

## 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.

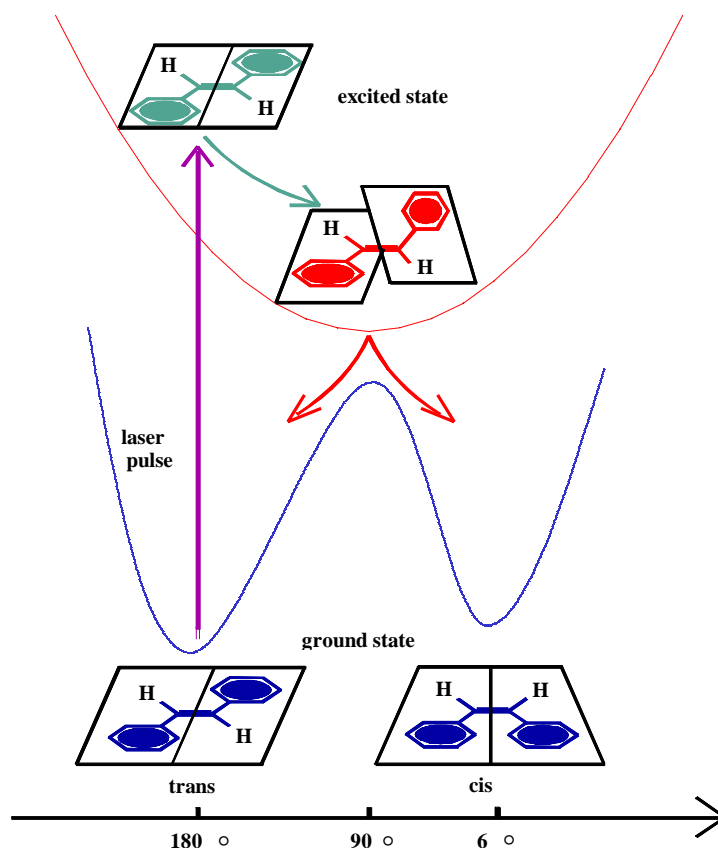


	<b>Experiment title:</b> <b>Picosecond Time Resolved X-ray Scattering of trans-Dibromoethylene and trans-Stilbene in non polar Solvents: Probing Solvent-Supported Large Amplitude Motion</b>	<b>Experiment number:</b> CH-707
<b>Beamline:</b>	<b>Date of experiment:</b> (might be not correctly reminded) from: 24/11/99 to: 28/11/99	<b>Date of report:</b> 01/08/00
<b>Shifts:</b>	<b>Local contact(s):</b> M. Wulff	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants (* indicates experimentalists):</b>  *Techert, Simone Old Address: ESRF, BP 220, 38043 GRENOBLE CEDEX New Adress: Max Planck Institute for Biophysical Chemsitry, Dep. 010, 37070 Goettingen, Germany  Geis, Armin & Wulff, Michael (ESRF, Grenoble)  Jens Als Nielsen, The Niels Bohr Institut, University of Copenhagen		

## Report:

Experiment No CH-707 aimed at the determination of the largest conceivable intramolecular motion of a small organic system triggered by a photo-reaction. The idea was to probe the trans/cis isomerisation (and/or other resolvable structural rearrangements) of trans-stilbene with picosecond time-resolved X-ray scattering. The isomerisation reaction of trans-stilbene is summarised in Fig. 1. The underlying idea was that – assuming a non-dissipative relaxation process – different time-points might be assigned to different geometrical configurations if the isomerisation was slow enough to be tracked by 80 - 100 ps x-ray pulses. The configurational changes can be probed as changes in the diffuse x-ray scatter signal of t-stilbene in some solvent. As this method makes visible all intermediates of a photo-cycle – both light-active and non-light-active ones – it provides a possibility to probe structures which can be studied only indirectly by common optical spectroscopic methods.

Here, the photochemistry of t-stilbene dissolved in methanol was investigated. Since the inverse rate constant of the isomerisation is about 40 ps at room temperature and normal pressure [1], and since the x-ray pulse length was about 80 ps, changes in the product state distribution (generation and enrichment of the cis product) and a partial population of the intermediate configurational states involved in the isomerisation process were expected as results.



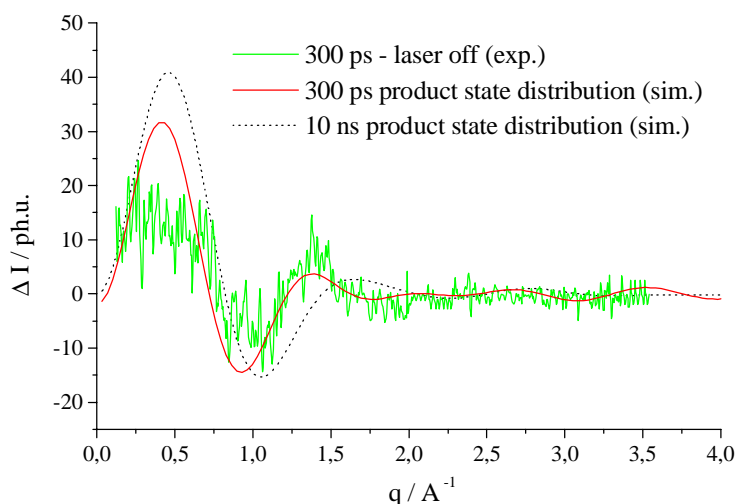
**Fig 1:** Isomerisation process of t-stilbene.

Fig. 2 shows the observed diffuse change of the scattered x-ray intensity for a 300 ps time point of t-stilbene (the electronically first-excited state of t-stilbene has a lifetime of ca. 2 ns, the inverse rate constant of the isomerisation takes 40 ps, 98 % of the excited molecules isomerise [1 and references therein].)

Obviously, there is a modulation of the scattered x-ray signal  $\Delta I$ . Although  $\Delta I$  is very small in amplitude it is slightly bigger than the readout noise of the detector (at that time a Princeton CCD camera).

In the simulated signal, the change of the product state distribution for a 300 ps time point, the (still) populated intermediate configurations during the isomerisation and an excitation level of 30 % were included. Although the phase of the experimental intensity change is correctly described, relative to the experimental signal, the amplitude of the measured signal is much smaller than the simulated one. One explanation could be that the theoretical model on which the simulation is based does not completely describe the state distribution during the 300 ps time point. However, in order to exclude experimental artefacts like spatial insensitivities on the detector surface, which could influence the integrated radial intensity, the experiment should be repeated with the new device recently installed at ID09-TR.

A comparison with the simulated signal for a 10 ns time-point shows that different distributions are formed for different time points and that these distributions can clearly be distinguished.



**Fig 2:** Measured and simulated 300 ps timepoint of the isomerisation reaction.

First this experiment aimed at demonstrating the possibility to track complex photochemical reactions where only large amplitude motions and no dissociation reactions are involved in solution. From the preliminary result obtained during the run in November 1999 this seemed to exist. Assuming that the simulation derived from high-level ab initio and semiempirical calculations [for the simulations only, see 2] match well the data in phase, there are non-negligible differences in the amplitude of the signal.

In order to exclude experimental artefacts causing the difference in the amplitude of the signal the experiment has to be repeated. Further time-points have to be measured to fit into a time-dependence.

Additional theoretical considerations have to be made also, e.g. the influence of large amplitude motions like the torsion of one phenyl-moiety around the ethylenic double bond around the other phenyl-moiety [3,4]. This experiment also shows that time-resolved x-ray scattering is presumably suitable for resolving relaxation processes of an isomerisation, which are smaller in configurational changes than  $180^\circ$ .

Further the results show, that especially with regard to excess energy the excitation wavelength of 266 nm – in comparison to the excitation wavelength of 310 nm - does not significantly change the photochemistry [5].

Based on the yielded experimental results

- a) further experiments in the liquid phase are necessary.

However, the following work should be carried out before:

- b) a detailed, high-resolution analysis of the relaxation processes of the first excited state in t-stilbene crystals (lifetime of 2.1 ns, see submitted proposal) as done for the excited state dynamics of N,N-dimethylaminobenzonitrile [4].

References:

- [1] R. Mohrschladt, J. Schroeder, J. Troe and P. Vöhringer, *J. Chem. Phys.* **101**, 7566 (1994).
- [2] S. Techert and S. Schmatz, in preparation for *Z. Phys. Chemie (special issue 2000)*.
- [4] J. S. Baskin, L. Banares, S. Pedersen and A. H. Zewail, *J. Phys. Chem.* **100**, 11920 (1996).
- [5] A. Zewail, nobel prize lecture 1999.
- [6] J. Schroeder, private communication.
- [7] S. Techert, F. Schotte and M. Wulff, submitted to *Phys. Rev. Lett.* (2000).