



Experiment title:
X-ray diffractio and emission properties of dyes under pressure

Experiment number:
CH1020

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ID09A

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9

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Report:

In **CH-1020** we studied the x-ray diffraction behaviour of organic laser dye solids under pressure. Spectroscopically we discovered an optical resonance Raman band around 4500 cm^{-1} which shifts as a function of pressure in a non-monotonic way suggesting several phase transitions up to 3 GPa.

In this proposal we performed XRD studies as a function of pressure in order to investigate the corresponding structural changes. Figure 1 presents the 1D diffraction pattern of the laser dye for 2 different pressures after radial integration of the 2D diffraction pattern with Fit2D.

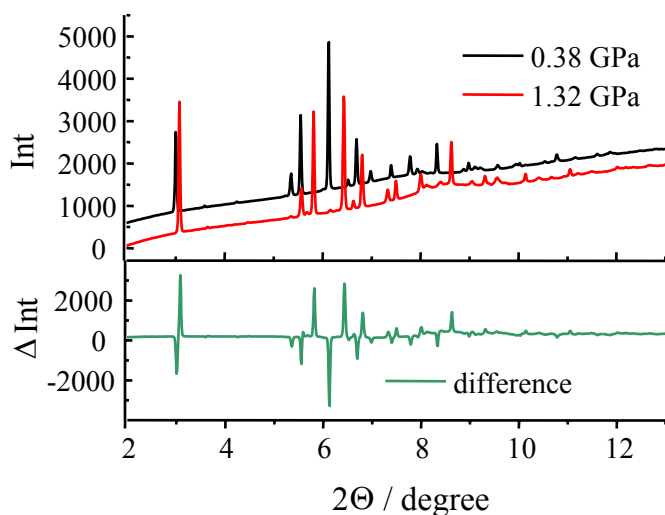


Figure 1: Powder spectra at $p=0.38$ and 1.32 GPa.

Most pronounced are the shifts of the Bragg diffraction peaks upon pressure increase suggesting major volume changes. Indeed, organic dyes are loosely packed in the crystal lattice with typical distances on the order of 5 Å making it easy to squeeze the material.

However, next to these changes in unit cell dimensions, detailed structural analysis based on Rietveld refinement strategies suggest interesting reorganisations within the chromophore unit itself. For the refinement we used the rigid body approach by dividing the chromophore molecule in two subunits with the freedom of rotation against each other. The rotational changes are presented by the change of the dihedral angle ϕ . Changes in ϕ can also be used in order to monitor local order – disorder phenomena in the system.

Figure 2 summarises the changes of ϕ under different conditions inducing disorder in the system: Exponential dependencies of ϕ -changes are found upon light excitation (figure 2, top left), nearly linear changes are found upon decrease of temperature (figure 2, bottom left), and a non-monotonic behaviour has been found upon pressure increase (figure 2, top right). The comparison between the refined changes suggest, that the response function of the intramolecular degrees of freedom are similar for light-excitation at early time points, pressure increase up to 1.5 GPa and temperature decrease up to 3.6 K with an first increase of dihedral angle followed by a decrease. However, the pressure-dependent studies suggest major reorganisations beyond 1.5 GPa leading to a thermodynamic state, which cannot be reached by a decrease of temperature up to 3.6 K. Note, that the dihedral angle can also indirectly be derived out of the visible absorption spectra of the dyes [1].

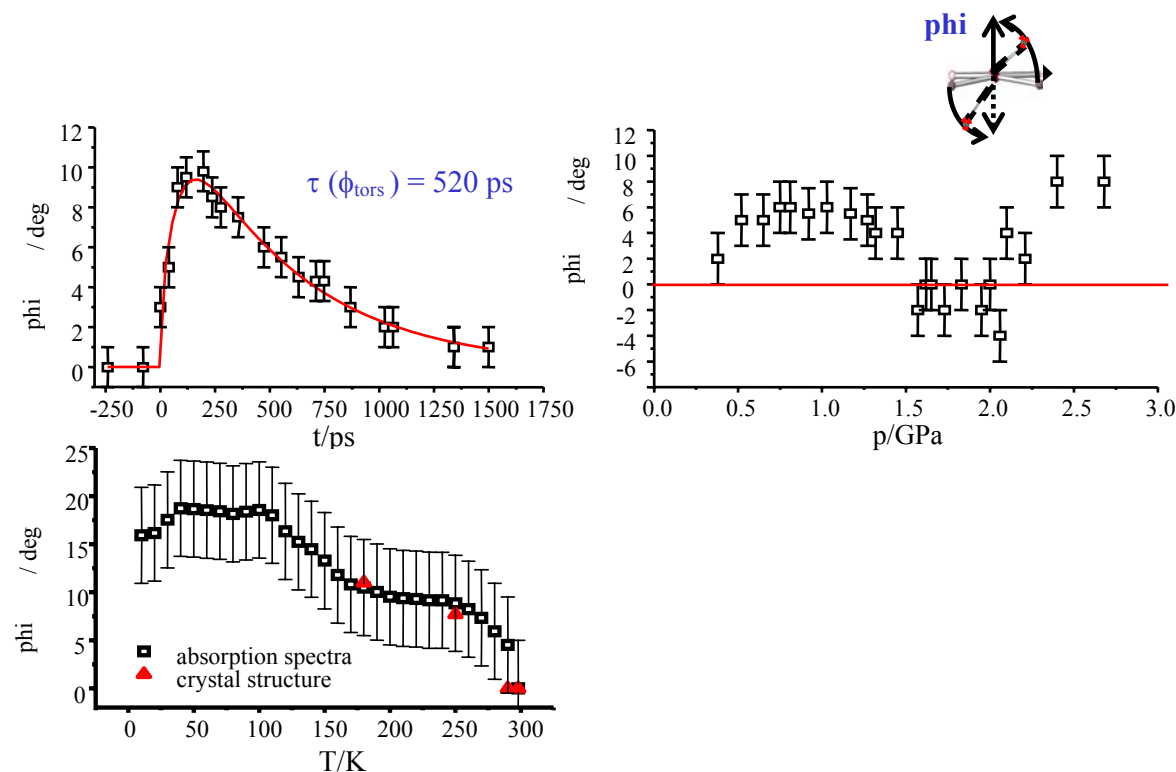


Figure 2: Order-disorder phenomena in laser dye solids in comparison: light-induced disorder, temperature-induced disorder and pressure-induced disorder. Light-induced, non-equilibrium intramolecular structural rearrangements.

The results of these measurements have recently been submitted [2].

References

- [1] J. Davaasambuu, P. Durand, S. Techert, *J. Synchrotron Rad.* **11**, 483-489 (2004).
 [2] S. Techert, G. Busse, A. Ramos, B. Frederichs, S. Schmatz, M. Hanfland, *J. Chem. Phys.*, submitted (2006).