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Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 04 Oct 2006.

To cite this article: Jaak Kekas , Artur Suisalu & Valter Zazubovich (1996): Anomalous Hole Spectra of Chlorin-Doped Low-Temperature Glasses, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 291:1, 215-222

To link to this article: http://dx.doi.org/10.1080/10587259608042750

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Mol. Cryst. Liq. Cryst., 1996, Vol. 291, pp. 215–222
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ANOMALOUS HOLE SPECTRA OF CHLORIN-DOPED LOW-TEMPERATURE GLASSES

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Abstract Spectral holes have been measured for chlorin dopant educt and photoproduct states in six disordered systems: in glasses of *o*-terphenyl, benzophenone, polystyrene, ethanol, and triethylamine and on the surface of Al_2O_3 powder at 5 K. In contrast to the conventional picture of zero-phonon holes and phonon sideholes observable in the educt state, no zero-phonon hole is observable in the photoproduct state in glasses yet the absorption spectra exhibit a peculiarity resonant with the burning frequency ("Λ-spectra"). A more complicated superpositional picture has been observed for Al_2O_3 powder The low-temperature hole spectra of an impurity in a 1D elastic lattice have been calculated and demonstrated to match qualitatively well the experimental observations. Physical relevance of such a model is discussed.

INTRODUCTION

The existence of narrow zero-phonon lines (ZPL) in optical spectra of impurities in different solids ranging from high-quality monocrystals[1] to strongly disordered (amorphous) materials[2,3] has been proved by different spectroscopic techniques including fluorescence line narrowing[1,2] and spectral hole burning[3,4]. Quantitatively the spectra depend on a system, but general features of vibronic impurity spectra are ZPLs of a width approaching a life-time-limited value at $T \to 0$ K and more or less intensive broad phonon sidebands (PSB)[5] observed in a large variety of systems. Such a picture stems from the phonon energy distribution ($\sim \Omega^2$, where Ω is the phonon frequency), characteristic for a 3D lattice and from the elastic nature of the deformation of a 3-dimensional host matrix (the shift u scaling as r^{-2} with the distance from the impurity considered as an elastic defect[6]).

It was demonstrated recently[7] that under some circumstances (phototransformation-induced local deformation) homogeneous impurity spectra in low-temperature disordered systems may acquire qualitatively different features: with no

zero-phonon lines observable still exhibiting a characteristic low-frequency peculiarity. In this report we will extend these studies to include, in particular, a novel system of chlorin molecules physisorbed on the surface of aluminum oxide.

EXPERIMENTAL

Chlorin (7,8-dihydroporphin) was used as a dopant. The choice of the dopant was motivated by the existence of an efficient intramolecular phototransformation process (turning of the central proton pair by 90°) in a chlorin molecule[8] which is accompanied by a large distortion of the molecule resulting in a photochromic shift to higher energies of about 60 nm. This reaction is photo- and thermoreversible.

Benzophenone, triethylamine, *o*-terphenyl and ethanol glasses were produced by rapid cooling of liquid solutions to liquid nitrogen temperature. Glassy polystyrene film was produced by evaporating a low-molecular-weight solvent from a dye-polymer solution. Evaporation of solvent was used to deposit chlorin onto Al_2O_3 powder surface.

The photoproduct was created at 5 K by an incandescent lamp excitation by using red filters not transmitting light at <600 nm. This enabled us to burn out the whole educt band between 620-650 nm without photoinducing back reaction in the product band located between 560-590 nm.

Absorption and excitation spectra were measured and the hole burning was carried out by using a CR-499 tunable dye laser of about 10 GHz linewidth. Fluorescence spectra were recorded on a DFS-24 0.8 m double spectrometer under a broad-band excitation. In all the experiments the temperature was stabilized at 5 K.

RESULTS

The results are depicted in Figs. 1 and 2 for o-terphenyl glass and Al_2O_3, respectively. In both systems the educt $S_1 \leftarrow S_0$ absorption spectra (curves 1 in Figs. 1, 2 left) are typical structureless gaussian bands of glassy matrices with widths (FWHM) of about 200 cm^{-1}. The product state absorption spectra (curves 1 in Figs. 1, 2 right) are shifted about 55 nm to the higher energies from the corresponding educt spectra and their widths of about 400 cm^{-1} are larger than those of the corresponding educt conformations.

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Curves 0 in Figs. 1, 2 (right) trace the absorption in the actual region before creation of the photoproduct. Its level is essentially lower than that of the photoinduced absorption.

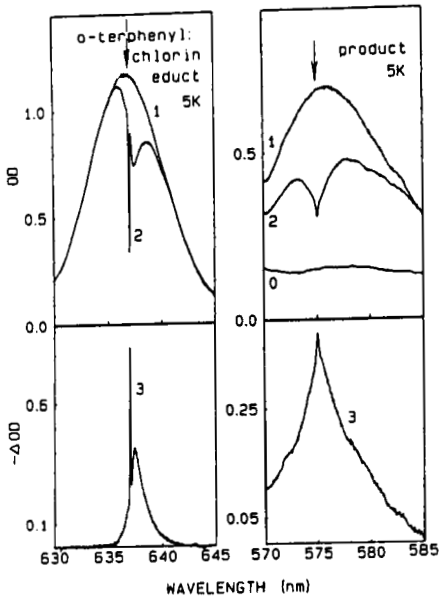

FIGURE 1 Left: The absorption spectra of chlorin in the educt conformation in glassy *o*-terphenyl; Right: The same for the photoproduct conformation. Arrow indicates the burning wavelength. Numbers: see text.

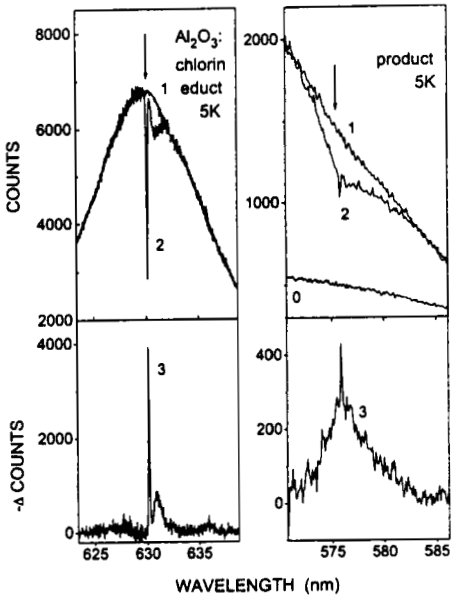

FIGURE 2 Left: The excitation spectra of chlorin in the educt conformation on aluminium oxide powder surface. Right: The same for the photoproduct conformation. Arrow indicates the burning wavelength. Numbers: see text.

The hole spectra for both the educt and the product conformation (curves 3) have been obtained as the difference of the absorption spectra before (1) and after (2) burning at the indicated position near the band maximum. The hole spectra for benzophenone, polystyrene, triethylamine and ethanol glasses (not depicted) have been observed to be similar to the spectrum in glassy *o*-terphenyl.

The hole in the product fluorescence spectrum (Fig.3) was obtained using a similar procedure of calculating the difference of the product fluorescence spectra before and after burning at the indicated wavelength. However, because of a very high yield of the back reaction a repeated procedure of product creation and hole burning was used during the recording. The high yield of the back reaction is also the reason for quite a low S/N ratio.

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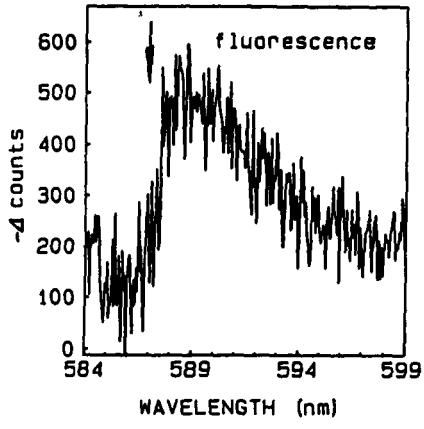

FIGURE 3 Hole in the fluorescence spectrum of chlorin photoproduct in *o*-terphenyl glass. Arrow indicates the burning wavelength.

DISCUSSION

Educt spectra

In Figs 1,2 (curves3, left) one can see typical asymmetric picture characteristic for weak or medium electron-phonon coupling at large burning fluencies when the burning via ZPL is strongly saturated already[9]. The broader sideholes located at *lower* frequencies from ZPHs are due to the dopant molecules burnt out via their PSBs and contributing to the absorption with their ZPLs[9]. A spectral gap between the maxima of ZPH and PSH due to the 3D Debye density of phonons (and the corresponding coupling) is also clearly observable in the spectra.

Product spectra

The hole burning in the chlorin product absorption/excitation spectra in glasses results in qualitatively different holeshapes ("Λ-spectrum", Fig.1 right). These spectra are characterized by the following features: (i) no ZPH is observable, (ii) spectrum is symmetric, (iii) from both higher and lower frequencies with respect to the resonant one hole spectrum exhibits a monotonous decrease with a hint to singularity at the resonant frequency.

The spectral hole, measured in product emission spectrum in *o*-terphenyl (Fig 3) is asymmetric, with an abrupt increase at the burning frequency (note that the hole is not peaked at the burning frequency) and monotonous decrease towards lower energies.

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Note, that chlorin photoproduct exhibits relatively intensive ZPLs in *crystalline* matrices (*n*-octane[10], crystalline phases of benzophenone[11] and o-terphenyl), and ZPHs of a width comparable to the holewidth in educt lines of the corresponding system can be burnt in these lines[10,12]. It is unlikely that the observable holeshapes are due to a drastically shortened lifetime of the excited state in the product conformation in glasses (lifetimes as short as 100 fs must be involved). In this case Lorentzian holeshapes are expected. In the cases of benzophenone and o-terphenyl it would also be unclear why the change of the phase state of the matrix should involve such a dramatic reduction of the lifetime.

The mirror symmetry of product hole (curve 3 in Fig.1, right) at quite a large depth indicates that the burning process is still far from saturation[9]. This is another proof of the absence of a narrow ZPL of high peak intensity in the product spectrum which becomes saturated at much lower fluencies and in the case of higher intensities produces a strongly asymmetric hole shape (the case of the educt conformation).

The product hole spectrum for Al_2O_3 powder deposited chlorin (Fig.2, right, curve 3) differs from the educt hole spectrum (Fig.2, left, curve3) as well as from the product hole spectra in glassy matrices. It may be interpreted as a superposition of a relatively weak "crystalline" spectrum exhibiting a sharp zero-phonon line and a more intensive Λ-spectrum characteristic of glassy matrices. In this connection it is of interest to recall the earlier results by Sauter and Bräuchle[13]. These authors observed in hole-burning experiments on octaethylporphyrin physisorbed on γ-alumina (γ-Al_2O_3) a superposition of zero-phonon holes of essentially different widths: a narrow and integrally weak one of about 1 GHz FWHM at 4.5 K and a much broader one of about 30 GHz FWHM. It is tempting to assign these holes to two different deposition modes of probe molecules (in "crystalline" and "glassy" surrounding), which yield in the case of chlorin photoproduct a zero-phonon hole and a Λ-hole, respectively.

Model Calculations

It is of interest to compare the above-discussed experimental findings with the calculated for a 1D elastic chain vibronic impurity spectra[7]. Referring to the latter paper for details we demonstrate in Figs. 4, 5 the calculated holeshapes in excitation (absorption) and fluorescence spectra, respectively. In these calculations a broad site energy distribu-

tion and mirror symmetry of homogeneous absorption and fluorescence spectra is assumed. The parameter α characterizes the strength of electron-phonon coupling and is given by the ratio of elastic deformation and Debye energies. Note that dimensionless integral Stokes' losses are infinite in this model for arbitrary small (but finite) values of α. As a consequence, this model yields no ZPLs. However, at $\alpha < ½$ the hole spectrum in excitation becomes divergent at the burning frequency.

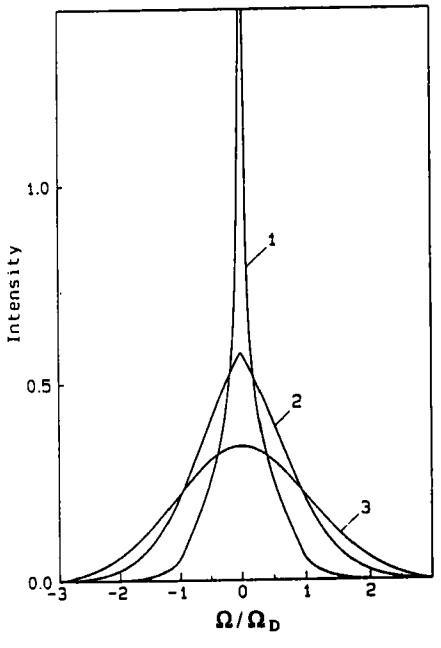

FIGURE 4 Calculated holes in absorption/excitation spectra of an impurity in 1D elastic chain for T=0 and α = 0.5 (1), 1 (2), 2 (3).

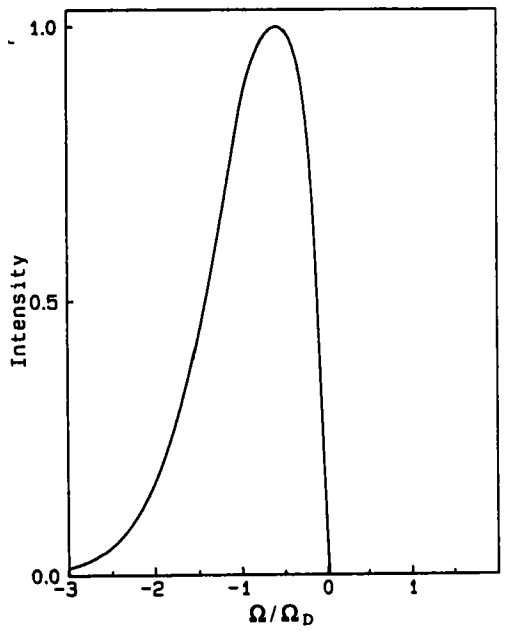

FIGURE 5 Calculated hole in emission spectrum of an impurity in 1D elastic chain for T=0 and α=0.5.

A comparison of experimental hole spectra of Figs. 1,2 and 3 with the ones calculated for the 1D elastic chain (Fig.4 with Figs. 1, 2 and Fig.5 with Fig. 3 respectively) demonstrates that the calculated spectra mimic the experimental spectra quite well for a *weak* electron-phonon coupling (curves 1, 2 in Fig.4 and Fig. 5).

Could such a similarity bear any physical meaning? We propose a following (quite a crude) reasoning. A transition to the product conformation may induce in a glass a local strain strong enough to create a local structural defect, e.g. a planar (micro)crack. In

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such a "cracked" state the deformation field that builds up upon the electronic transition, is qualitatively different. As far as the forces between the host particles across the crack are essentially weaker than those in the bulk material, the deformation acquires a quasi-1D nature.

One more observation supports indirectly the discussed picture. Different widths of the educt and photoproduct (inhomogeneous) spectra may be related to the different conditions of formation of the corresponding local state (relaxed local strains in quasi-equilibrium freezing-in of the educt at the liquid-glass transition and strong local strains induced by the phototransformation in the solid state). Thus the Λ-holes and large inhomogeneous broadening of the photoproduct spectra may be a dynamic and a static reflection of the same physical situation, respectively.

CONCLUSIONS

We have shown that in five different glasses - in molecular glasses of *o*-terphenyl and triethylamine (both nonpolar), benzophenone (polar), in a hydrogen-bonding glass of ethanol and in a polymeric glass of polystyrene, the homogeneous dopant spectra revealed by spectral hole burning acquire quite unusual features upon the phototransformation of the dopant (chlorin). Such spectra contain no zero-phonon lines, yet they exhibit a resonant singularity. A more complicated picture observable for chlorin physisorbed on the surface of Al_2O_3 powder hints to two qualitatively different depostion modes. An extension of the experimental research to other classes of disordered solids seems also promising as a possible way of probing local elastic/inelastic properties of different types of solids.

We have argued that it is a strong local deformation, resulting in the formation of a microcrack, that can lead to these observations. The resulting local dynamics in this case can be simulated by that of an elastic 1D lattice. More elaborated and realistic models may essentially contribute to our understanding of structure and dynamics of glasses.

The work was partly supported by the Estonian Science Foundation grant no. 2268 and by the Volkswagen-Stiftung.

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