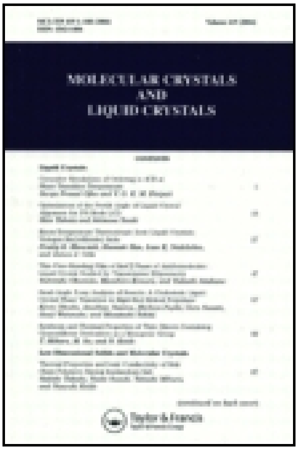

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Inhomogeneous Photochemistry and Hole Burning in Dihydrophenazine Doped Molecular Crystals

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INHOMOGENEOUS PHOTOCHEMISTRY AND HOLE BURNING IN DIHYDROPHENAZINE DOPED MOLECULAR CRYSTALS

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Abstract A series of photochemical products of 5,10 dihydrophenazine (PH_2) doped in fluorene (Fl) crystals can be observed via optical and ESR spectroscopy upon two photon excitation of PH_2. ESR spectra reveal the formation of host-guest triplet radical pairs as a product of a double hydrogen abstraction. The non-planar PH_2 ground state leads to a strong site distribution. Photochemical hole burning experiments indicate that this distribution determines to some extent the reaction rate.

INTRODUCTION

In contrast to liquid phase reactions, solid state reactions between host and guest molecules in doped molecular crystals allow the investigation of the reaction mechanism for different yet well defined reaction geometries. In principle, all host molecules near a guest molecule are potential reaction partners. The reaction rates, however, are expected to depend substantially on the position of the host molecule with respect to the guest molecule involved in the reaction. Furthermore, even small changes in the reaction geometry such as distortion of the lattice geometry caused by thermally activated nuclear fluctuations or non-substitutionally incorporated guest molecules will strongly influence the reaction rate.

The effect of nuclear fluctuations on the reaction rate has been widely investigated[1] and can be regarded as a dynamical approach to study the reaction mechanism for different reaction geometries. To our knowledge, however, the role of the reaction geometry has not yet been investigated under what one may call "static" conditions. In this case a suitable reaction system should allow the investigation of the same reaction under different yet well defined relationships of the reaction partners to each other. Unfortunately, systems which fullfill these requirements are scarce.

Recently, however, we have reported that in PH_2 doped Fl single crystals several distinct host-guest pairs indeed undergo a photochemical reaction yielding the same reaction products[2,3]. Furthermore, hole burning experiments have given strong indications that the chemical reaction rates are also influenced by a disorder in the reaction geometry presumably due to the non-planarity of the PH_2 guest molecules . Disordered reactions have already been observed, e.g., in glasses[7].

In this communication we will present some new results together with a summary of the observed PH_2 photochemistry and recent hole burning experiments.

EXPERIMENTAL

Preparation of the fluorene host material, the crystal growing procedure and PH_2 synthesis is described in Ref.6 and Refs. therein. The ESR spectrometer has been described elsewhere[3]. Details of the experimental setup used for hole burning are given in Ref.4 and 5.

RESULTS AND DISCUSSION

While in solution PH_2 is found to be highly unstable, it can be stabilized by substitution into Fl single crystals. Upon excitation of PH_2, however, irreversible decomposition of PH_2 and the formation of a series of photoproducts is observed. The primary step in understanding the reaction scheme affords a detailed characterization of PH_2 itself. This has been published previously[6]. Summarizing these results we have found that the nuclear configuration in the S_1 and T_1 states of PH_2 is essentially planar, whereas in the ground state, PH_2 is bent along the N-N axis thus having a butterfly-like structure. The change of nuclear configuration upon photoexcitation thus, in particular, involves the photochemically active N-H groups. Furthermore, the S_1 - S_0 transition of PH_2 was found to be symmetry forbidden borrowing intensity via a Herzberg-Teller coupling mechanism from a low-lying S_2 state. The coupling is achieved by a non-totally symmetric skeletal vibration with an energy of 750 cm^{-1},as is readily seen in the optical emission spectra. Most likely the 750 cm^{-1} vibration again involves a strong motion of the N-H groups.

The non-planar ground state of PH_2 is expected to lead to a distortion of the Fl host lattice and requires, to some extent, a redistribution of the neighbouring lattice molecules. A site distribution of PH_2 molecules is therefore not unlikely. Indeed, the optical spectra show broad linewidths in both the emission[6] and absorption spectra[4,6] even at 1.5 K. The absorption origin at 415 nm at 1.5 K has a linewidth of about 20 cm^{-1} whereas linewidths below 1 cm^{-1} are typical for molecular crystals.

Recently. we have reported that pumping on an individual absorption band with a tunable dye laser and subsequent scanning of the PH_2 fluorescence or phosphorescence excitation spectrum revealed spectral holes at the pumping wavelength as well as at corresponding positions in other vibrational transitions in the excitation spectrum[4]. A typical spectrum taken at 1.5 K is shown in Fig.1. Note the marked differences in linewidths between the hole where burning occurred and the holes in other vibronic transitions. This can be explained by a distribution of vibronic frequencies[5,8]. Intense broadband uv-irradiation using the light of a 100 W Hg lamp in the 300-400 nm region does not refill the holes. This proves the photochemical nature of the hole burning .

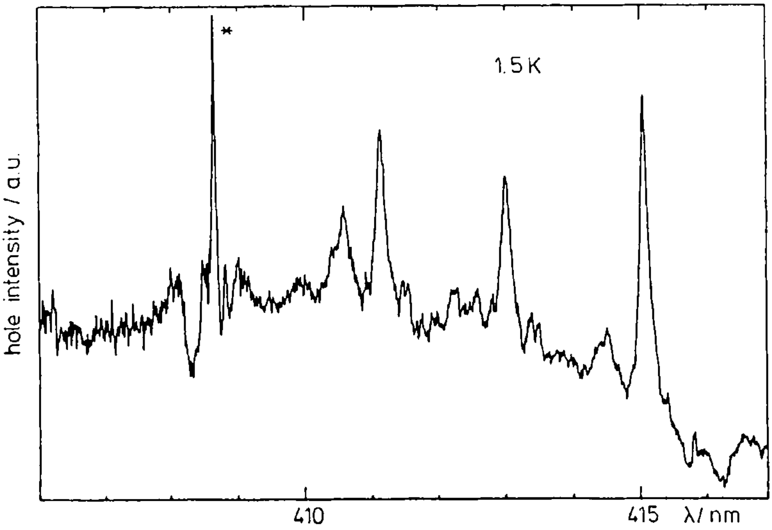

FIGURE 1 Hole spectrum of PH_2 obtained by subtracting the phosphorescence excitation spectra before and after burning at (*).

One of the major findings of these hole burning experiments is that, no matter in which vibrational transition the holes were burnt, the intensity ratios of the holes in the various vibrational transitions do not correspond to the intensity ratios in the excitation spectrum before hole burning. An enhancement of the "forbidden" absorption origin is shown in all cases. These results indicate that the spectral distribution is related to a distribution of the reaction rates. This is also supported by the observed spectral changes in the PH_2 fluorescence and phosphorescence spectra after prolonged broadband uv-irradiation[5]. Furthermore, the decomposition of PH_2 following broadband uv-excitation shown in Fig.2, reveals a strong deviation from a monoexponential decay. This is an independent indication of a distribution of reaction rates.

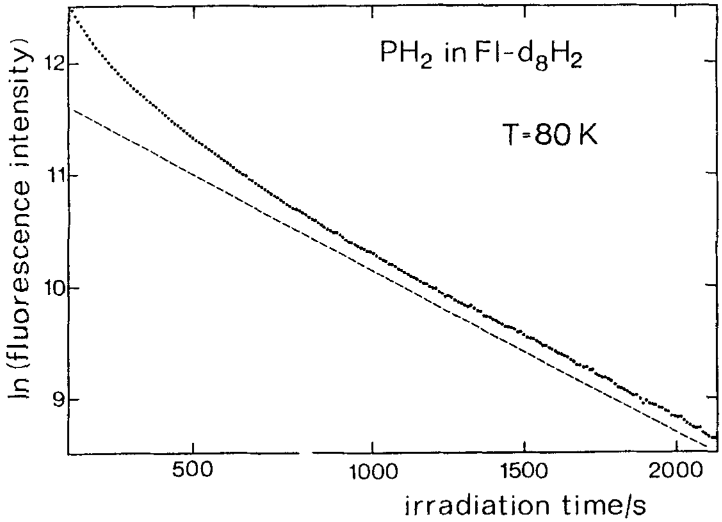

FIGURE 2 Logarithmic plot of the integral PH_2 luminescence intensity as a function of uv-irradiation time. The broken line demonstrates an assumed exponential decay.

The primary step of the PH_2 decomposition involves a two-photon process as can be seen in Fig.3. PH_2 doped in Fl was irradiated several times for 20 minutes. The remaining PH_2 luminescence was monitored after each irradiation cycle. The PH_2 decomposition is clearly enhanced if, in addition to the uv-light, the sample is also irradiated with light of wavelengths greater than 435 nm, which is well below the absorption origin of PH_2. Most likely a higher excited triplet state, T_j, is the photochemically active state as has been observed for various PH_2 derivatives in solution[9].

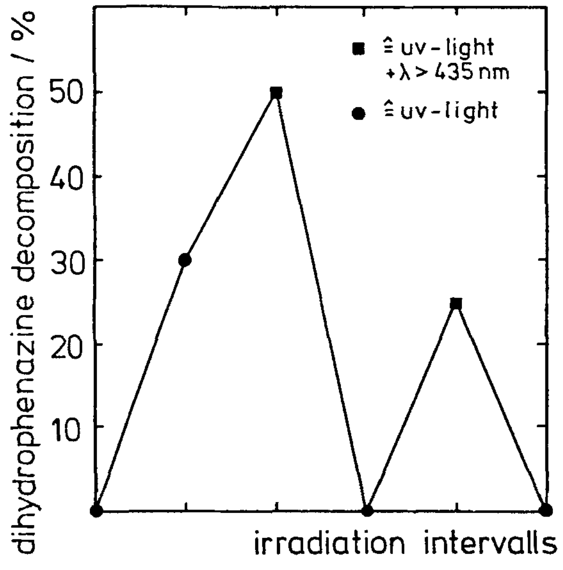

FIGURE 3 Relative change of PH_2 luminescence after uv-irradiation, with and without additional long-wave excitation at twenty minute intervals.
(●) - longwave irradiation turned off
(■) - longwave irradiation turned on

A series of photochemical products of PH_2 doped in Fl can be observed upon uv-excitation of PH_2. At temperatures below 80 K, ESR spectra reveal the formation of stable triplet $PH^{\bullet}...Fl^{\bullet}$ radical pairs as result of a hydrogen abstraction both from PH_2 and one of its individual Fl neighbours[3]. Radical pairs AB, AB', AB" can be observed (the notation is given in Fig. 4). Due to the different reaction geometries, the formation rates and thermal stability of these products vary considerably as can be seen in Fig. 5 for the case of the formation of two representative radical pairs. There are indications that the double hydrogen ab-

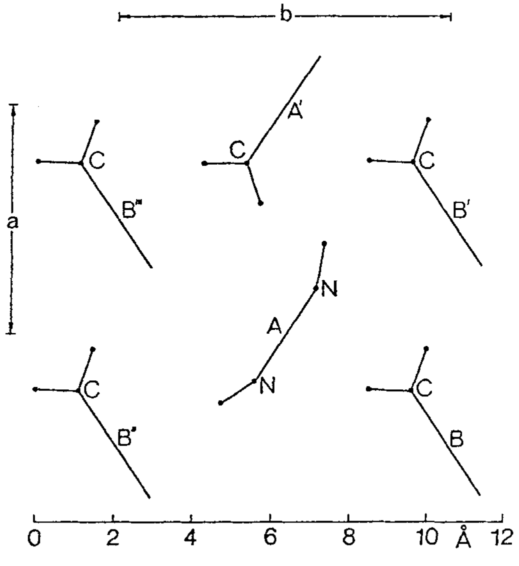

FIGURE 4 Crystallographic ab reaction plane of PH_2 in Fl. The points indicate the relevant C,N and H atoms. The non-planar ground state of PH_2 has been incorporated substitutionally into the lattice.

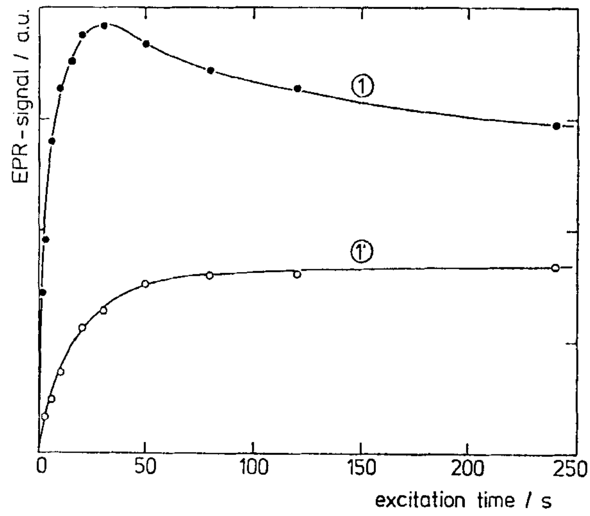

FIGURE 5 ESR intensity of the two possible radical pairs formed by (AB) molecules upon uv-irradiation at 35 K.

straction results in the formation of molecular hydrogen . The radical pairs can be bleached by long wavelength irradiation (λ>420nm) or during a temperature cycle up to room temperature. In addition to the formation of the radical pairs, formation of phenazinyl radical ($PH^{\bullet}$) is also observed after extended uv-irradiation[3].

At least three photoproducts can be detected by optical spectroscopy[4]. The investigation of the corresponding reaction kinetics turned out to be rather difficult as product formation and decomposition continues on a time scale of minutes in the dark following uv-irradiation. Some preliminary results have been discussed in Ref.4.

CONCLUSIONS

The combination of hole burning, optical, time resolved optical and ESR spectroscopy reveals a distribution of sites as well as a distribution of photochemical reaction rates both for PH_2 decomposition and the formation of triplet radical pairs. It is not clear yet whether the observed inhomogeneous distribution of PH_2 reaction rates is primarily determined by the distribution of reaction coordinates or the distribution of binding energies in PH_2 itself due to the variations in the electronic structure. In the first case selective optical excitation within the distribution should influence the formation of distinct radical pairs. Experiments combining optical hole burning with ESR spectroscopy might therefore settle this question.

In this communication we have presented results which clearly demonstrate that molecular crystals can also show a distribution of reaction rates, an observation which has so far only been reported for much more disordered systems like glasses[10]. With respect to a microscopic description of reactions, molecular crystals provide the opportunity to characterize the geometries determining the reaction kinetics in much more detail. The example of PH_2 in Fl already shows that minor changes of molecular symmetry and geometry influence guest-host reaction rates considerably.

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