![ESRF logo] **ESRF**	**Experiment title:** Time Resolved Diffraction study of Azobenzene Photoisomerization	**Experiment number:** CH-1905
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Report:

In this experiment a time resolved diffraction study has been carried out on a 12 mM solution of Azobenzene molecules in Methanol. The aim was to observe the trans-cis photoisomerization of the azobenzene molecule upon irradiation with UV ligth at 350 nm that is a classic issue in molecular photochemistry and has been widely studied for many possible applications. This experiment represents a challenge for at least two main reasons: the investigations of the possibility to apply the Time resolved diffraction technique to light molecules photophysics and photochemistry and the study of the reaction itself whose steps and timescales of the structural changes are not completely clarified. For this experiment a jet-system has been used to get a solution flux with a speed such that the sample in the scattering volume would be completely renewed in the 1 ms interval between the X-rays pulses defined by the chopper maximum frequency. The jet make the solution flowing in air avoiding the use of a capillary system with its heating contribution to the differential scattering signal. The X-rays scattering lenght is so defined by the 0.3 mm thickness of the jet. As the incidence of the UV pulse is almost collinear to the one of x-rays the concentration has been chosen to get an absorption of around 1 A on a 0.3 mm lenght:

due to the high cross section of the chromophore this concentration allows the most of photons in the laser pulse to be absorbed homogenously in the scattering volume but the dilution is still high to prevent solute solute contribution in the scattering signal. The scattering spectra are collected on the MAR ccd as function of the time delays between the the x-rays and laser pulse. As the photophysics is supposed to be very fast the chosen delays are -100,0,50,100 and 400ps where the time is taken in respect to the center of the 100ps long X-ray pulse. Due to the low molecular weight of the solution a 1000 repetition of 5 s exposure have been collected for each time delay in order to get the extremely good statistic observable in figure 1. Here the differences are reported for the different TD: as can be observed the shape of the signal seems to be the same for all the time delays a part for the intensity which is proportional to the integral of the pulse after the UV irradiation. This is clearly enhanced in figure 2 where the integral of the differences (dots) is rescaled on the measured integral of the x-ray pulse (solid line) matching perfectly its shape a part for a shift in the supposed TD of -15 ps: so our 0ps TD catch the structure at 35ps from the irradiation. As then the signal seems not to have further changes we can confine the structural photodynamics to faster timescales. Although we cannot see the reaction steps remains the question if we are able or not to discriminate between a signal coming from the isocore heating of the methanol and the structural contribution of the isomerization? Figure 3 compares the 400ps difference signal (dots) to a molecular dynamics simulation of methanol at two different Temperatures and constant volume (red-solid line): the simulation seems to match very well the features of the signal apart for the lower Q region where the main structural differences due to the cis-azobenzene structure are expected (see blue-dashed line). Unfortunately the MD simulation is not completely reliable in such Q region due to finite-size effects: to clarify this point an experiments has been suggested to produce a simple methanol isocore heating signal by infrared pulses. This experiment should give a definite answer to our problem.
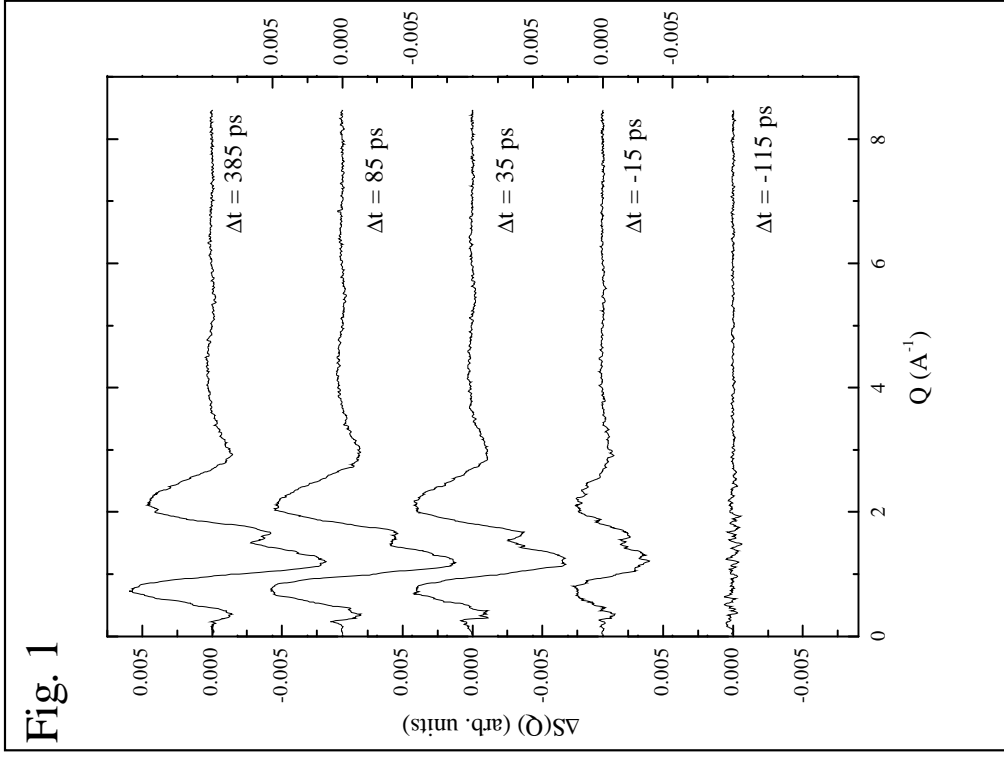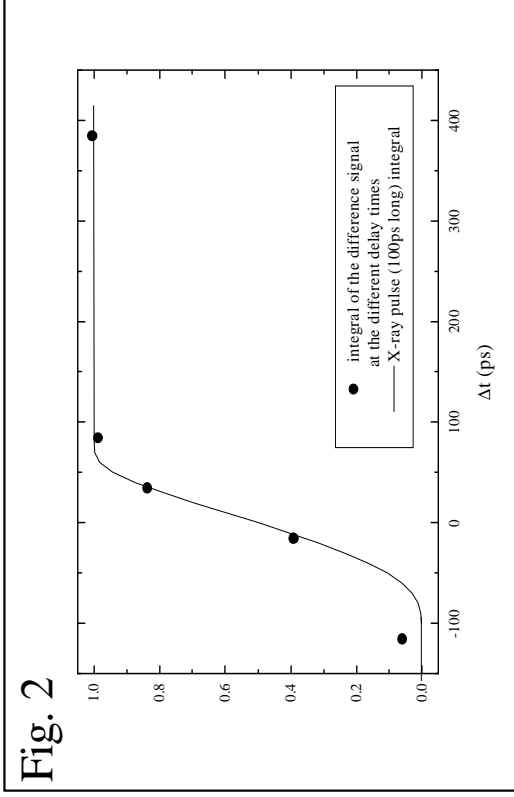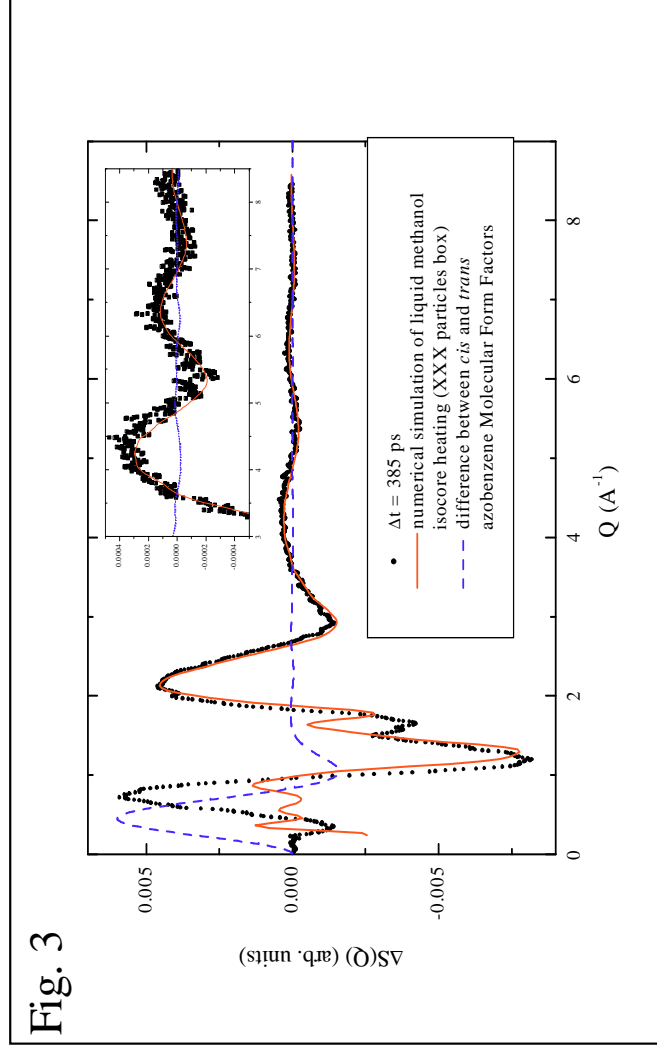
Fig. 1

ΔS(Q) (arb. units)

Δt = 385 ps
Δt = 85 ps
Δt = 35 ps
Δt = -15 ps
Δt = -115 ps

Q (A⁻¹)

Fig. 2

- integral of the difference signal at the different delay times
- X-ray pulse (100ps long) integral

Δt (ps)

Fig. 3

ΔS(Q) (arb. units)

Δt = 385 ps
- numerical simulation of liquid methanol isocore heating (XXX particles box)
- difference between *cis* and *trans* azobenzene Molecular Form Factors

Q (A⁻¹)