EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

http://193.49.43.2:8080/smis/servlet/UserUtils?start

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Real-Time X-Ray Studies of Charge-Induced Molecular Deformations in Conducting Organic Materials	**Experiment number**: CH-1647
Beamline:	**Date of experiment**: from: July 17th 08:00 to: July 22nd 08:00	**Date of report**: July 27th
Shifts:	**Local contact(s)**: Qingyu Kong	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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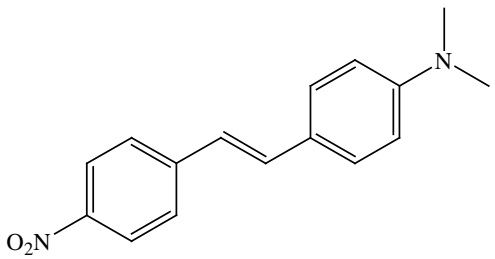
Report:

At ID09B we have studied the light-induced structural changes in a single crystal of 4,4'-dimethylaminonitro-stilbene (DANS):



The hypothesis that we sat out to test was whether the unit cell expands as a result of the large dipole moment of the excited-state molecule. In hybrid mode complete sets of diffraction data were collected at time delays between the femtosecond laserpulse and the X-ray pulse ranging from –300 ps to 50 μs. The employed wavelengths were chosen so that the light penetrates the crystal to various degrees (λ = 400 nm, A = 1.2; λ = 560 nm, A = 0.55; λ = 600 nm, A = 0.1). The laser repetition rate was 1 kHz (giving rise to 1000 laser/X-ray sequences per second). For each of the wavelengths an initial assessment of the maximum laser power had to be carried out to maximize the number of excited molecules. At laser energies higher than 10 μJ pulse^{-1} we experienced burning of the crystals at all three wavelengths. It was not possible to increase the pulse energy by decreasing the absorption from 0.55 to 0.1, this is taken to indicate that reason for the decomposition of the crystals is not single-photon absorptions but rather multi-photon ablation processes. The laser beam was focused to a diameter of 300 μm whereas the diameter of the X-ray pulse was 50 μm. Based on these dimensions, a pulse energy of 10 μJ pulse^{-1} and a matter-in-matter concentration of roughly 2 M the number

of molecules is estimated to outnumber the number of photons by a factor of 10000:1 – a ratio which is not leaving optimism for the observation of laser-induced changes in the X-ray scattering. Upon subtraction of the CCD diffraction images that result from an isolated X-ray shot and a laser/X-ray sequence we did, however, observe a significant change in the position of the diffraction spots towards larger lattice spacings in the case of the light exposed crystal (scattering at smaller angles, Fig. 1).

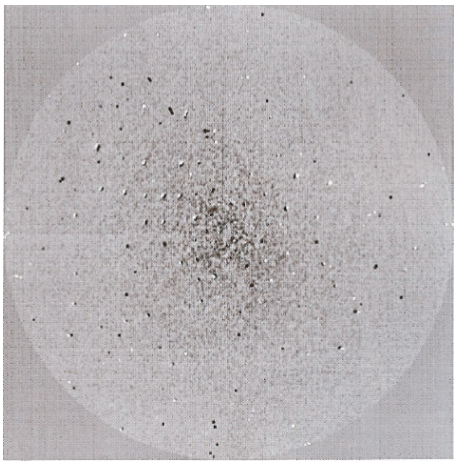


Fig. 1. The difference between a diffraction image taken at a 300 ps time delay between the laser pulse and the X-ray pulse and an image taken without exposing the crystal to laser light

This difference image remained unchanged from one pulse sequence to the next which means that the new "crystal-state" induced by the laser has a life time of more than one millisecond. The change was shown to be fully reversible by taking another set of diffraction images and noting that they did not differ from the initial ones. We took the millisecond decay to indicate either the existence of a triplet state or simply to reflect a heat-induced coherent motion of the molecules in the crystal. Work is in progress to index the data and ultimately to solve the laser-induced structure.

Given the low excitation efficiency we also attempted an experiment where the single crystal was substituted for a powder. This enabled the formation of very thin layers and therefore a larger molecule-to-photon ratio. The result of such a powder experiment is shown in Fig. 2; also in this case there is a noticable difference between the diffraction images that are obtained with and without exposure to the laser. Yet again the difference signal persists for milliseconds, thus, no new behaviour is induced by exciting a larger number of molecules – again it would seem that the lattice spacing increases upon exposure to light.

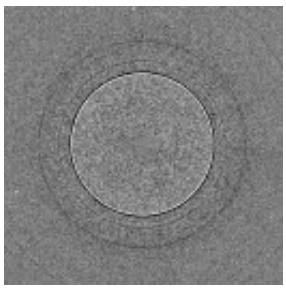
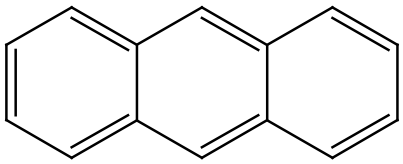


Fig. 2. Difference plot that results from the powder scattering from a sample with and without laser exposure

In addition to DANS we also studied single crystals of antracene:



The aim was to see if this more transparent molecule could be exposed to a higher photon flux. The interesting process in the case of antracene is a dimerisation process which is induced at one wave length and reversed at another. In this case a difference was also observed and the decay of the laser-induced process seems to most faster which might indicate that it is a result of a chemical change. We did not have sufficient time to explore the reaction in the other direction; a process that is induced by another colour.

In order for time-resolved X-ray studies to be generally applicable a larger excited-molecule to photon ratio is required. It would seem from this study that conventional organic crystals will burn under such conditions. We will attempt to device a grazing-incidence method for single-crystals in order to limit the X-ray pulse to probe the uppermost layer of the crystal, i.e., the layer that has been excited.