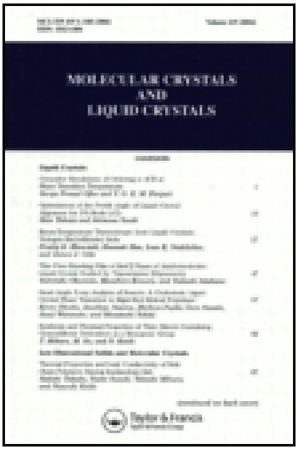

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SPECTRAL HOLE-BURNING INVESTIGATIONS IN THE RESTRICTED GEOMETRY OF MOLECULAR SIEVES

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Abstract Low-temperature spectroscopy and persistent spectral hole-burning have been used to characterize several aspects of the dynamics of physiadsorbed chromophores and amorphous phases confined to the Å-lengthscale voids of molecular sieves. It is shown that subtle differences of geometric factors, i.e. the relationship between molecular size and form and the confining void play a decisive role in the mobility and dynamics of thiazine dyes encapsulated in solvent-free faujasite structures. Additional solvent in the pores forms an amorphous phase which allows the formation of persistent spectral holes. Spectral diffusion in some of the solvent/molecular sieve systems is largely reduced due to the effect of the restricted geometry on the structure of the amorphous phase and/or the spatial distribution of two-level systems. For a hydrated $AlPO_4$-5 host with phthalocyanine-zinc derivates efficient hole formation has been demonstrated up to 80 K, the highest temperature for which stable non-photochemical holes have been reported so far.

Keywords: hole burning, phthalocyanine, adsorbed, amorphous, site-selective spectroscopy, spectral diffusion

INTRODUCTION

Investigations in recent years have shown that the dynamics of molecular probes and condensed phases can be dramatically modified if they are confined to geometrically restricted environments like membranes, polymers or the pores of sol-gel glasses and molecular sieves[1]. In this paper we will describe investigations of a variety of chromophores encapsulated in molecular sieves, inorganic crystalline structures like e.g. aluminosilicates (also known as zeolites) or aluminophosphates whose main characteristic is a well-defined porous structure (cages, channels, etc.) on an Å-lengthscale. Figure 1 shows as an example the so-called faujasite structure exhibiting cages with an inner diameter of 13 Å. These molecular sieves constitute an ideal example for a restricted geometry and allow the isolation and stabilization of encapsulated chromophores. Site-selective low-temperature spectroscopy and especially persistent spectral hole-burning (PSHB) have been used as extremely sensitive tools in the study of dynamical processes in glasses, crystals and on surfaces[2]. In this report we want to demonstrate how these techniques can contribute to a refined understanding of the chromophore/solvent/molecular sieve materials. We will

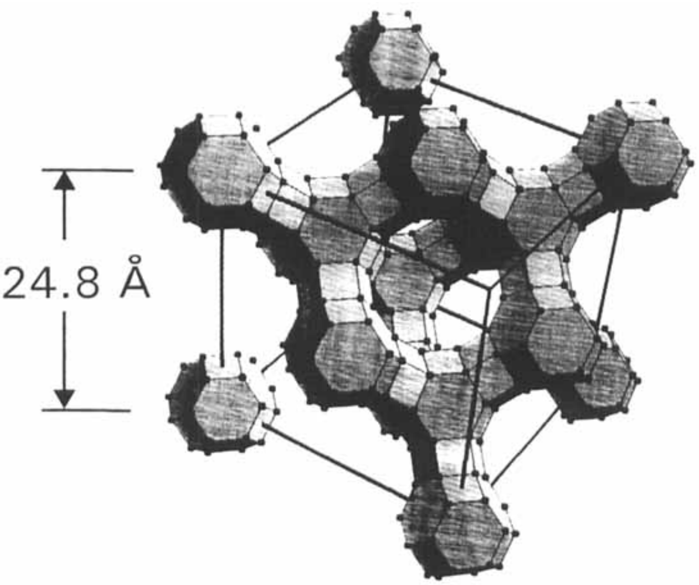

Figure 1: Schematic picture of the faujasite framework structure.

focus here on three facettes of these systems. In the first part low-temperature dynamics of thionine in a solvent-free faujasite structure will be described and attributed to reorientational dynamics of the chromophore within the faujasite supercage. These dynamics depend critically on the size of the molecule in relationship to the surrounding void. In the second set of investigations the pores of the molecular sieve have been filled with additional solvent (e.g. water, ethanol) and the chromophore will serve as a probe of the structure and dynamics of the glassy phase formed by this solvent in the porous structure at low temperature. In the third part PSHB in a hydrated aluminophosphate will be described and the specific properties of this guest/host system which allow the formation of non-photochemical holes at liquid nitrogen temperature will be discussed.

EXPERIMENTAL PROCEDURES

Depending on the molecular sieve host, two different preparation methods were employed. In the case of the zeolite systems with the faujasite structure the molecular sieve was synthesized first and the chromophores were incorporated later by cation exchange from aqueous solution followed by ethanolic extraction. For the aluminophosphates the dye molecules were dissolved in the aqueous starting mixture of the template synthesis and the inorganic molecular sieve framework was built around the chromophores[3]. In both cases typical dye concentrations are of the order of $5 \cdot 10^{-7}$ $mol\,g^{-1}$ corresponding to a mean chromophore distance of about 120 Å. Solvent-free or dehydrated samples were prepared by heating the sample up tp 120 °C under the reduced pressure of 10^{-5} torr and sealing it in a glass cuvette. Hydrated samples were stored over saturated aqueous KCl solution for a couple of days. Other solvents were incorporated into the pores of the molecular sieve by immersing the crystals into the respective liquid.

The optical experiments were performed in a combined He flow/bath cryostat with a scanning actively stabilized ring dye laser pumped by an Ar ion laser or a Xe lamp/monochromator combination. All spectra were recorded by fluorescence detection.

LOW-TEMPERATURE DYNAMICS OF THIONINE IN A FAUJASITE LATTICE

Although there is a large number of experimental and molecular simulation studies of the dynamics (in particular translational diffusion) of atoms and small molecules (e.g. methane) in molecular sieves[4] there is much less information about the photophysical properties and the molecular mobility of large adsorbates e.g. dye molecules inside the cavities of the molecular sieve[5]. On one hand the dynamics of these systems are interesting because it is possible to study molecular motion in the limit of a very high degree of geometrical restriction. On the other hand the properties of these chromophore/molecular sieve samples are important with respect to applications as e.g. photoredox systems or nonlinear optical materials[6].

Spectrum a in figure 2 shows the fluorescence excitation spectrum at T = 1.3 K of a slowly cooled sample of thionine in a Na-Y host, a zeolite of the faujasite type depicted in fig. 1. The sample exhibits a relatively weak fluorescence with an excitation maximum at λ = 640 nm. Upon heating the sample the fluorescence increases and the maximum shifts to higher energy. At T = 175 K the sample shows the excitation spectrum b in fig. 2 with a maximum at λ = 627 nm. This change is completely reversible: slow cooling back to 1.3 K reproduces spectrum a. However, if the sample is cooled very rapidly back to 1.3 K the spectrum b is preserved. Obviously the high-temperature species can be stabilized at low temperature. Even after many cycles of this kind the two excitation spectra and their respective intensities can be reproduced under the appropriate conditions. Besides this thermally induced change the two species (which we will call A and B corresponding to the spectra a and b) can be converted into each other through a photoinduced process. Illumination of the low temperature form A at T = 1.3 K with an excitation wavelength λ = 640 nm induces the formation of species B with the spectrum b and vice versa. The peculiar characteristics of this low-temperature phototransformation under monochromatic

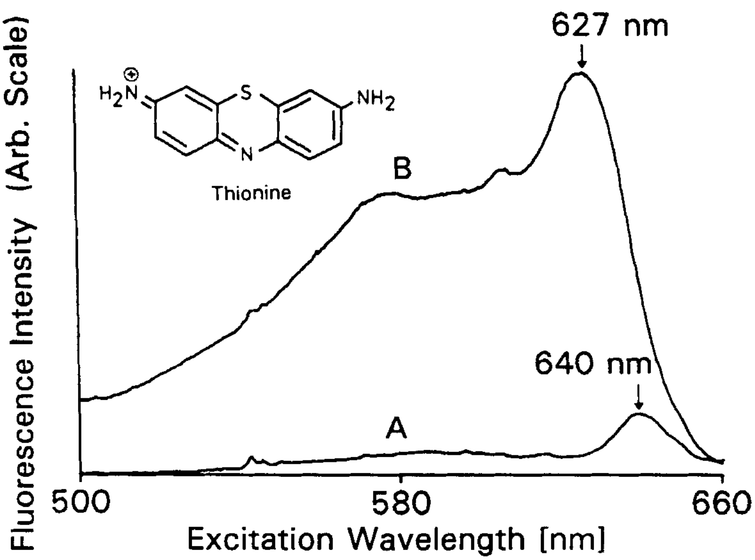

Figure 2: Fluorescence excitation spectra of a dehydrated thionine/Na-Y sample (a) after slow cooling to T = 1.3 K and (b) heating to T = 175 K.

excitation conditions like formation of sharp antiholes at the excitation wavelength will be described elsewhere[7].

For a quantitative characterization of the energies involved in the ground state transformation temperature dependent measurements have been performed. Over a large temperature range the relative contributions of the two forms A and B to the fluorescence excitation spectrum follow an Arrhenius behaviour and a corresponding plot gives a ground state energy difference of $\Delta E = 200\ cm^{-1}$. Through optical pumping an excess population of form B can be generated and the relaxation of the system back to the A ↔ B equilibrium at various temperatures can be tracked optically through the fluorescence intensity. The decay of this excess population follows monoexponential kinetics and the temperature dependence of the decay constant can again be described by an Arrhenius law from which a barrier height of $\Delta V = 120\ cm^{-1}$ can be extracted. A schematic illustration of the energy scheme associated with the A ↔ B interconversion is shown in figure 3. The role of the triplet state and very inefficient persistent spectral hole-burning (HB) processes out of the excited state will be treated elsewhere[7].

What is most interesting in this case is the microscopic picture associated with the double well potential which is clarified by two observations. Firstly, if additional solvent molecules are incorporated into the host, i.e. if the molecular sieve is hydrated again or

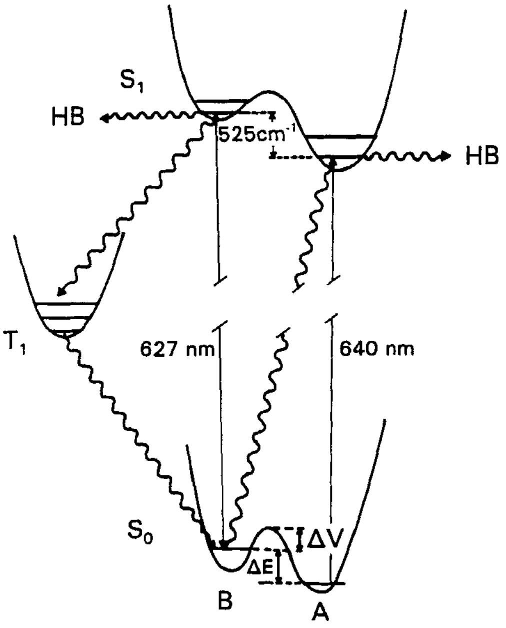

Figure 3: Schematic model of the energy level scheme and transitions characterizing the A↔B transformation of thionine in a solvent-free Na-Y host (for further details see text).

if it is immersed in ethanol, the A ↔ B equilibrium disappears. Only one stable form can be detected optically. Additional solvent molecules fill up the residual empty space in the faujasite structure and suppress any spatial mobility of the encapsulated chromophore. Therefore we associate the two spectral forms A and B with two different guest-host conformations and the transformation with a reorientational/conformational motion of the thionine chromophore. Secondly, we have also investigated solvent-free methylene blue/Na-Y samples. In methylene blue (MB) the four amine hydrogens of thionine are replaced by methyl groups, i.e. the photophysical and photochemical properties of MB and thionine are very similar but MB is slightly bulkier. For MB/Na-Y it is not possible to induce a change of the excitation spectrum at low temperature by warming or illuminating the sample. In our opinion the steric restraints induced by the slightly larger size of MB compared to thionine increase the barrier height ΔV drastically and prevent any low-temperature conformational change in the MB/Na-Y system.

SPECTRAL HOLE CHARACTERISTICS IN SOLVENT-FILLED AlPO$_4$-5 SYSTEMS

In all solvent-free chromophore/molecular sieve systems investigated no persistent spectral holes could be found or the hole-burning efficiency was extremely small as for the thionine/Na-Y sample discussed above. However, upon hydrating the molecular sieve or immersing it in an organic solvent burning efficiencies comparable to bulk glasses were detected. From all our observations it is evident that the solvent molecules in the porous structure of the molecular sieve form an amorphous phase at low temperature with additional degrees of freedom, so-called two-level systems (TLSs), as found in bulk glasses which can couple to the electronic transition of the chromophore[2]. In glasses the characteristics of the burnt spectral hole (e.g. the lineshape, the temporal evolution of the hole, its temperature dependence) are dominated by the interaction of the chromophore with the TLSs of the surrounding glass and are therefore a probe for the dynamics of the amorphous phase[8].

The investigations so far have revealed one major difference for the holes in the solvent-filled molecular sieves and those in the corresponding bulk glasses. Most bulk glasses exhibit a considerable broadening of the spectral hole, i.e. an increase of the linewidth with time, a phenomenon called spectral diffusion[9]. This effect is due to the broad spectrum of relaxation rates of the TLSs in the non-equilibrium glass system and the concomitant shifts of the electronic transition frequency of the probe molecule. This hole broadening is strongly reduced or completely suppressed in the solvent-filled porous systems studied so far. As an example figure 4 shows the time dependence of the linewidth of spectral holes with oxazine 1 as the probe molecule. Whereas in bulk ethanol the linewidth increases with a rate of 0.9 Ghz/decade, the corresponding values are 0.0 and 0.15 GHz/decade in a hydrated and an ethanol-immersed AlPO$_4$-5 molecular sieve. AlPO$_4$-5 is an aluminophosphate with essential one-dimensional channel-like pores with an inner diameter of 7.8 Å. To understand this difference the exact relationship between the glass dynamics and the spectral holewidth has to be known. It can be shown[8] that there are essentially three parameters which enter this relationship. These are the energy and relaxation rate distribution of the TLSs in the glass, the coupling of the TLSs to the chromophore and the spatial distribution of the TLSs with respect to the chromophore. Whereas a change in the type of coupling seems very unlikely the spatial distribution of the TLSs is certainly different in the molecular sieve (one has to imagine the solvent in the AlPO$_4$-5 pore as an amorphous phase with one-dimensional character). As the amorphous phase in the pore is characterized by a high surface to volume ratio and is susceptible to specific surface interactions one can also expect the structure of the glass and because of that the relaxation

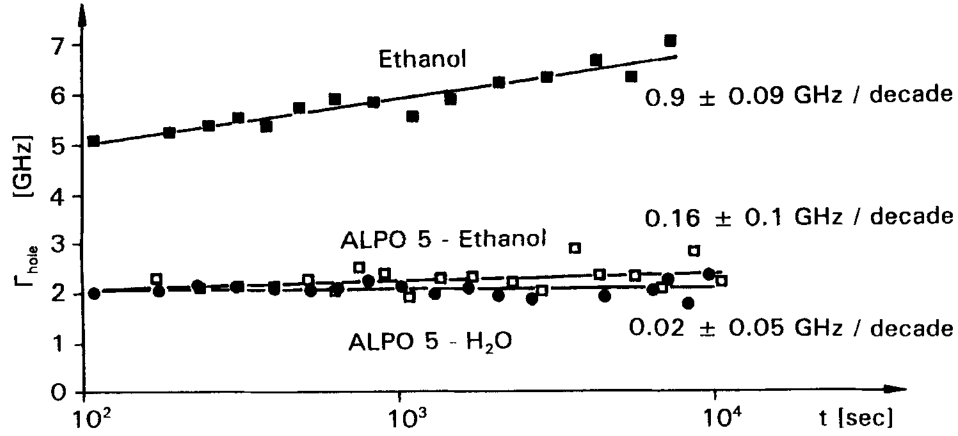

Figure 4: Temporal evolution of the spectral holewidth for oxazine 1 at T = 2 K in (i) bulk ethanol, (ii) $AlPO_4$-5 with ethanol-filled porous channels, (iii) $AlPO_4$-5 with water-filled porous channels.

rate distribution of the TLSs to be modified with respect to the bulk glass. Theoretically it is possible to distinguish between the effect of reduced dimensionality, i.e. modified spatial distribution, and different glass structure, i.e. altered relaxation rate distribution by e.g. an exact analysis of the spectral line shape. Experimentally such an unambiguous line shape analysis has turned out to be very difficult. However, we hope that through a systematic variation of host pore size and geometry as well as inner surface interaction we will be able to separate and characterize those two effects in the future. It should be mentioned at this point that the temporal evolution of the hole area, i.e. the hole filling is comparable in solvent-filled molecular sieves and in bulk phases. In general hole filling is associated with so-called extrinsic TLSs[9] whose microscopic origin is the interaction of the chromophore with the frozen next neighbour solvent shell. With this in mind the hole filling experiments indicate that at least the structure of the local solvent shell around the chromophore is similar in the porous host and the bulk glass.

HIGH-TEMPERATURE HOLE-BURNING OF PHTHALOCYANINE ZINC DERIVATES IN HYDRATED $AlPO_4$-5

In most systems persistent spectral holes can only be burnt at temperatures below 30 K. This limitation to liquid helium temperatures is one of the major factors impeding an application of these materials in a high-density frequency-domain optical data storage

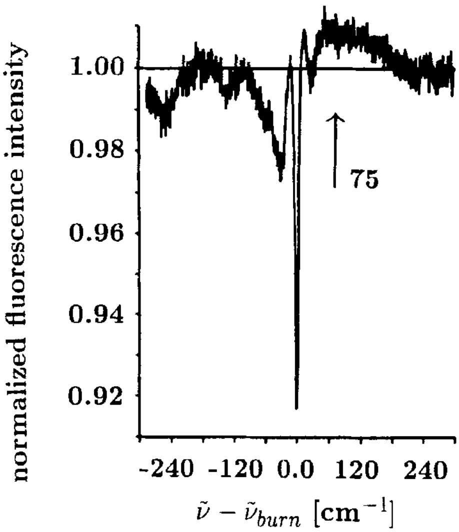

Figure 5: Deep saturated hole of ZnTaP in hydrated AlPO$_4$-5 burnt at T = 20 K.

medium[2]. It is in general brought about by two factors. Firstly the stability of the holes depends on the height of the product-educt barrier associated with the burning process. With increasing temperature higher and higher barriers can be crossed and the spectral holes associated with these barriers become transient ones due to reconversion. For this reason all high-temperature (meaning above liquid nitrogen temperature = 77 K) hole-burning systems known so far are based on a photochemical mechanism[10] with a relatively well-defined and high product-educt barrier. The second important factor is the change of the spectral lineshape with increasing temperature. The spectral hole contains two contributions: the purely eletronic transition, the so-called zero-phonon line (ZPL), and the phonon side band (PSB). The relative contribution of the ZPL to the total area of the hole is given by the Debye-Waller (DW) factor and decreases with increasing temperature while at the same time the linewidth of the ZPL increases. To observe well-resolved ZPLs at high temperature it is therefore necessary that the system investigated has a large DW factor.

In the following results from investigations of an AlPO$_4$-5 host loaded with the iodine salt of tetra-(N-ethyl-2,3-pyridino)-tetraazaporphyrine-zinc (ZnTaP) and water or chloroform as additional pore-filling solvents are described. It is well-established that chromophores of this type can undergo high efficiency one-photon or two-photon induced donor-acceptor electron transfer[11]. Figure 5 shows a deep spectral hole burnt into a sample of hydrated ZnTaP/AlPO$_4$-5 at 20 K. At a distance of 30 cm^{-1} to the right and left of

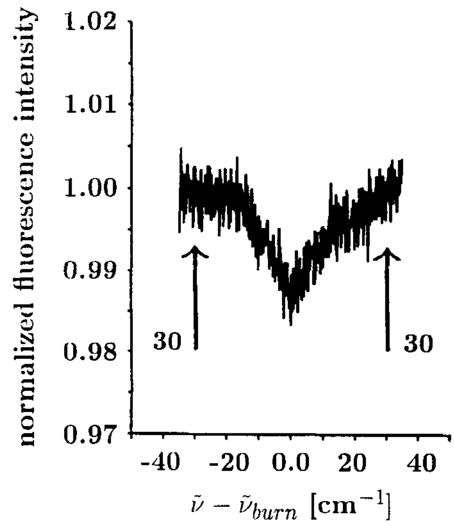

Figure 6: Shallow spectral hole of ZnTaP in hydrated $AlPO_4$-5 burnt at T = 80 K.

the ZPL the PSB and pseudo-PSB can be seen. On the high energy side of the ZPL the product band with a maximum at 75 cm^{-1} is clearly visible. This rules out one-photon electron transfer as the burning mechanism. No photon-gating indicative of a two-photon electron transfer could be observed in two colour hole-burning investigations. Temperature cycling experiments reveal a low thermal stability of the holes: holes burnt at 2 K are completely erased if the temperature is cycled to T = 30 K and back. From these findings one can conclude that the burning process in these samples is non-photochemical and associated with the amorphous solvent phase within the pores.

Although the burning efficiency decreases continously with increasing temperature, it is possible to burn stable holes in hydrated samples up to temperatures of 85 K. As an example a 19 cm^{-1} wide hole burnt at 80 K in a hydrated ZnTaP/$AlPO_4$-5 sample is shown in figure 6. The maximum attainable temperature with chloroform as pore-filling solvent is 50 K. To our knowledge, this is the first system for which non-photochemical hole-burning at liquid nitrogen temperature has been observed. In context of the prerequisites of HTHB discussed above this must be attributed to two facts. Obviously the hydrogen bonded amorphous water phase within the pores contains an appreciable number of TLSs with high energy barriers providing stable double-well potentials even at 80 K. In addition to that the electron-phonon coupling to the water/inorganic host is small, and the energy of the phonon side band is relatively large leading to DW factors clearly above 0.1 even at 80 K allowing the observation of clearly resolved ZPLs at high temperature.

CONCLUSIONS

We have characterized low-temperature dynamics of thionine molecules in the solvent-free supercages of a Na-Y faujasite lattice and demonstrated that very subtle changes of the molecular size have a dramatic influence on reorientational/conformational motion within the surrounding supercage. Spectral diffusion for chromophores in solvent-filled molecular sieves is largely reduced demonstrating the high sensitivity of the spectral hole to the structure and/or topology of the pore-restricted amorphous phase. The observation of non-photochemical high-temperature hole-burning in hydrated $AlPO_4$-5 hosts with phthalocyanine-zinc derivates is attributed to the combined effect of the stiff molecular sieve lattice and the hydrogen-bonded amorphous phase leading to a high Debye-Waller factor and high-barrier two-level systems.

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