NON-PHOTOCHEMICAL HOLE BURNING IN THE MIXED MOLECULAR CRYSTAL PENTACENE IN BENZOIC ACID

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Non-photochemical hole burning is observed in the mixed molecular crystal pentacene in benzoic acid. The homogeneous linewidth is obtained from photon echo measurements. Hole burning is monitored with absorption spectrometry and photon echo detection. Spontaneous hole filling is observed and the rate of hole filling is reported.

1. Introduction

Persistent hole burning in inhomogeneously broadened absorption bands of organic molecules imbedded in low-temperature glasses or matrices is a well-known phenomenon. The effect is termed either photochemical hole burning (PHB) [1] or non-photochemical hole burning (NPHB) [2-4]. The spectral holes produced in PHB are due to the disappearance of resonant guest molecules which have undergone photochemical reaction to a non-resonant species. In NPHB, however, the holes result when guest molecules on resonance with the laser migrate to another part of the inhomogeneous line, presumably due to a change in the local environment. A model for NPHB in glasses put forth by Small and co-workers [4] attributes this to the relaxation of surrounding glass molecules to a different stable minimum in potential energy which is accessible upon optical excitation. In glasses, the hole width is much wider than would be predicted by the guest fluorescence lifetime.

PHB has also been observed in mixed molecular crystals [5-8]. In some of these experiments low-temperature hole widths are consistent with homogeneous linewidths due totally to the fluorescence lifetimes [8]. Until now, no reports of NPHB in mixed molecular crystals have appeared in the literature. We report here the observation of hole burning of pentacene in benzoic acid crystals (PC/BZA), which we believe is an example of NPHB. PC is photostable in other hosts such as naphthalene and p-terphenyl [9-11]. In the experiments described below we observe complete spontaneous recovery of the burned absorption line at constant temperature (complete hole filling), demonstrating that PC has not undergone an irreversible chemical change.

This paper presents preliminary results for hole burning of PC/BZA. In addition, the results of photon echo experiments are discussed. The hole burning was monitored by photon echo detection and absorption spectrometry. The holes were burned with a laser whose bandwidth (≈15 GHz) is much greater than the homogeneous linewidth (≈7 MHz) and therefore a comparison of the hole width and photon echo measurements of the homogeneous linewidth is not yet possible. The BZA crystal consists of hydrogen-bonded dimers [12]. Results of experiments in which the BZA acidic hydrogens have been replaced with deuteriums are presented and possible mechanisms are discussed.

2. Experimental

The picosecond photon echo system used in these experiments has been described previously [9]. The photon echo experiments were performed using ≈10 μJ, 30 ps light pulses at a repetition rate of 400 Hz tuned to the pentacene origin, 588 nm. A dye laser single pulse is split into two excitation pulses with appropriate energies (≈0.2 μJ and ≈1 μJ) and variable temporal delays for the photon echo decay experiment. In the echo-monitored hole burning experiments, a fix-
ed, 1 ns separation between the excitation pulses was used. The excitation pulses are then directed to the sample, located in a liquid-helium dewar pumped to 1.6 K.

Polarized transmittance spectra were recorded using a high-pressure xenon arc lamp, a 1 m Spex Czerny–Turner scanning spectrometer in second order and an EMI 9658 phototube. The arc lamp was focused onto the entrance slit of the monochromator and a sheet polarizer was mounted on the exit slit. The polarized light was focused on the sample which was mounted on a 600 μm pinhole to ensure that the echo and absorption experiments were performed on the same spot in each crystal.

Crystals of PC/BZA were grown from the melt using standard Bridgman techniques. The BZA was extensively zone-refined and the PC, obtained from Aldrich, was used without further purification. The S0 → S1 PC transition in BZA is strongly a-axis polarized. In mounting samples a conoscopic microscope with crossed polarizers was used to locate the optic axes to ensure that the crystal a-axis was parallel to the laser polarization and the polarized light from the monochromator. Crystal concentrations were measured from a-axis polarized transmittance spectra and crystal thickness.

3. Results

Photon echo decay measurements were made on low-concentration, low-optical-density [13] (OD) PC/BZA crystals. Within experimental error the observed T2 is identical to 2T1 = 40 ns [14]. T1 was obtained by fluorescence lifetime measurements. (Since hole burning was slowly occurring during the photon echo measurements, there is a small degree of uncertainty in the T2 result.) The separation between the echo excitation pulses was then fixed at 1 ns and the change in echo intensity with time due to hole burning was monitored. Fig. 1 shows this change for an ≈ 10^-6 mole/mole, ≈ 0.5 mm thick pentacene in benzoic acid crystal. As discussed in the text, the initial rapid loss of signal is due to molecules which are on resonance and driven coherently by the laser. The slower loss rate is due to molecules which are off resonance. The loss of echo signal reaches steady state after ≈ 20 min.

Fig. 1 Photon echo monitored hole burning in an ≈ 10^-6 mole/mole, ≈ 0.5 mm thick pentacene in benzoic acid crystal. As discussed in the text, the initial rapid loss of signal is due to molecules which are on resonance and driven coherently by the laser. The slower loss rate is due to molecules which are off resonance. The loss of echo signal reaches steady state after ≈ 20 min.

The NPHB of PC/BZA is unique in that, after ≈ 2 h, we observe a full recovery of echo signal while at constant temperature, i.e. the hole has completely disappeared. The circles in fig. 2 show the recovery of the echo signal. The vertical coordinate is the ratio of echo signal to maximum echo signal observed. The horizontal coordinate is the time since burning was discontinued. This recovery data corresponds to the rate of hole filling. It was obtained by blocking the excitation pulses and occasionally unblocking them for ≈ 4 s to measure the photon echo signal. The amount of hole burning during unblocking is negligible. The plot shows that echo signal recovery is almost complete after 90 min.

In fig. 3 the results of absorption measurements are displayed. Fig. 3a shows the transmittance spectra of a PC/BZA crystal before and after laser irradiation. The transmittance of the line after burning has increased. Because high-power non-linear laser excitation is used, a broad region of the spectral line is burned away. In fig. 3b results for a crystal with a broader inhomogeneous line are shown. The laser was not tuned to the
1.0

\[ \text{PC/BZA} \]

\[ \text{OD}^2 \]

Fig. 2. Hole filling monitored by photon echo and absorption spectroscopies. The vertical coordinate is the ratio of the signal to the maximum signal observed and the horizontal coordinate is the time since burning was discontinued. The circles show the recovery of the echo signal. Recovery is almost complete after 90 min. Also plotted (squares) is the spectrally measured recovery of the \((\text{OD})^2\), since the echo signal is proportional to the square of the OD. It is clear that the recoveries of the spectrum and echo are identical.

4. Discussion

There are several differences between NPHB in glasses and NPHB in the PC/BZA mixed crystal. The most striking difference is that at a given burn temperature the holes persist for many hours in glasses [4], whereas in the PC/BZA crystal full recovery of peak OD is observed after \(\approx 2\) h. It has been suggested in a detailed theoretical analysis [15] that recovery from hole burning in glasses should occur. Another difference is that the OD typically changes by 10–20% in glasses [4] but 40–50% changes are observed in the experiments reported here. (\(\approx 80\%\) changes have been observed using a narrow-band dye laser [14].)

In glasses the inhomogeneous lines are very broad [2–4]. Hole burning at a particular frequency in the inhomogeneous line results in increased OD in some other region of the inhomogeneous line, generally a few wavenumbers away [4]. Examining fig. 3, it is seen that a reduction of OD at the spectral peak does not result in increased OD in the wings of the line. Furthermore, the time to reach saturation in PC/BZA is \(\approx 20\) min compared to 130 min in the particular case of tetracene in glycerol/DMSO/DMF and the hole was burned in PC/BZA with 2 mW/mm² while that in the glass was burned with 10 mW/mm² in a much narrower bandwidth. Thus PC/BZA seems to be an exception to the suggestion of Klafter and Silbey [15] that the high density of very-low-frequency modes in glasses leads to greater hole-burning efficiency than in crystalline solids.

The quantum yield for hole burning can be determined from the long-time, steady-state absorbance loss, the absorbance recovery time (from fig. 3), the PC flu-
orescence lifetime and the repetition rate of the laser \( \pi \)-pulses. For PC/BZA a quantum yield estimate of between \( 10^{-5} \) and \( 10^{-6} \) is obtained. This is similar to the results found in glasses, e.g. tetracene in ethanol/methanol has a quantum yield of \( \approx 10^{-6} \) while in glycerol/DMSO/DMF it has a quantum yield of \( \approx 10^{-4} \) [4].

At this early stage in our investigation we can only speculate about the mechanism behind the NPHB of PC/BZA. The UV spectrum of pure BZA crystals at liquid-helium temperature [16] shows that two-photon absorption by BZA of 588 nm light, the wavelength used to excite PC, is not a possibility. This demonstrates that the NPHB mechanism must involve some type of coupling of the excited PC to the BZA crystal lattice and not direct absorption of laser light by the host crystal. Also, we performed an experiment on PC/BZA in which the BZA acidic hydrogens were exchanged for deuteriums. The exchange was close to complete. The PC absorption was blue-shifted in the deuterated host and consisted of three closely spaced peaks. The bluest peak was 24 cm\(^{-1}\) from the PC absorption line in the non-deuterated BZA crystal. In the order red to blue, the three peaks probably correspond to increasing numbers of deuteriums present on the BZA dimers interacting with a PC molecule. The shift in the PC spectrum upon deuteration of BZA indicates significant interaction between the PC and the acidic groups. The most important result of the experiments in the deuterated BZA crystals is that attempts to burn holes were unsuccessful. There was no decrease either in the echo signal or in the peak OD, indicating either the absence of hole burning or that hole burning is very slow in the deuterated host. Additional discussion of this point occurs in ref. [14].

These results strongly suggest that the hydrogen bonds of the BZA dimers are involved in the hole-burning mechanism. Replacement of hydrogens by deuteriums results in stronger hydrogen bonds. In carbon tetrachloride solution, the BZA hydrogen bond strengths per mole of monomers are 5.3 kcal and 7.9 kcal for hydrogens and deuteriums, respectively [17]. Let us treat the BZA crystal lattice as a two-level system [4] where the two minima in potential energy correspond to two stable conformations of the hydrogen-bonded dimer. Upon optical excitation of the PC, the barrier for interconversion is reduced and some BZA molecules near excited PCs undergo interconversion, changing the PC energy. When the PC returns to the ground state, the BZA remains in the new conformation for some time, but there is gradual return to the more stable form. This could be responsible for the observed hole filling. We can then attribute the lack of NPHB in deuterated BZA to stronger hydrogen bonds. If the barrier were large enough, no interconversion, and thus no hole burning, would occur.

The observation of NPHB in the PC/BZA mixed crystal system demonstrates that NPHB is a more general phenomenon than had been previously demonstrated, i.e. NPHB is not restricted to glasses. We are currently pursuing a variety of experiments to understand this system more fully [7]. These experiments include hole burning with a narrow-band laser, comparison of hole widths with photon echo experimental results, temperature studies, and absorption and emission studies to determine the nature of the species formed by NPHB.

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