



## 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 via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

### ***Reports supporting requests for additional beam time***

Reports can 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:**

Tracking the electron transfer in a RuCo photocatalyst using time-resolved X-ray scattering

**Experiment number:**

CH-3608

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

from: 28 Nov 2012 to: 04 Dec 2012

**Date of report:****Shifts:**

15

**Local contact(s):**

Dmitry Khakhulin, Michael Wulff

*Received at ESRF:***Names and affiliations of applicants (\* indicates experimentalists):**

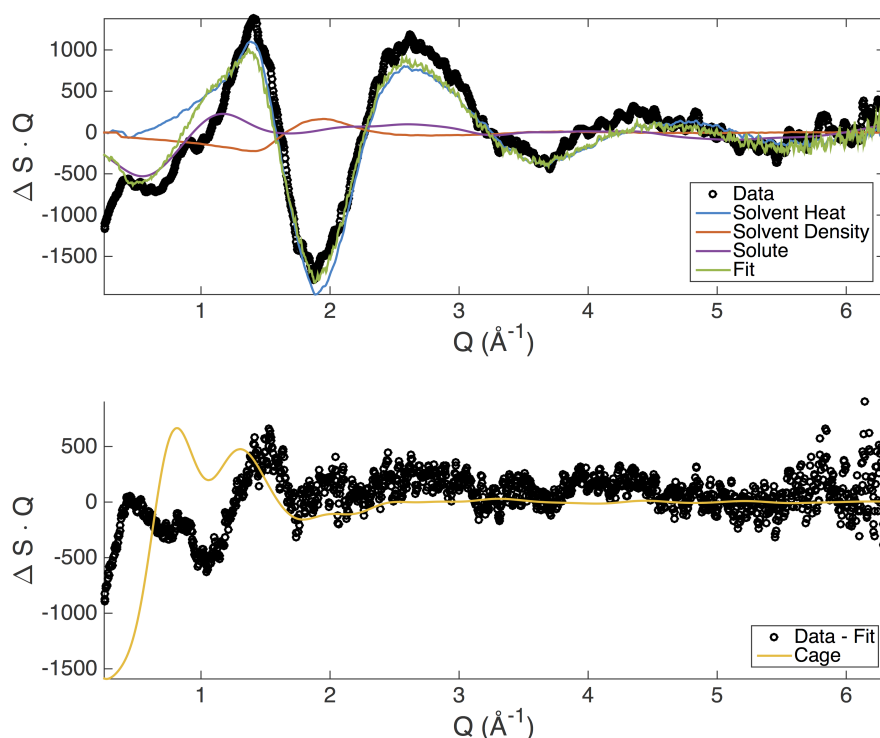
Tobias Harlang\*  
Martin Meedom Nielsen  
Sophie Canton  
Martin Kristoffer Haldrup\*  
Tim Brandt van Driel\*  
Asmus Ougaard Dohn  
Kasper Skov Kjaer\*  
Robert Hartsock\*

**Report:**

The aim of the experiment was to investigate the structural response associated with photo-induced electron transfer in a Ru-Co photocatalytic model system (see beamtime application for further details about the scientific background).

During the beamtime, we successfully measured time-resolved X-ray diffuse scattering (XDS) of the Ru-Co molecule and a series of reference compounds in solution. Additionally, we were able to implement an X-ray emission spectroscopy (XES) setup at the beamline, which allowed us to record time-resolved XES data simultaneously with the XDS experiment. The XES setup formed the basis of the permanent XES setup that still exists at the beamline today.

*Figure 1 X-ray diffuse scattering of the Ru-Co complex in acetonitrile solution. Top panel: The data (black) has been fitted to solvent heat and density changes (blue and red) and a structural change of the solute molecules based on DFT calculations (purple). Lower panel: The residual from the fit contains features at the low-Q region that cannot be described by the*



The XDS data of the Ru-Co molecule recorded 3 ns after excitation is shown in figure 1. The majority of the signal can be described by solvent heat/density and a solute signal based on DFT calculations of the ground state and excited state structures. With the best fit, however, there is still a small residual that cannot be fitted by these components.

The solute fit corresponds to a structural change of 0.2 Å, associated with a population of the  $^2\text{Ru(III)}\text{-}^4\text{Co(II)}$  high spin state, as sketched in figure 2. This confirms photo-induced electron transfer from the ruthenium site to the cobalt site, which was the main objective of the beamtime. The current challenge is to describe the solvent-cage interactions in a better way. Figure 2, lower panel shows the residual of the fitted data plotted against the solvent-cage scattering based on a molecular dynamics simulation of the solvent response. Such classical descriptions of the solvent response have been proved effective for molecules that have similar dipole moments in the ground state and excited state. In this case, however, the electron transfer changes the electronic environment around the Ru-site and Co-site drastically, and thus a quantum mechanical description of the solute-solvent interaction is required.

Currently, we are working with colleagues from DTU chemistry to simulate the Ru-Co in acetonitrile solutions with a quantum mechanics/molecular mechanics hybrid framework. The output from these simulations is expected to describe the solvent-cage effects observed in the data in a way that allows us to optimize the fit even more. Thus, we will not only learn about the solvent interactions of this photocatalytic model system, but we will also be able to further refine the structural information about the excited state molecule.

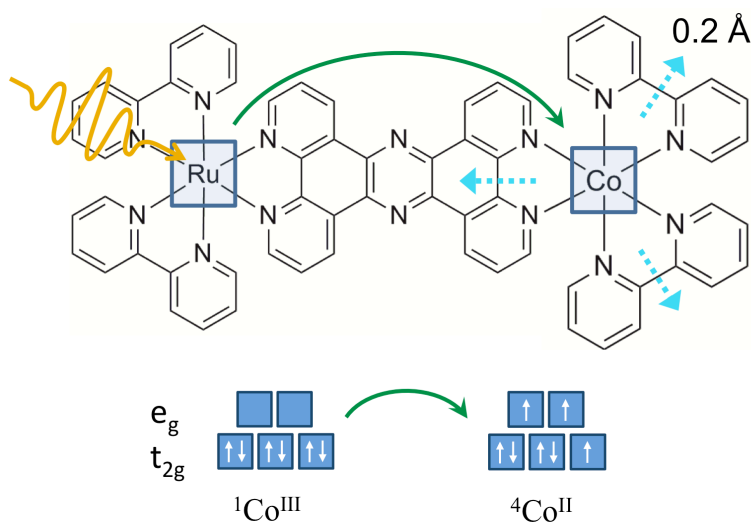


Figure 2 Illustration of the process observed in the experiment. The ruthenium center is excited with visible light, which induces electron transfer to the cobalt site. The electron transfer results in a population of the antibonding  $e_g$  orbital, which causes an expansion of the Co-N bond by 0.2 Å.