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# Ultrafast induced excited state absorption in organically doped xerogels

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Vanadyl-phthalocyanines have been trapped in different silica-based xerogel matrices. Nonlinear ‘reverse saturable absorption’ behavior has been observed for femtosecond and nanosecond pulse excitation at 620 nm. Nanosecond experiments could be fitted using a classical 3-energy-level model. However, the time scales are such that the behavior observed with femtosecond pulses cannot be correctly interpreted with the same model. © 1999 Elsevier Science B.V. All rights reserved.

Some organic molecules present, at given wavelengths, reverse saturable absorption (RSA) behavior: they are transparent for low-energy pulses and absorbent for high-energy optical pulses. The reasons are that the excited states are more absorbent than the ground state at certain wavelengths, and that these first excited states have long lifetimes. Such materials should be of great interest for applications like optical limiting and they have already been extensively studied in solution [1–4]. Furthermore, their optical-limiting function can be enhanced by coupling effective two-photon absorption with reverse saturable absorption [5]. They have also been

recently shown to strongly modify laser dynamics when they are inserted in a laser cavity [6]. Using the sol–gel process, which allows the incorporation of organic molecules in solid vitreous matrices at low temperature, it is possible to trap some of these molecules in solid xerogel matrices [7–10].

Chloro-aluminum-phthalocyanines (ClAlPc) doped xerogels have been demonstrated to act as reverse saturable absorbers when excited at 532 nm by 10 ns or 30 ps pulses [11,12]. Furthermore, a detailed analysis concerning ClAlPc in solutions has been reported with 30 ps excitation pulses at 532 nm [13]. Characteristic parameters as excited-state recombination time (7 ns) and reorientational time (7 ps) have been determined experimentally with precision. One can now wonder about the behavior that would be recorded in a femtosecond timescale, i.e. with pulses much shorter than these characteristic

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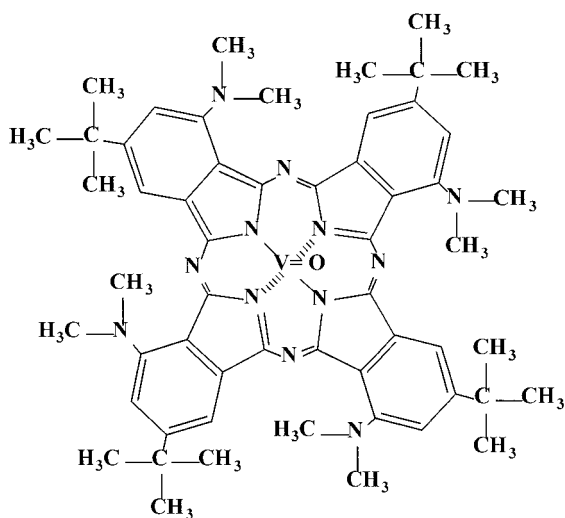


Fig. 1. Representation of the vanadyl 3,10,17,24-tetra-(tert)butyl-1,8,15,22-tetrakis(dimethylamino)-29H,31H-phthalocyanine (called VPC).

times. However, ClAlPc present an intense absorption band (Q band) near 670 nm, and additional vibrational bands between 600 and 670 nm. Therefore, they are not adapted to realize reverse saturable absorption experiments with current femtosecond lasers emitting in the red part of the visible spectrum. In order to obtain materials that are low absorbent in the whole visible range, it is necessary to use molecules that present a Q-band shifted to the near infrared. In the case of phthalocyanines, different parameters influence the position of the Q-band: the substituents, the nature of the metal atom and of the macrocycle. In particular, highly substituted phthalocyanines and naphthalocyanines present their absorption Q-band shifted far away towards the near infrared [14,15]. However, they often present a low solubility, which makes their use in sol-gel chemistry difficult. It has been possible to synthesize vanadyl-phthalocyanine-doped xerogels. The complete name of this molecule, that will be called VPC, is given in Fig. 1. It is highly substituted, in particular with donor groups  $N(CH_3)_2$ , which leads to an absorption Q-band shifted to  $\lambda_{max} = 810$  nm. Let us note that  $\lambda_{max} = 700$  nm for non-substituted vanadyl-phthalocyanines [14,16]. Experiments could also be performed with our VPC-doped xerogels in the red part of the spectrum. Moreover, ultrafast

excited state absorption measurements could be performed in a femtosecond timescale at 620 nm (the use of this specific wavelength is imposed by our femtosecond liquid dye laser system).

Doped xerogel samples were prepared from methyl-triethoxysilane (MTEOS) or vinyl-triethoxysilane (VTEOS). The details of this type of synthesis of silica based sols and gels are given in Ref. [17]. Briefly, the hydrolysis of silicon alkoxide was performed under acidic conditions with acetone as common solvent. After several hours hydrolysis at room temperature, a small amount of amine modified silane (3-triethoxysilylpropylamine) was added. Acetonic solution of VPC was then added to yield a concentration of  $10^{-4}$  mol  $l^{-1}$ . Afterwards, the resulting sol was cast into polypropylene cylindrical-shaped moulds and sealed. Gelation occurred within one week at  $60^\circ C$ . The samples were left to dry for another 2 weeks at the same temperature. After drying, optically clear and dense inorganic-organic hybrid xerogels (60 mm diameter and 1–2 mm thick) were obtained. The absorption spectrum of the VPC-doped MTEOS matrix is presented in Fig. 2. This sample is 1.1 mm thick and the VPC concentration in the xerogel is  $\sim 3 \times 10^{-4}$  mol  $l^{-1}$ . The absorption spectrum of a VPC-doped acetone solution is presented for comparison. Both spectra are quite similar, except a slight difference of the vibronic structure of the Q-band near 720 nm. It could be due to

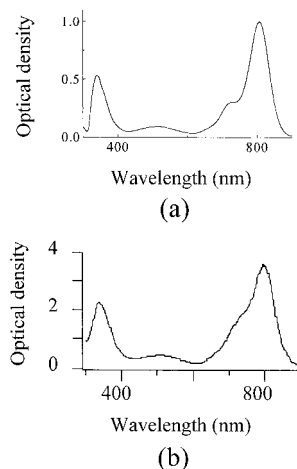


Fig. 2. Absorption spectrum of a VPC-doped acetone solution (curve a) and of the VPC-doped MTEOS sample (curve b).

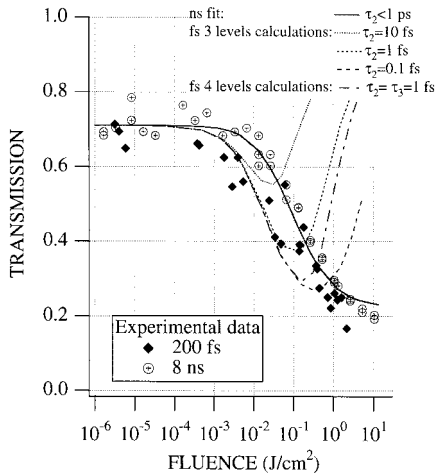


Fig. 3. Measurements of the transmission of a vanadyl-phthalocyanine (VPc) doped MTEOS matrix, as a function of incident fluence for 8 ns (circles) and 200 fs (diamonds) optical pulses. Fitting curves obtained in the cases of 8 ns with a classical 3-energy-level model, and theoretical calculations for 200 fs incident pulses using the same model, or a modified 4-energy-level model.

the aggregation of a few phthalocyanine molecules in the xerogel.

Ultrafast RSA experiments have then been realized using a VPc-doped MTEOS matrix at the wavelength of 620 nm. Experiments have been performed using 200 fs pulses issued from a passive mode-locked dye laser. We have realized single-shot measurements, so that there was no cumulative population of the excited states from one pulse to the other. As the laser output energy was very unstable, it was necessary to add a reference measurement. The transmitted energy and the incident energy were compared for each pulse. The laser beam was focused on the sample to an irradiated surface of  $\sim 25 \mu\text{m}$  radius, and was collimated through the sample. The output beam was collected using a  $f/2.5$  aperture lens. The main part of the transmitted beam was thus collected to measure nonlinear absorption properties. Other mechanisms, like nonlinear scattering or nonlinear refraction were not taken into account. The transmission of the samples was measured for incident pulses whose fluence was between  $1 \mu\text{J cm}^{-2}$  and  $2 \text{ J cm}^{-2}$ . Experimental results are reported in Fig. 3. An optical limiting behavior is clearly exhibited by the sample with femtosecond pulses. This is

the first report, to the best of our knowledge, of such a fast transmission switching process with solid state reverse saturable absorbers. Ultrafast optical limiting involving other processes had been previously demonstrated in the case of metal/semiconductor phase transition in  $\text{VO}_2$  materials [18].

The behavior of our sample has then been characterized in a nanosecond timescale for comparison. Reverse saturable absorption experiments have been performed using 8 ns optical pulses at the same wavelength of 620 nm. Pulses were issued from a sulforhodamine dye laser. It was pumped by a frequency doubled Q-switched Nd:YAG laser. The laser beam was focused with a 100 mm focal length lens on the sample to a surface of  $\sim 85 \mu\text{m}$  of radius. After propagation through the medium, the output beam was collected using a  $f/2.5$  aperture lens. The transmission of the sample was measured for different incident fluences between  $1 \mu\text{J cm}^{-2}$  and  $10 \text{ J cm}^{-2}$ . Experimental results obtained with the VPc-doped MTEOS matrix are reported in Fig. 3. A typical reverse saturable absorption behavior is observed. It must be pointed out that the nonlinear threshold (incident fluence where the transmission begins to decrease) is different for 8 ns and 200 fs incident pulses. A simplified explanation can be given using the schematic 3-energy-level model classically used and presented in Fig. 4. Let us also consider the singlet states  $S_0$ ,  $S_1$  and  $S_2$ . The transmission begins to decrease when some molecules are in the first excited state: it means that the  $S_0$ – $S_1$  transition must have been first ‘saturated’. In the case of 200 fs incident pulses, the  $S_1$  lifetime ( $\sim 1$  ns) is much longer than the pulse duration. In the

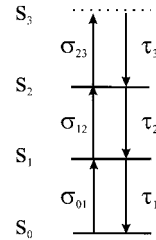


Fig. 4. (Full line levels) Classical 3-energy-level model used to interpret reverse saturable absorption, notations defined in the text. (With dashed line level) Extra excited state level may be taken into account, using a ‘ladder’ type energy diagram.

case of 8 ns incident pulses, the  $S_1$  lifetime is shorter than the pulse duration: the molecules that are excited first from  $S_0$  to  $S_1$  can decay to the ground state before the end of the pulse. The  $S_0$ – $S_1$  transition ‘saturation’ requires thus higher incident fluences and the nonlinear threshold is higher. The experimental results have been fitted using the classical 3-energy-level model used in such cases to confirm this interpretation (see the full line in Fig. 3). The model has been previously described in Ref. [12]. Three singlet states  $S_0$ ,  $S_1$  and  $S_2$  are considered. Femtosecond pulses are much shorter than the intersystem crossing decay times from singlet to triplet states. The influence of triplet states can thus be neglected in this case. We have used the same model with nanosecond pulses for sake of simplicity. In this simulation, the laser pulse is assumed to have a gaussian temporal shape. The fitting curve is presented in Fig. 3. The parameters that have been used to fit the experimental data are the following:  $\sigma_{01} = 1.3 \times 10^{-21} \text{ m}^2$ ,  $\sigma_{12} = 1.4 \times 10^{-20} \text{ m}^2$ ,  $\tau_1 = 1 \text{ ns}$ ,  $\tau_2 < 1 \text{ ps}$ , where  $\sigma_{01}$  (resp.  $\sigma_{12}$ ) is the absorption cross-section from  $S_0$  to  $S_1$  (resp.  $S_1$  to  $S_2$ ) and  $\tau_1$  (resp.  $\tau_2$ ) is the  $S_1$  (resp.  $S_2$ ) lifetime. The sample was 1.1 mm thick. The concentration of the VPc molecules in the matrix was  $3 \times 10^{-4} \text{ mol l}^{-1}$ .  $\sigma_{01}$  was determined from the linear transmission, the sample thickness, and the dopant concentration. The first excited state lifetime  $\tau_1$  was independently estimated by fluorescence decay experiments. They showed that this time was  $\sim 1 \text{ ns}$ . The second excited state lifetime was estimated to be much shorter, but nanosecond experiments did not allow to determine it precisely. Using the fitting parameters obtained in the nanosecond experiments, we have then calculated the behavior that our sample should exhibit with 200 fs incident pulses. Let us keep in mind that the use of the rate equation approximation will open to criticism for very high fluences (e.g.,  $2 \text{ J cm}^{-2}$ ) in such ultrafast regime. Coherent effects should then be considered: indeed, for the maximum irradiance to be simulated ( $10^{13} \text{ W cm}^{-2}$ ), the Rabi frequency ( $\sim 10^{13} \text{ s}^{-1}$ ) approaches the inverse rate of the phase ( $\sim 10^{14} \text{ s}^{-1}$ ) [19]. However, the rate equation approximation is well justified for smaller irradiances, and the similarity of behaviors recorded in nanosecond and femtosecond regimes is such that we have used the same rate equation analysis. Calcu-

lated curves obtained with three different values of  $\tau_2$  are presented in Fig. 3. We can observe that the 3-energy-level model gives a correct quantitative description of our observations concerning the nonlinear threshold: it is higher in the case of 8 ns pulses.

But another point must be discussed: even if the first experimental points are in good agreement with the fitting curve, the transmission should theoretically increase again for high incident fluences (‘saturation’ of the  $S_1$ – $S_2$  transition). This is not observed experimentally. We could start explaining our experimental results with the 3-energy-level model assuming  $\tau_2 < 0.1 \text{ fs}$ , which is not realistic. The problem of the ‘non-saturation of  $S_1$ – $S_2$  transition’ has been discussed in the case of HITCI-doped solutions in order to explain the behavior that was observed with 15 ps pulses at 532 nm: absorption between higher excited states has been demonstrated to become an important factor [19,20]. Our model has then been modified to take another excited state  $S_3$  into account. We have calculated the expected behavior assuming that the  $S_2$ – $S_3$  transition is present in the case of our sample (see dashed lines in Fig. 4). The fitting parameters that have been used are the following:  $\sigma_{01} = 1.3 \times 10^{-21} \text{ m}^2$ ,  $\sigma_{12} = 1.4 \times 10^{-20} \text{ m}^2$ ,  $\sigma_{23} = 3 \times 10^{-20} \text{ m}^2$ ,  $\tau_1 = 1 \text{ ns}$ ,  $\tau_2 = 1 \text{ fs}$ ,  $\tau_3 = 1 \text{ fs}$ . The  $\sigma_{23}$  absorption cross-section has been deliberately supposed to be very high. The theoretical curve obtained with this model is presented in Fig. 3. The theoretical transmission is observed to increase again for incident fluences higher than  $0.1 \text{ J cm}^{-2}$ , after ‘saturation’ of the  $S_1$ – $S_2$  and  $S_2$ – $S_3$  transitions. Experimentally, the transmission of the sample continues to decrease at  $1 \text{ J cm}^{-2}$  with 200 fs incident pulses. It thus indicates that this sole explanation of one other absorbent higher excited state is not sufficient, each molecule having to absorb a large number of photons very quickly.

Different sol–gel samples have then been tested to verify that the ultrafast behavior observed is not an exception. The environment of the VPc molecules has been first modified: they have been incorporated in a VTEOS matrix. Similar ultrafast optical limiting properties have been exhibited by this solid sample. Silicon naphthalocyanines molecules have then been incorporated in a MTEOS matrix. A reverse sat-

urable absorption behavior has been observed with 8 ns and 200 fs pulses at 620 nm. The linear transmission of the sample is 60%. A continuous decrease of the transmission is observed in the femtosecond timescale when the incident fluence becomes  $> 10^{-2}$  J cm $^{-2}$ . The transmission reaches 20% for fluences of  $> 1$  J cm $^{-2}$ . Moreover, no saturation of the absorption is observed for such high fluences.

In summary, the classical 3-energy-level model seems to be not sufficient to interpret correctly the behavior which is observed with intense 200 fs incident pulses, in the case of some phtalocyanines. Different assumptions can be done to explain the experimental measurements. The optical limiting behavior observed with intense ultrashort pulses could be partially due to the existence of two-photon absorption between the ground state  $S_0$  and an higher excited state  $S_x$ . It could also be partially explained by nonlinear scattering processes due to small absorptive aggregates or by biexcitonic decay processes from the higher excited state. Yet such ultrafast optical limiting, so similar in femtosecond and nanosecond excitation regimes, is not well understood at high fluences. Time-resolved pump and probe transmission saturation experiments have to be carried out, using the 200 fs pulses. They should enlighten this phenomenon. Nevertheless, ultrafast optical switching has been demonstrated with solid state reverse saturable absorbent materials.

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