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Spectral hole burning and electron–phonon coupling in aluminum phthalocyanine tetrasulfonate doped inorganic hosts with and without water addition

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Abstract

The earlier discovery by G.J. Small and his group of the exceptional hole burning properties of aluminum phthalocyanine tetrasulfonate (AlPT) in hyper quenched water encouraged us to look for other suitable hosts in which such properties could be preserved. The non-photochemical hole burning behavior of AlPT in various hosts: dense inorganic or hybrid xerogels, light aerogels and porous Vycor glasses soaked with dye-doped water is investigated. The crucial role played by water or the silanol groups in xerogel pores is underlined by our experiments, the hole burning efficiency becoming quite low in a hybrid xerogel or in a dried porous glass. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Spectral hole burning; Aluminum phthalocyanine tetrasulfonate; Electron–phonon coupling; Xerogels

1. Introduction

The aluminum phthalocyanine tetrasulfonate (AlPT) is a hydrosoluble dye which has demonstrated high persistent spectral hole burning performances when it is embedded in hyperquenched water [1–3], an amorphous ice prepared under extreme conditions. A flow of very small ($\sim 1\mu\text{m}$ diameter) droplets of water is hyperquenched onto a cold substrate at a few K under vacuum. Other efficient hole burning systems with AlPT have also been reported to date including

hyperquenched ethanol [3] and methanol [3], gelatin films [4], polymeric hosts like water-containing poly(2-hydroxyethylmethacrylate) [5]. In a previous paper, which is closely related to this one, we have also partly reported our results on the persistent spectral hole burning (PSHB) performances of AlPT in various inorganic hosts [6].

Our interest is motivated by the search of suitable hosts, i.e. practical solids, stable at room temperature. The hole burning mechanism reported for AlPT in hyperquenched water is believed to be due to re-arrangements occurring among the hydrogen bond links formed at the periphery of the guest hydrosoluble phthalocyanine and water molecules from the host. The high amorphous character of the host assures a large

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density of unstable TLS in the surrounding of the guest chromophore, which can explain the elevated hole burning efficiency observed for a so-called non-photochemical hole burning system.

Therefore, a natural idea is to trap the AlPT in a silicate xerogel, i.e. a dense inorganic material in which the dopant molecules can be permanently trapped in pores with nanometric sizes. With tetraethoxy-silane (TEOS) as a precursor, glass-like pure silicate xerogels in which silanol groups (Si-OH) cover favorably the surface of the pores are synthesized. Two other inorganic hosts have also been studied for comparison: a light aerogel with large size pores and a commercial porous Vycor glass [7]. For both latter systems, the AlPT molecules dissolved in water were introduced by impregnation. In the present paper, we compare and discuss the performances of these three systems, with respect to their PSHB efficiency, hole burning kinetics and electron–phonon coupling on a broad temperature range between 5 and 80 K.

2. Results and discussion

Experimental details for sample preparation and the setup used have been described in previous papers [6,8] and they will not be repeated here. However, one point should be added. It concerns the doping of the light aerogel hosts. They revealed to remain highly fragile despite a densification process performed by heating the samples up to 1000°C. The strong capillary forces due to the superficial tension of water (73 dyn/cm² at 18°C) destroyed the sample after each attempt to soak it in a dye doped water solution. Achieving the impregnation process was obtained with the

encapsulation of the AlPT dye dissolved in water in hydrophilic micelles, which form protecting drops in an hydrophobic solvent like heptane chosen to have a lower superficial tension (about 20 dyn/cm²). The micelles were created with the addition of the usual tensio-active agent AOT to the dye water solution. The characteristics of the samples studied are reported in Table 1 for comparison.

2.1. Summary of results

We first summarize the experimental results obtained and partially reported in [6]. High-resolution hole burning experiments have been performed on two dye doped xerogels TEOS:AlPT and VTEOS:AlPT, the former being a pure silicate host and the latter being a hybrid one with organic vinyl groups CH=CH₂ permanently linked to the silicate network. With typical burning power density of 3 μW cm⁻², easily detectable holes are burnt in about 1 s at 1.8 K in the mineral host. A comparatively much weaker efficiency is observed with the hybrid host, at such a point that further experiments were not continued. However, this important result demonstrates the crucial role played by the silanol groups at the surface of the pores. The temperature dependence of the homogeneous width between 1.8 and 12 K is reported in Fig. 1 for AlPT in a TEOS xerogel. By measuring a burned hole after a delay between burning and probing (up to 3 h), a hole broadening is observed, correlated with a decrease of the hole depth, the hole area remaining constant, demonstrating evidence of spectral diffusion (Fig. 2). The influence of fluence and temperature has been studied with low-resolution hole burning experiments on three purely inorganic hosts, the TEOS xerogel,

Table 1

Host	Xerogel TEOS	Xerogel VTEOS	Aerogel/AOT	Vycor/H ₂ O
Nature	Inorganic	Hybrid	Mixed	Inorganic
Density (g/cm ³)	1.3	1.3	0.5	1.5
Porosity	Closed	Closed	Open	Open
Pore diameter (nm)	1–2	1–2	9–10	4–5
“Organic carpet”	Si-OH	Si-C ₂ H ₂	H ₂ O	Si-OH, H ₂ O

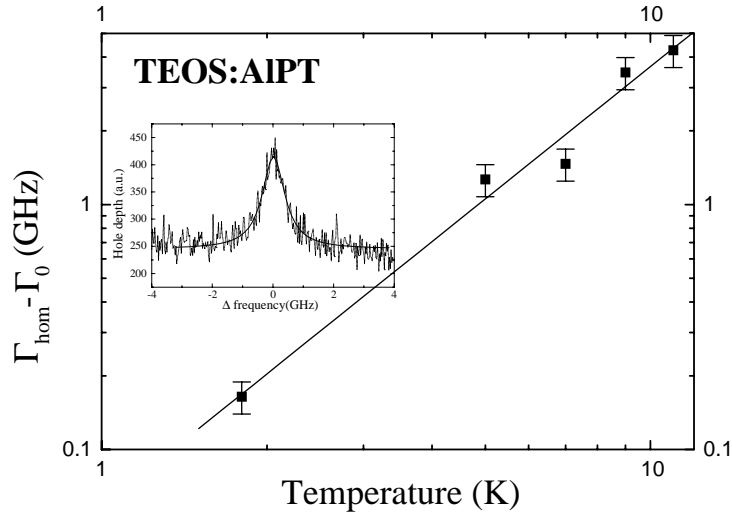


Fig. 1. Temperature dependence of the homogeneous width as resulting from high-resolution hole burning experiment on a AIPT doped TEOS xerogel sample. The inset shows an example of a hole burnt at 1.8 K, $t_b = 1$ s, $P_b = 4 \mu\text{W}/\text{cm}^2$, $\lambda_b = 679.172$ nm. The fit gives $\Gamma_{\text{hom}} = 0.06T^{1.8}$.

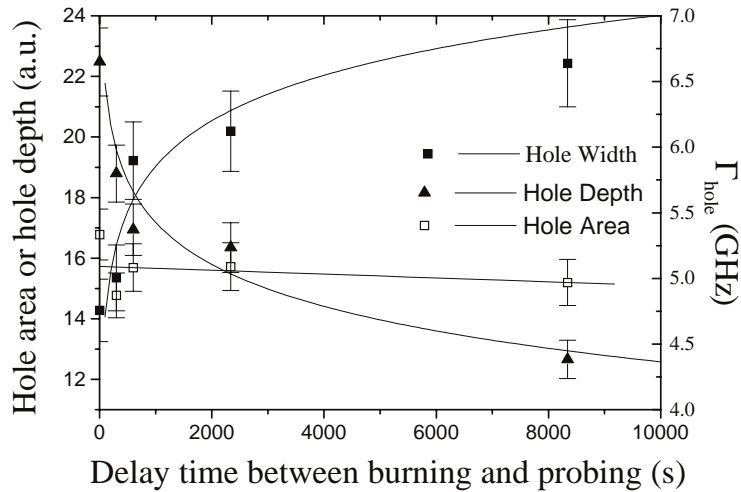


Fig. 2. Hole width, hole depth and hole area monitored at successive probing time delayed after burning showing evidence of spectral diffusion at $T = 5$ K in a AIPT doped xerogel sample.

the light aerogel and the porous Vycor glass. Efficient hole burning is observed in the three hosts studied, with the TEOS xerogel at any time and with the aerogel or the Vycor glass being introduced into the cryostat just after their immersion in a water solution containing AIPT. With dried dye doped aerogel or porous Vycor,

holes are hardly burnt using the same usual conditions as for dye doped TEOS samples. Also, this result demonstrates the necessary presence of water in these open porous hosts. The dependence of burned holes with the burning time and the temperature at burning for AIPT in TEOS and in Vycor/ H_2O is shown in Fig. 3. The hole profiles

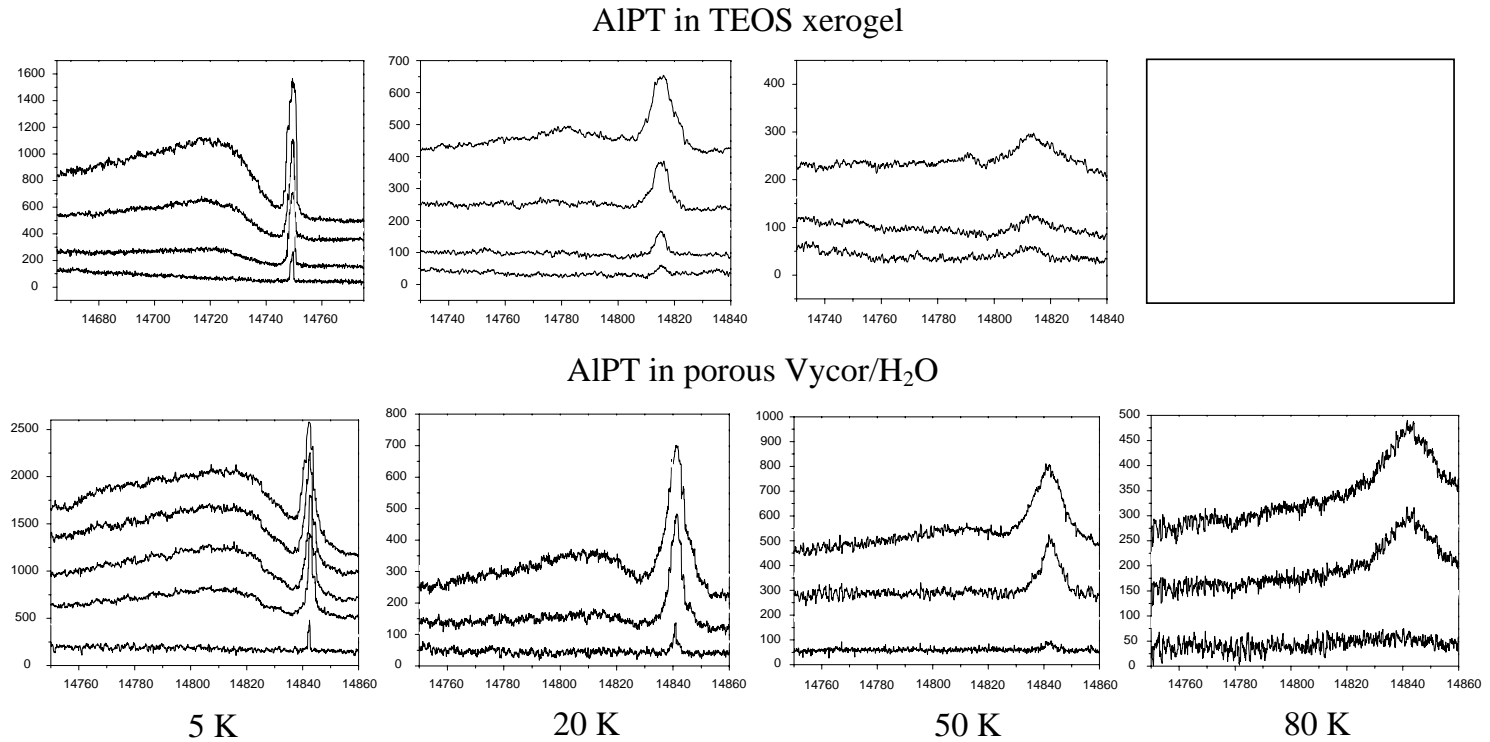


Fig. 3. A sampling of different recorded hole spectra for different temperatures (horizontal spread) and for different burning time (vertical spread) between 1 and 3200 s. Records on top are from AlPT doped TEOS xerogel and the blank rectangle means that no hole was registered at 80 K. Records on bottom are from AlPT doped porous Vycor/H₂O glass.

drawn in the figure are obtained from the change of the optical density before and after burning as

$$\Delta\text{DO}(v) = \text{DO}(v)_{\text{before burning}} - \text{DO}(v)_{\text{after burning}}.$$

Some noticeable experimental differences between the two inorganic hosts are apparent in the figure. First, the shape of the pseudo-phonon side band (PSB) recorded at 5 K under high fluence appears with a single peak maximum at 30 cm^{-1} from the zero-phonon line (ZPL) in TEOS and with two peaks respectively at 35 and about 80 cm^{-1} in Vycor/ H_2O . Second, the highest temperature at which PSB is still observed is about 50–60 K for AlPT in TEOS and 80 K or a little higher for AlPT in Vycor/ H_2O . In the latter host, detectable persistent holes were burnt in 10 s (fluence = 14 mJ). A minimum homogeneous FWHM of about $9\text{--}10\text{ cm}^{-1}$ has been measured, to be compared with the value of 3.2 cm^{-1} reported by Small for AlPT in buffered HGW at 77 K [4]. We also notice that the hole shape recorded at 80 K resembles the line shape reported by Mikami et al. [9] for AlPT dissolved in interstitial water in a poly(acrylamide) gel, also at high temperature (110 K) in fluorescence line narrowing experiments. We used a simulation program to model the set of data shown in Fig. 3, playing with fluence and temperature changes.

2.2. Details of the simulation program

We followed a simple model for hole burning early proposed by Friedrich and Haarer [10] and re-visited by Jankowiak et al. [11]. The homogeneous spectrum of one molecule is modeled by a Lorentzian profile $L(v)$ for the zero-phonon line (ZPL) accompanied with a phonon side band (PSB) [11]:

$$h(v - v') = \alpha L(v - v') + \sum_{i=0}^{\infty} e^{-S} \sum_{j=0}^i \frac{(nS)^{i-j} ((n+1)S)^j}{(i-j)!j!} \times L_j(v - v' - (i-2j)\omega_m),$$

where α is the Debye–Waller factor: $\alpha = e^{-(2n+1)S}$, n is the mean occupation number of a phonon mode and S the Huang–Rhys factor which

characterize the linear electron–phonon coupling. The unburned inhomogeneous band results from the convolution of the homogeneous profile with the inhomogeneous distribution assumed to be a Gaussian. Whereas the $L(v - v')$ is a normalized Lorentzian function with a FWHM $\Gamma_{\text{hom}}(T)$ to express the homogeneous profile of the zero-phonon line, the phonon side band is simulated with the combination of a Lorentzian profile on one side and a Gaussian profile on the other side as

$$L(v - v' - (i-2j)\omega_m) = \frac{\Gamma_i/2\pi}{(v - v' - (i-2j)\omega_m)^2 + (\Gamma_i/2)^2}$$

if $v > (i-2j)\omega_m$

$$L(v - v' - (i-2j)\omega_m) = \frac{1}{\Gamma_i} \sqrt{\frac{\ln 2}{\pi}} \times \exp \left[- \left(\frac{v - v' - (i-2j)\omega_m}{\Gamma_i / \sqrt{2 \ln 2}} \right)^2 \right]$$

if $v \leq (i-2j)\omega_m$.

This allows to consider only 4 unknown parameters: ω_m , S , Γ_{hom} and Γ_1 as there is the following relation between the width Γ_1 of a phonon profile associated to 1 phonon width Γ_i involving i overtones: $\Gamma_i = \Gamma_1 \sqrt{|i-2j|}$. The engraving process is modeled assuming a selective burning at a frequency ν_B such as the number of molecules remaining from the initial number N_0 , after a burning time τ is

$$N_{\nu_B, \tau} = N_0 \exp[-\sigma I_B \phi \tau L(\nu_B - v')],$$

where I_B is the burning intensity, σ the absorption coefficient, ϕ the phototransformation quantum yield and $L(\nu_B - v')$ the homogeneous profile with a ZPL centered at ν_B . In this approach, the dispersion rate of the yield ϕ is assumed to be weak and this expression is only rigorously valid far from saturation. In order to take into account the problem of saturation, we introduce a dependence of the absorption coefficient σ with the intensity I . We used the quantity $A = \sigma I_B \phi \tau$ as an adjustable parameter to represent the fluence. The simulated hole profile is obtained as the difference between the unburned and the burned

inhomogeneous profiles obtained after a convolution of the homogeneous shapes over the inhomogeneous distribution assumed to be a Gaussian with a fixed width. We then proceeded along the following way: for each different temperature, a simulated profile is fitted on the corresponding experimental data. From the fit, the parameter values are extracted with their dependence with the fluence.

The mean phonon frequency ω_m , which can differ from the peak phonon frequency, is then deduced from the experimental data. For each temperature, we varied the accumulated burning time between 1 and 3200 s, corresponding to typical fluence changes from 1.5 to 4800 mJ with 1.5 mW laser power, with a non-focused beam. Fits were made automatically and from the comparison, one determined the widths of the ZPL and of the PSB, as also the Debye–Waller factor α_{DW} . An example of such a fit is shown in Fig. 4. From the model and the fits obtained at different temperatures, we have extracted the evolution of α_{DW} with temperature, which gives access to the Huang–Rhys factor S , the homogeneous width and its change with the temperature or with the fluence and the changes of the Stokes

shift with temperature. The Debye–Waller factor has been determined at several temperatures both for the TEOS and the porous Vycor glass and its temperature dependence is shown in Fig. 4. Such data were reported yet in our previous paper together with another example of a fitted hole [6]. A determination of the respective Huang–Rhys factors is then possible from these data. We found S values of 0.13 for porous Vycor/H₂O and 0.26 for TEOS in satisfactory agreement with the values published by Small for AlPT in HGW [12]. The S values obtained for these systems are much better than the ones (about $S = 1$) we extracted for quinizarin (1,4 dihydroxy-anthraquinone) in an alumino-silicate xerogel [13].

2.3. Comparison between the three hosts studied and with others

We have followed the hole growth versus the fluence for the three inorganic hosts studied. For all the samples studied, the absorption in the region of hole burning was adjusted to have an optical density close to 1. Therefore, we can estimate the hole burning efficiency in a simple way by comparing the slopes of the curves

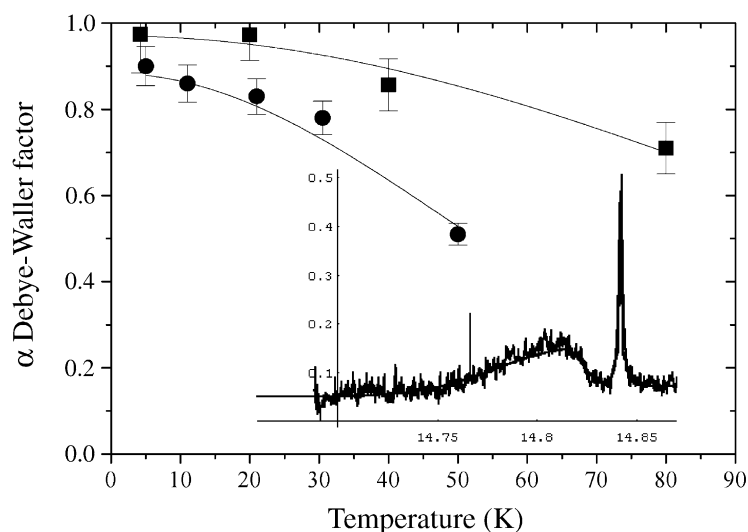


Fig. 4. Debye–Waller factor versus temperature. From the fit, the following values for the Huang–Rhys factor S and the phonon frequency Ω are $S = 0.26$, $\Omega = 22$ cm⁻¹ for AlPT in Xerogel (closed circles) and $S = 0.13$, $\Omega = 27$ cm⁻¹ for AlPT in porous Vycor/H₂O (closed squares). The inset shows a comparison of an experimental hole profile (AIPT in Vycor, $T = 5$ K, $t_b = 120$ s, $P_b = 1.4$ mW) with a simulated profile (fitted parameters: $F_{hom} = 0.01$ cm⁻¹, $F_{inh} = 330$ cm⁻¹, $\alpha_{DW} = 0.98$).

Table 2

Host at 4–5 K	Phonon peak frequency (cm ⁻¹)	Γ_{hole} at 5 K (GHz)	Huang–Rhys factor	Technique [Reference]
HGWater fresh	38	0.15 (0.55) ^a	~0.2	PSHB [3,14]
Buffered HGW	36	0.16	0.22	PSHB [4]
Gelatin	—	<30	—	PSHB [4]
HGEthanol	26	1.5 (8.5) ^a	0.43	PSHB [3]
HGMethanol	17	2.0 (30) ^a	0.36	PSHB [3]
Poly HEMA/H ₂ O	31	1.3 (1.75) ^a	0.4	PSHB [5]
PAAm gel	33	—	—	FLN [9]
Hydrolyzed PAAm gel	38	—	—	FLN [9]
TEOS xerogel dry	30	2.6	0.26	PSHB [6] ^b
Vycor/H ₂ O	35	—	0.13	PSHB [6] ^b
Aerogel/H ₂ O/AOT	26	—	—	PSHB [6] ^b

^aThe values are given for samples after annealing. Between parenthesis, the values measured in fresh samples are recorded.

^bThis work.

representing the hole depth change versus the burning time for a constant irradiation power. From this comparison, it results that the three hosts have comparable hole burning efficiencies. We remind that an exponential growing of the hole depth is associated with a narrow distribution of tunnelling parameters, i.e. to non-dispersive kinetics associated with a photochemical hole burning mechanism. In contrast, a logarithmic curve corresponds to a broad distribution of tunnelling parameters, i.e. to dispersive kinetics associated with non-photochemical (photophysical) mechanisms. For the AIPT in the TEOS xerogel, as well as for the two other inorganic hosts, AIPT in porous Vycor/H₂O and AIPT in the light aerogel/AOT/H₂O, the hole depth growth versus fluence is closer to logarithmic evolution, in agreement with a non-photochemical hole burning mechanism.

We have followed a rather tedious way to evaluate the Debye–Waller factor for the several samples and at different temperatures. We believe that it is the more precise way. Another possibility involves the direct deduction of the Huang–Rhys factor S from the maximum relative hole depth measured just at the saturation limit as the saturated depth is given by e^{-S} at very low temperatures (rigorously at $T = 0$ K) [1]. The measurement of α_{DW} has also been performed using photon-echoes or 4-wave mixing techniques [14]. As a main result of the present work, particularly in the porous Vycor/H₂O glass, the

linear electron–phonon coupling revealed to be sufficiently low to allow rather good hole burning performances up to 80 K. A comparison between several AIPT doped systems is presented in Table 2.

3. Conclusion

We demonstrate the rather good hole burning performances of three new hosts for the water soluble AIPT dye: an inorganic xerogel, a hybrid aerogel and a porous Vycor glass. The crucial role played by water or the silanol groups in xerogel pores is underlined by our experiments, the hole burning efficiency becoming quite low in a hybrid xerogel or in a dried porous glass.

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