



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>

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal (“relevant report”)

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a “*preliminary report*”),
- even for experiments whose scientific area is different from the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as “relevant report(s)” in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

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.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number 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: Investigation of the photoactivation mechanism of $\text{Fe}_3(\text{CO})_{12}$ using time-resolved x-ray solution scattering

Experiment number:
CH-6493

Beamline: ID09	Date of experiment: from: Nov. 29, 2022 to: Dec. 4, 2022	Date of report: Sep. 11, 2023
Shifts: 12	Local contact(s): Mikhail Kozhaev	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

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Report:

The goal of our experiment was to study the photodynamics of triirondodecacarbonyl ($\text{Fe}_3(\text{CO})_{12}$) and how they depend on excitation wavelength and solvent. In particular, previous optical spectroscopic studies suggested that the $\text{Fe}_3(\text{CO})_{12}$ complex forms intermediates with elongated Fe-Fe bonds, and dissociates into various subcomponents such as $\text{Fe}(\text{CO})_4$, $\text{Fe}_2(\text{CO})_8$, or their isomers (**Figure 1a**). The formation time constants for these transient products range within several hundreds of picoseconds and slightly depend on excitation wavelengths (267, 400 nm) (**Figure 1b**).

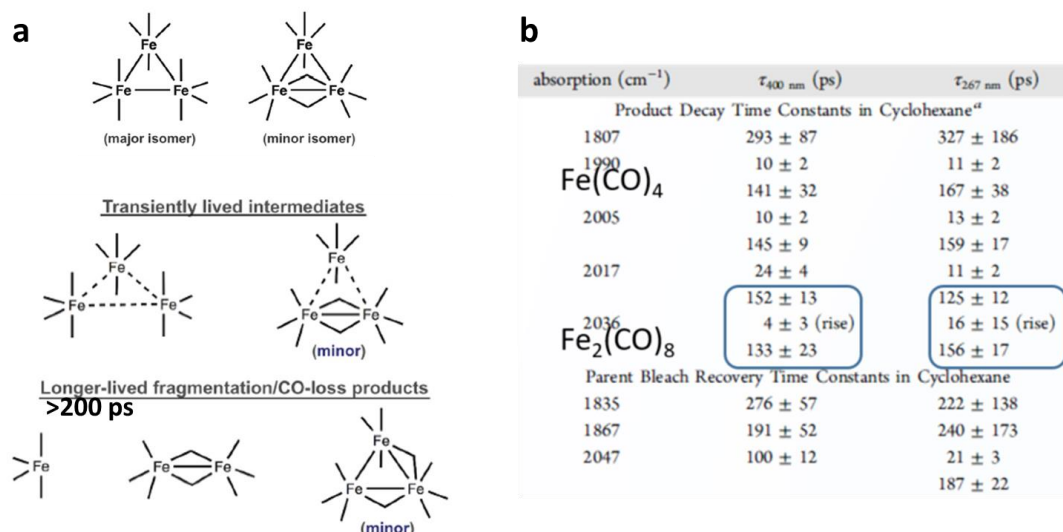


Figure 1. Reported transient structures and their formation time constants revealed by previous time-resolved optical spectroscopy studies.

Table 1. TRXSS measurement of $Fe_3(CO)_{12}$.

Sample	Conc.	Laser	Time delays
$Fe_3(CO)_{12}$ in CHX	1	1.6 (267)	50 ps + 3 pts / decade
	0.6	1.6 (400)	50 ps + 3 pts / decade
$Fe_3(CO)_{12}$ in MeOH	2	1.6 (267)	50 ps + 1 pt / decade
	2	4.2 (267)	50 ps + 2 pts / decade

* Concentration (mM) / Laser fluence (mJ/mm²) / Laser wavelength (nm)

Table 2. TRXSS measurement of solvent dye.

Sample	Laser	Time delays
AzoBr dye in CHX	1.1 (400)	100 ps, 1 ns, 10 ns, 31.6 ns, 100 ns, 316 ns, 1 us
	1.6 (400)	100 ps, 1 ns, 10 ns, 31.6 ns, 100 ns, 316 ns, 1 us
AzoBr dye in MeOH	1.6 (267)	100 ps, 1 us
	4.2 (267)	100 ps, 1 us

* Concentration (mM) / Laser fluence (mJ/mm²) / Laser wavelength (nm)

In this work, we utilized time-resolved x-ray solution scattering (TRXSS), a prominent tool to visualize the structural dynamics in liquids and solutions, to precisely extract chemical structure of each intermediate. We conducted the TRXSS measurement of $Fe_3(CO)_{12}$ in two different solvents, cyclohexane and methanol, and at two different wavelengths, 267 and 400 nm (**Table 1**). The x-ray scattering signals from heated solvents were measured in a separate experiment using a well-known heat dye (Br-derivative of azobenzene complex) (**Table 2**).

We azimuthally integrate the scattering images to obtain a set of static 1D curves that have momentum (q) as x-axis. Then, we subtracted the curves collected at positive time delays with those at negative time delays to generate difference x-ray scattering curves. Finally, we performed a singular value decomposition (SVD) to decompose the collected data $\Delta S(q,t)$ into time-independent structural components ($U(q)$), their temporal evolutions ($V(t)$) and relative importance in the data (S). The experimental results about the TRXSS data of $Fe_3(CO)_{12}$ at 400 nm in cyclohexane (**Figure 2**) and that at 267 nm in cyclohexane (**Figure 3**) were summarized. We also compared the momentum-space scattering curve $U(q)$ and the kinetics of the primary component $V(t)$ with that obtained in methanol for comparison (**Figure 4**) and concluded that both the structural dynamics and kinetics remains almost independent on solvents.

Based on the regression fit using a sum of multiexponential functions, we extracted a number of time constants from the time-dependent right singular vectors ($V(t)$). The obtained components and time constants will be transferred to the kinetic analysis (KA) that constraint the model-associated scattering curves encrypting structural information at each kinetic step. We will use a theoretical model combining the scattering signals from solute, cage, and solvent to fit these curves and the respective structural dynamics at each step. Details of the analysis is still ongoing and we have a plan to publish the results by a scientific paper in the future.

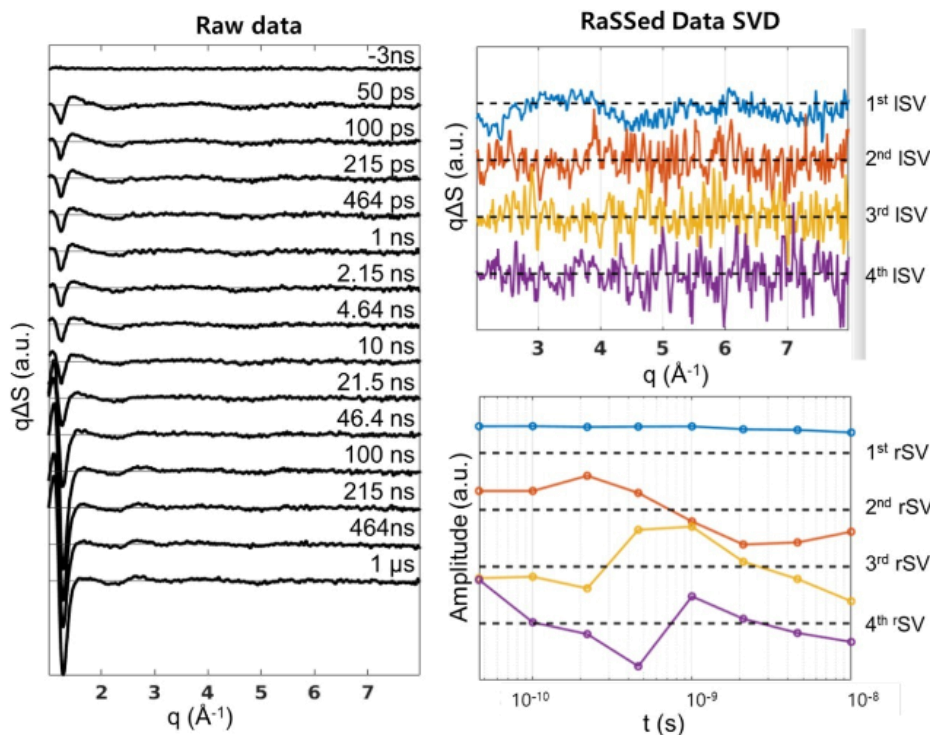


Figure 2. Time-resolved x-ray scattering curves (left) and the SVD results (right) of the TRXSS data for $Fe_3(CO)_{12}$ in cyclohexane excited at 400 nm.

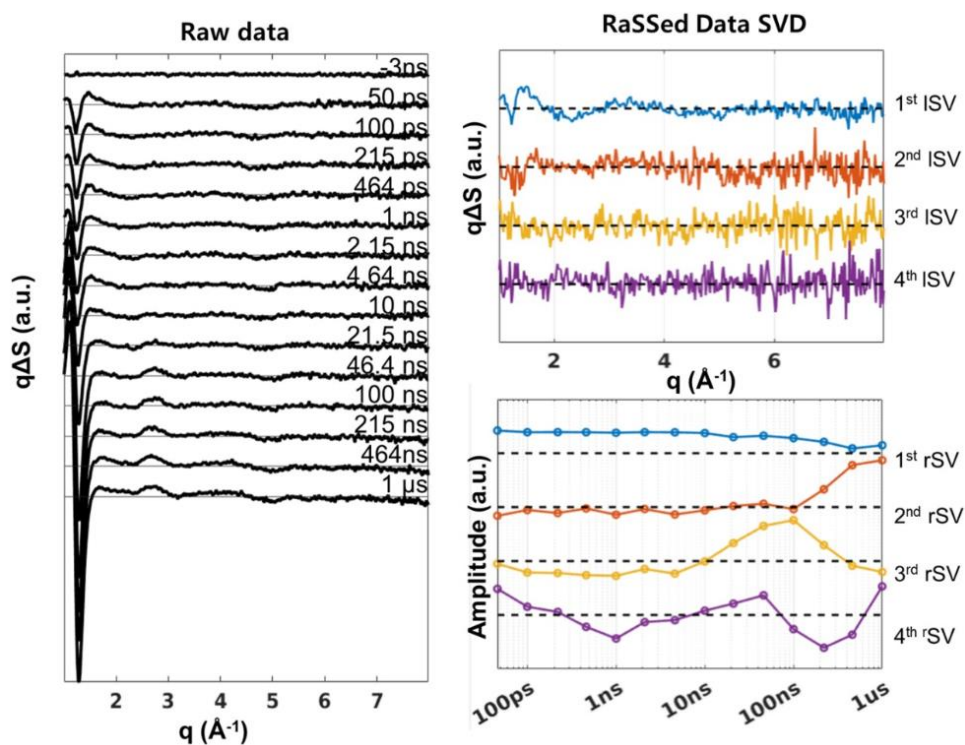


Figure 3. Time-resolved x-ray scattering curves (left) and the SVD results (right) of the TRXSS data for $Fe_3(CO)_{12}$ in cyclohexane excited at 267 nm.

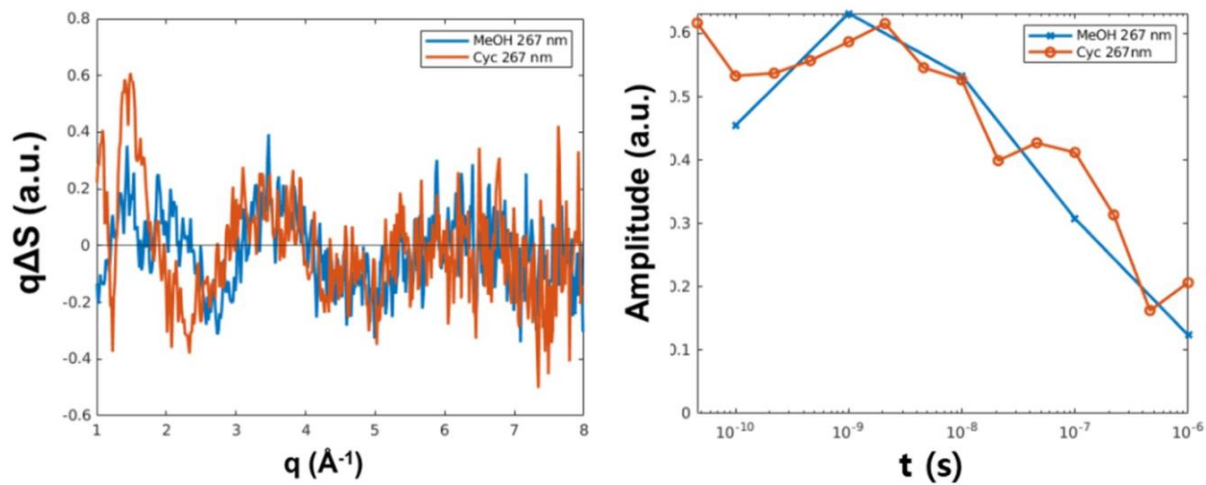


Figure 4. $U(q)$ and $V(t)$ comparison of the primary components for the TRXSS data of $Fe_3(CO)_{12}$ in cyclohexane and methanol. The excitation wavelength was 267 nm.

