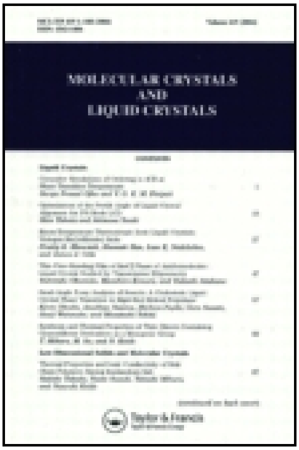

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Proton Motions and Holeburning Mechanisms in Molecular Solids

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PROTON MOTIONS AND HOLEBURNING MECHANISMS IN MOLECULAR SOLIDS

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Abstract Holeburning mechanisms based on proton motions in organic solids are discussed. Studies in model crystalline systems are used to identify and to characterize in detail processes involving methyl group spin conversion, tautomerization, and reversible hydrogen transfer reactions. All these mechanisms should also be operative in glasses.

INTRODUCTION

Spectral holeburning in condensed molecular phases at low temperatures has become an important topic over the past decade. Beyond its potential use for optical memories,[1-3] this phenomenon has proven to be the most useful line narrowing technique in condensed phases. The understanding of the reaction mechanisms leading to the bleaching of the excited dye molecule is an other interesting issue. Several mechanisms leading to the appearance of spectral holes have been identified and others have been suggested.[2] While the situation is fairly straightforward for some photochemical processes which can occur even at the lowest temperatures (dissociation, ionization and electron transfer, proton transfer) other photoinduced changes are more subtle and involve rearrangements of the dye-host system which are not so well characterized and understood. In organic glasses, in particular, it has been suggested that two-level tunneling systems are involved in the formation of holes[3] but the precise nature of these has not been elucidated. Holeburning could always be observed in hydrogen bonded solids and the hole formation and evolution was shown to depend strongly on deuteration, suggesting rearrangements of the hydrogen bond networks.[2] The complexity of the inhomogeneous distribution of local environments, reflected in the transition energies, reaction and relaxation rates and other molecular properties (distortions of the nuclear and electronic structure) makes precise observations and the identification of specific processes more difficult in amorphous hosts. Crystalline host materials are better adapted for such studies and can be used as model systems for situations encountered also in glasses. The spectral information is simplified because of the geometrical restrictions but the range of properties is also more limited so that situations, commonly encountered in glasses, may not be so easily found in a crystal.

In studies of hydrogen tunneling phenomena in doped molecular crystals at low temperatures we have used the optical transitions of dye molecules as very sensitive probes of the structure and the relaxation dynamics of changes induced by the optical excitation of the dye in the (well defined) crystalline environment.[5-14] Holeburning, fluorescence line narrowing, and time resolved spectroscopy were used to identify and to characterize proton tunneling along hydrogen bonds in benzoic acid[5-9] and methyl group tunneling of di-methyl-s-tetrazine in durene[10,11]. In addition reversible hydrogen transfer reactions between the dye and the matrix have been identified and characterized in these experiments.[12-14] All of these well defined phenomena should also occur and give rise to holeburning in disordered solids where any such detailed characterization is more difficult if not impossible. Taken in isolation, the dye chromophore is not altered after the excitation - relaxation cycle and these processes would be classified as so-called "photophysical" holeburning. In the following we shall briefly discuss rotational and translational proton tunneling with regard to its relevance to holeburning and describe in more detail recent results on reversible hydrogen transfer reactions which are thought to be very general phenomena in hydrogen bonded solids and may well be the single most important processes for photophysical holeburning.

METHYL GROUP NUCLEAR SPIN CONVERSION

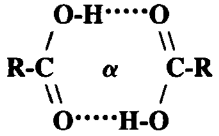
In condensed phases the rotation of a methyl group is hindered by a potential which has intra as well as intermolecular contributions. This potential reduces the free rotation to torsional vibrations (librations) around the potential minima positions. Because of tunneling through the finite barriers separating the potential minima the levels corresponding to these librations are split. Observed tunneling splittings (in the ground librational state) range from 5.3 cm^{-1}, corresponding to a free rotor, to values of kHz or less.[15,16] Because of the identity of the three protons the potential is strictly threefold symmetric and the tunneling levels of A and E spatial symmetry are associated with a nuclear spin of 3/2 and 1/2 respectively. Relaxation between tunneling levels of different nuclear spin ("spin conversion") is very slow at low temperatures but is accelerated by the interaction with paramagnetic species. Even at low temperatures the lowest tunneling levels are thermally populated, and as upon electronic excitation the tunneling splitting is changed, all spectral lines are split by a value equal to the difference, δ, of tunneling splitting in the ground and excited electronic state. This small splitting is usually hidden by inhomogeneous broadening but was recently revealed by holeburning experiments.[10,11] Of particular interest in the present context was the observation that spin conversion is significantly faster in the paramagnetic triplet state, which is reached via intersystem crossing from the optically excited singlet state. The optical pumping cycle results therefore in a net transfer of population between tunneling levels of the selectively excited molecules producing a hole at the frequency of the laser used for burning and an enhanced absorption ("antihole") due to the population surplus at $\pm\delta$. This hole/antihole pattern disappears on the scale of the spin conversion time in the ground state.

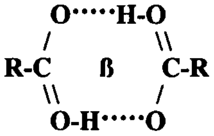
Almost all organic glasses contain methyl groups so that this phenomenon should be quite general. In a glass the barrier heights are distributed so that the antihole is smeared out over a frequency interval of up to ± 5.3 cm^{-1} and is no longer visible. When the methyl rotor is strongly hindered in the ground state the lifetime of the hole can be very long (hours to weeks at liquid helium temperatures).

TAUTOMERIZATION

Photoinduced proton displacements are a well established holeburning mechanisms, for example in the "inner" tautomerization of free base porphyrin and phthalocyanine as well as in the molecule-matrix tautomerism of quinizarin.[2]

The two tautomers of a carboxylic acid dimer:





are related by a concerted displacement of the two acid protons. Such dimers constitute a model for two-level systems as postulated in glasses. In a condensed phase environment the *α* and ß tautomers have in general different energies. Their interconversion has been characterized in detail and is a relatively fast process occurring on a nsec time scale. At low temperatures this tautomerization was induced and monitored in benzoic acid crystals doped with various dye molecules.[5-8] Because of the short lifetime of the unstable tautomer this process does not lead to the formation of stable spectral holes. In the centrosymmetric crystal two equivalent dimers sandwich the dye. For each dimer, the energy difference, W, of the *α* and ß tautomers is dominant so that the symmetric *αα* and ßß configurations of the dimer-dye sandwich have extremal energies.

Recently we have discovered a case where the coupling of these two dimers across the dye exceeds the value of W so that the polar *α*ß and ß*α* configurations are stabilized and lowest in energy. This level pair can be considered as a new two-level system. Relaxation between these levels involves the simultaneous tautomerization of two dimers (i.e. the concerted motion of four protons) and is slowed down considerably. In the specific case of benzoic acid the rates corresponding to a "simple" *α* -> ß and to a concerted *α*ß -> ß*α* tautomerization differ by over 8 orders of magnitude, which may be due to an unusually symmetric arrangement of the energy levels in this case.

Extending the picture to an ensemble of two-level systems as postulated in glasses one can in the same way construct a hierarchy of two-level systems of increasing complexity and with rates that decrease for relaxation processes that require the simultaneous flipping of two two-level systems of lower order. The rates of these processes can become sufficiently slow as to provide a possible mechanism for holeburning. It remains to be explored in how far these ideas do apply in glasses.

REVERSIBLE HYDROGEN TRANSFER

Photoinduced, reversible hydrogen transfer reactions between the dye and the host lattice can also lead to the a change of the environment of the dye, displacing the transition energy and producing a spectral hole under selective irradiation. This mechanism was postulated to occur in doped benzoic acid[12] where the irradiation of some guest molecules (in particular pentacene) leads to the appearance of spectrally well defined products corresponding to the guest in a defect environment.[17] These defect structures

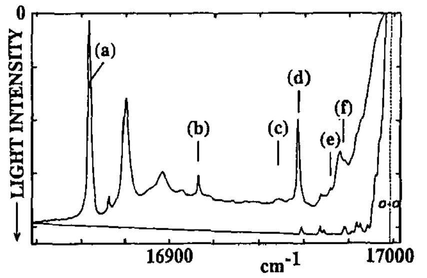


FIGURE 1 Absorption spectra of pentacene in benzoic acid at 1.5 K, illustrating the appearance of additional absorption lines under illumination (marked a to f, top trace) as compared to a spectrum recorded in the dark (bottom trace).

anneal spontaneously via tunneling even at the lowest temperatures on time scales ranging from ms to hours or more. This mechanism was questioned on the ground that the excitation energy is not sufficient for a proton (hydrogen) transfer to occur in the isolated dye-matrix molecule complex.[18] However the overall energetics of the reaction must include the solvation of the reaction intermediates and is therefore more difficult to evaluate. Because of the small quantum yields and the short lifetimes of the intermediates it has not been possible to directly resolve this issue by transient spectroscopy. Selective deuteration of the guest host system, on the other hand, offers an excellent handle on this problem. This was used in pentacene doped benzoic acid, which is particularly well adapted for a more detailed characterization.

Figure 1 illustrates the appearance of additional pentacene absorption lines under irradiation. The quantum yield of producing the defect sites lies in the range of 10^{-4} to 10^{-5} and the lifetime of these defect sites ranges from seconds and less to hours. In the acid deuterated host, analogous defect sites are produced but the yields are diminished by several ($\approx$4) orders of magnitude and the lifetimes increase by a factor of 10^3 and more (depending on the specific defect site). During the crystal growth, in the melt of the deuterated acid, part of the protons (up to 6) of pentacene are exchanged, so that the spectra show multiplets of lines corresponding to the different isotopically labelled pentacene molecules (these molecules are labelled D_0 to D_6 according to the number of protons exchanged). As however these isotopic replacements occur at random, there exist, except for D_0 and D_6, different isomers, for example two inequivalent mono-deuterated species (central position 6 or next to center position 5). As the deuteration shifts of these different isomers are very similar, the corresponding spectral lines are not fully resolved. We have therefore also prepared, via synthesis, specifically labelled molecules. With these materials we have made the following observations:

a) Selective irradiation of the D_0 to D_6 lines gives rise to a distribution of defect sites, the relative abundances of which depend upon the isotopic labelling of pentacene. This is shown in Fig. 2 for the (d),(e), and (f) defect sites produced by irradiation of D_2, D_5, and D_6 in a deuterated host.

b) The relative emission intensity of the D_0 to D_2 lines (selective deuteration in the center of pentacene) in protonated acid does not follow the relative abundance as measured in absorption. Figure 3 shows that the intensity ratio of absorption vs emission is smaller by a factor of about 6 for D_1 as compared to D_0 and D_2. Such an anomaly is also observed for D_3 molecules but is not seen for molecules D_1, both deuterated at next to center positions.

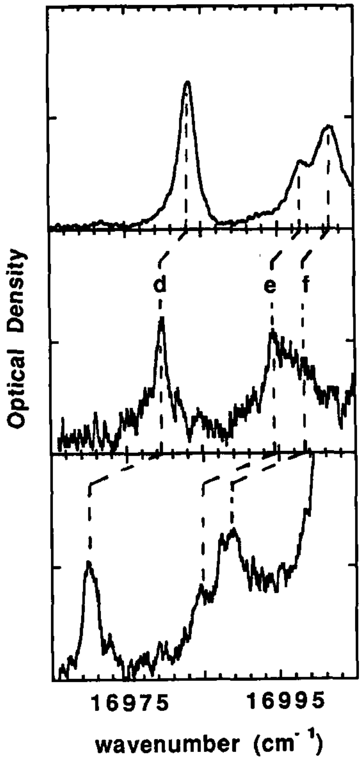
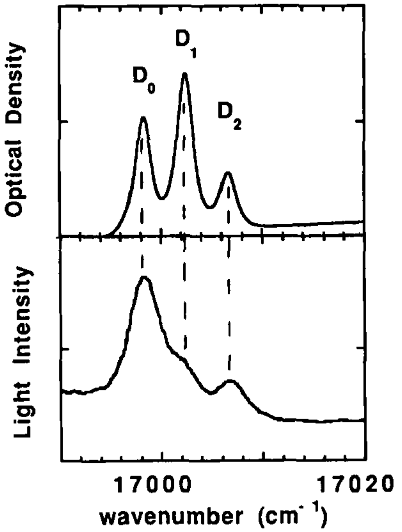


FIGURE 2 (left) Relative intensities of defect site absorption lines obtained after selective irradiation of D_6 (top), D_5 (middle), and D_2 (bottom) labelled pentacene in deuterated benzoic acid.

FIGURE 3 (bottom) Absorption and fluorescence of pentacene, selectively deuterated at the central positions, in protonated benzoic acid.



c) The yield of photoproducts is different for differently labelled molecules. Figure 4 shows this fact for the defect site (a) in protonated acid where the yield for D_0 is higher by a factor of more than 2 as compared to D_1 and to D_2 for molecules deuterated in next to center positions.

The fluorescence lifetime of pentacene is known to vary by more than of a factor of two in different substitutional sites of p-terphenyl, a fact that was traced to a large increase of competing intersystem crossing (ISC).[19,20] This large variation of the ISC rate was attributed to a distortion of pentacene, enhancing the spin-orbit coupling.[21] Observation b) indicates a significant decrease of the fluorescence lifetime for specifically deuterated pentacene molecules, which in analogy with the documented site effect is also attributed to a change of the ISC rates. We have observed that the yield of photoproducts follows the relative fluorescence intensities rather than the triplet populating ISC rates and conclude that the reaction occurs out of the excited singlet state. Observations a) and c) demonstrate that motions of the protons of pentacene are involved in the reaction leading to the creation of defect sites.

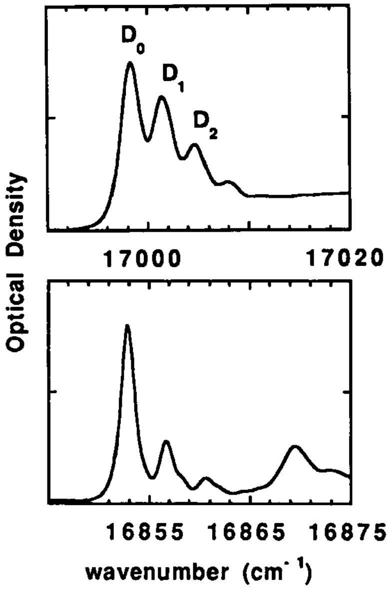


FIGURE 4 Absorption at the electronic origin and at the spectral position of the defect sites of pentacene, deuterated at the next to center positions in protonated benzoic acid. The sample had been homogeneously irradiated so that all isotopic species were equally excited.

The transient abstraction by the excited pentacene of an acid proton (or hydrogen atom) from the benzoic acid is a model which can rationalize all observations made for this as well as other systems (Figure 5). The protonated dye is highly unstable with respect to the ground state and releases the proton with significant translational energy, so that a variety of defect structures (corresponding to differently displaced acid protons in the matrix) is created.

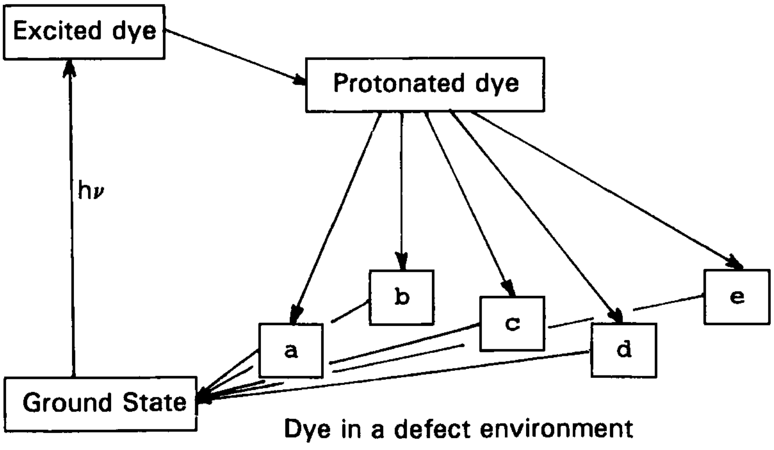


FIGURE 5 Reaction scheme leading to the production of defect sites by reversible proton (hydrogen) transfer reactions.

The population of these defect sites provides a reservoir for holeburning. The efficiency of the reservoir states in holeburning depends on the rates of populating and depopulating them, very short lived reservoir states are ineffective. Upon deuteration of the host both, rates are decreased, but as more reservoir states become effective the overall holeburning efficiency may even increase. This was observed for example in durene doped with di-methyl-s-tetrazine,[11] and was also claimed for the pentacene/benzoic acid system, even though in this case the triplet state was invoked as reservoir.[18]

CONCLUSION

All the examples discussed here have in common the fact that the dye molecule is not chemically altered after the spectral hole is formed. It is a photoinduced change of the environment that produces a shift of the transition frequency, a phenomenon called "photophysical" holeburning. These processes are closely related to spectral diffusion, a process in which the transition energy of an optical center varies slowly in time. This variation may be a random walk in transition energy space for a single center and/or occurs in a random uncorrelated fashion for an ensemble of centers so that the frequency address of a class of optical centers defined by a sharp transition energy at time zero becomes diffuse as time increases. Photophysical holeburning can be viewed as an optically induced spectral diffusion process in which the migration of the optical center is faster in the excited than it is in the ground state. This picture has found support in recent beautiful experiments on matrix isolated single molecules.[22,23] While we have used single crystalline matrices in order to identify and to characterize some of the basic mechanisms, the same processes should also contribute to holeburning in glasses. Single molecule spectroscopy in glasses will allow a similar indepth study in these complex systems as was done here in the ordered environment of a crystal.

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