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Reverse saturable absorption in solid xerogel matrices

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Aluminophthalocyanine (APC) and fullerene carbon 60 (C_{60}) have been studied engaged in different silica matrices. The reverse saturable absorption properties of these doped xerogels have been compared to those of reference solutions of APC and C_{60} . We show that reverse saturable absorber molecules retain their properties even when they are enclosed in the pores of a solid xerogel matrix.

In most dye chromophores, an increase in incident intensity leads to an increase in the transmission which becomes nonlinear at high intensities. Such molecules are therefore called saturable absorbers. Some chromophores, on the contrary, become less transparent as the incident intensity increases and are called reverse saturable absorbers. The use of both types of chromophores has been suggested in the last few years, especially in laser cavities as mode locking or pulse-shaping media¹⁻³ or as optical limiters.⁴

Most authors propose a simple energy-level model to describe saturable as well as reverse saturable absorption (Fig. 1). The incident photons excite absorber molecules from the ground state S_0 to the first excited state S_1 with an absorption cross-section $\sigma_{gr}(\lambda)$. The excited molecules then relax very rapidly to the lowest energy levels of S_1 . From there the population of the first excited state may either decay to the ground state with an absorption recovery time τ_{gr} or be excited to a higher excited state S_2 by absorbing incident photons; this excited-state absorption is characterized by a cross-section $\sigma_{ex}(\lambda)$. At a given incident wavelength λ , if $\sigma_{gr} > \sigma_{ex}$ the molecule behaves like a saturable absorber. On the opposite, if the absorption cross section from the first excited state S_1 up to a higher excited state S_2 is larger than the absorption cross section from the ground state S_0 to the first excited state S_1 ($\sigma_{ex} > \sigma_{gr}$), the molecule is a reverse saturable absorber. Note that two types of applications of a reverse saturable absorber in a laser cavity exist depending on the values of the first excited state recovery time τ_{ex} and of the incident pulse width τ_L : molecules with $\tau_{ex} > \tau_L$ may be used for pulse smoothing or power limitation, and reverse saturable absorbers with $\tau_{ex} < \tau_L$ lead to pulse shortening or energy limitation.

Reverse saturable absorption has already been observed with many molecules in solution.^{5,6} Do these molecules still behave like reverse saturable absorbers when they are enclosed in a solid medium, for example in a xerogel matrix, as recent results⁷ seem to indicate with APC? Should this be the case, their application as optical limiters in solid state lasers would be of great interest. To answer this question, we have studied two types of reverse saturable absorbers engaged in the pores of a gel matrix: organic ones, like aluminophthalocyanine (APC), and in-

organic ones, e.g., fullerene carbon 60 (C_{60}).

Oxide gel matrices have been prepared by the sol-gel method using metal alkoxides as precursors. In all cases, the initial sol was prepared with a mixture of both silicon (Si) and zirconium (Zr) precursors in an organic solvent: tetraethoxysilane $Si(OC_2H_5)_4$ (TEOS) or one of its organic-inorganic hybrid derivatives was used as a silicon precursor, while zirconium butoxide $[Zr(OBu)_4]$ provided zirconium atoms. Chromophores were added to this initial solution: aluminophthalocyanine was enclosed in three different types of matrices derived from either TEOS, methyltriethoxysilane (MTEOS) or vinyltriethoxysilane (VTEOS), and the solvent used was ethanol (EtOH). For C_{60} , we used benzene (C_6H_6) as the solvent and the silicon precursor was vinyltriethoxysilane (VTEOS). The initial doping concentrations were 4×10^{-4} mol/l for APC and 1.4×10^{-5} mol/l for C_{60} .

Gel samples were obtained by slow hydrolysis condensation of such alkoxide solutions in a wet atmosphere. As previously reported,⁸ this process leads after complete drying to clear and dense xerogels which exhibit a closed porosity. In xerogels, organic groups (methyl- CH_3 or vinyl- $CH=CH_2$) still remain attached to the silicon atoms and may induce modifications on chromophore molecule/gel

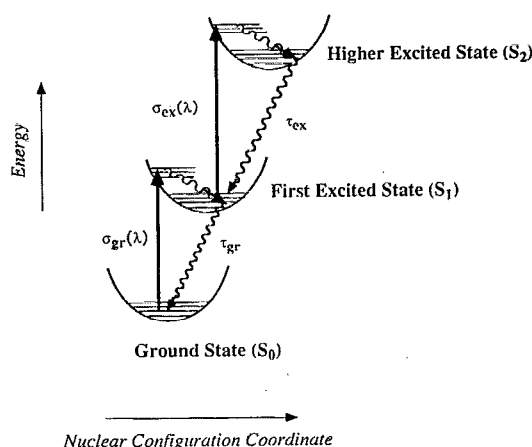


FIG. 1. Classical energy-level model of saturable and reverse saturable absorbers.

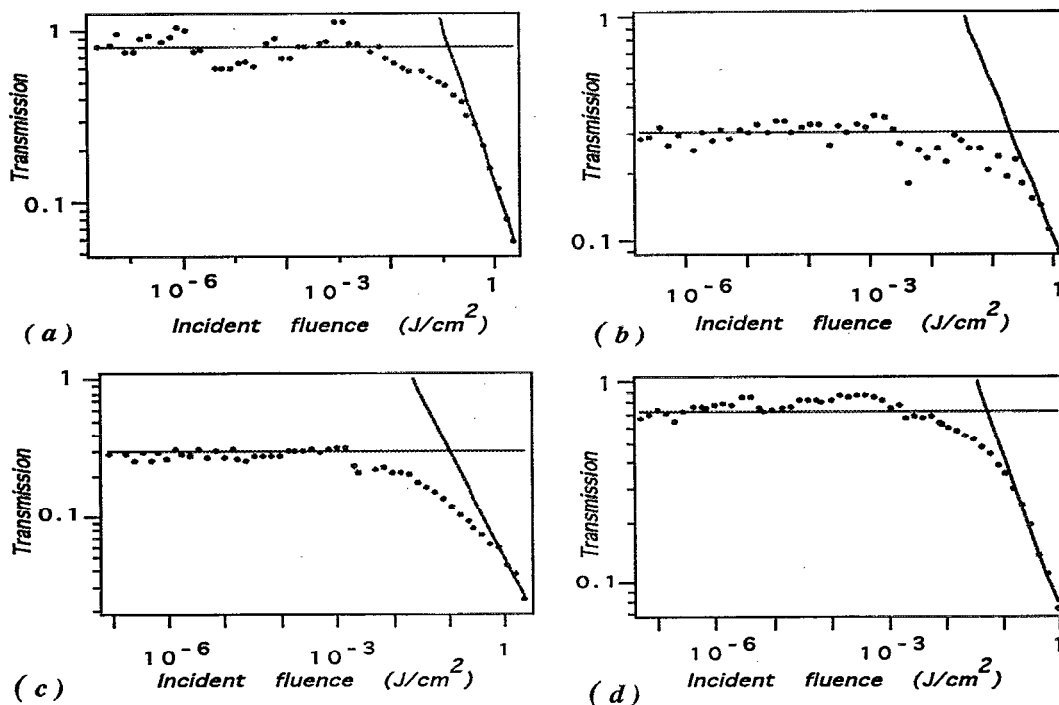


FIG. 2. Transmission of APC vs incident fluence: (a) in an ethanol solution, (b) in a TEOS matrix, (c) in a MTEOS matrix, (d) in a VTEOS matrix.

matrix interactions. We have already shown that such modifications occur in gels doped by a saturable absorber (Malachite Green)^{9,10} where both the size and the chemical composition of the substituted organic groups notably modify those interactions and consequently the recovery times of the excited dye molecules.

Xerogel samples were about 1 mm thick. In order to compare the results obtained, respectively, on the gel samples and on reference solutions, these solutions were placed in 1 mm thick cells. Drying of the xerogels classically involves an important shrinkage of the samples, leading to an increase of the actual dye concentration. Therefore the dye concentrations of our reference solutions have been chosen to be approximately the same as the dye volumic concentrations in the solid matrices.

The reference solution of APC was prepared with ethanol C_2H_5OH as the solvent, with a concentration of 4×10^{-3} mol/l, which is supposed to be the actual APC volumic concentration in the gel sample after shrinkage (whereas its concentration in the original sol was 4×10^{-4} mol/l, i.e., assuming that shrinkage reduces the volume to the tenth of its initial value). C_{60} was studied with benzene C_6H_6 as the solvent, with a concentration of 1.4×10^{-4} mol/l in the solution and in the final xerogel.

Both series of measurements (successively on gel samples and on reference solutions) were made under the same experimental conditions. Incident radiation consisted of an 8 ns long pulse at a wavelength $\lambda=532$ nm obtained from a frequency doubled Nd-YAG laser with energies up to 5 mJ. The laser beam was focused on the samples with a diameter of about 500 μ m and transmitted light was received and measured with a calibrated photodiode.

Absorption spectra of the reverse saturable absorbers,

both in solutions and in gels, show that the green incident radiation (at $\lambda=532$ nm) is on the short wavelength edge of the principal absorption band of these molecules.

Figure 2 shows the evolution of the transmission of aluminophthalocyanine molecules as a function of the increasing incident fluence (energy per surface unit), in solution (a) as well as enclosed in a gel matrix (b), (c), and (d). Classical behavior⁵ is observed in the ethanolic solution of APC [Fig. 2(a)]. Above a region where the transmission is initially linear and constant, it breaks down very rapidly beyond a fluence threshold of about 10^{-1} J/cm². Fluence thresholds are estimated as the point of intersection between the straight lines corresponding to each region of the graphs (see linear interpolation on Figs. 2 and 3). Values of the nonlinear threshold intensity I_{th} are obtained by dividing these fluence saturation thresholds by the duration of the optical pulses (8 ns). The constant part of the transmission curve (linear absorption) leads, for APC in solution, to a value of about 7×10^{-18} cm² for the ground-state absorption cross-section σ_{gr} which is in agreement with previous studies^{1,2} on this type of organic molecules. Assuming that the incident nonlinearity threshold intensity I_{th} can be given by:¹

$$I_{th} = h\nu / \sigma_{gr} \tau_{gr} \quad (1)$$

where $h\nu$ is the energy of an incident photon, the value of I_{th} yields a ground-state recovery time τ_{gr} of about 3 ns. These first measurements do not allow us to give a precise value of the excited-state absorption cross-section σ_{ex} , but the decrease of the transmission beyond I_{th} clearly shows that $\sigma_{ex} > \sigma_{gr}$.

Figures 2(b)–2(d) present the same evolution study when APC is engaged in, respectively, TEOS, MTEOS,

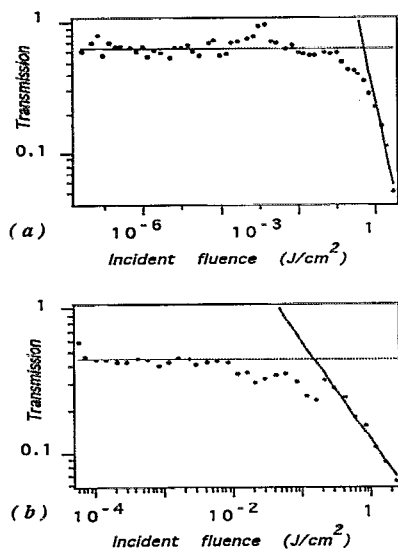


FIG. 3. Transmission of fullerene C_{60} vs incident fluence: (a) in a benzene solution, (b) in a VTEOS matrix.

and VTEOS based silica matrices. As we expected, a good reverse saturable absorption behavior can be obtained even when the molecules are enclosed in a solid gel matrix. In all instances, the value of I_{th} does not seem to be notably different from that measured in solution. Values of σ_{gr} calculated from these curves (10^{-18} – 5×10^{-18} cm^2) are slightly smaller than that obtained in the ethanol solution. Recovery times τ_{gr} (over 10–20 ns) are longer than the one evaluated when the aluminophthalocyanine molecules freely move in their ethanolic solution.

The same comparison can be made between the transmission evolution of fullerene C_{60} in a benzene solution [Fig. 3(a)] and that of C_{60} in a VTEOS gel matrix [Fig. 3(b)]. Even encaged in a solid medium, the C_{60} molecule clearly remains a reverse saturable absorber. The nonlinearity threshold (between 10^{-1} and 1 J/cm^2) does not significantly vary when the molecules are enclosed in the pores. On the contrary, the linear transmission value of the doped gel sample at 532 nm is smaller than that of the benzene solution. Consequently the ground-state absorption cross-section σ_{gr} slightly decreases from 12×10^{-17} cm^2 in the benzene solution to 7×10^{-17} cm^2 in the gel matrix. Besides the ground-state absorption recovery time τ_{gr} follows the same evolution as for aluminophthalocya-

nine: it increases from about 50 ps in solution to about 270 ps when C_{60} dopes a xerogel matrix.

In both cases, APC and C_{60} , we thus found that the nonlinearity (or saturation) threshold I_{th} is not significantly modified when the molecules are trapped in the gel pores. Nevertheless, their ground-state absorption cross-section σ_{gr} seems to slightly decrease, whereas their ground-state absorption recovery time τ_{gr} increases. According to Eq. (1), these opposite evolutions do not contradict the relative invariability of I_{th} we observed. Moreover, we have already shown⁹ in the case of a saturable absorber (Malachite Green) that, in the type of xerogel we use, the movements of the dye molecules are impeded by the solid matrix. This generally leads to an increase in the $S_1 \rightarrow S_0$ relaxation time, i.e., in τ_{gr} in comparison to that measured in solution. This interpretation seems to be also valid for reverse saturable absorbers like APC. Further experiments are required to show the influence of the features (size, polarizability,...) of the organic groups (methyl, vinyl) which cover the internal surface of the xerogel pores on the values of σ_{gr} , τ_{gr} , σ_{ex} and τ_{ex} as well as to directly measure the ground-state recovery time τ_{gr} .

As a conclusion, we have shown that usual reverse saturable absorbers still possess their characteristic properties when they are encaged in the pores of a solid xerogel matrix. Only σ_{gr} and τ_{gr} seem to have slightly different values from those observed with the same molecules in solution, σ_{gr} decreasing while τ_{gr} becomes longer. These materials may have large applications as reverse saturable absorbers for mode locking or pulse shaping in solid medium lasers or as solid optical limiters.

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