



## 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.


**Experiment title:**

Structural Properties of Excimer Formation in Pyrene Crystals

**Experiment number:**

ME-1186

<b>Beamline:</b> ID09B	<b>Date of experiment:</b> from: 22/07/2006 to: 26/07/2006	<b>Date of report:</b> Wednesday, October 25, 2006
<b>Shifts:</b>	<b>Local contact(s):</b> Friederike Ewald	<i>Received at ESRF:</i>

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**Report:**

At ID09B we have studied the structural changes in thin films of pyrene and  $\alpha$ -perylene induced by excimer formation. Both pyrene and  $\alpha$ -perylene have a sandwich-like crystal structure, where the molecules are packed in pairs giving ideal conditions for excimer formation (see Fig. 1).

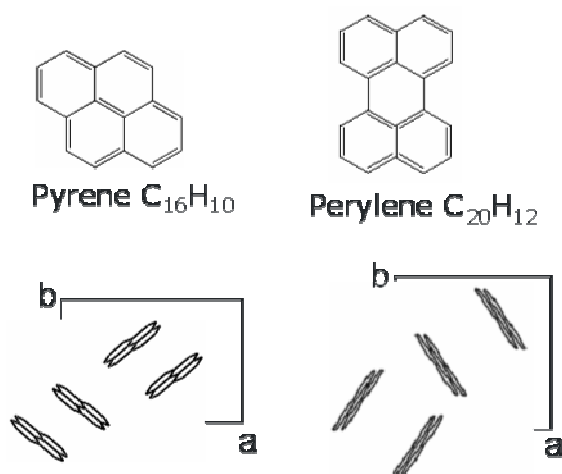


Fig. 1: The molecular structure of pyrene and perylene as well as the unit cells of pyrene and  $\alpha$ -perylene crystals projected along the normal to the ab-plane.

An attractive feature of the thin film geometry is that it provides a straight forward way of limiting the effective scattering volume by scaling the thickness of the film (e.g. 200 nm) and the length of the sample (here 5 mm) to match the volume probed by the X-rays with the volume pumped by the laser.

Several experiments have been carried out studying the formation dynamics and lifetimes of the excimers by using either fluorescence measurements, luminescence measurements or transient absorption

spectroscopy [3-14], but the structural changes caused by excimer formation in these crystalline compounds have so far only been predicted through calculations. The calculations have shown the excimer formation to be accompanied by a decrease of the distance between the two molecules [1, 2], hence we would expect the structure of the thin films to undergo a change.

Earlier experiments have shown the formation time of the excimers to be of the order of several hundred femtoseconds with lifetimes in the order of 100ns [3-14], hence the 50-100ps time resolution at ID09B is well suited for observing the structural dynamics of the thin films as the excimers decay.

Our preparations for the measurements at ESRF revealed instability issues of the thin pyrene films, with respect to film evaporation under ambient conditions. We have found that these issues can be resolved using cooled substrates during deposition, storage, and measurements. However, to avoid these complications in the very first time-resolved experiments on thin film structures, we decided to focus on perylene, a material with similar properties as pyrene, and which is stable at room temperature.

Based on our previous investigations of the optical absorption properties of  $\alpha$ -perylenes films, the excitation wavelength was chosen to be the second harmonic of the femtosecond laser at ID09B (390nm). At this wavelength the sample has a good absorption and can survive excitation for several hours at a repetition rate of 1 kHz, making the wavelength ideal for these experiments. The laser was focussed to cover the whole area probed by the X-rays (5 mm  $\times$  200  $\mu$ m). When the laser was running at full power, the energy of each pulse at the film was about 20  $\mu$ J, which we estimate corresponds to about 0.5-1% of the molecules in the film forming excimers, assuming a quantum efficiency of 1, which is a good assumption as no monomer fluorescence is observed from  $\alpha$ -perylenes.

The X-rays are incident on the sample at a grating angle (0.2 degrees), sufficiently above the angle of total external reflection of the substrate to avoid complications of refraction effects, but low enough to keep scattering from the amorphous glass substrate low in comparison to the diffraction peaks. The high degree of crystallinity and texture of the perylene films, as evident from the diffraction pattern shown in Fig. 2, allowed us to resolve individual reflections both using monochromatic and polychromatic (3% BW) X-ray radiation. Relaxing the demands on monochromaticity provided a 500 fold increase in available X-ray flux, greatly facilitating the data acquisition.

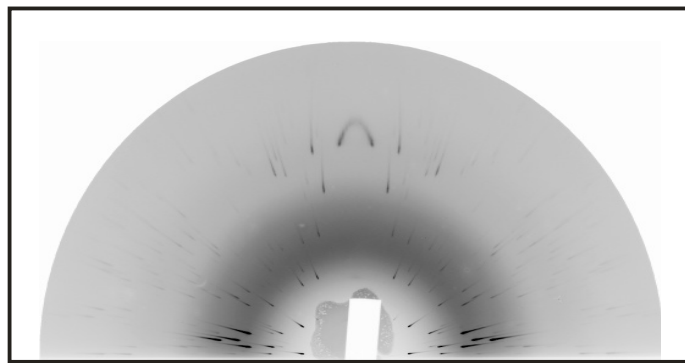


Fig 2. 2D diffraction pattern from a thin film of  $\alpha$ -Perylene with a pump-probe delay of – 3ns. Radial elongation of diffraction peaks is due to the polychromatic beam (3%BW) used. The small azimuthal width of diffraction peaks reflects the high alignment of mosaic crystallites. The amorphous halo originates from the glass substrate.

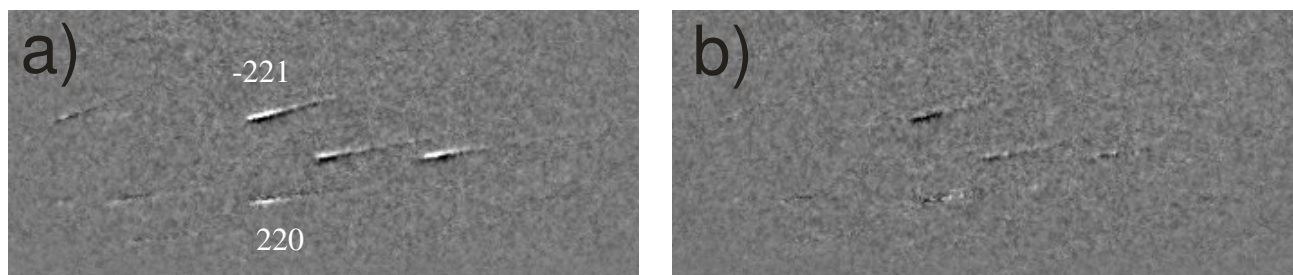


Fig. 3A zoom in on the bottom right region of two difference images from an  $\alpha$ -perylenes thin film cooled to 220K during the experiments – a) difference between patterns at 10ns delay and at the negative delay – b) difference between patterns at 10 $\mu$ s delay and at the negative delay. Colorscale from white (lowest) to black (highest).

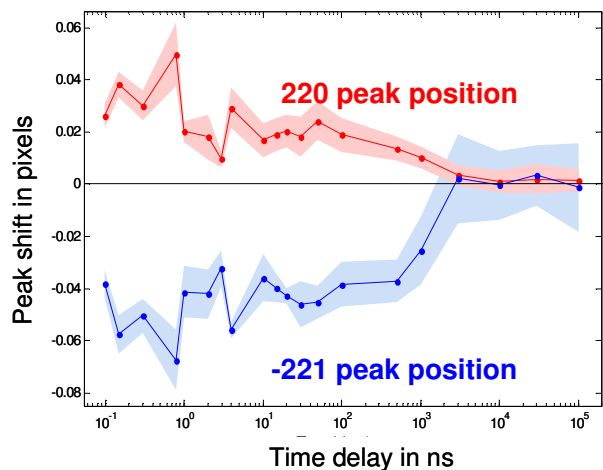


Fig 4 Azimuthal peak position as function of time at -55°C. Shaded areas correspond to one standard deviation around the mean value of 10 repetitions of the experiment.

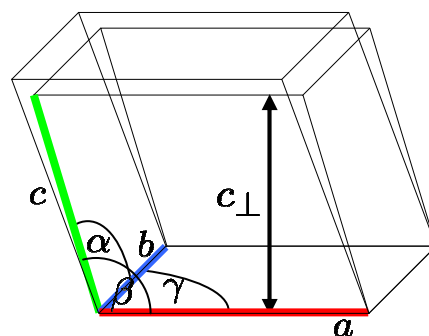


Fig 5 Unit cell of  $\alpha$ -perylene – showing the different angles and axes, as well as a sketch of the transient deformation (exaggerated for clarity)

The difference images show large peaks shifts in the azimuthal direction, cf. Fig. 3. The shifts are already present at 150 ps and are completely gone after about 1-100  $\mu$ s depending on the thickness and the temperature of the film.

A semi-quantitative interpretation of peak shifts suggests an increase of the unit cell volume. The monoclinic angle  $\beta$  as well as the unit cell “height” ( $d_{001}$ ) increases slightly while the other unit cell parameters stay essentially constant (see Figs. 4 and 5). The observed variations in azimuthal peak width decay much faster than the corresponding shifts in position. This suggests a collective effect of a high fraction of scattering unit cells undergoing a slight elastic deformation, which is supported by the apparently unchanged structure factors of the various reflections.

We recorded data to compare the changes for two different thicknesses of the films (200nm and 700nm), we also used a cryostat during the experiments giving us the possibility to investigate the influence of temperature on the structural dynamics (298K and 220K). Finally, we acquired data with different pump intensities in order to study the structural dynamics as a function of exciton density, as previous work have shown evidence of exciton-exciton annihilation at high exciton densities [13].

The data analysis has so far led us to conclude that the peak shifts are mainly due to change in the  $\beta$ -angle of the unit cell. We observe differences in the time-behaviour of the peaks depending on thickness and temperature of the sample as well as the laser intensity. Further analysis is in progress.

## References:

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