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LASER INDUCED HYDROGEN MOTION IN ORGANIC CRYSTALS AT LOW TEMPERATURE

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We study here a laser induced reaction leading to a rearrangement of the acid protons in benzoic acid crystals at very low temperature. This hydrogen motion results from the electronic excitation of pentacene molecules substitutionally included into a benzoic acid host matrix, protonated or deuterated. The growth of a deuterated benzoic acid crystal doped with pentacene leads to a partial deuteration of pentacene molecules, resulting in several origin bands in the absorption spectrum. The dynamics of the system following non selective and selective laser irradiations of the differently deuterated pentacene molecules is analyzed in terms of hydrogen rearrangements.

Introduction.

Hydrogen motion in solids at low temperature is intensively studied with a wide variety of methods. Among them, optical spectroscopy is a very sensitive one, specially when performed on crystals giving narrow spectral lines. Carboxylic acid crystals represent a class of model systems commonly used for studies on proton transfer [1-5]. In such a system where two molecules associate to form a dimer bound by two hydrogen bonds, the hydrogen motion consists in a double exchange of the acid protons along the two hydrogen bonds giving rise to a tautomer form. For an isolated dimer the two tautomer forms are identical and the potential energy may be represented by a symmetrical double well. In the crystal the two forms are no longer equivalent and the double well becomes asymmetric, modifying the protons dynamics. An optical way of monitoring the proton movement is to replace a dimer by a dye impurity: any change in the dye environment, a tautomerization in the neighboring dimer for example, is reflected in its absorption spectrum. A particularly interesting feature of such a system is that the optical excitation of the dye molecule induces the desired environmental change which is then probed using the same dye molecule. By such a method, it was possible to study the protons tunneling mechanism in mixed thioindigo/benzoic acid crystals at very low temperature [6].

In the system studied here, composed of benzoic acid (BA) as the matrix and pentacene (PC) as the impurity, it has been proved that the induced modification of the neighborhood was not a double proton exchange but a more severe rearrangement [7]. This conclusion was drawn from the fact that the induced changes were very long-lived (10 orders of magnitude longer than in the tautomerization case), and that the energy difference between the two states was at least 30 times larger than the one reported in the literature for a tautomerization in a BA crystal [8]. A proposed mechanism was an

opening of an hydrogen bond followed by a reorientation of the O-H bond, or even an exchange of a proton between the matrix and its host. A decisive test for these questions was a deuteration of the benzoic acid. We present here some results on the effect of this deuteration on the absorption spectrum of pentacene. They first show that a deuteration of pentacene is already performed during the crystal growth and can be clearly analyzed /9/, and that the lifetimes of the photoproducts obtained after laser irradiation are lengthened by about two orders of magnitude. Moreover selective irradiations on the differently deuterated pentacene molecules indicate that they behave differently with respect to their environment.

Sample preparation and deuteration.

During the growth of the mixed PC/d-BA (d for deuterated) crystal by standard Bridgman technique a partial deuteration takes place, and according to the duration of the crystal growth it is possible to get PC molecules where at maximum 6 hydrogens have been replaced by deuteriums. These substitutions are imaged on fig.1, showing the absorption spectra in the origin region of crystals grown during 0.5, 2 and 6 days. The different lines are labelled D_0 , D_1 , ..., D_6 for pentacene molecules bearing 0 to 6 deuteriums.

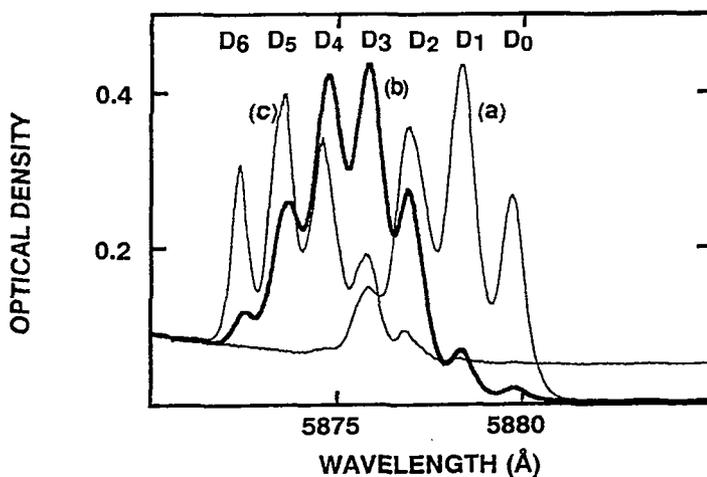


Figure 1 : Absorption spectra of partially deuterated pentacene in deuterated benzoic acid at 1.6 K, after (a): half a day, (b): 2 days, (c): 6 days of crystal growth.

This particular feature allows to prepare samples containing more or less deuterated PC molecules and gives the interesting possibility to selectively excite a chosen D_i class of PC molecules.

Selective and non-selective laser irradiations.

Two types of laser irradiations have been performed: selective ones, as described above, achieved with a spectrally narrowed dye laser (FWHM ≈ 1 cm^{-1}), or non-selective ones using the 514 nm Ar^+ laser line. In the latter case the photon energy is high enough to excite simultaneously the seven class of PC molecules defined previously.

Fig.2 shows the absorption spectra of a crystal grown during 2 days recorded before and after a non-selective laser irradiation. On the lower trace are only visible the 7 origin lines of the non-irradiated PC molecules.

On the upper trace clearly appear several sets of lines reproducing more or less faithfully the origin set. Each set is assigned to a photoproduct i.e. a modification in the environment of the PC molecules, but two differently deuterated PC molecules contribute differently inside a given set. This behaviour is deduced from fig.3 for which a selective irradiation was applied to the D_6 line of a crystal grown 6 days: the position of the different D_6 -photoproducts may be used to find their positions in the sets of fig.2, and then to determine the positions of the other D_1 photoproducts in the same set.

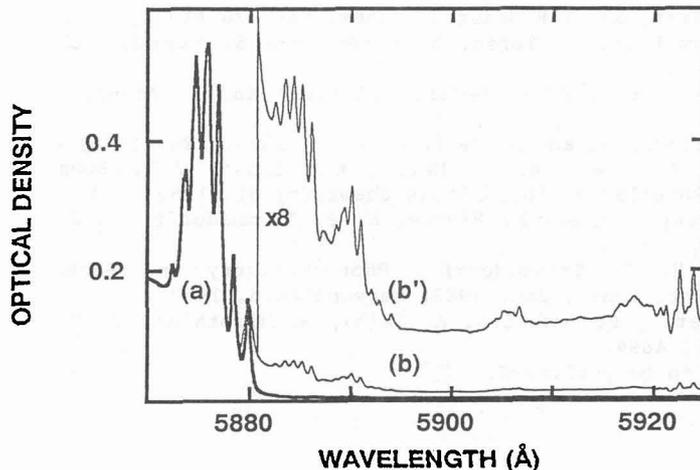


Figure 2 : Absorption spectra of d-pentacene in d-benzoic acid at 1.6 K, (a) before irradiation, (b) after non selective irradiation with the 5145 Å line of an Ar^+ laser; (b') is a 8x expansion of (b), arbitrarily shifted on the D.O. scale for better clarity.

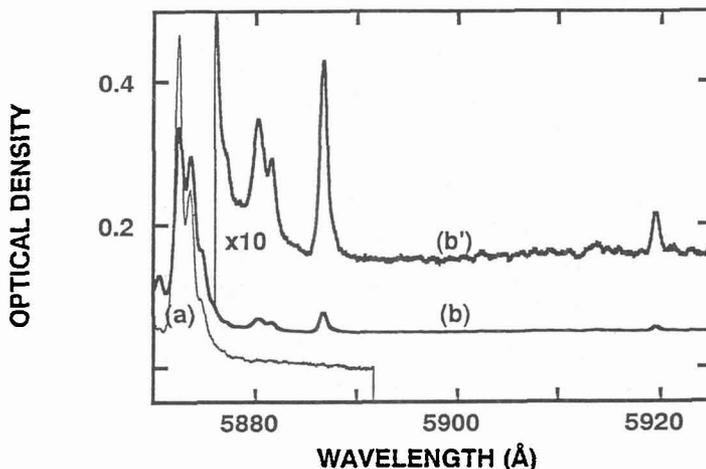


Figure 3 : Absorption spectra of d-pentacene in d-benzoic acid at 1.6 K, (a) before excitation, (b) after selective excitation of the D_6 origin line; (b') is a 10x expansion of (b). (b) and (b') are arbitrarily shifted on the D.O. scale.

Lifetime measurements have been done on the photoproducts obtained under selective irradiation. They gave lifetimes of 100 to 500 hours, more than 100 times longer than the lifetimes measured in a protonated matrix.

All these results confirm the role of the acid proton in the formation of the photoproducts seen on the PC absorption spectra. The exact nature of formation process is still not understood but new informations will be given by further selective irradiations of the D₀ to D_s origin lines.

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