

## 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:**

Simultaneous breaking of two metal-metal bonds: Light-induced ion-release from a trinuclear Ir-Ag-Ir complex

**Experiment number:**

CH-2826

**Beamline:****Date of experiment:**

from: 12/5/09 (9/9/09) to: 17/5/09 (13/09/09)

**Date of report:**

24/2/2010

**Shifts:****Local contact(s):**

Marco Cammarata, Michael Wulff, Laurent Guerin

*Received at ESRF:***Names and affiliations of applicants (\* indicates experimentalists):****\*Prof. NIELSEN, Martin Meedom****\*Ph.D. stud. CHRISTENSEN Morten / +45 5190 6970 / +45 353 20460 / mc@fys.ku.dk****\*Post. Doc. HALDRUP M. Kristoffer / +45 22983720 / / haldrup@fys.ku.dk****Dr. HARRIT Niels / NanoScienceCenter, Copenhagen University, Universitetsparken 5, DK-2100 Copenhagen /****+45 353 21846 / +45 353 20460 / harrit@nano.ku.dk****Report:**

The purpose of experiment CH-2826 was to investigate the process of photo-induced bond breakage and ion-release from the tri-metallic compound  $\text{AgIr}_2(\text{dimen})_4$ , see Figure 1 in the beamtime application. Basic feasibility of the proposed experiment had been established previously, cf. The Beamtime Application for CH-2826, and indeed the first measurements of the non-encapsulating  $\text{Ir}_2(\text{dimen})_4$  compound in acetonitrile yielded good results, as Figure 1 shows. -Of primary importance in this plot is the presence of clearly visible oscillations at high values of the scattering vector  $Q$ , indicating the possibility for good structural refinement.

To investigate the bond breakage and ion-release process, silver was added to the circulating solution as  $\text{AgPF}_6$ . Upon restarting the data collection, it became

evident that the promising preliminary results presented in the beamtime applications Figure 2 were not reproduced, e.g. the expected drop in low- $Q$  intensity in the difference scattering images was not observed. Following prolonged data acquisition, the lack of a signal indicating dissociation was confirmed and increasing instability of the sample flow and jet was becoming evident. Following extensive cleaning of the flow system, a good signal from the contraction of the  $\text{Ir}_2(\text{dimen})_4$  host compound was recovered, but laser timing had been lost due to loss of mode-lock on the laser system, possibly due to faulty aircondition and thus lack of temperature control in the experimental hutch. Extensive work by the beamline staff on the laser system was not successful in re-establishing the femtosecond laser system to adequate working conditions. On this background it was decided to use the DM50 530 nm pump-laser system, although the 1 $\mu$ s pulse length

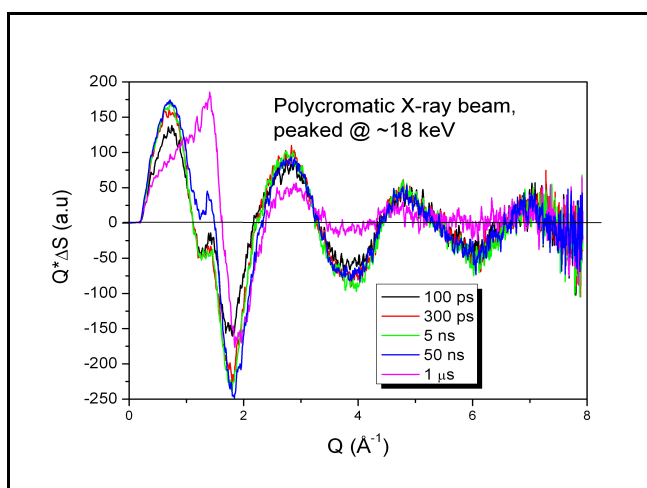


Figure 1: Data on  $\text{Ir}_2(\text{dimen})_4$  obtained May 2009

would preclude studying the ultrafast ion-release process. However, it was felt that good data on the host compound could be acquired.

Experiment continued with the long laser pulse, but was significantly hampered by the lack of temperature control in the hutch, as this led to several instabilities in the beamline setup, such as occasional drop-out of the high-speed chopper, despite intense efforts on the part of the beamline staff. However, in spite of the instabilities, high-quality data were acquired under these somewhat unusual conditions on both solvent + inert chromophore ( $\text{CH}_3\text{CN}/\text{KMnO}_4$ ) as well as on the  $\text{Ir}_2(\text{dimen})_4$  compound; this is shown in Figure 2.

Based on the very good quality (S/noise and S/background) of the low-time-resolution data, it was decided in consultation with the beamline staff to attempt a liquid-state experiment using monochromatic radiation, as opposed to the usual polychromatic and exceptionally intense X-radiation from U17. This entails a drop of at least two orders of magnitude in the X-ray intensity, but may yield benefits in terms of increased structural resolution. As Figure 4 shows, this trial experiment was successful and has allowed some interesting considerations regarding optimum experiment design in terms of spectral X-ray intensity distribution and overall intensity.

In summary, technical difficulties ultimately due to faulty airconditioning in the experimental hutch and an unstable fs laser system precluded the acquisition of high-quality data on the originally proposed ion-release process, although basic feasibility was reconfirmed. However, discussions with the beamline staff resulted in a switch to experimental conditions with much lower time resolution, but higher signal strength, that led to data of high quality on the host compound, which is in itself of scientific interest.

As compensation for the beamtime lost due to technical difficulties, we were invited for additional beamtime at ID09B in September 2009. Unfortunately, an unexpected reaction between the Ag ions and a co-precipitate of one of the  $\text{Ir}_2(\text{dimen})_4$  precursor compounds prevented us from obtaining good data on the ion-release process, but several related key experiments were successful during this experimental run, most importantly very good 10 ps “time-slicing” data on the Ir host compound were obtained. We expect that the analysis of this and related data sets will result in the first determination of the excited-state structure of the  $\text{Ir}_2(\text{dimen})_4$  compound in solution, and expect to submit these results for publication in 2010. These results will also provide a solid foundation on which to interpret later data on the ion-release process. We gratefully acknowledge the helpfulness and competence of the ID09B staff, especially when faced with difficulties of a technical nature beyond their control.

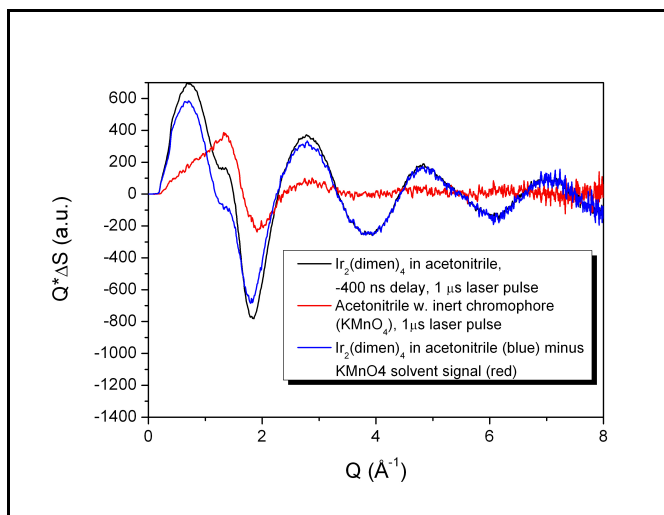


Figure 2: Low time resolution, high S/N data on  $\text{Ir}_2(\text{dimen})_4$  and solvent with inert chromophore

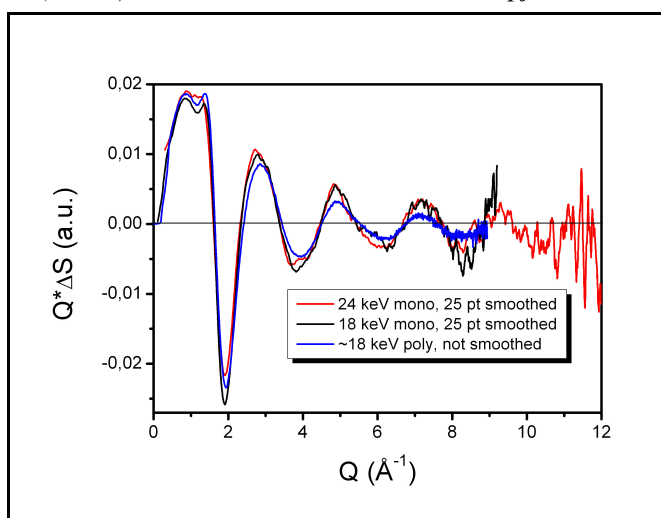


Figure 3: Comparison of mono- and polychromatic experiments

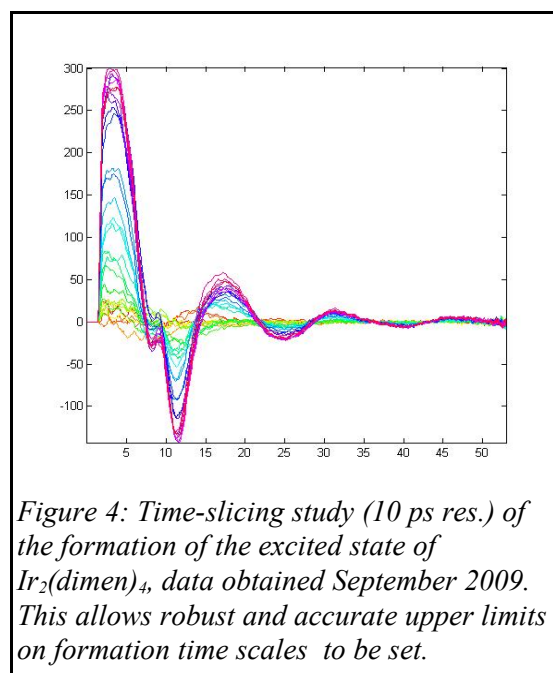


Figure 4: Time-slicing study (10 ps res.) of the formation of the excited state of  $\text{Ir}_2(\text{dimen})_4$ , data obtained September 2009. This allows robust and accurate upper limits on formation time scales to be set.