

## Spectral hole burning: Spontaneous and photoinduced tunneling reactions in low temperature solids

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*Abstract:* Spectral hole burning is frequently observed in molecular solids when a solute dye molecule in a solvent matrix at very low temperature is irradiated with light having a narrow frequency bandwidth. This phenomenon relies on photo induced changes of the absorption spectrum of the solute. All photochemical reactions lead in principle to such changes, but the extreme sensitivity of the method makes it particularly suitable for the characterization of reactions that occur at cryogenic temperatures with very small yield and that would be difficult to observe by conventional methods. Here we will discuss in more detail the contribution of proton tunneling reactions to spectral hole burning and in particular new results obtained in pentacene doped benzoic acid crystals, which is an excellent model system.

### Introduction

Spectral hole burning is the frequency selective bleaching of the absorption spectrum of a material, which leads to an increased transmission (a "spectral hole") at the selected frequency.<sup>1</sup> Two basic requirements, that must be met for the observation of this phenomenon, are: 1) *The spectrum is inhomogeneously broadened* and 2) *the material undergoes, subsequent to light absorption, a modification which changes its absorption spectrum*. Typical materials include dye molecules dissolved in suitable host matrices and the frequency selective irradiation is usually realized by a narrow band laser.

The requirement of inhomogeneous broadening means that chemically identical molecules have different transition frequencies since they experience different environments. As a consequence, only a subset of the ensemble of molecules will be excited by a narrow band light source. For electronic transitions of dye solutes in organic solvents inhomogeneous broadening ( $\Gamma_{inh}$ ) typically lies in the range of 100 to 1000  $\text{cm}^{-1}$ . The precision with which it is possible to selectively address a subset of molecules is determined by the homogeneous line width ( $\Gamma_{hom}$ ) of the transition. This homogeneous line width is determined by the lifetime ( $T_1$ ) of the excited level and by fluctuations of the transition energy due to motions of the environment (so-called pure dephasing processes characterized by  $T_2^*$ ). At room temperature the contribution to the line width, due to thermal fluctuations, is comparable to the inhomogeneous width, while in the limit of very low temperatures the line width is entirely determined by the decay of the initially excited state. In dye molecules with intense  $S_0 \leftrightarrow S_1$  transitions typical lifetimes of  $S_1$  are  $5 \cdot 10^{-9}$  sec, corresponding to a homogeneous line width of  $\Gamma_{hom} = 10^{-3} \text{ cm}^{-1}$ . The ratio of  $\Gamma_{inh}/\Gamma_{hom} = 10^6$  implies that selective excitation allows to distinguish, by their "frequency address" an equal number of subsets of solute molecules. The spectral resolution obtained via hole burning in low temperature solids is increased by the same factor, which not only makes this phenomenon an attractive technique to record high resolution spectra but also opens interesting perspectives for optical data storage and processing.<sup>1-3</sup> For analytical purposes this increased sensitivity allows, for example, to detect photochemical changes in 1 out of  $10^8$  dye

molecules in a small volume of  $\approx (10\mu\text{m})^3$ , so that photochemical hole burning is well suited for the study of photochemical reactions, occurring at low temperatures with very small yield.

In order to effectively obtain this gain in resolution and in sensitivity, the pure electronic 0-0 transition must be excited directly, since fast relaxation processes usually shorten the lifetime of higher levels involving the simultaneous excitation of internal or external vibrations (vibronic bands or phonon sidebands) by several orders of magnitude so that the homogeneous line widths of these transitions increase correspondingly and the selectivity is lost. The relative intensity of the 0-0 transition in an electronic spectrum is given by the product of the Franck-Condon and Debye-Waller factors, which describe the coupling of the electronic excitation with internal (intra molecular vibrations) and external (phonons) nuclear modes respectively. This product should therefore be sufficiently large. Molecules, which upon electronic excitation undergo large geometry changes and/or large changes of the electronic charge distribution are therefore unfavorable candidates for hole burning studies.<sup>3</sup>

The modification of the material subsequent to light absorption can be induced by a variety of different processes.<sup>1,3,4</sup> The simplest case is that of a photochemical reaction of the dye itself. Examples of materials, where such so-called "photochemical hole burning" is observed, are free base porphyrins and phthalocyanines in a variety of hosts. Here the photochemical reaction is the tautomerization of the inner protons. Hole burning is also observed as a result of the ionization or the dissociation of the guest molecule, the first example being *s*-tetrazine in a variety of host matrices. Even when the dye itself is chemically unchanged hole burning will occur when the environment of the dye is altered. Since transition frequencies are spectrally shifted in a new environment, a spectral hole is created at the old transition frequency at which the dye molecule was excited. This process is termed "photo physical hole burning" and is nearly always reversible so that original spectrum can be recovered and the hole is erased. This "hole filling" can be spontaneous or it may be induced by raising the temperature or irradiating the sample with light of a different frequency. In fact the distinction and the borderline between photochemical and photophysical hole burning is often artificial: Photophysical hole burning can be regarded as supramolecular photochemical hole burning and, as will be discussed below, photophysical hole burning can be the result of reversible photochemical reactions that lead, in particular in glasses, to rearrangements of the environment of the dye, which displace the transition frequency sufficiently to create a spectral hole. While photophysical hole burning is very frequently observed in disordered solids (glasses), the structural changes of the environment as well as the mechanisms leading to such changes have rarely been established.<sup>4</sup> An indication of the importance of proton displacements comes from significant deuteration effects on the rates of hole burning and recovery ("hole filling") that have been observed for these processes. In several crystalline host systems photophysical hole burning was also observed. Here the geometry is better defined and it becomes in principle possible to gain more detailed information about the changes induced in the environment of a dye as well as about the reaction mechanisms leading to these changes.

Hole burning, which apparently is fully reversible, has been observed in a large number of crystalline guest-host systems. Among these, doped benzoic acid crystals have proven to be particularly interesting model systems for "photo physical hole burning".<sup>5-14</sup> In this matrix it is the acid protons that are displaced from their regular positions so that the dye finds itself in a "defect environment". Since the proton defect positions in this crystalline matrix are well defined, the absorption lines of a dyes in such "defect sites" are sharp and discrete so that it becomes possible to characterize in detail yields of formation, rates of recovery, thermal stability, deuteration effects, etc.. We will review here recent work that has led to the identification of the reaction mechanism leading to the creation of proton defect positions and to a characterization of these defect sites.<sup>9-14</sup>

### Properties of benzoic acid host crystals

In the crystal, benzoic acid forms symmetric dimers linked by two hydrogen bonds. In the monoclinic unit cell, the two symmetry equivalent dimers occupy centers of inversion. Substitutional mixed crystals are formed by replacing one acid dimer of the host by a guest molecule of similar size. Since single crystals of benzoic acid with high optical quality are fairly easily grown by Bridgeman techniques,<sup>15</sup> this material has been used as a host matrix for a variety of guest molecules. In particular for pentacene and different indigo dyes it has been shown that the dye guest can be used to induce and to monitor two different types of displacements of the acid protons of the host matrix from their regular positions.<sup>16</sup> One of these processes is the tautomerization of the benzoic acid dimers and an other a more severe rearrangement of the acid protons.

**Tautomerization:** For each benzoic acid dimer there exist two tautomer structures which are inter converted by a concerted transfer of the two acid protons. In the crystal, the tautomers have different energies: At low temperatures only the most stable form is populated and the protons are frozen in an ordered configuration, while at higher temperatures the crystal contains a random mixture of both tautomers so that the acid protons are no longer ordered. Using indigo dyes as a probe it has been possible to fully characterize the tautomerization reaction at low temperatures when proton tunneling dominates.<sup>7,17-22</sup> Under these conditions the tautomerization occurs on a nanosecond time scale and is slowed down by about three orders of magnitude in the deuterated crystal.

Here we will be concerned with an other reaction which leads to displacement of the protons to positions separated by larger energy barriers. This reaction occurs on much slower time scale of longer than  $\mu\text{sec}$  to many hours and is responsible for spectral hole burning in producing long lived holes. Even though the two types of reactions are distinct and occur on completely different time scales, there are some interesting connections. On the one side, hole burning was used to perform high resolution spectroscopy and to thereby unravel the tunneling level structure resulting from the tautomerization of benzoic acid dimers, mentioned above.<sup>21</sup> Inversely it was found that the efficiency of hole burning depends strongly on the tautomer configuration of the benzoic acid dimers of the host next to the dye guest (see below).<sup>8</sup>

### Hole burning in pentacene doped benzoic acid

There are several common features, that are observed for hole burning of all different dye guest molecules in benzoic acid host crystals: The process is fully reversible so that the original absorption spectrum is recovered. This hole recovery occurs spontaneously in the dark on time scales ranging from sub-second to hours and more and becomes independent of temperature in the limit of low temperatures. The rate of hole recovery can be increased by raising the temperature or by irradiating the sample at different wavelengths. After hole burning, increased absorption is observed in a frequency range close ( $\pm 150 \text{ cm}^{-1}$ ) to the original absorption of the dye and this new absorption decays as the hole is filled. Within experimental accuracy, the integral optical density is conserved by this spectral redistribution of absorption. The rates of all processes are slowed down by many orders of magnitude in a deuterated matrix (only the acid protons are exchanged). All these features are best exemplified and have been studied in more detail for pentacene as a guest.

Figure 1 (top) shows the absorption of pentacene in benzoic acid in the region of the electronic origin. The observation of a single, sharp 0-0 line at  $16998.3 \text{ cm}^{-1}$  is consistent with the fact that in the host matrix there is only one physically acceptable way in which pentacene can replace a benzoic acid dimer. Subsequent to laser irradiation at the frequency of the electronic 0-0 line ( $75 \text{ min.}, \approx 50 \text{ mW/cm}^2$ ), the bottom spectrum is observed. All new absorption lines in the bottom trace are 0-0 lines of spectra that have the same vibrational structure as the original spectrum and are thus attributed to pentacene molecules. The spectral shift indicates that the environment of the guest has been changed. The shift of transition frequency is typical for site shifts commonly observed in mixed crystal spectra. All new lines decay with lifetimes of up to several hours showing that the new sites are metastable. Since the bottom spectrum was recorded ca. 10 min. after laser irradiation, sites with shorter lifetimes have already decayed. These short lived sites are observed in emission or in absorption under continuous irradiation. More than 20 such sites could be identified. The rates of producing these defect sites as well as their decay rates are decreased by factors of up to  $10^5$  in the deuterated matrix. These large deuteration effects prove that the defect sites are linked with a displacement, from their regular positions, of protons of the host matrix. Both, the very large deuteration effect and the observation that the rates reach temperature independent finite values at low temperatures demonstrate that all processes occur by proton tunneling. Since tunneling rates scale with the square of the tunneling matrix element, the deuteration effect can be used to estimate properties of the barriers (height, width) over which the protons are displaced from their regular position. Reasonable combinations of values, consistent with the largest observed deuteration effect of  $10^5$ , are barriers in the range of several  $10^3 \text{ cm}^{-1}$  combined with proton displacements over 1 to 2 Å.

### Relaxation and inter conversion of defect sites

The ensemble of defect sites is metastable and decays. After leaving an irradiated sample for a sufficiently long time in the dark the spectrum becomes identical to the one recorded prior to irradiation, demonstrating that the displaced protons have returned to their original stable positions. This relaxation process, however,

is not necessarily direct and protons, returning to the stable position may do so by passing through other metastable positions, corresponding to different defect sites. This communication of defect sites is observed by monitoring their population via the intensity of the corresponding 0-0 absorption lines. Figure 2 illustrates this *spontaneous site inter conversion* for a group of lines at energies of 52.3 to 74.3  $\text{cm}^{-1}$  above the 0-0 line of the stable site at 16998.3  $\text{cm}^{-1}$ . Such cascading relaxation processes can be monitored provided that the intermediate sites are sufficiently long-lived so that their population increase becomes measurable. In fact our observation suggest the possibility that most relaxation paths of protons from more stable defect sites pass through less stable sites before returning to their regular positions.

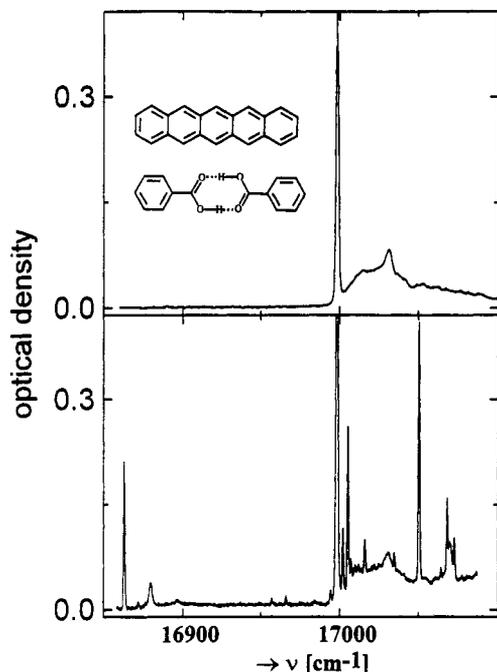


Fig. 1 Absorption spectrum of pentacene in benzoic acid at 1.6 K prior (top) and subsequent (bottom) to laser irradiation at 16998.3  $\text{cm}^{-1}$ .

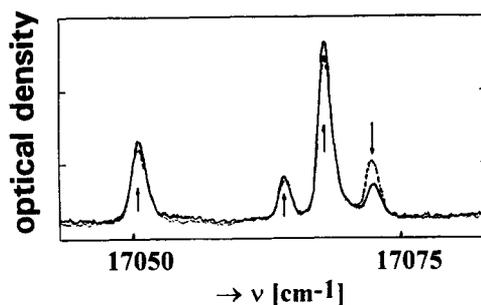


Fig. 2 Spontaneous site interconversion in the dark. The spectra, represented by broken and full lines respectively, were recorded at an interval of 3 hours and the arrows indicate the intensity changes.

Population redistribution between different defect sites is also induced by irradiation. Just as the 0-0 line of the stable site, 0-0 lines corresponding to defect sites can be hole burned and other defect sites are produced. Figure 3 illustrates this *photo induced site inter conversion* for the line at 17050.6  $\text{cm}^{-1}$ . Remarkably, the efficiency of this process is higher by more than two orders of magnitude than the efficiency observed for the stable site. Irradiation with 50  $\text{mW}/\text{cm}^2$  for only 20 sec completely erases the line at 17050.6  $\text{cm}^{-1}$  and produces the bottom spectrum of Fig. 3, where the intensity of some existing lines is increased and a new weak line at 17059  $\text{cm}^{-1}$  is created. In addition weak lines between 17005 and 17010  $\text{cm}^{-1}$  have also been erased. This latter observation is explained by the fact that any site can also weakly be excited via phonon side bands extending to higher energies of the 0-0 line and will be erased if the efficiency of hole burning is sufficiently high.

In many regards the ensemble of defect sites can be regarded as a disordered solid and this ensemble indeed exhibits many of the characteristics observed for the ensemble of dye molecules doped into a glass. The spread of transitions energies of the different defect sites of over 200  $\text{cm}^{-1}$  is comparable to the inhomogeneous width commonly observed for electronic transitions in glasses. Site inter conversions are also observed for dye molecules in glasses and can be represented as relaxation processes between different local minima on a multidimensional potential energy surface as shown as cartoon in Fig. 4. There are two main differences, which are however not essential for this comparison: 1) In contrast to a doped glass the ensemble of defect sites is not conserved at longer times, but decays to the stable substitutional site of the doped crystal. 2) In a glass the distribution of sites is continuous, while the defect sites in the crystalline

model system represent discrete classes of molecules occupying various well defined sites (if we neglect the small inhomogeneous width of about  $1 \text{ cm}^{-1}$  observed for a given defect site).

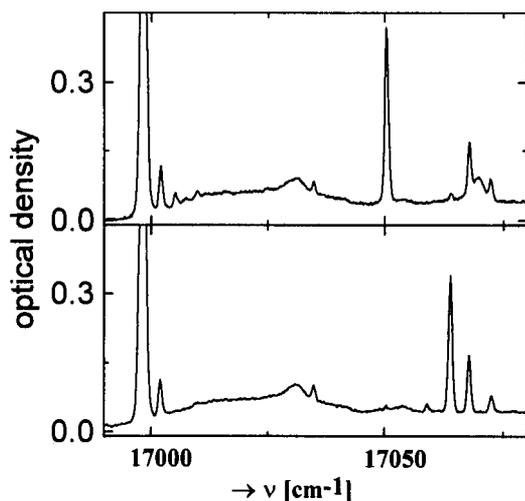


Fig. 3 Photo induced site inter conversion. Spectra recorded before (top) and after (bottom) irradiation of the defect site at  $17050.6 \text{ cm}^{-1}$ .

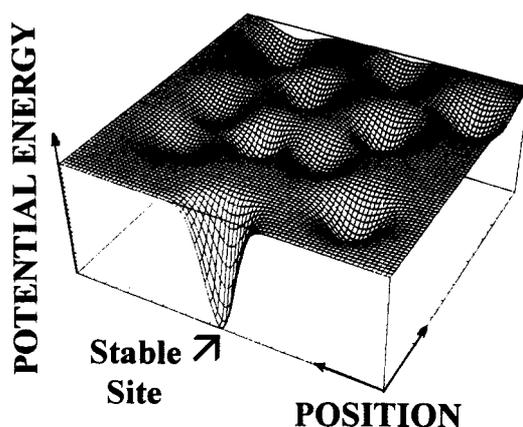


Fig. 4 Cartoon of the potential energy surface for displaced protons in benzoic acid.

#### Reaction mechanism leading to the generation of defect sites

Excluding the inner tautomerization of the acid dimers (see above), the mildest possible form of a defect involves the breaking of one hydrogen bond of an acid dimer and the reorientation of the corresponding acid hydrogen on a circle defined by the C-O-H angle of about  $110^\circ$ . The maximum hydrogen displacement in this case is about  $1.7 \text{ \AA}$  and the defect would have a dipole moment of about 2.5 Debye. A number of different defects can be created in this way as the hydrogen displacement can occur on different neighboring benzoic acid dimers, and several potential minima may exist on the circles defined above. A more severe defect would be created if the O-H bond is broken and the proton is displaced to some interstitial position. In this case the distances over which protons are displaced can be greater and the number of possible defect structures can be very large.

Both scenarios of creating "mild" or "severe" defects require a mechanism which leads to the displacement of the (acid) hydrogen atom. In previous work we have proposed that a reversible proton/hydrogen transfer reaction between the host and the guest could create the defect structures.<sup>6</sup> An energy diagram of this reaction scheme is given in Fig. 5: Pentacene, in the excited state ( $\text{PC}^*$ ), abstracts a proton/hydrogen from the matrix, but this hydrogenated pentacene ( $\text{PC-H}$ ) is unstable and dissociates into ground state pentacene and the proton/hydrogen which is released back to the matrix, not necessarily to its original position but to a displaced position such as described above, so that pentacene finds itself in a defect site ( $\text{PC}_i$ ). Excitation of pentacene in a defect site triggers an analogous reaction. The spontaneous site inter conversions are indicated by broken arrows in Fig. 5.

Searches for the reaction intermediate, i.e. hydrogenated pentacene, by ESR and optical spectroscopies have been unsuccessful. The low yield of the reaction as well as a very short lifetime of the  $\text{PC-H}$  intermediate limit the concentration of reaction intermediates and explain this failure. The ESR experiment does indicate that the defect structures (which can be created in sufficient concentration) are not associated with radical pairs. In order to substantiate the proposed mechanism, we have made measurements of the yield of producing different defect sites as a function of selective deuteration of pentacene. These yields are expected to change since the proposed reaction mechanism involves not only the motion of the acid hydrogen atoms of the host but also a motion of the pentacene hydrogen atoms (see Fig. 6). For a variety of different partially deuterated pentacene molecules we have found that reaction yields depend indeed significantly (up to a factor of 10) upon the selective deuteration of the guest. Both the efficiency of depleting, by light irradiation, the stable site and the efficiency of populating a given defect site were found

to depend on the partial deuteration of pentacene. In addition it was found that the rate of intersystem crossing was strongly influenced by this partial deuteration so that the relative populations of the lowest excited singlet and triplet states varied accordingly.<sup>23</sup> Since the yield of creating defect sites follows the singlet state population it is proven that the reaction occurs out of this state.

The mechanism proposed in Fig. 5 suggests that some new defects, created via irradiation of an existing defect, may not be accessible directly by irradiation of the stable site and would correspond to "double" defects, where two different protons have been displaced (e.g. PC<sub>5</sub> in Fig. 5). Conceivably some of these structures are centrosymmetric if the two hydrogen displacements occur on either side of the pentacene guest and are related by the center of inversion of the crystal. Stark measurements which verify this proposition are presented below.

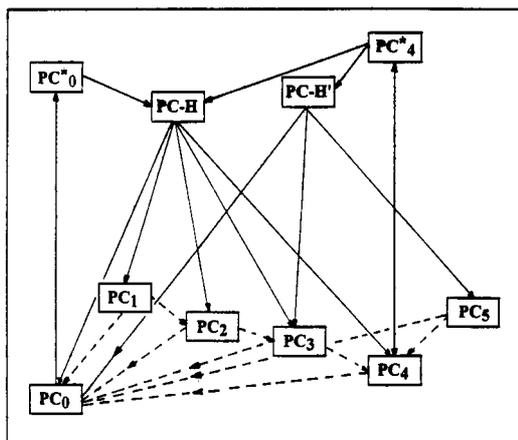


Fig. 5 Schematic energy diagram for the reaction leading to the creation of defect sites.

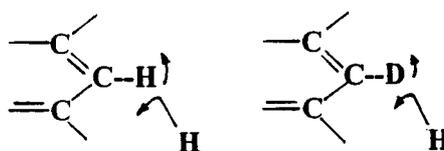


Fig. 6 Illustration of the effect of deuteration of pentacene on the reversible hydrogen atom transfer reaction.

#### Local crystal field at the defect sites

When one proton of the host matrix next to a pentacene guest is displaced and a defect site is created, the center of inversion is lost and the crystal field will have a dipolar component which induces a dipole moment in pentacene. The orientational degeneracy of such a defect site is lifted in an applied electric field and the corresponding spectral lines are split by  $2\Delta\mu \cdot F$ . While the transition frequency in the centrosymmetric site is displaced by  $-\frac{1}{2}F \cdot \Delta\alpha \cdot F$ , where  $\Delta\mu$  and  $\Delta\alpha$  are the changes, upon electronic excitation, of the dipole moment and the polarizability of pentacene and  $F$  is the electric field in the crystal resulting from the applied field. Defining the crystal field,  $F_c$ , as being equal to an externally applied field that induces the same dipole moment, i.e.  $\mu = \alpha \cdot F_c$ , allows to evaluate  $F_c$  at defect sites by comparing the line shift of the stable site with line splittings of defect sites. Such measurements had previously confirmed the polar character of all defect sites with transition energies lower than that of the stable site. The crystal field strengths were found to be different for each site and to lie in the range of  $10^6$  V/cm.<sup>16</sup> Having discovered sites with transition energies to the blue of the stable site that might be assigned to double defects, such measurements were repeated for this spectral region and are shown in Fig. 7. The measurements in a modulated electric field clearly show weak signals which equal the first derivative of the absorption lines of the stable site at  $16998.3 \text{ cm}^{-1}$  and of a nearby defect site at  $17002.2 \text{ cm}^{-1}$  and correspond to a small shift to lower energy of these transitions by equal amounts for the two lines. This measurement proves that the defect site giving rise to the line at  $17002.2 \text{ cm}^{-1}$  is a double defect in which two protons are displaced symmetrically on either side of the pentacene guest. The modulated signals for the three lines at  $17064$ ,  $17068.4$ , and  $17072.6 \text{ cm}^{-1}$  are stronger and are fitted by second derivatives of the absorption lines. These signals reflect the larger splitting of the lines by values which differ by a factor of about two among the three lines. All other lines in Fig. 1, which are attributed to defect sites, are also split in an applied field and correspond therefore to polar sites. The transition energy of the only site, that could with confidence be attributed to a symmetric double defect, is close to the one of the stable site: This observation suggests that a major contribution to the site shifts may come from the crystal field which is expected to be smallest for symmetric sites.

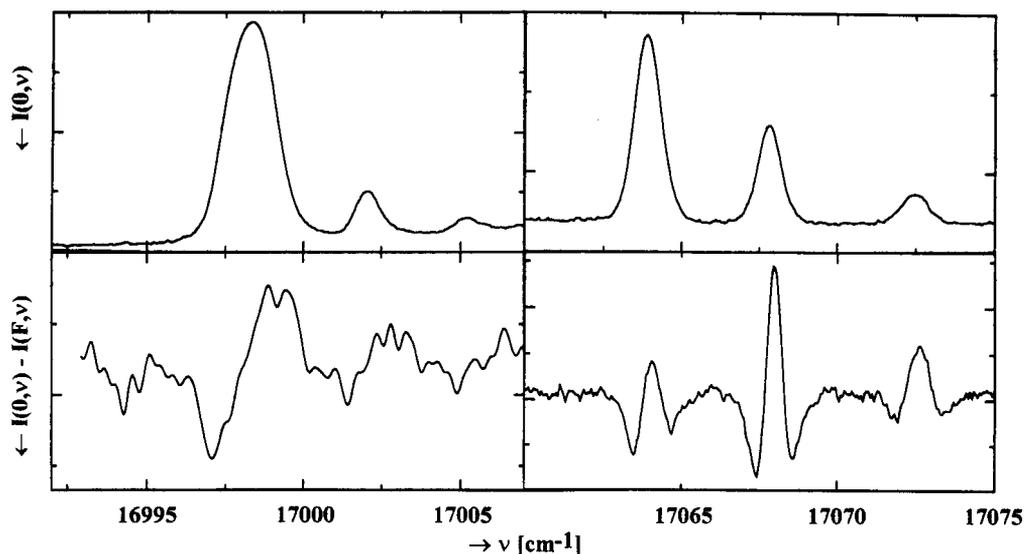


Fig. 7 Measurements of electric field induced line shifts and splittings for the stable and different defect sites. The top traces are the absorption spectra on a linear light intensity scale in zero field, and the bottom trace is the difference of light intensity measured without and with field by applying a square wave modulated electric field of 50 kV/cm along the crystal  $c'$  axis.

## Conclusion

The demonstration, that in many dye doped crystals light induced reversible proton/hydrogen transfer reactions between the excited dye and the matrix occur by tunneling at cryogenic temperatures and lead to structural rearrangements in the environment of the dye, suggests that such reactions occur in a quite general fashion in condensed phases. These reactions offers an appealing explanation for mechanisms that contribute to so-called photophysical hole burning in glasses. Being reversible, such reactions would be essentially unobservable at higher temperatures, where the spectral selectivity, that allows to discern different environments, is lost. In the specific case of pentacene, the reaction discussed above had been questioned on the ground that the excitation energy available would not be sufficient to break an O-H bond as required here.<sup>24</sup> This argument is certainly valid for free reaction partners but neglects corrections to the energy balance in the condensed phase that may be significant. The very strong increase of reactivity in metastable defect sites, where slightly more energy is available, suggests that the excess energy for the stable site may indeed be just at minimal limit required so that any, however small, increase of energy has a strong influence on the reaction rate.

Not surprisingly, all experiments indicate that the reaction is very sensitive to small geometry changes in the reaction partners. For thioindigo, for example, it was found that the yield of hole burning changed by over two orders of magnitude for different tautomer configurations of the neighboring benzoic acid dimers,<sup>8</sup> even though only on one side of the centrosymmetric guest molecule the acid proton is displaced along the intermolecular hydrogen bond by 0.7 Å. This change in reactivity was observed only in the deuterated matrix but not in the protonated: As the reaction occurs from the short lived singlet state and as tautomerization is faster than the singlet decay in protonated but much slower in the deuterated matrix this different behavior can be rationalized. An other indication of the sensitivity to small changes of the topology comes from the fact that out of the about 20 defect sites analyzed only one is a symmetric double defect, while on statistical grounds more are expected if the reactivities of positions in pentacene related by a center of inversion where to be independent.

The use of single crystals in the present work has allowed to identify the reaction mechanism, as in a crystal matrix the spectral selectivity is sufficient to distinguish different sites in the host and different isotopic species of the guest. These advantages are however lost at higher temperatures when the spectral selectivity is no longer sufficient. A detailed analysis, such as presented here, would be impossible in glasses, where

such selectivity is lost. Neither hole burning and not even single molecule spectroscopy, a powerful technique that has recently emerged and allows to follow the behavior of individual molecules in glasses,<sup>25,26</sup> would be able to provide, for example, as detailed information about isotope effects, since it is impossible in a glass to produce sites that are basically identical, except for the isotopic composition.

There are many challenging extensions of the present studies: An obvious question, because of the high sensitivity to the geometry, is the influence of pressure on the reaction. Since tunneling reactions are so sensitive to energy barriers attempts have been made to observe the influence on reaction rates of external electric fields, but the expected effect was below the detection limit, so that more precise measurements will be required.

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