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OPTICAL PROPERTIES OF DYE MOLECULES ADSORBED ON FRACTAL STRUCTURES

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We present preliminary measurements of the optical properties of Rhodamine B molecules adsorbed or trapped in porous matrices such as Vycor 7930 glass, silica xerogels and aerogels. The electronic transfer between donor and acceptor molecules adsorbed on such fractal structures is also discussed; a fast sub-picosecond resolution experiment is proposed to study this process.

1. Introduction

Porous glasses such as Vycor 7930, aerogels and xerogels are typical self-similar structures with dilatation symmetry referred to as fractals [1]. In condensed matter physics other disordered systems, such as linear and branched polymers, surfaces resins, proteins etc., can also be characterized by a fractal geometry over the microscopic scale.

These structures are described by three distinct dimensions:

d – the spatial dimension of the Euclidean space.

$\bar{d}$ – The fractal dimension which relates the number of sites $N(R) \sim R^{\bar{d}}$.

$\bar{\bar{d}}$ – The spectral dimension (fracton) which characterizes the density of states and the time dependence of the number of sites visited $N(t) \sim t^{\bar{\bar{d}}/2}$ [2–4].

Klafter and Blumen [5] have recently calculated the ensemble averaged decay of an excited donor molecule due to randomly distributed traps (acceptor molecules) deposited on a fractal structure of Hausdorff dimension $\bar{d}$. While for regular lattices the direct (unistep) and indirect (multistep) trapping and reaction processes are both governed by the Euclidian dimension d, for fractal structures however, the direct processes (respectively the multistep processes) must be described by the Hausdorff dimension $\bar{d}$ (respectively the multistep spectral dimension $\bar{\bar{d}}$). For low density of acceptors (probability of the

occupation of fractal sites $p \ll 1$) and for direct trapping, the survival probability $\psi(t)$ of the excited donor is given by

$$\psi(t) = \exp\left[-pA\left(\frac{t}{\tau}\right)^{d/s} - \frac{t}{\tau}\right],$$

where s is the order of the multipolar interaction, τ is the radiative decay lifetime of the donor, A is a time independent proportionality factor.

Even et al. [6] have recently tested this model studying the direct, long range, singlet–singlet intermolecular electronic energy transfer EET between Rhodamine B (RB, donor molecule) and Malachite Green (MG, acceptor molecule) trapped on the inner surface of a porous glass (Vycor 7930) by measuring the fluorescence decay of the RB + MG system after a short laser pulse (5 ps) excitation of the RB at 573 nm. The value found for the fractal dimension was $\bar{d} = 1.74 \pm 0.12$ for effective concentrations of Rhodamine $\bar{C}_A = 5.1 \times 10^{-4}$ M and of Malachite Green $\bar{C}_A = 5.1 \times 10^{-4}$ M. $\bar{C}_D = 6 \times 10^{-5}$ M.

We have recently started a similar study with porous glass Vycor 7930, aerogels and xerogels doped with the same dyes. The technique to be used is however different and is briefly described. Preliminary results are described of some optical properties of Rhodamine B adsorbed or trapped in various porous matrices.

2. Sample preparation

2.1. Porous Glass Vycor 7930

Samples were cut in small plates of $5 \times 5 \times 1$ mm³ and dipped for 48 h into methanol dye solutions of various concentrations. They were dried in vacuum for 24 h at ambient temperature. The samples were easily leached in methanol but not in water.

2.2. Silica xerogel

Doped silica xerogels were prepared by mixing methanol dye solutions with TMOS and water (molar proportion 4 to 1). The samples were dried at ambient temperature for one week. These glasses were neither leachable in water nor in methanol; this shows that the dye molecules are either completely trapped in rigid cases or in pores having a rigid entrance opening smaller than the diameter of the dye molecules.

2.3. Silica aerogels

Silica aerogels were prepared by mixing an equal volume of methanol and TMOS and adding water up to a molar ratio of $H_2O/TMOS = 4$. The wet gels were aged for a few days and then dried using the hypercritical technique developed by Woignier [7]. The incorporation of the dye solutions was similar

to that in section 2.1. These glasses are only slightly leachable in water but easily leached in methanol.

3. Absorption and luminescence spectra

An example of the absorption spectra of Rhodamine B in the various matrices is shown in fig. 1 for (a) pure methanol solution (8×10^{-4} M), (b) a Vycor glass prepared with the same solution and (c) a xerogel (7.1×10^{-3} M).

Fig. 2 shows the absorption spectra of the Vycor samples prepared with different Rhodamine B concentrations in methanol. Several preliminary observations can be drawn. The absorption constant of the Rhodamine B is much higher for the Vycor plates than for the solutions. This effect depends on the dye concentration in the solution and is all the greater the smaller the dye concentration (factor ~ 10(resp. ~ 2) for $C = 2 \times 10^{-4}$ M (resp. $C = 10^{-3}$ M)). For the Vycor samples the position of the main absorption band in the visible is strongly dependent on the dye solution concentration. This indicates that the porous structure is very selective with respect to aggregation processes. The nature of the silica groups on the wall of the silica cage (silanol Si–OH and/or siloxanes Si–O–Si) is probably responsible for this variation. Our results indicate that monomers are preferentially adsorbed and that the dimer concentration stays low even for solution concentrations up to 10^{-3} M. This is an important result since the dimerization and aggregation of laser dyes have strong effects on the spectral and lasing properties and is the main cause for concentration quenching of the dye luminescence. The shift observed in absorption is also reflected in emission. Fig. 3 shows the emission spectra observed for 4 Vycor samples prepared with different solution dye concentration.
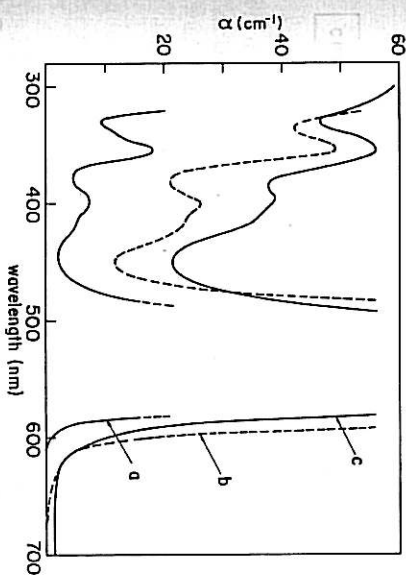

Fig. 1. Optical absorption spectra normalized to a sample thickness of 1 cm of Rhodamine B in: a: methanol solution $C = 8 \times 10^{-4}$ M; b: a Vycor glass prepared by dipping in the same solution (Glass 4); c: a Xerogel ($C = 7 \times 10^{-3}$ M).
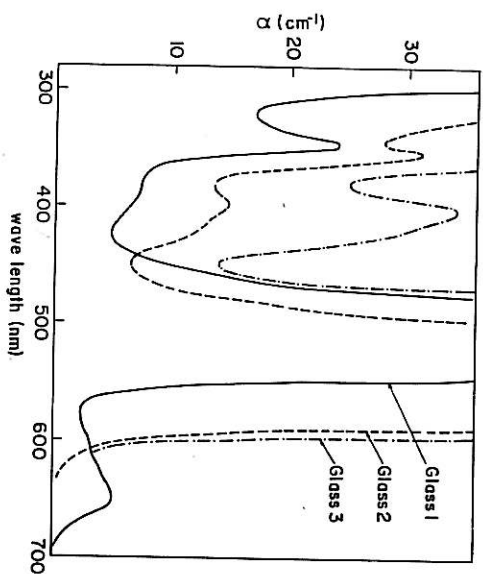
Fig. 2. Optical absorption spectra of Vycor porous glasses prepared with various concentrations of Rhodamine B in methanol. Glass 1: $C = 2 \times 10^{-4}$ M in solution. Glass 2: $C = 2 \times 10^{-3}$ M in solution. Glass 3: $C = 8 \times 10^{-4}$ M in solution.

Fig. 3. Emission spectra of the same Vycor porous glasses excited by a pulse nitrogen laser $\lambda = 337$ nm, ~ 200 kW.

4. Optical technique for EET studies

Fig. 4 shows schematically the energy levels of Rhodamine B and Malachite Green. Rhodamine B molecules are exited by a fast laser pulse at 310 nm ($\Delta t \sim 80 \times 10^{-15}$ s) obtained by frequency doubling a colliding pulse mode-
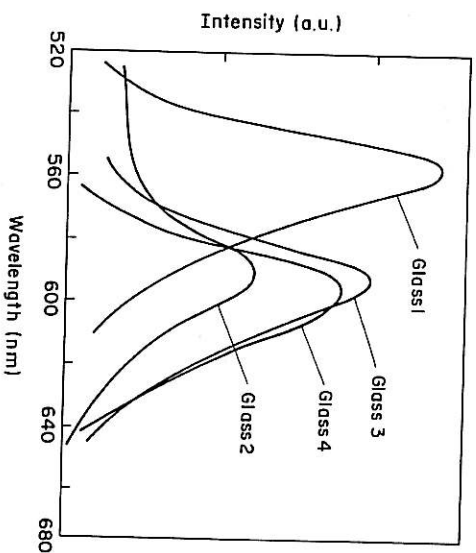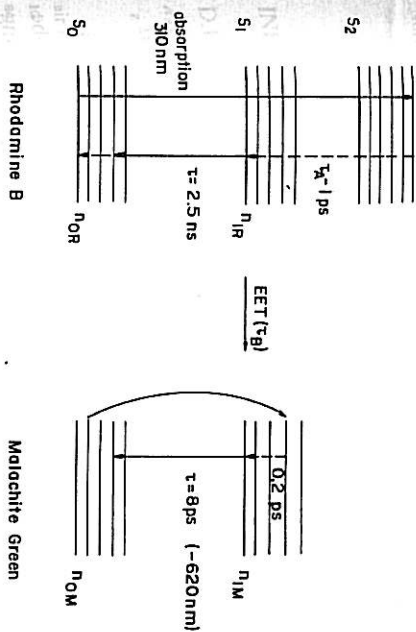
Fig. 4. Schematic energy levels of Rhodamine B and Malachite Green showing the absorption, emission and the electronic transfer (EET) occurring during the optical cycle.

locked dye laser (CPM) emitting 20 mW at 620 nm with a 100 MHz frequency [8]. In a time shorter than 10^{-12} s the excited molecules relax to the lower vibrational S_1 singlet state. From this level the electronic energy is either transferred to the Malachite Green molecules or emitted as fluorescence. To probe the decay of the relaxed population n_{IR} we can use the 620 nm beam which can be time delayed ($0 < \Delta t < 2 \times 10^{-9}$ s) with respect to the 310 nm excitation beam. The experimental arrangement used is shown in fig. 5.

The probe beam will suffer two effects: it will be amplified proportionally to the Rhodamine B population n_{IR} since these molecules have a high stimulated emission cross-section at 620 nm (gain) and it will also be absorbed by the Malachite Green molecules which have a high absorption cross-section
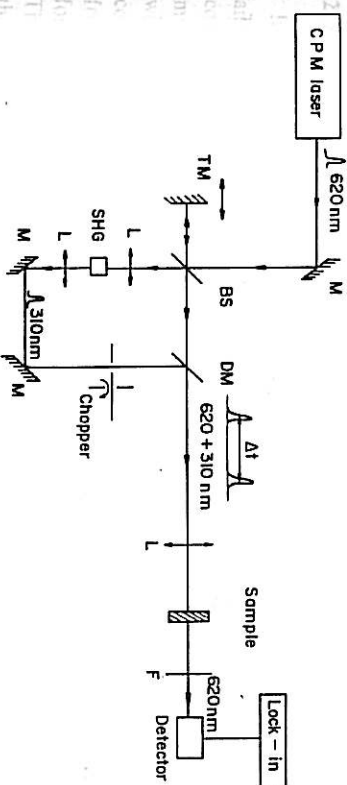

Fig. 5. Proposed optical arrangement of probe the decay of the excited dye molecules with fast subpicosecond transmission pulse delay spectroscopy. M = mirror; L = lens; TM = translating mirror; BS = beam splitter; DM = dichroic mirror; F = low pass optical filter. The time delay can be adjusted between 0 and 2×10^{-9} s.
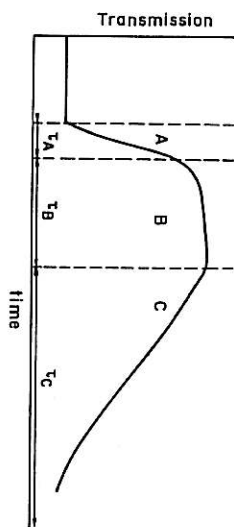
Fig. 6. Expected time variation of the transmitted light intensity $\tau_A = 1 \times 10^{-12}$ s, $\tau_B = 8 \times 10^{-12}$ s and $\tau_C \gtrsim 1 \times 10^{-9}$ s (see text).

at this wavelength (maximum peak absorption). The transmission of the probe beam should vary in a manner similar to the scheme shown in fig. 6. During the excitation, the transmission of the probe beam will increase due to the gain effect and the decrease of the ground state population n_{0R} of the Malachite Green which are promoted to their excited state through the electronic energy transfer (region A and B) with characteristic times $\tau_A = 10^{-12}$ and $\tau_B \sim 8 \times 10^{-12}$ s and then will fall off to its initial value during the decay of n_{1R} (and n_{1M}) with a characteristic time $\tau_C \gtrsim 1 \times 10^{-9}$ s (region C).

The subpicosecond resolution will allow us to observe two interesting phenomena. One is related to the fast relaxation of the Rhodamine B excited molecule to the lowest singlet excited state S_1 (region A). This is an intramolecular process and should not be drastically affected by the fact that the molecules are adsorbed or trapped in a porous glass. The second reflects the building up of the excited state population of the Malachite Green (region B). The characteristic time constant should be of the order of the decay time of the Malachite Green ($\sim 8 \times 10^{-12}$ s) and should be affected by the fractal structure of the matrices. The last region C will definitely be affected by the nature of the fractal structure and the characteristic time constant must be smaller than the decay time of the Rhodamine B alone.

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