

NONPHOTOCHEMICAL HOLE BURNING AND INTERSYSTEM CROSSING IN THE PENTACENE/BENZOIC ACID SYSTEM: DEUTERIUM EFFECTS

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Received 11 February 1985

We report a study of the extent of nonphotochemical hole burning in the mixed crystal system pentacene in benzoic acid (PC/BZA) as a function of burn time and burn intensity. Comparison is made to PC in BZA with deuteriums replacing the carboxylic acid hydrogens (d-BZA). Absolute hole-burning efficiencies, antihole recovery rates, and pentacene intersystem crossing rates and lifetimes are reported for the two hosts. Hole burning is shown to occur from the first singlet state. The absolute hole-burning efficiency is an order of magnitude greater in d-BZA, while the antihole recovery rate is a factor of three slower. A two order of magnitude reduction in the *apparent* hole-burning efficiency upon deuteration of BZA, which was reported previously, is shown to be due to a dramatic increase in PC's intersystem crossing rate in d-BZA.

1. Introduction

Recently, the mixed molecular crystal system, pentacene in benzoic acid (PC/BZA) was shown to exhibit nonphotochemical hole burning (NPHB) [1,2]. This crystalline system is unusual in that it exhibits hole burning by a phenomenon which is external to the optically excited molecule. Hole burning in crystals has involved either an irreversible chemical change of the chromophore [3,4], i.e., photochemical hole burning (PHB), or reversible intramolecular changes in the chromophore, such as hydrogen bond rearrangements [5,12]. In the PC/BZA system, optical excitation of the pentacene to the first singlet state results in a hydrogen bond rearrangement of an adjacent benzoic acid hydrogen bonded dimer [1,2]. The change in the BZA hydrogen bonds modifies the local environment of the pentacene and shifts its energy. If a narrow band laser is used for excitation, a spectral hole is burned into the pentacene S_1 origin and a number of new absorption peaks appear. These peaks arise from absorption by pentacene molecules in modified lattice sites.

There are a number of inequivalent benzoic acid dimers surrounding each pentacene which, upon burning, gives rise to the various antihole

absorption peaks. A detailed study of the holes and antiholes and their relationship to the nature of inhomogeneous broadening has been presented [6]. The principal antihole (site I) at 16872 cm^{-1} contains 70% of the integrated antihole intensity, and is 135 cm^{-1} to the red of the PC/BZA origin [2]. The site I antihole reverts with a lifetime of 45 min, refilling the hole [6]. The spontaneous reversion occurs in the dark at 1.8 K. The reversion can also be induced optically, i.e., irradiation of the site I antihole fills the original hole.

In this paper we present experiments on PC/BZA and pentacene in benzoic acid with deuteriums replacing the carboxylic acid hydrogens (PC/d-BZA). The hole burning is shown to occur from a pathway involving the first singlet state. Intersystem crossing to the first triplet causes a population bottleneck and retards hole burning. The experiments demonstrate that deuteration of BZA dramatically increases the pentacene intersystem crossing (ISC). This increase in ISC reduces the *apparent* hole-burning efficiency at high laser power. Previously the hole-burning efficiency was reported to be a factor of 100 smaller in d-BZA than in BZA [2]. By examining the extent of hole burning as a function of laser intensity and burn time we have determined that the absolute

hole-burning efficiency is actually greater by an order of magnitude in d-BZA than it is in BZA. This is in contrast to the site I antihole recovery time, which is a factor of three *slower* in d-BZA.

The change in ISC is shown to arise from a shift in the pentacene second triplet state, T_2 , below S_1 upon host deuteration. This opens an efficient ISC pathway not available to pentacene in the undeuterated BZA host. The increase in hole-burning efficiency and the decrease in antihole recovery rate with deuteration of the host are discussed in terms of possible models for the hole-burning process.

The benzoic acid crystal is only one of a wide class of materials composed of hydrogen bonded dimers, hydrogen bonded linear chains of molecules, and hydrogen bonded molecular networks. Currently, the dynamics of hydrogen bond rearrangements are under intensive investigation [7,8,10]. The fact that optical excitation of a guest chromophore can trigger a hydrogen bond rearrangement is intriguing but not understood. This phenomenon has been observed in a number of substituted BZAs [9] and for chromophores other

than pentacene in BZA [10]. It seems likely that optical hole burning by hydrogen bond rearrangement will occur in many hydrogen bonded materials. This paper provides information which will be useful in understanding hole burning in hydrogen bonded systems.

2. Experimental procedures

A Coherent 599-21 single mode cw scanning dye laser pumped by 1.25–2.5 W of the 514 nm line of a Coherent Innova 90-5 argon ion laser was used both for burning holes and recording holes and antiholes. Maximum dye laser power was 110 mW with ~ 3 MHz bandwidth. Holes and antiholes were monitored by fluorescence excitation using an EMI 9658 PMT filtered with Hoya R625 and R640 cutoff filters. The experimental setup is shown in fig. 1. A Nova 2/10 computer was used to scan the laser and collect data. A pickoff of the excitation beam was sent into an EMI 9781R PMT so that variations in laser power over the course of a scan could be normalized out of the

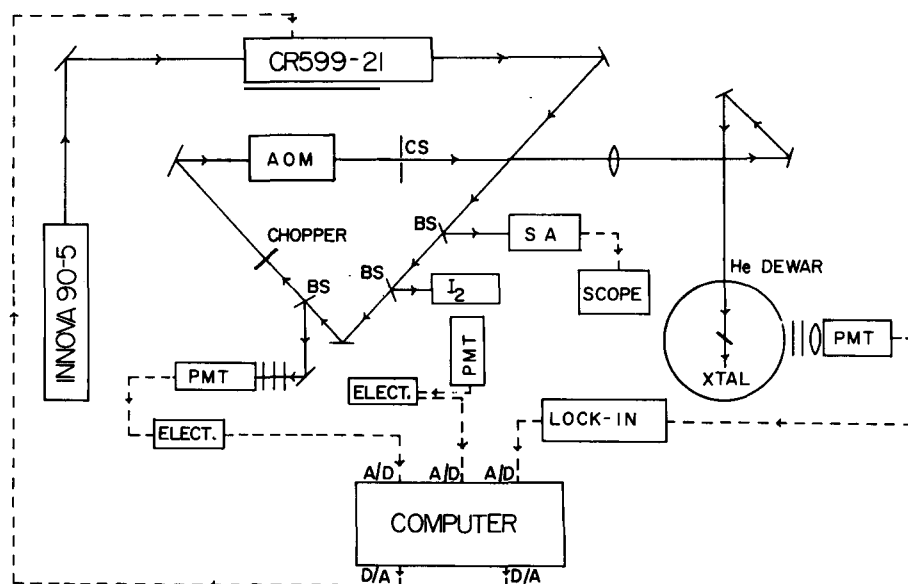


Fig. 1. Experimental setup for nonphotochemical hole burning. This system utilizes a single-mode scanning cw dye laser pumped by 2.5W of the 514 line of an Ar^+ laser. BS = beam splitter; CS = camera shutter; SA = Tropel 240 spectrum analyzer; Elect = electrometer; AOM = acousto-optic modulator; I_2 = gaseous I_2 cell for extract frequency determination.

excitation spectra. Several scans were averaged to improve signal-to-noise.

The experiments involved keeping the fluence, i.e., number of photons hitting the sample fixed while varying the laser power and burn time in an inverse manner. Attenuation of the laser beam without displacing the beam to ensure that the same area of the crystal that was burned is probed was accomplished by using the deflected beam of an acousto-optic modulator as the excitation beam. This allowed for accurately determined attenuation over almost four orders of magnitude. A calibrated camera shutter was used to time short burns (19 ms–2 s), and a stopwatch was used for longer burn times.

The PC/BZA and PC/d-BZA crystals were grown from the melt by the Bridgman technique. The pentacene was obtained from Aldrich and used after vacuum sublimation. Benzoic acid (Baker analyzed reagent 0076) was recrystallized from deionized water and extensively zone-refined (> 800 passes) before use. Deuterated benzoic acid (acid proton substituted only, d-BZA) was prepared by refluxing a saturated solution of zone-refined BZA in D₂O under nitrogen atmosphere for ~ 48 h, followed by recrystallization by slow cooling to 0°C and filtering. The refluxing, recrystallization, and filtering procedures were repeated three times. The extent of deuteration determined by NMR was 95%.

Crystal samples were mounted so that the transition polarized along the short axis of PC was parallel to the laser polarization. Low concentration ($\sim 3 \times 10^{-6}$ moles PC/mole BZA) samples were used. All experiments were performed at 1.8 K.

3. Results

The dependence of the burning time on the hole depth when the fluence is kept constant can be explained with a simple rate-equation model. The model involves three levels, as shown in fig. 2. In this case, the hole burning occurs out of the first singlet level, S₁. A model in which hole burning occurs out of the triplet level was considered but found to be inconsistent with experimental results.

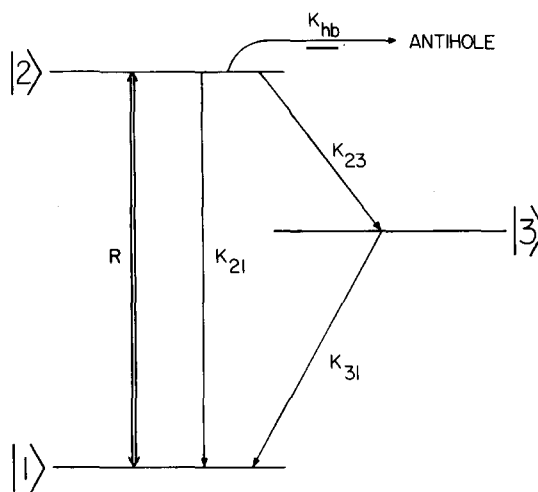


Fig. 2. Level system for the rate equation model. R is the pumping rate. K_{21} includes both radiative and nonradiative contributions, and K_{23} is the intersystem crossing rate, so that $1/\tau_F = K_{21} + K_{23}$, where τ_F is the fluorescence lifetime. K_{31} also includes both radiative and nonradiative processes. K_{hb} is the hole-burning rate constant. The rate constant for returning from the metastable state is small compared to the other rate constants in this system and has been neglected.

It was determined conclusively that the model based on hole burning from S₁ is appropriate for this system. The rate equations for the populations of levels |1>, |2>, and |3> (see fig. 2) are given by:

$$\dot{\rho}_{11} = R(\rho_{22} - \rho_{11}) + K_{21}\rho_{22} + K_{31}\rho_{33}, \quad (1a)$$

$$\dot{\rho}_{22} = R(\rho_{11} - \rho_{22}) - K_{21}\rho_{22} - K_{hb}\rho_{22} - k_{23}\rho_{22}, \quad (1b)$$

$$\dot{\rho}_{33} = K_{23}\rho_{22} - K_{31}\rho_{33}. \quad (1c)$$

Similar equations have been presented for the steady-state case in which no significant amount of population is hole-burned and there is no significant triplet population build-up [11]. A system in which hole burning occurs out of the triplet level has been analyzed with a similar kinetic model [12]. Note that no return of population from the hole-burned metastable state is included in the model. This is because the majority of the hole-burned population forms an antihole (metastable state) which is long-lived compared to the time scale of the experiments and to the inverse of the rate constants involved in the kinetics.

The parameters used in the analysis are defined as follows. R is the pumping rate.

$$R = \chi^2 \frac{1}{T_2} / 2 \left(\Delta^2 + \frac{1}{T_2^2} \right). \quad (2)$$

χ is the susceptibility, where $\chi^2 = 2\mu^2 I / \hbar^2 \epsilon_0 c$. T_2 for PC/BZA and PC/d-BZA have been measured experimentally using both hole-burning and photon-echo techniques [2]. These values are listed in table 1. Using $\mu = 0.7 D$ for the $S_0 \rightarrow S_1$ transition of pentacene, $R = 6987 I \text{ s}^{-1}$ for PC/BZA and $R = 3047 I \text{ s}^{-1}$ for PC/d-BZA for resonant excitation ($\Delta = 0$). I is the intensity of the incident beam in W/m^2 .

K_{23} and K_{21} can be expressed in terms of the fluorescent lifetime, τ_F , and the intersystem crossing yield, Y . The intersystem crossing yield is given by $Y = K_{23} / (K_{21} + K_{23})$. Since $K_{21} + K_{23} = 1/\tau_F$, then $K_{23} = Y(1/\tau_F)$, and $K_{21} = (1 - Y)1/\tau_F$. It should be noted that K_{21} and K_{31} include both radiative and nonradiative contributions. The fluorescent lifetimes for both systems have been measured experimentally and are listed in table 1. The three triplet lifetimes for the T_x , T_y , and T_z sublevels of pentacene/naphthalene mixed molecular crystals have been measured using electron spin-echo techniques [13]. As an estimate for the triplet lifetime in PC/BZA and PC/d-BZA, an average of the T_x , T_y , and T_z sublevels was taken, and each was weighted by its relative populating rate. The estimated effective triplet lifetime is $19 \mu\text{s}$, so that $K_{31} = 5 \times 10^4 \text{ s}^{-1}$. K_{hb} is the absolute hole-burning rate constant.

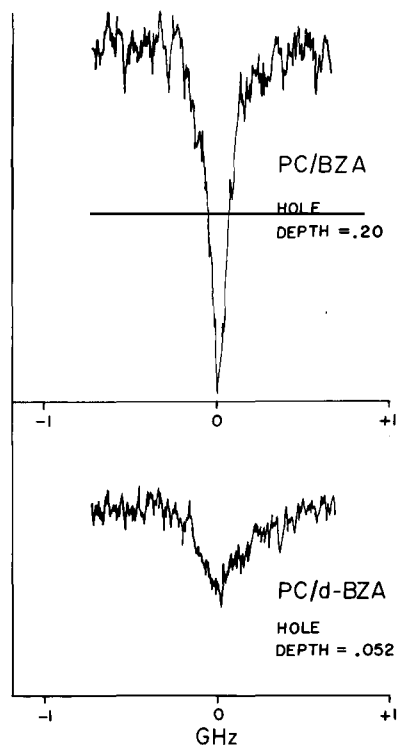


Fig. 3. Comparison of hole depths for PC/BZA and PC/d-BZA. Both samples were burned with the same laser intensity for the same amount of time. The absolute hole-burning efficiency is ten times greater for PC/d-BZA than for PC/BZA, but the hole depth for PC/d-BZA is considerably smaller than that in PC/BZA under identical burning conditions. The drastic increase in ISC yield in PC/d-BZA causes the hole-burning efficiency for PC/d-BZA to appear much less than that for PC/BZA. See text.

Table 1
Results

	T_2	τ_F	Y	K_{hb}	Hole-burning efficiency ^d	1/e Antihole recovery time
PC/BZA	39.0 ns ^a	20.0 ns ^a	0.007 ± 0.001	1.3 ± 0.2 s ⁻¹	2.0 × 10 ⁻⁶	47 min
PC/d-BZA	17.0 ns ^a	9.0 ns ^a	0.60 ± 0.05	14.9 ± 0.5 s ⁻¹	1.5 × 10 ⁻⁵	135 min
PC/PTP ^b						
O ₁	40.8 ns	21.7 ns ^c	0.005 ± 0.001 ^c			
O ₂	43.5 ns	22.7 ns	0.004 ± 0.001 ^c			
O ₃	17.5 ns	9.3 ns	0.64 ± 0.02 ^b			
O ₄	17.2 ns	9.4 ns	0.61 ± 0.02 ^b			

^a Ref. [2]. ^b Ref. [16]. ^c Ref. [17]. ^d The hole-burning efficiency is defined as the number of molecules burned/photons absorbed.

The set of three coupled differential equations (eqs. (1a)–(1c)) are solved by standard matrix inversion techniques to give the population of the three levels (ρ_{11} , ρ_{22} , ρ_{33}) as a function of burn time as the fluence is kept constant. The hole depth (as a fraction) will be given by $(1 - (\rho_{11} + \rho_{22} + \rho_{33}))$ if the total number of molecules is normalized. Figure 3 shows a PC/BZA hole and a PC/d-BZA hole-burned with the same fluence for a moderate intensity.

For a given fluence, the calculated hole depths as a function of burn time are fit to the measured (fractional) hole depths using a nonlinear least-squares analysis which has been modified from one written by Bevington [14]. Only the intersystem crossing yield (Y) and hole-burning rate constant (K_{hb}) are adjustable parameters. Unique fits to the data were obtained which are independent

of the initial choice for Y and K_{hb} . The fits were also insensitive to changes in the estimated value for the triplet lifetimes. Fits were obtained from data sets with a variety of different fluences and a number of different samples to give the values of Y and K_{hb} for both PC/BZA and PC/d-BZA listed in table 1. Figure 4 shows representative fits to the data for the protonated and deuterated cases.

Further information on the kinetics of the system is provided by the antihole recovery times. The disappearance in the dark of the site I antihole for PC/BZA and PC/d-BZA was found to be exponential, with $1/e$ times listed in table 1.

4. Discussion

Table 1 presents the experimental results for pentacene in BZA and in d-BZA as well as parameters relating to pentacene in another host crystal, p-terphenyl (PC/PTP). PC/PTP, which does not undergo hole burning, has four inequivalent sites in the PTP lattice. This results in four absorption origins labeled $O_1 - O_4$ [15]. These sites differ only in the twist angle of the PTP rings surrounding the pentacene sites. Consider the first two columns of the table. For PC in BZA, d-BZA and the four sites in PTP, the homogeneous dephasing time, T_2 , is equal to twice the excited state lifetime, τ_F , within experimental error. At the low temperature of these experiments (1.8K), population relaxation is the dominant line-broadening mechanism. The variations in T_2 's are due exclusively to the variations in the lifetimes.

Column three of table 1 lists the intersystem crossing yields. The yields for PC/BZA and PC/d-BZA were determined by the experiments discussed in section 3. The O_1 and O_2 PC/PTP yields were determined by fluorescence recovery measurements [17]. The O_3 and O_4 yields were measured using picosecond stimulated photon echo experiments [16]. At first glance, the large increase in ISC yield in going from BZA to d-BZA is surprising. Deuteration is a very small change in the host lattice. However, the four sites in PC/PTP exhibit this same behaviour, demonstrating that the large changes in lifetime and ISC are not

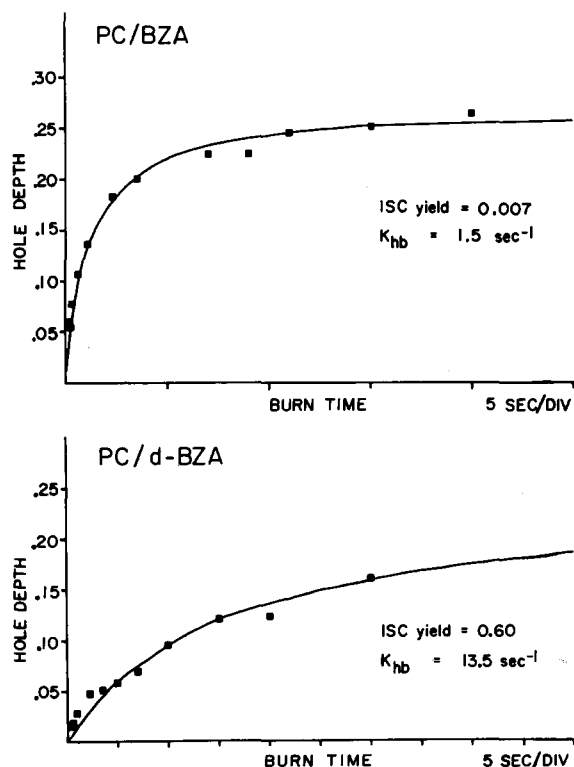


Fig. 4. Result of constant fluence experiments, in which hole depth is measured as a function of burn time. The solid curves are the theoretical fits to the data using eq. (1). The variable parameters used in the fits were ISC yield and K_{hb} .

peculiar to or intimately involved with the hole-burning phenomenon.

In PC/PTP the differences in ISC yields and the concomitant differences in lifetimes have been ascribed to shifts in the pentacene second triplet state, T_2 [16]. In O_1 and O_2 , T_2 is somewhat above S_1 . Intersystem crossing must occur to T_1 . In a system such as pentacene in which both S_1 and T_1 are $\pi\pi^*$ states derived from the same molecular orbitals, direct spin-orbit coupling is forbidden [18]. Therefore the ISC yield is low. In contrast, O_3 and O_4 have T_2 below S_1 , opening an allowed ISC route and producing a high ISC yield. The decrease in lifetime occurs because ISC is an important radiationless relaxation pathway for O_3 and O_4 .

In the PC/BZA systems, deuteration of the BZA carboxylic acid groups results in a slight increase in the lattice unit cell dimensions [19]. Like the ring twist differences in the O_3 and O_4 sites in PC/PTP, the lattice change is sufficient to bring T_2 below S_1 in PC/d-BZA, resulting in a high ISC yield and a fast S_1 lifetime. In fact the increase in ISC upon deuteration could be accurately estimated strictly from the decrease in lifetime. The similarity between lifetimes and ISC yields for the BZA hosts and the four sites of PTP supports the accuracy of the fits to the hole-burning data.

Earlier it was reported that the decrease in lifetime in PC/d-BZA was in some manner intimately related to the hole-burning process [2]. While not related to the hole-burning mechanism, the increase in ISC yield does substantially affect the *apparent* hole-burning efficiency in PC/d-BZA under high-intensity illumination. The *apparent* hole-burning efficiency is the number of molecules burned divided by the number of photons calculated to be absorbed using the low power optical density of the sample. The high ISC yield in PC/d-BZA results in a substantial triplet bottleneck. Under high intensity illumination, considerable population resides in the T_1 state, decreasing the effective optical density of the S_0 to S_1 absorption, and therefore the hole burning is greatly reduced (see fig. 3). This fact led to an initial report that upon deuteration the hole-burning efficiency decreased by a factor of 100.

Column five of table 1 shows that the absolute hole-burning efficiency, i.e., the number of molecules burned divided by the number of photons absorbed, is actually an order of magnitude greater in PC/d-BZA than in PC/BZA. Column four gives K_{hb} , the rate constant for hole burning, obtained from the fits of the data to eq. (1). K_{hb} is a pseudo-first-order rate constant, representing what may be a very complex multistep process involving a number of rate constants. Within experimental error, K_{hb} increases an order of magnitude upon deuteration of BZA.

In column six of table 1 the site I antihole recovery times are listed. The disappearance of the antihole and the filling of the hole occur ~ 3 times slower in PC/d-BZA than in PC/BZA. Thus deuteration of the BZA carboxylic acid groups increases the hole-burning rate but decreases the rate of hole filling.

The changes produced upon deuteration suggest that the hole-burning process is not a single step process governed by a first-order rate constant. In a normal single-step process involving hydrogens, deuteration generally reduces the rate constant a factor of ~ 6 at 298 K because it lowers the vibrational zero-point energy, effectively increasing the height of the potential barrier which must be crossed for the process to occur. However, since the ratio of proto and deuterio first-order rate constants is proportional to $e^{-\Delta E/KT}$, where ΔE is the difference between the vibrational zero-point energies, then at the low temperature at which these experiments were performed, deuteration should cause a single-step activated process to slow down by orders of magnitude. The increase upon deuteration of the hole-burning rate constant, K_{hb} , can be understood only if K_{hb} is a pseudo-first-order constant that actually represents a multistep process with one or more intermediates. Then K_{hb} will be a ratio of sums of rate constants, and it is possible for K_{hb} to increase even if the individual rate constants which control the overall process decrease upon deuteration.

The spontaneous hole filling which occurs in the dark, also does not appear to be consistent with a single-step process. The site I antihole reversion is temperature independent at low temper-

ature (~ 2 K to ~ 20 K), indicating a tunneling process [21]. NMR studies have also shown tunneling to be important at low temperature in pure BZA crystals [22]. Taking a value of 1.0 \AA for the barrier width, a simple calculation yields a barrier height of 20 cm^{-1} for $K_{\text{H(tunneling)}}/K_{\text{D(tunneling)}}$ equal to the experimentally determined value of 3. This barrier height is inconsistent with the temperature dependence of the antihole recovery rate [21]. In the temperature range 20–100 K, the antihole recovery rate appears as an activated process with an activation energy of 400 cm^{-1} , i.e., $K = A \exp[-\Delta E/kT]$ with $\Delta E = 400 \text{ cm}^{-1}$ and A of $\sim 10^2$ [21]. Furthermore, studies of pure BZA have shown that the hydrogen bond tautomerization is an activated process, with an activation energy of 400 cm^{-1} and $A = 2 \times 10^{11}$ [20]. Transition state theory gives the A factor as

$$A = \frac{ekT}{h} \exp(\Delta S^\ddagger/k),$$

where h is Planck's constant, k is the Boltzmann's constant, T is the temperature and ΔS^\ddagger is the entropy change for the transition state. At $T = 100$ K and for $\Delta S = 0$, $A = 6 \times 10^{12}$. It is not physically possible for ΔS^\ddagger to be a sufficiently large negative number to bring A for the antihole recovery down to the observed value of $\sim 10^2$, since the tautomerization is essentially a unimolecular reaction. This and the discrepancy in barrier heights obtained from the deuteration experiments and the temperature dependent recovery experiments suggest that the rate constant for the antihole recovery (hole filling) is a pseudo-first-order constant that actually represents a multistep process.

Fluorescence lifetime measurements of thioindigo dye doped into BZA and d-BZA have resulted in estimates for $K_{\text{H(tunneling)}}$ and $K_{\text{D(tunneling)}}$ in BZA and d-BZA at liquid helium temperatures [10]. The excited state values reported are $K_{\text{H(tunneling)}} = 4.5 \times 10^8 \text{ s}^{-1}$ and $K_{\text{D(tunneling)}} = 4.9 \times 10^6 \text{ s}^{-1}$. This observed isotope effect is more consistent with a single-step tunneling process with a barrier height of 430 cm^{-1} , which is similar to that of pure BZA. However, it

is necessary to emphasize that the thioindigo/BZA system is significantly different from the PC/BZA system in many aspects. When thioindigo is used as the chromophore, thermal population of different tautomeric forms of BZA and d-BZA is observed at liquid helium temperatures. No detectable metastable photoproducts are formed upon hole burning, and the hole-filling time is on the order of one minute. No hole burning is observed when d-BZA is the host. It appears that the differing guest–host interactions in the pentacene and thioindigo systems have caused the potential surfaces describing the tautomerization to shift dramatically such that the dynamics of the processes are different.

Finally, it has been suggested that hydrogen abstraction from BZA was responsible for hole burning in PC/BZA although hydrogen bond tautomerization occurs in thioindigo/BZA and pure BZA [21]. This idea arose out of an attempt to thermally produce antihole population. Since no antihole was observed after raising a PC/BZA sample to 120 K and then quenching in liquid helium, it was postulated that the ground state of the antihole was at least 1000 cm^{-1} higher in energy than the normal ground state of PC/BZA.

In the experiment described above, it was assumed that the system had come to thermal equilibrium before it was quenched at liquid helium temperature. However, thermal equilibrium could not occur on the time scale of the experiment if the energy levels differ by 1000 cm^{-1} . The 1000 cm^{-1} is an indication of a barrier height rather than difference in energy between the two states. Therefore, the failure to observe thermal population of the site I antihole at 120 K is not inconsistent with a hydrogen bond tautomerization mechanism for the hole burning. Furthermore, given that the typical energy required to break an O–H bond is $\sim 40000 \text{ cm}^{-1}$ (111 kcal/mole) and the pentacene excited state energy is only $\sim 17000 \text{ cm}^{-1}$, it seems that the proposed hydrogen atom abstraction mechanism is energetically unfeasible. To date, all existing evidence is consistent with a tautomerization mechanism. However, the nature of the forward and reverse processes are not yet understood in detail.

4. Concluding remarks

We have presented the results of constant fluence hole-burning experiments for PC/BZA and PC/d-BZA which are analyzed in terms of a rate-equation model. Fits to the model show that hole burning occurs from the first singlet state, and gave values for the absolute hole-burning efficiencies and intersystem crossing yields for the two systems. It is shown that the intersystem crossing yield for PC increases three orders of magnitude when the host lattice is deuterated. The changes in guest–host interactions produced by a slight lattice expansion in d-BZA causes the second triplet state to shift in energy below S_1 , opening up an allowed intersystem crossing pathway.

Earlier it was reported that the hole-burning efficiency for PC/d-BZA was two orders of magnitude less than for PC/BZA. However, in PC/d-BZA under high intensity illumination the very high ISC yield causes a significant amount of population to reside in the triplet state. When this effect is taken into account, the absolute hole-burning efficiency of PC/d-BZA is demonstrated to be an order of magnitude greater than that of PC/BZA.

The hole-burning and hole-filling processes were discussed in terms of the effect of deuteration on tunneling and thermally activated processes using the concepts of unimolecular reaction transition state theory. This analysis leads to the conclusion that both hole burning and hole filling involve complex multistep pathways. Future experiments on the temperature dependence of hole-burning efficiencies in both PC/BZA and PC/d-BZA as well as the temperature dependence of the hole-burning efficiencies of the antiholes in these systems will aid considerably in our understanding of the hole-burning mechanism.

Acknowledgement

We would like to thank Dr. Howard Lee for extensive collaboration on preliminary experiments and Professor John I. Brauman for very helpful discussions pertaining this work. This work was supported by the National Science Founda-

tion, Division of Materials Research (Grant #DMR84-16343). C.A.W. would like to thank the National Science Foundation for a predoctoral fellowship.

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