover, just by modifying the amount of dye incorporated to the gel glass, the maximum of the emission spectrum as well as the lifetime values may vary over a wide range of values (from 581 to 609 nm,  $\approx 28$  nm, and from 3.58 to 5.52 ns,  $\approx 2$  ns). The properties of these gel glasses should make these systems very good candidates for the preparation of solid tunable laser dyes.<sup>79,82</sup>

**Acknowledgment.** The authors are grateful to CICYT for the research grant MAT95-0040-C02-01 and to C. Alonso for technical support.

## References and Notes

- Avnir, D.; Levy, D.; Reisfeld, R. *J. Phys. Chem.* **1984**, *88*, 5956.
- Brinker, C. J.; Scherer, G. W. *Sol Gel Science*; Academic Press: San Diego, 1990.
- Hench, L. L.; West, J. K. *Chem. Rev.* **1990**, *90*, 33.
- Ulrich, D. R. *J. Non-Cryst. Solids* **1988**, *100*, 174.
- Sakka, S. *J. Non-Cryst. Solids* **1985**, *73*, 651.
- Pope, E. J. A.; Mackenzie, J. D. *MRS Bull.* **1987**, *12*, 29.
- Sanchez, C.; Ribot, F. *Proceedings of the 1st European Workshop on Hybrid Organic–Inorganic Materials (Synthesis, Properties and Applications)*; Sanchez, C., Ribot, F., Eds.; Gauthier-Villars: Paris, 1993; p 9.
- Avnir, D.; Kaufman, V. R. *Langmuir* **1986**, *2*, 717.
- Leveau, B.; Herlet, N.; Livage, J.; Sanchez, C. *Chem. Phys. Lett.* **1993**, *206*, 15.
- del Monte, F.; Levy, D. *Chem. Mater.* **1995**, *7*, 292.
- Levy, D.; Avnir, D. *J. Phys. Chem.* **1988**, *92*, 4734.
- Preston, J.; Novinson, T.; Kaska, W.; Dunn, B.; Zink, J. I. *J. Phys. Chem.* **1990**, *94*, 4167.
- Levy, D.; Serna, C. J.; Otón, J. M. *Mater. Lett.* **1991**, *10*, 470.
- Zhang, Y.; Prasad, P. N.; Burzynski, R. In *Chemical Processing of Advanced Materials*; Hench, L. L., West, J. K., Eds.; Wiley: New York, 1992; p 825.
- Boilot, J. P.; Chaput, F. *J. Sol-Gel Sci. Technol.*, in press.
- Braun, S.; Rappoport, S.; Zusman, R.; Avnir, D.; Ottolenghi, M. *Mater. Lett.* **1990**, *10*, 1.
- Ellerby, L.; Nishida, C.; Nishida, F.; Yamanaka, S. A.; Dunn, B.; Valentine, J. S.; Zink, J. S. *Science* **1992**, *25*, 1113.
- Levy, D.; del Monte, F.; Lopez-Amo, M.; Oton, J. M.; Datta, P.; Matias, I. *J. Appl. Phys.* **1995**, *77*, 2804.
- Canva, M.; Dubois, A.; Georges, P.; Brun, A.; Chaput, F.; Ranger, A.; Boilot, J. P. Sol–Gel Optics III. *Proc. SPIE* **1994**, *2288*, 276.
- Levy, D.; Esquivias, L. *Adv. Mater.* **1995**, *7*, 120 and references cited therein.
- Levy, D. *Chem. Mater.* **1997**, *9*, 2666.
- Narang, U.; Bright, F. V. *Chem. Mater.* **1996**, *8*, 1410.
- Innocenzi, P.; Kozuka, H.; Yoko, T. *J. Phys. Chem. B* **1997**, *101*, 2285.
- Martini, I.; Hartland, G. V.; Kamat, P. V. *J. Phys. Chem. B* **1997**, *101*, 4826.
- Casalboni, M.; Senesi, R.; Prossposito, P.; De Matteis, F.; Pizzoferrato, R. *Appl. Phys. Lett.* **1997**, *70*, 2969.
- López-Arbeloa, I.; Rothagi-Mukherjee, K. K. *Chem. Phys. Lett.* **1986**, *128*, 474.
- López-Arbeloa, I.; Ruiz-Ojeda, P. *Chem. Phys. Lett.* **1981**, *79*, 347.
- López-Arbeloa, F.; Ruiz-Ojeda, P.; López-Arbeloa, I. *J. Lumin.* **1989**, *44*, 105.
- López-Arbeloa, F.; Urrecha-Aguirresacona, I.; López-Arbeloa, I. *Chem. Phys.* **1989**, *130*, 371.
- Itho, K.; Chiyokawa, Y.; Nakao, M.; Honda, K. *J. Am. Chem. Soc.* **1984**, *106*, 1620.
- Kanezaki, E. *Mol. Cryst. Liq. Cryst.* **1996**, *275*, 225.
- Kemnitz, K.; Tamai, N.; Yamazaki, I.; Nakashima, N.; Yoshihara, K. *J. Phys. Chem.* **1986**, *90*, 5094.
- Wang, H.; Harris, J. M. *J. Phys. Chem.* **1995**, *99*, 16999.
- Rohatgi, K. K. *J. Mol. Spectrosc.* **1968**, *27*, 545.
- Nakashima, N.; Yoshihara, K.; Willig, F. *J. Chem. Phys.* **1980**, *73*, 3553.
- Kemnitz, K.; Yoshihara, K. *J. Phys. Chem.* **1991**, *95*, 6095.
- Muto, J. *J. Phys. Chem.* **1976**, *80*, 1342.
- Drexhage, K. H. In *Topics in Applied Physics*; Schäfer, F. P., Ed.; Springer: Berlin, 1973; Vol. 1, p 144.
- Narang, U.; Jordan, J. D.; Bright, F. V.; Prasad, P. N. *J. Phys. Chem.* **1994**, *98*, 8101.
- Avnir, D.; Kaufman, V. R.; Reisfeld, R. *J. Non-Cryst. Solids* **1985**, *74*, 395.
- Pouxviel, J. C.; Dunn, B.; Zink, J. I. *J. Phys. Chem.* **1989**, *93*, 2134.
- Fujii, T.; Ishii, A.; Anpo, M. *J. Photochem. Photobiol. A: Chem.* **1990**, *54*, 231.
- Fujii, T.; Nishikiori, H.; Tamura, T. *Chem. Phys. Lett.* **1995**, *233*, 424.
- Innocenzi, P.; Kozuka, H.; Yoko, T. *J. Non-Cryst. Solids* **1996**, *201*, 26.
- Nishikiori, H.; Fujii, T. *J. Phys. Chem. B* **1997**, *101*, 3680.
- Ramette, R. W.; Sandell, E. B. *J. Am. Chem. Soc.* **1956**, *78*, 4872.
- Faraggi, M.; Peretz, P.; Roshental, I.; Weinraub, D. *Chem. Phys. Lett.* **1984**, *103*, 310.
- Ferguson, J.; Mau, A. W. H. *Chem. Phys. Lett.* **1972**, *17*, 543.
- López-Arbeloa, I. *J. Photochem.* **1982**, *18*, 161.
- Hammond, P. R. *J. Chem. Phys.* **1979**, *70*, 3884.
- Kawahigashi, M.; Hirayama, S. *J. Lumin.* **1989**, *43*, 207.
- El-Daly, S. A.; Okamoto, M.; Hirayama, S. *J. Photochem. Photobiol. A: Chem.* **1995**, *91*, 105.
- Lackowicz, J. R.; Laczko, G.; Cherk, H.; Gratton, E.; Limkeman, M. *Biophys. J.* **1984**, *46*, 463.
- Levy, D.; Ocaña, M.; Serna, C. J. *Langmuir* **1994**, *10*, 2683.
- Bevington, P. R. *Data Reduction and Error Analysis for the Physical Sciences*; McGraw-Hill: New York, 1969; p 336.
- Gratton, E.; Linkeman, M. *Biophys. J.* **1983**, *44*, 315.
- El Baraka, M.; Deumié, M.; Viallet, P. J. *Photochem. Photobiol. A: Chem.* **1991**, *62*, 195.
- Deumié, M.; El Baraka, M. *J. Photochem. Photobiol. A: Chem.* **1993**, *74*, 255.
- Kobayashi, Y.; Imai, Y.; Kurokawa, Y. *J. Mater. Sci. Lett.* **1988**, *7*, 1148.
- Narang, U.; Wang, R.; Prasad, P. N.; Bright, F. V. *J. Phys. Chem.* **1994**, *98*, 17.
- López-Arbeloa, T.; Tapia-Estébez, M. J.; Lopez-Arbeloa, F.; Uretxa-Aguirresacona, I. *J. Lumin.* **1991**, *48–49*, 400.
- Vogel, M.; Rettig, W.; Sens, R.; Drexhage, K. H. *Chem. Phys. Lett.* **1988**, *147*, 452.
- Itho, K.; Honda, K. *Chem. Phys. Lett.* **1982**, *87*, 213.
- Eyal, M.; Reisfeld, R.; Cherniyak, V.; Kaczmarek, L.; Grabwska, A. *Chem. Phys. Lett.* **1991**, *176*, 531.
- Kemnitz, K.; Murao, T.; Yamazaki, I.; Nakashima, N.; Yoshihara, K. *Chem. Phys. Lett.* **1983**, *101*, 337.
- Korobov, V. E.; Chibisov, A. K. *J. Photochem.* **1978**, *9*, 411.
- Bojarski, P.; Matczuk, A.; Bojarski, C.; Kowski, A.; Kuklinski, B.; Zurkowska, G.; Diehl, H. *Chem. Phys.* **1996**, *210*, 485.
- Lin, C. T.; Mahlougji, A. M.; Li, L.; Hsiao, M. W. *Chem. Phys. Lett.* **1992**, *193*, 8.
- Taguchi, T.; Kirayama, S.; Okamoto, M. *Chem. Phys. Lett.* **1994**, *231*, 561.
- Chambers, R.; Kajiwar, T.; Kearns, D. R. *J. Phys. Chem.* **1974**, *78*, 380.
- Kemnitz, K.; Yoshihara, K.; Tani, T. *J. Phys. Chem.* **1990**, *94*, 3099.
- Vyshkvarko, A. A.; Kiselev, V. F.; Paschenko, V. Z.; Plotnikov, G. S. *J. Lumin.* **1991**, *47*, 327.
- Liang, Y.; Moy, P. F.; Poole, J. A.; Ponte Goncalves, A. M. *J. Phys. Chem.* **1984**, *88*, 2451.
- Nasr, C.; Liu, D.; Hotchandani, S.; Kramat, P. V. *J. Phys. Chem.* **1996**, *100*, 11054.
- Kasha, M.; Rawls, H. R.; El-Bayoumi, M. A. *Pure Appl. Chem.* **1965**, *11*, 371.
- Porter, G. *Proc. R. Soc. London, Ser. A* **1978**, *362*, 281.

- (77) McRae, E. G.; Kasha, M. *J. Chem. Phys.* **1961**, *11*, 38.
- (78) Morgenthaler, M. J. E.; Meech, S. R. *J. Phys. Chem.* **1996**, *100*, 3323.
- (79) Selwyn, J. E.; Steinfeld, J. I. *J. Phys. Chem.* **1972**, *76*, 762.
- (80) Ballet, P.; Van der Auweraer, M.; De Schyver, F. C.; Lemmtyinen, H.; Vuorimaa, E. *J. Phys. Chem.* **1996**, *100*, 13701.
- (81) Sadkowsiki, P. J.; Fleming, G. R. *Chem. Phys. Lett.* **1978**, *57*, 526.
- (82) Rahn, M. D.; King, T. A. *Appl. Opt.* **1995**, *34*, 8260